Advanced cathodes and electrolytes for rechargeable zinc-ion batteries

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**ADVANCED CATHODES AND ELECTROLYTES FOR
RECHARGEABLE ZINC-ION BATTERIES**

VERMA VIVEK

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

ADVANCED CATHODES AND ELECTROLYTES FOR RECHARGEABLE ZINC-ION BATTERIES

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Prof. Madhavi Srinivasan

Authorship Attribution Statement

This thesis contains material from 5 papers published in the following peer-reviewed journals in which I am listed as first/co-first author.

Chapter 2 is published as two papers:

Verma, V., Kumar, S., Manalastas Jr, W., Satish, R. and Srinivasan, M., 2019. *Progress in rechargeable aqueous zinc - and aluminum - ion battery electrodes: challenges and outlook*. Advanced Sustainable Systems, 3(1), p.1800111. DOI:10.1002/adsu.201800111

The contributions of the co-authors are as follows:

- Prof. Madhavi provided the initial direction to write the manuscript
- Dr. Manalastas and Dr. Sathish guided in revising the manuscript
- I and Kumar gathered the content, curated the data and wrote the first manuscript draft.

Verma, V., Kumar, S., Manalastas Jr, W., & Srinivasan, M. (2021). *Undesired Reactions in Aqueous Rechargeable Zinc Ion Batteries*. ACS Energy Letters, 6, 1773-1785.

The contributions of the co-authors are as follows:

- I wrote the manuscript
- Kumar helped me in editing the manuscript
- Dr. Manalastas helped me in making the conclusion figures and editing the manuscript
- Prof. Madhavi supervised the project.

Chapter 4 is published as Verma, V., Kumar, S., Manalastas Jr, W., Zhao, J., Chua, R., Meng, S., Kidkhunthod, P. and Srinivasan, M., 2019. *Layered VOPO₄ as a cathode material for rechargeable zinc-ion battery: effect of polypyrrole intercalation in the host and water concentration in the electrolyte*. ACS Applied Energy Materials, 2(12), pp.8667-8674. DOI:10.1021/acsaem.9b01632

The contributions of the co-authors are as follows:

- I carried out the synthesis, electrochemical testing, XRD characterization and analysis and wrote the manuscript.
- Prof. Madhavi supervised the project
- Kumar carried out the XPS and XANES analysis
- Dr. Zhao helped me in fabrication of the coin cell and EIS measurements
- Dr. Manalastas helped me in EIS data analysis and editing the manuscript.
- Kumar, Dr. Chua, Meng and Dr. Kidkhunthod helped me in collecting the XANES data.

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The contributions of the co-authors are as follows:

- Prof Madhavi supervised the project
- I did the electrochemical testing, pH studies and XRD analysis
- Kumar synthesized the material, carried out the XANES and XPS, and Raman analysis
- I and Kumar wrote the manuscript.
- Dr. Chua helped in collecting the XANES and Raman spectroscopy data.
- Dr. Hao helped in collecting and analyzing the TEM data.
- Dr. Kidkhunthod, Dr. Sattayaporn and Prof de Groot helped in the analysing the XAS data and editing the XAS section in the manuscript
- Dr. Manalastas and Dr. Rojviriya helped in collecting and analyzing the X-ray tomography data.

Abstract

Increasing energy demands has led to the rise in the harvest of renewable energy sources such as solar and wind energy for grid-scale energy storage. However, the intermittent energy output from these resources demand efficient ways to store the electrical energy. Rechargeable batteries can be a promising technology. However, the widely used Li-ion batteries might not be apt for grid-scale storage application considering the rising cost of Li-based resources and safety concerns. Rechargeable zinc-ion batteries (RZIBs) can be a better alternative to Li-ion batteries. RZIBs use zinc metal as an anode which is 1) inexpensive, recyclable and easier to handle, 2) has a higher volumetric capacity than Li metal and 3) Zn^{2+} is divalent and hence can theoretically transfer twice the charge per ion when compared to Li^+ . However, the present RZIBs show a severe capacity fading during cycling and a limited operational lifetime. A poor operational lifetime will mean frequent replacement of the battery pack which at a large grid-scale level will not be very economical. This suboptimal performance is due to a lack of better cathode materials and the electrolyte formulations. The aim of this thesis is two-fold : First, this thesis explores different classes of cathode materials as a reversible zinc-ion storage host. Phosphate-based intercalation-type cathode materials were tested and in depth zinc-ion intercalation mechanism was elucidated. Furthermore, as an alternative to the intercalation-storage mechanism, reversibly storing zinc-ions via conversion-type mechanism was demonstrated for the first time and the conversion mechanism was elucidated in depth. Second, the electrolyte formulations were found to initiate a lot of undesired reactions which also limits the battery operational lifetime. Hence novel electrolyte formulations were designed to limit the undesired reactions. Using the developed cathodes and electrolyte formulations, full cell RZIB battery performance with high operational lifetimes were demonstrated. The results and the various strategies adopted in designing the cathode materials and the electrolyte formulations should provide necessary guidelines in improving the RZIB performance on a practical scale.

Lay Summary

The imminent need for harvesting renewable energy sources calls for integrating solar and wind energy systems in the electrical grid. However, the energy production and consumption from these systems fluctuates with time. Therefore, efficient ways to store the electrical energy is needed and rechargeable battery technology can be a promising approach. Although, the Li-ion batteries are widely used in portable electronics, this technology is not well suited for large grid-scale energy storage. The portable electronics requirements hinge on high gravimetric energy and power density. On the other hand, since the grid-scale energy batteries are stationary and large scale, the primary considerations are safety, operational lifetime, and material/fabrication/installation cost. Even though Li-ion batteries possess good energy and power densities, we still have safety concerns and rising cost of the raw materials. Rechargeable Zinc-Ion Batteries (RZIBs) can be a promising alternative to the Li-ion batteries. RZIBs use zinc metal as an anode which is inexpensive, easily recyclable and can be handled in ambient air. Furthermore, zinc metal as an anode has a much higher volumetric energy density compared to Li battery anodes, implying that the stationary batteries can be much smaller in size. Finally, zinc metal shows better stability in water which also opens the option to use water instead of organic solvents in the electrolytes. However, the lab-scale developed RZIBs so far show a slow degradation of the cathode and electrolyte materials during the operation which limits the lifetime of the batteries. A smaller lifetime will imply frequent replacement of the grid-scale batteries which can incur a heavy maintenance cost. Hence, the main aim of this thesis is to improve the operational lifetime of the battery by exploring better cathode materials and electrolytes. Different classes of cathode materials were studied including the in-depth mechanism for zinc ion storage and the material degradation during runtime. Furthermore, the degradation of the presently used electrolytes were also studied and novel electrolytes were formulated to mitigate the runtime degradation. Using the newly developed cathode and electrolytes, full RZIBs were fabricated with high operational lifetimes. The cathode and the electrolyte design strategies in this work can be used as guidelines to improve RZIB performance from a practical application standpoint.

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Reproduced with permission from ref.^[29]

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Figure 5.12 SEM images of a), b) separator and c) zinc metal anode after long cycling (>100 cycles) of a Zn-FeVO₄ battery.

Figure 6.1 a) The image of the $\text{ZnCl}_2/\text{EG}=1:3$ electrolyte and $\text{Zn}(\text{OTf})_2/\text{EG}=1:5$ electrolyte, b) DSC test for the two prepared electrolytes, c) and d) the ionic conductivity and the viscosity trends of the two electrolyte systems, e) and f) the voltage window measurement for the two systems which are also compared with the corresponding aqueous electrolytes. The voltage window was determined using the cutoff current density of $1\mu\text{A}/\text{cm}^2$.^[13]

Figure 6.2 Transference number calculation for the two electrolyte systems. The voltage profile after the application of the constant current of 5 mV is recorded along with the impedance spectra before and after the polarization. The EIS spectra are then fitted using a model circuit to obtain the charge-passivation resistance values. The resistance and the current values are then used to calculate the transference number.

Figure 6.3 a), b) and c) Evolution of FTIR spectra on increasing the $\text{Zn}(\text{OTf})_2$ salt concentration in EG. d) schematic of the expected bidentate EG chelation on the zinc-ion center.

Figure 6.4 Evolution of the FTIR spectrum on increasing the ZnCl_2 salt concentration in

EG.

Figure 6.5 a) and b) The Fourier transformed EXAFS spectrum of the electrolyte systems. Schematic of the zinc coordination structure in $\text{Zn}(\text{OTf})_2/\text{EG}$ system in c) dilute and d) saturated salt concentration levels. e) the schematic of the zinc coordination structure in the dilute concentrations of ZnCl_2/EG (molar ratio 1:18).

Figure 6.6 Optical images of aged zinc foils in various electrolytes after three weeks of aging time. The optical images and the corresponding ex-situ XRD patterns are shown. The # marked peaks are from the BZS precipitates of $\text{Zn}(\text{OTf})_2$ but with different interplanar spacing due to the difference in the number of interlayer water molecules.^[44-45]

Figure 6.7 The Zn|Zn stripping/plating test in various electrolytes.

Figure 6.8 The post-mortem coin cell optical images after the Zn|Zn stripping/plating test in various electrolytes.

Figure 6.9 Ex-situ post mortem optical micrograph and SEM for $\text{Zn}(\text{OTf})_2$ in a) EG and b) water and c) their XRD diffraction patterns. Optical micrograph and SEM and for ZnCl_2 in d) EG and e) water and f) their XRD diffraction patterns.

Figure 6.10 Cycling stability of FeVO_4 (left) and InVO_4 (right) in water and EG-based electrolytes.

Figure 6.11 Schematic for the evolution of zinc coordination structure on tuning the zinc salt concentration and the anion coordination strength.

Figure 7.1 Comparison of operational lifetime, energy density and power density of the RZIBs developed in the thesis with literature. Energy density (based on mass of cathode) is plotted in X-axis (log scale) and the operational lifetime in days is plotted on Y-axis (log scale). Each data point is sourced from a study from the Appendix Table A 5. Each data point is color coded for power density as shown in the color palette to the right (log scale). The rough range of energy and power density for Li-ion, Pb-acid and electrochemical capacitors are marked. The two common family of V- based and Mn-based cathode materials

are also zoned to show the rough range of the energy densities and the operational lifetimes. The square-shaped data points are from this thesis work.

Abbreviations

AFM	Atomic Force Microscope
AN	Acetonitrile
BZS	Basic Zinc Salt
CV	Cyclic Voltammetry
DES	Deep Eutectic Solvent
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive X-ray Spectroscopy
EG	Ethylene Glycol
EIS	Electrochemical Impedance Spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
FTIR	Fourier Transform Infrared Spectroscopy
GCD	Galvanostatic Charge Discharge
GITT	Galvanostatic Intermittent Titration Technique
HER	Hydrogen Evolution Reaction
HOMO	Highest Occupied Molecular Orbital
LSV	Linear Sweep Voltammetry
LUMO	Lowest Unoccupied Molecular Orbital
OCV	Open Circuit Voltage
OER	Oxygen Evolution Reaction
PPy	Polypyrrole
RZIB	Rechargeable Zinc Ion Battery
SCE	Standard Calomel Electrode
SEI	Solid Electrolyte Interphase
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope

TFSI	trifluoromethanesulfonylimide
TGA	Thermo Gravimetric Analysis
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
Zn(OTf) ₂	zinc trifluoromethanesulfonate or zinc triflate

Chapter 1

Introduction

This chapter introduces the need for the development of rechargeable batteries for grid-scale energy storage and explains how the rechargeable zinc ion batteries (RZIB) fit in the present scenario. The RZIB technology is also compared with the well-established Lithium ion and Lead acid batteries to highlight the similar and differences in terms of the performance metrics. Furthermore, this chapter also outlines the objective and scope of this thesis work. Finally, this chapter provides a brief overview of the following chapters summarizing the context, the novelty of the work and the significant findings from each of the studies.

1.1 Background and significance

The rise in the economy and the earth's population is also increasing the energy demands. At the same time, the limited fossil fuel resources and a rise in the pollution levels has shifted our attention to renewable energy resources such as solar and wind energy, especially for grid-scale energy storage.^[1-2] However, the unpredictable and intermittent nature of these resources makes a smooth and continuous supply to the industry and household rather difficult. To solve this problem, battery energy storage systems can be one of the promising solutions to regulate the energy demand and the supply.^[3] Since the battery energy storage systems used will be at a large scale in megawatts, factors such as: cost, safety, scalability and sustainability will be the major selection criteria.^[4-5] The widely used rechargeable Li-ion batteries in portable electronics might not be the ideal choice for this application due to limited resources of the Li reserves and safety concerns.^[6]

As the alternatives, batteries using monovalent cations such as Na and K and multivalent cations such as Mg, Al, Ca, Zn have been intensively investigated in the recent years.^[5, 7-9] Among the mentioned metals, Zn metal as an anode has many advantages (Figure 1.1). Firstly, zinc metal is inexpensive and has one of the highest volumetric energy densities. This opens up the possibility of making smaller sized batteries for stationary applications where the size plays an important role compared to the weight. Secondly, among all the metals mentioned above, zinc metal can be handled easily in air and moisture without the spontaneous formation of an oxide layer.^[10] Thirdly, zinc metal has also shown reversible zinc electrodeposition/dissolution in water-based electrolytes, indicating that the rechargeable zinc ion batteries (RZIBs) can be paired with water containing electrolytes and can be assembled in ambient air environment.^[11-12] Finally, the RZIBs can be easily recycled given the fact that: 1) primary alkaline zinc batteries forms one of the main sources for the recycling of zinc and 2) zinc is one of the most profitable metals to recycle and even higher than Al and Fe.^[13]

the RZIB can be easily recycled given the fact that 1) primary alkaline batteries are recycled to some e

zinc metal is one of the most profitable metal to recycle second only to copper. These advantages have the potential to make the RZIBs suitable for grid-scale energy storage applications.

Figure 1.1 Comparison of few monovalent and multivalent metals as a rechargeable battery anode. Reproduced with permission from ref. [14]

For any battery to be used in the grid-scale energy storage, few key criteria are to be considered that are different as compared to portable electronics application. Firstly, since the grid-scale batteries will be at much larger scales, the installation and replacements costs are going to be very high and hence the operational lifetimes of the battery should be very long. Secondly, higher gravimetric energy densities are better, but are not as critical as in the case of portable electronics applications since these batteries will be stationary. Thirdly, the power density of the grid-scale energy storage is better if higher, but the requirements will differ based on the design of the system.

1.2 Problem Statement

Table 1.1 here shows comparison of present RZIBs to two of the commercially used rechargeable battery technologies to understand where do the current RZIB performance actually stands. Compared to Li-ion and lead acid batteries, the RZIBs have advantages in few of the following fields including: 1) high power density due to the high ionic

conductivity of aqueous electrolytes, 2) better safety, 3) low cost. However, there are few other fields which hinders the successful commercialization of this technology. While the Li-ion battery or Pb acid battery can operate for years, the operational lifetimes for RZIBs are very low (less than a month). This poor lifetime is the consequence of severe capacity fading which is more prominent at slow cycling rates. The capacity fading values at slow cycling rates (< 500 mA/g) is in the range of 0.1 - 5 % per cycle, which is at least one order higher (or worse) when compared to Li-ion batteries (0.02-0.04). The maximum number of cycles is also thus limited to 300 cycles or less due to the high capacity fading.

Table 1.1 Comparison of rechargeable zinc ion battery performance metrics with few well established battery technologies

Battery Type	Energy density (Wh/kg)	Power density (W/kg)	Safety	Cost \$/Wh	Capacity fade (%/cycle)	Max cycles	Operational lifetime
Li-ion battery	120-160	200-300	Flammable	300-1000	0.02-0.04	>1000	>1 year
Pb-acid battery	30-40	60-110	Pb is toxic	100-300	~	>1000	> 1year
RZIB	100-400 (cathode), 50-80 (full cell)	1,000-20,000	safer	~65	0.001-0.1 (fast), 0.1-5 (slow)	1,000-20,000 (fast), <300 (slow)	<20 days

Data for Li-ion battery and Lead acid battery taken from refs^[15-18] RZIB cost ref^[19] and the data for other RZIB metrics are from the Appendix Table A. 3 and Table A. 5

The poor RZIB operational lifetimes has been ascribed to high cathode material dissolution currently used in the aqueous electrolytes. Furthermore, many other undesired reactions due to electrolyte-cathode interactions and electrolyte-zinc anode interactions making the cycling process irreversible and further enhances the capacity fading problem. Hence, to improve the operational lifetime, better cathodes materials and electrolytes formulations have to explored.

The problem statement will take in the following form:

This thesis explores fundamental understanding and exploration of cathode host structures along with tuning of zinc electrolyte formulations for a reversible zinc ion storage with improved cycle stability (battery operational lifetime) of RZIB.

1.3 Objective and Scope

To improve the operational lifetime of RZIBs the objectives are twofold. The first one is identify better cathode host structure which allows for reversible zinc-ion storage. Once a suitable cathode material is identified, the next target will be to develop a better electrolyte which should minimize all the known undesired reactions at both the cathode-electrolyte interface and also the zinc metal anode-electrolyte interface.

Developing a better zinc-ion storage host structure can be achieved by the following objectives:

- Exploring the cathode host materials beyond the currently used materials.
- Exploring alternative zinc-ion storage mechanism to the currently studied intercalation-type storage mechanism.
- Studying crystal structure evolution and oxidation state of transition metal centers to elucidate the zinc ion storage mechanism.

Developing a better zinc electrolyte formulation can be achieved by the following objective:

- Identifying the undesired reactions in the currently used electrolytes at the cathode and the anode interfaces.
- Designing a new electrolyte formulation to mitigate these side-reactions
- Studying the molecular level interaction to explain the differences in the electrolyte properties and the extent of the undesired reactions

1.4 Dissertation Overview

The thesis is divided into 7 chapters.

Chapter 1 introduces the background, overview scope and objective of this thesis. Furthermore, it also provides the layout and the brief summary for each of the following chapters.

Chapter 2 sets the context of the RZIB technology by providing the relevant literature. This chapter begins by looking at the working mechanism of the RZIB technology along with understanding the various components. This chapter will also discuss the various cathode materials that have been used in RZIB and various design challenges associated in identifying a new host structure. Furthermore, various shortcoming that stem from the currently used zinc electrolyte formulations are also elaborated.

Chapter 3 discusses the synthesis methods, battery fabrication protocols, characterization techniques and the methods used for the data analysis. The rationale for choosing the methods and analysis is also highlighted.

Chapter 4 focuses on exploring intercalation-type phosphate cathode host structures as an alternative to currently used oxide based intercalation-type structures. Few selected phosphate host structures were investigated as a reversible zinc-ion storage host structure. The synthesis method, material characterization, fabrication of the device including the optimization of the electrolyte to enhance the battery operational lifetime are discussed. Furthermore, the zinc ion storage mechanism is elucidated using various ex-situ characterization techniques.

Chapter 5 explores the conversion-type zinc ion storage mechanism as an alternative to the widely studied intercalation-type mechanism. The chapter starts by investigating binary oxides which have shown conversion reaction with Li ions. The reversible zinc-ion storage behavior were unsatisfactory and therefore, ternary oxides were then explored using the metal vanadate family as an example. The best performing material, FeVO_4 , was chosen for an in-depth zinc-ion storage mechanism study by investigating the phase evolution via various ex-situ characterization studies.

Chapter 6 is based on formulating ethylene-glycol based zinc electrolyte to mitigate the undesired reactions observed in chapters 4 and 5. The physical property of the electrolytes such as viscosity, ionic conductivity, thermal phase stability are discussed. Furthermore, compatibility with the zinc metal anode and the FeVO_4 cathode material are compared with the water-based electrolytes to compare the extent of the undesired reactions. Finally, a full cell using the ethylene-glycol based electrolytes is used to fabricate Zn- FeVO_4 cell and the effect of mitigating the side-reactions on the improvement of battery performance and the operational lifetime is discussed.

Chapter 7 aims at putting the results from the previous chapters into the perspective of RZIB technology in general. The merits and demerits of strategies used in the developing the cathode materials and electrolyte formulations are highlighted. Based on the studies, this chapter will highlight the unresolved challenges both at the practical performance level and the fundamental level for researchers to focus on.

1.5 Findings and Outcomes

This research led to several novel outcomes such as:

1. Application of polypyrrole-intercalated VOPO_4 as a reversible zinc-ion intercalation host structure:
 - Elucidated the zinc ion storage mechanism in a layered type phosphate intercalation material.
 - Established the inverse relationship between the battery kinetics and the capacity retention in electrolytes with high water content.
2. Application of FeVO_4 as a as a reversible zinc-ion conversion host structure
 - Described the conversion based zinc-ion storage mechanism for the first time.
 - Established the similar and differences between the conversion reactions in lithium and zinc chemistry
3. Formulation of ethylene glycol-based electrolyte for RZIBs:
 - Identified the undesired reactions occurring at the electrolyte-electrode interface in water-based electrolytes.

- Elucidated the molecular level salt-solvent interactions in the ethylene glycol based electrolyte.
- Correlated the molecular interactions with the observed reduction in the undesired electrolyte side-reactions in an RZIB.

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Chapter 2

Literature Review

This chapter gives an overview in the field of rechargeable zinc ion batteries. It begins by introducing the basic working principles and the various components involved in making an RZIB. Furthermore, various cathode host structures and the electrolyte formulations used in the literature are discussed. Various zinc storage mechanisms in the host structure and the challenges associated are discussed. Finally, different classes of the electrolyte formulations are also discussed and their merits and demerits are also highlighted.

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- Verma, V., Kumar, S., Manalastas Jr, W., & Srinivasan, M. (2021). *Undesired Reactions in Aqueous Rechargeable Zinc Ion Batteries*. ACS Energy Letters, 6, 1773-1785. Reproduced with permission, Copyright 2021, American Chemical Society

2.1 The construction of Rechargeable Zinc-ion batteries (RZIBs)

The construction of RZIBs is very similar to the conventional Li-ion batteries and has three main components: anode, electrolyte and the cathode (Figure 2.1). The anode in the case of RZIB will be the zinc metal which acts as a reserve of zinc ions in the system. The cathode will be the host structure which will store the zinc ions when the battery is used up or discharged. The cathode material must have a redox center (such as a transition metal) to balance the electronic charge of the system when the zinc ions enter the host structure. Finally the electrolyte, which is a zinc salt dissolved in a solvent, is the medium through which the zinc ions can travel between the cathode and the anode. During the discharging step, the zinc metal will dissolve in the electrolyte as Zn^{2+} ions and the excess electrons are released into the external circuit. At the cathode side, the Zn^{2+} ions from the electrolyte are inserted into the cathode host structure and the electrons from the external circuit are also accommodated to balance the electrical charge. This phenomenon occurs in reverse when the battery is charged.

Figure 2.1 Schematic of a RZIB during the discharge process

2.2 Electrolytes for RZIBs

The electrolytes can be formulated with zinc salts dissolved in organic solvents or water. Some of the zinc salts and the electrolytes used in the RZIB studies are discussed below.

2.2.1 Zinc salts

In the case of electrolytes the most commonly used zinc salts are zinc sulphate and $\text{Zn}(\text{OTf})_2$. Other zinc salts which have also been used are zinc acetate, zinc chloride, zinc nitrate and $\text{Zn}(\text{TFSI})_2$.^[1] While the zinc salt of chlorides and nitrates are corrosive and strongly oxidizing, $\text{Zn}(\text{TFSI})_2$ is very expensive and has very poor solubility in water.^[2-3] ZnSO_4 is inexpensive and can be sufficiently dissolved in water, but cannot be dissolved in organic solvents which cannot separate the ionic Zn^{2+} and SO_4^{2-} units.^[4] On the other hand, triflate anion (OTf^- or CF_3SO_3^-) has only single charge (instead of double charge unlike SO_4^{2-} ion) and hence the salt is not as polar as compared to the zinc sulphate and can be dissolved both in organic and water solvents and hence is the most widely used zinc salt in the RZIB studies.

2.2.2 Organic electrolytes for RZIB

While majority of the RZIB studies have utilized aqueous electrolytes, very few studies use organic solvent based zinc electrolytes. Han et al. have studied the organic solvent based on $\text{Zn}(\text{TFSI})_2$ or $\text{Zn}(\text{OTf})_2$ salt and some of the electrochemical properties are mentioned in the Table 2.1.

Table 2.1 Electrochemical properties of organic solvent based zinc electrolytes

Electrolyte	Ionic conductivity (mS/cm)	Voltage window (V vs Zn^{2+}/Zn)
0.1 M $\text{Zn}(\text{OTf})_2$ in AN	20	3.6
0.1 M $\text{Zn}(\text{TFSI})_2$ in AN	25	3.8
0.1 M $\text{Zn}(\text{TFSI})_2$ in PC	5	3.4

Data in this table is taken from ref^[5]

The organic electrolytes have some advantages over the widely used aqueous electrolytes. First, the electrochemical stability voltage window of these electrolytes are quite high and are higher than ~ 3 V (Figure 2.2a).^[5] Second, organic electrolytes are relatively inert and do not initiate a lot of undesired reactions such as non-uniform zinc electrodeposition and electrolyte decomposition as seen in aqueous electrolytes.^[6-7] We discussed this in more detail in the section 2.4.

Figure 2.2 (a) Anodic stability limit for few organic solvent based zinc electrolytes. Reproduced with permission from ref. [5] (b) Comparison of de-solvation energies of zinc electrolytes in organic or water solvent. Reproduced with permission from ref.[8]

However, these electrolytes are not well suited for RZIB for grid-scale applications due to a lot of disadvantages. First, these solvents tend to be very flammable and defeats the safety aspect of the RZIBs. Second, the kinetics in these electrolytes tend to be sluggish when compared to the aqueous electrolytes: meaning the RZIB performance at high current rates are very poor.^[9-10] This is due to the poor ionic conductivities compared to aqueous electrolytes ($\sim 40\text{-}60\text{ mS/cm}$). Furthermore, while the zinc salts are highly ionic due to the high charge-to-size ratio of the zinc cations, the organic solvents are not very polar when compared to water. Hence, the zinc cation-anion pairs still exist in the electrolyte which have to be broken when intercalating inside the cathode host structures (Figure 2.2b).^[3, 11] The energies needed for this desolvation is much higher in organic solvents. However, addition of water to the dry organic electrolytes can create a wet cathode-electrolyte interface and can lower the desolvation energy penalties.^[12]

2.2.3 Aqueous electrolytes for RZIB

When water is used as the electrolyte solvent, the voltage window becomes much more limited due to the oxidation and the reduction reactions of the water and is also a function of pH of the aqueous electrolyte. This can be estimated using the Pourbaix diagram (Figure 2.3). Pourbaix diagram for any material is the phase stability diagram at various potential and pH values which are derived thermodynamically using the Nernst equation. The Pourbaix diagram for water shows that water is only stable in a small voltage window of 1.23 V. At more positive voltages, the water oxidizes to oxygen gas and at lower voltage

values, water reduces to hydrogen gas. The voltage window of 1.23 V remains constant as a function of pH and only the absolute position of the window shifts.

Figure 2.3 Pourbaix diagram showing the electrochemical stability window for water. Reproduced with permission from ref.[13]

Aqueous electrolytes have many advantages over the conventionally used organic solvent based electrolytes. Firstly, the manufacturing cost are much lowered not only because of the solvent cost, but it also adds an advantage of the battery fabrication in the ambient environment and eliminating the stringent drying protocols used in Li-ion batteries.^[14] Secondly, the aqueous electrolytes when compared to the flammable organic solvents are much safer and reduces the risk of hazards especially at the grid-scale level. Thirdly, the ionic conductivities of the aqueous electrolytes (10-60 mS/cm)^[15] are at least an order higher compared to the organic electrolytes (1-10 mS/cm),^[15] hence the rate performance of the battery can be much better. Because of all these advantages most of the RZIB studies have employed the use of aqueous electrolytes. Some of the aqueous electrolytes used in RZIB are listed in the Table 2.2

Table 2.2 Electrochemical properties of few aqueous zinc electrolytes

Zinc salt	electrolyte concentration	Ionic conductivity (mS/cm)	Voltage window (V)	pH	Ref
ZnSO ₄	3 M	~40	2.3	4.2	[15]
Zn(NO ₃) ₂	1 M	-	1.5	-	[16]
Zn(ClO ₄) ₂	1 m	7	2.4	4.9	[17]
ZnCl ₂	30 m	29	2.3	5.7	[18]
Zn(OTf) ₂	1 M	60	2.4	4.5	[15]
Zn(TFSI) ₂	1 M	-	-	-	[19]

2.3 Cathode Materials for RZIB

Majority of the cathode active materials investigated are manganese-based oxides and vanadium-based oxides. Apart from these two broad classes of materials, few other type of materials such as Prussian blue analog, sulphide and organic materials have also been explored.

2.3.1 Manganese-based oxides

These materials are attractive candidates as they are low cost, environmentally benign, and abundant. Manganese oxide can occur in various polymorphs wherein the basic MnO₆ units can connect in various ways to give a variety of layer and tunnel type structures (Figure 2.4).

α -MnO₂: This polymorph is the most widely studied RZIB cathode host structure due to its large tunnels size of 4.6 Å. The cathode can deliver a capacity of more than 200 mAh/g at ~1.3 V. However, there are many challenges associated such as rapid capacity fading and unclear zinc ion storage mechanism. Some of the proposed zinc ion storage mechanisms are discussed below.

Figure 2.4 MnO_2 polymorphs. The octahedra represent MnO_6 octahedra with spin-up (purple) and spin-down (brown) configurations. The birnessite and buserite structures. MnO_6 octahedra: brown polyhedra and water molecules: white spheres, respectively. Reproduced with permission.^[14]

zinc ion insertion/extraction mechanism: This is the most widely reported mechanism.^[20] Here, zinc-ions insert into the α - MnO_2 structure which is followed by a reversible phase transformation of α - MnO_2 to layered birnessite, buserite or spinel ZnMn_2O_4 structure.^[21-23]

Lee et al. have shown that Zn^{2+} intercalate into the α - MnO_2 host structure and the oxidation state of Mn will reduce to +3 state (Figure 2.5a).^[21] This +3 state will undergo a disproportionation reaction to form +4 and +2 states. +2 state will dissolve and hence some of the MnO_6 units will disappear turning the structure to a layered birnessite. In the charging process, the structural transformation occurs in the reverse order. A similar mechanism is also shown by Alfuruqi et al, with one difference being that the new phase formed after discharge is the spinel ZnMn_2O_4 phase.^[22] Furthermore, this mechanism is also reported in β - MnO_2 and γ - MnO_2 by few studies.^[24-25]

Proton and zinc-ion co insertion mechanism: Sun et al. reported this mechanism.^[26] They showed that discharge process occurs at two distinct plateaus in GCD curve indicating insertion of two different kind of ions (Figure 2.5b). From GCD and GITT (Figure 2.5b,c), Region I had a smaller overpotential and hence was ascribed to small sized proton insertion, whereas the region II had a large overpotential and hence was ascribed to the high charge-density zinc-ions. Furthermore, when only using MnSO_4 without ZnSO_4 salt in the

electrolyte, only one voltage plateau similar to the region I was observed (Figure 2.5c). Hence, region II plateau never appears due to the absence of zinc ions in the electrolyte. Additionally, Sun et al also showed that proton insertion also contributes to the capacity by showing that the poor capacities observed in a dry organic electrolyte improves when adding water in the electrolyte.^[26]

Figure 2.5 (a) Transformation of cryptomelane (α -MnO₂) into Zn–birnessite via Mn²⁺ dissolution. White spheres: K⁺, red spheres: water molecules. Reproduced with permission.^[21] (b), GCD profile of Zn-MnO₂ system showing two different regions. (c) GITT profiles where each discharge pulse was applied for 120 s at 50 mA/g with 4 h rest. (d) Discharge curve for MnO₂ cathode in 0.2 M MnSO₄ solution with or without ZnSO₄ in the electrolyte. Reproduced with permission.^[26]

Figure 2.6 Proton induction α - MnO_2 conversion. (a) TEM image of α - MnO_2 nanorod electrodes in the discharged state. b) STEM-HAADF image showing the elemental distribution in the α - MnO_2 nanorods after the first discharge shows that Zn is present in the adjacent flakes but not inside the nanorods. Reproduced with permission.^[27]

Proton induced host structure conversion: In this proposed mechanism, the protons react with the MnO_2 host structure and zinc ions never react with the MnO_2 structure.^[27] The protons reaction with MnO_2 forms MnOOH and the lost protons will lead to an increase in the pH which will cause the zinc salts in the electrolyte to precipitate locally as Basic Zinc Salt (BZS) $\text{ZnSO}_4[\text{Zn}(\text{OH})_2]_3 \cdot x\text{H}_2\text{O}$ (Figure 2.6) around the MnO_2 nanorods. The BZS precipitation is discussed in detail later in the sections 2.4.2 and 2.4.7. To further confirm that the zinc ions are not stored into the MnO_2 material, STEM-EDS was taken. The zinc species was detected only in the BZS flake and not in the MnO_2 material itself. Even in this study the cathode capacities are very limited in dry organic electrolyte, but improves on the addition of water in the electrolyte indicating that the main ion driving the reaction is not zinc but protons.

Dissolution/Deposition mechanism: In the mechanism, during discharging step, the Mn from the host structure will dissolve into the electrolyte and the BZS of the zinc salt from the electrolyte will precipitate onto the cathode surface (Figure 2.7).^[28] Guo et al. showed that during the first discharge step the cathode host structure reacts with the water molecules and Mn^{2+} ions will dissolve. The simultaneously released OH^- ions will react with the zinc salts and thus the BZS will precipitate. Upon charging, the BZS will react

with the dissolved Mn^{2+} to form birnessite MnO_2 . From the second cycle onwards, the same process will be observed in the birnessite host structure.

Figure 2.7 Dissolution/deposition mechanism in $\alpha\text{-MnO}_2$ as proposed by Guo et al.^[28]

Hence, to this date, the zinc ion storage mechanism remains controversial.

$\beta\text{-MnO}_2$: There are two proposed mechanisms. Islam et al. have shown that in the initial stages the zinc ions intercalate in the $\beta\text{-MnO}_2$ structure which slowly transforms to the spinel ZnMn_2O_4 structure and the formation of the BZS is also observed.^[24] In the later cycles the zinc ion insertion takes place in the spinel- ZnMn_2O_4 structure.

Zhang et al. proposed that the beta structure converts to a layered busenite structure in the initial cycle.^[29] In the later cycles, the zinc ion insertion occurs into the zinc busenite structure. This is reflected in the very different CV and GCD profiles in the first and the later cycles (Figure 2.8a,b). Ex-situ XRD pattern also shows that the host structure phase transforms after the first cycle (Figure 2.8c).

$\gamma\text{-MnO}_2$: Alfuruqi et al. have shown that the initial discharge process, the structure will partially transform to spinel ZnMn_2O_4 phase (Figure 2.9).^[25] On further discharging, a new zinc intercalated tunnel type $\gamma\text{-Zn}_x\text{MnO}_2$ phase will gradually form. In much later stage, the zinc inserted $\gamma\text{-MnO}_2$ phase will transform to a layered zinc inserted MnO_2 structure

Zn_yMnO_2 . All the newly formed phases will revert back to the original $\gamma\text{-MnO}_2$ during the charging step.

Figure 2.8 The zinc ion storage mechanism in $\beta\text{-MnO}_2$ as proposed by Zhang et al. Reproduced with permission from ref.^[29]

Todorokite- MnO_2 : This material has a largest one dimensional tunnel structure of all the polymorphs. However, the zinc ion storage capacity observed is very less ($\sim 100 \text{ mAh/g}$).^[30] This is ascribed to the fact that many metal cations such as Na, K, Cu ions and also water molecules are pre-occupying the tunnels of this framework to support the structure.

Spinel-Type ZnMn_2O_4 : Knight et al. have previously shown that the ZnMn_2O_4 spinel structure is not the best host structure as the zinc diffusion in the host structure is very sluggish due to the high electrostatic interaction between the zinc ions and the host structure, due to the close proximity of 16c sites and the MnO_6 octahedra (Figure 2.10).^[31]

Figure 2.9 The zinc ion storage mechanism in γ - MnO_2 as proposed by Alfuruqi et al. Reproduced with permission from ref.^[25]

Hence Zhang et al. created some Mn vacancy deficiency in the cathode host structure $\text{ZnMn}_{1.86}\text{Y}_{0.14}\text{O}_4$ /carbon composite, where Y denotes the vacancies.^[16] This makes the electrostatic repulsion much lesser when the zinc ions are diffusing inside the host structure and gets stored in the 8a tetrahedral sites. The RZIB can deliver a capacity of 150 mAh/g at 50 mA/g current density for a duration of 500 cycles. Some of the reported Manganese-based oxide cathode RZIB performance are shown in Table 2.3.

Figure 2.10 Schematic showing the movement of zinc ions inside a spinel ZnMn_2O_4 structure. The zinc ions must occupy 8a tetrahedral sites by diffusing through the 16c octahedral sites. The purple octahedra represents the MnO_6 octahedra.

Table 2.3 RZIB performance of few manganese-based oxides

Cathode	Current rate	Voltage V vs Zn^{2+}/Zn	Capacity (mAh/g)	Retention (% at cycles)	Ref
α - MnO_2	6C	1.5	210	~100% at 100	[20]
α - MnO_2	10 mA/g	1.5	205	62% at 30	[21]
α - MnO_2	1540 mA/g	1.4	285	92% at 5000	[27]
β - MnO_2	200 mA/g	1.4	180	75% at 200	[24]
β - MnO_2	2000 mA/g	1.4	150	94% at 2000	[29]
γ - MnO_2	50 mA/cm ²	1.5	200	63% at 40	[25]
δ - MnO_2	83 mA/g	1.5	170	91.8% at 100	[32]
$\text{ZnMn}_{1.86}\text{Y}_{0.14}\text{O}_4/\text{C}$	500 mA/g	1.4	150	94% at 500	[16]

2.3.2 Vanadium-based oxides

Vanadium transition metal can exist in multiple oxidation states.^[33] Furthermore, the vanadium oxygen polyhedra is very flexible which gives rise to a wide variety of crystal structures.^[34] The most widely studied class of materials in this family are bilayered vanadium oxides, metal intercalated layered vanadium oxides and NASICON structures.

Bilayered vanadium pentoxide: Xero- V_2O_5 has a distorted polyhedra and exists in the form of a bilayered structure.^[33] These layers can further expand when water molecules insert between the bilayers to form $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (Figure 2.11a).^[35] These intercalated water molecules provide the electrostatic shielding to the intercalating zinc ions which can

improve the solid state zinc ion diffusion.^[36-37] Yan et al. showed that if the intercalated water molecules are removed by heating the sample, the cycling performance is very poor (Figure 2.11b).^[38]

Figure 2.11 (a) Crystal structure of $V_2O_5 \cdot nH_2O$, the blue spheres indicate water molecules. (b) The cycling stability of V_2O_5 with (VOG) and without structural water (VOG-350). Reproduced with permission from ref.^[38] (c) The zinc ion insertion mechanism in $Zn_{0.25}V_2O_5 \cdot nH_2O$ as proposed by Kundu et al.^[39]

Kundu et al. have studied a cathode material: $Zn_{0.25}V_2O_5 \cdot nH_2O$.^[39] The crystal structure of this material is similar to xero- V_2O_5 , with only one difference being that ZnO_6 octahedra also exist along with the water molecules in the interlayer (Figure 2.11c). However, the zinc ion insertion mechanism is still ambiguous today for a hydrated layered xero- V_2O_5 material. Some studies have shown that during the zinc ion insertion, the interlayer spacing of the host structure decreases,^[10, 40-43] other reports have shown that it can increase.^[38, 44-46]

Kundu et al. and other similar studies have shown that the interlayer spacing in the host structure will reduce because the pre-intercalated water molecules are expelled out during the zinc ion insertion and an increased electrostatic attraction between the layers (Figure 2.11c).^[10, 40-43] On the other hand, few other studies have shown that the zinc ion insertion

occurs together with the water molecules from the solvent and hence the spacing will increase.^[38, 44-46]

Metal vanadates: Vanadium polyhedra can arrange in many other ways. For instance, crystal lattice framework of VO_4^{3-} (orthovanadates), $\text{V}_2\text{O}_7^{4-}$ (pyrovanadates) or $[\text{V}_3\text{O}_8]_n^{n-}$ are possible.^[47] These crystal structure frameworks are then charge balanced with cations and/or water molecules which can give rise to a variety of crystal structures of the general formula $\text{M}_x\text{V}_y\text{O}_z.n\text{H}_2\text{O}$ usually in a layered or tunnel structure form. Some of the cathode materials are listed in the table. The zinc ion storage mechanism is ambiguous in this class of cathode materials and some of the reported charge storage mechanisms are discussed below.

Layered metal-ion (Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+}) intercalated V_2O_5 material have been actively studied since the pre-intercalated metal ions can increase the interlayer spacing between the vanadium-oxygen layers and hence reduce the electrostatic interaction of the host structure with the zinc ions. $\text{Ca}_{0.25}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ (CVO) is similar to xero- V_2O_5 structure with extra CaO_7 polyhedra in the interlayer acting as ‘pillars’ (Figure 2.12a).^[41] The interlayer spacing further increases when this material comes in contact with water and the interlayer spacing can increase further by 3.5 Å. From the charge-discharge storage perspective, the interlayers contract during the zinc ion insertion similar to the case for $\text{Zn}_{0.25}\text{V}_2\text{O}_5.n\text{H}_2\text{O}$ reported by Kundu et al.^[41]

LiV_3O_8 has a layered V-O framework, and Li^+ ions are present in the interlayer. Alfaruqi et al. showed that in the initial discharging step, the zinc ion inserts in the host structure via a solid solution route (Figure 2.12b).^[48] In the intermediate stages, a two-phase reaction occurs and the two phases stoichiometric ZnLiV_3O_8 phase and the previously formed solid-solution phases occur in equilibrium. In the final stage, the zinc-ions insert in the $\text{Zn}_x\text{LiV}_3\text{O}_8$ phase ($x>1$) phase via a solid-solution mechanism.

The zinc ion storage mechanism in $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (NVO) has been elucidated by He et al. Instead of any solid-solution phenomena, a new phase $\text{Zn}_x\text{Na}_{0.33}\text{V}_2\text{O}_5$ phase appears with $0<x<0.96$ along with the original NVO phase (Figure 2.12c).^[49]

Figure 2.12 (a) Comparison of crystal structures of $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (left) and $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (CVO) (right).^[41] (b) zinc ion storage mechanism in LiV_3O_8 . Reproduced with permission from ref.^[48] (c) zinc ion storage mechanism in $\text{Na}_{0.33}\text{V}_2\text{O}_5$. Reproduced with permission from ref.^[49]

Wan et al. have shown a proton and zinc co-intercalation mechanism in the $\text{NaV}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$.^[50] They show that protons and zinc ions simultaneously get stored in the cathode during the cycling process (Figure 2.13). The XRD results show that the BZS of the ZnSO_4 (or $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$) salt is also formed reversibly during the discharge/charge step. The BZS is formed from the zinc cation, sulphate anion and the OH^- ions from the water molecule and the protons from the water molecule insert in the host

structure as evident from the NMR studies. Furthermore, the XPS studies also showed that the zinc ions are also simultaneously inserted in the host structure. The three type of Zn^{2+} peaks correspond to the intercalated zinc ions in the host, two zinc environments in the $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$ phase corresponding to the $\text{Zn}(\text{OH})_2$ and ZnSO_4 environments.

Figure 2.13 Proton and zinc charge storage mechanism in $\text{NaV}_3\text{O}_{8.1.5}\text{H}_2\text{O}$. (a) charge-discharge process (b) ex-situ cathode material XRD (c) ex-situ proton NMR and (d) ex-situ Zn 2p XPS. Reproduced with permission from ref. [50]

Vanadium-based NASICON structure: The NASICON framework consists of VO_6 and PO_4 polyhedra connected to get a general formula of $\text{A}_x\text{V}_2(\text{PO}_4)_3$ where A is a mono/divalent cation (Figure 2.14a). Compared to the oxides, the phosphate group can enhance the battery voltage from the average values of 0.6-0.7 V in vanadium based oxides to ~ 1.1 V in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. [51] The mechanism was proposed wherein during the first discharge step, $2/3$ of the Na ions are electrochemically removed and the phase will convert to $\text{NaV}_2(\text{PO}_4)_3$. Thereafter, only Zn^{2+} ions will reversibly insert into the host structure. The electrochemical performance of few vanadium-based RZIB cathode materials are shown in Table 2.4.

Table 2.4 RZIB cathode performance of few vanadium-based materials.

Cathode	Current rate	Voltage V vs Zn ²⁺ /Zn	Capacity (mAh/g)	Retention (%) at cycles)	Ref
V ₂ O ₅ .nH ₂ O	6000 mA/g	0.5	230	91.3% at 900	[38]
Zn _{0.25} V ₂ O ₅ .nH ₂ O	2400 mA/g	0.7	230	92% at 1000	[39]
anhydrous V ₂ O ₅	5000 mA/g	0.6	400	91% at 4000	[46]
Na _{0.33} V ₂ O ₅	1000 mA/g	0.6	220	72% at 1000	[49]
Na ₂ V ₆ O ₁₆ .3H ₂ O	40 C	0.7	150	80% at 1000	[52]
Ca _{0.25} V ₂ O ₅ .nH ₂ O	23 A/g	0.7	70	96% at 3000	[41]
VO ₂	10 A/g	0.7	120	79% at 10000	[53]
Na ₃ V ₂ (PO ₄) ₃	50 mA/g	1.1	97	74% at 100	[51]

2.3.3 Other cathode materials

Prussian Blue Analogs: These materials are metal organic framework of the form A_xMM'(CN)₆.yH₂O where A= metal cation or water molecule and both M and M' are transition metals (Figure 2.14b). Zhang et al. have investigated a rhombohedral Zn₃[Fe(CN)₆]₂ as a RZIB cathode material.^[54-55]

The crystallographic orientation was found to govern the RZIB performance. The cathode material was synthesized with different crystallographic facets and hence the morphologies were also different (Figure 2.14c). The cycling behavior was very different for different morphologies and the performance varied in the following order: cubo-octahedron > truncated octahedron > octahedron (Figure 2.14d). This was ascribed to the exposure of 100-type of planes which increased the access of the zinc ions to the diffusion channels easy. On the other hand, the octahedron has only 111-type planes exposed which have less atomic planar density and hence are more prone to dissolve in the electrolyte. These family of materials are not so attractive as the capacities are very poor (~60 mAh/g).

Figure 2.14 (a) Crystal structure of NASICON $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, orange polyhedra: VO_6 , magenta polyhedra: PO_4 green spheres: Na ions. (b) Crystal structure of a typical hexacyanoferrate structure where the A site can be occupied by cations or water molecules. Reproduced with permission from ref.^[56] (c) and (d) Cycling performance of $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ with different crystal facets exposed. Reproduced with permission from ref.^[54-55]

Few other type of cathode materials are also investigated which are summarized in the Table 2.5. Beyond transition metal oxides, transition metal chalcogenides have shown much improved zinc ion mobility in the host structures such as Mo_6S_8 .^[57] This can be ascribed to the fact that the sulfide host structures are more covalent (or less ionic) and hence the electron cloud is well delocalized and hence the electronic charge can be redistributed during the discharging step when the zinc ions are inserted. For these reasons, a high cathode capacity of 600 mAh/g can be achieved. However, a much covalent framework will also reduce the zinc intercalation potential and the voltage observed was only ~ 0.34 V.

Figure 2.15 Zinc ion storage mechanism in calix(4)quinone. Reproduced with permission from ref.^[58]

Organic cathode materials such as Calix(4)quinone has also been investigated (Figure 2.15).^[58] This is an organic molecule with open bowl structure and eight C=O functional groups. These functional groups can store the zinc ions by the "ion-coordination mechanism" where the zinc cations coordinate to the O atoms of the carbonyl groups and the carbonyl groups are also simultaneously reduced. This material has been shown to bind to up to three zinc cations as shown in the Figure 2.15. One drawback of these organic materials is the very poor electronic conductivity and hence a lot of carbon additives have to be added to make the cathode electrode. Some of the cathode materials and their RZIB performance is shown in Table 2.5

Table 2.5 RZIB performance of few other type of cathode materials.

Cathode	Current rate	Voltage V vs Zn^{2+}/Zn	Capacity (mAh/g)	Retention (%) at cycles)	Ref
$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	300 mA/g	1.7	52.5	81% at 100	[55]
CuFeCN_6	60 mA/g	1.73	52.5	97% at 100	[59]
VS_2	50 mA/g	0.65	193	98% at 200	[60]
Mo_6S_8	600 mA/g	0.35	85	90% at 350	[57]
Calix(4)quinone	500 mA/g	1	150	87% at 1000	[58]
Tetrachloro-1,4-benzoquinone	43 mA/g	1.1	200	65% at 30	[61]

2.4 Challenges in the RZIB

Although aqueous electrolytes are advantageous to the RZIB system, they also bring in a lot of demerits. Aqueous electrolytes are also responsible for a lot of undesired reactions with the zinc metal anode and the cathode electrodes active not only during the battery operation, but some of them are active even when the battery is not in use.^[62] Because of these undesired reactions, the operational lifetimes of the RZIBs are much shorter. Furthermore, the choice of the cathode materials for RZIB are also mostly limited to very few classes of materials. Even within these classes of materials the zinc ion storage mechanisms are not very reversible or ambiguous. We will discuss some of these limitations stemming from the cathode material and the electrolyte perspective.

2.4.1 Simultaneous zinc metal corrosion and hydrogen evolution reaction (HER)

Generally, the zinc aqueous electrolytes are mildly acidic in nature and pH for the electrolytes used are in the range of ~3-7.^[15] The acidic nature can be explained by the strong polarizing nature of the divalent nature of the Zn^{2+} ions. The zinc ion center in the hydrated $\text{Zn}[(\text{H}_2\text{O})_6]^{2+}$ complex can act as Lewis acid and hydrolyze the coordination water molecules to produce free protons which will make the electrolytes acidic in general.^[63-64]

Figure 2.16 a) Pourbaix diagram of zinc in water, taken from ref.^[62] The shaded regions represent the potential of the zinc metal when in contact with water without any potential bias applied (A) and during the zinc electrodeposition process in RZIB (B). b) and c) zinc foil before and after being aged in 1 M zinc sulphate solution d) and e) SEM image of the zinc foils before and after the aging experiment. Reproduced with permission.^[62]

How stable will the zinc metal be when in contact with these mildly acidic electrolytes can be predicted using a Pourbaix diagram.^[65] This is a potential-pH diagram which determines the thermodynamically stable state of the zinc metal/ion in water using Nernst equation (Figure 2.16a). When the RZIB is not in use, then there is no external potential bias to the zinc metal. In this scenario, when the zinc metal is in contact with the electrolyte, the system will lie somewhere in the region A. In this condition, the zinc metal is in a favorable state to oxidize/dissolve into the electrolyte as Zn^{2+} ions and the protons from the water to reduce to hydrogen gas as Hydrogen evolution reaction (HER). Because of these two reactions, the zinc metal will corrode.^[66] This process is experimentally verified by Hao et al.^[67] by soaking zinc metal in zinc sulphate solution as shown in the Figure 2.16 b,c.

Notably, when the RZIB is in use and the battery is charged (or the zinc ions are being electrodeposited on the zinc metal anode) the potential of the zinc metal anode is in the region B,^[62] (Figure 2.16a) where the HER and the zinc metal corrosion will be even more prominent. The HER process can cause increased pressure due to the gas build up in a sealed battery which can lead to the battery swelling or even a rupture.^[68]

2.4.2 Basic Zinc Salt (BZS) precipitation at the zinc metal anode

During the HER process, the protons in the vicinity of the zinc metal anode are lost as hydrogen gas and hence the local pH will rise.^[67] This triggers the zinc salts in the electrolytes to precipitate out as basic zinc salts (BZS).^[67, 69] For instance, a zinc sulphate based BZS was observed when zinc metal was immersed in these aqueous zinc sulphate electrolyte as shown in Figure 2.16 d,e.^[67, 69]

BZSs are derivatives of layered double hydroxides (eg. $\text{Mg}(\text{OH})_2$)^[70] where the cations are zinc and the zinc polyhedra forms layered sheets with extra zinc salt anions and water molecules in the interlayer spacing with the general formula: $[\text{Zn}_x(\text{OH})_y(\text{A}^{n-}_{(2x-y)/n})]_m \cdot m \text{H}_2\text{O}$ ^[71]. BZSs are found to precipitate in all RZIB system regardless of the zinc salt (or the zinc salt anion used) – sulphate, nitrate, acetate, perchlorate, triflate.^[62] Some of the BZS are shown in the Figure 2.17. Notably, the crystal structures of the BZS with larger salt anions such as acetate and triflate are still not solved yet.^[72-74]

Figure 2.17 Crystal structures of (a) brucite, $\text{Mg}(\text{OH})_2$, and basic zinc salts (b) $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, (c) $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, and (d) $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, where gray polyhedra indicate ZnO_4 or ZnO_6 , yellow tetrahedra SO_4 , and blue NO_3 units, are orange sphere are O, white spheres H_2O , and green spheres Cl. Reproduced with permission from ref.^[62]

The BZS precipitation can trigger various problems in RZIB. First, the BZS crystal structure often contains crystal water.^[73] This implies that the water solvent will eventually be used up and given that the zinc salt solubility is limited,^[1, 75] the zinc salts will crystallize out causing the battery to dry out and ultimately leading to cell failure.^[76] Secondly, the BZS are layered structures and hence they precipitate out in the form of loose sheets and not uniform SEI layer.^[72-73] Therefore, even after the BZS is formed, the electrolyte and the zinc metal will still be in contact and therefore, the HER, zinc corrosion and the BZS precipitation process will occur continuously.^[67, 69]

2.4.3 Non-uniform zinc deposition and zinc dendrites

Compared to organic electrolytes, aqueous electrolytes show a higher ionic conductivities which can be detrimental at the zinc metal anode.^[62] The zinc deposition process at the zinc metal anode starts by the nucleation step during which zinc clusters are formed at the zinc metal surface.^[77] The cluster formation process is governed by the excess energy applied beyond the thermodynamic potential for zinc deposition process in the form of overpotential.^[78] The minimum stable size for the cluster to form is determined by $r_{\text{crit}} = (2\gamma V_m)/(F\eta_n)$ where γ is the zinc-electrolyte interface energy, V_m is the molar volume of zinc, η_n is the nucleation overpotential.^[78] A smaller r_{crit} is desirable for the zinc deposition to be more uniform, while a large r_{crit} implies that the zinc deposition will be with very few

clusters and hence the deposition will be very non-uniform. Notably, from the equation increasing the overpotential is one way to make the zinc deposition more uniform as has been experimentally demonstrated by Yang et al.^[69] by using Deep Eutectic Solvent electrolytes as shown in Figure 2.18a,b.

Figure 2.18 Zinc deposition uniformity when the zinc deposition overpotential is increased from (a) 1 M $\text{Zn}(\text{ClO}_4)_2$ aqueous electrolyte (low) to (b) $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ /succinonitrile (1:8) electrolyte (high). Reproduced with permission.^[69] (c) Evolution of zinc metal anode surface with an applied zinc plating overpotential of 200 mV. Reprinted with permission.^[79] (d) AFM images of zinc nucleation and growth process in 1 M ZnSO_4 electrolyte. Reprinted with permission.^[77] Effect of changing the current rate density from (e) 20 mA to (f) 2 mA on the zinc deposition uniformity. Reprinted with permission.^[15]

The growth step follows the nucleation step where the zinc atoms are deposited onto the existing zinc clusters and as a result the cluster size will grow.^[78] Because it is more favorable for zinc atoms to deposit on the existing clusters than onto depositing on a flat zinc surface,^[80] a faster growth phenomena can cause the zinc deposition to be highly non-uniform and can even cause dendrites to appear as shown in the Figure 2.18c,d.

Notably, the current rate can also affect the uniformity of the zinc deposition process. Glatz et al.^[15] have shown that the zinc deposition is uniform at faster current densities, but is very non-uniform at slower current rates (Figure 2.18e,f). At fast current rates, the kinetics of the aqueous electrolytes starts to reach the limiting case and the zinc ion transfer is hampered. As a result, the overpotentials needed for the zinc ion supply will also be higher according to Butler-Volmer equation.^[78] Hence, a higher overpotential will reduce the r_{crit} making the zinc deposition more uniform. At the same time, the dendrite tips cannot also grow due to sluggish zinc ion kinetics again making the deposition more uniform. However, at slow current densities the zinc ion transfer kinetics will occur as expected and the zinc deposition process will be non-uniform causing dendrites to appear.

2.4.4 Oxygen Evolution Reaction (OER)

During the charging step as the voltage of the cathode is pushed to positive values, the water in the electrolyte can reach the borderline conditions for the water oxidation reaction: $6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$; $E = 1.23 \text{ V vs SHE}$.^[81] Since many of the cathode materials are V or Mn based oxides, which can catalyze the OER process, the OER process can occur at an accelerated rate.^[82-84] The OER process will lead to the evolution of the oxygen gas and can lead to cell rupture^[85] or even drying out of the water solvent from the electrolyte.^[76]

2.4.5 Limited zinc-ion solid state diffusion inside the cathode host

The high charge-to-size ratio of zinc cations can have a high electrostatic interaction with the host structure and hence can limit the diffusivity of the zinc cations.^[86] As a result of which the transfer of zinc ions from a liquid electrolyte (which provides high mobility to the zinc ions) will be hindered as soon as the zinc ions reach at the electrolyte-electrode interface. This explains why many of the studies have claimed that the zinc ions are rather stored on the cathode surface in the form of BZS precipitate rather than inside the bulk.^[74]

Or in other words, the cathode performance tend to be pseudocapacitive in nature rather than bulk ion storage.^[46, 53, 87-88] This also explains why the RZIBs can show a very high rate performance wherein the rate performance are much better than the best rate performances of Li-ion batteries as shown in the Table 1.1. However, at slow cycling rates or at longer operating time durations, another problem arises as discussed below.

2.4.6 Cathode Material Dissolution

The transition metals such as Mn and V from the cathode materials are susceptible to dissolve in the aqueous electrolytes. This is evident when we look at the Pourbaix diagram of Mn and V as shown in the Figure 2.19.^[14, 89] RZIB when in operation, the voltage of the cathode is cycled from 0 to 1.2 V vs SCE. Given that the aqueous electrolytes are mildly acidic, a thermodynamic force exists to reduce a solid cathode active material MnO_2 to Mn^{2+} ion which can easily dissolve into the electrolyte and many experiments have confirmed the same.^[21, 29] Similarly, vanadium based compounds are also unstable in the typical operational voltage range of 0 to 0.6 V vs SCE. The solid V_2O_5 phase will slowly dissolve in the aqueous electrolyte as $[\text{VO}]^{2+}$ ion.^[90] The slow dissolution of the transition metal ions into the electrolyte will imply that the active material is lost as the battery operates and hence the capacity will fade out as the cycling progresses.^[62] Since the transition metal dissolution is time bound phenomena, it has been more noticeable when the cycling rates are slower or when RZIBs are run for very long durations.^[62] This dissolution and the capacity fading hence limits the maximum lifetime of the RZIB.

Figure 2.19 Pourbaix diagram of transition metals Mn and V. The voltages are on SCE scale. Reproduced with permission.^[91]

2.4.7 Proton insertion and the BZS precipitation at the cathode

Many of the charge storage mechanisms discussed earlier have shown that the protons ions intercalate into the host structure, either predominantly or along with the zinc ions.^[74] The preferential insertion of protons over zinc ions has been ascribed to a smaller ionic size and a smaller charge-to-size ratio of the protons compared to the zinc ions.^[50]

Figure 2.20 Schema for pH evolution near the cathode vicinity in MnO_2 -Zn system with ZnSO_4 as electrolyte. Reproduced with permission from ref.^[72]

Along with the insertion of the protons into the cathode host structure, the BZS from the zinc electrolyte salt also forms on the cathode surface as seen in many mechanisms discussed above (Figure 2.20). This can be ascribed to an increase in the pH locally in the vicinity of the cathode and the BZS tend to precipitate at more basic pH values.^[74, 92-94] The BZS buffers the pH fluctuations near the cathode surface via dissolution and precipitation during the reversible proton insertion/deinsertion.^[72] For the BZS precipitation/dissolution to occur reversibly the salt should remain attached to the cathode surface for ionic/electronic transfer.

However, the salts are attached to the cathode surface by weak van der Waals forces and are prone to detach when the battery is left to rest after discharging.^[72] Once the BZS is detached, the pH will shift to very acidic values during the proton deinsertion process. Hence the proton concentration in the cathode vicinity will be much higher and therefore,

further egress of the protons from the cathode will be hindered.^[72] Therefore, the charge/discharge of the RZIB battery is no longer reversible.

2.5 Strategies to improve RZIB performance:

The above mentioned challenges calls for better cathode host structures and electrolyte formulations.

2.5.1 . Cathode materials

Majority of the cathode materials are limited to the oxides based on Manganese and Vanadium transition metals. The true zinc ion intercalation in these materials have been ambiguous. Furthermore, the transition metals have been found to dissolve and hence the capacity fading is high and the operational lifetime is low. One strategy could be to explore host structure materials beyond the oxide materials to polyanionic materials such as phosphates. These framework have been shown to be very rigid and stable framework in the Li-ion systems. These stable frameworks can stabilize the transition metal ions and might suppress their dissolution.

Given the fact that the intercalation behavior is bound to be difficult inside the host structure, the other strategy could be to explore conversion-reaction type host structure wherein the zinc ions are not stored inside the host cathode structure but as a separate phase after a chemical reaction. These two strategies will be explored in the Chapters 4 and 5.

2.5.1 Electrolyte formulations

Because of the above mentioned undesired side reactions in the aqueous electrolytes, which are more prominent especially at slower cycling rates,^[62] the observed capacity fading in aqueous electrolytes is very high as shown in Figure 2.21. (As an example, a 5 %/cycle capacity fade will imply that a starting cathode capacity of 100 mAh/g will lose 5 mAh/g of capacity after each charge-discharge cycle).

Figure 2.21 Capacity fade (in the units %/cycle, on the log scale) for aqueous electrolytes and DES-type electrolytes at slow cycling rates (< 500 mA/g). Each point here represents an RZIB study listed in the table in appendix Table A. 3 and Table A. 4. The blue and red zoned regions indicate the magnitude of the capacity fade or the Y-axis range. Reproduced with permission from ref.^[62]

To reduce the unwanted side reactions observed in aqueous electrolytes, shifting from aqueous electrolytes to Deep Eutectic Solvent (DES)-type electrolytes has been recently found to be effective.^[66, 69, 95-96] These electrolytes have also been shown to slow down the capacity fade as shown in Figure 2.21.

DES electrolytes in general form by a mixture of salt with a hydrogen bond donor. The salt is usually made from ammonium, phosphonium or Lewis acid like Zn^{2+} or Al^{3+} cations and the salt anion can be halide ion. The hydrogen bond donor species are in general alcohol, carboxylic acid, or amide containing groups. These species have lone pair of electrons which can be donated to the cations and hence the salt and the polar species can interact. This interaction can be strong enough to break the solid lattice of their individual solid salt and the hydrogen bond donors components. Hence, the resulting mixture can exist in the liquid form at temperatures lower than the melting temperature of the individual salt and the hydrogen bond donor species.^[97] DES-type electrolytes share a lot of similarities such as physical and chemical properties with the conventionally used ionic liquid type

electrolytes. Some of these properties include wide electrochemical stability voltage window, wide thermal stability window, low vapor pressure etc. However, DES-type electrolytes are less expensive and can be even made in ambient air.^[69, 98]

Figure 2.22 Comparison of zinc metal corrosion in (left) LiTFSI/Zn(TFSI)₂/urea/water DES-type electrolyte, (center) 0.25 M LiSO₄ + 0.5 M ZnSO₄ in water, and (right) 0.5 M LiTFSI + 0.5 M Zn(TFSI)₂ in water. (b) HER process while zinc deposition in (top) 0.5 M LiTFSI + 0.5 M Zn(TFSI)₂ in water and (bottom) LiTFSI/Zn(TFSI)₂/urea/water DES-type electrolyte. (c) Symmetric zinc-zinc stripping/plating behavior in Zn(TFSI)₂/acetamide = 1:7 DES and 1 M Zn(TFSI)₂ electrolytes with the inset showing the optical image of the zinc foils post-cycling. (d) bulging of coin cells due to H₂ gas build-up during the stripping/plating process for 30 cycles at 1 mA/cm² in a symmetric Zn|Zn cell in Zn(TFSI)₂/acetamide = 1:7 DES electrolyte (left) and 1 M Zn(TFSI)₂ (right) (e) BZS precipitation on the zinc foil surface in 1 M Zn(ClO₄)₂ aqueous electrolyte (ZW) and Zn(ClO₄)₂·6H₂O/succinonitrile = 1:8 electrolyte (ZS). Reproduced with permission from refs.^[66, 69, 95]

Zhao et al. made a DES-type electrolyte using LiTFSI/Zn(TFSI)₂/urea/water in a molar ratio of 1:0.05:3.8:2.^[66] They demonstrated that the zinc metal corrosion and the HER process observed in the aqueous electrolytes can be mitigated in the DES-type electrolyte as shown in the Figure 2.22a,b. Furthermore, a reduced HER process in the DES-type electrolyte will also enhance the reversibility of zinc dissolution and the zinc deposition

process during the battery runtime. Qui et al made a $\text{Zn}(\text{TFSI})_2/\text{acetamide}$ DES electrolyte and showed that the zinc stripping/plating process is more reversible compared to aqueous electrolyte (Figure 2.22c).^[95] The suppressed HER process reduces the unnecessary hydrogen gas build up inside the coin cell, unlike the one with aqueous electrolyte which bulges (Figure 2.22d). Finally, the BZS precipitation in the zinc metal anode is also suppressed as depicted by the ex-situ XRD studies of the post mortem zinc anode surface (Figure 2.22e).^[69]

Table 2.6 Physical and electrochemical properties of DES-type zinc electrolytes

Electrolyte	Molar Ratio	Conductivity (mS/cm)	Viscosity (mPa/s)	window (V)	Ref
$\text{ZnClO}_4 \cdot 6\text{H}_2\text{O}/\text{succino nitrile}$	1:8	5.52	25.4	2.5	[69]
$\text{LiTFSI}/\text{Zn}(\text{TFSI})_2/\text{urea}/\text{water}$	1:0.05:3 .8:2	1.85	139	2.2	[66]
$\text{Zn}(\text{TFSI})_2/\text{acetamide}$	1:7	0.31	789	2.4	[95]
$\text{LiTFSI}/\text{Zn triflate}/\text{acetamide}$	1:0.05:3 .5	0.35	290	2.5	[99]

The DES-type electrolytes have high viscosities and low ionic conductivity compared to aqueous electrolytes (Table 2.6). This property makes the zinc deposition morphology more uniform compared to aqueous electrolyte. The lower ionic conductivities in these electrolytes will make the zinc deposition overpotential much higher.^[66, 100] Hence, the zinc deposition phenomena will become similar to the case of zinc deposition in aqueous electrolytes at very high current rates wherein the zinc deposition overpotentials are higher and the zinc nucleation phenomena dominates leading to a much uniform zinc electrodeposition. The lower ionic conductivities also ensure that the zinc ion reserves close to the dendrite tips are not replenished fast and hence the zinc dendrite growth will also suppress.^[66, 69, 95]

At the cathode-electrolyte interface, absence of water molecules in the system and the high viscosities have been shown to reduce the transition metal dissolution phenomena.^[69, 101] Finally, a bigger potential window also ensures that the OER reaction at the cathode material surface will also be suppressed.

In Li-aqueous system, addition of Li salts such as LiTFSI in very high concentrations of upto ~ 21 m, and hence reducing the water solvent molecules, have been shown to reduce a lot of undesired reactions in the aqueous electrolytes.^[102] The super concentrated electrolytes then behaves like the DES-type electrolytes in terms of physical, chemical and electrochemical properties and all the above mentioned benefits, in theory, will be seen.^[62] However, the same is very difficult to achieve in the zinc aqueous electrolytes as the solubility of most zinc salts in water are less than ~4 m.^[1, 75] This is because unlike Li, Na or K salts, the zinc ion is divalent and has a high charge-to-size ratio which makes the dissociation of the zinc cation and the salt anion much more challenging which limits the zinc salt solubility.^[3] With the cap of 4 m zinc salt solubility, the water content of the system is still higher than 90 mol% and is still present in abundance.^[62] Nevertheless, few studies could still add highly soluble K or Li salts along with zinc salts in water to make a Zn-K hybrid battery or Zn-Li hybrid battery.^[103-106]

2.6 Conclusion

To conclude, this chapter reviews the various cathode materials that have been used as a RZIB cathode host structures. The various known storage mechanisms have been elucidated and the challenges from the cathode material perspective are also highlighted. Considering the challenges in the cathode host structure, few design strategies are highlighted which will be tested in the next few chapters. Furthermore, the various undesired reactions that stem from the aqueous electrolytes are also studied. These guidelines will be used for the formulation of new zinc electrolyte.

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Chapter 3

Experimental Methodology

This chapter explains the various experimental techniques used during course of this thesis work. The chapter begins by explaining the various synthesis techniques which were used to make the cathode materials. Thereafter, various material characterization techniques used to determine the physical or chemical properties, microstructure and crystal structure are discussed. Finally, last part of this chapter explains various battery fabrication and electrochemical techniques used to obtain the electrochemical data such as charge-discharge behavior, cathode material activity and electrolyte voltage window.

3.1 Synthesis techniques

3.1.1 Solid-state synthesis

This synthesis technique involves mixing the precursors via grinding and then heating them at a high temperature to get the final product. The precursors can also be made into the form of compact pellet to ensure good contact between the precursor materials. The reaction mixture is then placed in a alumina crucible and then heating either in ambient air environment or in an inert atmosphere as required based on the condition to achieve the final product.

The working principle of this synthesis technique is based on thermodynamics where the thermodynamically stable state of the final product is determined using the phase diagram. Furthermore, high temperatures also help in improving the diffusion kinetics of the reactants and as a result the time needed to complete the reaction also reduces.^[1]

In this thesis, solid state synthesis was used to synthesize the β -VOPO₄ material and also in the final stage of the FeVO₄ synthesis. The furnace used in the synthesis was the Carbolite muffle furnace.

3.1.2 Hydrothermal synthesis

This synthesis technique works on the principle of dissolving the precursor salts in water or any other solvent and then heating the mixture in a sealed Teflon lined container inside a stainless steel autoclave. Since the vessel is sealed, the water on heating will increase its boiling point to values beyond the room temperature and pressure conditions. As a result, the liquid inside the vessel can reach the supercritical fluid conditions where the solvent properties such as the dielectric constant values and the salt solubilities will show a drastic change.^[2] More specifically, the dielectric constant values will decrease on increasing the temperature and as a result the dissolved precursors will form a lot of small nuclei to give rise to a variety of nanostructures.^[3] The advantages of this synthesis technique is that the phases can be formed at much lower temperatures at increased pressure and at much faster rates compared to reactions in open air.

In this thesis, hydrothermal synthesis route is used for the synthesis of FeVO_4 and InVO_4 cathode materials. The reaction vessel used in this study are 45 mL acid digestion vessel autoclave from Parr Scientific products, USA which was kept in a steel autoclave and then heated in Thermofisher air oven.

3.2 Material characterization

3.2.1 X-ray diffraction

X-ray diffraction technique is one of the heavily used techniques in this thesis work. This technique has been used to identify the phase of the material, either of the powder material obtained after the synthesis or during the ex-situ characterization of the either the anode or the cathode electrodes.

Every crystalline material can act as a diffraction grating and the spacing of the diffraction grating depends on the atomic spacing of the material for a particular plane. It can so happen that when a monochromatic X-ray beam is shined on a material at a particular angle, the atoms of the material scatter the X-rays constructively and a strong signal comes out of the material again. This behavior can be easily explained using the principle of Bragg's law: $2d \sin\theta = n\lambda$.^[4] For a given X-ray source, the wavelength is fixed and the order of the diffraction, n , is usually 1. Therefore every set of diffraction planes which have a unique d -spacing will show a diffract the incoming X-ray beam constructively at a particular angle 2θ .

This principle is used for the construction of the X-ray diffraction instrument. A monochromatic X-ray source is produced using a copper cathode ray tube, which is passed through filters to make the beam monochromatic and then passed through parallel plates to adjust the beam spread before it hits the sample. The beam then hits the sample and the diffracted X-rays from the sample is detected using a detector at any given angle as the detector can move in a circle in a range of 2θ angle. As the detector moves, the θ values where the Bragg law are satisfied, the X-ray counts will be very high because of the constructive interference. The result of the scan will then be the intensity of the X-ray counts detected as a function of 2θ angle.

The 2θ angles or the d-spacing with the relative intensities can then be used to match the phase of the material to any of the previously reported crystal structures from a database. Furthermore, the 2θ positions of the material can also be used to calculate the unit cell type and the dimensions using Pawley fitting. Finally, using a full Rietveld refinement, which fits the data using both the intensity and the 2θ angles, the unit cell dimensions along with the fractional coordinates of each atom inside the unit cell can also be deduced.^[4-5]

In this thesis, Pawley fitting has been used to calculate the interplanar spacing for the synthesized VOPO_4 family of materials. Pawley fitting has also been used for ex-situ samples to find the d-spacings of the new phases formed after charge-discharge process on both the anode and the cathode surface. Finally, full Rietveld refinement has been used to characterize the unit cell shape and the atomic coordinates of the synthesized FeVO_4 nanorods.

3.2.2 X-ray Absorption Spectroscopy

The basic principle of this technique is that X-rays is shined on a material with enough energy to excite a core level electron from a specific element in the material which will result in the absorption of the X-ray photons.^[6] The absorption of the X-rays is calculated relative to the X-ray photon counts of the incoming beam. This is done for a range of X-ray energies and therefore the X-ray photons absorption as a function of X-ray energy can be obtained. A typical XAS signal will look like the Figure 3.1 shown below. The whole spectrum can be divided into two parts- X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS).

XANES region contains the pre-edge region, where the absorption is very low and reduces on increasing the energy. As we go to higher energy regions the absorption rises sharply as the incoming X-ray energy matches with the energy of the core level electron. The position (or the energy) of the rising edge gives an idea of the oxidation state of the element.

Figure 3.1 A typical XAS spectrum. Reproduced from ref.^[6]

EXAFS region is the energy portion at energy values after the rising edge and contains a lot of perturbations in the absorption. The perturbations is caused by the modulations in the X-ray photon absorption response as the photoelectron ejected off from the core level can be scattered back from the adjacent atoms in a constructive and destructive fashion, depending on the energy of the X-ray photons. Therefore, the EXAFS region can give the information about the local environment and the surroundings of the absorbing atom.^[6]

In this study, XANES was used to determine the oxidation state for the transition metal of the synthesized powders. Furthermore, the EXAFS region was used to estimate the Zn^{2+} coordination environment in the zinc based ethylene glycol electrolytes. These experiments were carried out in Synchrotron Light Research Institute (SLRI), Thailand at beamline 5.2 in the fluorescence mode. The electron energy used was 1.2 GeV with a beam current of 80 to 150 mA and the photon flux is around 10^{11} photons per second. Germanium (220) double crystal was used as a monochromator. The measurement were carried out 5 times per sample in the k range of $12 \text{ \AA}^{-1}$ and then averaged. The data analysis was carried out using the Athena and Artemis software.

3.2.3 Raman Spectroscopy

This technique is used to observe the type and the nature of the vibration of the chemical bonds in a solid, liquid or gas specimen. A monochromatic light is shined on the sample and the sample can show elastic or in-elastic scattering of the photons. The inelastic scattering is when the energy (or the frequency) of the scattered photons is modulated by the sample. The photons are interacting with the sample can have an increased energy (called anti-stoke scattering) or a decrease in the energy (stoke-scattering) as shown in

Figure 3.2. This shift in the frequency occurs as the system energy state changes to a different vibration level. The difference in the energy level will involve a specific change in the energy of a chemical bond which can be used as a fingerprint to identify the chemical bonds present in the system.^[7]

Figure 3.2 Two different process for inelastic scattering. Reproduced from ref.^[8]

In this thesis, Raman spectroscopy has been used for studying the phase evolution of the FeVO_4 system during the charge-discharge cycling. Since this method works on with chemical bonds and does not need any long range ordering of the atoms, this method was suitable when the starting structure amorphizes and the XRD technique could not give any information on the amorphous materials. Witec Alpha 300 SR (Ar laser, 488 nm) was used for the purpose.

3.2.4 X-ray Photoelectron Spectroscopy

This technique works on the principle of photoelectric effect and gives the chemical information from the surface of the sample. A monochromatic X-rays is shined on the sample using an X-ray source using a Mg or Al target since they generate almost monochromatic X-rays. The X-rays will hit the sample kept under vacuum conditions and if the X-rays have sufficient energies to knock off core level electrons from the atoms, the photoelectrons will be ejected out with some kinetic energy and can be estimated using the following equation^[9]: $h\nu = KE + BE + \Phi$, where $h\nu$ is the energy of the incoming photon, KE is the kinetic energy of the ejected photoelectron and BE is the binding energy or the minimum energy needed to knock off the core level electron. Φ is the work function of the spectrometer and is constant for an experiment. KE can be estimated in the instrument, Φ and $h\nu$ are known for the instrument, therefore the BE can be calculated. Furthermore, the

BE of a given atom is modulated by the oxidation state and the surrounding atoms. Therefore, BE can give an idea of the chemical state of the scanned atom.

In this work, XPS technique was used to identify the oxidation states of the vanadium transition metal of the VOPO_4 family in the synthesis stage. Furthermore, this technique was also used to identify the oxidation state of the transition metals in the VOPO_4 and FeVO_4 ex-situ electrodes to elucidate the zinc ion storage reaction mechanism.

3.2.5 Scanning Electron Microscope

SEM is one of the most widely used microscopy technique in materials science. The image resolutions can go down to 50 nm since the wavelength of the electron beam can be made much smaller than the visible light as in the case of an optical microscope. Furthermore, the SEM can give the image in three dimension due to a large depth of field. The working mechanism basically involves scanning one of the various signals generated when an electron beam hits the sample surface.

An electron beam is generated in the electron gun either by heating the filament or by using an electric field. This electron beam is then focused on a spot on the surface of the sample using various magnetic lenses. When the electron beam hits the sample surface the electron-sample interaction will then produce a lot of signals such as primary electrons, secondary electrons, characteristic X-rays, Auger electrons etc. as shown in the Figure 3.3. Furthermore, even though the signal is generated in a lot of locations inside the sample, the signal slowly attenuates before it can be detected and therefore each signal has a specific interaction volume with the sample. Each type of signal gives a characteristic information about the sample. For instance, the secondary electrons have very low interaction volume and very low energy and therefore this signal gives an information about the surface morphology. Primary or the backscattered electrons are deflected at an angle depending on the nuclear charge and therefore backscattered electrons give an information about the elemental composition of the specimen.^[10]

Figure 3.3 Electron beam and material interaction. Reproduced from ref.^[11]

In this thesis JEOL FESEM 6340 was used to observe the morphology of the synthesized FeVO_4 and VOPO_4 family of materials. Furthermore, the surface morphology of the zinc metal anode after the stripping/plating tests in various electrolytes were also observed.

3.2.6 Transmission Electron Microscope

When compared to SEM, the electron beam is produced at much higher kinetic energies and as a result the wavelengths of the electron beam become even smaller thus improving the resolution to less than 10 nm. The major difference as compared to SEM is that the sample is made very thin and therefore, the primary electron beam can transmit through and can be used as the signal.

The electron beam is produced by heating a tungsten filament. At high voltage bias anode, the ejected electrons can be accelerated at very high kinetic energies. This electron beam is then passed through a series of condenser lenses which can then pass through the objective lens before reaching the sample. The beam, after crossing the sample, passes through the intermediate and the projector lens. The intermediate lens allows for the selection of the type of image to choose from either the image or the diffraction pattern at the back focal plane of the objective lens (Figure 3.4).^[12]

In this thesis work, TEM was used to image the FeVO_4 nanorods. The measurement was conducted on a JEOL JSM 2100 F machine.

Figure 3.4 TEM cross section during the operation in the diffraction pattern mode (left) and imaging mode (right). Reproduced from ref.^[12]

3.2.7 Fourier Transform Infrared Spectroscopy

This technique gives an idea of the presence of functional groups present in the sample. The sample, solid or liquid, is irradiated with a white light of the wavelength 500 to 4000 cm^{-1} and the fraction of photons transmitted or absorbed by the sample relative to sample holder without the sample is measured.

Each functional group in the sample will absorb the photons at a unique wavelength which will be characteristic to the functional group and the mode of the vibration. Furthermore, if the functional group is known, the characteristic wavelength of the absorption can shift in wavelength which can give a rough idea about the local change in the bonding environment for that specific bond.^[13]

In this work, FTIR was used to confirm the presence of the polypyrrole polymer after its in-situ polymerization in the VOPO_4 material. The FTIR was also used to confirm the bonding characteristic between the ethylene glycol molecule and the zinc ion center in the ethylene glycol based electrolytes.

3.2.8 Thermo Gravimetric Analysis (TGA)

This technique measures the weight of the sample as a function of temperature, when the temperature is ramped up at a constant rate. The change in the weight of the sample can be used to determine the mass fraction of the volatile component in the sample such as adsorbed water, crystal water, decomposition, oxidation etc.

The measurement is done by placing the sample in alumina crucible kept over a platinum pan connected to a high precision balance. The whole setup is placed inside a furnace and the furnace environment is then purged using air or an inert gas such as nitrogen. The weight of the sample setup is continuously measured as the temperature is ramped up and the data we obtain is the weight percent as a function of the temperature.

In this thesis, TGA was used to quantify the water content in the VOPO₄- based synthesized materials.

3.2.9 Differential Scanning Calorimetry (DSC)

DSC is a technique which can give an idea of the thermal phase transitions occurring in the sample, solid or liquid. The sample is heated/cooled and the heat energy supplied/released is measured as a function of temperature. This technique can give information about the crystallization behavior, melting point, glass transition temperature etc.^[14]

The measurement is carried out in two sample holders simultaneously, with and without the sample inside. The difference in the heat flow is measured between the two sample holders which gives an estimate of how much excess or less heat flow was needed to maintain the temperature-time profile as compared to the empty sample holder. Hence, the data in the form of heat flow as a function of temperature can be collected. The heat flow peaks and valleys at specific temperatures can correspond to the melting or crystallization processes at that temperature while a sloping heat flow can indicate a second order phase transformation such as glass transition.

In this thesis, DSC was used to measure the crystallization temperatures of the ethylene glycol and water based electrolytes.

3.3 Electrochemical Analysis

3.3.1 Electrochemical Testing Setup

All the electrochemical measurements are done either in the three electrode setup or in the two electrode setup in the form of coin cell.

Three-electrode Setup: In the case of three electrode setup, we have three electrodes namely: the negative, positive and the reference electrodes. All the three electrodes are then submerged in an electrolyte as shown in Figure 3.5. The reference electrode used in the studies is the Ag/AgCl (KCl saturated) type reference electrode which has a fixed voltage of 0.22 V vs SHE.^[15] Having a reference electrode gives an advantage of finding the voltage of the positive electrode on an absolute scale and is independent of the system. If the setup is used as a battery system, the negative electrode is zinc metal and the positive electrode is the cathode electrode used. The three electrode setup can also be used to measure the electrochemical voltage window of the electrolyte. In this configuration, for the positive and negative electrodes, a current collector titanium was used.

Figure 3.5 Three electrode setup (left) and the close up showing the working, counter and the reference electrodes (right).

Coin-cell assembly: coin cell (2016-type) construction is a two electrode cell configuration without the reference electrode. In this study, the coin cells were used for two purposes: 1) for testing the electrochemical performance of the full cell RZIBs for a given cathode material and an electrolyte, and 2) for testing the electrolyte compatibility and reversibility with the zinc metal anode in the form of Zn|Zn stripping/plating test.

For making the full cell RZIB, first the cathode electrode was fabricated. First, the cathode active material, Super P carbon and PVDF binder (having a weight ratio of 6:2:2) are stirred overnight in dimethylformamide solvent to obtain a slurry. The mixed slurry is then drop casted on either a stainless steel or titanium circular disks of 12 mm diameter and then kept in vacuum oven for one day for drying. The dried electrodes are then used as the positive electrodes. For the negative electrodes, zinc metal (Goodfellow, 0.25 mm thickness) is cut as 16 mm circular disk and used as the anode. The separator used was porous glass fiber (Whatman, UK). CR2016 is assembled in ambient air conditions with the zinc metal anode, the separator soaked in the appropriate electrolyte and the cathode. For the Zn|Zn stripping/plating tests, the whole procedure remains the same, with only one difference being that zinc foil is used both the sides of the separator to act as the negative and the positive electrode.

3.3.2 Cyclic Voltammetry (CV)

CV is an electrochemical characterization technique where the voltage difference between two electrode terminals is varied between two fixed values at a fixed linear rate (as a function of time) for a fixed number of cycles and the current response between the electrodes is recorded. The data is presented in the form of I-V graph and a current peak in the scan will indicate a redox reaction. The CV data can give crucial information in an electrochemical system such as, the rough voltage values where the oxidation or the reduction reaction occur and the reversibility of these redox reactions over cycles.^[16]

In this study, CV was carried out in Solartron 1470E. The CV data was recorded for the full cell RZIBs to estimate the voltage values of the redox reactions, which was then used to determine the voltage window range for running the charge-discharge test for the RZIBs.

3.3.3 Linear Sweep voltammetry

LSV technique is very similar to the CV technique described previously with slight differences. Unlike CV, LSV is not cyclic and is carried out starting from the voltage of the system at rest (also called as Open Circuit Voltage (OCV)) to a fixed voltage value either on the positive side (positive sweep) or on the negative side (negative sweep) of the OCV.^[17] LSV technique is used in this study to determine the electrochemical stability

window of the electrolyte. The high currents observed during the positive or the negative sweeps will indicate the voltage values where the electrolytes are getting oxidized or reduced respectively, and we can estimate the voltage window of the electrolytes.^[18] The LSV test in this study was done on Biologic SP-300 to measure the voltage window of the electrolyte formulations.

3.3.4 Galvanostatic Charge-Discharge Test

In GCD test, a constant current is applied between the positive and the negative electrode terminals of the coin cell. The current is applied between a fixed voltage range and the voltage variation of the system is recorded as a function of time. The time taken to reach the voltage limits can be used to calculate the capacity and hence we can obtain the data in the form of voltage vs capacity.^[19]

The GCD test can give a lot of valuable information about the system. In this study, GCD tests were carried out using Neware system. The GCD tests on full cell RZIBs were done to: 1) estimate the cathode capacity of the cathode active material at different current rates, 2) identify the nature of the cathode material reaction during the zinc storage from the charge-discharge profiles.^[19] 3) reversibility of the charge/discharge reactions after multiple cycles. GCD tests were also done in symmetric Zn|Zn cells to check the reversibility of the zinc stripping/plating process for any given electrolyte.

3.3.5 Electrochemical Impedance Spectroscopy

This technique is used to delineate the electronic and ionic kinetics in an electrochemical system. To use this technique an AC voltage signal is applied to the system with a very small amplitude over a range of frequencies. At different applied frequency, the system will show a different response in the amplitude and shift in the phase of the output current. The impedance response at each frequency is then recorded. In most cases, the electronic response predominates at high frequency range which gives the information about the electron transfer kinetics at high frequency ranges. On the other hand, ionic movement predominates at a low frequencies since they are heavier and the ionic diffusion kinetics is reflected in the impedance at low frequency range.^[20] A typical EIS spectrum is shown in the Figure 3.6 in the Nyquist plot of real and imaginary part of the impedance (X and Y

axis respectively).^[21] The semicircle in the high frequency range gives an indication of charge transfer kinetics at the electrode-electrolyte interface. And the straight line after the semicircle represent the Warburg impedance which gives an indication of the solid state diffusion phenomena. The interpretation of the EIS results is done by fitting the impedance response to an equivalent model circuit.

Figure 3.6 A typical Nyquist plot and the equivalent circuit to fit the impedance data. Reproduced from ref.^[21]

In this work, the impedance spectroscopy has been used to compare the charge-transfer kinetics at the electrode-electrolyte interface. Furthermore, this technique is also used to measure the cationic transference number, which gives an idea of the fraction of ionic conductivity coming from the cations in the overall ionic conductivity value in the ethylene glycol based electrolyte formulations made.

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Chapter 4

Intercalation-based phosphate cathode host structures for reversible zinc ion storage

This chapter explores intercalation-type phosphate-based host structures for reversible zinc ion intercalation/deintercalation. The study begins by exploring few tunnel-type host structures which were found to reversibly store Li^+ ions. However, these materials failed to store Zn-ions due to high electrostatic interactions between the small tunnel host structure and the zinc ions. Hence, open layered-type phosphate based host structures were synthesized and tested for reversible zinc ion storage. Polypyrrole intercalated VOPO_4 (PPy- VOPO_4) was found to reversibly store zinc ions with optimized electrolyte and hence the zinc ion storage mechanism was studied in-depth. Finally, the advantages and disadvantages of the phosphate-based intercalation host structures from RZIB perspective are highlighted.

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4.1 Introduction

When compared to Li^+ ions, Zn^{2+} has a higher charge-to-size ratio or a higher charge density. This high charge density of the Zn^{2+} ions strongly polarizes the cathode host structure and limits the ionic diffusivity inside the host structure.^[1] The high charge density can also induce a high degree of structural distortion in the host structure and as a result, the structure can collapse.^[2] A high structural integrity and a highly stable framework should allow for longer battery operational lifetimes without a severe host structure dissolution in the aqueous electrolytes.^[3]

In the Li-ion systems, phosphate polyanionic based three dimension framework has been widely explored as alternative host structures to the oxide based materials.^[4] These type of frameworks have been found to be very stable and hence allow for Li ion intercalation/deintercalation in a very reversible way and thus the operational lifetime and the number of charge/discharge cycles are very high.^[4] The stable framework might also be beneficial for zinc ion storage in two ways: 1) the high stability will allow the insertion of divalent zinc-ions without a large degree of structural distortion or structural collapse. 2) the high stability should also be more resistant to cathode material dissolution in the aqueous electrolytes and hence improve the battery operational lifetime. 3) an added benefit can be a higher intercalation voltage compared to the oxides.^[5] Hence, this chapter will focus on exploring phosphate based materials for reversible zinc-ion storage.

4.2 Experimental Methods

Material Synthesis: LiFePO_4 used in this study is the commercial powder. $\beta\text{-VOPO}_4$ was synthesized via a solid state method. Ammonium dihydrogen phosphate (99.9%, Sigma Aldrich) and Vanadium pentoxide (99.6%, Sigma Aldrich) was grinded in the stoichiometric ratio and then annealed at 700 °C for 8 hours in an air furnace.

Synthesis of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was carried out following the technique mentioned by De.^[6] Stoichiometric ratio of the materials V_2O_5 (99.6%, Sigma Aldrich), phosphoric acid (85%, merck) were added in deionized water and was refluxed at 115 °C for a duration of 20 h. The end product is a yellow powder which was collected by vacuum filtration and washed with acetone and ethanol several times and then air dried at 60 °C.

Using the $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ material as a precursor, Polypyrrole intercalated VOPO_4 (PPy- VOPO_4) was synthesized using the technique described by De et al.^[6] In a 1:1 molar ratio of pyrrole and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, the precursors were dispersed in molecular sieves dried ethanol in two separate beakers and stirred for 2 hours. After that, the two dispersion mixtures were mixed together and then left to stir for 24 h without any heating. The product was then collected using the vacuum filtration technique and then washed multiple times in dry ethanol and then dried in air oven at 60 °C overnight to get the final powder.

Material Characterization: The XRD diffractogram of the synthesized materials were collected using a Bruker D8 Advance machine using Copper $\text{K}\alpha$ source in a Bragg-Brentano geometry. For the case of VOPO_4 family of materials, Pawley fitting was done using the TOPAS 3 software to calculate the interlayer spacing. The morphology of the VOPO_4 family of the materials was characterized using JEOL, JSM-7600F SEM. XPS scan were taken using Kratos AXIS Supra using Al $\text{K}\alpha$ source. The XPS spectrum analysis was done using Casa XPS. All spectrums were calibrated with the N1s pyrrolic main peak at 399.6 eV.^[7-8] FTIR spectrum was recorded using Perkin-Elmer FTIR spectrometer for 32 scans in the wavenumber range of 400-4000 cm^{-1} to get the average.

Electrochemical Measurements: The electrochemical testing was done in a coin cell of 2016 type. Cathode electrodes were made using a stainless steel mesh as the substrate and then drop casting the slurry and then vacuum drying the coated substrate at 60 °C overnight. The slurry was made by mixing the appropriate active material with PVDF binder and super P carbon with a weight ratio of 60:20:20 using N-methyl-2-pyrrolidone solvent. The mass loading was 1-2 mg per electrode. In the case of aqueous electrolytes, 1 M $\text{Zn}(\text{OTf})_2$ (zinc triflate) in deionized water was used. For the aqueous/non-aqueous hybrid electrolyte 1 M $\text{Zn}(\text{OTf})_2$ in acetonitrile with appropriate water amount was used. Cyclic voltammetry test were done using Solartron machine and the GCD studies were done in the BTS Neware equipment. The EIS measurement was carried out in Biologic SP-200.

4.3 Results and Discussion

4.3.1 Preliminary investigation on tunnel-type phosphates (LiFePO_4 and $\beta\text{-VOPO}_4$)

LiFePO_4 has been one of the most widely used and also commercially available phosphate material in Li-ion system. It is a stable framework which intercalates Li-ions in its 1-D tunnels. Furthermore, few previous studies have demonstrated that Li from the framework can be electrochemically removed in aqueous electrolytes and other ions such as Na can then be reversibly intercalated/deintercalated in the host structure.^[9] The same studies were also repeated in the zinc system, but the results were unsatisfactory. Although Li could be successfully be removed from the host structure, the capacities during the zinc ion insertion/deinsertion were very poor (Figure 4.1).

Figure 4.1 Attempt of zinc insertion and extraction in delithiated LiFePO_4 .

$\beta\text{-VOPO}_4$ is another phosphate material which has been shown to reversibly intercalate/deintercalate Li-ions in the tunnel structure.^[10] However, this material was also found to be electrochemically inactive for zinc-ion insertion (Figure 4.2). Based on the results from these two materials, we can conclude that although the framework might be stable, the high charge density and the high electrostatic interactions between the divalent zinc ions and the host structure hinders the zinc ion 1-D diffusion inside the tunnel structure.^[2, 11] Hence, phosphate material with relatively open structure such as layered materials which are not limited to 1-D diffusion pathways for zinc diffusion and lower electrostatic interaction are explored.

Figure 4.2 XRD pattern of the synthesized β -VOPO₄ material. Attempt of zinc insertion/extraction in the β -VOPO₄ material.

4.3.2 Layered-type phosphates: VOPO₄-based materials

VOPO₄·2H₂O is a material that exists as a layered phase with a high interlayer spacing.^[12] The high interlayer spacing, created by the pre-intercalated water molecules between the VOPO₄ layers, can minimize the electrostatic repulsion and hence make the zinc ion migration inside the host easy.^[3, 13-14] The interlayer water molecules between the VOPO₄ layers have also been replaced by organic species such as polypyrrole to improve the electrical conductivity and hence improve the electrochemical performance in the Li-systems.^[15] Hence, these materials were chosen as the next phosphate based materials to investigate their reversible zinc-ion storage.

4.3.3 Characterization of VOPO₄·2H₂O & polypyrrole-VOPO₄ (PPy- VOPO₄)

The crystal structure of the VOPO₄·2H₂O powder material can be confirmed to be matching with the previously published reports (JCPDS 04-014-1253) (Figure 4.3a).^[16] The crystal structure has been described well by Tachez et al. and is depicted in the Figure 4.3b.^[17] Briefly, the crystal structure is made up of vanadium octahedra attached to the phosphate tetrahedra in a sheet like structure. These sheets are then intercalated by the loosely held water molecules in the interlayer.^[12] The VOPO₄ layer (where the layers lie in the a-b plane) and the water intercalated layer is then repeated in the c-axis to build the full crystal structure. The (001) peak intensity is very high which indicates at the crystal has a preferred orientation wherein the planes perpendicular to the c-axis (or the VOPO₄ layers) are stacked and hence the structure is sheet like.

Figure 4.3 (a) XRD pattern for VOPO₄·2H₂O and the PPy-VOPO₄. b) and c) the crystal structures of VOPO₄·2H₂O and the PPy-VOPO₄ d) SEM micrograph of PPy-VOPO₄, e) V 2p XPS data for the VOPO₄ material before and after and the polypyrrole intercalation.

The X-ray diffraction pattern of the VOPO₄ material after polypyrrole insertion (PPy-VOPO₄) resembles to some of the previously published work (Figure 4.3a).^[6, 18] Since the polypyrrole insertion between the layers is expected to only change the interlayer VOPO₄ spacing without disturbing the layers, the unit cell dimensions only in the c-axis is expected to change.^[12] This is also evident in the XRD pattern where only the *l* dependent peaks shift but the *l* independent (020) peaks still remains at the original location. The shifting of the *l*-dependent peaks to higher 2θ angles indicates a contraction of the c-axis or the VOPO₄ interlayer planes are coming closer to each other. This is reflected in the unit cell dimension when calculated after Pawley fitting of the XRD patterns where the c-unit cell length shrinks from 7.43 Å to 6.72 Å (the calculation is based on the (001) plane). The replacement of water with the polypyrrole molecules results in shrinking of the interlayer spacing and this can be ascribed to the fact that the interlayer bonding of polypyrrole is much stronger than that of water as suggested by De et al.^[18] Another key difference that appears after intercalation of polypyrrole into the layers is that the material long range ordering or the crystallite size is smaller which is evident when the peaks of the new material appear much broader when compared with the case before polypyrrole intercalation.^[6]

Figure 4.4 FTIR spectra for $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and PPy-VOPO_4 .

Table 4.1 The assignment of FTIR peaks

Peaks (cm^{-1})	$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$	Peaks (cm^{-1})	PPy-VOPO_4
680	V-O-P bending	680	V-O-P bending
985	V=O stretch	1058	P-O stretch
1080	P-O stretch	977	V=O stretch
947	V-O stretch	924	V-O stretch
1616	H-O-H bending	1300-1388, 1566	C-N stretch
3000-3600	O-H water stretch	1566	C=C stretch
		3400 (broad)	N-H stretch

Values are matched from the refs^[6, 18-21]

The SEM image for the PPy-VOPO_4 shows the sheets or the flake like morphology appears after the polypyrrole intercalation. This is consistent with our previous observation that the unit cell is changed along the c-axis and the material crystalline size also reduces. Furthermore, FTIR studies also confirm the presence of the polypyrrole species (Figure 4.4 and Table 4.1) and the chemical composition as determined using the TGA and the CHN analyzer was found to be $(\text{PPy})_{0.4}\text{VOPO}_4 \cdot 1.17 \text{H}_2\text{O}$ (Figure 4.5).

Figure 4.5 TGA for PPy-VOPO_4 and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

To confirm the nature of interaction between the pyrrole units and the host VOPO₄ layers the oxidation state of the vanadium transition metal was determined before and after the polypyrrole interaction (Figure 4.3e). The majority of the vanadium ions shows as oxidation state of +5 oxidation state with a binding energy of 518.7 eV with a small fraction of +4 oxidation state at 516.8 eV.^[22-23] After the polypyrrole intercalation, two key differences are observed. First, the fraction of +4 to +5 ions is much higher. This indicates that the vanadium ions now are in the mixed oxidation state of +4 and +5. Secondly, both the peaks for +4 and +5 oxidation state are now shifted to a lower binding energy and this behavior is consistent when other carbon-based materials are intercalated between the VOPO₄ layers.^[23]

4.3.4 Effect of polypyrrole insertion in the VOPO₄ layers

The polypyrrole addition to the host structure improves the electronic conductivity of the material in two ways. Firstly, as the vanadium now is present in a mixed oxidation state of +4 and +5, which will give rise to an improved electronic conductivity as the d-orbitals are not fully empty and the electron cloud is delocalized over neighboring V ion centers.^[24-25] Secondly, the polypyrrole units themselves are present in the partially oxidized state, which can be seen as an analogous to doped polypyrrole, and thus is also electronically conductive.^[6, 18] As a result of these two phenomena, the overall electronic conductivity of the material is higher. Because of this high electronic conductivity, the charge transfer resistance (depicted by the semicircle size as ascribed by Kundu et al.^[26]) also reduces as shown in Figure 4.6a.

Furthermore, the polypyrrole pre-intercalation also gives an added benefit of improving the structural integrity of the host structure which is reflected in the battery cycling behavior (Figure 4.6b). Without the polypyrrole pre-intercalation VOPO₄·2H₂O structure could not show a stable cycling stability and the capacity dropped rapidly. This is due to the loss of very weakly bonded water molecules in the interlayer which can be easily lost from the host structure as also evident in the ex-situ XRD data (Figure 4.7).^[12, 27] However, the capacity retention was much more stable after the polypyrrole intercalation which showed an improvement from 25 to 90 % in the first 30 cycles (Figure 4.6b). This behavior is analogous to the other layered-type vanadium-based host structures which when

preintercalated with other ions between the interlayers can maintain the structural integrity during repeated guest ion intercalation and deintercalation.^[28]

Figure 4.6 a) EIS spectra and b) cycling stability comparison for the two materials. c) and d) effect of addition of water in 1 M Zn(OTf)₂/acetonitrile electrolyte on the capacity and the charge transfer resistance of the PPy-VOPO₄ cathode material.

Figure 4.7 Ex-situ XRD for cycled VOPO₄·2H₂O shows that the interplanar spacing shrinks irreversibly.

4.3.5 Effect of Water amount in electrolyte on PPy-VOPO₄ battery performance

An aqueous electrolyte will be an ideal electrolyte to run the PPy-VOPO₄ cathode battery. However, the cathode material powder is unstable in water as it slowly dissolves. The other choice would have been to use non-aqueous solvent such as acetonitrile-based electrolyte. Although the material is stable in this solvent the battery could not show any significant capacity which is most likely due to the fact that the battery kinetics are very poor in non-aqueous zinc electrolytes (Figure 4.6c).^[26] However, a hybrid acetonitrile/water electrolyte showed some working capacities in the battery and therefore the hybrid electrolyte was optimized first before carrying out the other studies.

On increasing the water content in the 1 M Zn(OTf)₂/ acetonitrile electrolyte the capacity was observed to increase (Figure 4.6c). Impedance spectroscopy was used to determine the reason the increasing capacities on increasing the water content. As it can be seen from the Figure 4.6d that the charge transfer resistance, which is indicated by the size of the semicircle, is reducing on increasing the water content. Kundu et al. have ascribed this charge transfer resistance to the desolvation energies of the Zn²⁺ ion transfer at the electrolyte-electrode interface.^[26] Previous studies have shown that the desolvation energy penalty of multivalent cations is much reduced in water as compared to other organic solvents such as acetonitrile or carbonates.^[26, 29]

However, addition of more water in the electrolyte beyond a an optimal value of 10 vol% does not provide any added benefits. Although the capacities appear to increase slightly, the capacity retention values becomes quite poor especially at much longer cycling duration (Figure 4.8). This can be ascribed to the severe material dissolution due to water when the water is available in sufficient concentrations. Hence, a compromised trade-off is optimized at 10 vol% water in the system in order to improve the battery kinetics but at the same time to also ensure that the material dissolution is kept to a minimum and thus the battery cycling stability is not suffering.

Figure 4.8 Effect of excessive water addition in the electrolyte on the cycling stability of the PPy-VOPO₄ cathode material.

4.3.6 Electrochemical investigation of PPy-VOPO₄ battery

Cyclic voltammogram was first used to determine the electrochemical activity of the PPy-VOPO₄ material. The curve showed three pairs of oxidation and reduction reactions (Figure 4.9a). The CV profile resembles the studies where the VOPO₄-based cathode was used in lithium, magnesium and potassium systems.^[27, 30-31] These studies have described the appearance of multiple peaks to a guest ion insertion in multiple steps inside the host structure.^[30] Furthermore, polypyrrole itself does not give any redox peak in CV indicating that the redox reactions are driven by the change in the oxidation states of the vanadium transition-metal ions (Figure 4.10).

The full cell battery performance was studied using the GCD tests (Figure 4.9b). When the battery is cycled at a current rate of 100 mA/g, the battery showed a high operational lifetime of 455 hours or nearly 350 cycles. The cycling profile indicates that initially the capacity values drop in the first few cycles, rises to a maximum and then drop down again. The initial drop in the first few cycles is caused by the irreversible zinc ions insertion into the host structure which cannot be deintercalated again. These sites are then blocked as more zinc ions cannot be stored in these locations and hence the capacities will drop initially.^[32-33] Thereafter, the capacities values rise continuously and this can be ascribed to an gradual activation of the cathode material. This initial drop and then the rise has also been seen in other RZIB systems.^[32-35]

Figure 4.9 Electrochemical performance of the PPy-VOPO₄ cathode material with the optimum water amount of 10 vol% in the 1M Zn(OTf)₂/acetonitrile electrolyte. a) CV b) cycling stability at 0.1 A/g and c) rate capability test.

Notably, the activation process is very slow and lasted for nearly first 200 cycles. This behavior has also been observed in non-aqueous electrolytes before and is due to the slow reduction of the charge-transfer resistance at the zinc metal anode interface via progressive electrochemical polishing.^[26] Finally, the capacities starts to drop as the material also starts to dissolve slowly in the electrolyte as the time progresses. The rate performance of the battery is also shown in the figure where it can be seen that after testing the battery at much higher current densities, the capacity can still be retained to almost the full value once the current density is reduced again (Figure 4.9c).

Figure 4.10 CV for only polypyrrole material shows no redox peaks.

4.3.7 Structural Characterization of the optimized PPy-VOPO₄ battery

The zinc ion storage mechanism is then studied using the ex-situ XRD characterization technique (Figure 4.11). The peak positions in the cathode electrode are compared in the charged and discharged states. When compared to the pristine sample, the (001) and the (002) peaks are shifted to higher angles in the discharged sample. This is an indication that the layered material undergoes a contraction. The interplanar distance (when calculated using the 001 plane) contracts from 6.72 Å to 6.39 Å. This reduction in the layer spacing is because the intercalated zinc ions, with high charge-density, when present in the interlayer pulls the layers closer to each other via the electrostatic interaction and is also observed in other layered materials.^[13, 34, 36] When the cathode is charged again, the (001) and (002) peaks again shifts to the locations of the pristine sample and hence showing that the zinc ions are released back into the electrolyte from the host structure.

XPS studies were used to confirm the insertion and deinsertion of zinc ions. The Zn 2p XPS spectra is first compared in the pristine, charged and the discharged samples (Figure 4.11b). The pristine sample shows that the zinc ions are absent in the sample. In the case of discharged sample, Zn 2p_{3/2} (1022.07 eV) and Zn 2p_{1/2} (1045.27 eV) peaks confirm the presence of zinc ions. On charging the cathode, the Zn 2p peak intensities are much lower indicating that the zinc ions are expelled in the charging step. However, the intensity of the peaks is not full reduced to zero, indicating that some zinc ions are still present in the

sample, which is expected from our charge-discharge results that some amount of zinc ions will be irreversibly stored in the host structure in the initial cycles. These results are also consistent with the observations of the zinc insertion inside a layered vanadium oxide host structure where in the initial cycles, some zinc ions are trapped in the host structure. After these initial cycles, the host structure then stores the zinc ions reversibly.^[13]

Figure 4.11 ex-situ characterization studies for PPy-VOPO₄ cathode material. a) XRD b) Zn 2p XPS data c) V 2p_{3/2} XPS data. d) The proposed zinc storage mechanism.

Vanadium XPS studies gives more details on the battery reaction mechanism during the charge-discharge process (Figure 4.11c). The binding energies of the pristine sample at two locations are 517.8 and 516.3 eV. The peaks shift to lower binding energies at the values of 517.1 and 516 eV when the cathode is discharged implying that the vanadium ions are now present in the reduced states. The peaks again shift to higher binding energies when

the battery is charged indicating a reoxidation of the vanadium ion centers. The final binding energy values were found to be 517.5 and 516.3 eV. Even though during the charging step, the peaks move towards the higher binding energy values, the final peak position is still at a lower binding energy compared to the pristine sample. This can be ascribed to the fact that the vanadium-ion centers are not fully oxidized, and is expected since some of the zinc ions remain trapped in the interlayer during the initial charge-discharge cycles as evident in the XPS analysis of the zinc ions. Based on the ex-situ analysis, the overall reaction mechanism can be summarized in Figure 4.11d.

4.4 Conclusion

To conclude, various phosphate materials have been investigated as a reversible zinc storage host structure. The tunnel-type structures such as olivine-LiFePO₄ and the β -VOPO₄ which can reversibly store Li ions via 1-D diffusion channel pathways failed to store Zn²⁺ ions due to high charge density and the electrostatic repulsion. To mitigate the strong electrostatic interaction, open layered-type phosphate materials were tested. VOPO₄·2H₂O shows an open layered structure which could show Zn²⁺ ion storage behavior, but the process was not reversible due to the structural collapse as the water molecules are weakly bonded and can easily be lost. The structural integrity was improved when the interlayer water molecules were replaced by polypyrrole and the battery could show a reversible zinc ions storage for upto 350 cycles at a discharge voltage of 1.1 V and a maximum capacity of 86 mAh/g.

While testing PPy-VOPO₄, however, the material showed severe dissolution in the water solvent. Therefore, the water content in the electrolyte was reduced by adding acetonitrile co-solvent. The acetonitrile solvent reduced the cathode dissolution problem, but also made the battery kinetics sluggish and hence the cathode capacities were limited. Therefore, the acetonitrile and the water solvent ratio had to be tuned to find a right balance between the improvement in the battery kinetics and minimizing the cathode material dissolution. With optimum electrolyte, a maximum operational lifetime of 14 days (350 cycles at a rate of 100 mA/g) could be achieved.

Hence, based on the study of phosphate materials, the host structural integrity was found to be a governing factor in reversible zinc-ion intercalation. While the relatively closed structure such as tunnel-type intercalation materials were found to be stable, the zinc-ion insertion was difficult due to strong electrostatic interactions. On the other hand, open layered-type VOPO_4 based structures did allow zinc-ion storage but had very poor structural stability and were found to either collapse or dissolve in the electrolyte solvent. Hence, simple intercalation-based storage mechanism have the aforementioned challenges and exploration of zinc-ion storage via mechanism beyond the intercalation mechanism is needed.

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Chapter 5

Conversion based oxide host structures for reversible zinc ion storage

This chapter explores conversion-type storage mechanism as an alternative to the intercalation-type storage mechanism studied in the previous chapter. The study begins by exploring binary transition metal oxides which have shown to store Li ions via the conversion storage mechanism, but this family of materials was not found to be able to store zinc ions reversibly. Hence, the ternary oxide family, RVO_4 ($R=Fe, In, Al, Cr$) family which have shown reversible Li storage via conversion mechanism were also tested for zinc-ion storage. $FeVO_4$ showed the best electrochemical performance in this family of materials, hence the conversion-ion storage mechanism was studied in depth using various ex-situ characterization techniques and compared with the Li-ion chemistry.

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5.1 Introduction

An alternative mechanism to the simple intercalation process for electrochemically storing guest cations can be via a conversion or redox reaction which has been well studied in Li systems.^[1] In Li system, the Li^+ ions react with the transition metal oxide host structure to form Li_2O reversibly via the following reaction mechanism: $\text{Li}^+ + \text{M}_x\text{O}_y \rightarrow \text{Li}_2\text{O} + \text{M}$.^[1] Since the guest cation is stored as a separate oxide phase and not within the host structure as in the case of intercalation mechanism, the structural integrity of the starting host material is not a requirement.^[2] Furthermore, the conversion-type material have shown much higher capacities when compared to intercalation-type materials.^[1] Although few other multivalent ions such as Mg and Al are shown to be electrochemically active with conversion-type materials, the conversion-reaction mechanism for multivalent ions is still not very well explored.^[3-4]

5.2 Experimental Methods

Materials and Synthesis:

All the binary oxides used in this study were commercial powders with the particle size <250 nm. The powders used were Co_3O_4 (50nm, 99.5%, Sigma Aldrich), SnO_2 (100 nm, 99% Sigma Aldrich), Sb_2O_3 (250 nm, 99.9%, Sigma Aldrich) RuO_2 (99.9%, Sigma Aldrich), Bi_2O_3 (200 nm, 99.8%, Aldrich), Fe_2O_3 (100 nm, Nanostructured & Amorphous Materials, Inc.)

InVO_4 : This was synthesized using the technique described by Li et al.^[5] 2 mmol of $\text{InCl}_3 \cdot \text{H}_2\text{O}$ (99%, Sigma Aldrich) and 2 mmol of Sodium metavanadate were mixed in 40 mL distilled water in two separate beakers till a transparent solution was obtained. Then ammonium metavanadate was slowly added to the indium chloride solution under constant magnetic stirring to form a turbid solution. This mixture was then transferred to autoclave and then heated at 180 °C for 12h. After the reaction was completed a brown precipitate is obtained which is washed with distilled water and ethanol several times and then air dried.

FeVO_4 : Stoichiometric amount of iron nitrate (99.9%, Sigma Aldrich) and ammonium metavanadate (99%, Sigma Aldrich) are separately dissolved in deionized water. These two solutions are then mixed under constant stirring. The mixture was then transferred to

autoclave and heated at 160 °C for 5 hours. The resultant product was then washed with DI water and acetone and then calcined in air furnace at 500 °C for 2 hours.

CrVO_4 and AlVO_4 were synthesized by a precipitation followed by calcination route.^[6] The stoichiometric ratio of ammonium metavanadate (99%, Sigma Aldrich) and the metal nitrate solution (99%, Sigma Aldrich) are mixed to get a clear solution. Then ammonium hydroxide solution is added slowly to increase the pH value to 2.5 and the obtained precipitate was washed and dried and then calcined in air furnace at 500 °C for 2 hours.

Material characterization: The XRD for all the synthesized materials was carried out using in a Bruker D8 Advance machine in Bragg- Brentano configuration using a Cu $K\alpha$ radiation. The ex-situ XRD pattern of the cycled electrode were also recorded the same way. The cycled electrodes were retrieved after opening the coin cells and then washed with distilled water. The morphology of the FeVO_4 material were characterized using FESEM, JEOL JSM-7600F and TEM JEM-2100F. Raman measurements for the ex-situ studies were done in WITec, Alpha300 SR Raman using a 488 nm incident wavelength. XPS measurements were done using Kratos AXIS Supra using a Al $K\alpha$ source and the peak analysis was done in Casa XPS software. The X-ray tomography was carried out at beamline 1.2W SLRI, Thailand at 1.2 GeV and 150 mA current. A polychromatic radiation using 2.2T multipole wiggler via a Be window was shined on the sample and the mean energy of the beam was 6 keV. The FeVO_4 electrodes were made onto 10 micron thick Ti foil and were cut into 1 mm wide strips and then place on the sample holder. For each sample 1801 sample orientations were scanned at 180 degree rotation. The imaging was done in the absorption contrast mode. The 3D volume resolution was 2.88 microns. The data analysis was done using ImageJ and Drishti software.

Electrochemical measurement: The electrochemical testing was done in a coin cell of 2016 type. Cathode electrodes were made using a Titanium foil 30 micron thick as the substrate and then drop casting the slurry and then vacuum drying the coated substrate at 60 °C overnight. The slurry was made by mixing the appropriate active material with PVDF binder and super P carbon with a weight ratio of 60:20:20 using N-methyl-2-pyrrolidone solvent. The mass loading was 1-2 mg per electrode. The electrolyte used was 1 M

$\text{Zn}(\text{OTf})_2$ in water. CV and EIS measurements were done on Solartron Analytical 1470E. The in-situ pH measurement was done in a flooded beaker cell with 15 mL electrolyte in a Zn-FeVO_4 system using M300 Mettler Toledo pH meter and the measurement was done at a duration of every one minute.

5.3 Results and Discussion

5.3.1 Preliminary investigation on binary transition metal oxides

Since a lot of binary transition metal oxides were shown to be electrochemically active for Li ion storage, the same materials were explored for the zinc ion storage system. Some of the commercially available binary oxides were electrochemically tested such as Co_3O_4 , SnO_2 , Sb_2O_3 , RuO_2 , Bi_2O_3 , and Fe_2O_3 . While most of the binary oxide materials were found to be electrochemically inactive for zinc ion storage, the ones which were found to be electrochemically active showed a drastic capacity fade within the first few cycles (Figure 5.1). This has also been usually observed with some conversion oxides in the Li system which can be due to poor electronic conductivity of the host matrix and/or due to large volumetric expansion.^[7] The volumetric expansion problem could be mitigated if the host also contains additional unreactive elements which may not participate in the reaction but can still hold the matrix together. Hence, ternary metal oxides were explored.

Figure 5.1 Charge-discharge curves for a) Fe_2O_3 , b) RuO_2 and c) Bi_2O_3 .

5.3.2 Ternary Oxides: metal vanadates

The metal vanadates, RVO_4 , where R is a trivalent metal ion, like Fe, In, Al have been tested as a conversion-type host structure for reversible Li ion storage.^[6] In Li systems, InVO_4 and FeVO_4 materials have shown high capacities of values higher than 500 mAh/g

and were shown to be reversible for more than 50 cycles.^[8] Additionally, FeVO_4 material has shown to be electrochemically active for other multivalent ions such as Mg and Al with the capacity values greater than 180 mAh/g.^[3-4] However, the exact reaction mechanism has not been explored yet. For these reasons, the study of conversion-type storage mechanism for zinc-ion storage was done using RVO_4 family of materials.

Figure 5.2 Preliminary investigation of RVO_4 ($\text{R}=\text{Al}, \text{Cr}$) shows that these materials are inactive for zinc ion storage.

5.3.3 Preliminary investigation of RVO_4 ($\text{R}=\text{Al}, \text{Cr}, \text{Fe}, \text{In}$)

Similar to the Li-ion system, AlVO_4 and CrVO_4 were found to be inactive for zinc-ion storage (Figure 5.2). The XRD fitting details are given in the Table A. 1. The materials were inactive which was ascribed to a very ionic R-O bond ($\text{R}=\text{Al}$ or Cr). If the R-O bond is highly ionic, the V-O bond is very covalent and hence very stable and therefore doesn't have any driving force for introduction of guest cation (or infusion) in the host structure.^[6] On the other hand, both InVO_4 and FeVO_4 were seen to be electrochemically active for zinc-ion storage as also observed for the case of Li-ion storage (Figure 5.3). Since the initial capacity of the FeVO_4 material is much higher than the InVO_4 material as discussed later,

FeVO_4 material was chosen to understand the conversion-type storage mechanism in-depth for the zinc-ion storage in the rest of the chapter.

Figure 5.3 Preliminary investigation of InVO_4 cathode material shows its active for reversible zinc ion storage.

5.3.4 FeVO_4 : material characterization

Figure 5.4 Material characterization for synthesized FeVO_4 a) XRD pattern b) crystal structure c)

SEM micrograph and d), e) TEM images and f) TEM-EDX of a FeVO₄ nanorod.

The FeVO₄ material synthesized was single phase as can be confirmed from the XRD data (Figure 5.4a). The material is triclinic with the space group of P-1 with the lattice parameters of $a = 6.714(1)$ Å, $b = 8.066(1)$ Å, $c = 9.352(1)$ Å, $\alpha = 96.68(1)^\circ$, $\beta = 106.67(1)^\circ$, $\gamma = 101.53(1)^\circ$, similar to a previous report (Figure 5.4b).^[9] The full Rietveld fitting details is shown in Appendix

Table A. 2 The morphology of the synthesized FeVO₄ is in the form of nanorods as can be seen in the TEM and SEM images (Figure 5.4c,d,e). The length of the nanorods is roughly 4 to 5 micrometers and the diameter is in the range of 200-300 nm. The homogeneity of the elements in the sample can also be seen in the TEM-EDX image (Figure 5.4f).

5.3.5 FeVO₄: Electrochemical Activity

The electrochemical activity of the FeVO₄ material for zinc ion storage was first tested using a CV test (Figure 5.5a). The first negative or cathodic sweep showed a sharp reduction reaction at 0.6 V followed by a broad peak roughly at 0.3 V. After this first reduction sweep, the oxidation and the reduction in the subsequent steps were seen to be reversible at the voltage values of roughly 0.6 and 0.4 V respectively. This behavior indicates that the first discharge process shows some irreversible reactions which have also been observed with Li and K ion storage in FeVO₄ host structure previously.^[10-11]

The galvanostatic charge-discharge curves gives more details of the observations made in the CV test (Figure 5.5b). The first discharge cycle shows a voltage plateau at around 0.65 V which is followed by a gradual sloping profile. The voltage plateau is not observed in the subsequent charging and discharging cycles and only a gradual sloping profile is observed and this observation is consistent with the CV profile. The flat voltage plateau is also commonly observed in the conversion-type reaction of other transition metal oxides,^[7, 12-14] and have been ascribed to irreversible two phase reaction in the initial cycle.^[14-15] The phases involved in this step were explored using the XRD studies later in this chapter. Furthermore, the irreversibility in the first step is also reflected in the capacity values where the discharge capacity drops from 348 to 272 mAh/g in the second cycle.

Figure 5.5 a) CV and b) GCD curves of Zn-FeVO₄ system using 1 m Zn(OTf)₂/water electrolyte. c) and d) the cycling stability test at two different current rates. e) the evolution of EIS spectrum in the first few cycles for high current rate test at 3 A/g.

5.3.6 FeVO₄: Electrochemical Performance

The electrochemical performance of the FeVO₄ material in the RZIB system was done using the charge-discharge cycling test at both slow and fast rates of 60 mA/g and 3000 mA/g, respectively (Figure 5.5c,d). At slow rates, the battery could run reversibly for 140 cycles and could still retain a capacity of 156 mAh/g or 57.3 % of the second discharge

capacity. On the other hand, at a fast current density of 3000 mA/g, the cathode can still maintain a high discharge capacity of 180 mAh/g for more than 300 cycles. However, unlike the case for slow rate testing, the capacity increases in the first few cycles. This rise in the capacities is also consistently observed in other RZIBs tested at fast rates and has been ascribed to the gradual activation of the electrodes when the zinc-ions are kinetically limited to react with the host structure.^[16-18] This behavior is also reflected in the EIS measurement showing a high charge transfer resistance in the initial cycles, which later reduces after 20 cycles (Figure 5.5e). The rate capability test for the system is also shown in Figure 5.6. It is to be noted that at very high current rates of 5 A/g, the system can show very poor capacities which can be pointed out to the limiting diffusion reaction involved in the phase changes.

Figure 5.6 Zn-FeVO₄ system rate capability test.

5.3.7 Phase evolution of FeVO₄ during zinc ion storage

The evolution of the phases during the charge-discharge process was studied by the ex-situ XRD (Figure 5.7). During the first discharge step, the ex-situ XRD was taken just before the battery reached the plateau state, after the plateau state and at the end of the discharge as shown in the inset of the Figure 5.7. Thereafter, for the subsequent cycles the ex-situ

XRD were taken for the 4th cycle discharge and charge, 4D and 4C respectively and in a similar way for the 10th cycle.

Figure 5.7 Ex-situ XRD characterization of the FeVO_4 cathode electrodes at various charge-discharge states.

In the first discharge step, FeVO_4 phase is still present before the plateau is reached (at 0.7 V), but the phase amorphized when the battery is discharged further below the plateau voltage (0.6 V). Hence, the FeVO_4 phase amorphized during the two phase reaction and this observation is consistent with Li conversion reaction with transition metal oxides.^[7, 15] Moreover, in all of the subsequent cycles, the crystalline FeVO_4 phase was not detected in the cathode implying that the amorphization that occurred in during the two phase reaction is irreversible and it is only the amorphous matrix that is responsible for the zinc ion storage. Additionally, in the subsequent cycles ZnO (PDF-01-083-6338), metallic Fe (PDF- 04-017-1577), and $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (PDF- 00-057-0572), were detected and has been discussed below.^[19-21]

ZnO phase: ZnO phase appears after the plateau region (0.6 V) and then the peak intensity grows stronger until the end of the first discharge cycle (1D). Hence, the ZnO phase starts forming after the plateau voltage and is continuously formed until the end of the discharge

cycle. Thereafter, in the subsequent cycles, ZnO phase disappears in the charging step (4C and 10C) and appears again in the discharging step (4D and 10D), indicating that zinc ions are stored reversibly in the form of ZnO phase after reaction with the host structure.

During the plateau reaction, metallic Fe is also simultaneously formed as ZnO phase is formed and the FeVO₄ host structure amorphizes and this is also observed in the Li-FeVO₄ system.^[8, 22] Furthermore, the metallic Fe is present in all the systems indicating that this phase is also formed irreversibly. Although the phase is permanently present in all the samples, the lattice parameters were seen to change during the charging and the discharging step as shown by the shift in the peak position in the Figure 5.7. Pawley fitting for the charged and the discharged electrodes (10C and 10D) showed a lattice parameter of 2.9090(7) Å and 2.922(1) Å respectively. The exact reason for this shift is still not very clear. However, the formation of Zn-Fe alloying is unlikely as the change in the lattice parameter is in the scale of picometer.^[23-24]

Finally, third phase detected after the plateau region was, Zn₃V₂O₇(OH)₂.2H₂O (PDF- 00-057-0572) which is a layered type structure as shown in the Figure 5.8a.^[19] This phase is present in all the samples indicating that the formation of this phase is irreversible. This phase is expected to form when the pH of the electrolytes turn more basic to values higher than 5.^[21] In-situ pH measurement shows that pH of our electrolyte shifts to more basic values as the battery runs and goes to values higher than 6 (Figure 5.8b). The shift in pH indicates that the electrolyte is turning basic which can be caused by the zinc corrosion reaction and the simultaneous proton loss via the hydrogen evolution reaction.^[25] Since the electrolyte decomposition occurs continuously the RZIB runs, the amount of this phase also increases at much later cycles as can be seen by more intense Zn₃V₂O₇(OH)₂.2H₂O peaks in the 10th cycle compared to 4th cycle.

Figure 5.8 Crystal structure of the $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ phase and (right) the in-situ pH evolution of the Zn-FeVO₄ system in the first few cycles.

5.3.8 Redox reactions of the transition metal centers

The changes in the oxidation state of the transition metal centers Fe and V can give more information about the reaction mechanism. The Fe oxidation state is measured using XPS studies for the pristine, charged and the discharged sample as shown in the Figure 5.9a. The pristine sample shows Fe in +3 state at two binding energies which should represent the two different coordination environment of trigonal bipyramidal and octahedral in the triclinic-FeVO₄ crystal structure.^[22] After discharging, the binding energy of the green model peak shifts to lower binding energies indicating that Fe²⁺ species is also present which again converts to +3 oxidation state during charging.^[26] This behavior is consistent with the observation made in RVO₄ type materials with Li where the trivalent species R reduces to oxidation states between 0 and +3 when during discharging.^[8] Furthermore, metallic Fe was also observed in the discharged sample as expected from the XRD results.^[27-29] However, no metallic Fe was detected in the charged sample unlike XRD results, and this anomaly can be due to the difference the sample area probed in the two different techniques wherein XRD is bulk technique and XPS is surface technique. Hence XPS and XRD studies have shown that some of the Fe species permanently converts to metallic Fe and the remaining Fe reversibly converts between +2 and +3 oxidation states during battery cycling.

The XPS spectrum of V 2p_{3/2} range is also shown for the pristine, discharged and the charged samples (Figure 5.9b). The pristine sample shows that the oxidation state of V is in +5 state.^[30] On discharging, another peak appears at lower binding energy which can be

fitted with the +4 oxidation state indicating a reduction of the vanadium ion during the zinc ion storage. Furthermore, after charging both the +5 peak and +4 peak are still present in the sample. However, the intensity of the +4 oxidation state peak reduces, indicating that most of the V ion species are again oxidized back to +5 state while some V ions remains irreversibly reduced to +4 state. This irreversible reaction is expected as we see an irreversible amorphization of the FeVO_4 matrix and the formation of irreversible phase $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$.

Figure 5.9 a) and b) ex-situ XPS studies on the cycled FeVO_4 electrodes and c) ex-situ Raman studies.

5.3.9 Local structure evolution of FeVO_4

Since the FeVO_4 original crystal structure amorphizes in the first cycle and the long range ordering of the host structure is lost, Raman studies were carried out to understand more details at the short range ordering (Figure 5.9c). The pristine sample shows V-O-V deformation in the range of 300 to 550 cm⁻¹, V-O-Fe bridging and V-O-Fe stretching in the range of 550 to 770 cm⁻¹ and bridging V-O-Fe stretching between 700 and 880 cm⁻¹ and terminal V-O stretching between 880 to 950 cm⁻¹.^[3, 31-33] In the discharged samples (4D and 10D) the 300-550 peaks red-shifts and recovers during charging as also observed in other Li systems and indicates a reversible local expansion of the crystal lattice.^[34] The 700-1000 range peaks becomes a broad single peak at 850 cm⁻¹ after discharging the

process and is reversible. This behavior has also been observed during the Li insertion in V_2O_5 host structure.^[35] Finally, though all the Raman spectra are not identical, the overall profile switches reversibly between the charged states (4C, 10C and pristine) and the discharged states (4D and 10D). This indicates that even though the $FeVO_4$ structure loses the long range order, as seen in the XRD studies, the structure still reversibly reacts in the short range order.

5.3.10 3D morphological evolution of $FeVO_4$

The conversion-type reaction mechanism are also expected to show a volume change and therefore, X-ray tomography was used to study the volume change visually at the sub millimeter scale (Figure 5.10). Pristine, charged and discharged samples are compared. The high X-ray absorption or the dense area represents the bulk material (red colored) and the low absorption region represents the surface material (blue colored).

When comparing the images, the pristine sample shows a flat and smooth morphology because of the electrode fabrication process. On discharging (4D) the sample surface becomes rougher and is expected when a new phase is formed which is consistent with the conversion reaction. The sample surface relatively smoothens in the charged sample (4C) and the same behavior is also observed in the charged and discharged samples in the 10th cycle. The bulk material volume expansion can be estimated by the porosity analysis. The porosity values were (in %): 9.9 in pristine, 13.9 in 4D, 12.3 in 4C, 15.4 in 10D and 13.2 in 10C. Hence, the porosity is increased upon discharging which decreased reversibly upon charging. Therefore, the material reorganization is not only observed at the angstrom level as seen in the XRD and Raman measurements but also in the sub millimeter scale which further supports the conversion-type storage mechanism.

Figure 5.10 Representative tomography images of pristine, 4D, 4C, 10C and 10D electrode showing morphological evolution in electrode upon discharge-charge. Blue and red colors represent low and high X-ray attenuating phases, respectively. The smaller adjacent figures shows the red and the blue region separately.

5.3.11 FeVO₄ Reaction Mechanism

The overall reaction mechanism can be deduced based on all the above studies (Figure 5.11). During the first discharging step: the FeVO₄ material amorphizes along with the formation of two new phases: ZnO and metallic Fe. The Zn²⁺ ions from the electrolyte is reversibly stored in the cathode as the ZnO phase and the metallic-Fe formed is irreversible. The transition metals V and Fe in the amorphous matrix oxidize and reduce reversibly with changes in the local or short-range order as seen in the Raman and XPS studies. The reaction mechanism after the 2nd cycle for zinc ion storage will be: $a\text{-FeVO}_4 + x\text{Zn}^{2+} + xe^- \rightleftharpoons a\text{-FeVO}_{(4-x)} + x\text{ZnO}$. Furthermore, the electrolyte decomposition due to HER reaction leads to increase in the electrolyte pH which leads to the formation of $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ as a side-reaction product.

Figure 5.11 The proposed conversion reaction mechanism in the Zn-FeVO₄ system.

5.3.12 Limitations in the Zn-FeVO₄ system from the aqueous electrolyte

Although the cathode material showed good reversibility of the zinc ion storage during the charge and the discharge cycles, some of the battery failed abruptly after ~100-150 cycles. The coin cells were opened and was found that the separator from the zinc metal anode side are damaged (Figure 5.12a,b). The surface of the zinc foil also showed sharp plate like morphology as shown in Figure 5.12c. This indicates the zinc deposition occurs in a highly non-uniform way which can pierce the separator and hence causing a short circuit and causing the running battery to die. Furthermore, the formation of the Zn₃V₂O₇(OH)₂·2H₂O phase was also the result of electrolyte decomposition via HER. Hence, the electrolyte forms one of the cause to limit the operational battery lifetime and better electrolytes are to be explored.

Figure 5.12 SEM images of a), b) separator and c) zinc metal anode after long cycling (>100 cycles)

of a Zn-FeVO₄ battery.

5.4 Conclusion

This chapter explores the conversion-type zinc ion storage in the cathode material. Few of the binary transition metal oxides were tested and none of them could show a reversible zinc ion storage behavior. Then the cathode host oxide structures with two metal ions were explored in RVO₄ (R=Fe, In, Al, Cr) material family and few materials in this family could reversibly store zinc ions. FeVO₄ showed the best electrochemical performance in this material class and therefore an in-depth zinc ion storage behavior was studied. The mechanism explored here resembled closely to the mechanism observed in the Li-FeVO₄ system. The guest cation or zinc-ions are stored as ZnO. Furthermore, the host structure amorphized after the first discharge step and metallic Fe is also formed. In terms of the electrochemical performance the cathode host structure could show a high 2nd discharge capacity of 272 mAh g⁻¹ at 60 mA/g and also a high reversibility of 300 cycles at a high current rate of 3 A g⁻¹ and retaining a high capacity value of ~180 mAh g⁻¹. We also note that conversion based cathode materials Li and Na systems although have been under intensive research had difficulties in commercialization. The same trend might hold true with RZIB system.

From the electrolyte formulation perspective, the battery also showed some undesired reactions related to the aqueous electrolyte. Firstly, the electrolyte decomposition via HER lead to an increase in the pH of the electrolyte and therefore Zn₃V₂O₇(OH)₂·2H₂O as a side-reaction product were formed on the cathode. Furthermore, the zinc deposition morphology at the anode were not very uniform and in some cases the zinc anode could damage the separator leading to a sudden failure of a running battery. Finally, the cathode capacity was seen to fade especially at slow cycling rates. At 60 mA/g, only ~57% of the initial capacity could be retained after 140 cycles and this fading can be ascribed to the cathode material dissolution in aqueous electrolyte during cycling.^[36] Hence, a better electrolyte is to be explored for harnessing the full potential of the cathode materials and making a long lasting RZIB.

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Chapter 6

Ethylene Glycol-based zinc electrolyte formulation for reversible zinc ion storage

This chapter aims at exploring a better electrolyte to mitigate the challenges in the widely used aqueous electrolytes as observed in the literature and also in the previous two chapters. Ethylene Glycol which shares a lot of similarity with water as a solvent was used to make the zinc electrolyte formulations. The physico-electrochemical properties of the electrolyte formulations were studied and the synchrotron EXAFS and FTIR techniques were used to get insights in the salt-solvent molecular level interactions. Finally, the EG-based electrolytes were compared to the conventional aqueous electrolytes from the RZIB perspective. Compared to the aqueous electrolytes, the EG-based electrolytes showed: 1) a suppressed zinc metal corrosion at rest, 2) expanded voltage stability windows upto 2.2 V, 3) enhanced zinc stripping/plating durations up to 2.4 times longer than aqueous electrolytes, 4) much uniform zinc electrodeposition morphology, and 5) improved cycling stability by more than two times due to a limited cathode material dissolution.

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6.1 Introduction

Aqueous electrolytes are the most widely used electrolyte for RZIB. Nevertheless, the aqueous electrolytes are not the best choice for RZIBs because of various factors. Firstly, as shown in the previous chapters, the cathode host structure can dissolve in the aqueous electrolytes which can cause the cathode capacity to fade out during repeated charging/discharging.^[1] Secondly, even at the electrolyte and the zinc metal anode interface, the zinc deposition during the charging or the zinc plating process can be highly non-uniform. The non-uniformity of the zinc metal anode deposition can lead to the formation of dendrite which can grow to big enough size and can damage the battery separator and can ultimately lead to cell failure. Thirdly, the voltage window of the water-based electrolyte is low and thus the electrolyte can lead to a continuous decomposition either via HER at the zinc metal anode during the discharging step or by OER at the cathode during the charging step.^[2-3] Therefore, exploring other type of electrolytes is of crucial importance to prevent these undesired reactions.

Deep Eutectic solvent (DES)-type electrolytes can be an alternative to the conventional aqueous electrolyte. The polar protic molecules which can also act as a hydrogen bond donor such as urea and acetamide have been used to dissolve zinc salts to form liquid zinc electrolyte formulations.^[2-3] These electrolytes have demonstrated better zinc anode compatibility and much less capacity fading.^[3-4] The zinc salts can dissolve in these medium because these molecules can act as Lewis/Bronsted acid-based and can interact with the zinc salt cation and the anion.^[5-7] Among the various choices of the hydrogen bond donor species, Ethylene Glycol can be a promising solvent for the zinc salt electrolyte formulations. Most other hydrogen bond donor species are solid, and therefore the zinc electrolyte formulations are difficult and the resulting formulations are very viscous and in some cases other diluting agent such as water had to be added to reduce the viscosity.^[3] Ethylene Glycol (EG) on the other hand, is liquid and therefore the electrolyte formulation process can be much easier. Furthermore, the EG molecules also have O-H groups and shares a lot of solvent properties with water including high polarity, high donor number, high dielectric constant as shown in the

Table 6.1 (values taken from ^[8-9]).

Table 6.1 Solvent properties of water and ethylene glycol

Solvent	Formula	Melting Point (°C)	Boiling Point (°C)	Donor Number	Dielectric Constant	Polarity (Debye)
Water	H ₂ O	0	100	18	80.2	1.85
Ethylene Glycol	(CH ₂ -OH) ₂	-12.6	197.6	20	41.4	2.36

In this chapter EG has been explored as an alternative solvent to water for the zinc electrolyte formulations. Two salts were used in this study with two different anion coordination strength. The anion coordination strength of the triflate anion is very weak and the anion coordination strength of the chloride anion is very strong.^[10-11] For these reasons, ZnCl₂ and zinc triflate (Zn(OTf)₂) salts were used. The two extreme anion coordination strengths were used so that a general scenario of the salt- solvent interaction can be deduced when any other zinc salt is used. The work begins by measuring the physical properties of the electrolytes. Thereafter, the salt-solvent interactions were characterized to explain some of the physical properties observed. Finally, the EG electrolyte was compared with the conventional aqueous electrolytes to check the compatibility with the zinc metal anode and also with the cathode materials to see the improvements in the full cell battery performance.

6.2 Experimental Methods

Electrolyte formulation: Ethylene glycol (99%, Sigma Aldrich) was kept in molecular sieves for a day to dry any absorbed moisture. Zn(OTf)₂ (98%, Sigma Aldrich) and Zinc chloride (anhydrous, 98%, sigma aldrich) are added in appropriate stoichiometric amount to the EG solvent and then heated to 60 °C with continuous stirring for 5 h. The electrolyte are then placed in glass vials with molecular sieves.

Physical Property characterization: DSC measurement was carried out using Q10 TA instruments at a scan rate of 5 °C per minute by first cooling the samples to -80 °C and then heating them up to a temperature of 40 °C. The viscosity were measured using Brookfield DV3T rheometer. Specific ionic conductivity was measured in Orion 3 star,

Thermoelectron corporation USA. The water content of the electrolytes are measured in CA-200 Coulometric Karl Fisher Titrator, Mitsubishi Chemical. The cationic transference number was calculated using Bruce-Vincent method^[12] in Biologic SP-200 machine. A constant voltage polarization of 5mV (ΔV) was applied for 18 h and the initial and the final passivation resistance (R_o and R_s) was found by fitting the first semicircle EIS data. $T = (I_s(\Delta V - I_o R_o)) / (I_o(\Delta V - I_s R_s))$ was used to calculate the transference numbers. LSV was used to measure the voltage window of the electrolytes in a three electrode setup using Ag/AgCl as the reference electrode and Ti as both working and the counter electrodes at a scan rate of 3 mV/s and the cutoff current density of 1 $\mu A/cm^2$.^[13]

Electrolyte structural characterization: FTIR measurement were carried out in Nicolette iS50 ATR Thermo Scientific for the range of 500-4000 cm^{-1} and averaged after 32 scans. EXAFS measurement was carried out at BL 5.2, SLRI Thailand. Zn K-edge was scanned at a beam current of 80 mA. Germanium 220 was used as a monochromator up to a maximum k range of 12 $\text{\AA}^{-1}$ and averaged for 5 scans. The data analysis was done using Athena and Artemis software and the S_o^2 value was estimated to be 0.61 using a standard 2 m Zn(OTf)₂ in water electrolyte.

Electrochemical characterization: The full cell performance was carried out in the same way in 2016 type coin cell as described in the experimental methods section of chapter 5. The zinc stripping/plating tests was also carried out in a similar way but with zinc foils being used as both the anode and the cathode.

Post-mortem zinc stripping/plating test: XRD pattern were collected in Bruker D8 Advance diffractometer in Bragg-Brentano geometry. The aged zinc foils or the zinc foils from the stripping/plating coin cells were washed with deionized water and dried in air before collecting the XRD pattern. The SEM images were collected using FESEM JEOL, JSM-7600F.

6.3 Results and Discussion

6.3.1 Physical Property Characterization

Salt solubility and stability: The salts $\text{Zn}(\text{OTf})_2$ and zinc chloride show high solubilities in the EG solvent and the maximum molar ratios that can be achieved are 1:5 and 1:3 respectively as shown the Figure 6.1a. These liquid electrolyte formulations can remain stable in the liquid state even after 10 months. The water content, when measured using the Karl Fisher titration, is roughly 1.2 to 1.4 wt%. The liquid phase stability is also seen at low temperatures as the electrolytes do not crystallize to temperatures as low as $-80\text{ }^\circ\text{C}$ when measured using DSC (Figure 6.1b). This high stability in the liquid phase can be ascribed to the anti-freezing behavior of EG.^[14]

Ionic conductivity and viscosity: Since the DES-type electrolytes are in general more viscous than the conventional aqueous electrolytes, the ionic conductivity and the viscosity were measured (Figure 6.1c,d). The ionic conductivity was in the range of 0.1 to 2.5 mS/cm. This range of ionic conductivities is less by one order when compared to conventional aqueous electrolyte ($\sim 40\text{--}60\text{ mS/cm}$).^[15] However, these values are still comparable to other DES based electrolytes ($0.01\text{--}0.1\text{ mS/cm}$)^[7] and larger than the polymer based electrolytes ($10^{-4} - 10\text{ mS/cm}$).^[16] Furthermore, the separate contributions coming from the cations and the anions in the electrolyte formulations can be estimated by calculating the transference numbers. The transference number for saturated $\text{Zn}(\text{OTf})_2$ and zinc chloride electrolytes were found to be 0.52 and 0.44 respectively (Figure 6.2), and is of the same order when compared with other DES type electrolytes ($\sim 0.5\text{--}0.6$).^[2, 17] The ionic conductivity shows an initial increase, peaks at a point and then starts to reduce again (Figure 6.1c,d). This behavior will be explained after the structural characterization.^[18-19]

Figure 6.1 a) The image of the ZnCl₂/EG= 1:3 electrolyte and Zn(OTf)₂/EG=1:5 electrolyte, b) DSC test for the two prepared electrolytes, c) and d) the ionic conductivity and the viscosity trends of the two electrolyte systems, e) and f) the voltage window measurement for the two systems which are also compared with the corresponding aqueous electrolytes. The voltage window was determined using the cutoff current density of 1μA/cm².^[13]

Electrochemical stability voltage window: The electrochemical voltage window of the electrolytes for a EG based saturated formulation, dilute formulation along with one of the conventional aqueous electrolyte is measured for both the zinc chloride and the Zn(OTf)₂ salts and is shown in the Figure 6.1e,f. When compared to the conventional aqueous electrolytes, the dilute EG electrolytes almost show a similar voltage stability window. However, as the electrolyte salt concentrations reaches to near saturation values, the

voltage stability window are much larger when compared to the voltage window of the conventional aqueous electrolytes. A voltage window of 2.2 V and 1.6 V was observed in the $\text{Zn}(\text{OTf})_2$ and the zinc chloride systems respectively and a similar expansion has also been observed with other DES type electrolytes.^[2]

Figure 6.2 Transference number calculation for the two electrolyte systems. The voltage profile after the application of the constant current of 5 mV is recorded along with the impedance spectra before and after the polarization. The EIS spectra are then fitted using a model circuit to obtain the charge-passivation resistance values. The resistance and the current values are then used to calculate the transference number.

Notably, the voltage window expansion is observed mostly on the anodic sweep and not much towards the cathodic sweep. This is due to the fact that the negative current during the cathodic sweep is not solely the electrolyte decomposition but has a combined contribution of the zinc electrodeposition phenomena as well.^[20] Hence, even if the HER process is suppressed, the zinc electrodeposition process will still be active and contribute to the negative current in the reduction sweep of the LSV scan. Nevertheless, the reduction

in the HER process can be confirmed via other studies as shown later in this work. The voltage window of chlorides in general are observed to be smaller than the triflate based electrolytes because the chloride ions are prone to oxidize at higher voltage values.^[16, 21]

The trends in the ionic conductivity, viscosity, electrolyte voltage window can be explained once we elucidate the zinc salt solvent interactions. The next section will focus on the structural characterization aspect via the FTIR and the EXAFS characterization techniques.

6.3.2 Structural Characterization

FTIR: FTIR technique was used to observe the changes in the bonds of the EG solvent molecules as any interaction of the EG molecules with the zinc salts is expected to locally modify the bonds in the EG molecule. The $\text{Zn}(\text{OTf})_2$ salt concentration is increased in the EG solvent and the evolution of FTIR spectra is recorded and shown in the Figure 6.3.

The Figure 6.3a shows a peak at 3300 cm^{-1} which represents the O-H stretching vibrations in the EG molecule.^[22] As we increase the $\text{Zn}(\text{OTf})_2$ salt concentration, the peak intensity diminishes which indicates that the fraction of free or the uncoordinated EG molecules in the system is much lower.^[23-24] Furthermore, the peaks width also increases and as a result the overall peak becomes much broader along with a shift to smaller wavenumbers. This shift has also been observed in other multivalent ion salts in EG.^[25-26]

In Figure 6.3b, two peaks can be observed which can be ascribed to the C-O stretching vibration.^[22] On increasing the zinc salt concentrations, we see that the peaks shift to lower wavenumbers region and this same behavior has also been observed in the Ni and Co complexes formed with the EG molecules.^[27-28] This shift is an indication that the C-O bond in the EG molecule becomes weaker and is expected when the electron loan pair from the oxygen ions are donated to the zinc ions as shown in the figure.^[25-26] Furthermore, no indication of emergence of new shoulder peaks or peak splitting were observed. This is an indication that each of the oxygen atom in the ethylene glycol molecules has exactly same electron density implying that both the oxygen atoms are bonded to the zinc ion center or the ligand is bidentate.^[25-26, 29]

Figure 6.3 a), b) and c) Evolution of FTIR spectra on increasing the $\text{Zn}(\text{OTf})_2$ salt concentration in EG. d) schematic of the expected bidentate EG chelation on the zinc-ion center.

Finally, in Figure 6.3c, the peaks at 882 cm^{-1} represents the CH_2 rocking and the peak at 860 cm^{-1} represents the C-C stretching respectively.^[22] When the O atoms bind to the zinc ion centers the carbon atoms bonded to the oxygen is also affected and as a result the C-C bond and the C-H bond are also affected and this same effect has also been observed in other multivalent metal ion complexation with the EG molecules.^[26]

The same trend in the FTIR data has also been observed in the series of the zinc chloride salt as well (Figure 6.4), indicating that the EG molecule can act as a bidentate ligand in this system as well and is independent of the salt anion used. EXAFS studies can give an even better understanding of the nature of the EG molecule interaction with the zinc ion center for both the triflate and the chloride system.

Figure 6.4 Evolution of the FTIR spectrum on increasing the ZnCl_2 salt concentration in EG.

EXAFS: The EXAFS signals were recorded for four cases: zinc chloride and zinc triflate in EG at dilute salt concentrations and also at the near saturation levels and is shown in the Figure 6.5a,b. The zinc K-edge EXAFS data can give an idea about the coordination shell around the zinc ion center. Every coordination shell, which is a group of equidistant atoms from the zinc ion center, will give rise to a peak in the EXAFS spectrum. The data fitting can give an information about the number of the atoms present in the coordination sphere (which for the first shell can be called as the coordination number) and the type of the atom by fitting the intensities.^[30] The data fitting can also give an idea of the distance of the coordination sphere from the zinc ion center with the phase modulation corrected. All the spectra have no major peaks that appear after a radial distance of $3.5 \text{ \AA}$ which indicates that in all the samples there are no fixed coordination sphere present at distances farther than roughly $3.5 \text{ \AA}$. In other words, the samples show an amorphous behavior away from the zinc ion center. However, high intensity peaks can be seen at distances close to the zinc ion center as explained below and the data analysis results are shown in the Table 6.2.

Figure 6.5 a) and b) The Fourier transformed EXAFS spectrum of the electrolyte systems. Schematic of the zinc coordination structure in $\text{Zn}(\text{OTf})_2/\text{EG}$ system in c) dilute and d) saturated salt concentration levels. e) the schematic of the zinc coordination structure in the dilute concentrations of ZnCl_2/EG (molar ratio 1:18).

Table 6.2 EXAFS fitting details for the electrolytes

Sample	Element	N^a	$R(\text{\AA})^b$	$\Delta E_o (\text{eV})^c$	σ^{2d}	R-factor ^e
$\text{Zn}(\text{OTf})_2/\text{EG}$ (1:18)	O	5.6^λ	2.072	8.268	0.004	0.007
	C	5.2^λ	2.865	8.268	0.007	
$\text{Zn}(\text{OTf})_2/\text{EG}$ (1:5)	O	5.5^λ	2.076	8.362	0.005	0.003
	C	3.8	2.894	8.362	0.005	
ZnCl_2/EG (1:18)	Cl	2.4	2.223	1.253	0.003	0.001
	O	1.8	2.083	1.253	0.002	
ZnCl_2/EG (1:3)	Cl	2.1	2.215	-1.323	0.002	0.018
	O	1.4	2.073	-1.323	0.003	

^a Number of atoms. ^b Distance from zinc-ion ^c Shift in energy at $k=0$. ^d Mean square disorder in R. ^e Fractional misfit ^λ The number of atoms appears less than 6 since the second shell C peak has a high contribution to the first shell O atoms as also observed previously.^[5, 31]

Zn(OTf)₂/EG system: When the salt concentrations are low (1:18), a high intensity peak is observed roughly at 1.6 Å (Figure 6.5a). This peak could be fitted with 6 oxygen atoms which are equidistant from the zinc ion center at a distance of ~ 2.07 Å.^[32] Note that the calculated bond distance is higher when compared to the peak position in the figure which occurs due to the phase shifts in the signal.^[30] Furthermore, the second peak appears as a shoulder peak at 2.2 Å is also seen in the spectrum. This peak could be fitted with roughly 6 carbon atoms at an average distance of 2.8 Å. The similar combination of 6 O atoms and 6 C atoms at the distances mentioned here were also observed in Ni²⁺- Ethylene glycol complex.^[5] The structure was described to be comprising of three EG molecules and all of them bind to the transition metal-ion center in a bidentate way.^[33-34] Indeed, a similar combination of three EG molecules coordinating a zinc ion center has also been experimentally found using the XRD studies of solids of Zn²⁺ - EG complexes.^[11, 35] Based on these arguments, this electrolyte formulation will have a similar Zn²⁺-EG chelation as shown in the Figure 6.5c.

When the Zn(OTf)₂ salt concentration reaches the saturation levels, the first peak could be fitted with roughly 6 oxygen atoms, while only 4 carbon atoms were needed to fit the second peak (Table 6.2). This combination of the number of carbon and oxygen atoms indicate that only 2 EG molecules are now bonded to the zinc ion center. This trend of reduction in the solvent molecule is expected from the FTIR results which indicated that the system becomes deprived of the solvent molecules. Similar trend of a reduction in the solvent-salt interaction has also been observed in systems with saturation level zinc salt concentrations with other hydrogen bond donors.^[2, 36] These studies also pointed out that the salt anion remains attached to the zinc ion center. This result can indicate that the remaining two oxygen atoms in the first coordination sphere most likely are contributed from one triflate anion, and thus the rough expected structure will be from 2 EG molecules forming a bidentate ligand with the zinc ion center and one triflate anion still attached to the zinc ion center as shown in the Figure 6.5d.

ZnCl₂/EG system: Since the coordination strength of the chloride anion is higher than the triflate anion,^[11] the observed EG chelation occurs at a much lower extent. The presence of both the Cl and O atoms in the first coordination sphere even at a dilute concentrations

supports the argument Figure 6.5b. This trend indicates that unlike the case of triflate anion which were not bonded to the zinc ion center at dilute concentrations, the chloride anion is bonded to the zinc ion center even at dilute concentrations. The EXAFS spectrum could be fitted with 2 Cl atoms and 2 O atoms at a distance of 2.3 Å and 2.07 Å, respectively. From our FTIR results we expect the EG molecules to act as a bidentate ligand, hence we would expect the zinc ion center to be bonded to 2 chlorine atoms and 1 EG molecule as shown in the Figure 6.5e.

When the zinc salt concentrations reach the saturated levels, EXAFS fitting shows that the total coordination number of the first coordination sphere (sum of the coordination number of O and Cl) reduces from a value of 4 to 3.5. Zou et al have also shown that in systems with very high ZnCl_2 concentrations, the overall coordination number of the first shell will drop to values less than 4.^[37] This observation is an indication of the formation of the zinc-chloro polymeric species.^[18, 37-38] Although the full structural details of the zinc-chloro species is not fully elucidated yet, these systems have in general shown that zinc ion centers are predominantly coordinated to the chloride ions and not the solvent.^[38-39]

6.3.3 Structure-physicochemical properties correlation

With some structural insights between the salt-solvent interactions, the trends in the physicoelectrochemical properties can be explained. For both the zinc chloride and the $\text{Zn}(\text{OTf})_2$ salts, increasing the salt concentration in the EG lead to a continuous increase in the viscosity (Figure 6.1c,d). This can be explained from the FTIR results where the amount of unbonded EG molecules were seen to decrease as most of the EG solvent molecules were bonded to the zinc ion center. Therefore, the lack of free solvent molecules will increase the viscosity as also seen in few other studies.^[18, 40-41] When looking at the conductivity trend, the conductivity values first increase, peaks out and then reduces again, and this trend is consistent with other concentrated electrolytes developed (Figure 6.1c,d).^[19, 41] The initial increase in the conductivity is due to the increase in the number of free salt ions.^[41] However, the EXAFS results indicated that the zinc cation-anion aggregate pairs instead of free ions were mostly observed at the saturation levels. The loss of free and mobile ions in the system together with an increase in the viscosity will decrease the ionic mobility and hence the conductivity of the system will reduce.^[18, 40]

The expansion of the voltage window at the saturated salt concentrations are also linked to the salt-solvent interactions (Figure 6.1e,f). At nearly the saturation salt levels, most of the O atoms of the EG solvent molecules donate their electron loan pair to the zinc ion center. Yoshida et al. have found that in the case of Li-glyme electrolytes, when the O atoms from the glyme molecules donate the electron loan pairs to the lithium ion center, the highest occupied molecular orbital (or HOMO) levels of the solvent molecules are lowered which can enhance the anodic stability of the electrolytes.^[42] Furthermore, the shortage of free solvent molecules will also reduce their activity and also contributing to expand the anodic stability window of the electrolyte.^[43]

To explore the application of these saturated EG electrolytes in RZIBs, we investigate the electrochemical performance of these systems in the following section.

6.3.4 Electrochemical characterization

Figure 6.6 Optical images of aged zinc foils in various electrolytes after three weeks of aging time. The optical images and the corresponding ex-situ XRD patterns are shown. The # marked peaks are from the BZS precipitates of $\text{Zn}(\text{OTf})_2$ but with different interplanar spacing due to the difference in the number of interlayer water molecules.^[44-45]

Since aqueous electrolytes were found to initiate corrosion reactions in the zinc metal anode even at rest,^[46] the same test was carried out with the EG based electrolytes. The zinc foils were dipped in the aqueous electrolytes and also in the EG based electrolytes and were left to be aged for a duration of three weeks (Figure 6.6).

The zinc foils dipped in the EG based electrolytes were more or less similar to the pristine zinc foil with no change in the color and even the XRD pattern of the zinc foil indicated that no new phases were formed. However, the zinc foiled dipped in the aqueous electrolytes showed that a passivation layer forms on the zinc foil. The XRD scan, as expected, revealed that the passivation layer formed is due to the basic zinc salt precipitates of their corresponding zinc salts.^[4, 47-48] The similar corrosion and the formation of the basic zinc salt precipitation at the zinc metal anode is also seen with other zinc salts with different anions such as sulphate and perchlorate ions.^[4, 46-47] The authors explained that the basic zinc salts are formed when the zinc electrolyte pH values shift to more basic values.^[48] In this study, the pH of the electrolytes will locally shift to basic values when the mildly acidic electrolytes comes in contact with the zinc metal and a spontaneous redox reaction of zinc metal oxidation/corrosion to aqueous zinc-ion and the reduction of protons from aqueous electrolyte to hydrogen gas.^[46] The lost protons during this process will cause the pH to rise and cause the basic zinc salt precipitation. Since the basic zinc salt formation need water (as seen in their crystal structure), the basic zinc salt could not precipitate out in the EG based electrolytes where the water contents were negligible.^[4, 49-50]

In order to investigate if EG-based electrolytes have any advantage in making the zinc stripping/plating process more reversible when compared to their aqueous counterparts, galvanostatic stripping/plating tests were performed (Figure 6.7). The triflate based EG electrolyte could show a reversible stripping/plating behavior for more than 600 h or longer than 2.4 times when compared to the aqueous counterpart. Even the zinc chloride-EG system showed a longer battery runtime by 2.7 times when compared to the water-based electrolyte. One difference in the stripping/plating profile in EG electrolytes when compared to the aqueous electrolytes was that the overpotential values were higher which can be ascribed to the smaller ionic conductivity values when compared to the water-based electrolytes.^[2-3]

Figure 6.7 The Zn|Zn stripping/plating test in various electrolytes.

Furthermore, visual examination of the coin cells indicated that the water based electrolytes showed a swelling (Figure 6.8). This swelling has also been observed in other previous studies and have been ascribed to the hydrogen gas buildup when water from the aqueous electrolytes decompose.^[2] The EG based electrolytes when cycled did not show any such swelling, indicating that the electrolyte decomposition is much suppressed.

Figure 6.8 The post-mortem coin cell optical images after the Zn|Zn stripping/plating test in various electrolytes

Ex-situ XRD and SEM, and optical images were checked to observe the changes on the surface of the zinc foil during the stripping/plating process (Figure 6.9). The EG based systems showed that the zinc foil remains smooth and the separators remain intact. On the other hand, the separators in the water based electrolytes were seen to be damaged and pierced. The SEM investigation of the zinc foil indicated that the deposited zinc morphology is highly non uniform and has a layered morphology with sharp edges which can damage the separator. Zinc deposition morphology on the other hand, were more uniform in the EG based electrolyte. The XRD investigation on the zinc foils again showed a similar behavior as the aging experiment and the corresponding BZS precipitates were found on the surface of the zinc foil. These precipitates are expected to appear in layer or sheet like morphology and is consistent with the SEM morphologies observed on the zinc foils with aqueous electrolytes.^[4, 46]

Finally, to estimate if the EG based electrolytes can help in mitigating the cathode capacity fading observed in the aqueous electrolytes, full cell RZIBs were assembled using FeVO_4 and InVO_4 systems in EG based electrolytes (Figure 6.10). In both the cases of FeVO_4 and InVO_4 , we see that the initial capacities in the EG based electrolytes is lower compared to their aqueous counterpart. This can be ascribed to the lower ionic conductivity in the EG electrolyte and is also observed with other DES-type electrolytes.^[2-3] Nevertheless, the capacity retention in the subsequent cycles is much better in the EG based electrolytes. For instance, the capacity retention in the FeVO_4 system improved from 33.8% to 66% when shifting from water to the EG electrolyte system. This can be ascribed to a suppressed cathode material dissolution in the EG electrolytes when compared to the aqueous electrolytes.^[51-53] Therefore, the saturated EG-based electrolytes mitigate the unwanted cathode-electrolyte and also the anode-electrolyte interactions to improve the full cell battery performance.

Figure 6.9 Ex-situ post mortem optical micrograph and SEM for Zn(OTf)₂ in a) EG and b) water and c) their XRD diffraction patterns. Optical micrograph and SEM and for ZnCl₂ in d) EG and e) water and f) their XRD diffraction patterns.

Figure 6.10 Cycling stability of FeVO_4 (left) and InVO_4 (right) in water and EG-based electrolytes.

6.4 Conclusion

In this chapter, an alternative to aqueous electrolyte was developed using Ethylene Glycol as a solvent. The Ethylene glycol solvent is polar protic solvent which can be used to make zinc electrolyte formulations in ambient air environment with a high shelf life of 10 months and can remain stable in liquid state even at temperatures as low as -80°C . The high solubilities of zinc salts in EG to a molar ratio of 1:5 or higher reduces the free EG solvent molecules which can expand the anodic stability and hence expand the voltage stability window up to 2.2 V.

As a zinc battery electrolyte, EG based electrolyte mitigated few of the undesired reactions at both the anode and the cathode interface. At the zinc anode interface, EG electrolytes suppressed corrosion reaction, basic zinc salt precipitation and hydrogen evolution reaction and hence extending the reversibility of zinc stripping/plating test by more than 2.4 times. At the cathode interface, the cathode material dissolution was suppressed and hence the capacity retention was enhanced by two folds.

Figure 6.11 Schematic for the evolution of zinc coordination structure on tuning the zinc salt concentration and the anion coordination strength.

Finally, the salt-solvent interactions were elucidated using FTIR and EXAFS structural characterization. The studies showed that the zinc coordination sphere depends on the anion coordination strength and also the salt concentration as depicted in the Figure 6.11. When the salt concentration and the anion coordination strength both are low (as in the case of dilute $\text{Zn}(\text{OTf})_2$ electrolyte in EG), the zinc ion centers are fully chelated by the solvent. The other extreme case was the case of saturated ZnCl_2 electrolyte where the salt concentration and the anion coordination strength both are high. In this scenario it was observed that the zinc ion will still be predominantly bonded to the anions and thus the cation-anion aggregates can be observed. The other intermediate cases will be the cases where: 1) the anion coordination strength is high and the salt concentration is low (dilute ZnCl_2 electrolyte), or 2) the anion coordination strength is low and the salt concentration is high (saturated $\text{Zn}(\text{OTf})_2$ electrolyte). These cases have shown that both the solvent and the zinc salt anion will coordinate with the zinc ion center. Thus, these findings provide a guideline for estimating the coordination sphere of the multivalent cations when selecting the chelating solvent, salt and the salt concentration for multivalent-ion electrolytes (Zn, Mg, Ca, Al) where high salt cation-anion dissociation is desirable.

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Chapter 7

Conclusion and Future Work

This chapter aims at summarizing all the results obtained while designing zinc-ion cathode host structures and the zinc electrolyte formulations. The merits and demerits of each strategy are also highlighted to get a broader perspective. Furthermore, from the battery performance viewpoint, the RZIBs developed in these studies were also compared with other RZIBs in the literature. A performance comparison is also provided with Li-ion and Pb-acid battery technology to understand the performance gaps that still remain to be solved. Finally future work to develop better zinc host structures and electrolytes for improved battery performance are also suggested.

7.1 Perspective

The aim of this thesis was to explore novel zinc ion storage host structures and zinc electrolyte formulations which can allow for a reversible Zn^{2+} ion storage with a long operational lifetime. The initial literature studies were done to identify the host structure which have already been studied and various challenges associated with the reversible zinc ion storage from the cathode host structure perspective. Furthermore, the various type of electrolytes used and the challenges associated with the electrolytes are also presented.

From the cathode host structure perspective, intercalation-type phosphate host structures and conversion-type oxide host structures were investigated for reversible zinc-ion storage. The merits and demerits for both the type of cathode host structures from the RZIB performance perspective are elaborated. Furthermore, this thesis also elucidated an in-depth conversion-storage mechanism study for multivalent cations using zinc ions as an example for the first time. Finally, a novel ethylene glycol based electrolyte was designed and compared with the aqueous electrolyte to demonstrate a decrease in the undesired reactions and an improvement in the battery operational lifetimes.

7.2 Results Summary

Table 7.1 Performance metrics for the RZIB systems developed in this thesis work.

Cathode	electrolyte	Voltage (V)	Best capacity mAh/g	Current density A/g	cycles	Energy density Wh/kg _{cathode}	Power density W/kg _{cathode}	Capacity fade (%/cycle)	Operational lifetime (days)
PPy-VOPO ₄	1 m Zn(OTf) ₂ /AN with 10 vol% H ₂ O	1.1	86	0.1	350	94	110	0.15	14
FeVO ₄	1 m Zn(OTf) ₂ in water	0.6	272	3	300	163	1800	0.1	27
FeVO ₄	Zn(OTf) ₂ /EG molar ratio 1:5	0.6	170	0.1	500	102	60	0.06	35

7.2.1 Intercalation-type phosphate host structures for reversible zinc-ion storage

Considering the success of the phosphate based intercalation materials in Li systems due to high structural stability, few of the phosphate materials such as LiFePO_4 , $\beta\text{-VOPO}_4$, and layered VOPO_4 family were explored as reversible zinc-ion storage host structure. The tunnel-type intercalation cathode materials (LiFePO_4 and $\beta\text{-VOPO}_4$) were found to be electrochemically inactive for zinc ion intercalation due to high electrostatic interaction of the host structure with the zinc-ions.

The layered-type VOPO_4 host structures could mitigate the strong host-cation interaction and hence could show better capacities during zinc ion intercalation. However, layered $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ structure would collapse due to the removal of weakly bonded interlayer molecules during repeated charge-discharge. Hence polypyrrole was used to displace the interlayer water molecules and was in-situ polymerized between the VOPO_4 sheets to improve the structural integrity of the host structure. The layered structure remains intact and the electronic conductivity improves by one order of magnitude. For testing this host structure in the RZIB system, the aim was to use water based zinc electrolyte to test this cathode material, however, this material showed severe dissolution in water. Hence, the water content of the electrolyte was tuned to get the best compromise between the cathode material dissolution and the battery reaction kinetics by adding acetonitrile organic solvent. The zinc ion storage mechanism was then explored using ex-situ XRD and XPS studies. The zinc ions were stored between the VOPO_4 layers via a reversible contraction/expansion of the host structure. The battery performance is shown in Table 7.1.

The suboptimal battery performance can be ascribed to the following reasons: 1) poor rate performance as a large amount of acetonitrile had been added and the kinetics is relatively poor in organic solvents. 2) even though the voltage of the battery can be increased from ~ 0.6 V to 1.1 V from vanadium oxides to vanadium phosphate, the energy density is still low due to the limited capacity. This limited capacity can be due to the extra weight of the phosphate group. 2) the battery operational lifetime is very low (14 days) and this can be ascribed to the severe material dissolution and/or poor structural integrity. Therefore, having a very closed host tunnel-type structure (eg LiFePO_4 and $\beta\text{-VOPO}_4$) can stifle the zinc ion diffusion inside the host. On the other hand having a very open layered-type

structure can have limited structural integrity and might result in severe cathode dissolution or structural collapse. For these reasons, we explore zinc ion storage mechanism beyond simple intercalation process.

7.2.2 Conversion-type oxides host structures for reversible zinc-ion storage

The previous study found that the intercalation-storage mechanism was one main reason which restricted the choice of the cathode materials and also the electrochemical performance. Unlike the intercalation mechanism where the cathode host structure remains intact during the insertion/removal of guest cation, conversion-type mechanism involves a chemical reaction between the host structure with the guest cation to form a new phase reversibly. Hence, as an alternative, conversion (redox) storage mechanism was explored. The materials to be tested for zinc-ion storage were chosen considering their electrochemical activity in the Li system. It was found that binary oxides were either inactive or showed a severe capacity drop in the initial few cycles of reversibly storing zinc-ions. Hence, a ternary oxide metal vanadate series which has been well studied for Li system was tested for zinc system. FeVO_4 material in metal vanadate series showed the best electrochemical performance and hence the conversion zinc-ion storage mechanism was studied in-depth in FeVO_4 .

The zinc ion storage mechanism was elucidated using ex-situ XRD, XPS and Raman techniques. The mechanism revealed that during the first discharge cycle (zinc being stored in the cathode host structure), two irreversible phase transformation occurs: 1) the FeVO_4 host structure amorphises, 2) metallic Fe phase is also formed irreversibly. Thereafter, the Zn^{2+} ions are reversibly stored as ZnO phase and both the Fe and V transition metals from the amorphous- FeVO_4 matrix have been shown to drive in the zinc ion storage. The reaction mechanism is found to be very similar to the Li-ion storage.

The FeVO_4 battery performance is shown in Table 7.1. Although the battery energy density and power density are better than the VOPO_4 battery, several key challenges still remain to be solved to improve the battery operational lifetime: 1) the capacity fading is still prevalent especially at slow rates. 2) the zinc anode showed highly non-uniform deposition and the separator was seen to be damaged leading to sudden battery failure after longer

cycling times. 3) Undesired by products were formed as the electrolyte decomposition occurred and the pH of the electrolyte changed. The electrolyte plays a direct role in initiating the mentioned unwanted reactions and therefore, a new zinc electrolyte was formulated to improve the battery operational lifetime.

7.2.3 Ethylene Glycol based zinc electrolytes for reversible zinc ion storage

Similar to water, EG is chosen as a polar protic solvent with O-H groups and a high dielectric constant. Furthermore, EG has also been shown to act as a hydrogen bond donor to form Deep Eutectic Solvent (DES)-type electrolytes. Some of the previously explored DES-type zinc electrolytes have shown great promise in extending the zinc battery lifetime by limiting many of the undesired reactions. However, the hydrogen bond donor species used were often solid and hence the electrolytes are very viscous. EG on the other hand is liquid and can make the electrolyte formulation much easier.

Two zinc salts, zinc chloride and $\text{Zn}(\text{OTf})_2$, were used to make EG based zinc electrolyte. Their physical and electrochemical properties including the thermal transition temperature, viscosity, ionic conductivity, and voltage window were measured and compared with the conventional water based electrolytes. The results revealed that the ionic conductivity and viscosity of these electrolytes are poor compared to the water based electrolytes. However, the voltage stability window is bigger almost by 30%. Furthermore, the Zn^{2+} metal coordination sphere were also analyzed in these electrolytes to identify the salt cation-salt anion-EG solvent interactions to explain the trends in the physical and the electrochemical properties.

Additionally, from the electrolyte for zinc batteries perspective, the EG-based electrolytes were compared with the conventional water electrolytes for the zinc metal anode stability, reversible zinc stripping/plating and the full cell Zn-FeVO_4 cathode performance. The EG-based electrolytes showed a much slower zinc metal corrosion and the undesired side-reactions either during zinc metal aging test or during the zinc stripping/plating test. Furthermore, the zinc deposition morphology was also much uniform compared to the water based electrolytes. All these factors improved the reversibility of zinc stripping/plating lifetime by 250%. Furthermore, from the FeVO_4 full cell RZIB

perspective, the dissolution of the vanadium transitional metal was also reduced and therefore, the cathode capacity retention of the Zn-FeVO₄ system was seen to almost double in the EG based electrolytes and hence the capacity fading was lower and the operational lifetime was much better (Table 7.1).

7.3 Comparison of three different electrolytes used in this thesis

Since the electrolytes for RZIBs are still in preliminary testing stages, different electrolytes were used for optimizing the best performance for a given cathode material. While choosing the electrolyte, the zinc salt used was Zn(OTf)₂ and the solvent was changed between water, acetonitrile and ethylene glycol. The comparison of the electrolytes is represented in the Table 7.2.

Table 7.2 Comparison of the different family of electrolytes used in this thesis work.

Electrolyte	Cost (SGD/ kg)	Ionic conductivity (mS/cm)	Boiling point (°C)	Viscosity mPa.s	Voltage window (V)	Zinc metal corrosion	Zinc plating uniformity	Cathode material dissolution
2 m Zn(OTf) ₂ in water	2135	60	100	1	1.7	High	Low	High
1 m Zn(OTf) ₂ in acetonitrile	3327	5~10	81	1	3.3	Low	High	Low
Zn(OTf) ₂ in EG molar ratio (1:5)	3445	1~2	197	500	2.2	low	high	low

The data in this table is taken from the thesis work and from ref.^[1-3]

As evident from the comparison, there is not an ideal candidate for the electrolyte choice as every type of electrolytes have some merits and demerits. While water based electrolytes are not that expensive and have low viscosity and high ionic conductivity, they tend to initiate a lot of undesired reactions such as cathode material dissolution, zinc metal corrosion and highly non-uniform zinc deposition morphology. Acetonitrile based

electrolytes can limit most of the undesired reactions seen in aqueous electrolytes, however, they have very poor ionic conductivity and most importantly are highly flammable and hence not the optimal choice from safety standpoint. DES-type electrolytes based on urea, acetamide or ethylene glycol based electrolytes can also suppress the undesired side-reactions in the RZIB system, but have poor battery kinetics due to viscosity and are expensive compared to other types of the electrolytes.

7.4 Comparison of full cell RZIB performance with literature

Figure 7.1 Comparison of operational lifetime, energy density and power density of the RZIBs developed in the thesis with literature. Energy density (based on mass of cathode) is plotted in X-axis (log scale) and the operational lifetime in days is plotted on Y-axis (log scale). Each data point is sourced from a study from the Appendix Table A. 5. Each data point is color coded for power density as shown in the color palette to the right (log scale). The rough range of energy and power density for Li-ion, Pb-acid and electrochemical capacitors are marked. The two common family of V- based and Mn-based cathode materials are also zoned to show the rough range of the energy densities and the operational lifetimes. The square-shaped data points are from this thesis work.

Most other studies have been using aqueous electrolytes with either Mn-based or V-based cathodes (Figure 7.1). These RZIBs have both merits and demerits. Since the ionic conductivities of water-based electrolytes are very high the battery kinetics are very fast and as a result the power densities of most of the systems are comparable to the electrochemical supercapacitors (~ 1000 to $10,000$ W/kg). In terms of energy density, Mn-based cathodes have higher energy density than V-based RZIB cathodes as the redox potential is higher (~ 1.4 V for Mn-based compared to ~ 0.7 V for V-based). However, as water also induces a lot of undesired reactions in the system leading to a rapid capacity fade, the operational lifetime of these systems are quite low and they last from anywhere between 1 day to about 20 days. Mn in general suffer from more severe dissolution hence the best operational lifetimes are lower when compared to V-based RZIB cathodes. From a practical standpoint, a very low operational lifetime can have huge implications as a grid-scale energy storage device when the battery pack sizes and the replacement cost both can be very high.

The energy densities of the RZIBs developed in this thesis are lower than the reported V- or Mn-based cathode materials. When compared to other V-based or Mn-based cathodes (eg. V_2O_5 or MnO_2) where all the transition metal center ions are involved in the zinc-ion storage behavior, the lower energy density of PPy-VOPO₄ cathode comes from the extra weight of the unreactive phosphate group and for FeVO₄ comes from the extra Fe centers which irreversibly transform to metal Fe and do not involve in reversible Zn-ion storage. In terms of power density, the PPy-VOPO₄ battery and FeVO₄ in EG electrolyte are very poor (~ 100 W/kg) due to the poor kinetics in AN-based electrolyte and due to the high viscosity in the EG-based electrolytes. FeVO₄ in water due to the high ionic conductivity of water shows a high power density of ~ 1000 W/kg. Nevertheless, the energy density and the power densities are still comparable to the commercial Pb-acid or Li-ion batteries.

The merits of RZIB systems developed in this thesis work are the better operational lifetimes than the values reported in the literature. The PPy-VOPO₄ system showed an operational lifetime of about 14 days, the FeVO₄ in aqueous electrolyte showed a lifetime of about 25 days and with EG electrolyte could show a long lifetime of more than 35 days. This improvement can be ascribed to a mitigated undesired reactions which occur to a large

extend in other RZIB studies. Although the energy and power densities are not on par with the other reports, higher operational lifetimes will make the battery more economical when upscaled and the replacements and maintenance becomes costly.

7.5 Future Work

7.5.1 Development of other conversion based oxides

Using FeVO_4 , we have shown that the storage of multivalent zinc-ions is feasible via the conversion mechanism and shares a lot of resemblance to the Li-ion storage chemistry. The similarity in the zinc and lithium conversion storage mechanism can also be used as a guideline to design other conversion based host structures beyond vanadium to other transition metals with higher redox potential in order to improve the battery voltage and also the energy density.

7.5.2 Development of novel zinc electrolytes

The development of a robust zinc electrolyte is of urgent importance for testing any RZIB cathode material and also to curb the undesired reactions, to limit the capacity fade and improve the operational lifetime. Since the DES-type electrolytes and the aqueous electrolyte offers some benefits in their own way, a hybrid electrolyte concept might be able to harness the best benefits from both the type of electrolytes. The DES-type electrolytes are costly, viscous and renders very poor kinetics. Adding water in controlled amounts can improve the battery kinetics while reducing the electrolyte cost.^[4] Having water solvent in limited amounts will also ensure that the undesired reactions such as zinc metal corrosion, hydrogen evolution reaction and cathode material dissolution are also limited.

From the zinc salt perspective, zinc triflate shows the best electrochemical performance compared to the other zinc salts such as zinc sulphate, acetate or chloride. However, the salt cost is also high which can bring up the overall cost of the RZIB. Therefore, other zinc salts which can be upscaled at much lower cost should be explored.

7.6 Concluding Remarks

This thesis titled “Advanced cathodes and electrolytes for rechargeable zinc ion batteries”, has successfully developed an intercalation-type and a conversion-type cathode host material for reversible zinc ion storage. The zinc ion storage mechanism has been elucidated using several ex-situ characterization techniques. The zinc-ion storage mechanism can be used as a guideline in designing better host structures for reversible zinc ion storage with better energy densities. Furthermore, the undesired reactions in the widely used aqueous electrolytes in the RZIB system are also elucidated and these factors deteriorate the battery performance and hence limiting the battery operational lifetime. A DES-type electrolyte was designed to mitigate some of the undesired reactions. The merits and demerits of different types of electrolytes are presented and therefore, better electrolytes can be designed under these considerations to improve the battery operational lifetime.

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Appendix

Table A. 1 Pawley fitting data for RVO₄ series of materials (R=Al, Cr, In). The distances are in angstroms (Å) and the angles are in degrees (°)

AlVO₄	R_{wp} = 12.3
Space Group	P-1
a	6.5398(2)
b	7.7583(6)
c	9.1333(8)
α	96.157(5)
β	107.252(8)
γ	101.410(7)
CrVO₄	R_{wp} = 7.05
Space Group	Cmcm
a	5.5815(1)
b	8.2383(2)
c	5.9964(1)
InVO₄	R_{wp} = 4.26
Space Group	Cmcm
a	5.7604(1)
b	8.5292(1)
c	6.5814(1)

Table A. 2 Rietveld refinement for FeVO_4 . The refinement was done using the space group triclinic $P\bar{1}$ and an occupancy of 1 for all the sites. The refinement matches with the reported FeVO_4 structure PDF 01-071-1592. with following parameters. $a = 6.714(1) \text{ \AA}$, $b = 8.066(1) \text{ \AA}$, $c = 9.352(1) \text{ \AA}$, $\alpha = 96.68(1)^\circ$, $\beta = 106.67(1)^\circ$, $\gamma = 101.53(1)^\circ$; Crystal size Lorentzian (nm) = 63.0(14); R_{wp} : 1.28 and R_p : 1.11; GOF: 1.64.

Atom	Wyckoff Site	x	y	z	Occupation factor
Fe1	2i	0.772(4)	0.695(3)	0.418(2)	1
Fe2	2i	0.467(3)	0.894(2)	0.216(2)	1
Fe3	2i	0.968(3)	0.304(2)	0.009(2)	1
V1	2i	0.008(4)	1.003(3)	0.255(3)	1
V2	2i	0.205(4)	0.605(2)	0.343(2)	1
V3	2i	0.518(3)	0.296(3)	0.122(3)	1
O1	2i	0.628(8)	0.512(7)	0.234(6)	1
O2	2i	0.267(8)	0.425(7)	0.426(6)	1
O3	2i	0.102(9)	0.725(7)	0.427(6)	1
O4	2i	0.113(9)	0.080(7)	0.418(7)	1
O5	2i	0.449(9)	0.756(6)	0.378(6)	1
O6	2i	0.764(9)	0.887(7)	0.258(6)	1
O7	2i	0.560(8)	0.136(7)	0.240(6)	1
O8	2i	0.140(10)	0.907(8)	0.213(7)	1
O9	2i	0.366(8)	0.743(6)	0.055(6)	1
O10	2i	0.242(9)	0.284(6)	0.027(6)	1
O11	2i	0.953(8)	0.113(6)	0.158(6)	1
O12	2i	0.052(8)	0.525(7)	0.157(6)	1

Table A. 3 The capacity fading (%/cycle) data for few RZIB studies using water-based electrolytes at a slow current density of 500 mA/g or below. The data has been sorted in chronological order.

Cathode	electrolyte	Initial capacity	final capacity	Cycling rate (mA/g)	no of cycles	Avg. capacity fading (%/cycle)	Ref	Year
todorokite-MnO ₂	1 M ZnSO ₄	-	-	50	50	0.34	[1]	Dec 2013
ZnHCF	1 M ZnSO ₄	-	-	300	100	0.24	[2]	Sep 2014
α - MnO ₂	1 M ZnSO ₄	-	-	42	30	1	[3]	Apr 2015
α -MnO ₂	1 M ZnSO ₄	-	-	83	50	0.8	[4]	Aug 2015
δ - MnO ₂	1 M ZnSO ₄	-	-	83	100	0.56	[5]	Nov 2015
Na ₃ V ₂ (PO ₄) ₃ /C	0.5 M Na acetate + 0.5 M Zn acetate	-	-	50	200	0.115	[6]	Mar 2016
Na ₃ V ₂ (PO ₄) ₃	0.5 M zinc acetate	-	-	50	100	0.26	[7]	Jul 2016
Na ₂ MnFe(CN) ₆	1 M Na ₂ SO ₄ + 1 M ZnSO ₄	-	-	80	200	0.435	[8]	Nov 2016
LiV ₃ O ₈	1 M ZnSO ₄	-	-	133	75	4.166	[9]	Feb 2017
MnS	1 M ZnSO ₄	-	-	100	500	0.36	[10]	Mar 2017
V _{1-x} Al _x O _{1.52} (OH) _{0.77}	1 M ZnSO ₄	156	120	15	50	0.654	[11]	Apr 2017
V doped MnO ₂	1 M ZnSO ₄	-	-	66	100	0.51	[12]	May 2017
α -MnO ₂ /C	1 M ZnSO ₄	-	-	66	50	0.62	[13]	Jul 2017
β - MnO ₂	3 M Zn(OTf) ₂ + 0.1 M Mn(OTf) ₂	275	225	200	100	0.181	[14]	Sep 2017
β - MnO ₂	1 M ZnSO ₄ + 0.1 M MnSO ₄	-	-	200	200	0.125	[15]	Oct 2017
V ₂ O ₅	1 m Zn(OTf) ₂	201	73	100	90	0.707	[16]	Nov 2017

$\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	1 M ZnSO_4	150	-	200	300	0.106	[17]	Dec 2017
spinel- Mn_3O_4	2 M ZnSO_4	-	-	500	300	0.0933	[18]	Jan 2018
$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 1.63\text{H}_2\text{O}$	3 M $\text{Zn}(\text{OTf})_2$	296	231	100	100	0.2195	[19]	Feb 2018
$\text{Na}_{1.1}\text{V}_3\text{O}_{7.9}$	1 M $\text{Zn}(\text{OTf})_2$	223	171	300	100	0.2331	[20]	Jul 2018
VO_2/rGO	1 M ZnSO_4	365	288	50	200	0.1	[21]	Sep 2018
$\text{NaV}_6\text{O}_{15}$	1 M ZnSO_4	-	-	100	150	0.126	[22]	Mar 2019
LiMn_2O_4	0.5 $\text{Zn}(\text{TFSI})_2$ + 0.5 M LiTFSI	110	10	200	700	0.4545	[23]	Mar 2019
$\beta\text{-MnO}_2$	2 M ZnSO_4	-	-	200	100	0.57	[24]	Mar 2019
$\delta\text{-MnO}_2$	1 M ZnSO_4 + 0.1 M MnSO_4	-	-	100	100	0.33	[25]	May 2019
$\text{Ca}_{0.20}\text{V}_2\text{O}_5 \cdot 0.80\text{H}_2\text{O}$	1 M ZnCl_2	300	100	50	20	3.33	[26]	May 2019
$\text{Ag}_{0.333}\text{V}_2\text{O}_5 @ \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	3 M $\text{Zn}(\text{OTf})_2$	321	282.5	500	100	0.1	[27]	Jul 2019
V_2O_5	1 M ZnTFSI	180	80	100	100	0.55	[28]	Nov 2019
FeVO_4	0.1 M $\text{Zn}(\text{OTf})_2$	275	156	60	140	0.357	[29]	Mar 2020
poly(2,3-dithiino-1,4-benzoquinone)	$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water (1:8)	140	25	319	250	0.328	[30]	Jul 2020

Table A. 4 The capacity fading (%/cycle) data for few RZIB studies using DES-type electrolytes or Zn hybrid batteries using superconcentrated Zn/K or Zn/Li electrolytes. The data has been sorted in chronological order.

Cathode	electrolyte	Initial capacity	final capacity	Cycling rate (mA/g)	no of cycles	Avg. capacity fading (%/cycle)	Ref	Year
V_2O_5	1 m Zn TFS + 21 m LiTFSI in water	215	204	100	160	0.0319	[16]	Nov 2017
LiMn_2O_4	1 m $\text{Zn}(\text{TFSI})_2$ + 21 m LiTFSI	66	50	66	500	0.0484	[31]	Apr 2018

LiMn ₂ O ₄	LiTFSI: Zn(TFSI) ₂ :acetamide (molar ratio 1:0.05:3.5)	-	-	118	150	0.09	[32]	Aug 2018
LiMn ₂ O ₄	LiTFSI:Zn(TFSI) ₂ : urea: water (1:0.05:3.8:2)	92	76	40	600	0.0289	[23]	Mar 2019
V ₂ O ₅	ZnTFSI:acetamide (molar ratio 1:7)	110	100	100	200	0.0455	[28]	Nov 2019
MnO ₂	1 m Zn acetate + 30 m K acetate	309	247	100	5	0.0334	[33]	Jun 2020
poly(2,3-dithiino- 1,4-benzoquinone)	Zn(ClO ₄) ₂ in Succinonitrile molar ratio 1:8	112	105	319	1000	0.009	[30]	Jul 2020
LiFePO ₄	30 m K acetate + 3 m Li acetate + 3 m Zn acetate in water	-	-	158	400	0.0589	[34]	Dec 2020

Table A. 5 Performance metrics: Energy density, power density and operational lifetime for few RZIB studies from the literature

Cathode	electrolyte used	Voltage (V)	Best capacity (mAh/g)	Initial Capacity (mAh/g)	Avg. Capacity (mAh/g)	current rate (mA/g)	cycle	Operational lifetime (hours)	capacity fade %/cycle	Energy Density (Wh/kg)	Power Density (W/kg)	Ref
α -MnO ₂	1 M ZnSO ₄ + 1 M Zn nitrate	1.45	210	135	100	1200	100	16.6	0	304.5	1740	[35]
α -MnO ₂ / graphene	2 M ZnSO ₄ + 0.2 M MnSO ₄	1.42	382	150	130	3000	3000	260	0.002	542.44	4260	[36]
α - MnO ₂ /C FP	2 M ZnSO ₄ + 0.2 M MnSO ₄	1.4	290	50	55	1950	10000	564.1	0.0065	406	2730	[37]
β -MnO ₂	3 M Zn(OTf) ₂ + 0.1 M Mn(OTf) ₂	1.3	225	150	130	2000	2000	260	0.003	292.5	2600	[38]

δ -MnO ₂	1 M ZnSO ₄ + 0.2 M MnSO ₄	1.4	266	125	120	2000	2000	240	0.0081	372.4	2800	[39]
O deficient - MnO ₂	1 M ZnSO ₄ +0.2 M MnSO ₄	1.4	345	120	105	5000	2000	84	0.01	483	7000	[40]
ZnMn ₂ O ₄ /graphene	1 M ZnSO ₄ + 0.05 M MnSO ₄	1.4	221	80	80	1000	2500	400	0.0012	309.4	1400	[41]
Zn stabilized MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	1.45	275	121	88	3000	2000	117.3	0	398.75	4350	[42]
MnO ₂ /P EDOT	2M ZnCl ₂ + 0.4 M MnSO ₄	1.4	366	310	280	1110	300	151.3	0.054	512.4	1554	[43]
V ₂ O ₅	saturated ZnSO ₄	0.7	225	132	120	10000	6200	148.8	0.0029	157.5	7000	[44]
V ₂ O ₅	2 M Zn(OTf) ₂	0.75	401	315	250	2000	1000	250	0.027	300.75	1500	[45]
V ₂ O ₅ ·n H ₂ O/Graphene	3 M Zn(OTf) ₂ + 0.1 M vanadium sol	0.85	374	300	220	6000	900	66	0.0322	317.9	5100	[46]
V ₂ O ₅ ·1.6 H ₂ O	3 M Zn(OTf) ₂	0.7	426	300	300	10000	5000	300	0.001	298.2	7000	[47]
V ₃ O ₇ ·H ₂ O	1 M ZnSO ₄	0.65	375	270	245	3000	200	32.6	0.1	243.75	1950	[48]
V ₆ O ₁₃	3 M Zn(OTf) ₂	0.68	360	230	230	4000	2000	230	0.004	244.8	2720	[49]
V ₆ O ₁₃ ·n H ₂ O	3 M Zn(OTf) ₂	0.75	395	300	262	5000	1000	104.8	0.013	296.25	3750	[50]
Na _{0.33} V ₂ O ₅	3 M Zn(OTf) ₂	0.75	367	218	218	1000	1000	436	0.007	275.25	750	[51]
Ag _{0.33} V ₂ O ₅	2M Zn(OTf) ₂	0.7	200	250	100	3000	700	46.6	0.0014	140	2100	[52]
Mn _x V ₂ O ₅ ·nH ₂ O	3 M Zn(OTf) ₂	0.6	415	260	260	4000	2000	260	0.004	249	2400	[53]
Cu _{0.1} V ₂ O ₅ ·0.08 H ₂ O	2 M ZnSO ₄	0.61	359	204	180	10000	10000	360	0.0012	218.99	6100	[54]

$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 1.63\text{H}_2\text{O}$	3 M $\text{Zn}(\text{OTf})_2$	0.7	352	155	140	5000	6000	336	0.0016	246.4	3500	[19]
$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 2.14\text{H}_2\text{O}$	1 M ZnSO_4 + 0.2 M Na_2SO_4	0.75	466	145	130	20000	2000	26	0.005	349.5	15000	[55]
$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$	1 M ZnSO_4	0.82	361	152	150	14440	1000	20.7	0.02	296.02	11840.8	[56]
$\text{NaV}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$	1 M ZnSO_4 + 1 M Na_2SO_4	0.62	380	165	160	4000	1000	80	0.018	235.6	2480	[57]
$\text{H}_2\text{V}_3\text{O}_8$	3 m $\text{Zn}(\text{OTf})_2$	0.7	423	173	136	5000	1000	54.4	0.006	296.1	3500	[58]
$\text{H}_2\text{V}_3\text{O}_8/\text{graphene}$	3 m $\text{Zn}(\text{OTf})_2$	0.8	394	270	240	6000	2000	160	0.0065	315.2	4800	[59]
$\text{K}_2\text{V}_6\text{O}_{16} \cdot 2.7\text{H}_2\text{O}$	1 M ZnSO_4	0.6	239	178	178	6000	500	29.6	0.036	143.4	3600	[60]
$\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	1 M ZnSO_4	0.8	248	163	145	4000	1000	72.5	0.015	198.4	3200	[61]
$\text{Zn}_{0.25}\text{V}_2\text{O}_5$	1 M ZnSO_4	0.7	282	278	260	2400	1000	216.6	0.019	197.4	1680	[62]
$\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	1 M ZnSO_4	0.7	340	80	80	22560	5000	35.4	0.0024	238	15792	[63]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}$	2 M $\text{Zn}(\text{OTf})_2$	1.42	92	50	46	1000	4000	368	0.0012	130.64	1420	[64]
VO_2	3 M $\text{Zn}(\text{OTf})_2$	0.9	274	133	120	10000	10000	240	0.0021	246.6	9000	[65]
VO_2	1 M ZnSO_4	0.6	283	97	83	3000	5000	276.6	0.0028	169.8	1800	[66]
rGO/VO_2	3 M $\text{Zn}(\text{OTf})_2$	0.6	276	240	240	4000	1000	120	0.01	165.6	2400	[67]
$\text{CoFe}(\text{CN})_6$	4 M $\text{Zn}(\text{OTf})_2$	1.75	173	109	109	3000	2200	159.8	0	302.75	5250	[68]
$\delta\text{-MnO}_2$	2 M ZnSO_4 + 0.1 M MnSO_4	1.3	278	150	106.5	6160	10000	345.7	0.0002	361.4	8008	[69]
Mn_2O_3	2 M ZnSO_4 + 0.1 M MnSO_4	1.45	148	73.6	75	2000	2000	150	0.0175	214.6	2900	[70]

V ₂ O ₅	3 M ZnSO ₄	0.8	224	100	121	1000	400	96.8	0.0825	179.2	800	[71]
VO ₂	3 M Zn(OTf) ₂	0.8	357	350	357	2000	300	107.1	0.029	285.6	1600	[72]
Li _x V ₂ O ₅ · nH ₂ O	2 M ZnSO ₄	0.7	470	300	225	10000	1000	45	0.037	329	7000	[73]
Ca _{0.24} V ₂ O ₅ ·0.83 H ₂ O	1M ZnSO ₄	0.8	340	70	70	27200	5000	25.7	0.0013	272	21760	[63]
Dendriti c V ₁₀ O ₂₄ ·1 2H ₂ O	3 M Zn(OTf) ₂	0.6	164	80	80	10000	3000	48	0.002	98.4	6000	[74]
MoS ₂	3 M Zn(OTf) ₂	0.6	240	98	83	1000	2000	332	0.016	144	600	[75]
Co _{0.24} 7V 2O ₅ 0.9H 2O	4 M Zn(OTf) ₂	1.7	432	163	154	10000	7500	231	0.0013	734.4	17000	[68]
NaCa _{0.6} V ₆ O ₁₆ ·3 H ₂ O	3 M Zn(OTf) ₂	0.7	347	231	217	2000	2000	434	0.0017	242.9	1400	[76]
(NH ₄) ₂ V 6O ₁₆ ·1.5 H ₂ O	3 M Zn(OTf) ₂	0.8	385	139	120	8000	10000	300	0.0025	308	6400	[77]
NH ₄ V ₃ O ₈ 1.9H ₂ O	3 M Zn(OTf) ₂	0.6	463	207	166	10000	2000	66.4	0.0095	277.8	6000	[78]
V ₂ O ₅ ·1.6 H ₂ O	3 M Zn(OTf) ₂	0.75	426	300	284	10000	5000	284	0.001	319.5	7500	[47]
Na _x V ₂ O ₅ · nH ₂ O	3 M Zn(OTf) ₂	0.67	459	362	330	10000	1800	118.8	0.0093	307.53	6700	[79]
NH ₄ V ₄ O 10	3 M Zn(OTf) ₂	0.75	147	100	72	2000	5000	360	0.0059	110.25	1500	[80]
VO ₂ (D)	3 M ZnSO ₄	0.8	408	300	120	10000	30000	720	0.0023	326.4	8000	[81]
V ₂ O ₃ @ C	3 M Zn(OTf) ₂	0.7	350	240	175	5000	4000	280	0.0025	245	3500	[82]

$\text{Na}_{0.44}\text{Mn}_{1.5}\text{O}_4 \cdot \text{H}_2\text{O}$	2 M ZnSO_4 + 0.2 M MnSO_4	1.4	278	108	106	7600	10000	278.9	0.0002	389.2	10640	[69]
rod like anhydrous V_2O_5	3 M $\text{Zn}(\text{OTf})_2$	0.71	464	317	275	2000	2000	550	0.0066	329.44	1420	[83]
$(\text{NH}_4)_2\text{V}_{10}\text{O}_{25} \cdot 8\text{H}_2\text{O}$	2 M ZnSO_4	0.7	385	222	215	10000	1000	43	0.0063	269.5	7000	[84]
Acetalene Black/ V_2O_5	3 M $\text{Zn}(\text{OTf})_2$	0.7	340	329	329	10000	5000	329	0.0016	238	7000	[85]

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