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**AQUEOUS RECHARGEABLE SODIUM-ION ENERGY
STORAGE**

Rodney Chua Yong Sheng

School of Materials Science and Engineering

2020

AQUEOUS RECHARGEABLE SODIUM-ION ENERGY STORAGE

Rodney Chua Yong Sheng

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

2020

Statement of Originality

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

06 July 2020

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RODNEY CHUA YONG SHENG

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06 July 2020

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PROFESSOR MADHAVI SRINIVASAN

Authorship Attribution Statement

This thesis contains materials from 3 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 4 is published as a) **R. Chua**, Y. Cai, Z.K. Kou, R. Satish, H. Ren, J.J. Chan, L. Zhang, S.A. Morris, J. Bai, M. Srinivasan, 1.3 V superwide potential window sponsored by Na-Mn-O plates as cathodes towards aqueous rechargeable sodium-ion batteries, Chem. Eng. J. 2019, 370,742-748. DOI: 10.1016/j.cej.2019.03.251

The contribution of the co-authors are as follows:

- Prof. Madhavi provided the initial project direction.
- I wrote the manuscript drafts. The manuscript was revised by Prof. Madhavi, Dr. Cai and Dr. Kou.
- I co-designed the study with Dr. Cai.
- I performed the synthesis and electrochemical testing at School of Materials Science and Engineering.
- J.J Chan and I conducted the scanning electron microscopy, while the transmission electron micrographs and spectra were collected by Dr. Zhang and Dr. Ren from the Facility for Analysis, Characterization, Testing, and Simulation.
- Dr. Morris, Dr. Satish, Dr. Bai and I collected, processed and analyzed the powder X-ray diffraction data from Beamline 28-ID-2 X-ray powder diffraction of the National Synchrotron Light Source II, Brookhaven National Laboratory, United States.

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The contribution of the co-authors are as follows:

- Prof. Madhavi and Dr. Sennu provided the initial project direction.
- Dr. Sennu and I wrote the manuscript drafts and analyzed the data. The manuscript was revised by Prof. Madhavi, Dr. Hanna, S.S.H. Dintakurti and Dr. Aravindan.
- I co-designed the study and fabricated the electrochemical cell with Dr. Sennu.
- Dr. Sennu and I performed the synthesis and electrochemical testing at School of Materials Science and Engineering.
- I performed the synthesis of the cathode material while Dr Sennu synthesized the activated carbon for the anode material.
- I performed the confocal Raman spectroscopy while S.S.H. Dintakurti performed the nuclear magnetic resonance spectroscopy.
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- Dr. Morris, Dr. Satish, Dr. Bai and I collected and analyzed the powder X-ray diffraction data from Beamline 28-ID-2 X-ray powder diffraction of the National Synchrotron Light Source II, Brookhaven National Laboratory, United States.
- S. Kumar, V. Verma, S.Meng, and I collected the X-ray Absorption Near-Edge Structure (XANES) spectra in Synchrotron Light Research Institute (Public Organization), Thailand.
- S. Kumar, Dr. Kidkhunthod and I analyzed the XANES data.
- I performed the Fourier Transform Infrared and confocal Raman spectroscopies and analyzed the data.
- P.Q. Lim and I performed the nuclear magnetic resonance spectroscopy and water contact angle measurement and analyzed the data.
-

06 July 2020

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RODNEY CHUA YONG SHENG

Abstract

Aqueous rechargeable sodium-ion energy storage (ARSIES) is proposed as a promising alternative to the state-of-art lithium-ion batteries due to its abundance of natural reserves (water and sodium salts), excellent fire safety and environmental benignity. Towards enabling ARSIES for large-scale energy storage applications, it is imperative to develop electrode material with high charge storage capacity with superior rate capability and low-cost electrolytes that can enable long cycle lifespan. Due to the nature of the aqueous system, the main challenges lie in the various parasitic side reactions associated with water that limits the electrochemical stability window and undermines the cycle stability of the cell. In this thesis, a tunnel-type sodium manganese oxides (NMO), is used as a model cathode, owing to its high theoretical storage capacity and the ease of fabrication. The charge storage and its failure mechanism of the NMO in the aqueous system, are thoroughly investigated and characterized. A series of strategies based on electrode modification and electrolyte engineering are designed and optimized to realize the ideal full cell for the ARSIES. Also, as a proof-of-concept, an array of green, ultralow-cost, and low concentrated electrolytes has been successfully developed based on the novel concept of hydrogen-bonding interaction between co-solvents. The unique hydrogen bonding interactions in the hybridized electrolytes can effectively suppress the water activities as well as the parasitic side reactions associated with water, thereby enabling the superior electrochemical performances with long cycle stability of NMO. The novel findings from this study and the proposed future works could provide guidelines and inspire more research and developments for the practical application of next-generation ARSIES.

Lay Summary

In this modernized era, society consumes a great deal of energy stored in fossil fuels to power both stationary and portable electronic devices. Despite the low cost of extraction and distribution of the energy from fossil fuel, the increasing rate of combustion of fossil fuels to meet the electricity demands has generated a lot of pollutions, which contributed to global warming. Towards building a sustainable society, clean energy has to be derived from solar, wind, and tidal sources. However, this posed a great challenge for the conventional state-of-art lithium-ion batteries for large-scale energy storage applications due to its limited resources and inherent fire safety issue. Aqueous rechargeable sodium-ion energy storage (ARSIES) has been a promising alternative due to its abundant resources, high safety, and high ionic conductivity of the aqueous system while having similar electrochemistry with lithium-ion counterpart. However, its practical application has been hindered by the narrow electrochemical stability window and the inferior life cycles of electrode materials in aqueous electrolytes due to parasitic side reactions associated with water. In this study, various strategies to enhance the rate capability and cycle stability of the electrode investigated the sodium-based material *via* electrode modifications and electrolyte engineering. In particular, sodium manganese oxide (NMO) is chosen as a model cathode, considering its unique tunnel-shaped structures that can accommodate a large quantity of sodium-ion. The NMO sodium charge storage mechanism is thoroughly investigated and characterized. Benefitting from the fundamental understanding of the NMO electrochemical behavior in the aqueous system, this has led to various scientific hypotheses and research findings. The novel research developments of this study serve as the guidelines for future research advances and breakthroughs for next-generation electrochemical energy storage applications.

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Abbreviations

AC	Activated Carbon
AGIPs	Aggregated Ion Pairs
ARSIES	Aqueous Rechargeable Sodium-Ion Energy Storage
CIPs	Common Ion Pairs
CV	Cyclic Voltammetry
Di-water	Deionized water
DSC	Differential Scanning Calorimetry
Et	Ethanol
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
ESW	Electrochemical Stability Window
FTIR	Fourier Transform Infrared
FTIR-ATR	Fourier Transform Infrared- Attenuated Total Reflectance
GCD	Galvanostatic Charge and Discharge
HANE	Hybrid Aqueous/ Non-Aqueous Electrolyte
HRTEM	High Resolution Transmission Electron Microscopy
HOMO	Highest Occupied Molecular Orbital
ICN	Interwoven Carbon Network
LiTFSI	Lithium bis (trifluoromethanesulfonyl) imide
LIBs	Lithium-Ion Batteries
LSV	Linear Sweep Voltammetry
NaAc	Sodium Acetate
NaOTF	Sodium trifluoromethanesulfonate (NaCF_3SO_3)
NaFSI	Sodium bis(fluorosulfonyl)imide
NaTFSI	Sodium bis (trifluoromethanesulfonyl) imide
NMO	Sodium Manganese Oxide ($\text{Na}_{0.44}\text{MnO}_2$)
NMR	Nuclei Magnetic Resonance
PBA	Prussian Blue Analog

PEG	Polyethylene Glycol
PJAC	Prosopis Juliflora Activated Carbon
PVA	Poly (vinyl alcohol)
PVP	Polyvinylpyrrolidone
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEM	Scanning Electron Microscopy
SEI	Solid Electrolyte Interphase
SG	Sol-Gel
SLRI	Synchrotron Light Research Institute
SS	Solid State
SSC	Symmetric Supercapacitor
SSIPs	Solvent Separated Ion Pairs
TEM	Transmission Electron Microscopy
T _m	Melting point
TEAOTF	Tetraethylammonium triflate
XANES	X-ray Absorption Near-Edge Structure
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter introduces the need for a green, safe, and low-cost aqueous rechargeable sodium-ion energy storage system for large scale storage and utilization of renewable energy resources. Towards designing and engineering the ideal ARSIES cell for practical applications, the significant challenges, and the underlying failure mechanisms of the cell in the aqueous system are identified. Following the scope and objectives of this thesis are defined. Finally, an overview of the chapters is provided together with the significant research findings and outcomes highlighted.

1.1 Background and significance

In today's modern society, there is an ever-rising dependence on fossil fuels for energy to power small to large electronics ranging from mobile phones to electric vehicles.^{1, 2} However, there is a growing concern over the finite supply of fossil fuels as well as the negative environmental impact of the carbon dioxides by-product that is contributing to global warming.^{2, 3} Towards a sustainable society, there is a need to adopt and harness alternative clean energy resources such as solar, wind, and tidal power.^{4, 5} However, these resources are intermittent and require efficient large scale electrochemical storage systems. Conventional lithium-ion batteries (LIBs) have been a promising candidate for electrochemical energy storage systems due to their high energy density and coulombic efficiency.⁶⁻⁸ However, due to the fast depletion rate of lithium reserves, it is not sustainable for large scale energy storage applications.⁹⁻¹¹

In these regards, aqueous rechargeable sodium-ion energy storage (ARSIES) system has garnered researchers' attention as a promising alternative to LIBs.¹²⁻¹⁵ It is mainly because of the high availability (sixth most abundant element in Earth's crust) and wide distribution of sodium reserves, which makes it economical (**Table 1.1**) for widespread employment. Moreover, the use of aqueous-based electrolyte possesses inherent high safety and does not require stringent fabrication environment. These attractive attributes of ARSIES have enabled it to be a low-cost, safe, and highly sustainable energy storage system for the grid-scale application.

Table 1.1. Characteristics of lithium and sodium.¹²

Lithium	Sodium	Category
0.76	1.06	Cation radius (Å)
6.9 g mol ⁻¹	23 g mol ⁻¹	Atomic weight
0	0.3 V	E° (vs. Li/Li ⁺)
\$5000/ton	\$150/ton	Cost, carbonates
3829	1165	Capacity (mAh g ⁻¹), metal
Octahedral and tetrahedral	Octahedral and prismatic	Coordination preference

1.2 Problem Statement

Although ARSIES offers high safety and low-cost advantages as compared to LIBs, there are still challenges faced by ARSIES that hindered its practical application, as identified in the following.^{13, 15} Firstly, the aqueous system has lower energy density than its non-aqueous counterpart due to the narrow thermodynamics electrochemical stability window (ESW) of water (~ 1.23 V), which limits both the upper and lower cutoff of the operating voltages as shown in **Figure 1a**.¹³ Beyond the cutoff voltages, undesired water decomposition, and the evolution of H_2 and O_2 would occur. As a result, it restricts the selection of electrode materials to those that have appropriate redox reactions within the stable ESW of water (**Figure 1b**). Secondly, the electrode materials may encounter electrode dissolution in the aqueous electrolyte, leading to the loss of active material and resulting in the capacity fading and inferior cycling stability of the cell. Thirdly, the presence of protons in water may co-insert into the host electrode during electrochemical cycling, leading to the blocked alkali metal-ion diffusion pathways, resulting in decaying performance or even catastrophe cell failure. A scheme showing the various parasitic side reactions in the aqueous system that undermines the cell cycling stability is as summarized in **Figure 1-2**. Therefore, to achieve the ideal ARSIES, it is vital to develop cathode materials with high capacities and enhance its cycling stability by suppressing these parasitic side reactions through electrode modification and electrolyte engineering.

Figure 1-1. (a) Electrochemical stability of water at different pH and (b) suitable electrode materials with redox reaction within the electrochemical stability window of water. The orange dotted line illustrates the H_2 and O_2 evolution limits in a pH-neutral solution.¹³

Figure 1-2. The various parasitic side reactions in the aqueous system.

The problem statement will take in the form as follows:

“This thesis describes and validates the feasibility of aqueous rechargeable sodium-ion energy storage system with an optimized electrode/electrolyte that has the potential to deliver high power and energy density with long cycle lifespan to function as an alternative source of the energy storage system.”

1.3 Objective and Scope

This thesis aims to design and engineer the cathode and the electrolytes to maximize the power and energy density output of the aqueous rechargeable sodium-ion energy storage system. Towards realizing the ideal design for ARSIES, the electrode and electrolyte modifications will be tailored based on the underlying working and failure mechanisms of the cell, determined through systematic characterization using in-house laboratory as well as synchrotron-based techniques on the pristine and cycled samples.

The objective and scope statement will take in the form as follows:

“The current research is concerned with the synthesis of sodium-ion based cathode material(s) and electrolyte engineering with systematic characterizations to understand the working and failure mechanism to enhance the battery’s power and energy density, and cycle lifespan for application as energy storage devices.”

1.4 Thesis Organization

This thesis addresses the challenge of structural and electrochemical instability of cathode in the aqueous electrolyte due to the various parasitic side reaction associated with water. In this thesis, a high theoretical capacity sodium manganese oxide ($\text{Na}_{0.44}\text{MnO}_2$; NMO) is employed as a model cathode material for aqueous rechargeable sodium-ion energy storage (ARSIES).

Chapter 1 introduces the background and advantages of employing ARSIES for large scale energy storage applications. Further, the challenges and issues faced in ARSIES are highlighted and discussed. Most importantly, the objective and scope that provide the research direction for the thesis are laid out. In addition, an overview of the thesis organization is provided for understanding the purpose and rationale of each chapter.

Chapter 2 reviews the literature on the selection criteria and the state-of-art cathode material towards building an ideal ARSIES. More importantly, this chapter identifies the research gaps that structures the objective of this thesis. In particular, the high theoretical capacity sodium manganese oxide suffers from inferior energy density, and electrode instability in the aqueous system due to the parasitic side reactions associated with water are highlighted and discussed. The potential state-of-art electrode modification and electrolyte engineering strategies to overcome the challenges in the aqueous system are discussed.

Chapter 3 describes the synthesis and characterization techniques employed in this study. These include the basic principle and its application rationales of these techniques in detail. Further, the fabrication and electrochemical testing of the cell are described.

Chapter 4 focuses on the electrode modification *via* morphological control of NMO as the cathode materials for ARSIES. The synthesis and characterization techniques of the NMOs are described. Further, the electrochemical performances of the NMOs are evaluated in the diluted electrolyte in a three-electrode configuration. A combination of *ex-situ* characterization techniques is employed to uncover the morphological and phase evolution of NMOs.

Chapter 5 focuses on the full cell construction of ARSIES using the modified NMO from chapter 4 as the cathode, biomass-derived activated carbon as the anode, and the designed electrolyte based on “water-in-bisalt”- mixed anion formulation. The solution structure of the designed electrolyte is investigated by a combination of confocal Raman spectroscopy and theoretical simulation. The interactions of cation, anion, and water molecules are elucidated. The electrochemical performance of the full cell is evaluated and compared with the state-of-art energy storage systems.

Chapter 6 focuses on electrolyte engineering to construct low-cost ARSIES towards practical applications. Low concentrated electrolytes are designed by hybridizing polar protic solvent with water, which expands the voltage window and suppresses the parasitic side reactions. A series of spectroscopic and interfacial techniques are employed to determine the effect of hydrogen-bonding interaction in the hybridized electrolytes. The cycle stability of NMOs tested in the hybridized electrolyte, and the state-of-art “water-in-salt” electrolytes are compared. *Ex-situ* characterizations, including synchrotron-based X-ray absorption near edge structure, are further employed to determine the chemical and structural evolution of NMOs.

Chapter 7 concludes the overall study and summarizes the significant findings and the novel outcomes of the study. Further, the future works that can be useful in advancing the field of ARSIES are discussed.

1.5 Novel Findings and Outcomes

The novelties in this study are as follows:

- NMO plates synthesized *via* the PVP-assisted sol-gel route achieved the widest applicable potential window of 1.3 V (with deep discharge) in the aqueous system for the first time. *Ex-situ* characterization techniques uncover the *in-situ* formation of sheet-like structures on the NMO plates during electrochemical cycling that could act as passivation layers against the parasitic side reactions.
- A full cell construction of NMO//biomass-derived activated carbon cycled in the formulated pH regulated “water-in-bisalt” electrolyte can cycle over a wide potential range up to 2.8 V with superior energy and power densities even at demanding conditions (high 60 °C and low – 20 °C temperatures).
- A new class of electrolytes formulated by hybridizing polar protic solvent with water enable the usage of a wide array of green and low-cost sodium-based salts, enabling the long cycle lifespan of NMO. The unique hydrogen bonding interaction between the ethanol-water significantly suppresses the parasitic side reactions such as electrode dissolution and proton co-intercalation.

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Chapter 2

Literature Review

In this chapter, it provides an overview of aqueous rechargeable sodium-ion energy storage (ARSIES) as the green and low-cost alternative to lithium-ion technologies for large scale energy storage application. Its basic working principle is introduced. Based on the literature, the selection of $\text{Na}_{0.44}\text{MnO}_2$ as the ideal cathode for ARSIES is reviewed and discussed. More importantly, this chapter identifies the research gaps that structures the objective of this thesis. Further, a comprehensive list of potential strategies to overcome the challenges of side reactions in ARSIES based on electrode modifications and electrolyte engineering are identified from the literature.

2.1 Overview of Aqueous Rechargeable Sodium-ion Energy Storage

Aqueous rechargeable sodium-ion energy storage (ARSIES) system is an attractive alternative to lithium-ion technologies for the grid-scale energy storage applications. The significant advantage of employing the ARSIES system is the vast availability of sodium reserves in the Earth's crust (~ 1000 times more abundant than lithium; **Figure 2-1**), which leads to its low-cost ($\sim 30\%$ cost reduction).^{1, 2} Besides, the assembly can be done in ambient conditions without the need for stringent measures (e.g., moisture and oxygen), which significantly reduces the fabrication cost. Moreover, the use of aqueous electrolytes also substantially raises the safety level of the energy storage system in terms of flammability and toxicity towards large scale employment.

ARSIES share the same basic working principle and electrochemical setup configuration with the lithium-ion cells (**Figure 2-2**).^{2, 3} When the cell is charged using a power supply, the sodium is deintercalated from the cathodes and transferred into the electrolytes and intercalate into the anode. Meanwhile, the electrons are transported *via* the external circuit from the anode to the cathode to maintain the overall charge balance. The as-mentioned steps are reversed during the discharge process to power the load.

Figure 2-1. Earth's crust- An overview of the elemental availability.²

Despite having a similar working principle as commercialized lithium-ion cell, the ARSIES still faced several challenges that hindered its practical applications.⁴⁻⁷ One of the major problems is the limited choice of active materials due to the narrow electrochemical stability window ($\sim 1.23\text{V}$) of water (ESW).⁷ Beyond the ESW, electrolyte decomposition with severe evolution of gases (O_2 and H_2) would occur, leading to catastrophe cell failure.⁵ Another major issue lies in the inferior short lifespan of the electrodes in an aqueous system due to the degradation of active materials by the parasitic side reactions associated with water. The degradation effects on the electrodes include dissolution, structural/phase transformation, and irreversible sodium de-/insertion due to proton co-intercalation during electrochemical cycling. In these regards, this literature review mainly focuses on the fundamental electrochemistry and its applied strategies to overcome the as-mentioned challenges. In particular, the reviewed strategies include the electrode modification on the cathode material and electrolyte engineering towards the realization of ARSIES.

Figure 2-2. Electrochemical configuration of ARSIES.³

2.2 Cathodes for ARSIES: Selection criteria and consideration

2.2.1 Cathodes- Redox reactions within water decomposition potential

Due to the presence of water in the electrolyte, the water decomposition reaction (Equation 1) would limit the upper and lower cut-off potential of the cell. In particular, the oxygen and hydrogen evolution reactions would occur at the cathode (Equation 2) and anode (Equation 3), respectively. Therefore, to build an ARSIES, the electrode has to be chosen based on its redox potential within the thermodynamic voltage of water decomposition ($E^\circ \sim 1.23$ V calculated based on Equations 4 and 5).^{7, 8}

Water decomposition reaction:

Cathode:

Anode:

$$\Delta G^\circ = -nFE^\circ \quad (4)$$

$$E^\circ \text{ water decomposition} = \frac{-\Delta G^\circ}{nF} \quad (5)$$

where,

ΔG° is the Gibbs free energy change of the water decomposition process ($\Delta G^\circ = 237.1$ kJ mol⁻¹ at standard condition; where the temperature is 25 °C and pressure is 1 atm),

n is the transfer electron number (in this case, 2e⁻ are transferred),

F is the Faraday constant (96485 C mol⁻¹),

and E° water decomposition is the minimum thermodynamic voltage for water decomposition to occur.

2.2.2 Na_{0.44}MnO₂ (NMO) as promising cathode for ARSIES

The cathode with high energy and power densities are highly desired in building an ideal ARSIES. In these regards, the selection of materials with high theoretical capacities (calculated based on Equation 6) and good electrode kinetic (e.g., sodium-diffusion, calculated based on Equation 7) becomes the essential priority since these contribute towards the overall energy and power densities, respectively. As shown in **Figure 2-3**, it presents the various cathode candidates that have the redox potential within the electrochemical stability window of water. Among them, sodium manganese oxide (Na_{0.44}MnO₂; NMO) is one of the most promising candidates due to its suitable redox potential within the electrochemical stability of water and its high theoretical capacity. Due to its robust and unique tunnel-shaped structure (**Figure 2-4a**), it is capable of accommodating up to 0.44 mol of sodium-ions (**Figure 2-4b**) corresponding to a high capacity of ~121 mAh g⁻¹ (calculated based on Equation 6).⁹ In 2010, Whitacre and co-workers were the first to employ NMO with activated carbon and 1 M sodium sulfate (Na₂SO₄) as the cathode, anode, and electrolyte, respectively.¹⁰ They found that the cell exhibits not only electrochemical characteristics nominally similar to the NMO tested in a non-aqueous system but also an appealing rate capability of NMO as the cathode in ARSIES.

2.2.3 Electrode modification of NMO

Subsequently, Kim et al. have further improved the charge transfer resistance of NMO by synthesizing the NMO rod-shaped particles *via a* modified Pechini method.¹¹ In their study, they also compared the electrode kinetics of NMO in both aqueous (0.5 M Na₂SO₄) and non-aqueous (1 M NaClO₄) systems (**Figure 2-5**). They have demonstrated the superior sodium ion diffusion capability within NMO in the aqueous system (1.08×10^{-13} to 9.15×10^{-12} cm²s⁻¹; calculated based on Equation 7) as compared to that of the non-aqueous electrolyte (5.75×10^{-16} to 2.14×10^{-14} cm²s⁻¹) determined from Equation 6.¹¹

Figure 2-3. Comparison of the redox potential of the various electrode materials for ARSIES.³

Theoretical capacity calculation based on Faraday's law:

$$Q_{\text{theoretical}} = \frac{nF}{3600 \times M_w} \text{ mAh g}^{-1} \quad (6)$$

where

Q is the theoretical capacity of the active material,

n is the number of ions de/-insertion,

F is the Faraday constant (96485 C mol⁻¹),

Mw is the molecular weight of the active material.

Sodium-ion diffusion coefficient (D_{Na^+})¹¹:

$$D_{\text{Na}^+} = 0.5 \left[\frac{V_m}{nFAZ_w} \left(\frac{dE}{dx} \right) \right]^2 \quad (7)$$

where,

D_{Na^+} is the sodium-ion diffusion coefficient within a material,

V_m is the molar volume of the material,

F is the Faradaic constant (96,486 C mol⁻¹),

A is the area of contact between the electrode and electrolyte,

Z_w is the Warburg coefficient,

$\frac{dE}{dx}$ is the slope of electrode potential versus the composition (galvanostatic charge-

discharge) curve.

Figure 2-4. (a) Crystal structure of $\text{Na}_{0.44}\text{MnO}_2$. (b) Calculated voltage profile (red) line and the charging and discharging experimental data (dotted black line) at 0.1 C.⁹

Figure 2-5. Cyclic voltammety curves of NMO tested in aqueous (0.5 M Na_2SO_4 ; blue curve) and non-aqueous (1 M NaClO_4 ; red curve) electrolytes.¹¹

2.2.4 Adjusted cut-off potential of NMO in the aqueous system

Interestingly, it is noteworthy that the lower cut-off potential in which the NMOs are cycled in the aqueous system is higher than that in the non-aqueous system (**Figure 2-5**). In 2017, Whitacre and co-workers reported that the NMO would suffer from parasitic side reactions, such as the dissolution of the NMO is cycled below the lower cut-off potential of 0.1 V vs. NHE, which result in the loss of capacity.¹² In this regard, due to the smaller electrochemical potential window, the reported NMOs tested in the aqueous system delivered lower capacities values (ranging between ~30 to ~48 mAh g⁻¹) than in non-aqueous system, as summarized in Table 2-1.¹⁰⁻¹³

2.2.5 Doping of NMO

Previously, Wang et al. proposed the sodium-rich elemental-doped NMO [Na_{0.66}Mn_{0.66}Ti_{0.34})O₂ *via the* solid-state method in the hope of stabilizing the NMO structure for improved long term cycling performance.¹⁴ However, the half cell is only able to deliver 74 mAh g⁻¹ corresponding to insertion of 0.28 mol of sodium-ions when tested in the non-aqueous system at ~0.1C (11.8 mA g⁻¹). This is lower than the theoretical capacity of Na_{0.44}MnO₂ (~121 mAh g⁻¹; insertion of 0.44 mols of sodium-ions), possibly due to the altered electrochemical behaviour of the doped NMO (related to charge ordering and sodium-ion vacancy ordering). Even though the doping strategy has indeed improved cycling stability, it comes with a large sacrificial loss in the overall energy density that needs to be further considered.

2.2.6 Surface modification of NMO

Previously, the carbon coating of LiFePO₄ (15 wt% carbon) was one of the strategies employed by Luo et al. to enhance the cycle stability of the lithium-ion cell.¹⁵ Recently, Whitacre and co-workers proposed an optimized surface-modified Na_{0.44}MnO₂ with the nano-Al₂O₃ coating (4wt%) synthesized *via the* solid-state synthesis process to improve the capacity retention at lower discharge potential (~ -0.2 vs. Ag/AgCl).¹⁶ With the widen

potential window, the nano- Al_2O_3 coated NMO is able to achieve a higher capacity of 57.4 mAh g^{-1} . Thus far, this coating strategy has shown promising capacity retention after ten cycles, while the long-term cycling has yet to be reported.

Table 2-1. Electrochemical performance comparison of NMO electrodes in ARSIES.

Cathode	Synthesis	Electrolytes	Potential Window (V vs. Ag/AgCl)	Current Density (mA g^{-1})	Discharge Specific capacity (mA h g^{-1})	Ref
$\text{Na}_4\text{Mn}_9\text{O}_{18}$ needle-like morphology	Solid-state	1 M Na_2SO_4	0 V - 0.7 V	30	~ 45	10
$\text{Na}_{0.44}\text{MnO}_2$ rods-shaped particles	Modified Pechini method	0.5 M Na_2SO_4	0 V - 0.7 V	24.2	~ 40	11
$\text{Na}_4\text{Mn}_9\text{O}_{18}$ needle-like morphology	Solid-state	1 M NaCl	-0.1 V – 0.75 V	25	~ 48	12
$\text{Na}_{0.44}\text{MnO}_2$	Not specified	1 M Na_2SO_4	0.1 V – 0.6 V	60.5	~ 30	13

2.3 Electrolyte Engineering

From the above discussion, the enhanced cycling stability of the electrodes is achieved *via* electrode modification. However, it is noteworthy that the electrolytes also plays a significant role in the overall physical and chemical characteristic of the cell. The safety level of the system is enhanced with water as the solvent. On the other hand, the electrochemical stability window of the cell is restricted by the thermodynamic of water. Thus, reducing the applicable potential window for the electrode, resulting in the reduced energy density of the cell. Further, the parasitic side reactions associated with water, such as the evolution of gases (O_2 and H_2), dissolution of electrode materials, proton co-intercalation into the electrode, among others, affect the stability of the cell. Here, in the following subsections, the focus will be on the different strategies (**Figure 2-6**) proposed

to overcome the as-mentioned limitations *via* electrolyte engineering, its rationale, and challenges towards the realization of ARSIES.^{10, 15, 17-24}

Figure 2-6. Various proposed strategies in electrolyte engineering.^{10, 15, 17-24}

2.3.1 Removal of dissolved oxygen and pH regulation (Strategy 1)

In 2010, Xia and co-workers had proposed the elimination of oxygen and tuning the pH of the electrolyte to enable the utilization of active materials and raise the cycling stability of the cell for aqueous lithium-ion batteries.¹⁵ The rationales for eliminating the oxygen and adjusting the pH are as follows: (1) Utilization of the active materials’ working potential. In the case of anode materials, the typical redox reaction is below 3V vs. Li/Li^+ . By removing the oxygen and tuning the pH, this allows the anode to undergoes its proper electrochemical redox reaction without being chemically oxidized (as explained in Examples A and B).¹⁵

Example A- In the presence of oxygen and water,

Potential of the lithium-ion intercalated compound, $V(x)$, (in equilibrium with oxygen

and water) at a particular pH:

$$V(x) = -\frac{1}{e} (u_{\text{Li}}^{\text{int}}(x) - u_{\text{Li}}^0) \quad (9)$$

where,

$u_{\text{Li}}^{\text{int}}(x)$ is the chemical potential of the intercalated lithium-ion in the lithium-ion intercalated compound,

u_{Li}^0 is the chemical potential of lithium in lithium metal,

and e is the magnitude of the electron charge.

$$V(x) = 4.268 - 0.059 \text{ pH (V vs. Li/Li}^+) \quad (10)$$

Based on Equation 9, suppose the pH of the electrolyte is 7, the equilibrium voltage would be $\sim 3.85 \text{ V vs. Li/Li}^+$. Even with the adjusted pH to 13, the equilibrium voltage remains at high value of $\sim 3.5 \text{ V}$. In this regard, unfortunately, there is no available anode with redox potential $> 3 \text{ V vs. Li/Li}^+$.

Example B- In the absence of oxygen,

Potential of the lithium-ion intercalated compound (in equilibrium with water) at a particular pH:

$$V(x) = 3.039 - 0.059 \text{ pH (V vs. Li/Li}^+) \quad (12)$$

Based on Equation 12, suppose the pH of the electrolyte is 7, the equilibrium voltage would be $\sim 2.626 \text{ V vs. Li/Li}^+$. By adjusting the pH to 13, the equilibrium voltage would be $2.272 \text{ V vs. Li/Li}^+$. In this case, anode such as $\text{LiTi}_2(\text{PO}_4)_3$ with redox at $2.45 \text{ V vs. Li/Li}^+$ can be utilized. Similarly, in ARSIES, $\text{NaTi}_2(\text{PO}_4)_3$ can be employed as the anode material.

(2) Suppression of proton co-intercalation. In the aqueous system, some of the cathodes (e.g., $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, LiCoO_2 , LiFePO_4 , etc.) are susceptible to the proton co-intercalation.^{15, 25, 26} During the discharge process (especially at low discharge potential), the protons in the water would co-intercalated with the alkali metal (e.g., Li^+ , Na^+ , etc.)

into the host structure. This parasitic side reaction leads to an irreversible alkali metal de/insertion in the subsequent cycles, which undermines the cycle stability of the cell. By increasing the pH of the electrolyte for $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and LiCoO_2 to pH 11 and 9, respectively, the proton co-intercalation side reaction could be suppressed.^{25, 26} However, the alkaline environment of the electrolyte could decompose some cathodes, such as LiFePO_4 .¹⁵ In this case, it would require additional carbon coating on the cathode, which acts as a protective layer to achieve the overall cycling stability.

By removing the dissolved oxygen and tuning pH, indeed, this could offset the water decomposition potential for the utilization of the active materials and improve the cycle stability of the cell. However, the overall applicable potential window of the cell is still limited, restricting the energy density of the system. Therefore, to expand the electrochemical stability window, electrolyte-oriented strategies have to target the water species (H^+ and OH^-) that are accountable for the water decomposition, along with the several parasitic side reactions.

2.3.2 Concentrated electrolytes

Recently, there has been a significant breakthrough in overcoming the narrow electrochemical stability window of the electrolyte through the reduction in free water activities and the formation of solid electrolyte interphase (SEI) layers *via* concentrated electrolytes. The fundamental concepts and challenges will be discussed in the following.

2.3.2.1 “Water-in-salt” (WIS) electrolytes (Strategy 2)

In 2015, Wang and co-workers first proposed the novel “water-in-salt” (WIS) strategy to significantly expand the electrochemical stability window (ESW) to ~ 3.0 V (1.9-4.9 V vs. Li/Li^+) by using a highly concentrated 21 m lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) electrolyte.¹⁸ Subsequently, in 2017, Wang and co-workers also demonstrated the WIS concept in ARSIES by using 9.26 m sodium trifluoromethane sulfonate (NaCF_3SO_3 ; NaOTF), which remarkably expand the ESW up to 2.5V (-1.2 V to 1.3V vs. Ag/AgCl).²⁷

Shortly, Battaglia and co-workers have also proposed the highly concentrated 35 m NAFSI as the WIS electrolyte, which further expand the ESW up to ~ 2.6 V for ARSIES.²⁸

The novel concept of WIS is to alter the physical and chemical interactions between the water species (H^+ and OH^-) with the concentrated salt (cation and anion) in the electrolyte, to suppress the water activities. In a dilute electrolyte, as the water molecules outnumber the salt, the cations (e.g., Li^+ or Na^+) are solvated by water molecules inside a double layer solvation sheath as shown in **Figure 2-7a**. It leads to the large dissociation of cation along with the presence of a large amount of loosely bounded and unbound free water molecules. However, in concentrated electrolytes, as the water molecules to cation molar ratio decreases, the cation (Lewis acid; Li^+ or Na^+) coordination with the water molecules increases. Accordingly, the water molecules (or dissociated OH^-) would donate its electrons from the lone pair of the oxygen atoms to the cations (Li^+ or Na^+). This leads to a negative shift in the energy of the highest occupied molecular orbital (HOMO), increasing the oxidative stability of the electrolyte.^{18, 28, 29}

Figure 2-7. Illustration of the interaction between the salt (cations and anions) and water molecules in (a) “salt-in-water” and (b) “water-in-salt” electrolytes.¹⁸

Further, as the water molecules are unable to neutralize the electrostatic field created by the formal charge on the cation, the water solvation sheath is partially replaced by the anion-containing cation solvation sheath (e.g., $TFSI^-$, OTF^- , etc.), as shown in **Figure 2-7b**.^{18, 27} As a result, the interaction between the cation (Li^+ or Na^+) with the anion interaction becomes intimate. This interaction can be probed using spectroscopic

techniques such as Raman and nuclei magnetic resonance (NMR; ^{17}O NMR) spectroscopies. Consequently, based on the computational study (density functional theory calculation) of the WIS electrolytes, it is found that the anions' reduction potential is raised (**Figure 2-8**) and occurs before the water decomposes.^{18, 27} This favors the formation of the solid electrolyte interphase (SEI), which in turn, stabilizes the water molecules against the reducing surfaces of the anodes.

Figure 2-8. The reduction potential of OTF⁻ anions.²⁷

More recently, Lee et al. proposed the low-cost “WIS” electrolyte using a concentrated 17 m NaClO₄.³⁰ It can provide a full electrochemical stability window of up to 2.7 V (-1.2 V to 1.5 V Ag/AgCl). Unlike the sulfates- and nitrates- based salts, the high solubility of sodium perchlorates salt enables the hydration of water molecules to its cations, comparable to the organic solutes such as the NaCF₃SO₃ (NaOTF; 9.26 m) and LiTFSI (21 m) as shown in **Figure 2-9**. It enables the suppression of free water activities responsible for the parasitic side reactions. In addition, unlike the other WIS electrolytes, the 17 m NaClO₄ electrolyte is able to form the SEI layer without the reduction of its anions during electrochemical cycling. The formation of the SEI layer, composed of sodium carbonates, oxides, and hydroxides, enables the cycling stability of the cell.

Figure 2-9. Raman spectra of various saturated electrolytes and pure water.³⁰

2.3.2.2 “Water-in-bisalt” electrolytes (Strategy 3a-3c)

Indeed, the novel WIS concept proposed has significantly expanded the electrochemical stability window of the electrolytes. In brief, this expansion of the window is achieved through the following:

- (1) **Increase in oxidative stability:** At high salt concentration, the strong coordination of alkali ions with the water molecules leads to the negative shift in the highest occupied molecular orbital (HOMO), resulting in higher oxidative stability.
- (2) **Formation of SEI layer which suppresses hydrogen evolution reaction:** Due to the altered solvation sheath with high salt concentration, the anions have intimate contact with the alkali-ion. This interaction increases the reduction potential of the anions, enabling it to form SEI on the anode, which in turn, protecting the water molecules from the reductive surface of the anode.

However, the efficiency of the formation of the SEI layer depends on salt concentration.¹⁹ In particular, the maximum solubility of the given salts (e.g., LiTFSI- max solubility 21 m) placed a significant restriction on the further expansion of potential window and

suppression of water activities. In this regard, there have been a few remarkable strategies proposed to overcome this limitation for the Li-ion cells applications that are valuable to consider when designing the electrolytes for ARSIES.¹⁹⁻²⁴

2.3.2.2.1 “Water-in-bisalt”- Mixed anion electrolyte (Strategy 3a)

Inspired by the ability of the saturated electrolyte to dissolve another salt with similar chemical properties, Wang and co-workers formulated a “water-in-bisalt” with mixed anion electrolyte based on 21 m LiTFSI and 7 m LiOTF to achieve a higher cation to water molar ratios (0.5:1).^{19, 31, 32} The formulated WIS with mixed anion electrolyte enables the enhanced reductive stability of the cell (**Figure 2-10a and b**) while maintaining similar oxidative stability behavior compared to the WIS (21 m LiTFSI) electrolyte (**Figure 2-10c**). In aqueous sodium-ion energy storage, Hu and co-workers have also formulated the mixed anion electrolyte based on (9 m NaOTF + 2 m NaTFSI) as well as other aqueous sodium ion-based electrolyte formulations which will be further elaborated in the following.

Figure 2-10. (a) The electrochemical window of the Li-ion based full cell and the different electrolytes (21 m LiTFSI + 7 m LiOTF and 21 m LiTFSI). The enlarge regions near the (b) cathodic and (c) anodic extremes.¹⁹

2.3.2.2.2 “Water-in-bisalt”-Mixed cation electrolyte (Strategy 3b)

Given the potential widespread energy storage applications, there is a concern over the sustainability and cost of the electrolyte as the amount of salt required for WIS is substantial. To address these concerns, Bao and co-workers formulated the green and low-cost “water-in-bisalt” mixed cation acetates-based (8 m LiOAc and 32 m KOAc) electrolyte.²⁰ Taking advantage of the high solubility of potassium acetates and applying as a “water-in-bisalt” with the lithium acetate as the electrolyte, it can achieve a remarkably large electrochemical stability window of up to 2.7 V (-1.3 V to 1.4 V) with water to cation ratio of 1.3.^{20, 33} Importantly, this concept is particularly useful in the context of aqueous based energy storage mainly because of the low solubility of the majority of sodium-based salts (as shown in Table 2-2).²¹ As compared to the “water-in-bisalt” mixed anion electrolyte formulation based on (9m NaOTF + 2m NaTFSI; Table 2-2), a higher salt concentration electrolyte could be achieved with “water-in-bisalt” mixed cation electrolyte (9 m NaOTF + 8m KOTF; Table 2-2).²¹

2.3.2.2.3 “Water-in-bisalt” – Mixed inert-cation electrolyte (Strategy 3c)

Despite the higher concentration achieved *via* mixed cations electrolyte formulation, there is still concern about the mixed cation co-intercalation to the electrodes that could result in a detrimental effect on the cell cycling performance.^{21, 34, 35} In these regards, Hu and co-workers proposed a new class of “water-in-bisalt” mixed inert-cation electrolyte consisting of tetraethylammonium triflate (TEAOTF) salt.²¹ The formulated electrolyte consisting of NaOTF and TEAOTF mixture can reach up to an ultrahigh concentration of 31 m (9 m NaOTF+ 22 m TEAOTF), expanding the full electrochemical stability window up to 3.3 V (-1.7 V to 1.6 V vs. Ag/AgCl) as shown in **Figure 2-11**. Attributing to the large ionic radius of TEA⁺ cation (3.6 Å), this avoids the mixed cation co-intercalation process, even in the open structure framework of Prussian blue analog (PBA).²¹ Further, this electrolyte formulation can effectively suppress the transition metal dissolution of Na_{1.88}Mn[Fe(CN)₆]_{0.97}·1.35 H₂O (PBA) cathode, and enabling the superior cycle stability of full cell (PBA//NaTiOPO₄) with an excellent energy density of 71 Wh kg⁻¹.

Figure 2-11. The electrochemical potential window of 9 m NaOTF electrolyte and (9 m NaOTF + 22 m TEAOTF) electrolyte from the linear sweep voltammetry measurement taken at a scan rate of 10 mV s^{-1} .

Table 2-2. The sodium-based salts and its saturated concentration.²¹

Category	Salt	Saturated concentration (mol kg ⁻¹ ; m)
^a “Salt-in-water” electrolytes	Na ₂ SO ₄	2
	NaCl	6
	NaOAc	4.5
	NaNO ₃	10
^b “Water-in-salt” electrolytes	NaClO ₄	17
	NaOTF	9.3
	NaTFSI	9
	NaFSI	35
“Water-in-bisalt”- Mixed anion		
Electrolytes	NaOTF + NaTFSI	9 m NaOTF + 2 m NaTFSI
“Water-in-bisalt”- Mixed cation		
electrolytes	NaOTF + KOTF	9 m NaOTF + 8 m KOTF
“Water-in-bisalt” Mixed inert-cation electrolytes		
	NaOTF + TEAOTF	9 m NaOTF + 22 m TEAOTF

^a “Salt-in-water” electrolytes are defined as the ratios of the volume and weight of dissolved salt to the water in the solutions < 1 .

^b “Water-in-salt” electrolytes are defined as the ratios of the volume and weight of dissolved salt to the water in the solutions > 1 .

2.3.2.3 Hydrate melt (Strategy 4)

In ARSIES, due to the lower hydration energies of the majority of sodium salts, they have significantly lower solubility limits than lithium counterparts.²² As a result, the single sodium-based salt would reach saturation at a much lower concentration, such as 8 m for NaTFSI and 9 m for NaOTF.²² Therefore, the molar ratio of the water to cation remains high, with the non-negligible amount of unbounded water molecules remaining. As mentioned previously, several parasitic side reactions are associated with these free water molecules, which severely undermines the cycle stability of the cell. Further, cell cycling stability could be jeopardized if the saturated electrolyte would crystallize over time.³⁶

To address these issues, Yamada and co-workers recently proposed the novel hydrate melt electrolyte with ternary anions for both Na^+ and K^+ based systems.²² In particular, an optimized eutectic system $\text{Na}(\text{PTFSI})_{0.65}(\text{TFSI})_{0.14}(\text{OTF})_{0.21} \cdot 3\text{H}_2\text{O}$ was formulated for the ARSIES application.²² This formulated electrolyte has a full electrochemical stability window of up to 2.7 V (**Figure 2-12**). As asymmetric anions possess high vibrational mobility and flexibility, the highlight of this strategy is the incorporation of asymmetric (PTFSI⁻) anions $[\text{N}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_2\text{F}_5)]^-$ (**Figure 2-13**) to the NaTFSI-NaOTF mixture to achieve an overall high concentration (18.5 m) while reducing the viscosity of the electrolyte and suppressing the crystallization.²²

Figure 2-12. Electrochemical stability window of the different electrolytes.²²

As compared to the saturated NaTFSI (8 m) electrolyte, the sodium-ions of the hydrate melt can coordinate more effectively with the water molecules as indicated by the sharp O-H vibration peak at 3568 cm^{-1} and the absence of the broad band in its Raman spectrum

(**Figure 2-14a**). From the snapshot obtained from the DFT simulation, the largely uncoordinated water molecules of the low concentration 1.2 m NaTFSI electrolyte is indicated by the abundant presence of the water molecules' hydrogen bonding (**Figure 2-14a**). In contrast, almost all water molecules are coordinated with the sodium-ions, with negligible hydrogen bonding in the sodium hydrate melt (**Figure 2-14b**), emphasizing the effectiveness of this strategy in suppressing water activities for ARSIES.

Figure 2-13. The different chemical structures of the anions used in sodium hydrate melt.²²

Figure 2-14. Structural characterization of the electrolytes. (a) Raman spectra of the various electrolytes solution. Snapshots obtained the DFT simulations of (b) 1.2 m NaTFSI aqueous electrolyte and (c) $\text{Na}(\text{PTFSI})_{0.65}(\text{TFSI})_{0.14}(\text{OTf})_{0.21} \cdot 3\text{H}_2\text{O}$. (Light-colored surfaces represent the hydrogen bonding among the water molecules)²²

2.3.3 “Molecular crowding” electrolyte (Strategy 5)

Since the birth of WIS concept, the majority of its later improved derivatives have been utilizing the high concentration of fluorinated based salt to achieve suppression in water activities coupled with the formation of stable SEI for successive expanded window application. However, these pose a significant concern in terms of cost, sustainability, and

environmental impact when employed in large-scale energy storage applications. In these regards, Lu and co-workers proposed the novel “molecular crowding” electrolyte for Li-ion based system.²³ Formulated using the polyethylene glycol (PEG) as the water-miscible crowding agent with a low concentration of only 2 m LiTFSI salt as the electrolyte (2 m LiTFSI-94%PEG-6% H₂O), this presents as a promising low-cost and environmentally friendly strategy to address the former concerns. Further, with the introduction of water, it significantly raises the overall fire safety of the 2 m LiTFSI-94%PEG-6% H₂O electrolytes as compared to the non-aqueous system (**Figure 2-15a**) and the solid-state PEO polymer counterpart (**Figure 2-15b**). Due to its strong hydrogen-bonding interactions with the water molecules, this electrolyte (2 m LiTFSI-94%PEG-6% H₂O) exhibit a broader electrochemical stability window (up to 3.2V; **Figure 2-16a**) and its higher effectiveness in suppressing the hydrogen evolution reaction (**Figure 2-16 b-d**), than most of the proposed WIS formulations. This novel strategy holds great potential when transplanted to ARSIES in many promising aspects.

Figure 2-15. Flammability test. (a) 2 m LiTFSI-94%PEG-6% H₂O vs commercial electrolyte (b) comparison among 2 m LiTFSI-94%PEG-6% H₂O, 2 m LiTFSI-PEG and 2 m LiTFSI-PEO.²³

Figure 2-16. (a) Electrochemical stability window of the different electrolytes. (b-d) Online electrochemical mass spectroscopy monitoring of hydrogen evolution of the full cell (coated $Li_4Ti_5O_{12}/LiMn_2O_4$) in the 1st galvanostatic charge and discharge cycled in the various electrolytes.²³

2.3.4 Hybrid aqueous/non-aqueous electrolyte (Strategy 6)

The previous strategies (2 to 5) are mainly based on the high salt concentration to achieve the suppression of water activities, with the majority of them able to form the SEI layer during the reduction process. However, as the formation of the SEI layer is strongly dependent on the salt concentration, this imposes a significant challenge when designing the electrolytes for ARIES due to the low solubility of its salts. In this regard, the hybrid aqueous/ non-aqueous electrolyte (HANE) proposed by Wang and co-workers is an attractive strategy to achieve the stable formation of SEI layers *via* two stepwise reduction process of Li_2TFSI and $Li^+_2(DMC)$ aggregates (**Figure 2-17**), which eliminate the heavy reliance on the salt for SEI formation.²⁴ Remarkably, the optimized hybridized electrolyte (HANE) exhibits an unprecedented electrochemical stability window of up to 4.1 V (**Figure 2-18**). Moreover, credited to the presence of the water, this electrolyte maintains good fire safety without any combustion observed during the open fire combustion test (**Figure 2-19**). It clearly emphasized the importance of hybridizing the aqueous and non-

aqueous solvents to harness the safety and non-toxicity characteristics of the aqueous system and the enhanced electrochemical stability of the non-aqueous system.

Figure 2-17. (a) Liquid structure of HANE (H₁D₁). (b) Schematic illustration of the stepwise formation of the SEI on the anode in HANE.²⁴

Figure 2-18. The electrochemical stability window of the full cell (LiNi_{0.5}Mn_{1.5}O₄//Li₄Ti₅O₁₂) cycled in HANE.²⁴

Figure 2-19. Open flame combustion test using a propane-oxygen torch.²⁴

As shown in **Figure 2-20** and **Table 2-3**, it compares the electrochemical stability window for electrolytes formulated *via* different electrolyte engineering strategies. By overcoming the various challenges in the aqueous system, each approach presents its own unique set of capabilities and limitations. These strategies provide valuable insight into achieving the suppression of the water activities and effective formation of the SEI to expand the narrow electrochemical potential window of water, opening up many new possibilities for ARSIES.

Figure 2-20. Comparison of the electrochemical stability window of the different electrolyte systems.¹⁷⁻²⁴

Table 2-3. Summary of the various electrolyte systems.

Salt	Molality (mol kg ⁻¹ ; m)	Electrolyte conductivity (mS cm ⁻¹)	Electrochemical stability window	Molar ratio water to cation (Li ⁺ or Na ⁺)	Ref
Strategy 2: “Water-in-salt” (WIS) electrolyte					
LiTFSI	21 m	~10	1.9 V -4.9V vs. Li/Li ⁺ (3.0 V)	2.6	18
NaOTF	9.26 m	50	-1.2 V to 1.3V vs. Ag/AgCl (2.5V)	6.5	27
NaFSI	35 m	~ 8.0	-1.2 V to 1.4 V vs. Ag/AgCl (2.6 V)	1.5	28
NaClO ₄	17 m	108.0	-1.2 V to 1.5 V vs. Ag/AgCl (2.7 V)	3.27	30
Strategy 3a: “Water-in-bisalt”: Mixed Anion					
LiTFSI + LiOTF	21 m LiTFSI 7 m LiOTF	6.5	1.83 V-4.9 V vs. Li/Li ⁺ (3.07 V)	2.0	19
Strategy 3b: “Water-in-bisalt”: Mixed cation					
LiOAc+ KOAc Li _{0.2} K _{0.8} OAc. 1.3H ₂ O	32 m KOAc 8 m LiOAc	5.3	-1.3 V to 1.4 V vs. Ag/AgCl (2.7V)	~1.3	20
Strategy 3c: “Water-in-bisalt”: Mixed inert-cation					
NaOTF + TEAOTF Na _{0.29} TEA _{0.71} OTF 1.79 H ₂ O	9 m NaOTF 22 m TEAOTF	11.2	-1.7 V to 1.6 V vs. Ag/AgCl (3.3V)	1.79	21
Strategy 4: Hydrate melt electrolyte					
Sodium Hydrate Melt Na(PTFSI) _{0.65} (TFSI) _{0.14} (OTF) _{0.21} . 3H ₂ O	18.5 m	14.0	-1.0 V to 1.7 V vs. Ag/AgCl (2.7 V)	3.0	22
Strategy 5: Molecular crowding aqueous electrolyte					
LiTFSI-94%PEG-6% H ₂ O	2 m LiTFSI	0.8	1.3 V to 4.5V vs. Li/Li ⁺ (3.2 V)	Not specified	23
Strategy 6: Hybrid aqueous/ non-aqueous electrolyte					
LiTFSI -H ₂ O/ LiTFSI-DMC (H ₁ D ₁)	~14 m LiTFSI	~3.5	1.0 V to 5.1 V vs. Li/Li ⁺ (4.1 V)	Not specified	24

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Chapter 3

Experimental Methodology

This chapter covers the fundamental aspect of the electrodes synthesis, characterization techniques, cell assembly, and electrochemical testing. In the first section, the role of Polyvinylpyrrolidone (PVP) as a chelating agent to achieve the ideal cathode material for aqueous recharge sodium-ions energy storage (ARSIES) is highlighted and discussed. In the second section, the suites of characterization techniques used to elucidate the morphological, structural, and chemical evolution of the electrode as well as to probe the physical and chemical behavior of electrolytes will be elaborated. Finally, the assembly and various electrochemical testing will be presented.

3.1 Synthesis

3.1.1 Solid-state method

The solid-state method is one of the most widely employed technique to synthesize the inorganic materials by mixing of different precursors together and heating the mixture in a furnace till a set temperature at an optimized heating rate and duration. ¹

3.1.1.1 Principle¹

The commonly used precursors (e.g., acetates, nitrates, and carbonates) of the final product are ground together to achieve sufficient contact between the particles. Depending on the precursors melting points (T_m), the heating temperature is typically set above the $2/3 T_m$ for the materials to be reactive based on Tammann's rule.² In the heating process, the precursors react together, forming both the final product and by-product in the form of gases.

3.1.1.2 Applications

In this work, a solid-state method employed to synthesize the $\text{Na}_{0.44}\text{MnO}_2$ particles as a control sample.

3.1.2 Role of Polyvinylpyrrolidone (PVP) in polymer assisted sol-gel synthesis

3.1.2.1 Principle³

With the introduction of polyvinylpyrrolidone (PVP) as a chelating agent with the colloidal metal dispersion in the sol-gel synthesis, the imide group (N and O atoms) of PVP is able to interact with the individual unit of the metal colloid (**Figure 3-1**). Such interaction enables the stabilized particle growth process and facilitates nucleation formation.^{4, 5}

Figure 3-1. Schematics showing the particle growth process *via* solid-state (SS) and PVP-assisted sol-gel (SG) methods.³

3.1.2.2 Applications

Due to its ability to suppress the agglomeration of as-synthesized materials *via* the PVP-assisted sol-gel route, it is a promising technique to synthesize the ideal electrode materials for battery application.^{3, 6} This technique is used in the study to synthesize the homogenous rods and plates-like morphologies of $\text{Na}_{0.44}\text{MnO}_2$ for electrochemical performance evaluation.

3.2 Material Characterization

3.2.1 X-ray Diffraction (XRD)

XRD is widely used to determine the phase, crystal structures, and the presence of any impurities of the as-synthesized sample.

3.2.1.1 Principle⁷

When the X-ray typically from the $\text{CuK}\alpha$ source strike a crystalline sample over a range of angle (2θ), constructive interference will be generated when Bragg's law is met, as shown in **Figure 3-2**. Bragg's law relates the wavelength (λ) of the $\text{CuK}\alpha$ source to the diffraction angle (θ) and the lattice distance (d), hence when the crystalline sample is tested

over a known range of angle with known X-ray source, the lattice distance values can be calculated from the peak position with certain values of intensity that are generated for the sample. These sets of lattice distance values, in turn, indicate the phases or orientation of the samples. [7]

Figure 3-2. Bragg's Law.⁷

3.2.1.2 Applications

XRD is used in this study to determine the phase of the pristine and cycled materials. The model of XRD used: Bruker D8 Avance XRD using $\text{CuK}\alpha$ radiation with wavelength 1.5404 Å. TOPAS software is used for Rietveld refinement of the diffraction pattern collected to check the crystallinity and atomic arrangement of the crystals.

3.2.2 Scanning Electron Microscopy (SEM)

SEM is typically employed to examine the morphology and determine the particle size distribution of the synthesized materials.

3.2.2.1 Principle^{8,9}

The operational condition for SEM is at room temperature (~300 K) and in vacuum pressure of $\sim 10^{-10}$ Torr. The resolution of the SEM is a dependent electron probe size with a typical value of 1-2 nm. There are two types of signals collected when the electrons strike the

sample, namely inelastic scattering from the secondary electrons and elastic scattering from the backscattered electrons. The low energy secondary electrons which can only escape near the surface within the depth ranging from 5-50 nm provides the topographic information, whereas the backscattered electrons which can escape from the interaction volume with a depth ranging from 50-300 nm is collected for elemental composition contrast as shown in **Figure 3-3**.

Figure 3-3. A typical electron beam interaction with the sample.⁸

3.2.2.2 Applications

SEM was used in this study to observe the morphology of the pristine and cycled materials. Model of SEM used in this study: JEOL FESEM 6340 and 7600F.

3.2.3 Energy Dispersive X-ray Spectroscopy (EDX)

EDX is a qualitative analytical technique used for the chemical composition and distribution analysis of the sample.

3.2.3.1 Principle^{10, 11}

The sample is bombarded with a beam of electrons, which creates electron vacancies resulted from the ejected electrons from the atoms. These vacancies are filled with electrons at a higher energy state, and an X-ray (characteristic X-ray) is emitted to balance the difference in energy between the two electrons' states. An energy dispersive X-ray spectrometer is used to measure the energy, counts, and distributions of the emitted X-ray, which are element specific.

3.2.3.2 Applications

EDX was used in this study to map the elemental composition and distribution of the pristine and cycled materials. The EDX detector used in this study was attached to the SEM JEOL 7600F.

3.2.4 Transmission Electron Microscopy (TEM)

TEM uses a high energy electron source for illumination as opposed to the light microscope, which uses a light source to create the image, as shown in **Figure 3-4**.¹²

3.2.4.1 Principle¹³

The resolution of TEM is dependent on accelerating voltage, for example, at 200 kV, the resolution is up to 0.2 nm.¹² As the electron beam penetrates through the thin section of the material, the electrons are scattered and focused on either an image or diffraction pattern. To obtain the image pattern, the intermediate lens is focused on the image plane of the objective lens. On the other hand, the diffraction pattern is obtained by focusing the intermediate lens on the back focal plane of the objective lens.¹² With the elastically and coherent electrons interact with the thin sample as shown in **Figure 3-5**, high-resolution TEM can be employed to examine the crystal arrangement and orientation, an example of Si [110] orientation is as shown in **Figure 3-6**.¹²

Figure 3-4. Schematic of light microscope vs. transmission electron microscope.¹²

Figure 3-5. Types of electrons.¹²

Figure 3-6. HRTEM image of silicon [110] orientation.¹²

3.2.4.2 Applications

TEM is employed to observe the morphology of the pristine and cycled samples at a higher resolution. Model/Software of TEM used in this study: JEOL 2100F/ Gatan Digital Micrograph

3.2.5 Selected Area Electron Diffraction (SAED)

SAED is a crystallographic experimental technique performed in a TEM.

3.2.5.1 Principle

In the TEM, a thin sample ($\sim 100\text{nm}$ thick) is subjected to high energy electrons (~ 100 to 400 keV). These electrons undergo diffraction when Bragg's law is satisfied. For a highly crystalline sample, the SAED pattern consists of bright spots, while the SAED patterns of the amorphous sample include only ring-like patterns, as shown in **Figure 3-7a and b**, respectively.^{14, 15} A polycrystalline sample would consist of both the bright spots and ring-like pattern, as shown in **Figure 3-7c**. The different phases of the materials would have characteristic SAED patterns, and these are identified by indexing the spots or rings, as shown in **Figure 3-7a and c**.

Figure 3-7. SAED image of (a) $\text{Na}_2\text{Mn}_3\text{O}_7$ single-crystal (b) amorphous cobalt phosphides (c) polycrystalline cobalt phosphides.^{14, 15}

3.2.5.2 Applications

SAED is used as a diffraction technique to identify the crystal structures of the pristine and cycled materials. SAED is conducted in tandem with TEM (JEOL 2100F). The software used to analyze and index the SAED patterns includes Micrograph and Image J.

3.2.6 X-ray Absorption Near-Edge Structures (XANES)

3.2.6.1 Principle¹⁶

X-ray Absorption Near-Edge Structure (XANES) spectroscopy is a technique used for determining the oxidation states for the specific element in a sample of interest. This technique is one of the inner shell spectroscopies in which the X-ray would interact with the deep-core electrons, and such interaction would result in the change as a function of photon energy. When the photon (incoming X-ray) interacts with the deep-core electron (e.g., 1s electron is excited for a K-edge spectrum). This electron will be shifted to the unoccupied state above the Fermi energy, creating a core-hole. In a short period of time (~1-2 femtoseconds), the higher-lying electron would fill in the core-hole. At this point, either a photon or an Auger electron would be emitted. In particular, each element has its own characteristic excitation and fluorescence energies. Therefore, the valence of the element can be determined even in a heterogeneous sample. The XANES measurement used in this study is conducted in the Synchrotron Light Research Institute (SLRI) in Thailand. As shown in **Figure 3-8a and b** are the schematic and the actual layout of the instrument in the Synchrotron Light Research Institute (SLRI).

Figure 3-8. (a) Schematic and (b) actual layout of the XANES instrument in SLRI.¹⁷

3.2.6.2 Applications

In battery research application, XANES is typically employed to determine the valence states and chemical evolution of the pristine and cycled electrodes.¹⁸

3.3 Electrolyte Characterization

3.3.1 Confocal Raman Spectroscopy

Confocal Raman spectroscopy is a spectroscopic technique mainly used to determine the various vibrational modes of the molecules. The Raman spectra give the molecular fingerprint, and it is different for different molecules.

3.3.1.1 Principle¹⁹

Raman spectroscopy uses the inelastic scattering of photons, usually from a source of monochromatic light such as a laser. The laser beam is directed onto the sample, which

results in different types of scattering, as shown in **Figure 3-9**. When the sample is exposed to monochromatic light, the sample absorbs light, and a major portion of the light is transmitted through the sample. A minute part of the light is scattered by the sample in all directions. If the scattered light has the same frequency as the incident light, the scattering is Rayleigh scattering. On the other hand, if the scattered light has a different frequency as the incident light, it is known as the Raman scattering.

The electrons have different vibrational levels, defined by specific energy differences. When a monochromatic incident light interacts with an electron in the sample, the electron absorbs energy from the incident photon and rises to a virtual state of energy. The energy transferred is given the formula $E = h\nu$ (Planck's equation), where ν is the frequency of the incident photon. The electron then falls back to an energy level by losing energy. If the energy lost equals the energy of the incident photon, the electron falls back to its initial vibrational level and, in this process, emits another photon. Since the energy lost is equivalent to the energy of the incident photon, the released photon has the same frequency as the incident photon, which gives rise to Rayleigh scattering. If the electrons lose energy from the virtual state and fall back to a different vibrational level, the energy lost by the electron is different than the energy absorbed from the incident photon. As a result, the photon emitted by the electron has energy different than the incident photon, which gives rise to Raman scattering.

Depending upon the final energy of the electron or final vibrational level of the electron, Raman scattering can be separated into Stokes and anti-Stokes lines. The electron absorbs energy if the frequency of the scattered photon is less than the frequency of the incident photon, Stokes lines are observed on the Raman spectrum. On the other hand, the electron releases energy when the frequency of the emitted photon is greater than the incident photon, anti-Stokes lines are observed.

Figure 3-9. Energy-level diagram with the various states associated with confocal Raman spectroscopy.¹⁹

3.3.1.2 Applications

Confocal Raman spectroscopy is useful in determining alkali cation hydration of the water molecules interaction (e.g., in the high concentrated aqueous electrolyte) as well as the hydrogen bonding interaction between ethanol and water cosolvent based electrolyte.^{20, 21}

3.3.2 Fourier Transform Infrared (FTIR) Spectroscopy

3.3.2.1 Principle²²

In infrared spectroscopy, a sample of interest is irradiated with the polychromatic infrared electromagnetic radiation. As a result, some of this radiation is absorbed by the sample, while the remaining of the radiation is transmitted to the detector. By studying the spectrum of the transmitted radiation, it is possible to obtain information on the chemical structure of the sample. At the specific amount of energy of the exciting electromagnetic radiation, it can be transferred to a molecule and cause the vibration of the molecule uniquely. A different wavelength exciting radiation is required to initiate the various vibration modes of the molecule.

As shown in **Figure 3-10**, it shows the various components of the Fourier transform infrared spectrometer. The components consist of a radiation source, beam splitter, two mirrors (one fixed and one movable), and the photodetector. Typically, the sample is loaded in front of the detector.

Figure 3-10. Components of FTIR.²²

When the radiation from the IR source reaches the splitter, half of the beam passes through the splitter to the fixed mirror while the other half is reflected in the movable mirror. When these two beams reach the mirrors, they are reflected back toward the splitter. At the splitter, both beams are split again, causing part of the radiation reflected from the fixed mirror and movable mirrors to recombine and go through the sample into the detector. Meanwhile, the other part of the radiation that was reflected by the mirrors goes back to the radiation source. Constructive interference is created when both mirrors are set at an equal distance from the splitter, causing the two beams to reach the detector in the same phase.

At this point, the radiation reaching the detector has the highest intensity. However, if the movable mirror is moved by $\lambda/2$, the intensity of the radiation reaching the detector drops because the two recombined beams are no longer in-phase and cancel each other out, which is known as destructive interference.

Thus, in order to carry out the measurement, the movable mirror is shifted, resulting in an interferogram by measuring the intensity of the radiation that reaches the detector. The interferogram holds spectral information in the time domain. It is then converted into a spectrum with the frequency domain by Fourier transform process.

3.3.2.2 Applications

FTIR is useful in determining the molecular interaction (e.g., hydrogen bonding) of the electrolyte (or solvents).^{21, 23}

3.3.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

3.3.3.1 Principle²⁴

The nuclear magnetic resonance (NMR) is useful in identifying the carbon and hydrogen framework in the inorganic compound. NMR could only work for certain nuclei having either an odd number of proton or neutron (e.g., ^1H , ^{13}C , ^{31}P , etc.). Each of these protons has a positive charge and a property called spin. These moving protons would generate its own magnetic field. In a set of these protons, the protons would have random orientations (**Figure 3-11**). When an applied magnetic field is applied to this set of protons, the protons would either aligned with or against it. The former nuclei are known as the α spin state, while the latter nuclei are known as the β spin state (**Figure 3-11**).

Figure 3-11. Schematic illustrating the randomly arranged protons and the different spin states (α and β) when an external magnetic field is applied.²⁴

Since the α spin state is lower energy than in β spin state, the majority of the protons or hydrogen nuclei will be in the α spin state as it is more stable. The difference in the energy between the α and β spin states is called the ΔE . This difference in energy is dependent on the strength of the applied magnetic field. To switch the hydrogen nuclei from the α spin state to the β spin state, the radiofrequency with sufficient energy would be needed. If the nuclei fall back to from the β to α state, the radiofrequency energy is emitted. And this would again take the radiofrequency energy to promote it back to the β spin state. When it is flipping back and forth between the α and β spin states, it is in resonance. Thus, the term nuclear magnetic resonance. The energy difference between the α and β spin states can be calculated using the following formula:²⁴

$$\Delta E = h \times \nu \quad (1)$$

$$\Delta E = h \times (\gamma/2\pi \times B_0) \quad (2)$$

where

ΔE is the difference in the energy between the α and β spin states

h is the Planck's constant,

ν is the frequency of the energy required for the protons to go into a spin state,

γ is the gyromagnetic ratio,

and

B_0 is the strength of the applied magnetic field.

As shown in **Figure 3-12**, it shows the overview block diagrams for the instrumentation of the NMR spectrometer.²⁴ The main components for the NMR consist of radiofrequency source and the magnetic field. The sample of interest is loaded between the poles of the magnet. The radiofrequency radiation is then transmitted and detected *via* the same coil on the probe. Later, either the magnetic field or the radiofrequency is regulated until the resonance condition is met for the nuclei of interest. The absorbed radiofrequency energy of the sample and its resulting signal would then be detected on the receiver coils, amplified and recorded.

Figure 3-12. Components of NMR. ²⁴

3.3.3.2 Applications

^1H NMR is useful in determining the hydrogen bonding interaction and the proton ratio in the ethanol-water cosolvents.²¹

3.3.4 Contact Angle Measurement

The static sessile drop method is commonly employed for contact angle measurement due to its direct approach in determining the angle formed between the liquid (electrolyte)-solid (substrate) interface. ²⁵

3.3.4.1 Principle²⁵

In the sessile drop technique, the contact angle is probed by a contact angle goniometer. The instrument includes an optical module to capture the liquid-solid interface with the aid of the incorporated image analysis software, formed angle (θ_c) of the interface could be measured (**Figure 3-13**).

Figure 3-13. An illustration of the contact angle measurement of the liquid on the stainless-steel substrate.

3.3.4.2 Applications

Contact angle measurement is a useful technique in determining the wettability of the electrolyte. ²¹

3.3.5 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is one of the most frequently used techniques for thermal analysis. This technique is used to study the behavior of materials as a function of temperature or time. Melting points, crystallization behavior, and chemical reaction are some of the many properties and processes that can be measured by DSC.

3.3.5.1 Principle²⁶

DSC measures the heat flow produced in a sample when it is heated, cooled, or held isothermally at a constant temperature. Depending on the type of sample, it may undergo one or more phase changes during the heating or cooling process. As shown in **Figure 3-14**, it shows the typical thermal effects that would occur when an amorphous plastic such as polyethylene terephthalate is heated.^{26, 27} This includes the glass transition (T_g), cold crystallization (T_c), and the melting point (T_m).

Figure 3-14. An illustration of the DSC curve.

Figure 3-15. An overview of the DSC instrument.²⁸

As shown in **Figure 3-15**, it shows an overview of the DSC instrument. In a DSC experiment, the heat flow from the furnace to the sample is measured relative to the heat flow to reference material. The sample and reference crucibles are identical except that the reference crucible is typically empty. They are loaded directly on top of the sensor and surrounded by a heated chamber or furnace. The sensors consist of thermocouples that would then detect the heat flow. The thermocouple guarantee that the heat flow is accurately measured. The temperature sensor in the furnace would also regulate the temperature *via* a heater. A cooling option is often necessary to perform experiments below room temperature. In this case, cooling is achieved by means of a flow of air around the furnace or by using a cryostat or an intracooler. The measurement curve generated by the computer (x-axis: temperature and y-axis: heat flow in mW) would provide valuable information such as the enthalpy of melting and the specific heat capacity of the materials.

3.3.5.2 Applications

DSC is useful in determining the crystallization of the electrolyte to evaluate its suitability for low-temperature storage and for cell application.²⁹

3.3.6 Viscosity measurement

3.3.6.1 Principle³⁰

Based on Newton's law, the viscosity (η) can be defined as the shear stress (τ) divided by the shear rate ($\dot{\gamma}$). Therefore, the instrument to measure the viscosity, are typically based on the two-plates model, as shown in **Figure 3-16**. The sample is loaded between the two parallel plates. Shear will be applied by moving the top plate while the bottom plate is fixed (rigid). A device (rheometer) will be used to record the amount of shear force (F) *via* the torque as well as the velocity of the plate at various points. And since the shear area (A) and gap distance (h) between the plates are known, the viscosity of the sample can be determined.

Figure 3-16. Viscosity determined by the amount of shear stress and shear rate based on the two-plates model.

3.3.6.2 Applications

Viscosity measurement is commonly employed in electrolyte studies as it is one of the important parameters that would affect the electrochemical performance of the cell.³¹

3.3.7 Conductivity measurement

3.3.7.1 Principle ³²

In an electrolyte, it contains both the positively and negatively charged ion. When a pair of conductive plates are dipped into the electrolyte, connected to the battery source, a complete circuit is formed, as shown in **Figure 3-17**.

Figure 3-17. Basic set up for conductivity measurement.

When the voltage is applied, the positively charged ions of the electrolyte will move towards the plate connected to the negative terminal of the battery while this applies the opposite manner for the negative charge ions. In this way, the resistance (R) can be defined as:

$$R = \rho \times (L/A)$$

where

R is the resistance,

P is the resistivity,

L is the distance between the plates,

and

A is the surface area of the plate.

Since the conductivity (k) is defined as the inverse of resistivity ($1/\rho$) and according to Ohm's law, the resistance can be defined as voltage (V) divided by current (I), where V and I are known values, the following equation can be further expressed as follows:

$$\text{Conductivity (k)} = I/V \times (L/A)$$

3.3.7.2 Applications

Conductivity measurement is commonly employed in electrolyte studies as it is one of the important parameters that would affect the electrochemical performance of the cell.³¹

3.4 Electrochemical Cell Assembly and Testing

3.4.1 Electrode preparation

The as-synthesized powder for active material is mixed with conducting carbon (Super P, Timcal) and binder (teflonized acetylene black-2) in the mass ratio of 8:1:1. In the case of $\text{Na}_4\text{Mn}_9\text{O}_{18}$ full cell, the active materials mass ratio for $\text{Na}_{0.44}\text{MnO}_2$ (working) to activated carbon (counter) is 1: 2.5. The composite powders are pressed onto the titanium foil substrate, which acts as a current collector at a pressure of 6 tons. The electrodes are vacuum dried overnight at 60 °C to eliminate any residual solvent.

3.4.2 Cell assembly

For three-electrodes configuration, $\text{Na}_{0.44}\text{MnO}_2$ active material, platinum foil, and silver/silver chloride (Ag/AgCl) are employed as the working, counter, and reference electrode, respectively (**Figure 3-18**). The sodium-based salts are dissolved in DI water as electrolytes. In the full cell configuration, it is fabricated using a coin cell (2032) with the electrodes (working- $\text{Na}_{0.44}\text{MnO}_2$, counter-activated carbon) sandwiching a glass microfiber filter paper soaked with 150 μl of sodium-based electrolyte.

Figure 3.18. Three-electrodes setup.

3.4.3 Linear Sweep Voltammetry (LSV)

3.4.3.1 Principle³³

Linear sweep voltammetry (LSV) technique is where the output current is measured as a function of time and as a function of the potential between the working and reference electrodes. The potential is varied linearly and ends at a specified potential.

3.4.3.2 Applications

LSV technique is used in this study to evaluate the potential where the oxygen and hydrogen evolution takes place in the aqueous electrolytes.³⁴

3.4.4 Cyclic Voltammetry (CV)

3.4.4.1 Principle³⁵

Cyclic voltammetry (CV) is carried out between a working and a reference electrode at a specified fixed scan rate (mV s^{-1}). When an increase and decreased in current response

recorded over a certain voltage range is observed, these correspond to either oxidation (positive y-axis) or reduction (negative y-axis) potential of the material, as shown in **Figure 3-19**. The reversibility of the redox reaction of the material is determined by the ability of the materials to have the same oxidation and reduction intensity and position peaks as the previous cycle.

Figure 3-19. Typical peak profile using cyclic voltammetry technique illustrating the oxidation and reduction reaction.³⁵

3.4.4.2 Applications

CV technique is employed in this thesis to probe the electrochemical reaction of the electrode.

3.4.5 Galvanostatic Charge and Discharge (GCD)

3.4.5.1 Principle³⁶

Galvanostatic charge and discharge technique apply a constant current to the cell and scan across a set limit range of potential over a period. The time for a cell to fully charge and discharge can be used to calculate the specific capacity of the cell (mAh g^{-1}) with the active mass and fixed current rate known. An example of the charge and discharge profile of doped and undoped vanadium samples is as shown in **Figure 3-20**.³⁶

Figure 3-20. Example of galvanostatic charge and discharge profile of doped and undoped vanadium samples.³⁶

3.4.5.2 Applications

GCD technique is used in this thesis to evaluate the electrochemical performance of the electrode, such as the cycling stability and rate performance.

3.4.6 Electrochemical Impedance Spectroscopy (EIS)

3.4.6.1 Principle³⁵

To measure the electrolyte (R_{Ω}), charge transfer (R_{ct}), and the capacitive double layer (C_d) resistances, electrochemical impedance spectroscopy measurement is done by sweeping an alternating potential across the electrochemical cell over a range of specified frequencies. [9] This results in a range of alternating current, which is then measured for its respective impedance value. At higher frequencies, that is where the region of kinetic control, whereas for lower frequencies, corresponds to the region of mass transfer control, as shown in **Figure 3-21** and the equivalent circuit, as shown in **Figure 3-22a and b**.³⁵

Figure 3-21. Nyquist plot of a model electrochemical configuration.³⁵

Figure 3-22. (a) The equivalent circuit for the Nyquist plot and (b) Equivalent components of Z_f .³⁵

3.4.6.2 Applications

EIS technique is used in this thesis to study the electrode-electrolyte interphase and ions diffusion kinetics.

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Chapter 4

Morphology control of $\text{Na}_{0.44}\text{MnO}_2$ as a cathode material for aqueous rechargeable sodium-ion energy storage

In this chapter, a superwide applicable potential window (1.3 V) of $\text{Na}_{0.44}\text{MnO}_2$ (NMO) has been reported in the aqueous system for the first time. It is achieved via electrode modification of NMO through the PVP-assisted sol-gel route, which could yield uniform rods and plates structure depending on annealing conditions, with high phase purity and crystallinity. Preliminary electrochemical performance evaluation of NMO is tested in both a non-aqueous and aqueous system to gain an understanding of the electrode kinetics. Subsequently, the NMO cycling stability and rate performances are compared to that of NMO particulates. Ex-situ characterization of the cycled electrode unveiled the interesting discovery of a sheet-like structure forming on NMO rods and plates, which potentially acts as a passivation layer against degradation activities associated with the aqueous system. This work provides the guideline for the electrode morphological influence on the electrochemical performances for ARSIES.

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4.1 Introduction

The need for high capacity cathodes for aqueous rechargeable sodium-ion energy storage (ARSIES) has been emphasized in the literature. Among the various transition metal-based cathodes employed in ARSIES, manganese-based cathodes are attractive due to its suitable redox reaction potential range within the thermodynamic limits of water.¹⁻⁷ In particular, a tunnel- typed sodium manganese oxides, $\text{Na}_{0.44}\text{MnO}_2$ (NMO) has been one of the most widely investigated cathode material in both non-aqueous and aqueous systems.^{1-3, 5, 6, 8, 9} Owing to its uniquely large tunnel structures, $\text{Na}_{0.44}\text{MnO}_2$ can accommodate a high amount of sodium-ions (up to 0.44 mol Na-ions) with attractive theoretical capacity ($\sim 121 \text{ mAh g}^{-1}$). However, there are several challenges faced by NMO in an aqueous system due to the various parasitic side reactions associated with the water solvent.

One of the major problems is the inferior cycle instability, especially during deep discharge, which could be potentially due to manganese (Mn^{2+}) dissolution, proton co-insertion into the active material during electrochemical cycling, among others.¹⁰ To overcome the cycle instability of NMO, some studies adjust the lower cut-off potential, which has proven success in cycling NMO reversibly, however, with a significant sacrificial loss of NMO's energy density.^{1, 3} There are also a few strategies proposed, such as elemental doping and coatings of NMO, to enhance its cycle stability.^{4, 6} However, these works have yet to demonstrate high energy density with the long cycle life of NMO. There are also several studies related to electrolyte modification in the aqueous system that could potentially enhance electrode cycle stability. The electrolyte engineering will be further discussed in the subsequent chapters (Chapter 5 and 6).

In this chapter, the main focus is on electrode modification of NMO, *via* a novel polyvinylpyrrolidone (PVP)- assisted sol-gel route. Meanwhile, the NMO (particulates) is synthesized *via* a simple solid-state method for comparison. The preliminary studies of NMOs are done in both a non-aqueous and aqueous system. Subsequently, a series of electrochemical testings are done to evaluate the cycle stability and rate performance of NMOs at deep discharge potential. Finally, a combination of *ex-situ* characterization

techniques are employed to gain insight into the structural and phase evolution of the NMOs (pristine and cycled electrodes).

4.2 Experimental Methods

4.2.1 Material synthesis

Sodium acetate anhydrous (Purity 99%, Merck) and manganese (II) acetate tetrahydrate (99.99% trace metal basis, Aldrich) in a weight ratio of 1:2, were added into 5 mL of ethanol and stirred overnight. 0.2 g mL⁻¹ of polyvinyl pyrrolidone (PVP, Mw= 360,000, Fluka) were added into de-ionized water and stirred overnight. Both solutions were mixed and stirred for another 6 hours. The final solution was then calcined in a muffle furnace at 750 °C and 900 °C with a heating rate of 3 °C min⁻¹ for 8 hours to obtain NMO rods and plates. For the solid-state synthesis of NMO particulates, both sodium acetate anhydrous and manganese (II) acetate tetrahydrate were grounded together in a weight ratio of 1:2 and calcined at 900 °C with the same heating rate and duration.

4.2.2 Material characterization

The pristine, ground samples were loaded into a capillary Kapton tube holder with a diameter of 0.50 mm with a 0.01 mm wall thickness. 2D X-ray diffraction (XRD) patterns of the as-prepared pristine samples were then collected with a wavelength of 0.2405 Å and a detector to sample distance of 1.20 m using Beamline 28-ID-2, National Synchrotron Light Source II, Brookhaven National Laboratory.¹¹ The collected 2D X-ray diffraction data were then calibrated using a Nickel standard and integrated using Fit2D software. The Rietveld refinements of the XRD pattern were carried out using the TOPAS 6.0 software. The 2θ values presented in the graph have been converted to Cu Kα wavelength of 1.5406 Å. The morphological characterizations were obtained by field emission scanning electron microscope (FESEM JSM-7600F, JEOL), and high-resolution transmission electron micrographs were obtained using the JEOL 2100F TEM. The elemental composition was

obtained by using the energy-dispersive X-ray spectroscopy (EDX) coupled to the JEOL 2100F TEM.

4.2.3 Electrochemical characterization

The working electrodes were prepared by firstly grounding the NMO powders with the Super P carbon using mortar and pestle. The teflonized acetylene black (TAB) binder is later added into the mixture with further grounding to form a pellet. The composition of NMO powder, Super P carbon, and TAB is in a weight ratio of 8:1:1, respectively. Then, the pelletized mixture is pressed onto the titanium mesh (Good Fellow) using a hydraulic press machine with a pressure of 10 MPa. The area of the pellet is $3\text{ mm} \times 3\text{ mm}$, with an active material mass loading of around 2 mg. In aqueous setup, platinum foil (99.99% metals basis, Alfa Aesar) and Ag/AgCl (saturated KCl) were employed as counter and the reference electrode, respectively. 1 M Na_2SO_4 (Purity >99%, Sigma Aldrich) dissolved in argon purged de-ionized water was used as the electrolyte. For the non-aqueous setup, sodium metal foil (Sigma Aldrich) was used as both counter and reference electrode while 1 M NaClO_4 (Purity $\geq 98\%$, Sigma Aldrich) in 1:1 (v/v) ethylene carbonate (EC): propylene carbonate (PC) was used as the electrolyte. Cyclic voltammetry (CV) was carried out using Solartron 1256 B. The CV measurements in aqueous electrolyte were taken in three potential ranges as follows: (i) -0.3 V to 1.2 V, (ii) -0.4 to 1.2 V and (iii) -0.8 V to 1.2 V vs. Ag/AgCl. The CV measurement in the non-aqueous system was taken in the potential range between 2.0 V to 4.0 V vs. Na/Na^+ . EIS measurements were taken on pristine and cycled NMO samples in the frequency range between 100 kHz to 0.1 Hz on a Solartron 1256B. Galvanostatic charge and discharge (GCD) measurements were carried out using the Neware BTS system. All the electrochemical measurements were conducted under ambient pressure and temperature conditions.

4.3 Results and Discussion

4.3.1 Crystal structures and morphologies of as-synthesized Na_{0.44}MnO₂

The crystal structures of the as-synthesized of Na_{0.44}MnO₂ (NMO) powders were confirmed using high energy X-ray powder diffraction (XPD), and the lattice parameters were refined using Rietveld refinement methods. As shown in **Figure 4-1a and b**, all the diffraction peaks of the as-synthesized NMOs can be well indexed to the orthorhombic Na_{0.44}MnO₂ phase (crystal group: *Pbam*; PDF: 04-018-3147). Based on the Rietveld refinement on the X-ray powder diffraction data, the lattice structure parameters of the as-synthesized NMO plates is calculated to be $a = 9.0841(6) \text{ \AA}$, $b = 2.6408(1) \text{ \AA}$ and $c = 2.8238(2) \text{ \AA}$, with a lattice volume of $677.42(7) \text{ \AA}^3$. Subsequently, the unique structure of NMO is as illustrated in **Figure 4-1c**. The NMO structure framework is built up with the connections of polyhedrons (MnO₅ and MnO₆). In this framework, it consists of two types of tunnels (O- and S-shaped). A total of three sodium-ion sites (Na 1, Na 2, and Na 3) can be found in these tunnels (viewed from the c-axis). Specifically, in the smaller O-shaped tunnels, there is one sodium-ion site (Na 1), while the larger S-shaped tunnels have two sodium-ion sites (Na 2, and Na 3).

The morphologies of the as-synthesized NMO powders were characterized using field emission- scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). The SEM images of the as-synthesized NMO are as shown in **Figure 4-2**. It can be observed that inhomogeneous particulates (**Figure 4-2a**) were synthesized from the simple solid-state reaction. Meanwhile, the NMO synthesized via the sol-gel route without PVP yielded rods- (**Figure 4-2b**) and plates- (**Figure 4-2c**) like structures that are not uniformly distributed, with chunks of particulates still present. On the other hand, uniform rods-like structures (lengths: 5.0-8.0 μm , widths: 0.2-0.5 μm) and plates-like structures (lengths: 3.0-7.7 μm , widths: 1.8-6.0 μm) were successfully yielded *via* PVP-assisted sol-gel synthesis route (**Figure 4-2d and e**, respectively). The reason for the uniform growth of the NMOs (rods and plates) can be attributed to the interaction between the imide groups

of PVP and the metal ions of NMO precursors, which can suppress the agglomeration, enhance the nucleation process and stabilize the particle growth.¹²⁻¹⁴ Meanwhile, the different NMO morphologies (plates and rods) observed is due to the different annealing temperature, where the rod-like structure would start to form at a lower temperature and fused at the higher annealing temperature.

Figure 4-1. (a) XRD patterns of as-synthesized NMO powders and (b) NMO plates indexed with its corresponding diffraction peaks. (c) Crystal structure of NMO.

Figure 4-2. SEM images of as-synthesized NMO *via* different techniques- (a) solid-state, (b and c) sol-gel without PVP, and (d and e) sol-gel with PVP at different annealing temperatures.

Figure 4-3. TEM images (a and c) and high-resolution TEM (HRTEM) images (b and d) of as-synthesized NMO plates.

From the TEM image (**Figure 4-3a**), it can be observed that the NMO plates consist of a bundle of flakes stacked together. Further, the high-resolution TEM (HRTEM) image

(**Figure 4-3b**) shows well-defined lattice fringes with an interplanar spacing of 0.28 nm and 0.26 nm, corresponding to the (001) and (0100) crystal planes of NMO, respectively, well matching to the obtained XRD results. It also confirms the highly ordered crystal arrangement of NMO with crystal growth along the [001] direction. Such anisotropic NMO plates structure formation could possibly due to the faster crystal growth along the [001] plane directions as compared to other directions based on the orthorhombic lattice structure of NMO. As shown in **Figure 4-3c**, the magnified TEM confirms the stacking of several adherent flakes to form slab-like NMO plates. It is noteworthy that these slab-like structures consist of parallel plates, and there is no obvious grain-boundary from each other. This could potentially provide open [001] channels for fast sodium-ion diffusion. Further, as shown in **Figure 4-3d**, it can be observed that the adjacent flakes have lattice fringes with the same interplanar spacing of 0.45 nm, corresponding to (200) plane. This result demonstrates that the flakes have crystallized and formed a very well interlaced structure during the annealing process, which can potentially reduce the sodium-ion diffusion barrier and enhance the electrochemical performances.

4.3.2 Electrochemical performances of $\text{Na}_{0.44}\text{MnO}_2$

4.3.2.1 Preliminary testings of NMO in the non-aqueous and aqueous system: Electrode kinetics and reversible redox reaction potential range assessment

Cyclic voltammetry (CV) measurements were used to probe the electrode kinetics and the reversibility of the NMO plates in both the aqueous (1 M NaSO_4 in Di water) and non-aqueous systems (1 M NaClO_4 in EC: PC 1:1 v/v). In the non-aqueous electrolyte, the NMO plates exhibit a redox reaction in a wide potential range (between 2 V to 4 V vs. Na/Na^+). Moreover, it can achieve a high reversible capacity of 104.3 mAh g^{-1} at a current rate of 100 mA g^{-1} (**Figure 4-4b**). On the other hand, the NMO rods and plates tested in the aqueous system (**Figures 4-4c and d**, respectively) exhibit reversible redox reaction in a smaller potential range (between -0.3 V to 1.2 V vs. Ag/AgCl) as compared to the NMO tested in the non-aqueous system. As shown in **Figure 4-4d**, the assigned peaks (I-V)

corresponds to the specific (de-)insertion of sodium-ions into the respective sodium sites (Na 1, Na 2, and Na3), as summarized in **Table 4-1**.

Since the NMOs tested in both systems are the same, the narrower potential window of NMO could be attributed to parasitic side reactions associated with the aqueous system.¹⁰ Possible reasons for the irreversible sodium (de-)insertion process of NMO below the cut-off potential of -0.3 V vs. Ag/AgCl could be due to the degradation activities such as proton co-insertions into active material or dissolution of active material (e.g., Mn^{2+}) into the aqueous electrolyte upon electrochemical cycling.¹⁰ (**Note:** The investigation/modification of electrolytes is beyond the scope of this chapter, and it will be addressed in the subsequent chapters on electrolyte engineering.) Interestingly, it is noteworthy that the as-synthesized NMO rods and plates in this work present a significantly larger applicable potential window (-0.3 V to 1.2 V vs. Ag/AgCl), with a lower cut-off discharge potential, as compared to the reported NMOs tested in the aqueous system (potential window ranging between 0 to 0.75 V vs. Ag/AgCl).^{1-3, 5}

Figure 4-4. (a) CV of NMO plates tested in the aqueous and non-aqueous systems. (b) GCD curves of NMO plates tested in a non-aqueous system at 100 mA g⁻¹. CV of NMO tested in the aqueous system at various lower cut-off potentials (c) NMO rods and (d) NMO plates.

Table 4-1. Oxidation and reduction peaks of NMO plates and the corresponding sodium-ions (de-)insertion sites.

	Oxidation (V vs. Ag/AgCl)	Reduction (V vs. Ag/AgCl)	Oxidation (V vs. Na/Na ⁺)	Reduction (V vs. Na/Na ⁺)	Ma <i>et al</i> ⁹ Na site
Peak I	-0.19	-0.25	2.72	2.66	Na 3
Peak II	0.09	0.05	3.00	2.96	Na 2
Peak III	0.18	0.15	3.09	3.06	Na 1
Peak IV	0.32	0.28	3.23	3.19	Na 2
Peak V	0.54	0.51	3.45	3.42	Na 2

4.3.2.2 Electrochemical performance evaluation of NMO

Here, we prepared the homogenous NMO rods/ 750 (+) and plates/ 900(+) as well as the NMO particulate/ 900 ss as a control sample. To evaluate the NMO cycle stability performance, galvanostatic charge and discharge (GCD) tests are conducted on the NMO samples at a current density of 100 mA g⁻¹ over 100 cycles. As shown in **Figure 4-5a-c**, the initial two cycles of NMO maintain at a specific discharge capacity around ~70 mAh g⁻¹. Among them, the NMO plates exhibit the highest initial specific discharge cycle 77.2 mAh g⁻¹. After 100 cycles, the NMO rods and plates (synthesized via PVP-assisted sol-gel route) still exhibit high specific discharge capacity ~60 mAh g⁻¹ (**Figure 4-5a and b**), as compared to NMO particulates (synthesized *via* simple solid-state method) with significantly lower specific discharge capacity close to ~40 mAh g⁻¹ (**Figure 4-5c**). As observed in **Figure 4-5d**, the NMO particulates exhibit a faster decay rate with a capacity loss close to ~40% in the first 20 cycles (~2.14 % capacity loss per cycle). On the other hand, the NMOs rods and plates exhibit superior cycling stability with a low decay rate of only ~ 0.5% capacity loss per cycle in the first 20 cycles and stabilize in the subsequent cycles. Thus far, the NMO plates present the best electrochemical cycle stability performance. This can be attributed to the unique chemical bonded NMO plates structures that effectively accommodate the (de-)insertion of sodium-ions. As compared to reported NMOs tested in mild aqueous electrolytes (**Figure 4-5e** and **Table 4-2**), it is noteworthy that the NMO plates in this work can cycle reversibly in the broadest potential range of 1.3 V and delivering the highest specific discharge capacity (77.2 mAh g⁻¹) with sodium-ion (de-)insertion up to 0.28 mol Na-ions. Moreover, the NMO plates also exhibit excellent rate capabilities (**Figure 4-5f**) with specific discharge capacity close to ~50 mAh g⁻¹, even at a high energy density of 500 mA g⁻¹ (~4.1 C).

Figure 4-5. Galvanostatic charge and discharge (GCD) cycles of NMO (a) rods, (b) plates, and (c) particulates. (d) GCD of NMOs over 100 cycles. (e) Comparison of NMO electrochemical performance with reported NMOs.^{1-3, 5} (f) Rate performances of NMOs.

Table 4-2. Electrochemical performance comparison of NMOs in ARSIES.

NMOs tested in ARSIES	Potential Window (V vs. Ag/AgCl)	Current Density (mA g ⁻¹)	Discharge Specific capacity (mAh g ⁻¹)	Ref
Na _{0.44} MnO ₂ nanorods	0 V - 0.7 V	24.2	~ 40	3
Na ₄ Mn ₉ O ₁₈ nanorods	0 V - 0.7 V	30	~ 45	1
Na ₄ Mn ₉ O ₁₈ nanorods	-0.1 V - 0.75 V	25	~ 48	2
Na _{0.44} MnO ₂	0.1 V - 0.6 V	60.5	~ 30	5
Na _{0.44} MnO ₂ plates	-0.3 V - 1.0 V	100	77.2	This work

To gain further insight into the electrochemical behaviours of NMOs, the electrochemical impedance spectroscopy (EIS) measurements were conducted on the pristine and cycled (100th cycle) NMO samples. **Figure 4-6** presents the Nyquist plots of the NMO samples and the fitted equivalent circuit (inset of **Figure 4-6**). The charge transfer resistance at interfaces (R_{ct}) values of the NMO samples (pristine and 100th cycle) are presented in **Table 4-3**.

Figure 4-6. Electrochemical impedance spectroscopy (EIS) measurements with fitted curves of NMO plates, rods, and particulates electrodes before and after cycling along with the corresponding equivalent circuit given as insets.

Table 4-3. Charge-transfer resistance values of pristine and cycled (after 100 cycles at 100 mA g⁻¹) of NMO plates, rods, and particulates electrodes.

NMO	Plates	Rods	Particulates
Before cycles /Ω	15.4	10.9	10.8
After cycles /Ω	3.7	6.4	20.6

Interestingly, after 100 cycles, the R_{ct} value of NMO particulates increases almost two-folds while the R_{ct} values of NMO rods and plates decrease. It could be due to the fragmentation and agglomeration of the NMO particulates after cycling that lead to the poor connection between the electrodes and current collector. In contrast, the NMO plates have a low R_{ct} value of (3.7 Ω) and a sloping straight line at low-frequency region (**Figure 4-6**) after cycling as compared to the higher R_{ct} values of rods (6.4 Ω) and particulates (20.6 Ω), emphasizes the excellent charge transfer and ion diffusion electrochemical behavior of NMO plates. Further, the apparent sodium-ion diffusion D_{Na+} can be estimated from the inclined line in the Warburg region (**Figure 4-7**) using the following equation ¹⁵:

$$D = R^2 T^2 / (2 A^2 n^4 F^4 C^2 \sigma^2) \quad (1)$$

where,

R is the universal gas constant,

T is the absolute temperature,

A is the surface area of the electrode,

n is the number of transferred electrons per molecule during reduction,

F is the Faraday constant (96500 C mol⁻¹),

C is the sodium-ions concentration in electrode (9.81×10^{-3} mol cm⁻³) ^{3, 16},

σ is the Warburg coefficient associated with Z_{re} ($Z_{re} \propto \sigma \omega^{-1/2}$).

The value of σ can be derived from the slope of the fitted line. Based on the above equation (1), the calculated D_{Na+} value of NMO plates is 4.69×10^{-12} cm² s⁻¹, higher than that of the NMO rods (4.43×10^{-12} cm² s⁻¹) and the NMO particulates (2.2×10^{-12} cm² s⁻¹), which indicates the enhanced sodium-ion diffusion kinetics of NMO plates.

Figure 4-7. Linear fits of the Z_{re} vs. $\omega^{-1/2}$ curves of the NMO electrodes in the low-frequency region.

4.3.3 Post-mortem characterizations of Na_{0.44}MnO₂

4.3.3.1 Passivation sheet-like structure forming on NMO rods and plates after cycling

To gain further insight into the morphology changes of NMOs after electrochemical cycling, *ex-situ* SEM measurements were conducted on NMO samples after 100 cycles. As expected, the cycled NMO plates (**Figure 4-8a**) and rods (**Figure 4-8b**) maintained its uniform morphologies. On the other hand, the cycled NMO particulates (**Figure 4-8c**) possess agglomeration of fragmentized particles. Interestingly, passivation sheet-like structures can be observed on the top surface of the cycled NMO plates and rods (**Figure 4-8d and e**, respectively), which is absent on the cycled NMO particulates electrode. The sheet-like structure on NMO plates is further confirmed using the TEM (**Figure 4-9a**). The chemical composition of the sheet-like structure on the cycled NMO plates is tested using TEM coupled with energy-dispersive X-ray spectroscopy (TEM-EDX). Based on the TEM-EDX analysis (**Figure 4-9b**), it indicates the presence of sodium, manganese, and oxygen elements. (Cu and C elements attributed to TEM grid) Further, the HRTEM unveils the lattice fringes with the spacing of 0.25 nm (**Figure 4-9c**), which could correspond to the (200) plane of sodium-birnessite. Moreover, based on the selected area electron

diffraction (SAED) pattern (**Figure 4-9d**), it exhibits three diffraction rings, which could be assigned to the (200), (004), and (31-1) planes of sodium-birnessite, $\text{Na}_{0.55}\text{Mn}_2\text{O}_4$ (JCPDS No. 43-1456).

The sodium-birnessite sheet-like structure discovered on the cycled NMO plates and rods could be formed during electrochemical cycling, possibly due to the uniformly synthesized NMOs that provide sufficient active sites for deposition on the electrodes. Nevertheless, this is one of the important contributing factors towards the superior cycling stability of NMO plates and rods. It can potentially provide more sodium intercalation sites and stabilized the electrode structure (e.g., prevent pulverization). In addition, this sheet-like structure could also act as a passivation layer against any possible side reactions on the electrode associated with the aqueous system.

Figure 4-8. SEM images of the cyclized NMOs taken from cross-section and top view: (a, d) plates, (b, e) rods and (c, f) particulates. The corresponding magnified images are inset of Figure 4-8d–f.

Figure 4-9. (a) TEM image, (b) EDX analysis, (c) HRTEM image, and (d) SAED pattern of the sheet-like structure on the surface of the cycled NMO plates electrode.

4.4 Conclusion

In conclusion, $\text{Na}_{0.44}\text{MnO}_2$ (NMO) rods and plates were successfully synthesized via the PVP-assisted sol-gel route. For the first time, the superwide applicable potential window (1.3 V) for NMO has been demonstrated in the mild aqueous electrolyte in ARSIES. Benefitting from the robust, chemically bonded structures of NMOs, it enables NMOs to achieve excellent cycle stability even with deep discharge (-0.3 V vs. Ag/AgCl) as well as high rate capability. Further, postmortem studies have unveiled the sheet-like structures (sodium-birnessite) on NMOs that could have contributed towards the superior long term cycle stability of NMOs. This study opens a new pathway for developing low-cost and high-performance cathode materials to broaden the applicable potential window towards high energy and power density for ARSIES.

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1.3V superwide potential window sponsored by Na-Mn-O plates as cathodes towards aqueous rechargeable sodium-ion batteries

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BACK

CLOSE WINDOW

Chapter 5

A pH regulated “water-in-bisalt” mixed anion electrolyte towards full cell application of ARSIES

In this chapter, the aim is to design and construct an ideal full cell for aqueous rechargeable sodium-ion energy storage (ARSIES). In the full cell configuration, the NMO plate is employed as the cathode, and the anode is composed of the biomass-derived activated carbon. Meanwhile, the electrolyte is designed based on a pH regulated “water-in-bisalt” mixed anion strategy. The physical and chemical properties of the various electrolyte formulations are characterized. A combination of spectroscopic technique and computational study is used to determine the solution structure. The formulated electrolyte (35 M NaFSI + 5 M NaAc) can effectively suppress the water activities, which enables a wide electrochemical stability window up to 3.1 V. Moreover, the formulated electrolyte also exhibits stable and superior electrochemical stability, even at extreme temperature conditions.

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5.1 Introduction

Towards realizing the ideal full cell design for aqueous rechargeable sodium-ion energy storage (ARSIES), the design and compatibility of cell components (cathode, anode, and electrolyte) are vital to achieving the desired electrochemical performance. For the full cell configuration, the NMO plates with a widen applicable potential window developed in the previous chapter is employed as the cathode. Meanwhile, environmentally benign and easily derived activated carbon is used as the anode material.

What is an ideal electrolyte for ARSIES? Based on the literature, the major problem with aqueous electrolytes is the intrinsically narrow electrochemical stability window and its parasitic side reactions associated with water.^{1, 2} These challenges render the unsatisfactory energy density and cycle life of the aqueous-based cell for practical applications. Therefore, it is essential for the ideal electrolyte to “scavenge” these free water molecules to suppress its parasitic activities.

A significant breakthrough was made in the aqueous system when Wang and co-workers first proposed the novel “water-in-salt” (WIS) concept to expand the narrow electrochemical stability window of water.^{3, 4} By dissolving a high concentration of fluorinated salt (e.g., 21 mol kg⁻¹ LiTFSI) into the water, the salt formed strong alkali cation coordination with the water molecules’ Lewis base oxygen lone pairs, thereby suppressing the water activities.³⁻⁵ As a consequence, the highest occupied molecular orbital of the water molecules shifted towards the lower energy, increasing the oxidative stability of the electrolyte (upper cut-off potential). Meanwhile, due to the salt outnumbering the water molecules, the primary solvation sheath of the water molecules with the alkali cation is altered with the salt anions replacing these water molecules and having intimate alkali cations-anions interactions (e.g., Li⁺-TFSI⁻). As a result, the reduction potential of these anions shifted to a higher potential than the decomposition potential of water, enabling the formation of stable electrode interphase (SEI) on the anode. The SEI layers prevent the anode from decomposing the water molecules, thereby kinetically expanding the cathodic limits (lower cut-off potential) of the electrochemical stability window.

It is noteworthy that the WIS strategy is dependent on the salt solubility and the anion reduction products to achieve the SEI layer.⁶ Among the various sodium-based salts, NaFSI is the most attractive candidate due to its ultra-high solubility up to 37 m as compared to its sodium-based counterparts. In 2017, Battaglia and co-workers proposed the 35 m NaFSI as a WIS electrolyte for ARSIES, which exhibits a remarkable electrochemical stability window (ESW) of 2.6 V.⁵

Interestingly, despite the wide ESW enabled by the 35 M NaFSI, there has been no report evaluating its reliability in facilitating long term cycling stability of the cell. In this work, it is found that the 35 M NaFSI electrolyte exhibits an acidic pH (~2.5). Such acidic nature of the electrolyte may be detrimental to the electrode stability towards the practical application of ARSIES.⁷ Recently, there are also reports emphasizing the importance of having a mild pH electrolyte (pH close to 7) not only for stable cell operation but also for the possibility of application in wearable and biocompatible devices.^{7, 8}

Inspired by the dual salt system adopted in the “water-in-bisalt” strategy, herein, a green and low-cost sodium acetate is introduced as a secondary salt to alleviate the acidic electrolyte to a near-neutral pH (~6.5). The formulated electrolyte (35 M NaFSI + 5 M NaAc) not only expanded the ESW to ~3.1 V, but it also enables excellent cycle stability of the full cell. Moreover, owing to the higher thermal stability of the formulated electrolyte, it also renders stable cell operation even at demanding temperature conditions (-20 °C and 60 °C).

5.2 Experimental Methods

5.2.1 Material synthesis

5.2.1.1 Preparation of NMO

The NMO plates cathode is synthesized *via* the PVP-assisted sol-gel route, as mentioned in Chapter 4.⁹

5.2.1.2 Preparation of activated carbon from *Prosopis juliflora* plant

The dried small pieces of *Prosopis juliflora* woods were charred at 200 °C in an air oven. Next, the finely grounded black powder was activated with potassium hydroxide (1:4 wt. %) under the flowing of N₂ gas at 900 °C for 3 hours (PJAC). Finally, the activated product was repeatedly washed with water and ethanol, then subsequently dried at 80 °C.

5.2.2 Material characterization

The crystalline phase of the synthesized materials was analyzed by an X-ray diffractometer (XRD, Bruker D8 Advance) using CuK α radiation operated at 40 kV. The surface morphological and internal structural aspects were examined with a field emission scanning electron microscope (JOEL JSM- 7600F) and a high-resolution transmission electron microscope (JEOL 2100F). The ionic conductivity of the electrolytes was measured by a conductivity meter (CyberScan COND 610, EU TECH) at room temperature (25 °C). Prior to the conductivity measurement, the electrode accuracy was ensured by a 12880 $\mu\text{S cm}^{-1}$ calibration solution. Differential scanning calorimetry (TA Instruments- DSC Q10) studies were performed with a heating rate of 5 °C min⁻¹ under the nitrogen atmosphere. The viscosity of the electrolyte solution was analyzed in a steady shear and sinusoidal Rheometer (MCR 501, Anton Paar Physica, Ostfildern, Germany) with an Anton Paar CP25-1/TG 25-mm diameter cone-plate geometry with a cone angle of 1°. Raman spectra of the electrolytes were collected on a confocal Raman spectrometer (Alpha300 SR, WITec; laser wavelength $\lambda = 488 \text{ nm}$) between 100 to 4000 cm⁻¹ at ambient temperature.

5.2.3 Computational details

All the computations were done using the *Gaussian 09* suite of software. All the structures shown were optimized using the M06-2x density functional, which is highly successful in simulating chemistry in the condensed phase. The Pople-styled 6-31+G(d,p) basis-sets were used throughout. In addition to implicitly including the water molecules in our system,

the popular SMD implicit solvation model was employed. All the structures are energy minimized following the Berny algorithm and do not contain any imaginary frequency as assessed from harmonic frequencies.

5.2.4 Electrochemical characterization

The electrochemical stability window measurement of electrolytes and electrodes were carried out in a three-electrode cell with respect to the Ag/AgCl (sat. KCl solution) reference electrode. The platinum foil (99.99% metals basis) was served as both working and counter electrode for electrolyte studies, whereas employed only as a counter electrode for electrode perspective. The full cell is fabricated using a coin cell (2032) with the electrodes sandwiching a glass microfiber filter paper (Whatman GF/F) soaked with 150 μ l of WIS electrolyte (35 M NaFSI +5 M NaAc in Di). The cells were subjected to rest for 12 h at room temperature prior to the electrochemical measurements. The linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with Solartron 1256B electrochemical workstation. Galvanostatic charge-discharge measurements were conducted using a battery tester (Neware BTS) at various temperatures (-20, 25, and 60 °C) ranges.

5.3 Results and discussion

5.3.1 Full cell design for ARSIES

As shown in **Figure 5-1**, it depicts the full cell design for an ARSIES. To meet the criteria for the ideal ARSIES, the cell should be able to deliver the following:

- (1) High energy and power densities
- (2) Good cycle life
- (3) Versatile (e.g., stable in wide operating temperature range)

Due to the narrow potential window and the several parasitic side reactions associated with water that could undermine the cell performance, the electrodes and electrolytes are carefully chosen and modified to overcome the challenges in the aqueous system. For the cathode material, the NMO plates with a widen applicable potential window, as demonstrated in Chapter 4, is employed. One of the most commonly used anodes in energy storage is the activated carbon due to its low-cost, abundance, and reliable electrochemical performance.^{10, 11} Here, the anode employed is the abundant and environmental benign activated carbon derived from wood (Prosopis juliflora activated carbon; PJAC).¹² The as-synthesized PJAC is characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HR-TEM) techniques as shown in **Figure 5-2**. The two broad XRD reflections for PJAC (**Figure 5-2a**) corresponds to the (002) and (110) planes of typical amorphous carbon.¹² **Figure 5-2b** shows the SEM images of potassium hydroxide activated PJAC with its naturally existing rigid carbon skeleton, and the porous-structured carbon layers over the surface resulted from the activation process. **Figure 5-2c** shows the HR-TEM image of PJAC with its graphene-like PJAC layered carbons curled and randomly arranged, which results in a highly disordered structure.¹²

Figure 5-1. A schematic illustrating the full cell design for ARSIES.

Figure 5-2. (a) XRD (b) SEM (c) HR-TEM of the biomass-derived activated carbon (PJAC).

5.3.2 Electrolyte design and optimization

Sodium bis(fluorosulfonyl)imide (NaFSI) was proposed by Battaglia and co-workers as the promising salt for WIS application in ARSIES due to its high solubility limit ~35 M which enables a cell voltage window up to 2.6 V.⁵ However, it is found that the 35 M NaFSI electrolyte has a highly acidic pH of ~2.5. On the consideration that most battery components are susceptible to degradation in the acidic environment, the 35 M NaFSI electrolyte is still not ideal for ARSIES towards practical application. Inspired by the dual system in “water-in-bisalt” proposed by Wang and co-worker, 5 M of sodium acetates salt is added to neutralize the pH of 35 M NaFSI electrolyte to a pH of ~6.5. Its effects on the physical, chemical properties of the electrolyte are investigated.

5.3.2.1 Ionic conductivity and viscosity

Towards ideal electrolyte design for ARSIES, two of the key indicators for evaluating the electrolyte include both the ionic conductivity and viscosity, which determine the rate capabilities of the cell.^{13, 14} As presented in **Figure 5-3a**, it shows the ionic conductivity and viscosity measurements (25 °C) of the NaFSI electrolytes at varying concentrations and the binary mixtures with sodium acetates. At the saturation limit of NaFSI (35 M), it exhibits a conductivity of 12.3 mS cm⁻¹, which is in good agreement with the previous report.⁵ The high ion mobility at such a high concentration is attributed to the lower charge

density of sodium-ions compared to that of lithium counterpart.⁵ Further, the 35 M NaFSI electrolyte possesses a viscosity of 75.9 mPa s. Upon the addition of 5 M acetates, the conductivity of the electrolyte (35 M + 5 M) slightly decreases to $\sim 7.1 \text{ mS cm}^{-1}$ with an increase in the viscosity (121 mPa s). Nevertheless, as compared to other WIS based electrolytes, the observed conductivity and viscosity of 35 M + 5 M are considered to be in an ideal range for charge storage applications.¹⁵⁻¹⁷

Figure 5-3. The comparison (a) viscosity and ionic conductivity and (b) differential scanning calorimetry of the different sodium-ion based electrolyte solutions.

5.3.2.2 Evaluation of the electrolytes' thermal properties

The broad temperature applicability of the electrolyte is highly desired for the ideal ARSIES cell to operate stably and efficiently in cold and hot environments. Accordingly, the differential scanning calorimetry (DSC) is employed to evaluate the phase changes in the various concentration and binary mixture of WIS based electrolytes between -90 °C to 40 °C (**Figure 5-3b**).

At a low concentration (1 M NaFSI), the sharp endothermic (T_m) observed at ca. 0 °C corresponds to the ice melt of frozen water while the exothermic peak observed at -35 °C corresponds to the crystal-crystal phase transition. Upon the increase in NaFSI concentration to 10 M, the exothermic peak shifted towards the lower temperature (-40 °C) can be attributed to the decreased activity of free water favoring the

crystal-crystal phase transition. As expected, this also results in the absence of ice melts peak, which means that the electrolyte could remain stable in the liquid state above -40°C . At a higher concentration (20 M), both the T_c and T_m peaks disappear over the entire testing range, with the appearance of the glass transition (T_g) peak at -77.8°C , which typically refers to highly viscous sample.¹⁸ A similar characteristic thermal peak can also be observed in the binary electrolyte (35 M + 5 M) with the T_g shifted to the higher temperature ($\sim 57^{\circ}\text{C}$), due to increased ionic interaction strengths.¹⁸ Importantly, the linear heat flow without any fluctuation in heat flow value observed above -55°C manifest that the 35 M + 5 M electrolyte potentially can remain stable in a broad temperature range even in extreme temperature conditions.

5.3.2.3 Determination of solution structure

In order to gain insight into the variation in the solution structure, confocal Raman spectroscopy was conducted. As shown in **Figure 5-4**, the Raman spectra were recorded for the various electrolyte samples, including the pure water with the wavenumber ranging between 100 to 4000 cm^{-1} . The Raman spectra obtained were then deconvoluted to extract the single Raman band, as shown in **Figure 5-4c-f**.¹⁹

Figure 5-4. Raman spectrum of different concentrated all Na-ion based electrolyte solutions.

5.3.2.3.1 Solution structure at low concentration

Similar to the Raman spectrum of the pure water, the Raman spectra of 1 M NaFSI, 1 M NaAc, and 1 M NaOH (**Figure 5-4a**) exhibit the typical broad Raman band between 2900 to 3700 cm^{-1} , which corresponds to the free water molecules in various hydrogen bonding environments.^{5, 20} In such a case, the water cluster and the unbound ions can be presented as solvent-separated ions pairs (SSIPs), as shown in **Figure 5-5**.

Figure 5-5. Solvent separated ion pairs.

5.3.2.3.2 Solution structure at high concentration: From the perspective of FSI⁻ anion

As the concentration of the NaFSI with NaAc salt increase in the electrolyte (**Figure 5-4a and b**), the as-mentioned broad Raman band shift toward the higher wavenumber ($\sim 3565 \text{ cm}^{-1}$) coupled with the reduction in overall intensity and narrower reflection. This phenomenon is well-known as the hydration to cation (coordination of sodium-ions with the water molecules).^{5, 20} In general, the FSI⁻ anion can exist in two different conformation states, namely *cis* and *trans* conformers.²¹ Based on previous reports, the original NaFSI bands are observed at 298, 320, and 353 cm^{-1} (**Figure 5-4c**) corresponds to the *cis* conformer of FSI anion.^{19, 22, 23} On the other hand, the deviation in the vibrational bands is found to be around 256, 314, and 370 cm^{-1} (**Figure 5-4c**) for the concentrated NaFSI (35 M) electrolyte, with the deviations, further increase for 35 M + 5 M electrolyte. Such deviations suggest that the *trans* conformers are preferred when the FSI⁻ binds with the sodium and acetate ions.²⁴ Specifically, upon the addition of sodium acetates to 35 M NaFSI electrolyte, the deviation of vibrational frequencies near 313 cm^{-1} corresponds to

the rocking vibrational mode of SO_2 of FSI^- . This deviation is potentially due to the partial replacement of the water molecules with the larger acetate ions in the sodium solvation sheath, leading to the increased steric repulsion with the neighboring FSI^- anions. Further, with the addition of sodium acetates to 35 M NaFSI electrolyte, the bending vibration of the S-N-S band (731 cm^{-1}) is drifted to 741 cm^{-1} (**Figure 5-4d**). This can be ascribed to the FSI^- anions solvated to the sodium ions with the bonded acetate ion, with structure existing as contact ion pairs (CIPs) or aggregate ion pairs (AGIPs) configurations (**Figure 5-6**).²⁴

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Figure 5-6. Common ion pairs (CIPs) and aggregated ion pairs (AGIPs).

5.3.2.3.3 Solution structure at high concentration: From the perspective of acetate anion

As shown in **Figure 5-4d**, the band appearing at 935 cm^{-1} corresponds to the C-C stretching band at a lower concentration of acetate is attributed to the interaction between the acetate anions with the water molecules. At a higher concentration of acetates anions, the C-C stretching band is shifted towards the higher wavenumber (943 cm^{-1}) due to the polarization of the C-C bonds in the mixture.²⁶ Therefore, to further examine the aggregation behavior of the sodium acetates salt in 35 M NaFSI solution, the variation in the COO^- asymmetric stretching mode would be of interest. At a low concentration of sodium acetate (1 M) solution, the presence of the band at 1421 cm^{-1} (**Figure 5-4e**) is an indication of the SSIPs.²⁷ With the increase of sodium acetate concentration and the mixture with NaFSI salt in the electrolyte, this shifting of this COO^- stretching band towards the higher wavenumber ($\sim 1440\text{ cm}^{-1}$) suggests the alteration in the coordination environment. This could be due to the various interactions of acetate anions with water molecules, sodium, and FSI ions, forming the CIPs and AGIPs. In particular, in the 35 M NaFSI solution, the single cation-based aggregates species formed by the single anion is AGIP-I (**Figure 5-6**). On the other hand, the presence of the both FSI⁻ and acetates anions coordinated with the single cation (Na^+) through the different coordinating sites could form various configurations of anion dominated AGIPs (e.g., AGIP-II, III and IV) as shown in **Figure 5-6**. As shown in **Figure 5-4f**, it depicts the stretching vibration mode of the C-H band located at 2945 cm^{-1} , and the asymmetric vibration of *cis* C-H bond arises from the energy distorted methyl group (3015 cm^{-1}). This coordination environment remains complex to interpret due to the presence of several unassigned modes within this region. Thus, further studies are necessary to comprehend this impressive WIS electrolyte system.

5.3.2.3.4 Solution structure: Computational study

To further determine the most probable solution structure of the binary mixture (35 M + 5M), *ab initio* density functional computation was performed. To set up the model for the

Figure 1 displays four molecular structures (a, b, c, d) showing the relative orientation of the S_2O_2 molecule (yellow and red spheres) relative to the S_2O molecule (purple, yellow, and red spheres) in the $\text{S}_2\text{O}_2\text{-S}_2\text{O}$ complex. The structures are labeled with their relative energies in kcal/mol: (a) 7.95, (b) 7.24, (c) 0.00, and (d) 7.84. The atoms are color-coded: S (yellow), O (red), C (grey), and H (white). Dashed lines indicate hydrogen bonds.

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5.3.3 Electrochemical testing

5.3.3.1 Electrochemical stability window of electrolytes

To evaluate the electrochemical stability of the concentrated NaFSI electrolyte with sodium acetate electrolytes, the linear sweep voltammetry (LSV) is performed at a scan rate of 0.1 mV s^{-1} . As presented in **Figure 5-8**, it shows the anodic and cathodic limits of the various electrolytes. The overall electrochemical stability window is widened from $\sim 2.6 \text{ V}$ (35 M NaFSI) to 3.1 V (35 M + 5 M NaAc) vs. Ag/AgCl. In particular, with the higher sodium content in the electrolyte, it enables stronger coordination of cations with the water molecules, thereby enabling the shift of the highest occupied molecular orbital to more negative energy, expanding the oxidative stability (anodic limit).^{4, 5, 16} Also, with the alteration in the water solvation sheath and the aggregation of the anions due to higher salt concentration, it can possibly result in the shift in the FSI⁻ reduction potential for the formation of SEI layer, thereby expanding the cathodic limit of the 35 M + 5 M electrolyte.²⁹

Figure 5-8. Electrochemical stability window of the concentrated electrolytes.

5.3.3.2 Cathode and anode mass balancing

The full-cell NMO//PJAC is assembled with 35 M NaFSI +5 M NaAc as the electrolyte solution. Prior to full cell assembly, both anode and cathode charges have to be balanced by adjusting the mass ratio of the active materials based on three-electrode performance with platinum foil and Ag/AgCl as counter and the reference electrode, respectively (**Figure 5-9**). Based on the capacity obtained from the PJAC (**Figure 5-9a**) and NMO (**Figure 5-9b**) materials in the half-cell studies, the optimized mass ratio is fixed at 2.5:1.

Figure 5-9. Half-cell studies of (a,c) PJAC and (b,c) NMO.

5.3.3.3 Full cell testing: Optimization of cell cut-off potential

To determine the optimal cut-off potential, the full cell (NMO//PJAC) is scanned in various potential ranges using cyclic voltammetry (CV) technique at a scan rate of 0.1 mV s^{-1} as shown in **Figure 5-10a**. The as-observed CV curves exhibit the quasi-rectangular shape indicates the involvement of two different mechanisms consisting of (de-)intercalation as well as adsorption/desorption of charge carriers. Based on the optimization, the potential range is set as 0 to 2.8 V for the subsequent electrochemical testing. Beyond this upper cut-off potential ($>2.8\text{V}$), it could potentially trigger parasitic side reactions such as oxygen evolution and electrolyte decomposition.

5.3.3.4 Full cell testing: Electrochemical performance evaluation

As shown in **Figure 5-10b**, it depicts the CV curves of the full cell (NMO//PJAC) scanned at higher scan rates varying from 5 to 50 mV s^{-1} between 0 to 2.8 V at 25°C .

The as-observed CV curves (**Figure 5-10b**) exhibit the distorted rectangular shape curves without prominent redox peaks suggest the capacitive dominant behavior with a limited amount of sodium ion intercalation/de-intercalation. Similarly, this shape can also be observed in the CV curves at different testing temperatures, as shown in **Figure 5-11a and b**.

Figure 5-10c presents the galvanostatic charge and discharge (GCD) curves of the full cell at various current densities ranging from 0.1 to 4 A g^{-1} at 25°C . Accordingly, the GCD profiles display the non-linear sloping curves resembling the characteristic co-existence of battery and capacitor properties, in good agreement with CV measurements. As the current rates increases, the discharge time is decreasing due to the inaccessible electrochemical active area and also the limited sodium ion diffusion kinetics. The similar electrochemical characteristic was also recorded at high (60°C) and low (-20°C) temperature conditions.

To evaluate the long term cycle stability performance at different temperature conditions, both the full cells tested in 25°C and 60°C are cycled at a current rate of 1 A g^{-1} , while the

full cell tested in $-20\text{ }^{\circ}\text{C}$ is cycled at a 0.2 A g^{-1} over 5000 cycles. As shown in **Figure 5-10d**, approximately 88, 73, and 92% of the initial capacities were maintained after 5000 cycles at 25, 60, and $-20\text{ }^{\circ}\text{C}$, respectively. While the full cells tested in the $-20\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$ exhibit excellent cycling stability, the inferior performance at $60\text{ }^{\circ}\text{C}$ was mainly attributed to the dissolution of the transition metal from the battery electrode and electrolyte decomposition. Remarkably, the full cell (NMO//PJAC) still exhibits superior energy and power energy density as compared to the other reports (**Figure 5-12** and **Appendix A1**). For instance, when tested at $60\text{ }^{\circ}\text{C}$, a maximum specific energy density of 52 Wh kg^{-1} is achieved at a power density of 700 W kg^{-1} . Even at a substantially high power density of 5600 W kg^{-1} , the full cell still retained a maximum energy density of 38 Wh kg^{-1} . Moreover, at a low temperature of $-20\text{ }^{\circ}\text{C}$, the full cell is still able to deliver an energy density of 38 Wh kg^{-1} at a power energy density of 70 W kg^{-1} . The electrochemical performance for the full cell tested in this work with 35 M+5 M electrolytes is highly comparable to the organic electrolyte based hybrid charge storage system (regardless of Li^+ , Na^+ , and K^+).³⁰⁻³² Further, it is also better than the other reports based on the other WIS system (as summarized in **Appendix A1**).^{17, 33, 34}

As discussed, the remarkable electrochemical performance of NMO//PJAC is mainly attributed to the synergistic effects between the NaAc and NaFSI salts, which provides a pH neutral environment, effectively suppresses the water activities and forming the unique solution structure that could expand the electrochemical stability window of the electrolyte. This study emphasizes not only the requirement for a well-structured high capacity active material but also the importance of electrolyte engineering to attain high power and energy density with superior cycling stability.

Figure 5-10. (a) The voltage range profile, (b) cyclic voltammetry at different scan rates, and (c) the charge/discharge pattern of the PJAC//NMO asymmetric capacitor at 25 °C. The comparison (d) Nyquist plots and (e) cycling profile of the PJAC//NMO asymmetric capacitor in 35M+5M electrolyte at different temperatures.

Figure 5-11. The cyclic voltammetry curves and charge/discharge patterns of the PJAC//NMO asymmetric capacitor recorded at (a, b) 60 °C and (c, d) -20 °C, respectively.

Figure 5-12. Ragone plots of the PJAC//NMO ASC at different temperatures of 60, 25, and -20 °C and other reported works.

5.4 Conclusion

In this study, the rationally developed mixed anions based “water-in-bisalt” electrolyte enables the excellent operation of NMO//PJAC full cell in the wide operating temperature and potential range. The green and low-cost NaAc salt is not only utilized to neutralize the acidic pH of the NaFSI electrolyte but also triggers the formation of AGIP to expand the electrochemical stability window of the electrolyte up to 3.1 V. Further, the enhanced stability with excellent cycling performance realized at different temperatures is paralleled by *ab initio* studies. Overall, this study adopted a simple yet effective strategy to design and extend the exploration of various combinations of fluorine and/or non-fluorinated salts in the aqueous-based system to realize the safe, versatile, and high-performance full cell for ARSIES.

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Supersaturated “water-in-salt” hybrid electrolyte towards building high voltage Na-ion capacitors with wide temperatures operation

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Chapter 6

Green and low-concentrated electrolytes enabled by hydrogen-bonding interaction for ARSIES

In this chapter, the aim is to develop low-cost and sustainable electrolytes for ARSIES towards large-scale energy storage applications. Due to the several parasitic side reactions associated with water, it severely undermines the cycle stability of the cell and impeding the usage of low concentrated salt electrolytes. Here, the novel concept of hydrogen bonding to suppress water activities and parasitic proton-co insertion is proposed. As a proof of concept, the hydrogen bonding is achieved through the hybridization of polar and protic ethanol solvent with water as an electrolyte cosolvent. The hydrogen bonding interaction of the hybridized electrolytes is investigated via a series of spectroscopic techniques. Further, the hypothesis is validated by electrochemically testing the as-synthesized NMOs in an array of electrolytes formulated using low concentration sodium-based salts dissolved in the hybridized cosolvent. Ex-situ characterizations consisting of in-house and synchrotron-based techniques are employed to determine the morphological, structural, and chemical evolutions.

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6.1 Introduction

In the previous Chapter 5, the full cell of ARSIES has been demonstrated using the highly concentrated electrolyte (pH regulation and “water-in-bisalt” mixed anions strategy) to suppress the water activities and enable the broad applicable potential window of the cell. Importantly, the need to “scavenge” the free water molecules to mitigate the parasitic side reactions associated with water have been emphasized. Since the birth of the “water-in-salt” (WIS) concept, it has spawned many innovative strategies based on concentrated salt electrolytes to achieve high cation to water molar ratio to suppress the water activities.¹⁻⁸

However, there are still challenges with the WIS-based approach that needs to be addressed. Firstly, the WIS strategy may not be feasible for large scale applications due to the concern over its high cost (**Appendix A2**) and environmental impact with a considerable amount of fluorinated salts required. Secondly, since the WIS-based strategy could only be applied to salts possessing high solubility limits, most of the green and low-cost sodium-based salts with low solubilities could not be employed. Thirdly, based on the WIS mechanism for suppressing water activities *via* alkali cation coordination with the water molecules Lewis base oxygens' lone pairs, the protons of the free water molecules have yet to be bounded. Hence, the possibilities of proton co-intercalations into the host electrode could occur during electrochemical cycling, resulting in cell fading.

Herein, a new class of electrolytes based on hydrogen bonding interaction *via* the hybridization of polar and protic ethanol and water as a cosolvent has been proposed. As a proof-of-concept, ethanol has been chosen due to its high miscibility with water and its protic characteristic which enables the unique hydrogen bond formations with water molecules through both (O-H_{water}•••O-H_{ethanol}) and (O-H_{ethanol}•••O-H_{water}) interactions.⁹⁻

¹¹ In this manner, both the oxygens and protons of the water molecules are bounded, thereby effectively suppressing the water activities, and potentially inhibiting the proton co-intercalation side reaction during electrochemical cycling of the cell. Further, this approach

has no dependence on salt concentration for reducing the water activities, thus, opening many possibilities for green and low-concentration salts to be employed in ARSIES.

The hydrogen bonding interaction between the ethanol and water is first investigated using spectroscopic techniques such as confocal Raman, Fourier transform infrared-attenuated total reflectance (FTIR-ATR), and nuclear magnetic resonance (NMR). To validate the hypothesis, the as-synthesized NMO is employed as the model cathode electrochemically cycled in an array of low concentrated salts (acetates, chlorides, and perchlorates) dissolved in the optimized ethanol-water cosolvents electrolytes. A combination of *ex-situ* characterizations consisting of in-house and synchrotron-based techniques are employed to determine the morphological, structural, and chemical evolutions.

6.2 Experimental Methods

6.2.1 Synthesis of $\text{Na}_{0.44}\text{MnO}_2$ plates

The $\text{Na}_{0.44}\text{MnO}_2$ is prepared based on the optimized polyvinylpyrrolidone (PVP)-assisted sol-gel synthesis route, as described in Chapter 4.^{9, 12}

6.2.2 Material Characterization

The phases of the pristine and cycled NMO were analyzed by an X-ray diffractometer (XRD, Bruker D8 Advance) using $\text{CuK}\alpha$ radiation operated at 40 kV. The morphological characterizations were obtained by field emission scanning electron microscope (FESEM JSM-7600F, JEOL), and high-resolution transmission electron micrographs were obtained using the JEOL 2100F TEM. Mn K-edge spectra of the cycled samples were collected at Beamline 5.2 at Synchrotron Light Research Institute (SLRI), Thailand. The beam can operate from 1.2 keV to 12.1 keV with a resolution of 2×10^{-4} . The spectra were recorded in fluorescence mode using a 4-element silicon-drift detector. Manganese (II) oxide (MnO , 99.99%, Alfa Aesar), manganese (III) oxide (Mn_2O_3 , 99%, Aldrich), and manganese (IV) oxide (MnO_2 , $\geq 99\%$, Sigma-Aldrich) were used as references. The background was

subtracted, and intensities normalized for XANES analyses using the ATHENA software from the Demeter Suite.¹³ The ionic conductivity of the electrolytes was measured with a CyberScan Series 600 waterproof portable meter (Eutech Instruments) at room temperature.

6.2.3 Preparation and characterization of electrolytes

To test the hydrogen bonding interaction, mixtures of ethanol (EMSURE[®], absolute for analysis) and Di water in different volume ratios (5:1, 4:2, 3:3, 2:4, 1:5) were prepared. The hydrogen bonding strength of the ethanol-water mixtures was probed using confocal Raman (excimer laser wavelength 488 nm, WiTec), Fourier transform infrared-attenuated total reflectance (FTIR-ATR, Nicolette) spectroscopy and nuclear magnetic resonance (NMR, Bruker). For the confocal Raman measurements, a total of 20 accumulations with an integration time of 1 s per accumulation is acquired for each sample spectra. For the FTIR-ATR measurements, 20 μl of the sample was placed directly on the total reflectance accessory. The IR spectra were recorded between 500 and 4000 cm^{-1} at a resolution of 2 cm^{-1} using Omnic software. To enhance the signal to noise ratio, a total of 64 scans were averaged for each spectrum. IR data were used without any further data processing.¹H NMR chemical shifts of the hydroxyl groups in ethanol-water mixtures were obtained in ambient temperature with a Bruker NMR Advance 400 (400 MHz) with a total of 16 scans per sample. “Water-in-salt” electrolytes were prepared using 17 m sodium perchlorate (Purity $\geq 98.0\%$, Sigma Aldrich) and 9.26 m sodium trifluoromethanesulfonate (Solvionic) dissolved in Di water. Binary ethanol-water electrolytes and single Di water electrolytes were prepared using 1 M sodium acetate anhydrous (Purity 99%, Merck), 0.1 M sodium chloride (Purity $\geq 99.5\%$, Sigma Aldrich) and 1 M sodium perchlorate (Purity $\geq 98.0\%$, Sigma Aldrich), dissolved into the highest ethanol to water volume ratio (v/v) of 5:1 and pure Di water, respectively. Contact angle measurements of the electrolytes were recorded using contact angle system OCA 15 Pro (Dataphysics), and the water contact angles were measured using the SCA20 software. The total amount of

electrolyte samples used for the contact angle measurement was 4 μL and injected onto a stainless steel substrate at a flow rate of 1 $\mu\text{L s}^{-1}$.

6.2.4 Electrochemical characterization

The working electrodes were prepared by first grounding the NMO powders with the Super P carbon using mortar and pestle. The teflonized acetylene black (TAB) binder was later added into the mixture with further grounding to form a pellet. The composition of NMO powder, Super P carbon, and TAB was in a weight ratio of 8:1:1, respectively. The pelletized mixture was pressed onto the titanium mesh (Good Fellow) using a hydraulic press machine with a pressure of 10 MPa. The area of the pellet is 3 mm $\times$ 3 mm, with an active material mass loading of around 2 mg. In aqueous setup, platinum foil (99.99% metals basis, Alfa Aesar) and Ag/AgCl (saturated KCl) were employed as counter and the reference electrode, respectively. The full cell was assembled by using zinc foil (Good Fellow) as both the counter and reference electrode. Cyclic voltammetry (CV) was carried out using Solartron 1256 B. The CV measurements in aqueous electrolytes were taken in potential ranges of -0.4 V to 0.7 V vs. Ag/AgCl. Galvanostatic charge and discharge (GCD) measurements were carried out using the Neware BTS system.

6.3 Results and Discussion

The cosolvents of the ethanol and water are first prepared by mixing them in different volume ratios denoted as x:y (Et:Di). To determine the existence and hydrogen bonding strength of the ethanol-water cosolvents, a combination of spectroscopic techniques such as confocal Raman, Fourier-transformed infrared-attenuated total reflectance, and ^1H nuclear magnetic resonance (NMR) are employed.

6.3.1 Structural characterization

Figure 6-1a presents the Raman spectra of the ethanol-water at various volume ratios between 2700 to 4000 cm^{-1} . Meanwhile, the Raman peaks assignment to the different

modes of vibrations is as listed in **Appendix A3**.¹⁴⁻¹⁷ Due to the abundant hydrogen bonding environments among the water molecules in the pure water ($\text{Di H}_2\text{O}$), it exhibits a broad and pronounced band that corresponds to the symmetric O-H stretching band ($\sim 3254\text{ cm}^{-1}$) and the asymmetric O-H stretching vibration ($\sim 3411\text{ cm}^{-1}$). Further, the free O-H of the water molecules is characterized by the weak shoulder peak around 3613 cm^{-1} . Upon introduction of ethanol, the asymmetric CH_2 and symmetric CH_3 stretching modes of ethanol appear. Clearly, with the increasing ethanol volume ratios, the broad Raman band gradually reduces in intensities, and the free O-H peak diminishes. This indicates the weakening in water-water hydrogen bonding interactions and reduced free water activities with increasing ethanol concentration. Meanwhile, with an increase in ethanol concentration, the Raman shift of CH_2 and CH_3 stretching modes (**Figure 6-1b**) towards the lower wavenumbers suggests the new formation of hydrogen bonds between the ethanol and water molecules.

Figure 6-1c presents the FTIR spectra of the ethanol-water focusing on the H-O-H bending vibrational band of water molecules.^{18, 19} With the increasing ethanol concentration, the H-O-H bending vibrational bands of the cosolvents exhibit shift toward the higher wavenumber region, indicating the strengthening of hydrogen bonds of the water molecules' hydrogens. This could be attributed to the strengthened hydrogen bonding between the oxygens of ethanol with the hydrogens of water molecules with increasing ethanol content.

To further elucidate the hydrogen bonding behavior of ethanol and water, the ^1H nuclear magnetic resonance (NMR) measurements are conducted on the ethanol-water cosolvents. As shown in **Figure 6-1d**, the protons corresponding to the O-H group of ethanol and water molecules exhibit the chemical shift values of 5.86 and 4.77 ppm, respectively. As the ethanol concentration increases, the ethanol-water mixtures exhibit a downfield shift trend approaching higher ppm values. This phenomenon indicates the deshielding of hydrogen on the hydroxyl groups with increasing ethanol content, suggesting the strengthening of hydrogen bonds between the ethanol and water molecules. Among the various ethanol-water ratios, 5:1 Et-Di exhibits the highest downfield shield. Further, based on the

calculated proton ratios (O-H, CH₂, and CH₃ in ethanol-water mixtures),²⁰ 5:1 Et-Di also exhibits the lowest protons ratio number associated with the O-H groups (**Figure 6-1e**). These results demonstrate the strongest hydrogen bonding interaction between the ethanol and water molecules in 5:1 Et-Di cosolvents.

Based on the above discussion, the simplified models for the molecular associations in the water and ethanol-water cosolvents are as illustrated in **Figure 6-1f and g**, respectively. In the water, the water molecules have weak hydrogen bonding interaction among themselves with the existence of free water molecules. On the other hand, in the ethanol-water cosolvents, water-water hydrogen bonding interactions are broken, and new hydrogen bonds are formed between the ethanol and water molecules. Importantly, the hydrogens of the water molecules are also bounded by the oxygens of the ethanol owing to the protic characteristic of ethanol. Therefore, it is highly anticipated that the ethanol-water cosolvents (5:1 Et-Di) could potentially suppress the parasitic proton co-intercalations side reactions, enabling the cell stability and long cycle life span for ARSIES applications.

Figure 6-1. (a, b) Raman spectra, (c) Fourier transform infrared- attenuated total reflectance (FTIR-ATR) spectra, (d) ¹H nuclear magnetic resonance (NMR) spectra of water and ethanol-water cosolvents. (e) Integrated proton ratio number of protons in the different hydrogen atoms environment (CH₂, CH₃, and OH) of ethanol-water solvents. Illustration of (f) water and (g) ethanol-water intermolecular interactions. (Adapted with

permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

6.3.2 Electrochemical testing

Since the hypothesis of the “hydrogen bonded” is to enable low concentration salt for the ARSIES application, the hybridized electrolyte is formulated by dissolving 1 M NaAc into the ethanol-water cosolvents (denoted as 1 M NaAc-Et/Di). Meanwhile, the non-hybridized electrolyte is formulated by dissolving 1 M NaAc into water (denoted as 1 M NaAc-Di) for comparison. To elucidate the effect of hybridized electrolytes on the electrochemical performance of the electrode, the as-synthesized NMO is employed as the model cathode in the typical three-electrode setup.

Cyclic voltammetry was employed to determine the electrochemical stability window (ESW) of the electrolytes and to evaluate the NMO electrode kinetics in both electrolytes. As shown in **Figure 6-2a**, the hybridized exhibits a wider ESW (up to ~2.5 V) as compared to the non-hybridized electrolyte (~1.8 V). The expanded window of the hybridized electrolyte indicates the suppressed water decomposition reaction. This is potentially attributed to the effective suppression of water activities *via* the strengthened hydrogen bonding between the ethanol and water molecules. More importantly, the hybridized electrolyte has provided a considerable wide electrochemical stability window for the applied electrodes, given the low amount of salt required.

The cyclic voltammetry curves of the NMOs tested in 1 M NaAc-Di and 1 M NaAc-Et/Di are depicted in **Figure 6-2 b and c**, respectively. A total of 7 redox peaks (as labeled I-VII) observed correspond to the de-/insertion of sodium into the various sodium sites (Na 1, Na 2, and Na 3) in the NMO tunnel-shaped structures as summarized in **Appendix A4**.²¹⁻²⁷ In brief, the Na 1 sites are in the smaller O-shaped tunnel while the Na 2 and Na 3 sites are located together in the larger S-shaped tunnel of NMO (**Figure 6-2d**).^{21-23, 26}

As shown in **Figure 6-2b**, the CV curves of NMO cycled in the non-hybridized electrolyte (1 M NaAc-Di) exhibits a decreasing current intensity after each cycle, which indicates the irreversible sodium de-/insertion processes. Particularly, a larger reduction in intensities is observed in redox peaks associated with sodium de-/insertion to Na 2 and Na 3 sites. In principle, the sodium ions located at Na 2 and Na 3 are more susceptible to experiencing electrostatic repulsion due to the higher sodium content within the S-shaped tunnel than that of the O-shaped tunnel (Na 1).²² Therefore, it is postulated that the “proton-rich” environment of the non-hybridized electrolyte could have favored the proton-co-intercalation side reaction, inducing the electrostatic repulsion in the S-shaped tunnel and impeding the subsequent sodium-ions de-insertion processes.

Figure 6-2. (a) Electrochemical stability window of the hybridized (1 M NaAc-Et/Di) and non-hybridized electrolytes (1 M NaAc-Di). Cyclic voltammetric profiles of NMOs tested in (b) hybridized and (c) non-hybridized electrolytes. (d) Crystal structure of NMO showing the various sodium sites located in the S- and O- shaped tunnels. (Adapted with permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

In stark contrast, the CV curves of the NMO cycled in the hybridized electrolytes are almost overlapping over the 10 cycles, indicates the excellent sodium-ion de/insertion processes into the various sodium sites (**Figure 6-2c**). This can be attributed to the intrinsic hydrogen bonding interaction between the ethanol and water molecules, suppressing the water protons co-insertion side reaction.

Figure 6-3a and b compare the galvanostatic charge and discharge (GCD) profiles of the NMO cycled in the non-hybridized (1 M NaAc-Di) and hybridized electrolyte (1 M-NaAc-Et/Di), respectively. As shown in **Figure 6-3a**, at a current density of 100 mA g^{-1} , the NMO cycled in the non-hybridized electrolyte can deliver a specific discharge capacity of 71.6 mAh g^{-1} . However, by the 5th discharge cycles, the specific discharge capacity has been reduced by 22.6 %. On the other hand, the NMO cycled in the hybridized electrolyte delivered a higher initial discharge capacity and maintaining a high capacity of 76.8 mAh g^{-1} , with retention close to 100 % after 5 cycles. This is in excellent agreement with the overlapping CV curves of NMO, indicating the superior sodium diffusion kinetics of NMO enabled by the hybridized electrolyte.

To elucidate the variation in the chemical evolution of NMO cycled in the non-hybridized and hybridized electrolyte, *ex-situ* X-ray absorption near-edge structures (XANES) measurement are performed. **Figure 6-3c** depicts the normalized Mn K-edge profiles for the commercial powder (reference), pristine NMO, and the fully discharge NMO samples.

In the pristine state of NMO, its Mn K-edge of NMO exhibits similar characteristics as the commercial MnO_2 powder, which indicates an average manganese oxidation state close to +4. After the 1st full discharge cycle, both the *ex-situ* NMO electrodes cycled in the hybridized and non-hybridized electrolytes exhibit the shift in Mn K-edge toward the lower binding energy.²⁸ This indicates a decrease in the oxidation state of manganese. Interestingly, there is a difference in the oxidation states of NMOs after the discharge. For the discharge NMO sample cycled in the hybridized electrolyte, its Mn K-edge resembles the Mn K-edge of commercial Mn_2O_3 powder, indicating an average oxidation state close to Mn^{3+} . On the other hand, the discharge NMO sample cycled in the non-hybridized electrolytes exhibits an absorption edge in between the Mn K-edges of MnO and Mn_2O_3 ,

indicating a mixed in valences state of +2 and +3. Importantly, the presence of Mn^{2+} species highlighted the possibility for the occurrence of a disproportionation reaction ($\text{Mn}^{3+}_{(\text{s})} \rightarrow \text{Mn}^{4+}_{(\text{s})} + \text{Mn}^{2+}_{(\text{aq})}$), which could lead to the dissolution of manganese, resulting in the loss of NMO active material.^{22, 29-31} Therefore, this could explain the rapid capacity fading of NMO when electrochemically cycled in the non-hybridized electrolyte as compared to the NMO cycled in the hybridized electrolyte.

Figure 6-3. Galvanostatic charge and discharge profiles of NMOs tested in (a) non-hybridized and (b) hybridized electrolytes. (c) Synchrotron-based X-ray absorption near edge structures (XANES) curves of NMOs in pristine and full discharge states. The comparison of (d) rate capability and (e) long term cycling stability of NMOs tested in different electrolytes. (Adapted with permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

The rate performance of the NMO cycled in the hybridized and non-hybridized electrolytes is further evaluated, as shown in **Figure 6-3d**. Clearly, the NMO cycled in the hybridized electrolyte has a better rate capability with high capacities of 90.8, 81.0, 67.6, 42.2 mAh g⁻¹ at current densities of 50, 100, 200, 500 mA g⁻¹. Moreover, the NMO cycled in the

hybridized electrolyte can recover back to a high capacity of 91.6 mAh g⁻¹ (50 mA g⁻¹), more than 2 times the capacity of NMO cycled in the non-hybridized electrolyte.

The long-term cycle stability of the NMOs is evaluated in hybridized (1 M NaAc-Et/Di), non-hybridized (1 M NaAc-Di), as well as the state-of-art “water-in-salt” electrolytes (17 m NaClO₄ and 9.26 m NaCF₃SO₃) for comparison (**Figure 6-3e**). For the NMO cycled in the hybridized electrolyte at a current density of 100 mA g⁻¹, it exhibits a high specific discharge capacity of 76 mAh g⁻¹. Moreover, even after 100 cycles, the NMO electrode still maintained a high capacity of 75 mAh g⁻¹, with capacity retention ~99% more than 2 times that that of NMO cycled in the non-hybridized electrolyte (48%).

Remarkably, the cycling stability of NMO cycled in the hybridized electrolyte is more superior than that of NMOs cycled in the “water-in-salt” electrolytes (capacity retention after 100 cycles: 17 m NaClO₄ → **25.6%** and 9.26 m NaCF₃SO₃ → **27.4%**). Even after 1000 cycles, the NMO cycled in the hybridized electrolyte still maintained excellent electrochemical stability with a capacity decay rate of only 0.024% as compared to that of NMO cycled in the non-hybridized electrolyte (0.087%). This emphasized the importance of the suppressed water protons’ activities via the unique hydrogen bonding interactions of ethanol and water molecules for enabling the superior cycling stability. Further, the intrinsic hydrogen bonding between the ethanol and water also enhanced the wettability of the hybridized electrolyte (22.4°; **Figure 6-4**), facilitating the excellent electrode/electrolyte interfacial contact for efficient sodium-ion transport processes.

Figure 6-4. Contact angle comparison of the different electrolytes. (Adapted with permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

6.3.3 Postmortem characterizations

To investigate the morphological and structural evolutions of the NMO cycled in the hybridized and non-hybridized electrolytes, *ex-situ* XRD, SEM, TEM with EDS mapping measurements were conducted.

In comparison to the morphology of pristine NMO (**Figure 6-5a**), the NMO cycled in the non-hybridized electrolyte after 5 cycles (**Figure 6-5b**) exhibits the partial fragmented plate structure. Based on the as-discussed XANES results, the presence of Mn^{2+} indicates the occurrence of a disproportionation reaction could lead to the dissolution of active material. Therefore, the loss of NMO active materials observed in (**Figure 6-5b**) in the non-hybridized electrolyte has resulted in the decaying capacity. In contrast, the NMO cycled in the hybridized electrolyte (**Figure 6-5c**) exhibits smooth plate morphology, highlighting the important role of the hydrogen bonding interaction in the hybridized electrolyte for stabilizing the electrode structure.

Ex-situ XRD measurement of the pristine and cycled electrodes are presented in Figure 6-5 d and e. As compared to the pristine state of NMO, the XRD patterns of the NMO cycled in the non-hybridized electrolytes starts to exhibit an additional diffraction peak (around 26°) after 200 cycles (**Figure 6-5d and e**) and remained a mixed-phase after 500 cycles (**Figure 6-5e**). After 1000 cycles, the NMO has undergone the full phase transformation into MnOOH (PDF 04-010-4788), indicating the irreversible phase transformation of NMO cycled in non-hybridized electrolytes. On the other hand, the NMO cycled in the hybridized electrolyte maintained its original NMO phase (PDF 04-018-3147) even after 1000 cycles (**Figure 6-5d**), demonstrating the excellent structural stability of NMO in the hybridized electrolyte. Based on the results, the proposed de-/insertion process of NMO in the hybridized electrolyte is as follows:

On the other hand, in the case of NMO cycled in the non-hybridized electrolyte, the sodium ions and water protons are co-intercalated into the host during the discharge. As discussed

earlier, the presence of the protons could induce the electrostatic repulsion with the sodium ions, hindering the subsequent sodium ion de-/insertion process.²² Therefore, the proposed reaction for NMO cycled in the hybridized electrolyte is formulated as follows:

Figure 6-5. Postmortem characterizations. (a) SEM image of pristine NMO. SEM images of cycled NMO in (b) non-hybridized and (c) hybridized electrolyte after 5 cycles. (d) XRD patterns of pristine and NMOs cycled in hybridized and non-hybridized electrolytes after 1000 cycles. (e) XRD patterns of NMO cycled in non-hybridized electrolytes after different cycles. (f) *Ex-situ* TEM, HR-TEM (inset), (g) SAED, and (h) TEM-EDS mapping of NMO

cycled in non-hybridized electrolytes after 1000 cycles. (i) *Ex-situ* TEM, HR-TEM (inset), (j) SAED, and (k) TEM-EDS mapping of NMO cycled in hybridized electrolytes after 1000 cycles. (Adapted with permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

Further evidence on the structural evolution of NMO is confirmed by the *ex-situ* TEM and the TEM-EDS analysis on the cycled NMO samples. As shown in **Figure 6-5f**, the NMO cycled in the non-hybridized electrolyte exhibiting the nanorods morphology. The inset of **Figure 6-5f** presents the high-resolution TEM (HRTEM) image of the nanorods, showing the well-resolved lattice fringes with the interplanar distance of 0.34 nm. Accordingly, this corresponds to the (-111) crystal plane of the MnOOH. Similarly, the diffraction spots, as shown in the SAED pattern (**Figure 6-5g**), can be indexed to both (-111) and (002) planes of the MnOOH, consistent with the XRD results. From the TEM-EDS mapping of cycled NMO in the non-hybridized electrolyte (**Figure 6-5h**), it shows the newly formed nanorods show the presence of Mn and O elements with the absence of the sodium element, confirming the phase transformation into MnOOH. Due to the combination disproportionation reaction leading to the dissolution of Mn²⁺ species and the irreversible proton co-intercalation process, these lead to the accumulation of MnOOH, resulting in inferior electrochemical stability of NMO in the non-hybridized electrolyte.

On the other hand, the NMO cycled in the hybridized electrolyte maintained its plate morphology after 1000 cycles (**Figure 6-5i**). Meanwhile, its SAED pattern (**Figure 6-5j**) displays its single-crystalline structure oriented along the [001] direction, and its HR-TEM image (**inset of Figure 6-5i**) presents its lattice spacing of 0.45nm, which correspond to the (200) plane of the pristine NMO. Further, the TEM-EDS elemental image of NMO cycled in the hybridized electrolyte (**Figure 6-5k**) also confirms the uniform elemental distributions (Na, Mn, and O elements).

As shown in **Figure 6-6a**, it summarized the hydrogen bonding interactions between the ethanol and water molecules in the hybridized electrolyte. It enabled the reversible sodium-ion de-/insertion into the NMO by suppressing the proton-co intercalation process and stabilizing the NMO structure. Meanwhile, in **Figure 6-6b**, it illustrates the free water molecules of the non-hybridized electrolyte and the proton-co insertion with the sodium ion into the host, resulting in the irreversible phase transformation of MnOOH.

Figure 6-6. Schematics illustrating the (a) ethanol-water and (b) water system. (Adapted with permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

6.3.4 A proof of concept

The “hydrogen bonding” concept with water molecules by introducing ethanol into the water as cosolvents have opened the possibilities for low concentration salt to be employed for the ARSIES application. Here, for instance, the application of ethanol-water cosolvents has also applied to other low concentration salts such as sodium chloride (0.1 M) and

sodium perchlorate (1 M). As shown in **Figure 6-7**, the reversible sodium-ion de/insertion processes and superior cycling stability of NMOs have been successfully demonstrated in the hybridized electrolyte containing the low concentration salts as compared to its non-hybridized counterparts.

Figure 6-7. Galvanostatic charge and discharge profiles of NMOs cycled in non-hybridized electrolytes (a) 0.1 M NaCl in Di, (b) 1 M NaClO₄ in Di and hybridized electrolyte (c) 0.1 M NaCl in Et/Di and (d) 1 M NaClO₄ in Et/Di. (e and f) Cycling stability of NMOs in cycled in the hybridized and non-hybridized electrolytes. (Adapted with permission from Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, ACS Appl. Mater. Interfaces 2020, 12, 22862-22872. Copyright 2020 American Chemical Society.)

6.4 Conclusion

In summary, a new class of electrolytes based on hybridizing ethanol-water cosolvents has been proposed. Benefitting from the unique hydrogen bonding interaction between the ethanol-water in the electrolyte, the parasitic side reactions such as electrode dissolution and proton co-intercalation during the electrochemical cycling process can be effectively suppressed. Furthermore, the introduction of ethanol enables the breaking and reorganization of the water-water molecules network, thereby improving the surface wettability of the electrolyte. This hybridized electrolyte enables the NMO to deliver high specific discharge capacity up to 81 mAh g^{-1} and exhibits superior cycling stability (low capacity decay rate per cycle of 0.024%) over 1000 cycles at 100 mA g^{-1} . Importantly, the hybridized electrolyte formulation has successfully opened a wide array of low-concentrated sodium-based salts (acetates, chlorides, and perchlorates) to enable the long cycle lifespan of NMO. Overall, this novel hydrogen bonding concept opens doors to low-cost and greener electrolyte formulations for ARSIES as well as other aqueous-based systems toward practical large-scale energy storage applications.

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Electrolytes Enable Low-Cost and Long-Lifespan Sodium-Ion
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Chapter 7

Conclusion and Future Work

In this final chapter, the key findings and outcomes of the studies are placed into perspective and summarized. The novel contributions and the highlights of the strategies proposed based on electrode modification and electrolyte engineering to overcome the major challenges in the aqueous system are emphasized. The scope and the possible strategies that could be adopted in future work are laid out toward designing the ideal aqueous rechargeable sodium-ion energy storage (ARSIES) for practical applications.

7.1 Perspective

This thesis aimed to develop the ideal cathode and electrolyte for aqueous rechargeable sodium-ion energy storage (ARSIES) with high energy and power densities as well as long cycle life. Due to the nature of the aqueous electrolyte, there are several parasitic side reactions associated with water that hindered the practical application of ARSIES. In these regards, the literature on the various strategies based on state-of-art electrode modifications and electrolyte engineering was reviewed. Following, the gaps in the reported strategies to achieve high energy density with good cycle stability, in particular, with low salt concentration electrolytes, were identified. The problem statements were crafted and set as a foundation towards innovating ideas and approaches to overcome the challenges.

In this work, the high theoretical capacity $\text{Na}_{0.44}\text{MnO}_2$ (NMO) material is investigated as the cathode for ARSIES. Due to the parasitic side reactions in the aqueous system, its energy densities and cycling stability have been severely undermined. Here, a combination of electrode modification and electrolyte engineering enables it to be reversibly cycled in a wider potential window. The full cell application of NMO paired with the environmentally friendly activated carbon as the anode in the modified “water-in-bisalt” (WIS) electrolyte has demonstrated superior energy density, even in weathering conditions. Through the systematic investigation of the failure mechanism of the cathode in low salt concentration electrolytes, the importance of hydrogen bonding interaction with the water was identified. The proposed hybridized co-solvent electrolytes with strengthened hydrogen bonding interaction with the water in aqueous electrolytes enable a wide array of green, low-cost sodium-based salts such as (chlorides, acetates, and perchlorates) to be successfully employed in ARSIES. This work brings us one step closer towards harnessing the highly abundant seawater with low salt concentration as the electrolyte for the practical application of ARSIES.

7.2 Summary of results

7.2.1 Morphology control of $\text{Na}_{0.44}\text{MnO}_2$ as a cathode material for aqueous rechargeable sodium-ion energy storage

- The NMO sample with uniform plate-like morphology was successfully yielded *via* a PVP-assisted sol-gel route.
- With the stabilization of the NMO structure through the PVP-assisted sol-gel route, the applicable potential window of NMO plates cathode has been significantly widened up to 1.3 V.
- A sheet-like (sodium birnessite) protective layer is discovered on the cycled sample that enabled the superior cycle stability performance of NMO

7.2.2 A pH regulated “water-in-bisalt” mixed anion electrolyte towards ARSIES full cell applications

- A full cell has been assembled with the scalable and green resources as active materials (cathode- NMO, anode-biomass derived activated carbon) for supercapacitor applications and modified electrolytes based on state-of-art WIS concept.
- The novel utilization of sodium acetate not only neutralizes the acidic pH of NaFSI “water-in-salt” electrolyte but also further suppresses the water activities *via* anions (FSI^- and OAc^-)-water- Na^+ associations.
- The pH regulated “water-in-bisalt” mixed anion electrolyte also enables the cell to achieve superior power and energy densities even at demanding conditions ($-20\text{ }^\circ\text{C}$ and $60\text{ }^\circ\text{C}$).

7.2.3 Green and low-concentrated electrolytes enabled by hydrogen-bonding interaction for ARSIES

- A new class of electrolytes based on the hybridization of ethanol-water co-solvents has been proposed to suppress the parasitic side reactions associated with water *via* the strengthened hydrogen bonding interaction between the ethanol and water molecules.
- The hybridized electrolyte (1 M NaAc-Et/Di) enables the NMO to deliver high specific discharge capacity up to 81 mAh g⁻¹ and exhibits superior cycling stability (low capacity decay rate per cycle of 0.024%) over 1000 cycles at 100 mA g⁻¹.
- The NMO cycled in the hybridized electrolyte exhibits excellent structural and phase stability.
- In contrast, the NMO cycled in the non-hybridized electrolyte (1 M NaAc in Di), suffered from severe structural degradation (loss of active materials due to dissolution of Mn²⁺) and underwent irreversible phase transformation to MnOOH.
- The hybridized electrolyte formulation also opened up different low-concentrated sodium-based salts such as chlorides, and perchlorates to enable better cycling stability of NMO than its non-hybridized electrolyte counterparts.

7.3 Novel contributions

- NMO plates cathode material synthesized *via* the PVP-assisted sol-gel route achieved the widest applicable potential window of 1.3 V as compared to other reported NMOs in the aqueous system for the first time.
- *Ex-situ* characterization techniques uncover the *in-situ* formation of sheet-like structures on the NMO plates during electrochemical cycling that could act as passivation layers against the parasitic side reactions.
- A full cell construction of NMO//biomass-derived activated carbon cycled in the formulated pH regulated “water-in-bisalt” electrolyte can cycle over a wide potential range up to 2.8 V with superior energy and power densities even at demanding conditions (high 60 °C and low – 20 °C temperatures).

- A new class of electrolytes formulated by hybridizing ethanol-water as co-solvents opens up a wide array of green and low-cost sodium-based salts enabling the long cycle lifespan of NMO. The unique hydrogen bonding interaction between the ethanol-water significantly suppresses the parasitic side reactions such as electrode dissolution and proton co-intercalation during the electrochemical cycling of NMO.

7.4 Future Work

7.4.1 Formation of cathode electrolyte interface layer

From the literature, preliminary effort in employing atomic layer deposition to coat a thin layer of nano- Al_2O_3 on the surface of NMO has demonstrated the enhanced electrochemical kinetic and improved cycle stability of NMO over a few cycles.¹ Also, in this thesis, it is found that the *in-situ* formation of the birnessite with the sheet-like structure on NMO surfaces exhibits enhanced electrochemical stability. This sheet-like structure could act as a passivation layer to protect the cathode from the side reaction associated with the water. Therefore, future work can explore different types of coatings (e.g., carbon, TiO_2 , etc.).²⁻⁷ The coatings could be performed by either synthesis routes (e.g., polyol method, solvothermal, etc.) or post-synthesis deposition techniques (e.g., pulse laser deposition, chemical vapor deposition, etc.) for effective coatings of the cathode, to enhance the cell cycling stability in the aqueous system.²⁻⁷

7.4.2 Functionalizing seawater as the electrolyte for ARSIES

Towards large scale energy storage application, seawater (~ 0.5 M NaCl) presents itself as a promising candidate as the aqueous electrolyte for ARSIES due to its high abundance.⁸ However, based on recent research effort, it would require complex cell design and costly high concentrated salts with perfluorinated anions before the seawater can be utilized.⁹ In this study, we have identified the importance of hydrogen bonding with water molecules in suppressing the parasitic side reaction associated with water. The study also demonstrated the superior cycling stability of NMO in low- concentrated sodium chloride

using the green and low-cost hybridized electrolyte system. However, due to the presence of superoxide radicals among the other impurities in seawater, its direct application as an electrolyte has yet to be realized, and research effort is still in progress.¹⁰⁻¹² Future work can focus on the chemical species present in seawater, elucidating its effect on the electrochemical performance of the cell and neutralizing/eliminating them *via* functionalization of the seawater (e.g., with additives, solutes with hydroxyl groups) toward scalable, green and low-cost electrolyte of ARSIES.¹¹⁻¹³

7.5 Concluding remarks

In conclusion, the studies covered in this thesis includes the development of the NMO cathode with excellent electrochemical performance and electrolyte formulations that are able to suppress the parasitic side reactions of water-based on electrode modification and electrolyte engineering. Importantly, a wide array of green and low-concentrated sodium-based salts (acetates, chlorides, and perchlorates) is enabled by the hybridized electrolyte system based on unique hydrogen bonding with the water molecules. With a more in-depth understanding and promising results, it brings us one step closer towards harnessing the abundant seawater as the electrolyte for ARSIES in large scale energy storage applications. Overall, this thesis provides a guideline to understand and overcome the challenges in the aqueous system and opens new avenues for groundbreaking research in aqueous rechargeable sodium-ion energy storage.

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List of Publications

1. **R. Chua**, Y. Cai, P.Q. Lim, S. Kumar, R. Satish, W. Manalastas Jr, H. Ren, V. Verma, S. Meng, S.A. Morris, P. Kidkhunthod, J. Bai, M. Srinivasan, Hydrogen-bonding interactions in hybrid aqueous/nonaqueous electrolytes enable low-cost and long-lifespan sodium-ion storage, *ACS Appl. Mater. Interfaces* 2020, 12, 22862-22872. DOI: 10.1021/acsami.0c03423
2. **R. Chua**, Y. Cai, Z.K. Kou, R. Satish, H. Ren, J.J. Chan, L. Zhang, S.A. Morris, J. Bai, M. Srinivasan, 1.3 V superwide potential window sponsored by Na-Mn-O plates as cathodes towards aqueous rechargeable sodium-ion batteries, *Chem. Eng. J.* 2019, 370, 742-748. DOI: 10.1016/j.cej.2019.03.251
3. S. Petnikota, **R. Chua (co-first author)**, Y. Zhou, E. Edison, M. Srinivasan, Amorphous vanadium oxide thin films as stable performing cathodes of lithium and sodium-ion batteries, *Nanoscale Res. Lett.* 2018, 13, 363. DOI: 10.1186/s11671-018-2766-0
4. P. Sennu, **R. Chua**, S.S.H. Dintakurti, J.V. Hanna, R.O. Ramabhadran, V. Aravindan, M. Srinivasan, Supersaturated “water-in-salt” hybrid electrolyte towards building high voltage Na-ion capacitors with wide temperatures operation, *J. Power Sources* 2020. (Just accepted)
5. S. Petnikota, **R. Chua**, K.M. Boopathi, R. Satish, F. Bonaccorso, V. Pellegrini, M. Srinivasan, An insight into the electrochemical activity of Al-doped V₂O₃, *J. Electrochem. Soc.* 2020. DOI: 10.1149/1945-7111/ab971e
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7. Y. Cai, S. Kumar, **R. Chua**, V. Verma, Y. Du, Z. Kou, H. Ren, H. Arora, M. Srinivasan, Bronze-type vanadium dioxide holey nanobelts as high performing cathode material for aqueous aluminium-ion battery, *J. Mater. Chem. A* 2020. DOI: 10.1039/D0TA03986A

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9. S. Petnikota, J.J. Toh, J.Y. Li, **R. Chua**, M. Srinivasan, Citric acid assisted solid state synthesis of V_2O_3 , $\text{V}_2\text{O}_3/\text{C}$ and $\text{V}_2\text{O}_3/\text{graphene}$ composites for Li-ion battery anode applications, *ChemElectroChem* 2019, 6, 493-503. DOI: 10.1002/celec.201801244
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List of Abstract and Presentation

1. **R. Chua**, Y. Cai, S. Kumar, V. Verma, M. Srinivasan, EN03.05.04: A Novel Ethanol/Water Binary Electrolyte Enabling Superior Cycle Stability of Na-Mn-O Cathode for Aqueous Rechargeable Sodium-Ion Batteries. Materials Research Society (MRS) Fall Meetings & Exhibit **2019**, Boston Massachusetts, 29 Nov- 4 Dec (**Best Poster Nominee**)

Appendix

Appendix A1. Comparison of electrochemical performance with other reported works.

Active materials	Electrolyte	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Voltage (V)	Temperature (°C)	Ref
PJAC//Na _{0.44} MnO ₂ ASC	35 M NaFSI + 5 M NaAc	52 55 38	700 140 70	2.8	60 25 -20	This work
Polyaniline-derived carbon nanorods SSC	21 M LiTFSI	29.6	1100	2.2	25	1
Porous Carbon Monolith SSC	5 M LiTFSI	24	480	2.4	25	2
N/O codoped porous carbons	7 M LiTFSI	30.5	1000	2.2	25	3
Mn ₅ O ₉ /FeOOH	21 M LiTFSI/PVA	49.3	~1050	3.2	25	4
Fe ₃ O ₄ //MnO ₂	21 M LiTFSI	35.5	~152	2.2	25	5
N/S/O doped carbon SSC	7 M LiTFSI	37.7	~180	2.3	25	6
Nitrogen-doped porous carbon SSC	20 M LiTFSI	33	300	2.4	25	7
ICN //Li ⁺ -MnO ₂	21 M LiTFSI: 1 M Li ₂ SO ₄	55.7	1000	2.8	25	8
Commercial AC SSC	31.3 M LiTFSI	30.4	228	2.4	25	9
YP-50F carbon SSC	17 M NaClO ₄	23.7	~1100	2.3	25	10
Na _{0.55} Mn ₂ O ₄ .1.5 H ₂ O//AC	17 M NaClO ₄	21	1200	2.4	25	11
Commercial graphene nanoplatelets SSC	30 M [BMIm]Cl	36	870	3	-20	12
LMO//AC	40.4 M KAc+ 9.8 M LiAc	58	65	2	25	13

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Appendix A2. Cost comparison of various electrolytes based on different salts. The cost of all chemicals is from Merck.

Salt	Cost (S\$ g ⁻¹)	Molecular weight (g mol ⁻¹)	Concentration (mol kg ⁻¹ ; m)	Electrolyte cost (S\$ L ⁻¹)
C ₂ F ₆ NNaO ₄ S ₂ (NaFSI)	87.4	303.14	35	35 m = 927,305.3
NaCF ₃ SO ₃	11.12	172.06	9.26	9.26 m = 17,717.2
NaClO ₄	0.624	122.44	17	17 m = 1,298.8
NaClO ₄	0.624	122.44	1	1 M = 76.4
NaCl	0.096	58.44	0.1	0.1 M = 0.6
CH ₃ COONa	0.266	82.03	1	1 M = 21.8

Appendix A3. Mode of vibrations corresponding to the various peaks in Raman spectra of ethanol-water cosolvents.¹⁻⁴

Raman shift (cm ⁻¹)	Mode of vibrations
~436	Bending vibrations of C-C-O
~882	Skeletal CCO stretching
~1048	Skeletal CCO deformation
~1088	CO stretching
~1275	Deformation wagging
~1453	Wagging
~1482 (weak)	Bending vibrations of CH ₃
~1633	Bending vibrations of water
~2878	Symmetric CH ₂ stretching
~2926	Symmetric CH ₃ stretching
~2971	Asymmetric CH ₃ stretching
~3254	Symmetric O-H stretching
~3411	(a) Symmetric O-H stretching vibrational mode of asymmetrically bonded water molecules (b) Water molecules with bifurcated hydrogen bonds
~3613 (weak)	Vibrational mode of free OH

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Appendix A4. Cyclic voltammetry (CV) oxidation and reduction peaks of NMO tested in 1 M NaAc-Et/Di and its corresponding sodium-ions de/insertion sites.

Peak	Oxidation (V vs. Ag/AgCl)	Reduction (V vs. Ag/AgCl)	Sodium-ions de/insertion site ¹
I	-0.324	-0.400	Na 2
II	-0.105	-0.197	Na 1
III	0.020	-0.050	Na 3
IV	0.196	0.124	Na 2
V	0.282	0.235	Na 1
VI	0.439	-0.341	Na 2
VII	0.655	0.586	Na 2

References for A4

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