



ADAM MICKIEWICZ UNIVERSITY IN POZNAŃ

*FACULTY OF CHEMISTRY*

# THESIS

presented by:

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**“Metal and Covalent organic framework (MOFs, COFs) electrodes for high efficiency energy storage systems”**

**“Elektrody oparte na sieciach metaloorganicznych i kowalencyjnych sieciach organicznych (MOF, COF) do zastosowań w wysokowydajnych systemach magazynowania energii”**

to obtain the rank: **Doctor of Adam Mickiewicz University in Poznań**

Specialty: **Chemistry**

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*"I dedicate this thesis to  
my incredible father,  
Muhammad Sarwar.  
Thank you for everything,  
for being the reason I  
learned to fly."*



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# Acknowledgements

I would like to express my deepest gratitude to everyone who supported me throughout my PhD journey. First and foremost, I thank my parents and siblings for their unwavering love, patience, and encouragement, which have been my foundation through every challenge.

I extend my sincere thanks to my supervisors, Dr. Artur Ciesielski at Institut de Science et d'Ingénierie Supramoléculaires UMR7006, (Université de Strasbourg) and at the Center for Advanced Technologies (Adam Mickiewicz University in Poznań) and Dr. Dawid Pakulski at the Center for Advanced Technologies (Adam Mickiewicz University in Poznań), who welcomed me at the beginning and introduced me to the domain of laboratory work. Our discussions, including moments of sharing knowledge, have been invaluable in shaping my research and growth as a researcher.

I am also grateful to Prof. Paolo Samorì for the opportunity to work in the Nanochemistry Laboratory in Strasbourg, France, and to Dr. Verónica Montes García for her mentorship, guidance, and encouragement, which inspired me to strive for excellence.

I would like to thank all my friends, lab mates, and colleagues who have made the lab a stimulating and collaborative space, enriching me both professionally and personally. Living and studying in Poland as an international student has been a transformative experience. The culture, warmth of people, and vibrant academic community have made my journey not only productive but deeply memorable.

Finally, I extend my gratitude to everyone who has helped me in any way, directly or indirectly, during the preparation of this work. This achievement is possible thanks to your support.

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# Abstract

The growing global demand for efficient and sustainable energy storage technologies has accelerated the search for new, advanced electrode materials that combine high capacity, long cycling stability, and versatility across diverse electrochemical systems. Porous frameworks including metal–organic frameworks (MOFs), carbonized MOF-derived carbons (CMOFs), and covalent organic frameworks (COFs) have emerged as a highly promising class of materials for this purpose, owing to their tunable porosity, large specific surface areas, and the possibility of incorporating redox-active sites directly into the framework structure. Despite considerable recent progress, the rational design of such materials for specific battery chemistries remains an open challenge, and the structure–function relationships governing their electrochemical behavior are not yet fully understood. This thesis mainly focuses on three complementary studies, each targeting a distinct porous framework electrode material and electrochemical energy storage system. The first study concerns a dual metal–organic framework combining manganese and iron ions with trimesic acid (Mn-Fe-BTC DMOF) as a cathode material for lithium metal batteries (LMBs). The second study investigates MOF-5-derived carbon materials (CMOF-5) obtained at systematically varied carbonization temperatures as cathodes for zinc-ion hybrid supercapacitors (ZnHSCs). The third study evaluates a redox-active covalent organic framework built from tetrakis(4-aminophenyl)-1,4-phenylenediamine (TPA) and naphthalene diimide (NDI) units (COF TPA-NDI) for application in aluminum-ion batteries (AIBs).

Moreover, the doctoral thesis is divided into six chapters:

**Chapter 1** defines the global context of energy storage challenges and highlights the need for sustainable advanced energy storage systems (ESS). It describes the fundamental operating principles and comparative performance of batteries, supercapacitors, and hybrid energy storage devices. The chapter then explains the structure, working mechanisms, and limitations of conventional lithium-ion batteries (LIBs), providing the foundation for a discussion of emerging next-generation ESS. Particular focus is given to LMBs, ZnHSCs, and AIBs, examining their electrochemical operating principles, key performance benefits, and cathode-related limitations. Subsequently, the chapter

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identifies cathode materials as a critical bottleneck across these three ESS and introduces MOFs and COFs as promising cathode materials. A systematic review of their structural characteristics, electrochemical advantages, and reported performance in various energy storage applications is provided. The chapter concludes by outlining the specific research objectives and scope of the present study.

**Chapter 2** describes the comprehensive set of characterization techniques employed in this thesis to investigate the synthesized materials at the structural, chemical, morphological, and electrochemical levels. Further, it discusses the post-mortem and ex situ characterization techniques employed to investigate structural and chemical changes occurring in the materials during long-term cycling, providing insights into their performance and degradation mechanisms.

**Chapter 3:** In the first study, bimetallic Mn-Fe-BTC DMOF was synthesized via a one-step hydrothermal method and comprehensively characterized by Powder X-ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), and nitrogen adsorption analysis. The bimetallic strategy was shown to combine the high specific surface area of Fe-BTC ( $1125 \text{ m}^2 \text{ g}^{-1}$ ) with the chemical stability characteristic of Mn-BTC, yielding a thermally stable framework with an average pore diameter of 1.6 nm. Electrochemical evaluation in CR2032 coin cells demonstrated outstanding specific capacities of  $1292 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ , far exceeding those of the corresponding mono-metal BTC frameworks. After 100 charge–discharge cycles, the DMOF retained  $687 \text{ mA h g}^{-1}$  with a Coulombic efficiency approaching 100%. Post-mortem XPS, XRD, and SEM analyses revealed that the electrode largely preserved its structure and chemical composition after prolonged cycling, with the sustained cyclic stability attributed to strong  $\pi$ – $\pi$  interactions between conjugated carboxylate linkers, reinforcing the three-dimensional framework. However, over 100 cycles, EIS analysis revealed a notable increase in charge transfer resistance ( $R_{ct}$ ), from  $60 \text{ }\Omega$  to  $189 \text{ }\Omega$ , suggesting progressive interfacial changes at the electrode surface, which could result from electrolyte–electrode interactions or partial structural reorganization during repeated lithiation/delithiation.

**Chapter 4:** In the second study, pristine MOF-5 was carbonized under inert atmosphere at five temperatures between 600 and  $1000 \text{ }^\circ\text{C}$  to yield a systematic series of CMOF-5 materials. Comprehensive characterization by SEM, XRD, XPS, Raman spectroscopy, TGA, and BET analysis revealed a temperature-dependent evolution of zinc and ZnO species within the carbon matrix: ZnO formed at lower temperatures was partially reduced to metallic Zn at  $800 \text{ }^\circ\text{C}$ , and the resulting zinc completely evaporated at  $1000 \text{ }^\circ\text{C}$ , leaving a porous carbon framework with a specific surface area of  $2151 \text{ m}^2 \text{ g}^{-1}$

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and a pore volume of  $1.87 \text{ cm}^3 \text{ g}^{-1}$ . Among all samples, CMOF-5 carbonized at  $1000^\circ\text{C}$  delivered the highest specific capacitance of  $268.93 \text{ F g}^{-1}$  at  $1 \text{ mV s}^{-1}$ , an energy density of  $166.9 \text{ W h kg}^{-1}$ , and a power density of  $9234 \text{ W kg}^{-1}$ , with 88% capacitance retention after 10,000 cycles. Kinetic analysis confirmed a progressive increase in diffusion-controlled faradaic contributions with increasing carbonization temperature, establishing a clear structure–property correlation.

**Chapter 5:** The third study focused on the design, synthesis, and computational characterization of COF TPA-NDI, a redox-active covalent organic framework combining an electron-donor tetrakis(4-aminophenyl)-1,4-phenylenediamine unit and an electron-acceptor naphthalene diimide unit for aluminum-ion battery applications. PXRD, BET, TEM, and solid-state  $^{13}\text{C}$  NMR confirmed the crystalline, hierarchically porous structure of the COF, with pore sizes of 1.64 and 3.4 nm. The charge storage mechanism was elucidated through a multi-level density functional theory (DFT) investigation and molecular calculations at the M06-2X/6-311++G\*\* level, which identified preferred binding sites and interaction energies for all relevant ionic species of the ionic liquid electrolyte ( $\text{Cl}^-$ ,  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{EMIm}^+$ ,  $\text{AlCl}^+$ ) within the COF pores, while periodic DFT calculations in VASP confirmed the structural stability of the framework and identified AA stacking as the preferred arrangement, consistent with experimental diffraction data. The calculations established that anions interact preferentially with oxidized TPA units during charging, while cations interact with reduced NDI units during discharging, providing a rigorous mechanistic foundation for further COF-based AIB electrode optimization.

**Chapter 6** presents the general conclusion and outlook.

Collectively, these findings establish clear structure–property relationships in each system and identify key directions for future development, including ternary framework compositions, multi-stage carbonization protocols, and simulation- and AI-guided materials discovery. Together, these advances lay a strong scientific foundation for the practical deployment of porous framework electrodes in next-generation, sustainable energy storage technologies.

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# Streszczenie

Rosnące globalne zapotrzebowanie na efektywne i zrównoważone technologie magazynowania energii przyspieszyło poszukiwania nowych, zaawansowanych materiałów elektrodowych, łączących wysoką pojemność, długotrwałą stabilność cykliczną oraz uniwersalność w różnych układach elektrochemicznych. Materiały porowate, w tym sieci metaloorganiczne (MOF), materiały węglowe powstałe w procesie karbonizacji (CMOF) oraz kowalencyjne sieci organiczne (COF), okazały się wysoce obiecującą klasą materiałów w tym zakresie, dzięki modyfikowalnej porowatości, dużej powierzchni właściwej oraz możliwości wprowadzenia centrów redoks-aktywnych bezpośrednio w strukturę sieci. Mimo znacznego postępu poczynionego w ostatnich latach, racjonalne projektowanie tego typu materiałów dla konkretnych chemii ogniw pozostaje wciąż otwartym wyzwaniem, a zależności strukturalno-funkcjonalne determinujące ich zachowanie elektrochemiczne nie są jeszcze w pełni poznane.

Niniejsza rozprawa skupia się głównie na trzech komplementarnych badaniach, z których każde dotyczy odrębnego materiału elektrodowego oraz odpowiadającego mu elektrochemicznego systemu magazynowania energii. Pierwsze badanie dotyczy bimetalicznej sieci metaloorganicznej łączącej jony manganu i żelaza z kwasem trimezynowym (Mn-Fe-BTC DMOF) jako materiału katodowego dla baterii litowo-metalicznych (LMB). Drugie badanie obejmuje materiały węglowe pochodzące z sieci metaloorganicznej MOF-5 (CMOF-5) otrzymywane w procesie karbonizacji prowadzonej w zmiennych temperaturach, wykorzystywanych jako materiały katodowe w hybrydowych ogniwach cynkowo-jonowych (ZnHSC). Trzecie badanie dotyczy oceny redoks-aktywnej kowalencyjnej sieci organicznej zbudowanej z jednostek tetrakis(4-aminofenilo)-1,4-fenyleneodiaminy (TPA) oraz diimidu naftalenowego (NDI) (COF TPA-NDI), przeznaczonej do zastosowania w bateriach glinowo-jonowych (AIB).

Praca doktorska została podzielona na 6 rozdziałów:

**Rozdział 1** przedstawia wyzwania związane z magazynowaniem energii i podkreśla potrzebę otrzymywania nowych zrównoważonych, zaawansowanych systemów magazynowania energii (ESS). Przytoczone są również podstawowe zasady działania i porównanie wydajności baterii, superkondensatorów i urządzeń hybrydowych. Następ-

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nie opisano strukturę, mechanizmy działania i ograniczenia konwencjonalnych baterii litowo-jonowych (LIB). Szczególna uwaga poświęcona jest bateriom litowo-metalicznym (LMB), hybrydowym superkondensatorom cynkowo-jonowym (ZnHSC) i bateriom glinowo-jonowym (AIB), z analizą ich elektrochemicznych zasad działania, kluczowych korzyści wydajnościowych oraz ograniczeń związanych z katodą. Następnie rozdział identyfikuje materiały katodowe jako krytyczne ograniczenie we wszystkich trzech systemach ESS. Zaproponowano układy MOF i COF wraz z ich systematycznym przeglądem właściwości strukturalnych, zalet elektrochemicznych oraz udokumentowanej wydajności. Rozdział kończy się nakreśleniem konkretnych celów badawczych i zakresu niniejszego opracowania.

**Rozdział 2** opisuje kompleksowy zestaw technik charakteryzacji zastosowanych w niniejszej rozprawie do badania zsyntetyzowanych materiałów na poziomach strukturalnym, chemicznym, morfologicznym i elektrochemicznym. Ponadto omawia techniki post-mortem i ex situ stosowane do badania zmian strukturalnych i chemicznych zachodzących w materiałach podczas długotrwałego procesu ładowania/rozładowania, zapewniając wgląd w mechanizmy ich wydajności i degradacji.

**Rozdział 3** rozpoczyna część eksperymentalną dysertacji, w której bimetaliczny układ MOF (Mn-Fe-BTC DMOF) został zsyntetyzowany w jednoetapowej reakcji hydrotermalnej i kompleksowo scharakteryzowany za pomocą proszkowej dyfrakcji rentgenowskiej (PXRD), spektroskopii w podczerwieni z transformatą Fouriera (FTIR), spektroskopii Ramana, spektroskopii fotoelektronów wzbudzonych promieniowaniem X (XPS), skaningowej mikroskopii elektronowej (SEM), analizy termogravimetrycznej (TGA) oraz analizy adsorpcji azotu. Wykazano, że strategia bimetaliczna łączy wysoką powierzchnię właściwą charakterystyczną dla sieci metaloorganicznej z jonem żelaza Fe-BTC ( $1125 \text{ m}^2 \text{ g}^{-1}$ ) ze stabilnością chemiczną charakterystyczną dla sieci metaloorganicznej z jonem manganu Mn-BTC, dając termicznie stabilny szkielet o średniej wielkości porów wynoszącej 1,6 nm. Ocena elektrochemiczna przeprowadzona w ogniwach guzikowych CR2032 wykazała wyjątkowo wysokie pojemności właściwe na poziomie  $1292 \text{ mA h g}^{-1}$  przy gęstości prądu  $0,1 \text{ A g}^{-1}$ , znacznie przewyższające wartości odpowiadających im jednometalicznych szkieletów. Po 100 cyklach ładowania-rozładowania Mn-Fe-BTC DMOF zachował pojemność na poziomie  $687 \text{ mA h g}^{-1}$  przy wydajności kulombowskiej bliskiej 100%. Analizy post-mortem metodami XPS, XRD i SEM wykazały również, że elektroda w dużej mierze zachowała swoją strukturę i skład chemiczny po długotrwałym procesie ładowania/rozładowania, a utrzymującą się stabilność cykliczną przypisano silnym oddziaływaniom  $\pi$ - $\pi$  między sprzężonymi łącznikami karboksylowymi, wzmacniającymi trójwymiarowy szkielet. Niemniej jednak w ciągu 100 cykli analiza EIS wykazała istotny wzrost oporu przeniesienia ładunku ( $R_{ct}$ ) z 60

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$\Omega$  do 189  $\Omega$ , co wskazuje na postępujące zmiany międzyfazowe na powierzchni elektrody, mogące wynikać z oddziaływań elektrolit–elektroda lub częściowej reorganizacji strukturalnej podczas powtarzanego litowania/delitowania.

**Rozdział 4** przedstawia badania, w których niezmodyfikowany MOF-5 poddano karbonizacji w atmosferze gazu obojętnego w pięciu temperaturach z zakresu 600–1000 °C, otrzymując systematyczną serię karbonizatów CMOF-5. Szczegółowa charakteryzacja metodami SEM, XRD, XPS, spektroskopią Ramana, TGA oraz analizą BET wykazała zależną od temperatury zmianę zawartości cynku i jego tlenku (ZnO) w matrycy węglowej: ZnO powstający w niższych temperaturach był częściowo redukowany do metalicznego Zn przy 800 °C, a powstały w ten sposób cynk całkowicie odparował w temperaturze 1000 °C, pozostawiając porowatą strukturę węglową o powierzchni właściwej 2151 m<sup>2</sup> g<sup>-1</sup> i objętości porów 1,87 cm<sup>3</sup> g<sup>-1</sup>. Wśród wszystkich próbek CMOF-5 karbonizowany przy temperaturze 1000 °C wykazał najwyższą pojemność właściwą na poziomie 268,93 F g<sup>-1</sup> przy szybkości skanowania 1 mV s<sup>-1</sup>, gęstość energii 166,9 W h kg<sup>-1</sup> oraz gęstość mocy 9234 W kg<sup>-1</sup>, przy retencji pojemności na poziomie 88% po 10 000 cykli. Analiza kinetyczna potwierdziła postępujący wzrost udziału procesów faradajowskich kontrolowanych dyfuzją ze wzrostem temperatury karbonizacji, ustalając jednoznacznie korelację struktura–właściwość.

**Rozdział 5** skoncentrowany jest na projektowaniu, syntezie i charakterystyce obliczeniowej redoks-aktywnej kowalencyjnej sieci organicznej COF łączącej jednostkę trifenyloaminy (TPA), będącą donorem elektronów, z jednostką diimidu naftalenowego (NDI), będącą akceptorem elektronów, przeznaczonej do zastosowań w bateriach glinowo-jonowych. Analizy PXRD, BET, TEM oraz NMR <sup>13</sup>C w ciele stałym potwierdziły krystaliczną, hierarchicznie porowatą strukturę COF o rozmiarach porów 1,64 oraz 3,4 nm. Mechanizm magazynowania ładunku wyjaśniono za pomocą badań obliczeniowych wykorzystujących metodę teorii funkcjonału gęstości (DFT). Stosując funkcjonał M06-2X z bazą 6-311++G\*\*, zidentyfikowano preferowane miejsca wiązania i energie oddziaływań dla wszystkich form jonowych elektrolitu (Cl<sup>-</sup>, AlCl<sub>4</sub><sup>-</sup>, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>, EMIm<sup>+</sup>, AlCl<sub>2</sub><sup>+</sup>) w obrębie porów COF, podczas gdy periodyczne obliczenia DFT w programie VASP potwierdziły stabilność strukturalną szkieletu oraz wskazały upakowanie AA jako preferowany układ, zgodny z eksperymentalnymi danymi dyfrakcyjnymi. Obliczenia wykazały, że aniony oddziałują preferencyjnie z utlenionymi jednostkami TPA podczas ładowania, podczas gdy kationy oddziałują ze zredukowanymi jednostkami NDI podczas rozładowania, co stanowi solidną podstawę mechanistyczną dla dalszej optymalizacji elektrod w bateriach glinowo-jonowych na bazie COF.

**Rozdział 6** przedstawia ogólne wnioski i perspektywy. Otrzymane wyniki ustanawiają wyraźne zależności struktura–właściwości w każdym prezentowanym systemie i

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identyfikują kluczowe kierunki przyszłego rozwoju, w tym trójskładnikowe kompozycje szkieletowe, wieloetapowe protokoły karbonizacji oraz odkrywanie materiałów sterowane badaniami teoretycznymi wspomagane sztuczną inteligencją. Reasumując, przedstawione osiągnięcia tworzą solidną podstawę naukową dla praktycznego wdrożenia elektrod na bazie porowatych elektrod szkieletowych w zrównoważonych technologiach magazynowania energii nowej generacji.



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# Abbreviations and Symbols

## General Abbreviations

### II Abbreviation Description

|            |                                                                    |
|------------|--------------------------------------------------------------------|
| AC         | Activated Carbon                                                   |
| AC         | Alternating Current (in EIS context)                               |
| AIB        | Aluminum-Ion Battery                                               |
| ATR        | Attenuated Total Reflectance                                       |
| BET        | Brunauer-Emmett-Teller                                             |
| BTC        | 1,3,5-benzenetricarboxylic acid (Trimesic acid)                    |
| CE         | Coulombic Efficiency                                               |
| CNT        | Carbon Nanotube                                                    |
| COF        | Covalent Organic Framework                                         |
| CP-MAS NMR | Cross-Polarization Magic Angle Spinning Nuclear Magnetic Resonance |
| CPE        | Constant Phase Element                                             |
| CV         | Cyclic Voltammetry                                                 |
| DC         | Direct Current                                                     |
| DFT        | Density Functional Theory                                          |
| DFT (pore) | Density Functional Theory (for pore size distribution)             |
| DMOF       | Dual Metal-Organic Framework                                       |
| DSC        | Differential Scanning Calorimetry                                  |
| DTA        | Differential Thermal Analysis                                      |
| EC         | Ethylene Carbonate                                                 |
| EDLC       | Electric Double-Layer Capacitor                                    |
| EDS/EDX    | Energy-Dispersive X-ray Spectroscopy                               |
| EES        | Electrochemical Energy Storage                                     |
| EIS        | Electrochemical Impedance Spectroscopy                             |
| EMC        | Ethyl Methyl Carbonate                                             |
| EMImCl     | 1-Ethyl-3-methylimidazolium chloride                               |
| ESCA       | Electron Spectroscopy for Chemical Analysis                        |
| ESP        | Electrostatic Potential                                            |
| ESS        | Energy Storage System                                              |
| EV         | Electric Vehicle                                                   |
| FE-SEM     | Field Emission Scanning Electron Microscopy                        |

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FTIR Fourier Transform Infrared Spectroscopy  
FWHM Full Width at Half Maximum  
GCD Galvanostatic Charge-Discharge  
HOMO Highest Occupied Molecular Orbital  
HRTEM High-Resolution Transmission Electron Microscopy  
HSC Hybrid Supercapacitor  
IL Ionic Liquid  
IUPAC International Union of Pure and Applied Chemistry  
LIB Lithium-Ion Battery  
LMB Lithium Metal Battery  
LUMO Lowest Unoccupied Molecular Orbital  
MIL Materials Institute Lavoisier  
MOF Metal-Organic Framework  
MWCNT Multi-Walled Carbon Nanotube  
NDI Naphthalenediimide  
NMP N-Methyl-2-pyrrolidone  
NMR Nuclear Magnetic Resonance  
NP Nanoparticle  
PANI Polyaniline  
PBA Prussian Blue Analog  
PCP Porous Coordination Polymer  
PTFE Polytetrafluoroethylene (Teflon)  
PVDF Polyvinylidene Fluoride  
PXRD Powder X-ray Diffraction  
rGO Reduced Graphene Oxide  
RS Raman Spectroscopy  
SBU Secondary Building Unit  
SC Supercapacitor  
SEI Solid Electrolyte Interphase  
SEM Scanning Electron Microscopy  
SHE Standard Hydrogen Electrode  
SOC State of Charge  
SSA Specific Surface Area  
TGA Thermogravimetric Analysis  
TPA Tetrakis(4-aminophenyl)-1,4-phenylenediamine  
UV-Vis Ultraviolet-Visible Spectroscopy  
XPS X-ray Photoelectron Spectroscopy

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XRD X-ray Diffraction

ZIB Zinc-Ion Battery

ZnHSC Zinc-Ion Hybrid Supercapacitor

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## Chemical and Electrochemical Symbols

### II Symbol Description (Unit)

|              |                                                                  |
|--------------|------------------------------------------------------------------|
| $A$          | Effective area / Surface area of the electrode ( $\text{m}^2$ )  |
| $a$          | Constant in power law                                            |
| $b$          | Exponent in power law (determines capacitive/diffusion behavior) |
| $C$          | Capacitance (F/g or F)                                           |
| $c$          | Concentration of electrolyte ( $\text{mol cm}^3$ )               |
| $D$          | Grain size / Diffusion coefficient ( $\text{m}^2/\text{s}$ )     |
| $d$          | Inter-planar spacing / Distance (nm, $\text{\AA}$ )              |
| $E_B$        | Binding energy (eV)                                              |
| $E_{kin}$    | Kinetic energy of ejected electron (eV)                          |
| $F$          | Faraday constant ( $96485 \text{ C mol}^{-1}$ )                  |
| $f$          | Frequency (Hz)                                                   |
| $h$          | Planck's constant ( $\text{eV}\cdot\text{s}$ )                   |
| $I$          | Current (A)                                                      |
| $i$          | Current density (A/g or $\text{mA}/\text{cm}^2$ )                |
| $J$          | Current density (A/g)                                            |
| $k$          | Shape constant (Debye-Scherrer)                                  |
| $M_w$        | Molecular weight ( $\text{g mol}^{-1}$ )                         |
| $m$          | Mass of active material (g)                                      |
| $n$          | Order of diffraction / Number of electrons transferred           |
| $Q$          | Capacity ( $\text{mAh}/\text{g}$ ) / CPE constant                |
| $R$          | Gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )       |
| $R_{CT}$     | Charge transfer resistance ( $\Omega$ )                          |
| $R_S$        | Internal/Series resistance ( $\Omega$ )                          |
| $T$          | Absolute temperature (K)                                         |
| $t$          | Discharge time (h or s)                                          |
| $W_f$        | Work function of the spectrometer (eV)                           |
| $Z$          | Impedance ( $\Omega$ )                                           |
| $Z'$         | Real part of impedance ( $\Omega$ )                              |
| $Z''$        | Imaginary part of impedance ( $\Omega$ )                         |
| $\beta$      | Full width at half maximum (FWHM) (radians)                      |
| $\Delta t$   | Discharge time (s)                                               |
| $\Delta V$   | Voltage window (V)                                               |
| $\delta$     | Warburg coefficient ( $\Omega \text{ s}^{1/2}$ )                 |
| $\epsilon_0$ | Permittivity in vacuum                                           |

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$\epsilon_r$  Relative permittivity  
 $\eta$  Overpotential (V)  
 $\theta$  Bragg's angle / Diffracting angle ( $^\circ$ )  
 $\lambda$  Wavelength ( $\text{\AA}$ , nm)  
 $\nu$  Scan rate / Frequency (V/s, Hz)  
 $\pi$  Pi constant (3.14159)  
 $\sigma$  Electrical conductivity (S/m)  
 $\tau$  Time constant  
 $\varphi$  Phase angle ( $^\circ$  or rad)  
 $\omega$  Angular frequency ( $\text{rad s}^{-1}$ )

# Contents

|                                                                                                                                 |            |
|---------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>Acknowledgements</b> . . . . .                                                                                               | <b>ii</b>  |
| <b>Abstract</b> . . . . .                                                                                                       | <b>iii</b> |
| <b>Streszczenie</b> . . . . .                                                                                                   | <b>vi</b>  |
| <b>Chapter 1 – Introduction</b> . . . . .                                                                                       | <b>1</b>   |
| 1.1. Global Energy Storage Challenges and the Need for Sustainable Advanced Energy Storage Systems (ESSs) . . . . .             | 1          |
| 1.2. Electrochemical Energy Storage Technologies: Batteries, Supercapacitors, and Hybrid Devices . . . . .                      | 3          |
| 1.2.1. Batteries . . . . .                                                                                                      | 4          |
| 1.2.2. Supercapacitors . . . . .                                                                                                | 6          |
| 1.2.3. The Hybrid Devices . . . . .                                                                                             | 8          |
| 1.3. Limitations of Conventional LIBs and the Shift Toward Next-Generation Chemistries . . . . .                                | 10         |
| 1.3.1. Structure and working Principle of LIBs . . . . .                                                                        | 11         |
| 1.3.2. Limitations and Challenges . . . . .                                                                                     | 12         |
| 1.4. Lithium Metal Batteries (LMBs): High-Energy Promises and Key Challenges                                                    | 15         |
| 1.4.1. Working Principle of LMBs . . . . .                                                                                      | 15         |
| 1.4.2. Fundamental Advantages . . . . .                                                                                         | 16         |
| 1.4.3. Key Challenges . . . . .                                                                                                 | 17         |
| 1.5. Zinc-Ion Hybrid Supercapacitors (ZnHSCs): Performance Advantages and Cathode Design Requirements . . . . .                 | 20         |
| 1.5.1. Operating Principle . . . . .                                                                                            | 23         |
| 1.5.2. Performance advantages . . . . .                                                                                         | 25         |
| 1.5.3. Cathode Design Requirements . . . . .                                                                                    | 27         |
| 1.6. Trivalent Aluminum-Ion Batteries (AIBs): Materials Rationale, Charge Storage Complexity, and Cathode Constraints . . . . . | 29         |
| 1.6.1. Working Principle . . . . .                                                                                              | 31         |

|                                                                                                    |           |
|----------------------------------------------------------------------------------------------------|-----------|
| 1.6.2. Charge Storage Complexity in AIBs . . . . .                                                 | 33        |
| 1.6.3. Performance Advantages . . . . .                                                            | 36        |
| 1.6.4. Cathode Constraints . . . . .                                                               | 37        |
| 1.7. Cathode Materials as a Central Bottleneck in LMBs, ZnHSCs, and AIBs . .                       | 38        |
| 1.8. Metal Organic Frameworks (MOFs): Structural Features, Electrochemical<br>Advantages . . . . . | 41        |
| 1.8.1. Development Of Porous materials . . . . .                                                   | 41        |
| 1.8.2. Development of MOFs . . . . .                                                               | 43        |
| 1.8.3. Structural Features . . . . .                                                               | 44        |
| 1.8.4. MOFs as Cathode for various Energy Storage Devices . . . . .                                | 45        |
| 1.8.5. Pristine MOF as cathode material for Lithium Batteries . . . . .                            | 46        |
| 1.8.6. MOF derivatives and composite cathodes for Lithium batteries . . . . .                      | 48        |
| 1.8.7. Pristine MOFs for ZnHSCs . . . . .                                                          | 51        |
| 1.8.8. MOFs derivatives for ZnHSCs . . . . .                                                       | 53        |
| 1.9. Covalent Organic Frameworks (COFs) . . . . .                                                  | 57        |
| 1.9.1. Structural Features of COFs . . . . .                                                       | 58        |
| 1.9.2. COFs electrodes for Energy storage devices . . . . .                                        | 59        |
| 1.9.3. COFs cathodes in AIBs . . . . .                                                             | 60        |
| 1.10. Research Objectives and contents . . . . .                                                   | 63        |
| <b>Chapter 2 – Characterization Techniques . . . . .</b>                                           | <b>65</b> |
| 2.1. Qualitative Characterizations . . . . .                                                       | 65        |
| 2.1.1. X-Ray Diffraction . . . . .                                                                 | 65        |
| 2.1.2. Raman Spectroscopy . . . . .                                                                | 67        |
| 2.1.3. Fourier Transform Infra-Red Spectroscopy (FTIR) . . . . .                                   | 70        |
| 2.1.4. X-Ray Photon Spectroscopy (XPS) . . . . .                                                   | 71        |
| 2.1.5. Thermogravimetric analysis (TGA) . . . . .                                                  | 73        |
| 2.2. Morphological Characterizations . . . . .                                                     | 75        |
| 2.2.1. Scanning Electron Microscopy (SEM) . . . . .                                                | 75        |
| 2.3. Electrochemical Characterizations . . . . .                                                   | 76        |
| 2.3.1. Cyclic Voltammetry (CV) . . . . .                                                           | 77        |
| 2.3.2. Galvanostatic Charge-Discharge (GCD) . . . . .                                              | 78        |
| 2.3.3. Electrochemical Impedance Spectroscopy (EIS) . . . . .                                      | 80        |
| 2.4. Postmortem and Ex situ characterizations . . . . .                                            | 83        |
| 2.5. Instrumental techniques used for characterizations of experimental section .                  | 84        |
| 2.5.1. Chapter 3 . . . . .                                                                         | 84        |
| 2.5.2. Chapter 4 . . . . .                                                                         | 86        |

|                                                                                                                                                              |            |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| 2.5.3. Chapter 5 . . . . .                                                                                                                                   | 86         |
| <b>Chapter 3 – Dual metal–organic framework (D-MOF) based on Mn–Fe and trimesic acid as a high-performance cathode for lithium metal batteries . . . . .</b> | <b>89</b>  |
| 3.1. Introduction . . . . .                                                                                                                                  | 90         |
| 3.2. Experimental Section . . . . .                                                                                                                          | 91         |
| 3.2.1. Synthesis of Mn-Fe-BTC DMOF . . . . .                                                                                                                 | 91         |
| 3.2.2. Preparation of Electrode material . . . . .                                                                                                           | 92         |
| 3.2.3. Structural and morphological characterizations . . . . .                                                                                              | 92         |
| 3.3. Results and Discussion . . . . .                                                                                                                        | 93         |
| 3.4. Electrochemical Characterizations . . . . .                                                                                                             | 96         |
| 3.4.1. Results and Discussion . . . . .                                                                                                                      | 96         |
| 3.5. Postmortem Analysis . . . . .                                                                                                                           | 98         |
| 3.6. Conclusion . . . . .                                                                                                                                    | 101        |
| <b>Chapter 4 – Impact of MOF-5 Derived Carbonization Temperature on the Performance of Zinc-Ion Energy Storage . . . . .</b>                                 | <b>102</b> |
| 4.1. Introduction . . . . .                                                                                                                                  | 103        |
| 4.2. Experimental Section . . . . .                                                                                                                          | 104        |
| 4.2.1. Synthesis and carbonization of MOF-5 . . . . .                                                                                                        | 105        |
| 4.2.2. Preparation of Electrode material . . . . .                                                                                                           | 105        |
| 4.2.3. Morphological and Structural characterizations . . . . .                                                                                              | 106        |
| 4.3. Results and Discussion . . . . .                                                                                                                        | 106        |
| 4.4. Electrochemical Characterizations . . . . .                                                                                                             | 114        |
| 4.4.1. Results and Discussion . . . . .                                                                                                                      | 114        |
| 4.5. Conclusion . . . . .                                                                                                                                    | 125        |
| <b>Chapter 5 – A Donor–Acceptor Covalent Organic Framework as an Ambipolar Cathode for High-Performance Aluminum-Ion Energy Storage System . . . . .</b>     | <b>126</b> |
| 5.1. Introduction . . . . .                                                                                                                                  | 127        |
| 5.2. Experimental Section . . . . .                                                                                                                          | 129        |
| 5.2.1. Synthesis of NDI dialdehyde . . . . .                                                                                                                 | 129        |
| 5.2.2. Synthesis of COF TPA-NDI . . . . .                                                                                                                    | 129        |
| 5.2.3. Preparation of Electrode material . . . . .                                                                                                           | 130        |
| 5.2.4. Morphological and Structural characterizations . . . . .                                                                                              | 130        |
| 5.3. Results and Discussion . . . . .                                                                                                                        | 130        |



|                                                             |            |
|-------------------------------------------------------------|------------|
| 5.3.1. PXRD Structural Simulations (DFT) . . . . .          | 134        |
| 5.4. Electrochemical Characterizations . . . . .            | 136        |
| 5.4.1. Results and Discussion . . . . .                     | 136        |
| 5.5. Postmortem Analysis . . . . .                          | 144        |
| 5.6. Electrochemical kinetic analysis . . . . .             | 148        |
| 5.7. Ex situ charge storage mechanism study . . . . .       | 148        |
| 5.8. Density functional theory (DFT) calculations . . . . . | 155        |
| 5.9. Conclusion . . . . .                                   | 158        |
| <b>Chapter 6 – General Conclusion and Outlook . . . . .</b> | <b>159</b> |
| <b>Statement of Work . . . . .</b>                          | <b>164</b> |
| <b>Scientific Achievements . . . . .</b>                    | <b>165</b> |
| <b>Conferences and Internships . . . . .</b>                | <b>167</b> |
| <b>Bibliography . . . . .</b>                               | <b>168</b> |

# List of Figures

|      |                                                                                                                                                                     |    |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.1  | Overview of ESS technology and application [1]                                                                                                                      | 2  |
| 1.2  | Global Battery Storage Capacity Addition 2020-2025 [3]                                                                                                              | 3  |
| 1.3  | Illustration of Batteries, Supercapacitors and Hybrid devices                                                                                                       | 4  |
| 1.4  | Basic setup of the battery (Daniel Cell) [13]                                                                                                                       | 5  |
| 1.5  | Working principle of Supercapacitor [11]                                                                                                                            | 6  |
| 1.6  | Schematic diagram of (a) a EDLC, (b) a pseudocapacitor and (c) a hybrid capacitor. Ref. [19]                                                                        | 7  |
| 1.7  | Schematic diagram of (a) EDLC, (b) pseudo-capacitor (c) a hybrid capacitor along their charge/discharge profile (d,e,f) respectively [22]                           | 9  |
| 1.8  | Modified coin cell of LIBs [33]                                                                                                                                     | 11 |
| 1.9  | Schematic illustration of the lithium intercalation/de-intercalation reaction mechanism in a LIBs non-aqueous electrolytes [33]                                     | 12 |
| 1.10 | Schematic illustration of the principal limitations of conventional LIBs                                                                                            | 14 |
| 1.11 | Configuration of LMBs [44]                                                                                                                                          | 16 |
| 1.12 | LMBs and LIBs energy density comparison [45]                                                                                                                        | 17 |
| 1.13 | LMBs Advantages along key challenges                                                                                                                                | 18 |
| 1.14 | Scheme of dilemma of issues in LMBs [49]                                                                                                                            | 19 |
| 1.15 | 10 years development of ZnHSCs                                                                                                                                      | 21 |
| 1.16 | Working mechanism of ZnHSCs [63]                                                                                                                                    | 23 |
| 1.17 | Schematic illustrations of (a) Capacitor type materials (b) Battery type materials [64]                                                                             | 24 |
| 1.18 | Comparison of volumetric and specific capacities, cost of metals, and redox potentials are considered promising parameters for the battery cathode [71]             | 26 |
| 1.19 | Ragone plots declare the performance comparison of different energy storage devices, capacitors, supercapacitors, batteries, and Zn-ion hybrid supercapacitors [72] | 27 |
| 1.20 | Challenging characteristics of ZnHSCs                                                                                                                               | 28 |
| 1.21 | The key breakthrough of the evolutionary timeline of AIBs                                                                                                           | 31 |
| 1.22 | a-b Schematic configuration of an Aluminum ion cell [90]                                                                                                            | 32 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |    |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.23 | Schematic illustration of chloroaluminate ionic liquid based AIBs using cathodes with different charge storage mechanisms [93] . . . . .                                                                                                                                                                                                                                                                                                                                   | 34 |
| 1.24 | The schematic electrochemical illustration of metal-based cathode of AIB [94] . . . . .                                                                                                                                                                                                                                                                                                                                                                                    | 35 |
| 1.25 | Comparison of (a) abundance, (b) cost, (c) volumetric capacity, (d) gravimetric capacity, (e) density and (f) electrode potential vs. SHE of Li, Na, Mg, K, Zn, Ca and Al [95] . . . . .                                                                                                                                                                                                                                                                                   | 36 |
| 1.26 | Major cathode challenges in AIBs and their impact on electrochemical performance . . . . .                                                                                                                                                                                                                                                                                                                                                                                 | 38 |
| 1.27 | Infographic illustrations of key challenges, materials, and performance bottlenecks of cathodes in LMBs, ZnHSCs, and AIBs . . . . .                                                                                                                                                                                                                                                                                                                                        | 41 |
| 1.28 | Important turning points in the discovery of useful porous materials [83]                                                                                                                                                                                                                                                                                                                                                                                                  | 42 |
| 1.29 | Schematic representation of MOF and construction parts within MOFs [106] . . . . .                                                                                                                                                                                                                                                                                                                                                                                         | 43 |
| 1.30 | Schematic representation of the three generations of porous materials [108]                                                                                                                                                                                                                                                                                                                                                                                                | 44 |
| 1.31 | Different types of MOF prepared by using same organic linker terephthalic acid with different metals [109] . . . . .                                                                                                                                                                                                                                                                                                                                                       | 45 |
| 1.32 | Schematic Illustration of MOF based Materials for Rechargeable Batteries [115]. . . . .                                                                                                                                                                                                                                                                                                                                                                                    | 46 |
| 1.33 | Structure of MIL-101(Fe). a) The SBU (blue, Fe; red, O; stick, C; green, Cl; H is omitted for clarity), b) The windows and pores of MIL-101(Fe) c) First five voltage profiles. d) Differential capacity for the first 5 cycles. e) Cyclic capacity. f) Initial cycle CE when rested for various time intervals between discharge/charge (C/20) [116]. . . . .                                                                                                             | 47 |
| 1.34 | a) Schematic of MOF-derived metal oxide coating over NCM-622. b) Charge/discharge curves at 0.2 C, c) Rate capability, d) Cycling performance of pristine and coated NCM-622 [127] . . . . .                                                                                                                                                                                                                                                                               | 50 |
| 1.35 | Schematic illustrations of a typical EDLC supercapacitor and development strategies of MOFs for [116]. . . . .                                                                                                                                                                                                                                                                                                                                                             | 52 |
| 1.36 | Schematic diagram of the Zn//ZnHCF battery. (b) Rate capability of the Zn//ZnHCF battery, (c) Galvanostatic charge and discharge curves at different current densities of the Zn//ZnHCF-PANI battery, (d) Schematic of the Mn(BTC) cathode//ZIF-8@Zn anode ZIBs. (e) Cycling performance at 1 A g <sup>-1</sup> in 2 M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub> electrolyte, (f) Rate capability of Zn//Mn-H <sub>3</sub> BTC-MOF-4 hybrid battery [149, 150] . . . . . | 54 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |    |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.37 | a) Schematic illustration of MO-ZMO HOs with FESEM/TEM images of Mn-MIL SO, Zn/Mn-MIL SO and MO-ZMO HO samples. (b) Rate performance based on discharging curves, (c) Illustration of the Mn valence state distribution in ZMO QD@C. (d) FTIR spectra and (e) long-term cycle test of ZMO QD@C at $1 \text{ A g}^{-1}$ [150] . . . . .                                                                                                                                                                                                                                                  | 55 |
| 1.38 | Synthesis of the first COF (COF-1) by self-condensation of 1,4-benzenediboronic acid . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 57 |
| 1.39 | Basic topological diagrams for the COFs with hexagonal pores [175] . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 58 |
| 1.40 | Basic topologies for designing 2D COFs and 3D [180] . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 59 |
| 1.41 | Timeline and progress of COFs for applications in the different ESSs. [181]                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 60 |
| 1.42 | Schematic representation of the synthesis route of TpBpy-COF. b) GCD capacities for AIB in 0.01–2.3 V. [181] . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 61 |
| 1.43 | Schematic illustration of the a) DAQ-TpO/CNT multiple redox sites. b) Galvanostatic discharge/charge profiles of DAQ-TpO/CNT, DAQ-TpO, and CNT [181, 184]. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                      | 62 |
| 2.1  | Schematic representation of X-ray Diffractometer . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 66 |
| 2.2  | Schematic Diagram of X-ray Diffraction (Bragg's Law) . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 66 |
| 2.3  | Types of scattering in Raman Spectroscopy . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 68 |
| 2.4  | Working Principle of FTIR . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 70 |
| 2.5  | Working principle of XPS . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 73 |
| 2.6  | Schematic illustration of TGA setup . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 74 |
| 2.7  | Schematic of SEM setup . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 76 |
| 2.8  | CV shapes for different energy storage devices . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 78 |
| 2.9  | GCD curves for different energy storage devices . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 79 |
| 2.10 | The Impedance Z plotted as a vector quantity using polar coordinates . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 81 |
| 2.11 | Components of an equivalent circuit model and Nyquist plot . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 81 |
| 2.12 | Typical Nyquist plots for various circuits, from simplest to common. (a) pure resistor, R (b) pure capacitor, C (c) R and C in series connection, (d) R and C in parallel connection; (e) R and C in parallel connection and in series with a solution resistance (RS), where $R_{CT}$ denotes the charge transfer resistance of the interface, (f) the same circuit with additional in-series capacitance and (g) Randles–Ershler equivalent circuit, most commonly used for fitting ESS devices, where W stands for Warburg element (diffusion parameter for low frequencies. . . . . | 82 |
| 2.13 | Postmortem and ex-situ characterization of working electrodes . . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 85 |
| 3.1  | Synthetic protocol of Mn-Fe-BTC DMOF. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 92 |

|      |                                                                                                                                                                                                                                                                                                                |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 3.2  | (a) Raman spectra of BTC (black line) and Mn-Fe-BTC (red line), (b) FTIR spectra of BTC (black line) and Mn-Fe-BTC (red line), (c) TGA analysis of Mn-Fe-BTC DMOF. . . . .                                                                                                                                     | 93  |
| 3.3  | (a) SEM image of Mn-Fe-BTC DMOF, (b) N <sub>2</sub> isotherm adsorption/desorption isotherm analysis, (c) pore size distribution, (d) PXRD spectra of BTC (black) and Mn-Fe-BTC DMOF (red). . . . .                                                                                                            | 95  |
| 3.4  | XPS (a) Fe2p and (b) Mn2p spectra of Mn-Fe-BTC DMOF. . . . .                                                                                                                                                                                                                                                   | 95  |
| 3.5  | (a) CV curves for Mn-Fe-BTC DMOF at 0.1 mV/s, (b) Galvanostatic charge-discharge voltage profiles of Mn-Fe-BTC DMOF after 1, 10 and 50 cycles. . . . .                                                                                                                                                         | 97  |
| 3.6  | (a) GCD profiles, (b) specific capacity at different current densities of Mn-Fe-BTC DMOF, (c) EIS analysis, (d) cyclic performances. . . . .                                                                                                                                                                   | 98  |
| 3.7  | XPS (a) Fe2p, (b) Mn2p, and (c) C1s spectra of Mn-Fe-BTC DMOF electrode after 100 charge/discharge cycles. . . . .                                                                                                                                                                                             | 99  |
| 3.8  | (a) Powder XRD of pristine Mn-Fe-BTC DMOF electrode (black) and after 100 charge/discharge cycles (red), (b) SEM image of Mn-Fe-BTC DMOF electrode after 100 cycles, (c) EIS spectra after 1 cycle (black) and 100 cycles (red), (d) CV curves at 0.1 mV/s after 1 cycle (black) and 100 cycles (red). . . . . | 100 |
| 4.1  | Synthetic pathway of CMOF-5_X samples, being X the carbonization temperature. . . . .                                                                                                                                                                                                                          | 105 |
| 4.2  | (a) Raman spectrum, (b) PXRD, (c) nitrogen adsorption/desorption isotherms, and (d) TGA in air curve of pristine MOF-5. . . . .                                                                                                                                                                                | 106 |
| 4.3  | SEM images of a) MOF-5 and CMOF-5 carbonized at: b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C and f) 1000 °C. . . . .                                                                                                                                                                                            | 107 |
| 4.4  | High magnification of SEM images of a) MOF-5 and CMOF-5 carbonized at b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C and f) 1000 °C. . . . .                                                                                                                                                                       | 108 |
| 4.5  | (a) XRD patterns of all CMOF-5 samples, (b) XPS survey spectra of all CMOF-5 samples, (c) TGA in air curves of all CMOF-5 samples. . . .                                                                                                                                                                       | 109 |
| 4.6  | Fitted Raman spectra of all CMOF-5 samples. . . . .                                                                                                                                                                                                                                                            | 111 |
| 4.7  | Ratio of the band intensities a) $I_D/I_G$ , b) $I_{D'}/I_G$ , c) $I_{D''}/I_G$ , d) $I_{D^*}/I_G$ of all CMOF-5 samples. . . . .                                                                                                                                                                              | 112 |
| 4.8  | Nitrogen adsorption/desorption isotherms of all CMOF-5 samples. . . .                                                                                                                                                                                                                                          | 113 |
| 4.9  | (a-e) IV curves and (f) electrical conductivity of all CMOF-5 samples. .                                                                                                                                                                                                                                       | 114 |
| 4.10 | CV curves of all CMOF-5 samples at different scan rates. . . . .                                                                                                                                                                                                                                               | 116 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                        |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.11 | GCD profiles of all CMOF-5 samples at different current densities. . . .                                                                                                                                                                                                                                                                                                                                                               | 117 |
| 4.12 | (a) CV curves at scan rate of 1 mV/s, (b) GCD profiles at a current density of 0.1 A/g, (c) capacitances at different scan rates and (d) Nyquist plots of commercial AC and CMOF-5_1000 sample. . . . .                                                                                                                                                                                                                                | 118 |
| 4.13 | (a) CV curves at scan rate of 1 mV/s, (b) GCD profiles at current density of 0.1 A/g, (c) capacitance values at various scan rates, (d) Nyquist plots for all CMOF-5 samples, cycling stability test after 10000 cycles for (e) CMOF-5_600, (f) CMOF-5_700, (g) CMOF-5_800, (h) CMOF-5_900, and (i) CMOF-5_1000. . . . .                                                                                                               | 119 |
| 4.14 | The equivalent electric circuit models used for fitting the Nyquist plots.                                                                                                                                                                                                                                                                                                                                                             | 121 |
| 4.15 | Ragone Plot for all CMOF-5 samples. . . . .                                                                                                                                                                                                                                                                                                                                                                                            | 122 |
| 4.16 | Fitting plots between $\log(i)$ and $\log(v)$ at various peak currents. Capacitive contribution and diffusion-controlled contribution of all CMOF-5 samples at various scan rates. . . . .                                                                                                                                                                                                                                             | 124 |
| 5.1  | Synthetic illustration for COF TPA-NDI. . . . .                                                                                                                                                                                                                                                                                                                                                                                        | 129 |
| 5.2  | (a) ATR-FTIR spectrum of COF TPA-NDI, NDI and TPA, (b) TGA analysis of COF TPA-NDI. . . . .                                                                                                                                                                                                                                                                                                                                            | 131 |
| 5.3  | (a) $^{13}\text{C}$ CP-MAS NMR; (b) HRTEM; (c) PXRD (inset corresponds to a magnification of the region between $16\text{-}25^\circ$ ) and (d) nitrogen adsorption/desorption measurements and pore size distribution of COF TPA-NDI. . . . .                                                                                                                                                                                          | 131 |
| 5.4  | SEM images of COF TPA-NDI at different magnifications. . . . .                                                                                                                                                                                                                                                                                                                                                                         | 132 |
| 5.5  | (a) EDX spectrum of COF TPA-NDI (inset represents the magnification of 0-1 keV region); (b) SEM image of COF TPA-NDI, (c-e) EDX mapping of element distribution in COF TPA-NDI: (c) carbon, (d) nitrogen, and (e) oxygen. . . . .                                                                                                                                                                                                      | 133 |
| 5.6  | (a-b) HRTEM images of COF TPA-NDI at different magnifications. . .                                                                                                                                                                                                                                                                                                                                                                     | 133 |
| 5.7  | A) Simulated XRD structure of COF TPA-NDI. a) view of AA symmetry along c; b) view of AA symmetry along b; c) view of AA symmetry along a. B) Simulated XRD structure of COF TPA-NDI. a) view of AB symmetry along c; b) view of AB symmetry along b; c) view of AB symmetry along a, C) Experimental (black line), simulated AA stacking (blue line) and simulated AB stacking (red line) PXRD diffractograms of COF TPA-NDI. . . . . | 135 |
| 5.8  | The experimental powder XRD pattern and their Pawley refinement for AA-stacking (a) and AB-stacking (b). . . . .                                                                                                                                                                                                                                                                                                                       | 135 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |     |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.9  | (a) Scheme of COF TPA-NDI    EMImCl/AlCl <sub>3</sub>    Al energy storage system; (b) CV curve at 1 mV/s; (c) GCD profiles at various current densities; (d) specific charge capacity (blue points), specific discharge capacity (black points) and coulombic efficiency (red points) at various current densities; (e) Nyquist plot; (f) long-term cycling performance of COF TPA-NDI as cathode in Al-ESS at current density 5 A/g. . . . .                                                              | 137 |
| 5.10 | Chemical structure of NDI-TPA COF based on NDI and TPA redox-active units with their corresponding molecular weight and number of electrons transferred in redox reactions. . . . .                                                                                                                                                                                                                                                                                                                         | 139 |
| 5.11 | SOC retention of the COF TPA-NDI electrode as a function of current density. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                        | 140 |
| 5.12 | The equivalent electric circuit models used for fitting the Nyquist plot. .                                                                                                                                                                                                                                                                                                                                                                                                                                 | 141 |
| 5.13 | Tauc plot for NDI, TPA and COF TPA-NDI. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 141 |
| 5.14 | Electrochemical performance comparison of COF TPA-NDI electrodes with and without conductive carbon additive (Super P). (a) CV profiles at 1 mV/s for electrodes with Super P (red curve) and without Super P (black curve). (b) CV profiles recorded at different scan rates, (c) rate capability and corresponding coulombic efficiency at increasing current densities and (d) GCD profiles at different current densities of COF TPA-NDI electrodes without conductive carbon additive (Super P). . . . | 142 |
| 5.15 | Corresponding linear relation between $\omega^{-1/2}$ and $Z'$ in the low frequency region of the Nyquist plot of COF TPA-NDI. . . . .                                                                                                                                                                                                                                                                                                                                                                      | 143 |
| 5.16 | SEM images of COF TPA-NDI electrode after 5000 charge/discharge cycles at different magnifications. . . . .                                                                                                                                                                                                                                                                                                                                                                                                 | 145 |
| 5.17 | SEM image of COF TPA-NDI electrode after 5000 charge/discharge cycles. EDX mapping of element distribution in COF TPA-NDI electrode after 5000 charge/discharge cycles: (b) carbon, (c) nitrogen and (d) oxygen. . . . .                                                                                                                                                                                                                                                                                    | 146 |
| 5.18 | EDX spectra of COF TPA-NDI electrodes: pristine (black spectrum) and after 5000 charge/discharge cycles (red spectrum). . . . .                                                                                                                                                                                                                                                                                                                                                                             | 147 |
| 5.19 | Ragone plot for COF TPA-NDI employed in Al-ESS. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 147 |
| 5.20 | (a) CV curve of COF TPA-NDI recorded at various scan rates; (b) fitting plots between $\log(i)$ and $\log(v)$ at various peak currents; (c) capacitive and diffusion-controlled contributions at various scan rates. . . . .                                                                                                                                                                                                                                                                                | 149 |
| 5.21 | (a-e) Capacitive contribution and diffusion-controlled contribution of COF TPA-NDI fraction for the CV curves recorded at different scan rates.                                                                                                                                                                                                                                                                                                                                                             | 150 |

|      |                                                                                                                                                                                                                                                                     |     |
|------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.22 | PXRD diffractogram of COF TPA-NDI in pristine, discharged, charged states, and Super P. . . . .                                                                                                                                                                     | 151 |
| 5.23 | HRXPS of COF TPA-NDI electron in pristine, discharge and charged states for (a) Cl2p; (b) O1s; (c) C1s; (d) N1s. (e) schematic illustration of proposed charged storage mechanism. . . . .                                                                          | 153 |
| 5.24 | XPS (a) Survey and (b) Al2p spectra of COF TPA-NDI in pristine, discharged and charged form. . . . .                                                                                                                                                                | 154 |
| 5.25 | TPA-NDI unit employed for DFT calculations. Red and blue circles correspond to pore regions explored for studying the interaction between the unit model and anions and cations, respectively. . . . .                                                              | 156 |
| 5.26 | (a) ESP of TPA-NDI repeating unit in charged state, neutral state and discharged state; (b) corresponding binding energy of the most stable TPA-NDI repeating unit in charged state, neutral state and discharged state with the corresponding counterions. . . . . | 157 |
| 5.27 | HOMO-LUMO energy gaps (in eV) for the isolated TPA-NDI unit (in black colour) and for the charged (left) and discharged (right) states interacting with anions and cations, respectively. . . . .                                                                   | 157 |



# Chapter 1

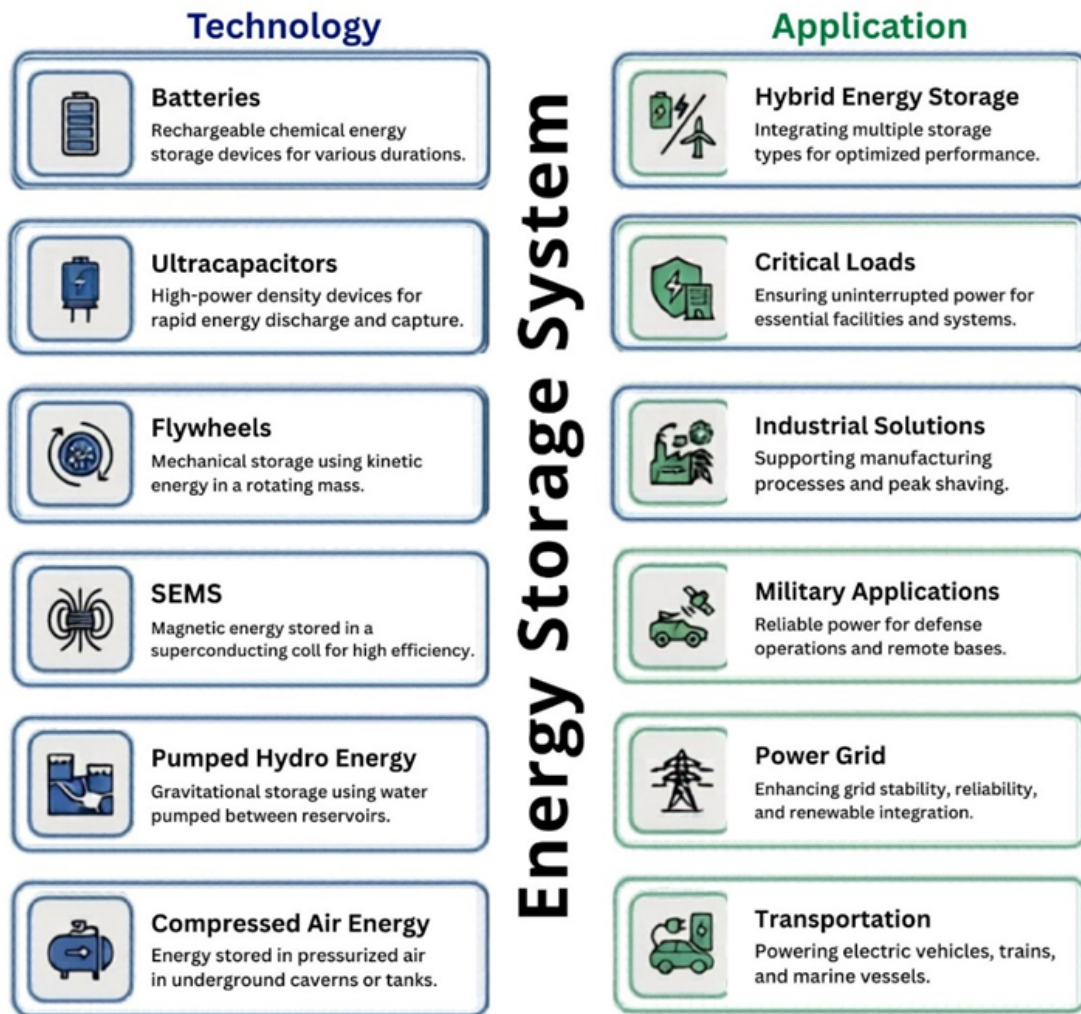
## Introduction

### 1.1 Global Energy Storage Challenges and the Need for Sustainable Advanced Energy Storage Systems (ESSs)

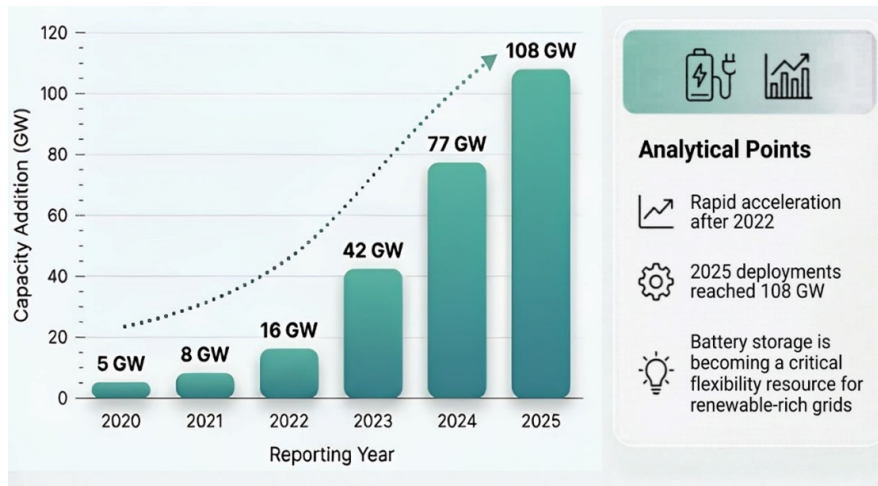
*“The stone age didn’t end because we ran out of stones. It ended because we found something better.” — Sheikh Ahmed Zaki Yamani*

The increasing concern of climate change coupled with massive depletion and consumption of fossil fuels has prompted global shift towards renewable sources of energy [1]. As of 2016, fossil fuels continue to contribute approximately two-thirds of global electricity production, significantly increasing atmospheric ( $\text{CO}_2$ ) levels beyond 400 ppmv, with emissions projected to rise progressively between 2015 and 2040 [2]. Consequently, significant emphasis has been placed on the transition towards sustainable, environmentally friendly, economically viable, and safe sources of renewable energy such as hydropower, geothermal energy, and solar energy. Figure 1.1 illustrates an overview of major energy storage technologies and their key application domains in modern energy systems. This contemporary energy transition has made storage a structural requirement rather than a technical supplement. As variable renewable sources such as solar and wind expand, electricity production does not align with demand, while electrified transport and distributed systems create more complex load profiles. Under these conditions, storage technologies, especially batteries as identified by the International Energy Agency (2024) [3], are essential to maintain reliability, flexibility, resilience, renewable integration, and decentralized electricity access. As illustrated in Figure 1.2, the global addition of battery storage capacity increased dramatically from 5 GW in 2020 to 108 GW in 2025, highlighting the accelerating integration of renewable

energy into modern grids.



**Figure 1.1:** Overview of ESS technology and application [1]



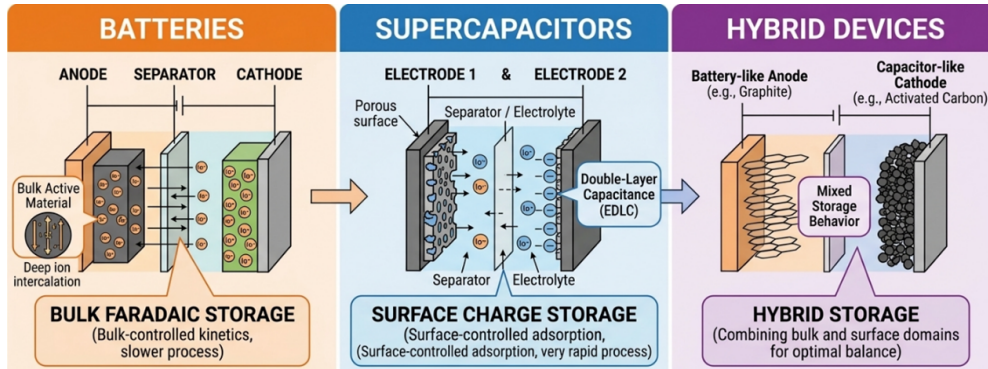
**Figure 1.2:** Global Battery Storage Capacity Addition 2020-2025 [3]

Lithium-ion batteries (LIBs) remain the commercial standard, offering high energy density, round-trip efficiency, and broad applicability across consumer electronics, electric vehicles, and grid storage [4–6]. However, ongoing concerns over thermal safety, critical raw material dependency, and recycling complexity have highlighted the limitations of over-reliance on a single technology platform [7, 8]. These concerns have driven advanced electrochemical storage towards diversification. Hybrid electrochemical technologies, integrating multiple charge carriers, storage modes, and reaction mechanisms are increasingly explored as the traditional battery-capacitor dichotomy proves insufficient [9, 10]. In this context, lithium-metal batteries (LMBs), zinc-ion hybrid supercapacitors (ZnHSCs), and aluminum-ion batteries (AIBs) have emerged to address distinct limitations of conventional LIBs. LMBs pursue higher energy density, ZnHSCs offer safety and rapid charge storage, and AIBs leverage aluminum’s natural abundance and multielectron redox capability [9]. The common challenge across all three systems is translating system-level promise into viable electrode chemistry. The present thesis addresses these challenges through the rational design of cathode materials that are redox-active, structurally stable, and ion-accessible for next-generation energy storage technologies

## 1.2 Electrochemical Energy Storage Technologies: Batteries, Supercapacitors, and Hybrid Devices

Electrochemical energy storage technologies are broadly classified into batteries, supercapacitors and hybrid devices. Liu et al. (2025) [11] consider these electrochemical ESS to be a common electrochemical family as shown in Figure 1.3, these devices differ not

only in energy and power characteristics but also in their dominant storage mechanisms, performance strengths, and practical limitations.



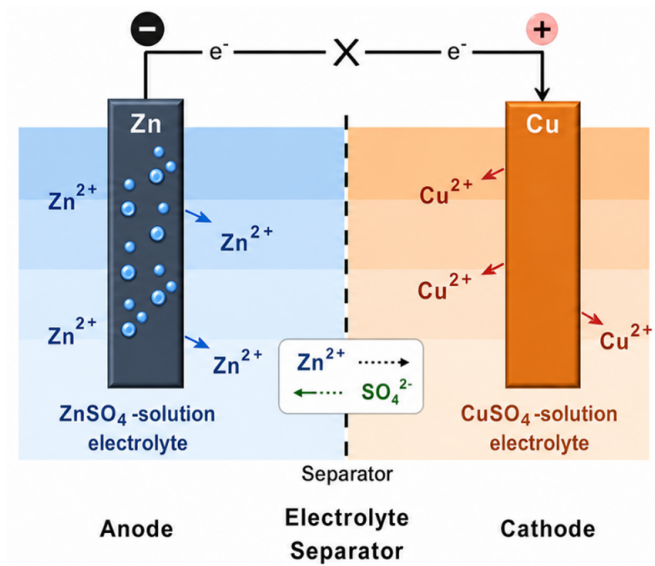
**Figure 1.3:** Illustration of Batteries, Supercapacitors and Hybrid devices

### 1.2.1 Batteries

Benjamin Franklin was the first scientist to coin the term battery when in 1748 [12], he described a series of capacitors connected in some of his experiments with electricity. It is out of this analogy that the term battery came into existence as a means by which a set of devices are used to create a greater effect than each device could individually create. However, today the two Italian scientists, Luigi Galvani and Alessandro Volta are universally acknowledged as fathers of the electrochemical cells. Batteries are closed systems, having charge-transfer mechanism with the anode and cathode and taking an active role in the redox reaction as "active masses". In other words, energy storage and conversion take place in the same compartment. Figure 1.4 demonstrates the basic setup mechanisms of the batteries [11, 13],

They are divided into two categories according to the capacity of electrical recovery when chemical energy is converted fully into electrical energy during discharge such as;

- primary batteries  $\longrightarrow$  *non – rechargeable*
- secondary batteries  $\longrightarrow$  *rechargeable*



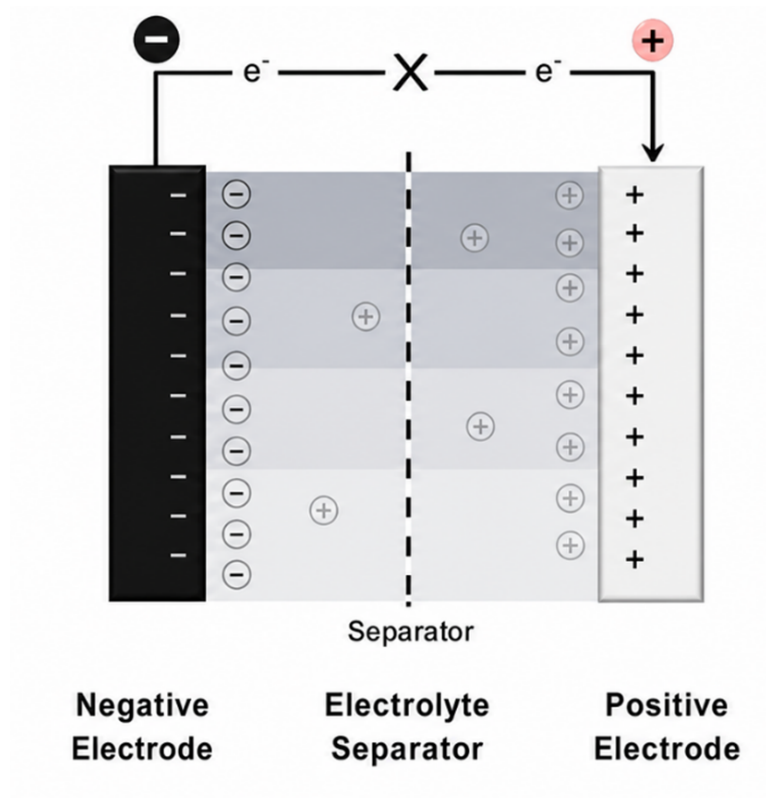
**Figure 1.4:** Basic setup of the battery (Daniel Cell) [13]

The electrochemical reaction cannot be reversed in the primary batteries. Once they are discharged, discarded, disposed of, and chemically recycled. In any case primary batteries are found to have numerous applications because of timeframe of usability, high energy density at low discharge rate, ease of use and compactness. Secondary batteries are known as rechargeable batteries, in which the electrochemical reaction can be reversed by using current through the battery toward the path inverse to that of discharge. They remain the most familiar electrochemical storage devices because they are built around Faradaic charge storage and are therefore capable of delivering comparatively high energy densities. They rely on oxidation and reduction reactions where ions are taken into, though, or across active materials with electrons being exchanged via the external circuit. Practically, this may be intercalation, conversion, alloying or more complicated redox processes in solid-state systems based on the chemistry of the systems. Rudra et al. (2024) [14] describe this difference in simple terms by drawing the line between rechargeable batteries and supercapacitors based on the nature of their storage mechanism, i.e. batteries are those systems which are controlled by Faradaic processes as opposed to those which are controlled by surface-limited electrostatic accumulation. This is obviously the benefit of this arrangement. Storing charge in the bulk of the active material as opposed to just at the interface allows storing a higher volume of energy per unit mass or volume. The fact that the ions must travel through the bulk material, however, makes the process of charging and discharging slower. Structural stress and interfaces degradation may also occur in the interface between the electrode, current collector, separator, and electrolyte due to repeated cycling. On the other hand,

supercapacitors accumulate charge primarily by processes on the surface-controlled mechanism [15]. Thus, batteries are more appropriate when high energy density and sustained energy delivery are required, whereas supercapacitors are more suitable when high power, fast charging, and long cycle life are the priority.

### 1.2.2 Supercapacitors

In the 1990s, NEC company produced and named the capacitor as the "supercapacitor" [16], which has since become the name used worldwide. Supercapacitors follow a different electrochemical process. They put an emphasis on the rate and reversibility of charge accumulation and release at or near the electrode surface, instead of emphasizing the amount of charge that can be stored deep within the electrode. Figure 1.5 represents the basic working mechanisms of the Supercapacitor [17].

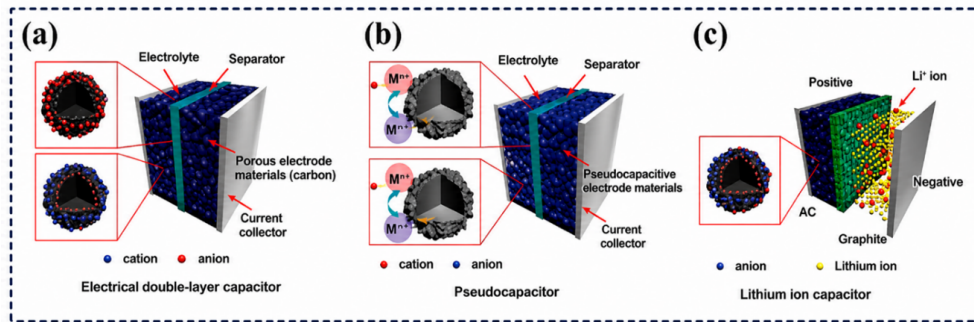


**Figure 1.5:** Working principle of Supercapacitor [11]

As a result of the dominance effects at the surface (and near) the supercapacitors can deliver high power density, high charge and discharge rates, and high cycle life. These characteristics are popular in applications where rapid response is more important than the maximum stored energy, such as regenerative braking, short duration power backup, pulse delivery, and high-rate auxiliary systems. The familiar limitation is lower energy



density relative to batteries, but that limitation should not be treated as a simple weakness. It is the price of a design philosophy that privileges speed, reversibility, and cycling stability over deep bulk storage. The stored energy can be due to either electrostatic ion adsorption, high-speed surface redox reaction, or both. Based on these charge storage mechanisms. Because of the rising demand for energy storage applications and hybrid cars, the market of supercapacitors was forecasted to grow to more than 409 million dollars in 2020 to over 720 million dollars in 2025 [18]. It is generally divided into three main types shown in figure 1.6 including an electric double layer (EDLC) supercapacitor, pseudo-supercapacitor and a hybrid supercapacitor [19]. The types vary based on the symmetries of the electrode material used and the mechanism by which it uses the material to store energy, and electric charge. EDLC supercapacitors holds the majority shares in the commercial market. There are a few pseudo-supercapacitor models which are not well known and spread, and the hybrid supercapacitors are currently limited only to the research area.



**Figure 1.6:** Schematic diagram of (a) a EDLC, (b) a pseudocapacitor and (c) a hybrid capacitor. Ref. [19]

## EDLC

In 1879, Helmholtz came up with the electric double layer theory which was to become the theoretical basis of supercapacitor development [20]. The first proposal of the patent of a small double-layer capacitor as a storage of energy by Becker was made in 1957 with carbon materials having high specific surface area as the electrodes. The SOHIO company published a patent to use carbon materials with high specific surface area to make electric double layer electrodes in 1968 [21]. The EDLCs shown in figure 1.6(a) storage energy is through electrostatic adsorption of the charges on the electrode/electrolyte interfaces without any redox-reaction at the electrode/electrolyte interface during the charge/discharge process shown in Figure 1.7(a). Profiting from the physical electrostatic process, the EDLCs exhibited a complete and fast charge/discharge

procedure, which showed a rapid response potential changing. The EDLCs capacity can be determined in the following manner:

$$C = \frac{\epsilon_r \epsilon_0 A}{d}$$

where  $\epsilon_r$  and  $\epsilon_0$  are relative permittivity and permittivity in vacuum,  $A$  and  $d$  means the effective area and distance between electrode and electrolyte.

### **Pseudo-capacitors**

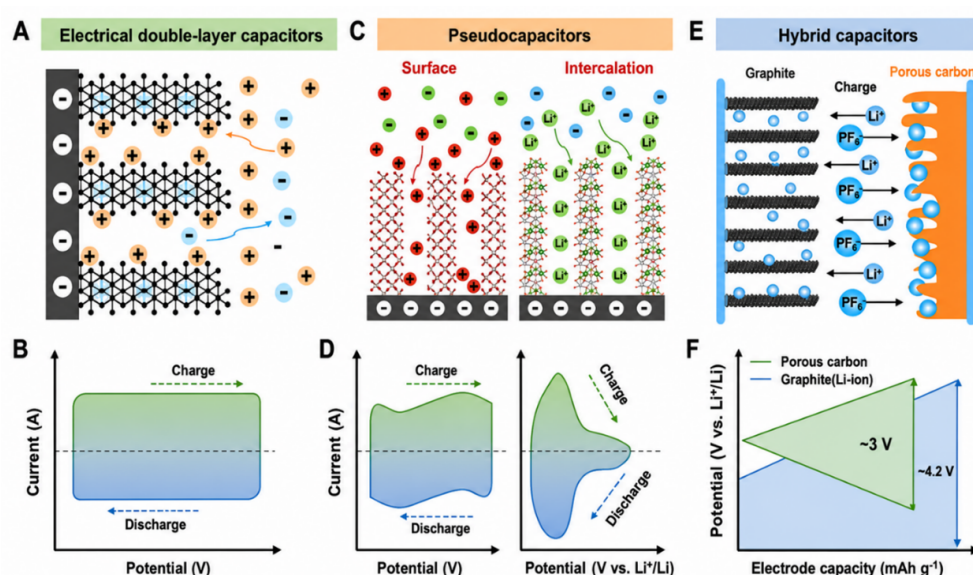
The working principle of pseudo-capacitors relies on fast and reversible Faradaic reactions. The Faraday process provided pseudo-capacitive, like metal oxides and conductivity polymers in figure 1.6(b) [22]. Three major processes can be used to obtain charge storage in pseudo-capacitors. The former reaction is a surface redox reaction, and an ion reacts with active sites on the surface of the electrode. The second is intercalation pseudo-capacitance, in which the electrode is intercalated with ions, but no significant structural changes take place (figure 1.7b). The third is underpotential deposition where the ions get deposited on the electrode surface at more positive potential than their standard deposition potential. When charging is going on, electrolyte ions are transported towards the electrode and undergo reversible redox reactions. During discharging, the opposite process takes place where the stored energy is given out through the external circuit. Pseudo-capacitors can offer higher power density, since they have faster reactions than the slower reactions of the bulk diffusion-controlled reactions in batteries. Simultaneously, since Faradaic charge transfer helps in energy storage, they usually offer greater capacitance compared to EDLCs. In most cases, the pseudo-capacitors had a higher energy density. However, it is still a great challenge for the widen application due to its poor cyclic stability.

### **1.2.3 The Hybrid Devices**

The Hybrid supercapacitors are the advanced electrochemical energy storage devices that combine the charge storage properties of electrical double-layer capacitors and battery-type or pseudocapacitive electrodes. one electrode behaves like a capacitor-type electrode, usually storing charge by the electrostatic attachment of ions to the electrode surface, and the other electrode behaves like a battery-type or pseudocapacitive electrode, storing charge through Faradaic redox reactions [23]. The primary aim of the hybrid supercapacitors is to fill the gap between batteries and conventional supercapacitors. Hybrid supercapacitors are widely categorized into various types because of the high



energy density and the power density which is comprised of asymmetric supercapacitors, battery-type hybrid supercapacitors and lithium-ion capacitors. Asymmetric supercapacitors are typically constructed by using one EDLC-type carbon electrode and one pseudocapacitive electrode. Battery-type electrodes consist of pseudo-capacitive (metal oxide) and capacitor-like electrodes (porous carbon) [24]. Lithium-ion capacitors offer higher energy density than conventional EDLCs. They have a lithium-ion battery-type anode and an activated carbon cathode, while maintaining better power capability than many batteries. Special applications that need high power density and moderate cycling stability can be done with this hybrid supercapacitor (Figure 1.6-1.7c).



**Figure 1.7:** Schematic diagram of (a) EDLC, (b) pseudo-capacitor (c) a hybrid capacitor along their charge/discharge profile (d,e,f) respectively [22]

The difference between batteries and supercapacitors, at the same time introduces a more difficult design problem. Once electrodes operate by different mechanisms, device performance depends on how effectively their kinetics, capacities, voltage ranges, and interfacial behaviors can be balanced. Hybrid devices therefore do not dissolve the battery-supercapacitor distinction [25]. They should be viewed more as purpose-designed systems which attempt to integrate energy-oriented and power-oriented storage in the same electrochemical platform. They demand long-term energy supply, rapid power response, reasonable safety, long life cycle, manufacturability and cost control usually together. One way of attempting to electrochemically respond to that multi-concurrent problem is with hybrid devices. This is evident when Mandal et al. (2025) [26] review hybrid supercapacitor electrode materials and claim that the main challenge here is to reduce the energy-power density distance by developing superior

materials engineering but not by name alone. Their discussion gives vigorous emphasis on formation of nanostructures, heterostructures, conductive frameworks and hybrid morphology of electrodes, not as decorative material approaches, but as viable solutions to the kinetic bottlenecks, and an unstable cycling. Electrochemical storage technologies cannot be discussed merely at the device level. They must also examine through the evolving capabilities of electrode materials. A hybrid architecture can be tuned to privilege of one regime (battery-type) over another (supercapacitor) depending on the application. This is why the study of electrochemical ESS cannot stop at formal definitions. It must proceed into materials chemistry. It is here where the current chapter must shift towards more specific classification and analysis into electrochemistry. Lithium-Ion/metal battery (LIBs, LMBs), zinc-ion hybrid supercapacitors (ZnHSCs) and aluminum-ion battery (AIBs) are not presented as single subjects. They emerge as different attempts to negotiate the same unresolved problem in electrochemical storage, namely, how to achieve stronger energy performance, faster charge handling, longer lifetime, and greater sustainability without transferring the problem to unstable or poorly matched electrode materials.

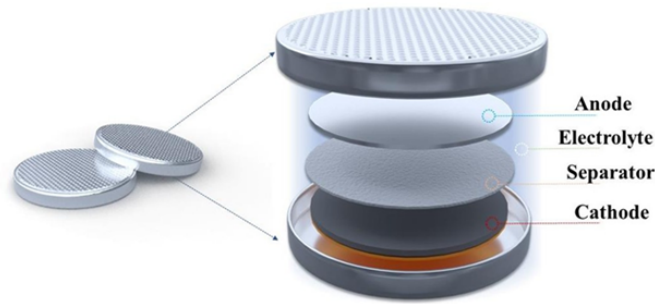
### **1.3 Limitations of Conventional LIBs and the Shift Toward Next-Generation Chemistries**

In 1974, M. Stanley Whitting built the first lithium battery using metallic lithium and titanium disulfide ( $\text{TiS}_2$ ) as working electrodes for fast kinetics [27]. Whittingham and Winn et al. in 1976 investigated the electrochemical properties of the  $\text{Li/TiS}_2$  battery. After that, Jürgen Otto Besenhard discovered reversible charge and discharge reactions between lithium and cathodic oxides in graphite [28]. Some battery cells were assembled at that time, but their capacity quickly declined after several cycles. In 1979, Goodenough and his co-authors reported lithium cobalt oxide ( $\text{LiCoO}_2$ ) as a new cathode with a voltage of 3.9 V vs.  $\text{Li}^+/\text{Li}$  [29]. This was inspired by the earlier work on sodium cobalt oxide ( $\text{Na}_x\text{CoO}_2$ ) by the Rao group [30].  $\text{LiCoO}_2$  has been widely used as a cathode material for decades because it shows greater stability in air and better electrochemical performance than  $\text{NaCoO}_2$ . Additionally, Rachid Yazami's group [31] addressed the fading capability in the early 1980s during their studies on the reversible electrochemical intercalation of lithium in graphite. In the 1980s, many groups dedicated their efforts to experimenting with and developing cathode materials for lithium-ion batteries (LIBs). A commercial breakthrough occurred in 1991 when Sony launched their battery [32]. Since then, many developments and investigations

have been proposed and explored for widespread applications of LIBs.

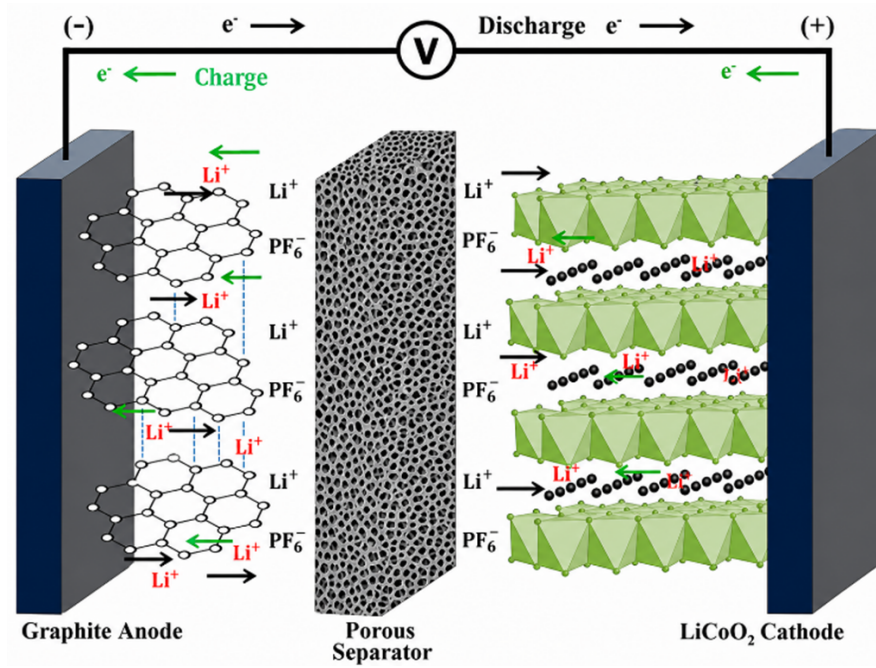
### 1.3.1 Structure and working Principle of LIBs

The basic structure and types of all the lithium-ion batteries (LIBs) and modified coin cell of LIBs have four major parts shown in figure 1.8. [33]



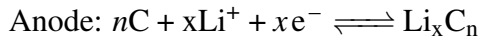
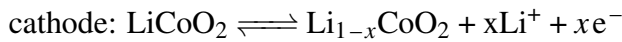
**Figure 1.8:** Modified coin cell of LIBs [33]

As a secondary rechargeable battery, the charging and discharging process of the lithium-ion battery relies on the round-trip transfer of  $\text{Li}^+$  between the two electrodes. Figure 1.9 is a schematic diagram of the working principle of a commercial lithium-ion battery, the positive electrode is  $\text{LiCoO}_2$ , and the layered graphite is used as negative electrode. During discharge, lithium ions and electrons are simultaneously extracted from the positive electrode and transported in opposite directions: lithium ions diffuse into the electrolyte through the electrode/electrolyte interface, and electrons are transferred to the high-voltage state through the contact interface between the electrode and the current collector. Finally, lithium ions and electrons pass through the anode/current collector interface and are stored in the anode material through two different pathways to complete the discharge process. The opposite is the charging process: lithium ions are extracted from the negative electrode and re-inserted into the positive electrode material in a lithium-deficient state through the electrolyte. At the same time, electrons are transferred from the negative electrode to the positive electrode balance voltage through the external circuit. Through the round-trip transfer of lithium ions between the positive and negative electrodes, the process of charging and discharging lithium-ion batteries is constructed shown in figure 1.9.



**Figure 1.9:** Schematic illustration of the lithium intercalation/de-intercalation reaction mechanism in a LIBs non-aqueous electrolytes [33]

The specific reaction formula is as follows



### 1.3.2 Limitations and Challenges

The lithium-ion standardized batteries were not in line with the peak. This featured reversible intercalation chemistry, cycle life that was relatively high, comparatively high gravimetric and volumetric energy density, and an industrial base that could be refined to consumer electronics, electric vehicles and electric storage. Characteristics of LIBs in portable electronic devices are given in Table 1.1.

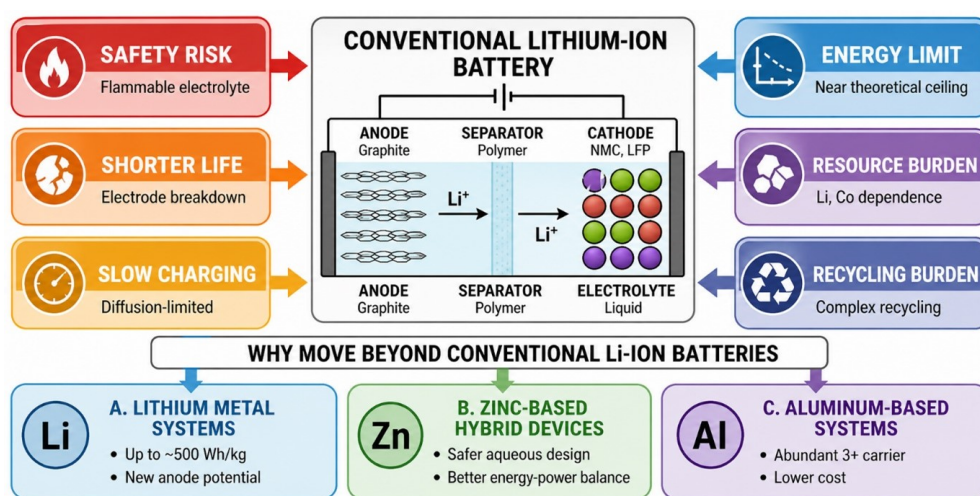
In LIBs, graphite is commercially used as an anode material. It has a theoretical specific capacity of 372 mAh/g [34], which is very low for energy storage. The main reason to use graphite as the anode material is referred to its advantage of having a low potential profile at about 0.1–0.2 V during its discharging and its low and favorable cost range.

**Table 1.1:** Characteristics of LIBs used in Portable electronic devices

| Characteristics                                    | Li-ion battery |
|----------------------------------------------------|----------------|
| Gravimetric energy density ( $\text{Wh kg}^{-1}$ ) | 170-250        |
| Volumetric energy density ( $\text{Wh L}^{-1}$ )   | 350-700        |
| Battery voltage (V)                                | 3.7            |
| Cycle life (to 80% of the initial capacity)        | 500-2000       |
| Self-discharge per month (%)                       | <10            |
| Fast charging time (h)                             | 1 or less      |
| In use since                                       | 1991           |
| Toxicity                                           | Low            |
| Overcharge tolerance                               | Low            |
| Operating temperature range ( $^{\circ}\text{C}$ ) | -20 to 60      |

Xiao et al. (2025) [35] show that concerted movement of  $\text{Li}^+$  along the electrodes, electrolytes, and interfaces is the rate ability of LIBs and that all the paths are bottlenecks in the critical conditions of charging. The issue is thus institutional. The process of sluggish diffusion in solid state, polarization of the concentration at the interfaces, local heating and plating of lithium, are all converged as the charging rates increase. This is why the idea of fast charging is one of the most obvious examples of how traditional LIB architecture poses a barrier to further increases in performance. Chemistry can be improved, certainly, but the improvement requires increasingly sophisticated control of material structure and interfacial kinetics, which is another sign that the present platform is being pushed toward its practical limits. Safety poses an equally serious challenge, and it should not be reduced to a matter of rare catastrophic events. The real problem is that the common LIB design uses flammable liquid electrolytes and the chemically active interfaces the stability of which varies with the age of the battery. Adebajo et al. (2025) emphasize this argument by relating the long-term degradation of cathodes, anodes, and electrolytes to the operational safety, thermal instability, and instability under severe conditions [36]. This degradation hazard correlation has contributed to the push of chemistry and architecture towards achieving intrinsic benefits of safety. Luo et al. (2024) [37] frame this problem by stating that it is precisely because a conventional liquid-electrolyte LIBs cannot provide both that solid-state lithium batteries and the trend towards a more-environmentally-friendly and higher-energy mix of these batteries is possible. A second reason, which is more specific and more practical, is that, when higher energy density becomes a hard imperative, traditional LIB architecture starts to compromise safety margins and interfacial stability is too fast. Peiseler et al. (2024) [38] demonstrate that the carbon footprint of LIBs is highly influenced by sourcing and processing of constituent materials, with lithium, nickel and cobalt being highly variable

in their impact on emissions. Another study by Dixit et al. (2024) [39] takes the debate a step further by considering battery packs as long-lasting storage of locked critical reserves to decide that a large-scale deployment will increase material vulnerability despite an increase in storage capacity. Collectively, these works move the discussion to the next level where LIBs are not merely reliant on rare materials. The challenges to LIB recycling include but are not limited to design barriers, pretreatment bottlenecks, constraints of economics, and uneven infrastructure. It is challenging to ignore the wider picture, conventional LIBs have constraints beyond discharge voltage, specific capacities, or cycle retention. They reveal information about energy production, waste management, and the potential for material manufacturing loops at the global scale.



**Figure 1.10:** Schematic illustration of the principal limitations of conventional LIBs

Vedhanarayanan and Seetha Lakshmi (2024) [40] argue that resource pressure, safety risks associated with liquid electrolytes, and theoretical limits of conventional Li ion chemistry have accelerated serious interest in alternatives such as solid-state batteries, lithium-sulfur systems, and other metal-ion chemistries. Lithium-metal systems respond to the need for increased power density. The hybrid devices based on zinc respond to the issues of safety, power capacity, and price. Aluminum-based systems respond to the demand to find abundant multivalent charge carriers, regardless of their own cathode and electrolyte challenges, represents three distinct responses to the widening gap between the capabilities of conventional LIBs and the increasing demands of modern energy storage as illustrated in Figure 1.10. Each of these electrochemical systems will be investigated and discussed in detail in the experimental chapters.

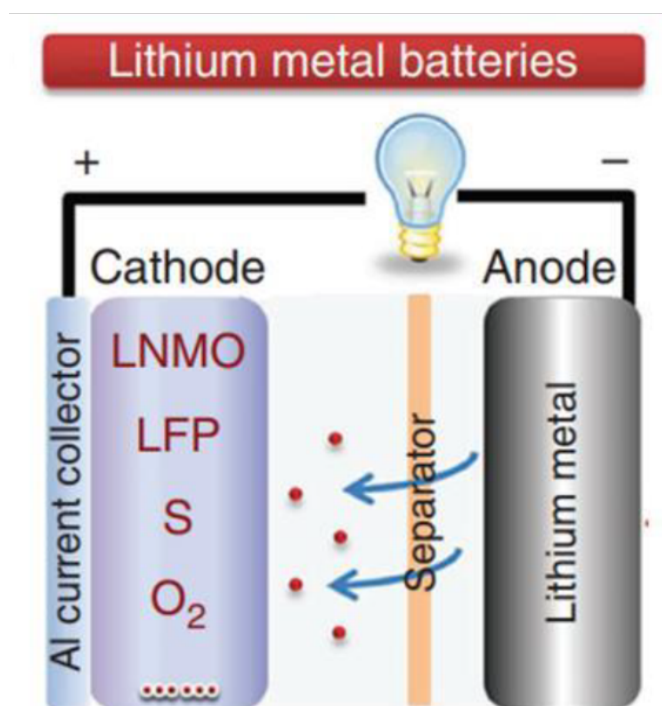
## 1.4 Lithium Metal Batteries (LMBs): High-Energy Promises and Key Challenges

In a conventional LIB there is no Li metal. Graphite is dominantly used as the anode. All  $\text{Li}^+$  ions are originally stored in the cathode side in LIBs. During charge,  $\text{Li}^+$  ions de-intercalate from the cathode lattice and insert into the layered structure of graphite (Fig. 1a). Some  $\text{Li}^+$  cations are irreversibly consumed for the solid electrolyte interphase (SEI) formation on graphite surfaces during charge [34]. Thereby, in the subsequent discharge process, fewer  $\text{Li}^+$  ions return into the NMC structure compared to the amount of  $\text{Li}^+$  ions that leave from the NMC. Accordingly, CE is less than 100%. Lithium metal batteries are of interest as they response a question that traditional lithium-ion chemistry has to some extent ignored. Scientists have been working to incorporate Li metal into next-generation, high-energy-density, rechargeable Li metal batteries with much increased stability over the span of four decades. Primary lithium metal batteries (LMBs) were proposed by Exxon [41,42] as early as the 1970s. However, because of the technology limitations back then, these primary LMBs were non-rechargeable, leading to high cost and severe environmental issues. In the 1980s, Moli Energy designed the first-generation rechargeable LMBs, which possess a high gravimetric energy density of 100-200 Wh  $\text{kg}^{-1}$  and high volumetric energy density of 200-300 Wh  $\text{L}^{-1}$  [43].

### 1.4.1 Working Principle of LMBs

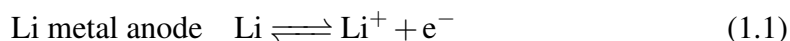
For the formation of  $\text{Li}^+$ , metallic Li loses one electron in the electrolyte to dissolve and during the discharge process it moves towards cathode and intercalate or react with cathode material.  $\text{Li}^+$  disassociates from cathode material during the charging process and migrates via electrolyte and form metallic Li depositing it on the surface of anode /current collector as shown in figure 1.11 [44].





**Figure 1.11:** Configuration of LMBs [44]

The LMBs depend on the electrochemical reaction of lithium metal used as anode as shown in eq 1.1.



During this repeated charge/discharge process, side reactions occur between Li metal and components in electrolyte that reduces Coulombic efficiency and consequently worse cycling stability as compared to LIBs. That's why in LMBs excess Li metal is commonly used to overcome this problem and to balance this unnecessary but inevitable consumption of Li metal.

### 1.4.2 Fundamental Advantages

Most important advantage of LMBs over LIBs is energy density. LIBs have specific energy of  $250 \text{ Wh kg}^{-1}$ , once the anode is replaced by Li metal, it delivers specific energy of  $440 \text{ Wh kg}^{-1}$  shown in figure 1.12. Transition to Li-S and Li-O systems can further boost the specific energy to  $650 \text{ Wh kg}^{-1}$  and  $950 \text{ Wh kg}^{-1}$  respectively. Therefore, Li metal has been widely regarded as the best alternative anode material because to its exceptionally low redox potential ( $-3.040 \text{ V}$  versus a standard hydrogen electrode) and ultrahigh theoretical specific capacity ( $3,860 \text{ mAh g}^{-1}$ ) [45].



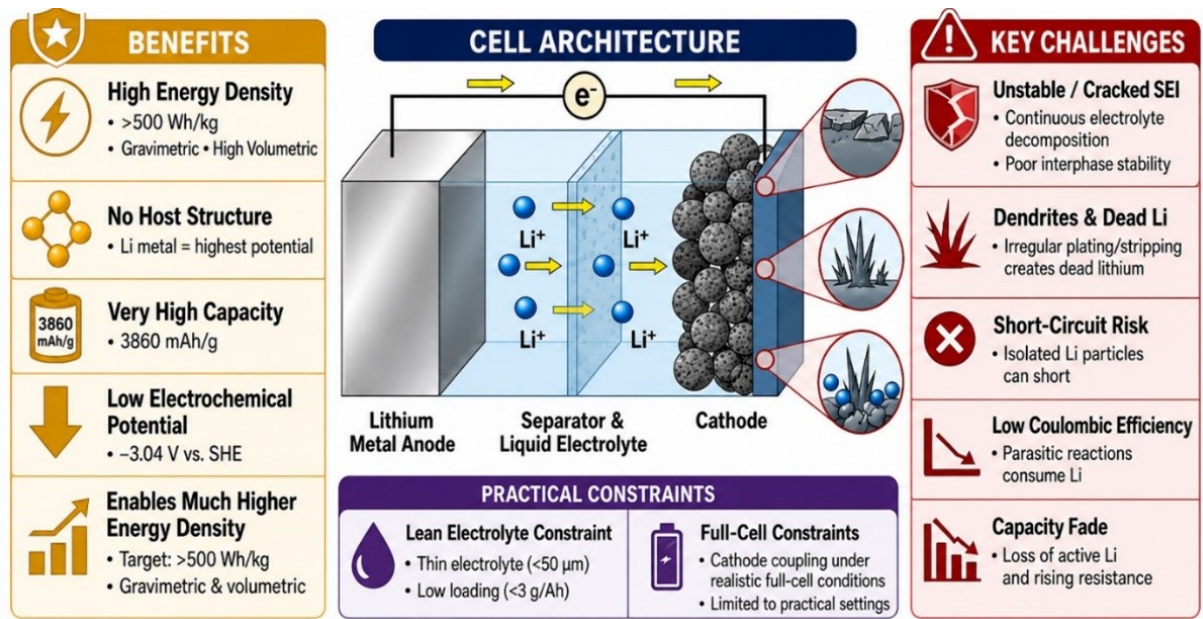


**Figure 1.12:** LMBs and LIBs energy density comparison [45]

The substitution of graphite by metallic lithium alters the balance of mass and volume in the entire cell in a fundamental sense as lithium metal does not require a host structure to store Li and thus eliminates much of the inactive mass of intercalation type anodes. Yang et al. (2024) [46] consider this to be the main reason why LMB technology is still so attractive, as it can potentially provide volumetric energy densities higher than  $1000 \text{ Wh L}^{-1}$  provided the cell can be optimized when one operates in realistic conditions. Burton et al. (2025) [47] reaches a similar conclusion from the perspective of solid-state systems, where lithium metal is viewed as a route to gravimetric and volumetric energy densities that conventional Li-ion configurations struggle to match. The attraction of LMBs, then, is not difficult to understand. Their promise begins with the thermodynamic and structural advantages of lithium metal itself.

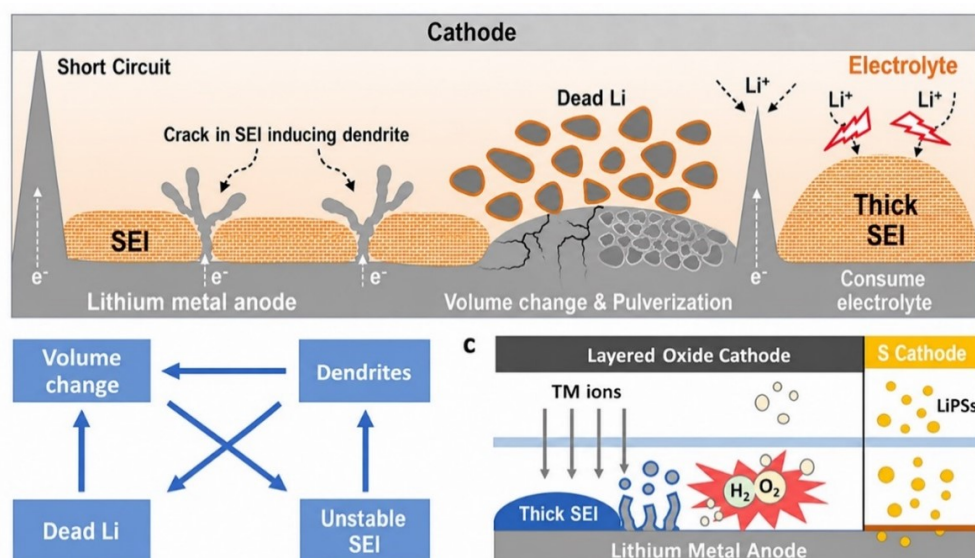
### 1.4.3 Key Challenges

That promise, however, only becomes meaningful when it is transformed from material-level application to full-cell reality. Burton et al demonstrated in 2025 [47] that thickness restriction of lithium is necessary in case of lithium-based batteries to achieve the volumetric goals that were used to justify their existence in the first place. That is to say that lithium metal is not valuable because it is metallic lithium. The anode must be thin, reversible, and manufacturable enough to make the intrinsic benefit of the anode to be viable at the level of the pack. This difference between the promise of theory and the design that can be comprehended is at the core of the problem of LMB and the field has since shifted beyond the euphoric comparisons with graphite towards a more serious dialogue of cell-wide measurements. As shown in figure 1.13, lithium metal batteries combine a strong theoretical energy advantage with a set of tightly coupled interfacial and full-cell challenges that still limit their practical deployment.



**Figure 1.13:** LMBs Advantages along key challenges

The first major obstacle is interfacial instability. Lithium metal is an extremely reactive material, and the reactivity ensures that the electrode is never simply left in the electrolyte as an inert source of current. Wang and Wang (2025) [48] indicate that electrolyte chemistry controls the formation, structure and composition of the solid electrolyte interphase (SEI), or develops to dendritic growth, low coulombic efficiency and continuous side reactions. Dendrites, dead lithium, rising impedance, and electrolyte depletion are not separate anomalies. They are linked manifestations of a chemically unstable interface that cannot sustain highly reversible plating and uncovering over long cycling periods. A closely related issue is that the lithium metal surface does not degrade in a simple or uniform manner. The SEI is spatially heterogeneous, compositionally dynamic, and mechanically fragile under repeated deposition and stripping. Vishweswariah et al. (2025) [49] pointed out that the structural characteristics of the SEI, directly related to efficiency and battery life. They have also specified the formation of dendrites as shown in figure 1.14. So how to stabilize a chemically evolving interface whose failure can be electrochemically affluent over a long period before catastrophic shorting can happen, is one of the most difficult problems in LMB research. In that light, the interphase design is not a supporting subject in LMB research but also one of the conditions according to which the system becomes viable. Cycle life provides another measure of how far LMBs still stand from standard deployment. This is because reversibility with idealized testing conditions talks about what would happen with more realistic behavior under full cells, as real energy storage would demand.



**Figure 1.14:** Scheme of dilemma of issues in LMBs [49]

Liu et al. (2024) [50] discussed accelerated aging in LMBs, lifetime degradation can be learned and understood in response to coupled cell behavior and not reduced to a single failure signature. Their work is significant in that it drives the field out of simplistic diagnostics. The aging of LMBs is no one-parameter story. This challenge becomes even more severe once the battery is evaluated under practical full-cell constraints instead of generous laboratory conditions. Zhang et al. (2024) [51] consider LMBs with Ni-rich layered oxide cathodes and demonstrate that the commercial imperative to reach energy densities beyond  $500 \text{ Wh kg}^{-1}$  is immediately challenged by the severe yet realistic demands, such as lean electrolyte-to-capacity ratios of less than  $3 \text{ g Ah}^{-1}$ , cathode mass loadings of more than  $3 \text{ mAh cm}^{-1}$ . In this case, the lithium metal anode is compelled to react with high-loading, high-voltage cathodes with much stricter interfacial and transport tolerances. This is where most of the apparently robust LMB strategies start to fail. Lithium morphology is not the sole killer of practical lithium metal batteries. They are also constrained by the difficulty of making thin lithium, efficient electrolyte, and cathode operation coexist within one stable cell. There is an implication of that full cell view as to the present thesis. LMB failure cannot be an anode-only cycle life. Cathode behavior is also directly related to lithium-metal stability, particularly when high-energy designs are needed with Ni, Fe, Mn-rich oxides, high-areal loading and limited stack pressure. Cathode strain, contact loss, interface fracture, and electrode-level stress redistribution can reshape anode behavior in ways that make cathode design inseparable from lithium-metal reversibility. For a study concerning MOF- and COF-based cathodes, this point is especially important. The cathode is not a secondary variable in LMB

development. It is part of the control problem. LMBs will continue to be one of the promising paths to high-energy rechargeable systems, due to the ability of lithium metal to provide a negative electrode arrangement that graphite cannot compete with. Yet the electrochemical performance remains constrained by unstable interphases, limited Coulombic efficiency, lithium loss, demanding full-cell conditions, and the need for much firmer integration between electrolyte, anode, and cathode than conventional LIBs require. Therefore, the central objective of Chapter 3, is to develop a dual-metal organic framework-derived cathode to improve cycling stability, suppress dendritic growth and high Coulombic efficiency. That is why LMBs are best understood not as a finished successor to LIBs, but as a high-potential system whose success depends on resolving multiple coupled materials problems at once.

## **1.5 Zinc-Ion Hybrid Supercapacitors (ZnHSCs): Performance Advantages and Cathode Design Requirements**

Mobile electronics and electric vehicles have developed at an accelerated rate in recent times, which have created increased demands on ESS in terms of energy and power densities, stability, safety and reduced cost of production. The alkaline metal, including lithium (Li), sodium (Na), and potassium (K), in the traditional SCs, are highly reactive. Also, organic electrolytes, which are explosive, are a considerable safety hazard. Also, the scarcity and uneven supply of lithium results have contributed to increasing its price. To counter these obstacles, technologies to store divalent ions have been invented as alternatives to new ESS. Compared to monovalent metal ion systems (e.g.  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), divalent metal ion systems (e.g.  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) have several advances, including faster charge transfer, higher capacity and greater energy density. To achieve both features on device, substitution of both SCs and batteries has been suggested as HSCs. The fabrication of HSCs includes a capacitive/pseudocapacitive-electrode and another battery-type Faradic-electrode, and the rest of the parameters are the same as standard SCs. Development of ZnHSCs has only gained projection in the past decade, as shown in Figure 1.15. The development of ZnHSC cathode materials has evolved through several significant research thrusts, each of which explored a specific performance bottleneck, yet key challenges remain unresolved.



**Figure 1.15:** 10 years development of ZnHSCs

Early fundamental work established the basic viability of the ZnHSCs concept. In 2016, Yuheng Tian et al. first assembled a ZnHSC using a zinc anode and oxidized carbon nanotubes as the cathode, with a  $\text{ZnSO}_4/\text{PVA}$  electrolyte, achieving a capacitance of  $53 \text{ F g}^{-1}$ . [52] In 2018, Liubing Dong et al. reported ZnHSC in aqueous zinc sulfate ( $\text{ZnSO}_4$ ), a high safety and ultralong cycle life with active carbon and zinc metal as electrodes. This device demonstrated a capacity of  $121 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  current density with an energy density of  $84 \text{ Wh kg}^{-1}$ . [53] Concurrently, Heng Wang et al. explored ZnHSC of active carbon//Zn in a  $1 \text{ M}$  zinc trifluoromethanesulfonate ( $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ ) electrolyte mixed with acetonitrile (AN). [54] These early works however relied on conventional carbon cathodes with limited surface utilization and no deliberate pore engineering, leaving substantial room for improvement.

A second research approach focused on heteroatom doping and structural carbon engineering to enhance charge storage. In 2019, Haozhe Zhang et al. introduced N-doped porous carbon for ZHSCs, achieving an energy density of  $107 \text{ Wh kg}^{-1}$  at  $4.2 \text{ A g}^{-1}$ . Their work highlighted a pseudocapacitive storage mechanism facilitated by nitrogen dopants on the carbon cathode, forming C-O-Zn bonds. [55] In 2020, Juan Zeng by using an in-plane printing technique obtained flexible solar-charging micro ZnHSCs. [56] After that, Cheng Wang et al. proposed a ZnHSC based on "water-in-salt" hydrogel electrolyte with an energy density of  $271 \text{ Wh kg}^{-1}$  and an outstanding cycling life. [57]. Despite these advances, a persistent gap in this body of work is the challenge of simultaneously achieving high energy density and high power density, as heavily doped or thick carbon electrodes often suffer from sluggish ion transport within their interior pores.

A third thrust explored anode instability through interfacial engineering. In 2022, Yongzheng Zhang et al. extended a spraying MXene-based polypyrrole (MXene-mPPy) layer on a zinc foil, forming a dendrite-free Zn metal anode (MXene-mPPy/Zn) with high charge capabilities. [58]. In 2023 a pseudo-capacitor-type anode was developed by Faqi Ji et.al [59] where polyimide (PNDIE) was directly grown on multiwalled carbon nanotubes (MWCNT) and polythiophene-coated  $\text{Na}_0.55\text{MnO}_2$  carbon cloth-

based battery type cathode (PEDOT- $\text{Na}_0.55\text{MnO}_2/\text{CC}$ ). It offers a lightweight structure and efficient working mechanism, with a energy density of  $10.7\text{ Wh kg}^{-1}$  and high-power density of  $192.2\text{ W kg}^{-1}$ . In 2024 Dandan Li et.al reported a biocompatible thin, wet-adhesive and flexible ZnHSC (0.142mm) [60]. It is composed of gel electrolyte-integrated Zn anode with a MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ )-based cathode. It exhibited an areal capacitance of  $482.58\text{ mF cm}^{-2}$  and an energy density of  $7.37\text{ mWh cm}^{-3}$ . While these approaches demonstrate impressive integration of anode protection and device flexibility, but the focus on cathode-level design and energy density improvements remained largely unexplored.

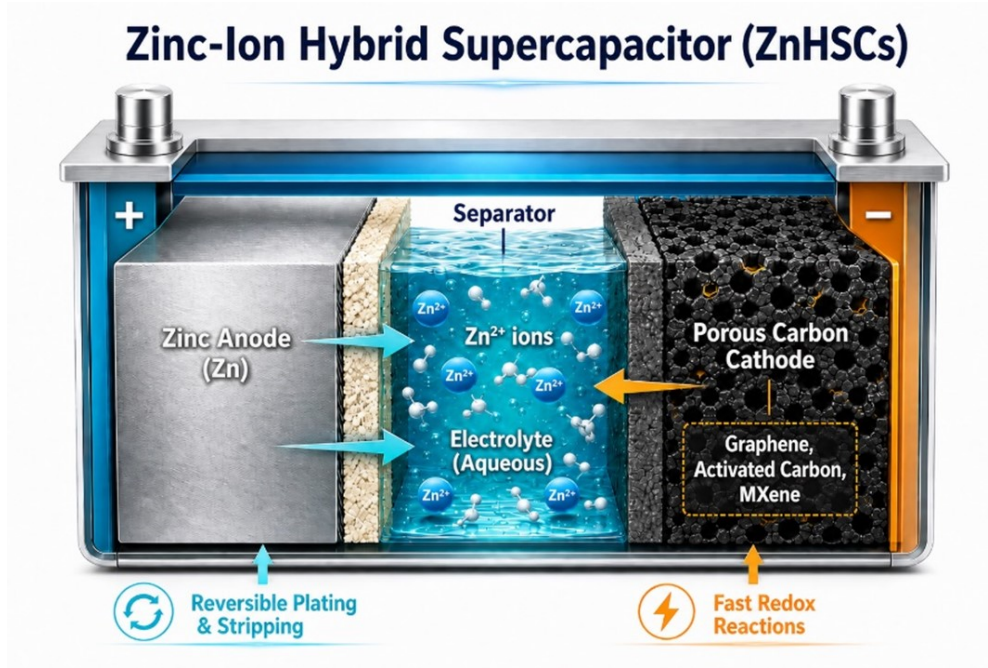
To address the dual challenge of ion diffusion and energy density, more recent efforts have turned toward advanced 2D and porous framework-derived cathode materials Haiping Wang et.al [61] in 2025 presented a ZnHSC with reduced graphene oxide and 3D porous  $\text{K}^+$ -intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$ - ( $\text{K}^+$ - $\text{Ti}_3\text{C}_2\text{T}_x$ -RGO) hydrogel as cathode and Zn foil anode. It exhibited high specific capacitance of  $253.86\text{ Fg}^{-1}$  and an impressive energy density of  $141.03\text{ Whkg}^{-1}$  and power density of  $999.99\text{ Wkg}^{-1}$ . Recently in 2026 Entong Zhou et.al reported a surfactant-modulated MOFs-derived nanocarbon cathodes [62]. They presented sodium dodecyl sulfate (SDS) surfactant-modulated ZIF-8 precursor with porous structure and rich N/O/S heteroatoms, and the resultant nanocarbon cathode delivered capacitance of  $292.5\text{ F/g}$  (50% more than the pure ZIF-8-derived carbon), superior cycling stability with 100% capacitance retention over 7000 charge/discharge cycles. The charge storage mechanism in SDS-modulated ZIF-8-derived nanocarbon cathode is a capacitive process-dominated mechanism, where rich heteroatom sites and hierarchically porous structure promote high-capacity and fast ion storage.

Overall, the literature findings reveals three persistent gaps in ZnHSC cathode development, conventional and doped carbon approaches still struggle to achieve optimized porosity for efficient ion transport, while high energy density cathodes generally suffer from poor rate capability due to limited active-site accessibility at high current densities. Furthermore, although MOF-derived carbons show strong promise, as demonstrated by Zhou et al.[62], a systematic understanding of how precursor chemistry, carbonization conditions, and heteroatom content collectively govern cathode performance remains underdeveloped. These gaps directly motivate the carbonized MOF-5-derived cathode developed in Chapter 4 of this thesis.



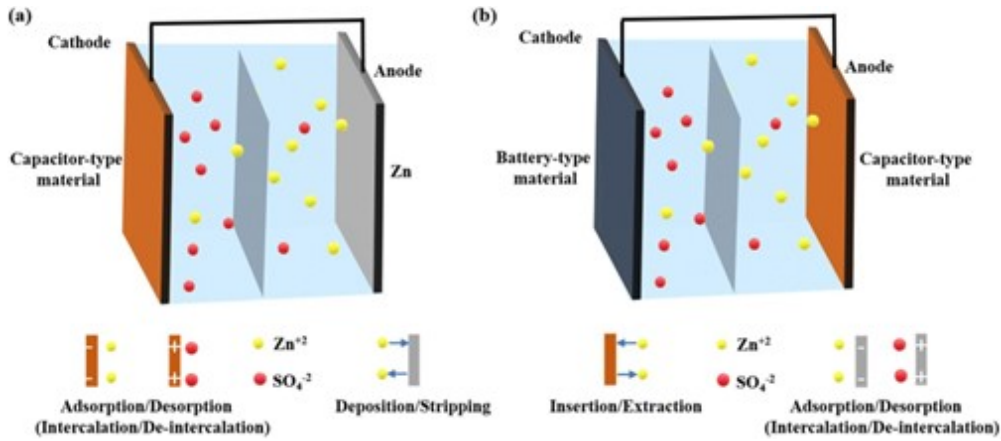
### 1.5.1 Operating Principle

Figure 1.16 follows directly from that asymmetry. In a standard aqueous ZnHSC, zinc is stripped and plated at the negative electrode, and charge is stored at the positive electrode by adsorption, surface redox or ion confinement amongst other fast  $\text{Zn}^{2+}$  accessible processes that are dependent on the material used in each case [63].



**Figure 1.16:** Working mechanism of ZnHSCs [63]

The charge storage mechanism is attained by physical interaction of the surface of the electrode and chemical interaction (redox reaction) by the EDLCs and pseudocapacitors, respectively. These capacitor type working materials are composed of carbon or Pseudocapacitive materials and battery-type electrode materials mainly consists of Zn metal and metal oxides i.e. manganese-based oxides, or vanadium-based oxides, which may offer higher storage capacity than traditional supercapacitors [64]. The visualization of the charge storage mechanism of battery type and capacitor type is presented in figure 1.17.



**Figure 1.17:** Schematic illustrations of (a) Capacitor type materials (b) Battery type materials [64]

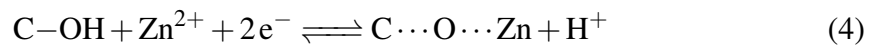
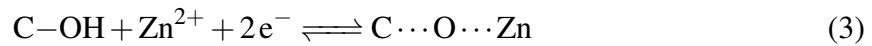
### Capacitor-type materials for ZnHSCs

In the charging mechanism, the anions adsorbed/intercalated on/into the surface-active sites of the cathode electrode, storing the energy by the formation of EDLC/faradaic intercalation. Simultaneously, Zn ions immigrated and deposited onto the Zn anode, which can be described as [65]:



The discharge process is the opposite of this charge mechanism where the  $\text{Zn}^{2+}$  ions and anions move back into the electrolyte, following a reversible deposition/stripping on Zn anode and desorption/de-intercalation on the carbon-based cathode.

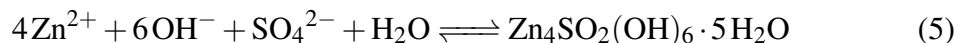
However, the revisionary electrochemical process of carbon-based materials based on the redox reaction of electrolyte ions at the surface/near-surface was proposed by following equations [66]:



The combination of pseudocapacitive and EDLC through the chemical adsorption/desorption contributes to the output energy. Moreover, the side reaction can usually be observed, including the growth of the zinc dendrite, pH changing of the electrolyte



caused by the generation of the  $\text{OH}^-$  group from the  $\text{H}_2\text{O}$  splitting. This process can be described as follows (for example, in  $\text{ZnSO}_4$ ) [67]:

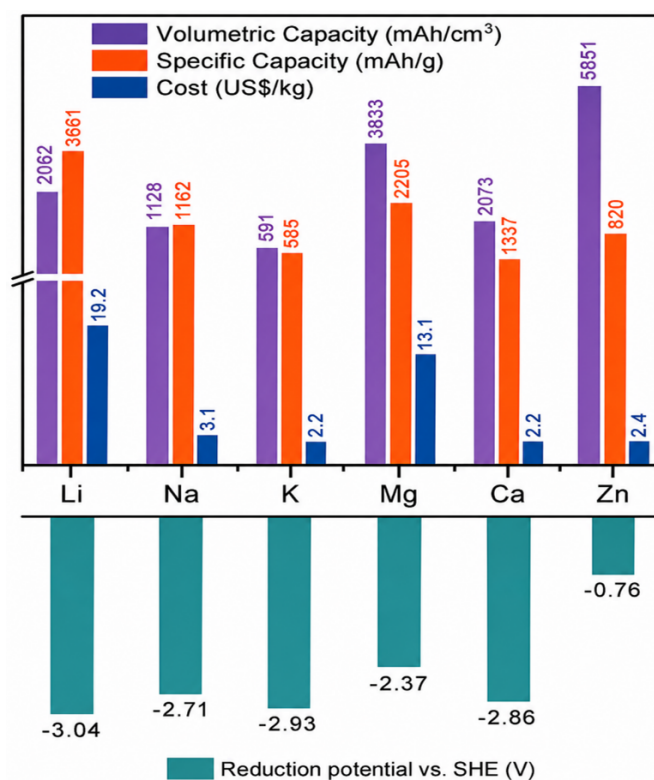


### **Battery-type materials for ZnHSCs**

The battery-type based materials showed a similar charge/discharge mechanism as the capacitor-type. The only difference in the battery-type materials is the storage mechanism of the  $\text{Zn}^{2+}$  through a reversible zinc ions insertion reaction  $\text{MnO}_2$ ) [68], co-insertion mechanism (vanadium (V) oxide ( $\text{V}_2\text{O}_5$ )) [69] or the conversion reaction ( $-\text{MnO}_2$ ) [70].

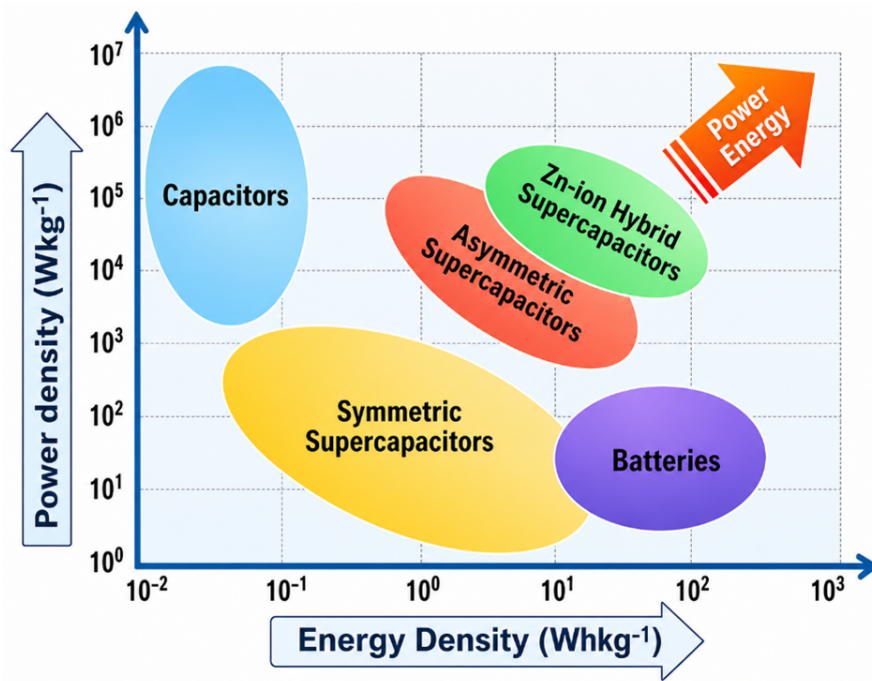
## **1.5.2 Performance advantages**

The attraction of ZnHSCs becomes easier to understand when they are studied against the limitations of both conventional batteries and conventional supercapacitors. ZnHSCs are quite attracting due to some key advantages. It is abundantly available, relatively inexpensive and more important environmentally safe than the flammable organic-based-electrolyte technologies. Meanwhile, the hybrid form provides a path to improved energy storage than an all-capacitor system of purely double-layer capacitor can typically offer, without sacrificing the fast response of capacitive systems. The metallic Zn has outstanding electrochemical properties, such as the low redox potential ( $-0.76\text{ V}$  vs. SHE) and high theoretical capacity ( $820\text{ mAh g}^{-1}$ ) and volumetric capacity ( $5851\text{ mAh cm}^{-3}$ ) [71]. Comparison of volumetric and specific capacities, cost of metals, and redox potentials are shown in figure 1.18.



**Figure 1.18:** Comparison of volumetric and specific capacities, cost of metals, and redox potentials are considered promising parameters for the battery cathode [71]

The ZHSC device is of great importance and maintains similar attractive characteristics to SCs while delivering superior energy density of batteries' level. As compared to monovalent, Zn divalent ions are doubly ionized in nature and only half of the  $\text{Zn}^{2+}$  ions require to be inserted/extracted from a host electrode material to deliver high theoretical capacities. Furthermore, due to the two-electron transfer reaction the utilization of divalent  $\text{Zn}^{2+}$  provides a twofold higher capacity than  $\text{Li}^+$ . In this aspect, comparison of power densities and energy densities of different energy storage devices has been summarized in the Ragone plot shown in figure 1.19 [72].

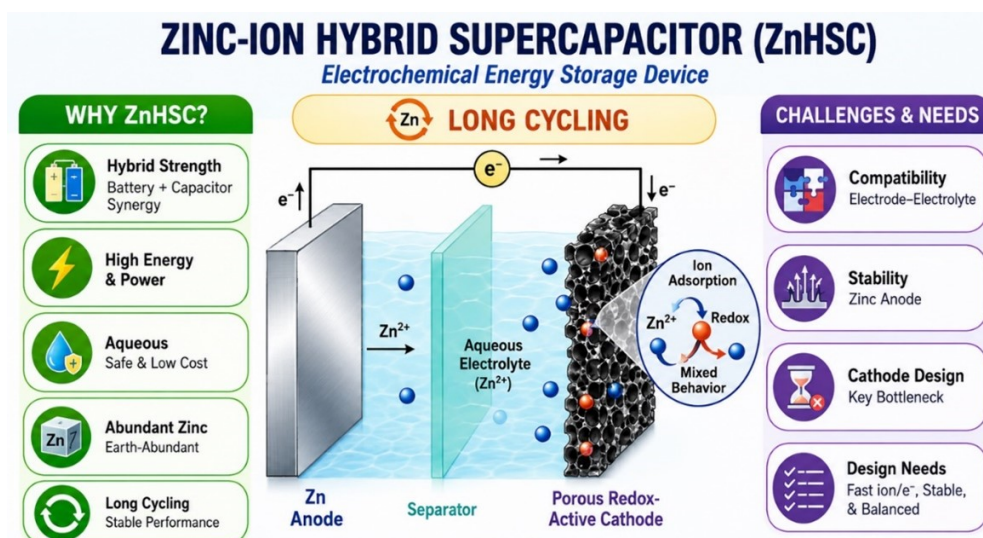


**Figure 1.19:** Ragone plots declare the performance comparison of different energy storage devices, capacitors, supercapacitors, batteries, and Zn-ion hybrid supercapacitors [72]

It is evident that ZHSCs possess considerably higher power density than numerous types of SCs, and the range of energy density is suitable for use in practical applications. However, the energy densities of ZHSCs are less than LIBs; they need to be improved up to the level of LIBs so that ZHSCs can be used for next-generation ESS.

### 1.5.3 Cathode Design Requirements

Key challenges of ZnHSC along with other features are shown in the figure 1.20. Loh et al. (2024) [73] state that in ZnHSCs formation of positive electrodes, the alteration of zinc-anode, as well as the fabrication of electrolytes, all appear to be a single inseparable problem. The cathode is another crucial component of ZHSC and is usually composed of carbon-metal oxides and 2D MXenes based materials.



**Figure 1.20:** Challenging characteristics of ZnHSCs

As during discharge cation ions move from anode to cathode and form electrons. Therefore, the selection of the cathode material is the critical factor to achieve excellent performance of the ZHSCs. The primary function of cathode material is to offer a stable  $Zn^{2+}$  structure that allows it to be chemically linked together with low energy and fast kinetics. Nevertheless, due to significant high atomic weight and large positive polarization of divalent  $Zn^{2+}$ , electrode materials seem ideal for  $Li^+$  ion capacitors found to be unsuitable for ZHSC. To solve this problem for ZHSCs, considerable efforts and reviews were performed by using various cathode materials. However, to meet the commercial demands, high-rate capability and energy density are still insufficient. Therefore, novel approaches for emerging new cathodes based on nanomaterials with improved structural stability are required for better  $Zn^{2+}$  kinetics and fast electron transport.

To achieve cathode materials with diverse and stable morphologies, the structure of the material can be tuned by properly modifying the reaction conditions. Materials with a stable structure during charging/discharging can buffer the volume changes and thereby increase the cycling performance of the materials. In fact, by increasing specific surface area and changing the pore structure, the electric double-layer capacitance performance of a material can be increased, because fast adsorption/desorption reactions and transport of electrolyte ions are only possible with large specific surface area and appropriate pore structure. To enhance pseudocapacitive performance, in the cathode materials heteroatoms are also inserted by various means. The hybrid design strategy can also strengthen the performance of cathodes by incorporating conducting polymers, organic molecules, and metal oxides. These rational material designs enhance the performance

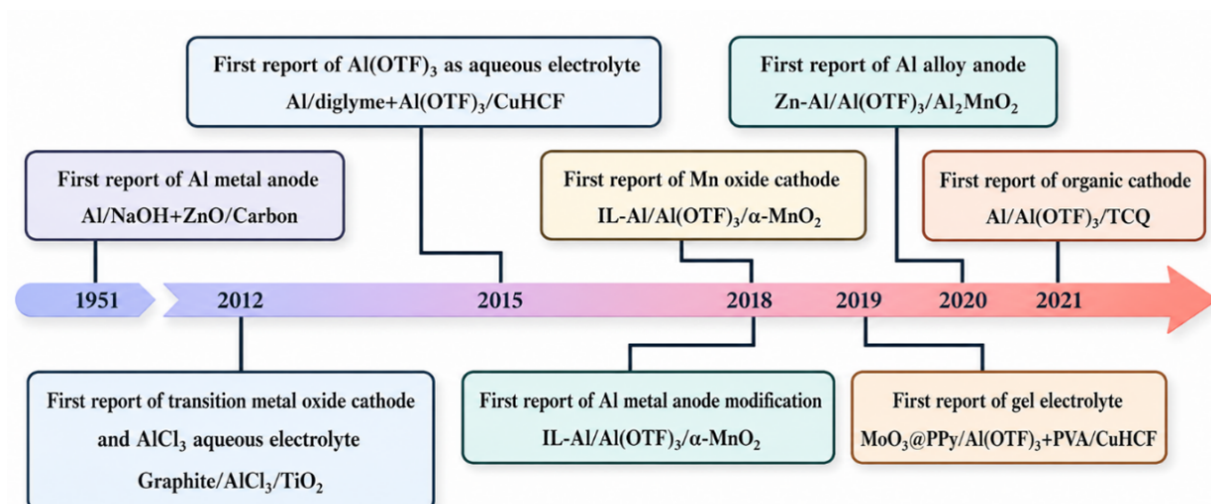
of cathode materials to make them more desirable for practical applications.

The next question that arises as a response to that requirement is: do you want the cathode to act more like a capacitor or like a battery? As Zhu et al. (2025) [74] suggest, the science of ZnHSCs has been progressively moving away from what they refer to as an incompatible principle, i.e., that electrode pairing in capacitors should be driven by either kinetically matching voltage-window coherent performance rather than isolated performance of either side. The energy output of a ZnHSC can potentially be increased by a battery-type cathode, although when its diffusion-limited behavior is too slow the device ceases to benefit from rate advantage which is the trait that convinced hybridization in the first place. A pure, capacitive carbon cathode, in contrast, can maintain fast response and a long life but might render the entire cell deficient in useful energy storage. The cathode design in ZnHSCs is therefore a matter of selective balance rather than maximizing any single property. Redox-active, the most surface-rich materials are not necessarily the strongest. They are the ones whose mechanism not only fits the zinc side closely enough to co-operate on the whole cell, but also to make the whole of the cell work coherently. Recent work on advanced carbon-based electrodes points in the same direction and clarifies why framework-derived materials have become so relevant. The design of heteroatomic-doped carbon electrodes to ZnHSCs, Ji et al. (2026) [75] argue that its design must rely on the quantitative control of pore architecture, distribution of active sites and doping chemistry rather than arbitrary increases in surface area. This kind of transformation is a natural progression to MOF- and COF-based cathodes. It is the peculiar control of porosity, the localization of heteroatoms, the configuration and architecture of redox sites. These cathode design requirements for ZnHSCs are directly addressed in Chapter 4, which presents a carbonized MOF-5-derived cathode engineered to deliver high capacity and long-term cycling stability. This segment addressed the recent advances and opportunities of different cathode materials currently used for ZHSC and predicted advancement to enhance the overall performance of the ZHSCs further.

## **1.6 Trivalent Aluminum-Ion Batteries (AIBs): Materials Rationale, Charge Storage Complexity, and Cathode Constraints**

A new battery system for electronic vehicles (EVs) started developing in 1900 by Thomas A. Edison. In 1901, his final nickel-iron battery patented in the USA (Edison,

1901) [76], became the most commercially successful invention of his career. Over 10 years, more than 50,000 experiments, along with withdrawal of the initial version of the battery from the market, he came up with the right combination of materials, lighter, more reliable, and threefold more "powerful" battery than the existing lead-acid battery as highlighted by Dyer and Martin [77] in 2010 to finally deliver the best commercially available battery. At present, demand for another breakthrough's technology is growing faster. Shortly, LIB is the highest energy- commercial product but there is an increasing demand for a new battery with an even higher energy density, better safety, and reduced costs, especially for EVs stationary storage, and mobile devices. In 2018, Schnell et al reported another most important drawback of the LIB system is the demand of the aprotic (non-aqueous, organic) liquid electrolyte for ionic transfer. That results in safety concerns, capacity fading, aging, wetting processes, and high cost during production. Flammability of the solvents obviously raises safety concerns, as various incidents of burning batteries were reported. Therefore, Governing Council of ICAO (International Civil Aviation Organization) has decided to ban the shipping of lithium-ion batteries as cargo in passenger aircraft. Due to these reasons, new promising and safer technologies than existing LIBs, with higher theoretical energy density such as multivalent batteries are required. Beyond LIBs, in recent years Na-ion, [78] K-ion, [79] Zn-ion, [80] Mg-ion, [81] Ca-ion, [82] and Al-ion batteries are becoming progressively popular [83, 84]. Aluminum-ion batteries (AIBs) due to their unique properties from aluminum are considered a potential candidate among these metal ions. Its superiority is mainly evident in two key aspects. Firstly, In the Earth's crust Al is the most abundant metal element (8% by weight) [82] Secondly, during redox mechanism Al undergoes a three-electrons process per atom, presenting an opportunity to create high energy density batteries. Since 1951, Figure 1.21 summarizes the significant milestones in the development of AIBs [85–87].



**Figure 1.21:** The key breakthrough of the evolutionary timeline of AIBs

In the earliest idea, aqueous electrolyte AlCl<sub>3</sub> was used with transition metal oxides-based cathodes which led the foundation for AIB research. Even though in 1857 Al was first reported as a battery anode, [85] it was not until 2011 that the first rechargeable AIB appeared, using a pristine Al metal anode and a V<sub>2</sub>O<sub>5</sub> nanowire cathode in an AlCl<sub>3</sub>/[EMIm]Cl ionic-liquid electrolyte [88], followed by a CuHCF cathode with the high-performance Al(OTf)<sub>3</sub> aqueous electrolyte in 2015.

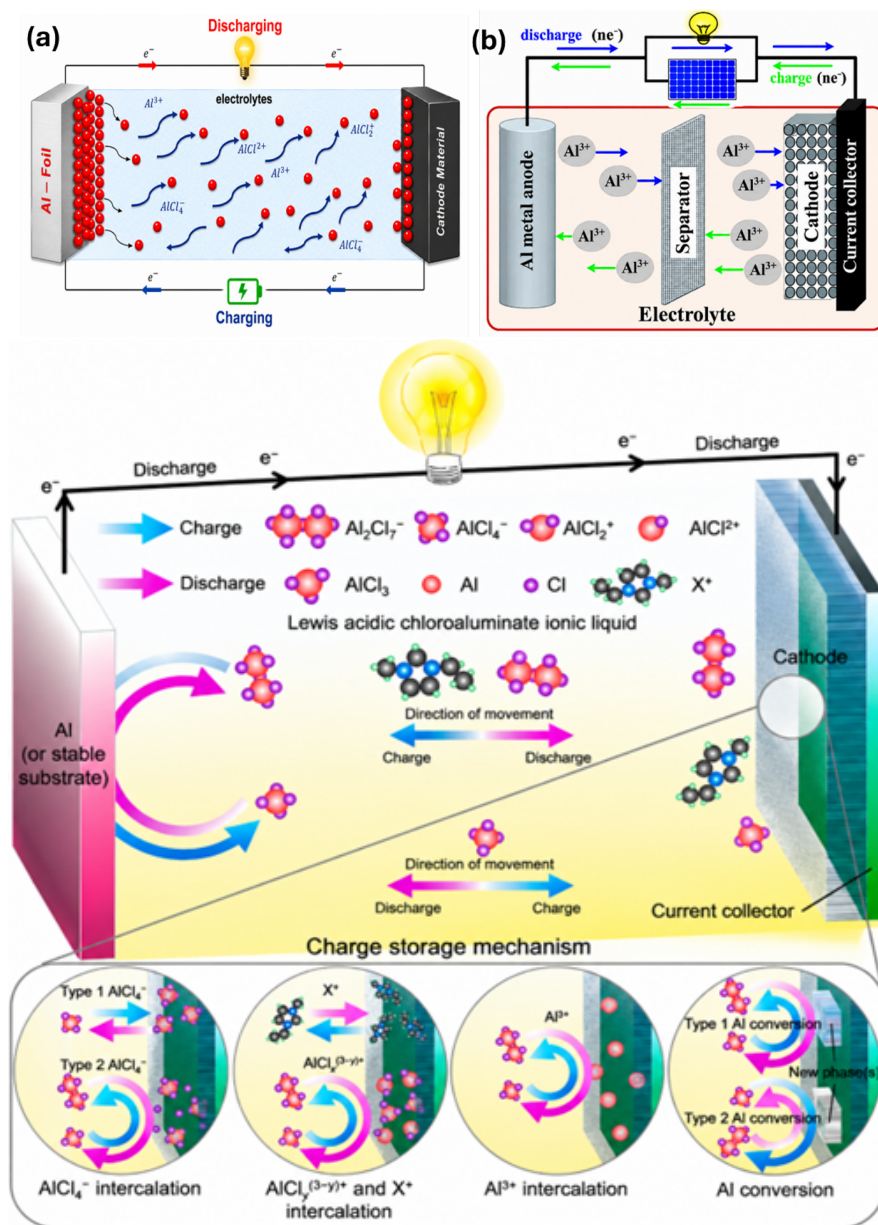
Between 2018 and 2021, important developments were achieved, introducing the first implementation of organic molecules (e.g., TCQ) and Mn-based oxides as cathodes, Al alloy anodes, interfacial engineering approaches for Al metal, and the development of Al(OTf)<sub>3</sub>-based gel electrolytes. It is also compatible with non-flammable and non-volatile ionic liquid electrolyte chloroaluminate ([EMIm]AlCl<sub>4</sub>), offering a substantial safety advantage over LIBs by eliminating the risk of formation of Li dendrites and short circuits [85, 89]. In conclusion, with its high specific capacity, minimal cost, superior safety, and robust compatibility with aqueous electrolytes, Al anodes present a stable ground for the advancement of AIBs with high potential for future ESSs.

### 1.6.1 Working Principle

AIBs are secondary batteries as their redox reaction is reversible. Among these rechargeable aqueous/non aqueous AIBs where Al metal used as anode are considered most promising ESS, It also has four fundamental components similar to all other batteries such as Al metal/foil as anode, metal sulfides, carbon based materials, selenides, spinel compounds, and organic macrocyclic compounds as a cathode material coated on stable



current collector (Nb, Mo, Ta etc.), separator and electrolyte enriched with aluminum complex ion for high ionic conductivity with low viscosity. As Al metal is used on the negative side of the electrode. Immediately after cell fabrication, AIBs are considered to be in the charged state.



**Figure 1.22:** a-b Schematic configuration of an Aluminum ion cell [90]

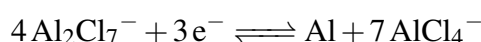
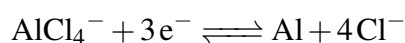
For all AIBs, during discharging, there is reversible electro-stripping where oxidation of metallic aluminum occurs, and aluminum ions and electrons travel through an aprotic or protic electrolyte from the anode to the cathode side via separator and reduction of cathode material takes place and during the charge process the reversible process



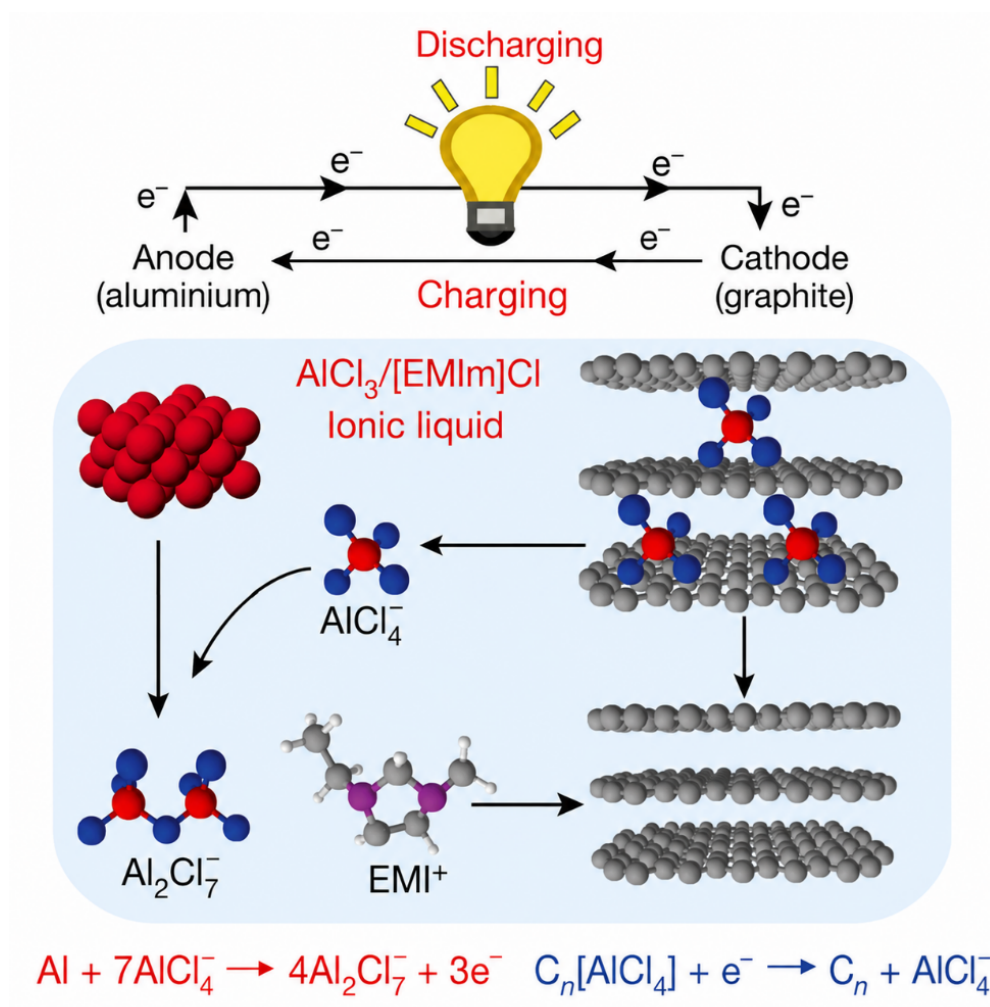
of electroplating occurs. Cathode materials are responsible either it gets converted into intercalated chloroaluminate anions compound [85] or a metal ligand complexes with multivalent Al-complex [84, 91, 92]. Overall, the redox reaction of battery (Fig. 1.22) [90] is centered on the insertion of different carrier ions like,  $\text{AlCl}_4^-$ ,  $\text{AlCl}_2^+$ ,  $\text{AlCl}^{2+}$ ,  $\text{AlCl}_3$  and  $\text{Al}_2\text{Cl}_7^-$  and  $\text{Al}^{3+}$  shown in figure 1.22 (a). Among them  $\text{Al}^{3+}$  has strong coulombic coordination interaction with electrolyte species and cathode materials, therefore, it might be expected that  $\text{Al}^{3+}$  will be the charge carrier, during battery charging and discharging shown in figure 1.22 (b).

## 1.6.2 Charge Storage Complexity in AIBs

To understand charge storage complexity of AIBs, electrolytes composed of aluminum chlorides and organic chloride salts have been investigated. The first ionic liquid-based rechargeable AIBs have promising Columbic efficiencies of 98% and ultrafast 7500 charge/discharge cycles without any noteworthy capacity decay at high current density (400 mA/g). This type of ionic liquid chloroaluminate electrolyte is categorized into three groups, such as basic, acidic and neutral, mainly depending on the molar concentration of  $\text{AlCl}_3$  in the electrolyte. Lower than 50% molar concentration of  $\text{AlCl}_3$  electrolytes dominates basic characteristics and contains primary anions  $\text{AlCl}_4^-$  and  $\text{Cl}^-$ . On the opposite,  $\text{AlCl}_3$  with more than 50% molar concentration results in acidic nature with  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  anions.



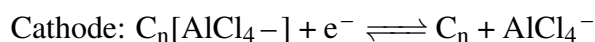
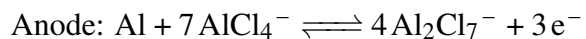
It can be clearly noticed from the equations that when it is acidic state, in the electrolyte there are only  $\text{Al}_2\text{Cl}_7^-$  and  $\text{AlCl}_4^-$  anions. Due to the lower steric hindrance and smaller ionic radius of  $\text{AlCl}_4^-$ , it may be inferred that insertion of the  $\text{AlCl}_4^-$  anion only takes place in organic ionic electrolytes owing to their exceptional acidic properties. It is a well-known fact that most solutions of aluminates in water are slightly alkaline because of the hydrolysis of  $\text{Al}^{3+}$  ions. The reversible  $\text{Al}^{3+}$  intercalation process is made possible by the presence of a large amount of  $\text{Al}^{3+}$  cations in these electrolytes. It is evident that only an acidic configuration accelerates electroplating and electro stripping of Al during charge/discharge mechanism. Consequently, depending on the type of cathode materials, several inserted ions in the acidic  $\text{AlCl}_3$  based ionic liquid electrolytes and their corresponding chemical intercalation has most importantly two types of charge storage complexity shown in the figure 1.23 will be discussed further.



**Figure 1.23:** Schematic illustration of chloroaluminate ionic liquid based AIBs using cathodes with different charge storage mechanisms [93]

### Intercalation of $\text{AlCl}_4^-$

From the above discussion it is concluded that in the charging and discharging process of positive electrode based on carbonaceous materials such as some polymers, graphite as well as graphene-based materials are responsible for  $\text{AlCl}_4^-$  intercalation/deintercalation mechanism. The reaction mechanism equations can be given as:

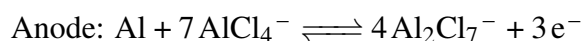
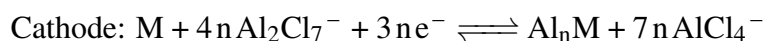


Where n is the molar ratio of carbon atoms to inserted anions in the cathode. In the discharge process of anode, the  $\text{AlCl}_4^-$  leaves the host materials and reacts with the Al anode to produce  $\text{Al}_2\text{Cl}_7^-$  with three electrons. Whereas at cathode side, the  $\text{AlCl}_4^-$  separates from the host layers initially inserted with  $\text{AlCl}_4^-$ . During the charging process, the reversible reaction occurs shown in figure 1.23 [93]. However, the

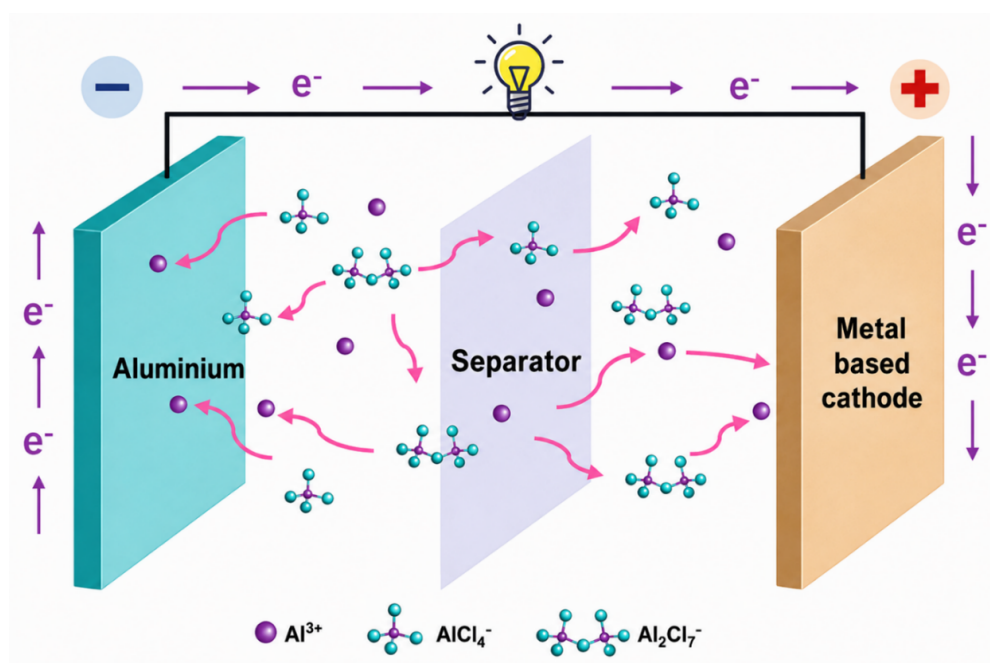
intercalation/deintercalation of  $\text{AlCl}_4^-$  is clearly related to the battery capacity and other properties of AIBs to some extent.

### Intercalation of $\text{Al}^{3+}$

According to studies, there are some other materials than carbonaceous materials which do not support intercalation of  $\text{Al}^{3+}$  and deliver limited capacity. Different kinds of metal based shown in figure 1.24 [94] for example, transition metal oxides and metal sulfide-based cathode facilitate the diffusion of  $\text{Al}^{3+}$  in the structure. Such as Vanadium oxide  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$ ,  $\text{Li}_3\text{VO}_4$ ,  $\text{Mo}_2 \cdot 48\text{VO}_9 \cdot 93$ ,  $\text{VS}_2$ , molybdenum sulfide  $\text{Mo}_6\text{S}_8$ ,  $\text{MoS}_2$  etc., are all representative. Intercalation mechanism of these materials is represented in the following equations.



where M is for metal-based cathode. Like the reaction on the anode side, as mentioned earlier the  $\text{Al}_2\text{Cl}_7^-$  anions are generated by the reaction of Al metal with the  $\text{AlCl}_4^-$  complex anions, while  $\text{Al}^{3+}$  cations freely intercalate into the cathode side to form a new aluminide. Charging process is the reverse of it. Incidentally,  $\text{Al}_2\text{Cl}_7^-$  anions showing in the electrolyte may imply that the mole ratio of  $\text{AlCl}_3$  in ionic electrolyte is higher than 1, which confirms the content referring to the electrolyte proportions already discussed in this section.

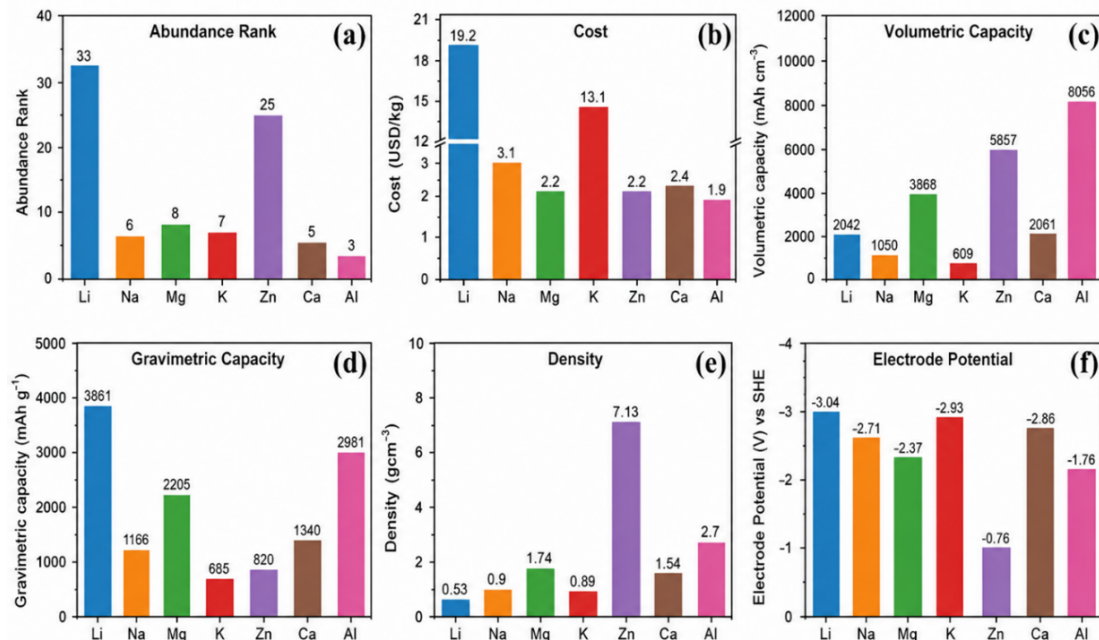


**Figure 1.24:** The schematic electrochemical illustration of metal-based cathode of AIB [94]

That kind of charge storage mechanism reveals that the term trivalent AIBs needs to be used with some precision. In broad chapter language, the field standard remains multivalent AIBs or, more cautiously, rechargeable AIBs. It combines strong materials rationale with electrolyte-dependent charge-storage complexity, which in turn makes cathode selection and cathode stability central challenges for practical implementation which will be discussed further in the next sections.

### 1.6.3 Performance Advantages

The AIBs have various advantages over performance, most important with its property of having three-electron redox ( $\text{Al}^{3+}/\text{Al}$ ) mechanism deliver high capacity, low practical reactivity owing to its protective native oxide layer, offer low cost, low flammability, easy handling and 3rd most abundant rank on Earth as compared to other metals (Li, Na, Mg, Zn, Ca, K). AIBs could offer a potential alternative to LIB systems. Aluminum offers low cost as compared to Li metal, ( 1.40 USD/kg vs 1450 USD/kg) impressive gravimetric capacity of 2,981 mAh g<sup>-1</sup> and the highest volumetric capacity at 8,056 mAh cm<sup>-3</sup> shown in figure [95]. Given its relatively low atomic weight, aluminum demonstrates great potential as an anode material.



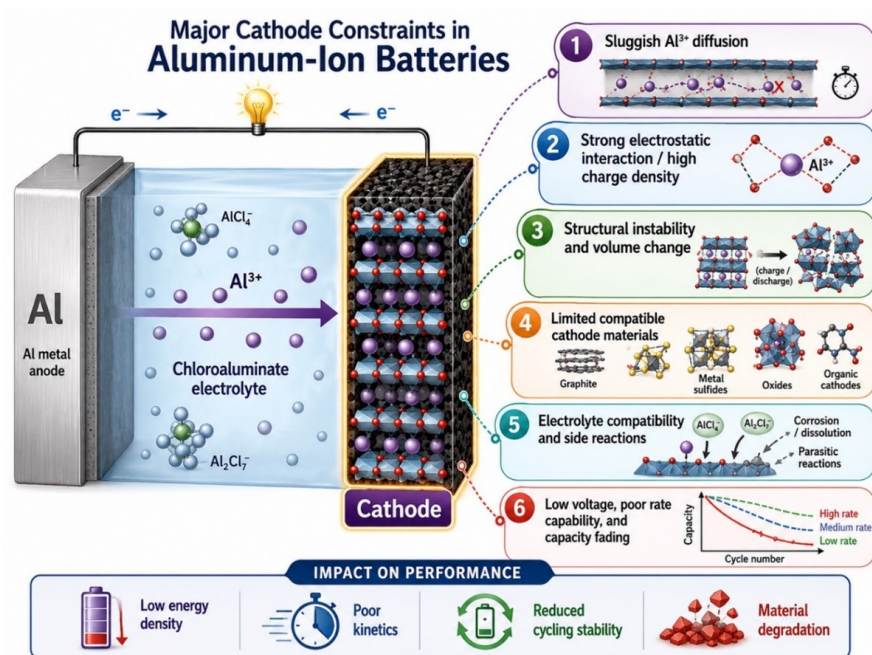
**Figure 1.25:** Comparison of (a) abundance, (b) cost, (c) volumetric capacity, (d) gravimetric capacity, (e) density and (f) electrode potential vs. SHE of Li, Na, Mg, K, Zn, Ca and Al [95]

AIBs exhibit significant advantages in terms of safety and non-toxicity of Al as well.

Moreover, multivalent metals are less susceptible to dendrite formation, which opens the potential as metal anodes for their practical application. In 2015, Dai et al. reported their ground-breaking work with the use of Al as an anode, a 3D graphitic foam as a cathode and as an electrolyte  $\text{AlCl}_3\text{-EmImCl}$  chloroaluminate ionic liquid (IL) was used. This AIB delivered a capacity of  $60 \text{ mAh g}^{-1}$  with 97% coulombic efficiency (CE) over 7500 cycles at room temperature. In addition, it was safe operation ensured non-flammability of the AIB. Moreover, this room temperature operating ionic liquid worked very well for ultrafast transportation of anions with high charging of the AIBs.

### 1.6.4 Cathode Constraints

Regardless of many advantages, AIB battery possesses few limitations as well. Formation of toxic  $\text{Cl}_2$  is one of the crucial problems because of the reaction of two  $\text{AlCl}_4^-$  at the cathode side. As has already been mentioned that the Al-storage mechanism is mainly based on the intercalation/deintercalation of  $\text{AlCl}_4^-$  anions in the graphite layer, therefore the capacity will always remain limited by the amount of electrolyte with moderate energy density, although graphite-based cathode has considerable cycling stability. Assuming metal ions of cathode as the redox center, one  $\text{Al}^{3+}$  insertion per formula unit and three electrons are accepted by the metal redox center namely a reduction by three valences. First, it is not easy to endure huge electron injections in a conventional cathode. Moreover, when electrons are injected into large numbers, the drastic change of the radius of the cations will lead to great structural changes and strains which will harm the host cathodes. Some key challenges associated with AIBs cathode materials have been summarized in the figure 1.26. Therefore, the design of novel cathode materials for Al storage becomes crucial to boost the device's energy density. Organic cathode materials are considered as a powerful alternative to improve the electrochemical performance of AIBs, not only because they have high theoretical capacities, sustainable production and structural tunability but also because they can store Al ions through a coordination reaction mechanism.



**Figure 1.26:** Major cathode challenges in AIBs and their impact on electrochemical performance

Conjugated carbonyl ( $\text{C}=\text{O}$ ) compounds (i.e., quinones and their derivatives) have shown great potential as redox-active materials because of their highly reversible electrochemical performance. Still several challenges are associated with the organic cathodes used in AIBs including slow kinetics, poor reversibility, difficulties related to the insertion of Al ions into the host structure as well as electrode-electrolyte interface problems [96]. That's why framework-based cathodes become so relevant in this chapter. Metal organic frameworks sit close to this design logic because they combine ordered porosity with chemically tunable coordination or covalent redox environments. Therefore, it is important to design cathode materials to avoid these limitations to improve the electrochemical performance of AIBs. These cathode constraints, therefore, are tackled in Chapter 5, where a covalent organic framework (COFs) based cathode is designed to improve ion diffusion kinetics and structural stability under repeated  $\text{Al}^{3+}$  insertion and extraction.

## 1.7 Cathode Materials as a Central Bottleneck in LMBs, ZnHSCs, and AIBs

These three batteries still lie inside the domain of cathode chemistry and are now electrochemically interesting. Lithium metal offers a significant increase in specific energy, zinc is safe and can be utilized with aqueous systems, and the benefit of aluminum



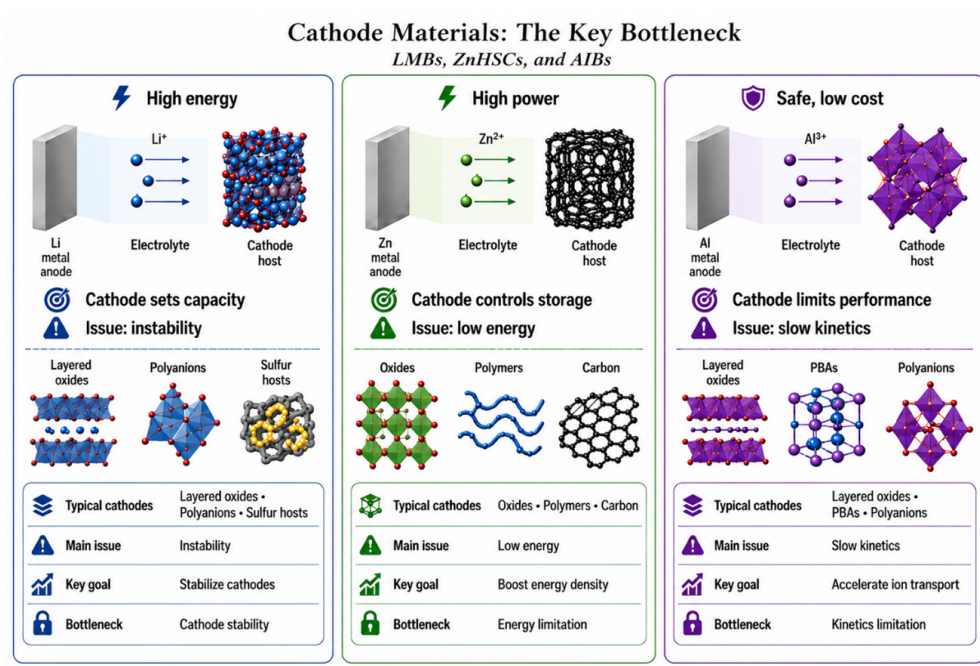
is that it is abundant and has multivalent redox. Xu et al. (2025) make a direct argument in LMBs that the energy density of the system is highly dependent on the cathode that is used with lithium metal. On the zinc side, Liu and Wu (2023) note that another reason why ZnHSCs are still miles away before they can be implemented is the development of the cathode. The same can be said about the example of the aluminum systems, where Zhao et al. (2025) divide the advances in the field into the most recent ones, namely the cathode charge-storage mechanisms. That has been explained in previous sections. This bottleneck becomes sharper in lithium metal batteries once the discussion shifts from idealized material properties to cell-level design. Lithium metal can be effectively utilized in situations where cathode can sustain a high areal capacity, moderate loading, interfacial stability and co-utilization of inactive mass. Shen et al. (2025) put this into perspective by shifting the focus of the materials innovation towards system engineering, which, in essence, is a way of stating that cathode selection cannot be decoupled with electrode loading, pouch-cell design, and realistic consideration of energy-density. This is interesting since most cathodes have only been shown to be effective in thin-electrode experiments but not in those experiments that scale the cell to realistic sulfur loading, lower electrolyte stock and lower volumetric requirements. The central difficulty is therefore not merely that some cathodes are chemically unstable. Also, the cathode is overloaded with large capacity, large voltage, mechanical strength, interface compatibility, and electrode architecture designs. When such requirements are combined the list of any attainable cathodes is reduced to a very small size.

The positive electrode of the ZnHSCs has another, but equally recalcitrant limitation. In this case the cathode must maintain the rapid charge-discharge characteristics of capacitive storage, in addition to providing sufficient reversible charge storage to elevate the energy of the device beyond that which a simple electric double-layer capacitor might be able to provide. According to Loh et al. (2024) such systems are yet to achieve their theoretical specific capacity, which reminds us that the hybrid view is constrained by the quality of its electrode materials, and not by cell marking. Ji et al. (2026) also note that to pay attention to high-level carbon materials and hetero atom engineering is essential but regular porosity is insufficient because carbon cathodes are still leading in the industry. The cathode is expected to provide ion-accessible pore structure, short diffusion pathways, surface chemistry to enhance the adsorption and desolvation of Zn-ions and sufficient electronic conductivity to eliminate rate collapse. This has been the reason why literature has been continuously trending towards doped carbons, hierarchical porous architecture and hybridized positive electrodes rather than the electrodes based on a bare surface area. That same intrinsic pressure is felt in even the direction adopted by Potham and Ramanujam (2023) which was to test an activated

carbon-organic composite cathode, the area was seeking ways of reducing the cathodes that could easily accommodate charge without the sacrifice of the rapid kinetics of the kind of device that it was. It is not the case with the failure mode of ZnHSCs. It is the need but to be accomplished to join capacitor-like speed, battery-like energy on one positive electrode.

Aluminum-ion batteries expose the cathode problem in an even more fundamental way because multivalent storage raises the bar for ion transport and structural tolerance. Ma et al. (2024) show that the cathode question sits at the center of both nonaqueous and aqueous AIB research, largely because candidate materials must handle complex insertion chemistry without sacrificing reversibility. Rechargeable Al systems based on graphite have low capacity, although subsequent carbonaceous systems or transition-metal-based systems remain a trade-off between capacity and rate capability and long-term stability. It is not difficult to observe the problem. Aluminum species are very active with host structures, diffusion can be slow, and the cathode can often be structurally or electrochemically inactive long before chemistry is viable in the sense of the implication of aluminum metal itself. Lin et al. (2025) illustrates why new cathode chemistries keep attracting attention by reporting a TiNbC/MXene cathode designed for reversible Al-complex ion storage. To attain a high energy density AIBs key feature is to design cathode materials that accommodate and release the  $\text{Al}^{3+}$  ions while discharging/charging. High output voltage and high-capacity featured cathode materials are crucial for practical high energy density AIBs. Graphite, graphene, sulfur, and metal sulfide are all found as promising positive electrode materials at an early age for fast charging and stable cycling stability. In recent days organic macrocyclic molecules have also shown promising electrochemical results. Seen together, these chemistries do not suffer from the same cathode problem, but they are all restrained for the same cathode reason summarized in figure 1.27.





**Figure 1.27:** Infographic illustrations of key challenges, materials, and performance bottlenecks of cathodes in LMBs, ZnHSCs, and AIBs

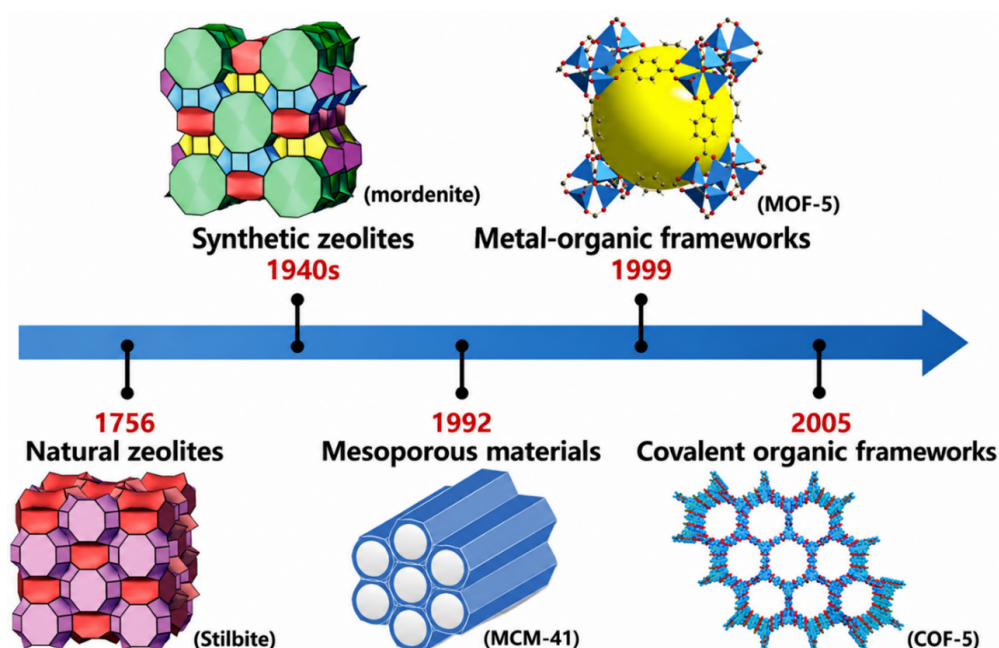
In LMBs, the cathode struggles to convert high theoretical energy into practical cell-level output under lean and high-loading conditions. In ZnHSCs, the cathode must compromise a challenging requirement between high-rate kinetics and significant energy density. The cathode must counter the basic retribution of multivalent ion transport and high host interaction within AIBs. This is what makes cathode design the critical bottleneck to all three systems. Although LMBs, ZnHSCs, and AIBs have different operating chemistries, as illustrated in the above sections, cathode materials are often a bottleneck due to the need to simultaneously control redox activity, ion transport, conductivity, and structural stability to achieve practical performance.

## 1.8 Metal Organic Frameworks (MOFs): Structural Features, Electrochemical Advantages

### 1.8.1 Development Of Porous materials

The chemistry of pores or confined spaces is extremely difficult but very useful for the solution of many problems by using host–guest interaction. Porous materials can be classified according to the size of the pores: microporous (<2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm). For their excellent structural properties, they

are widely used in ion exchange, adsorption, separation and catalysis [82, 83]. The natural occurrence of zeolites was first reported in 1756 in the aluminosilicate mineral stilbite, and the artificial production of zeolites started in the 1940s shown in figure 1.28 [97–101].

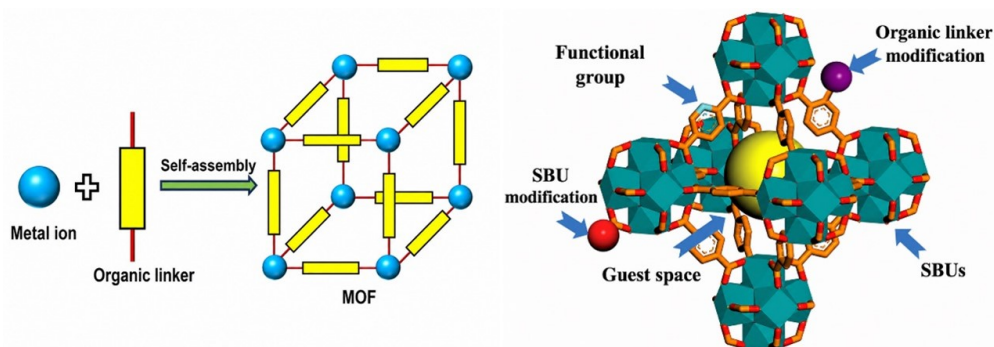


**Figure 1.28:** Important turning points in the discovery of useful porous materials [83]

They consist of inorganic compounds of principally Si, Al and O and have well defined sub-nanometric pores. The pores in zeolites permit molecules or ions of guests from entering, diffusing through and exchanging with the host. For this reason, zeolites are sometimes referred to as molecular sieves. They have valuable properties for their tunable composition and acidic sites and are used in detergents, adsorbents, petrochemistry and biomass conversion and energy storage systems. Zeolites, however, have some drawbacks such as the modulation of their pore surface at an atomic level is difficult, and there may be limited diffusion of large substrates. The invention of ordered mesoporous silica in 1992 opened the door to this large area of research due to its larger pores and potential in catalysis, sensing, electronics, energy storage and drug delivery [99]. As a result, in order to fill the gap between zeolites and mesoporous silica, the development of crystalline porous materials as heterogeneous catalysts and cathodes for energy storage as MOFs and COFs has been introduced [102–105]. MOFs are organic–inorganic hybrid coordination polymers consisting of metal ions and organic linkers, while COFs are porous organic polymers that are generated covalently from light-element building blocks which will be discussed later in detail in the next sections.

## 1.8.2 Development of MOFs

Li and Yaghi in 1995 used the term MOF for the first time [102]. Other groups have chosen to name their materials with a short description or acronym associated with the institute or university in which the new materials were developed, e.g., MIL (Materials Institute Lavoisier) or HKUST (Hong Kong University of Science and Technology). In some instances, new materials are just described by their chemical formula. IUPAC (International Union of Pure and Applied Chemistry) has defined MOF as a coordination network structure with potential voids created by organic ligands in the structure in 2013 [106]. Since the discovery of metal–organic frameworks (MOFs) (also referred to as porous coordination polymers (PCPs)), a new family of porous crystalline materials, their high surface area, structural flexibility, tunable structure and composition, and well-defined ordered framework, have made them highly attractive for use in a range of catalytic and energy storage applications. Such properties make MOFs well suited for the anchoring of atomic level catalysts. MOFs are built with metal-based nodes called secondary building units, or SBU and a variety of organic linkers shown in figure 1.29, such as nitrogen-containing ligands and carboxylic acid ligands.



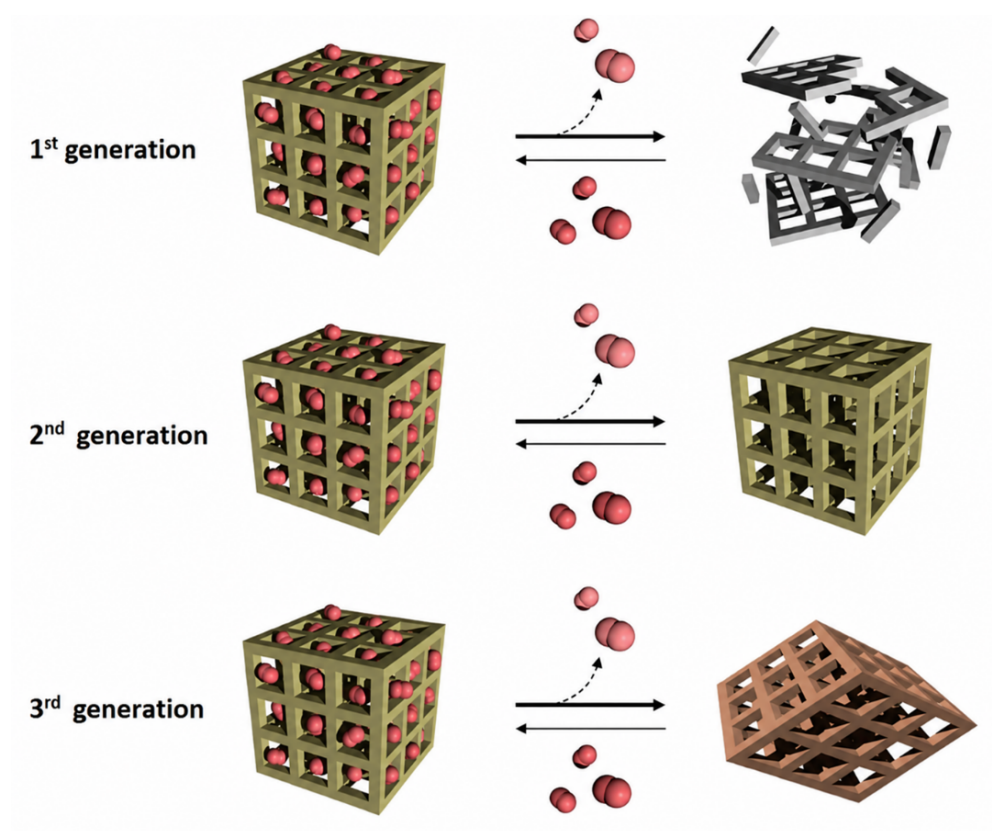
**Figure 1.29:** Schematic representation of MOF and construction parts within MOFs [106]

The distinguishing feature of MOFs is that their structure is tunable, unlike other porous materials. On the other hand, MOFs can be readily engineered for desired applications by incorporating or post-synthetic modifying metal nodes and/or organic linkers with designed optical, magnetic, and electronic properties among others. Conversely, MOFs have a well-defined and large number of pores that can host a variety of guest species such as quantum dots, metal complexes, metal salts, and "ship-in-bottle" species, and nanoparticles (NPs). These incorporations can be used to enhance MOF functionality by combining interactions. The novel properties of MOFs make it an attractive material for the study of structure–performance relationships, a fundamental issue in electrochemical storage devices. The information obtained from these types of studies

can then be used to rationally design future single-atom, dual-atom, and cluster materials as cathodes for energy storage applications.

### 1.8.3 Structural Features

Kitagawa and coworkers introduced three types of classification scheme shown in figure 1.30 of porous solids, including MOFs, according to how they react to the guest molecules, including gases, solvent molecules, drugs and other species incorporated into the pores [104, 107].

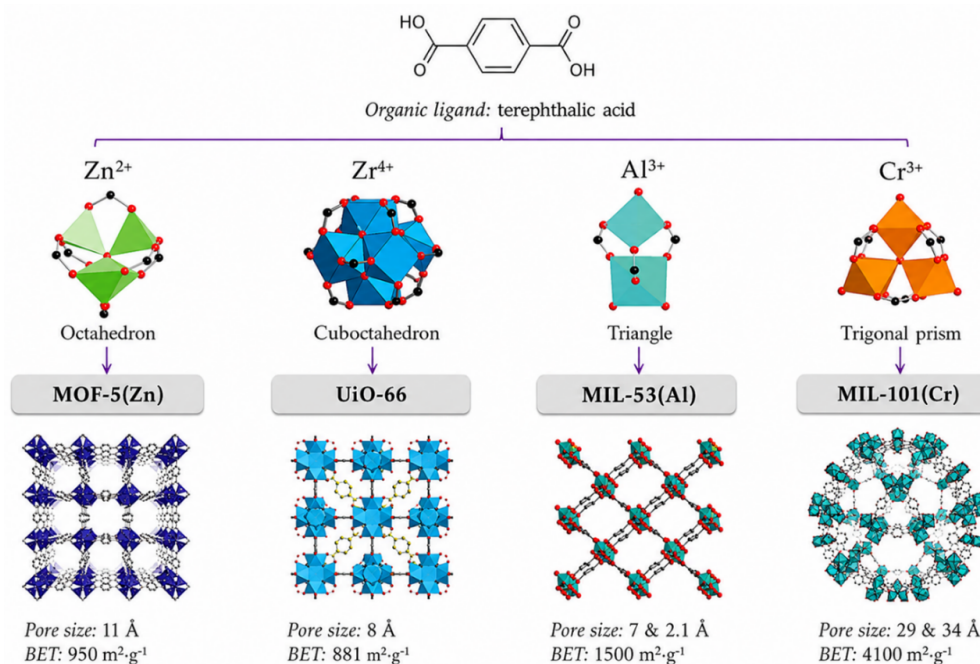


**Figure 1.30:** Schematic representation of the three generations of porous materials [108]

First generation: Materials with microporous frameworks that collapse the framework irreversibly when the guest molecules are removed. Second generation: Materials with strong and more rigid porous frameworks that be able to keep their crystallinity even in absence of guest molecules in pores. Third generation: Materials that have flexible and dynamic porous frameworks which can undergo reversible structural changes in response to external stimuli including changes in temperature and/or guest molecules. Furthermore, Omar Yaghi and co-workers in 2002, have shown the porosity and functionality of MOFs can be precisely controlled by rational design of organic linkers or



metal nodes in figure 1.31 [109]. This flexibility allows MOFs to have tunable and versatile properties without losing the basic topology. Consequently, MOFs can be used to fill the gap between microporous materials and mesoporous materials. Notable examples include the MIL-101 series, MIL-47 series, MIL-100 series, MIL-88 series, MOF-5 series, HKUST-1 series, UiO-66 series, and ZIF-8 series [110–114].



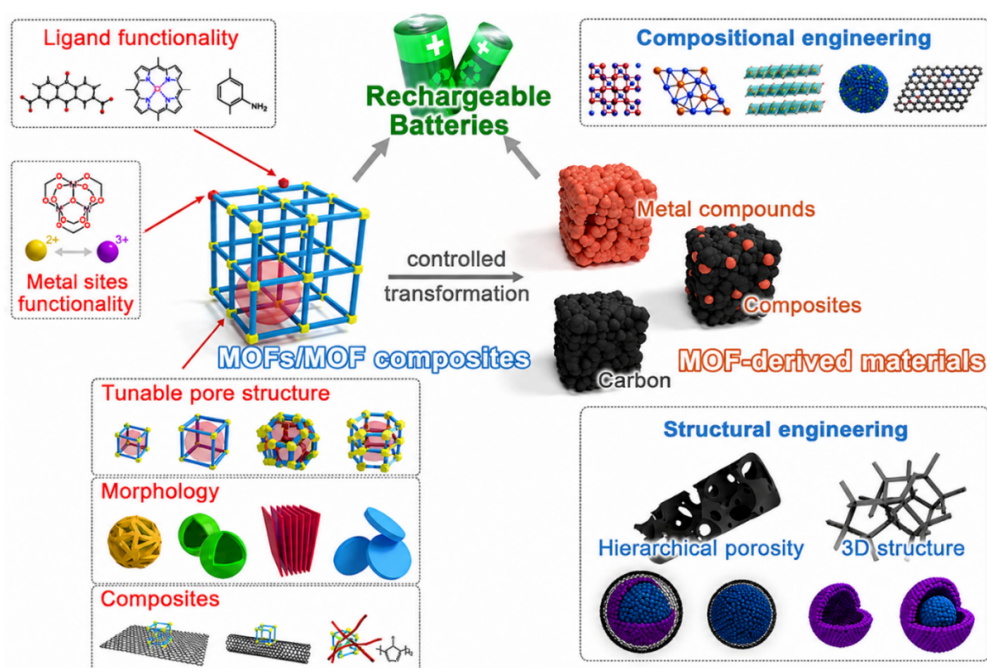
**Figure 1.31:** Different types of MOF prepared by using same organic linker terephthalic acid with different metals [109]

To date, BET analysis reveals that the surface area of MOFs can reach as high as 10,000 m<sup>2</sup> g<sup>-1</sup> which is greater than those generally reported for zeolites and activated carbon. This kind of high surface area MOFs plays a crucial role as a cathode material to enhance the storage capacity of electrochemical devices.

#### 1.8.4 MOFs as Cathode for various Energy Storage Devices

Researchers are continuously searching for materials to act as a cathode in many metal ion batteries and supercapacitors that are stable, have a high discharge specific capacity and are also inexpensive. Manganese-based materials are frequently investigated because of their high specific capacities, but they suffer problems of dissolution in electrolytes and low conductivity during charge–discharge cycles. Vanadium-based materials have high discharge capacities but have disadvantages of high toxicity and high costs. The limitations of Prussian blue cathode materials are low discharge specific capacities and

poor stability. Moreover, little knowledge has been gained on the impact of electrolyte pH on the battery performance under charge–discharge cycles and the role of electrolyte additives in enhancing the battery mechanisms, which needs further exploration. Issues like the uneven deposition of the Li and zinc anode, which can result in the formation of dendrites capable of perforating the separators and short circuiting the battery, must also be resolved. The problems of zinc anodes include hydrogen and oxygen evolution reactions, and corrosion. Finding appropriate cathode materials is the chief hurdle for commercialization of ZnHSCs. Therefore, this thesis focuses on the latest developments in using MOFs and their derivatives as cathode materials shown in figure 1.32 [115] for different energy storage devices most importantly rechargeable lithium-based batteries and supercapacitors such as ZnHSCs.

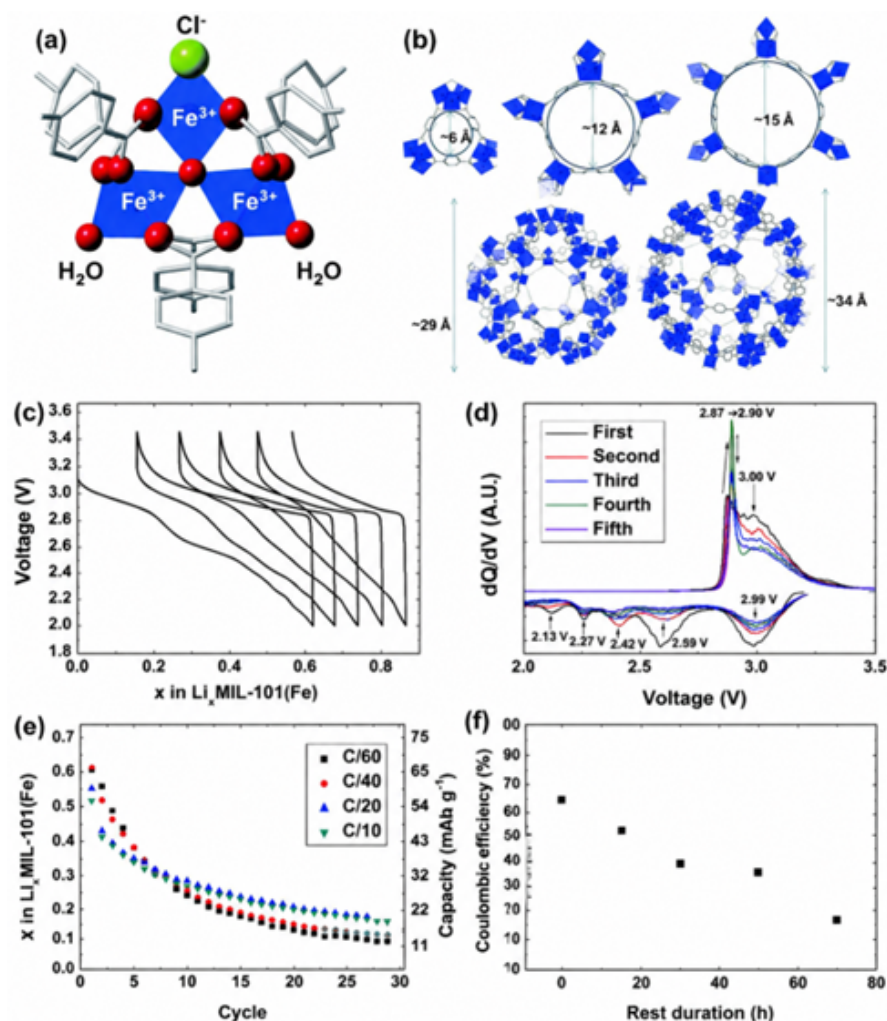


**Figure 1.32:** Schematic Illustration of MOF based Materials for Rechargeable Batteries [115].

### 1.8.5 Pristine MOF as cathode material for Lithium Batteries

MOFs are useful redox materials in electrochemical processes because of the redox active metal ions and charge storing organic ligands. These materials have high porosity, which facilitates the migration of various metal ions, and they have a structural stability that promotes their service life in lithium-based batteries during cycling and high capacitance in supercapacitors. MOFs offer superior properties compared to other porous materials, due to their different structures, ordered pores and multiple metal-ligand combinations. Iron's widespread availability (5.1% in earth's crust), low toxicity, redox activity and

biodegradability have led to a wide exploration of Fe-based metal–organic frameworks (Fe-MOFs) as cathode materials for rechargeable batteries.



**Figure 1.33:** Structure of MIL-101(Fe). a) The SBU (blue, Fe; red, O; stick, C; green, Cl; H is omitted for clarity), b) The windows and pores of MIL-101(Fe) c) First five voltage profiles. d) Differential capacity for the first 5 cycles. e) Cyclic capacity. f) Initial cycle CE when rested for various time intervals between discharge/charge (C/20) [116].

The unsaturated Fe(III) centers and the oxygen atoms of organic ligands result in strong Fe–O bonds, which help stabilize the porous structure and improve the capacity the materials have for lithium based batteries. Tarascon et al. in 2007 developed a successful Fe-MOF cathode called MIL-53(Fe), where Fe(III) is in a higher oxidation state. The design sought to create mixed-valence states to increase electrochemical activity with lithium. The electrochemical performance of MOFs such as NCHU-3 and Zn<sub>4</sub>O(1,3,5–benzenetribenzoate)<sub>2</sub> exhibited better reversibility that might be attributed to the stabilization of M–O bond and delocalization of electrons in 3d transition metals. The reversible capacity of MIL-53(Fe) was almost 75 mAh/g, and 70 mAh/g at 50

cycles. The reversible intercalation of Li and Fe (III) reduction to Fe (II) was confirmed by studies. Moreover, Meng's group reported MIL-101(Fe) as a cathode material electrochemically active MOF for Lithium batteries [117]. The secondary building unit (SBU) of MIL-101(Fe) was ordered of a carboxylate bridged, Fe<sup>3</sup> complex, as shown in Fig 1.33(a). The performance of MIL-101(Fe) was also found to be good, with the capacity to accommodate 0.62 Li<sup>+</sup>/Fe, compared to MIL-68(Fe) with Coulombic efficiency of 79% for the first cycle. MIL-101(Fe) exhibited reduced capacity retention after few cycles, which is mainly considered to be due to Fe<sup>2+</sup>  $\rightleftharpoons$  Fe<sup>3+</sup> relaxation. Reversibility was strongly affected by the lithiation/delithiation rate, as demonstrated from cycle tests with different current density table batteries are shown in the Table 1.2 along their electrochemical performance.

**Table 1.2:** Pristine MOFs Cathodes and Their Electrochemical Performances in Li batteries

| MOF         | Formula                             | Rate     | Cap. (mAh/g) | Cyc. | Ref   |
|-------------|-------------------------------------|----------|--------------|------|-------|
| MIL-136     | MIL-136(Ni)                         | 10 C     | 20           | 50   | [118] |
| MIL-136     | MIL-136(Co)                         | 10 C     | 82           | 50   | [118] |
| MIL-47      | V <sup>IV</sup> (O)(bdc)            | 100 mA/g | 82           | 50   | [119] |
| MOF-2       | Cd(II)MOF                           | 50 mA/g  | 36.6         | 50   | [120] |
| SNNU-73     | CoLi(BTC)(DMA)* <i>n</i>            | 50 mA/g  | 67.5         | 50   | [121] |
| SNNU-74     | CoLi(BTC)/(DMA)(DO)/* <i>n</i>      | 50 mA/g  | 41.5         | 50   | [122] |
| UiO-66      | (ZrO(OH))(1,4-benzenedicarboxylate) | 50 mA/g  | 118          | 50   | [123] |
| MIL-53(Fe)  | [Fe <sup>III</sup> (OH).F.(OCCHCO)] | 0.025 C  | 71           | 50   | [124] |
| MIL-68(Fe)  | Fe(OH)(bdc).(dmf)* <i>x</i>         | 0.02 C   | 72           | 12   | [125] |
| MIL-101(Fe) | [Fe(O)(Cl)(RCOO)(L)]                | 0.2 C    | 100          | 100  | [117] |
| MIL-116(Fe) | MIL-116(Fe).2HO                     | 0.2 C    | 100          | 100  | [116] |

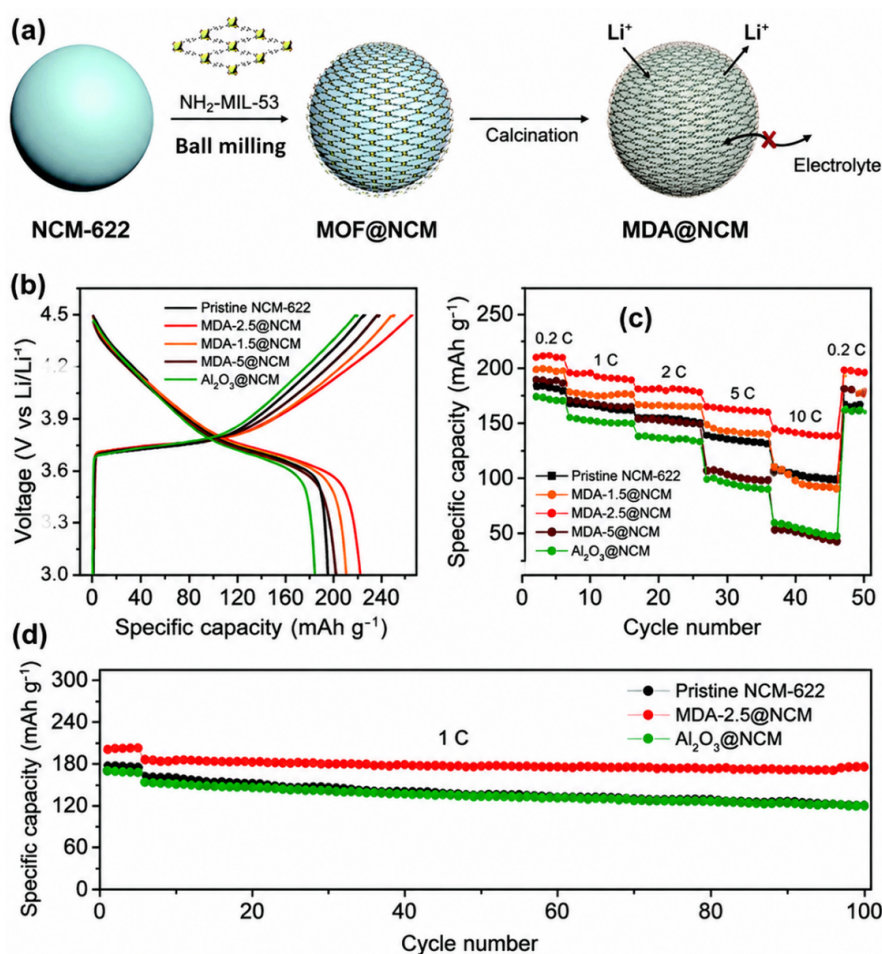
### 1.8.6 MOF derivatives and composite cathodes for Lithium batteries

However, there are several drawbacks of MOF cathodes such as slow rate performance, degradation in the structure during cycling, electrolyte decomposition and low thermostability. To overcome these problems, many strategies have been used, among the best of which is MOF template-mediated synthesis. This approach can produce a variety of nanostructures based on the MOF, alleviating the constraints that are present in conventional cathode materials. Most significantly, MOF cathodes provide complete control over their structural and morphological features, addressing challenges like complex MOF synthesis, low energy density, and short cycle life. One strategy is the surface modification of high-performance commercial cathode materials with MOFs or MOF derived materials to improve the stability of the electrode during cycling. Another



method is thermal processing of pristine MOFs to form metal nanostructures and porous carbonaceous materials which are later directly employed as cathodes in lithium battery applications. Wang et al. reported a material coated with alumina (MDA) on the surface of the well-known cathode material  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  (NCM-622) as demonstrated in Fig 1.34 [116]. NCM-622 was selected because of its high capacity, which is mainly due to the high-Ni content of the transition metal sites. Several problems might still make this cathode material unsuitable for commercialization. The high nickel content decreases the structural stability and causes the loss of lattice oxygen on charging to 4.5 V vs  $\text{Li}^+/\text{Li}$ , which can result in a number of electrolytes induced side reactions. This leads to a higher surface impedance, lower discharge capacity and low cycling stability [126].

To solve the above issues, an  $\text{NH}_2$ -MIL-53 MOF coating precursor was first synthesized by the solvothermal method and NCM-622 by the co-precipitation method. MOF was subsequently ball-milled with NCM-622 at a certain mass ratio and the MOF modified NCM-622 was then calcined at 600 °C in air to obtain MDA-2.5@NCM. The 2.5% MDA coating was well dispersed on NCM-622 and had an amorphous structure, which was derived from the MOF. Under this modification, it was found that the initial discharge capacity of the NCM-624 was improved to 196.5 mAh g<sup>-1</sup> compared to NCM-622, which was 188.3 mAh g<sup>-1</sup>, while 183.3 mAh g<sup>-1</sup> was achieved with 92.7% capacity retention after 100 cycles at 1 C (Fig. 1.34d) [116].



**Figure 1.34:** a) Schematic of MOF-derived metal oxide coating over NCM-622. b) Charge/discharge curves at 0.2 C, c) Rate capability, d) Cycling performance of pristine and coated NCM-622 [127]

The surface protection of NCM-622 minimizes side reactions and the amorphous structure stabilizes the crystalline structure, which enhances the electrochemical performance of NCM-622. Li<sub>2</sub>FeSiO<sub>4</sub>/C cathode composites were prepared by using Fe-BTC-MOF prepared by a hydrothermal method and then treated using a solid-state microwave assisted process along with nanosilica and C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Li·2H<sub>2</sub>O [128]. The amount of carbon had a significant impact on the crystal size, morphology, and electrochemical performance of these composites of Li<sub>2</sub>FeSiO<sub>4</sub>/C. The charge transfer resistance of these composites was found to be the smallest, and the Li<sup>+</sup> diffusion coefficient was largest due to their uniform carbon coating and porous structure. The composites with 19.3 wt% carbon exhibited a first discharge capacity of 117 mAh g<sup>-1</sup> at a 2C rate with about 97.4% capacity after 100 cycles. Various MOF-derivatives/composite cathode with their EC performance are given in Table 1.3.

**Table 1.3:** MOF derivatives/composites cathodes and their electrochemical performances in Li batteries

| Material                   | DC/CC (mAh/g) | RC/rate       | Cycles | Ref   |
|----------------------------|---------------|---------------|--------|-------|
| UiO-66@LiCoO               | 155/—         | 134/2325 mA/g | 100    | [129] |
| UiO-66@LiCoO               | 155/—         | 108/2325 mA/g | 100    | [129] |
| MIL-53@LiCoO               | 151/—         | 120/2325 mA/g | 100    | [130] |
| MIL-53@LiCoO               | 151/—         | 111/2325 mA/g | 100    | [130] |
| MOF@NCM                    | 196/—         | 183.31        | 100    | [126] |
| LLO@MOF                    | 254/—         | 270/0.4 C     | 100    | [131] |
| UiO-66-F4@LLO              | 279.8/—       | 200           | 72%    | [132] |
| LiFePO <sub>4</sub> /ZIF-8 | 200           | 99%           | 100    | [133] |
| ZIF-67@Ni-rich NCM         | 210/—         | 199.7/0.1     | 50     | [134] |

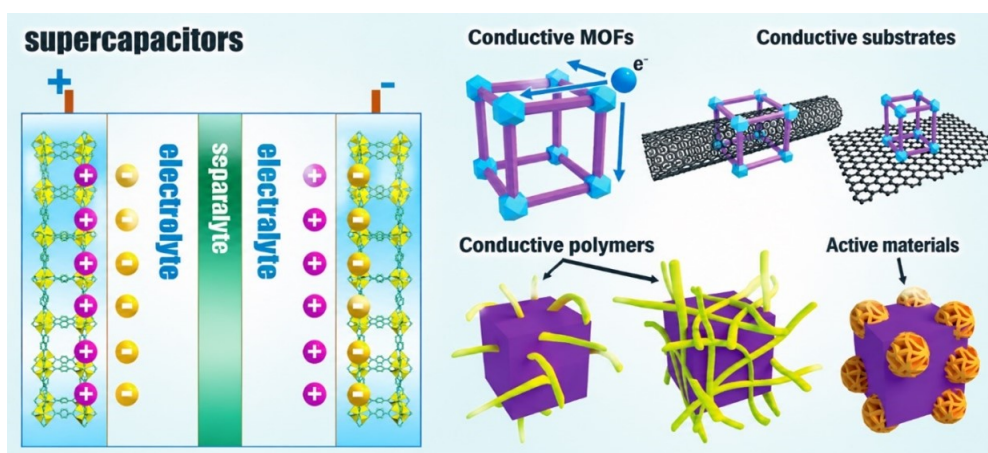
Moreover among these MOF-derivatives there are somehow limited number of metals attached to ligands available in 2D conductive MOFs (c-MOFs). Therefore MOFs with dual metal-ligands have a much larger number of chemical compositions and can be designed with highly tunable topological structures with high surface area [135, 136] which can help to broaden the range of electrochemical properties of 2D MOF-based electrode materials. Because of the competitive coordination effect from the different metals with ligands, constructing dual metal-ligand based MOFs in one step is challenging for Lithium storage which we have developed and will be discussed in detail in chapter 3.

### 1.8.7 Pristine MOFs for ZnHSCs

With their highly porous structure, MOFs and their composites have been shown to have potential applications in supercapacitors, especially in electrochemical double layer capacitors (EDLCs, Figure 1.35) [127]. Conventional MOFs, however, suffer from poor electrical conductivity, and structural instability [137, 138]. This built-in disadvantage must be taken into account for electrochemical processes using these pristine MOFs, which have a very high surface area but limited theoretical capacitance, compared with the more widely used activated carbon. Yaghi and co-workers have synthesized 23 nanosized conventional MOFs (nMOFs) in 1.0 M tetraethylammonium tetrafluoroborate ((C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>)–acetonitrile electrolyte with different pore sizes and shapes, and applied

them as active materials of supercapacitors electrodes.

For zinc-metal ion ESS, Prussian blue (PB) and its analogues (PBAs) are the most suitable MOFs materials credits to their crystal structure with large nanocavity gaps that allow efficient insertion and extraction of  $\text{Zn}^{2+}$ . Liu's group used a high-temperature co-precipitation method to synthesize two types of zinc hexacyanoferrates with diamond-shaped structures. ZIBs are assembled according to the process shown in Fig. 1.36a. As seen in Fig. 1.36b, the Zn//ZnHCF batteries with a discharged capacity of  $65.4 \text{ mAh g}^{-1}$  at a 1 C rate, with definite discharge platforms at 1.6 V. To improve the capacity of ZnHCF cathode, Huang et al. harnessed a polyaniline (PANI) coating to the ZnHCF. As shown in Fig. 1.36c, the Zn//ZnHCF-PANI batteries show two stable charge/discharge cycles and a specific capacity of  $130 \text{ mAh g}^{-1}$  ( $0.2 \text{ A g}^{-1}$ ). Due to the coating of PANI electrochemical performance was enhanced and it has ability to prevent degradation.



**Figure 1.35:** Schematic illustrations of a typical EDLC supercapacitor and development strategies of MOFs for [116].

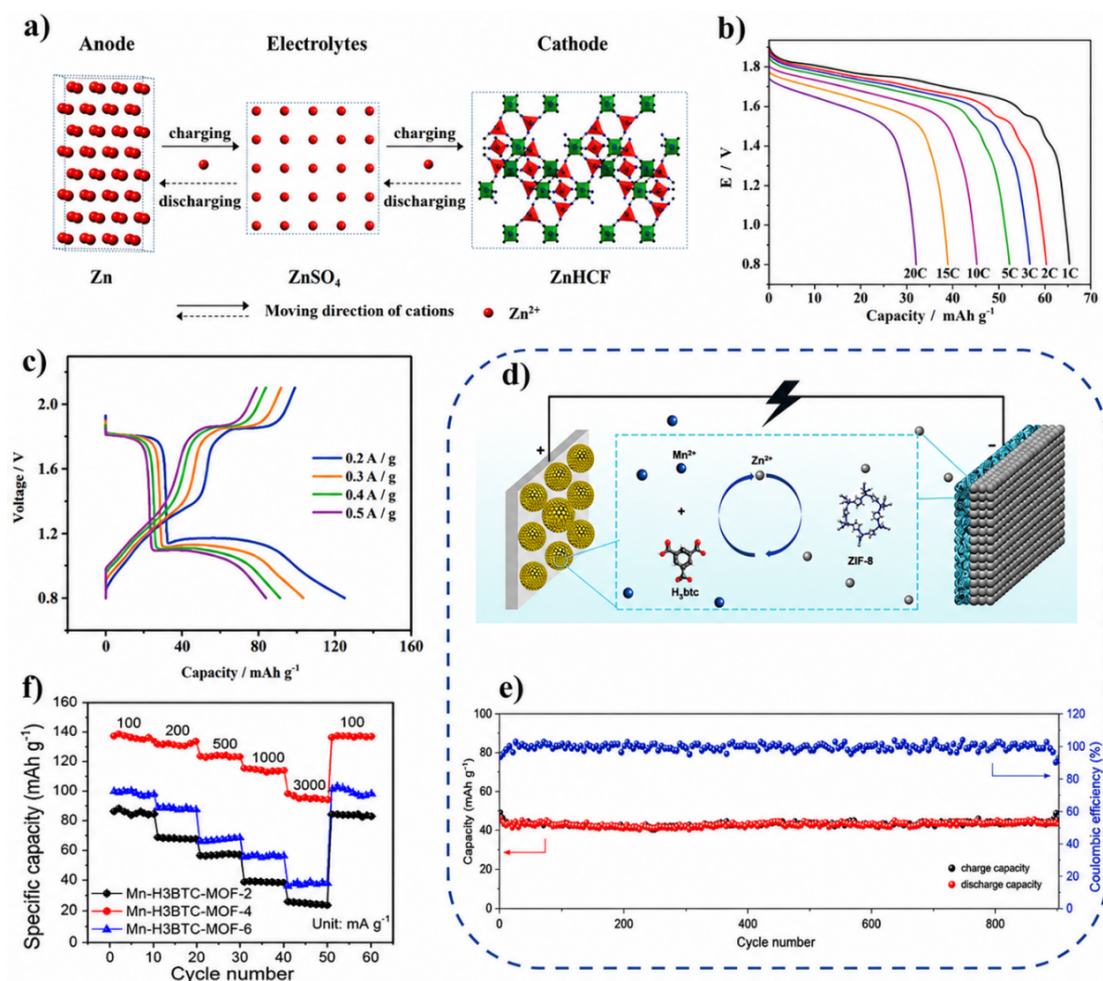
Moreover, a variety of 1D c-MOFs (Cu-BTA) was reported by Liang et al. as the cathode for Zn hybrid device. It is synthesized by coordination ultrasmall 1,2,4,5-benzenetetramine (BTA) ligands with polyvalent copper ions. BTA can effectively increase the proportion of active groups ( $-\text{C}=\text{N}$ ) in the material system, while the synergistic redox reaction of transition metal ions ( $\text{Cu}^{2+}/\text{Cu}^{+}$ ) provides additional energy storage capacity as the second active site. Therefore, the high crystallinity Cu-BTA electrodes possess a reversible capacity of  $330 \text{ mA h g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ . Some other MOFs based cathode for Zn metal ion ESS are given in Table 1.4.

**Table 1.4:** Electrochemical properties of MOFs based cathode for Zn hybrid devices

| Cathode                                                         | Cap. (mAh/g) | J (A/g) | Ret. (%) | Cycles | S.A. (m <sup>2</sup> /g) | Ref   |
|-----------------------------------------------------------------|--------------|---------|----------|--------|--------------------------|-------|
| N-1T MoS <sub>2</sub>                                           | 149.6        | 0.1     | 97.4     | 600    | 24.4                     | [139] |
| Ni/Ni <sub>3</sub> S <sub>2</sub>                               | 379.0        | 0.34    | 83.0     | 1000   | 54.0                     | [140] |
| MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> | 277.8        | 0.1     | 80.0     | 5000   | 16.8                     | [141] |
| Cu-BTA-H                                                        | 330.0        | 0.2     | 68.0     | 500    | 25.2                     | [142] |
| Bi-PYDC                                                         | 286.7        | 0.1     | 95.2     | 10000  | 137.0                    | [143] |
| NiHCF/rGO                                                       | 94.5         | 0.005   | 80.0     | 1000   | 88.2                     | [144] |
| MnHCF-15                                                        | 130.0        | 0.05    | 84.5     | 1000   | 142.0                    | [145] |
| MZHCF-7                                                         | 48.0         | 0.05    | 99.6     | 500    | 144.0                    | [146] |
| Mn-PBA-3                                                        | 100.0        | 5.0     | 99.6     | 800    | 145.0                    | [147] |
| MnHCF/NCDs                                                      | 130.0        | 0.05    | 91.0     | 1000   | 147.0                    | [148] |

### 1.8.8 MOFs derivatives for ZnHSCs

Kang's team selected four types of metal ions to link two organic ligands, resulting in the formation of five MOFs derivatives named Mn(BTC), Mn(BDC), Fe(BDC), Co(BDC), and V(BDC). Among these, Mn(BTC) stands out due to its favorable Zn<sup>2+</sup> storage capacity, making it an effective cathode material for Zn hybrid devices. In addition, a ZIF-8@Zn anode was developed by coating ZIF-8, which helps regulate the dissolution-deposition behavior. Above Figure 1.36d shows a schematic of the Mn(BTC) cathode paired with the ZIF-8@Zn anode in ZIBs. These batteries maintain 92% of their initial capacity after 900 cycles at a current density of 1 A g<sup>-1</sup> (Fig. 1.36e). According to existing literature, coordination-unsaturated MOFs have been synthesized as electrode materials, facilitating efficient Zn<sup>2+</sup> transport and electron exchange. Figure 1.36f shows the performance rate of three samples. The Zn//Mn-H<sub>3</sub>BTC-MOF-4 batteries display a capacity reduction from 138 mA h g<sup>-1</sup> to 98 mA h g<sup>-1</sup> when the current density increases from 0.1 A g<sup>-1</sup> to 3 A g<sup>-1</sup>.



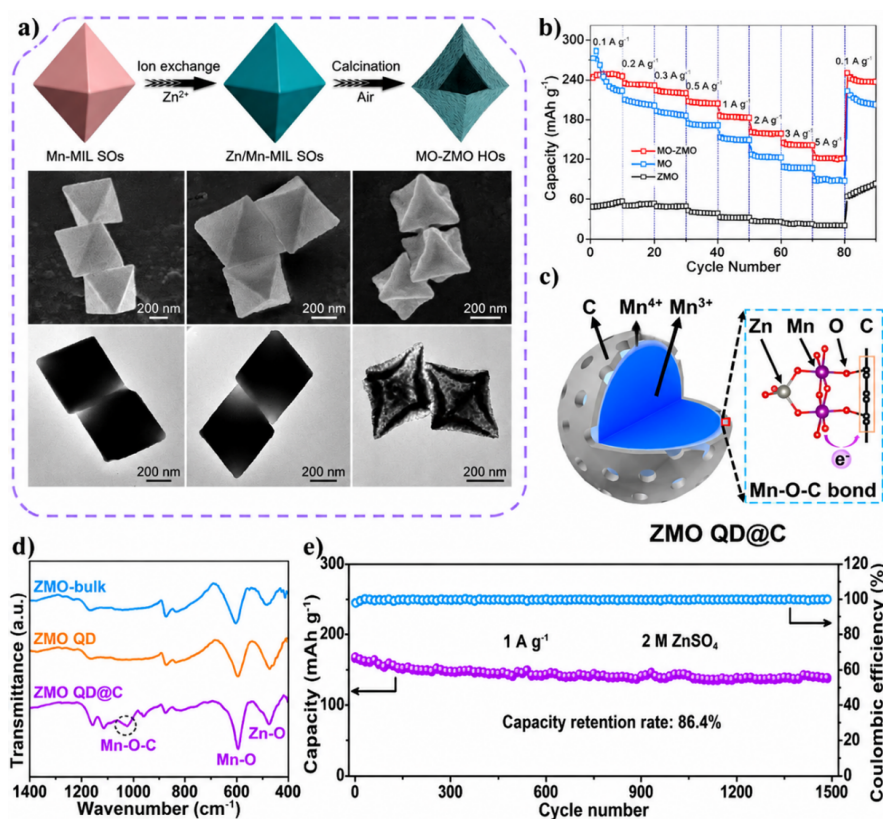
**Figure 1.36:** Schematic diagram of the Zn//ZnHCF battery. (b) Rate capability of the Zn//ZnHCF battery, (c) Galvanostatic charge and discharge curves at different current densities of the Zn//ZnHCF-PANI battery, (d) Schematic of the Mn(BTC) cathode//ZIF-8@Zn anode ZIBs. (e) Cycling performance at 1 A g<sup>-1</sup> in 2 M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> electrolyte, (f) Rate capability of Zn/Mn-H<sub>3</sub>BTC-MOF-4 hybrid battery [149, 150]

Lou et al. [149] prepared Mn<sub>2</sub>O<sub>3</sub>–ZnMn<sub>2</sub>O<sub>4</sub> hollow octahedra (MO-ZMO HOs) from Mn-MIL octahedra via cation exchange and annealing shown in figure 1.37(a). The MO-ZMO HO sample retains its octahedral shape, though the particle size shrinks during calcination. The design of hollow heterostructures and double phases provides dense active sites, resulting in a specific capacity of 247.4 mAh/g at 0.1 A/g in figure 1.37(b). The carbon framework enhances ion diffusion, conductivity, and stabilizes the material. Niu et al. integrated Mn<sub>3</sub>O<sub>4</sub> quantum dots with carbon to create a ZMO QD@C electrode [150], showing a mixed manganese valence state in figure 1.37(c). The Mn<sup>4+</sup> concentration at the cathode-carbon matrix interface and Mn<sup>3+</sup> inside the QDs, along with Mn–O–C bonds, prevent manganese dissolution. The ZMO QD@C in figure 1.37(d) electrode maintains 143.9 mAh/g after 1500 cycles, with 86.4% capacity



retention at 1 A/g shown in figure 1.37(e).

Moreover Vanadium-based MOFs are known for their stability. Mondal et al. used MIL-100(V) as a cathode material, citing its high surface area (2320 m<sup>2</sup>/g), stability in aqueous electrolytes, and diverse valence states of V ions. MIL-100(V) showed a discharge capacity of 362 mAh/g at 0.2 A/g, with 95.45% capacity retention after 3500 cycles at 5 A/g. Its excellent performance is attributed to its porous structure and electrochemically active sites. Ru et al. used MIL-47, a vanadium-based MOF with a 1D rod-like structure, for AZIB cathodes. MIL-47 showed 320 mAh/g at 0.1 A/g and 86 mAh/g after 70 cycles at 1 A/g, with enhanced electron transport due to its open structure. Some MOF-derived composite as cathodes for Zn hybrid devices are given in Table 1.5 with their electrochemical performance.



**Figure 1.37:** a) Schematic illustration of MO-ZMO HOs with FESEM/TEM images of Mn-MIL SO, Zn/Mn-MIL SO and MO-ZMO HO samples. (b) Rate performance based on discharging curves, (c) Illustration of the Mn valence state distribution in ZMO QD@C. (d) FTIR spectra and (e) long-term cycle test of ZMO QD@C at 1 A g<sup>-1</sup> [150]

**Table 1.5:** MOF-derived composite as cathodes for Zn hybrid devices

| Cathode                                      | Cap. (mAh/g) | J (A/g) | Ret. (%) | Cycles | S.A. (m <sup>2</sup> /g) | Ref   |
|----------------------------------------------|--------------|---------|----------|--------|--------------------------|-------|
| Mn(BTC)                                      | 112          | 0.05    | 92       | 1500   | —                        | [151] |
| Mn-<br>H <sub>3</sub> BTC-<br>4              | 138          | 0.1     | 93.5     | 3000   | 21.8                     | [152] |
| MOF-73                                       | 815          | 0.25    | 92       | 1000   | —                        | [153] |
| Mn-<br>MOF/CNT                               | 260          | 0.05    | 100      | 900    | 111.8                    | [154] |
| Mn <sub>2</sub> O <sub>3</sub>               | 435          | 0.1     | 98       | 1000   | 117.6                    | [155] |
| Mn <sub>3</sub> O <sub>4</sub> @C            | 335          | 0.2     | 100      | 1900   | 145                      | [156] |
| $\delta$ -<br>MnO <sub>2</sub> -<br>CNA      | 346.7        | 0.5     | 90.4     | 50000  | —                        | [157] |
| MnO/C                                        | 172.3        | 0.5     | 90.6     | 900    | 175.2                    | [158] |
| C-MnO <sub>2</sub>                           | 160          | 1.0     | 81       | 2000   | 136                      | [159] |
| $\alpha$ -<br>Mn <sub>2</sub> O <sub>3</sub> | 225          | 0.05    | 53.3     | 1700   | 24.1                     | [160] |
| MnO@C                                        | 456          | 0.05    | 84.2     | 2000   | —                        | [161] |
| t-<br>MnO@C                                  | 743          | 0.05    | 92       | 20000  | 29.8                     | [162] |
| Ni-<br>MnO/PC                                | 347.4        | 0.1     | 91.1     | 6000   | 250.3                    | [163] |
| KMO/CNFs                                     | 472          | 0.3     | 90       | 1000   | 283.1                    | [164] |
| ZnCo-<br>MnO/C                               | 428.9        | 0.1     | 98.7     | 3000   | —                        | [165] |
| MIL-<br>100(V)                               | 362.0        | 0.1     | 95.45    | 3500   | 866                      | [166] |
| MIL-47                                       | 320.0        | 0.1     | 57       | 70     | 700                      | [167] |
| p-<br>VO <sub>x</sub> @C                     | 464.3        | 0.2     | 84.2     | 2000   | 22                       | [168] |
| P-V <sub>2</sub> O <sub>5</sub>              | 293.0        | 0.1     | 61       | 2000   | 11.4                     | [169] |
| ZnVO-<br>800                                 | 314.0        | 0.1     | 90       | 3000   | 126.5                    | [170] |
| N/C@V <sub>2</sub> O <sub>3</sub>            | 258.0        | 0.1     | 71.0     | 4500   | 13.1                     | [171] |
| V <sub>2</sub> O <sub>3</sub> @C-<br>CC      | 448.0        | 0.1     | 96.5     | 1500   | 14.6                     | [172] |
| V <sub>2</sub> O <sub>5</sub>                | 284.0        | 0.1     | 99.6     | 1400   | 119.3                    | [173] |
| ZMO<br>QD@C                                  | 320.6        | 0.1     | 86.4     | 1500   | 240.4                    | [174] |

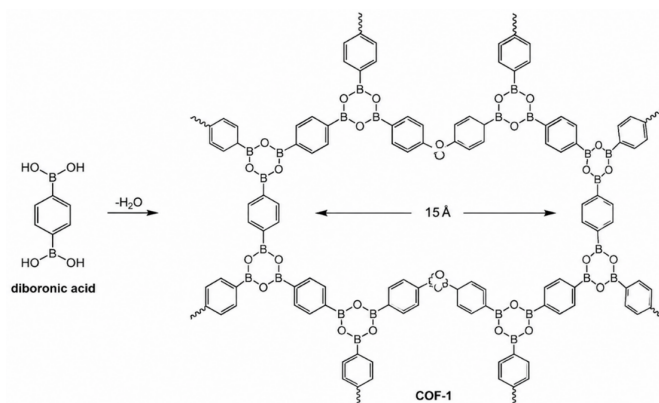
Materials with expanded layered structures often provide more redox active sites and shorter ion diffusion paths, thus enhancing the electrochemical performance of the cathode materials. In future research, various improvement strategies could be used to develop new MOFs and their derivative cathode materials for ZnHSCs such carbonized



MoF-5 which will be discussed in detail in chapter 4.

## 1.9 Covalent Organic Frameworks (COFs)

Organic materials are famous for their environmentally friendly attributes, diversity, low cost and sustainability. Their intrinsic features allow for a great deal of design flexibility regarding structure, morphology and functionality to accommodate a variety of cations. Covalently Organized Framework (COFs) is a new class of crystalline materials with these characteristics and importantly the COFs structure is permanently porous with covalently linked organic building blocks. This has made COFs a subject of much interest and they have been applied in fields like catalysis, gas storage, sensors, and energy storage. Nevertheless, the mechanisms and application of COFs in Aluminum-ion battery (AIBs) are still not well studied. To fill this gap, it is essential to synthesize COFs that can host Al ions, understand their electrochemical behavior and charge storage mechanism, and offer guidelines for designing high-performance COF cathodes for aqueous/non aqueous AIBs.



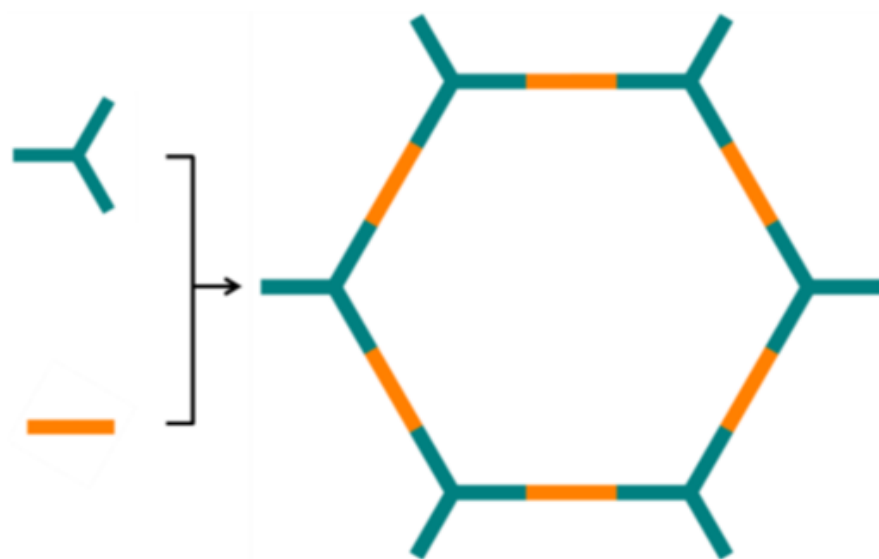
**Figure 1.38:** Synthesis of the first COF (COF-1) by self-condensation of 1,4-benzenediboronic acid

Yaghi group in 2005 introduced covalent organic frameworks (COFs) (Figure 1.38), which are 2D or 3D [175] materials formed by covalent linking of organic precursors with strong covalent bonds to form porous crystalline materials [176]. Because of the easy tunability of the geometry and pore size of COFs through the choice of building-blocks, precise control of physical and chemical properties is possible. The porous channels in COFs are well defined, and mass transfer is improved, which makes them possible application in catalysis, separation, sensing and electrode materials. Moreover, the diversity of building blocks and synthesis strategy allows the incorporation of many electrochemical redox groups in COFs. Many synthesis pathways for COFs have

been developed since the first COF was synthesized via self-condensation of boronic acids (Figure 1.38), and flexibility can be achieved to synthesize COFs for different uses [176–179].

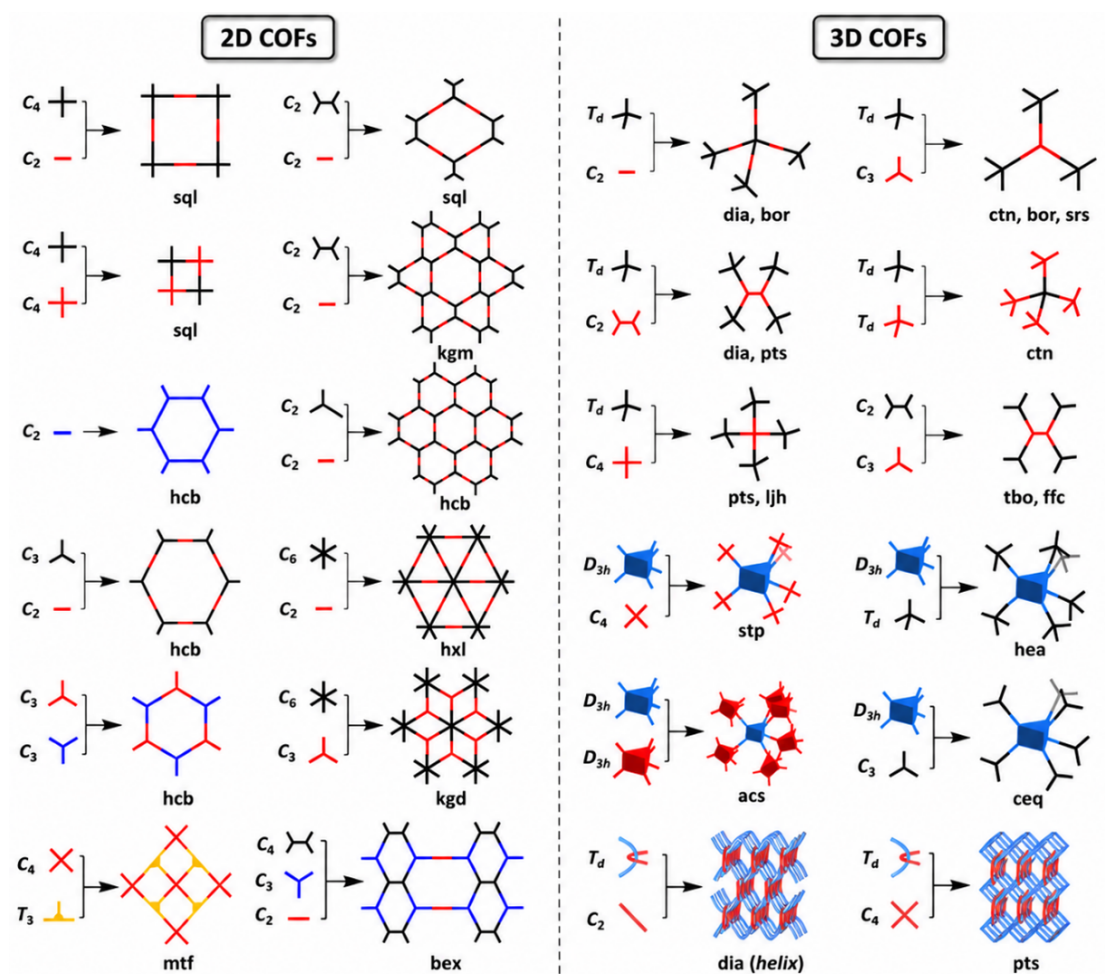
### 1.9.1 Structural Features of COFs

In COFs for each covalent bond to be oriented correctly, the monomers used should have relatively stiff backbones with the reactive sites in different geometries. Figure 1.39 shows the basic design concept for COFs having hexagonal pore.



**Figure 1.39:** Basic topological diagrams for the COFs with hexagonal pores [175]

COFs have diversity of ligands and linkers with different functional groups and geometries. They have been divided into two types of topologies, 2D and 3D shown in the figure 1.40. These Organic materials are composed of lightweight elements, such as C, H, O, and N, affordable and sustainable, which not only offer structural versatility but also facilitate molecular design and functional modulations. They have various applications in ESS most importantly cathode material in various metal ion hybrid devices, batteries and supercapacitors.

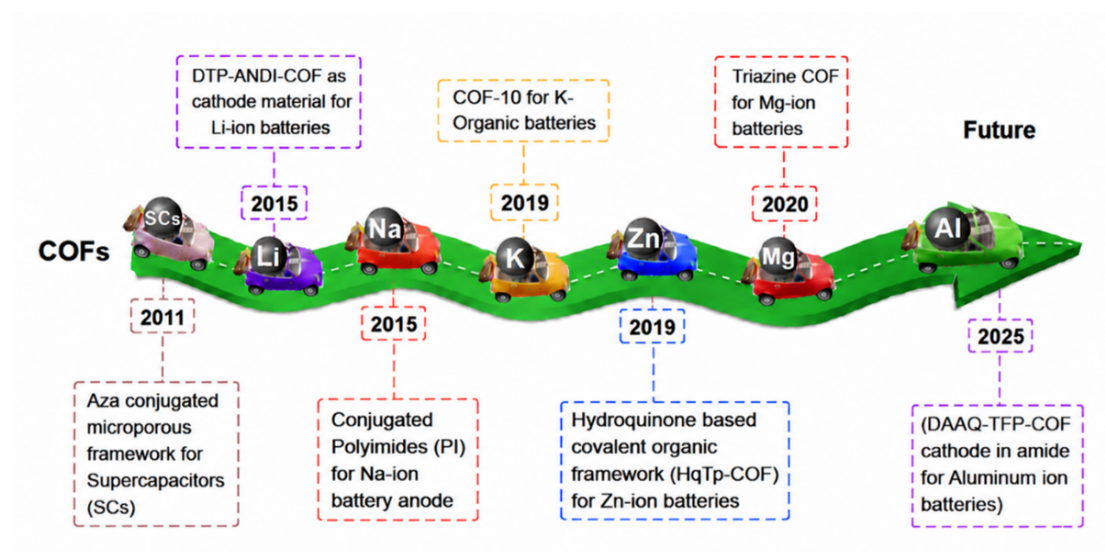


**Figure 1.40:** Basic topologies for designing 2D COFs and 3D [180]

### 1.9.2 COFs electrodes for Energy storage devices

COFs possess several attractive properties, which have led to their emerging as promising materials for next-generation rechargeable metal-ion batteries such as Tunability of porous architecture, linker units of different lengths can be used to adjust the pore size, and optimise the pore and channel structure for efficient ion transport. Framework functionalization, the wide variety of organic components available as building blocks provides a degree of flexibility for the post-modification or design of pre-functionalized components into the COF framework. This flexibility enables the tuning of the electrochemical properties of COFs, including specific capacity and discharge voltage, which are essential for batteries with excellent performance. The covalent bonding of organic units, hydrogen bonding and  $\pi$  -  $\pi$  stacking interactions in COFs make them highly soluble in both aqueous and non-aqueous electrolytes during electrochemical reactions, resulting in long cycling stability of COF electrodes. Global availability and non-toxicity

of raw materials used to produce COFs are all light elements, which are low-cost, environmentally friendly and even degradable. These materials are non-toxic and sustainable, in contrast to the toxic inorganic heavy metals. The distinctive properties make COFs a promising material to be developed into advanced electrode materials in different energy storage technologies. Development of various ESS devices based on COFs are shown in the figure 1.41 [180]. For the future applications COFs potential as a cathode material will be explored for AIBs.



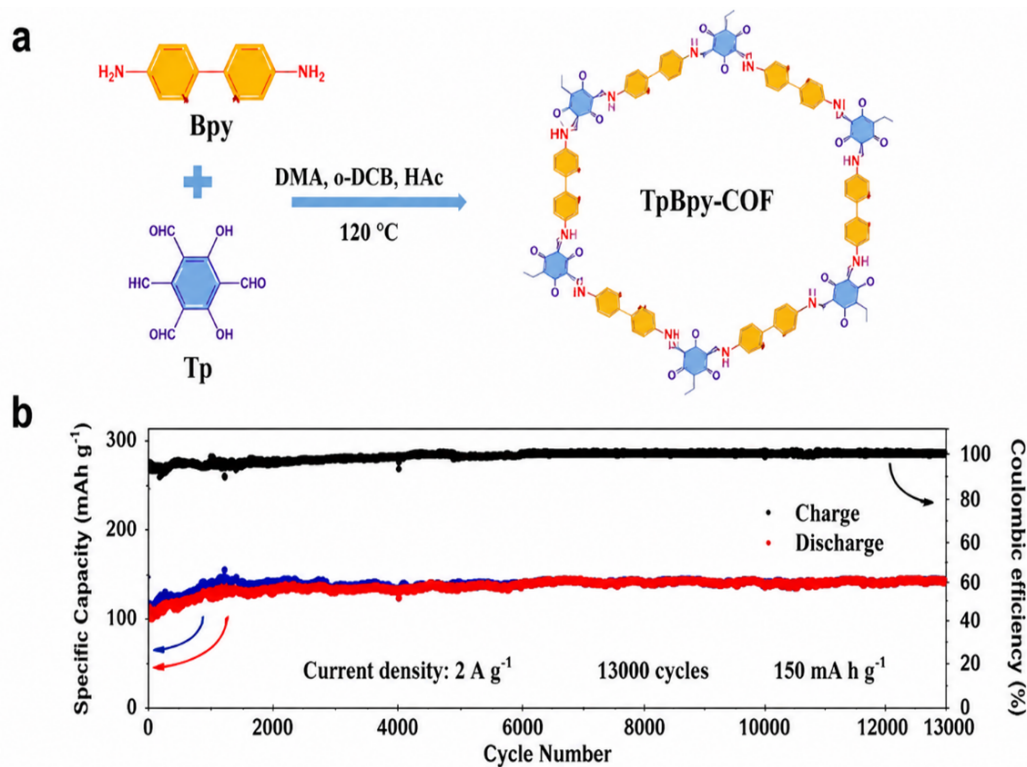
**Figure 1.41:** Timeline and progress of COFs for applications in the different ESSs. [181]

### 1.9.3 COFs cathodes in AIBs

Aluminum-ions batteries (AIBs) are a promising alternative showing increased safety, lower cost and higher energy density for applications in large-scale power grids and electric vehicles.  $\text{Al}^{3+}$  ions, however, have a high charge density and they strongly interact with the host lattice, which restricts the number of host materials that can facilitate reversible deintercalation of  $\text{Al}^{3+}$  ions. That's why these materials tend to encounter capacity and lifecycle problems.  $\text{AlCl}_3$ -[Emim]Cl is the most used electrolyte in AIBs, which allows for reversible intercalation and deintercalation of  $\text{AlCl}_4^-$  or  $\text{Al}_2\text{Cl}_7^-$  anions. Lu et al. were inspired by the graphite layers being able to accommodate  $\text{AlCl}_4^-$ , and he designed COFs containing 2,2-bipyridine as the cathode material (TpBpy-COF) shown in figure 1.42a [182].

The X-ray diffraction confirmed that the structure of TpBpy-COF is 2D layered, enabling  $\text{AlCl}_4^-$  diffusion to occur. Theoretical calculations revealed that TpBpy-COF acts as a semiconductor with a bandgap of 1.59 eV, thereby improving electron transport. The IR spectra showed that the C=C bonds did not change, but C=N bonds

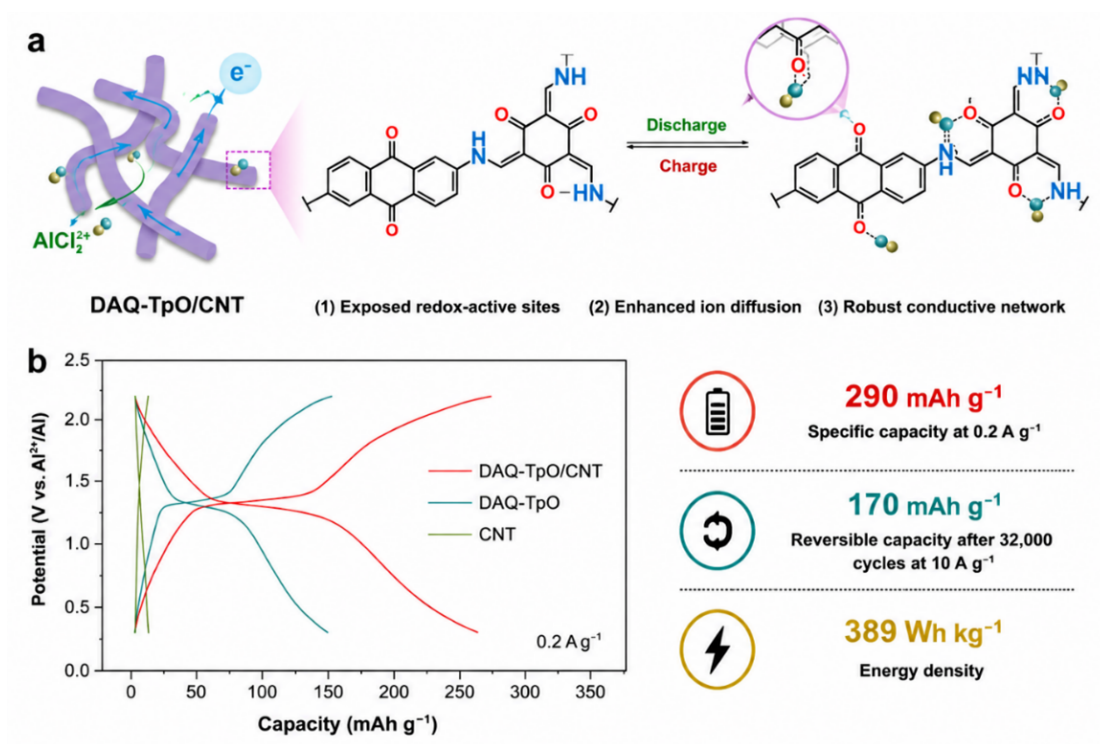
did, suggesting good interaction with  $\text{AlCl}_4^-$ . Consequently, the electrode exhibited a high long cycle stability with  $150 \text{ mAh g}^{-1}$  after 13,000 cycles at  $2 \text{ A g}^{-1}$  shown in figure 1.42(b).



**Figure 1.42:** Schematic representation of the synthesis route of TpBpy-COF. b) GCD capacities for AIB in 0.01–2.3 V. [181]

More recently Peng et al. fabricated the Al-Organic battery cathode materials based on  $\text{C}=\text{O}$  groups supported by CNT shown in figure 1.43(a) based on COF [183]. Batteries is  $290 \text{ mAh g}^{-1}$  at  $0.2 \text{ A/g}$ . The reversible capacity is  $170 \text{ mAh g}^{-1}$  after 32,000 cycles at  $10 \text{ A g}^{-1}$  with an energy density of  $389 \text{ Wh kg}^{-1}$  in the figure 1.43(b). Such a remarkable performance is due to the multiple  $\text{C}=\text{O}$  and  $\text{C}-\text{N}$  groups available for storing many  $\text{AlCl}_2^+$  ions through a pseudocapacitive process. Moreover, the COF network and conductive CNT channels play a synergetic role, further enhancing the structural stability and facilitating diffusion of ions and electrons, which results in excellent efficiency and durability of the AIBs.





**Figure 1.43:** Schematic illustration of the a) DAQ-TpO/CNT multiple redox sites. b) Galvanostatic discharge/charge profiles of DAQ-TpO/CNT, DAQ-TpO, and CNT [181, 184].

In the synthesis of COFs, usually a mixture of polar and nonpolar solvents is employed as the reaction medium for reversible covalent bond formation. Solvents, catalyst, reaction temperature and reaction time are important parameters used to thermodynamically control the reaction. Many COF cathodes and their electrochemical performance have given in Table 1.6.

**Table 1.6:** Various COFs cathode and their electrochemical performance in AIBs

| COFs Material                  | Active Materials (Proportion)           | Init. Cap. (mAh/g) | J (A/g) | Cycles | Ref   |
|--------------------------------|-----------------------------------------|--------------------|---------|--------|-------|
| DAQ-TpOMe (DATP) COFs          | DAQ + TpOMe (60% COF + 40% CNT)         | 140                | 2       | 100000 | [185] |
| DAQ-TpO COFs                   | DAQ + TPO (COF:CNT $\approx$ 80:20)     | 290                | 10      | 320000 | [183] |
| 2D-NT-COF                      | TTTA + NTCDA (COF:CNT = 70:30)          | 132                | 1       | 4000   | [186] |
| Phenanthrenequinone (PQ)-based | PQ triangle (PQ- $\Delta$ ) derivatives | 110                | 2       | 5000   | [187] |
| Heterocyclic quinone polymer   | TABQ + PYT (PYTQ:CNT = 2:1)             | 295                | 1       | 4000   | [188] |

The crystallinity and porosity of the COFs obtained depend on these variables. Thanks to the global efforts of researchers, COF synthesis has expanded from the original boroxine and boronate-ester linked COFs [176] to a variety of other linkages such as borosilicate, triazine, imine, hydrazone, borazine, squaraine, azine, phenazine, imide, double-stage, spiroborate, C=C, amide, viologen, hypercoordinate silicon, urea and 1,4-dioxin [189–197]. Solubility of COFs depends on the size of systems and types of reactive units. Some examples include boroxine-based COFs (which degrade in water) and Schiff-base linked COFs (which tend to be unstable under basic conditions). Imide-based COFs, on the other hand, are known to be structurally robust. We have developed a novel COF by imine condensation reaction as a cathode material for AIBs which will be discussed in chapter 5.

## 1.10 Research Objectives and contents

However, electrochemical energy storage (EES) systems have yet to be practically implemented due to the lack of high-performance electrode materials. The design of 2D materials, with higher specific surface areas for ion adsorption and enhanced ion transport capacities (than bulk materials) are also more recent lines of effort. Nevertheless, although great progress has been achieved, the "cathode bottleneck" is still a challenging issue for LMBs, ZnHSCs, and AIBs. High energy systems typically have structural degradation and slow reaction rates in LMBs. Although ZnHSCs are safer and more cost-effective, they still face challenges in achieving hierarchical porosity to promote efficient

ion diffusion and exposure of active sites. AIBs have even more challenges because the charge density of  $\text{Al}^{3+}$  ion is high, which leads to strong electrostatic interactions between  $\text{Al}^{3+}$  and the ions in the electrolyte, which slows down the ion diffusion and renders most of the cathode materials structurally unstable.

The structures of COFs and MOFs are highly tunable and have large surface areas. The low electronic conductivity of MOFs and chemical instability in many common electrolytes, and the need for complex structural modifications for high-rate applications of COFs, are challenges that must be addressed. The purpose of this research is to provide a unified approach and to fill this gap from the previous studies that dealt with these ESS as isolated problems. Therefore main objective of the chapter 3 is to design a bimetallic dual-metal organic framework (DMOF) via one step hydrothermal method as a cathode for LMBs and demonstrate that the synergistic interaction between two metal centers, combined with high redox-site density and a well-defined pore architecture, leads to high surface area, high capacity and cycling stability compared to monometallic analogues. In Chapter 4, the aim is to develop a hierarchically porous carbon cathode through controlled carbonization of (CMOF-5) and establish that the resulting material provides sufficient electronic conductivity, active-site exposure, and structural integrity to meet the energy and power density requirements of ZnHSCs. Focus of chapter 5 is to design a covalent organic framework-based (COFs) cathode with ordered pore channels and a high density of redox-active sites, and to demonstrate its ability to accommodate  $\text{Al}^{3+}$  ion insertion and extraction with improved ion diffusion kinetics and long-term structural stability AIBs. This thesis will overall examine the key features of MOFs and COFs including their pore structure, density of redox-sites, and their engineering for conductivity, and how these features can be harnessed to solve the cathode challenges of LMBs, ZnHSCs and AIBs. These materials will be systematically characterized by the following techniques and electrochemical measurements (Chapter 2) and detailed results and analysis will be presented (Chapter 3-5). In the final chapter, Chapter 6, conclusions will be drawn from the main experimental results presented in this thesis. The dissertation closes with a discussion of future research directions, outlining the opportunities and remaining challenges that must be addressed to further advance MOF and COF-based cathode materials for practical energy storage applications.



## Chapter 2

# Characterization Techniques

### 2.1 Qualitative Characterizations

#### 2.1.1 X-Ray Diffraction

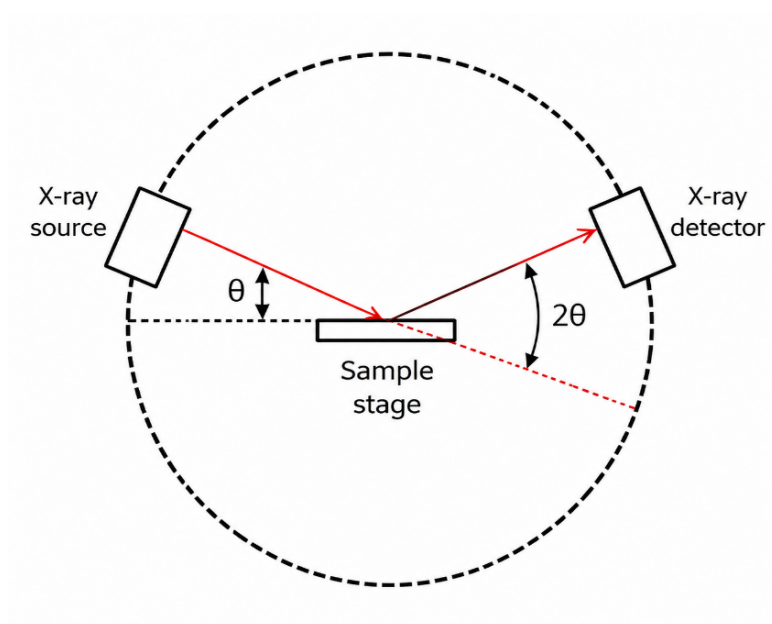
When a monochromatic beam of x-rays having some wavelength irradiates a material, the beam of light is dispersed by atoms of that material which further produces diffracted beam of higher intensity. That intensity of the diffracted light is then determined by scattering of atoms of material. If the angle of incident light is  $\theta$  then the angle of observed constructive or destructive interference will be  $2\theta$  from incident light as well as  $\lambda$  is the wavelength, if it satisfies the Bragg's equation [198]. It can also be written as in following equation:

$$2d \sin \theta = n\lambda \quad (2.1)$$

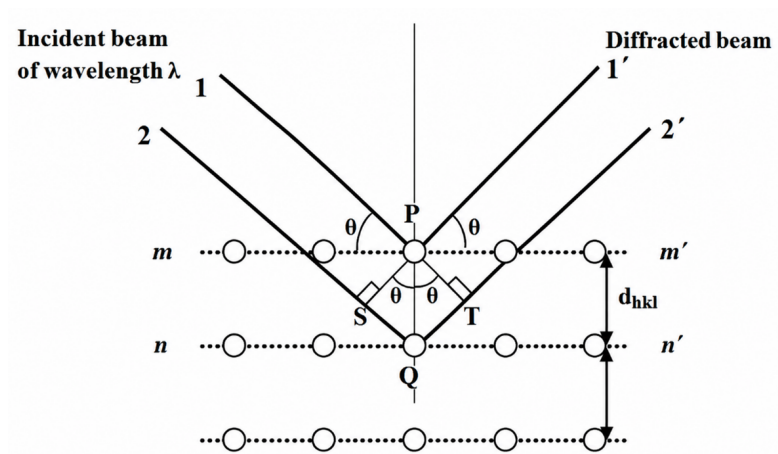
Where  $d$  is inter-planar spacing creating diffraction,  $\theta$  is diffracting angle and  $n$  is known as order of diffraction.

Bragg's law connects wavelength of monochromatic light to the lattice spacing in a crystal and the diffraction angle [199]. These rays are then observed, operated and counted. Because of random direction of powdered sample, the diffraction of lattice has been obtained and by the range of  $2\theta$  angle the sample can be scanned. Diffracted peaks are converted to interplanar spacing which allows the recognition of sample because sample has its unique interplanar spacing. We can calculate particle size, interplanar spacing, texture co-efficient, and grain size through Bragg's law equation. The interplanar spacing is the distance between two consecutive planes of a structure.

Diffractometers contain three components as shown in figure 2.1 i.e. X-Ray Tube/source, Specimen (Sample stage) and X-ray detector. X-rays are produced in



**Figure 2.1:** Schematic representation of X-ray Diffractometer



**Figure 2.2:** Schematic Diagram of X-ray Diffraction (Bragg's Law)

a vacuum tube which contains high voltage to accelerate electrons. They escaped through a cathode to higher velocity. These electrons strike with metal target (anode) to create x-rays. When wavelength of incident light is close to the interplanar spacing then the diffracted beam of light takes place as shown in figure 2.2. This experiment is performed at room temperature.

The grain size can be calculated by using the Debye-Scherrer's formula as given [200,201]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2.2)$$

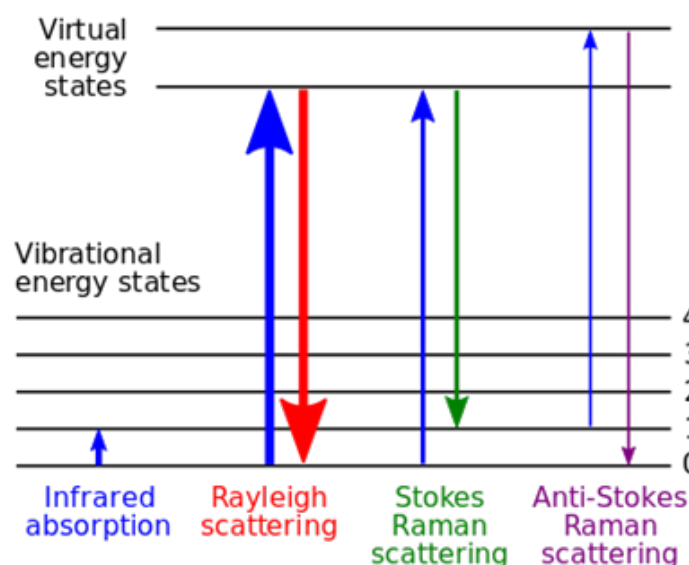
Where  $k$  is the constant having value 0.9,  $\lambda$  is the Cu-K $\alpha$  wavelength and its value is 1.54 Å,  $\beta$  is full width half maximum (FWHM),  $\theta$  is the Bragg's angle. The beam of light is diffracted at half maximum of a selected peak called  $\beta$ , whereas X-ray's wavelength is represented as  $\lambda$  in the present experiment [202]. To get information from solid state materials, powder XRD can be used [203]. It consists of two types of instruments for analysis: the XRD powder camera and the X-ray diffractometer. In the powder camera method, cylindrical photographic film placed around the specimen where diffraction maxima or cones are recorded while about diffractometer it's working has already mentioned. Powder X-ray diffraction (XRD) is particularly useful to determine the structure of insoluble two-dimensional materials, such as graphene derivatives [204]. For detailed structural analysis, Rietveld refinement can be applied to extract precise lattice parameters and atomic positions [205].

In this thesis, XRD was performed to determine the intended crystal structures and phase composition of as synthesized MOFs and COFs. Structural data were confirmed by PXRD by using Bruker AXS D8 Advance diffractometer ( $2\theta$  resolution:  $\pm 0.01^\circ$ ) in Bragg-Brentano geometry with CuK $\alpha_1$  radiation ( $\lambda = 1.5406$  Å).

### 2.1.2 Raman Spectroscopy

Raman scattering is a technique built on Raman Effect which states that frequency of dispersed light opposes frequency of monochromatic light that based on inelastic scattering of incident light correspond vibrating molecules [206]. It analyzes molecular vibrations. In Raman scattering, sample is irradiated by monochromatic light that interacted with atoms of specimen and develops scattered light. This scattered radiation having different frequency than that of incident light is utilized to build a Raman spectrum.

This spectrum appears because of inelastic impact between sample molecules and



**Figure 2.3:** Types of scattering in Raman Spectroscopy

incident light. When incident light strikes the sample, it is scattered randomly. Most of the frequency of scattered radiation is same as frequency of incident light that comprises Rayleigh scattering. A little amount of frequency of scattered radiation is different from incident light that comprises Raman scattering shown in figure 2.3. Stokes lines occur when incident radiation's frequency is greater than scattered radiation's frequency and when it is lower than frequency of scattered light then antiStokes line arose in Raman spectrum. The scattered light is computed at right angle to incident light [207]. Stokes lines are extremely intense than anti-Stokes line & computed in Raman spectroscopy because Raman lines include transformations from lower to higher energy levels. Anti-Stokes lines are computed with fluorescing specimens because interference is caused by fluorescence with Stokes lines. Raman scattering is dependent on incident light's wavelength. The modes of Raman are same as Infrared modes. The Raman modes are produced by variation in polarizability while Infrared modes are generated by change in dipole moment. Interface between incident photon and electric dipole of molecules provides magnification of Raman Effect. Vibrational modes which don't have a change in the dipole moment are inaccessible in Infrared but can be studied by Raman spectroscopy. A Raman spectrum is a graph of the intensity of the scattered photons against the frequency of the scattered photons. The difference between the frequencies of the incident and scattered photons is called "Raman shift", which is measured in wavenumbers ( $\text{cm}^{-1}$ ). The change in photon frequency is not significant and is not important, but the absolute frequency is important, making Raman spectroscopy frequency independent, thus permitting the use of a variety of laser sources [208]. The

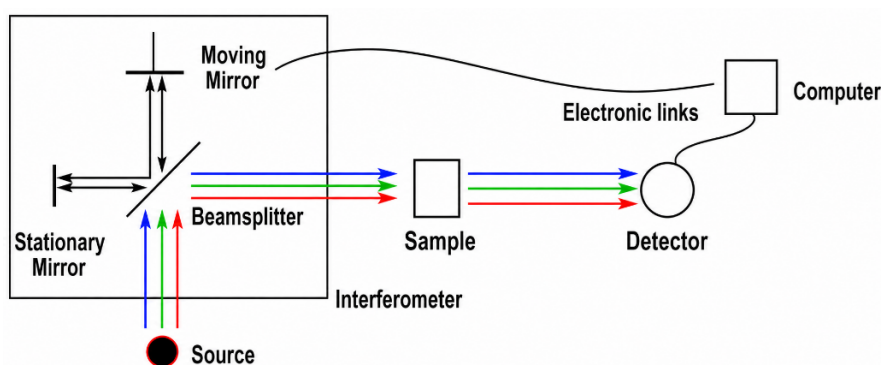
Raman Spectroscopy is instrumented in the following way: There are three main parts to a Raman spectrometer, the laser, the collection device, and the spectrograph. The Raman signal is excited by a coherent laser beam. The collection device is used to filter out the Rayleigh-scattered photons (which have the same frequency as the incident photons) and to prevent background noise from the fiber-optic cables from reaching the spectrograph, leaving only the Raman-scattered photons to reach it. Each scattered photon is then detected and recorded by a detector coupled to the spectrograph, which records the intensity profile of the photon. Room-temperature Raman spectroscopic investigations of the dispersion properties of metal oxides have been carried out.

A Raman spectrum has several peaks which are an outcome of the intensity and wavelength of the Raman scattered light. The peaks relate to specific molecular bond vibrations, either single bonds (C-C, C=C, N-O, C-H, etc.) or collective vibrations (breathing modes of the benzene ring, polymer chain vibrations, lattice dynamics, etc.). In addition to vibrational fingerprinting, Raman spectroscopy (RS) can also provide information about the chemical structure of the material, including details about its phase, polymorphism, and the presence of contaminants or impurities. Every molecule or material has a spectral ‘fingerprint’ so Raman spectroscopy can be used to quickly identify and differentiate materials. This is typically done using reference spectra databases, commonly called spectral libraries, in which thousands of reference spectra are systematically searched to find the closest matches to an unknown sample. Combined with mapping and/or imaging systems, it can be even more useful, allowing us to create spatially resolved chemical images. These images are useful for studying the distribution of individual components, polymorphs, and phases, and local variations in crystallinity, particularly at the molecular scale. The scope of this spectroscopy greatly broadened in 2006 when the first Raman characterization of graphene was provided by Ferrari, et al. [209]. Ever since, it has emerged as a staple method in determining the quality, integrity and number of layers in two-dimensional materials (2DMs) that are exfoliated. The present state of it as a main approach for measuring disorder in graphitelike systems is well established [210–212].

Due to the variety of redox-active sites in COFs and MOFs, Raman Spectroscopy is broadly used in the characterization of these materials. In this dissertation, the changes in the vibrational modes of the samples were studied by using a Raman Microscope (Renishaw inVia) with an excitation wavelength of 532 nm.

### 2.1.3 Fourier Transform Infra-Red Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is extensively used to analyze the chemical composition of diverse inorganic and organic substances and their constituents. The process involves passing infrared radiation through a sample and measuring the wavelengths that are absorbed by the sample. The resulting infrared absorption bands give information on the molecular structure and composition of the material [213] as well as the intensity of the absorption at each wavelength. Infrared radiation is absorbed by material at a specific wavelength, which leads to molecular transition to a higher energy state from a lower energy state, which also results in changes in the dipole moments. The strength of the absorption bands depends on the number of energy levels available and the likelihood of transitioning from one configuration of dipole moments to another. The infrared spectrum contains information about the molecular structure of a specific material that can be deduced [214]. The general absorption region, which is the part of the spectrum used most often, is from the 400 to 4000  $\text{cm}^{-1}$  region. The basic parts of a FTIR spectrometer are: Radiation source, Interferometer, Sample compartment (holder), Amplifier, Analog-to-digital (A/D) converter, Detector, Output device (computer). The radiation spectrum created by the radiation directed onto a target material is an interference-based radiation spectrum in the infrared region, obtained using an interferometer. The Michelson interferometer consists of two mirrors, one fixed and one movable, and a beam splitter. The beam splitter splits the incident light into two beams that are directed towards both mirrors.



**Figure 2.4:** Working Principle of FTIR

In this process the two beams are combined again in the interferometer, creating optical interference shown in figure 2.4. The resulting interference pattern is recorded in the form of an interferogram, which represents the intensities of the interference spectrum. This recombined radiation is then focused on the detector, after interacting with the sample. The signal detected is then amplified to increase its strength and

sent to an analog-to-digital (A/D) converter that converts the analog signal to a digital signal. Finally, the digitized signal is sent to an output device (computer) and a Fourier transform is performed to change the interferogram into a traditional infrared absorption spectrum.

FTIR spectroscopy identifies functional groups in a molecule by irradiating it with infrared radiation. The technique is applicable to solid, liquid, and gaseous samples. The infrared region lies between the visible and microwave regions and is divided into three sub-regions: near-IR ( $14000\text{--}4000\text{ cm}^{-1}$ ), mid-IR ( $4000\text{--}400\text{ cm}^{-1}$ ), and far-IR ( $400\text{--}40\text{ cm}^{-1}$ ). The technique records the amount of IR radiation absorbed by the sample, which induces molecular vibrations and changes in dipole moment. The absence of a dipole moment indicates that the molecule is infrared-inactive. The resulting spectrum plots IR light intensity, expressed as absorbance or percentage transmittance, against wavenumber ( $\text{cm}^{-1}$ ).

Unlike traditional IR spectroscopy, which required selecting specific radiation ranges for each functional group a lengthy and time-consuming process, FTIR bombards the sample with an energy pulse simultaneously, generating an interferogram in the time domain. A Fourier transform then converts this interferogram into a frequency-domain spectrum. Since infrared radiation is low in energy, it cannot excite electrons but instead induces two main types of molecular vibrations. Stretching vibrations involve changes in bond length and can be symmetric or asymmetric. Bending vibrations cause changes in bond angle without altering bond length and are further classified into in-plane (scissoring and rocking) and out-of-plane (wagging and twisting) modes shown in the figure 2.5 [215–217]. \*[FTIR has also proven valuable in studying clay minerals and layered materials [218], which is relevant to the structural analysis of MOFs and COFs.]\*

In this dissertation, FT-IR was used to confirm the formation of an imine bond in the COF structure and its stretching and vibrational modes and the presence of carbonyl group in the form of aldehydes by using IR recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. For the MOF structure asymmetric and symmetric vibrations of the carboxylate groups of the organic ligand and shift after their interaction with metal ion was confirmed within the range of  $500\text{--}3500\text{ cm}^{-1}$  by using PerkinElmer Spectrum Two IR spectrometer ATR mode.

#### 2.1.4 X-Ray Photon Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) has its roots in 1887 when Hertz discovered the photoelectric effect. The technique became practical in the 1950s and became widespread after the

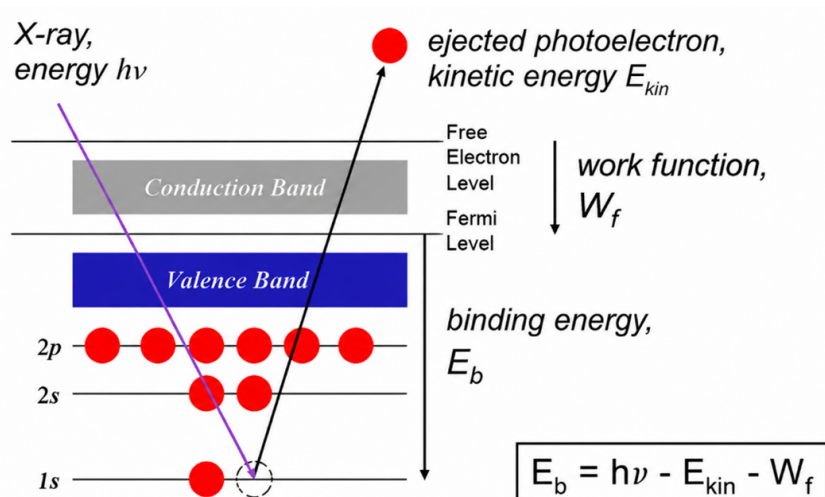
Nobel Prize in Physics was awarded to the Swedish scientist Manne Siegbahn in 1981 for his pioneering work in XPS [219]. XPS is a powerful surface-sensitive analytical instrument which can be used to characterize the elemental composition of surface layers, as well as to gain insight into atomic interactions, chemical bonding, layer thickness, size of nanoparticles and surface functionalization of materials [220]. It is an element detector which can detect the elements with a sensitivity of 0.1–1% and can detect all the elements except hydrogen and helium. XPS is a non-destructive technique which allows surface reactions to be studied in the range from 2 to 10 nm deep. The analysis is performed by analyzing the variation in the emission angle of the electrons that are ejected from the material's surface or by changing the excitation energy. Samples thicker than 10 nm cannot be examined because artifacts introduced by ionic doping and atomic intermixing in film depth profiling limit the maximum thickness of samples that can be examined. Other complications can be encountered due to oxidation state change and preferential elemental etching. The position of spectral bands is determined by the element, its orbital structure and the chemical context in which it is located, such as its location of heteroatoms in the structure. The number of electrons counted from the sample is found to be correlated with the peak intensities. The binding energies, the shape of peaks, spin-orbit doublets, multiple splitting, peak asymmetries, overlaps and satellite structures are all important for the correct interpretation of the data in the spectral deconvolution process [221–223]. In XPS measurements, core-level electrons are removed from atoms in the sample being measured. The binding energy of each ejected electron is a unique value determined by the core level, element source and local chemistry of the electron. The principle involved in this process is based on the first law of thermodynamics, the conservation of energy, which states that the energy of the incident X-ray photon is divided into binding energy and ejected electron energy. This relationship is expressed as,

$$E_B = h\nu - E_{kin} \quad (2.3)$$

Where the energy of the incident X-ray photons (with  $h$  being Planck's constant and  $\nu$  the frequency of X-ray photons), composed of  $E_B$ , the binding energy, and  $E_{kin}$ , is the kinetic energy of the ejected electron, but this is only valid if the samples are in a gaseous state, and the zero point is the vacuum level. In addition, there is a correction to be added for specimens, shown in figure 2.6.

For which the energy properties are macroscopic, this is the work function of the spectrometer  $W_f$ , which is the minimum energy needed to detach the most loosely bound electrons from the Fermi level. The modified equation for solid samples is then:





**Figure 2.5:** Working principle of XPS

$$E_B = h\nu - E_{kin} - W_f \quad (2.4)$$

The binding energy of the core-level electron with respect to the Fermi level of the sample appears in the expression  $E_B$  and  $E_{kin}$  denotes the kinetic energy and work function  $W_f$  measured by the spectrometer. XPS is a very common and powerful method of studying the chemical surface structure which includes the content of carbon and oxygen, and the binding energy (eV) of functional groups [224].

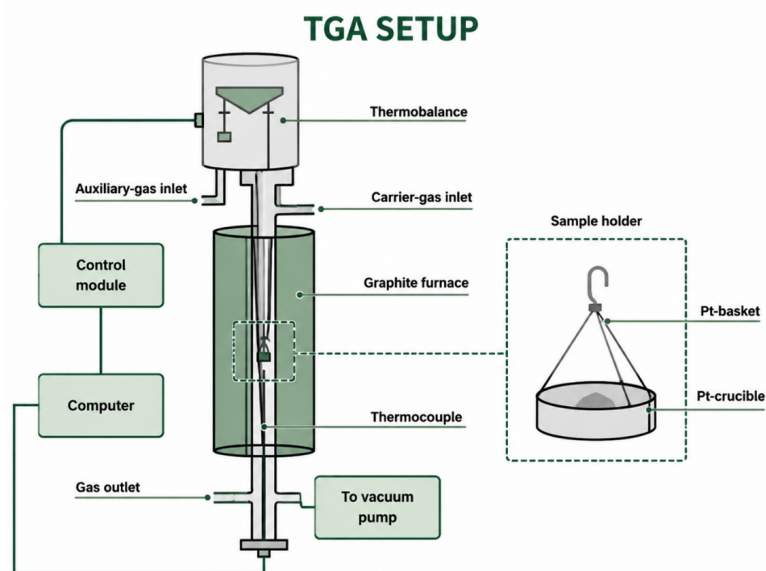
In this dissertation, XPS was used for the confirmation of the desired MOFs and COFs, their chemical composition and surface chemistry with K-Alpha X-ray photoelectron spectrometer (Thermo Scientific) equipped with an aluminum X-ray source (energy 1.4866 keV), operating at a vacuum level of  $10^{-8}$ - $10^{-9}$  mbar in the main chamber. The spot size of the X-ray beam was fixed at 400  $\mu\text{m}$ .

### 2.1.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique that monitors changes in the mass of a sample as it is subjected to controlled heating or cooling. It provides critical insights into a material's thermal stability, composition, and decomposition behavior [225, 226]. A typical TGA system consists of several key components: a sample pan, a high-sensitivity microbalance for detecting mass changes, a furnace for precise temperature control, a temperature regulation system, and a gas supply system capable of maintaining either an inert or reactive atmosphere. Sample temperature is continuously monitored by a thermocouple, while a data acquisition system records

mass loss as a function of either temperature or time shown in the figure 2.7.

In practice, the sample is placed in the pan and subjected to a controlled, gradual temperature increase. As the temperature rises, the sample may undergo mass loss through various thermally driven processes, including evaporation, decomposition, or oxidation. These changes are captured by the microbalance and plotted as a thermogravimetric curve, which conveys essential material characteristics such as decomposition temperatures, residual mass content, and overall thermal stability, all of which are fundamental to understanding a material's behavior under thermal stress. Due to its versatility, TGA finds broad application across material science, polymer chemistry, and environmental testing.



**Figure 2.6:** Schematic illustration of TGA setup

In thermogravimetric analysis, mass changes of samples from 1 mg to a few grams can be measured while the sample is heated up to 1600 °C in a furnace in both constant and variable gas flow. Every compound yields a distinct thermogram containing information on its thermal and oxidative stability, multicomponent composition, product lifetime, decompositions and moisture or volatile content [227, 228]. It is possible to identify several characteristic temperature regions in a typical thermogram. At temperatures below 150 °C the loss in weight is mostly attributed to the evaporation of solvents, the release of trapped gases, and the release of low molecular weight volatiles. In the temperature range of 150 °C to 250 °C, chemisorbed water is released, and there is a start of the decomposition of small additives. In the range of temperatures higher than 250 °C, the most significant thermal decomposition process takes place between the onset temperature and the end set temperature. In addition to the end set temperature,

non-volatile residues (metals, inorganic ashes) are left behind. Metals, under oxidizing conditions, can, however, be oxidized and gain mass as a result of the formation of higher oxidation states. TGA can also be combined with a thermal analysis technique like differential scanning calorimetry (DSC) or differential thermal analysis (DTA) to measure the heat flow as well as mass loss during the measurement [229]. The extension of the analytical capability is that it allows detect thermally driven events that do not involve mass change, such as crystallization, melting, solid-solid phase transition and glass transition.

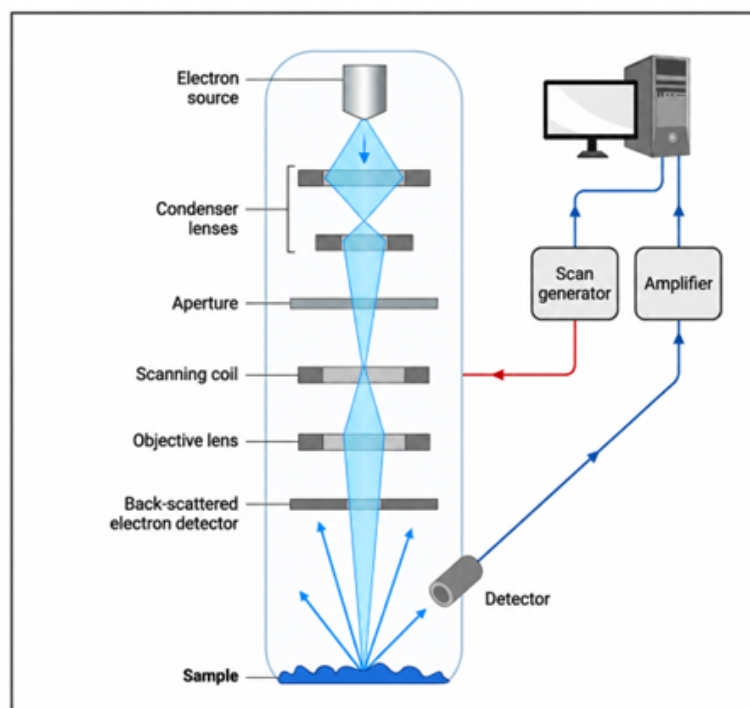
In this thesis different ranges of TGA instruments in nitrogen were used to study the thermal stability and mass loss of the MOFs and COFs samples by using suitable heating rate and temperature.

## **2.2 Morphological Characterizations**

### **2.2.1 Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) has been widely adopted for the morphological characterization of various materials, largely owing to the relative simplicity of specimen preparation [230]. In this technique, a tungsten filament (cathode) generates thermionic electrons with a potential difference of 1.0 to 30.0 kV, accelerated toward the anode shown in figure 2.8. Operating under a vacuum of less than  $10^{-5}$  Pa, the resulting electron beam is directed and focused onto the sample surface using condenser and objective electromagnetic lenses, scanning it line by line in a manner analogous to a cathode ray tube. When the sample interacts with the electron beam, it generates various signals, including secondary electrons, backscattered electrons, Auger electrons, and X-rays. These signals are detected by specialized detectors and processed by imaging software to create high-resolution grayscale images. Secondary electrons, primarily produced by outer-shell electrons released through inelastic scattering, are key to imaging surface topography [231, 232].

In contrast, backscattered electrons, resulting from high-angle elastic scattering between the beam and sample, provide compositional contrast. These signals are electronically amplified and processed to produce a detailed image of the sample's surface. SEM is often paired with Energy Dispersive X-ray Spectroscopy (EDS) for qualitative and semi-quantitative analysis of the sample's chemical composition. While secondary and backscattered electrons offer morphological images, the X-ray spectrometer reveals elemental details, enhancing the SEM-EDS combination for comprehensive material characterization. The resolution in SEM depends on the focused electron beam spot



**Figure 2.7:** Schematic of SEM setup

size and the interaction volume of primary electrons within the sample. High-end SEM systems can resolve features below 1 nm, making them crucial for high-magnification imaging and compositional analysis, though not at the atomic scale. Non-conductive samples require surface pretreatment prior to imaging to prevent charge accumulation. This is typically achieved through sputter coating, in which the specimen is placed inside a chamber filled with argon gas under ultra-high vacuum, alongside a gold or carbon target. A high voltage is applied to ionize the argon gas, and the resulting ions are accelerated toward the target, dislodging atoms that subsequently deposit as a thin, uniform conductive layer onto the specimen surface. This coating significantly enhances the specimen's visibility and signal quality during SEM imaging.

In this thesis SEM images were recorded with a FEI Quanta FEG 250 instrument S3 (FEI corporate, Hillsboro, Oregon, USA) to observe the morphological changes of synthesized MOFs and COFs.

## 2.3 Electrochemical Characterizations

Electrochemistry enables the investigation of both heterogeneous and homogeneous reactions. Electrochemical techniques allow for the precise measurement of electron transfer processes, interfacial behavior, electrolyte properties, and surface reactions

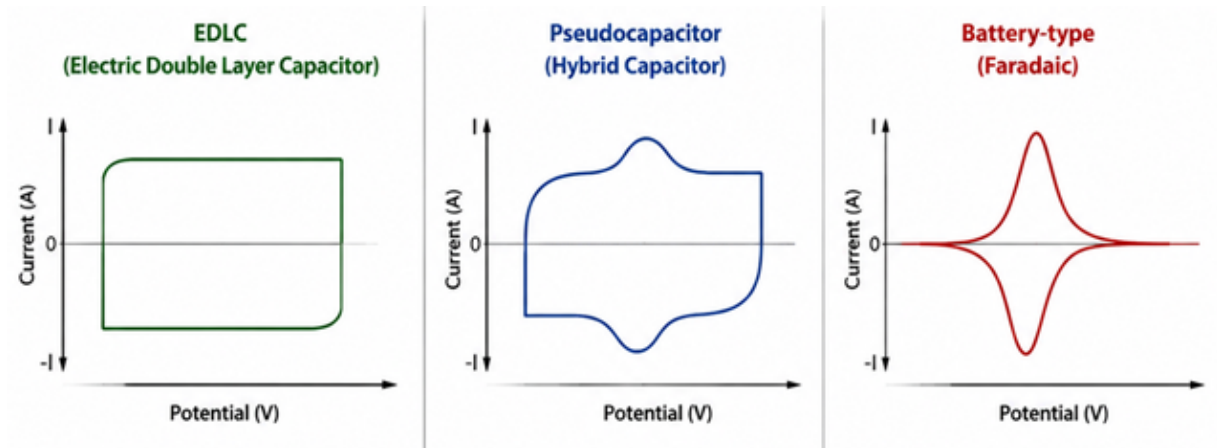
occurring at the electrode. Owing to these capabilities, electrochemistry plays a central role in energy conversion and storage systems. In the context of these energy storage devices, key electrochemical methods include cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) testing among others. Reactions occurring at the electrode-electrolyte interface can be deconvoluted into distinct elementary processes including mass transport, charge transfer, and adsorption each of which operates at a characteristic rate and timescale, as well as within a specific voltage window.

### 2.3.1 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is an electrochemical method that quantifies the current response of an electrochemical material to the applied potential [233]. This can be done in a two-electrode or three-electrode configuration, depending on the precision and control desired in the measurements. Both systems involve the potential being cycled in a specified voltage range and various scan rates, while the current response is measured in the form of I-V curve, resulting in a cyclic voltammogram, which helps to understand the underlying electrochemical processes. A two-electrode system composed of a working electrode and a counter electrode. This set-up is easier to build and is used for testing practical energy storage devices like supercapacitors and batteries. A reference electrode is added to a three-electrode system to give a stable and well-defined potential reference to which the potential of the working electrode can be precisely controlled. The counter electrode is always used to complete the circuit and to carry the current, and the reference electrode helps measure the potential. This setup provides high levels of precision and is especially well-suited for in-depth studies of electrochemical kinetics, redox reaction mechanisms and material stability. In any configuration, CV provides important data related to the reversibility of the reaction, charge transfer kinetics, and electrochemical stability [234,235]. The electrochemical behavior of the material being studied is reflected by the sum of the diagnostic features of the voltammogram, such as redox peak currents, peak potentials, and peak separations.

The specific shape of the I-V CV curve can be used to distinguish energy storage devices, such as supercapacitor exhibit a rectangular curve without peaks EDLC (capacitive behavior), HSCs exhibit both rectangular and peak features (pseudocapacitance) and batteries exhibit distinct redox peaks (faradaic reactions). Such differences are due to the different charge storage mechanisms in each system as shown in the figure 2.9 [236–238].

In this thesis CV measurements were performed in a two-electrode system by using



**Figure 2.8:** CV shapes for different energy storage devices

Autolab PGSTAT128N Potentiostat/Galvanostat instrument with a Metrohm Autolab DuoCoin Cell Holder (Metrohm AG) at room temperature for LMBs, ZnHSCs and AIBs.

To calculate the capacitance from the CV following equation was used,

$$C = \frac{\int I \Delta V}{m v \Delta V} \quad (2.5)$$

Where  $C$  represents capacitance (F/g),  $I$  shows current (A),  $\Delta V$  voltage window (V),  $\int I \cdot \Delta V$  is the area of the CV curve,  $v$  is the scan rate (V/s) and  $m$  (g) is the mass of active material in 1 electrode. For the calculation of the capacitive/diffusion contribution in the hybrid system following equations were used

$$i = a v^b \quad (2.6)$$

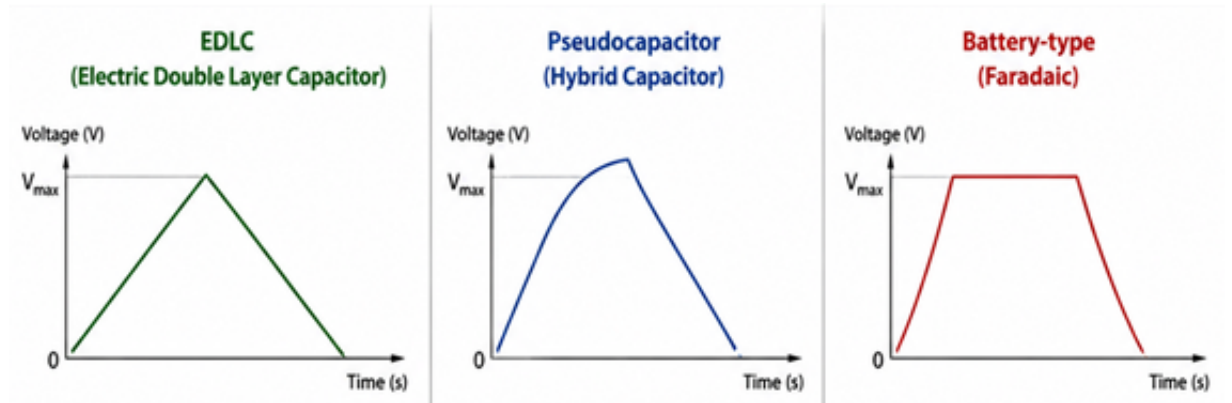
$$\log i = a + b \log v \quad (2.7)$$

Where  $i$  is the current (A) and  $v$  is the scan rate (V/s).

### 2.3.2 Galvanostatic Charge-Discharge (GCD)

Galvanostatic Charge-Discharge (GCD) is an important method to characterize the electrochemical performance of an energy storage device [239, 240]. In this method, a constant current is applied to the charging and discharging of the device which gives information on the following important parameters. Specific capacity, energy and power densities, voltage profiles, time curves and cycling stability can be obtained from GCD testing. Specific capacity is a measure of how much a device can store energy and power

densities show the efficiency of a device in the energy storage and delivery process. The voltage profile gives information about the rate at which the charge or discharge happens, which is reflected in the voltage profile, and whether there are any plateau regions. Further, GCD test is also useful for evaluating the system either EDLC, Pseudo or battery type by time-voltage curves shown in figure 2.10. It is also crucial to determine cycling stability in terms of capacity retention and coulombic efficiency of repeated charge and discharge cycles. The information is vital for general efficiency, cyclic stability and suitability of the device in different applications [241, 242].



**Figure 2.9:** GCD curves for different energy storage devices

In this thesis GCD was performed by using Neware Battery Tester (BTS-4008T-5V/10mA, Neware Technology Company, China) at different current densities for MOF and COF based cathode in LMBs, ZnHSCs and AIBs.

To calculate capacity following equation was used,

$$C = \frac{I \bullet \Delta t}{3.6 \bullet m} \quad (2.8)$$

Where  $Q$  represents capacity (mAh/g),  $I$  correspond to current (A),  $\Delta t$  is discharge time (s) and  $m$  (g) is the mass of active material in 1 electrode.

While Energy density was calculated from the equation:

$$\text{Energy density} = \text{Capacity} \times \Delta V \quad (2.9)$$

Where Energy density (Wh/kg), Capacity (mAh/g),  $\Delta V$  is voltage window.

Power density was calculated from the equation:

$$\text{Power density} = \frac{\text{Energy density}}{t} \quad (2.10)$$

Where power density (W/kg) and  $t$  (h) is the discharge time.

### 2.3.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements for energy storage devices are often used to get information about battery resistance, charge-transfer resistance and electrolyte resistance, diffusion coefficient often for open circuit potential under certain conditions [243, 244]. The advantage of EIS tests is to accompany rest of the electrochemical results which provide better understanding for the internal electrochemical methods.

Small sinusoidal alternating current (AC) is applied with the voltage  $U(t)$  to the material for EIS and its equivalent circuit model testing. AC response  $I(t)$  will be obtained at various phase angles for the same frequency value. The applied AC voltage is given as,

$$U(t) = U_0 \sin(\omega t) \quad (2.11)$$

Where  $U_0$  is the voltage amplitude and  $\omega$  is the radial frequency expressed as  $\omega = 2\pi f$ , thus the AC response  $I(t)$  is,

$$I(t) = I_0 \sin(\omega t + \varphi) \quad (2.12)$$

Where  $I_0$  is the amplitude of current response and  $\varphi$  is the phase angle.

As Ohm's law shows that, impedance is the product of the applied voltage and current denoted by:  $|Z| = U_0/I_0$  as the modulus of the impedance, the impedance has the form,

$$Z(\omega) = U(t)/I(t) = |Z| \sin(\omega t) / \sin(\omega t + \varphi) \quad (2.13)$$

Because impedance is a vector quantity, it is written in the form of complex function:

$$Z(\omega) = Z' - jZ'' \quad (2.14)$$

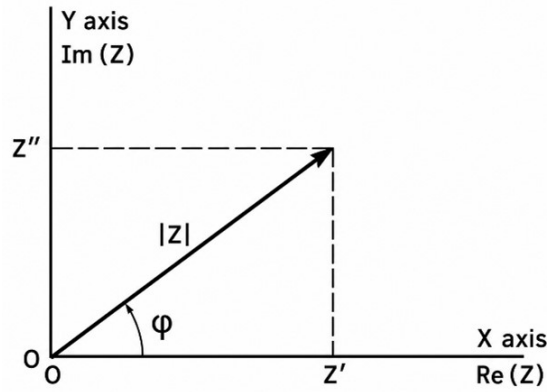
As shown Figure 2.11, indicates that impedance has real and imaginary parts, so relationships between these quantities can be written as,

$$Z' = |Z| \cos \varphi \quad (2.15)$$

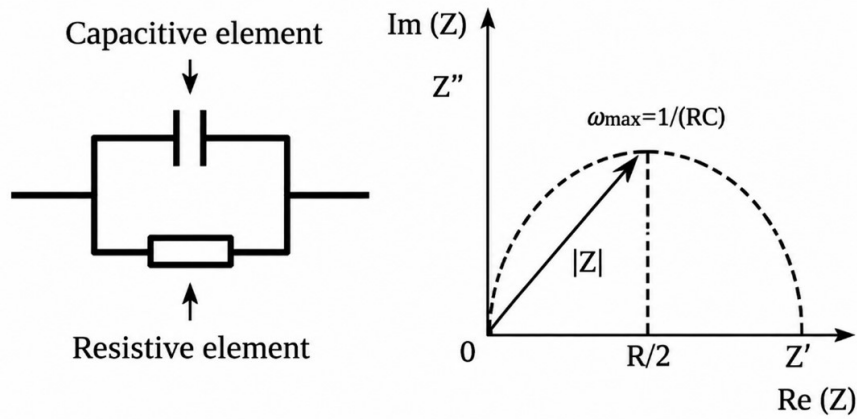
$$Z'' = |Z| \sin \varphi \quad (2.16)$$

$$\varphi = \tan^{-1}(Z''/Z') \quad (2.17)$$





**Figure 2.10:** The Impedance  $Z$  plotted as a vector quantity using polar coordinates



**Figure 2.11:** Components of an equivalent circuit model and Nyquist plot

Nyquist plotting with equivalent circuit fitting is used to plot the obtained results as shown in Figure 2.12 [245, 246].

A constant phase element (CPE) is another non-resistant circuit which is not a resistor, inductor or capacitor. It is sometimes a non-ideal capacitor. Its impedance can be written as,

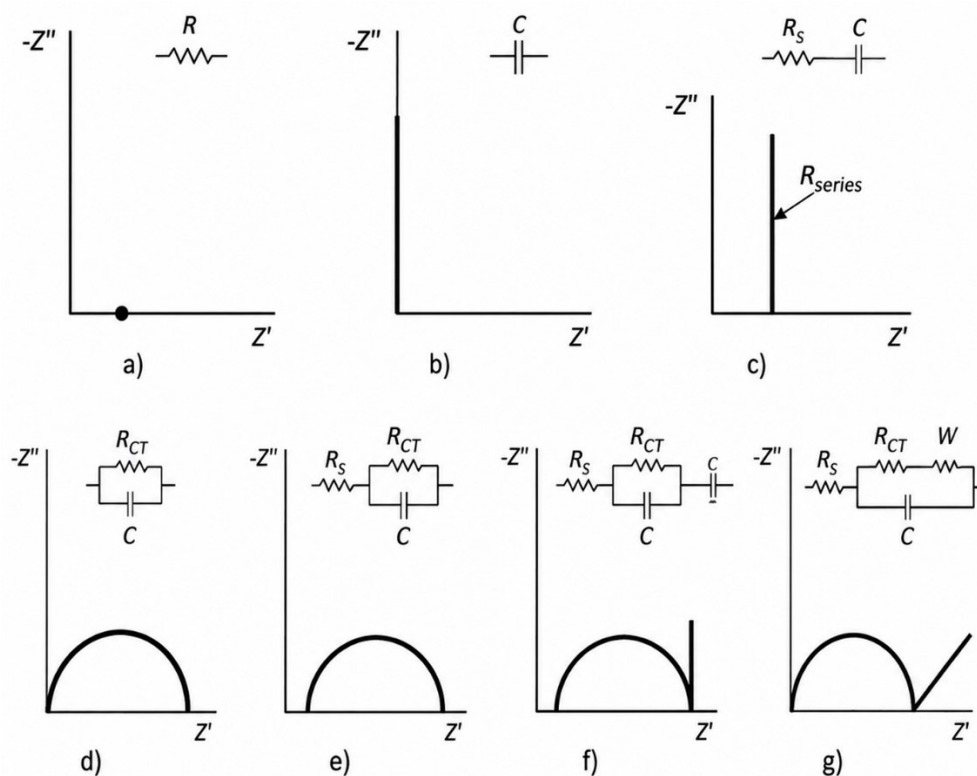
$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad (2.18)$$

When the value of  $n$  is 1, then CPE is referred to as perfect capacitor, when its value is 0 then CPE is called as resistor and when value of  $n$  is -1 then CPE is known as a perfect inductor. The phase angle  $\phi$  of CPE is always constant and can be written as,

$$\phi = -n \cdot 90^\circ \quad (2.19)$$

CPE begins to be a Warburg element when flow of current is limited by ionic

diffusion. In that case, the value of  $n$  will be 0.5. Normally, this value has been used when diffusion through corrosion outcomes controls corrosion rate. For a real system, when it consists of an imperfect layer of specimen, the value of  $n$  lies between 0.5 and 1 [247–249].



**Figure 2.12:** Typical Nyquist plots for various circuits, from simplest to common. (a) pure resistor,  $R$  (b) pure capacitor,  $C$  (c)  $R$  and  $C$  in series connection, (d)  $R$  and  $C$  in parallel connection; (e)  $R$  and  $C$  in parallel connection and in series with a solution resistance ( $R_s$ ), where  $R_{CT}$  denotes the charge transfer resistance of the interface, (f) the same circuit with additional in-series capacitance and (g) Randles–Ershler equivalent circuit, most commonly used for fitting ESS devices, where  $W$  stands for Warburg element (diffusion parameter for low frequencies).

For the fitting of the resulting curve with equivalent circuit models, the device properties can be obtained quantitatively, as illustrated in Figure 2.13. For an electrochemical analysis a diffusion process can form impedance called Warburg impedance ( $Z_w$ ) as shown in figure 2.13(g). That impedance is frequency and AC potential dependent impedance. At the high frequencies, the Warburg impedance gives small value, because the diffusion rate of the reactants is low, while at low frequencies, the diffusion rate of reactants is high in length, so the Warburg impedance has high value. EIS or equivalent circuit modelling allow detailed information of the electrochemical processes to be gained, allowing parameters such as charge transfer, electrolyte resistance, SEI forma-

tion or capacitance to be extracted. This makes it easier to better utilize the material, to identify degradation and to optimize the efficiency of the system.

In this dissertation EIS measurements were performed on Autolab PGSTAT128N Potentiostat/Galvanostat instrument with a Metrohm Autolab DuoCoin Cell Holder (Metrohm AG) at room temperature at different frequency ranges. Moreover, diffusion coefficient ( $D$ ) was calculated by using following equation,

$$D_{\text{Al}}^{\text{EIS}} = \frac{R^2 \cdot T^2}{2 \cdot A^2 \cdot n^4 \cdot F^4 \cdot c^2 \cdot \delta^2} \quad (2.20)$$

where  $R$  is the gas constant ( $8.314 \text{ J (mol K)}^{-1}$ ),  $T$  is the absolute temperate (298 K),  $A$  is the surface area of the electrode,  $n$  is the electron-transfer number,  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $c$  is the concentration of electrolyte ( $0.001 \text{ mol cm}^{-3}$ ), and  $\delta$  is the Warburg coefficient derived from the linear relation between  $\omega^{1/2}$  and  $Z_0$  ( $61.3 \text{ } \Omega \text{ s}^{-1/2}$  for (TPA-NDI COF)).

## 2.4 Postmortem and Ex situ characterizations

Postmortem analysis is conducted on the electrode from the disassembled cell to assess the structural integrity and electrochemical stability of the electrode material after long cycling usually a fully used/dead state [250, 251]. The spotlight here is not on the mechanism but on whether the material preserved its reliability after long cycling use. The electrode is gently removed from the cell in an argon-filled glovebox/open environment, washed with anhydrous solvent, dried, and then analyzed. The cycled electrode is used to evaluate the crystallinity of the electrode by XRD after repeated charge/discharge cycles. The diffraction patterns of the pristine and post-cycled electrodes are compared to detecting any peak shifts, peak broadening or disappearance of the characteristic peaks that suggest structural change, loss of long-range order and/or phase change due to cycling. The surface morphology of the electrode is studied by SEM. The mechanical stability of the electrode material under repeated ion insertion and extraction is evaluated by assessing any changes in the particle morphology, cracking, agglomeration or delamination from the current collector. In order to investigate the surface chemical composition and oxidation state of the cycled electrode, XPS is used to probe the surface. This allows for confirmation of reversible redox activity and identification of any irreversible side reactions and/or electrolyte decomposition products that may have built up on the electrode surface during cycling. Changes in charge transfer resistance and ionic diffusion properties are followed by performing EIS before and after cycling. If the resistance increases after cycling, it is an indication that

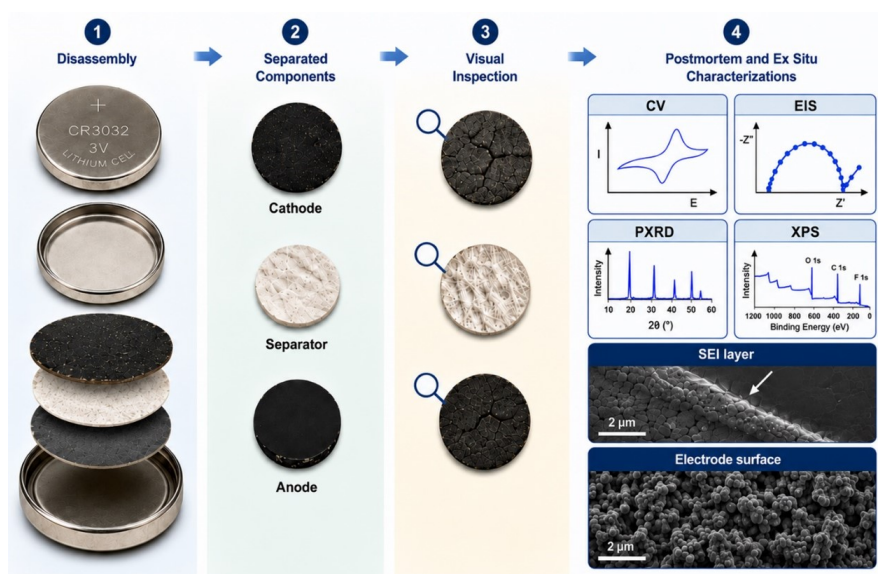
the electrode/electrolyte interface has degraded, and if it does not, then the behavior is stable. Moreover, CV is obtained on the post-cycled electrode to ensure the reversible redox peaks are preserved even after prolonged cycling, which indicates that the charge storage mechanism is retained. The postmortem characterizations results show that the overall structure, morphology and chemical nature of the electrode material have not changed due to cycling, thus confirming the suitability of this material as a stable electrode for energy storage applications as shown in figure 2.14 [252,253].

Moreover, fully charged, fully discharged and pristine states of the electrode material are accessed by disassembling the cells at those states and taking out the electrodes for ex-situ characterization to gain deeper understanding of the structural and chemical evolution of the electrode material at different stages of charge [254]. The extracted electrodes are rinsed with anhydrous solvent after they were extracted and dried under vacuum before characterization to prevent any interference from solvent residues and moisture. To monitor changes in the crystal structure of the electrode material with the charge state, ex situ XRD measurements are performed. The diffraction patterns obtained during different charge levels were compared with that of the pristine electrode to identify any reversible or irreversible structural changes because of the insertion and extraction of ions, surface chemical composition and oxidation states and material's morphology at various electrochemical states are examined by ex situ SEM and XPS analysis. These measurements gave direct visual evidence of any structural changes, particle swelling or shrinking and the retention of the overall electrode architecture between charge and discharge states. Additional ex situ measurements are also taken at specific states of charge (SOCs) to compare electrochemical properties with the structural and chemical results. The ex-situ characterization results complement each other to give a complete picture of the charge storage mechanism, substantiating the reversible structural and chemical changes that occur in the electrode material during cycling, as well as the ion interaction mechanism proposed.

## **2.5 Instrumental techniques used for characterizations of experimental section**

### **2.5.1 Chapter 3**

In chapter 3, the powder X-ray diffraction (PXRD) patterns were obtained using a Bruker AXS D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) over a  $2\theta$  range from  $6^\circ$  to  $60^\circ$ . The specific surface area and total pore volume were measured



**Figure 2.13:** Postmortem and ex-situ characterization of working electrodes

using a ASAP 2050 (Micromeritics) surface area and porosity analyzer. The sample was degassed at 100 °C for 12 hours under vacuum before analysis. A PerkinElmer TGA 8000 thermogravimetric analyzer was used to perform thermogravimetric analysis (TGA) over the temperature range from 25 to 800 °C under a  $\text{N}_2$  atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$ . Fourier-transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum Two IR spectrometer using an attenuated total reflectance (ATR) mode within the range of 500-3500  $\text{cm}^{-1}$ . Raman spectra were obtained using a Renishaw InVia Reflex system. The spectrograph used a high-resolution grating (1200 grooves  $\text{cm}^{-1}$ ) with additional bandpass filter optics, a confocal microscope, and a 2D-CCD camera. The excitation was carried out using a 785 nm laser excitation beam, with a 100 $\times$  objective, 0.02 mW maximum power and 10 s acquisition time. The chemical valence states were determined using a Thermo Scientific KAlpha X-ray photoelectron spectrometer (XPS) with a mono-chromatized Al  $\text{K}\alpha$  anode as the X-ray source (1.486 eV) at a vacuum level of  $10^{-8}$ – $10^{-9}$  mbar in the main chamber. The spot size of the X-ray beam was fixed at 400  $\mu\text{m}$ . The electrochemical performance of the as-prepared Mn-Fe-BTC DMOF was assessed in a two-electrode system. The galvanostatic charge/discharge (GCD) measurements were performed using a Neware battery test system and recorded in the voltage range of 0-3.0 V at current densities ranging from 0.1 to 2 A/g. The cyclic voltammetry (CV) analysis was performed using the Biologic MPG-2 instrument with scan rates of 0.5 and 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) was conducted with an amplitude of 10 mV and a frequency range of 100 kHz to 10 MHz. All the electrochemical analyses were performed at room

temperature.

### 2.5.2 Chapter 4

In chapter 4, the morphology and surface structure of the samples were investigated by SEM, using a Quanta 250 FEG, FEI. Specific surface area and total pore volume were analyzed through nitrogen adsorption/desorption isotherms, using the BET model and Density Functional Theory (DFT), and was performed with an ASAP 2050 (Micromeritics). XRD patterns were carried out using D8 Bruker Diffractometer with Cu lamp ( $K\alpha_1 = 1.5418 \text{ \AA}$ ) to determine the crystal structure and phase composition of the samples. TGA was performed using the TGA/DSC 2 (Mettler Toledo) instrument at the heating rate of  $10 \text{ }^\circ\text{C/min}$  from room temperature to  $1000 \text{ }^\circ\text{C}$  in air to study the thermal stability and mass loss of the samples. Raman spectra were recorded using Via Raman Microscope (Renishaw) with the excitation wavelength of  $532 \text{ nm}$  to provide information on the vibrational modes of the samples. XPS analyses were performed with a K-Alpha X-ray photoelectron spectrometer (Thermo Scientific) equipped with an aluminum X-ray source (energy  $1.4866 \text{ keV}$ ), operating at a vacuum level of  $10^{-8}$ - $10^{-9}$  mbar in the main chamber. The spot size of the X-ray beam was fixed at  $400 \text{ }\mu\text{m}$ . XPS was used to determine the chemical composition and surface chemistry of the samples. Electrical conductivity measurements were conducted on films of different materials; Ag paste was used to connect the samples to the probe station. The electrical conductivity of the pellets was measured with a probe station, under ambient conditions, using a Keithley 2626A SourceMeter unit. The IV curves were recorded by sweeping the voltage from 0 to 2 V and from 2 to 0 V. The electrochemical performance of two-electrode systems was assessed using CV, and EIS on Autolab PGSTAT128N Potentiostat/Galvanostat instrument with a Metrohm Autolab DuoCoin Cell Holder (Metrohm AG) at room temperature. CV was performed at scan rates of 1 - 500 mV/s in the voltage range between 0 and 1.8 V. EIS measurements were recorded with a frequency range of 0.01 Hz to 1 MHz. The GCD tests were performed on Neware Battery Tester (BTS-4008T-5V/10mA, Neware Technology Company, China). GCD curves were tested at current densities ranging from 0.1 to 5 A/g.

### 2.5.3 Chapter 5

In chapter 5, the composition, structure, and texture properties of materials were investigated by powder XRD patterns (Bruker AXS D8 Advance X-ray diffractometer). TGA decomposition curves were recorded in the range  $25$ - $1000 \text{ }^\circ\text{C}$  operating under nitrogen

atmosphere, with a thermal step of 10 °C/min on a Mettler Toledo TGA/SDTA851e system. XPS (Thermo Scientific K-Alpha X-ray photoelectron spectrometer) equipped with an aluminum X-ray source (energy 1.4866 keV) at a vacuum level of  $10^{-8}$ - $10^{-9}$  mbar in the main chamber. The spot size of the X-ray beam was fixed at 400  $\mu$ m. The specific surface area was measured using a Micromeritics ASAP 2050 surface area and porosity analyzer. Before the nitrogen sorption measurements, the samples were outgassed for 12 hours at 95 °C. Adsorption isotherms were calculated for nitrogen adsorption at 77 K and pressure up to 1 bar. Transmission Electron Microscopy (TEM) images were obtained using a JEOL JEM-2200FS EFTEM/STEM drying an ethanol suspension of the samples on C/Cu grids. Scanning Electron Microscopy (SEM) images and Energy-dispersive X-ray spectroscopy (EDX) were recorded with a FEI Quanta FEG 250 instrument S3 (FEI corporation, Hillsboro, Oregon, USA). Solid state nuclear magnetic resonance  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III HD spectrometer coupled with an 11.7 T wide bore superconducting magnet operating at 125.76 MHz  $^{13}\text{C}$  Larmor frequency. All spectra were recorded at 298 K stabilized temperature using the magic-angle spinning technique for high-resolution NMR spectroscopy in the solid state using 4 mm rotors. The spinning frequency was 10 kHz. Infrared spectra (IR) were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. Selected absorption bands are reported by wavenumber ( $\text{cm}^{-1}$ ). Solid-state ultraviolet-visible (UV-Vis) diffuse reflectance spectra were recorded using a Jasco spectrophotometer equipped with an integrating sphere. The COF or monomer samples were finely ground and mixed with  $\text{BaSO}_4$  as a non-absorbing reference matrix. The optical band gap was determined from the corresponding Tauc plot obtained from the diffuse reflectance data. Geometrical optimization of isolated structures of TPA, NDI were performed using density functional theory (DFT) at the M062X/6-311++G\*\* level, followed by analysis of their vibrational frequencies to characterize the structures obtained as energy minima. These computations were performed using Gaussian16. The description for the vibrational modes and its assignment to the theoretical IR spectra was performed by visual inspection of the atomic displacements for each vibrational mode. Density functional theory (DFT) calculations for the energy storage mechanism were carried out with Gaussian 16 at the M062X/6-311++G\*\* level. For the COF TPA-NDI, used as simplified model a TPA-NDI unit in the neutral state from which two electrons were removed or added to represent the charged and discharged states, respectively. Extended periodic structures of COF TPA-NDI were optimized with the plane-wave DFT approach at PBE+D3(BJ) level of theory using the VASP code. All atomic positions and lattice parameters were relaxed. K-point integration was performed using the  $\Gamma$  point only. The convergence criteria were set to  $10^{-5}$  eV for electron density and

$10^{-2}$  eV/Å for forces. Simulations were carried out for the monolayer cell (672 atoms). The monolayer was simulated by setting the length of the cell vector perpendicular to the plane of the COF to  $\|c\| = 20$  Å, adding a thick layer of vacuum. Next, AA and AB stacked 1x1x2 cells (1344 atoms) were optimized with the use of BAFF force field. From the calculated models, simulated XRD spectra were obtained, assuming Cu-K $\alpha$  1.54 Å wavelength as the X-ray source. The electrochemical performance of COF TPA-NDI electrodes was evaluated by CV and EIS on Autolab PGSTAT128N Potentiostat/Galvanostat instruments at room temperature. CV measurements were conducted at scan rates between 1 and 6 mV/s over a voltage range of 0 to 2.4 V. EIS data were collected over a frequency range from 0.01 Hz to 1 MHz. GCD tests were performed using a Neware Battery Tester (BTS-4008T-5V/10mA, Neware Technology Company, Guangdong, China), with GCD curves recorded at current densities from 0.1 to 5 A/g.



## Chapter 3

# Dual metal–organic framework (D-MOF) based on Mn–Fe and trimesic acid as a high-performance cathode for lithium metal batteries

High performance Lithium-Metal Batteries (LMBs) require electrode materials with high storage capacity, structural stability, and electrochemical tunability. Metal-organic frameworks (MOFs) are promising candidates with their highly porous structures, high surface area and chemically diverse coordination sites. MOFs based on BTC (1,3,5-benzenetricarboxylic acid) have a high density of redox-active sites and structural flexibility, but mono-metal BTC frameworks suffer from low electronic conductivity, low surface area, and high capacity fading over prolonged cycling. To address these shortcomings, a dual metal strategy was adopted wherein both Manganese (Mn) and Iron (Fe) were introduced in a single BTC framework, in order to achieve greater charge storage capacity and cycling stability. Thereby a novel Mn-Fe-BTC dual metal–organic framework (DMOF) was prepared via facile one-step hydrothermal method and explored as a cathode material for LMBs. CV and GCD studies revealed that as a cathode material, the Mn-Fe-BTC-based DMOF exhibited a high initial capacity of  $1385 \text{ mA h g}^{-1}$  and  $687 \text{ mA h g}^{-1}$  after 100 cycles which demonstrated its potential for high performance energy storage devices.

### 3.1 Introduction

The escalating risks associated with resource depletion, environmental pollution, and geopolitical instability have intensified the global pursuit of renewable energy sources, including tidal, wind, and solar power. The effective integration of these intermittent renewable energy sources into existing power grids necessitates the deployment of large-scale ESS. Lithium-ion batteries (LIBs) have established themselves as indispensable to modern technological applications, among the most extensively adopted electrochemical storage technologies owing to their high energy density, extended cycle life, and low self-discharge rates [255–257]. Within the broader LIB family, LMBs which employ lithium metal as the anode offer significantly greater energy densities, thereby broadening their applicability and enhancing overall device performance. The cathodes currently used in conventional LMBs are based on transition metal oxides such as lithium cobalt oxide ( $\text{LiCoO}_2$ ), lithium iron phosphate ( $\text{LiFePO}_4$ ), lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ), nickel manganese cobalt oxide (NMC), nickel cobalt aluminum oxide (NCA), or lithium nickel oxide ( $\text{LiNiO}_2$ ), which are known to have excellent theoretical specific capacities [258–263]. However, issues such as increasing material cost, structural instability, energy density limitations, capacity fading, and safety concerns have inspired a lot of research into the development of new and eco-friendly cathode materials. MOFs, which consist of metal ions linked to organic ligands, have proven to be highly promising materials for LMB cathode applications, due to their extremely high surface area, tunable pore architecture, and customizable functional properties, all of which are favorable for efficient lithium-ion diffusion and improve battery performance [264, 265]. The first Fe-based MOF (MIL-53) has been used as a cathode for LIBs with a low specific capacity of  $75 \text{ mAh g}^{-1}$ . Since then, a wide variety of MOFs have been studied as cathode and anode materials; however, the use of many of these in LMBs has been hindered by their low specific capacity, poor electrical conductivity and poor cycling stability. Understanding the Li ion storage mechanisms is therefore key to overcoming these limitations. The two main storage methods include intercalation/insertion, which tends to have a relatively low storage capacity and conversion, which is mostly based on the redox activity of the central metal ions in the MOF structure but has poor cycling stability. There are several proposed mitigation strategies to overcome the limitations of cyclability of the conversion type mechanism. A strategy is to design MOF architectures which allow redox reactions to take place in the organic linkers, combining the structure rigidity of inorganic clusters with the conformational flexibility of organic ligands to keep the 3D framework stable during the electrochemical cycling. Moreover, the use of organic linkers with aromatic cores has been demonstrated to increase  $\pi$ – $\pi$  interactions

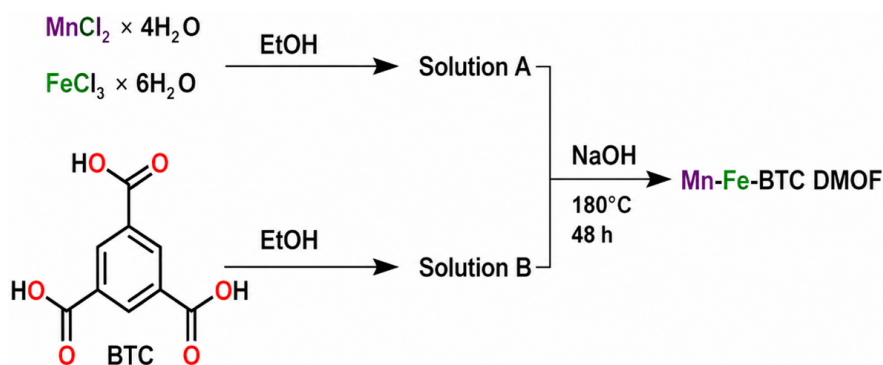
to further improve the chemical stability of the MOF structure. MOFs such as those based on the BTC linkers have demonstrated remarkable electrochemical activity due to the redox active carbonyl groups that serve as  $\text{Li}^+$  ion hosts. The specific capacity of LMB applications of monometallic BTC-based MOFs is systematically evaluated and reversible specific capacities are 740, 1085, 694 and 1021  $\text{mAh g}^{-1}$  for Cu-BTC, Ni-BTC, Mn-BTC and Fe-BTC, respectively [266–269]. Notably, Fe-BTC possesses a substantially higher specific surface area of  $1125 \text{ m}^2 \text{ g}^{-1}$  relative to Cu-BTC ( $489.4 \text{ m}^2 \text{ g}^{-1}$ ), Ni-BTC ( $551 \text{ m}^2 \text{ g}^{-1}$ ), and Mn-BTC ( $23.8 \text{ m}^2 \text{ g}^{-1}$ ). Although the surface area of Mn-BTC is relatively small, it shows almost no structural changes after 100 charge/discharge cycles, in contrast, the other monometallic BTC-based MOFs show irreversible structural changes during prolonged cycling. One significant improvement that Zheng et al. reported was a bimetallic MOF (Mn-Co-BTC) which was designed to improve electrochemical performance [270]. A bimetallic Mn-Co-BTC MOF with a specific capacity of  $819 \text{ mAh g}^{-1}$  was synthesized, compared to the previously reported monometallic MOF of Mn-BTC, which had a specific capacity of only  $694 \text{ mAh g}^{-1}$ . After 600 galvanostatic cycles at a current density of  $1 \text{ A g}^{-1}$ , the Mn-Co-BTC still exhibited a significant lithium storage capacity of  $337 \text{ mAh g}^{-1}$ , suggesting its potential for high performance electrochemical energy storage applications. The bimetallic configuration is clearly effective for improving  $\text{Li}^+$  ion transport kinetics, and for stabilizing the structure under cycling, which is important for the development of MOF-based cathodes in LMBs. This is a very promising, but under-explored approach. Based on the excellent electrochemical performance and large specific surface area of Fe-BTC as well as the excellent structural stability of Mn-BTC, it is expected that the synthesis of Mn-Fe-BTC bimetallic MOF can produce even better electrochemical performance in LMBs, providing a rational design strategy to prepare high-performance cathode materials for the next generation of energy storage applications.

## 3.2 Experimental Section

### 3.2.1 Synthesis of Mn-Fe-BTC DMOF

To synthesize Mn-Fe-BTC DMOF shown in Figure 3.1, one-step hydrothermal method was used.

First, a solution (Solution A) was prepared by dissolving 1.5 g of manganese chloride tetrahydrate ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) and 0.5 g of iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) into 60 mL of EtOH. On the other hand, a second solution (Solution B) was prepared 1 g of BTC in 20 mL of EtOH. Solution A was gradually added to solution B under



**Figure 3.1:** Synthetic protocol of Mn-Fe-BTC DMOF.

magnetic stirring. After the addition of solution A was completed, 0.2 g of NaOH was added. After that, the solution was carefully transferred into a stainless-steel autoclave and placed in an oven at a temperature of  $180^\circ\text{C}$  for 48 hours. The sample was collected by centrifugation after the autoclave naturally cooled down. It was then washed multiple times with deionized water and ethanol and finally dried at  $80^\circ\text{C}$  for 24 hours in an oven. A Pink powder was obtained with yield 87 % with reference to BTC.

### 3.2.2 Preparation of Electrode material

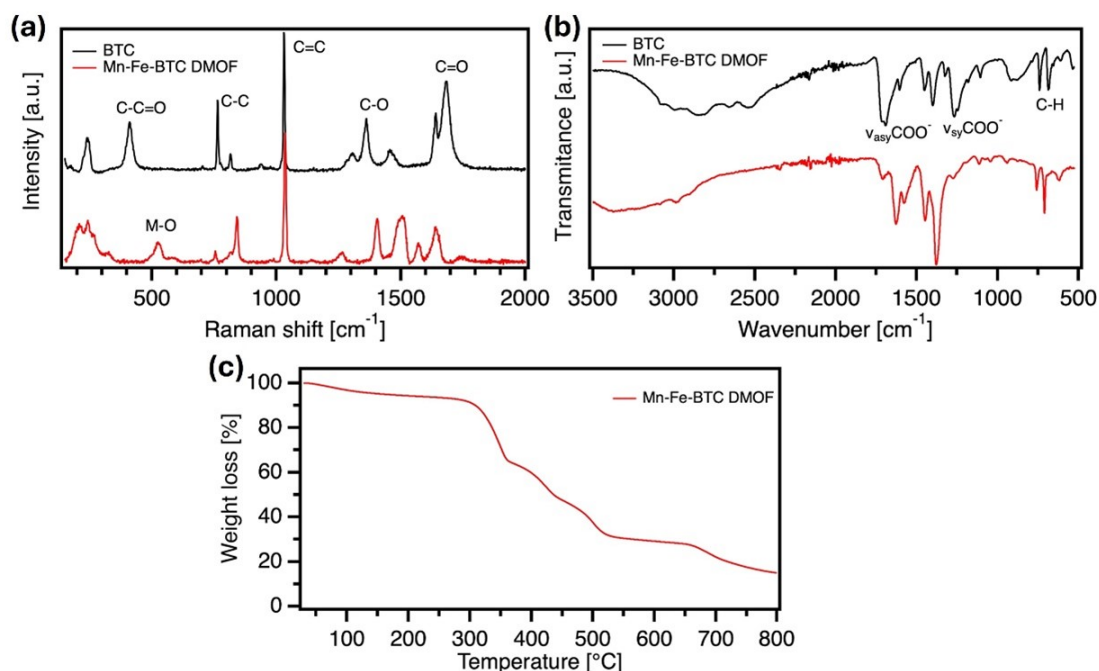
The cathode was prepared by mixing 75 wt% of Mn-Fe-BTC DMOF, 15 wt% of PVDF binder, and 10 wt% of conductive carbon black in NMP. The slurry was evenly spread over Cu foil, creating a  $200\ \mu\text{m}$ -thick layer using a doctor blade. Cu foil was used as a current collector because the operating potential window of the electrode remained below 3.7 V vs.  $\text{Li}/\text{Li}^+$ , which is the oxidation threshold of copper. Within this potential range, Cu foil remains electrochemically stable and does not undergo dissolution, making it a viable current collector for this system. Additionally, Cu foil provided better mechanical adhesion with the MOF-based slurry compared to other materials [271]. Further the electrodes were heated at  $120^\circ\text{C}$  in a vacuum oven overnight. Afterward, 18 mm discs were cut and used as cathodes. The assembling process was performed in a glovebox under a controlled argon (Ar) atmosphere, ensuring that the concentration of  $\text{O}_2$  and  $\text{H}_2\text{O}$  remained below 0.1 ppm. Two electrode systems as coin cells were used where a Li-foil was employed as an anode, along with a glass microfiber as a separator. The electrolyte consisted of a solution of 1 M  $\text{LiPF}_6$  in EC: DEC: EMC (1:1:1 vol%).

### 3.2.3 Structural and morphological characterizations

To confirm the structure, chemical composition and morphology of synthesized DMOF Raman Spectroscopy, FTIR, XRD, XPS, BET, TGA and SEM were performed.

### 3.3 Results and Discussion

The chemical structure of Mn-Fe-BTC DMOF is first confirmed by Raman spectroscopy shown in Figure 3.2(a). The Raman spectrum of Mn-Fe-BTC DMOF demonstrates the characteristic peak of BTC at 998 (C=C), 1005  $\text{cm}^{-1}$ . The formation of Mn-Fe-BTC DMOF is confirmed by the appearance of a new peak at 495  $\text{cm}^{-1}$ , corresponding to the metal–oxygen interactions. Furthermore, the vibrations at 381  $\text{cm}^{-1}$  correspond to O=C=O, at 1332  $\text{cm}^{-1}$  to C–O and at 1653  $\text{cm}^{-1}$  to C=O of BTC. In Mn-Fe-BTC DMOF, these vibrational peaks are shifted to 293, 1375 and 1612  $\text{cm}^{-1}$ , respectively due to the bonding of metal-carboxylate. The FTIR spectrum of BTC shown in Figure 3.2(b) displayed peaks at 1694 and 1262  $\text{cm}^{-1}$  attributed to asymmetric and symmetric vibrations of the carboxylate groups and a peak at 738  $\text{cm}^{-1}$ , assigned to the C–H vibration of the benzene ring. In agreement with the Raman analysis, in the FTIR spectrum of Mn-Fe-BTC DMOF, the asymmetric and symmetric vibrations of the carboxylate groups are shifted to 1627 and 1381  $\text{cm}^{-1}$ , respectively, due to their interactions with the metal ions. Both Raman and FTIR analyses confirm the presence of metal–oxygen interactions.



**Figure 3.2:** (a) Raman spectra of BTC (black line) and Mn-Fe-BTC (red line), (b) FTIR spectra of BTC (black line) and Mn-Fe-BTC (red line), (c) TGA analysis of Mn-Fe-BTC DMOF.

The TGA analysis of Mn-Fe-BTC was carried out in a systematic way as shown in Figure 3.2(c). The thermogram obtained shows that the thermal resistance of Mn-Fe-BTC is also significant. A significant weight loss is observed at around 310  $^{\circ}\text{C}$  as

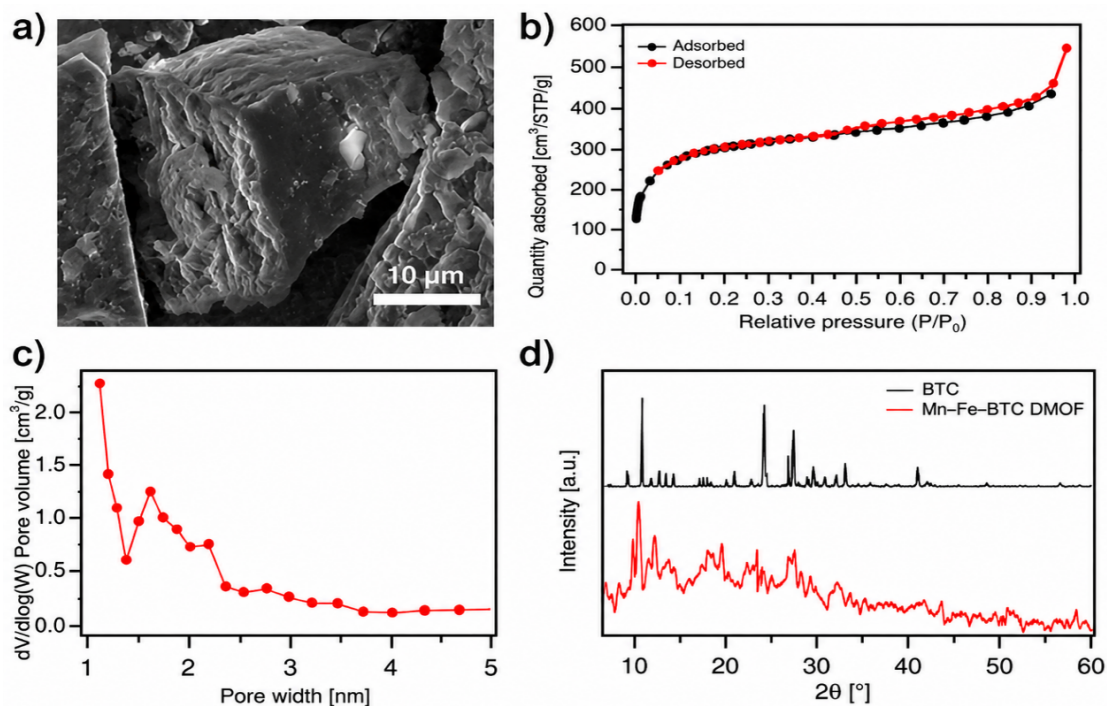
seen in the  $T_{d10}$ , where only 10% of the material is decomposed. This shows the good structural strength of Mn-Fe-BTC at high temperature. Furthermore, high temperature ( $> 350\text{ }^{\circ}\text{C}$ ) is necessary to achieve major thermal decomposition of the Mn-Fe-BTC DMOF framework. This higher temperature decomposition is mainly attributed to the decomposition of the linkers of BTC (1,3,5-benzenetricarboxylate), backbone of the metal-organic framework. In general, it is noted that the framework of the Mn-Fe-BTC is very stable up to high temperatures above  $300\text{ }^{\circ}\text{C}$ , which suggests its suitability for applications with high thermal stability.

The morphology and microstructure of the Mn-Fe-BTC DMOF was systematically investigated by SEM and  $\text{N}_2$  adsorption/desorption isotherm shown in Figure 3.3(a) and (b). The SEM images show that the Mn-Fe-BTC DMOF consists mainly of well-defined cubic structures on the micrometer scale, suggesting uniform crystallinity and particle growth. The  $\text{N}_2$  adsorption/desorption study at low temperature offers information about the textural properties of the material. Specific surface area (SSA) was calculated by using the BET model, and the pore size distribution was determined from the DFT model [272]. The Mn-Fe-BTC DMOF has a high SSA of  $1045\text{ m}^2\text{ g}^{-1}$  and an average pore diameter of 1.6 nm. In comparison to this, the surface area is slightly lower than that of Fe-BTC ( $1125\text{ m}^2\text{ g}^{-1}$ ) but significantly higher than for Mn-BTC ( $23.8\text{ m}^2\text{ g}^{-1}$ ), suggesting that the addition of Mn does not appreciably decrease the surface area in the dual-metal framework. Furthermore, the  $\text{N}_2$  adsorption/desorption isotherms show an H3 hysteresis loop typical of loosely aggregated particles with slit-like pores, which could account for the accessible porosity and adsorption capabilities of the material. Powder XRD was then used to further investigate the crystal structure of Mn-Fe-BTC shown in Fig. 3.3(c).

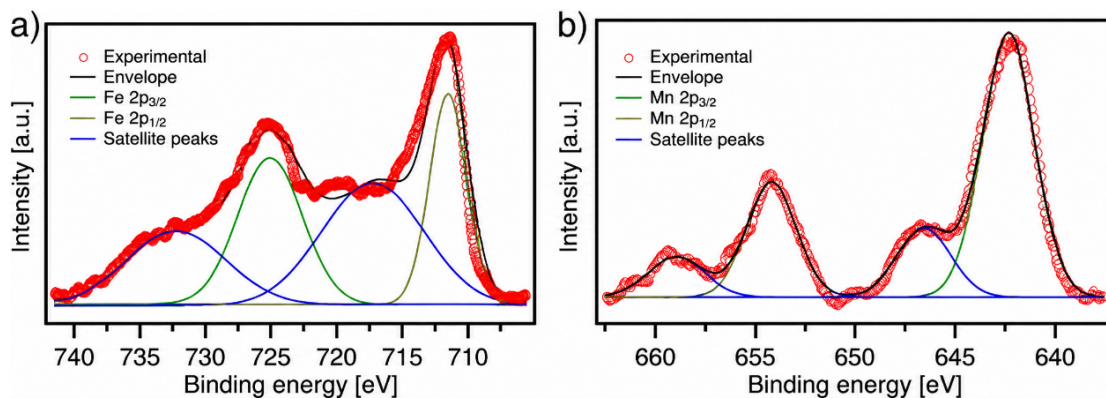
The diffraction pattern exhibited peaks at  $9.4$ ,  $9.9$ ,  $17.6$ ,  $19.2$ ,  $26.5$  and  $31.7^{\circ}$ , in agreement with those reported for previously synthesized Mn-Fe-MOFs using terephthalic acid linkers indicating that both metal centers were successfully incorporated into an ordered framework. Prominent peak at  $2\theta = 10.7^{\circ}$  which is observed in pristine BTC is not seen in the Mn-Fe-BTC pattern, further confirming the formation of new crystalline dual-metal framework and suggesting structural changes due to Mn substitution. These results indicate that Mn-Fe-BTC has a highly porous morphology with slit-like pores, along with a well-defined crystalline structure.

Furthermore, XPS analysis was used to confirm the nature of the metal ion in DMOF shown in Figure 3.4.

The high-resolution XPS spectrum of Fe 2p, shown in Figure 3.4(a), shows two obvious peaks characteristic of the  $\text{Fe}^{3+}$  oxidation state. The peak at a binding energy level of  $711.6\text{ eV}$  corresponds to the Fe  $2p_{3/2}$  core-level transition, while the peak



**Figure 3.3:** (a) SEM image of Mn-Fe-BTC DMOF, (b)  $\text{N}_2$  isotherm adsorption/desorption isotherm analysis, (c) pore size distribution, (d) PXRD spectra of BTC (black) and Mn-Fe-BTC DMOF (red).



**Figure 3.4:** XPS (a) Fe2p and (b) Mn2p spectra of Mn-Fe-BTC DMOF.

at 724.8 eV corresponds to the Fe 2p<sub>1/2</sub> transition. The observed spin-orbit splitting conforms that iron in the framework exists solely as Fe<sup>3+</sup>. In contrast, the XPS spectrum of Mn 2p, presented in Figure 3.4(b), also shows two main peaks, which are attributed to Mn<sup>2+</sup>. The peak at 642.2 eV is ascribed to the Mn 2p<sub>3/2</sub> transition, while the peak at 644.9 eV corresponds to Mn 2p<sub>1/2</sub>. Taken together, the XPS data specifies clear and reliable evidence for the incorporation of both Fe<sup>3+</sup> and Mn<sup>2+</sup> ions into the organic framework. The well-resolved peaks and their binding energies demonstrate that each metal is present in its expected oxidation state, supporting the successful formation of a bimetallic material. These results not only confirm the presence of both metal ions in the organic framework but also confirm the structural reliability of the framework, highlighting the material's potential for applications where defined bimetallic centers are crucial.

### 3.4 Electrochemical Characterizations

The electrochemical performance of DMOF active material vs. Li/Li<sup>+</sup> is investigated by CV, GCD and EIS. Two electrode systems were employed where a coin cell (CR2032) was assembled with Mn-Fe-BTC DMOF active material as a cathode and Li metal as an anode.

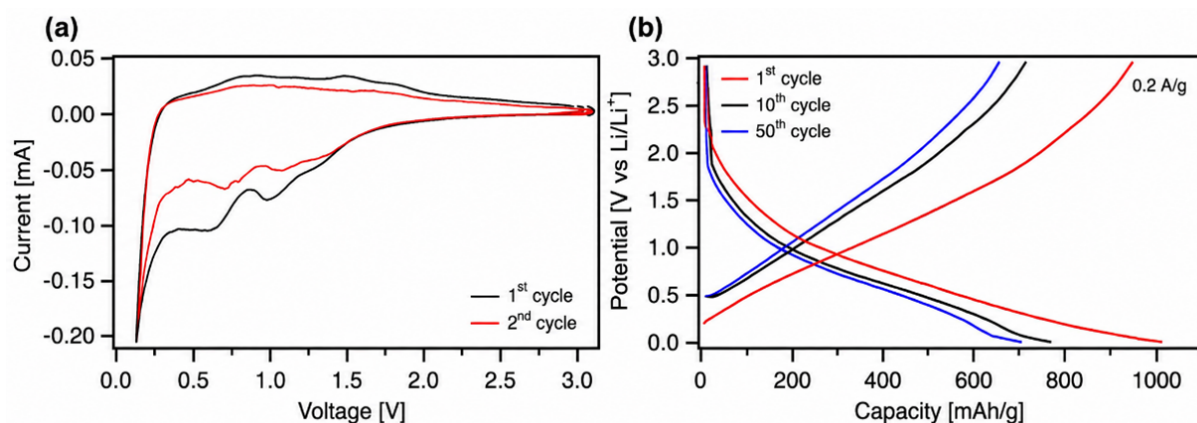
#### 3.4.1 Results and Discussion

First two CV scans of Mn-Fe-BTC DMOF electrode in the potential window of 0.01–3.0 V are shown in Figure 3.5. During the first discharging cycle, three peaks are observed at 1.37, 0.99 and 0.63 V, respectively. The broad small peak at 1.37 V could be linked with an irreversible reaction related to the formation of solid electrolyte interface (SEI) layers due to electrolyte decomposition.

The peak at around 0.99 V may be ascribed to the reduction of Mn ions. The last broad peak centered at 0.63 V might be attributed to the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> as well as the insertion of Li<sup>+</sup> ion to the organic framework. The corresponding anodic broad peaks, centered at 0.85, 1.50 and 1.85 V, respectively, indicate the Li extraction from the aromatic C<sub>6</sub> ring/carboxylate moieties as well as the reversible oxidation of the metal ions. The broad anodic peaks probably indicate a continuing, multistep process for lithium extraction.

The electrochemical performance from GCD of the Mn-Fe-BTC electrode is assessed over the initial cycles at a current density of 0.2 A/g shown in Figure 3.5(b). The initial discharge capacity of the Mn-Fe-BTC DMOF electrode is above 1000 mA h g<sup>-1</sup> but

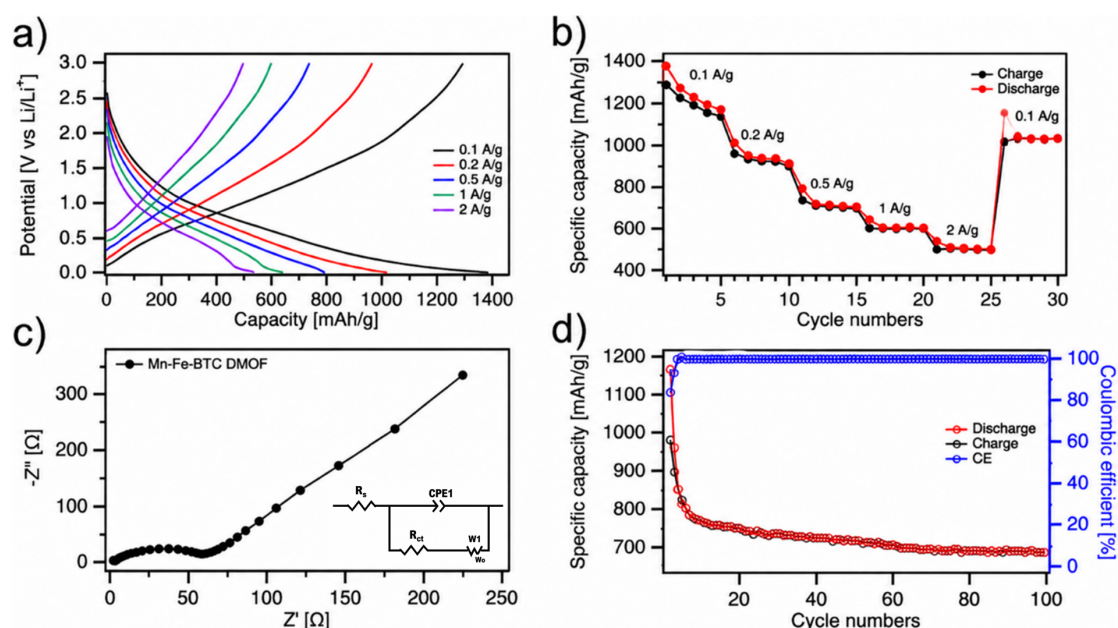




**Figure 3.5:** (a) CV curves for Mn-Fe-BTC DMOF at 0.1 mV/s, (b) Galvanostatic charge-discharge voltage profiles of Mn-Fe-BTC DMOF after 1, 10 and 50 cycles.

after 10 cycles it decreases to  $765 \text{ mA h g}^{-1}$ . However, after around 50 cycles, the Fe-Mn-BTC DMOF electrode exhibits a stable capacity for reversible lithium storage of about  $710 \text{ mA h g}^{-1}$ , implying good cycling stability. Moreover, we observed that the charge–discharge plateaus shift systematically during sequential cycles, likely due to the increase in resistance and the SEI formation. GCD of the Mn-Fe-BTC electrode is also performed at different current densities from 0.1 to  $2 \text{ A g}^{-1}$ , as illustrated in Fig. 3.6(a, b). The reversible specific charge/discharge capacities at 0.1, 0.2, 0.5, 1 and  $2 \text{ A g}^{-1}$  delivering 1292/1385, 962/1016, 735/792, 597/640, 496/537  $\text{mAh g}^{-1}$ , respectively. Mn-Fe-BTC displays significantly higher specific capacity at high current densities ( $597/640 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$  and  $496/537 \text{ mAh g}^{-1}$  at  $2 \text{ A g}^{-1}$ ) compared to single metal Mn-BTC ( $435/433 \text{ mA h g}^{-1}$  at  $1 \text{ A g}^{-1}$ ), Fe-BTC ( $302/304 \text{ mA h g}^{-1}$  at  $2 \text{ A g}^{-1}$ ) and bimetallic MOF with BTC linkers Mn-Co-BTC MOFs ( $445 \text{ mAh g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ ) [270] and other MO based materials given in Table 3.1 according to literature.

More importantly, a high specific capacity of around  $1050 \text{ mAh g}^{-1}$  is recovered when the current density is reduced from 2 to  $0.1 \text{ A g}^{-1}$ , proving the potential of the DMOF framework. Electrochemical impedance spectroscopy (EIS) data is analyzed using Nyquist plots shown in Fig. 3.6(c) and the experimental results are well-fitted with the equivalent circuit given in inset 3.6 (c). DMOF material exhibits a low  $R_{ct}$  of  $60 \Omega$  implying that dual MOFs allow for efficient and rapid transfer of charge (electrons or ions) at the electrode surface. Another demanding feature of the novel Mn-Fe-BTC DMOF electrode is its robust long-term cyclability at a rate of  $200 \text{ mA g}^{-1}$ , as demonstrated in Fig. 3.6(d). After the first three cycles, the coulombic efficiency of the Mn-Fe-BTC DMOF rapidly increased to 99.9% and remains around 100% throughout the subsequent cycles. After 100 charge/discharge cycles, a high specific capacity of  $687 \text{ mAh g}^{-1}$  is still obtained for Mn-Fe-BTC DMOF. The high chemical stability of



**Figure 3.6:** (a) GCD profiles, (b) specific capacity at different current densities of Mn-Fe-BTC DMOF, (c) EIS analysis, (d) cyclic performances.

DMOF electrode can be ascribed to the presence of conjugated carboxylates, which hold aromatic cores with strong  $\pi$ – $\pi$  interactions.

**Abbreviations:** Mn-BDC: Manganese-1,4-benzenedicarboxylate, Fe-MOF: Iron metal organic frameworks, Mn-BTC: Manganese Benzene-1,3,5-tricarboxylate, NiFeMn-BTCA: nickel, iron and manganese benzene-1,2,4,5-tetracarboxylate trimetallic organic framework, MnCo-T: manganese cobalt trimesic acid, Ni/Mn-BTC: nickel, manganese benzene 1,3,5-tricarboxylate, Fe-BDC: Iron 1,4-benzenedicarboxylate, H<sub>8</sub>L-Fe-MOF: Iron ethene-1,1,2,2-tetrayltetrakis(benzene-4,1-diyl)tetrakisphosphonic acid.

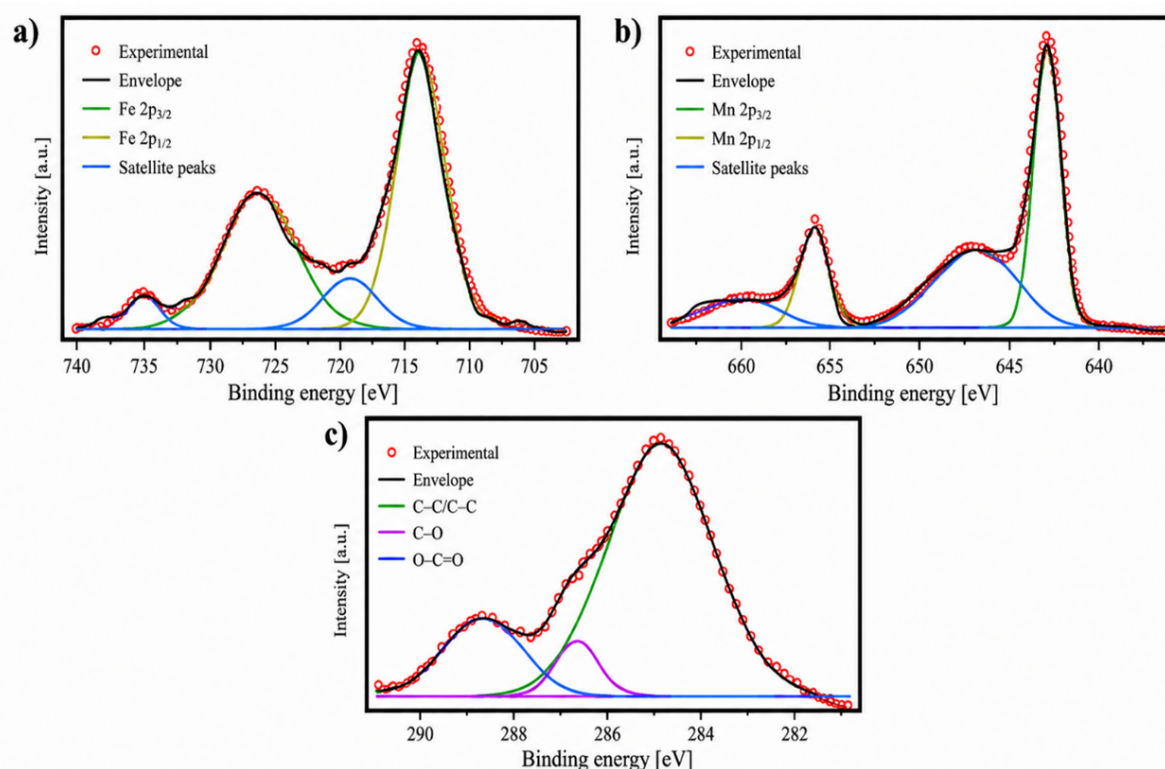
### 3.5 Postmortem Analysis

To determine the chemical stability of Mn-Fe-BTC DMOF a series of ex situ characterizations are performed in Figs. 3.7 and 3.8 (a, b, c, d) including XPS, Powder XRD, SEM, EIS and CV. Figure 3.7 displays the high-resolution XPS spectra of Fe 2p, Mn 2p, and C 1s for Mn-Fe-BTC DMOF after 100 cycles. Notably, the XPS spectra exhibit no significant changes compared to the pristine state for any of the elements, demonstrating the DMOF's outstanding chemical stability during electrochemical cycling.

Likewise, the XRD analysis in Fig. 3.8(a) shows consistent peaks with no shifts, verifying the structural integrity of the active material. Additionally, SEM analysis in Fig. 3.8(b) after cycling reveals that the structure remains porous and that the pores have

**Table 3.1:** Electrochemical performance of various Mn and Fe-based MOFs electrodes previously reported for LMBs.

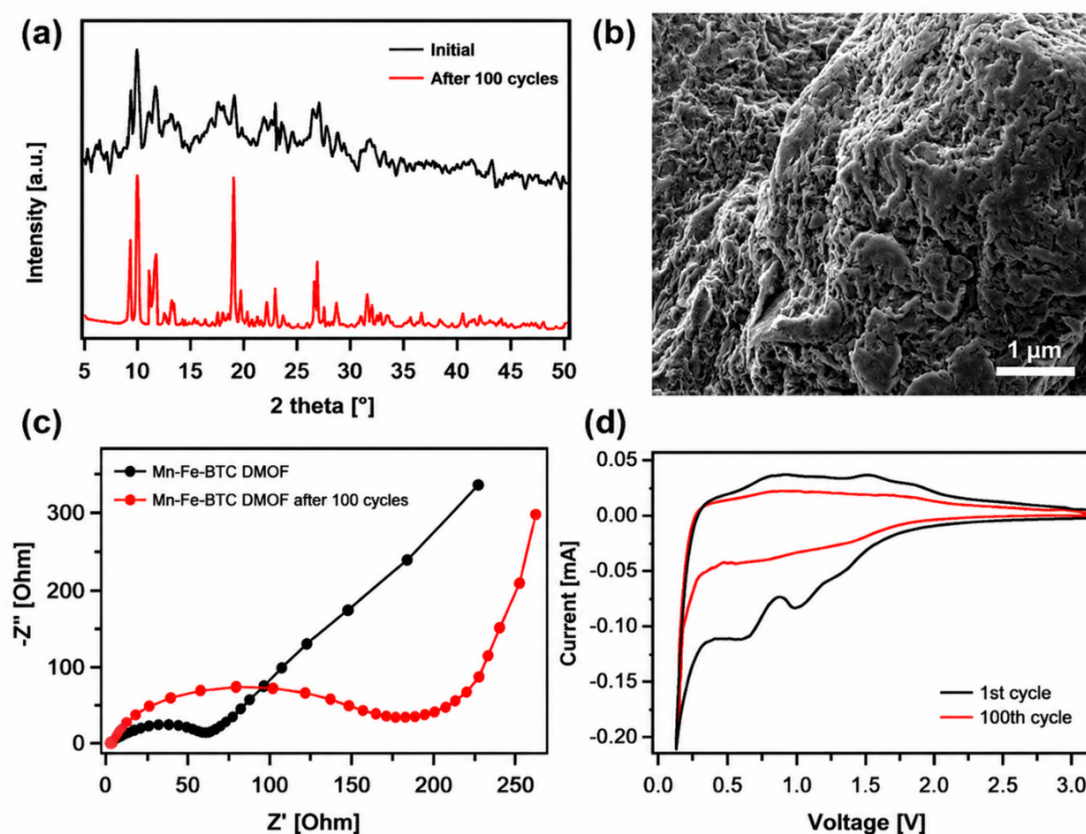
| Electrode                                                                  | S.A. (m <sup>2</sup> /g) | J (A/g)    | Cap. (mAh/g) | Cycles     | Ret. (mAh/g) | Ref              |
|----------------------------------------------------------------------------|--------------------------|------------|--------------|------------|--------------|------------------|
| Mn-BDC                                                                     | 6.135                    | 0.1        | –            | 100        | 974          | [255]            |
| C/Fe-MOF (after calcination)                                               | –                        | 0.1        | 1124         | 50         | 975          | [256]            |
| Mn-BTC (after calcination)                                                 | 24.9                     | 0.1        | 630          | 60         | 582          | [257]            |
| NiFeMn-BTCA                                                                | 263.23                   | 0.1        | 802          | 100        | 624          | [258]            |
| Mn <sub>1.8</sub> Fe <sub>1.2</sub> O <sub>4</sub> MOF (after calcination) | 124                      | 0.2        | 2300         | 60         | 827          | [259]            |
| MnO/ZnO@C MOF (after calcination)                                          | 117.9                    | 2          | 1396         | 1000       | 636          | [261]            |
| MnCo-T                                                                     | 9.15                     | 1          | –            | 600        | 337          | [260]            |
| Ni/Mn-BTC (after calcination)                                              | 12.8                     | 1.257      | 1049         | 400        | 258          | [262]            |
| Fe-BDC                                                                     | –                        | 0.03       | 280          | 40         | 175          | [263]            |
| Mn-BDC (after calcination)                                                 | 4.12                     | 0.1        | 961          | 100        | 653          | [264]            |
| H <sub>8</sub> L-Fe-MOF                                                    | 204                      | 0.05       | –            | 50         | 275          | [265]            |
| <b>Mn-Fe-BTC DMOF</b>                                                      | <b>1045</b>              | <b>0.1</b> | <b>1385</b>  | <b>100</b> | <b>687</b>   | <b>This work</b> |



**Figure 3.7:** XPS (a) Fe2p, (b) Mn2p, and (c) C1s spectra of Mn-Fe-BTC DMOF electrode after 100 charge/discharge cycles.

not collapsed.

EIS and CV characterizations after 100 charge–discharge cycles are presented in Figs. 3.8(c) and (d). The Nyquist plots for Mn-Fe-BTC DMOF after 1 cycle (black) and 100 cycles (red) reveal an increase in  $R_{ct}$  from 60  $\Omega$  to 189  $\Omega$ , indicating the formation of a SEI on the electrode surface. As shown in Fig. 3.6(d), after a few cycles, the specific capacity becomes constant, suggesting that the SEI layer has reached a stable state. Importantly, no additional semicircles are observed, verifying the material’s stability.



**Figure 3.8:** (a) Powder XRD of pristine Mn-Fe-BTC DMOF electrode (black) and after 100 charge/discharge cycles (red), (b) SEM image of Mn-Fe-BTC DMOF electrode after 100 cycles, (c) EIS spectra after 1 cycle (black) and 100 cycles (red), (d) CV curves at 0.1 mV/s after 1 cycle (black) and 100 cycles (red).

The CV results support the EIS findings, showing that the increased resistance from SEI formation slows the charge-transfer process, resulting in reduced peak heights and a diminished overall CV response.



### 3.6 Conclusion

To conclude, a convenient hydrothermal method was used to successfully prepare a porous composite of dual metal–organic frameworks (Mn-Fe-BTC DMOF) as a cathode material for LMBs. The synthesized framework had a specific surface area of  $1045 \text{ m}^2\text{g}^{-1}$ , delivering a significant storage capacity of  $1385 \text{ mAh g}^{-1}$  at  $0.1 \text{ Ag}^{-1}$  and a low charge transfer resistance of  $60 \text{ }\Omega$  confirming favorable ion transport kinetics and accessible electroactive sites. However, the specific capacity declined to  $687 \text{ mAh g}^{-1}$  after 100 consecutive charge/discharge cycles, reflecting a notable degree of capacity fade. This decay is attributed to several interrelated degradation mechanisms operating within the electrolyte environment, that can progressively attack the metal–ligand coordination bonds within the MOF structure, leading to partial framework corrosion and loss of electrochemically active sites over prolonged cycling. Furthermore, CV analysis revealed a gradual attenuation and broadening of the redox peaks with an increasing number of cycles, indicating a diminished electrochemical accessibility of the active sites and increased kinetic polarization. EIS measurements further supported this finding, showing a progressive increase in charge transfer resistance from  $60 \text{ }\Omega$  to  $189 \text{ }\Omega$  over 100 cycles, consistent with the formation of a resistive electrode–electrolyte interphase layer arising from oxidative decomposition of carbonate solvents at the cathode surface. While the  $\pi$ – $\pi$  interactions within the DMOF framework contribute to structural resilience against volume changes during repeated lithiation/delithiation, they are insufficient to fully counteract the electrolyte-driven interfacial degradation and induced framework corrosion. Future strategies such as electrolyte additive engineering, surface passivation, or the use of more chemically stable electrolyte systems may significantly improve the long-term cyclability of DMOF-based electrodes. The findings collectively prove Mn-Fe-BTC DMOF to be a promising electrode candidate for next-generation LMBs to enhance efficiency and durability. However, for future investigations, ex situ XPS at intermediate states of charge or operando techniques such as X-ray absorption spectroscopy (XAS) and in situ Raman spectroscopy would provide a more definitive and quantitative deconvolution of the sequential redox contributions during lithiation and delithiation processes. More generally, this work provides a rational design principle for the engineering of functional porous materials to store charge for applications in energy storage, which is easily extendable to a variety of combinations of metal ions, alternative organic linkers, and a wide range of novel electrochemical applications.

## Chapter 4

# Impact of MOF-5 Derived Carbonization Temperature on the Performance of Zinc-Ion Energy Storage

The carbonization temperature of MOF-derived carbons critically governs their porous architecture, graphitization degree and ultimately their electrochemical performance in energy storage applications. In ZnHSCs, the structural and textural properties of the carbon electrode play a vital role in determining the reversible intercalation and de-intercalation kinetics of divalent  $\text{Zn}^{2+}$  ions in aqueous electrolyte. Despite the growing interest in MOF-derived carbons as electrode materials, the systematic influence of pyrolysis temperature on the structure-property relationships of MOF-5-derived carbons and their consequent impact on ZnHSCs performance remains insufficiently explored. In the present work, we systematically study the carbonization of MOF-5 with pyrolysis temperatures to evaluate how the carbonization temperature affects the physicochemical properties of these materials. The carbon material prepared at the optimal carbonization temperature 1000 °C, (CMOF-5\_1000) exhibited the best electrochemical performance with an outstanding specific capacitance of 268.93  $\text{Fg}^{-1}$ , high energy density of 166.9  $\text{Whkg}^{-1}$ , and high-power density of 9234  $\text{Wkg}^{-1}$  among all the synthesized samples. All these improved properties are attributed to the well-developed hierarchical porous structure, high degree of graphitic ordering and much lower charge transfer resistance obtained at this temperature. It is worth emphasizing that the simultaneous achievement of both high energy and high-power densities in the case of CMOF-5-1000 indicates the crucial importance of thermal treatment for the creation of carbon microstructures

with advanced energy storage properties. The results suggest that carbonized MOF-5 is an attractive and scalable nanoscopic electrode material for next-generation zinc based energy storage technologies which could be readily expanded to other MOF precursors and energy storage devices.

## 4.1 Introduction

Due to the increasing global energy crisis, it is becoming a critical issue to develop more and more efficient and reliable energy storage systems (ESS) that can supply a steady and stable energy supply [273]. Zinc ion-based energy storage systems (Zn-ESS) have gained many research interests due to their high theoretical capacity, abundance, low cost, and environmental benignity, among other electrochemical technologies [274]. Among the various anode materials considered, zinc metal is a very promising material for large-scale energy storage, due to its high volumetric capacity, natural safety, and relatively low redox potential [274]. Despite this, finding and developing optimal cathode material for the high-performance Zn-ESS is still a major challenge for the realization of such a device [275]. To identify a suitable candidate for the cathode, a wide variety of manganese dioxide ( $\text{MnO}_2$ ) [276], vanadium-based materials [277] and Prussian blue analogs (PBAs) [278] have been tested. Although they show reasonable electrochemical performance, they are intrinsically limited by several key issues, such as electrolyte dissolution, structural instability during repeated cycling and slow ion reaction rates, which significantly affect their cycling stability. However, activated carbon (AC) is an interesting cathode material because of its excellent electrical conductivity, high specific surface area and very good stability in the aqueous electrolyte environment [279]. It is, however, impossible to achieve high energy density by using it as a purely EDLC material, which makes it not very attractive for next generation high performance Zn-ESS [280]. Due to their outstanding and tunable physicochemical features, MOFs, which are a new class of porous nanostructured materials with a structurally diverse family of crystal structures, are becoming increasingly attractive cathode materials for Zn-ESS [276]. The unique characteristics such as the nanoscale compositional and structural controllability, exceptionally high specific surface area and high porosity accomplish them excellent host materials for electrochemical charge storage [281]. In addition, the site-specific carbonization or pyrolysis of the MOF precursors provides a valuable method to decorating the resulting porous carbon-based frameworks with high electrical conductivity while maintaining the metal species and natural hierarchical porosity of the precursor structure [282, 283]. In the vast array of MOFs available, there

are some specific electrochemical properties that are exclusively found in Zn-based MOFs including faster  $\text{Zn}^{2+}$  ion transport kinetics and greatly improved charge transfer properties at the electrode-electrolyte interface [284]. MOF-5, which was synthesized by linking  $\text{Zn}^{2+}$  ions with terephthalic acid, is one of the most representative and widely studied MOF systems in the literature, with over 5,000 studies reported to date [285]. Its well-defined topology, high BET surface area of up to  $3,800 \text{ m}^2 \text{ g}^{-1}$ , large pore volume of  $\sim 1.04 \text{ cm}^3 \text{ g}^{-1}$ , and remarkable thermal stability up to  $400^\circ\text{C}$  have established it as a benchmark framework and an ideal precursor for the fabrication of porous carbons via controlled pyrolysis [286, 287]. When MOF-5 is carbonized, MOF-5 starts to distribute ZnO species, and the species are gradually separated from the framework by thermal diffusion by analytically increasing the carbonization temperature and duration. Most significantly, it has recently been shown that a carboreduction process starts once the carbonization goes beyond a critical point, in which ZnO species transform progressively into metallic Zn [288, 289]. The resulting removal of ZnO and metallic Zn species from the carbon matrix is expected to create well-defined pore channels with proper dimensions to enable the accommodation of  $\text{Zn}^{2+}$  ions from the electrolyte during the discharge process and significantly improve the accessibility and transport of ions in the electrode structure. At the same time, the remaining species could play an active role in the overall energy storage mechanism by faradaic reactions, thus potentially increasing the energy density of the cathode material. Thus, the interaction between Zn and ZnO retention, pore structure evolution and electrochemical performance is a vital subject of study, and for systematic optimization, the carbonization temperature is an important variable to fine-tune the connection between these structural properties and electrochemical activity. In this chapter synthesis and characterization of carbonized MOF-5 is reported as a nanostructured cathode material for Zn-ESS. The effect of carbonization at various temperatures ranging from  $600$  to  $1000^\circ\text{C}$  are explored, and the resulting MOF-derived carbons' physicochemical properties including surface area, pore size electrical conductivity, and Zn/ZnO ratio are correlated with the observed electrochemical performance.

## 4.2 Experimental Section

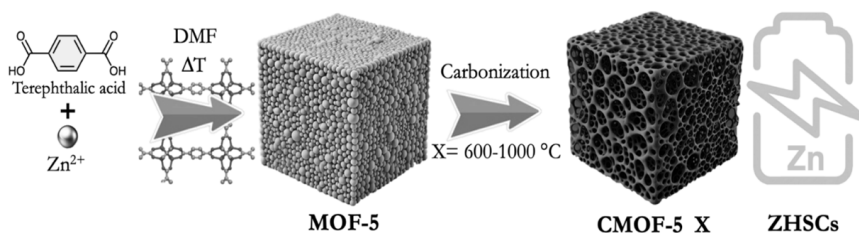
Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), zinc foil, terephthalic acid ( $\text{C}_6\text{H}_4(\text{COOH})_2$ ) and N-Methyl-2-pyrrolidone (NMP) were bought from Sigma Aldrich. N,N-dimethylformamide (DMF) was purchased from CARLO ERBA (France) and zinc trifluoromethanesulfonate ( $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  or  $\text{Zn}(\text{OTf})_2$ ) was purchased from Tokyo Chemical



Industry (TCI, Japan). Polyvinylidene fluoride (PVDF) binder, conductive carbon black (Super P – SP) and activated carbon (AC) were bought from Alfa Aesar (Germany).

### 4.2.1 Synthesis and carbonization of MOF-5

The synthesis of MOF-5 was based on a previously reported procedure [282, 283]. Briefly, a zinc nitrate tetrahydrate (982 mg, 3.75 mmol) and terephthalic acid (299 mg, 1.8 mmol) was dissolved in 360 mL of DMF to prepare the solution shown in Figure 4.1.



**Figure 4.1:** Synthetic pathway of CMOF-5\_X samples, being X the carbonization temperature.

The solution was then stirred at  $110\text{ }^{\circ}\text{C}$  for 48 hours. After this time, the solution was centrifuged at 8,000 rpm for 10 minutes to attain white powder. For its subsequent carbonization, the resultant powder was placed in a ceramic boat in a tube furnace, initially heated to  $110\text{ }^{\circ}\text{C}$  to eliminate residual solvent from the pores, and then heated to the desired temperature ( $600-1000\text{ }^{\circ}\text{C}$ ), maintained for two hours, and then cooled down to room temperature. The entire process was carried out under an inert argon atmosphere. In this chapter the samples will be represented as CMOF-5\_X, being X the carbonization temperature.

### 4.2.2 Preparation of Electrode material

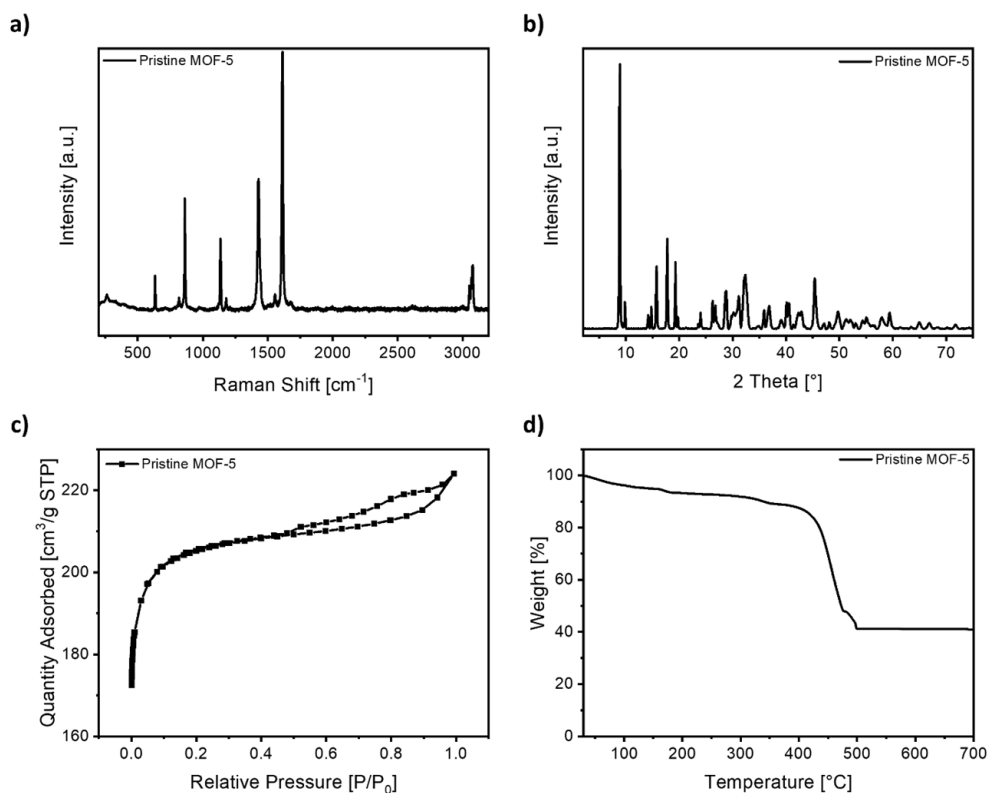
The electrochemical characterizations were performed in a two-electrode system using a coin cell composed of a cathode (*i.e.*, CMOF-5 or AC) and Zn foil as an anode glassy fibrous paper (Whatman GF/G) as a separator soaked with 3 M  $Zn(CF_3SO_3)_2$  bis(trifluoromethanesulfonate) as aqueous electrolyte. The cathode electrode is composed of 70 wt.% of CMOF-5\_X, 20 wt.% of Super P conductive carbon, and 10 wt.% of polytetrafluoroethylene (PVDF) as the binder. The two-electrode system was enclosed in CR2032-type cells.

### 4.2.3 Morphological and Structural characterizations

To confirm the structure, chemical composition and morphology of synthesized CMOF-5, SEM, XRD, XPS, TGA, Raman Spectroscopy and for the surface area and pore volume BET were performed.

## 4.3 Results and Discussion

Pristine MOF-5 material is synthesized through a solvothermal method by using a modified procedure by Park et al shown in Figure 4.2 in detail.

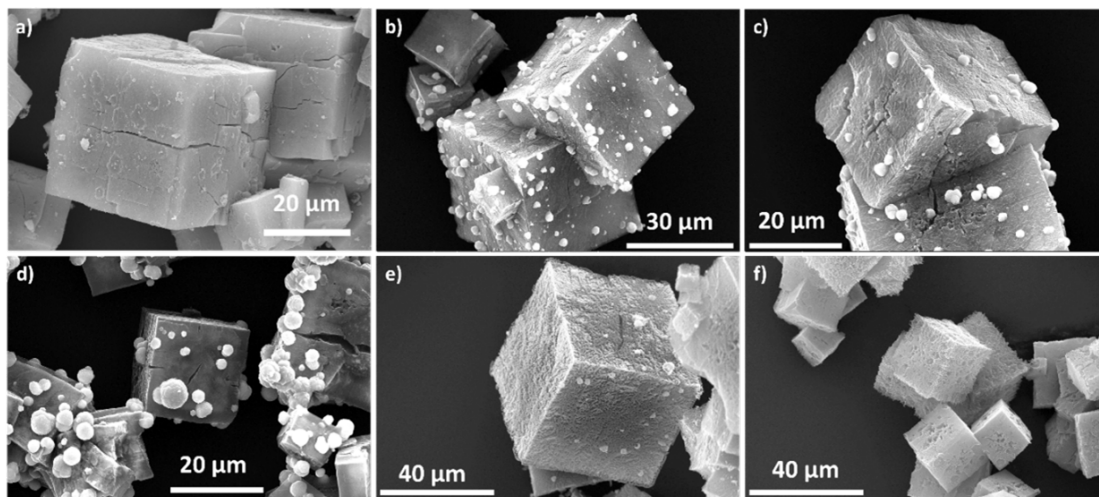


**Figure 4.2:** (a) Raman spectrum, (b) PXRD, (c) nitrogen adsorption/desorption isotherms, and (d) TGA in air curve of pristine MOF-5.

Raman spectroscopy is employed to confirm the chemical composition of MOF-5 (Fig. 4.2). Five major bands at 1615, 1433, 1140, 866 and 635 cm<sup>-1</sup> are observed, corresponding to the vibrational modes of carboxylic group and aromatic benzene ring of the terephthalic acid ligand, in agreement with previous reports [282]. The XRD pattern of pristine MOF-5 (Fig. 4.2b) reveals a close alignment between the diffraction peaks of the synthesized MOF-5 and the pattern reported previously for MOF-5 [290], indicating the successful synthesis of the MOF-5 material. The adsorption isotherms

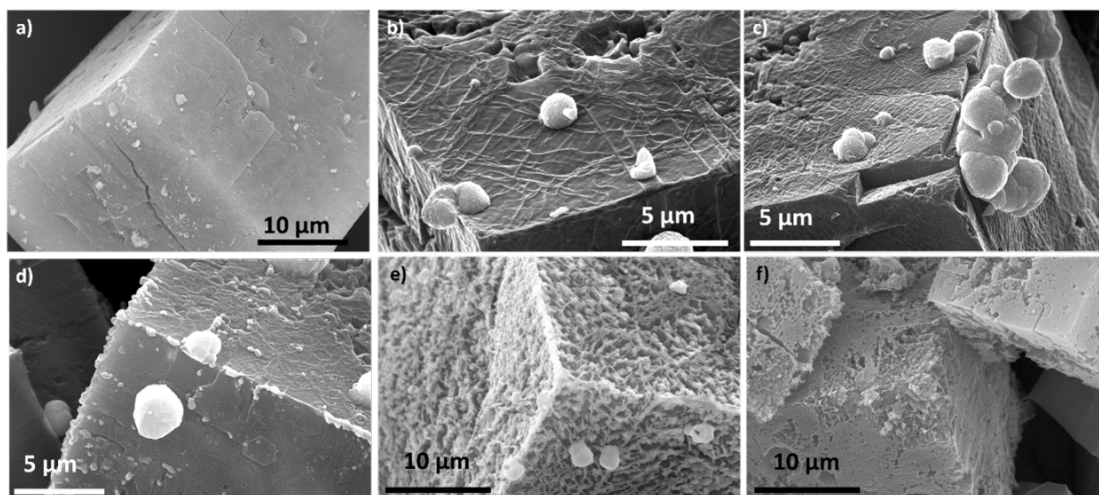
of MOF-5 exhibit type-I sorption isotherm, with steep rises appearing at a low relative pressure and type-IV sorption features with adsorption/desorption hysteresis at higher pressure. The calculated BET surface area of MOF-5 amounts to  $631.03 \pm 16.76 \text{ m}^2/\text{g}$  (Fig. 4.2c) and the DFT total pore volume amounts to  $0.26 \text{ cm}^3/\text{g}$  [282]. The thermal stability of pristine MOF-5, as assessed by TGA, is reported in Fig. 4.2d. It reveals a fast process with 45.5% weight loss in the temperature range of 400–450 °C for the crystal MOF-5, which corresponds to its structure decomposition [283]. MOF-5 is then carbonized (CMOF-5) under an inert atmosphere at different temperatures, ranging from 600 to 1000 °C shown in Figure 4.1.

To explore the carbonization mechanism of MOF-5, scanning electron microscopy (SEM) is first employed to examine the nanoscale morphology, specifically the size, shape, and surface structure, of CMOF-5 samples.



**Figure 4.3:** SEM images of a) MOF-5 and CMOF-5 carbonized at: b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C and f) 1000 °C.

Figures 4.3 and 4.4 reveal that the CMOFs assemble into large cubic aggregates with lateral sizes ranging between 10-25  $\mu\text{m}$ . Such unique morphology is retained independently on the carbonization temperature, yet the temperature plays a crucial role in the surface structure of the resulting materials. CMOF-5 materials obtained at 600 °C and 700 °C exhibit noticeable ZnO agglomerates on their surfaces. Upon reaching 800 °C, the agglomerates become larger, displaying cracks and defects in the cubic CMOF-5 structures, as well as small Zn or ZnO islands on their surface. This indicates that a significant portion of the ZnO has been removed from the CMOF-5 core structure, forming large agglomerates on the surface. Additional pores and defects in the carbon structure are simultaneously created during the ZnO migration to the CMOF-5 surface [283]. At 900 °C, the large agglomerates disappear, leaving only small Zn or

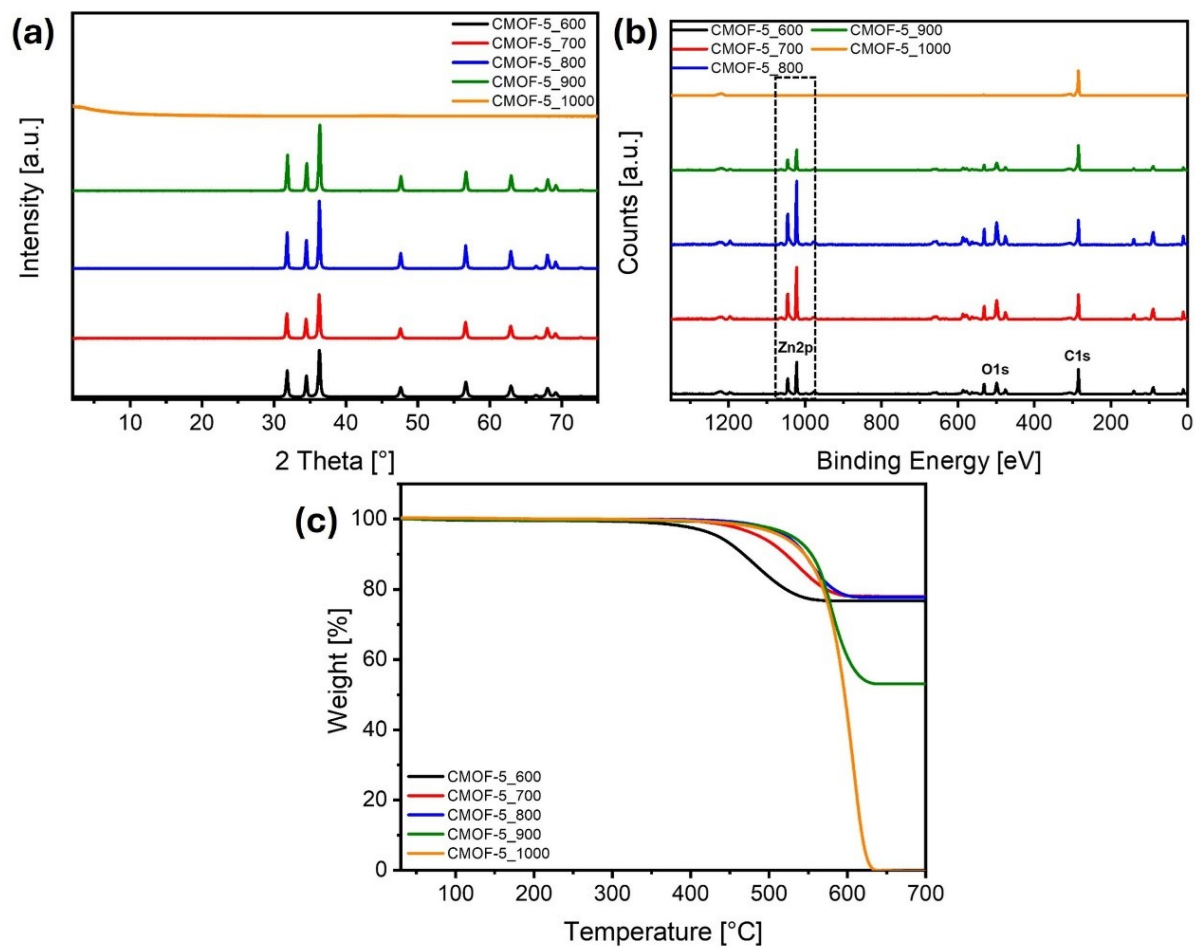


**Figure 4.4:** High magnification of SEM images of a) MOF-5 and CMOF-5 carbonized at b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C and f) 1000 °C.

ZnO clusters. Upon further heating to 1000 °C, all zinc species are evaporated and removed from the CMOF-5 structure [288,289].

XRD diffractograms of all the carbonized samples shown in Figure 4.5(a). In agreement with SEM results, the samples produced at carbonization temperatures ranging from 600 to 900 °C, display the characteristic sharp peaks attributed to ZnO [291]. Importantly, when the carbonization temperature reaches 1000 °C no traces of ZnO are observed, confirming the complete Zn removal of the MOF-derived carbon structure. To quantify the amount of Zn and ZnO on the CMOF-5 samples and the defectiveness of each sample, XPS shown in Figure 4.5(b) survey investigations, thermogravimetric analysis (TGA) shown in Figure 4.5(c).

XPS provides insight into the surface composition with a penetration depth of 1-10 nm, whereas TGA offers information on the composition throughout the entire sample. Fig. 4.5(b) shows the XPS survey spectra of all CMOF-5 samples, normalized by the carbon peak. With the rising carbonization temperature, a gradual increase in the presence of Zn and ZnO on the surface of CMOF-5 is observed, reaching its peak value for the sample carbonized at 800 °C, in line with SEM and XRD characterizations. Subsequently, there is a reduction in the amount of Zn and ZnO present on the sample obtained at 900 °C and at 1000 °C, with a complete evaporation of the Zn species occurring due to the carboreduction process [288,289]. Table 4.1 reports the quantitative data indicating the atomic proportions of each element present on the surface of all the carbonized samples, especially Zn/O ratio. While this ratio amounts to 0.57 for samples treated at carbonization temperatures of 600 and 700 °C, it rises up to 0.83 at 800 °C, due to the formation of metallic Zn. Subsequently, at 900 °C, the evaporation of metallic



**Figure 4.5:** (a) XRD patterns of all CMOF-5 samples, (b) XPS survey spectra of all CMOF-5 samples, (c) TGA in air curves of all CMOF-5 samples.

Zn begins (as the approximated evaporation temperature of Zn is 907 °C), leading to a reduction in the Zn/O ratio to 0.72. Finally, at a carbonization temperature of 1000 °C, all Zn species, including the ZnO integrated into the porous carbon matrix, disappear.

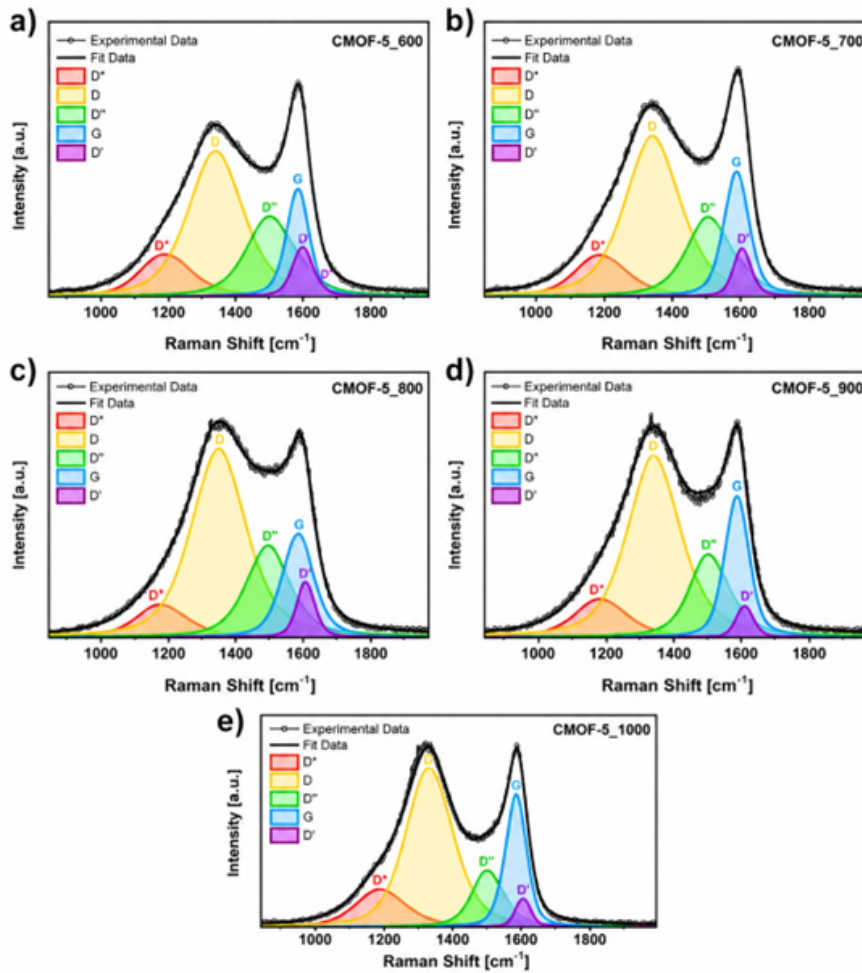
**Table 4.1:** Atomic contribution of elements on the surface in all CMOF-5 samples from XPS analysis.

| Sample      | C [At.%] | O [At.%] | Zn [At.%] | Ratio C/Zn | Ratio Zn/O |
|-------------|----------|----------|-----------|------------|------------|
| CMOF-5_600  | 76.9     | 14.7     | 8.4       | 9.15       | 0.57       |
| CMOF-5_700  | 74.5     | 16.2     | 9.3       | 8.01       | 0.57       |
| CMOF-5_800  | 69.6     | 16.6     | 13.8      | 5.04       | 0.83       |
| CMOF-5_900  | 86.6     | 7.8      | 5.6       | 15.46      | 0.72       |
| CMOF-5_1000 | 98.3     | 1.7      | —         | —          | —          |

TGA is then performed to assess the overall composition of the CMOF-5 samples, as depicted in Fig. 4.5(c). As observed in the TGA analysis of pristine MOF-5 in Fig. 4.2(d) and in agreement with previous reports [283], within the temperature range of 400-550 °C, the organic ligand undergoes thermal decomposition, generating gases such as carbon monoxide, carbon dioxide, and benzene. This process leads to the creation of a carbon matrix, maintaining the original MOF-5 structure as shown in SEM (Figs. 4.3, 4.4). Simultaneously, Zn<sub>4</sub>O clusters start transforming into ZnO at this stage. As can be seen in Fig. 4.5(c), the samples carbonized within the range of 600-800 °C display a comparable composition, comprising approximately 77% Zn and ZnO in weight. In contrast, the sample carbonized at 900 °C exhibits a notably reduced presence of zinc species, accounting for approximately 53% in weight, in full agreement with SEM, XRD and XPS. This is a clear indication of the occurrence of carboreduction. Briefly, the carbon species actively remove oxygen from the ZnO, resulting in the reduction of ZnO to metallic Zn and the production of carbon oxides such as CO and CO<sub>2</sub> as byproducts [288]. Upon increasing the carbonization temperature to 1000 °C, the zinc species are entirely evaporated (boiling point of Zn metal is 907 °C) from the material's structure, rendering the sample completely composed of porous carbon.

The Raman spectra of CMOF-5 samples shown in Figures 4.6 and 4.7 are deconvoluted by using five Lorentzian curves, which consist of the first-order Raman modes, namely: D, G, D', D'' and D\* in Figure 4.6 in an analogous manner to other carbon-based materials [292]. The D band typically arises from the breathing modes of sp<sup>3</sup>-hybridized carbon atoms, and it is associated with the presence of defects and disorder in the carbon lattice. Conversely, the G band corresponds to the E<sub>2g</sub> mode of sp<sup>2</sup>-hybridized carbon atoms and is indicative of the graphitic structure and the degree of order in the carbon lattice. The intensity ratio of D and G bands ( $I_D/I_G$ ) (Fig. 4.7) is frequently utilized

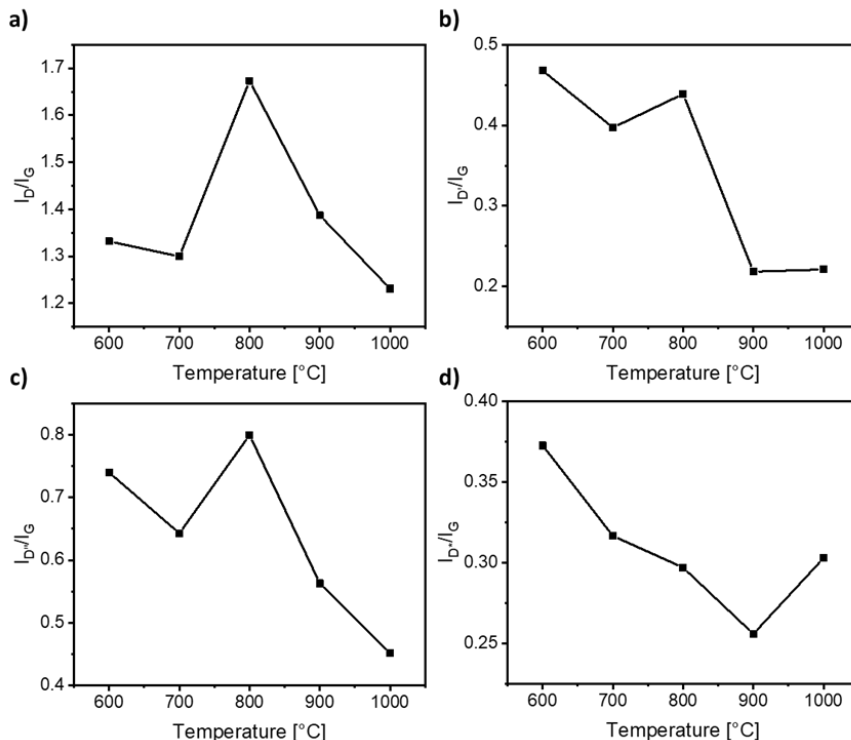
to quantify the extent of disorder in carbon-based materials. At 600 °C and 700 °C carbonization temperatures, the  $I_D/I_G$  ratio remains below 1.35, indicating a structure primarily composed of graphite-like carbon with a well-ordered arrangement. However, this trend shifts at 800 °C, where the  $I_D/I_G$  ratio reaches 1.65, indicating an increase in structural defects, in agreement with SEM analysis. This increase can be attributed to the extraction of zinc species from the core structure of the CMOF-5, which, while migrating to the surface, induces the formation of defects and new nanoscale pores along their path. Interestingly, at 900 °C and 1000 °C, the  $I_D/I_G$  ratio decreases, possibly due to carbon self-healing processes occurring at higher temperatures, consequently reducing the number of structural defects [293].



**Figure 4.6:** Fitted Raman spectra of all CMOF-5 samples.

The additional bands ( $D'$ ,  $D''$  and  $D^*$ ) originate from the defects within the graphitic framework of the carbon material. The  $I_{D'}/I_G$ ,  $I_{D''}/I_G$ , and  $I_{D^*}/I_G$  ratios are shown in Fig. 4.7(b), (c) and (d) respectively. The  $I_{D'}/I_G$ ,  $I_{D''}/I_G$  ratios follow the same trend as the  $I_D/I_G$  ratio with a maximum disorder reached when 800 °C is used as carbonization

temperature.

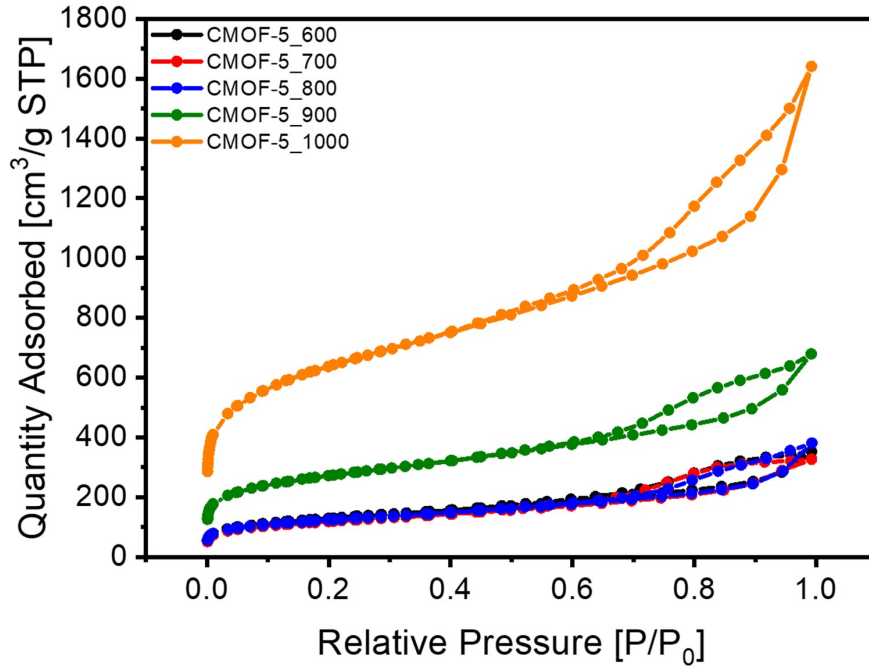


**Figure 4.7:** Ratio of the band intensities a)  $I_D/I_G$ , b)  $I_{D'}/I_G$ , c)  $I_{D''}/I_G$ , d)  $I_{D^*}/I_G$  of all CMOF-5 samples.

The specific surface area and total pore volume of all samples are assessed by using nitrogen adsorption/desorption isotherms shown in Fig. 4.8. The isotherms of the CMOF-5 samples exhibit a type IV shape, indicating the presence of both micro- and mesopores within the materials [294]. This coexistence of different pore sizes renders these materials well-suited for energy storage applications. Additionally, all isotherms display H3 type hysteresis loop, which is indicative of loosely assembled particles that form slit-like pores [295]. The specific surface area and total pore volume values for all samples are reported in Table 4.2. The samples carbonized within the range of 600-800 °C demonstrate constrained surface areas and pores due to the presence of zinc species, as indicated by their similar BET-specific surface area and total pore volume values.

However, when the carbonization of MOF-5 is performed at 900 °C, both the values of specific surface area and pore volume are significantly increased and can be attributed to the extraction of zinc species from the CMOF-5 core, thereby releasing the occupied space. Notably, the material carbonized at 1000 °C consists only of highly porous carbon frameworks, with a specific surface area of 2151 m<sup>2</sup>/g and fully accessible pores (1.87 cm<sup>3</sup>/g). Consequently, the BET findings align entirely with the findings from the SEM, XRD, XPS and Raman analyses, by confirming the removal of zinc species during





**Figure 4.8:** Nitrogen adsorption/desorption isotherms of all CMOF-5 samples.

**Table 4.2:** Texture parameters of all the obtained CMOF-5 samples.

| Sample      | BET surface area [m <sup>2</sup> /g] | Total pore volume [cm <sup>3</sup> /g] |
|-------------|--------------------------------------|----------------------------------------|
| CMOF-5_600  | 443.80 ± 4.59                        | 0.41                                   |
| CMOF-5_700  | 404.86 ± 4.18                        | 0.41                                   |
| CMOF-5_800  | 420.12 ± 4.50                        | 0.43                                   |
| CMOF-5_900  | 919.06 ± 11.27                       | 0.78                                   |
| CMOF-5_1000 | 2151.07 ± 27.17                      | 1.87                                   |

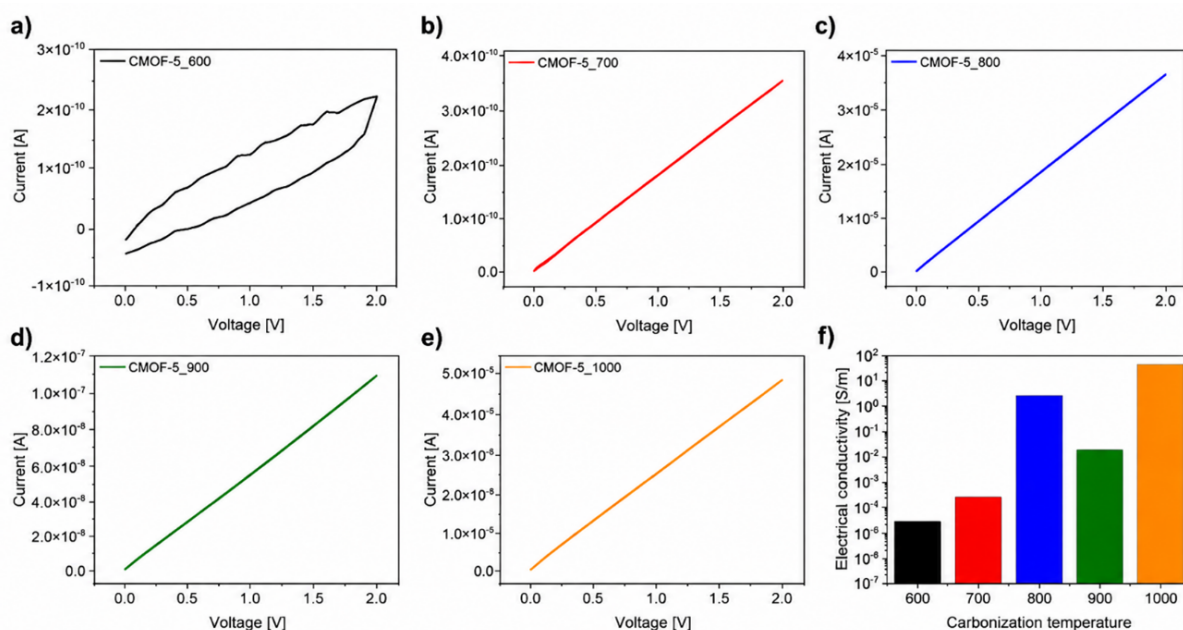
carbonization at temperatures exceeding 900 °C, leading to the creation of extra porosity within the CMOF-5 structure.

## 4.4 Electrochemical Characterizations

The electrochemical performance of CMOF-5 active material was investigated by electric conductivity (IV curves), CV, GCD and EIS. Two electrode systems were employed where a coin cell (CR2032) was assembled with CMOF-5 active material as a cathode and Zn metal as an anode.

### 4.4.1 Results and Discussion

To gain a greater understanding of the electrical performance of CMOF-5 samples, thin film conductivity measurements are performed and correlated with the Zn/ZnO content.



**Figure 4.9:** (a-e) IV curves and (f) electrical conductivity of all CMOF-5 samples.

I-V curves are obtained by applying a sweeping voltage between 0 and 2 V and between 2 and 0 V for all the carbonized samples (Fig. 4.9a-e). Film conductivities are then estimated and reported in Fig. 4.9f. The film's conductivity initially rises with the carbonization temperature, reaching a maximum at 800 °C, followed by a decrease at 900 °C, and subsequently, another increase at 1000 °C. The observed trend can be linked to the variation in Zn and ZnO contents within the samples. Below 800 °C, the predominant process involves the generation of ZnO, that migrates towards the surface

of CMOF-5, resulting in an increase in electrical conductivity. However, at 800 °C, the carboreduction of ZnO initiates, converting portions of ZnO into metallic Zn. The occurrence of this transformation is also evidenced by the Zn/O ratio evolution which is determined from the XPS survey spectra (Table 4.1). While this ratio amounts to 0.57 for samples treated at carbonization temperatures of 600 and 700 °C, it rises to 0.83 at 800 °C, due to the emergence of metallic Zn, that also determines a substantial increase in conductivity. Subsequently, at 900 °C, the evaporation of metallic Zn begins (as the approximated evaporation temperature of Zn is 907 °C), leading to a reduction in the Zn/O ratio to 0.72. Consequently, as metallic elements depart from the CMOF-5 structure, the overall electrical conductivity decreases. Finally, at a carbonization temperature of 1000 °C, all Zn species, including the semiconducting ZnO integrated into the porous carbon matrix, are removed, resulting in a notable enhancement in electrical conductivity.

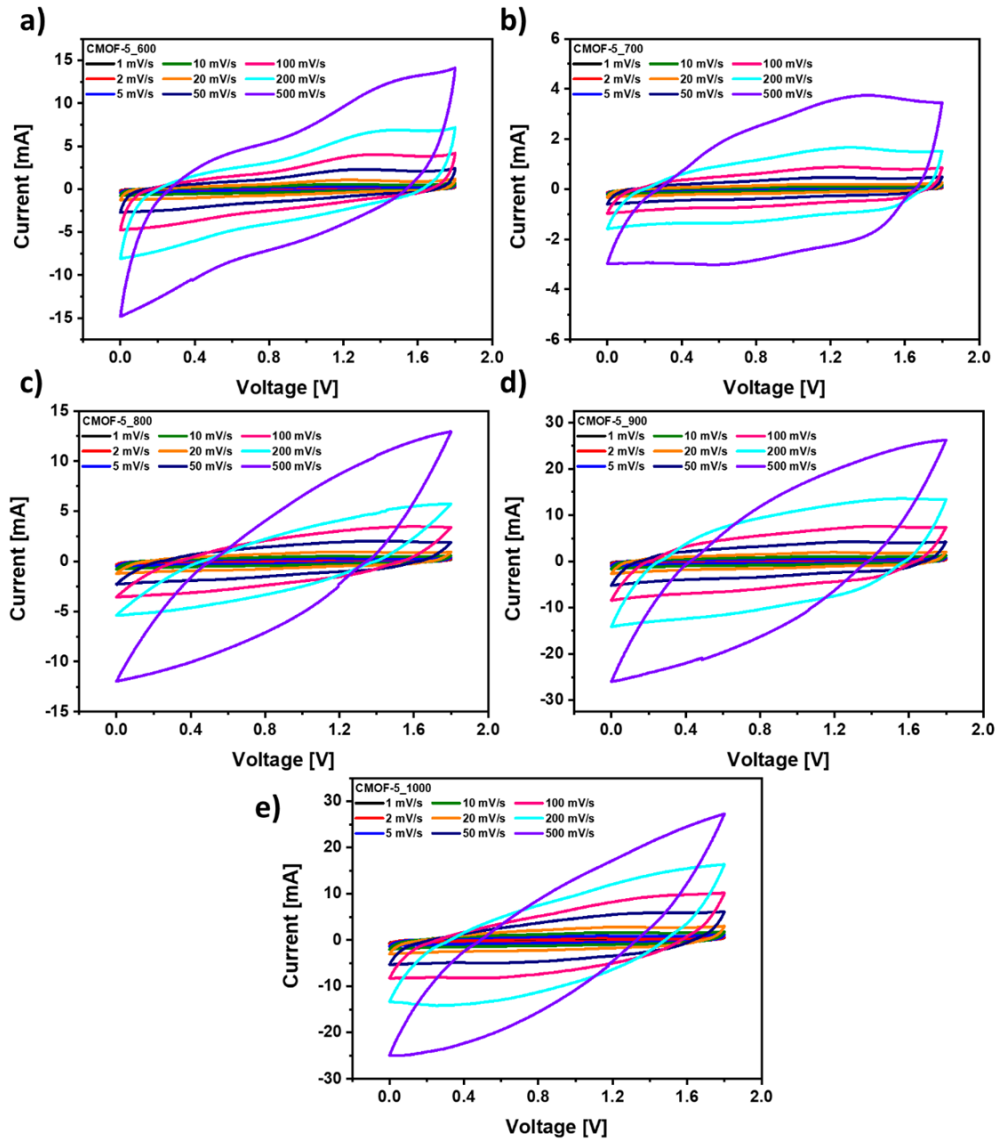
CV at different scan rates between 0-1.8 V were performed to determine the shapes of the curve to investigate the electrochemical behavior of all the CMOF-5 shown in Figure 4.10.

GCD was also measured at various current densities for all CMOF-5 from 0.1 to 5 A/g shown in Figure 4.11.

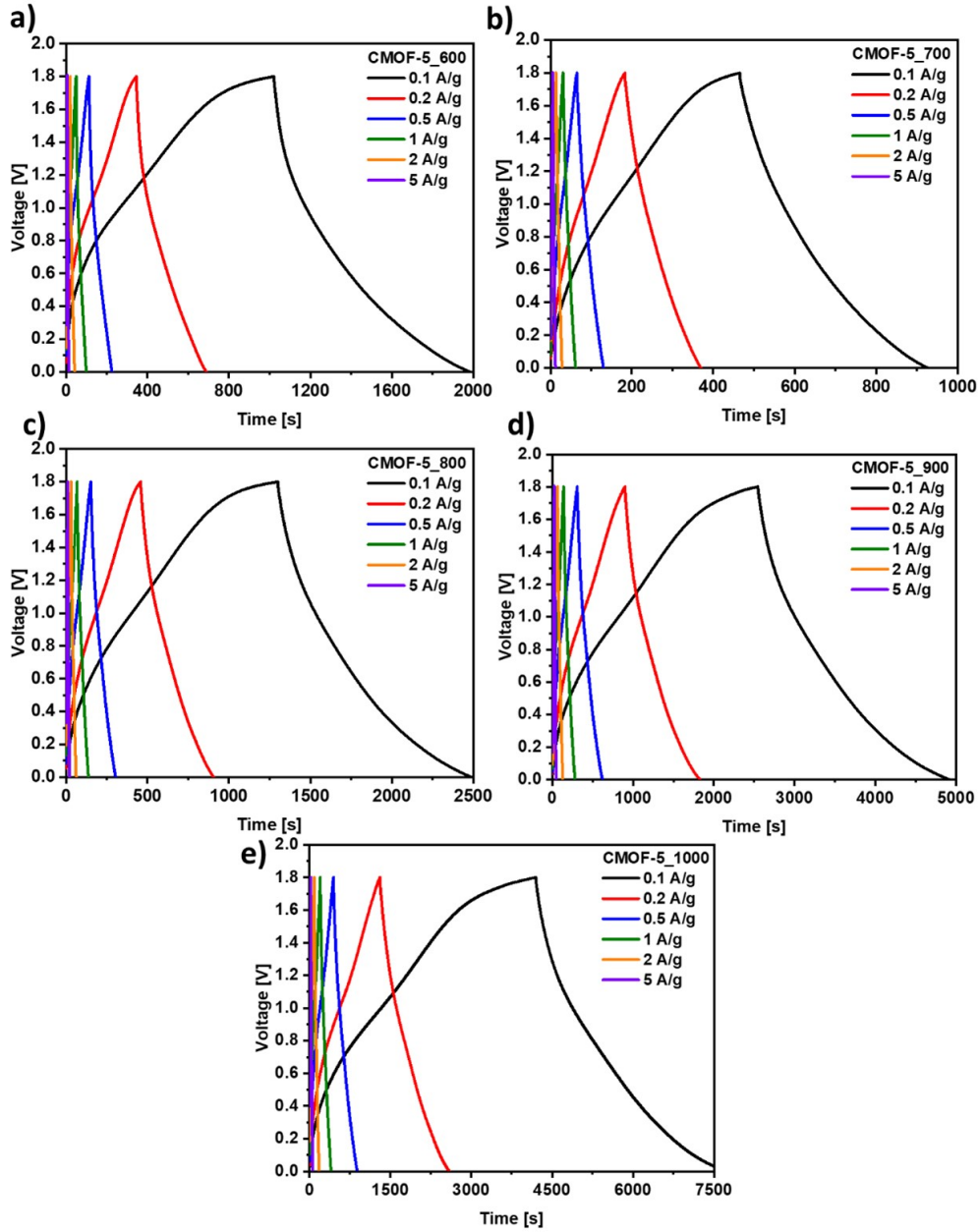
To compare electrochemical performance of CMOF-5 with Activated carbon (AC), AC was also measured for CV, GCD and EIS shown in Figure 4.12.

Fig. 4.13(a) and Fig. 4.10 show the CV curves and Fig. 4.13(b) and Fig. 4.11 the GCD profiles of CMOF-5\_X samples in the voltage range from 0 to 1.8 V at different scan rates and current densities, respectively. The CV and GCD profiles suggest a hybrid nature of the CMOF-5 electrodes. The quasi-rectangular shape of the CV curves and the nonlinear behavior of the GCD profiles imply a combination of electric double-layer capacitance and faradaic charge storage mechanisms, characteristic of asymmetric/hybrid energy storage systems [296]. Among the samples, MOF-5 carbonized at 1000 °C exhibits the largest curve area and the most rectangular CV shape at a scan rate of 1 mV/s as well as the longest discharge time in the GCD profile at 0.1 A/g, indicating superior electrochemical performance. Despite varying scan rates and current densities shown in Figs. 4.10 and 4.11, both CV and GCD profiles exhibit minimal deformation at high rates, indicating rapid kinetics and efficient energy storage behavior. In hybrid/asymmetric devices, we encounter nonlinear GCD profiles (Figs. 4.13b and 4.11), so it is necessary to determine the value of specific capacitance from CV curves (Fig. 4.13c and Table 4.3).

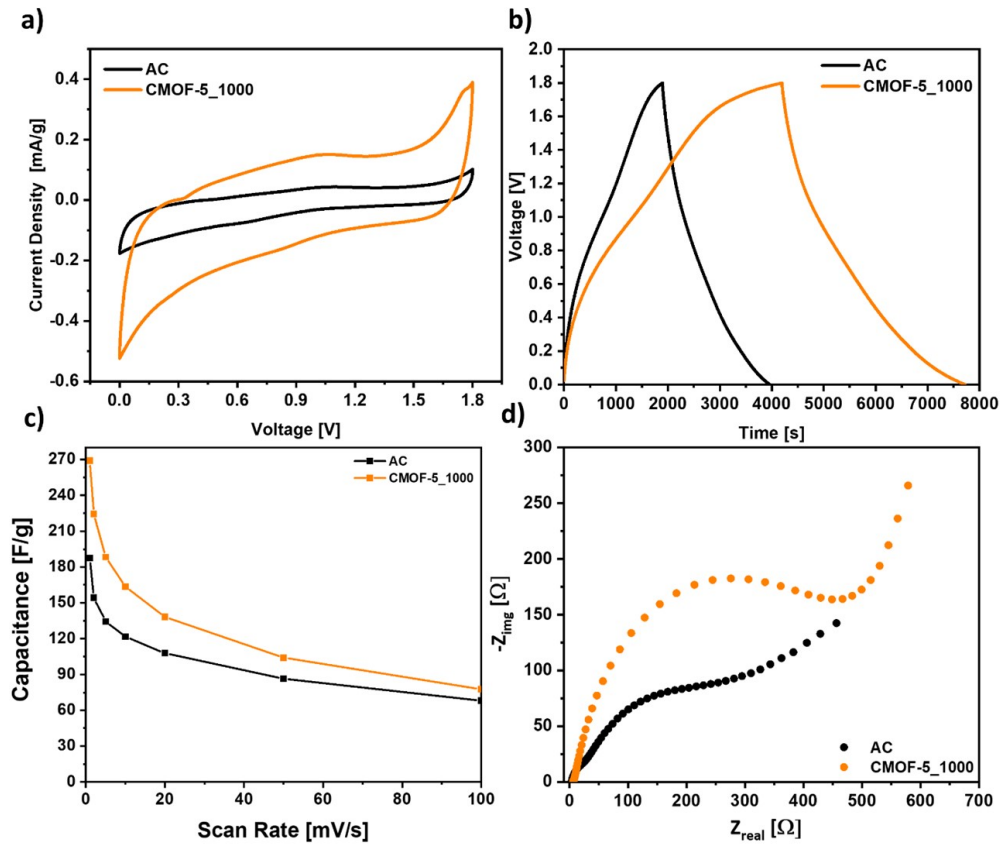
The lowest carbonization temperature (600 °C) exhibits a maximum specific capacitance of 133.51 F/g at 1 mV/s. The decrease in specific capacitance from CMOF-5\_600



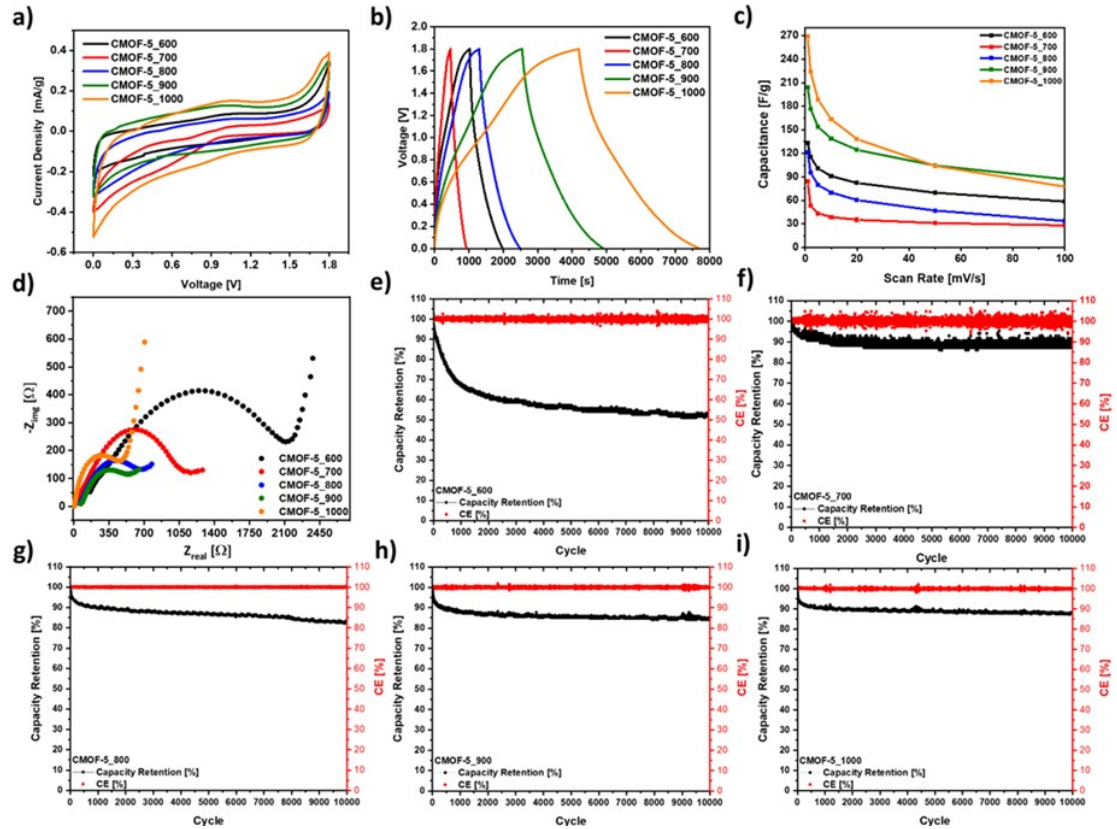
**Figure 4.10:** CV curves of all CMOF-5 samples at different scan rates.



**Figure 4.11:** GCD profiles of all CMOF-5 samples at different current densities.



**Figure 4.12:** (a) CV curves at scan rate of 1 mV/s, (b) GCD profiles at a current density of 0.1 A/g, (c) capacitances at different scan rates and (d) Nyquist plots of commercial AC and CMOF-5\_1000 sample.



**Figure 4.13:** (a) CV curves at scan rate of 1 mV/s, (b) GCD profiles at current density of 0.1 A/g, (c) capacitance values at various scan rates, (d) Nyquist plots for all CMOF-5 samples, cycling stability test after 10000 cycles for (e) CMOF-5\_600, (f) CMOF-5\_700, (g) CMOF-5\_800, (h) CMOF-5\_900, and (i) CMOF-5\_1000.

(133.51 F g<sup>-1</sup>) to CMOF-5\_700 (84.11 F g<sup>-1</sup>), despite the slight improvement in electrical conductivity at 700 °C, shows that charge storage in these MOF-derived carbon electrodes is controlled by a balance between electron transport and ion-accessible porosity, rather than by conductivity alone. Higher carbonization temperature can promote partial graphitization and facilitate electron movement through the carbon framework however, capacitance, particularly at low scan rates, strongly depends on the ability of Zn<sup>2+</sup> ions from the electrolyte to penetrate the pore network and reach the internal electroactive surface. In CMOF-5\_700, the XPS results indicate that a substantial amount of ZnO is still present, with a Zn/O ratio similar to that of CMOF-5\_600, while SEM and XRD suggest that these ZnO species begin to agglomerate and disrupt the porous carbon structure. This ZnO-induced pore blockage reduces electrolyte accessibility, limits Zn<sup>2+</sup> ion diffusion, and decreases the effective surface area available for charge storage, as also supported by the constrained BET surface area and pore volume values observed for the 600–800 °C samples. Therefore, although electrons can move slightly more efficiently in CMOF-5\_700, the restricted ionic transport and reduced access to active storage sites surpass the benefit of improved conductivity. This result highlights a competing effect between electronic conductivity and pore accessibility, enhanced conductivity can improve electrochemical performance only when the pore network remains sufficiently open to support efficient ion transport. The lower capacitance of CMOF-5\_700 should therefore be interpreted as evidence that ZnO-related pore barrier and framework disruption dominate over the modest conductivity improvement at this intermediate carbonization temperature. As a result, the capacitance of CMOF-5\_700 drops to 84.11 F/g. Starting at 800 °C, as supported by XPS, BET and electrical conductivity analyses, carboreduction takes place, driving the migration of zinc species to the surface. This process not only creates new channels but also leads to the gradual evaporation of zinc at higher temperatures. As a result, the CMOF-5\_800 and 900 samples exhibit specific capacitances of 121.23 and 204.4 F/g, respectively. Notably, although the CMOF-5\_900 sample has lower electrical conductivity compared to CMOF-5\_800, its significantly higher porosity enhances ion accessibility and dominates the charge storage process, leading to superior capacitance.

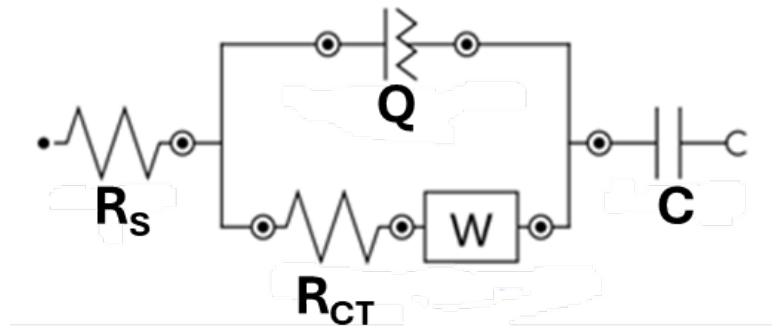
The highest capacitance, 268.93 F/g, is achieved for CMOF-5\_1000 sample, representing a 1.43-fold improvement over commercial activated carbon (AC) (Fig. 4.12). EIS provides valuable insight into the charge transport behavior of the CMOF-5 samples as a function of carbonization temperature. Nyquist plots in Fig. 4.13(d) are well fitted with the indicated circuit model shown in Figure 4.14. In the chosen equivalent circuit, the internal resistance ( $R_S$ ) and the charge transfer resistance ( $R_{CT}$ ) can be determined by the intercept on the real axis and the diameter of the semicircle, respectively shown



**Table 4.3:** Physical parameters and maximum specific capacitance of all obtained CMOF-5 samples.

| Sample      | Zn/O | BET (m <sup>2</sup> /g) | Pore vol. (cm <sup>3</sup> /g) | Cond. (S/m)             | Cap. (F/g) |
|-------------|------|-------------------------|--------------------------------|-------------------------|------------|
| CMOF-5_600  | 0.57 | 443.80 ± 4.59           | 0.41                           | 3.24 × 10 <sup>-5</sup> | 133.51     |
| CMOF-5_700  | 0.57 | 404.86 ± 4.18           | 0.41                           | 2.85 × 10 <sup>-4</sup> | 84.11      |
| CMOF-5_800  | 0.83 | 420.12 ± 4.50           | 0.43                           | 3.32                    | 121.23     |
| CMOF-5_900  | 0.72 | 919.06 ± 11.27          | 0.78                           | 0.02                    | 204.4      |
| CMOF-5_1000 | –    | 2151.07 ± 27.17         | 1.87                           | 50.15                   | 268.93     |

in Table 4.4 [296, 297].



**Figure 4.14:** The equivalent electric circuit models used for fitting the Nyquist plots.

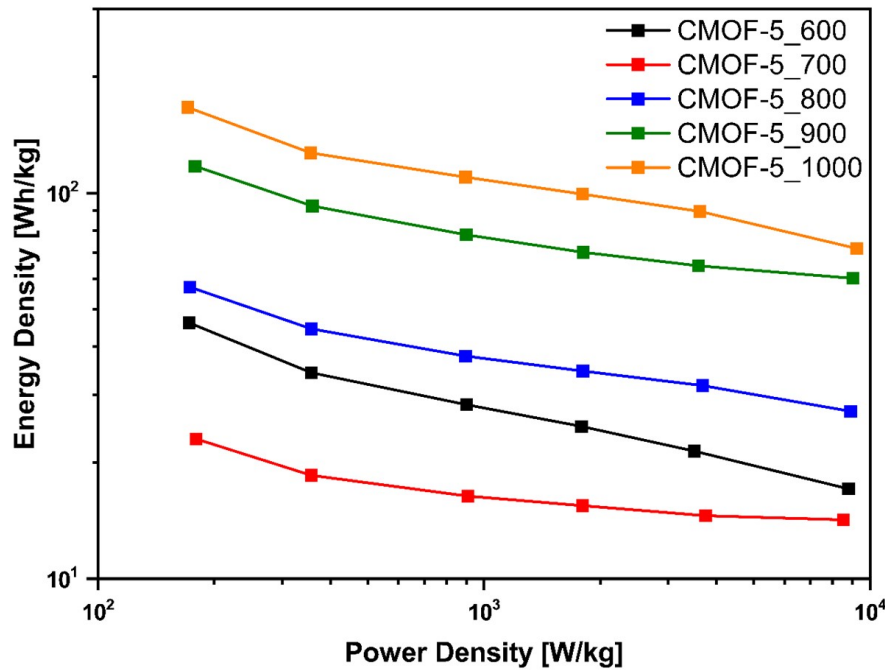
In this circuit model  $R_s$  represents the total internal resistance, which includes the interfacial contact resistance between the material and the current collector, the ohmic resistance of the electrolyte, and the intrinsic resistance of the current collector. It can be determined from the high-frequency region of the Nyquist plot by its intersection with the real axis.  $R_{CT}$ , on the other hand, corresponds to the interfacial charge transfer resistance, which is indicated by the diameter of the semicircle and reflects the resistance associated with electrochemical reactions at the electrode surface. Additionally, the semicircle accounts for a constant phase element (Q) arising from the double-layer capacitance behavior. In the middle-frequency region, the sloped transmission line represents the Warburg element (W), which characterizes the transport and diffusion of electrons and electrolyte ions within the electrode material pores.

As shown in Fig. 4.13(d), the Nyquist plots exhibit a clear evolution in shape from a battery-type response for CMOF-5\_600 and CMOF-5\_700 samples, to a mixed capacitive-battery character for CMOF-5\_800 and CMOF-5\_900, and finally to a nearly ideal capacitive profile for CMOF-5\_1000. Moreover, a significant decrease in the  $R_{CT}$  is observed, dropping from 2437  $\Omega$  for CMOF-5\_600 to just 488.4  $\Omega$  for CMOF-5\_1000. This substantial reduction in  $R_{CT}$  indicates that higher carbonization temperatures enhance the conductivity and optimize the pore structure, allowing more efficient electron

**Table 4.4:** Circuit parameters for the EIS measurements of CMOF-5.

| Sample [°C] | $R_S$ [ $\Omega$ ] | $R_{CT}$ [ $\Omega$ ] |
|-------------|--------------------|-----------------------|
| 600         | 92                 | 2437                  |
| 700         | 13.88              | 1296                  |
| 800         | 47.9               | 767                   |
| 900         | 65.56              | 570.3                 |
| 1000        | 6.738              | 488.4                 |

and ion transport at the electrode–electrolyte interface. The cycle stability of CMOF-5\_X is evaluated at a current density of 1 A/g (Figs. 4.13e-i). While carbonization at 600 °C results in only 52% capacitance retention after 10,000 charge/discharge cycles, all samples carbonized at temperatures above 700 °C retain over 85% of their initial capacitance, highlighting the enhanced chemical stability of the materials [281]. When assessing the potential practical applications of energy storage materials, it is crucial to report power density and energy density.



**Figure 4.15:** Ragone Plot for all CMOF-5 samples.

As shown in the Ragone plot depicted in Fig. 4.15, the CMOF-5\_1000 sample exhibits an impressive maximum energy density of 166.9 Wh/kg and a power density of 9234 W/kg [298, 299]. Additionally, the kinetics of the electrochemical processes occurring at CMOF-5\_X electrodes (Fig. 4.16) further confirm the truly hybrid nature of the active materials. As the carbonization temperature increases from 700 to 1000 °C,

a consistent rise in the diffusion-based contribution can be observed across all the scan rates. This enhancement is attributed to the carboreduction process, which facilitates the removal of surface Zn species, thereby improving the access to internal surfaces and pore channels, as well as enhancing ion diffusion during the charge/discharge cycles. An exception is observed for the CMOF-5\_700 sample, where a reduction in diffusion contribution is likely due to the formation of zinc species that disrupt the framework and block pores, limiting ionic transport, in agreement with the reduced capacitance value. Overall, the diffusion-controlled contribution increases from 55% for CMOF-5\_600 to 70.9% for CMOF-5\_1000 at a scan rate of 1 mV/s, highlighting the positive impact of high-temperature carbonization on charge storage dynamics.

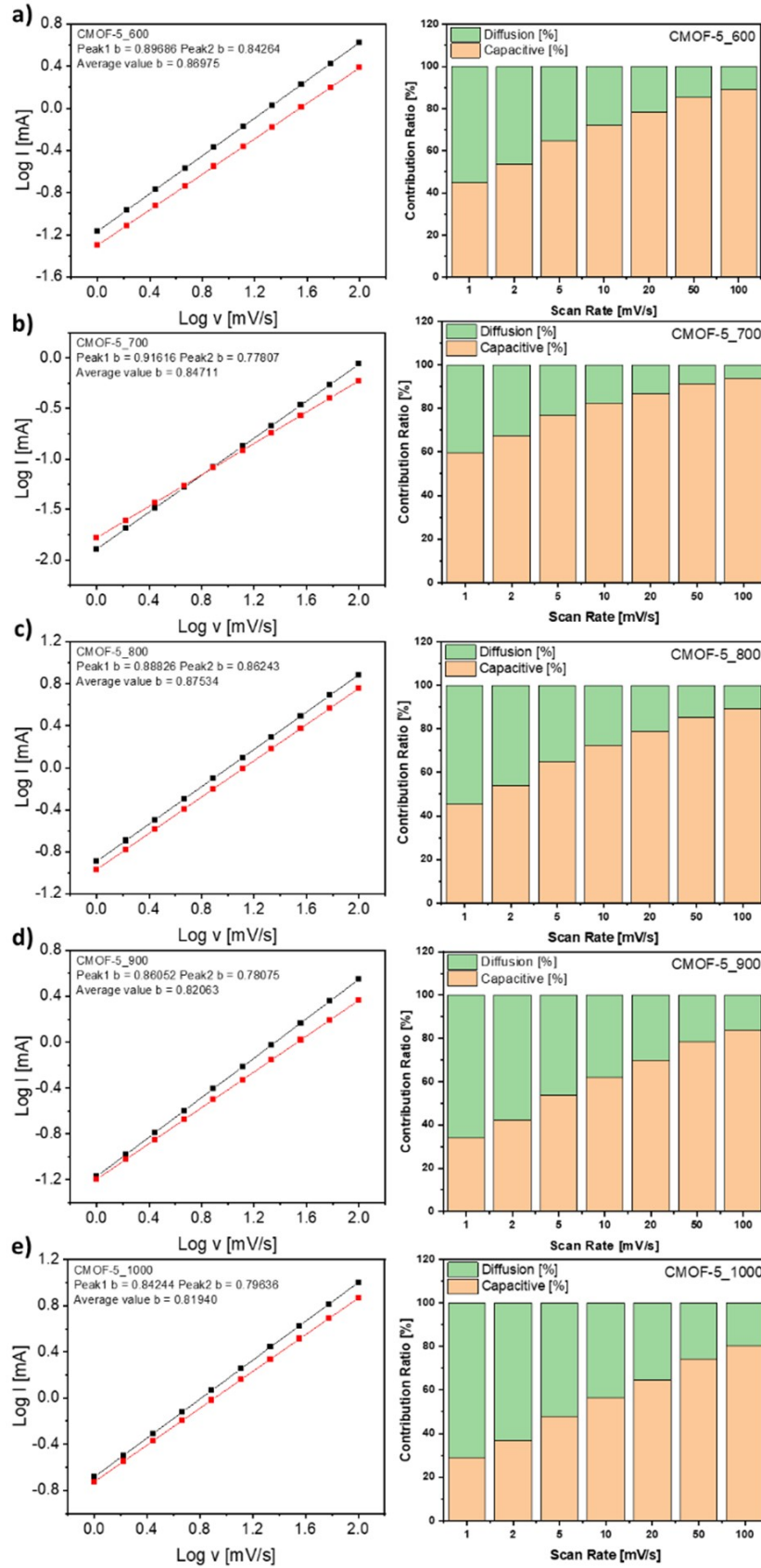
Comparison to previously reported cathode materials are given in Table 4.5.

**Table 4.5:** State of the art of the electrochemical performance of various cathode materials in Zn-ESS.

| Cathode            | Cap./Cap.                      | Rate                    | Cyc. (% , cycles)                     | E/P (Wh/kg, W/kg)                                        | S.A. (m <sup>2</sup> /g) | Ref              |
|--------------------|--------------------------------|-------------------------|---------------------------------------|----------------------------------------------------------|--------------------------|------------------|
| DFs                | 35.1 F/g                       | 0.2 A/g                 | 89.9%, 10000 @ 1 A/g                  | 70.7, 4395                                               | 3068                     | [300]            |
| oCNT               | 53 F/g                         | 10 mV/s                 | 100%, 5000 @ 500 mV/s                 | –, –                                                     | 211                      | [301]            |
| C2NN1-800-1-5      | 296.4 F/g                      | 0.2 A/g                 | 100%, 10000 @ 6 A/g                   | 133.4, 18000                                             | 1256                     | [302]            |
| AC                 | 259.4 F/g                      | 0.05 A/g                | 100%, 10000 @ 1.56 mA/cm <sup>2</sup> | 115.4 $\mu$ Wh/cm <sup>2</sup> , 0.16 mW/cm <sup>2</sup> | 1825                     | [279]            |
| MXene-rGO          | 128.6 F/g                      | 0.4 A/g                 | 95%, 75000 @ 5 A/g                    | 34.9, 2800                                               | –                        | [303]            |
| MPCs-3             | 209 F/g                        | 0.2 A/g                 | 100%, 10000 @ 2 A/g                   | 92.7, 7264                                               | 2807                     | [304]            |
| aMEGO              | 210 F/g                        | 0.1 A/g                 | 93%, 80000 @ 8 A/g                    | 106.3, 31400                                             | 2957                     | [305]            |
| RHC                | 149.8 F/g                      | 0.2 A/g                 | 95.9%, 3005 @ 2 A/g                   | 58.6, 10000                                              | –                        | [306]            |
| MDC                | 123 F/g                        | 0.2 A/g                 | 99%, 20000 @ 1 A/g                    | 7.5, 85000                                               | 270                      | [307]            |
| ZDC                | 341 F/g                        | 0.5 A/g                 | 75%, 20000 @ 1 A/g                    | 121.2, 16000                                             | 551.3                    | [308]            |
| MPC                | 289.2 F/g                      | 0.2 A/g                 | 96.7%, 10000 @ 10 A/g                 | 130.1, 7800                                              | 2125                     | [309]            |
| CMOF-5_600         | 133.51 F/g (20.1 mAh/g)        | 1 mV/s (0.1 A/g)        | 52%, 10000 @ 1 A/g                    | 46.1, 8794                                               | 444                      | this work        |
| CMOF-5_700         | 84.11 F/g (10.7 mAh/g)         | 1 mV/s (0.1 A/g)        | 88%, 10000 @ 1 A/g                    | 23.0, 8532                                               | 405                      | this work        |
| CMOF-5_800         | 121.23 F/g (26.4 mAh/g)        | 1 mV/s (0.1 A/g)        | 83%, 10000 @ 1 A/g                    | 57.1, 8895                                               | 420                      | this work        |
| CMOF-5_900         | 204.4 F/g (54.8 mAh/g)         | 1 mV/s (0.1 A/g)        | 84%, 10000 @ 1 A/g                    | 117.4, 9018                                              | 919                      | this work        |
| <b>CMOF-5_1000</b> | <b>268.93 F/g (73.7 mAh/g)</b> | <b>1 mV/s (0.1 A/g)</b> | <b>88%, 10000 @ 1 A/g</b>             | <b>166.9, 9234</b>                                       | <b>2151</b>              | <b>this work</b> |

*Abbreviations:* DFs – diamond fibers [300], oCNT - oxidized carbon nanotubes [301], C2NN1-800-1-5 - chitin-derived NaCl-templated and NaNO<sub>3</sub>-activated carbon [302], AC – activated carbon [279], MPCs – mesoporous carbons [304], aMEGO - porous carbon derived from chemical activated graphene (reference not provided in the list), RHC – rice husk derived carbon [306], MDC – MOF derived carbon [307], ZDC - ZIF-8 derived N-doped porous carbon [308], MPC - MIL-47 derived porous carbon active material [309].

For Zn-ion ESS, CMOF-5\_1000 delivers a compelling electrochemical performance, with a specific capacitance of 268.93F/g, an energy density of 166.9Wh/kg, and an outstanding power density of 9234W/kg. While some MOF-derived and carbon-based materials report higher energy densities (*e.g.*, VO<sub>0.9</sub>/C: 215Wh/kg), their maximum power densities are significantly lower – typically below 3000W/kg – limiting their rate capabilities. In contrast, CMOF-5\_1000 achieves a remarkable balance of high energy



**Figure 4.16:** Fitting plots between  $\log(i)$  and  $\log(v)$  at various peak currents. Capacitive contribution and diffusion-controlled contribution of all CMOF-5 samples at various scan rates.

and power density, which arises from the combination of material properties optimized through high-temperature carbonization. The high energy density is largely attributed to a dominant diffusion-controlled contribution (70.9%), reflecting faradaic charge storage processes supported by a highly porous structure ( $1.87\text{cm}^3/\text{g}$ ) and large surface area ( $2151\text{m}^2/\text{g}$ ). Meanwhile, the excellent power performance stems from the low charge transfer resistance ( $488.4\Omega$ ) and improved electrical conductivity ( $50.15\text{ S/m}$ ) provided by the graphitized carbon matrix, enabling rapid ion and electron transport. Together with excellent cycling stability (88% retention after 10,000 cycles at  $1\text{ A/g}$ ), this positions CMOF-5\_1000 among the few MOF-derived materials capable of delivering both high energy output and fast charge/discharge performance, making it a strong candidate for high-performance hybrid Zn-ion energy storage devices.

## 4.5 Conclusion

This study demonstrates the critical role of carbonization temperature in tuning the physicochemical and electrochemical properties of MOF-5-derived hybrid materials (CMOF-5\_X) for Zn-ion energy storage systems. By increasing the carbonization temperature from  $600^\circ\text{C}$  to  $1000^\circ\text{C}$ , we achieve substantial improvements in porosity, and electrical characteristics. The CMOF-5\_1000 sample exhibits exceptional characteristics, including a high specific surface area ( $2151\text{m}^2/\text{g}$ ), fully developed porosity ( $1.87\text{cm}^3/\text{g}$ ), excellent electrical conductivity ( $50.15\text{ S/m}$ ) and low charge transfer resistance ( $488.4\Omega$ ). These properties enable a unique combination of high energy density ( $166.9\text{Wh/kg}$ ) and high-power density ( $9234\text{W/kg}$ ), along with a specific capacitance of  $268.93\text{F/g}$  at  $1\text{mV/s}$ —outperforming commercial activated carbon and many previously reported MOF-derived and carbon materials. The dominant diffusion-controlled contribution (70.9%) further supports the enhanced energy storage capability, while 88% capacitance retention after 10,000 cycles at  $1\text{ A/g}$  confirms long-term stability. These results highlight the effectiveness of temperature-tuned carbonization as a scalable strategy for engineering MOF-based electrodes that deliver both high energy output and rapid charge/discharge performance in hybrid Zn-ion energy storage devices.

## Chapter 5

# A Donor–Acceptor Covalent Organic Framework as an Ambipolar Cathode for High-Performance Aluminum-Ion Energy Storage System

Engineering ambipolar redox activity with a pairing of electron-rich and electron-deficient building blocks in a covalent organic framework, in which donor and acceptor units play independent roles in charge storage, is particularly attractive for multi-electron cathode materials in aluminum-ion energy storage systems (Al-ESS). It is an exciting area including aluminum's natural abundance, high theoretical volumetric capacity, and intrinsic safety. The development of Al-ESS, however, is still hampered by the lack of cathode materials that can reversibly and efficiently store aluminum ions [85, 89]. COFs are promising candidates, structurally tunable architectures and redox-active sites with the ability to transfer out multi-electron reactions and fast ion transport [96, 135, 136, 310]. Nevertheless, they have been hindered in their use because they are poorly accessible and have low electronic conductivity. In this chapter a 2D donor–acceptor COF constructed from electron rich tetrakis(4-aminophenyl)-1,4-phenylenediamine (TPA) and electron deficient naphthalenediimide (NDI) used as an ambipolar cathode for rechargeable AIBs is reported. The resulting structure is highly crystallized and has various pores so that no conductive CNTs additives are required to facilitate charge transport. The TPA-NDI COF delivers a specific capacity of 270 mAh g<sup>-1</sup>, a specific energy of 447 Wh kg<sup>-1</sup> and excellent cycling stability, with 99% of its capacity maintained after 5,000 cycles. The combination of ex situ characterization and DFT calculations uncovers a reversible, multi-electron redox pathway that involves amine, imine and carbonyl sites

that coordinatively bind both the cationic and anionic species. The data are combined to form donor–acceptor engineering as a effective design strategy for next-generation COF cathodes for high-performance Al-ESS.

## 5.1 Introduction

With the prevalent use of electronic devices and electric vehicles, ESS that are sustainable, profitable, and economical are becoming more than just a necessity. LIBs have long been the central technology for this application and have been used in high demand applications with energy densities of 100–300 Whkg<sup>−1</sup>. However, lithium resources are limited and expensive, which makes the technology of LIBs difficult to level up in the long term and is a reason to look for alternatives that are more prevalent within the Earth’s crust [311–313]. Al-ESS are one of the most promising options for the future of energy storage. Aluminum has a combination of benefits that make it a unique material, it is the most abundant metal in the earth’s crust, it can be used with the non-flammable ionic liquid electrolytes, it is inherently safe, and it is low in toxicity. It’s theoretical volumetric capacity of 8,056 mAhcm<sup>−3</sup> is larger than that of lithium (3,860 mAhcm<sup>−3</sup>), suggesting that if it can be shown to overcome the materials problems. Al-ESS holds the potential to deliver volumetric energy densities nearly twice that of conventional LIBs, provided that suitable cathode materials with electrochemical compatibility are identified and developed [82–84, 92]. The cathode is the main drawback of Al-ESS and although aluminum metal proved to be a reliable anode, it is the electrode that will be the primary challenge in the performance of Al-ESS [85, 89]. Initial studies were on positive electrodes based on graphite, which have relatively good cycling stability, but only allow the storage of charge by intercalation and deintercalation of AlCl<sub>4</sub><sup>−</sup> anions. The mechanism is intrinsically limited by the availability of electrolytes and leads to limited energy densities that are not practical. The potential of organic electrode materials is more promising. Organic materials can host a variety of the Aluminum ion species, such as Al<sup>3+</sup>, AlCl<sup>2+</sup>, AlCl<sub>2</sub><sup>+</sup>, AlCl<sub>4</sub><sup>−</sup>, and Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup>, by coordination interaction, which allows for a much higher charge storage capacity and enhanced overall efficiency in comparison to graphite [96, 314]. COFs are particularly known for their excellent chemical and electrochemical stability amongst various types of organic electrode candidates [135, 136, 310, 315]. They have long, porous structures that are resistant to dissolution in electrolytes, ensuring long-lasting durability and promoting effective transport. More significantly, the flexibility that is inherent to the COF synthesis provides the ability to incorporate redox active monomers that can undergo multielectron,

multistep reactions, which is critical for achieving the high capacity. The inherent low electronic conductivity of most COFs, however, requires the addition of conductive CNTs, which makes device fabrication more complex and reduces the contribution of active material. A promising approach to overcome these limitations is based on ambipolar COFs in which both units are simultaneously electron-donating (p-type) and electron-accepting (n-type). When the donor sites are oxidized during charging, they gain a positive charge and can bind to the negative charged electrolyte species. At the time of discharge, acceptor sites are reduced (gain an electron) and become negatively charged and interact with cationic species. This dual-ion storage mechanism effectively balances charge, increases storage capacity and improves energy density. Furthermore, the  $\pi$ -conjugated backbone of the donor–acceptor COFs contributes to the intrinsic electronic conductivity and charge transfer, and tight spatial proximity of the donor/acceptor sites facilitates charge-carrier hopping and minimizes charge-transfer resistance. There are several studies that have shown the potential of this approach. A symmetric supercapacitor is constructed using a TTF–DAQ ambipolar COF, that was reported to show a specific capacitance of  $752 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  with 90% capacitance retention after 10,000 cycles [316]. Chatterjee et al. also demonstrated a 30% enhancement in the specific capacitance when pairing a TTF with a porphyrin acceptor as compared to a TTF–phenylene diamine analog [316]. Specifically, in Al-ESS, the 2D-NT-COF containing p-type triazine and n-type NDI monomers provided specific capacity of  $\sim 70 \text{ mAh g}^{-1}$  which further increased to  $132 \text{ mAh g}^{-1}$  with 30 wt% CNTs, retaining capacities of  $>97\%$  after 4,000 cycles [317]. Likewise, Peng et al. reported that the capacity of 2,4,6-trimethoxy-benzene-1,3,5-tricarbaldehyde (TpOMe–DAQ) ambipolar COF can be increased by 14% by introducing CNTs [184,318]. Regardless of all these advances, only a few ambipolar COFs have been tested for Al-ESS and the addition of CNTs is a near universal requirement, thus representing an important design gap.

To surmount this, here we report a 2D donor–acceptor COF based on the electron-rich monomer tetrakis(4-aminophenyl)-1,4-phenylenediamine (TPA) and the electron deficient naphthalenediimide dialdehyde (NDI) linked by imine bond to create a highly planar  $\pi$ -conjugated framework with strong intramolecular charge-transfer character. The redox property of the TPA donor and NDI acceptor extends potential window and enhances the cycling stability of the material when used as a cathode in Al-ESS. The resulting COF is highly crystalline with well-defined porosity and a large surface area giving an unprecedented specific capacity of  $270 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  and a capacity retention of  $> 99\%$  after 5,000 cycles at  $5 \text{ A g}^{-1}$ . Importantly, TPA-NDI COF is achieved without any CNT additives, and so is one of the few high-performing COF cathodes



reported so far that can realize the conductivity increase usually provided by the external additives by rational donor–acceptor engineering. Hierarchical ambipolar COF design is identified as a powerful pattern for next-generation organic cathodes and clearly provides a guiding principle for targeted development of organic materials for efficient, sustainable energy storage.

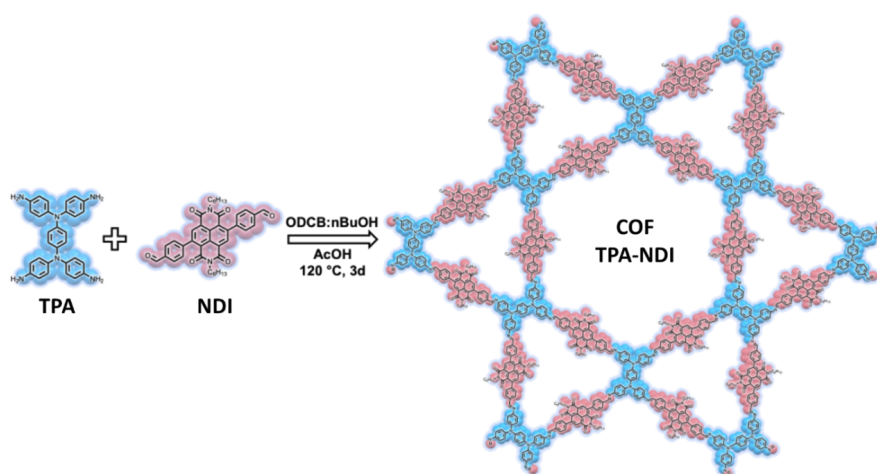
## 5.2 Experimental Section

All commercially available reagents and solvents used as received without further purification were purchased from Merck and BLD Pharm. Aluminum foil, stainless steel and tungsten rods were purchased by AEM metal company.

### 5.2.1 Synthesis of NDI dialdehyde

This compound was synthesized according to a modified literature procedure [319].

### 5.2.2 Synthesis of COF TPA-NDI



**Figure 5.1:** Synthetic illustration for COF TPA-NDI.

The COF TPA-NDI synthesis involves an imine condensation reaction between the organic monomers TPA and NDI illustrated in Figure 5.1. In a high-pressure vessel, NDI dialdehyde (0.173 mol, 112 mg) and TPA (0.087 mol, 41 mg) were dissolved in 5.2 mL of 1,2-dichlorobenzene and 5.2 mL of n-butanol and sonicated for 20 minutes. To the reaction mixture, 1.32 mL of acetic acid 6 M was added and degassed through freeze-pump-thaw (3 x 15 minutes). The reaction mixture was heated at 120 °C for 3 days. The reaction crude was collected by filtration, washed with DMF (20 mL), THF

(20 mL) and purified via Soxhlet extraction with THF for 24 hours. After drying for 16 hours in a vacuum oven at 60 °C, the COF product was in a black powder form in 46% yield.

### 5.2.3 Preparation of Electrode material

The cathodes were prepared as COF TPA-NDI (70 wt%, 21 mg) was combined with carbon black (20 wt%, 6 mg) and PTFE (10 wt%, 3 mg) in an agate mortar, using a few drops of NMP to create a uniform paste. The resulting slurry was then applied onto a carbon cloth electrode with a diameter of 0.8 cm and dried under vacuum at 80°C. The mass loading of COF TPA-NDI on each electrode was approximately 1 mg cm<sup>-2</sup>.

### 5.2.4 Morphological and Structural characterizations

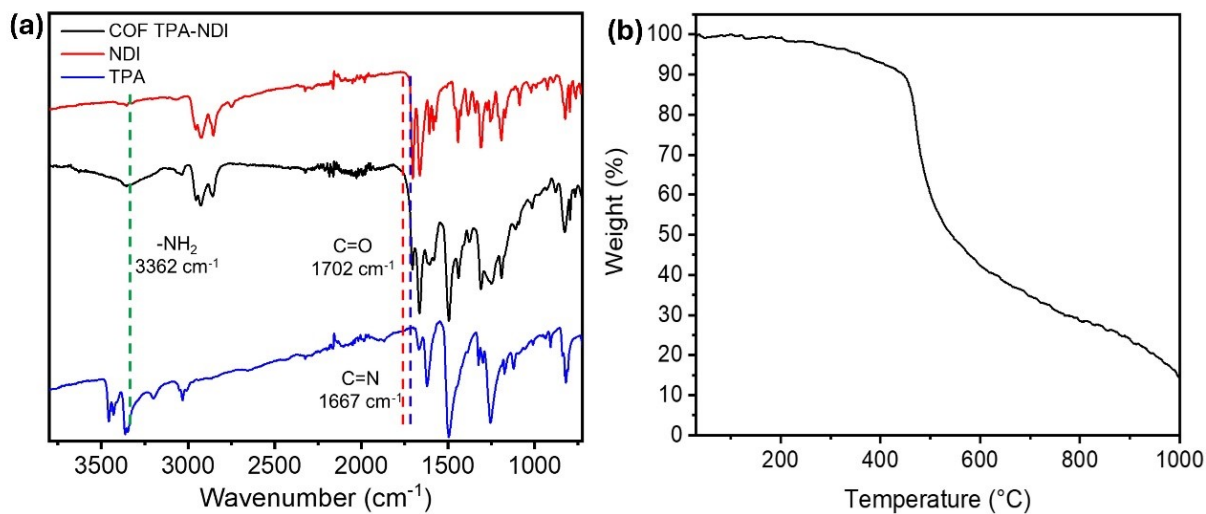
The composition, structure, and texture properties of materials were investigated by powder XRD patterns, TGA, XPS, TEM, SEM images and Energy-dispersive X-ray spectroscopy (EDX), Solid state nuclear magnetic resonance <sup>13</sup>C NMR spectra, Infrared spectra (IR) spectra with FTIR spectrometer in ATR mode, Solid-state ultraviolet-visible (UV-Vis) diffuse reflectance spectra. The optical band gap was determined from the corresponding Tauc plot obtained from the diffuse reflectance data.

## 5.3 Results and Discussion

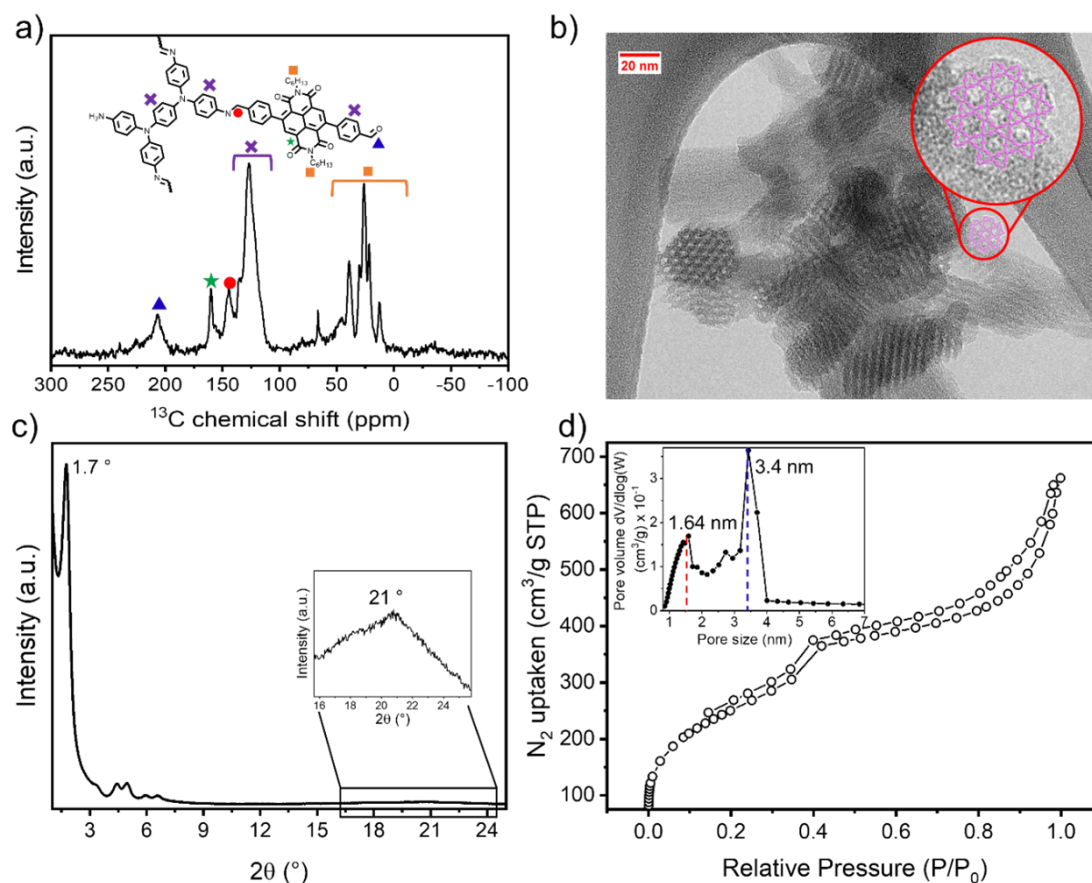
The successful formation of COF TPA-NDI is confirmed by the presence of imine bonds, as evidenced by solid-state <sup>13</sup>C cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) and attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopies shown in Figure 5.2(a) and Figure 5.3(a).

The ATR-FTIR spectrum of COF TPA-NDI reveals the expected imine stretching vibration at 1667 cm<sup>-1</sup> (Figure 5.2). Importantly, the minimal intensity of the NH<sub>2</sub> vibrational stretching peaks attribute to 3362 cm<sup>-1</sup> and the aldehyde C=O is 1702 cm<sup>-1</sup> provides strong evidence for complete COF formation. Further proof of imine bond formation is provided by the <sup>13</sup>C CP-MAS NMR spectrum, which displays a distinct signal at 144 ppm attributable to the <sup>13</sup>C of imine carbon, while the <sup>13</sup>C signals of aromatic moieties appear in the 137-112 ppm range in Figure 5.3(a).

The negligible presence of unreacted aldehyde <sup>13</sup>CHO subunits is indicated by a small peak at 207 ppm, and the peak at 160 ppm is attributed to the imide moiety from NDI repeating units [320, 321]. TGA of COF TPA-NDI shown in Figure 5.2(b)



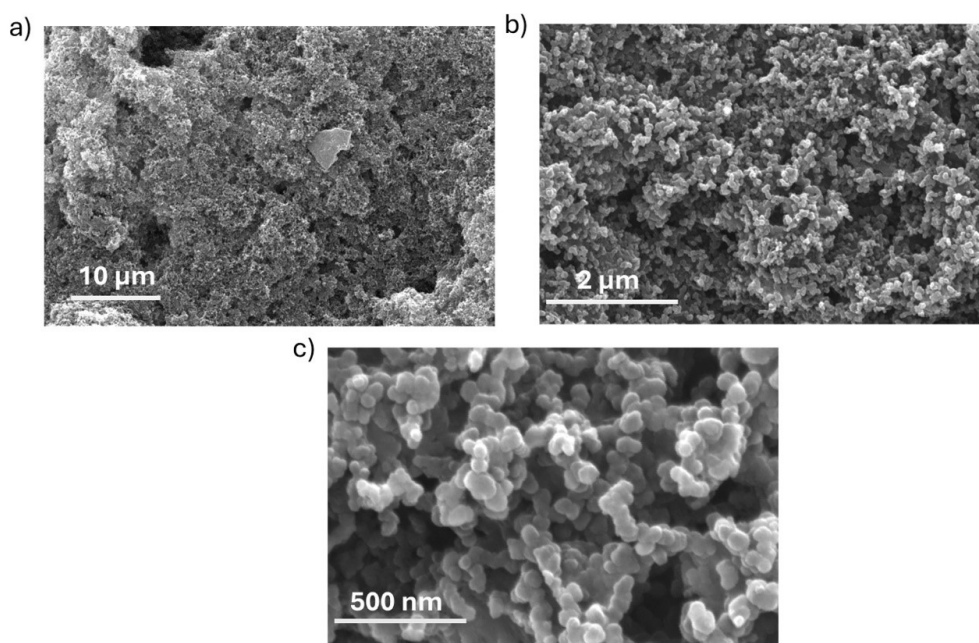
**Figure 5.2:** (a) ATR-FTIR spectrum of COF TPA-NDI, NDI and TPA, (b) TGA analysis of COF TPA-NDI.



**Figure 5.3:** (a)  $^{13}\text{C}$  CP-MAS NMR; (b) HRTEM; (c) PXRD (inset corresponds to a magnification of the region between  $16^{\circ}$ – $25^{\circ}$ ) and (d) nitrogen adsorption/desorption measurements and pore size distribution of COF TPA-NDI.

shows remarkable thermal stability, with values  $T_{d10}$  thermal decomposition of 10% weight of approximately 430 °C. Noteworthy, the main thermal decomposition of COFs occurs above 500 °C, corresponding to the rupture of the imine bonds and subsequent decomposition into oligomers and combustion products.

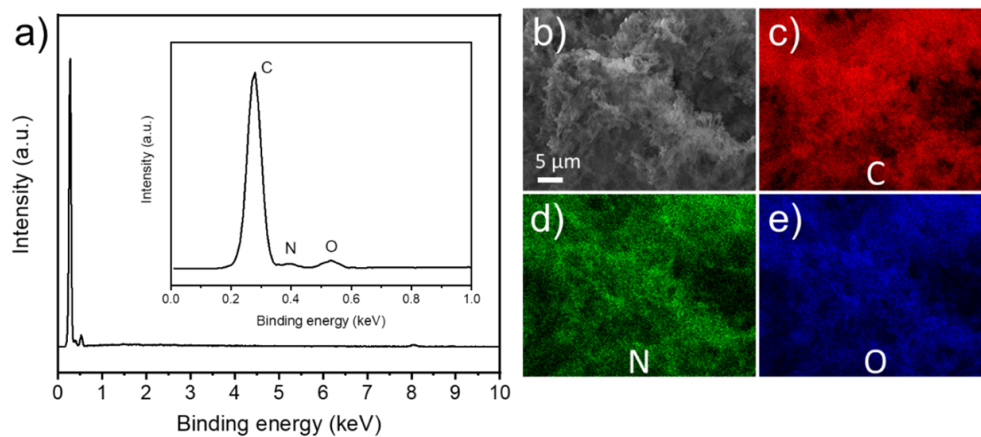
Scanning electron microscopy (SEM) images along Energy dispersive X-ray spectroscopy (EDX) mappings of COF TPA-NDI shown in Figures 5.4 and 5.5. SEM images of COF TPA-NDI show spherical particles with diameters of ~50-80 nm. EDX mapping confirms the homogeneous distribution of carbon, nitrogen and oxygen throughout the COF TPA-NDI structure.



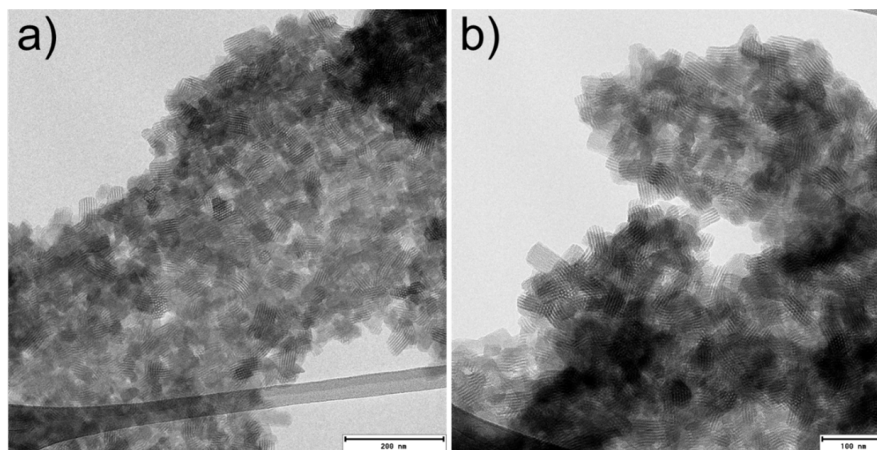
**Figure 5.4:** SEM images of COF TPA-NDI at different magnifications.

High-resolution transmission electron microscopy (HRTEM) images (Figures 5.3b, 5.6) of COF TPA-NDI reveal a nanotube morphology with a highly ordered periodic structure and pores around 5 nm in diameter. Particularly, Figure 5.3b shows some nanotubes oriented perpendicularly to the carbon film of the TEM grid, allowing estimation of an average domain size ~40 nm, while Figures 5.6(a) and 5.6(b) display nanotubes parallel to the grid with an average length of ~100 nm.

Powder X-ray diffraction (PXRD) analysis provides insights into the crystalline structure and ordering of the material. Specifically, COF TPA-NDI shows a high crystalline pattern with a sharp (1 0 0) peak at 1.7° and a peak at 21.0° related to the interlayer spacing of 0.42 nm. Moreover, other minor peaks at 3.4°, 4.4°, 4.9°, 6.0°, 6.6° can be observed in Figure 5.3(c). To shed further light on the structure of COF TPA-NDI, N<sub>2</sub> adsorption-desorption measurements are performed (Figure 5.3d). Pore



**Figure 5.5:** (a) EDX spectrum of COF TPA-NDI (inset represents the magnification of 0-1 keV region); (b) SEM image of COF TPA-NDI, (c-e) EDX mapping of element distribution in COF TPA-NDI: (c) carbon, (d) nitrogen, and (e) oxygen.



**Figure 5.6:** (a-b) HRTEM images of COF TPA-NDI at different magnifications.

size distribution analysis indicates that COF TPA-NDI is predominantly organized in the eclipsed AA-stacking mode. Specifically, the microporous nature of the COF is evidenced by the sharp increase in gas uptake at low-pressure ( $P/P_0 = 0-0.99$ ). The Horvath-Kawazoe method for micropore analysis (inset of Figure 5.3d) reveals two distinct micropores, measuring 1.6 and 3.4 nm. Additionally, the Brunauer-Emmett-Teller (BET) surface area, determined from  $N_2$  adsorption-desorption isotherms at 77 K (Figure 5.3d) is  $924 \text{ m}^2/\text{g}$ . The total pore volume for pores smaller than  $1128 \text{ \AA}$  evaluated at  $P/P_0 = 0.98$  amounts to  $1.02 \text{ cm}^3/\text{g}$ , highlighting the high porosity and well-defined structural organization of the COF.

### 5.3.1 PXRD Structural Simulations (DFT)

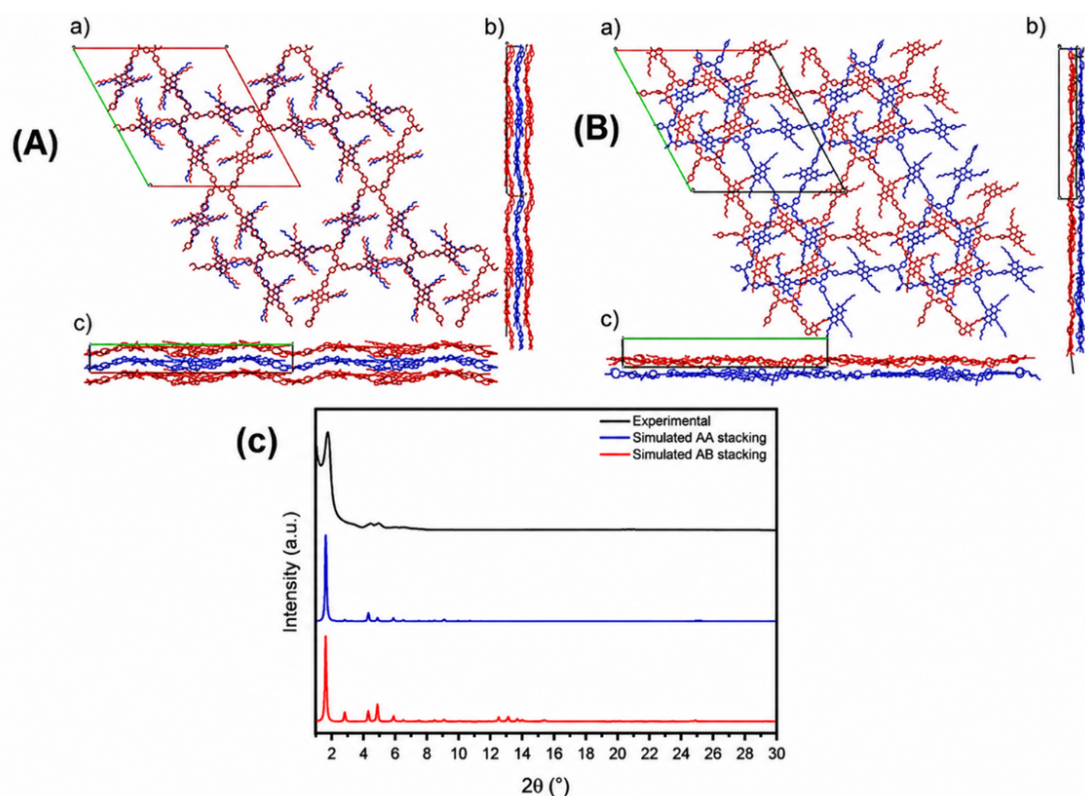
To investigate the crystal lattice arrangement of the COF, we simulate the PXRD pattern by using the density functional theory (DFT) calculated polymeric structure of COF with Kagome topology and unit parameters calculated are shown in Figure 5.7 and Table 5.1 respectively.

**Table 5.1:** Unit cell parameters of calculated COF TPA-NDI.

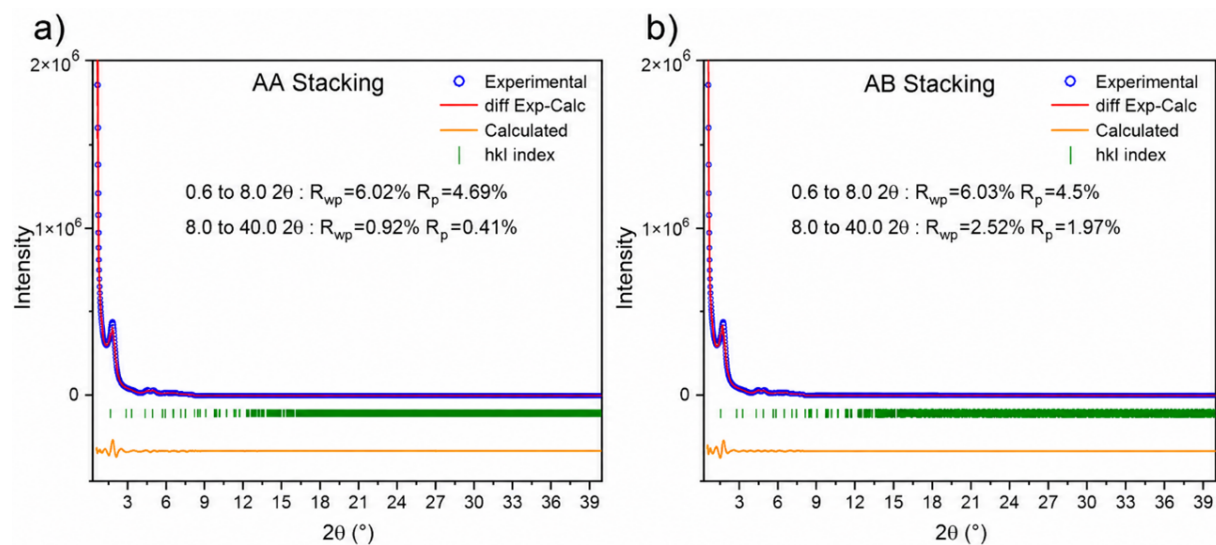
| Monolayer                                | Eclipsed (AA)                            | Staggered (AB)                           |
|------------------------------------------|------------------------------------------|------------------------------------------|
| $C_{330} H_{288} N_{30} O_{24}$          | $C_{660} H_{576} N_{60} O_{48}$          | $C_{660} H_{576} N_{60} O_{48}$          |
| $a = 62.517 \text{ \AA}, = 89.584^\circ$ | $a = 62.517 \text{ \AA}, = 89.580^\circ$ | $a = 62.517 \text{ \AA}, = 89.580^\circ$ |
| $b = 62.835 \text{ \AA}, = 90.041^\circ$ | $b = 62.835 \text{ \AA}, = 90.040^\circ$ | $b = 62.835 \text{ \AA}, = 90.040^\circ$ |
| $c = 20.000 \text{ \AA}, = 60.273^\circ$ | $c = 7.180 \text{ \AA}, = 60.270^\circ$  | $c = 7.180 \text{ \AA}, = 60.270^\circ$  |
| $V = 68222.4 \text{ \AA}^3$              | $V = 24491.4 \text{ \AA}^3$              | $V = 24354.9 \text{ \AA}^3$              |
|                                          | $d = 0.357 \text{ nm}$                   | $d = 0.36 \text{ nm}$                    |

Pawley refinement of AA- and AB-stacking models was also performed against the experimental PXRD data from  $0.6$  to  $8 \text{ } 2\theta$  and from  $8$  to  $40 \text{ } 2\theta$ . The  $R_{wp}$  and  $R_p$  values are very similar for both models (AA:  $R_{wp} = 6.02\%$ ,  $R_p = 4.69\%$  in  $0.6$  to  $8 \text{ } 2\theta$  range; AA:  $R_{wp} = 0.92\%$ ,  $R_p = 0.41\%$  in  $8$  to  $40 \text{ } 2\theta$  range; AB:  $R_{wp} = 6.03\%$ ,  $R_p = 4.50\%$   $0.6$  to  $8 \text{ } 2\theta$  range; AB:  $R_{wp} = 2.52\%$ ,  $R_p = 1.97\%$  in  $8$  to  $40 \text{ } 2\theta$  range), indicating that both AA- and AB-stacking well fit the experimental pattern shown in Figure 5.8 [322, 323]. In the light of this, it is not possible to unambiguously distinguish between AA and AB stacking due to their very similar diffraction features and comparable refinement quality.





**Figure 5.7:** A) Simulated XRD structure of COF TPA-NDI. a) view of AA symmetry along c; b) view of AA symmetry along b; c) view of AA symmetry along a. B) Simulated XRD structure of COF TPA-NDI. a) view of AB symmetry along c; b) view of AB symmetry along b; c) view of AB symmetry along a, C) Experimental (black line), simulated AA stacking (blue line) and simulated AB stacking (red line) PXRD diffractograms of COF TPA-NDI.



**Figure 5.8:** The experimental powder XRD pattern and their Pawley refinement for AA-stacking (a) and AB-stacking (b).

## 5.4 Electrochemical Characterizations

The electrochemical performance of COF TPA-NDI electrodes was evaluated using CV and GCD at various scan rates and current densities respectively. EIS data were collected at 0.01 Hz to 1 MHz. Two-electrode Swagelok cells with a tungsten rod were assembled inside a glove box to evaluate the electrochemical performance of the Al-ESS. A circular cathode electrode was layered with a glass fiber separator (Merck) and an aluminum foil anode, followed by the addition of  $\text{AlCl}_3$ /[EMIM]Cl (ratio 1.3) as the electrolyte. A steel spacer and spring were then added before sealing the cell for electrochemical measurements.

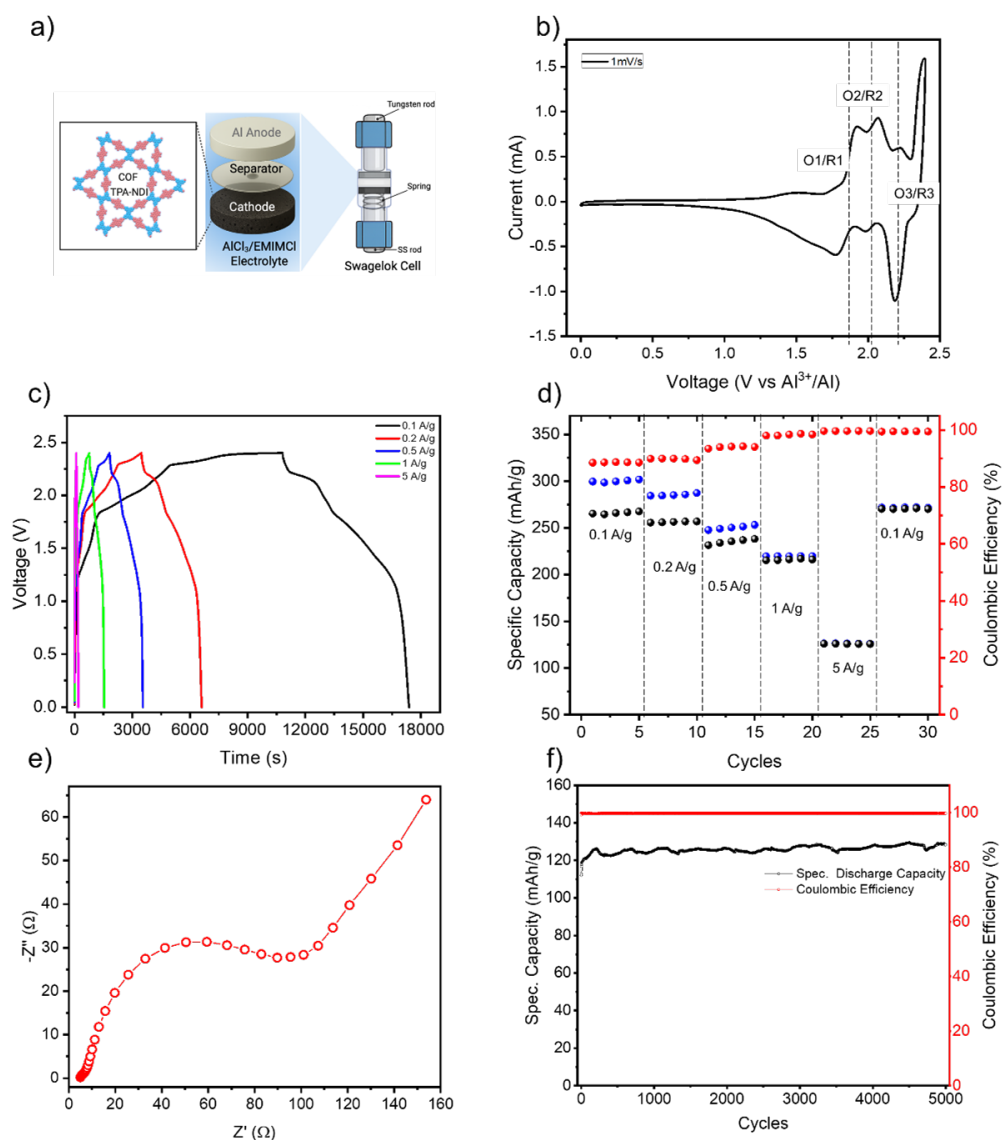
### 5.4.1 Results and Discussion

The electrochemical performance of COF TPA-NDI is evaluated in a Swagelok-type cell, (Figure 5.9(a)) using the COF material as cathode, aluminum metal foil as anode, and ionic liquid ( $\text{AlCl}_3$ /EMIMCl) as electrolyte. Figure 5.9(b) displays the cyclic voltammetry (CV) curve at 1 mV/s of COF TPA-NDI within a voltage window of 0–2.4 V. The CV curve exhibits three distinct redox peaks, with half-peak potentials at 1.83 V, 2.02 V, and 2.21 V, corresponding to O1/R1, O2/R2, and O3/R3, respectively.

The presence of these multiple redox peaks confirms a multi-step Faradaic process, indicating reversible redox reactions occurring at the active sites of the COF. However, in the voltage range of 0 to 1.5 V, the CV curve also displays a quasi-rectangular capacitive region, characteristic of non-Faradaic charge storage via electric double-layer capacitance. This indicates that COF TPA-NDI does not function purely as a battery-type or supercapacitor-type material, but rather as a hybrid energy storage system, where both redox reactions and capacitive charge storage contribute to the overall electrochemical performance [324, 325]. The GCD profiles at various current densities are shown in Figure 5.9(c) further support this hybrid behavior. Unlike pure battery-type materials, which exhibit well-defined plateaus, or supercapacitor-type materials, which show linear profiles, the charge-discharge curves of COF TPA-NDI display non-linear voltage profiles. This indicates the coexistence of Faradaic redox reactions and capacitive charge storage mechanisms.

The electrochemical performance of COF TPA-NDI, expressed as specific capacity, is determined from the GCD profiles recorded at different current densities (Figures 5.9(c, d)). COF TPA-NDI exhibits a high specific capacity, 267, 256, 238, 209 and 125 mAh/g at a current density of 0.1, 0.2, 0.5, 1 and 5 A/g, respectively. The theoretical capacity ( $C_t$ ) of COF TPA-NDI was estimated based on Faraday's law according to





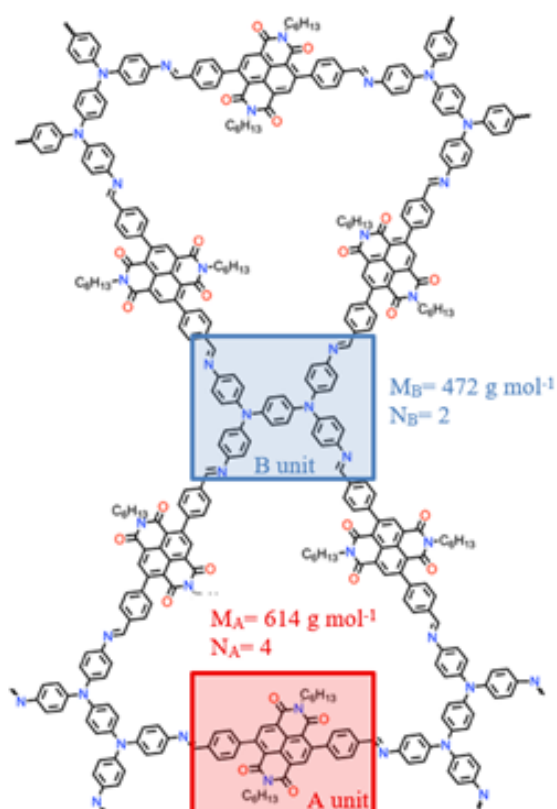
**Figure 5.9:** (a) Scheme of COF TPA-NDI || EMImCl/AlCl<sub>3</sub> || Al energy storage system; (b) CV curve at 1 mV/s; (c) GCD profiles at various current densities; (d) specific charge capacity (blue points), specific discharge capacity (black points) and coulombic efficiency (red points) at various current densities; (e) Nyquist plot; (f) long-term cycling performance of COF TPA-NDI as cathode in Al-ESS at current density 5 A/g.

Equation 5.1.

$$C_t = \frac{nF}{3600 \times (\frac{M_w}{1000})} \quad (5.1)$$

where  $F$  is the Faraday constant ( $96\,485\text{ C mol}^{-1}$ ),  $n$  is the number of electrons transferred per repeating unit of TPA-NDI, and  $M_w$  is the molecular weight of the repeating unit ( $\text{g mol}^{-1}$ ). As illustrated in figure 5.10, the framework is constructed from TPA (A unit) and NDI (B unit) building blocks. The molecular weight of the active unit  $M_A=614\text{ g mol}^{-1}$  and  $M_B= 472\text{ g mol}^{-1}$ . The repeating unit in TPA-NDI consists of 1/2 of a unit A and 1/4 of a B unit. Therefore, the molecular weight of the repeating unit in TPA-NDI is estimated to be  $M_w= 1/2 * 614 + 1/4 * 472 = 425\text{ g mol}^{-1}$ . The number of electrons associated with the redox reaction of unit A and B is 4 ( $N_A$ ) and 2 ( $N_B$ ) respectively. Thus, the number of electrons ( $n$ ) involved in each repeating unit of NDI-TPA is  $1/2 * 4 + 1/4 * 2 = 2.5$ . By applying above mentioned equation, the theoretical specific capacity of NDI-TPA is  $= 96485 * 2.5 / (3600 * 425/1000) = 157\text{ mAh g}^{-1}$ . The calculation methodology follows previously reported approaches for COF-based electrode materials [326, 327]. The experimentally achieved capacity of  $267\text{ mAh/g}$  exceeds the theoretical Faradaic maximum of  $157\text{ mAh/g}$  calculated by equation 5.1 and exceeds that of several state-of-the-art COF-based cathodes for Al-ESS (given in Figure 5.10, Table 5.2).

This result is fully consistent with and provides strong supporting evidence for the hybrid charge-storage mechanism established by our kinetics analysis. For instance, Zn-TABQ delivers  $198\text{ mAh/g}$  at  $0.05\text{ A/g}$  [328], while 2D-NT-COF and DAQ-TpO COF reach  $132\text{ mAh/g}$  [317] and  $134.6\text{ mAh/g}$  [184, 318], respectively. Even the CNT-containing DAQ-TpO COF-CNT composite achieves  $242.2\text{ mAh/g}$  at  $0.2\text{ A/g}$  [184], highlighting COF TPA-NDI as one of the highest-performing materials in terms of specific capacity. A major advantage of COF TPA-NDI is its ambipolar donor-acceptor design, which enhances intrinsic conductivity and charge transport efficiency. COF TPA-NDI exhibits excellent rate capability, as demonstrated in Figure 5.9 (d). Even at a high current density of  $5\text{ A/g}$ , the material retains a specific capacity of  $125\text{ mAh/g}$ , highlighting its ability to sustain efficient charge storage under fast charge-discharge conditions. Furthermore, when the current density returns to  $0.1\text{ A/g}$ , the specific capacity is almost fully recovered, indicating high reversibility and structural stability. The ability of COF TPA-NDI to retain its capacity across a wide range of current densities without relying on CNT additives underscores its intrinsic charge transport and robust ambipolar charge storage mechanism. This outstanding rate performance makes COF TPA-NDI a highly competitive cathode material for Al-ESS. In addition,

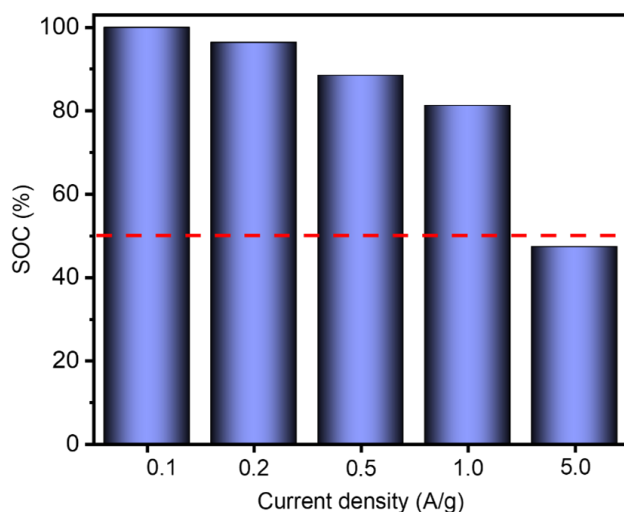


**Figure 5.10:** Chemical structure of NDI-TPA COF based on NDI and TPA redox-active units with their corresponding molecular weight and number of electrons transferred in redox reactions.

the state-of-charge (SOC) is calculated by equation 5.2.

$$SOC(J) = \frac{C_J}{C_{0.1}} \times 100\% \quad (5.2)$$

Where  $C_J$  is the discharge capacity at a given current density  $J$  and  $C_{0.1}$  is the discharge capacity at 0.1 A/g.

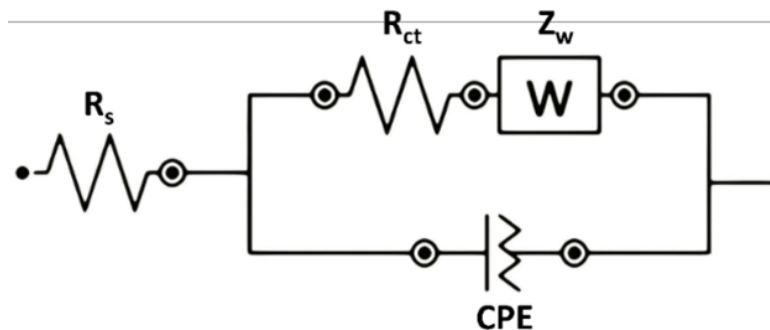


**Figure 5.11:** SOC retention of the COF TPA-NDI electrode as a function of current density.

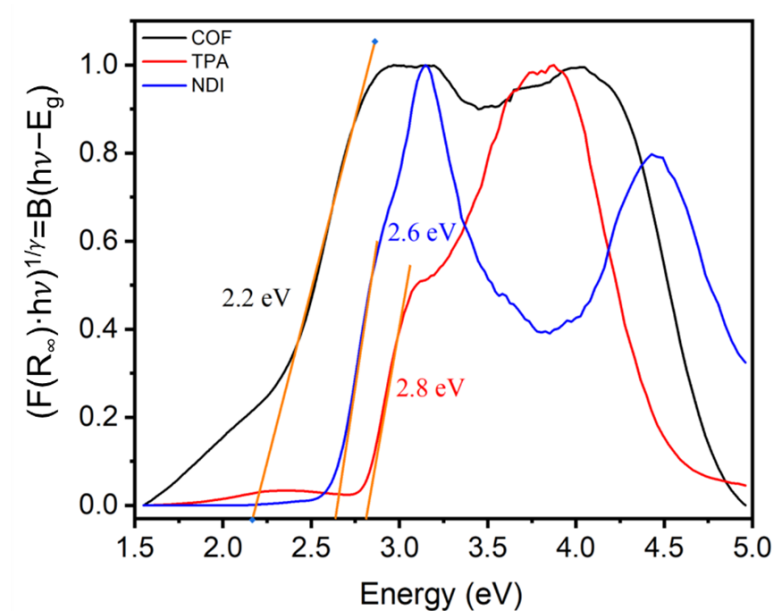
SOC retention as a function of current density demonstrates that a substantial fraction of the capacity remains accessible at high rates, with  $\sim 81\%$  retained at 1 A/g and  $\sim 47\%$  at 5 A/g relative to 0.1 A/g (Figure 5.11). This behavior indicates that charge storage remains largely kinetically accessible even under fast charge-discharge conditions, consistent with efficient electron and ion transport within the framework. The Nyquist plot in Figure 5.9(e) illustrates the EIS response of COF TPA-NDI, providing insights into its charge transport and ion diffusion properties. The experimental result is well fitted with the indicated circuit (Figure 5.12).

COF TPA-NDI exhibits a low charge transfer resistance ( $R_{ct}$ ) ( $96.5 \Omega$ ), indicating efficient interfacial charge transfer (electrons or ions) between the electrode's surface and the electrolyte or the external circuit. This superior charge transport efficiency can be directly correlated to the highly crystalline structure and well-ordered porosity of COF TPA-NDI. To further support the presence of intramolecular charge transfer and band gap narrowing in the donor-acceptor framework, the optical properties of the COF are investigated in the solid state.

The resulting optical band gap, derived from Tauc analysis of the diffuse reflectance data, is significantly reduced (2.2 eV) compared to those of the individual monomers (2.8 eV for TPA and 2.6 eV for NDI), confirming enhanced electronic delocalization

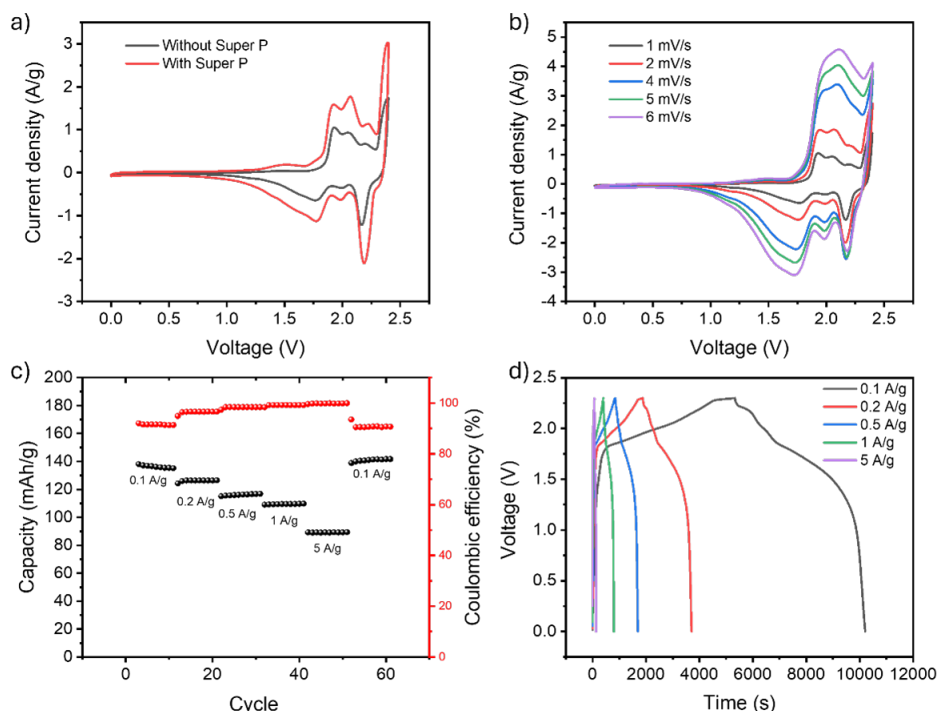


**Figure 5.12:** The equivalent electric circuit models used for fitting the Nyquist plot.



**Figure 5.13:** Tauc plot for NDI, TPA and COF TPA-NDI.

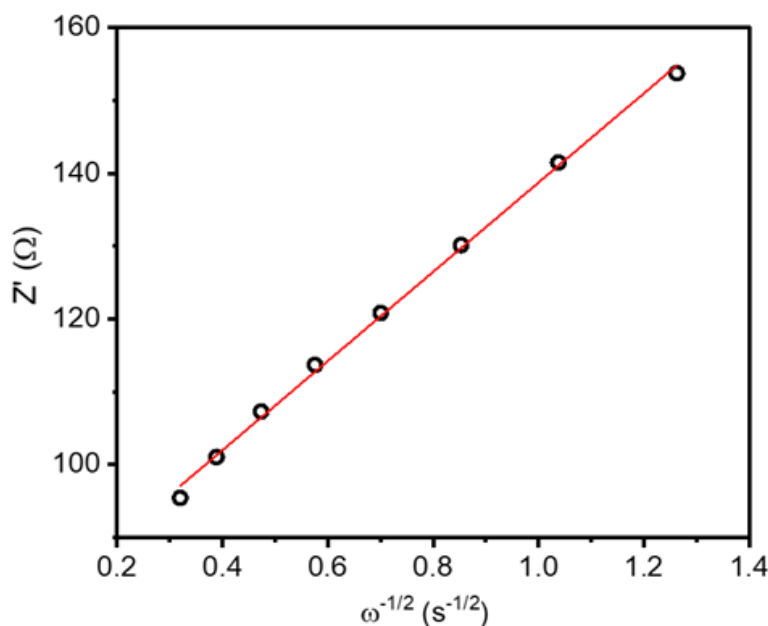
and intramolecular charge transfer within the framework (Figure 5.13). Because of the wide bandgap (2.2 eV), bulk DC conductivity could not be quantified by conventional 4-probe or 2-terminal methods, consistent with the insulating character of the pristine material under dark conditions. Instead, effective charge transport is validated at the device level through electrochemical performance metrics. To further assess the intrinsic conductivity of the COF, electrodes are also prepared without any conductive carbon additive (i.e., without Super P) shown in Figure 5.14.



**Figure 5.14:** Electrochemical performance comparison of COF TPA-NDI electrodes with and without conductive carbon additive (Super P). (a) CV profiles at 1 mV/s for electrodes with Super P (red curve) and without Super P (black curve). (b) CV profiles recorded at different scan rates, (c) rate capability and corresponding coulombic efficiency at increasing current densities and (d) GCD profiles at different current densities of COF TPA-NDI electrodes without conductive carbon additive (Super P).

While a decrease in capacity is observed (from  $\sim 260$  to  $\sim 140$  mAh/g at 0.1 A/g), the material retains significant electrochemical activity. The cyclic voltammetry profiles remain well-defined and preserve their characteristic redox features, although with reduced current response and slightly increased polarization compared to electrodes containing Super P. This indicates that the COF itself supports intrinsic charge transport, while conductive carbon primarily improves electrode-level percolation, reduces polarization, and enhances overall utilization of active material. These results confirm that long-range conductive scaffolds such as CNTs are not required for efficient operation.

The eclipsed AA-stacking mode, as confirmed by PXRD and  $N_2$  adsorption-desorption analyses, facilitates the formation of aligned  $\pi$ -conjugated pathways, which promote fast electron mobility across the framework. Simultaneously, the high surface area and interconnected micropores provide well-defined ion transport channels, ensuring efficient electrolyte ion diffusion. The Al ions diffusion coefficient ( $D_{Al}$ ), obtained from the Warburg impedance in the low-frequency region of the Nyquist plot in Figure 5.15 is estimated to be  $2.36 \cdot 10^{-12} \text{ cm}^2/\text{s}$  for COF TPA-NDI.



**Figure 5.15:** Corresponding linear relation between  $\omega^{-1/2}$  and  $Z''$  in the low frequency region of the Nyquist plot of COF TPA-NDI.

The high  $D_{Al}$  value confirms that the porous architecture and intrinsic ionic conductivity of COF TPA-NDI enable rapid Al ions transport kinetics, further reinforcing its suitability as a high-performance cathode material for Al-ESS.

The cyclability test of COF TPA-NDI, shown in Figure 5.9(f), demonstrates its exceptional long-term electrochemical stability under high-rate charge-discharge conditions. Over 5,000 charge-discharge cycles at 5 A/g, the material exhibits an ultralow capacity decay of only  $\sim 0.9\%$ , highlighting its robust structural integrity and efficient charge storage mechanism. Notably, the initial slight increase in capacity observed during the first cycles is likely due to an activation process, where the electrolyte gradually infiltrates the porous COF structure, optimizing ion accessibility and charge storage efficiency. Additionally, the battery device maintains an exceptionally high coulombic efficiency of 99.7%, indicating minimal side reactions and excellent reversibility throughout the prolonged cycling process. The superior charge-storage capability and

electrochemical stability of COF TPA-NDI can be directly attributed to its extended  $\pi$ -conjugation system, which facilitates efficient charge delocalization.

## 5.5 Postmortem Analysis

To evaluate the stability of the COF TPA-NDI electrodes, SEM, and EDX analyses are conducted after 5000 charge-discharge cycles (Figures 5.16-5.18).

Notably, the morphology of COF TPA-NDI cathodes remains largely unchanged, indicating that the structural integrity of the material is well-preserved even after prolonged cycling. The only noticeable modification is the surface incorporation of electrolyte-derived species, which suggests a minor interfacial interaction with the electrolyte but no significant degradation of the COF framework.

This observation confirms that COF TPA-NDI exhibits exceptional cycling stability, maintaining its electrochemical performance and structural robustness throughout long-term charge-discharge cycling.

The Ragone plot is shown in Figure 5.19.

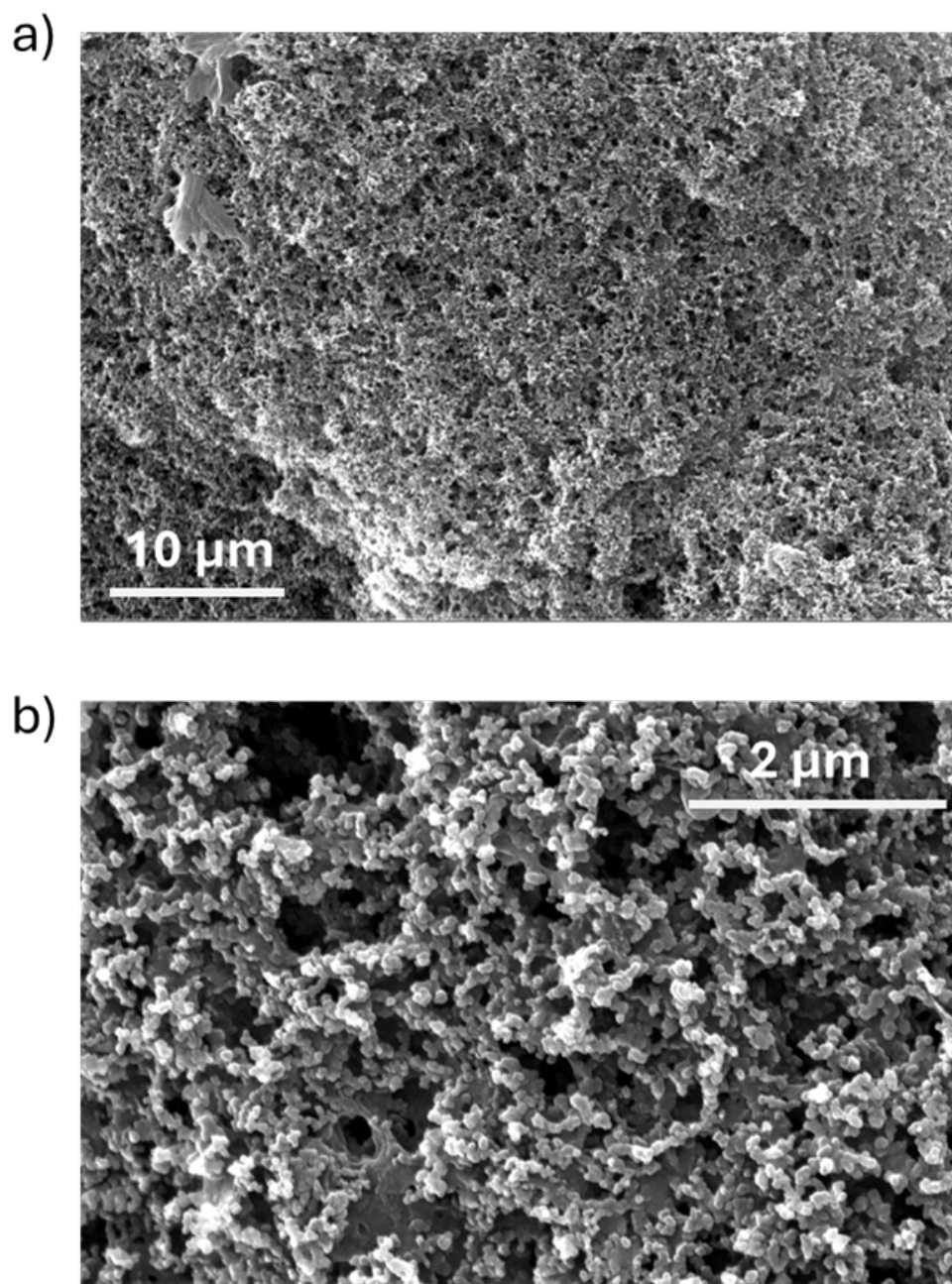
It highlights the exceptional specific energy and power density of COF TPA-NDI, achieving a maximum specific energy of 447 Wh/kg and a power density of 7 kW/kg. These values outperform previously reported common cathode materials for Al-ESS given in Table 5.2. It demonstrates the superior charge-storage capability of COF

**Table 5.2:** State of the art of the electrochemical performance of various cathode materials in Al-ESS

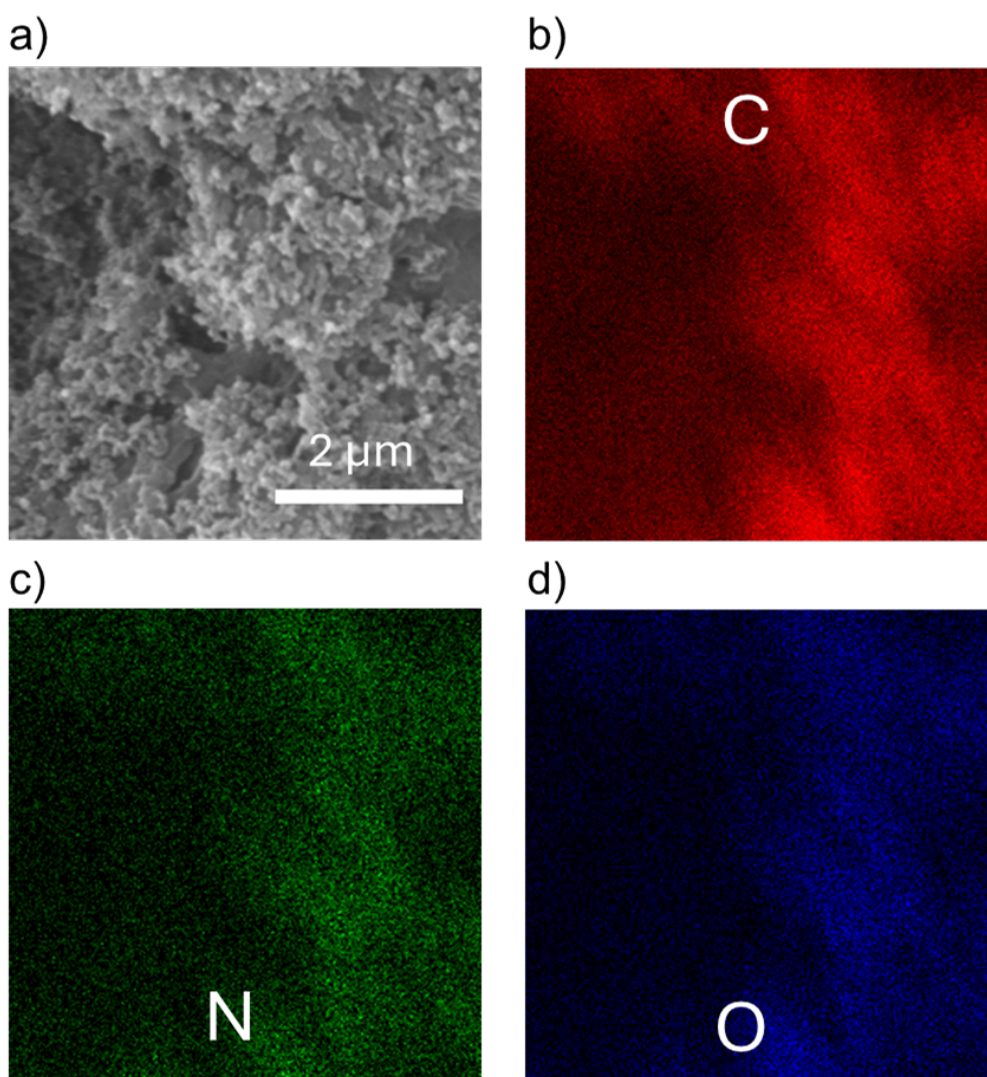
| Cathode      | Add.    | J (A/g) | Q (mAh/g) | Cycles | Retention (%)   | E / P (Wh/kg, kW/kg) | Ref   |
|--------------|---------|---------|-----------|--------|-----------------|----------------------|-------|
| COF TPA-NDI  | –       | 0.1     | 267       | 5000   | 99% at 5 A/g    | 447, 7               | [329] |
| Zn-TABQ      | –       | 0.05    | 198       | 5000   | 95% at 1 A/g    | 247, 1.01            | [330] |
| 2D-NT-COF30  | CNT 30% | 0.1     | 132       | 4000   | 99% at 1 A/g    | –                    | [186] |
| DAQ-TpO COF  | CNT     | 0.2     | 242.2     | 32000  | 90% at 10 A/g   | 389, 11.5            | [185] |
| DAQ-TpO COF  | –       | 0.2     | 134.6     | 32000  | 62% at 10 A/g   | –                    | [185] |
| DATP-CNT COF | CNT     | 0.2     | 160       | 10000  | 78% at 2 A/g    | ~240, ~1             | [185] |
| DATP COF     | –       | 0.2     | 145       | 500    | 90% at 0.5 A/g  | –                    | [185] |
| DAAQ-TFP-COF | –       | 0.05    | 113.9     | 400    | 82% at 0.05 A/g | 62, –                | [331] |
| TpBpy-COF    | CNT     | 0.5     | 245       | 13000  | 100% at 2 A/g   | –                    | [332] |

TPA-NDI. Unlike other COF-based cathodes that require CNT additives to enhance conductivity, COF TPA-NDI leverages its intrinsic ambipolar behavior, enabling efficient electron transfer and fast ion diffusion, as proved by EIS and GCD characterization. Moreover, its ability to sustain high specific energies even at elevated power outputs makes it a highly competitive cathode material, offering an efficient solution for next-generation Al-ESS with both high energy and power performance.

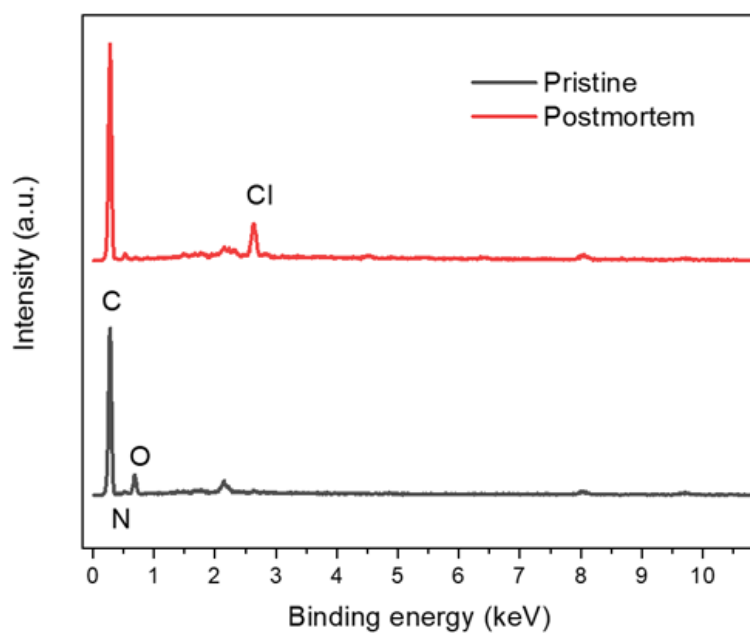




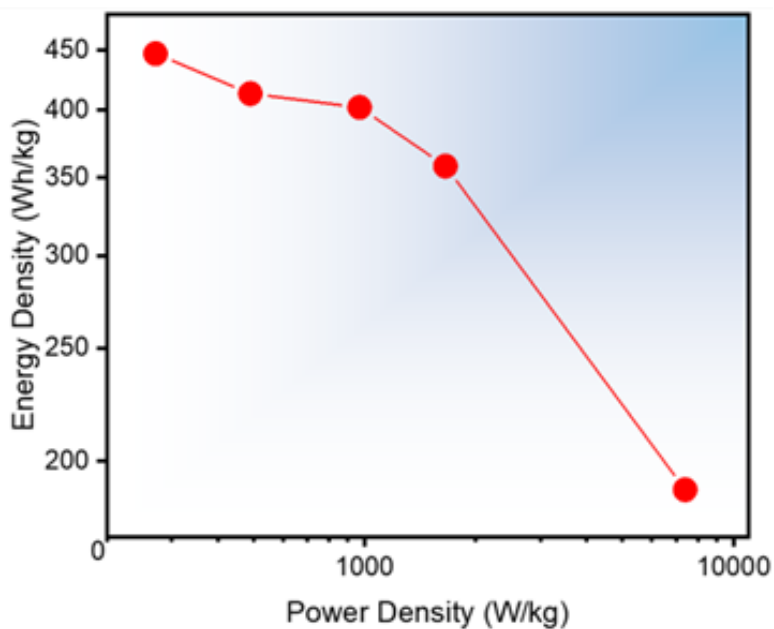
**Figure 5.16:** SEM images of COF TPA-NDI electrode after 5000 charge/discharge cycles at different magnifications.



**Figure 5.17:** SEM image of COF TPA-NDI electrode after 5000 charge/discharge cycles. EDX mapping of element distribution in COF TPA-NDI electrode after 5000 charge/discharge cycles: (b) carbon, (c) nitrogen and (d) oxygen.



**Figure 5.18:** EDX spectra of COF TPA-NDI electrodes: pristine (black spectrum) and after 5000 charge/discharge cycles (red spectrum).



**Figure 5.19:** Ragone plot for COF TPA-NDI employed in Al-ESS.

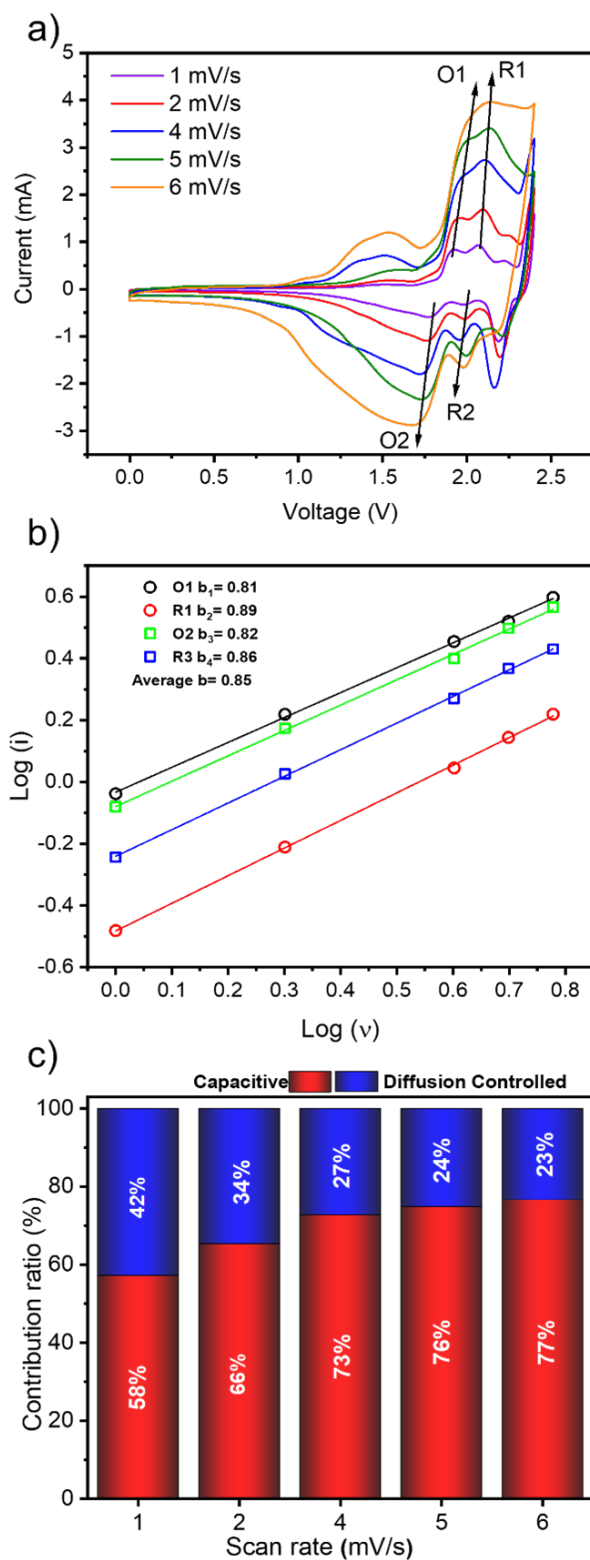
## 5.6 Electrochemical kinetic analysis

To gain insight into the charge storage mechanism of COF TPA-NDI, CV profiles at different scan rates are recorded in Figure 5.20(a). The CV curves display only a small peak shift within the scan rate range of 1 to 6 mV/s, indicating excellent electrochemical reversibility. The kinetics of the electrochemical processes occurring at the electrode are analyzed using the method proposed by Wu et al. [305]. The average *b*-value for COF TPA-NDI is determined to be 0.85, with individual *b*-values of 0.81, 0.89, 0.82, and 0.86 for different redox peaks, confirming a hybrid charge storage behavior that combines both capacitive and diffusion-controlled contributions shown in Figure 5.20(b). To further differentiate the capacitive and diffusion-controlled contributions at different scan rates, the current response is analyzed using the standard power-law relationship. The relative contributions of each mechanism are quantified and shown in Figures 5.20(c) and 5.21. At a scan rate of 1 mV/s, 42% of the total current is capacitive, while 58% is governed by a diffusion-controlled process. As the scan rate increases, the capacitive contribution becomes more dominant, reaching 77% at 6 mV/s. This trend indicates that at higher scan rates, charge storage is primarily capacitive, enabling rapid ion adsorption and charge accumulation at the electrode surface, whereas at lower scan rates, diffusion-controlled redox reactions contribute more significantly due to the increased time for ion insertion into the COF framework. These results confirm that COF TPA-NDI exhibits a charge storage mechanism predominantly governed by capacitive processes, particularly at high scan rates, where fast surface-controlled charge storage ensures efficient energy delivery. The coexistence of both capacitive and diffusion-controlled contributions enhances its hybrid electrochemical behavior, providing rapid charge storage capability along with high-capacity retention.

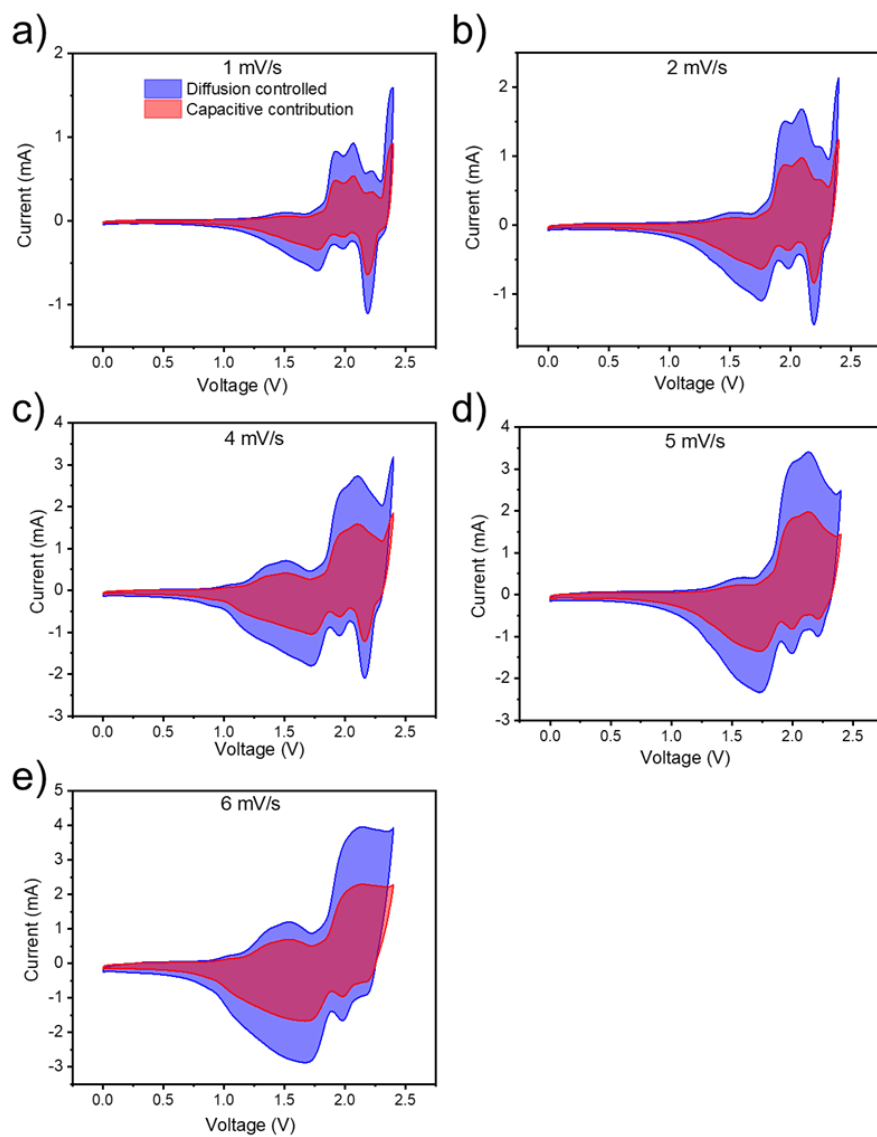
## 5.7 Ex situ charge storage mechanism study

To investigate the charge storage mechanism of COF TPA-NDI electrodes, PXRD (Figure 5.22) and high-resolution XPS (HRXPS) analyses (Figures 5.23(a-d) and Figure 5.24) are performed in the pristine, fully charged (2.4 V) and fully discharged (0 V) states.

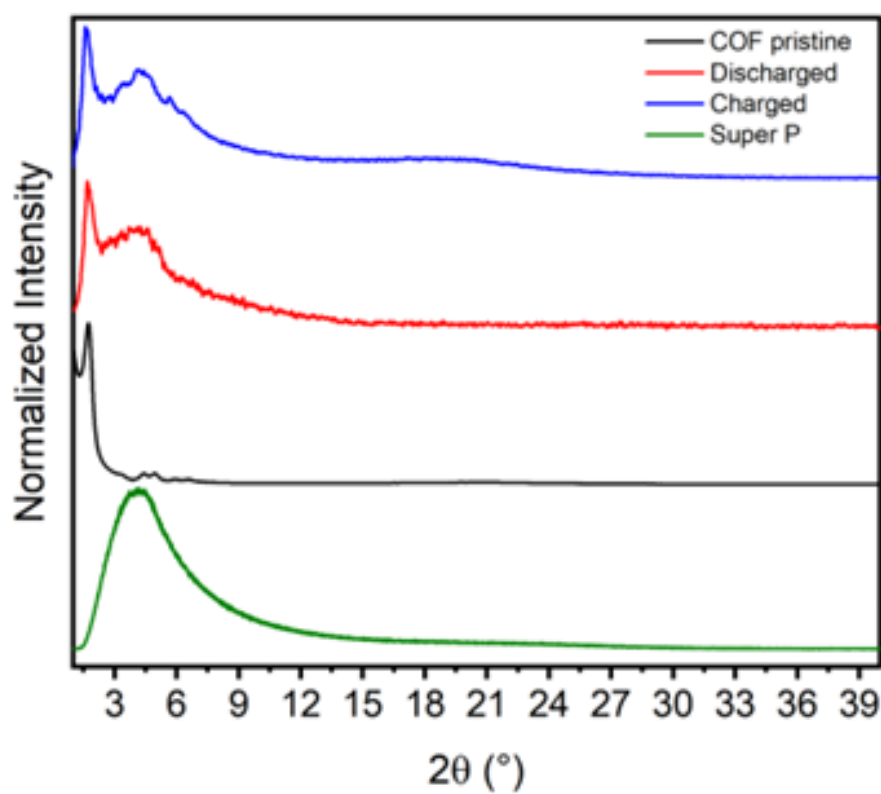
Ex situ PXRD measurements are conducted to investigate the structural evolution of the COF TPA-NDI electrode during electrochemical cycling (Figure 5.22). The diffraction patterns collected for the pristine, charged, and discharged states show that the characteristic peak at  $\sim 1.7^\circ$  is retained in all cases, indicating that the long-range crystalline order of the framework is well preserved upon cycling. In the region



**Figure 5.20:** (a) CV curve of COF TPA-NDI recorded at various scan rates; (b) fitting plots between  $\log(i)$  and  $\log(v)$  at various peak currents; (c) capacitive and diffusion-controlled contributions at various scan rates.



**Figure 5.21:** (a-e) Capacitive contribution and diffusion-controlled contribution of COF TPA-NDI fraction for the CV curves recorded at different scan rates.



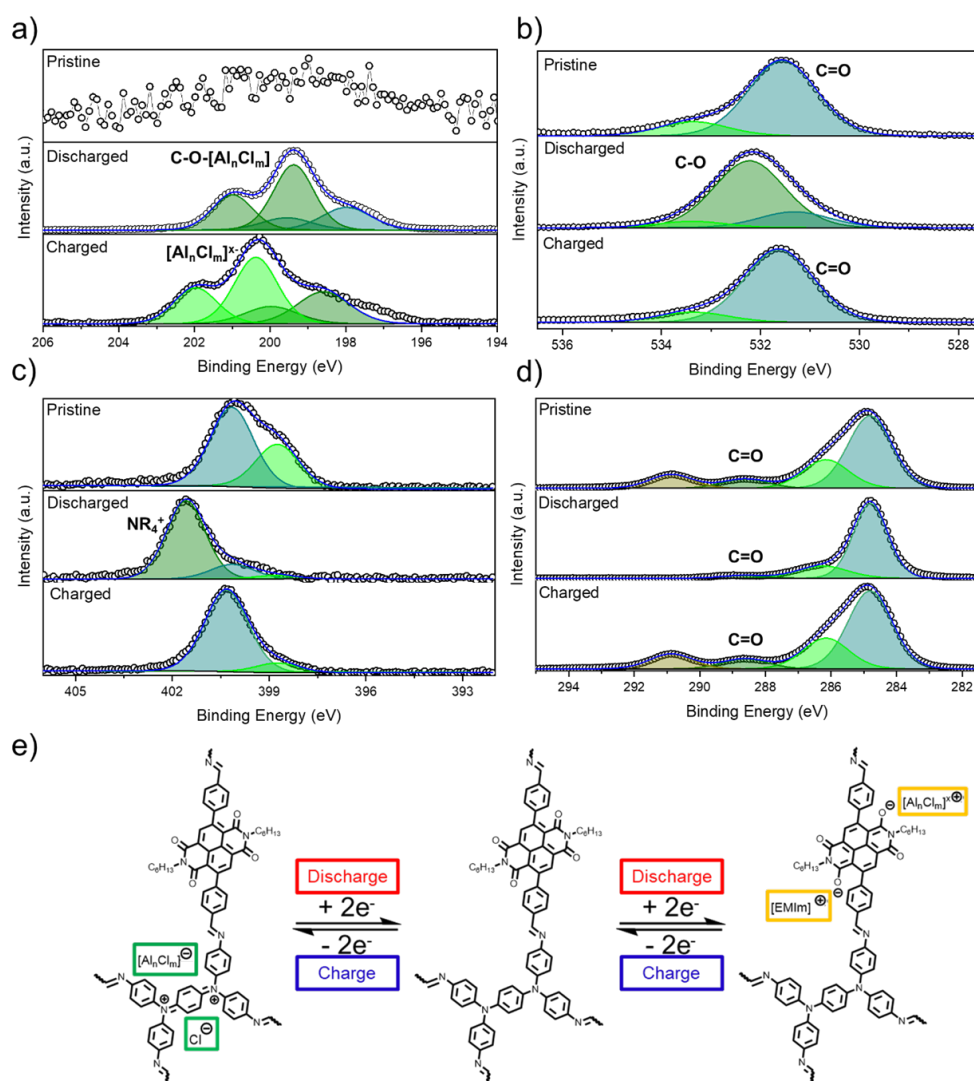
**Figure 5.22:** PXRD diffractogram of COF TPA-NDI in pristine, discharged, charged states, and Super P.

from  $2.4^\circ$  to  $8.2^\circ$ , the diffraction features of the COF are partially overlapped by the broad contribution of the conductive Super P, which dominates this range. Despite this limitation, no new peaks or significant peak shifts are observed between the different electrochemical states. The absence of any detectable structural change suggests that the charge storage process does not involve a classical intercalation mechanism associated with lattice expansion or contraction. Instead, this behavior is consistent with reversible redox reactions occurring within the intrinsic channels of the COF without perturbing its periodic structure. These findings, together with the electrochemical kinetics analysis, support a predominantly pseudocapacitive charge storage mechanism. To elucidate the aluminum complex ions present during charging and discharging, the ratio between Cl and Al is calculated from the survey spectra (Figure 5.24 a).

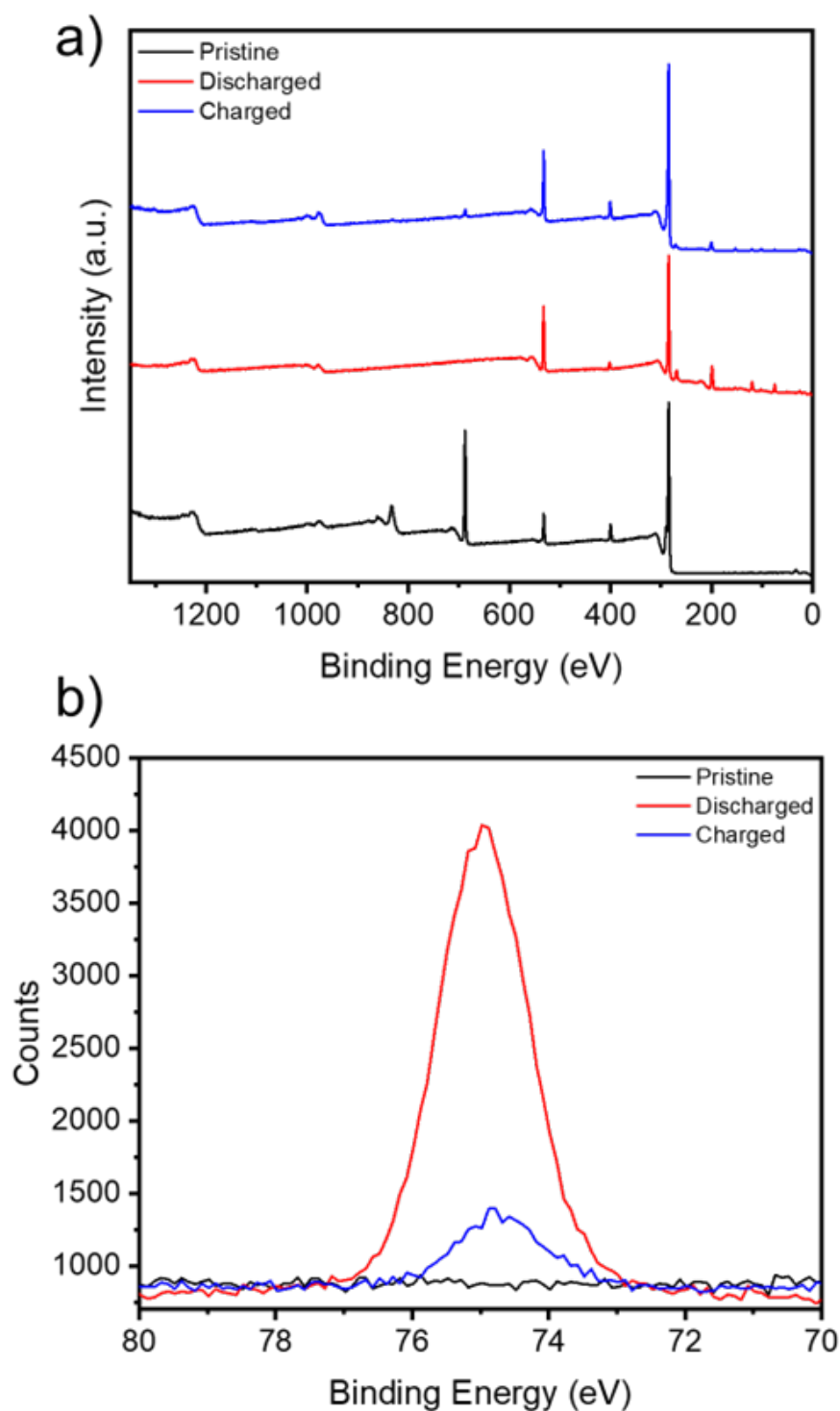
Due to the ambipolar nature of COF TPA-NDI, both p-type and n-type units are present, resulting in Al-Cl ions being detected in both charged and discharged states, as shown in the XPS survey and Al2p spectra in Figures 5.24(a, b). Notably, the Cl/Al ratio differs between the two states: approximately 3 in the charged state and about 1 in the discharged state. These Cl/Al ratios suggest that multiple ion species are involved in charging and discharging processes. Specifically, during charging,  $\text{Cl}^-$  and Al-Cl anions ( $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ) coordinate with the oxidized p-type donor sites, while during discharge, cations ( $\text{AlCl}_2^+$ ,  $\text{AlCl}^{2+}$  and  $\text{EMIm}^+$ ) stabilize the reduced n-type acceptor sites, ensuring efficient bidirectional charge storage.

In the discharged state (0 V), the Cl2p spectrum reveals the presence of two distinct peaks at 197.9 eV and 199.4 eV, corresponding to C-N–AlCl (from the imine bond) and C-O–AlCl (from the NDI unit) species, respectively (Figure 5.23a). These peaks indicate that during reduction,  $\text{AlCl}_2^+$  and  $\text{AlCl}^{2+}$  cations interact with both nitrogen and oxygen sites in the COF structure, stabilizing the negative charges formed on the COF framework. The Al-O interaction is further supported by the O1s HR XPS spectrum, which shows a significant transformation in oxygen-containing functionalities. In the discharge state, the dominant peak at 530.5 eV, that in the pristine state corresponds to C=O bonds of the NDI subunits, decreases in intensity, while a new peak emerges at 532.2 eV, indicating the reduction of carbonyl moieties to enolate groups (Figure 5.23b). This transformation is also evident in the C1s spectrum, where the flattening of the carbonyl peak at 290.5 eV further confirms the electrochemical conversion of C=O functionalities into enolates during the discharge process (Figure 5.23c). Additionally, the N1s spectrum in the discharged state shows a dominant peak at 401.6 eV, attributed to the quaternary nitrogen ( $\text{N}^+$ ) of the  $\text{EMIm}^+$  electrolyte, which interacts with the negatively charged enolate groups (Figure 5.23d). This coordination suggests that  $\text{EMIm}^+$  stabilizes the reduced enolate species, contributing to charge compensation and





**Figure 5.23:** HRXPS of COF TPA-NDI electron in pristine, discharge and charged states for (a) Cl2p; (b) O1s; (c) C1s; (d) N1s. (e) schematic illustration of proposed charged storage mechanism.



**Figure 5.24:** XPS (a) Survey and (b) Al<sub>2</sub>p spectra of COF TPA-NDI in pristine, discharged and charged form.

facilitating efficient charge storage.

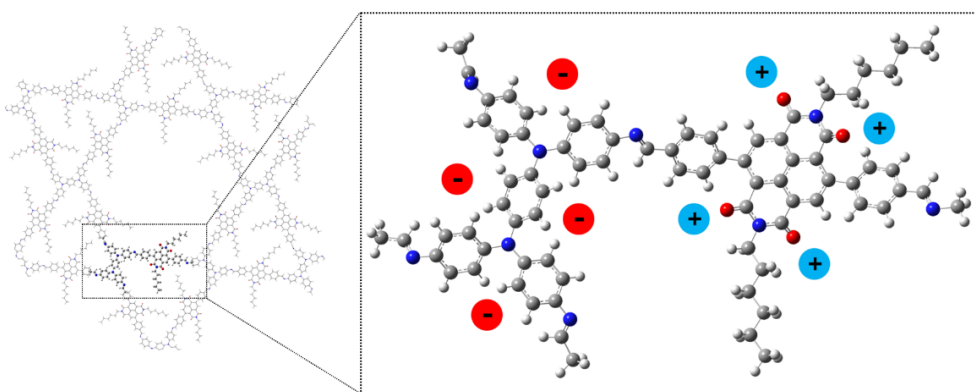
In the charged state (2.4 V), the Cl2p spectrum exhibits peaks at 198.55 eV and 200.4 eV, corresponding to  $\text{AlCl}_2^-$  or  $\text{Al}_2\text{Cl}_7^-$  anions and  $\text{Cl}^-$  species, respectively, that are strongly interacting with the p-type donor units in COF (*i.e.*, TPA) (Figure 5.23a). The oxidation of enolate groups back to carbonyl moieties is confirmed by the O1s spectrum, where the enolate peak disappears, and the C=O peak at 530.5 eV is fully restored (Figure 5.23c). The reoxidation process ensures the complete reversibility of the charge storage mechanism. Furthermore, in the N1s XPS spectrum, the quaternary nitrogen peak observed in the discharged state disappears, confirming the loss of  $\text{EMIm}^+$  coordination upon oxidation (Figure 5.23d).

These findings highlight the critical role of the donor and acceptor units in the charge storage mechanism of COF TPA-NDI. The n-type acceptor sites facilitate the coordination of cationic  $\text{AlCl}_2^+$ ,  $\text{AlCl}^{2+}$ , and  $\text{EMIm}^+$  species and stabilization of enolate groups during discharge, while the p-type donor sites interact with anionic  $\text{AlCl}_2^-$ ,  $\text{Al}_2\text{Cl}_7^-$ , and  $\text{Cl}^-$  species and stabilize the oxidized tertiary amine moieties during charge. This dual charge accommodation enables a highly reversible charge storage process, distinguishing COF TPA-NDI from conventional n-type COFs, which only interact with cationic species. The ability of COF TPA-NDI to store both cationic and anionic aluminum species leads to enhanced charge storage capacity, improved electrochemical reversibility, and superior cycling stability.

## 5.8 Density functional theory (DFT) calculations

DFT calculations are conducted to elucidate active sites and further understand the charge storage mechanism. On the one hand, we calculate the molecular electrostatic potential (ESP) of the TPA-NDI repeating unit shown in Figure 5.25 in the neutral state, charged state after removing 2 electrons and discharged state after adding 2 electrons.

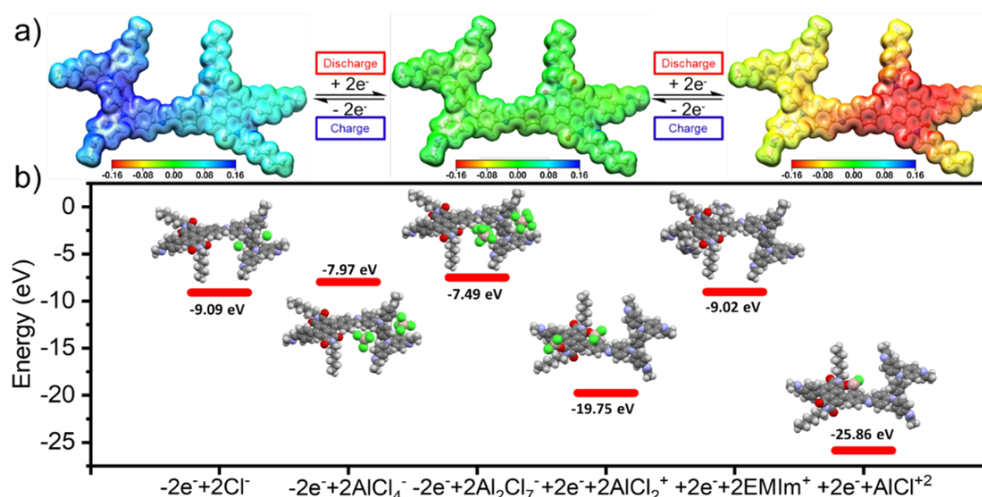
The obtained results (Figure 5.26a) provide evidence that, in the charged state, oxidation occurs upon extraction of two electrons mainly from the electron-rich p-type TPA frame (depicted as a dark blue region in the ESP). On the contrary, in the discharged state, the reduction after the injection of 2 electrons takes place in the electron-poor n-type NDI frame (the red region in Figure 5.26a). The different charge location in the charged and discharged states confirms the ambipolar behavior of COF TPA-NDI. The HOMO and LUMO orbitals shown in Figure 5.27 confirm this description, with the HOMO mainly distributed along the TPA moiety, while the LUMO orbital is located at the aromatic region of the NDI unit [333, 334]. On the other hand, the interactions



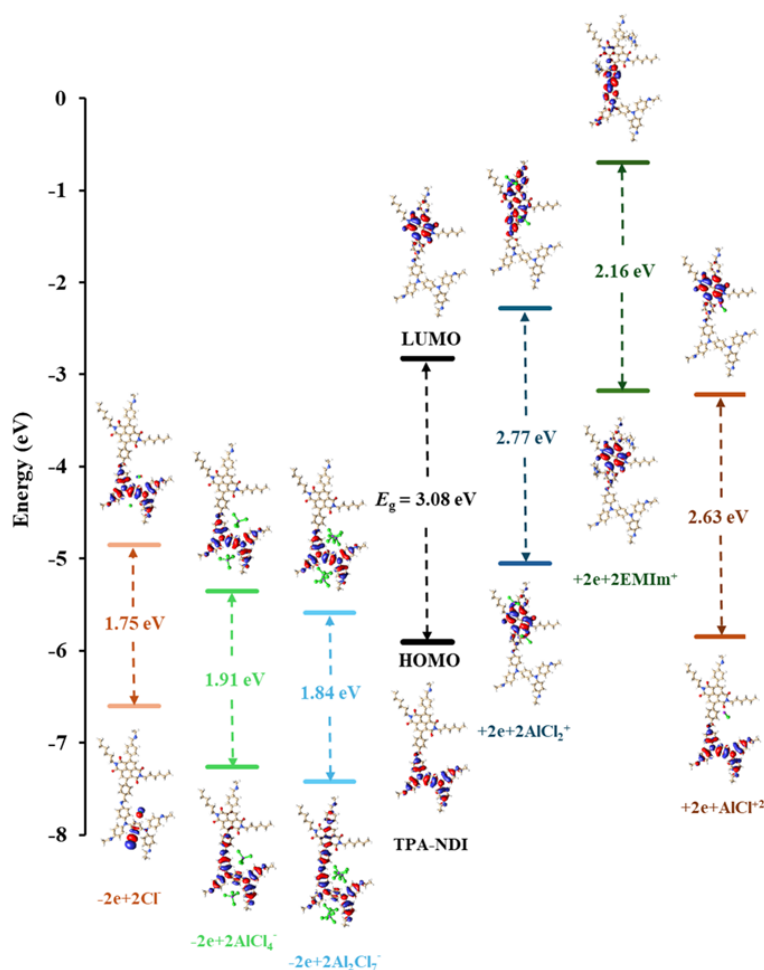
**Figure 5.25:** TPA-NDI unit employed for DFT calculations. Red and blue circles correspond to pore regions explored for studying the interaction between the unit model and anions and cations, respectively.

between electrolyte ions and COF framework in charged and discharged states are evaluated considering  $\text{Cl}^-$ ,  $\text{AlCl}_4^-$ , and  $\text{Al}_2\text{Cl}_7^-$  as anions, and  $\text{EMIm}^+$ ,  $\text{AlCl}_2^+$ , and  $\text{AlCl}^{2+}$  as cations. In the discharged state, the computed binding energies (Figure 5.25b) indicate that the preferred interaction for the anions corresponds to the smallest  $\text{Cl}^-$  species (-9.09 eV), which can be located closer to the positively charged regions of the TPA than other larger anions. The interactions for  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  with the oxidized TPA frame (-7.97 and -7.49 eV, respectively), although somewhat smaller to the one predicted for  $\text{Cl}^-$ , are also favorable and justify the presence of Al peaks in HRXPS spectrum of the charged state. In the discharged state, the stabilizing interactions of the  $\text{AlCl}_2^+$  and  $\text{AlCl}^{2+}$  cations with the reduced NDI frame are larger (-19.75 and -25.86 eV, respectively) than the one observed for  $\text{EMIm}^+$  (-9.02 eV). This difference can be attributed mainly to strong directional interaction between the reduced carbonyl group and the aluminum atom in the aluminum-based cations and the high steric hindrance of the EMIm group. Moreover, the interaction with both anions and cations reduces the HOMO-LUMO gap compared with that of the TPA-NDI isolated unit, suggesting an enhancement of the electronic conductivity (Figure 5.27).

Finally, it must be also noted that the optimized geometries obtained from DFT calculation indicate that electrolyte ions are principally located in the pores of the crystal structure and, although only interactions between ions and one TPA-NDI unit were considered, the small distance between the parallel COF TPA-NDI layers (around 3.6 Å) suggests that simultaneous interactions between several layers of the COF and the anions/cations can also occur [137, 138, 335].



**Figure 5.26:** (a) ESP of TPA-NDI repeating unit in charged state, neutral state and discharged state; (b) corresponding binding energy of the most stable TPA-NDI repeating unit in charged state, neutral state and discharged state with the corresponding counterions.



**Figure 5.27:** HOMO-LUMO energy gaps (in eV) for the isolated TPA-NDI unit (in black colour) and for the charged (left) and discharged (right) states interacting with anions and cations, respectively.

## 5.9 Conclusion

In this work, we have designed and synthesized a 2D donor–acceptor COF, TPA-NDI, as a high-performance cathode for Al-ESS. The COF integrates electron-rich TPA and electron-poor NDI into a crystalline microporous network (BET surface area: 924 m<sup>2</sup> g<sup>−1</sup>; pore sizes: 1.6 and 3.4 nm) that enables efficient diffusion of ions and intrinsic charge transport without the use of conductive additives. As a result, COF TPA-NDI delivers a record-specific capacity of 270 mAh/g at 0.1 A/g within COFs assessed as cathode materials in Al-ESS and maintains 125 mAh/g at 5 A/g, demonstrating an excellent rate capability. The material also exhibits exceptional durability, retaining >99% of its initial capacity over 5,000 cycles at 5 A/g, with a coulombic efficiency of 99.7%. Ex situ XPS and DFT analyses reveal a reversible multielectron charge-storage mechanism involving amine, imine, and carbonyl sites, with the framework coordinating both cationic (AlCl<sub>2</sub><sup>+</sup>, AlCl<sub>2</sub><sup>2+</sup>, EMIm<sup>+</sup>) and anionic (AlCl<sub>4</sub><sup>−</sup>, Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup>, Cl<sup>−</sup>) species. This ambipolar behavior enables effective charge compensation during both oxidation and reduction, enhances electrochemical reversibility, and is associated with the high specific capacity and long-term stability of the electrode. Furthermore, the intrinsic donor-acceptor electronic structure enables efficient charge transport without external conductive fillers, allowing the Al-ESS to reach a specific energy level of 447 Wh/kg and a power density of 7 kW/kg. Overall, these results demonstrate that donor-acceptor engineering is a promising strategy for creating intrinsically conductive COFs capable of fast multivalent-ion storage, offering a pathway toward next-generation aluminum-ion energy storage technologies.

## Chapter 6

# General Conclusion and Outlook

This thesis establishes that porous framework-based cathodes for energy storage cannot be designed by optimizing a single material parameter, such as surface area, conductivity, redox activity, or crystallinity, in isolation. Instead, high electrochemical performance emerges when three features are balanced within the same electrode architecture, accessible redox-active sites, ion-compatible pore environments, and efficient charge transport pathways. This shared design principle connects the three systems investigated in this thesis, namely Mn-Fe-BTC DMOF for lithium metal batteries, CMOF-5-derived carbons for zinc-ion hybrid supercapacitors, and donor–acceptor COF TPA-NDI for aluminum-ion energy storage. Although these materials operate in different electrolytes and involve different charge carriers, they collectively show that porous frameworks become effective cathodes only when their chemical functionality, pore architecture, and electronic structure are matched to the storage mechanism of the specific battery chemistry. In summary, the first study demonstrated that incorporating two metal centers within a single MOF framework is an effective strategy to increase the density and diversity of redox-active sites. In Mn-Fe-BTC DMOF, the coexistence of Mn and Fe centers, together with redox-active carboxylate linkers, enabled high lithium storage capacity and stable cycling. The material delivered a high initial discharge capacity of  $1385 \text{ mA h g}^{-1}$  and retained  $687 \text{ mA h g}^{-1}$  after 100 cycles, with nearly 100% Coulombic efficiency. These results indicate that the electrochemical response is not controlled by one redox center alone, but by the cooperative contribution of metal nodes and organic linkers within a stable porous framework. Post-cycling XPS, XRD, and SEM confirmed that the framework retained its structural and chemical integrity after cycling, while EIS revealed an increase in charge transfer resistance from 60 to  $189 \Omega$ . This suggests that the electrode remains structurally well framed, but the electrode–electrolyte interface, particularly SEI formation and evolution, becomes an

important factor controlling long-term performance. Therefore, the central contribution of this study is not only the development of a high-capacity DMOF cathode, but also the demonstration that dual-metal framework chemistry can be used to tune redox activity while maintaining structural stability during lithium storage. The second study showed that the performance of MOF-derived carbon electrodes depends strongly on the thermal evolution of residual metal species and their effect on pore accessibility. In the CMOF-5 system, carbonization temperature controlled ZnO formation, carboreduction to metallic Zn, Zn evaporation, graphitization, and pore development. The best-performing sample, CMOF-5\_1000, exhibited a high surface area of  $2151 \text{ m}^2 \text{ g}^{-1}$ , a pore volume of  $1.87 \text{ cm}^3 \text{ g}^{-1}$ , improved electrical conductivity, and a reduced charge transfer resistance of  $488.4 \Omega$ . These combined properties enabled a specific capacitance of  $268.93 \text{ F g}^{-1}$ , an energy density of  $166.9 \text{ Wh kg}^{-1}$ , a power density of  $9234 \text{ W kg}^{-1}$ , and 88% capacitance retention after 10 000 cycles. Importantly, this study also revealed that improved conductivity alone is insufficient to guarantee higher capacitance. The lower capacitance of CMOF-5\_700 compared with CMOF-5\_600, despite improved electrical conductivity, shows that ZnO-related pore obstruction can dominate over the benefit of better electron transport. This result is one of the most important mechanistic findings of the thesis because it demonstrates that ion-accessible porosity, rather than nominal conductivity or total surface area alone, determines whether charge storage sites can actually participate in electrochemical reactions. The third study extended this framework design concept to an organic crystalline system by using donor–acceptor COF chemistry to enable ambipolar charge storage in aluminum-ion electrolytes. COF TPA-NDI was designed by combining electron-donating triphenylamine units and electron-accepting naphthalene diimide units within an ordered imine-linked porous framework. This architecture provides complementary redox sites for interaction with both anionic and cationic electrolyte-derived species. Solid-state NMR confirmed imine bond formation, PXRD and DFT supported the crystalline AA-stacked structure, TEM confirmed the ordered lattice, and BET analysis revealed hierarchical pores of 1.64 nm and 3.4 nm. DFT calculations further showed that anions preferentially interact with oxidized TPA units during charging, while cations interact with reduced NDI units during discharging. This establishes a dual-ion storage mechanism in which the donor and acceptor units play complementary electrochemical roles. The key contribution of this study is therefore the demonstration that pore geometry and redox-site polarity can be rationally coupled to control ion selectivity and charge storage in aluminum-based electrolytes.

For the first time, these studies in this thesis also explained that each system converged around the same underlying strategy, introducing two chemically distinct, simultaneously active components into a single porous framework, rather than relying on one



dominant active site or property. In Mn-Fe-BTC DMOF, two redox-active metal centres ( $\text{Mn}^{2+}/\text{Fe}^{3+}$ ) share the same carboxylate-linked framework, giving two parallel charge-storage pathways instead of one. In CMOF-5, the carbonization process generates a framework whose performance is governed by the competing presence of two components, the evolving carbon matrix and the residual Zn/ZnO phase, which determines whether ion transport or electron transport is rate-limiting. In COF TPA-NDI, the donor (TPA) and acceptor (NDI) units provide two electronically distinct redox sites within the same pore wall, enabling selective interaction with both anionic and cationic electrolyte species. Taken together, these three studies further establish that the most crucial design requirement for porous framework cathodes is not the independent maximization of redox activity, conductivity, or porosity, but the integration of these properties into an electrolyte-specific architecture. A framework with many redox sites will underperform if ions cannot access them. A highly conductive carbon will show limited capacitance if pore channels are blocked. A crystalline COF with tunable redox units will be ineffective if its pore geometry does not accommodate the relevant electrolyte species. Therefore, the single most important insight for designing porous framework cathodes is that electrochemical performance is governed by the coupling between redox chemistry and ion-accessible transport pathways. In practical terms, the active site must be chemically capable of storing charge, physically accessible to the electrolyte ion, and electronically connected to the current collector. Only when these three conditions are satisfied simultaneously can porous frameworks deliver high capacity, fast kinetics, and stable cycling. This conclusion also reframes how porous framework electrodes should be evaluated. Conventional descriptors such as BET surface area, crystallinity, electrical conductivity, and redox-site density remain essential, but they are incomplete when considered separately. In the CMOF-5 study, surface area and conductivity must be interpreted alongside pore blockage, Zn/ZnO evolution, and ion diffusion. Similarly, the Mn-Fe-BTC DMOF study shows that high capacity must be interpreted together with SEI evolution and interfacial resistance. The COF TPA-NDI study shows that pore size must be evaluated not only geometrically, but also chemically, in terms of selective interaction with  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{EMIm}^+$ , and related electrolyte species. Thus, this thesis supports a more integrated structure–performance framework in which cathode performance is understood through the interaction of framework chemistry, pore architecture, electrolyte identity, and interfacial evolution.

The results of this thesis raise several specific directions that should guide future work. For the Mn–Fe–BTC DMOF, the most important question is what governs SEI evolution and charge-transfer resistance beyond the first 100 cycles. This could be addressed by extending cycling to 500–1000 cycles while performing periodic EIS.

Although post-mortem characterisation confirmed structural stability after cycling, the rise in resistance indicates that interfacial processes continue to influence performance. Future work should therefore determine whether this increase originates mainly from SEI thickening, electrolyte decomposition, partial blockage of framework pores, or changes in the oxidation states of Mn and Fe during extended cycling. A second question is how the Mn:Fe ratio affects redox contribution, structural stability, and SEI chemistry; systematically varying this ratio could reveal whether the observed performance arises from an optimal balance between the two metal centres or from a single dominant component. A third direction is to examine whether linker functionalisation can stabilise the electrode–electrolyte interface while preserving the high capacity provided by the dual-metal framework.

For the CMOF-5 system, the central open question is whether a multi-stage carbonisation strategy can outperform the single-temperature route used here. The present results show that ZnO migration, carboreduction, Zn evaporation, graphitisation, and pore formation occur over different temperature ranges, so a single final temperature may not allow independent control of all of these processes. Future work should test stepwise protocols that first promote controlled ZnO migration and defect formation, followed by optimised Zn removal and carbon-framework stabilisation, to determine whether beneficial mesoporosity and graphitic conductivity can be retained while avoiding pore collapse or excessive defect healing. A related direction is to examine whether partial retention of Zn or ZnO can be beneficial when its distribution is controlled. The poor performance of CMOF-5\_700 suggests that uncontrolled ZnO agglomeration blocks pores, yet finely dispersed residual Zn species may still contribute to pseudocapacitive storage or improve electrolyte interaction; future studies should therefore distinguish between harmful ZnO agglomerates and potentially useful atomically dispersed or nanoscale Zn-containing sites.

For the COF TPA-NDI, the most important unresolved question is how pore geometry controls selectivity between  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  during charge storage. The DFT results suggest that these electrolyte-derived ions interact differently with the donor and acceptor units, but the relative contribution of each species under operating conditions remains unclear. Future work should therefore establish whether pore size, pore polarity, and the local electrostatic environment can be tuned to favour one aluminium-chloride species over another – a question of particular importance because  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  differ in size, charge distribution, and role in aluminium-ion electrochemistry. A second question is how the donor–acceptor ratio influences ambipolar storage: increasing the density of TPA units may improve anion storage during charging, while increasing the NDI content may enhance cation interaction during discharge, although changing this ratio may also

affect crystallinity, pore ordering, and electronic delocalisation. A third direction is to investigate whether stronger electronic coupling between the donor and acceptor units can improve conductivity without sacrificing the ion-accessible porosity that enables dual-ion storage.

Overall, this thesis indicates that a porous-framework cathode should be regarded as an electrochemical environment rather than merely a porous solid. This principle provides a unified basis for the future development of MOF, MOF-derived-carbon, and COF cathodes for lithium, zinc, aluminium, and other emerging energy-storage systems.

## Statement of Work

The experiments and analysis data presented in this dissertation have been conducted and described by me, unless otherwise stated below. Contributions from others, including collaborative experimental work, computational studies, and characterization performed by external parties, are explicitly acknowledged at the appropriate points throughout the writing.

In chapters 3, 4 and 5, PXRD, XPS and SEM were carried out by Dr. Verónica Montes and BET measurements were performed by Dr. Wojciech Kukułka from Center for Advanced Technologies, Adam Mickiewicz University in Poznań.

In chapter 5 Solid-state  $^{13}\text{C}$  (CP-MAS NMR) was done in collaboration with Dr. hab. Michał Bielejewski, Prof., at Institute of Molecular Physics, Polish Academy of Sciences Poznań. And all the density functional theory (DFT) calculations were carried out in collaboration with Dr. Mateusz Wlazło working at the Chemical and Biological Systems Simulation Lab, Centre of New Technologies of University of Warsaw.

The projects reported in this thesis were designed with Prof Dr. Artur Ciesielski and Dr. Dawid Pakulski.

## Scientific Achievements

### Publications included in the dissertation:

1. Sarwar, S.; Montes-García, V.; Stachowiak, M.; Chudziak, T.; Kukułka, W.; Valentini, C.; Karoń, K.; Pakulski, D.; Ciesielski, A. *Mn–Fe dual metal–organic framework based on trimesic acid as a high-performance electrode for lithium metal batteries*. **Nanoscale Adv.** 2024, 6 (21), 5301–5305, IF = 6.3
2. Kukułka, W.; Montes-García, V.; Sarwar, S.; Pakulski, D.; Samorì, P.; Ciesielski, A. *Enhancing zinc-ion energy storage: impact of MOF-5 derived carbonization temperature on performance*. **J. Mater. Chem. A** 2025, 13 (28), 22755–22760, IF = 9.5
3. Valentini, C.; Montes-García, V.; Kukułka, W.; Sarwar, S.; Bielejewski, M.; Wlazło, M.; Greco, R.; Pankratova, V.; Pérez Juste, I.; Pakulski, D.; Samorì, P.; Ciesielski, A. *Donor–acceptor covalent organic framework enables ambipolar charge storage in aluminum-ion energy storage*. **Adv. Energy Mater.** 2026, e71198, IF = 25.5

### Publications not included in the dissertation:

1. Ahmad, F.; Shahzad, A.; Sarwar, S.; Inam, H.; Waqas, U.; Pakulski, D.; Bielejewski, M.; et al. *Gel polymer electrolyte composites in sodium-ion batteries: synthesis methods, electrolyte formulations, and performance analysis*. **J. Power Sources** 2024, 619, 235221, IF = 8.4
2. Ahmad, F.; Bielejewska, N.; Świergiel, J.; Sarwar, S.; Pakulski, D.; Bielejewski, M. *Correlation of adaptive ion transport and electrochemical properties of thermally reversible Li-ion supramolecular gel electrolytes in Li-ion batteries*. (In Preparation)
3. Sarwar, S.; Montes-García, V.; Pakulski, D.; Ciesielski, A. *Unlocking superior*

*electrochemical performance of laser reduced graphene oxide (LrGO) from symmetric supercapacitor to asymmetric zn ion hybrid energy storage system. (In Preparation)*

# Conferences and Internships

## Conferences

All conferences held during PhD studies are presented below.

- LEAPS INNOV Battery Research Forum 2025 Int. Conference and Exhibition 27-29/01/2025 Helmholtz-Zentrum Berlin, Germany. (Poster Presentation)
- 10th Polish Conference Graphene and other 2D materials 2025 Conference and Exhibition 9-12/09.2025, Świnoujście, Poland. (Poster Presentation)

## International internship:

- **Country:** France
- **Institution:** Université de Strasbourg, Institut de Science et d'Ingénierie Supramoléculaire (I.S.I.S.).
- **Type of stay:** In the frame of ERASMUS+ Program
- **Duration time:** 15.09.2024 – 15.01.2025
- **Description of activities:**

During an internship at the Institut de science et d'ingenierie supramoleculaires in Strasbourg, France, I synthesized metal nanoparticles using colloidal methodologies and fabricated plasmonic platforms via layer-by-layer techniques, optimizing their structural and physicochemical properties for surface-enhanced Raman scattering (SERS)-based mycotoxin sensing. I performed multiscale characterization of the synthesized materials using XPS, SEM, STEM, AFM, and UV-vis spectroscopy, and designed experimental setups to enhance the sensitivity and specificity of the SERS platforms. Through this experience, I developed strong expertise in nanoparticle synthesis, plasmonic substrate fabrication, and advanced material characterization techniques in materials science and chemical sensing research.

- **Supervisor:** Dr. Verónica Montes García



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## Saira Sarwar

### “Metal and Covalent organic framework (MOFs, COFs) electrodes for high efficiency energy storage systems”

#### Streszczenie pracy w języku polskim

Rosnące zapotrzebowanie na zrównoważone magazynowanie energii przyspieszyło poszukiwania elektrod łączących wysoką pojemność, stabilność i uniwersalność. Sieci metalo-organiczne (MOF), karbonizaty MOF (CMOF) oraz kowalencyjne sieci organiczne (COF) – są obiecującymi kandydatami dzięki regulowanej porowatości, dużej powierzchni właściwej i aktywnym centrom redoks. Praca przedstawia trzy uzupełniające się badania dotyczące odmiennych elektrod i układów elektrochemicznych. Pierwsze badania dotyczyły bimetalicznego układu MOF Mn-Fe-BTC jako katody baterii litowych (pojemność 1292 mAh g<sup>-1</sup> przy 0,1 A g<sup>-1</sup> oraz 687 mAh g<sup>-1</sup> po 100 cyklach). Drugie badania dotyczyły skarbonizowanej sieci MOF-5 w zakresie temp. 600-1000°C jako materiału dla hybrydowych superkondensatorów cynkowo-jonowych. Próbkę wygrzaną w 1000°C wykazała pojemność 269 F g<sup>-1</sup> i 88% zachowania pojemności po 10000 cyklach. Trzecie badania opisują układ COF typu donor–akceptor (TPA-NDI) w bateriach glinowo-jonowych. Obliczenia DFT wyjaśniają mechanizm magazynowania ładunku poprzez oddziaływania anionów/kationów odpowiednio z utlenionymi jednostkami TPA i zredukowanymi NDI. Badania te przedstawiają zależności struktura–właściwości i dowodzą, że racjonalne projektowanie poprzez strategie bimetaliczne, kontrolowaną karbonizację i architektury donor–akceptor stanowi wszechstronną platformę dla magazynowania energii nowej generacji.

Słowa kluczowe: Elektrody z porowatej sieci, Sieci metalo-organiczne (MOF), Kowalencyjne sieci organiczne (COF), Elektrochemiczne magazynowanie energii, Temperatura karbonizacji

## Summary in English

The growing demand for sustainable energy storage has accelerated the search for advanced electrode materials combining high capacity, long cycling stability, and versatility. Metal–organic frameworks (MOFs), MOF-derived carbons (CMOFs), and covalent organic frameworks (COFs) have emerged as promising candidates due to their tunable porosity, large surface areas, and redox-active sites. This thesis presents three complementary studies targeting distinct porous framework electrodes and electrochemical systems. The first investigates a bimetallic Mn-Fe-BTC MOF as a cathode for lithium metal batteries, achieving 1292 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and 687 mAh g<sup>-1</sup> after 100 cycles. The second study examines carbonized MOF-5 at 600–1000 °C for zinc-ion hybrid supercapacitors; the 1000 °C sample delivered 269 F g<sup>-1</sup> and 88% retention after 10,000 cycles. The third evaluates a donor–acceptor COF (TPA-NDI) for aluminum-ion batteries, with DFT calculations explaining the charge storage mechanism involving anion/cation interactions with oxidized TPA and reduced NDI units, respectively. Collectively, these studies establish clear structure–property relationships and demonstrate that rational framework design through bimetallic strategies, controlled carbonization, and donor–acceptor architectures offer a versatile platform for next-generation energy storage.

**Keywords:** Porous Framework Electrodes, Metal–Organic Frameworks (MOFs), Covalent Organic Frameworks (COFs), Electrochemical Energy Storage, Carbonization Temperature

Opis rozprawy doktorskiej:

|                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |
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| <b>Wydział</b>                                             | Chemii                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <b>Instytut/Zakład</b>                                     | Laboratorium Materiałów Hybrydowych (CZT)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| <b>Tytuł pracy w jęz. polskim</b>                          | Elektrody oparte na sieciach metaloorganicznych i kowalencyjnych sieciach organicznych (MOF, COF) do zastosowań w wysokowydajnych systemach magazynowania energii                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| <b>Tytuł pracy w jęz. angielskim</b>                       | Metal and Covalent organic framework (MOFs, COFs) electrodes for high efficiency energy storage systems                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| <b>Język pracy</b>                                         | Angielski                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| <b>Słowa kluczowe w jęz. polskim (max 5)</b>               | 1. Elektrody z porowatej sieci<br>2. Sieci metalo-organiczne (MOF)<br>3. Kowalencyjne sieci organiczne (COF)<br>4. Elektrochemiczne magazynowanie energii<br>5. Temperatura karbonizacji                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| <b>Słowa kluczowe w jęz. angielskim (max 5)</b>            | 1. Porous Framework Electrodes<br>2. Metal–Organic Frameworks (MOFs)<br>3. Covalent Organic Frameworks (COFs)<br>4. Electrochemical Energy Storage<br>5. Carbonization Temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| <b>Streszczenie pracy w jęz. polskim (max 1400 znaków)</b> | Rosnące zapotrzebowanie na zrównoważone magazynowanie energii przyspieszyło poszukiwania elektrod łączących wysoką pojemność, stabilność i uniwersalność. Sieci metalo-organiczne (MOF), karbonizaty MOF (CMOF) oraz kowalencyjne sieci organiczne (COF) – są obiecującymi kandydatami dzięki regulowanej porowatości, dużej powierzchni właściwej i aktywnym centrom redoks. Praca przedstawia trzy uzupełniające się badania dotyczące odmiennych elektrod i układów elektrochemicznych. Pierwsze badania dotyczyły bimetalicznego układu MOF Mn-Fe-BTC jako katody baterii litowych (pojemność 1292 mAh g <sup>-1</sup> przy 0,1 A g <sup>-1</sup> oraz 687 mAh g <sup>-1</sup> po 100 cyklach). Drugie badania dotyczyły skarbonizowanej sieci MOF-5 w zakresie temp. 600-1000°C jako materiału dla hybrydowych superkondensatorów cynkowo-jonowych. Próbką |

|                                                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |
|----------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                      | <p>wygrzana w 1000°C wykazała pojemność 269 F g<sup>-1</sup> i 88% zachowania pojemności po 10000 cykli. Trzecie badania opisują układ COF typu donor–akceptor (TPA-NDI) w bateriach glinowo-jonowych. Obliczenia DFT wyjaśniają mechanizm magazynowania ładunku poprzez oddziaływania anionów/kationów odpowiednio z utlenionymi jednostkami TPA i zredukowanymi NDI. Badania te przedstawiają zależności struktura–właściwości i dowodzą, że racjonalne projektowanie poprzez strategie bimetaliczne, kontrolowaną karbonizację i architektury donor–akceptor stanowi wszechstronną platformę dla magazynowania energii nowej generacji.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
| <p><b>Streszczenie pracy w jęz. angielskim (max 1400 znaków)</b></p> | <p>The growing demand for sustainable energy storage has accelerated the search for advanced electrode materials combining high capacity, long cycling stability, and versatility. Metal–organic frameworks (MOFs), MOF-derived carbons (CMOFs), and covalent organic frameworks (COFs) have emerged as promising candidates due to their tunable porosity, large surface areas, and redox-active sites.</p> <p>This thesis presents three complementary studies targeting distinct porous framework electrodes and electrochemical systems. The first investigates a bimetallic Mn-Fe-BTC MOF as a cathode for lithium metal batteries, achieving 1292 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and 687 mAh g<sup>-1</sup> after 100 cycles. The second study examines carbonized MOF-5 at 600–1000 °C for zinc-ion hybrid supercapacitors; the 1000 °C sample delivered 269 F g<sup>-1</sup> and 88% retention after 10,000 cycles. The third evaluates a donor–acceptor COF (TPA-NDI) for aluminum-ion batteries, with DFT calculations explaining the charge storage mechanism involving anion/cation interactions with oxidized TPA and reduced NDI units, respectively.</p> <p>Collectively, these studies establish clear structure–property relationships and demonstrate that rational framework design through bimetallic strategies, controlled carbonization, and donor–acceptor architectures offer a versatile platform for next-generation energy storage.</p> |
| <p><b>liczba stron</b></p>                                           | <p>220</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |