### **Development of Ionic Liquid-Assisted Manganese**

### **Oxide for Energy Storage Applications**

Thesis submitted to

Indian Institute of Technology Jammu For the award of the

Degree of

### **Doctor of Philosophy**

in **Physics** 

By

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Under the supervision of

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Department of Physics Indian Institute of Technology, Jammu Jammu and Kashmir, India (181221) June 2023

#### Declaration

I hereby declare that the matter embodied in this thesis entitled "**Development of Ionic Liquid-Assisted Manganese Oxide for Energy Storage Applications**" is the result of investigations carried out by me in the Department of ABC, Indian Institute of Technology, Jammu, India, under the supervision of **Dr. Rahul R. Salunkhe** and it has not been submitted elsewhere for the award of any degree or diploma, membership etc. In keeping with the general practice in reporting scientific observations, due acknowledgements has been made whenever the work described is based on the findings of other investigators. Any omission that might have occurred due to oversight or error in judgment is regretted. A complete bibliography of the books and journals referred in this thesis is given at the end of each chapter.

June, 2023 Indian Institute of Technology, Jammu (Signature) Ved Prakash Joshi 2018RPH0031

### Certificate

The thesis titled " **Development of Ionic Liquid-Assisted Manganese Oxide for Energy Storage Applications,**" submitted by **Ved Prakash Joshi** for the award of the degree of Doctor of Philosophy, has been carried out under my supervision at the Department of Physics of the Indian Institute of Technology, Jammu. The work is comprehensive, complete, and fit for evaluation.

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#### Abstract

The need for effective energy storage systems has prompted the investigation of new materials for supercapacitors and zinc-ion batteries. This thesis centers on synthesizing electrode materials based on manganese oxide, utilizing an approach that involves the assistance of an ionic liquid. The aim is to improve these energy storage systems' electrochemical efficiency and durability. Manganese oxide is synthesized using an eco-friendly and straightforward approach, using ionic liquids as templates and reaction media. Ionic liquids' distinct characteristics aid in regulating particle size, morphology, and crystal structure, leading to enhanced electrochemical features of the produced manganese oxide. Various characterization techniques, including X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and electrochemical analysis, are utilized to examine the structural, morphological, and electrochemical features of the produced manganese oxide materials. The results indicate the successful synthesis of manganese oxide nanorods with customized properties for energy storage purposes. The electrochemical efficacy of manganese oxide substances is assessed in zinc-ion batteries and supercapacitors. Manganese oxide demonstrates favorable characteristics such as high specific capacitance, exceptional cycling stability, and excellent rate capability in supercapacitor applications. These traits render it a promising contender for practical energy storage mechanisms. Manganese oxide exhibits excellent electrode performance in zinc-ion batteries, with notable features such as high reversible capacity, favorable rate capability, and good cycling stability. This thesis thoroughly investigates the ionic liquids assisted manganese oxide for use in supercapacitors and zinc-ion batteries. The findings demonstrate the capability of these materials as advanced electrode contenders for future energy storage devices, presenting noteworthy progressions in the realm of electrochemical energy storage.

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## List of Abbreviations and Acronyms

ESD	_	Energy storage devices
EESD		Electrochemcial Energy storage devices
SCs	-	Supercapacitors
TMOs	-	Transition metal oxides
LIBs	_	Lithium-ion batteries
PLBs	-	Post-lithium batteries
ZIBs	_	Zinc-ion batteies
AZIBs	_	Aqueosus zinc-ion batteries
SE	_	Specific energy
SP	_	Specific power
e	_	Electron
1D	-	One-dimensional
2D	_	Two-dimensional
3D	_	Three-dimensional
EDL	_	Electric double-laver
EDLCs	_	Electric double-layer capacitors
Zinc	_	Zn
SHE		Standard hydrogen electrode
HER		Hydrogen evolution reaction
SSA	_	Specific surface area
CNT	_	Carbon nanotubes
AC	_	Activated carbon
nm	_	Nanometer
SEI	_	Solid electrolyte interphase
XRD	_	X-ray diffraction
XRT	_	X-ray tube
FESEM	_	Field emission scanning electron microscope
FCCI	_	Flectron channeling contrast imaging
FRSD	_	Electron backscatter diffraction
HRTEM	_	High-resolution transmission electron microscope
FFIS	_	Electron energy loss spectroscopy
VDS	_	X ray photoelectron spectroscopy
AI 5 FTID	_	Fourier transform infrared
	_	Attenuated total reflectance
CV	_	Cuelie voltammetry
CCD	_	Coluenestatio cherge discharge
CE	_	Coulombia officionay
		Electrochemical impedance spectroscopy
		Columnostatic intermittent titration technique
		Chamical both deposition
	_	Drynower Emmett Teller
	_	Engager disconsister V new and stressonny
EDS	—	Analysis management
AK 2E	-	Analytic reagent
5년 2년	-	I nree electrode
2E	-	I wo electrode
HEK	-	Hydrogen evolution reaction
PBAs	_	Prussian blue analogues
TMDs	_	Transition metal dichalcogenides

PVDF	_	Polyvinylidene fluoride
NMP	_	N-Methyl-2-pyrrolidone
BB	-	1-Butyl-3-methylimidazolium tetrafluoroborate
MnO <sub>2</sub>	-	Manganese dioxide
BB-M	-	1-Butyl-3-methylimidazolium tetrafluoroborate
		derived MnO <sub>2</sub>
ET	-	1-Ethyl-3-methylimidazolium
		bis(trifluoromethylsulfonyl)imide
ET-M	-	1-Ethyl-3-methylimidazolium
		bis(trifluoromethylsulfonyl)imide derived MnO <sub>2</sub>
BT	_	1-Butyl-3-methylimidazolium
		bis(trifluoromethylsulfonyl)imide
BT-M	_	1-Butyl-3-methylimidazolium
		bis(trifluoromethylsulfonyl)imide derived MnO <sub>2</sub>
ASC	-	Asymmetric supercapacitor
NiO	-	Nickel oxide
$Co_3O_4$	-	Cobalt oxide
IL	-	Ionic liquid
SS	-	Stainless steel
MO	-	MnO <sub>2</sub> synthesize using chemical precipitate
		method
ILMO	-	IL-derived MnO <sub>2</sub>
MnSO <sub>4</sub> .H <sub>2</sub> O	-	Manganese sulfate monohydrate
NH4OH	-	Ammonium hydroxide
ZnSO <sub>4</sub> .7H <sub>2</sub> O	-	Zinc sulfate heptahydrate
KMnO <sub>4</sub>	-	Potassium permanganate
$H_2O_2$	-	Hydrogen peroxide
OCV	-	Open circuit voltage
SOC	-	State of charge
ICDD	-	International Centre for Diffraction Data
FWHM	-	Full width at half maxima
R <sub>CT</sub>	-	Charge transfer resistance
Z <sub>Re</sub>	-	Real impedance
Z <sub>Im</sub>	-	Imaginary impedance
SAED	-	Selected area electron diffraction

## List of Symbols and Units

S	_	Seconds
h	_	Hours
Wh kg <sup>-1</sup>	_	Watt Hour per
		Kilograms
W kg <sup>-1</sup>	_	Watt per
		Kilograms
Н	_	Hours
°C	_	Degree Celsius
Ω	_	Ohm
cm	_	Centimeter
nm	_	Nanometer
%	_	Percentage
F g <sup>-1</sup>	_	Farad per Gram
$mV s^{-1}$	_	Milli Volt per
		Second
mg	_	Milli Gram
mAh g⁻¹	_	Milli Hour per
		Gram
Å	_	Angstrom
$\mathcal{E}_0$	_	Permittivity of
		free space
$\mathcal{E}_r$	_	Relative
		permittivity
τ	_	Relaxation time
Hz	_	Hertz
at%	_	Atomic percent
eV	_	Electron Volt

### **List of Publications**

- Joshi, V. P.; Kumar, N.; Pathak, P. K.; Tamboli, M. S.; Truong, N. T. N.; Kim, C. D.; Kalubarme, R. S.; Salunkhe, R. R. Ionic Liquid Assisted Synthesis of Mixed Phase Manganese Oxide Nanorods for High-Performance Aqueous Zinc Ion Battery. ACS Appl. Mater. Interfaces https://doi.org/10.1021/acsami.3c01296, 2023.
- Joshi, V. P.; Kumar, N.; Yadav, R. S.; Pathak, P. K.; Kornweitz, H.; Salunkhe, R. R. Nanoarchitectured Cobalt Ruthenium Phosphate for High-Performance Asymmetric Supercapacitor Application. *Batteries & Supercaps* (Submitted) 2023.
- 3. Joshi, V. P.; Pathak, P. K.; Kumar, N.; Salunkhe, R. R. Asymmetric Supercapacitors Using Manganese Oxide Nanorods and Activated Carbon. *ChemistrySelect* 2022, *7*, e202203183.
- Joshi, V. P.; Sahoo, B.; Kumar, N.; Pathak, P. K.; Rath, D.; Salunkhe, R. R. Mixed Phase Nickel-Cobaltite for High Energy Density Flexible Solid-State Supercapacitor using Cathodic Overpotential Synthesis Route. *ChemNanoMat* 2023, e202200571.
- Pathak, P. K.; Joshi, V. P.; Kumar, N.; Salunkhe, R. R. Sea-Urchin-like Iron-Cobalt Phosphide as an Advanced Anode Material for Lithium-Ion Batteries. *Mater. Adv.* 2022, 3, 7235–7240.
- Joshi, V. P.; Kumar, N.; Salunkhe, R. R. Nanoporous Metal Oxides for Supercapacitor Applications. In *Chemically Deposited Nanocrystalline Metal Oxide Thin Films*; Springer International Publishing: Cham, 2021; pp 601–621.

### **List of Conferences**

- Ved Prakash Joshi, Rahul R. Salunkhe, High-performance aqueous zinc ion batteries of mixed-phase manganese oxide nanorods, International Conference on Nanotechnology for Better Living, May 25-29,2023, NIT Srinagar, J & K, India
- Ved Prakash Joshi, Rahul R. Salunkhe, Ionic liquid assisted growth of manganese oxide nanorods for long life asymmetric supercapacitors, National Conference on Energy Materials & Devices, December 16-18, 2022, IIT Jodhpur, Rajasthan, India.
- Ved Prakash Joshi, Prakash Pathak, Rahul R. Salunkhe, α-MnO<sub>2</sub> nanorods for supercapacitors and Zinc-ion battery, Industry-Academia Conclave 2022, IIT Jammu, May 20-21, 2022, Convention center, Jammu, J & K, India.
- 4. Ved Prakash Joshi, Rahul R. Salunkhe, α-MnO<sub>2</sub> nanorods for long life asymmetric supercapacitors, Energy Materials & Device Physics, IIT Jammu, Department of Physics, December 20-21, 2021, Jammu, J & K, India.

## **Introduction and Literature Background**

#### Overview

This chapter introduces energy storage devices (ESD) and the involvement of transition metal oxides (TMOs) in electrodes for supercapacitors (SCs) and Zinc-ion batteries (ZIBs). The chapter addresses the current situation where population expansion, urbanization, and industrialization have increased energy consumption over time. However, burning fossil fuels still meet most of the world's energy demands, contributing to climate change and other environmental issues. This chapter then discusses how clean and green energy storage options are essential for achieving net-zero emissions. SCs and batteries have the ability to store energy generated from renewable sources and discharge it as required, thereby ensuring a dependable and consistent energy supply. ESD can also improve energy availability in rural areas that are difficult to connect to the grid. The chapter also explores the advantages of TMOs for ESD and highlights the inability of classical materials to achieve high device performance. This chapter presents a comprehensive analysis of the literature concerning the performance of TMOs in SCs and ZIBs. The chapter includes a tabulated overview of the existing research. Furthermore, the fundamental characteristics of ionic liquids (ILs) as precursor for TMOs are explored, and the potential application in ESD is assessed. Finally, the chapter concludes by discussing the purpose and arrangement of the dissertation.

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#### 1.1 Introduction

The COVID-19 pandemic and the Russia-Ukraine conflict have significantly impacted the global energy market. The pandemic led to decreased demand for oil and gas, causing prices to drop, while the war in Ukraine raised concerns about energy security. Figure 1.1 (a) displays global fossil fuel consumption data for 2021, as published by Our World in Data.<sup>[1]</sup>

a Fossil fuel consumption, 2021



**Figure 1.1** (a) Fossil fuel consumption worldwide in 2021, based on data from Our World in Data. (b) Breakdown of fossil fuel consumption by type (coal, oil, and natural gas).<sup>1</sup> (c) Renewable energy generation by technology from 2010 to 2021, based on the Net Zero scenario.

The figures offer insight into the annual total energy consumption of various nations. Figure 1.1 (b) shows the worldwide utilization of coal, oil, and gas from 1800 to the present. Since 1950, there has been a significant increase in the consumption of fossil fuels, and this usage

has approximately doubled since 1980. Additionally, there has been a shift in fuel preference from relying solely on coal to oil and natural gas. Coal is becoming less popular as an energy source in many world regions while the oil and gas industries are rapidly expanding. These events have accelerated the shift towards renewable energy sources, with many countries implementing policies to support the transition. Figure 1.1 (c) show the increasing consumption of renewable energy solutions in the last decade. Solar is the fastest-growing technology; however, the 150 GW added in 2021 is barely one-third of the average annual additions needed to fulfil Net Zero Scenario objectives. Hydropower and biofuel growth should be twice the average of the last five years, while wind installations should double. These popular technologies require significantly more work to align with the Net Zero Scenario trend.<sup>[2]</sup> Solar, wind, and hydropower still supply most of the green energy compared to other sources. The move towards renewable energy sources will reduce the environmental impact of energy consumption, improve energy security, and promote economic growth.

#### **1.2 Renewable Energy and Challenges**

Climate change and the running down of fossil fuels necessitate using sustainable and renewable resources to address these challenges. The importance of safe and efficient energy storage and distribution rises as the globe moves towards renewable energy sources. Energy production from solar, hydro, biomass, and wind are consequently increasing.<sup>[3,4]</sup> Electrochemical energy storage and distribution innovations are essential due to the limited availability of hydro and biomass resources and the intermittent nature of wind and solar energy. These innovations should focus on accommodating power from renewable sources and addressing the challenges their intermittent nature poses.<sup>[5]</sup> There is a continuous global demand for clean energy storage and delivery, driving the development of new technologies. This process is complex and challenging, requiring advancements in material science, energy conversion storage efficiency, and safety. Despite these challenges, the development of such technology is critical to achieving a sustainable energy future. Renewable energy sources including sun, hydro, wind, and biomass are depicted in Figure 1.2. which offer clean energy that can be stored in ESD. Transitioning from fossil-based to renewable energy can lead to energy savings and a more streamlined energy delivery system by generating electricity onsite from renewable sources. This requires research into electrochemical energy storage (EES) technologies and materials to provide a consistent energy source. The ESD includes SCs, batteries, and fossil fuels, which can be utilized in electric vehicles, smart grids, residential and industrial applications.



**Figure 1.2** Schematic depiction of renewable energy sources and ESD, along with their diverse applications.

#### **1.3 Electrochemical Energy Storage Devices (EESD)**

EESD change electrochemical energy into electrical energy using either electrosorption or redox reactions.<sup>[6]</sup> Batteries, fuel cells, and SCs are practical and effective energy conversion and storage devices. As a result of the ground-breaking research conducted by Whittingham, Scrosati, and Armand, Sony launched lithium-ion batteries (LIB) in 1990.<sup>[7]</sup> The energy density (ED) of these batteries, which can reach 180 Wh kg<sup>-1</sup>, makes them the best available. Still, they also come at a high price. Despite extensive work on producing Li-ion and other improved secondary batteries using nanomaterials, until recently, SCs received far less attention. Li-ion batteries' relatively sluggish power delivery or absorption has resulted in the demand for quicker and more powerful ESD.<sup>[8]</sup>

SCs have received increased attention in recent years due to their high specific power (SP), long lifespan, and ability to bridge the SP and specific energy (SE) gap between capacitors (high SP) and batteries/fuel cells (high SE).<sup>[9]</sup> For over 20 years, researchers have been exploring and examining these devices. Figure 1.2 shows the main components of various types of these systems. Figure 1.3 demonstrations a Ragone plot showing the SE, and SP relationship for the most crucial ESD. They have a different way of storing and delivering electricity than conventional and fossil fuels. But we need to make significant changes to their performance to meet the higher demands of future systems, such as portable electronics, hybrid electric vehicles, and large industrial equipment. We can do this by making new materials and learning more about the nanoscale electrochemical interfaces.



Figure 1.3 Ragone plot shows the SP vs. SE for different ESD,

**Table 1.1** Analysing the characteristics of ESD such as standard capacitors, SCs, and batteries to various performance criteria.

Parameters	Capacitor	SCs	Battery	
C-V curve	Current (A)	Current (A)	Current (A)	
Cycle life	>500000	>100000	<1000	
Cell voltage	0-1 V	0-4 V	1-5 V	
Capacitance/capacity	~µF to mF range	~ upto	-	
		1000 F		
SE (Wh kg <sup>-1</sup> )	<0.1	1-10	10-200	
SP (W kg <sup>-1</sup> )	>10000	1000-2000	50-200	
Kinetics	Ultra-fast	Very fast	Slow to fast	
Nature of charge	Electrostatically	Reversible ion	Intercalation/deintercala	
storage		adsorption/ redox	tion, or change in	
		reaction/intercalati	oxidation state	
		on		
Materials	Metals	Carbon-	Materials with high	
		based/transition	theoretical capacity	
		metal-based	(LiCoO <sub>2</sub> , LiMn <sub>2</sub> O <sub>4</sub> )	
		oxides/hydroxides		
		/sulfides		
Charge/discharge time	<b>Charge/discharge time</b> $10^{-6}-10^{-3}$ (s)		0.3-10 (h)	
i-v relationship	i ∝ v	$i \propto v^b \ (0.5 \le b \le 1)$	$i \propto v^{0.5}$	
Limitation	-	Electrolyte and	Reaction kinetics,	
		electrode	Conductivity of active	
		resistivity/kinetic	material	
		limitation		

**Table 1.1** summarises the main differences between conventional capacitors, SCs, and batteries. The most notable thing is that SCs have decent SE and SP values despite their short

charge-discharge times. Unlike batteries, SCs have a long cycle life that is worth considering. However, rechargeable batteries have higher SE and SP values but need longer charge times.

#### **1.4 TMOs for Energy Storage**

The significance of electrode materials in ESD, such as batteries and SCs, is paramount. The device's performance is determined by various factors such as SE, SP, and cycle life.<sup>[10]</sup> The enhancements in electrode materials, exemplified by LIB and SCs based on carbon,<sup>[11]</sup> metal oxide/hydroxide/sulfides/carbide,<sup>[12]</sup> MXene,<sup>[13]</sup> and polymer,<sup>[14]</sup> have substantially elevated these energy storage systems' overall efficiency and capabilities. Metal oxides present various benefits compared to carbon-based materials, MXene, and polymer-based electrodes when used in energy storage devices. Metal oxides possess significant theoretical capacity, indicating their potential to store higher energy.<sup>[15]</sup> They offer enhanced stability, facilitating prolonged cycling and heightened durability.<sup>[16]</sup> Furthermore, metal oxides present the potential for multi-electron redox reactions, allowing for increased energy density.<sup>[17]</sup> In contrast, MXene exhibits a layered structure in two dimensions, enabling rapid ion diffusion and adequate charge transportation and improving power density.<sup>[18]</sup> The adjustability of their surface chemistry facilitates enhanced electrochemical efficacy and adaptability to diverse electrolytic environments. Electrodes based on polymers present several benefits, such as flexibility, low weight, and straightforward manufacturability.<sup>[19]</sup> It is possible to engineer them in a manner that outcomes in a high specific surface area (SSA) and porosity, thereby facilitating growth in charge storage capacity. In addition, polymers offer mechanical durability and chemical resilience, thereby enhancing the overall lifespan of the energy storage apparatus.<sup>[20]</sup> Metal oxides are low-cost and easily synthesized. Using metal oxides in electrodes is mainly responsible for ESD success. In Figure 1.4 main advantages of TMO. It shows multiple oxidation state, high specific capacity/capacitance, high conductivity, low-cost in nature. Pseudocapacitance arises from surface-bound reversible redox reactions or unrestricted reactions in contact with an electrolyte, rather than solid-state ion diffusion.<sup>[21]</sup> Metal oxides have demonstrated at least an order of magnitude greater capacitance/capacities and energy densities than carbon-based materials.<sup>[22]</sup> However, due to these ongoing reactions, the morphology of the metal oxide materials can get deformed, and the initial phase might be altered, leading to poor cycle stability for commercial applications.<sup>[23]</sup> They also show electrochemical faradaic reactions between ions at the electrolyte and the electrode in suitable potential ranges. Metal oxides such as RuO<sub>2</sub>,<sup>[24]</sup> MnO<sub>2</sub>,<sup>[25]</sup> NiO,<sup>[26]</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>[27]</sup> Co<sub>3</sub>O<sub>4</sub>,<sup>[28]</sup> etc., are used in energy storage devices for electrode material. Their potential use as a

pseudocapacitive material has been investigated using various synthesis methods. Oxide materials based on manganese are advantageous for ESD due to their tunable redox behavior, high theoretical specific capacitance, large potential window, low-priced, and low environmental impact.<sup>[29]</sup> The unique tunnel structure of manganese oxide allows for bulk redox reactions and a more comprehensive range of available oxidation states than with most other transition metals.<sup>[30]</sup> The disadvantages of manganese oxide include limited cycle stability and poor electrical conductivity.<sup>[31]</sup> Therefore, scientists strive to enhance the functionality of manganese oxide-based electrodes by modifying their morphology, mixing in conductive species, and producing nanostructures.



Figure 1.4 Main advantages of TMO for ESD.

#### 1.4.1 Properties of TMOs for Energy Storage

Metal oxides have been the subject of intense study for ESD due to their several properties, such as good surface area, oxidation state, high electrolyte and electrode interaction zone, short ion distances path, and in some cases, electrochemical reactions with high mass loading become possible. The performance of each specific electrode depends on various factors, including the production of a suitable nanomaterial, as well as the design and construction of the electrode.

**Porosity:** Porosity is the existence of empty spaces or voids inside a substance, such as a metal oxide, and is referred to as the presence of porosity. These spaces give surface area for

reactions to occur and can assist the passage of ions or electrons, which can be utilized in ESD. Due to their large SSA, metal oxides with high porosity have demonstrated potential for use as electrodes in SCs and batteries. One example of such a material is nanoporous materials. However, managing porosity is essential to obtaining optimal performance, as either an excessive amount of porosity or an insufficient amount of porosity can have a detrimental influence on the energy storage capabilities of the material.<sup>[32]</sup> Regarding the effectiveness of energy storage, the size and distribution of pores in metal oxide are two crucial factors to consider. Micropores are tiny pores with dimensions ranging from 1-2 nm. They are responsible for the high SSA and the fast ion diffusion. Mesopores have sizes ranging from 2 to 50 nm and are responsible for increased storage capacity and improved conductivity. Macropores are bigger holes that have sizes that are greater than 50 nanometres, and potential to play a part in promoting mass movement and accommodating volume changes during electrochemical processes.<sup>[33]</sup> More evidence for the significance of pore size optimizations in energy storage devices comes from the heuristic model published in 2006 by Chimola et al. for electrolyte ion size matching with pore size in the considerable augmentation of capacitance values.<sup>[34]</sup>

**Surface area:** Metal oxides' ability to store energy relies mainly on their surface area. More electrochemical processes may occur with a larger surface area, allowing for more excellent energy storage. Electrode materials in batteries and SCs have been shown to benefit from metal oxides with high surface areas, such as those having nanoporous architectures. However, surface area management is essential for optimal energy storage since too much can cause instability and poor performance. Therefore, it is crucial to investigate and enhance the surface area to create effective energy storage materials. Large surface areas coupled to pore channels filled with electrolytes allow for rapid electron and metal ion diffusions in nanoporous architecture.

**Oxidation state:** Many transition metals have numerous readily available stable oxidation states, enabling the facile oxidation or reduction of one oxide to another while preserving the morphology.<sup>[35]</sup> In ESD like batteries and SCs, a metal oxide's oxidation state is crucial in the material's capacity to store and release energy. For instance, these compounds may store more electrical charge because there are more opportunities for electron transport in high-oxidation-state metal oxides. That's why they work so well in large energy storage systems. In addition, a metal oxide's stability and cycling performance during charging and discharging cycles can be affected by the degree to which the oxide has been oxidized.<sup>[36]</sup> Longer cycle

life and higher performance can be achieved using oxides that maintain a constant oxidation state. The effectiveness of energy storage devices relies on several factors, including the metal oxide's electrical conductivity and surface area, which can be affected by its oxidation state. Generally, a metal oxide's oxidation state is essential in deciding whether it may be used in energy storage applications.

**Conductivity:** ESD need high conductivity for charge collection and transfer. Lowtemperature synthetic procedures that create out-of-equilibrium lattice defects can increase ionic and electronic conductivity.<sup>[37]</sup> The conduction band receives electrons (e<sup>-</sup>) to compensate for positively charged oxide ion vacancies caused by oxygen removal. Surfaces respond quickly, resulting in a positive surface potential. Due to extra electrons, oxygendeficient oxides with a high SSA are expected to have a higher electrical conductivity.<sup>[38]</sup> TMO may be doped with additional ions from the reaction media during synthesis. These may be adsorbed at the surface to create charge space regions or integrated into bulk oxide to create more ionic defects.<sup>[39]</sup> Thus, many adsorbed or dissolved dopant ions will increase oxide conductivity.

**Tunable free volume:** The capacity to control the amount of free space or voids inside a material or structure is known as tunable free volume. Metal oxides' highly tunable free volume is crucial for improving their performance in battery applications. Researchers have shown that modifying the free volume in the metal oxide electrode can improve the SSA and porosity of the material, enhancing ion transport and the material's ability to store energy. Adjusting the free volume, battery life, and performance can be improved by influencing the electrode's structural stability and cycling performance. In metal-ion batteries, oxide electrodes expand greatly in volume upon ion insertion, it allows the active material to expand into the empty spaces.<sup>[40]</sup> However, a too-porous structure can diminish the electrode's volumetric storage capacity. Thus, it is crucial to find the optimal packing density.

**Morphology:** The efficiency of a metal oxide battery can be drastically altered by its morphology. The term "morphology" describes the atomic structure and arrangement of the oxide substance. The oxide's surface area and capacity to support effective charge transfer during energy storage operations can be affected by particle size, shape, and porosity. Electrochemical performance, including energy storage capacity, cycle stability, and overall efficiency, can be improved by carefully designing the morphology of materials. Therefore, the creation of high-performance energy storage systems necessitates the careful study of

metal oxide morphology. Altering the structure and morphology of metal oxides is presented as a viable solution to these problems. One-dimensional (1D) nanostructures, twodimensional (2D) nanosheet, and three-dimensional (3D) nanotubes interconnected and porous architectures are just a few examples of the types of metal oxide nanomaterials that can be used to improve the rate capability of metal oxide electrodes by reducing the diffusion distance and increasing the active SSA for ions during the intercalation processes. These nanomaterials' structural and cyclic stability can be improved because of the substantial void space provided by the hierarchical pores within or between them.

Low toxicity and environmental impact: Nanomaterials that undergo substantial chemical reactions upon exposure to external conditions are increasingly used in cutting-edge nanotechnologies. Rapid increment in the production of complex TMOs containing elements like Co and Ni that have the potential for considerable detrimental biological effects are caused by the extensive adoption of LIB for energy storage in mobile gadgets and electric cars.<sup>[41]</sup> To help evaluate the environmental effect of energy storage technologies, this Perspective summarises some of the technical factors underlying complex oxide materials. It illustrates some of the chemical processes that need to be understood.

#### 1.4.2 Limitation of the TMOs for Energy Storage

TMO have a lot of potential as electrode materials for ESD, but they also have several drawbacks. A significant hurdle is their poor electrical conductivity, which might prevent effective charge transfer during energy storage procedures. Large volume fluctuations occur in many TMOs when charging and discharging, which causes mechanical stress and eventual material breakdown. Inadequate cycle stability is problematic since repetitive charging and discharging might irreversibly alter the oxide's structure. The high price and restricted supply of some transition metals can also be obstacles to the widespread manufacture of these materials. Last but not least, there is rising concern over the environmental effect of their manufacturing and disposal. Resolving these issues is vital for expanding the use of TMO in energy storage.

#### 1.4.3 Literature Survey for Different TMOs for SCs

TMOs have the potential to achieve significant levels of energy storage, particularly when utilized as electrode materials for SCs, because of their inexpensive cost, eco-friendly, and high capacitance. TMOs have been demonstrated to be an advanced electrode material for high SE and high SP for ESD. Nanoarchitecture design, mixing oxide composites with several

oxidation states are examples of such approaches. High theoretical specific capacitances, less expansive, and reversible redox reactions make TMOs (Ni, Co, Fe, Mn, V, etc.) a popular alternative to carbon-based SCs. Suitable electrochemical activities can be found in TMOs, although their typically poor conductivity reduces their rate capability. As a result of their low ionic, and electronic conductivities, their actual practical capacitances greatly exceed theoretical predictions. **Table 1.2** shows different metal oxide/hydroxide-based electrodes reported in the literature for SC application. Introducing doping in TMOs to improve redox activity, conductivity and mixing oxide composites with various oxidation states are only a few of the recent ways investigated to adjust their nanostructures.

**Table 1.2** Different metal oxide/hydroxide-based materials reported in the literature for SC application.

<b>S.</b>	Materials	Electrolyte	Capacitance	Specific	Specific	Synthesis method	Ref.
No.			(F g <sup>-1</sup> )	energy	power		
				(Wh	(W		
				kg <sup>-1</sup> )	kg <sup>-1</sup> )		
1	ZnWO <sub>4</sub> /SnO <sub>2</sub>	2M KOH	56.7	-	-	Solvothermal	[42]
2	Amorphous MnO <sub>2</sub>	0.25M	200	_	_	Precipitation method	[43]
		Na <sub>2</sub> SO <sub>4</sub>					
3	λ-MnO <sub>2</sub>	0.5M	241	_	_	Wet solution method	[44]
		$K_2SO_4$					
4	E-MnO <sub>2</sub>	1M	115	-	-	Wet chemical method	[45]
		Na <sub>2</sub> SO <sub>4</sub>					
5	MnO <sub>2</sub>	1M	288	39.5	2000	Wet chemical method +	[46]
		Na <sub>2</sub> SO <sub>4</sub>				template method	
6	CuO/CuO <sub>2</sub> /Cu	3M KOH	1480	9.7	3748.4	Solgel method	[47]
7	CoMCNFs@MnO <sub>2</sub>	4M KOH	265	19.27	3628.3	Electrospinning +	[48]
						chemical bath deposition	
8	MnCo <sub>2</sub> O <sub>4</sub>	6M KOH	290	-	_	co-precipitation method	[49]
9	CMGP	1M NaCl	241	17	_	chemical	[50]
						oxidative polymerization	
						method	
10	NiO	1M KOH	1000	_	_	Electrodeposition	[51]
11	MnWO <sub>4</sub> -rGO	6M KOH	288	-	-	Hydrothermal	[52]

10			1 7 1			Ъ. Л. 11	[53]
	N1-WO <sub>3</sub>	2M KOH	171	-	-	Microwave irradiation	[33]
13	WO <sub>3</sub>	1M H <sub>2</sub> SO <sub>4</sub>	246	-	-	Microwave-assisted wet	[54]
						chemical route	
14	WO <sub>3</sub>	0.5M	148	-	-	precipitation	[55]
		$H_2SO_4$					
15	SnWO <sub>4</sub>	ЗМ КОН	242	-	-	Microwave synthesis	[56]
16	CNT-CoWO <sub>4</sub>	3M KOH	1486	12	-	Hydrothermal synthesis	[57]
17	RuO <sub>2</sub> .xH <sub>2</sub> O	0.5M	768	26.7	-	Sol-gel method	[58]
		H <sub>2</sub> SO <sub>4</sub>					
18	SnO <sub>2</sub>	0.1M	285	-	-	Sol-gel method	[59]
		Na <sub>2</sub> SO <sub>4</sub>					
19	In <sub>2</sub> O <sub>3</sub>	1M	190	-	-	Potentiodynamic	[60]
		Na <sub>2</sub> SO <sub>3</sub>					
20	Bi <sub>2</sub> O <sub>3</sub>	1M NaOH	98	-	_	Electrodeposition	[61]
21	V <sub>2</sub> O <sub>5</sub>	2M KCl	350	-	-	Solvothermal	[62]
22	Fe <sub>3</sub> O <sub>4</sub>	1M	170	-	-	Wet chemical	[63]
		Na <sub>2</sub> SO <sub>3</sub>					
23	Sr-RuO <sub>3</sub>	6M KOH	270	-	_	Direct optimizing	[64]
						pyrolysis	
24	Hydrous-RuO <sub>2</sub>	1M	236	18.7	500	Hydrothermal method	[65]
		Na <sub>2</sub> SO <sub>4</sub>					
25	SnO <sub>2</sub>	1M	260	27.2	24800	AAO template method	[66]
		Na <sub>2</sub> SO <sub>4</sub>					
		T	MO-based cor	nposite fo	r SC		
1	rGO/V <sub>2</sub> O <sub>5</sub>	1M H <sub>2</sub> SO <sub>4</sub>	120.6	24.12	17770	Chemical method	[67]
2	rGO/MnO <sub>2</sub>	1M	140.3	19.5	1864.3	Microwave irradiation	[68]
		Na <sub>2</sub> SO <sub>4</sub>					
3	Co <sub>3</sub> O <sub>4</sub> /rGO	1M KOH	278	-	-	Hydrothermal	[69]
4	MoO <sub>3</sub> /Graphene	1M	148	-	-	Solvothermal	[70]
		Na <sub>2</sub> SO <sub>3</sub>					
5	Graphene/NiO	6M KOH	429.7	-	-	Hydrothermal	[71]
6	Graphene/Fe <sub>2</sub> O <sub>3</sub>	3M KOH	445	63	-	Hydrothermal	[72]
7	rGO/WO <sub>3</sub>	1M H <sub>2</sub> SO <sub>4</sub>	287	-	-	Hydrothermal	[73]

8	3DG/TiO <sub>2</sub>	3M KOH	235.6	-	-	Chemical synthesis	[74]
9	Nb <sub>2</sub> O <sub>5</sub> /rGO	LiClO <sub>4</sub>	321	-	-	Hydrothermal	[75]
10	Fe <sub>3</sub> O <sub>4</sub> -rGO	1M KOH	169	-	-	Solvothermal	[76]
11	Fe <sub>2</sub> O <sub>3</sub> /NG	1M	260.1	-	-	Hydrothermal	[77]
		Na <sub>2</sub> SO <sub>4</sub>					
12	TiO <sub>2</sub> /C	0.5M	274.2	-	-	Hydrothermal	[78]
		Na <sub>2</sub> SO <sub>4</sub>					
13	Graphene/V <sub>2</sub> O <sub>5</sub>	1M	288	-	-	Hydrothermal	[79]
		Na <sub>2</sub> SO <sub>4</sub>					
14	rGO-NiFe <sub>2</sub> O <sub>4</sub>	1M	215.7	23.7	4500	Hydrothermal	[80]
		Na <sub>2</sub> SO <sub>4</sub>					
15	rGO/LaAlO <sub>3</sub>	1M KOH	283	57	22608	gel route and low-	[81]
						temperature combustion	
						method	
16	MnO <sub>2</sub> /3DGH	5M LiCl	345	7.4	3000	Electrodeposition	[82]
17	GA-RuO <sub>2</sub>	1M H <sub>2</sub> SO <sub>4</sub>	348	-	-	Template method	[83]
18	MnMoO <sub>4</sub> /CoMoO <sub>4</sub>	2M NaOH	204.1	28.4	-	Chemical synthesis	[84]
19	Ti-Fe <sub>2</sub> O <sub>3</sub> @PEDOT	5M LiCl	311.6	0.89	0.44 W	Hydrothermal method	[85]
				mWh	cm <sup>-3</sup>		
				cm <sup>-3</sup>			
20	CNT/MnO <sub>2</sub> /GR	1M	486.6	24.8	-	Electrodeposition	[86]
		Na <sub>2</sub> SO <sub>4</sub>					
21	Yb <sub>2</sub> O <sub>3</sub> /rGO	0.5M	240	26.8	-	Chemical precipitation	[87]
		Na <sub>2</sub> SO <sub>4</sub>				method	
22	Mn <sub>3</sub> O <sub>4</sub> ND@NG	EMIMBF <sub>4</sub>	158.9	1244	29900	Solvothermal	[88]
23	V <sub>2</sub> O <sub>5</sub> -rGO	1M LiClO <sub>4</sub>	129.7	13.3	625	Chemical precipitate +	[89]
						Hydrothermal	
24	MnO <sub>2</sub> /BPC	1M	139.6	-	-	Hydrothermal	[90]
		Na <sub>2</sub> SO <sub>4</sub>					
25	MnO <sub>2</sub> /HC	1M	340	33.3	14.8	Hydrothermal	[91]
		Na <sub>2</sub> SO <sub>4</sub>					
### 1.4.4 Literature Survey for Different TMOs for ZIB

The potential of TMOs as cathode materials for aqueous zinc-ion batteries (AZIBs) is widely acknowledged owing to their high theoretical capacity, sufficient reserves, cost-effectiveness, and diverse valence states. The limited conductivity, susceptibility to structural degradation, and sluggish reaction kinetics of TMOs have impeded their potential utilization in AZIBs. In Mn oxides (usually MnO<sub>2</sub>), zinc (Zn) is stored by four reaction mechanisms: coinsertion/extraction,  $Zn^{2+}$  intercalation, phase conversion, and dissolution-deposition



Figure 1.5 Typical illustrations of electrode materials that use the  $Zn^{2+}$  insertion/extraction process.

process.<sup>[92,93]</sup> These multi-electron reactions may create metal oxides with high specific capacities. Because of their promise as cathode materials for ZIBs, metal oxides with improved SSA, conductivity, and morphology are being developed. Volume expansion occurs during intercalation in most oxide topologies (of Mn and V), resulting in poor cyclic stability. For aqueous ZIB, the intercalation of Zn<sup>2+</sup> ions shown in **Figure 1.5** depicts the charging and discharging processes. According to previous studies, <sup>94,95</sup> High hysteresis in the charge-discharge process is another drawback of Mn- and V-based oxides as electrode materials.<sup>[94,95]</sup> In **Table 1.3**, AZIBs and the electrochemical behaviors of many metal oxides are reported based on the literature.

**Table 1.3** Different cathode materials, including metal oxide and carbon composite, reported in the literature for ZIB application.

S. No	Electrode	Electrolyte	Specific Synthesis		Cycling	Ref.
	material		capacity	method	stability	
			(mAh g <sup>-1</sup> )			
1	ZMO@PCPs	1M ZnSO <sub>4</sub> +	176.8 @	Hydrothermal	90.3%	[96]
		0.05M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	method		
2	ZMO NDs/rGO	1M ZnSO <sub>4</sub> +	207.6 @	Chemical	-	[97]
		0.1M MnSO <sub>4</sub>	0.2 A g <sup>-1</sup>	synthesis		
3	ZMO	1M ZnSO <sub>4</sub> +	134.7 @	Hydrothermal	59.2%	[98]
		0.05M MnSO <sub>4</sub>	86 mA g <sup>-1</sup>	method		
4	Porous ZMO	1M ZnSO <sub>4</sub> +	225 @	Chemical	80%	[99]
		0.1M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	synthesis		
5	ZMO@Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	1M ZnSO <sub>4</sub> +	172.6 @	Hydrothermal	92.4%	[100]
		0.1M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	method		
6	ZMO@N-	1M ZnSO <sub>4</sub> +	221 @	Hydrothermal	97.4%	[101]
	graphene	0.05M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	method		
7	ZMO@C	3M	150 @ 50	Chemical	94%	[102]
		Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	mA g <sup>-1</sup>	synthesis		
8	ZMO@C	2M ZnSO <sub>4</sub> +	481 @	Chemical	90%	[103]
		0.1M MnSO <sub>4</sub>	0.2 A g <sup>-1</sup>	synthesis		
9	ZMO/Mn <sub>2</sub> O <sub>3</sub>	1M ZnSO <sub>4</sub>	151.9 @	Solvothermal	-	[104]
			0.1 A g <sup>-1</sup>	method		
10	ZNCMO@N-	2M ZnSO <sub>4</sub> +	204.4 @	Hydrothermal	79%	[105]
	rGO	0.2M MnSO <sub>4</sub>	10 mA g <sup>-1</sup>	method		
11	α-MnO <sub>2</sub> /rGO-	3M	248.8 @	Hydrothermal	85.9%	[106]
	PPy	Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.5 A g <sup>-1</sup>	method		
12	α-MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	233 @ 83	Hydrothermal	63%	[107]
			mA g <sup>-1</sup>	method		
13	α-MnO <sub>2</sub>	2M ZnSO <sub>4</sub>	285 @	Hydrothermal	92%	[108]
			C/3	method		
14	γ-MnO <sub>2</sub>	Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	105 @ 10	Electrolytic	65%	[109]
		in	$\mu$ A/cm <sup>2</sup>	manganese		

		PC+EC+PVDF		dioxide		
15	γ-MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	285 @	Redox reaction	63%	[110]
			0.05	process		
			mA/cm <sup>2</sup>			
16	γ-MnO <sub>2</sub> -	2M ZnSO <sub>4</sub> +	301 @	Hydrothermal	64.1%	[111]
	graphene	0.4M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	method		
17	β-MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	270 @	Microwave-	75%	[112]
			0.1 A g <sup>-1</sup>	assisted		
				hydrothermal		
				method		
18	β-MnO <sub>2</sub>	3M	258 @	Hydrothermal	94%	[113]
		$Zn(CF_{3}SO_{3})_{2} +$	0.65 C	method		
		0.1M				
		Mn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>				
19	Mn <sub>3</sub> O <sub>4</sub>	2M ZnSO <sub>4</sub>	239.2 @	Chemical	73%	[114]
			0.1 A g <sup>-1</sup>	synthesis		
20	ε-MnO <sub>2</sub>	2M ZnSO <sub>4</sub> +	290 @ 90	Electrodeposition	0.0007%	[115]
		0.2M MnSO <sub>4</sub>	mA g <sup>-1</sup>		decay	
21	Na <sub>0.56</sub> V <sub>2</sub> O <sub>5</sub>	3M ZnSO <sub>4</sub> +	317 @	Hydrothermal	87%	[116]
		0.5 Na <sub>2</sub> SO <sub>4</sub>	0.1 A g <sup>-1</sup>			
22	Zn <sub>0.25</sub> V <sub>2</sub> O <sub>5</sub> .nH <sub>2</sub> O	1M ZnSO <sub>4</sub>	300 @ 1	Microwave	80%	[117]
			С	hydrothermal		
				technique		
23	Ca <sub>0.25</sub> V <sub>2</sub> O <sub>5</sub> .nH <sub>2</sub> O	1M ZnSO <sub>4</sub>	340 @	Hydrothermal	96%	[118]
			0.2 C	method		
24	K <sub>0.23</sub> V <sub>2</sub> O <sub>5</sub>	2M	284 @	Hydrothermal	92.8%	[119]
		Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	0.1 A g <sup>-1</sup>	method		
25	Mn <sub>0.15</sub> V <sub>2</sub> O <sub>5</sub> .nH <sub>2</sub> O	1M Zn(ClO <sub>4</sub> ) <sub>2</sub>	367@	Microwave	_	[120]
			0.1 A g <sup>-1</sup>	hydrothermal		
				technique		
26	Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	1M ZnSO <sub>4</sub>	248 @ 50	Hydrothermal	85%	[121]
			mA g <sup>-1</sup>	method		
27	Mn <sub>3</sub> O <sub>4</sub> @C	2M ZnSO <sub>4</sub> +	331.5@	Solvothermal	-	[122]

		0.2M MnSO <sub>4</sub>	0.2 A g <sup>-1</sup>	method		
28	VOPO <sub>4</sub>	21M	139 @	Chemical	93%	[123]
		LiTFSI/1M	0.05 A g <sup>-1</sup>	precipitation		
		Zn(Tr) <sub>2</sub>		method		
29	α-MnO <sub>2</sub>	2M ZnSO <sub>4</sub> +	272 @ 50	Hydrothermal	70%	[124]
		$1M MnSO_4 +$	mA g <sup>-1</sup>	method		
		0.1M H <sub>2</sub> SO <sub>4</sub>				
30	α-MnO <sub>2</sub> /OLC	1M ZnSO <sub>4</sub> +	218 @	Hydrothermal	93%	[125]
		0.1M MnSO <sub>4</sub>	123 mA	method		
			g <sup>-1</sup>			
31	MnO <sub>2</sub> NDs/rGO	2M ZnSO <sub>4</sub> +	294 @	Solvothermal	90.1%	[126]
		0.1M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	method		
32	V <sub>2</sub> O <sub>3</sub> @CD	3M ZnSO <sub>4</sub>	281.9 @	Evaporation-	89%	[127]
			50 mA g <sup>-1</sup>	induced self-		
				assembly		
				technique		
33	MnO	2M ZnSO <sub>4</sub>	272 @	-	80.7%	[128]
			0.1 A g <sup>-1</sup>			
34	δ-MnO <sub>2</sub>	1M ZnSO <sub>4</sub> +	170@	Chemical	-	[129]
		0.1M MnSO <sub>4</sub>	0.1A g <sup>-1</sup>	synthesis method		
35	Mn <sub>3</sub> O <sub>4</sub> @NC	2M ZnSO <sub>4</sub> +	280 @	Two steps	-	[130]
		0.1M MnSO <sub>4</sub>	0.1 A g <sup>-1</sup>	hydrothermal		
				method		

### 1.5 Ionic Liquid-Assisted TMOs for Energy Storage

EESD has entered a new era with the advent of ILs as an environmentally acceptable and promising reaction medium. In addition to serving as electrolytes in batteries and SCs, ILs are used as media for materials synthesis and components in the fabrication of highly designed functional materials.<sup>[131]</sup>. ILs are a class of molten salts that have garnered interest as solvents for metal oxide-based energy storage systems. The high thermal stability, good conductivity, low volatility, and wide potential window of ILs make them potential candidates for use in EESD. These qualities of ILs during the past decade have made them one of the most rapidly expanding "green" media.<sup>[132]</sup> Hydrophobicity, hydrophilicity, reactivity, and other properties

can be introduced into these materials due to their versatile synthesis methods. **Table 1.4** shows electrode materials synthesis using IL for SCs. The IL-assisted method provides several unique advantages, including the ability to regulate particle size and shape and to stabilize emerging phases.<sup>[133]</sup>

	IL-assisted metal oxide for SC								
S.	Materials	Electrolyte	Capacitance	Specific	Specific	Synthesis method	Ref.		
No.			(F g <sup>-1</sup> )	energy	power				
				(Wh	(W kg <sup>-1</sup> )				
				kg <sup>-1</sup> )					
1	Carbon/TiO <sub>2</sub>	1M KOH	152.8		-	Ionothermal	[134]		
						synthesis			
2	Co-Fe LDH	2M KOH	456	-	-	Ionothermal	[135]		
						synthesis			
3	Co <sub>3</sub> O <sub>4</sub>	2M KOH	238.4	-	-	Ionothermal	[136]		
						synthesis			
4	ZnCo <sub>2</sub> O <sub>4</sub>	2M KOH	311.26 mAh	21.2	12000	Ionothermal	[137]		
			g <sup>-1</sup>			synthesis			
5	RuO <sub>2</sub>	1M KOH	200	17.4	8200	IL-assisted	[138]		
6	Co(OH) <sub>2</sub>	3M KOH	859	-	-	Ionothermal	[139]		
						synthesis			
7	$\beta$ -Co(OH) <sub>2</sub>	6M KOH	613	20.05	13400	IL-assisted	[140]		
						hydrothermal			
8	β-Ni(OH) <sub>2</sub> /rGO	6M KOH	1875	-	-	IL-assisted	[141]		
						hydrothermal			
9	$Co_3O_4$	6M KOH	813.1	-	-	IL-assisted	[142]		
						hydrothermal			
10	Cu <sub>2</sub> O	6M KOH	790	64.2	10040	IL-assisted one-	[143]		
						pot synthesis			
11	NiO/CNT	1M H <sub>2</sub> SO <sub>4</sub>	521	_	_	IL-assisted	[144]		
						method			
12	Fe <sub>2</sub> O <sub>3</sub>	1М КОН	230		_	IL-assisted ball	[145]		
	10203		200						

Table 1.4 Different electrode materials, synthesized using IL for SCs application.

						milling	
13	$g-C_3N_4/\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	2.5M	260	-	-	IL-assisted	[146]
		$Li_2SO_4$				solvothermal	
14	NiCo <sub>2</sub> O <sub>4</sub>	2M KOH	764	-	-	IL-assisted	[147]
						synthesis	
15	rGO/SnO <sub>2</sub>	1M	1012	-	-	Two-step method	[148]
		Na <sub>2</sub> SO <sub>4</sub>				using IL	
16	MNN/IL-GP	1M	411	-	-	Electrodeposition	[149]
		Na <sub>2</sub> SO <sub>4</sub>				on IL-modified	
						graphene	
17	Cu <sub>2</sub> O	1M KOH	119	-	-	IL-assisted	[150]
						electrodeposition	
18	MnO <sub>2</sub> / PEDOT:	0.5M	533 F cm <sup>-3</sup>	-	-	Electrodeposition	[151]
	PSS/CNTs	Na <sub>2</sub> SO <sub>4</sub>				on IL-modified	
						CNTs	
19	NiOOH/Ni(OH) <sub>2</sub>	1M KOH	986	-	-	IL-assisted	[152]
						electrodeposited	
20	CuCo <sub>2</sub> O <sub>4</sub>	ЗМ КОН	421 mAh	-	-	DES assisted	[153]
			g <sup>-1</sup>			method	
21	NiCo <sub>2</sub> O <sub>4</sub>	6M KOH	879	54	_	Microwave-	[154]
						assisted synthesis	
22	Co <sub>3</sub> O <sub>4</sub>	3M KOH	1010	-	-	DES assisted	[155]
						hydrothermal	
23	RuCo <sub>2</sub> O <sub>4</sub>	2M KOH	372 mAh	59.7	32060	DES assisted	[156]
			g <sup>-1</sup>			method	
24	Mn <sub>3</sub> O <sub>4</sub> @N-	1M	183	34	-	DES assisted	[157]
	doped carbon	Al(NO <sub>3</sub> ) <sub>2</sub>				method	

By incorporating ILs into the synthesis and assembly of TMOs, it is possible to improve the performance and stability of the resulting materials. This has led to the development a range of ILs-assisted TMO based energy storage systems, which show great potential for use in high-performance batteries and SCs. Figure 1.6 (a) (metal oxide for ESD) shows the present literature report trend, and Figure 1.6 (b) (ILs-aided materials for ESD) illustrates their

widespread use in EESDs. It shows that the popularity of TMOs is constantly rising, and substantial research has been done in the last three years on metal oxides formed from ILs.



**Figure 1.6** Literature reported (a) metal oxide for energy storage and (b) metal oxide synthesized from IL for energy storage. The information was found on the Web of Science site.

### 1.6 Summary and Literature Gaps

SCs and ZIBs exhibit great potential as energy storage systems with diverse applications. The present summary elucidates the utilization of an approach involving IL for augmenting the efficacy of SCs and bridging the research void in this domain. The rationale for conducting this study is rooted in the imperative for energy storage solutions capable of providing optimal power density and extended cyclic stability. SCs benefit from quick charging and discharging rates, whereas ZIBs offer high energy density. Nonetheless, both technologies encounter obstacles such as restricted energy storage capacity and deterioration throughout recurrent charge-discharge cycles. To surmount these constraints, scientists have utilized an approach assisted by the IL, which requires the integration of ILs into the electrode constituents. The methodology mentioned above augments the capacitance and durability of SCs while simultaneously facilitating the reversible intercalation/deintercalation of Zn-ions in ZIBs. Despite notable advancements in SCs and ZIB research, a knowledge gap in ILs' influence on these technologies' electrochemical efficacy persists. By examining various compositions and concentrations of ILs, researchers endeavor to enhance the effectiveness of SCs and ZIB, filling the existing literature's void and propelling the progression of effective energy storage mechanisms. To summarise, implementing an approach involving ILs in

enhancing SCs and ZIBs exhibits the potential to augment their efficiency and fill the existing research void. Additional investigation in this field will make a valuable contribution to advancing energy storage technology, creating more efficient ESD with improved SP and cycle life.

### **1.7 Thesis orientation**





This thesis aims to investigate the IL-assisted synthesis of metal oxide materials, specifically MnO<sub>2</sub>, for their application in energy storage devices such as SCs and ZIBs. The unique properties of ILs, such as their ionic conductivity and ability to act as templates for the formation of nanomaterials, make them attractive candidates for use in synthesizing metal oxides. This work aims to develop high-performance energy storage devices with improved efficiency and durability by optimizing the synthesis process and characterizing the resulting materials. The production and configuration of SC electrodes and cathode material for ZIBs

are crucial, necessitating specific properties such as a broad potential window, excellent conductivity, high SE, high SP, and quick charging/discharging rates. Thus, the amalgamation of the advantages of IL and  $MnO_2$  presents a highly efficient approach to optimize the electrochemical performance of metal oxide. Regrettably, there is no available documentation regarding the synthesis of  $MnO_2$  synthesized using ILs utilizing for SC and ZIB. Therefore,  $MnO_2$  has been selected as the material of interest for the current investigation to explore its potential for use in SCs and ZIBs. Figure 1.7 Shows the goals of this work. More specifically, this thesis seeks to accomplish the following objectives:

- > To design and development of  $MnO_2$  by simple and cost-effective IL-assisted method.
- To investigate the impact of IL on structural and morphological properties of MnO<sub>2</sub>, further to optimize a phase for optimum performance.
- > To optimize IL for stable and high performance for SCs and battery applications.
- Advanced characterization methods such as XPS, FESEM, HRTEM, XRD, Raman spectroscopy, and N<sub>2</sub> adsorption-desorption analyses for surface area investigations will be used to investigate the physiochemical characteristics of synthesized materials.
- To employ CV, GCD, EIS, and GITT to analyze the electrochemical characteristics of assynthesized materials electrodes to determine their capability for usage in SCs and Zn-ion batteries.

This thesis comprises five chapters, with the present chapter as an introductory section. The subsequent sections describe the arrangement and content of these chapters.

**Chapter 1.** The first chapter provides an outline of the significance of energy storage devices in modern society, focusing on the environmental impact of energy storage solutions and the relevance of SCs and ZIBs. In addition, it examines the wide variety of existing electrode materials for ZIBs and SCs, including their benefits and limitations exhaustively. It also highlights the unique properties of metal oxides derived from the IL, making them superior to the chemical synthesis for charge storage. In addition, a comprehensive tabular summary of the numerous metal oxide-based materials used as electrodes for both ZIBs and SCs is provided, emphasizing their electrochemical behavior.

**Chapter 2.** It summarizes the compounds and materials utilized in the research and the numerous synthesis protocols employed. Using a room-temperature precipitation technique, we synthesized MnO<sub>2</sub> and IL-assisted MnO<sub>2</sub> for our study. In addition, the details of preparing MnO<sub>2</sub> nanostructures by different ILs are discussed in depth. The chapter also discusses the tools and methods used to describe the materials as they are made, such as XRD, Raman spectroscopy, BET nitrogen adsorption-desorption analysis, FESEM, EDS, HRTEM, and XPS. The chapter also talks about how to prepare electrodes, analyze electrochemistry, and use methods to figure out the electrochemical features of SCs and LIBs.

**Chapter 3.** Here, we show how to make MnO<sub>2</sub> by green ionothermal synthesis at room temperature. During this process, we changed the ILs to improve synthesis. For the preparation of MnO<sub>2</sub>, we have used ILs called 1-Ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [ET], 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [BT], and 1-Butyl-3-methylimidazolium tetrafluoroborate [BB]. ET-M, BT-M, and BB-M are the abbreviations for the MnO<sub>2</sub> made by these different IL. Furthermore, all the samples are also tested for SCs applications.

**Chapter 4**. This chapter uses IL to synthesize 1D, mixed-phase  $MnO_2$  nanorods. Morphological, structural, and XPS studies for IL-assisted  $MnO_2$ , here IL act as a morphology-directing agent, and introducing mixed phases. The  $MnO_2$  nanorods synthesized this way are used as a cathode material in a coin-cell arrangement for ZIBs. Ex situ XPS, XRD, and comprehensive electrochemical investigation confirm high reversibility in the insertion/extraction of  $Zn^{2+}$  from  $MnO_6$  octahedra. Based on the results of this research,  $MnO_2$  nanorods may be used to create high-performance, long-lasting battery electrode materials.

**Chapter 5.** This chapter introduce a synopsis of the dissertation's findings and outcomes. The research shows that SCs and ZIBs can use electrodes made from pure  $MnO_2$  and IL-derived  $MnO_2$ . Large SSA, hierarchical pore structure, morphology, and better ionic conductivity contribute to the enhanced performances of SCs and ZIBs cathode applications. This research on  $MnO_2$  nanorods has future possibilities beyond only energy storage and conversion.

#### Reference

- [1] H. Ritchie, M. Roser, P. Rosado, *Our World Data* 2022.
- [2] "Renewable Electricity 2022, International energy agency, https://www.iea.org/reports/renewable-electricity. (accessed 2023-05-01),"
- [3] A. Qazi, F. Hussain, N. A. Rahim, G. Hardaker, D. Alghazzawi, K. Shaban, K. Haruna, *IEEE Access* 2019, 7, 63837–63851.
- [4] A. A. Kebede, T. Kalogiannis, J. Van Mierlo, M. Berecibar, *Renew. Sustain. Energy Rev.* 2022, 159, 112213.
- [5] P. Simon, Y. Gogotsi, *Nat. Mater.* **2008**, *7*, 845–854.
- [6] P. Li, Y. Bräuniger, J. Kunigkeit, H. Zhou, M. R. Ortega Vega, E. Zhang, J. Grothe, E. Brunner, S. Kaskel, Angew. Chemie Int. Ed. 2022, 61,
- [7] J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359–367.
- [8] Y. Wang, L. Zhang, H. Hou, W. Xu, G. Duan, S. He, K. Liu, S. Jiang, J. Mater. Sci. 2021, 56, 173–200.
- [9] S. Najib, E. Erdem, *Nanoscale Adv.* **2019**, *1*, 2817–2827.
- [10] Y. Wang, X. Wu, Y. Han, T. Li, J. Energy Storage 2021, 42, 103053.
- [11] R. Kumar, E. Joanni, S. Sahoo, J.-J. Shim, W. K. Tan, A. Matsuda, R. K. Singh, *Carbon N. Y.* 2022, 193, 298–338.
- [12] N. S. Shaikh, S. B. Ubale, V. J. Mane, J. S. Shaikh, V. C. Lokhande, S. Praserthdam,
   C. D. Lokhande, P. Kanjanaboos, *J. Alloys Compd.* 2022, 893, 161998.
- [13] K. Liang, R. A. Matsumoto, W. Zhao, N. C. Osti, I. Popov, B. P. Thapaliya, S. Fleischmann, S. Misra, K. Prenger, M. Tyagi, E. Mamontov, V. Augustyn, R. R. Unocic, A. P. Sokolov, S. Dai, P. T. Cummings, M. Naguib, *Adv. Funct. Mater.* 2021, *31*, 2104007.
- [14] S. Sardana, A. Gupta, K. Singh, A. S. Maan, A. Ohlan, J. Energy Storage 2022, 45, 103510.

- [15] M. Kandasamy, S. Sahoo, S. K. Nayak, B. Chakraborty, C. S. Rout, *J. Mater. Chem. A* 2021, *9*, 17643–17700.
- [16] Y. Ma, X. Xie, W. Yang, Z. Yu, X. Sun, Y. Zhang, X. Yang, H. Kimura, C. Hou, Z. Guo, W. Du, *Adv. Compos. Hybrid Mater.* 2021, *4*, 906–924.
- [17] C. An, Y. Zhang, H. Guo, Y. Wang, Nanoscale Adv. 2019, 1, 4644–4658.
- [18] S. Venkateshalu, A. N. Grace, Appl. Mater. Today 2020, 18, 100509.
- [19] Z. Wang, M. Zhu, Z. Pei, Q. Xue, H. Li, Y. Huang, C. Zhi, *Mater. Sci. Eng. R Reports* 2020, 139, 100520.
- [20] Y. Wang, F. Chen, Z. Liu, Z. Tang, Q. Yang, Y. Zhao, S. Du, Q. Chen, C. Zhi, Angew. Chemie Int. Ed. 2019, 58, 15707–15711.
- [21] V. Augustyn, P. Simon, B. Dunn, *Energy Environ. Sci.* 2014, 7, 1597.
- [22] R. Liang, Y. Du, P. Xiao, J. Cheng, S. Yuan, Y. Chen, J. Yuan, J. Chen, *Nanomaterials* 2021, 11, 1248.
- [23] R. R. Salunkhe, Y. V. Kaneti, Y. Yamauchi, ACS Nano 2017, 11, 5293–5308.
- [24] S. Korkmaz, İ. A. Kariper, O. Karaman, C. Karaman, Ceram. Int. 2021, 47, 34514– 34520.
- [25] T. Yue, B. Shen, P. Gao, *Renew. Sustain. Energy Rev.* 2022, 158, 112131.
- [26] S. Xiong, S. Jiang, J. Wang, H. Lin, M. Lin, S. Weng, S. Liu, Y. Jiao, Y. Xu, J. Chen, *Electrochim. Acta* 2020, 340, 135956.
- [27] A. Gupta, S. Sardana, J. Dalal, S. Lather, A. S. Maan, R. Tripathi, R. Punia, K. Singh,
   A. Ohlan, ACS Appl. Energy Mater. 2020, 3, 6434–6446.
- [28] X. Hu, L. Wei, R. Chen, Q. Wu, J. Li, *ChemistrySelect* **2020**, *5*, 5268–5288.
- [29] A. Zhang, R. Zhao, L. Hu, R. Yang, S. Yao, S. Wang, Z. Yang, Y. Yan, Adv. Energy Mater. 2021, 11, 2101412.
- [30] R. Yang, Y. Fan, R. Ye, Y. Tang, X. Cao, Z. Yin, Z. Zeng, Adv. Mater. 2021, 33, 2004862.
- [31] W. Guo, C. Yu, S. Li, Z. Wang, J. Yu, H. Huang, J. Qiu, Nano Energy 2019, 57, 459-

472.

- [32] R. Du, Y. Wu, Y. Yang, T. Zhai, T. Zhou, Q. Shang, L. Zhu, C. Shang, Z. Guo, Adv. Energy Mater. 2021, 11, 2100154.
- [33] H. Zhang, B. Wang, X. Yu, J. Li, J. Shang, J. Yu, Angew. Chemie 2020, 132, 19558– 19570.
- [34] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, Science 2006, 313, 1760–1763.
- [35] K. Jiang, P. Xiong, J. Ji, J. Zhu, R. Ma, T. Sasaki, F. Geng, Acc. Chem. Res. 2020, 53, 2443–2455.
- [36] L. Wang, X. Xie, K. N. Dinh, Q. Yan, J. Ma, Coord. Chem. Rev. 2019, 397, 138–167.
- [37] B. L. Ellis, P. Knauth, T. Djenizian, Adv. Mater. 2014, 26, 3368–3397.
- [38] T. Xiong, Y. Zhang, W. S. V. Lee, J. Xue, Adv. Energy Mater. 2020, 10, 2001769.
- [39] Q. Huang, G. Chen, P. Zheng, W. Li, T. Wu, Funct. Mater. Lett. 2021, 14, 2130005.
- [40] X. Su, Q. Wu, J. Li, X. Xiao, A. Lott, W. Lu, B. W. Sheldon, J. Wu, Adv. Energy Mater. 2014, 4, 1300882.
- [41] R. J. Hamers, *Chem. Res. Toxicol.* **2020**, *33*, 1074–1081.
- [42] S. Vinayaraj, K. Brijesh, P. C. Dhanush, H. S. Nagaraja, *Phys. B Condens. Matter* 2020, 596, 412369.
- [43] Y. Zhang, C. Sun, P. Lu, K. Li, S. Song, D. Xue, *CrystEngComm* **2012**, *14*, 5892.
- [44] O. Ghodbane, J.-L. Pascal, F. Favier, ACS Appl. Mater. Interfaces 2009, 1, 1130–1139.
- [45] D. Han, X. Jing, P. Xu, Y. Ding, J. Liu, J. Solid State Chem. 2014, 218, 178–183.
- [46] Y. Dai, L. Chen, V. Babayan, Q. Cheng, P. Saha, H. Jiang, C. Li, J. Mater. Chem. A 2015, 3, 21337–21342.
- [47] M. Mamizadeh, S. M. Masoudpanah, M. S. Bafghi, M. P. Dabir, *J. Energy Storage* 2023, 63, 106989.
- [48] X. Sun, T. Xu, J. Bai, C. Li, ACS Appl. Energy Mater. 2019, 2, 8675–8684.

- [49] M. A. Akhtar, V. Sharma, S. Biswas, A. Chandra, *RSC Adv.* **2016**, *6*, 96296–96305.
- [50] K. V. Sankar, R. K. Selvan, J. Power Sources 2015, 275, 399–407.
- [51] Y. Ghalmi, F. Habelhames, A. Sayah, A. Bahloul, B. Nessark, M. Shalabi, J. M. Nunzi, *Ionics (Kiel).* 2019, 25, 6025–6033.
- [52] J. Tang, J. Shen, N. Li, M. Ye, J. Alloys Compd. 2016, 666, 15–22.
- [53] R. D. Kumar, Y. Andou, S. Karuppuchamy, J. Alloys Compd. 2016, 654, 349–356.
- [54] P. Palanisamy, K. Thangavel, S. Murugesan, S. Marappan, M. Chavali, P. F. Siril, D.
   V. Perumal, *J. Electroanal. Chem.* 2019, *833*, 93–104.
- [55] A. V. Salkar, A. P. Naik, V. S. Joshi, S. K. Haram, P. P. Morajkar, *CrystEngComm* 2018, 20, 6683–6694.
- [56] S. R. Ede, S. Kundu, ACS Sustain. Chem. Eng. 2015, 3, 2321–2336.
- [57] V. Lokhande, S. J. Lee, A. Lokhande, J. H. Kim, T. Ji, *Mater. Chem. Phys.* 2018, 211, 214–224.
- [58] J. P. Zheng, P. J. Cygan, T. R. Jow, J. Electrochem. Soc. 1995, 142, 2699–2703.
- [59] K. Rajendra Prasad, N. Miura, *Electrochem. commun.* **2004**, *6*, 849–852.
- [60] K. R. Prasad, K. Koga, N. Miura, Chem. Mater. 2004, 16, 1845–1847.
- [61] T. P. Gujar, V. R. Shinde, C. D. Lokhande, S.-H. Han, J. Power Sources 2006, 161, 1479–1485.
- [62] H. Y. Lee, J. B. Goodenough, J. Solid State Chem. 1999, 148, 81–84.
- [63] S.-Y. Wang, K.-C. Ho, S.-L. Kuo, N.-L. Wu, J. Electrochem. Soc. 2006, 153, A75.
- [64] P. M. Wilde, T. J. Guther, R. Oesten, J. Garche, J. Electroanal. Chem. 1999, 461, 154–160.
- [65] H. Xia, Y. Shirley Meng, G. Yuan, C. Cui, L. Lu, *Electrochem. Solid-State Lett.* 2012, 15, A60.
- [66] F. Grote, Y. Lei, *Nano Energy* **2014**, *10*, 63–70.
- [67] A. Viswanathan, A. N. Shetty, J. Energy Storage 2020, 27, 101103.

- [68] V. M. Vimuna, A. R. Athira, K. V. Dinesh Babu, T. S. Xavier, *Diam. Relat. Mater.* 2020, 110, 108129.
- [69] A. Numan, N. Duraisamy, F. Saiha Omar, Y. K. Mahipal, K. Ramesh, S. Ramesh, *RSC Adv.* 2016, 6, 34894–34902.
- [70] M. Y. Ho, P. S. Khiew, D. Isa, W. S. Chiu, C. H. Chia, J. Mater. Sci. Mater. Electron.
   2017, 28, 6907–6918.
- [71] Y.-G. Zhu, G.-S. Cao, C.-Y. Sun, J. Xie, S.-Y. Liu, T.-J. Zhu, X. B. Zhao, H. Y. Yang, *RSC Adv.* 2013, 3, 19409.
- [72] H. Gholipour-Ranjbar, M. R. Ganjali, P. Norouzi, H. R. Naderi, *Ceram. Int.* 2016, 42, 12097–12104.
- [73] J. C. Pieretti, T. B. Trevisan, M. M. M. de Moraes, E. A. de Souza, S. H. Domingues, *Appl. Nanosci.* 2020, 10, 165–175.
- [74] S. Li, H. Jiang, K. Yang, Z. Zhang, S. Li, N. Luo, Q. Liu, R. Wei, J. Alloys Compd.
   2018, 746, 670–676.
- [75] M. Murugan, R. M. Kumar, A. Alsalme, A. Alghamdi, R. Jayavel, *Chem. Phys. Lett.* 2016, 650, 35–40.
- [76] Q. Ke, C. Tang, Y. Liu, H. Liu, J. Wang, Mater. Res. Express 2014, 1, 025015.
- [77] P. Zhao, W. Li, G. Wang, B. Yu, X. Li, J. Bai, Z. Ren, J. Alloys Compd. 2014, 604, 87–93.
- [78] J. Wang, W. Li, Y. Ge, J. Shen, Y. Zhao, Y. Zhang, J. Yuan, Ceram. Int. 2017, 43, 2876–2880.
- [79] M. Lee, S. K. Balasingam, H. Y. Jeong, W. G. Hong, H.-B.-R. Lee, B. H. Kim, Y. Jun, Sci. Rep. 2015, 5, 8151.
- [80] Y.-Z. Cai, W.-Q. Cao, Y.-L. Zhang, P. He, J.-C. Shu, M.-S. Cao, J. Alloys Compd. 2019, 811, 152011.
- [81] T. N. Vinuth Raj, P. A. Hoskeri, H. B. Muralidhara, C. R. Manjunatha, K. Yogesh Kumar, M. S. Raghu, J. Electroanal. Chem. 2020, 858, 113830.
- [82] T. Zhai, X. Lu, H. Wang, G. Wang, T. Mathis, T. Liu, C. Li, Y. Tong, Y. Li, Nano

Lett. 2015, 15, 3189–3194.

- [83] Z.-S. Wu, Y. Sun, Y.-Z. Tan, S. Yang, X. Feng, K. Müllen, J. Am. Chem. Soc. 2012, 134, 19532–19535.
- [84] L.-Q. Mai, F. Yang, Y.-L. Zhao, X. Xu, L. Xu, Y.-Z. Luo, Nat. Commun. 2011, 2, 381.
- [85] Y. Zeng, Y. Han, Y. Zhao, Y. Zeng, M. Yu, Y. Liu, H. Tang, Y. Tong, X. Lu, Adv. Energy Mater. 2015, 5, 1402176.
- [86] Y. Jin, H. Chen, M. Chen, N. Liu, Q. Li, ACS Appl. Mater. Interfaces 2013, 5, 3408–3416.
- [87] H. R. Naderi, M. R. Ganjali, A. S. Dezfuli, P. Norouzi, RSC Adv. 2016, 6, 51211– 51220.
- [88] L. Liu, L. Su, J. Lang, B. Hu, S. Xu, X. Yan, J. Mater. Chem. A 2017, 5, 5523–5531.
- [89] C. Y. Foo, A. Sumboja, D. J. H. Tan, J. Wang, P. S. Lee, Adv. Energy Mater. 2014, 4, 1400236.
- [90] G. Yang, S.-J. Park, J. Alloys Compd. 2018, 741, 360–367.
- [91] M. Yang, D. S. Kim, S. B. Hong, J.-W. Sim, J. Kim, S.-S. Kim, B. G. Choi, *Langmuir* 2017, 33, 5140–5147.
- [92] X. Guo, J. Zhou, C. Bai, X. Li, G. Fang, S. Liang, *Mater. Today Energy* 2020, 16, 100396.
- [93] G. Liang, F. Mo, H. Li, Z. Tang, Z. Liu, D. Wang, Q. Yang, L. Ma, C. Zhi, Adv. Energy Mater. 2019, 9, 1901838.
- [94] G. Zhou, D.-W. Wang, P.-X. Hou, W. Li, N. Li, C. Liu, F. Li, H.-M. Cheng, J. Mater. Chem. 2012, 22, 17942.
- [95] G. Zhou, D.-W. Wang, F. Li, L. Zhang, N. Li, Z.-S. Wu, L. Wen, G. Q. (Max) Lu, H. M. Cheng, *Chem. Mater.* 2010, 22, 5306–5313.
- [96] C. Yang, M. Han, H. Yan, F. Li, M. Shi, L. Zhao, J. Power Sources 2020, 452, 227826.
- [97] Z. Yao, D. Cai, Z. Cui, Q. Wang, H. Zhan, Ceram. Int. 2020, 46, 11237–11245.

- [98] X. Wu, Y. Xiang, Q. Peng, X. Wu, Y. Li, F. Tang, R. Song, Z. Liu, Z. He, X. Wu, J. Mater. Chem. A 2017, 5, 17990–17997.
- [99] V. Soundharrajan, B. Sambandam, S. Kim, S. Islam, J. Jo, S. Kim, V. Mathew, Y. Sun, J. Kim, *Energy Storage Mater.* 2020, 28, 407–417.
- [100] M. Shi, B. Wang, Y. Shen, J. Jiang, W. Zhu, Y. Su, M. Narayanasamy, S. Angaiah, C. Yan, Q. Peng, *Chem. Eng. J.* **2020**, *399*, 125627.
- [101] L. Chen, Z. Yang, H. Qin, X. Zeng, J. Meng, J. Power Sources 2019, 425, 162–169.
- [102] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, J. Am. Chem. Soc. 2016, 138, 12894–12901.
- [103] S. Wang, S. Zhang, X. Chen, G. Yuan, B. Wang, J. Bai, H. Wang, G. Wang, J. Colloid Interface Sci. 2020, 580, 528–539.
- [104] S. Yang, M. Zhang, X. Wu, X. Wu, F. Zeng, Y. Li, S. Duan, D. Fan, Y. Yang, X. Wu, J. Electroanal. Chem. 2019, 832, 69–74.
- [105] Y. Tao, Z. Li, L. Tang, X. Pu, T. Cao, D. Cheng, Q. Xu, H. Liu, Y. Wang, Y. Xia, *Electrochim. Acta* 2020, 331, 135296.
- [106] T. Niu, J. Li, Y. Qi, X. Huang, Y. Ren, J. Mater. Sci. 2021, 56, 16582–16590.
- [107] M. H. Alfaruqi, J. Gim, S. Kim, J. Song, J. Jo, S. Kim, V. Mathew, J. Kim, J. Power Sources 2015, 288, 320–327.
- [108] H. Pan, Y. Shao, P. Yan, Y. Cheng, K. S. Han, Z. Nie, C. Wang, J. Yang, X. Li, P. Bhattacharya, K. T. Mueller, J. Liu, *Nat. Energy* 2016, 1, 16039.
- [109] G. Kumar, S. Sampath, Solid State Ionics 2003, 160, 289–300.
- [110] M. H. Alfaruqi, V. Mathew, J. Gim, S. Kim, J. Song, J. P. Baboo, S. H. Choi, J. Kim, *Chem. Mater.* 2015, 27, 3609–3620.
- [111] C. Wang, Y. Zeng, X. Xiao, S. Wu, G. Zhong, K. Xu, Z. Wei, W. Su, X. Lu, J. Energy Chem. 2020, 43, 182–187.
- [112] S. Islam, M. H. Alfaruqi, V. Mathew, J. Song, S. Kim, S. Kim, J. Jo, J. P. Baboo, D. T. Pham, D. Y. Putro, Y.-K. Sun, J. Kim, J. Mater. Chem. A 2017, 5, 23299–23309.
- [113] N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, Nat. Commun.

**2017**, *8*, 405.

- [114] J. Hao, J. Mou, J. Zhang, L. Dong, W. Liu, C. Xu, F. Kang, *Electrochim. Acta* 2018, 259, 170–178.
- [115] W. Sun, F. Wang, S. Hou, C. Yang, X. Fan, Z. Ma, T. Gao, F. Han, R. Hu, M. Zhu, C. Wang, J. Am. Chem. Soc. 2017, 139, 9775–9778.
- [116] P. Gao, Q. Ru, H. Yan, S. Cheng, Y. Liu, X. Hou, L. Wei, F. Chi-Chung Ling, *ChemElectroChem* 2020, 7, 283–288.
- [117] D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah, L. F. Nazar, *Nat. Energy* 2016, *1*, 16119.
- [118] C. Xia, J. Guo, P. Li, X. Zhang, H. N. Alshareef, Angew. Chemie Int. Ed. 2018, 57, 3943–3948.
- [119] W. Zhang, C. Tang, B. Lan, L. Chen, W. Tang, C. Zuo, S. Dong, Q. An, P. Luo, J. Alloys Compd. 2020, 819, 152971.
- [120] H. Geng, M. Cheng, B. Wang, Y. Yang, Y. Zhang, C. C. Li, Adv. Funct. Mater. 2020, 30, 1907684.
- [121] B. Sambandam, V. Soundharrajan, S. Kim, M. H. Alfaruqi, J. Jo, S. Kim, V. Mathew,
   Y. Sun, J. Kim, *J. Mater. Chem. A* 2018, *6*, 3850–3856.
- [122] C. Yin, J. Chen, C.-L. Pan, Y. Pan, J. Hu, ACS Appl. Energy Mater. 2022, 5, 14144– 14154.
- [123] F. Wan, Y. Zhang, L. Zhang, D. Liu, C. Wang, L. Song, Z. Niu, J. Chen, Angew. Chemie Int. Ed. 2019, 58, 7062–7067.
- [124] Y. Chen, Z. Li, B. Li, Z. Zhang, J. Wei, B. Wang, Y. Huang, ACS Appl. Energy Mater.
  2023, 6, 3329–3336.
- [125] N. Palaniyandy, M. A. Kebede, K. Raju, K. I. Ozoemena, L. le Roux, M. K. Mathe, R. Jayaprakasam, *Mater. Chem. Phys.* 2019, 230, 258–266.
- [126] H. Tang, C. Liu, R. Zhou, T. Cai, C. Guo, X. Liu, Y. Zhu, J. Power Sources 2023, 566, 232915.
- [127] W. Zhou, G. Zeng, H. Jin, S. Jiang, M. Huang, C. Zhang, H. Chen, Molecules 2023,

28, 2147.

- [128] J. Wang, J.-G. Wang, H. Liu, Z. You, C. Wei, F. Kang, J. Power Sources 2019, 438, 226951.
- [129] C. Guo, H. Liu, J. Li, Z. Hou, J. Liang, J. Zhou, Y. Zhu, Y. Qian, *Electrochim. Acta* 2019, 304, 370–377.
- [130] M. Sun, D. Li, Y. Wang, W. Liu, M. Ren, F. Kong, S. Wang, Y. Guo, Y. Liu, *ChemElectroChem* 2019, 6, 2510–2516.
- [131] E. R. Parnham, R. E. Morris, Acc. Chem. Res. 2007, 40, 1005–1013.
- [132] R. D. Rogers, G. A. Voth, Acc. Chem. Res. 2007, 40, 1077–1078.
- [133] G. Gebresilassie Eshetu, M. Armand, B. Scrosati, S. Passerini, *Angew. Chemie Int. Ed.* 2014, *53*, 13342–13359.
- [134] R. Tao, T. Wang, J. Fan, H. M. Meyer, A. Y. Borisevich, C. Do-Thanh, S. Dai, *ChemNanoMat* 2022, 8, e202200075.
- [135] X. Ge, C. D. Gu, X. L. Wang, J. P. Tu, J. Mater. Chem. A 2014, 2, 17066–17076.
- [136] X. Ge, C. D. Gu, X. L. Wang, J. P. Tu, J. Phys. Chem. C 2014, 118, 911-923.
- [137] J.-H. Eum, D. Mandal, H. Kim, J. Electroanal. Chem. 2021, 892, 115299.
- [138] S. Sarkar, D. Mukherjee, R. Harini, G. Nagaraju, J. Mater. Sci. 2022, 57, 7680–7693.
- [139] B. G. Choi, M. Yang, S. C. Jung, K. G. Lee, J.-G. Kim, H. Park, T. J. Park, S. B. Lee, Y.-K. Han, Y. S. Huh, ACS Nano 2013, 7, 2453–2460.
- [140] M. Jana, P. Sivakumar, M. Kota, M. G. Jung, H. S. Park, J. Power Sources 2019, 422, 9–17.
- [141] W. Liu, C. Ju, D. Jiang, L. Xu, H. Mao, K. Wang, *Electrochim. Acta* 2014, 143, 135–142.
- [142] F. Li, C. Ruan, Y. Wang, L. Lei, New J. Chem. 2018, 42, 18659–18666.
- [143] Y. Lu, J.-L. Xu, S. Ren, Y.-N. Zhong, X. Gao, S.-D. Wang, RSC Adv. 2018, 8, 20182– 20189.
- [144] Y. Chen, X. Lu, B. Gao, J. Nanomater. 2014, 2014, 1-8.

- [145] H. Kahimbi, J. Jeong, D. H. Kim, J. W. Kim, B. G. Choi, Solid State Sci. 2018, 83, 201–206.
- [146] L. Xu, J. Xia, H. Xu, S. Yin, K. Wang, L. Huang, L. Wang, H. Li, J. Power Sources 2014, 245, 866–874.
- [147] Y. Zhu, X. Ji, R. Yin, Z. Hu, X. Qiu, Z. Wu, Y. Liu, RSC Adv. 2017, 7, 11123–11128.
- [148] V. H. Nguyen, J.-J. Shim, Synth. Met. 2015, 207, 110–115.
- [149] Y. Sun, Z. Fang, C. Wang, K. R. R. M. Ariyawansha, A. Zhou, H. Duan, *Nanoscale* 2015, 7, 7790–7801.
- [150] A. Yavuz, K. Kaplan, M. Bedir, J. Phys. Chem. Solids 2021, 150, 109824.
- [151] X. Guan, L. Zhao, P. Zhang, X. Song, J. Liu, L. Gao, *ChemistrySelect* 2019, 4, 2009– 2017.
- [152] A. Yavuz, N. Ozdemir, P. Y. Erdogan, H. Zengin, G. Zengin, M. Bedir, *Appl. Phys. A* 2019, 125, 494.
- [153] S. K. Shinde, S. S. Karade, N. C. Maile, H. M. Yadav, G. S. Ghodake, A. D. Jagadale, D.-Y. Kim, J. Mol. Liq. 2021, 334, 116390.
- [154] V. H. Nguyen, J.-J. Shim, Mater. Chem. Phys. 2016, 176, 6–11.
- [155] V. H. Nguyen, J.-J. Shim, Mater. Lett. 2015, 157, 290-294.
- [156] S. S. Karade, S. Lalwani, J.-H. Eum, H. Kim, Sustain. Energy Fuels 2020, 4, 3066– 3076.
- [157] N. Zdolšek, I. Perović, S. Brković, G. Tasić, M. Milović, M. Vujković, Materials (Basel). 2022, 15, 8540.

# Overview of the Methods of Synthesis, Physiochemical Characterization, and Electrochemical Techniques

#### **Overview**

The present chapter comprehensively analyses the experimental methodologies and protocols employed for preparing and characterizing materials utilized in the context of supercapacitors (SCs) and zinc-ion batteries (ZIBs). The present discourse delves into the comprehensive exposition of the electrode preparation process and the standard protocol for the assembly of coin cells. Moreover, the electrochemical assessment of assembled cells is scrutinized employing diverse methodologies, encompassing cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) profiles, galvanostatic intermittent titration technique (GITT), and electrochemical impedance spectroscopy (EIS),

The techniques illustrated in this chapter are essential for comprehending the fundamental principles that regulate the operation of SCs electrode and cathode for ZIB. Utilizing physiochemical characterization techniques can offer valuable insights into the microstructural and chemical properties of materials, thereby facilitating the optimization of cell performance. The electrode preparation, coin cell packing, and electrochemical analysis are crucial in advancing and commercializing such devices. Evaluating SCs' performance and potential applications necessitates the computation of their specific capacitance, specific energy (SE), and specific power (SP). This chapter provides a comprehensive overview of the experimental methods and procedures for preparing and characterizing ZIB and SCs.

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### 2.1 Theoretical Background

Transition metal oxides (TMOs) are essential in applications ranging from conversion to catalysis, sensing, and energy storage. TMOs with a specific surface area (SSA) and a porous structure that can be controlled are effective for achieving high SE with long-term stability.<sup>[1,2]</sup> The TMOs made using templated techniques have suitable porosity and surface area values.<sup>[3]</sup> Their complex synthesis method, limited availability and high cost of natural templates, and inability to be employed for large-scale manufacturing hampered their practical application. Therefore, finding the best synthesis process for creating TMOs is challenging. This chapter provides an overview of various synthesis methods. Understanding these techniques is essential to modify TMO characteristics and finding new applications.

The basic principles, charge storage processes and practical applications of supercapacitors (SCs) are introduced in this chapter. It discusses how SCs store and release energy and offers insights into their operating principles. The specific benefits of zinc-ion batteries (ZIBs) are also discussed in this chapter, along with their charge-discharge procedures, electrode materials, and general operation. This chapter thoroughly introduces SCs and ZIBs, covering their basic concepts. To better fulfil the needs of extensive range of applications, there is an ongoing effort to improve ZIBs and SCs in terms of their functionality, SE, and efficiency.

Characterization methods are crucial for comprehending and evaluating the efficiency of SCs and ZIB. Researchers may learn more about the materials' structures, morphologies, chemical compositions, and electrochemical properties using these techniques. EIS, FESEM, and XRD are only a few of the methods used to characterize materials for energy storage. Additional information can be collected by EDS, and XPS. Researchers may use this information to enhance the functionality and efficiency of these energy storage systems.

#### 2.1.1 Synthesis Methods for TMOs

Chemical synthesis techniques are used for TMO mass manufacturing because they are easy and inexpensive. Research on affordable chemical procedures for creating TMOs has been ongoing for several decades. These processes include chemical bath deposition (CBD),<sup>[4]</sup> electrodeposition,<sup>[5]</sup> the hydrothermal approach,<sup>[6]</sup> the sol-gel method,<sup>[7]</sup> and many more.<sup>[8,9]</sup> The nucleation and development of TMOs may be more precisely controlled using these methods.<sup>[10]</sup> **Figure 2.1** shows a common synthesis technique used to develop TMOs. In addition to providing large-scale and inexpensive manufacturing of different TMOs, these technologies may function under low-temperature settings (CBD, electrochemical deposition). The advancement of TMOs for energy storage relies heavily on chemical production techniques. These solutions involve the guided synthesis of TMOs with adjustable features to increase the electrode materials' functioning as functional materials.





#### 2.1.1.1 Chemical precipitation

The chemical precipitation method is a common synthesis approach to create metal oxides with specific characteristics for use in energy storage. In this technique, a precipitating agent separates metal ions from a solution. Metal oxide nanoparticles may be tailored to particular compositional, structural, and morphological needs by precisely regulating pH, temperature, and reaction time.<sup>[111]</sup> In energy storage, electrode materials in SCs and batteries from metal oxides synthesized by chemical precipitation have shown promising results. Besides possessing high specific capacitance and good cyclic stability, these TMOs also provide good rate performance. Because of their surface area and porosity, nanoparticles produced by chemical precipitation have high electrochemical activity and quick charge-discharge operations.<sup>[12]</sup> Manganese dioxide (MnO<sub>2</sub>),<sup>[13]</sup> nickel oxide (NiO),<sup>[14]</sup> and cobalt oxide (Co<sub>3</sub>O<sub>4</sub>)<sup>[15]</sup> are some of the metal oxides that have been synthesized utilizing the chemical precipitation approach. High redox activity, an abundance of redox sites, and superior electrical conductivity are all features that make these metal oxides ideal for use in energy storage.<sup>[16]</sup>

In conclusion, the chemical precipitation technique offers a flexible and efficient strategy for synthesizing metal oxides optimized for energy storage. Materials with improved electrochemical performance may be designed and optimized by manipulating the composition and structure of TMOs, which aids in developing energy storage systems. The chemical precipitation method has limited control over particle nucleation and growth, leading to inconsistent material properties and a wide size distribution. Moreover, the procedure can be time-intensive, necessitating numerous stages and extended reaction durations.<sup>[17]</sup> Moreover, it could entail the utilization of perilous chemicals and produce substantial waste, thereby giving rise to environmental apprehensions.

#### 2.1.1.2 Sol-gel

The sol-gel method is a flexible and commonly used way to make TMOs. This method produces a mix of metal alkoxides or salts into a precursor, then dissolves and cools to create a gel-like network. The gel is then dried and heated to turn it into a solid object made of metal oxide.<sup>[18]</sup> The sol-gel method confers various advantages in the production of TMOs. This technology affords individuals precise manipulation of materials' properties, composition, and morphology.<sup>[19]</sup> By employing appropriate precursors and reaction conditions, it is feasible to synthesize TMOs possessing the requisite characteristics for a

specific application. The sol-gel technique facilitates the integration of dopants and the synthesis of mixture materials. Sol-gel-made TMOs have a high SSA and a porous structure, which makes it easy for charges to move and improves their electrochemical performance.<sup>[20,21]</sup>

Overall, the sol-gel method is a helpful way to make metal oxide products with specific qualities that use to store energy. It can do many different things and make well-defined shapes, making it a good choice for creating new energy storage devices. The sol-gel method is disadvantaged by the intricate and delicate nature of its process parameters. Obtaining the desired material composition and structure can be difficult due to the requirement for accurate regulation of factors such as temperature, pH, and drying parameters. Moreover, the sol-gel technique's extended processing duration renders it unsuitable for mass production. Additionally, the process's cost-effectiveness is restricted by the expensive nature of organic precursors.

#### **2.1.1.3 Electrodeposition**

Electrodeposition is a way to make and put new materials on a conducting surface. It happens when metal ions in a fluid are reduced electrochemically on an electrode, which makes a layer or thin film. This method has many benefits, such as controlling the deposited material's surface area, morphology, and property.<sup>[22]</sup> But there are also some hurdles and problems with electrodeposition. One big problem is that the applied material might not stick well to the base. When there are problems with adhesion, the layer can peel off or come loose, hurting how well it works and lasts. Another problem is getting the deposition to be the same over the medium area. To ensure the deposit is even and uniform, you must carefully optimize solution percentage, current density, and deposition time.<sup>[23]</sup> Also, electrodeposition is limited by the lack of reasonable electrolyte solutions and substrates that work well together. Some materials may not be easy to electroplate because of their chemical qualities or the incorrect electroplating settings. There can also be problems with how well the applied material and the base work together, leading to unwanted reactions or degradation.

Electrodeposition is a flexible and widely used method for making new materials and depositing them. However, it is essential to think carefully about adhesion, uniformity, and compatibility issues to overcome the problems that come with it and make coatings or thin films that work well in energy storage and other applications.

### 2.1.1.4 Hydrothermal

The hydrothermal method is a way to make new materials by using high temperatures and high pressures in a water solution to create materials with a particular structure and shape.<sup>[24]</sup> This method makes metal oxides, nanoparticles, and nanocrystals exceptionally well.<sup>[25,26]</sup> The hydrothermal method has several benefits, such as making well-defined shapes, particles of the same size, and high-quality materials. It makes it possible to control the growth process very precisely, which leads to materials with better qualities that use for many things, like storing energy.<sup>[27]</sup> But the hydrothermal method has its problems and hurdles. During manufacturing, particles may stick or clump together, a common problem. High temperatures and pressures can cause particles to bump into each other and stick together. It makes the particles bigger and decreases their surface area, which could hurt how well the material works in energy storage devices.

Another problem is that the factors of a reaction, such as temperature, pressure, and reaction time, need to be carefully controlled. Even small changes to these factors can affect the size, shape, and electronic properties of the materials. Precise optimization is needed to get the desired shape and property.<sup>[28]</sup> Designing and running hydrothermal reactors can be complicated and expensive for large-scale synthesis.

Even with these problems, the hydrothermal method is still a valuable and widely used way to make materials with specific qualities. Researchers can use the hydrothermal process to create new materials for energy storage and other uses by figuring out how to stop particles from sticking together and adjusting the reaction settings to get the best results.

### 2.1.1.5 Ionothermal method (IL-assisted method)

Ionic liquids (ILs) are employed as both solvents and reactants in ionothermal synthesis, a methodology utilized for fabricating various materials. This approach enables the regulation of the produced entities' composition, structure, and characteristics. Ionothermal synthesis is done at low temperatures and has benefits like making a substance more soluble and easier to crystallize.<sup>[29]</sup> Compared to ILs, the molecular composition of the solvents utilized in hydrothermal and solvothermal synthesis stands out as a key distinction. Because of their ionic structure, ILs have unique characteristics such as low vapor pressures (and hence generate relatively little autogenous pressure at high temperatures).<sup>[30]</sup> ILs can act as a solvent and a possible template or structure guiding agent in ionothermal synthesis. Dai and colleagues first used ILs as the reaction media for producing inorganic compounds in

2000.<sup>[31]</sup> Since then, ionic liquids have been widely used to make several inorganic materials, including monodisperse Ir nanoparticles, microspheres of hollow titania, and aggregates of spherical  $TiO_2$ .<sup>[32]</sup> ILs are beneficial due to their extended hydrogen bond systems, low interface tensions, and incompatibility with organic solvents.<sup>[33]</sup> ILs have the potential to become a widely used tool in synthetic chemistry, opening up new avenues for the creation of nanomaterials.

Consistent and basic knowledge of the impact between ILs and products has not been reached, despite ionic liquids utilized to influence the crystal phase and shape of inorganic materials. Two factors contribute to this lack of knowledge: (1) it is difficult to gain a molecular understanding of the physicochemical characteristics of ILs, and (2) there has been very little study of the laws and relationships between molecular structures and the morphologies of the resultant inorganic materials.<sup>[34]</sup> To conclude, ionothermal synthesis is a pioneering approach for the production of TMOs and materials that are a combination of inorganic and organic components. The popularity of this methodology is on the rise, and it is reasonable to anticipate that forthcoming publications will detail novel and stimulating structures and advancements.

#### 2.2 Theoretical Background of Supercapacitors and Zn-ion Batteries

SCs and ZIBs, two examples of energy storage technologies, are indispensable in today's energy storage systems. SCs exhibit superior charge-discharge performance due to the effective separation of charges at the electrode-electrolyte interface, resulting in high SP and rapid charge-discharge capabilities.<sup>[35]</sup> ZIBs offer a higher energy density and potential environmental advantages than traditional lithium-ion batteries (LIBs). The reversible process of intercalation/deintercalation of Zn ions into the electrode materials is responsible for this achievement.<sup>[36]</sup> Optimizing the performance of these devices and improving performance for a extensive range of applications requires an understanding of the theoretical concepts behind these devices.

#### 2.2.1 Supercapacitors (SCs)

SCs utilise a separator permeable to ions and an electrolyte, along with two electrodes, to store electrical charge.<sup>[37]</sup> They have gained attention due to their exceptional capacitance and ability to endure infinite charge-discharge cycles. They store and release energy rapidly because of their design, which generally includes high-surface-area electrodes and

electrolytes.<sup>[38]</sup> SCs have probable applications in various fields, like portable electronics, renewable energy systems, and electric cars.



#### Figure 2.2 Schematic representation of capacitor, and SCs.

SCs works on the same principle as a traditional capacitor, that acts as a charge storage medium between electrodes and electrolytes. SCs comprise of two electrodes with current collectors and a separator, immersed in an electrolyte..<sup>[39]</sup> SCs use an electrolyte media that is electrically insulating but ionically conducting, in contrast to the dielectric material often used to separate the electrodes in a traditional capacitor.<sup>[40]</sup> In **Figure 2.2**, we see a simplified illustration of a standard capacitor and SC. Active material having a high SSA and a good ionic conductivity between the electrolyte and electrode are required to obtain a high specific capacitance in an electrochemical capacitor. **Equation 2.1** is commonly used to approximate the capacitance of an electrochemical capacitor.

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{2.1}$$

Here, Capacitance (F), free space permittivity ( $\mathcal{E}_0$ ), insulator relative permittivity ( $\mathcal{E}_r$ ), area of a single plate (A), and separation between parallel plates (d) are all inputs in this equation. Energy and power density are crucial considerations for an SCs system. **Equation 2.2**, it is possible to calculate an electrochemical capacitor's energy density (E).

$$\mathbf{E} = \frac{1}{2}CV^2 \tag{2.2}$$

Similarly, power density can be calculated using Equation 2.3,

$$\mathbf{P} = \frac{E}{t} \tag{2.3}$$

Where V is the device's operating voltage range, and t is the discharge time for a specific current density at which E and P calculations are performed.<sup>[41]</sup> EDLCs and Pseudocapacitors are two broad groups of SCs based on their charge storage techniques, as shown in **Figure 2.3**. Hybrid energy storage systems are, as the name suggests, a hybrid between SCs, and batteries, with an transitional behavior between EDLC and Faradaic processes, in the energy storage spectrum.<sup>[42]</sup> Carbon-based active electrode materials with a high SSA are often used in EDLCs because they have the ability to electrostatically store charges by absorbing ions at the electrode/electrolyte contact and releasing them when needed.<sup>[43]</sup> On the other hand, pseudocapacitors can store electrical charge through rapid and reversible redox methods at



**Figure 2.3** A categorization of SCs according to the different electrode materials, charge storage mechanism.

material surface.<sup>[44]</sup> Faradaic electrodes have a larger specific pseudocapacitance (usually  $300-1000 \text{ F g}^{-1}$ ) than carbon-based materials (about  $100-250 \text{ F g}^{-1}$ ).<sup>[45]</sup> Polyanilines,<sup>[46]</sup>

polypyrrole,<sup>[47]</sup> and polythiophenes<sup>[48]</sup> are examples of electronically conducting redox polymers, while TMOs like  $RuO_2$ ,<sup>[49]</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>[50]</sup> NiO,<sup>[51]</sup> and  $MnO_2$ <sup>[52]</sup> are examples of active pseudocapacitive materials. We'll explore these two energy storage techniques and their associated materials in the following.

#### 2.2.1.1 Electric Double-Layer Capacitor (EDLC)

EDLCs store energy through electrostatic adsorption of electrolyte ions onto active electrode materials. It follows that using easily accessible surface area and electrically conducting electrode materials is crucial to the high capacitance of EDLCs. EDLCs are typically prepared from carbon-based materials with a high SSA and strong conductivity. SCs based on carbons with desirable properties such as electrochemical stability, conductivity and easily accessible SSA can originate in a wide variety of inexpensive and readily available forms like graphene derivatives,<sup>[53]</sup> activated carbon,<sup>[54]</sup> carbon nanotubes,<sup>[55]</sup> and porous carbon.<sup>[56]</sup>



**Figure 2.4** (a) The electric double layer (EDL) is modelled by the classical theories. Copyright 2022, American Chemical Society<sup>59</sup> (b) Carbon sample average pore size vs. areal capacitance. The standard perspective assumes normalized capacitance declines with pore size. (c-e) Schematic illustration of solvated ions in pores with pore wall distances (c) higher than 2 nm, (d) between 1, and 2 nm, and (e) less than 1 nm.<sup>61</sup> Copyright 2006, American Association for the Advancement of Science.

Pore size, and capacitance in solvent-free IL electrolytes were the subjects of an experimental study by Simon and Gogotsi.<sup>[57]</sup> Based on their findings, the optimum capacitance is attained when the ion size is similar to pore size. Capacitance and specific surface area were studied by Ji et al. for many carbon-based electrodes.<sup>[58]</sup> The EDL model, proposed by Helmholtz, comprises two planes with opposite electrical charges, representing the electrode surface and counterions, as shown in **Figure 2.4 (a)**.<sup>[59]</sup> The double layer, consisting of two parallel

conductive sheets, has a separation comparable to the counterion radius. This results in a capacitance that is significantly larger than that of a typical dielectric capacitor by several orders of magnitude. EDL capacitors are commonly composed of porous electrodes and a concentrated electrolyte or ionic liquid to optimize the overall capacitance.<sup>[59]</sup> Carbon-based materials can facilitate both rapid ionic diffusion and high capacitance because of their small pore size and carefully managed specific surface area. Figure 2.4 (b-e) indicates that the impact of pore size on specific capacitance normalized by SSA is independent of surface area. The Gouy-Chapman-Stern model says that hydrated ions cannot enter holes that are smaller than 0.5 nanometer (nm) across. It also says that organic electrolytes cannot enter pores that are smaller than 1.0 nm across.<sup>[60]</sup> The best capacitive performance is seen in active materials with mesoporosity (around 3 to 5 nm in diameter). The pore diameter accommodates proper ion adsorption on adjacent pore walls, as it is approximately twice the radius of the solvated ions.<sup>[61]</sup> But Gogotsi and Simon did a study later and found something strange. They saw that capacitance went up a lot when the holes were smaller than the size of the electrolyte ions with water around them.<sup>[62]</sup> The mechanism for the increased capacitance of microporous materials is not fully understood. However, it supposed to include the incomplete desolvation of the ions upon entry to the few-nanometre-size pores of the carbon. The results of the experiments indicate that microporous materials exhibited a higher level of capacitance than their mesoporous counterparts. Charge storage in micropores of SCs differs from the more common Helmholtz and diffuse layer development at the solid-electrolyte interface. Consequently, the process of charge storage in such a scenario remains elusive. The potential decreases linearly from the surface to the inner and outer compact layers, with varying gradients. Equation 2.4 calculates the electrode's total double-layer capacitance, Cdl.

$$\frac{1}{c_{dl}} = \frac{1}{c_{Stern}} + \frac{1}{c_{Diff}}$$
(2.4)

EDLCs are "blocking electrodes" because they do not undergo redox reactions. It facilitates rapid energy intake and distribution, leading to increased efficiency. The solvent in the electrolyte is irrelevant to the charge storage process. it is possible to use a wider variety of solvents. Energy density is a limiting factor; hence efforts are being made to boost EDLCs' energy efficiency and increase their usable temperature range. Scientists first worked to improve the activation process and create high SSA activated carbon to increase the pore volume. Nevertheless, research has demonstrated that even samples with the highest porosity cannot increase the capacitance.

### 2.2.1.2 Pseudocapacitor

EDLCs are limited to applications that need the power supply for no more than a few seconds because of their low energy density, despite the remarkable advances in the characteristics of carbon-based materials. As a result, researchers are concentrating on developing new electrode materials to address the issue of SCs' relatively low SE. Using pseudocapacitive materials allows for the creation of SCs with increased energy densities. Conway<sup>[63]</sup> discovered a variety of faradaic pathways that can lead to capacitive electrochemical properties, including: redox pseudocapacitance (such as RuO<sub>2</sub>.nH<sub>2</sub>O), intercalation pseudocapacitance, and underpotential deposition shown in Figure 2.5.<sup>[64]</sup> Adsorption of a metal ion onto the surface of another metal results in the formation of a monolayer, considerably beyond its redox potential, this process is known as underpotential deposition.<sup>[65]</sup> Lead deposited on a gold electrode is an ancient but good example of underpotential deposition. A faradaic charge-transfer occurs when ions are electrochemically adsorbed onto or near the surface of a substance, creating a redox pseudocapacitance.<sup>[66]</sup> There is no change in crystallographic phase when ions undergo faradaic charge-transfer redox-active when they intercalate into material, resulting in intercalation pseudocapacitance.<sup>[67]</sup> Each of these three processes takes place either at the electrode/electrolyte contact or on the inner surface of a material. Still, they share a similar electrochemical signature due to correlation between potential and the magnitude of charge generated by adsorption/desorption processes.



**Figure 2.5** Pseudocapacitance can be produced by many distinct reversible faradic redox processes, including (a) underpotential deposition, (b) redox, and (c) intercalation pseudocapacitance. Copyright 2014, Royal Society of Chemistry.<sup>65</sup>

Several mechanisms, including those already discussed, can lead to pseudocapacity. We characterize pseudocapacitive energy storage by its response to (a) CV; (b) GCD; and (c) EIS. Scan rate (v, mV s<sup>-1</sup>) determines an experiment's duration in cyclic voltammetry. The response of a current to a certain scan rate will vary depending on whether the redox reaction is controlled by diffusion or the surface (capacitive). Current response varies with  $v^{1/2}$  for a redox reaction bounded by diffusion over semi-infinite linear path; current differs directly with v for a capacitive process.<sup>[68]</sup> Hence, relation can be expressed for the electric current at a specific voltage relevant to all materials.

$$I = k_1 v^{1/2} + k_2 v \tag{2.5}$$

Separation of the diffusion and capacitive currents is achieved by Calculating  $k_1$  and  $k_2$  values at different potentials. Using caution while employing this equation is essential, as the existing correlations do not set up the process. New nanostructured materials' performance has been measured using this method.

#### 2.2.1.3 Hybrid Capacitor

Hybrid composite electrode systems, which combine nanostructured carbons with pseudocapacitive materials like TMOs and electrically conducting polymers, can enhance the electrochemical performance of ECs by introducing pseudocapacitance effects.<sup>[69]</sup> A hybrid system at the material level necessitates a charge storage method resembling a battery and a capacitive process, either EDLC-type or pseudocapacitive. This is depicted in **Figure 2.3** (c). Hybridizing metal oxide electrodes with highly conductive carbons are commonly used to improve device performance. A high-energy and high-power energy storage device would be highly desirable. SCs have limited energy capacity, but researchers in this area have made significant progress. A hybrid energy storage system aims to combine the SE performance of batteries with the high SP characteristic and strong cycle life of SCs.

Power conversion electronics are necessary to separately manage the EDLC and battery in a hybrid energy storage system at the device level. Device like hybrid systems are frequently composed of multiple components, resulting in increased production complexity and higher costs, weight, or volume. Scientists are developing a method to merge SCs' potency and reusability with batteries' energy density. Material hybridization yields superior outcomes when compared to hybridization in external systems. TMO and activated carbon (AC) were hybridized to form an asymmetric supercapacitor (ASC), utilizing TMO as an active electrode material for batteries and activated carbon as a SC electrode material.<sup>[70]</sup> The ASC employs activated carbon as its negative electrode, while the TMO as its positive electrode. The hybrid system can leverage the high SE of the battery and the high SP of the SC due to their shared working potential window.

#### 2.2.2 Rechargeable batteries

Batteries are electrochemical devices capable of storing chemical energy and converting it into electrical energy. Batteries are composed of electrochemical cells, including a cathode, anode, and electrolyte. The electrolyte enables ion movement between electrodes, leading to electron flow through an external circuit when a battery is discharged.<sup>[71]</sup> Metal-ion rechargeable batteries employ metal ions as charge carriers.<sup>[72]</sup> The batteries store and release energy by reversibly intercalating and deintercalation metal-ions in electrode materials during charge-discharge.<sup>[73]</sup> Metal-ion batteries provide high energy density, extended cycle life, and stability.<sup>[74]</sup> Zinc is abundant and inexpensive metal-ions, have involved significant attention as possible substitutes for conventional LIBs.<sup>[75]</sup> Metal-ion batteries are an effective option for the development of future energy storage systems. Current research aims to enhance their performance, safety, and sustainability. The widespread demand for high-performance rechargeable batteries has led to their requirements and functions becoming common knowledge. The popularity of battery research increased significantly after Sony Co. introduced the first commercially available LIB. Over seven years, the literature volume on batteries has grown rapidly with researchers adding new publications.

Rechargeable batteries are preferred for portable electronics, power tools, and electric automobiles due to their high SE and SP. There is skepticism regarding the long-term viability of batteries as a solution for global portable energy storage. Lithium exhibits the lowest reduction potential among all elements, possesses the third lowest atomic mass, and exhibits one of the smallest ionic radii among monovalent ions.<sup>[76]</sup> Lithium reserves in the Earth's crust are adequate to meet the energy requirements of a worldwide fleet of automobiles. The expansion of Li-ion batteries into renewable energy applications can be hindered by rising prices, primarily responsible for cost-related issues. Li-ion batteries prioritize electrode materials to improve energy and power densities and reduce size and cost, minimizing the significance of Li as a cost factor.

#### 2.2.2.1 Transition from the Lithium Battery to Post-Lithium Battery

#### 2.2.2.2 Lithium-ion Batteries (LIBs)

Primary batteries undergo irreversible electrochemical reactions during discharge, leading to a depletion of electroactive compounds and a modification of electrode chemical composition.<sup>[77]</sup> Safety, energy density, cycle and shelf life, storage efficiency, and cost of manufacture are essential aspects of a rechargeable battery. The quantity of charge that may be transferred over time per electrode formula unit is constrained by conventional rechargeable batteries' solid electrodes and liquid electrolytes. Secondary batteries employ reversible electrochemical reactions, enabling discharge/charge cycles without modifying the electrode materials' chemical composition.<sup>[78]</sup> Secondary batteries, especially LIBs, are ideal for industrial applications such as portable electronics, electric cars, and renewable energy storage systems. Sony introduced the first commercial LIB in 1991.<sup>[79]</sup>. Lithium, the lightest metal, possesses a high electronegative potential (-3.04 V vs. SHE), making it a preferred choice for energy storage. LIBs can attain high energy and power densities due to these properties. LIBs offer advantages over other rechargeable batteries, including a broad operating potential range, absence of memory effect, and extended cycle life, rendering them a dependable energy storage alternative in the present market.<sup>[80]</sup> LIB exhibits superior characteristics than other rechargeable batteries, for example nickel-metal-hydride and nickel-cadmium.<sup>[81]</sup> These advantages include higher SE, longer lifecycle, and lesser selfdischarge rate. LIB is an electrical energy storage device that uses two electrodes-an anode and a cathode to store electrical energy as chemical energy. An electrolyte separates the electrodes, moving the ionic component of the chemical reaction inside the cell while pushing the electronic component outside the battery.<sup>[82]</sup> By examining and managing electrode passivation layers, accelerating the rate of Li<sup>+</sup> transfer across electrode/electrolyte interfaces, and finding electrolytes with more extensive windows while maintaining a Li<sup>+</sup> conductivity, scientists are refining the standard approach. Cell phones, laptops, digital cameras, and iPads are all part of the wireless revolution made possible by LIB. Figure 2.6 depicts the components and processes of LIB. The electrolyte conducts the ionic component of the chemical interaction between the electrode, but the electronic component must go through an external circuit to function. The two electrodes of a rechargeable cell undergo a reversible chemical reaction. Still, variations in electrode volume, chemical changes in the electrodeelectrolyte, or electrode degradation can result in an irreversible loss of capacity. A battery's cycle life refers to the maximum number of cycles a cell can undergo before losing 80% of its
original reversible capacity.<sup>[83]</sup> However, new approaches are required for batteries that do more than only power handheld devices. For example, electrode hosts with two-electron redox centers, cathode hosts that undergo displacement processes, and Li<sup>+</sup> solid electrolyte separator membrane development might be used.



#### Current collector

**Figure 2.6** Depicts the LIB configuration consisting of a LiCoO<sub>2</sub> cathode,  $Li^+$  electrolyte, and graphite anode.

The demand for portable electronics and the constraints of current battery technologies prompted the advancement of LIBs. Lithium serves as the anode material in these batteries, providing a superior energy density compared to other rechargeable batteries, rendering them suitable for portable electronic devices

# 2.2.2.3 Post-Lithium Batteries (PLBs)

LIB technology has revolutionized our lifestyle. The suitability of LIBs for large-scale applications is being questioned due to concerns regarding the escalating consumption and scarcity of raw materials such as Li, Co, and Ni, as well as environmental and economic issues. Despite the potential of LIBs, various obstacles must be addressed prior to their commercialization. Because of this, we need to find new ways to make batteries that use materials that are easy to get. PLBs are the top candidates due to their low cost, abundance, and eco-friendliness. PLBs that use multivalent charge carriers such as  $Mg^{2+}$ ,  $Zn^{2+}$ , and  $Al^{3+}$  exhibit increased theoretical capacity due to their ability to store multiple electrons.<sup>[84]</sup> Multivalent PLBs exhibit superior energy density compared to monovalent counterparts such as Na<sup>+</sup> and K<sup>+</sup>. Using aqueous electrolytes in PLBs can offer benefits such as enhanced safety

# Chapter 2

and simplified production processes. The crucial factors to consider in developing highperformance battery chemistries are the standard reduction potentials of electrode materials and the electrochemical stability of electrolytes. Aqueous electrolytes have a limited voltage range of 1.23 V due to the disparity between water's inherent oxidation and reduction potential. Water's limited electrochemical stability window (ESW) restricts the feasibility of employing several electronegative metals as anodes in high-voltage aqueous rechargeable pouch cell batteries (PLBs). The redox potentials of Al, Mg, and Ca (-1.66 V, -2.38 V, and -2.76 V vs. SHE, respectively) exceed the stability limit of the aqueous electrolyte. The cathode can be effectively shielded against deterioration and structural breakdown using a surface coating. The breakdown of cathode materials can be prevented by using dualconductive polymers like PEDOT and Co(III) rich-Co<sub>3</sub>O<sub>4</sub>, for example.<sup>[85]</sup> To aid in reactant dispersion and adsorption and to enhance electroconductivity, defects can be made. It is suggested that an anionic redox reaction increase energy density by boosting the operating voltage and adding to the capacity. For aqueous ZIBs, it is critical to investigate new cuttingedge cathode materials with a combination of high voltage, high capacity, and improved cycle lifespan.

Although it comes at the price of a constrained capacity, adding electron-withdrawing groups like  $PO_4^{3-}$  and  $F^-$  to the host structure can raise the working voltage.<sup>[86]</sup> Diverse electrolytes can be employed to increase the voltage window as well as two- or multiple-electron redox processes. More study is required to investigate and improve innovative cathode, anode, and electrolyte types. Aqueous ZIBs are extremely promising and will soon be used in practical applications.

## 2.2.2.4 Zinc-ion Batteries (ZIBs)

ZIBs are being increasingly recognized as a viable substitute for conventional LIBs. ZIBs employ zinc ions as the charge carrier and are a rechargeable battery type. Like LIB, they comprise of 2E (an anode and a cathode) separated by an electrolyte. Zinc ions are intercalated into the anode material and corresponding reactions occur at the cathode during discharge. Upon charging, the anode releases zinc ions back into the electrolyte.<sup>[86]</sup> The selection of the electrolyte in a ZIB is critical for its efficacy and safety. Organic solvents have conventionally been utilized as non-aqueous electrolytes in rechargeable batteries owing to their broad electrochemical stability range.<sup>[87]</sup> Non-aqueous electrolytes have drawbacks

such as high expense, flammability, and toxicity. Aqueous zinc-ion batteries (AZIBs) utilize water-based electrolytes, providing advantages over non-aqueous systems. Water-based electrolytes are safer and less susceptible to thermal runaway than non-aqueous electrolytes.<sup>[88]</sup> Improved safety is crucial for applications like automobiles and large-scale



Figure 2.7 A chronology of the developmental history of various types of zinc-based batteries.

energy storage, where it is essential to minimize the potential for fire or explosion. AZIBs have cost advantages over LIBs owing to the plentiful supply and affordable pricing of zinc, resulting in a reduction in the overall cost of the battery system. Zinc is a plentiful element and its extraction and processing methods are established technologies. ZIBs are a desirable choice for energy storage on a big scale due to their accessibility and cost-effectiveness. Water-based electrolytes exhibit superior ionic conductivity in comparison to numerous non-aqueous alternatives. Enhanced conductivity can increase the SP and SE of the battery, resulting in quicker charge and discharge rates.<sup>[89]</sup> Their affordability and abundance make them a viable option for large-scale energy storage, aiding the shift towards sustainable and renewable energy sources. Additional research and development are necessary to address remaining obstacles and enhance the efficiency of ZIBs for broad commercial deployment. Figure 2.7 provides a concise overview of the developmental history of ZIBs. Under slightly acidic conditions, there is no intermediary phase formation during Zn's oxidation to Zn<sup>2+</sup>.<sup>[90]</sup> Additionally, it displays a significant overpotential for the hydrogen evolution reaction (HER). The redox potential of zinc relative to SHE is -0.76 V, which is suitable for battery

operation due to the narrow operating window for gas (H<sub>2</sub> and O<sub>2</sub>) evolution in water.<sup>[91]</sup> The utilization of Zn in aqueous batteries is a well-established notion.. The battery's rechargeability is negatively impacted by the reduced active material, which limits the capacity of the charging process. This matter has been extensively debated in various publications and will not be addressed in this viewpoint. Alternatively, adjusting the solution's pH can prevent the formation of discharge products. Figure 2.8 shows different controlling factor for AZIB. Zn follows a direct reaction pathway to produce Zn<sup>2+</sup> ions during discharge when the pH levels are close to neutral.<sup>[92]</sup> The battery can be easily charged due to the absence of waste products, such as Zn-hydroxides and ZnO, allowing for the reduction of Zn<sup>2+</sup> to its metallic state (Zn<sup>2+</sup> + 2e–  $\rightarrow$  Zn). AZIBs have been revitalizing academic interest as post-LIB systems.



Figure 2.8 Overview of methods for controlling factors to resolve problems with ZIBs.

#### **Basic terminology in ZIBs:**

**Specific capacity:** The specific capacity of cathode/anode materials can be obtained by how much energy is made and how many electrons are involved in the electrochemical process. Equation 2.6 shows how to use the Faraday equation to choose a material's possible specific capacity. In this equation, Q is the total amount of electricity made, number of electrons in

the process is denoted by n., molecular weight (in g/mol) of the material being measured (M)., and 26.8 is the Faraday constant in Ah.

#### $Q = 26.8 \times n/M$ (2.6)

**Coulombic efficiency (CE):** The reversibility and capacity retention in ZIBs of an electrode are measured by its CE, which is given as a percentage (%). The charge capacity measurement to the release capacity is used to figure it out.

 $\eta = Qd/Qc \times 100\% \tag{2.7}$ 

**Specific energy:** The amount of energy that can be held per unit of weight or volume of an electroactive material is measured by its energy density or specific energy (SE). This is usually written as the SE (Wh kg<sup>-1</sup>) or the bulk ED (Wh/L). The ED can be improved by increasing the electrode's specific capacity by the battery's cell voltage.

Specific energy = Specific capacity x Cell voltage (2.8)

**Specific power:** SP is the ratio of electrical power provided per unit of mass (gravimetric power density) or volume (volumetric power density) of an electroactive substance, such as an electrode. So, it is possible to determine how much energy an electrode can release. Because they provide information about the electrode material's speed and efficiency in delivering power, gravimetric and volumetric power densities are crucial when building and assessing battery systems.

**Open circuit voltage and cell voltage:** Open circuit voltage (OCV) and cell voltage of a battery system are two of the most critical measurements. A battery's OCV is when no load or circuit is connected. Without the battery being connected to a charger or drained, the voltage reading is taken across its terminals. Since the OCV varies with the state-of-charge (SOC), it is a crucial metric in calculating the battery's SOC. Cell voltage, on the other hand, refers to the voltage of a single battery cell. Batteries are composed of multiple cells that are interconnected either in a series or parallel configuration. The voltage of a single cell is determined by the difference in potential between the cell terminals. Because it may reveal whether or not a cell is overcharged or undercharged, cell voltage measurements, both crucial indicators of a battery's health and performance, are complementary. A battery's SOC may be calculated using OCV, while individual cell voltages can be used to assess their health and efficiency. A battery's performance and lifespan can be improved by carefully monitoring these factors.

**Solid electrolyte interphase:** When an electrode material contacts the electrolyte in a battery, a thin layer known as a solid electrolyte interphase (SEI) develops. Products of electrolyte breakdown and electrode material make up the SEI. It serves as a shield against electrolyte breakdown and corrosion by isolating the electrode from the solution. The SEI film, which is generated during the first few cycles of charging/discharging, might affect a battery's performance and lifespan. A high lithium-ion transference number, film stability, and film conductivity are desirable qualities in an SEI. The battery's safety may potentially be compromised. The electrolyte and electrode material composition profoundly affects the creation and characteristics of the SEI layer.

**Charge Storage Mechanism:** While the precise response mechanism of ZIBs is still being investigated, a general outline may be provided as follows: Chemical conversion, intercalation of  $Zn^{2+}$ , and co-insertion of H<sup>+</sup> and  $Zn^{2+}$ .<sup>[93]</sup>  $Zn^{2+}$  intercalation reverses or extracts  $Zn^{2+}$  into or from a tunnel-type MnO<sub>2</sub> cathode while the electrolyte is a mild ZnSO<sub>4</sub> aqueous solution.<sup>[94]</sup> The process of H<sup>+</sup> insertion into host materials using layered framework



Figure 2.9 Example of charge storage mechanism for MnO<sub>2</sub>-based cathode

in aqueous electrolyte is required for H<sup>+</sup> and Zn<sup>2+</sup> co-insertion. In the chemical conversion process, During discharge,  $\alpha$ -MnO<sub>2</sub> reacts with proton to form MnOOH, while the OH<sup>-</sup> created reacts with H<sub>2</sub>O and ZnSO<sub>4</sub> to produce ZnSO<sub>4</sub>[Zn(OH)<sub>2</sub>]<sub>3</sub>.xH<sub>2</sub>O.<sup>[95]</sup> The reversibility of this process is evidenced by the recovery of the original  $\alpha$ -MnO<sub>2</sub> electrode upon charging. H<sup>+</sup> and Zn<sup>2+</sup> intercalate into the host material with either an open tunnel or a layered framework.

The charge storage in  $MnO_2$  is dominated by a proton intercalation of the solid-solution type that does not include  $Zn^{2+}$  co-insertion.<sup>[95]</sup> Figure 2.8 shows phase change in  $\gamma$ -MnO<sub>2</sub> during charging at initial to final voltage. The phenomena may be explained by the fact that desolvation and intercalation of protons are more easily accomplished at the hydroxyl/waterterminated oxide interface. Another hypothesised mechanism involves a chemical conversion between MnO<sub>2</sub> and MnOOH. This process may be reversed because the initial MnO<sub>2</sub> electrode is recovered after charging. Experiments with a higher degree of precision and more in-depth analytical approaches are required to elucidate the processes of manganese oxides.

#### 2.2.2.4.1 Cathode Materials for ZIBs

Regarding the performance of ZIBs, the electrode materials are paramount. TMOs, sulfides, and polyanionic compounds are some of the several materials being investigated for their potential use as cathodes. These materials need good electrical conductivity, Zn ion intercalation, and long-term stability to store and release energy in Zn-ion batteries. Researchers are developing cathode materials with high energy density, cycle stability, and cost-effectiveness to enhance ZIBs for diverse uses. They aim to develop cathode materials that meet all three criteria. The distinct properties of cathode architectures and morphologies are primarily accountable for their changing electrochemical performances (**Figure 2.10**).<sup>[95]</sup>

**Mn-Based cathode:** As ZIB cathodes, manganese oxides (MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, and Mn<sub>3</sub>O<sub>4</sub>) have been studied. High theoretical capacity (308 mAh g<sup>-1</sup>) and moderate discharge potential (1.35 V) of MnO<sub>2</sub> make it appealing.<sup>[96]</sup> Mn-based oxide is a highly researched cathode material for ZIBs due to its broad range of oxidation states, cost-effectiveness, and established synthesis process. Several reports indicate significant progress in the utilisation of Mn-based oxides as cathodes for ZIBs.<sup>[97]</sup> Despite the large number of recently published Mn-based oxides, there are still uncertainties regarding their electrochemical performance and how they compare to other Mn polymorphs and oxidation states. Classification of Mn-based oxides according to their oxidation states (MnO<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, and MnO), their polymorphs ( $\alpha$ -MnO<sub>2</sub> and  $\delta$ - MnO<sub>2</sub>) as ZIB cathode, common modification strategies to improve performance, and the impact of these strategies on performance enhancement.



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**Spinel-structured based cathode:** With the formula  $AB_2O_4$ , Spinel oxides are widely employed in metal-ion batteries. Spinels with high specific capacity and operating voltage, such as MgMn<sub>2</sub>O<sub>4</sub>, ZnMn<sub>2</sub>O<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and ZnCo<sub>2</sub>O<sub>4</sub> have been investigated as cathodes for ZIBs.<sup>[98,99]</sup> However, because of the significant electrostatic repulsion for lattice Zn<sup>2+</sup> diffusion, the perfect spinel structure was unsuitable for the Zn<sup>2+</sup> intercalation process. Ion doping techniques have been employed to increase the operating voltage and structural stability of LiCoO<sub>2</sub>, and it has been reported to dope Al or Ni/Mn into ZnCo<sub>2</sub>O<sub>4</sub>.<sup>[100]</sup> These findings support the use of doping to increase intercalation in spinels.

**Vanadium-based cathode:** ZIBs that feature vanadium-based cathode are particularly interesting due to their multi-electron redox reaction, high capacity, and large ion transport channel. The versatile V-O octahedral structure and multiple oxidation states of vanadium

have made vanadium-based compounds a popular research topic for ZIBs.<sup>[101]</sup> Vanadium, being an early transition metal, exhibits a slight volume change owing to the abundance of unoccupied nonbonding orbitals. The varying oxidation states of vanadium enable increased structural variability and functional adaptability in the incorporation of multivalent cations into vanadium-based compounds.<sup>[102,103]</sup> Vanadium can promote local electroneutrality by adjusting multiple oxidation states to stabilise the crystal structure and enhance the multivalent mechanism of cation diffusion. Vanadium's unique properties make it a viable option for cathode materials in ZIBs.<sup>[104]</sup>

Vanadium oxide exists in multiple oxidation states and forms, such as orthorhombic V<sub>2</sub>O<sub>5</sub>, double-layer V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O, V<sub>10</sub>O<sub>24</sub>, V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O, V<sub>6</sub>O<sub>13</sub>, VO<sub>2</sub>, and V<sub>2</sub>O<sub>3</sub>.<sup>[99,105]</sup> The orthorhombic V<sub>2</sub>O<sub>5</sub> and double-layer V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O possess a layered structure with an open channel, facilitating ion insertion between interlayers.<sup>[106]</sup> Vanadium oxides have been studied for other battery systems, including LIBs, for many years. However, they have demonstrated low voltage and inadequate ion storage capabilities.

**Prussian blue analogues (PBAs):** PBAs are structurally stable, abundant at redox-active areas, and have an open-framework 3D structure, making them ideal candidates for use as hosts in metal-ion batteries.<sup>[107]</sup> Cubic CuHCF, FeHCF, NiHCF, CoHCF, and ZnHCF are some of the PBAs that have been used as cathode materials for ZIBs.<sup>[108]</sup> Strategies to alleviate these issues include creating more vacancy sites and combining them with other active components, which help PBAs overcome their low specific capacity and unpredictable phase change. Recently, the idea of using a two-species redox process to boost Zn storage and prolong cycle stability has been presented.

**Organic compounds:** The high theoretical capacity, structural flexibility, element availability, environmental friendliness, and long-term viability of organic molecules make them desirable electrode materials. There are three distinct categories to describe them: n, p, and bipolar.<sup>[109]</sup> Various techniques used to enhance performance of these materials, including molecular structure regulation, incorporation of conductive carbon materials, and electrolyte optimisation.<sup>[110]</sup> Nevertheless, the electrochemical efficiency of organic electrode materials remains suboptimal in aqueous ZIBs. Organic compounds with active and electron-withdrawing groups should be rationally designed to enhance their specific capacity and voltages. Particle size and morphology significantly impact the practical capacity, rate performance, cycle life, and phase behaviours of organic compounds.<sup>[111]</sup>

**Other cathode materials:** Compounds in the chevrel phase having the generic formula  $M_xMo_6T_8$  (where M denotes metal cations and T denotes S, Se, or Te) are some of the other Zn-host materials identified.<sup>[112]</sup> Reversible Zn insertion is also possible in transition metal dichalcogenides (TMDs), such as VS<sub>2</sub> and MoS<sub>2</sub>. Recent research has shown that MoS<sub>2</sub>'s hydrophilicity is enhanced by adding oxygen, and the interlayer gap is expanded from 6.2 to 9.5.<sup>[113]</sup> This makes the intercalation of hydrated Zn<sup>2+</sup> possible, significantly reducing the desolvation drawback at interface. It is possible to improve the ion storage efficiency of various layered intercalation hosts by extending the interlayer gap and hydrophilicity engineering techniques.

**Metallic zinc anodes:** The chemical properties of metallic zinc make it a highly suitable option for utilization in aqueous batteries. Its abundance, high theoretical specific capacity, low potential , low toxicity, and inherent safety render it an excellent choice for this application.<sup>[114]</sup> Zn-based charge storage in ZIBs depends on the reversible electrochemical plating and stripping of Zn during the charging and discharging processes.<sup>[115]</sup> Zn dendrite development, low reversibility, and various adverse responses have hampered this anode study. Many methods exist to stabilise the Zn stripping/plating layer. Researchers created a low-voltage Zn<sup>2+</sup>-intercalated anode to replace the metal Zn anode.<sup>[116]</sup> High-performance Zn anodes must consider numerous challenges. High-specific surface 3D Zn-plated anodes require frame and pore structure optimisation. Zn alloying produces high-performance anodes. The Zn<sup>2+</sup>-intercalated anode, which uses the intercalation/de-intercalation process, exhibits weak conductivity, sluggish insertion/extraction kinetics, low energy density, structural collapse, and material dissolution.<sup>[116]</sup> Conductive agents, tunnel structures, crystal structural changes, tiny nanomaterials, and excellent crystallinity can overcome these issues.

**Electrolytes:** Significant effects on ZIB performance can be attributed to the electrolyte's electrochemical stability and ionic conductivity.  $Zn(CF_3SO_3)_2$ ,  $ZnCl_2$ ,  $ZnClO_4$ , and  $ZnSO_4$  are the most often used electrolytes.<sup>[117]</sup> One of the most critical factors in Zn anode performance in ZIBs is the solvation sheath structure of  $Zn^{2+}$  ions in aqueous electrolytes. The solvation sheath water molecules are tightly linked to the  $Zn^{2+}$  ion in a dilute electrolyte.<sup>[118]</sup> When plating, the diluted electrolytes provide a significant energy barrier for the hydrated  $Zn^{2+}$  to overcome to release themselves from the water molecules (desolvation). Because of this, Zn deposits over the anode become erratic. Increasing the electrolyte concentration helps control the  $Zn^{2+}$  ion's solvation sheath shape.<sup>[119]</sup> Zn<sup>2+</sup> has fewer water

molecules in its solvation shell in a concentrated electrolyte than in a diluted one. Therefore, the focused electrolyte provides a suitable environment for the desolvation of Zn<sup>2+</sup>, resulting in a smooth and uniform Zn deposition. Although rechargeable ZIBs show promise, there are outstanding issues that require resolution. Electrolyte techniques can regulate the solvation structure of zinc ions, while IL is an environmentally friendly solvent with minimal toxicity and biodegradability.<sup>[120]</sup> This study aims to create cosolvent electrolytes that can achieve high Coulombic efficiency and optimal full cell performance.

Electrolyte additive: Organic and inorganic electrolyte additions can stabilize the anode and cathode through electrochemical cycling, improving ZIBs performance. Although AZIBs show potential as energy storage devices, critical challenges remain unresolved. To enhance performance, it is crucial to investigate new electrolyte additives, create additives with multiple effects, and harness the synergistic effects of compound additives. Studying electrolyte structure is crucial for advancing electrolyte additives, and investigating gel electrolytes is a promising avenue for enhancing performance and minimising water content.<sup>[121]</sup> Electrolyte additive engineering is a promising approach that has been demonstrated to effectively address cathode and anode challenges through the addition of various additives to the electrolyte. MnSO<sub>4</sub> and other additives are included in the electrolyte to minimise cathode dissolution. MgSO<sub>4</sub> is utilised in the electrolyte to modify electrostatic interactions. Diethyl ether facilitates even  $Zn^{2+}$  deposition, while glucose regulates solvation structure, reducing anodic side reactions. The majority of research has focused on the additive's impact on either the cathode or anode in isolation. Limited efforts have been made to create electrolyte additives with multifunctional properties that can tackle issues on both electrodes.

**Separator:** Separators are not directly involved in electrochemical processes, but their microstructure and inherent features affect battery performance. Separators must be mechanically stable, thin, wettable, and ion-permeable. Glass fiber paper, cellulose membrane, and other polyolefin polymers are commonly utilized in ZIBs as separators.<sup>[122]</sup> Porous microstructures of varying pore diameters allow electrolyte ions to move freely across these separators. The capacity of an aqueous electrolyte to fill the pores of a porous separator that is well-wettable in water is essential for establishing homogenous ion transport.<sup>[123]</sup> Commercial porous separators are chemically neutral and do not include any functional

groups, allowing cations and anions to move through the pores while electrolytes are present readily.

#### 2.3 Physiochemical Characterizations of Materials

## 2.3.1 X-ray Diffraction (XRD)

XRD method is one of the most effective ways to identify the materials' crystal structure. XRD can determine the crystal structure of the compound, and it can also identify the various phases of the same compounds.<sup>[124]</sup> In the electromagnetic spectrum, X-rays are distinguished by their short wavelengths and high energy. X-rays are created when an electron traveling at high speed and accelerated by a high-voltage field collide with a metal target. X-rays are formed when the kinetic energy of moving electrons is turned into X-ray radiation by rapidly decelerating the electrons.<sup>[125]</sup> The following formula explains how the X-ray radiation's wavelength, measured in nanometres, and connected to the accelerating voltage of the electrons.



**Figure 2.11** (a) Schematic representation for X-ray generation, (b) working principle for XRD.

To generate X-rays, an X-ray tube (XRT) is required. The XRT shown in Figure 2.11 (a) is made up of two metal electrodes, a vacuum, and a stream of accelerated electrons. Applying a high voltage between these two electrodes causes the electron to collide quickly with the metal target (copper, iron, molybdenum, chromium). The windows of the XRT direct the X-rays that are created at the collision site. While the XRT may produce X-rays in various wavelengths, the XRD techniques call for a monochromatic X-ray source. Monochromatic radiation is generated by blocking out all other wavelengths of light using a nickel filter.

The principle of XRD is shown in Figure 2.11 (b). When an energetic electron collides with an atom, it bumps an electron out of the inner shell and creates a vacancy. X-rays of a particular wavelength and energy are produced when an outer-shell electron moves into the

void. High-intensity Cu K $\alpha$  radiation is frequently utilized for sample analysis. The crystal structure and phase of a material may be determined by measuring the d-spacing and comparing the peaks to the ICDD database.

Bragg's law governs the fundamental law of XRD in the crystalline structure, In this case, d represents the interlayer separation,  $\theta$  the incidence angle,  $\lambda$  is the wavelength of the light source, and n the diffraction order. Bragg's law can be expressed as:<sup>[126]</sup>

$$2dsin\theta = n\,\lambda \tag{2.10}$$

According to Scherrer's formula<sup>[127]</sup>, the crystallite size of the sample may be determined from the FWHM of the most intense diffraction line, as shown in the following equation.

#### $D = K\lambda/\beta \cos\theta \qquad (2.11)$

Grain size is denoted by D, peak FWHM angle in radians is, Bragg's angle is, and K is a constant. The values of 'K' might be anywhere from 0.89 to 1.39; however, they are typically near 1.

#### 2.3.2 Raman Spectroscopy

The material's chemical composition and structural features may be studied with Raman spectroscopy, a reliable analytical tool. It helps scientists identify and evaluate compounds by revealing their vibrational and rotational modes. Raman spectroscopy's underlying premise is the photon-matter interaction. Most of the incoming photons in a monochromatic illumination of a sample disperse elastically, keeping the same energy and frequency. Raman scattering, an inelastic scattering process in which dispersed photons acquire or lose energy, occurs only for a tiny percentage of the photons. The energy difference of the incident. and scattered photons represents vibrational energy levels inside the sample's molecules. Raman spectroscopy reveals the material's vibrational modes and molecular bonding by examining the energy changes in the scattered light.<sup>[128]</sup> Raman spectroscopy has various benefits for analyzing materials. Figure 2.12 shows Raman spectroscopy working when incident light interacts with sample. One primary advantage is that this method is non-destructive and requires minimal sample preparation before analysis. In situ and real-time measurements are possible thanks to direct analysis of solid, liquid, or gaseous materials. The Raman spectra of many compounds are distinctive due to their vibrational frequencies. Researchers can determine the molecular components of a sample by comparing the resulting spectra to reference databases or established standards. In addition, Raman spectroscopy can reveal information about a material's structure. Changes in crystallographic orientations, chemical

bond strengths, and phase changes can all be detected. Molecular conformations, chain lengths, and intermolecular interactions are all things that may be learned via the use of Raman spectroscopy, making it an ideal tool for the study of polymers. Raman spectroscopy may also be used to analyze heterogeneous materials, allowing scientists to determine the presence and properties of many phases or constituents inside a single material. By narrowing the laser's focus on a small area, spatially resolved Raman spectroscopy can reveal subtle differences in a sample's chemical and structural composition.



**Figure 2.12** (a) Schematic representation for the generation of Raman spectroscopy, and (b) Ray diagram shows the stokes generation, anti-stokes, and Rayleigh scattering processes.

In conclusion, Raman spectroscopy is a helpful non-destructive tool for gaining insight into materials' molecular composition, chemical bonds, and structural properties. It can be used in chemistry, materials science, pharmacology, forensics, and even medicinal studies. It is a helpful tool for learning about the characteristics and actions of many compounds because of the specific molecular information it can supply.

# 2.3.3 X-ray Photoelectron Spectroscopy (XPS)

XPS is a proper analytical method used in materials science to study materials' elemental makeup, chemical states, and surface features. It explains how solids, liquids, and thin films behave on their surfaces. The main idea behind XPS is that when X-rays interact on a sample, the photons can cause electrons in the inner rings of atoms to become excited and jump out of the material. These thrown-off electrons are called photoelectrons and carry information about the sample's elements and chemical surroundings. The XPS device measures the speed

and strength of the released photoelectrons. The binding energy (BE) of electrons is a characteristic property of an element and its chemical configuration, and it is equivalent to the energy required to bind the electrons.<sup>[129]</sup> By analyzing the BE of photoelectrons, XPS helps researchers understand the surface chemistry, reactivity, and electronic structure of materials. This makes it an essential tool for studying surfaces, interfaces, and thin films in many different material systems.



**Figure 2.13** (a) Depicts the instrumental arrangement for XPS measurements. (b) survey spectra of example metal oxide sample (c) working principle of elemental identification through XPS measurements.

XPS technique utilizing Al K $\alpha$  radiation can provide data on elements located within a few nm of the sample's surface. Electrons experience increased scattering when emitted from deeper regions within a sample. This constrains the depth from which photoelectrons can originate within a sample. XPS is a surface-sensitive technique (Figure 2.13) When analyzing materials, XPS has several benefits. First, it is a method that only works close to the surface, with an average probing depth of a few nm. This makes it an excellent tool for studying the surface layers and boundaries of materials, where the chemistry and processes at the surface are essential. To understand how things behave and get the most out of them in different situations, you need to be able to study their surface composition and chemistry. Another benefit of XPS is that it can work with numbers. XPS can tell how many different types of elements are in a material by measuring how strong the photoelectron spots are. This is done using calibration standards and sensitivity factors known for each component. This lets the atomic amounts be measured accurately. XPS can also give helpful information about an object's chemical bonds and electronic states. The chemistry changes of photoelectrons' BE tell us about the elements' oxidation states, coordination environments, and bonding interactions. This helps us determine how surfaces react, how substances stick to them, and how they work as catalysts. XPS can help find surface contamination, look at chemical changes caused by processing or the environment, and figure out how suitable coatings or thin films.

#### 2.3.4 Field Emission Scanning Electron Microscopy (FESEM)

FESEM is a robust image method often used in materials science to describe and analyze different types of materials. FESEM can take high-resolution image of a solid sample's surface topography and shape, giving important information about its morphology.<sup>[130]</sup> FESEM uses a field-emission electron source, which makes an electron beam very focused and small in spot size. This makes it possible to make detailed pictures with good spatial precision, usually within a few nm. One of the best things about FESEM is that it can take photos with great clarity at many magnifications. It gives experts an apparent look at the grain borders, roughness of the surface, cracks, and other flaws in a material's microstructure. FESEM can also show small features on the surface and tiny structures that may be hard to see with other imaging methods. FESEM is especially useful for looking at materials with complicated shapes or different parts. It can explain how different stages, particles, or parts of an object are spread out and put together. FESEM can also study how various processing factors, like heat treatment or mechanical bending, change a material's microstructure and surface properties. In addition to geographic imaging, FESEM has other imaging methods that can tell you much about a sample's makeup and how its elements are distributed. EDS is often used with FESEM. This lets the chemical elements in the materials be identified and mapped. This makes determining a material's elemental makeup, chemical heterogeneity, and elemental spread possible. FESEM also lets you use methods like electron channeling contrast imaging (ECCI) and electron backscatter diffraction (EBSD) to look at the surface of a material. EBSD tells you about crystallographic orientations, grain sizes, and phase identification. ECCI makes areas with crystallographic flaws or deformation traits stand out more. FESEM is used extensively in the study and development of materials science and in many different businesses. It is used to learn about metals, alloys, ceramics, plastics,

composites, semiconductors, and living materials.<sup>[131]</sup> Figure 2.14 shows the representation of the various components of the FESEM instrument.



**Figure 2.14** The FESEM's operational mechanism is illustrated in a schematic representation. FESEM is needed to understand how the structure of a material affects its properties, to create new materials, to evaluate how well a material works, and for quality control. FESEM is a robust imaging method that shows the surface topography, morphology of materials in high-resolution, three-dimensional images. Because it can show fine surface details and microstructural features, it is a handy tool for characterizing and analyzing materials in various science and industrial settings.

# 2.3.5 Energy Dispersive X-ray Spectroscopy (EDS)

EDS, often known as X-ray microanalysis or EDX, is a proper analytical method for elemental analysis in materials research. EDS gives chemical composition and elementary concentration information about a sample. EDS and SEM can simultaneously image and analyze materials.<sup>[132]</sup> An SEM-focused electron beam bombards the material during EDS examination. Electrons expel inner-shell electrons from sample atoms. Outer-shell electrons fill the vacancies, emitting distinctive X-rays. The sample's elements determine X-ray energy. EDS detectors assess X-ray energy and intensity, identifying and quantifying components. Researchers can establish the sample's elemental makeup from the X-ray spectrum. EDS enhances materials analysis. It delivers fast, non-destructive elemental analysis with little sample preparation. This makes it helpful in evaluating metals, alloys, ceramics, polymers, minerals, and biological samples. EDS analyzes bulk materials and thin films or coatings. EDS provides spatially resolved elemental data. EDS and SEM allow elemental mapping of the sample's surface. This lets you study elemental segregation, phase separation, and compositional changes. EDS excels in characterizing complicated materials like multi-phase alloys and composites. It can detect trace elements, contaminants, and dopants that dramatically affect material characteristics and performance. EDS may also reveal elemental diffusion, gradients, and environmental or processing-induced chemical changes. EDS can also identify the elemental composition of sample particles and features. It helps identify unfamiliar materials, analyze tiny areas, and validate phase or component composition.<sup>[133]</sup> Failure analysis, materials research, quality control, and process optimization employ EDS in many sectors. EDS is a potent elemental analysis tool in materials research. It identifies, quantifies, and maps components in a sample, revealing its chemical composition and distribution. EDS is vital for understanding materials' elements, characteristics, and application performance.

# 2.3.6 High-Resolution Transmission Electron Microscopy (HRTEM)

HRTEM is a sophisticated imaging method used in materials research to characterize and analyze materials at the atomic level. Researchers may study materials' crystal structures, lattice flaws, interfaces, and nanoscale characteristics with HRTEM's high-resolution pictures.<sup>[134]</sup> A stream of electrons passes through a tiny sample in HRTEM. A high-resolution electron microscope with improved optics and electron sources allows HRTEM to image materials with sub-angstrom resolution. Atoms and their configurations in a crystal

lattice may be seen at this resolution. HRTEM's atomic-level structural information is a significant benefit. HRTEM creates a picture from transmitted electrons to directly observe crystal features such as unit cells, lattice planes, and atomic groupings. This knowledge is essential for understanding material characteristics and behavior. HRTEM best studies nanoparticles, nanowires, and thin films. It can disclose flaws, dislocations, interfaces, and their size, shape, and crystalline structures.<sup>[135]</sup> Figure 2.15 displays the HRTEM instrument components. HRTEM characterizes alloys, catalysts, and semiconductors with complicated microstructures, where atomic-scale features affect their characteristics. In addition to imaging, HRTEM provides improved analytical methods. Crystal symmetry, orientation, and phase identification may be determined from chosen sample sections using electron diffraction patterns. Nanoparticles' crystal structure and symmetry can be determined through SAED. Lattice faults and interfaces may also be analyzed using HRTEM. It can image dislocations, stacking faults, grain boundaries, and point defects like vacancies or substitutional impurities.



**Figure 2.15** The HRTEM operational mechanism is illustrated in a schematic representation. HRTEM can be merged with electron energy-loss spectroscopy (EELS) and EDS for chemical and elemental information at atomic resolution.<sup>[136]</sup> This lets researchers link the structural, chemical, and elemental features of materials. HRTEM is a solid atomic-scale imaging and analysis tool. Crystal structures, lattice faults, interfaces, and nanoscale features

may be seen with high resolution. HRTEM helps materials scientists understand materials' fundamental characteristics, behavior, and performance.

## 2.3.7 Nitrogen Adsorption-Desorption Analysis

Nitrogen Adsorption-Desorption Analysis, often known as Brunauer-Emmett-Teller (BET) analysis, is a common materials science method for assessing solid materials' surface area, porosity, and pore size.<sup>[137]</sup> By revealing their textural features, this method helps explain material performance in diverse applications. The principle underlying this phenomenon is that gas molecules adhere to a material's surface in a manner that is proportional to the surface area available. The BET method is a nitrogen adsorption-desorption analysis that employs a mathematical model to interpret experimental data.<sup>[138,139]</sup> The study employs the instrument illustrated in Figure 2.16 (a). The BET method entails conducting nitrogen gas adsorption is quantified at various pressures, and a graph is generated by plotting the adsorbed amount against the relative pressure. The BET equation is employed to model the adsorption of gas molecules onto a material with a defined surface area.<sup>[140]</sup> Initially, the process entails degassing the material at a specific temperature. Subsequently, the cells were emptied and the void volume was measured using a controlled flow of helium gas. Pressure-controlled N<sub>2</sub> adsorption-desorption process is conducted. Different isotherms may be



Figure 2.16 (a) The instrument was utilized to conduct studies on surface area and pore size. b) displays the various stages of pore filling by  $N_2$  gas molecules and the corresponding isotherm profile.

observed depending on the material under investigation. Nitrogen adsorption-desorption analysis uses nitrogen gas molecules adsorbing to a material's surface. Nitrogen gas molecules adsorb onto material surfaces at low relative pressures. Analysis metrics like specific surface area are essential. It represents the material's surface area per mass or volume. Figure 2.16 (b) displays a single isotherm as an illustration. The isotherm's marked points correspond to distinct stages of  $N_2$  adsorption and desorption.

Nitrogen adsorption-desorption analysis also measures porosity and pore size distribution. The adsorption isotherm shape may identify the kind of porosity (micropores, mesopores, or macropores). Mathematical models like BJH and DFT can compute the pore size distribution.<sup>[141]</sup> Diffusion in porous materials requires this information. The method works on porous solids, catalysts, adsorbents, zeolites, activated carbon, and powders. Pharmaceuticals, energy storage, environmental science, and materials synthesis employ it for research, quality control, and process optimization. Nitrogen adsorption-desorption analysis is critical in materials science research and development to understand material performance and behavior in diverse applications.





Figure 2.17 FTIR spectrometer's basic operation.

In Material science, FTIR spectroscopy is used to examine and characterize materials. Materials research and development rely on it for molecular composition, structure, and bonding information.<sup>[142]</sup> FTIR spectroscopy is based on material-infrared light interaction. When a substance absorbs infrared radiation, its molecules vibrate. Depending on the material's chemical makeup, these vibrations may identify functional groups, contaminants, and molecular structures.<sup>[143]</sup> Non-destructive FTIR spectroscopy is a significant benefit. It analyzes samples without preparation. This is crucial when investigating fragile or precious materials. Figure 2.17 shows a basic diagram of FTIR and its working principle. FTIR spectroscopy reveals material properties. It can detect functional groups, including carbonyl, hydroxyl, and amino groups.

Researchers may identify bonds and their environments by examining infrared absorption peaks. FTIR spectroscopy also analyzes material crystallinity and phase composition. Crystal structures in crystalline materials may be identified and quantified using infrared absorption bands.<sup>[144]</sup> Understanding mechanical, thermal, and electrical qualities requires this knowledge. FTIR spectroscopy detects and analyzes chemical changes in materials. It tracks chemical processes, intermediates, and transformations. FTIR spectroscopy helps the industry with quality control and material characterization. It may test raw material composition and purity, detect contaminants, and evaluate product uniformity. Unknown samples may be recognized by comparing their spectra to a reference database, speeding up quality control. FTIR instrumentation has improved recently. Researchers may analyze complicated samples' component distribution and composition using FTIR and microscopy. Attenuated total reflection (ATR) FTIR spectroscopy may analyze samples in situ or in contact with other materials, making it suitable for many material systems.<sup>[145]</sup> Finally, material scientists need FTIR spectroscopy. Its non-destructive nature, molecular information, and material analysis adaptability make it vital for researching material composition, structure, and chemical changes. Researchers may use infrared light to study material qualities and behavior, advancing polymers, composites, medicines, and electronics.

## 2.4 Electrodes Preparation, Device Assemblies, and Background of

## **Electrochemical Techniques**

# 2.4.1 Slurry Preparation

In energy storage devices like SCs and ZIBs, electrode materials are essential components that store and discharge electrical energy via electrochemical reactions. A slurry composed of

active material, conductive additives, and a binder must be formulated to prepare electrodes. The slurry's preparation significantly impacts the electrochemical efficacy and stability of the final electrode. The active material, typically a carbon-based material or TMOs for ESD, is combined with conductive additives such as graphite or carbon black to prepare the slurry. These compounds improve the electrical conductivity of the electrode, allowing for efficient charge transfer during electrochemical processes. In addition, a binder is added to the slurry to enhance the adhesion between the electrode material and the current collector, thereby ensuring mechanical stability. The components of the slurry are combined in a solvent to create a homogenous suspension. The choice of solvent is contingent on the compatibility of the active ingredient and binder. The most common solvents are water, organic, or both. For consistent electrode coating, care must be taken to properly dispersion the active material and conductive additives and control the slurry's viscosity.

## 2.4.2 Electrode Preparation for SCs

After slurry preparation, the preparation of the electrodes is the next stage. Typically, the slurry is deposited on current collector, usually made of a conductive material such as metal foil or carbon fiber. Various techniques, such as doctor blade coating, spin coating, spray coating, and screen printing, can be utilized for the coating procedure. A thin slurry layer is applied to the current collector during doctor blade coating using a blade or drop cast. By modifying the blade separation, the thickness of the electrode coating can be adjusted. The spin coating process entails applying a small quantity of slurry to the current collector, then spinning at high velocities to distribute the slurry evenly. Spray coating entails atomizing the slurry into fine particles and then applying them to the current collector. The slurry is transferred to the current collector using a stencil in screen printing.

After the slurry has been deposited, the electrode is desiccated to remove the solvent and binder, leaving a solid electrode film. The dehydrating process is typically conducted in a vacuum oven or in an inert atmosphere to prevent oxidation and moisture absorption. For SCs, SS disk electrodes are used as current collectors. Zero-size polish paper and ultrapure water flow polished the SS (1 cm<sup>2</sup>). Ultra-micro balance (Mettler Toledo) calculated electrode mass. The slurry was drop-cast over the exposed SS substrate and dried at 110 °C for 10 h. SS 15-mm disk-shaped electrodes were polished using zero-sized polish paper and cleaned with DI water. The slurry was drop cast and dried to determine active mass loadings over various electrodes.

## 2.4.3 Three-electrode and Two-electrode Setups for SCs Studies

3E and 2E configurations are utilized for SC electrochemical characteristics. The 3E arrangement uses the working electrode (the electrode under examines), a counter electrode, and a reference electrode. The counter electrode is usually platinum based, and Ag/AgCl used as reference electrode, while the working electrode is the electrode mentioned above. This setup measures specific capacitance, electrochemical impedance, and cyclic voltammetry. Two electrodes (AC and TMO) utilized as working electrodes in the two-electrode configuration.





The 2E system evaluates SC energy density, power density, and cycle stability. Electrodes were immersed in electrolyte solutions after preparation. 3E experiments employed the coated electrode as the working electrode and Na<sub>2</sub>SO<sub>4</sub> solution as electrolytes. Figure 2.18 (a) depicts 3E measuring setup. Figure 2.18 (b) shows the Flat test cell assembly utilized for 2E measurements.

#### 2.4.4 Electrode Preparation and Coin Cell Packing for ZIBs Testing

For the study of ZIBs, the preparation of electrodes and the preparation of coin cells differ slightly from SCs because ZIB systems have different needs. ZIB electrodes are made by choosing suitable active materials, usually TMOs or sulfides. A slurry is made by mixing these materials with electrical chemicals and a binder. The slurry is put on a current collector, usually made of metal foil, and dried in a controlled environment. For electrical evaluation in ZIB tests, coin cells are often used. Coin cells have a working electrode, a counter electrode made of zinc metal, and a filter that has been soaked in an electrolyte. Most of the time, the electrode made, as explained above, is the working electrode, and the zinc metal is the counter electrode. The divider lets ions move between the electrodes without letting them touch each other directly. The coin cell is then covered to make sure the cell stays whole and to keep the electrolyte stable. The completed coin cell is then put through several electrochemical tests, such as CV, GCD cycling, and EIS. These tests tell us a lot about how well the ZIB system works, how much it can handle, and how stable it is. Materials study is critical for making electrodes, putting devices together, and learning about electrochemical techniques in energy storage. To accurately measure the performance of ZIB, the coin cells must be packed with suitable active materials, counter electrodes, and electrolytes.



**Figure 2.19** (a) A standard CV curve displaying both cathodic and anodic peaks, and (b) a GCD profile, (c) Nyquist plot depicts the process of determining various resistance values through graphical means.

Researchers can learn much from these methods and setups about how energy storage materials behave electrochemically.

## 2.4.5 Electrochemical Characterization Techniques

We used electrochemical workstations and a battery cycler (the standard Biologic SAS VSP, CHI 1150C, and Neware battery testing system) to do several electrochemical characterizations. These were CV, GCD, EIS, and GITT method. Most of the time, these methods are used to study the electrochemical features of SCs and ZIBs. The CV technique measures the relationship between current and voltage. The GCD technique, on the other hand, measures the relationship between current and voltage at different steady currents. EIS is a method for calculating a material's resistance and capacitance at different frequencies. Origin Lab software, used to process and plot the test data. This program used to study electrochemical data and make plots like Nyquist, Bode, and CV plots.

# 2.4.5.1 Cyclic Voltammetry (CV)

Cyclic voltammetry uses a triangle potential-time waveform to apply to an electrode and observe the current in an electrochemical cell. Unlike a 3E system, a 2E cell applies voltage between positive and negative electrodes. Time-varying voltage or potential is referred to as the scan rate. In a CV, voltage or time is graphed against electric current in an electrochemical cell. Cyclic voltammetry (CV) is used to evaluate electrodes and devices' energy storage capability in 3E, and 2E cell settings. CV may be used to analyse the reversibility of electrode reactions and energy storage system processes, among other complicated system properties.<sup>[146]</sup> The method gives information about the electrochemical processes happening at the electrode surface, such as the location of redox peaks, the rate of electrochemical reactions, and an estimate of the energy storage devices' capacitance. During a CV experiment, the potential goes back and forth between a starting and ending potential, typically at a set scan rate. The current reaction is recorded and plotted as a function of the applied potential as the potential sweeps. The result is a graph called a cyclic voltammogram (Figure 2.19 (a)). It shows peaks and patterns showing how the electrode's electrochemical processes are changing the voltage. The position and shape of the peaks give information about the redox processes, such as the redox potential, reversibility, and reaction rates. CV is used to study how SCs, batteries, catalysts, and other materials that conduct electricity behave. Equation 2.12 can be used to figure out the specific capacitance (Cs)., which involves computing the voltametric charge encompassed within the CV curve.<sup>[41]</sup>

$$C_{s} = \frac{\int_{V_{i}}^{V_{f}} i(V)dV}{mv(V_{f} - V_{i})}$$
(2.12)

Where i(V) is the current calculated from the CV curve, where m is the active mass loading, v is the scan rate (mV s<sup>-1</sup>), Vi is the initial potential, and V<sub>f</sub> is the final potential.

#### 2.4.5.2 Galvanostatic Charge-Discharge (GCD)

The GCD method is commonly utilised to analyse and predict how well electrode active materials store energy in real-world working situations. During a GCD test, an electrode is subjected to a constant current and charged-discharged between fixed voltage window. The resulting voltage change over time is then measured. The variation in GCD profiles of various ESD necessitates distinct handling of each material to compute its characteristic metrics.<sup>[147]</sup> Figure 2.19 (b) show process involves supplying a constant current to the device and monitoring the resulting voltage over time. The experiment's results in the charge-discharge curves provide information on the device's capacity, the voltage profiles during charging and discharging, and the impacts of rate performance.

Calculations of GCD were carried out on two-electrode cells utilizing the following equations: <sup>[41]</sup>

$$C_{s} = \frac{(i \times \Delta t)}{M \times (V_{f} - V_{i})}$$
(2.13)  
SE =  $\frac{C_{s} V^{2}}{M \times (V_{f} - V_{i})}$ (2.14)

$$SE = \frac{3}{7.2}$$
 (2.14)  
 $SP = \frac{3600 \times SE}{\Lambda t}$  (2.15)

Where "i" represents the charge/discharge current at time t (s), " $\Delta t$ " represents the discharge duration, and "V<sub>i</sub>" is initial potential and "V<sub>f</sub>" represents the final potential. "M" denotes the total active mass distributed over both electrodes.

#### 2.4.5.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is commonly employed for assessing the functionality of electrochemical capacitors, batteries, and other energy storage and conversion devices.<sup>[148,149]</sup> EIS entails the application of a low-magnitude alternating current (AC) signal across the electrochemical cell, followed by the measurement of the resultant current response. The frequency of the AC signal is modulated across a broad spectrum, commonly spanning from mHz to MHz. Following this, the measured impedance is plotted as a frequency function, characterized as the quotient of the applied voltage and the resultant current. The EIS data provides the opportunity to extract various parameters such as the solution resistance, double-layer capacitance, charge transfer

resistance, and Warburg impedance. The parameters mentioned above offer valuable insights into the kinetics of charge transfer mechanisms, ion diffusion, and the existence of interfaces or surface layers.<sup>[150]</sup> A Bode plot shows the frequency-dependent magnitude and phase response of EIS experiments, whereas a Nyquist plot shows the real and imaginary impedance components. The application of EIS analysis in practical scenarios enables the examination of active electrode materials' impedance, specific capacitance, equivalent series resistance, and charge storage mechanisms. The proposed technique involves the application of a sinusoidal perturbation signal with low amplitude, typically within the frequency spectrum of 100 kHz to 10 mHz, to an electrochemical system while it is at open-circuit voltage. The system's impedance is denoted as Z, comprised of the real component  $Z_{Re}$  and the imaginary component  $Z_{Im}$ .

The customary representation of impedance data is in the form of a Nyquist plot. The Nyquist plot commonly exhibits a semi-circular arc in the high-frequency domain, which suggests the existence of charge transfer resistance ( $R_{CT}$ ) and a linear region in the low-frequency range. The electrochemical reaction rate, which is highly correlated with the material's conductivity, is assessed through  $R_{CT}$ . The electrode resistance ( $R_S$ ) is represented by the point of intersection between the plot and the  $Z_{Re}$  axis, as illustrated in Figure 2.19 (c). Furthermore, it is possible to partition the high-frequency capacitive. EIS technique offers significant insights into the kinetics of electrochemical processes and the system's capacitance. Employing equivalent circuit models along with EIS data enables a more thorough understanding of the underlying electrochemical mechanisms, leading to improved efficiency of electrochemical cells.

# 2.4.5.4 Galvanostatic Intermittent Titration Techniques (GITT)

GITT is a widely employed electrochemical approach that enables the determination of the ionic diffusion coefficient and transport properties of ions within an electrochemical system.<sup>[151]</sup> This phenomenon finds significant utility in investigating ion diffusion within solid-state electrodes, including but not limited to LIBs and solid oxide fuel cells. Applying a constant current to the electrode initiates the ion diffusion process in GITT. Through voltage response analysis, it is possible to ascertain ions' diffusion coefficient and concentration profiles within the electrode.<sup>[152,153]</sup> The study of GITT offers significant contributions to understanding the transport properties of ions, the kinetics of diffusion, and mechanisms of

reaction that occur within electrode materials. This tool is highly effective in examining the functionality and conduct of energy storage systems while facilitating electrode materials' development and refinement to achieve superior electrochemical performance.<sup>[154]</sup>



Figure 2.20 a) A schematic illustration of a step in the GITT; b) The potential response, including  $\Delta E t$  (the overall transient voltage changes of the cell for a current I<sub>0</sub> over time ( $\tau$ ) and  $\Delta E_s$  (the change in steady-state voltage).

Fick's second law can be used to calculate GITT.<sup>[155]</sup>

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

The weight of active materials is denoted by  $m_B$  (g), while the molecular weight of active materials is denoted by  $M_B$  (g mol<sup>-1</sup>). The molar volume of the substance is represented by  $V_m$  (cm<sup>3</sup> mol<sup>-1</sup>), and the surface area is denoted by S (cm<sup>2</sup>). The pulse time of the current pulse is indicated by  $\tau$  (s). The parameter " $\Delta E_s$ " refers to the voltage difference observed at the conclusion of the relaxation period between two consecutive steps. On the other hand, " $\Delta E_\tau$ " denotes the variation in voltage between the initial and final stages during the discharge pulse time, after the iR drop has been removed. Figure 2.20 (a,b) exhibit the input pulse and corresponding GITT profile utilized for determining the values of  $\Delta E_s$  and  $\Delta E_\tau$ . To summarize, CV, GCD, EIS, and GITT are fundamental electrochemical methodologies in examining materials and electrochemical systems. The methods above offer significant insights into redox behavior, energy storage attributes, charge transfer mechanisms, and ion diffusion properties. By utilizing these methodologies, scholars can thoroughly comprehend the electrochemical efficacy and conduct of substances, culminating in creating more effective and refined energy storage mechanisms.

#### **2.5. References**

- [1] X. Guo, G. Zhang, Q. Li, H. Xue, H. Pang, *Energy Storage Mater.* 2018, 15, 171–201.
- [2] H. T. Tan, W. Sun, L. Wang, Q. Yan, *ChemNanoMat* **2016**, *2*, 562–577.
- [3] R. R. Poolakkandy, M. M. Menamparambath, *Nanoscale Adv.* 2020, 2, 5015–5045.
- [4] S. M. Pawar, B. S. Pawar, J. H. Kim, O.-S. Joo, C. D. Lokhande, *Curr. Appl. Phys.* 2011, 11, 117–161.
- [5] R. Li, Y. Li, P. Yang, D. Wang, H. Xu, B. Wang, F. Meng, J. Zhang, M. An, J. Energy Chem. 2021, 57, 547–566.
- [6] A. Nandagudi, S. H. Nagarajarao, M. S. Santosh, B. M. Basavaraja, S. J. Malode, R. J. Mascarenhas, N. P. Shetti, *Mater. Today Sustain.* 2022, 19, 100214.
- P. Jittiarporn, S. Badilescu, M. N. Al Sawafta, L. Sikong, V.-V. Truong, J. Sci. Adv. Mater. Devices 2017, 2, 286–300.
- [8] T. Guo, M.-S. Yao, Y.-H. Lin, C.-W. Nan, *CrystEngComm* **2015**, *17*, 3551–3585.
- [9] C. Yuan, H. Bin Wu, Y. Xie, X. W. D. Lou, Angew. Chemie Int. Ed. 2014, 53, 1488– 1504.
- [10] E. E. Finney, R. G. Finke, J. Colloid Interface Sci. 2008, 317, 351–374.
- [11] Y. Mao, T.-J. Park, F. Zhang, H. Zhou, S. S. Wong, *Small* **2007**, *3*, 1122–1139.
- [12] L. Zhou, Z. Zhuang, H. Zhao, M. Lin, D. Zhao, L. Mai, Adv. Mater. 2017, 29, 1602914.
- [13] T. Pan, H. Deng, S. Kang, Y. Zhang, W. Lian, C. Zhang, H. He, Chem. Eng. J. 2021, 417, 129246.
- [14] N. A. Mala, M. A. Dar, M. ud D. Rather, B. A. Reshi, S. Sivakumar, K. M. Batoo, Z. Ahmad, J. Mater. Sci. Mater. Electron. 2023, 34, 505.
- [15] K. Agilandeswari, A. Rubankumar, Synth. React. Inorganic, Met. Nano-Metal Chem. 2016, 46, 502–506.
- [16] W. H. Low, P. S. Khiew, S. S. Lim, C. W. Siong, E. R. Ezeigwe, J. Alloys Compd. 2019, 775, 1324–1356.
- [17] P. G. Jamkhande, N. W. Ghule, A. H. Bamer, M. G. Kalaskar, J. Drug Deliv. Sci. Technol. 2019, 53, 101174.
- [18] S. Dervin, S. C. Pillai, 2017, Advances in Sol-Gel Derived Materials and Technologies. Springer, Cham. pp. 1–22.
- [19] D. Y. Nadargi, J. L. Gurav, N. El Hawi, A. V. Rao, M. Koebel, J. Alloys Compd. 2010,

496, 436–441.

- [20] H. M. Tahir Farid, M. Noman Saeed, S. Gouadria, F. Farraj Alharbi, S. Aman, *ChemistrySelect* 2023, 8, DOI 10.1002/slct.202204283.
- [21] M. Parashar, V. K. Shukla, R. Singh, J. Mater. Sci. Mater. Electron. 2020, 31, 3729– 3749.
- [22] M. J. Kenney, J. E. Huang, Y. Zhu, Y. Meng, M. Xu, G. Zhu, W.-H. Hung, Y. Kuang,
  M. Lin, X. Sun, W. Zhou, H. Dai, *Nano Res.* 2019, *12*, 1431–1435.
- [23] R. Babaei-Sati, J. Basiri Parsa, M. Vakili-Azghandi, Synth. Met. 2019, 247, 183–190.
- [24] M. S. Whittingham, Curr. Opin. Solid State Mater. Sci. 1996, 1, 227–232.
- [25] X. Ji, Y. Zhu, X. Lian, B. Fan, X. Liu, P. Xiao, Y. Zhang, Ceram. Int. 2022, 48, 2281– 2288.
- [26] C. Niu, J. Qi, M. Tian, Ceram. Int. 2022, 48, 6874–6879.
- [27] A. Kaur, B. Bajaj, A. Kaushik, A. Saini, D. Sud, Mater. Sci. Eng. B 2022, 286, 116005.
- [28] C. Balamurugan, K. Cho, B. Park, J. Kim, N. Kim, Y. Pak, J. Kong, S. Kwon, *Chem. Eng. J.* 2022, 430, 132690.
- [29] X. Duan, J. Ma, J. Lian, W. Zheng, CrystEngComm 2014, 16, 2550.
- [30] R. E. Morris, Chem. Commun. 2009, 2990.
- [31] S. Dai, Y. H. Ju, H. J. Gao, J. S. Lin, S. J. Pennycook, C. E. Barnes, *Chem. Commun.* 2000, 243–244.
- [32] J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, J. Am. Chem. Soc. 2002, 124, 4228–4229.
- [33] E. R. Parnham, R. E. Morris, Acc. Chem. Res. 2007, 40, 1005–1013.
- [34] X. Duan, T. Kim, D. Li, J. Ma, W. Zheng, Chem. A Eur. J. 2013, 19, 5924–5937.
- [35] M. Zhong, M. Zhang, X. Li, *Carbon Energy* **2022**, *4*, 950–985.
- [36] D. Wang, Q. Li, Y. Zhao, H. Hong, H. Li, Z. Huang, G. Liang, Q. Yang, C. Zhi, Adv. Energy Mater. 2022, 12, 2102707.
- [37] Z. Zhai, L. Zhang, T. Du, B. Ren, Y. Xu, S. Wang, J. Miao, Z. Liu, *Mater. Des.* 2022, 221, 111017.
- [38] A. G. Olabi, Q. Abbas, A. Al Makky, M. A. Abdelkareem, *Energy* **2022**, *248*, 123617.
- [39] Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, *Chem. Rev.* 2018, 118, 9233–9280.

- [40] S. Zhang, N. Pan, Adv. Energy Mater. 2015, 5, 1401401.
- [41] A. Noori, M. F. El-Kady, M. S. Rahmanifar, R. B. Kaner, M. F. Mousavi, *Chem. Soc. Rev.* 2019, 48, 1272–1341.
- [42] Y. Kumar, S. Rawal, B. Joshi, S. A. Hashmi, J. Solid State Electrochem. 2019, 23, 667–692.
- [43] W. Yang, M. Ni, X. Ren, Y. Tian, N. Li, Y. Su, X. Zhang, Curr. Opin. Colloid Interface Sci. 2015, 20, 416–428.
- [44] R. Chen, M. Yu, R. P. Sahu, I. K. Puri, I. Zhitomirsky, Adv. Energy Mater. 2020, 10, 1903848.
- [45] G. Yu, X. Xie, L. Pan, Z. Bao, Y. Cui, *Nano Energy* **2013**, *2*, 213–234.
- [46] S. Grover, S. Goel, R. B. Marichi, V. Sahu, G. Singh, R. K. Sharma, *Electrochim. Acta* 2016, *196*, 131–139.
- [47] Z.-H. Huang, Y. Song, X.-X. Xu, X.-X. Liu, ACS Appl. Mater. Interfaces 2015, 7, 25506–25513.
- [48] Q. Lu, Y. Zhou, J. Power Sources 2011, 196, 4088–4094.
- [49] Q. Jiang, N. Kurra, M. Alhabeb, Y. Gogotsi, H. N. Alshareef, *Adv. Energy Mater.* 2018, 8, 1703043.
- [50] R. Li, J. Liu, *Electrochim. Acta* 2014, 120, 52–56.
- [51] A. K. Singh, D. Sarkar, G. G. Khan, K. Mandal, ACS Appl. Mater. Interfaces 2014, 6, 4684–4692.
- [52] N. Jabeen, Q. Xia, S. V. Savilov, S. M. Aldoshin, Y. Yu, H. Xia, ACS Appl. Mater. Interfaces 2016, 8, 33732–33740.
- [53] M. Liang, B. Luo, L. Zhi, Int. J. Energy Res. 2009, 33, 1161–1170.
- [54] L. Wei, G. Yushin, *Nano Energy* **2012**, *1*, 552–565.
- [55] S. Wen, M. Jung, O.-S. Joo, S. Mho, Curr. Appl. Phys. 2006, 6, 1012–1015.
- [56] C. Lei, F. Markoulidis, Z. Ashitaka, C. Lekakou, *Electrochim. Acta* 2013, 92, 183–187.
- [57] C. Largeot, C. Portet, J. Chmiola, P.-L. Taberna, Y. Gogotsi, P. Simon, J. Am. Chem. Soc. 2008, 130, 2730–2731.
- [58] H. Ji, X. Zhao, Z. Qiao, J. Jung, Y. Zhu, Y. Lu, L. L. Zhang, A. H. MacDonald, R. S. Ruoff, *Nat. Commun.* 2014, 5, 3317.
- [59] J. Wu, Chem. Rev. 2022, 122, 10821–10859.

- [60] K. B. Oldham, J. Electroanal. Chem. 2008, 613, 131–138.
- [61] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, *Science* (80-.).
  2006, 313, 1760–1763.
- [62] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Angew. Chemie Int. Ed.* 2008, 47, 3392–3395.
- [63] B. E. Conway, in *Electrochem. Supercapacitors*, Springer US, Boston, MA, **1999**, pp. 221–257.
- [64] V. Augustyn, P. Simon, B. Dunn, *Energy Environ. Sci.* 2014, 7, 1597.
- [65] E. Herrero, L. J. Buller, H. D. Abruña, *Chem. Rev.* 2001, 101, 1897–1930.
- [66] C. Xu, J. Mu, T. Zhou, S. Tian, P. Gao, G. Yin, J. Zhou, F. Li, Adv. Funct. Mater. 2022, 32, 2206501.
- [67] V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon, B. Dunn, *Nat. Mater.* 2013, 12, 518–522.
- [68] M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P.-L. Taberna, C. P. Grey, B. Dunn, P. Simon, *Nat. Energy* 2016, 1, 16070.
- [69] A. Muzaffar, M. B. Ahamed, K. Deshmukh, J. Thirumalai, *Renew. Sustain. Energy Rev.* 2019, 101, 123–145.
- [70] Q. Liu, H. Zhang, J. Xie, X. Liu, X. Lu, *Carbon Energy* **2020**, *2*, 521–539.
- [71] M. R. Palacín, Chem. Soc. Rev. 2009, 38, 2565.
- [72] Y. Liang, H. Dong, D. Aurbach, Y. Yao, *Nat. Energy* **2020**, *5*, 646–656.
- [73] R. Borah, F. R. Hughson, J. Johnston, T. Nann, *Mater. Today Adv.* 2020, *6*, 100046.
- [74] D. Zhang, H. Zhao, F. Liang, W. Ma, Y. Lei, J. Power Sources 2021, 493, 229722.
- [75] M. Song, H. Tan, D. Chao, H. J. Fan, Adv. Funct. Mater. 2018, 28, 1802564.
- [76] D. Deng, *Energy Sci. Eng.* **2015**, *3*, 385–418.
- [77] H. Chen, Z. Cao, J. Gu, Y. Cui, Y. Zhang, Z. Zhao, Z. Cheng, Q. Zhao, B. Li, S. Yang, *Adv. Energy Mater.* 2021, 11, 2003746.
- [78] J. Xu, H. R. Thomas, R. W. Francis, K. R. Lum, J. Wang, B. Liang, J. Power Sources 2008, 177, 512–527.
- [79] N. T, Prog. Batter. Sol. cells 1990, 209.
- [80] M. Li, J. Lu, Z. Chen, K. Amine, Adv. Mater. 2018, 30, 1800561.
- [81] H. Oman, *MRS Bull.* **1999**, *24*, 33–39.
- [82] J. Li, C. Daniel, D. Wood, J. Power Sources 2011, 196, 2452–2460.

- [83] J. Xie, Y.-C. Lu, Nat. Commun. 2020, 11, 2499.
- [84] Y. Liu, G. He, H. Jiang, I. P. Parkin, P. R. Shearing, D. J. L. Brett, *Adv. Funct. Mater.* 2021, *31*, 2010445.
- [85] L. Ma, S. Chen, H. Li, Z. Ruan, Z. Tang, Z. Liu, Z. Wang, Y. Huang, Z. Pei, J. A. Zapien, C. Zhi, *Energy Environ. Sci.* 2018, 11, 2521–2530.
- [86] W. Li, K. Wang, S. Cheng, K. Jiang, *Energy Storage Mater.* 2018, 15, 14–21.
- [87] M. S. Chae, J. W. Heo, H. H. Kwak, H. Lee, S.-T. Hong, J. Power Sources 2017, 337, 204–211.
- [88] T. Xue, H. J. Fan, J. Energy Chem. 2021, 54, 194–201.
- [89] L. Shan, Y. Wang, S. Liang, B. Tang, Y. Yang, Z. Wang, B. Lu, J. Zhou, *InfoMat* 2021, 3, 1028–1036.
- [90] W. Zhang, C. Zuo, C. Tang, W. Tang, B. Lan, X. Fu, S. Dong, P. Luo, *Energy Technol.* 2021, 9, 2000789.
- [91] C. Xie, Y. Li, Q. Wang, D. Sun, Y. Tang, H. Wang, *Carbon Energy* **2020**, *2*, 540–560.
- [92] K. Zhu, T. Wu, S. Sun, W. van den Bergh, M. Stefik, K. Huang, *Energy Storage Mater.* 2020, 29, 60–70.
- [93] L. Shan, Y. Yang, W. Zhang, H. Chen, G. Fang, J. Zhou, S. Liang, *Energy Storage Mater.* 2019, 18, 10–14.
- [94] X. Gao, H. Wu, W. Li, Y. Tian, Y. Zhang, H. Wu, L. Yang, G. Zou, H. Hou, X. Ji, Small 2020, 16, 1905842.
- [95] N. Zhang, X. Chen, M. Yu, Z. Niu, F. Cheng, J. Chen, Chem. Soc. Rev. 2020, 49, 4203–4219.
- [96] T. Xiong, Z. G. Yu, H. Wu, Y. Du, Q. Xie, J. Chen, Y. Zhang, S. J. Pennycook, W. S. V. Lee, J. Xue, *Adv. Energy Mater.* 2019, *9*, 1803815.
- [97] W. Shi, W. S. V. Lee, J. Xue, *ChemSusChem* **2021**, *14*, 1634–1658.
- [98] S. Xie, X. Li, Y. Li, Q. Liang, L. Dong, Chem. Rec. 2022, 22, e202200201.
- [99] J. Ding, H. Gao, D. Ji, K. Zhao, S. Wang, F. Cheng, J. Mater. Chem. A 2021, 9, 5258– 5275.
- [100] W. Kao-ian, A. A. Mohamad, W. Liu, R. Pornprasertsuk, S. Siwamogsatham, S. Kheawhom, *Batter. Supercaps* 2022, 5, DOI 10.1002/batt.202100361.
- [101] Y. Zhang, K. Rui, A. Huang, Y. Ding, K. Hu, W. Shi, X. Cao, H. Lin, J. Zhu, W. Huang, *Research* 2020, 2020, DOI 10.34133/2020/2360796.

- [102] Q. An, Q. Wei, P. Zhang, J. Sheng, K. M. Hercule, F. Lv, Q. Wang, X. Wei, L. Mai, Small 2015, 11, 2654–2660.
- [103] M. M. Huie, D. C. Bock, E. S. Takeuchi, A. C. Marschilok, K. J. Takeuchi, *Coord. Chem. Rev.* 2015, 287, 15–27.
- [104] Y. Zhao, C. Han, J. Yang, J. Su, X. Xu, S. Li, L. Xu, R. Fang, H. Jiang, X. Zou, B. Song, L. Mai, Q. Zhang, *Nano Lett.* 2015, 15, 2180–2185.
- [105] Y. Zhang, E. H. Ang, K. N. Dinh, K. Rui, H. Lin, J. Zhu, Q. Yan, *Mater. Chem. Front.* 2021, 5, 744–762.
- [106] C. M. Lewis, J. F. S. Fernando, D. P. Siriwardena, K. L. Firestein, C. Zhang, J. E. Treifeldt, D. V. Golberg, Adv. Mater. Technol. 2022, 7, 2100505.
- [107] G. Zampardi, F. La Mantia, Curr. Opin. Electrochem. 2020, 21, 84–92.
- [108] M. Zhang, R. Liang, T. Or, Y.-P. Deng, A. Yu, Z. Chen, Small Struct. 2021, 2, 2000064.
- [109] Z. Tie, Z. Niu, Angew. Chemie Int. Ed. 2020, 59, 21293–21303.
- [110] K. Zhu, T. Wu, S. Sun, Y. Wen, K. Huang, ChemElectroChem 2020, 7, 2714–2734.
- [111] L. Yan, X. Zeng, Z. Li, X. Meng, D. Wei, T. Liu, M. Ling, Z. Lin, C. Liang, *Mater. Today Energy* 2019, 13, 323–330.
- [112] Y. Cheng, L. Luo, L. Zhong, J. Chen, B. Li, W. Wang, S. X. Mao, C. Wang, V. L. Sprenkle, G. Li, J. Liu, ACS Appl. Mater. Interfaces 2016, 8, 13673–13677.
- [113] H. Shuai, R. Liu, W. Li, X. Yang, H. Lu, Y. Gao, J. Xu, K. Huang, *Adv. Energy Mater.* **2023**, *13*, 2202992.
- [114] T. Wang, C. Li, X. Xie, B. Lu, Z. He, S. Liang, J. Zhou, ACS Nano 2020, 14, 16321– 16347.
- [115] Z. Cao, P. Zhuang, X. Zhang, M. Ye, J. Shen, P. M. Ajayan, Adv. Energy Mater. 2020, 10, 2001599.
- [116] L. E. Blanc, D. Kundu, L. F. Nazar, Joule 2020, 4, 771–799.
- [117] L. Yuan, J. Hao, C.-C. Kao, C. Wu, H.-K. Liu, S.-X. Dou, S.-Z. Qiao, *Energy Environ. Sci.* 2021, 14, 5669–5689.
- [118] Q. Zhang, Z. Yang, H. Ji, X. Zeng, Y. Tang, D. Sun, H. Wang, SusMat 2021, 1, 432–447.
- [119] T. C. Li, D. Fang, J. Zhang, M. E. Pam, Z. Y. Leong, J. Yu, X. L. Li, D. Yan, H. Y. Yang, J. Mater. Chem. A 2021, 9, 6013–6028.

- [120] C. Liu, X. Xie, B. Lu, J. Zhou, S. Liang, ACS Energy Lett. 2021, 6, 1015–1033.
- [121] Y. Geng, L. Pan, Z. Peng, Z. Sun, H. Lin, C. Mao, L. Wang, L. Dai, H. Liu, K. Pan, X.
  Wu, Q. Zhang, Z. He, *Energy Storage Mater.* 2022, *51*, 733–755.
- [122] L. Li, S. Jia, Z. Cheng, C. Zhang, ChemSusChem 2023, 16, e202202330.
- [123] Y. Zong, H. He, Y. Wang, M. Wu, X. Ren, Z. Bai, N. Wang, X. Ning, S. X. Dou, Adv. Energy Mater. 2023, 13, 2300403.
- [124] H. Khan, A. S. Yerramilli, A. D'Oliveira, T. L. Alford, D. C. Boffito, G. S. Patience, *Can. J. Chem. Eng.* 2020, 98, 1255–1266.
- [125] H. Stanjek, W. Häusler, Hyperfine Interact. 2004, 154, 107–119.
- [126] L. R. B. Elton, D. F. Jackson, Am. J. Phys. 1966, 34, 1036–1038.
- [127] A. L. Patterson, *Phys. Rev.* **1939**, *56*, 978–982.
- [128] S. P. Mulvaney, C. D. Keating, Anal. Chem. 2000, 72, 145–158.
- [129] J. D. Andrade, in Surf. Interfacial Asp. Biomed. Polym., Springer US, Boston, MA, 1985, pp. 105–195.
- [130] K. D. Vernon-Parry, III-Vs Rev. 2000, 13, 40-44.
- [131] K. Akhtar, S. A. Khan, S. B. Khan, A. M. Asiri, in *Handb. Mater. Charact.*, Springer International Publishing, Cham, 2018, pp. 113–145.
- [132] M. Abd Mutalib, M. A. Rahman, M. H. D. Othman, A. F. Ismail, J. Jaafar, in *Membr. Charact.*, Elsevier, 2017, pp. 161–179.
- [133] M. Scimeca, S. Bischetti, H. K. Lamsira, R. Bonfiglio, E. Bonanno, *Eur. J. Histochem.***2018**, 62, 2841.
- [134] D. C. Joy, J. B. Pawley, Ultramicroscopy 1992, 47, 80-100.
- [135] S. R. Spurgeon, C. Ophus, L. Jones, A. Petford-Long, S. V. Kalinin, M. J. Olszta, R. E. Dunin-Borkowski, N. Salmon, K. Hattar, W.-C. D. Yang, R. Sharma, Y. Du, A. Chiaramonti, H. Zheng, E. C. Buck, L. Kovarik, R. L. Penn, D. Li, X. Zhang, M. Murayama, M. L. Taheri, *Nat. Mater.* 2021, 20, 274–279.
- [136] W. Grogger, F. Hofer, G. Kothleitner, B. Schaffer, Top. Catal. 2008, 50, 200-207.
- [137] P. Sinha, A. Datar, C. Jeong, X. Deng, Y. G. Chung, L.-C. Lin, J. Phys. Chem. C 2019, 123, 20195–20209.
- [138] D. Dollimore, P. Spooner, A. Turner, Surf. Technol. 1976, 4, 121–160.
- [139] F. Ambroz, T. J. Macdonald, V. Martis, I. P. Parkin, Small Methods 2018, 2, 1800173.
- [140] S. Lowell, J. E. Shields, M. A. Thomas, M. Thommes, 2004, pp. 58-81.
- [141] R. Bardestani, G. S. Patience, S. Kaliaguine, Can. J. Chem. Eng. 2019, 97, 2781–2791.
- [142] M. A. Mohamed, J. Jaafar, A. F. Ismail, M. H. D. Othman, M. A. Rahman, in *Membr. Charact.*, Elsevier, 2017, pp. 3–29.
- [143] O. Derkacheva, D. Sukhov, Macromol. Symp. 2008, 265, 61–68.
- [144] J. Schmitt, H.-C. Flemming, Int. Biodeterior. Biodegradation 1998, 41, 1–11.
- [145] C. Berthomieu, R. Hienerwadel, Photosynth. Res. 2009, 101, 157–170.
- [146] J. F. Rusling, S. L. Suib, Adv. Mater. 1994, 6, 922–930.
- [147] F. Licht, M. A. Davis, H. A. Andreas, J. Power Sources 2020, 446, 227354.
- [148] B. E. Conway, *Electrochemical Supercapacitors*, Springer US, Boston, MA, 1999.
- [149] M. D. Levi, D. Aurbach, J. Phys. Chem. B 1997, 101, 4630-4640.
- [150] B.-A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, J. Phys. Chem. C 2018, 122, 194–206.
- [151] Y. Zhu, C. Wang, J. Phys. Chem. C 2010, 114, 2830–2841.
- [152] S. D. Kang, J. J. Kuo, N. Kapate, J. Hong, J. Park, W. C. Chueh, J. Electrochem. Soc. 2021, 168, 120503.
- [153] S. D. Kang, W. C. Chueh, J. Electrochem. Soc. 2021, 168, 120504.
- [154] D. W. Dees, S. Kawauchi, D. P. Abraham, J. Prakash, J. Power Sources 2009, 189, 263–268.
- [155] B. Wu, G. Zhang, M. Yan, T. Xiong, P. He, L. He, X. Xu, L. Mai, Small 2018, 14, 1703850.

## Ionic Liquid-Assisted MnO<sub>2</sub> for Asymmetric Supercapacitor Application

### Overview

In the past decade, ionic liquids (ILs) have demonstrated significant potential for synthesizing inorganic materials. The superior characteristics of non-aqueous alternatives, such as low vapor pressure, good thermal stability, adjustable solubility, and adaptable synthesis methods, render them a better option than their aqueous counterparts. This study demonstrates the utilization of different ILs in producing  $\alpha$ -MnO<sub>2</sub> nanorods with asymmetric orientation. Nanorod formation exhibited higher energy favorability, and the incorporation of IL augmented the material's surface area and conductivity. The improved surface and conductivity of the material contribute to its enhanced supercapacitive performance, resulting in a capacitance of 352 F g<sup>-1</sup> when tested in a 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte. An asymmetric supercapacitor device was assembled using synthesized material and activated carbon. The device exhibits a high energy density of 28.5 Wh kg<sup>-1</sup> and a power density of 96.5 W kg<sup>-1</sup> when tested in 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

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### **3.1 Introduction**

Ionic liquids (ILs) offer a promising environmentally friendly alternative to conventional methods across various applications. An increasing amount of literature discusses the adaptability of properties to enhance effectiveness in diverse applications.<sup>[1–4]</sup> ILs are molten salts composed entirely of ions that display variable structural modifications by adjusting cations and anions at room temperature. In addition, they offer benefits such as reduced vapor pressure, temperature stability, high ionic conductivity, and extensive potential windows for electrochemical analysis. Moreover, these eco-friendly solvents serve as viable substitutes for hazardous organic solvents. Extensive research has been conducted on their potential use as electrolyte and reaction media in synthesizing active materials for supercapacitors.<sup>[5–8]</sup>

Symmetric supercapacitors have limited energy density due to using identical materials on both electrodes.<sup>[9]</sup> The device displays a hybrid nature derived from the combination of an electric double layer and pseudocapacitive type electrodes in an asymmetric configuration.<sup>[10]</sup> Numerous studies have been conducted on the asymmetric configuration of various metal oxides with activated carbon, as documented in the literature.<sup>[11]</sup> This approach facilitated researchers to attain higher energy densities (> 20 Wh kg<sup>-1</sup>) alongside standard power density levels.<sup>[12]</sup> Metal oxides are extensively studied as electrode materials due to their low cost, ease of processing, good conductivity and stability, multiple oxidation states, and environmentally friendly properties.<sup>[13,14]</sup> The synthesis route is a crucial factor in determining the practical feasibility of a given performance, among other factors. Ionothermal synthesis utilizing the structural and functional direction properties of ILs has been recognized as a promising method for producing advanced inorganic energy materials.<sup>[15,16]</sup> The dual function of IL as a solvent and template material is the primary advantage of this synthesis approach. Using RTILs in this process enables materials synthesis at ambient temperature, rendering it an eco-friendly and energy-efficient approach.<sup>[17,18]</sup> IL-based products can exhibit tunable nucleation, growth, and morphology owing to the unique characteristics of ILs, including a broad spectrum of cationic/anionic pairs. Ionothermal synthesis is a promising method for producing energy storage materials due to its eco-friendliness and precise manipulation of material properties.

Huh et al. utilized 1-butyl-3-methylimidazolium tetrafluoroborate IL to synthesize cobalt hydroxide ionothermally.<sup>[19]</sup> The addition of IL to cobalt hydroxide facilitated the customization of pore size, surface area, and pseudocapacitance in its application as a material

for supercapacitor electrodes. DFT simulations verified that the ionic liquid's cation and anion components facilitate hydrogen desorption/adsorption, resulting in a more favorable redox reaction on the Co(OH)<sub>2</sub> surface. The results emphasize the importance of ILs in synthesizing materials for energy storage. Nevertheless, the utilization of this technique to create highquality electrode materials for supercapacitor applications has been scarcely reported.<sup>[20,21]</sup> Metal oxides are being considered as potential electrode materials for energy storage devices due to their high theoretical capacitance and large surface area. MnO<sub>2</sub> is a popular electrode material for supercapacitor applications due to its high theoretical specific capacitance of 1370 F g<sup>-1</sup>, as reported in the literature.<sup>[22,23]</sup> An infrequent approach in the literature is the energyefficient room-temperature ionothermal synthesis of MnO<sub>2</sub> modification for SC.

We introduce a green synthesis ionothermal precipitation method for producing MnO<sub>2</sub> at room temperature. The technique was optimized by manipulating different ILs throughout the process. MnO<sub>2</sub> was synthesized using three different ionic liquids: 1-Ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][TFSI], 1-Butyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][TFSI], and 1-Butyl-3methylimidazolium tetrafluoroborate [Bmim][BF4], denoted as ET-M, BT-M, and BB-M, respectively. The integration of IL in the production process improved the surface kinetics of the material, resulting in the superior performance of the SC compared to  $\alpha$ -MnO<sub>2</sub> in its pure form. The development and confinement of nanorods were facilitated by the small size (0.5 nm) of the anion and cation present in the IL. The IL facilitates ion transport, hydrogen desorption, and adsorption, resulting in prompt and effective redox reactions in SC.<sup>[24-26]</sup> The ET-M exhibited a specific capacitance of 352 F g<sup>-1</sup> at 5 mV s<sup>-1</sup> due to the aforementioned improvements. The asymmetric supercapacitor (ASC) utilizing ET-M as active material demonstrated a high energy density of 28.5 Wh kg<sup>-1</sup> in 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

### **3.2 Experimental Section**

### **3.2.1 Chemicals required**

High-purity ionic liquids, including Emim-TFSI, Bmim-TFSI, and Bmim-BF4 (>98%), were purchased from Sigma-Aldrich. KMnO<sub>4</sub> (ACS reagent) was purchased from Loba Chemie Pvt

Ltd., while AR-grade methanol was obtained from SD fine chem limited. The ELGA ultrapure water system is utilized to obtain ultrapure water with a resistance of 18 M $\Omega$ .

### 3.2.2 Synthesis of MnO<sub>2</sub>, and IL-assisted MnO<sub>2</sub>

MnO<sub>2</sub> was synthesized via ionothermal method. A mixture of ultrapure water and methanol in a 3:1 ratio, measuring 20 ml, was subjected to reaction with 0.5 M KMnO<sub>4</sub>. Subsequently, 1 ml of [emim][TFSI] ionic liquid was added to the solution, which was then stirred and left at room temperature for 30 minutes. A reducing agent of 2 ml ethanol (AR) was added after 30 minutes. The solution underwent 12 hours of aging at room temperature under continuous stirring for 1h. The precipitate underwent vacuum filtration and was subsequently washed with ultrapure water and methanol for 12 hours. The resulting product was then vacuum dried at 80°C. The powder is subjected to a heat treatment at 600 °C for 5 hours to enhance its crystallinity, resulting in its designation as ET-M. MnO<sub>2</sub> was produced using [Bmim] [TFSI]



**Figure 3.1.** Schematic depicting the synthesis of  $MnO_2$  nanorods facilitated by ionic liquid. The precursor materials contain balls of various colors representing atoms of manganese, potassium, oxygen, carbon, hydrogen, sulfur, nitrogen, and fluorine.

and [Bmim][BF<sub>4</sub>] through a comparable method, resulting in pure MnO<sub>2</sub> without the need for the ionic liquid BT-M, BB-M, and MnO<sub>2</sub>. The detailed synthesis schematic is displayed in **Figure 3.1**.

### 3.2.3 Preparation of electrodes for Supercapacitors

Electrochemical analyses, such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), were performed using the CHI 1150 C equipment. The material was studied using (Three electrode) 3E and (Two electrode) 2E asymmetric cell configurations. The slurry and electrode preparation methodology is consistent with our prior publication.<sup>[27]</sup> The 3E measurements employed an active material-coated SS working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode in the presence of 1M Na<sub>2</sub>SO<sub>4</sub> as the aqueous electrolyte. Activated carbon served as the counter electrode for 2E measurements. The electrode mass loading was 1 mg cm<sup>-2</sup> for 3E measurements and 0.5 mg cm<sup>-2</sup> for 2E measurements.

### **3.3 Results and Discussion**

The ET-M sample was synthesized through ionothermal synthesis, using [emim][TFSI] as both the solvent and morphological guiding agent. The ionothermal process results in suspension



**Figure 3.2**. (a) Structural characterizations were performed on various samples using PXRD and FTIR techniques. PXRD data for BB-M, BT-M, MnO<sub>2</sub>, and ET-M were compared with ICDD data, (b) FTIR spectra for BB-M, BT-M, ET-M, and MnO<sub>2</sub> samples indicated the presence of metal-oxide bonds.

rather than solution due to the poor solubility of [emim][TFSI] in ultrapure water. IL functions

as a nucleation and growth catalyst in the solution, forming nanorods (in the case of pure  $MnO_2$ ), thereby decreasing the material's overall surface energy. PXRD was utilized to confirm the phase and crystallinity of the  $MnO_2$  and ET-M nanostructures. **Figure 3.2 (a)** displays the comparative XRD spectra of  $MnO_2$ , BBM, BTM, and ET-M samples. The experimental data for each diffraction peak were matched to the tetragonal  $MnO_2$  planes in the ICDD PDF-00-0440141. The prominent diffraction peaks of ET-M were observed at 20 angles of 25.7°, 28.8°, 36.4°, 37.6°, 49.9°, and 60°, corresponding to the (200), (220), (310), (400), (211), (411), and (521) crystallographic planes, respectively. Ionic liquid interaction with  $MnO_2$  resulted in the growth of additional peaks. The peaks were observed in all samples assisted by the ionic liquid, as depicted in **Figure 3.3 (a)**. The planes correspond to the I4/m space group and the tetragonal plane of  $MnO_2$ , with dimensions of a = b = 9.7845 Å and c = 2.8630 Å. The synthesized material displayed strong crystallinity, evidenced by prominent peaks at 28.8°, 37.6°, and 60°, as well as distinct peaks in the material. FTIR spectroscopy was employed to obtain a comprehensive and precise characterization of the synthesized material, as depicted in **Figure 3.2 (b)**. According to literature sources, the Mn-O vibrations of MnO<sub>6</sub> octahedra are



**Figure 3.3** (a) FTIR spectra of ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (ET), 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BT), and 1-Butyl-3-methylimidazolium tetrafluoroborate (BB), (b) XPS survey spectra were collected for pristine  $\alpha$ -MnO<sub>2</sub>, ET-M, BT-M, and BB-M to identify the elements present.

responsible for the bands observed at 702, 501, 436, and 417 cm<sup>-1</sup>, which fall within the 400-800 cm<sup>-1</sup> range.<sup>[28–30]</sup> An absorption band at 1112 cm<sup>-1</sup> was observed, which was assigned to the stretching of C-O and C=N.<sup>[31]</sup> Figure 3.3 (a) shows the observed peak intensity differences in ET-M FTIR, which can be attributed to the reaction of IL with Mn-O vibrations, among other peaks.

The XPS spectra were used to analyze the chemical composition and oxidation state. **Figure 3.4 (a)** displays survey spectra of the ET-M sample, which exhibit notable peaks corresponding to C 1s, O 1s, Mn 2p, K 2s, and F 1s. IL addition in the ET-M sample is confirmed by the F 1s peak, which was not observed in the pure  $MnO_2$  sample (**Figure 3.3 (b)**). The high-resolution narrow area spectra were utilized to analyze the oxidation states of ET-M samples with greater



**Figure 3.4** Elemental study to investigate chemical composition and oxidation states. It includes (a) survey spectra of ET-M and narrow region high-resolution XPS spectra for (b) Mn 2p and (c) O 1s.

precision. The Mn 2p peak in both the MnO2 and ET-M samples exhibit spin-orbit linked

components separated by approximately 11.7 eV, in agreement with the results reported in the literature.<sup>[32]</sup> The Mn 2p<sub>3/2</sub> narrow spectra region displayed notable peaks corresponding to the +4 oxidation state (643 and 653.8 eV), +3 oxidation state (641.9 eV and 652.8 eV), and +2 oxidation state (640.7 eV as shown in **Figure 3.4 (b)** after deconvolution). The normalized mole fractions for  $Mn^{2+}$ ,  $Mn^{3+}$ , and  $Mn^{4+}$  were determined to be 11.7%, 39.1%, and 49.2%, respectively, through analysis of the fitted peak in Mn 2p, despite the average valence state of Mn being +3.3. Satellite peaks were identified at 644.8, 648.2, and 655.3.<sup>[33–36]</sup> **Figure 3.4 (c)** shows deconvoluted O 1s spectra with three distinct oxygen bonds observed at characteristic energies of 529.4 eV, 531.1 eV, and 532.5 eV, corresponding to Mn–O–Mn, Mn–O–H, and H–O–H bonds, respectively.<sup>[37]</sup> The synthesized samples were analyzed using FESEM pictures for additional morphological information. The ET-M sample undergoes nanorod crystallization over time, as depicted in **Figure 3.5(a)**. The exposure of the precursor materials to ILs resulted



**Figure 3.5** Morphological analysis of ET-M sample. (a) FESEM images were obtained at low and (b) high magnifications. (c) EDS spectra indicate multiple elements in the specimen, while the inset displays the elemental mapping for Mn and O.

in the transformation of the structure into nanorods due to nucleation-growth kinetics. Due to its instability during the reaction, MnO<sub>2</sub> converts to nanorod form after an initial branching growth phase.<sup>[38]</sup> **Figure 3.5 (b)** displays the homogeneous size distribution of ET-M, which exhibits a typical nanorod shape. **Figure 3.5 (c)** displays EDS spectra and mappings indicating the presence of Mn, O, C, and K, consistent with XPS findings. The exceptional structural and morphological analyses of the synthesized sample and its high conductivity have sparked interest in investigating its electrochemical performance.

The electrochemical performance of MnO<sub>2</sub>, BB-M, BT-M, and ET-M electrodes was evaluated via CV in 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte, as depicted in **Figure 3.6**. The electrochemical performance of various MnO<sub>2</sub> samples was evaluated before optimization, (MnO<sub>2</sub>-400@3h, MnO<sub>2</sub>-500@3h, MnO<sub>2</sub>-600@3h, MnO<sub>2</sub>-600@4h, and MnO<sub>2</sub>-600@5h ( $\alpha$ -MnO<sub>2</sub>)) as shown in **Figure 3.7**. Figure 3.6 (a) shows that the ET-M sample has a higher specific capacitance than the MnO<sub>2</sub>, BB-M, and BT-M samples, as evidenced by its higher current and wider integral area in the CV curve. **Figure 3.6 (b)** displays the CV curves for different scan rates of the ET-M sample. MnO<sub>2</sub> CV curves display expected pseudocapacitive characteristics. The specific capacitance of the ET-M was measured at different scan rates, resulting in values of 352, 328, 300, 256, 210, and 154 F g<sup>-1</sup> for scan rates of 5, 10, 20, 50, 100, and 200 mV s<sup>-1</sup>, respectively.

The values obtained at scan rates of 5, 10, 20, 50, 100, and 200 mV s<sup>-1</sup> for the tested material are significantly better than those of pristine MnO<sub>2</sub> nanowires, with respective values of 263, 235, 184, 140, and 96 F g<sup>-1</sup>. Our material exhibits comparable capacitance to  $\alpha$ -MnO<sub>2</sub> (289 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>),<sup>[39]</sup> MnO<sub>2</sub>@CNTs/CNTs (149 F g<sup>-1</sup> at 0.2 A g<sup>-1</sup>),<sup>[40]</sup> and GO-MnO<sub>2</sub> (211 F g<sup>-1</sup> at 0.15 A g<sup>-1</sup>),<sup>[41]</sup> as reported in recent literature. **Figure 3.6 (c)** displays both samples' scan rate vs. capacitance curve, indicating that the ET-M sample has better retention than MnO<sub>2</sub>. The exceptional supercapacitive properties of the ET-M nanorods electrode can be attributed to its distinct textural shape, crystal structure, and surface area. The enhanced electron transport and reduced contact resistance at the junction in the ET-M sample can be attributed to the nanorods' greater surface area and contact points.

The ET-M nanorods' crystal structure comprises two  $[MnO_6]$  chains forming a 2×2 tunnel, facilitating the intercalation of cations into  $MnO_2$ . The nanostructure facilitates ion and electron diffusion over short distances by minimizing diffusion route lengths. This performance surpasses prior literature findings, as evidenced by Table 3.1.



**Figure 3.6** Electrochemical data analysis of the ET-M sample. (a) Comparison of CV curves of various samples at a scan rate of 20 mV s<sup>-1</sup>, (b) CV plots for the ET-M sample at different scan rates, and (c) Retention curve of specific capacitance versus scan rate for the ET-M sample. The CV curves of AC and ET-M were found to be appropriate for ASC assembly within the potential range of 0-0.8 V and -0.8 to 0.0 V, respectively, in 2E assembly studies. CV curves were obtained for the 2E ASC device of AC//ET-M using a scan rate of 20 mV s<sup>-1</sup> in 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The capacitive contribution for ET-M was determined using the Dunn method. Additionally, CV curves were recorded at various scan voltages.

The ASC conducted a study to explore the practical application of the synthesized material. The 2E testing was performed using activated carbon (AC) as the counter electrode and a 1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. The voltage window of 1.6 V was determined based on the CV voltage windows of AC and ET-M, as shown in **Figure 3.6 (d)**. The stable voltage range was determined by analyzing the CV curves between 0.8 V and 1.6 V, as depicted in **Figure 3.8**.

**Figure 3.6 (e)** displays CV plots showing the diverse pseudocapacitive curve shape observed at different scan rates. **Figure 3.6 (f)** illustrates that ET-M exhibits a capacitive contribution of 80.9% at 5 mV s<sup>-1</sup>. The significant capacitive contribution value of the material guarantees its exceptional capacity retention. The ET-M device shows low charge transfer and electrical resistance, as well as high capacitive-controlled capacitances.



The ASC device demonstrated varying specific capacitance values, ranging from 18.7 to 59.5

**Figure 3.7** Electrochemical performance of the  $\alpha$ -MnO<sub>2</sub> (a) CV plot comparison of  $\alpha$ -MnO<sub>2</sub> at 5 mV s<sup>-1</sup> and (b) specific capacitance of  $\alpha$ -MnO<sub>2</sub> at various scan rates for different samples.

F g<sup>-1</sup>, at different scan rates of 5 to 100 mV s<sup>-1</sup>. The superior supercapacitive performance of the ET-M sample suggests that utilizing ILs-assisted MnO<sub>2</sub> in both the electrode and electrolyte can result in a higher capacitive current compared to using pristine MnO<sub>2</sub>. Dunn's method was applied to determine electrode kinetic capacitances and charge storage mechanisms using CV curves at varying scan rates. The capacitance of all CV curves can isolate the processes of capacitive charge storage and diffusion-controlled insertion.

Electrode	Mass loading (mg.cm <sup>-2</sup> )	Specific capacitance (F.g <sup>-1</sup> )	Scan rate (mV.s <sup>-1</sup> )	Current density (A.g <sup>-1</sup> )	Electrolyte	Ref.
Mg-doped MnO <sub>2</sub>	10-15	145	2	-	0.5M Na <sub>2</sub> SO <sub>4</sub>	[42]
MnO <sub>2</sub>	2-3	222	2	-	0.5M Na <sub>2</sub> SO <sub>4</sub>	[43]
Graphene- MnO <sub>2</sub>	3	310	2	-	1M Na <sub>2</sub> SO <sub>4</sub>	[44]
Graphene- MnO <sub>2</sub>	-	320.59	-	0.5	1M Na <sub>2</sub> SO <sub>4</sub>	[45]
MnO <sub>2</sub> /PCNT/ MnO <sub>2</sub>	0.5	341.5	2	-	1M KOH	[46]
RGO/MnO <sub>x</sub>	2	202	1	-	0.5M Na <sub>2</sub> SO <sub>4</sub>	[47]
MnO <sub>2</sub>	2	185	-	0.5	1M Na <sub>2</sub> SO <sub>4</sub>	[48]
Birnessite MnO <sub>2</sub>	-	210	-	0.2	1M Na <sub>2</sub> SO <sub>4</sub>	[49]
K <sub>0.6</sub> MnO <sub>2</sub>	-	254	-	1	1M KTFSI	[50]
MnO <sub>2</sub>	0.28	269	-	0.3	1M Na <sub>2</sub> SO <sub>4</sub>	[51]
ET-M	0.5	352	5	-	1M Na2SO4	Our work

Table 3.1 3E performance of MnO<sub>2</sub> comparison with the previous literature reports.

The mesoporous structure and high specific surface area of ET-M nanorods facilitate the transportation of hydrated ions in the electrolyte to the working electrode surfaces (Figure 3.9). Impedance measurements were conducted on the samples to comprehend the charge transfer mechanism across the electrode-electrolyte interface. The Nyquist plot, displaying the impedance components (real and imaginary) as a function of frequency, was measured within the frequency range of 100 kHz to 1 mHz. Please refer to Figure 3.10 for the plot. The impedance values of the ET-M sample have significantly decreased. The Bode plot in Figure 3.10 (c) for ET-M//AC predicts a short time constant ( $\tau$ ) of 0.1 ms for the ASC device, indicating a fast ion diffusion process. The reported time constant value is shorter than those previously reported for graphene oxide (0.35 ms)<sup>[52]</sup> and carbon fiber-MnO<sub>2</sub> (39.1 ms)<sup>[53]</sup>. Figure 3.11 (a) displays the GCD curve of the ET-M device at a current density of 100 mA g<sup>-1</sup>.

Initially, a voltage drop occurred in the discharge curve caused by the internal resistance ( $R_i = ESR$ , equivalent series resistance) of the electrodes/active material. The device exhibits a specific capacitance of 80.24 F g<sup>-1</sup>, with a retention rate of 61% even after a 20-times increase in current density (at 2000 mA g<sup>-1</sup>), as depicted in Figure 3.11 (b). The performance metrics exceed the literature values for ASC devices (Table 3.2). Implementing ET-M nanorods can effectively enhance the electrochemical performance of electrodes by reducing resistance caused by charge transfer and ionic diffusion through shortened ion diffusion paths.<sup>[54]</sup> Furthermore, it enhances the electrochemical performance of the electrodes.



**Figure 3.8** Voltage window extension of ET-M in 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte for 2E ASC device. The optimized window for ASC device is 1.6 V.



**Figure 3.9** Surface area studies for ET-M sample (a) adsorption-desorption isotherms and (b) pore size distribution per the BJH model.

Aligned nanorods were found to be crucial for integrating SC devices, as no significant structural or electrochemical changes were observed after a prolonged process. ASC devices exhibit good real and imaginary capacitance values across various frequencies, as illustrated in Figure 3.11 (d). The device demonstrated a maximum real capacitance of 24.4 F g<sup>-1</sup> at a frequency of 4.5 mHz, and a maximum imaginary capacitance of 11.6 F g<sup>-1</sup> at 11.8 mHz. The cycling stability of the SC was evaluated through the GCD technique at a current density of 5000 mA g<sup>-1</sup>. The device exhibited remarkable stability, maintaining 72% of its initial capacitance even after 10000 cycles, as depicted in Figure 3.11 (e). The ASC device's energy and power densities were computed using GCD curves and graphed on the Ragone diagram, shown in Figure 3.11 (f). The device achieved a maximum energy density of 28.52 Wh kg<sup>-1</sup> at a power density of 96.52 W kg<sup>-1</sup>. The reported values surpass those of symmetric and asymmetric systems, including graphene/MnO<sub>2</sub> (6.8 Wh kg<sup>-1</sup> at 62 W kg<sup>-1</sup>)<sup>[55]</sup> and MnO<sub>2</sub>@R//NR-800 (9.2 Wh kg<sup>-1</sup> at 1283.7 W kg<sup>-1</sup>) <sup>[56]</sup>. For further comparison, refer to Table 3.2.



**Figure 3.10** Nyquist plots for ET-M//AC ASC, the inset shows the zoomed view for clear identification of semi-circular region, and Randles circuit used for the fitting of EIS data.



**Figure 3.11** 2E studies for assembled device (a) Discharge curves of ASC in the potential window of 0–1.6 V at a current density of 0.1 A g<sup>-1</sup>. (b) cell capacitance retention of ASC vs. current density plot. AC impedance studies for ET-M, (c) Bode plot, and (d) real and imaginary capacitance vs. log frequency graph. (e) Cyclic life test of the ASC device. (f) Ragone plot of AC//ET-M ASC at different applied currents compared to reported SC values in the literature (a=MnO<sub>2</sub>@R//NR-800<sup>[56]</sup>, b=Fe<sub>3</sub>O<sub>4</sub>//MnO<sub>2</sub><sup>[63]</sup>, c=MnO<sub>2</sub>//AG<sup>[69]</sup>, d=PEDOT//MnO<sub>2</sub><sup>[70]</sup>, e=MnO<sub>2</sub>//Graphene<sup>[71]</sup>.

Electrode	Specific	Current	Electrolyte	Energy	Power	Ref.
	capacitance	density		density	density	
	( <b>F.g</b> <sup>-1</sup> )	(A.g <sup>-1</sup> )		(Wh.kg <sup>-</sup>	(W.kg <sup>-</sup>	
				1)	1)	
AC-MnO <sub>2</sub> / AC-	83.3	0.5	1M NaOH	9.3	299	[57]
MnO <sub>2</sub>						
MnO <sub>2</sub> @R//NR-	137	0.5	1M Na <sub>2</sub> SO <sub>4</sub>	9.2	1283.7	[56]
800						
PANI-Grafted	407	0.125	1M H <sub>2</sub> SO <sub>4</sub>	11.4	875	[58]
MnO <sub>2</sub>						
MnO <sub>2</sub>	455	0.5	1M LiPF <sub>6</sub>	6.4	372	[59]
MnO <sub>2</sub> -coated	57.5	1 mA	1M Na <sub>2</sub> SO <sub>4</sub>	20.44	1600	[60]
CNT/ZNC						
MnO <sub>2</sub> -CNT/	68	10 mA	0.1M	4.5	33000	[61]
MnO <sub>2</sub> -CNT			Na <sub>2</sub> SO <sub>4</sub>			
MnO <sub>2</sub> //AC	30.8	0.1	1M Na <sub>2</sub> SO <sub>4</sub>	17.1	100	[51]
MnO <sub>2</sub> /AC	31	0.5	0.1M	17.3	605	[62]
			$K_2SO_4$			
Fe <sub>3</sub> O <sub>4</sub> /MnO <sub>2</sub>	20	0.22	0.1 M	7	820	[63]
			$K_2SO_4$			
AMEGO/MnO <sub>2</sub>	175	0.25	1M Na <sub>2</sub> SO <sub>4</sub>	24.3	24500	[64]
MnO <sub>2</sub> /FeOOH	51	0.5	1M Li <sub>2</sub> SO <sub>4</sub>	24	450	[65]
MnO <sub>2</sub> /Bi <sub>2</sub> O <sub>3</sub>	25.2	1.5 mA	1M Na <sub>2</sub> SO <sub>4</sub>	11.3	352.6	[66]
MnO <sub>2</sub> /Carbon	87.1	1.25	PVA/LiCl	27.2	979.7	[67]
fiber						
GHCS-	0.2	-	1M Na <sub>2</sub> SO <sub>4</sub>	22.1	100	[68]
MnO <sub>2</sub> /GHCS						
ET-M/AC	80.24	0.1	1M	28.53	96.53	Our
			Na <sub>2</sub> SO <sub>4</sub>			work

Table 3.2 2E data of MnO<sub>2</sub> asymmetric supercapacitor comparison with literature.

### **3.4 Conclusions**

In summary, we have documented the ionothermal synthesis of MnO<sub>2</sub> nanorods with the aid of IL, resulting in a straightforward process. Incorporating IL into the primary material enhanced its conductivity and surface area, improving SC performance. The ET-M electrode achieved a gravimetric capacity of 352 F g<sup>-1</sup> at a 5-mV s<sup>-1</sup> scan rate in a neutral 1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. The asymmetric SC device demonstrated a high gravimetric energy density of 28.5 Wh kg<sup>-1</sup> at a power density of 96.52 W kg<sup>-1</sup> and maintained 72% capacitance after 10000 charge/discharge cycles. The results of this study are anticipated to facilitate the advancement of eco-friendly ionothermal synthesis methods for producing more sophisticated materials. These materials will enhance their utilization in SCs and other energy storage and conversion areas.

### **3.5 References**

- [1] T. Zhang, T. Doert, H. Wang, S. Zhang, M. Ruck, *Angew. Chemie Int. Ed.* **2021**, *60*, 22148–22165.
- [2] Y. Liu, Q. Xu, R. Wang, Y. Zheng, L. Zhu, Z. Wang, W. Zheng, J. Mater. Chem. A 2020, 8, 797–809.
- [3] D. Tan, F. Wang, T. Pietsch, M. A. Grasser, T. Doert, M. Ruck, ACS Appl. Energy Mater. 2019, 2, 5140–5145.
- [4] D. Chen, T. Liu, P. Wang, J. Zhao, C. Zhang, R. Cheng, W. Li, P. Ji, Z. Pu, S. Mu, ACS Energy Lett. 2020, 5, 2909–2915.
- [5] G. G. Eshetu, M. Armand, H. Ohno, B. Scrosati, S. Passerini, *Energy Environ. Sci.* 2016, 9, 49–61.
- [6] M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, *Chem. Rev.* 2017, 117, 7190–7239.
- [7] S. K. Singh, A. W. Savoy, J. Mol. Liq. 2020, 297, 112038.
- [8] H. Liu, H. Yu, J. Mater. Sci. Technol. 2019, 35, 674–686.
- [9] N. Kumar, T. A. Wani, P. K. Pathak, A. Bera, R. R. Salunkhe, *Sustain. Energy Fuels* 2022, 6, 1762–1769.
- [10] Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, *Chem. Rev.* 2018, 118, 9233–9280.
- [11] Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, *Chem. Rev.* 2018, 118, 9233–9280.
- [12] Y. Qiu, Y. Zhao, X. Yang, W. Li, Z. Wei, J. Xiao, S.-F. Leung, Q. Lin, H. Wu, Y. Zhang, Z. Fan, S. Yang, *Nanoscale* 2014, 6, 3626–3631.
- [13] R. R. Salunkhe, Y. V. Kaneti, Y. Yamauchi, ACS Nano 2017, 11, 5293–5308.
- [14] N. Kumar, N. Bansal, R. R. Salunkhe, Chem. Commun. 2021, 57, 13748–13751.
- [15] T. Wang, H. Luo, Y. Bai, J. Li, I. Belharouak, S. Dai, Adv. Energy Mater. 2020, 10, 2001204.
- [16] J. Wu, Y. Wang, Y. Zhang, H. Meng, Y. Xu, Y. Han, Z. Wang, Y. Dong, X. Zhang, J. Energy Chem. 2020, 47, 203–209.
- [17] K. N. Manukumar, G. Nagaraju, B. Kishore, C. Madhu, N. Munichandraiah, *J. Energy Chem.* **2018**, *27*, 806–812.
- [18] F. A. Alharthi, G. Nagaraju, S. P. Vinay, Udayabhanu, N. Al-Zaqri, A. Alsalme, Int. J. Energy Res. 2020, 44, 8362–8371.
- [19] B. G. Choi, M. Yang, S. C. Jung, K. G. Lee, J.-G. Kim, H. Park, T. J. Park, S. B. Lee, Y.-K. Han, Y. S. Huh, ACS Nano 2013, 7, 2453–2460.
- [20] J. Liang, Z. Xiao, Y. Gao, X. Xu, D. Kong, M. Wagner, L. Zhi, *Carbon N. Y.* 2019,

143, 487–493.

- [21] J. Du, Y. Zhang, H. Lv, A. Chen, J. Colloid Interface Sci. 2021, 587, 780–788.
- [22] J. Qin, S. Wang, F. Zhou, P. Das, S. Zheng, C. Sun, X. Bao, Z.-S. Wu, *Energy Storage Mater.* 2019, 18, 397–404.
- [23] W. Du, X. Wang, J. Zhan, X. Sun, L. Kang, F. Jiang, X. Zhang, Q. Shao, M. Dong, H. Liu, V. Murugadoss, Z. Guo, *Electrochim. Acta* 2019, 296, 907–915.
- [24] A. Eftekhari, *Energy Storage Mater.* **2017**, *9*, 47–69.
- [25] D. S. Silvester, R. Jamil, S. Doblinger, Y. Zhang, R. Atkin, H. Li, J. Phys. Chem. C 2021, 125, 13707–13720.
- [26] I. Ruggeri, C. Arbizzani, S. Rapino, F. Soavi, J. Phys. Chem. Lett. 2019, 10, 3333– 3338.
- [27] N. Kumar, N. Bansal, Y. Yamauchi, R. R. Salunkhe, Chem. Mater. 2022, 34, 4946– 4954.
- [28] Z. Li, Y. Mi, X. Liu, S. Liu, S. Yang, J. Wang, J. Mater. Chem. 2011, 21, 14706.
- [29] D. Yan, P. Yan, S. Cheng, J. Chen, R. Zhuo, J. Feng, G. Zhang, Cryst. Growth Des. 2009, 9, 218–222.
- [30] J.-G. Wang, Y. Yang, Z.-H. Huang, F. Kang, Mater. Chem. Phys. 2013, 140, 643–650.
- [31] C. Wallar, D. Luo, R. Poon, I. Zhitomirsky, J. Mater. Sci. 2017, 52, 3687–3696.
- [32] E. S. Kim, H.-J. Lee, B.-H. Kim, *Electrochim. Acta* **2022**, *406*, 139883.
- [33] H. Jia, Y. Cai, X. Zheng, J. Lin, H. Liang, J. Qi, J. Cao, J. Feng, W. Fei, ACS Appl. Mater. Interfaces 2018, 10, 38963–38969.
- [34] R. Dong, Q. Ye, L. Kuang, X. Lu, Y. Zhang, X. Zhang, G. Tan, Y. Wen, F. Wang, ACS Appl. Mater. Interfaces 2013, 5, 9508–9516.
- [35] Y. Liu, Y. Jiao, B. Yin, S. Zhang, F. Qu, X. Wu, J. Mater. Chem. A 2015, 3, 3676– 3682.
- [36] N. Maile, S. K. Shinde, S. S. Patil, D.-Y. Kim, A. V. Fulari, D. S. Lee, V. J. Fulari, *Ceram. Int.* 2020, 46, 14640–14649.
- [37] G. Xie, X. Liu, Q. Li, H. Lin, Y. Li, M. Nie, L. Qin, J. Mater. Sci. 2017, 52, 10915– 10926.
- [38] D. Zheng, S. Sun, W. Fan, H. Yu, C. Fan, G. Cao, Z. Yin, X. Song, J. Phys. Chem. B 2005, 109, 16439–16443.
- [39] R. A. Davoglio, G. Cabello, J. F. Marco, S. R. Biaggio, *Electrochim. Acta* 2018, 261, 428–435.
- [40] P. Wu, S. Cheng, L. Yang, Z. Lin, X. Gui, X. Ou, J. Zhou, M. Yao, M. Wang, Y. Zhu, M. Liu, ACS Appl. Mater. Interfaces 2016, 8, 23721–23728.
- [41] S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, ACS Nano 2010, 4, 2822–2830.

- [42] L. Athouël, F. Moser, R. Dugas, O. Crosnier, D. Bélanger, T. Brousse, J. Phys. Chem. C 2008, 112, 7270–7277.
- [43] P. Wang, Y.-J. Zhao, L.-X. Wen, J.-F. Chen, Z.-G. Lei, Ind. Eng. Chem. Res. 2014, 53, 20116–20123.
- [44] J. Yan, Z. Fan, T. Wei, W. Qian, M. Zhang, F. Wei, Carbon N. Y. 2010, 48, 3825– 3833.
- [45] Y. Zheng, W. Pann, D. Zhengn, C. Sun, J. Electrochem. Soc. 2016, 163, D230–D238.
- [46] J. Wang, X. Guo, R. Cui, H. Huang, B. Liu, Y. Li, D. Wang, D. Zhao, J. Dong, S. Li, B. Sun, ACS Appl. Nano Mater. 2020, 3, 11152–11159.
- [47] Y. Wang, W. Lai, N. Wang, Z. Jiang, X. Wang, P. Zou, Z. Lin, H. J. Fan, F. Kang, C.-P. Wong, C. Yang, *Energy Environ. Sci.* 2017, 10, 941–949.
- [48] X. Wu, F. Yang, H. Dong, J. Sui, Q. Zhang, J. Yu, Q. Zhang, L. Dong, J. Electroanal. Chem. 2019, 848, 113332.
- [49] B. Ming, J. Li, F. Kang, G. Pang, Y. Zhang, L. Chen, J. Xu, X. Wang, J. Power Sources 2012, 198, 428–431.
- [50] T. Xiong, W. S. V. Lee, J. Xue, ACS Appl. Energy Mater. 2018, acsaem.8b01160.
- [51] X. Zhang, P. Yu, H. Zhang, D. Zhang, X. Sun, Y. Ma, *Electrochim. Acta* 2013, 89, 523–529.
- [52] Z. Wu, L. Li, Z. Lin, B. Song, Z. Li, K.-S. Moon, C.-P. Wong, S.-L. Bai, Sci. Rep. 2015, 5, 10983.
- [53] S. He, W. Chen, J. Power Sources 2015, 294, 150–158.
- [54] L. Miao, Z. Song, D. Zhu, L. Li, L. Gan, M. Liu, *Energy & Fuels* 2021, 35, 8443– 8455.
- [55] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, E. Xie, ACS Nano 2013, 7, 174–182.
- [56] M. Li, J. Yu, X. Wang, Z. Yang, Appl. Surf. Sci. 2020, 530, 147230.
- [57] P. Tagsin, P. Suksangrat, P. Klangtakai, P. Srepusharawoot, C. Ruttanapun, P. Kumnorkaew, S. Pimanpang, V. Amornkitbamrung, *Appl. Surf. Sci.* 2021, 570, 151056.
- [58] S. A. Jadhav, S. D. Dhas, K. T. Patil, A. V. Moholkar, P. S. Patil, *Chem. Phys. Lett.* 2021, 778, 138764.
- [59] R. S. Kalubarme, H. S. Jadhav, C.-J. Park, *Electrochim. Acta* 2013, 87, 457–465.
- [60] R. R. Salunkhe, H. Ahn, J. H. Kim, Y. Yamauchi, Nanotechnology 2015, 26, 204004.
- [61] A. L. M. Reddy, M. M. Shaijumon, S. R. Gowda, P. M. Ajayan, J. Phys. Chem. C 2010, 114, 658–663.
- [62] T. Cottineau, M. Toupin, T. Delahaye, T. Brousse, D. Bélanger, Appl. Phys. A 2006, 82, 599–606.

- [63] T. Brousse, D. Bélanger, *Electrochem. Solid-State Lett.* 2003, 6, A244.
- [64] X. Zhao, L. Zhang, S. Murali, M. D. Stoller, Q. Zhang, Y. Zhu, R. S. Ruoff, ACS Nano 2012, 6, 5404–5412.
- [65] W.-H. Jin, G.-T. Cao, J.-Y. Sun, J. Power Sources 2008, 175, 686–691.
- [66] H. Xu, X. Hu, H. Yang, Y. Sun, C. Hu, Y. Huang, *Adv. Energy Mater.* **2015**, *5*, 1401882.
- [67] N. Yu, H. Yin, W. Zhang, Y. Liu, Z. Tang, M.-Q. Zhu, Adv. Energy Mater. 2016, 6, 1501458.
- [68] Z. Lei, J. Zhang, X. S. Zhao, J. Mater. Chem. 2012, 22, 153-160.
- [69] M. Huang, Y. Zhang, F. Li, L. Zhang, R. S. Ruoff, Z. Wen, Q. Liu, Sci. Rep. 2015, 4, 3878.
- [70] J. Duay, E. Gillette, R. Liu, S. B. Lee, Phys. Chem. Chem. Phys. 2012, 14, 3329.
- [71] Z.-S. Wu, W. Ren, D.-W. Wang, F. Li, B. Liu, H.-M. Cheng, ACS Nano 2010, 4, 5835–5842.

## Ionic Liquid-Assisted MnO<sub>2</sub> for Zn-ion Battery Application

#### **Overview**

Aqueous zinc ion batteries (AZIBs) provide a safer and cost-effective energy storage solution by utilizing nonflammable water-based electrolytes. Although many research efforts are focused on optimizing zinc anode materials, developing suitable cathode materials is still challenging. In this study, one-dimensional (1D), mixedphase MnO<sub>2</sub> nanorods are synthesized using ionic liquid (IL). Here, the IL acts as a structure-directing agent that modifies MnO<sub>2</sub> morphology and introduces mixed phase, as confirmed by morphological, structural, and x-ray photoelectron spectroscopy (XPS) studies. The MnO<sub>2</sub> nanorods developed by this method are utilized as a cathode material for ZIBs application in the coin cell configuration. As expected, Zn//MnO<sub>2</sub> nanorods show a significant increase in their capacity to 347 Wh Kg<sup>-1</sup> at 100 mA g<sup>-1</sup>, which is better than bare MnO<sub>2</sub> nanowires (207.1 Wh Kg<sup>-1</sup>) synthesized by the chemical precipitation method. The battery is highly rechargeable and maintains good retention of 86 % of the initial capacity and 99% coulombic efficiency after 800 cycles at 1000 mA g<sup>-1</sup>. The *exsitu* XPS, XRD, and in-depth electrochemical analysis confirm that MnO<sub>6</sub> octahedrons experience insertion/extraction of Zn<sup>2+</sup> with high reversibility. This study suggests the potential use of MnO<sub>2</sub> nanorods to develop high-performance and durable battery electrode materials suitable for large-scale applications.

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### **4.1 Introduction**

With the growing number of applications for batteries, such as renewable energy storage and electric vehicles, many researchers focus on the development of multivalent metal ion batteries (for example, divalent magnesium (Mg), zinc (Zn), calcium (Ca), and trivalent aluminum (Al)) for improved battery safety, high energy density, charge-discharge rates, cost-effectiveness, and good cyclic life.<sup>[1,2]</sup> Along with abundant nature and low polarizabilities.<sup>[3]</sup> the two-electron redox  $(Zn^{2+})^{[4]}$  exhibits higher ionic conductivity (1 S cm<sup>-1</sup> for aqueous electrolytes)<sup>[5]</sup>. Zinc ion batteries (ZIBs) possess a low redox potential (-0.76 V vs. SHE)<sup>[6]</sup> compared to other negative electrodes and are cost-effective. These features make ZIBs viable for grid-scale applications, offering high specific energy and power. As noted in the literature, ZIBs face challenges related to cyclability, coulombic efficiency, and limited capacity.<sup>[7,8]</sup> Several cathode materials have been developed for ZIBs, including manganese ( $\alpha$ ,  $\beta$ ,  $\lambda$ ,  $\gamma$ ,  $\delta$ , and amorphous),<sup>[9,10]</sup> oxide/sulfides based on vanadium,<sup>[11]</sup> molybdenum,<sup>[12]</sup> sodium superionic conductors (NASICON)<sup>[13]</sup> type materials, and Prussian blue analogs.<sup>[14]</sup> Zn//MnO<sub>2</sub> batteries utilizing aqueous electrolytes are a secure alternative due to the plentiful availability of Zn and Mn. The formation of oxide and hydroxide byproducts in alkaline solutions leads to suboptimal cyclability and coulombic efficiency.<sup>[15]</sup> Efforts are concentrated on enhancing the stability of Zn//MnO<sub>2</sub> batteries for commercial viability.<sup>[16]</sup> Alshareef et al. achieved a high capacity of 232 mAh g<sup>-1</sup> through enhanced  $Zn^{2+}$  intercalation in the MoS<sub>2</sub> matrix. The experiments indicate that the performance is limited due to the intercalation energy barrier for  $Zn^{2+}$ .<sup>[17]</sup> Shi et al. investigated the surface chemistry and geometrical configuration of oxides in Mn-based ZIB to improve its performance by manipulating its phase.<sup>[18]</sup> The current research trends indicate that the exploration of innovative synthesis techniques and the utilization of mixed-phase cathode materials may result in a significant increase in capacity.

On the other hand, ionic liquids (ILs) are innovative and propitious materials providing ecofriendly and promising green solutions in a broad range of applications. The versatility of tuning the properties for optimizing their roles in diverse applications attracted the increasing interest of the scientific community.<sup>[19–21]</sup> ILs have been extensively researched as electrolytes and reaction media for synthesizing active materials in supercapacitors and batteries.<sup>[22–24]</sup> ILassisted synthesis using structural and functional direction properties of ILs has been the promising synthesis route for developing advanced inorganic energy materials.<sup>[25,26]</sup> This synthesis employs room-temperature ionic liquids (RTILs) to facilitate material synthesis at

ambient temperatures, rendering the process environmentally sustainable and energyefficient.<sup>[27,28]</sup> IL-assisted synthesis has advantages over conventional hydrothermal and solvothermal methods, such as lower temperatures, more straightforward operation, and normal pressure conditions, eliminating potential safety hazards.<sup>[29]</sup> Ionic liquids (ILs) possess stable properties and high decomposition temperatures, making them preferred over hydrothermal methods, especially for high-temperature synthesis.<sup>[30]</sup> ILs alter the polarity of the medium, which impacts surface energies and solvating strength, ultimately influencing material growth.<sup>[31]</sup> This approach offers significant potential for creating new materials, functionalities, and phases that are unattainable through conventional chemical methods.

We propose using IL-assisted synthesis to create mixed-phase MnO<sub>2</sub> nanorods for ZIBs, with IL serving as the solvent and morphology-directing agent. The IL-assisted reaction results in the formation of a suspension of precursor materials instead of a solution, owing to the limited solubility of [Emim][TFSI] in ultrapure water. The presence of the IL in the suspension induces a nucleation and growth mechanism that promotes the formation of nanorods, rather than nanowires, for pristine  $\alpha$ -MnO<sub>2</sub> (MO). This mechanism serves to minimize the total surface energy of the material. Using IL improves the surface area, redox kinetics, phase transition, and sample morphology. The mixed phase state is optimal for achieving efficient and consistent electrochemical performance. The aforementioned process can enhance structural stability and redox kinetics by significantly increasing the intercalation of  $Zn^{2+}$  and pseudocapacitive behavior. The structural and electrochemical differences of mixed-phase manganese oxide (MnO, MnO<sub>2</sub>, and Mn<sub>2</sub>O<sub>3</sub>) impact the performance of an electrode. The MnO<sub>6</sub> octahedra in the stacked MnO<sub>2</sub> structure exhibit exceptional capability for the intercalation and deintercalation of metal ions during battery cycling. MnO is a non-stoichiometric oxide with a higher capacity for metal ion retention compared to MnO<sub>2</sub>.<sup>[32]</sup> The electrochemical behavior of MnO<sub>2</sub> with mixed phases is contingent upon the relative proportions of the phases. The 3D architecture of MnO and Mn<sub>2</sub>O<sub>3</sub> facilitates rapid ion insertion and extraction, thereby mitigating stress concentration and improving cycling stability.<sup>[32]</sup> ILMO nanorods exhibit a significant capacity of 316 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> in aqueous electrolytes with the assistance of IL. The Zn//MnO<sub>2</sub> batteries exhibit a specific energy of 347.6 Wh kg<sup>-1</sup> and enhanced cyclic retention for the ILMO sample relative to the MO sample when subjected to a low current density of 100 mA g<sup>-1</sup>. Electrochemical tests, ex-situ characterizations, and diffusive capacitive contribution are utilized to investigate the mechanism underlying high performance.

### 4.2 Experimental section

### 4.2.1 Materials

N-methyl-2-pyrrolidone (NMP), [Emim][TFSI] (purity > 98%), and manganese sulfate monohydrate (MnSO<sub>4</sub>.H<sub>2</sub>O) were procured from Sigma-Aldrich. Potassium permanganate (KMnO<sub>4</sub>, ACS reagent) was procured from Loba Chemie Pvt. Ltd. Ammonium hydroxide (NH<sub>4</sub>OH, 28 wt% in water), 1-propanol, methanol (AR grade) and zinc sulfate heptahydrate (ZnSO<sub>4</sub>.7H<sub>2</sub>O) were obtained from SD fine chem limited. Ultrapure water (18 M $\Omega$ ) was collected from the ultrapure water system from ELGA LabWater America.

### 4.2.2 Synthesis of IL-derived MnO<sub>2</sub> (ILMO)

The IL-assisted process at room temperature was employed to synthesize ILMO samples. A solution was prepared by dissolving 0.5 M KMnO<sub>4</sub> and 0.72 g of [Emim][TFSI] in a 20 mL aqueous mixture of 1-propanol and ultrapure water (3:1) at room temperature. Subsequently, 2 mL of methanol was introduced as the reducing agent. The pH of the solution was raised to approximately ~9 by gradually adding 28 wt% NH<sub>4</sub>OH with moderate stirring. The precipitate was washed with ultrapure water and ethanol after 12 hours. The powder was amorphous initially and was crystallized into tetragonal MnO<sub>2</sub> by calcination at 600°C for 5 hours. The powders were stored and utilized for diverse materials and electrochemical analyses. Figure 4.1 (a) illustrates the dark-brown color of the ILMO sample following heat treatment.

### 4.2.3 Synthesis of MnO<sub>2</sub> (MO) by chemical precipitation method

The MO nanowires were synthesized via a chemical precipitation method for comparison. A solution of 0.5 M KMnO<sub>4</sub> was prepared by dissolving it in 20 mL of ultrapure water and stirring it for 30 minutes at room temperature. Subsequently, 2 mL of methanol was introduced as a reducing agent to the aforementioned solution. The solution was stirred for 1 hour and left to age at room temperature for 12 hours. After the reaction, a blackish-brown precipitate was obtained and purified by vacuum filtration and repeated washing with ultrapure water and methanol. The powder was dried at 80 °C using a vacuum method. The powder was subjected to varying temperatures (400 °C, 500 °C, and 600 °C) and durations (3, 4, and 5 h) to increase its crystallinity and form MO. The blackish brown-colored powder (Figure 4.1 (b)) obtained after heating was stored for future use.



**Figure 4.1** The initial samples are visually represented through photographs. Figure (a) depicts the dark-brown color of the bulk ILMO powder, whereas Figure (b) shows the blackish-brown color of the MO sample.

### **4.2.4 Electrochemical measurements**

Electrochemical analyses, such as CV and EIS, were conducted utilizing the CHI 1150C device. The Neware battery testing system was utilized to conduct charge-discharge experiments, galvanostatic intermittent titration technique (GITT), and stability tests. The material was analyzed for battery applications utilizing a CR2032 coin cell assembled in the laboratory. The slurry was formulated by combining ILMO (70%), carbon black (20%), and polyvinylidene fluoride (PVDF) (10%) in a conventional N-methyl-2-pyrrolidone (NMP) solution. The slurry was applied onto the current collector via the doctor blade method and dried overnight under vacuum at 110 °C. The current collector, which had been coated, underwent hot rolling to achieve uniform thickness. Subsequently, it was punched into a 16 mm disc shape using a disc cutter. The coin cell configuration consisted of a cathode with a coating, a 19 mm Whatman filter paper separator, and an anode composed of a 16 mm zinc foil (Figure 4.2). The coin cell was assembled under an argon atmosphere. The electrode's active mass loading for the battery measurements, named ILMO, ILMO-a, and ILMO-b, were 1.1, 2.5, and 4.6 mg cm<sup>-2</sup>, respectively. Ex-situ XPS analysis was conducted on charged and discharged electrodes at a current density of 100 mA g<sup>-1</sup>. The pristine electrode was used without undergoing any cycling process. The electrode underwent ex-situ XRD, FTIR, FESEM analysis through charging and discharging at varying voltages. Zn and Mn narrow region spectra were obtained at high resolution and deconvoluted through ThermoFisher Avantage software.



**Figure 4.2** A representation of the construction methodology for a coin cell component for battery utilizing zinc foil and ILMO.

### 4.3 Results and discussion

IL-assisted synthesis was utilized to create an ILMO nanorod as the cathode material for ZIBs. Figure 4.3 (a) schematically illustrates the synthesis process of the ILMO nanorods. In the absence of IL addition, the original material undergoes crystallization in the tunneled  $\alpha$ -phase of MnO<sub>2</sub>, as depicted in Figure 4.3 (b). IL-assisted synthesis promotes the creation of MnO<sub>2</sub> nanorods with mixed phases and enhanced energy stability. The XRD data obtained from the experiment was primarily matched with the tetragonal  $\alpha$ -MnO<sub>2</sub> (ICDD PDF: 00-044-0141),



Figure 4.3 (a) IL-assisted dense  $MnO_2$  nanorod production schematic. (b) MO sample crystal structure exhibits a 2x2 tunnel advantage for electrolyte ions intercalation.

with additional peaks attributed to MnO (ICDD PDF: 01-080-8705) and  $Mn_2O_3$  (ICDD PDF: 01-089-2809), which provided further evidence of the mixed phase present in ILMO.

Figure 4.4 (a,c) presents the PXRD spectra of MO and ILMO. Diffraction peaks were observed at 12.5°, 18°, 25.5°, 28.5°, 37.3°, 41.7°, 49.7°, 56.3°, 60°, 65.2°, 69.2° and 72.7° corresponding to crystallographic planes (110), (200), (220), (310), (211), (301), (411), (600), (521), (002), (541) and (312). The planes align with the tetragonal plane of  $\alpha$ -MnO<sub>2</sub>, which belongs to the I4/m space group. Mn<sub>2</sub>O<sub>3</sub> displays two diffraction peaks at 21.2° and 55.02°, whereas MnO exhibits three peaks at 29.6°, 30.68°, and 32.8°. Refer to Figure 4.4 (c) for a detailed comparison. The synthesized sample exhibits excellent crystallinity, as evidenced by intense peaks at 28°, 37°, and 60°, as well as prominent characteristic peaks.<sup>[33]</sup> The MnO peaks confirm the reduction of MnO<sub>2</sub> and provide additional evidence for the coexistence of multiple phases in the material. Additionally, the identified peaks correspond to Mn<sub>2</sub>O<sub>3</sub>, providing additional evidence for the MnO<sub>2</sub> phase transition. The mixed phase of manganese oxide and nanorod formation is attributed to the IL addition. The mixed-phase state is desirable for enhancing electrochemical performance due to the presence of defects. A tunnel structure is advantageous for enhanced electrolyte ion intercalation and is a promising option for battery utilization. Raman spectroscopy provided a more precise and thorough analysis of the synthesized material's structural information. The MO adopts a tetragonal body-centered structure with an I4/m space group, exhibiting characteristic  $A_g$  (6),  $B_g$  (6), and  $E_g$  (3) spectral bands.<sup>[34]</sup> Figure 4.4 (d,e) displays the Raman spectra of MO and ILMO, revealing three major peaks at 182, 572, and 633 cm<sup>-1</sup> and three minor peaks at 274, 382, and 481 cm<sup>-1</sup>. The sample's modes, which are consistent with existing literature, are all Mn-O vibrations below 1000 cm<sup>-1</sup>.<sup>[35]</sup> The MO exhibits two prominent peaks at 572 and 633 cm<sup>-1</sup> in the high-frequency range, which are associated with Ag spectroscopic species. These species arise from the movements of MnO<sub>6</sub> octahedra within a tetragonal hollandite-type framework.<sup>[36]</sup> Minor peaks for MO are detected at 279, 379, and 480 cm<sup>-1</sup>, whereas ILMO exhibits peaks at 274, 382, and 481 cm<sup>-1</sup>. The peak shift observed in the ILMO sample can be attributed to the Mn mixed phase state induced by the IL. Similar peak shifting has been observed for mixed-phase vanadium oxide.<sup>[37]</sup>



**Figure 4.4** (a,b) Powder XRD results to optimize MO through variations in temperature and heating duration. (c) Compares the PXRD spectra of the ILMO sample with the ICDD files of  $\alpha$ -MnO<sub>2</sub>, MnO, and Mn<sub>2</sub>O<sub>3</sub>. Deconvoluted Raman spectra for (d) MO and (e) ILMO showed metal and oxygen bond vibrational modes.



**Figure 4.5** FESEM images for (a) MO sample showing nanowire morphology, while for (b) nanorod morphology for ILMO sample at high magnification. (c) HRTEM images for the ILMO sample showing highly oriented crystallographic planes inside the nanorod at high magnification. (d) The SAED spot image of ILMO displays different phases using different colored balls and corresponding

Morphological characteristics were analyzed through FESEM and HRTEM images of the synthesized samples. The MO sample exhibits nanowire growth, as Figure 4.5 (a) depicts. In contrast, the IL-modified sample exhibits nanorod morphology attributed to the nucleation-growth kinetics of precursor materials. The inclusion of IL results in energetically unfavorable and unstable growth conditions for nanowires. A branching growth has facilitated the development of energetically favorable nanorods,<sup>[38]</sup> as depicted in Figure 4.5 (b).

The synthesized ILMO nanorods underwent HRTEM analysis. The synthesis process is effectively controlled, as evidenced by the distinct and well-developed individual nanorods.

The HRTEM image reveals the crystalline plane arrangement in the nanorods at higher magnification. Figure 4.5 (c) illustrates the (110) and (310) crystal planes present in the ILMO nanorods, which correspond to the PXRD spectra planes. Figure 4.5 (d) displays high-resolution bright-field scanning transmission electron microscopy micrographs that represent an ILMO sample. Selected area electron diffraction (SAED) analysis confirmed that the MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> phases correspond to the (220) and (440) plane families, respectively, as predicted by XRD data. The (1-21) plane family corresponds to the MnO phase, according to the ICDD PDF: 01-080-8705. Figure 4.6 (a,b) displays larger crystallographic planes determined through FFT and inverse FFT imaging.



**Figure 4.6** The ILMO sample's dominant crystallographic planes (1 1 0) and (3 1 0) are depicted in the enlarged inverse FFT images.



**Figure 4.7** Elemental and surface area study. (a) XPS survey spectra of ILMO inset display the atomic percentage of different elements. (b) Mn 2*p* narrow region spectra for ILMO confirm the various Mn oxidation state peaks. (c) Comparative O 1*s* narrow region spectra for ILMO and MO. (d) Adsorption-desorption isotherms for ILMO, inset shows the pore size distribution. (e) The STEM EDS spectra of the ILMO sample indicate a homogeneous dispersion of manganese and oxygen within the nanorod structure.


**Figure 4.8** (a) XPS survey spectra of the MO sample and (b) The narrow region spectra for the pristine MO sample to identify the chemical states or bonding configurations of the sample's elements. (c) The adsorption-desorption isotherms and pore size distribution for the MO sample.

XPS spectra in Figure 4.7 confirmed additional insights regarding chemical state and oxidation state identification. Figure 4.7 (a) displays survey spectra indicating the existence of C 1s, O 1s, Mn 2p, N 1s, and F 1s peaks in the ILMO sample (see Figure 4.8 (a,b) for MO XPS investigations) Both samples' high-resolution narrow region spectra were analyzed for Mn 2p and O 1s oxygen information, as shown in Figures 4.7 (b,c). ILMO exhibits mixed oxidation content, as indicated by its comparative high-resolution spectra. The O 1s spectra were analyzed through Gaussian XPS peak fitting. The analysis revealed the presence of lattice oxygen (O<sub>1</sub>) and adsorbed oxygen (O<sub>2</sub>) in ILMO. The amount of adsorbed water molecule (O<sub>3</sub>) was lower than that of O<sub>1</sub> and O<sub>2</sub>.<sup>[39]</sup> The Mn 2p peak in both samples exhibits a spin-orbit coupling component separation of approximately 11.7 eV, consistent with prior literature findings.<sup>[40]</sup> The XPS spectrum of ILMO revealed the presence of Mn 2p transitions at 642.1 eV (Mn 2p<sub>3/2</sub>) and 653.8 eV (Mn 2p<sub>1/2</sub>), with the Mn oxidation state contribution listed in Table 4.1. The Mn 2p<sub>3/2</sub> narrow spectra region displays notable peaks corresponding to different oxidation states: +4 at 642.9 and 654.6 eV, +3 at 641.8 and 653.5 eV, +2 at around 640.6 and 652.3 eV, and three satellite peaks at 644, 649.2, and 655.7 eV, as shown in Figure 4.7 (b).<sup>[41–46]</sup>

Peak	Deconvoluted Species'	At. %				
МО						
Mn 2p	Mn <sup>2+</sup>	20.3				
	Mn <sup>3+</sup>	36.7				
	$Mn^{4+}$	43				
ILMO						
Mn 2p	$Mn^{2+}$	10.8				
	Mn <sup>3+</sup>	38.1				
	$Mn^{4+}$	51.1				

Table 4.1 Mn 2p oxidation state contribution for MO and ILMO.

Surface area analyses were conducted using nitrogen adsorption-desorption isotherms at 77 K for both samples (Autosorb-iQ (Quantachrome)), as shown in Figures 4.7 (d) and Figure 4.8 (c). The ILMO sample demonstrated a higher specific surface area (SSA) of 46.12 m<sup>2</sup> g<sup>-1</sup> compared to the pristine MO sample's 28.5 m<sup>2</sup> g<sup>-1</sup>. This increase in SSA is greater than that of the recently reported Pt/ $\alpha$ -MnO<sub>2</sub> (20.56 m<sup>2</sup> g<sup>-1</sup>),<sup>[47]</sup> and  $\alpha$ -MnO<sub>2</sub>/R-MnO<sub>2</sub> (43 m<sup>2</sup> g<sup>-1</sup>).<sup>[48]</sup> The isotherm profiles of both materials were similar, but ILMO had a higher adsorbed volume than MO and exhibited a type-IV isotherm.<sup>[49]</sup> The presence of mesopores in the sample is

demonstrated by the pore size distribution shown in the inset of Figures 4.7 (d) and 4.8 (c). Table 4.2 presents the surface area and porosity analysis in detail. The high surface area and porosity of the ILMO sample contributed to its improved capacity.<sup>[50]</sup> The elemental confirmation was conducted through meticulous analysis of both samples' energy dispersive spectra (EDS), which were recorded at an accelerating potential of 10 kV. Figure 4.7 (e) presents the STEM EDS overlapped image and the Mn and O mapping. Refer to Figure 4.9 for MO sample EDS data. The samples' high surface area and nanoporous structure are advantageous for achieving optimal performance in the context of ZIBs.

Summary table								
XRD								
San	ıple		Peak position			Plane		
ILMO			12.5			(1 1 0)		
			18.0			(2 0 0)		
			25.5			(2 2 0)		
				28.5		(3 1 0)		
				37.3		(2 1 1)		
				41.7		(3 0 1)		
			49.7		(4 1 1)			
			56.3		(6 0 0)			
			60.2		(5 2 1)			
			65.2		(0 0 2)			
			69.7		(5 4 1)			
			72.7		(3 1 2	(3 1 2)		
Surface area & pore size								
Electrode	SBET	M <sub>BE</sub>	т	Langmuir	<i>t</i> -me	thod	Pore	Average pore
	(m <sup>2</sup>	$(m^2 g)$	g-	surface area	external	surface	volume	diameter
	g <sup>-1</sup> )	$\begin{vmatrix} 1 \end{pmatrix}$		$(m^2 g^{-1})$	area		$(cm^3 g^{-1})$	(nm)
					$(m^2 g^{-1})$			
MO	26.3	28.5	5	54.7	28	3.1	1.66	30.4
ILMO	43.4	46.1	1	86.4	46	5.1	4.2	30.4

**Table 4.2** Summary table is presented below, which includes XRD peak position for ILMO, surface area and pore size distribution for MO and ILMO.



**Figure 4.9** (a) EDS spectra indicate the presence of various elements in the MO sample. The elemental mapping of the MO sample reveals the existence of (b) Mn and (c) O elements within the material.

The electrodes of both materials were analyzed for their Zn-ion storage performance through cyclic voltammetry (CV) in an electrolyte of 2 M ZnSO<sub>4</sub> + 0.1 M MnSO<sub>4</sub> at a scan rate of 5 mV s<sup>-1</sup> and a voltage range of 0.8 - 1.9 V vs.  $Zn^{2+}/Zn$ , as depicted in Figure 4.10 (a). The analysis of redox peaks observed in the CV curves facilitated the comprehension of the charge storage kinetics of the ILMO cathode. This includes the solid diffusion or capacitive adsorption of H<sup>+</sup> and Zn<sup>2+</sup>. The electrochemical activity of the ILMO sample surpasses that of the pristine MO sample, as evidenced by the more significant area encompassed by the CV curve. Additionally, Figure 4.10 (b) displays the charge-discharge profiles for both substances. The ILMO exhibits a higher capacity compared to the MO sample due to its superior specific surface area, pore structure, and increased conductivity. The capacity of ILMO is 1.68 times greater than that of MO. Figure 4.10 (c) displays the ILMO's capacity at different current densities, namely 100, 200, 400, 600, 800, 1000, and 2000 mA  $g^{-1}$ . The specific capacity values were 316, 226.7, 196, 175.8, 147.9, 128, and 107.3 mAh g<sup>-1</sup>. The values obtained for the current density of 100, 200, 400, 600, 800, 1000, and 2000 mA  $g^{-1}$  are significantly higher than those of pristine MO nanowires. These values are 188.3, 141.8, 119, 102.3, 90.4, 81.3, and 63.3 mAh  $g^{-1}$ , respectively (Figure 4.10 (d)). The initial capacity of ILMO at 100 mA  $g^{-1}$  decreases due to mechanical stress or volume expansion during ion insertion and the formation of an unstable solid electrolyte interphase (SEI) layer.<sup>[51]</sup>

Our material exhibits superior performance in terms of high capacity compared to recently reported Zn ion storage systems such as todorokite-MnO<sub>2</sub> (108 mAh g<sup>-1</sup> at 0.3 A g<sup>-1</sup>),<sup>[52]</sup> Zn//MnO<sub>2</sub> nanofibers (290 mAh g<sup>-1</sup> at 90 mAh.g<sup>-1</sup>),<sup>[9]</sup> and Zn//MnO<sub>2</sub> (285 mAh g<sup>-1</sup> at 50 mA g<sup>-1</sup>).<sup>[53]</sup>



**Figure 4.10** Comparative electrochemical studies (a) CV curves of the MO and ILMO at 5 mV  $s^{-1}$  (b) Specific capacity plots for both samples at 100 mA  $g^{-1}$ . (c) Discharge/charge profiles at different current densities varying from 100 to 2000 mA  $g^{-1}$  for ILMO (d) Rate capability of MO and ILMO at different current densities. (e) Cycling performance with coulombic efficiency (CE) for ILMO and MO at 100 mA  $g^{-1}$ , and (f) Nyquist plots for Zn//MO and Zn//ILMO samples at 5 mV input signal; the inset shows the enlarged curve profiles.

The device exhibited high stability, with 74% initial capacity retention after 100 cycles and nearly 99% coulombic efficiency. In comparison, MO only retained ~46% capacity at 100 mA  $g^{-1}$ , as depicted in Figure 4.10 (e). The observed marginal capacity increments during cycling measurement at 100 mA  $g^{-1}$  in ILMO may be attributed to either electro activation or electrochemical rebuilding, which enhance a specific capacity.<sup>[54]</sup> The device exhibited capacity retention of 86% when subjected to long-term cyclability testing at 100 mA  $g^{-1}$ , as illustrated in Figure 4.11.

![](_page_149_Figure_1.jpeg)

![](_page_149_Figure_2.jpeg)

The ILMO sample exhibited excellent performance, which was corroborated by the EIS studies showing low impedance values. Figure 4.10 (f) illustrates a noteworthy reduction in impedance values for the ILMO sample. The Nyquist plot was obtained by measuring the impedance components (real and imaginary) against frequency in the range of 10 mHz to 100 kHz. The Nyquist plots indicate a lower resistance for the ILMO sample than MO. ILMO exhibits a charge transfer resistance of 47.3  $\Omega$ , whereas MO displays a significantly higher R<sub>ct</sub> of 649.9  $\Omega$ . The enhanced conductivity and capacity of the ILMO sample can be attributed to the reduced R<sub>ct</sub> compared to MO. The observed phenomenon can be attributed to the mixed phase in the material, which increases conductivity. Additionally, introducing IL results in a nanorod morphology that increases contact points and decreases R<sub>ct</sub> values.

Anode/Cathode	Electrolyte	Capacity	Cycles/capacity	Voltage	Ref.
		(mAh g <sup>-1</sup> )	retention	window	
α-MnO <sub>2</sub> //OLC	1M ZnSO <sub>4</sub>	168 @ 246 mA	93% after 100 cycles @ 246	1-1.8	[55]
	+0.1M	g <sup>-1</sup>	$mA g^{-1}$		
	MnSO <sub>4</sub>	•			
Zn//α-MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	195 @ C/20	70% after 30 cycles @ C/5	0.7-1.9	[56]
Zn//α-MnO <sub>2</sub>	1M	323 @ 16 mA g <sup>-</sup>	-	1-1.8	[57]
	ZnSO <sub>4</sub> (PH-4)	1			
Zn//V doped-	1M ZnSO <sub>4</sub>	266 @ 66 mA g <sup>-</sup>	49% after 100 cycles @ 66	1.0-1.8	[58]
MnO <sub>2</sub>		1	mA g <sup>-1</sup>		
Zn//ɛ-MnO <sub>2</sub>	$1M ZnSO_4 +$	221 @ 100 mA	92% after 500 cycles @ 500	0.6-1.9	[59]
	1M MnSO <sub>4</sub>	g <sup>-1</sup>	mA g <sup>-1</sup>		(00)
Zn//MnO <sub>2</sub>	2M	290 @ 90 mA g <sup>-</sup>	~ 58% after 20 cycle @ 1.3	1-1.8	[60]
	$ZnSO_4+0.2M$	1	С		
	MnSO <sub>4</sub>		(20) 6 50 1 @ 02	1010	[61]
$Zn//MnO_2$	IM ZnSO <sub>4</sub>	233 @ 83 mA g	63% after 50 cycles @ 83 mA $\sigma^{-1}$	1.0-1.8	[01]
Zn//MnO <sub>2</sub>	1M ZnSO <sub>4</sub>	108 @ C/2	-	0.7-2.0	[62]
Zn//MnO <sub>2</sub>	2M ZnSO <sub>4</sub>	313.5 @ 100	-	0.8-1.8	[63]
-		mA g <sup>-1</sup>			
Zn//MnO <sub>2</sub>	0.1M MnSO <sub>4</sub>	233 @ 30 mA g <sup>-</sup>	-	1.0-1.8	[64]
		1			
Zn//MnO	2M ZnSO <sub>4</sub>	292 @ 100 mA	-	1-1.9	[65]
		g <sup>-1</sup>			
Zn//MnO <sub>2</sub>	4.2M ZnSO <sub>4</sub>	265 @ 156 mA	88.37% after 1200 cycles @	0.8-1.9	[66]
	+ 0.1M	g <sup>-1</sup>	938 mA g <sup>-1</sup>		
	MnSO <sub>4</sub>	214 0 100 4		0.0.1.0	[67]
$Zn//MnO_2$	$2M ZnSO_4 +$	214 @ 100 mA	87.5% over 1000 cycles @	0.8-1.8	[67]
7//М0	0.5M MnSO <sub>4</sub>	g <sup>1</sup>	100 mA g *	0.9.1.7	[68]
	2 M $2$ M	150 @ 160 mA	-	0.8-1.7	[00]
Zn//CNT/MnO <sub>2</sub>	$3M_7nSO_4 +$	<u> </u>	86% after 1000th cycle @	08-19	[69]
	$0.1M MnSO_4$	mA g <sup>-1</sup>	$1000 \text{ mA g}^{-1}$	0.0 1.7	
Zn/MnO@NGS	$2M ZnSO_4 +$	272.5 @ 100	98% after 300 cycles @ 500	0.9-1.8	[70]
	0.2M MnSO <sub>4</sub>	mA g <sup>-1</sup>	mA g <sup>-1</sup>		
Zn//ILMO	2M ZnSO <sub>4</sub> +	316 @ 100 mA	86% over 1000 cycles @	0.8-1.9	This
	0.1M MnSO <sub>4</sub>	g <sup>-1</sup>	1000 mA g <sup>-1</sup>		work

#### Table 4.3 Compares the results from Zn//ILMO batteries with the previous literature.

The exceptional energy storage performance of the electrode can be attributed to the altered textural shape, crystal structure, and enhanced surface area of the ILMO. The increased number of contact points between nanorods decreases material resistance by providing more electron transport pathways and lower contact resistance at the junction. The crystal structure of ILMO nanorods comprises two chains of [MnO<sub>6</sub>] that form a  $2\times2$  tunnel, facilitating cation intercalation into  $\alpha$ -MnO<sub>2</sub>. The nanostructure facilitates ion and electron diffusion over short

![](_page_151_Figure_1.jpeg)

distances owing to its reduced diffusion route lengths. This performance exceeds previous reports, as shown in Table 4.3.

**Figure. 4.12** *Ex-situ* XPS measurements for ILMO cathode. (a) Zn//ILMO charge-discharge curve at 100 mA g<sup>-1</sup>,(b) Mn 2p spectra for pristine, charged, and discharged ILMO samples were obtained. A minor change in the Mn 2p spectra indicates the presence of  $Zn^{2+}$  in the cathode material. (c) The Zn 2p narrow area spectra explain the  $Zn^{2+}$  insertion while discharging.

Ex-situ XPS analyses were performed to comprehend the charge/discharge mechanism in the ILMO sample, as depicted in Figure 4.12 (a-c). Figure 4.12 (b) shows the oxidation state changes observed in the Mn 2p narrow spectra during cathode material charging and discharging. During cycling, Mn exhibits +2, +3, and +4 oxidation states in the deconvolution process. At a charge of 1.5 V and discharge of 1.3 V, the +4 oxidation state is dominant. However, the +3 oxidation state prevails over other possible oxidation states during the fully charged or discharged stage, as shown in Table 4.4. During charging, the cathode material 131

exhibits all oxidation states with slight variations in binding energy values, elucidating the lattice modifications resulting from Zn ion intercalation. The Mn spectra shift towards lower binding energy during discharge and return to their original position upon complete charging. The results demonstrate Mn valency changes during charging/discharging due to  $Zn^{2+}$  ion intercalation/extraction.<sup>[71]</sup> Figure 4.12 (c) displays the high-resolution Zn 2p narrow region spectra before testing, charging, and discharging. The absence of Zn content in the electrode prior to cycling is contrasted by the emergence of discernible Zn peaks during both charging and discharging, which elucidates the insertion of Zn ions into the cathode material. Upon discharge, the Zn 2p peak can be resolved into two distinct peaks, corresponding to intercalated Zn and adsorbed Zn. The intercalated Zn peak was absent during charging, but some Zn was adsorbed in the material. Ex-situ XPS analysis aids in comprehensively studying the Zn<sup>2+</sup> ion insertion between [MnO<sub>6</sub>] octahedrons, resulting in high capacity for ILMO.

Peak	Deconvoluted Species'	At. %			
	Mn <sup>2+</sup>	10.8			
Mn 2p (Pristine)	Mn <sup>3+</sup>	38.1			
	Mn <sup>4+</sup>	51.1			
	Charge upto 1.5 V				
	Mn <sup>2+</sup>	9.72			
	Mn <sup>3+</sup>	17.77			
Mn 2p (Charged)	Mn <sup>4+</sup>	72.51			
Charge upto 1.9 V					
	Mn <sup>2+</sup>	8.7			
Mn 2p (Charged)	Mn <sup>3+</sup>	53.9			
	Mn <sup>4+</sup>	37.4			
	Dicharge upto 1.3V				
	Mn <sup>2+</sup>	12.52			
Mn 2p (Discharged)	Mn <sup>3+</sup>	24.89			
	Mn <sup>4+</sup>	62.59			
Fully discharged					
	Mn <sup>2+</sup>	18.6			
Mn 2p (Discharged)	Mn <sup>3+</sup>	40.4			
	Mn <sup>4+</sup>	41			

**Table 4.4** Ex-situ study of the deconvoluted Mn 2p state contribution peak during charge and discharge.

The reversibility of the  $H^+/Zn^{2+}$  co-insertion/extraction process was confirmed through ex-situ XRD and ex-situ SEM analysis of Zn/ILMO cathodes. The electrolyte media initiates the proton insertion chemistry, as demonstrated by ex situ XRD and SEM measurements of the ILMO

electrode (Figures 4.13 and 4.14). The phenomenon occurs due to the ability of oxygen species in the host material to capture protons near the electrode surface through hydrogen bonding, thereby facilitating the insertion of H<sup>+</sup>. The absence of a hydrogen-bond-mediated surface in electrode materials in the absence of an oxygen medium impedes the insertion of H<sup>+</sup>. The ILMO electrode underwent charging at 1.31, 1.57, and 1.9 V and subsequent discharge at 1.67, 1.32, and 0.8 V, respectively, at a current density of 200 mA g<sup>-1</sup> for ex-situ XRD analysis (Figure 4.13 (a,b)). XRD data were obtained during various charging and discharging phases. New crystalline peaks were detected, including ZnMnO<sub>3</sub> (ICDD PDF: 00-065-0085), Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>.5H<sub>2</sub>O (ICDD PDF: 00-039-0688), and MnOOH (ICDD PDF: 01-075-1199), in addition to the peaks of the original ILMO sample.

![](_page_153_Figure_2.jpeg)

**Figure 4.13** *Ex-situ* XRD study was conducted on Zn//ILMO electrode at different charging and discharging voltages.

The observed phenomenon could be attributed to the significant  $Zn^{2+}$  and  $H^+$  insertion/extraction in the ILMO cathode. At 1.31 V charge, peaks resulting from the deintercalation of H+ from the ILMO host were detected, indicating the dissolution of  $Zn_4SO_4(OH)_6.5H_2O$  on the surface due to electrolyte reaction. The reversible dissolution and generation of  $Zn_4SO_4(OH)_6.5H_2O$ , and the appearance and disappearance of intrinsic diffraction peaks of ILMO during cycling, demonstrate its remarkable structural stability and cycle reversibility. Phase changes during charging/discharging in a high-volume electrolyte

environment result in a weaker diffraction peak signal. The reversible  $Zn//MnO_2$  chemistry with  $ZnSO_4 + MnSO_4$  electrolytes is proposed in the following reactions.

Cathode:  $3 \text{ Mn}^{2+} + 2 \text{ Zn}_4\text{SO}_4.5\text{H}_2\text{O} - 6e^- \rightleftharpoons 3 \text{ MnO}_2 + 2 \text{ SO}_4^{2-} + 8 \text{ Zn}^{2+} + 16 \text{ H}_2\text{O}$ 

Anode:  $Zn \rightleftharpoons Zn^{2+} + 2e^{-}$ 

Nanorod form was preserved in the fully charged cell, but their crystal structure was altered, with non-stoichiometric Mn (III, IV) layers now trapping water molecules in the interlayer spaces. Zinc ions can occupy interlayer vacancies, creating the  $(Zn_xMn_7O_{13}+y.5H_2O)$  phase. Figure 4.14 depicts linked nanorods exhibiting multiple interfaces. The SEM images shows cathode regeneration and the deposition of  $Zn_4(OH)_6SO_4.5H_2O$  during discharge. Manganese (III) undergoes a disproportionation reaction resulting in the formation of  $Zn_4(OH)_6SO_4.5H_2O$  upon increasing the pH of the electrolyte. Despite the persistence of nanorods morphology on the fully discharged cathode surface, the XRD diffraction peaks are exclusively associated with ILMO, suggesting that the majority of Mn(III) has transformed into Mn(II) and dissolved into

![](_page_154_Figure_5.jpeg)

**Figure 4.14** *Ex-situ* SEM investigation was conducted on (a, b) fully charged and (c, d) fully discharged cathode at different magnification scales.

the electrolyte, thereby restoring  $Zn_4(OH)_6SO_4 \cdot 5H_2O$ . We examined the morphologies of Zinc anodes to assess their stability post-charging and discharging. Figure 4.15 depicts the development of Zn dendrite outgrowth and nuclei following various cycling tests.

![](_page_155_Figure_2.jpeg)

**Figure 4.15** SEM photos of (a) fresh Zn anode was obtained, and ex-situ SEM examination of the Zn anode was performed after (b) 100 and (c) 800 cycles.

The pre-cycling asymmetry of Zn surfaces induces the nucleation process. After 100 cycles, certain nuclei exhibit dendrites with Zn edges. Corrosion of the Zn foil can affect the electrochemical performance of Zn-based batteries. Dendrite growth was observed on the Zn anode after 800 cycles, indicating its effective obstruction of zinc ion flow and dendrite formation. Additional evidence is present in the ex situ FTIR spectra, as depicted in Figure 4.16. The spectra indicate that the presence of signals at 1117, 1047, and 475-515 cm<sup>-1</sup> in Zn<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>· 5H<sub>2</sub>O is observed exclusively following the discharge of the electrode to state H.<sup>[72]</sup> The signals become absent upon charging the electrode to state A. Figure 4.17 displays ILMO mass loadings at different current densities. ILMO electrodes exhibit greater capacity than MO electrodes. The ILMO electrode (279.3 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup>) and the ILMO-b electrode (211.3 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup>).

The capacity retention was enhanced as the current density increase to 2000 mA  $g^{-1}$ , which was 20 times higher. The battery's capacity decreases as the active material mass increases due to a reduction in the electrolyte's ion transport capacity. The surface area available for charge storage is reduced in thick samples compared to thin samples. High-mass-loaded batteries exhibited improved capacity retention at higher current densities despite a slight decrease in performance. Increased current density mitigates mass loading effects by promoting greater ion flow through the electrolyte.

![](_page_156_Figure_1.jpeg)

Figure 4.16 *Ex-situ* FTIR measurement of the ILMO cathode was performed at various voltages.

![](_page_156_Figure_3.jpeg)

**Figure 4.17** Rate capabilities of ILMO, ILMO-a, and ILMO-b at varying current densities, given their respective mass loadings of 1.1 mg cm<sup>-2</sup>, 2.5 mg cm<sup>-2</sup>, and 4.6 mg cm<sup>-2</sup>.

![](_page_157_Figure_1.jpeg)

**Figure. 4.18** (a) The Zn//ILMO system underwent initial CV cycles at 0.2 mV s<sup>-1</sup> (b) CV obtained at various scan rates. (c) Linear correlation between log(v) and log(i) for peak 1 to peak 4 at varying potentials. (d) Zn//ILMO capacity contribution at 5 mV s<sup>-1</sup> (e) Initial 4 cycle GCD profiles at 100 mA g<sup>-1</sup> (f) Zn<sup>2+</sup> and H<sup>+</sup> storage contributions to capacity at varied current densities.

The electrode kinetics were analyzed by conducting multiple CV curves at different scan rates, as depicted in Figures 4.18 (a,b). Figure 4.18 (a) displays the CV curves for the first 6 cycles of ILMO, obtained at a scan rate of 0.2 mV s<sup>-1</sup> within the potential range of 0.8 to 1.9 V. The overlapping of CV curves in the cathodic/anodic scans indicates a high degree of reversibility in the ILMO cathode. The cyclic voltammetry curves of the ILMO cathode exhibit two pairs of redox peaks at 1.23/1.55 V and 1.37/1.61 V, which are indicative of the various cycles associated with ILMO cathodes. Figure 4.18 (b) illustrates the peak currents of the ILMO electrode at varying scan rates. The relationship between peak current (*i*) and scan rate (*v*) can be expressed as log *i* = log a + b. log*v*, where a and b are variable parameters. The value of b varies based on the charge storage behavior. b value of 0.5 suggests that charge storage is mainly governed by a solid-state ion diffusion mechanism.<sup>[73]</sup>

The ILMO cathode's b values at four redox peaks are 0.44 (peak 1), 0.45 (peak 2), 0.32 (peak 3), and 0.52 (peak 4), as shown in Figure 4.18 (c). These values indicate that the cathode's charge storage behavior is associated with diffusion-controlled processes. Increasing the scan rate from 0.2 to 2 mV s<sup>-1</sup> increases the capacitive contribution to the overall capacity of ILMO. The CV current "*i*" for the ILMO is contributed by both the capacitive-controlled effect  $(k_1.v)$ and the diffusion-controlled effect  $(k_2, v^{1/2})$ . Figure 4.18 (d) indicates that at a higher scan rate of 5 mV s<sup>-1</sup>, the pseudocapacitive contribution accounts for 81.8% of the total capacity. The electrochemical reaction kinetics related to the two-stage discharge plateaus were investigated to gain an understanding of the contribution of Zn<sup>2+</sup> and H<sup>+</sup> insertion performance, as depicted in Figure 4.18 (e). Galvanostatic discharge/charge patterns exhibit a turning point at 1.32 V discharge voltage during the initial cycle, when conducted at 100 mA g<sup>-1</sup>. Figure 4.18 (f) shows the plotted capacity based on the calculated contribution of Zn<sup>2+</sup> and H<sup>+</sup> storage capacity, with reference to the turning point. The decline in  $Zn^{2+}$  storage capacity ratio is directly proportional to the rise in current density, owing to the comparatively sluggish diffusion rate of  $Zn^{2+}$  ions compared to H<sup>+</sup> ions. The combined effect of capacitive and insertion mechanisms involving  $Zn^{2+}$  and  $H^+$  ions determines the overall capacity.

Furthermore, the GITT was employed to elucidate the ion transport kinetics and diffusion coefficients. Intermittent voltage spikes occur during discharge, as shown in Figure 4.19 (a). Region I exhibits lower overvoltage (71.5 mV) compared to Region II (286 mV), which can be attributed to the different diffusion rates. The abrupt voltage rise observed during a GITT measurement can be attributed to the combined effects of the electrolyte's ohmic and charge-transfer resistances. The resting voltage increase is attributed to ion diffusion. The combination of high voltage jumps and slow zinc ionic diffusion causes the overvoltage in region II. Figure 4.19 (b) illustrates that the ionic diffusion coefficients for Zn//ILMO ( $10^{-14}$ - $10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>) are higher than previously documented manganese-based electrodes.<sup>[74]</sup> The H<sup>+</sup> diffusion coefficient in region II ( $10^{-12}$ - $10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>) exceeds the Zn<sup>2+</sup> diffusion coefficient in region II ( $10^{-14}$ - $10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>), indicating a faster diffusion rate for H<sup>+</sup> ions compared to Zn<sup>2+</sup> ions. The study indicates that the nanorod structure produced by MnO<sub>2</sub> overgrowth through IL yields numerous activation sites, leading to improved electrochemical reactions, reduced ionic diffusion channels, and faster charge transfer and ionic diffusions.

![](_page_159_Figure_1.jpeg)

**Figure. 4.19** (a) GITT discharge profiles of the Zn//ILMO cell at 100 mA g<sup>-1</sup> (b) Zn//ILMO's computed diffusion coefficient of ions during discharge, (c) Rate capability comparison from earlier studies, and (d) Ragone plot comparing Zn/ILMO cell with other cathode materials reported for aqueous ZIBs.

Our material's performance was compared to previous reports<sup>[64,75–82]</sup> for Zn//MnO<sub>2</sub>, as depicted in Figure 4.19 (c). The cathode prepared in this study demonstrates good rate capabilities compared to previous research, potentially attributed to a network structure that facilitates enhanced electrolyte penetration and ion diffusion. Furthermore, we compared SE and SP values across the Ragone plot, as depicted in Figure 4.19 (d). The ILMO cathode demonstrated a significant specific energy (SE) ranging from 118 to 347.6 Wh kg<sup>-1</sup> at various specific power

(SP) levels ranging from 109.7 to 1743.5 W kg<sup>-1</sup>. These values are notable compared to other cathode materials for aqueous ZIBs (see Table 4.5 for a comprehensive comparison).

**Table 4.5** This study compares the specific capacity, voltage window, and specific energy values of  $MnO_2$  as the active material for ZIB with previously reported.

Materials	Specific capacity (mAh g <sup>-1</sup> )	Voltage (V)	Specific energy (Wh kg <sup>-1</sup> )	Ref.
α-MnO <sub>2</sub> nanofibers	285	0.9	210	[83]
a-MnO <sub>2</sub>	210	0.9	189	[84]
a-MnO <sub>2</sub>	306	1.05	290.7	[85]
β-MnO <sub>2</sub>	258	1.1	283.8	[86]
β-MnO <sub>2</sub>	270	0.8	216	[87]
γ-MnO <sub>2</sub>	285	0.8	228	[88]
δ-MnO <sub>2</sub>	252	0.8	201.6	[89]
Akhtenskite-type	290	0.8	232	[60]
MnO <sub>2</sub>				
Mn <sub>3</sub> O <sub>4</sub>	239.2	1.1	263.12	[90]
ZnMn <sub>2</sub> O <sub>4</sub>	150	1.1	165	[91]
This work	316	1.1	347.6	This work

#### **4.4 Conclusions**

IL-assisted synthesis for MnO<sub>2</sub> has resulted in enhanced surface area, redox kinetics, mixed phase, and controlled surface morphology compared to conventional synthesis methods. Our method for synthesizing mixed-phase MnO<sub>2</sub> is straightforward and does not require complex post-treatment procedures. The reversible insertion and extraction of  $Zn^{2+}$  are enhanced by the presence of a mixed phase in the MnO<sub>2</sub> lattice, which reduces the charge transfer resistance. We compare the effectiveness of MnO<sub>2</sub> nanorods and MnO<sub>2</sub> nanowires, which were produced using the conventional chemical precipitation method, for use in Zn-ion batteries. Using low-cost cathodes and anodes, along with aqueous electrolytes, can have high specific energy (~347 Wh kg<sup>-1</sup>) and good cycle life (~86% retention after 800 cycles). This makes it feasible to expand the application of these batteries for grid storage purposes. The results of this study are anticipated to facilitate the advancement of environmentally sustainable IL-assisted synthesis methods for producing more sophisticated binary metal oxides suitable for battery applications.

#### **4.5 References**

- Z. Pan, X. Liu, J. Yang, X. Li, Z. Liu, X. J. Loh, J. Wang, *Adv. Energy Mater.* 2021, *11*, 2100608.
- [2] Y. Liang, H. Dong, D. Aurbach, Y. Yao, *Nat. Energy* **2020**, *5*, 646–656.
- [3] J. Xie, Q. Zhang, *Small* **2019**, *15*, 1805061.
- [4] J. F. Parker, C. N. Chervin, I. R. Pala, M. Machler, M. F. Burz, J. W. Long, D. R. Rolison, *Science (80-. ).* 2017, 356, 415–418.
- [5] D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah, L. F. Nazar, *Nat. Energy* 2016, *1*, 16119.
- [6] N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao, Z. Niu, Angew. Chemie Int. Ed. 2021, 60, 2861–2865.
- [7] J. Wang, Y. Yang, Y. Zhang, Y. Li, R. Sun, Z. Wang, H. Wang, *Energy Storage Mater*.
   2021, 35, 19–46.
- [8] L. E. Blanc, D. Kundu, L. F. Nazar, *Joule* **2020**, *4*, 771–799.
- [9] Z. Liu, Y. Yang, S. Liang, B. Lu, J. Zhou, *Small Struct.* **2021**, *2*, 2100119.
- [10] J. Huang, Z. Wang, M. Hou, X. Dong, Y. Liu, Y. Wang, Y. Xia, *Nat. Commun.* 2018, 9, 2906.
- [11] N. Zhang, M. Jia, Y. Dong, Y. Wang, J. Xu, Y. Liu, L. Jiao, F. Cheng, *Adv. Funct. Mater.* 2019, 29, 1807331.
- [12] S. Li, Y. Liu, X. Zhao, Q. Shen, W. Zhao, Q. Tan, N. Zhang, P. Li, L. Jiao, X. Qu, *Adv. Mater.* 2021, *33*, 2007480.
- [13] G. Li, Z. Yang, Y. Jiang, C. Jin, W. Huang, X. Ding, Y. Huang, *Nano Energy* 2016, 25, 211–217.
- [14] L. Ma, S. Chen, C. Long, X. Li, Y. Zhao, Z. Liu, Z. Huang, B. Dong, J. A. Zapien, C.

Zhi, Adv. Energy Mater. 2019, 9, 1902446.

- [15] T. Zhang, Y. Tang, S. Guo, X. Cao, A. Pan, G. Fang, J. Zhou, S. Liang, *Energy Environ. Sci.* 2020, *13*, 4625–4665.
- [16] Z. Liu, Y. Yang, B. Lu, S. Liang, H. J. Fan, J. Zhou, *Energy Storage Mater.* 2022, 52, 104–110.
- [17] H. Liang, Z. Cao, F. Ming, W. Zhang, D. H. Anjum, Y. Cui, L. Cavallo, H. N. Alshareef, *Nano Lett.* **2019**, *19*, 3199–3206.
- [18] W. Shi, W. S. V. Lee, J. Xue, *ChemSusChem* **2021**, *14*, 1634–1658.
- [19] T. Zhang, T. Doert, H. Wang, S. Zhang, M. Ruck, Angew. Chemie Int. Ed. 2021, 60, 22148–22165.
- [20] Y. Liu, Q. Xu, R. Wang, Y. Zheng, L. Zhu, Z. Wang, W. Zheng, J. Mater. Chem. A 2020, 8, 797–809.
- [21] X. Wang, M. Salari, D. Jiang, J. Chapman Varela, B. Anasori, D. J. Wesolowski, S. Dai,
   M. W. Grinstaff, Y. Gogotsi, *Nat. Rev. Mater.* 2020, *5*, 787–808.
- [22] G. Hernández, M. Işik, D. Mantione, A. Pendashteh, P. Navalpotro, D. Shanmukaraj, R.
   Marcilla, D. Mecerreyes, J. Mater. Chem. A 2017, 5, 16231–16240.
- [23] M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, *Chem. Rev.* 2017, 117, 7190–7239.
- [24] G. Gebresilassie Eshetu, M. Armand, B. Scrosati, S. Passerini, *Angew. Chemie Int. Ed.*2014, *53*, 13342–13359.
- [25] T. Wang, H. Luo, Y. Bai, J. Li, I. Belharouak, S. Dai, Adv. Energy Mater. 2020, 10, 2001204.
- [26] X. Liu, C. Liu, W. Lai, W. Huang, Adv. Mater. Technol. 2020, 5, 2000154.
- [27] F. A. Alharthi, G. Nagaraju, S. P. Vinay, Udayabhanu, N. Al-Zaqri, A. Alsalme, Int. J.

Energy Res. 2020, 44, 8362–8371.

- [28] K. N. Manukumar, G. Nagaraju, B. Kishore, C. Madhu, N. Munichandraiah, J. Energy Chem. 2018, 27, 806–812.
- [29] E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* 2004, 430, 1012–1016.
- [30] E. R. Parnham, R. E. Morris, Acc. Chem. Res. 2007, 40, 1005–1013.
- [31] G. G. Eshetu, M. Armand, H. Ohno, B. Scrosati, S. Passerini, *Energy Environ. Sci.* 2016, 9, 49–61.
- [32] Y. Zou, A. Dong, Z. Guo, L. Ye, Y. Cui, M. Guo, L. Zhao, Q. Jiang, ACS Appl. Nano Mater. 2020, 3, 5612–5624.
- [33] B. Pandit, S. R. Rondiya, N. Y. Dzade, S. F. Shaikh, N. Kumar, E. S. Goda, A. A. Al-Kahtani, R. S. Mane, S. Mathur, R. R. Salunkhe, ACS Appl. Mater. Interfaces 2021, 13, 11433–11441.
- [34] D. Mondal, B. K. Paul, S. Das, D. Bhattacharya, D. Ghoshal, P. Nandy, K. Das, S. Das, *Langmuir* 2018, 34, 12702–12712.
- [35] Z. Yang, D. C. Ford, J. S. Park, Y. Ren, S. Kim, H. Kim, T. T. Fister, M. K. Y. Chan,
   M. M. Thackeray, *Chem. Mater.* 2017, 29, 1507–1517.
- [36] C. Julien, M. Massot, S. Rangan, M. Lemal, D. Guyomard, J. Raman Spectrosc. 2002, 33, 223–228.
- [37] Y. Huang, D. Zhang, Y. Liu, J. Jin, Y. Yang, T. Chen, H. Guan, P. Fan, W. Lv, Appl. Surf. Sci. 2018, 456, 545–551.
- [38] G. Xi, K. Xiong, Q. Zhao, R. Zhang, H. Zhang, Y. Qian, Cryst. Growth Des. 2006, 6, 577–582.
- [39] M.-K. Song, S. Cheng, H. Chen, W. Qin, K.-W. Nam, S. Xu, X.-Q. Yang, A. Bongiorno,

J. Lee, J. Bai, T. A. Tyson, J. Cho, M. Liu, Nano Lett. 2012, 12, 3483-3490.

- [40] H. Chen, C. Dai, F. Xiao, Q. Yang, S. Cai, M. Xu, H. J. Fan, S. Bao, Adv. Mater. 2022, 34, 2109092.
- [41] R. Ponnusamy, R. Venkatesan, M. Kandasamy, B. Chakraborty, C. S. Rout, *Appl. Surf. Sci.* 2019, 487, 1033–1042.
- [42] B. Dahal, T. Mukhiya, G. P. Ojha, K. Chhetri, A. P. Tiwari, A. Muthurasu, M. Lee, S.-H. Chae, T. Kim, D. C. Chung, H. Y. Kim, *Chem. Eng. J.* 2020, 387, 124028.
- [43] M. Liu, Q. Zhao, H. Liu, J. Yang, X. Chen, L. Yang, Y. Cui, W. Huang, W. Zhao, A. Song, Y. Wang, S. Ding, Y. Song, G. Qian, H. Chen, F. Pan, *Nano Energy* 2019, 64, 103942.
- [44] Z. Ma, H. Xu, Y. Liu, Q. Zhang, M. Wang, Y. Lin, Z. Li, X. He, J. Sun, R. Jiang, Z. Lei,
   Q. Li, L. Yang, Z. Liu, *J. Mater. Chem. A* 2022, *10*, 24216–24225.
- [45] Q. Dong, Q. Tian, S. Zhang, W. Zhang, Z. Chen, X. Han, W. Hu, J. Power Sources 2022, 550, 232143.
- [46] Y. He, D. Aasen, H. Yu, M. Labbe, D. G. Ivey, J. G. C. Veinot, *Nanoscale Adv.* 2020, 2, 3367–3374.
- [47] J. Liu, R. Younesi, T. Gustafsson, K. Edström, J. Zhu, *Nano Energy* **2014**, *10*, 19–27.
- [48] L. Trahey, N. K. Karan, M. K. Y. Chan, J. Lu, Y. Ren, J. Greeley, M. Balasubramanian,
   A. K. Burrell, L. A. Curtiss, M. M. Thackeray, *Adv. Energy Mater.* 2013, *3*, 75–84.
- [49] V. Sharma, S. Biswas, B. Sundaram, P. Haldar, B. Dubey, A. Chandra, ACS Sustain. Chem. Eng. 2019, 7, 5385–5392.
- [50] J. Zhang, M. Huang, B. Xi, K. Mi, A. Yuan, S. Xiong, Adv. Energy Mater. 2018, 8, 1701330.
- [51] Y. Zhang, P. Chen, Q. Wang, Q. Wang, K. Zhu, K. Ye, G. Wang, D. Cao, J. Yan, Q.

Zhang, Adv. Energy Mater. 2021, 11, 2101712.

- [52] T.-H. Wu, Y.-Q. Lin, Z. D. Althouse, N. Liu, ACS Appl. Energy Mater. 2021, 4, 12267– 12274.
- [53] M. Han, J. Yao, J. Huang, Y. Tang, X. Wu, B. Lu, J. Zhou, *Chinese Chem. Lett.* 2023, 34, 107493.
- [54] H. Huang, R. Xu, Y. Feng, S. Zeng, Y. Jiang, H. Wang, W. Luo, Y. Yu, *Adv. Mater.* **2020**, *32*, 1904320.
- [55] N. Palaniyandy, M. A. Kebede, K. Raju, K. I. Ozoemena, L. le Roux, M. K. Mathe, R. Jayaprakasam, *Mater. Chem. Phys.* 2019, 230, 258–266.
- [56] B. Lee, H. R. Lee, H. Kim, K. Y. Chung, B. W. Cho, S. H. Oh, *Chem. Commun.* 2015, 51, 9265–9268.
- [57] M. H. Alfaruqi, S. Islam, J. Gim, J. Song, S. Kim, D. T. Pham, J. Jo, Z. Xiu, V. Mathew,
   J. Kim, *Chem. Phys. Lett.* 2016, 650, 64–68.
- [58] M. H. Alfaruqi, S. Islam, V. Mathew, J. Song, S. Kim, D. P. Tung, J. Jo, S. Kim, J. P. Baboo, Z. Xiu, J. Kim, *Appl. Surf. Sci.* 2017, 404, 435–442.
- [59] L. Wang, X. Cao, L. Xu, J. Chen, J. Zheng, ACS Sustain. Chem. Eng. 2018, 6, 16055– 16063.
- [60] W. Sun, F. Wang, S. Hou, C. Yang, X. Fan, Z. Ma, T. Gao, F. Han, R. Hu, M. Zhu, C. Wang, J. Am. Chem. Soc. 2017, 139, 9775–9778.
- [61] M. H. Alfaruqi, J. Gim, S. Kim, J. Song, J. Jo, S. Kim, V. Mathew, J. Kim, J. Power Sources 2015, 288, 320–327.
- [62] J. Lee, J. B. Ju, W. Il Cho, B. W. Cho, S. H. Oh, *Electrochim. Acta* **2013**, *112*, 138–143.
- [63] X. Guo, J. Zhou, C. Bai, X. Li, G. Fang, S. Liang, *Mater. Today Energy* 2020, 16, 100396.

- [64] M. Chamoun, W. R. Brant, C.-W. Tai, G. Karlsson, D. Noréus, *Energy Storage Mater*.
   **2018**, *15*, 351–360.
- [65] Z. You, H. Liu, J. Wang, L. Ren, J.-G. Wang, Appl. Surf. Sci. 2020, 514, 145949.
- [66] B. W. Olbasa, F. W. Fenta, S.-F. Chiu, M.-C. Tsai, C.-J. Huang, B. A. Jote, T. T. Beyene,
   Y.-F. Liao, C.-H. Wang, W.-N. Su, H. Dai, B. J. Hwang, *ACS Appl. Energy Mater.* 2020,
   3, 4499–4508.
- [67] J. Cao, D. Zhang, C. Gu, X. Wang, S. Wang, X. Zhang, J. Qin, Z. Wu, Adv. Energy Mater. 2021, 11, 2101299.
- [68] O. Fitz, S. Ingenhoven, C. Bischoff, H. Gentischer, K. P. Birke, D. Saracsan, D. Biro, *Batteries* 2021, 7, 40.
- [69] L. Kang, M. Cui, F. Jiang, Y. Gao, H. Luo, J. Liu, W. Liang, C. Zhi, *Adv. Energy Mater.* **2018**, *8*, 1801090.
- [70] W. Li, X. Gao, Z. Chen, R. Guo, G. Zou, H. Hou, W. Deng, X. Ji, J. Zhao, *Chem. Eng. J.* 2020, 402, 125509.
- [71] K. Han, Z. Wang, F. An, Y. Liu, X. Qu, J. Xue, P. Li, ACS Appl. Mater. Interfaces 2022, 14, 4316–4325.
- [72] S. Li, C. Huang, L. Gao, Q. Shen, P. Li, X. Qu, L. Jiao, Y. Liu, *Angew. Chemie Int. Ed.* **2022**, *61*, DOI 10.1002/anie.202211478.
- [73] X. Gao, H. Wu, W. Li, Y. Tian, Y. Zhang, H. Wu, L. Yang, G. Zou, H. Hou, X. Ji, *Small* **2020**, *16*, 1905842.
- [74] X. Pu, X. Li, L. Wang, H. Maleki Kheimeh Sari, J. Li, Y. Xi, H. Shan, J. Wang, W. Li,
   X. Liu, S. Wang, J. Zhang, Y. Wu, ACS Appl. Mater. Interfaces 2022, 14, 21159–21172.
- [75] Z. Liu, D. Wang, Z. Tang, G. Liang, Q. Yang, H. Li, L. Ma, F. Mo, C. Zhi, *Energy Storage Mater.* 2019, 23, 636–645.

- [76] S. Chen, R. Lan, J. Humphreys, S. Tao, *Energy Storage Mater.* 2020, 28, 205–215.
- [77] J. Long, F. Yang, J. Cuan, J. Wu, Z. Yang, H. Jiang, R. Song, W. Song, J. Mao, Z. Guo, ACS Appl. Mater. Interfaces 2020, 12, 32526–32535.
- [78] Y. Tao, Z. Li, L. Tang, X. Pu, T. Cao, D. Cheng, Q. Xu, H. Liu, Y. Wang, Y. Xia, *Electrochim. Acta* 2020, 331, 135296.
- [79] L. Chen, Z. Yang, H. Qin, X. Zeng, J. Meng, H. Chen, *Electrochim. Acta* 2019, 317, 155–163.
- [80] S. Yang, M. Zhang, X. Wu, X. Wu, F. Zeng, Y. Li, S. Duan, D. Fan, Y. Yang, X. Wu, J. Electroanal. Chem. 2019, 832, 69–74.
- [81] L. Chen, Z. Yang, H. Qin, X. Zeng, J. Meng, J. Power Sources 2019, 425, 162–169.
- [82] M. H. Alfaruqi, S. Islam, D. Y. Putro, V. Mathew, S. Kim, J. Jo, S. Kim, Y.-K. Sun, K. Kim, J. Kim, *Electrochim. Acta* 2018, 276, 1–11.
- [83] H. Pan, Y. Shao, P. Yan, Y. Cheng, K. S. Han, Z. Nie, C. Wang, J. Yang, X. Li, P.
   Bhattacharya, K. T. Mueller, J. Liu, *Nat. Energy* 2016, *1*, 16039.
- [84] C. Xu, B. Li, H. Du, F. Kang, Angew. Chemie Int. Ed. 2012, 51, 933–935.
- [85] H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang,
   Y. Wang, F. Kang, B. Li, C. Zhi, *Energy Environ. Sci.* 2018, *11*, 941–951.
- [86] N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, *Nat. Commun.* **2017**, *8*, 405.
- [87] S. Islam, M. H. Alfaruqi, V. Mathew, J. Song, S. Kim, S. Kim, J. Jo, J. P. Baboo, D. T.
   Pham, D. Y. Putro, Y.-K. Sun, J. Kim, *J. Mater. Chem. A* 2017, *5*, 23299–23309.
- [88] M. H. Alfaruqi, V. Mathew, J. Gim, S. Kim, J. Song, J. P. Baboo, S. H. Choi, J. Kim, *Chem. Mater.* 2015, 27, 3609–3620.
- [89] M. H. Alfaruqi, J. Gim, S. Kim, J. Song, D. T. Pham, J. Jo, Z. Xiu, V. Mathew, J. Kim,

*Electrochem. commun.* **2015**, *60*, 121–125.

- [90] J. Hao, J. Mou, J. Zhang, L. Dong, W. Liu, C. Xu, F. Kang, *Electrochim. Acta* 2018, 259, 170–178.
- [91] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, J. Am. Chem. Soc. 2016, 138, 12894–12901.

#### **Summary and Conclusions**

#### Overview

In this chapter, we shall concisely outline the findings of the current dissertation. We shall provide a concise summary of the outcomes achieved by altering preparative parameters, conducting material characterizations, and evaluating their corresponding electrochemical performance. Moreover, this chapter's conclusion section shall explore the present study's importance in tackling the hurdles associated with energy storage. Although we recognize that the devices developed in this research are at the laboratory scale, we firmly believe that the discoveries made in this study hold substantial significance and shall serve as a valuable point of reference for future inquiries.

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#### 5.1 Summary

This study aimed to enhance the performance of manganese oxide (MnO<sub>2</sub>) for use in ESD, specifically supercapacitors (SCs) and zinc-ion batteries (ZIBs). The synthesis utilized an ionic liquid (IL) precursor and optimization techniques to improve the material's performance. The report presents a summary of the study's main findings and accomplishments. MnO<sub>2</sub> was synthesized using an IL precursor. The distinctive attributes of the IL enabled the production of MnO<sub>2</sub> with improved features suitable for energy storage purposes. The synthesis process was optimized to ensure reproducibility and consistency. Various ILs were studied as precursors to improve the characteristics of MnO<sub>2</sub>. The ideal IL for synthesizing MnO<sub>2</sub> was determined via methodical experimentation and comparative analysis. The optimization process yielded MnO<sub>2</sub> with enhanced electrochemical performance and stability. The impact of heating temperature and duration on MnO<sub>2</sub> synthesis was comprehensively investigated in conjunction with the selection of IL. The researchers fine-tuned the material's properties, such as crystallinity and particle size, by varying these parameters. The optimization process resulted in MnO<sub>2</sub> samples exhibiting enhanced structural and morphological features. The MnO<sub>2</sub> samples were characterized to comprehend their structural and morphological traits. XRD, FESEM, and HRTEM were utilized for crystal structure, particle size, and surface morphology analysis. The characterization findings yielded significant insights into the material's composition and verified the successful synthesis of MnO<sub>2</sub>. The electrochemical properties of MnO<sub>2</sub> were assessed via advanced methods, including CV and GCD measurements. The electrochemical workstation instrument and potentiostat were utilized for precise and dependable electrochemical measurements. The electrochemical analysis provided insight into essential parameters for energy storage applications, including MnO<sub>2</sub>'s capacitance, energy density, cycling stability, and rate capability. A summary table was created to present the performance metrics and significant findings of MnO<sub>2</sub> in its applications for SCs and ZIBs. Table 5.1 presented data on capacitance, energy density, cycling stability, rate capability, and other pertinent parameters. The table is a helpful reference for future research and offers a comprehensive summary of MnO2's energy storage capabilities. An ex-situ study was conducted to investigate the suitability of MnO<sub>2</sub> for ZIBs. The MnO<sub>2</sub> samples were characterized pre- and post-cycling in a ZIB configuration. The ex-situ analysis facilitated a comprehensive investigation of the material's stability, structural modifications, and

electrochemical performance during battery operation. The study yielded insights into the enduring performance and durability of MnO<sub>2</sub> as an electrode material in ZIBs.

 Table 5.1 Provides an overview of the electrochemical properties exhibited by synthesized materials.

S.N.	Sample code	Capacitance (F g <sup>-1</sup> )/ Capacity (mAh g <sup>-1</sup> )	Scan rate/ current density	Electrolyte	Capacity retention	Cyclic stability	
		<u> </u>	Supercapa	ncitor	<u> </u>		
1	MnO <sub>2</sub> - 400@3h	184	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	34.6 @ 100 mV s <sup>-1</sup>	-	
2	MnO <sub>2</sub> - 500@3h	195	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	28.6 @ 100 mV s <sup>-1</sup>	-	
3	MnO <sub>2</sub> - 600@3h	227	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	51.4 @ 100 mV s <sup>-1</sup>	-	
4	MnO <sub>2</sub> - 600@4h	240	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	47.8 @ 100 mV s <sup>-1</sup>	-	
5	MnO <sub>2</sub> - 600@5h	263	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	53.2 @ 100 mV s <sup>-1</sup>	-	
6	ET-M	352	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	59.6 @ 100 mV s <sup>-1</sup>	-	
7	BT-M	177	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	24 @100 mV s <sup>-1</sup>	-	
8	BB-M	159	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	51.8 @100 mV s <sup>-1</sup>	-	
9	AC	317	5 mV s <sup>-1</sup>	1M Na <sub>2</sub> SO <sub>4</sub>	52.3@ 100 mV s <sup>-1</sup>	-	
10	ET-M//AC	80.2	0.1	1M Na <sub>2</sub> SO <sub>4</sub>	61 @ 2 A g <sup>-1</sup>	72% @ 10000 cycle	
Zinc-ion Battery							
11	МО	188.3	100 mA g <sup>-1</sup>	2M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>	33.6 @ 2 A g <sup>-1</sup>	46%	
12	ILMO	316	100 mA g <sup>-1</sup>	2M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>	$33.9 @ 2 A g^{-1}$	74%	
13	ILMO-a	279.3	100 mA g <sup>-1</sup>	2M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>	38.4 @ 2 A g <sup>-1</sup>	-	
14	ILMO-b	211.3	100 mA g <sup>-1</sup>	2M ZnSO <sub>4</sub> + 0.1 M MnSO <sub>4</sub>	44.1 @ 2 A g <sup>-1</sup>	-	

#### **5.2** Conclusions

MnO<sub>2</sub> has the potential for use in ZIBs and SCs. Its favorable electrochemical properties facilitate efficient zinc ion intercalation and deintercalation during charge-discharge cycles. The material exhibits stability and electrochemical reactivity, rendering it a promising contender for future ZIB technology developments.

In summary, the use of IL-assisted synthesis of MnO<sub>2</sub> exhibits considerable potential for energy storage purposes. This study emphasizes the significance of optimizing MnO<sub>2</sub> for improved performance in SCs and ZIBs through the surface area, controlled morphology, crystalline structure, electrochemical reactivity, and stability. The method used to synthesize MnO<sub>2</sub> results in a material with desirable properties such as high SSA, controlled morphology, excellent electrochemical reactivity, and long-term stability. As a result, MnO<sub>2</sub> is a valuable material for energy storage applications. Additional research and development in this area may result in the feasible deployment of ESD based on MnO<sub>2</sub>, promoting sustainable and effective energy storage systems. Here are some conclusion points for this dissertation.

- Our synthesis approach is straightforward; the developed material has optimized phase and conductivity and can be mass-produced for commercial applications.
- Compared to traditional synthesis routes, ionothermal synthesis of materials has the advantages of improved surface area, fast redox kinetics, and tuned surface morphology.
- These materials represent the advantages of good stability, controlled phase and conductivity for improved electrochemical performance for ESD.
- We have reported the Ionothermal synthesis for the development of MnO<sub>2</sub> nanorods.
- In 1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte, the ET-M electrode has delivered an ultrahigh gravimetric capacity of 352 F g<sup>-1</sup> at a 5 mV s<sup>-1</sup>.
- ASC device shows high specific energy 28 Wh kg<sup>-1</sup> and 72% capacity retention up to 10000 cycles.
- ILMO shows a high specific capacity of 316 mAh g<sup>-1</sup> for ZIB and good cyclic retention.
- The SE of Zn||MnO<sub>2</sub> nanorods is higher than that of bare MnO<sub>2</sub> nanowires synthesized by the chemical precipitation method, with a value of 347 Wh Kg<sup>-1</sup> at 0.1 A g<sup>-1</sup>.
- GITT analysis shows diffusion of  $Zn^{2+}$  and  $H^+$  in during discharging the electrode.

This study effectively synthesized and enhanced MnO<sub>2</sub> by utilizing an IL precursor. MnO<sub>2</sub> samples were successfully enhanced for energy storage applications through meticulous synthesis optimization, characterization, and electrochemical investigations. This study's results show the potential of strengthening SCs and ZIBs' performance, stability, and efficiency.

#### 5.3 Outlook

This report examines the potential of IL-assisted metal oxides for energy storage applications. The subsequent sections identify binding domains for future investigation based on current research trends and favorable outcomes. This report primarily discusses IL-assisted synthesis for manganese oxide (MnO<sub>2</sub>), which can also be useful for other metal oxides. Researchers can utilize IL precursors to synthesize metal oxides like NiO, CoO, and Fe<sub>2</sub>O<sub>3</sub>. Investigating the electrochemical characteristics, durability, and efficacy of metal oxides produced using ILs will expand the selection of materials suitable for energy storage. Optimizing the synthesis parameters is essential for maximizing the performance of IL-assisted metal oxides. Research can investigate the use of various ILs, altering their concentrations, ratios, and combinations to improve the properties and performance of ESD.

Furthermore, exploring different synthesis parameters, such as reaction time, temperature, and precursor compositions, can enhance the electrochemical properties and structural properties of the materials. Hybrid and composite materials, formed by incorporating IL-assisted metal oxides with conductive polymers, carbon-based materials, or metal nanoparticles, offer a promising area for further investigation. Investigating hybrid and composite materials can result in synergistic outcomes, better kinetics of charge transfer, increased stability, and greater capacities for energy storage. The performance of mixed materials can be improved by designing and engineering new architectures, such as nanocomposites, core-shell structures, and hierarchical morphologies. Comprehensive characterization techniques are crucial for comprehending metal oxides' structural, morphological, and electrochemical features assisted by ILs. Advanced techniques, including in situ and operando analysis, atomic-resolution electron microscopy, spectroscopic methods, and surface-sensitive techniques, can provide researchers with a more comprehensive understanding of materials' behavior during energy storage. Advanced characterization techniques facilitate a complete understanding of the fundamental mechanisms that govern the electrochemical performance of metal oxides. This report discusses the potential applications of IL-assisted metal oxides beyond SCs and batteries in diverse energy storage systems. Subsequent studies may investigate the incorporation of these substances into alternative energy storage mechanisms such as fuel cells, electrochemical sensors, photovoltaics, and hybrid energy storage devices. Examining these materials' compatibility, performance, and stability across various energy storage systems will reveal novel prospects for their application. Efforts should focus on scaling up the synthesis process

and optimizing production techniques to implement IL-assisted metal oxides in energy storage devices practically. Cost-effective and scalable methods that preserve desired properties and performance are essential for successful commercialization. Collaboration among academia, industry, and policymakers will aid in translating these materials from the lab to large-scale manufacturing and commercialization. Environmental and safety considerations are crucial when dealing with any developing technology. Further research is needed to investigate the environmental impact, recyclability, and safety considerations related to producing, using, and disposing of metal oxides assisted by ILs. The widespread adoption of sustainable and environmentally friendly approaches requires the safe handling and operation of materials.

The utilization of liquid-assisted metal oxides shows potential for enhancing energy storage capabilities. Future research should investigate various metal oxides, optimize synthesis parameters, explore hybrid and composite materials, utilize advanced characterization techniques, integrate into diverse energy storage systems, address scalability and commercialization challenges, and consider environmental and safety aspects. Enhancing our comprehension of these materials can aid in creating dependable and eco-friendly energy storage technologies, facilitating the shift towards a more sustainable future.