Next generation electrolytes for sodium ion battery

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**NANYANG
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SINGAPORE

**NEXT GENERATION ELECTROLYTES
FOR SODIUM ION BATTERY**

DO MINH PHUONG

**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2020

NEXT GENERATION ELECTROLYTES FOR SODIUM ION BATTERY

DO MINH PHUONG

INTERDISCIPLINARY GRADUATE SCHOOL

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 plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Date

A handwritten signature in black ink, consisting of a stylized 'D' followed by a series of loops and a long horizontal stroke extending to the right.

Do Minh Phuong

Supervisor Declaration Statement

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

17 – Jan – 2020

A handwritten signature in black ink, appearing to read 'M. Srinivasan', with a stylized flourish at the end.

Prof. Madhavi Srinivasan

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as M. P. Do, N. Bucher, A. Nagasubramanian, I. Markovits, T. Bingbing, P. J. Fischer, K. P. Loh, F. E. Kühn, and M. Srinivasan. Effect of conducting salts in ionic liquid electrolytes for enhanced cyclability of sodium-ion battery. *ACS Applied Material & Interfaces* **11**, 23972-23981 (2019). DOI: 10.1021/acsami.9b03279.

The contributions of the co-authors are as follows:

- Prof Madhavi Srinivasan and Prof. Fritz E. Kühn provided the project direction.
- I prepared the manuscript drafts. The manuscript was revised by Dr Nicolas Bucher and Dr Arun Nagasubramania.
- I co-designed the study structure with Dr Arun Nagasubramania, Dr Nicolas Bucher and Dr. Iulius Markovits.
- Dr Arun Nagasubramania and Dr Nicolas Bucher synthesized the material.
- Dr. Pauline J. Fischer conducted the viscosity and the conductivity measurement.
- I performed battery assembly, electrochemical tests and analyzed the data at TUMCREATE LTD.
- Dr Tian Bingbing carried out the X-ray photoelectron spectroscopy in National University of Singapore with the support from Prof. Kian Ping Loh. I prepared the samples and interpreted data.

Chapter 5 is published as P. J. Fischer, M. P. Do, R. M. Reich, A. Nagasubramanian, M. Srinivasan and F. E. Kühn, Synthesis and physicochemical characterization of room temperature ionic liquids and their application in sodium ion batteries. *Physical Chemistry Chemical Physics* **20**, 29412-29422 (2019) DOI: 10.1039/c8cp06099a.

The contributions of the co-authors are as follows:

- Prof Madhavi Srinivasan, Prof. Fritz E. Kühn provided the project direction and edited the manuscript drafts.
- I and Dr. Pauline J. Fischer co-designed the study structure.
- I and Dr. Pauline J. Fischer wrote the drafts of the manuscript. The manuscript was revised together with Dr. Arun Nagasubramania and Dr. Robert. M Reich.
- Dr. Pauline J. Fischer performed the ionic liquids synthesis and the ionic liquid characterizations at Catalysis Research Center and Department of Chemistry, Technische Universität München.
- I performed the materials synthesis. I and Dr. Pauline assembled coin cells and performed electrochemical tests in TUMCREATE LTD. I analyzed the electrochemical data.

Chapter 6 is published as M. P. Do, P. J. Fischer, A. Nagasubramanian, J. Geder, F. E. Kühn, and M. Srinivasan. Investigation of the Electrochemical and Thermal Stability of an Ionic Liquid Based $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2/\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ Sodium-Ion Full-Cell. *Journal of The Electrochemical Society*, **166** (6), A944-A952 (2019). DOI: 10.1149/2.0261906jes.

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- Prof Madhavi Srinivasan, Prof. Fritz E. Kühn provided the project direction.
- I and Dr Pauline J. Fischer wrote the drafts of the manuscript. The manuscript was revised together with Dr. Arun Nagasubramania and Dr Jan Geder
- I performed the materials synthesis in TUMCREATE LTD. I assembled coin cells and performed electrochemical tests in School of Materials Science and Engineering, Nanyang Technological University.
- Dr Jan Geder performed Accelerating Rate Calorimetry at VDE Renewable Asia LTD.
- I performed the Differential scanning calorimetry and interpreted data.

17 – Jan – 2020

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Abstract

As the growing demand of portable consumer electronics, rechargeable sodium ion batteries (SIBs) have been an attractive alternative to lithium ion batteries owing to cost effectiveness and high natural abundance of sodium over lithium. Electrolyte is one of the vital components of lithium or sodium ion batteries, which can directly affect the performance (e.g. rate capability and long-term cyclability), as well as safety of a battery. During the last decade, room temperature ionic liquids (ILs) have been used as a solvent in many applications including electrolytes for electrochemical energy storage devices. It offers more thermally and electrochemically stability than other organic carbonate-based solvents. In this work, the comprehensive study on ionic liquid electrolytes for SIBs are presented on the aspect of electrochemical stability, thermal stability and high-voltage application.

First, the effect of different sodium conducting salts in cooperation with 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid was examined in Na ion half-cell using hollow spherical P2- $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$. The formation and the composition of cathode/anode electrolyte interphases are highly depending on the conducting salts. It is found that in comparison with NaTFSI and NaClO_4 , NaFSI is a superior choice for IL electrolytes.

Following, physical and electrochemical properties of a series of IL containing different cation and anion structures were investigated as individual and as electrolyte for SIBs. The relation of anion core structures, functional groups and cations to essential properties such as conductivity, viscosity, electrochemical and thermal stability had been drawn.

To prove the thermal advance of IL electrolytes in comparison with conventional organic electrolytes, full cell $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2/\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ were investigated. IL-based full cell is capable to operate at elevated temperature and safer than organic-based cell in calorimetry tests. The lower onset temperature and lower self-heating rate was observed when putting in high raising temperature.

Finally, ether-functionalize ILs which have advance in viscosity were characterized in detail in high voltage half-cell SIBs using hollow sphere $\text{Na}_{0.6}\text{Mn}_{0.63}\text{Ni}_{0.07}\text{Co}_{0.1}\text{O}_2$. The difference in cycling stability was observed as a result of cation core-structure effect to the stability of Na-electrolyte interphase.

In conclusion, the benefit of ionic liquid electrolytes over conventional organic electrolytes have been proved in term of long-term cyclability, thermal safety as well as high voltage application in SIBs half-cell and full-cell. A systematic review on the impacts of conducting salts, cation core structures and anion core structures to the physical properties and electrochemical properties was presented, which contributes to utilization of IL electrolytes. This have an influence on the development of a safe and stable high-energy SIB system.

Lay Summary

As the unceasing development of small-scale electronic devices and electrical vehicles, there is a growing demand for rechargeable energy storage. Lithium ion batteries (LIBs) have developed vigorously and become the most popular choice for charge storage systems. As a result, the available lithium sources would be exhausted due to the projected increase in consumption, and consequently, leads to the surge in the cost of Li metal. Sodium ion batteries (SIBs), as chemical analogy to lithium, turn into an attractive alternative to replace LIBs because of the higher natural abundance and the price advantages.

Apart from the pricing concern, energy density, life-span as well as safety need to reach consumer expectation. Electrolyte, which is the electrically conductive medium inside the batteries, has a crucial role in the battery's properties and performance. Conventionally, electrolyte is comprised of flammable organic solvents, posing a serious safety issue. Hence, the attempt to explore a safer generation of electrolyte is required. A bright candidate is ionic liquids (ILs), described as molten salts at room temperature. ILs exhibit beneficial properties in electrochemical and thermal behavior. In this thesis, a comprehensive study on ILs in SIB application is presented in both sodium ion full-cells (commercialisable, not containing Na metal inside) and sodium ion half-cells (which use Na as an electrode). The superiority in some aspects of IL electrolytes were investigated and introduced.

First, with the combination NaFSI, a cutting-edge salt in SIB research, and a type of IL, the Na half-cell showed a massive improvement in the cycling stability. It means that using IL electrolyte, the cell can have longer life-span than using the conventional one.

A suitable electrolyte needs to meet specific requirements on properties, such as viscosity, conductivity, thermal and electrochemical stability. By changing the structures of ILs, the thesis presented the effect of the structure to the desired properties. The result is beneficial for researchers to find the appropriate ILs meeting required features for their application.

Summary

The safety of IL electrolytes is then highlighted on a SIB full-cell system. The IL cells are able to operate at the elevated temperature while this is impossible for the organic cell to execute at high temperature because of the explosive reactions. Compare to the conventional organic cell, the IL cell can withstand at higher temperature, until 270°C with low heat release.

One of the drawbacks of conventional electrolyte is narrow, selective potential windows. Electrolyte would decompose and detriment the batteries. It restricts the development of high-voltage high-energy lithium/sodium ion batteries. Ionic liquid, in the other hand, has higher stability window, allows the cell to run at higher voltage. This property is demonstrated on chosen ILs in a developed SIB half-cell system before going to the conclusion and recommendation of the thesis.

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Abbreviations

ARC	Accelerating Rate Calorimetry
BET	Brunauer–Emmett–Teller
CEI	Cathode Electrolyte Interphase
CE	Counter Electrode
CV	Cyclic Voltammetry
DMC	Dimethyl Carbonate
DSC	Differential Scanning Calorimetry
EC	Ethylene Carbonate
EL	Electrolyte
FSI	Bis(fluorosulfonyl)imide
GCD	Galvanostatic Charge Discharge
HC	Hard Carbon
IL	Ionic liquid
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LIBs	Lithium Ion Batteries
LSV	Linear Sweep Voltammetry
NaNMC	$\text{P2-Na}_{0.6}\text{Mn}_{0.84}\text{Ni}_{0.06}\text{Co}_{0.1}\text{O}_2$
$\text{N}_{221,2\text{O}1}$	N,N-diethyl-2-methoxy-N-methylethanamonium
$\text{N}_{222,2\text{O}1}$	N,N,N-triethyl-2-methoxyethanamonium
NMR	Nuclear Magnetic Resonance
NCO	$\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$
NVO	$\text{Na}_{2.55}\text{V}_6\text{O}_{16}$
NMP	N-methylpyrrolidone
PC	Propylene Carbonate
$\text{Pip}_{1,2\text{O}1}$	1-(2-methoxyethyl)-1-methylpiperidinium
$\text{Pyr}_{1,2\text{O}1}$	1-(2-methoxyethyl)-1-methylpyrrolidinium
$\text{Pyr}_{1,4}$ TFSI	1-Butyl-1-Methylpyrrolidinium Bis(trifluoromethylsulfonyl)amide
PVdF	Polyvinylidene Fluoride
RE	Reference Electrode
SEI	Solid Electrolyte Interphase

SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SHR	Self-Heating Rate
SIBs	Sodium Ion Batteries
TEM	Transmission Electron Microscopy
TFSI	Bis(trifluoromethylsulfonyl)imide
WE	Working electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter introduces the background problem, motivation and objectives for this research. Sodium ion batteries has become a prospective candidate for energy storage sector, replacing lithium ion batteries due to the similar characteristic, high natural abundance and cost benefit. Electrolyte is a concerning factor to ensure the stable performance and safety of batteries. The conventional carbonate electrolytes are volatile and flammable, which poses a safety hazard for LIBs and SIBs.

Because of the non-volatility, non-flammability and high electrochemical stability window, ionic liquids are considered as electrolyte solvent in SIBs application. The research focuses on establishing, improving and demonstrating IL-based electrolytes in SIBs in the aspects of cycling stability, thermal safety and high voltage application.

1.1. Problem Statement

Safety, energy/power density and economic viability are the major research drivers in energy storage devices.[1-2] In present day, lithium-ion batteries have become one of the most sought after options for modern energy storage due to their high energy and power densities.[3] However, lithium is not very abundant and eventually the available lithium sources would be exhausted.[4-6] With increasing demand, the limited of lithium resource leads to the overpriced of Li metal as well as LIBs. In this regard, sodium-ion batteries (SIBs) are prospective candidates owing to the relative abundance of sodium, lower cost and similar energy storage characteristics.[7]

Electrolyte is one of the vital components of lithium or sodium ion battery, which can directly affect the performance (e.g. rate capability and long-term cyclability), and safety of batteries.[8-9] Recently, in LIBs or SIBs, the electrolytes are mainly carbonate based solvents (e.g. Ethylene carbonate, Propylene carbonate, Dimethyl carbonate, Diethyl carbonate, Dimethoxyethane etc.) that dissolve conducting Li/Na salts containing PF_6^- or ClO_4^- anions.[9-11]. The volatility and high flammability of these electrolytes pose a serious safety issue concerning the lithium or sodium ion batteries. [8, 12] As an example, because of the flammable hazard, alkali metal-ion battery is restricted to be carried on airplanes. In addition, operating temperature is limited due to the use of conventional organic electrolyte. LIBs/SIBs are not able to operate as normal at extreme conditions.[1] As a result of over-charging, the battery could be heated to high temperature and become swollen due to the electrolyte decomposition, posing the explosion hazard. Moreover, high voltage application is limited due to restricted electrolyte stability window (ESW).

Ionic liquids (ILs) are considered as promising candidate to overcome these drawbacks because of the non-flammability, non-volatility and high electrochemical and thermal stability. [13-15] When using ILs as electrolyte, the safety of the battery would be improved. Another advantage is promoting the formation of beneficial solid electrolyte interface (SEI) on the cathode and anode. The suitable SEI layer could enhance the cycling stability. [16-18] The application of ionic liquid could extend to other secondary ion battery systems, e.g. aluminum/zinc ion batteries and dual ion batteries.

A novel approach to safer and high-voltage IL-based electrolytes, which is applicable for Sodium ion batteries will be the focus of this work.

1.2. Objectives and Scope

IL electrolytes for SIBs contain sodium conducting salt and ionic liquid as solvent. There are various types of ionic liquid with different cation and anion structures. Hence, a comprehensive study on IL electrolytes components is necessary to implement them in SIBs with specific application. The goals of the research work are to improve and demonstrate ILs electrolytes which are more cycling stable, thermal safer and applicable for high-voltage sodium ion half-cell and full-cell system

The primary objectives of the research can be summarized as follows.

- To understand the mechanism of the electrode – electrolyte interactions by employing surface sensitive characterization techniques and electrochemical technique. By understanding the nature of SEI interphases and the interaction between electrode-electrolyte during the cycling, the performance of IL battery could be explained.
- To understand the effects of different conducting salts in the electrolyte on the performance $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ cathode in SIB. The most appropriate conducting salt with optimal concentration would be investigated.
- To compare and draw the relationship of different cation core structures, functional groups and anions in physio-chemical properties, especially, the viscosity, conductivity, thermal property and ESW of pure ILs as well as ILs incorporated with conducting salts.
- To demonstrate and prove the safety characteristic when using the IL-based electrolyte in SIB half-cell and full-cell systems by investigating the high-temperature operability and safety evaluation of explosive and propellant.
- To investigate the high-voltage performance in SIB application. This would broaden the usage of IL electrolytes and open the future for the development of high-voltage alkali metal-ion battery when the operating voltage is no longer to be restricted.

1.3. Dissertation Overview

The structure of this dissertation will be presented as follow

Chapter 1 provides a rationale for the research and outlines the goals and scope.

This thesis describes and validates the benefits of IL-based electrolytes system to displace carbonate-based electrolytes in SIB application in the aspects of cycling stability, safety and higher operating potential.

Chapter 2 reviews the literature concerning sodium ion batteries. The chapter covers the fundamental, historical and contemporary literature about cathode materials, anode materials and non-aqueous electrolytes for sodium-ion batteries. The safety concern regarding conventional organic electrolyte is described and the emphasis on needs of ionic liquids as promising alternatives is elaborated. In the latter part, fundamental properties of ionic liquids, their recent progresses in SIBs as a part of LIBs and research gaps are described.

Chapter 3 briefly portrays the experimental methodology, principles and analysis of characterization methods, electrochemical measurement employed in the thesis with rationale. The synthesis procedures of electrode materials, hollow sphere Na_xMnO_2 class with Co and Ni doping, nanowire $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ and ionic liquids, coin-cell preparation and assembly are presented. Basic physical characterization techniques related to materials and electrode surfaces are X-ray diffraction (XRD), Scanning electron microscope (SEM), Inductively coupled plasma Optical emission spectroscopy (ICP-OES) and X-ray spectroscopy. To assess the critical properties of ILs and ELs, conductivity, viscosity measurement, thermal stability analysis techniques are elaborated. The performance of ionic liquid electrolytes was investigated in coin cell setup. The principles of electrochemical measurements techniques such as cyclic/linear sweep voltammetry (CV/LSV), Galvanostatic charge/discharge cycling (GCD), electrochemical impedance spectroscopy (ESI) with technical terms are presented

Chapter 4 elaborates the effect of sodium conducting salts in in 1-butyl-1-methylpyrrolidinium bis(trifluoro-methylsulfonyl)imide to the electrochemical performance of spherical $\text{P2-Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_{2+z}$ / Na half-cell). The selection of sodium conducting salts would impact the decomposition pathway of TFSI anion,

hence the composition of cathode-electrolyte interface (CEI), which are characterized by XPS. The compatibility and stability of IL electrolytes in contact with metallic sodium was studied by Na stripping plating tests. It was found that the excellent capacity retention for the electrolyte consisting of NaFSI salt is related to the formation of stable CEI and SEI layers.

Chapter 5 elaborates a series of N-based core structure functionalized ionic liquids for SIB electrolyte application. By a consistent and uniform characterization of their physicochemical properties, evaluation of the viscosity, conductivity, and thermal and electrochemical stabilities resulted in clear structure–property relationships. For practical application in SIBs, series of IL electrolytes was first investigated on various SIBs systems, namely hard carbon/Na, $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2/\text{Na}$ or Na/Na symmetrical cells to give insight on the electrolyte capability.

Chapter 6 elaborates the superior in safety of IL electrolyte over conventional organic electrolyte in SIBs. The electrochemical performance and thermal stability of a SIB $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2 / \text{Na}_{2.55}\text{V}_6\text{O}_{16}$ full-cell containing an IL based electrolyte is evaluated and compared to a reference system employing a conventional organic electrolyte at ambient and elevated temperature. Further, for the first time the superior safety of an IL-based SIB full-cell over the organic analogue is proven using Accelerating Rate Calorimetry (ARC) underlining the benefits of the IL based electrolyte.

Chapter 7 elaborates ionic liquid electrolytes in high-voltage application. Four ether functionalize ionic liquids, Pyr_{1,2}O₁ TFSI, N_{222,2}O₁ TFSI, N_{221,2}O₁ TFSI and Pip_{1,2}O₁ TFSI in addition of 0.5M NaFSI were investigated comprehensively as electrolyte for high voltage sodium-ion battery. Investigated IL-based electrolytes show the high anodic stability, up to 5.0 V vs. Na/Na⁺, suggesting the suitability for high-voltage application. The cycling stability and rate performance in Na half-cell using P2- $\text{Na}_{0.6}\text{Mn}_{0.84}\text{Ni}_{0.06}\text{Co}_{0.1}\text{O}_2$ cathode material, in the potential range 1.5 V - 4.6 V are reported.

Chapter 8 draws the conclusion and implication of the thesis. Reconnaissance studies about developing high-voltage hollow spherical P2- $\text{Na}_{0.6}\text{Mn}_x\text{Co}_y\text{Ni}_z$ materials were

included. The outlook and recommendations for future work are proposed briefly.

1.4. Findings and Outcomes/Originality

The major findings and contribution of this research are summarized as followed

1. Establishing the relation of various conducting salts in IL electrolyte to the formation of SEI and CEI layers in Na half-cell systems. Regarding to cathode side, the CEI components was characterized and studied. Thereby, the reaction mechanism of IL decomposition or the CEI formation was proposed. The stability of different electrolytes in contact with Na metal during continuous Na stripping/plating condition was considered as a factor influencing the electrochemical stability of Na half-cell.
2. In Na/NCO half-cell system, NaFSI (0.5 M) in Pyr_{1,4}TFSI shows the best electrochemical performance with a significant improvement in cycling stability (90% capacity retention after 500 cycles at 50 mA g⁻¹ in a half cell versus Na metal anode), outperforms the conventional NaClO₄ (1 M) in EC/PC electrolytes (39% retention after 500 cycles) and IL electrolytes containing NaClO₄ and NaTFSI. The excellent capacity retention for the electrolyte consisting of NaFSI salt is related to the formation of a stable CEI and solid electrolyte interphase layers.
3. Correlating the cation core structures, cation ether functional group and anion of IL to the physical and electrochemical properties of pure IL and the electrolyte. Ether functionalized ILs were found to be promising in SIB application.
4. Establishing a safer SIB full cell employing IL electrolyte. The IL full cell is able to operate at 75°C without electrolyte decomposition, in contrast to the full cell containing organic electrolyte. For the first time, the superior safety of an IL-based SIB full-cell over the organic analogue is proven using Accelerating Rate Calorimetry (ARC) underlining the benefits of the IL based electrolyte.
5. Presenting high-voltage SIB half-cell using series of ether-functionalize IL electrolyte. When incorporating with NaFSI, investigated IL-based electrolytes shows the high anodic stability, up to 5.0 V vs. Na/Na⁺, suggesting the suitability for high-voltage application. The effect of core structure of IL in

electrolyte were examined in terms of cycling stability and rate performance in Na half-cell using P2-Na_{0.6}Mn_{0.84}Ni_{0.06}Co_{0.1}O₂ cathode material, in the operating potential from 1.5 V to 4.6 V. Core structure was found to affect significantly to the stability of Na anode interphase.

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Chapter 2

Literature Review

This chapter reviews the literature, recent progresses related to sodium ion batteries as promising substitutes for lithium ion batteries. First, the achievements in cathode and anode materials in SIB are deliberated. Due to stable structure, high discharge capacities and large operating voltages for cathode materials, sodium manganese oxides have received the most attention for low-cost and efficient SIB systems.

Besides electrode materials, electrolyte for SIBs and LIBs is a critical factor determining cycling stability, rate capability and safety of the systems. With the objective of developing safer electrolyte, the next part of the review focuses on non-aqueous electrolytes, containing sodium salts and various types of solvents, such as organic-based, sulfone-based, nitrile-based and ionic liquid.

In addition, ionic liquids become the most promising candidate for non-aqueous electrolyte owing to the negligible volatility, flammability, high thermal, electro-chemical stabilities, etc. In the final part, fundamental properties of ionic liquids, their recent progresses in SIBs and research gaps are described.

2.1. Sodium ion batteries

2.1.1. Sustainable energy storage

Along with safety, sustainability is also to be in the concern of scientists in energy storage research field. Recently, lithium-ion batteries have gone a huge way to be a leader in secondary (rechargeable) energy storage. The common in their application can be found in almost portable electronic devices or electric vehicle. LIBs equipped in electric vehicles is a useful alternate power source for combustion engines, help to reduce the consumption of fossil fuel in transportation. Large-scale LIBs are applied to store the electricity generated from green energy sources, such as solar cells or wind turbines. While LIB technology is quite mature, there remains huge demands regarding its safety and geographically-constrained Li mineral reserves, thereby making large-scale storage prohibitively expensive in the last few years. According to the reserves estimate of lithium in early 2015 showed by U.S. Geological Survey (fig. 5), the run out of lithium reserves will happen after 365 years.

Table 2.1 U.S. Geological Survey Mining and Reserves Data (Metric Tons)

	2013 production	2014 production	Reserves
United States	870	NA	38000
Argentina	2500	2900	850000
Australia	12700	13000	1500000
Brazil	400	400	48000
Chile	11200	12900	7500000
China	4700	5000	3500000
Portugal	570	570	60000
Zimbabwe	1000	1000	23000
Totals	33940	35770	13519000

To provident suppress the practical shortage of lithium, it is needed to find a replacement for Li in battery sector, which should have high natural abundance. Sodium becomes a promising candidate due to the high abundance and its low-cost resource. The properties of sodium, lithium, potassium and magnesium as charge carrier are compared below.

Table 2.2 Comparison properties between Li^+ , Na^+ , K^+ and Mg^{2+}

	Li^+	Na^+	K^+	Mg^{2+}
Atomic mass/ g mol^{-1}	6.94	23	39.1	24.31
Mass-to-electron ratio/ g mol^{-1}	6.94	23	39.1	12.16
Cation radius/ $\text{\AA}$	0.76	1.02	1.38	0.72
E° (vs SHE)/V	-3.04	-2.71	-2.93	-1.55
Melting point/ $^\circ\text{C}$	180.5	97.7	63.4	650.0
Coordination preference	Octahedral	Octahedral		Octahedral
	Tetrahedral	Prismatic		Tetrahedral

Figure 2.1 Scheme illustration for Sodium ion-battery working principle. Reproduced with permission. Copyright 2018 John Wiley and Sons [1]

Na-ion batteries have a similar working principle as Li-ion batteries, generally containing a separator separates the cathode and anode in Na-ion electrolyte medium. Alkali ions, as charge carriers, move between the two electrodes during the charge and discharge processes. Despite of the higher reducing potential ($E_{\text{Na}/\text{Na}^+}^0 = -2.7 \text{ V}$ vs

a Cathode

Working Potential / V (vs. Na⁺/Na⁻)

Specific Capacity / mAh g⁻¹

Layered O3, Layered P2, Polyanionic compounds, Prussian Blue Analogues, Organic Compound

b Anode

Working Potential / V (vs. Na⁺/Na⁻)

Specific Capacity / mAh g⁻¹

Carbonaceous, TMO, TMS, Metal alloy, Organic

c Electrolyte

Number of use in Ref. Paper

Salts, Solvents, Additives

d Binder

Number of use in Ref. Paper

Cathodes & Anodes Insertion reactions, Anodes Conversion & Alloying Reactions, Pellet, Film Self Supporting

Figure 2. 2. Recent progress in Sodium ion batteries. (A) Cathode material (B) Anode material (C) Electrolyte (D) Binder. [2] Published by The Royal Society of Chemistry

2.1.2. Cathode materials in sodium ion batteries

For SIBs, the cathode is required to accommodate Na cations reversibly at a high redox voltage > 2 V vs. Na/Na⁺ while the material having lower voltage < 2 vs. Na/Na⁺ is defined as anode material. The volume expansion of Na ion insertion and extraction should be small as possible for better cycling performance [3, 4]. In restrict of this review, major types of cathode material will be discussed.

2.1.2.1. Layered oxides

The dominant studied structure for the cathode material of both Lithium ion batteries (LIBs) and Sodium ion batteries (NIBs) is layered oxides of the type $\text{Na}_{1-x}\text{MO}_2$. Based on the stacking arrangement of sodium or lithium ions by oxygen within the interstitial layer of the crystal structure, there are 2 types of nomenclature notation for coordination, including trigonal prismatic (P) and octahedral (O), defined by Delmas

and Hagenmuller. The following number 2 or 3 is the number of stacking metal layers (repeated layer), e.g. ABCABC in O3, ABBA in P2 and ABBCCA in P3[5]. In some cases, the monoclinic distortion happens, indicated by prime (') symbol (e.g. O'3, P'3). In SIBs studies, O3-type and P2-type are 2 main groups of sodium transition metal oxide materials.

O3-type is stable when Na content is close to 1, the average oxidation state of M is close to 3+. When the de-/sodiation progresses, the material phase transforms reversibly between $O3 \leftrightarrow O'3 \leftrightarrow P3 \leftrightarrow P'3$. These transitions are low-energy gliding of MO_2 slab without the breaking of MO bond.

P2-layered metal oxides receive more attention than other types in NIBs because of the better cyclability and energy efficiency [6]. In P2-material, the Na content is in the range from 0.3 to 0.7. Metal ion has higher average oxidation state, above 3.3+. Na^+ can occupy 2 types of trigonal prismatic site: (1) contact 2 MO_6 octahedral along the faces; (2) contact 6 surrounding MO_6 octahedral along the edges. The distance of 2 adjacent sites are too short to be occupied simultaneously. During the desodiation, when Na content is lower than 0.46, P2 phase would transform toward O2 phase due to the rotation of MO_6 octahedra, M-O bond breaking and the contraction of the crystal structure. This process is unfavorable for stability of the material.

Single metal oxide

Due to the success of $LiCoO_2$ as cathode material in LIBs, P2- and O3- Na_xCoO_2 was first investigated and tested in Na systems from 1981 [7]. P2- Na_xCoO_2 was found to have the highest capacity of 95 mAh g^{-1} as well as the best capacity retention. Throughout electrochemical sodiation and desodiation, the P2 structure can maintain whereas there is an reversible interconversion between O3, O'3 and P'3 [6]. In addition, the diffusion coefficient of Na ion into Na_xCoO_2 is aslo comparable to Li material type, at $(0.7-1.9) \times 10^{11} \text{ cm}^2 \text{ s}^{-1}$.

Other type of layer oxides is $NaFeO_2$, e.g. α - $NaFeO_2$ [8], O3- $NaFeO_2$ [9]. It is thermally stable material which generate less heat at higher onset temperature (200°C

- 300°C) when compare to LiCoO_2 . [10] Nevertheless, it experiences server irreversible structure change when charging to 4.0 V vs Na/Na^+ . The irreversible deterioration results in noticeable capacity fading. For example, in $\alpha\text{-NaFeO}_2$, the oxidation state of iron (IV) is unstable. The removal of Na from this compound will lead to the structural distortions, hence hinders the reinsertion of Na ion. [8, 11] Despite of containing safe and inexpensive components, the implementation of NaFeO_2 is still strict. Recently, the use of iron oxide has been utilized for SIBs. Hollow $\gamma\text{-Fe}_2\text{O}_3$ could host Na ions into the cation vacancies in the voltage range from 1.1 – 4.0 V. At a high rate of 50 C, it delivered a capacity of 99 mAh g^{-1} with a reasonable capacity retention after 500 cycles. [12]

Vanadium oxides were first investigated for Na-insertion by West et al. in 1980s, including layer structure $\alpha\text{-Na}_x\text{V}_2\text{O}_5$, $\text{Na}_{1+x}\text{V}_3\text{O}_8$ and 3 dimensional $\beta\text{-Na}_x\text{V}_2\text{O}_5$. $\alpha\text{-V}_2\text{O}_5$ structures contain edge and corner-shared VO_5 , underwent a phase transition during Na^+ insertion. Recently, nanostructured bilayer $\alpha\text{-V}_2\text{O}_5$ has improved the interslab distance from 4.4 Å to 13.5 Å, with the morphology of nanoribbons with high porosity. The electrode showed a sloping charge-discharge curve in a range of 1.5 to 3.8 V, associated with $\text{V}^{5+/4+}$ redox reaction. Material can obtain a reversible capacity of ~ 250 mAh g^{-1} with good capacity retention after 300 cycles. Steffen et al. introduced nanorod material $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \cdot 0.6 \text{H}_2\text{O}$, consisting of VO_6 corner-sharing octahedra and V_2O_8 edge-sharing pyramids. [13] Na ions are located in both tetrahedral and octahedral cavities. Material provides initial capacities of 217 mAh g^{-1} (at 20 mA g^{-1}) and good rate capability. The sloping charge-discharge curve over the potential range from 1.25 V to 4 V offers the ability to use the material as anode and cathode material. $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ is a promising material to be applied for symmetrical full cell.

Another prospective candidate which has been researched is monoclinic $\text{O}'3 \text{NaNiO}_2$. When charging and discharging in the range 2-4 V, the poor coulombic efficiency was observed in the first cycle (160 and 114 mAh g^{-1} of charge and discharge capacity, respectively) [14]. In the first cycle, the amount of Na content remove is ~ 0.91 , while only ~ 0.52 Na is extracted during the subsequent cycles. [15] A good reversibility is obtained when the cut-off voltage for the material is limited to 3.7 V vs. Na/Na^+ . When

charge to 4.5 V, more Na ion could be extracted but the stability of the electrochemical progress is worsening.

In contrast with LiCrO_2 having poor reversible capacity, O3-NaCrO_2 can achieve a reversible capacity of 120 mAh g^{-1} . [16] 50% of Na can be reversibility extracted with a small polarization at 3.0V voltage plateau. Further sodium extraction beyond 3.6V would lead to the loss in the reversibility due to the irreversible phase transformation. This example brings to scientists a choice in looking into materials which inactive with LIBs. O3-NaCrO_2 is emphasized for its thermal stability. When compared to LiFePO_4 , which is known as the most thermal stable material for LIBs, NaCrO_2 is more stable in Accelerating rate calorimetry (ARC) test. [17]

Other single metal oxides investigated were O3- and P2- NaVO_2 . NaVO_2 had not been reported in SIBs before 2010. The capacity of O2-NaVO_2 and $\text{P2-Na}_{0.7}\text{VO}_2$ are 120 mAh g^{-1} and 100 mAh g^{-1} , respectively. The materials have operating voltage of 2 V, which is not an optimum level for cathode or anode application.

A interest is paid for manganese oxides and its combination with other transition metals which exists in several polymorphs. This specific type of oxides cathode material will be discussed in separate sections.

Binary/ternary metal oxides

The binary or ternary layer oxides which combines more than one transition metals is useful to adjust properties, such as increasing the average voltage or reversible capacity [18]. $\text{NaNi}_{0.6}\text{Co}_{0.4}\text{O}_2$ system was one of the first combinations to be examined, but only 0.4 Na was observed to reinsert into structure [19]. Other material based on NaCoO_2 with Mn doping was reported to have a capacity of 155 mAh g^{-1} with 0.45 Na cycling. However, their capacity retention was not shown [20]. $\text{P2-Na}_{2/3}[\text{Co}_{2/3}\text{Mn}_{1/3}]\text{O}_2$ show the suppression of Na^+ ordering in a range of $0.5 \leq x \leq 0.83$. [21] The biphasic compound of manganese and cobalt in $\text{Na}_{2/3}[\text{Mn}_x\text{Co}_{1-x}]\text{O}_2$ improve the capacity and deliver high rate performance. However, the capacity was majorly contributed in the voltage range of 1.5 V – 2.1 V. It reduces the energy density when applied as cathode for SIBs. The substitute of Co by Ca was reported by Matsui et al. in $\text{Na}_{2/3}$. [22] The presence of Ca^{2+}

in Na layers would help to suppress the phase transformation during the electrochemical process.

A $\text{P2-Na}_{2/3}\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ synthesized by sol–gel method could deliver a capacity of 110 mA h g^{-1} when cycled from 2.0 to 4.2 V. [23] The material has good rate capacity as well as cycling stability.

$\text{NaNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, an analogue of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ is mentioned as an example of ternary layered oxide material. It behaves a good capacity retention as well as rate capability in the voltage range 3.75 V – 2.5 V. The discharge capacity could further improve when increasing the cut-off voltage to 4.2 V but it would be detrimental to its stability [24].

$\text{Na}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ has a discharge capacity of 185 mAh g^{-1} in the voltage range of 2.5 V – 4.5 V. The optimum cut off voltage is 3.8 V. [25] When substituting by Fe ion, the capacity retention was improved when cycling in a voltage range of 2-4.3V. The content of Fe in the structure effect to the structural and thermal stability, as well as cycling retention and rate capacity.[26] With the increasing of Fe content, the discharge capacity reduce slightly. However, the conductivity of material increases, hence following by enhancing rate performance. Spherical based- NaNiO_2 materials with the substitution of Mn and Co were reported with a varied chemical composition, inner $\text{NaNi}_{0.75}\text{Co}_{0.22}\text{Mn}_{0.23}\text{O}_2$ and outer $\text{NaNi}_{0.58}\text{Co}_{0.06}\text{Mn}_{0.36}\text{O}_2$. [27] The material exhibits good performance, even at -20°C . Ti substitution results in superior cyclability and a discharge capacity of 120 mAh g^{-1} at 20 mA g^{-1} .

To the best of author's knowledge, the research on the combining layered oxide material has focused on the sodium manganese dioxide and its intercalations. Manganese based-oxide will be discussed further in the later part.

2.1.2.2. Polyanions compounds

Transition metal polyanion materials have remarkable thermal stability in comparison with metal oxide due to the presence of the covalent bonds (such as P and O) when

material is in charged state. However, polyanions usually exhibit lower conductivity relative to oxides. It is a requirement to employ material modifications as carbon coating to improve the conductivity, hence, increases the electrochemical performance.

From basic polyanion compound NaFePO_4 , there are some factors applied to modify the material, as followed (i) variation in Na charge carrier; (ii) partial or fully substitution Fe by other transition metal elements; (iii) combination anion system with F, OH or CO_3 ; (iv) combination phosphate (PO_4)³⁻ and pyrophosphate (P_2O_7)⁴⁻

Table 2. 3 List of possible phosphate phases material with theoretical specific capacity in Na-ion batteries. [28]

Compound	No. electron transfer	Redox couple	Voltage	Theoretical capacity / mAh g ⁻¹	Experimental capacity	Rep
NaFePO ₄ (amorphous)	1	Fe ^{3+/2+}	2.4	154	150	[29]
NaFePO ₄ (olivine)	1	Fe ^{3+/2+}	2.8	154	125	[29, 30]
NaFePO ₄ F	1	Fe ^{3+/2+}	2.0-3.8	124	100	[31]
NaVFePO ₄	1	V ^{5+/3+}	3-4.5 vs Li	143	107	[32]
Na ₃ V ₂ (PO ₄) ₃ F ₃	2	V ^{4+/3+}	2.0-4.2	128	120	[33, 34]
Na ₃ V ₂ (PO ₄) ₂ F	2	V ^{5+/4+}	3.0-4.2	156	87	[35]
Na ₂ [Fe _{0.5} Mn _{0.5}]PO ₄ F	1	Mn ^{3+/2+} Fe ^{3+/2+}	2.0-4.5	124	110	[36]
NaV _{0.96} Cr _{0.04} FePO ₄	1	V ^{5+/3+}	3.0-4.5	142	80	[37]
Na _{1.5} VOPO ₄ F _{0.5}	1	V ^{5+/4+} V ^{4+/3+}	3.6 and 4.0 V	130	87	[35, 38]
Na ₃ V ₂ (PO ₄) ₃	2	V ^{4+/3+} V ^{3+/2+}	3.4 V and 1.6V	118	~	

Phosphate and pyrophosphate

The most prominent cathode material is NaFePO₄ corresponding to the community of lithium analogue LiFePO₄ in LIBs. Unlike LiFePO₄, NaFePO₄ only can crystalize in maricite structure that is electrochemical inactive [5, 29, 39]. To prepare active NaFePO₄, sodium would be inserted into heterosite FePO₄ by electrochemical or

chemical method [30, 40]. In electrochemical tests of Na/NaFePO₄/Na cell, the olivine material exhibited an initial capacity of 125 mAh g⁻¹ with an operating voltage of 2.8 V, along with acceptable capacity retention (88%/50 cycles) [41]. Amorphous NaFePO₄ delivered a higher discharge capacity of 150 mAh g⁻¹ at low operating voltage (2.4 V). During the discharge process, FePO₄, Na_{0.7}FePO₃ and NaFePO₄ change simultaneously. Due to the large ion radius of Na⁺ relative to Li⁺, high charge-transfer resistance, slow diffusion of Na⁺ and high migration energy were observed.

To increase the operating voltage of the material, it is suggested introducing high electronegativity ion, for example fluoride. Na₂FePO₄F was first reported in 2007 which applied in LIBs. Langrock et al. synthesized carbon-coated hollow Na₂FePO₄F spheres, which exhibited a discharged capacity of 89 mAh g⁻¹ at 0.1 C. An excellent cycling stability was obtained, 80% retention over 750 cycles, which is explained by rapid ion diffusion and structure integrity [42].

Pyrophosphate Na₂FeP₂O₇ was introduced with a theoretical capacity of 97 mAh g⁻¹, not competitive in term of capacity. However, Na⁺ ion diffusion is improved compared to the phosphate-type material due to three-dimensionality and low energy for Na⁺ migration, resulting in the moderate rate performance.[43] Further investigation, Na_{3.32}Fe_{2.34}(P₂O₇)₂ exhibited a higher discharge capacity of 110 mAh g⁻¹. [44] The capacity retention and rate capability are superior to the previous material. Apart from FeP₂O₇, Branpanda et al. introduced triclinic structure β-Na₂MnP₂O₇ which provides a discharge capacity of 80 mAh g⁻¹ in an average voltage of 3.6 V. [45] Another pyrophosphate compound found is Na₂(VO)P₂O₇. [46] The redox couple associated is V^{5+/4+}, operating voltage is at 3.8 V.

To utilize the better Na⁺ diffusion of pyrophosphate compound and higher discharge capacity, the strategy is mixing phosphates compound as Na₄M₃(PO₄)₂P₂O₇. The low activation barrier for Na⁺ migration in all directions provide better Na⁺ diffusion. Na₄Fe₃(PO₄)₂P₂O₇ provides a reversible discharge capacity of 105 mAh g⁻¹ with the operating voltage of 3.2 V. [47] Na₄Co₃(PO₄)₂P₂O₇ has extraordinarily high operating voltage of 4.5 V because of the high-voltage Co^{2+/3+} redox reaction. At 25C-rate, material is still able to deliver a discharge capacity of 80 mAh g⁻¹. [48]

NASICON-type phosphate material

NASICON (Na^+ superionic conductor) has general formula $\text{A}_x\text{M}_2(\text{XO}_4)_3$ (where M = transition metal, X = Si^{4+} , P^{5+} , S^{6+} , Mo^{6+} , As^{5+} etc.) and a rhombohedral structure. Tetrahedral XO_4 corner-interlink with octahedral MO_6 . Na can occupy 2 different sites, octahedral sites and their 8-coordinate sites. In 2002, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ was first studied by Yamaki et al. Two plateaus were observed at 1.2 V and 3.4 V corresponding to V(II/III) and V(III/IV) respectively, however, the reversibility was poor, and the capacity was low (107 mAh g^{-1}) [49]. Based on 3D ion transport channels, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is extensively studied. The materials exhibit high diffusion rate and long cycle life. [50, 51] Similar compound $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ received a discharge capacity of 45 mAh g^{-1} in the first cycle [49].

Substitution of SO_4^{2-} , PO_4F^{2-} , $\text{P}_2\text{O}_7^{2-}$ and $(\text{P}_2\text{O}_7)_m(\text{PO}_4)$ for PO_4^{2-} would help to improve the operating voltage due to the introduction of greater ionicity, lower the energy of the redox couple. A modified of initial type, sodium transition metal sulfate fluorides, NaMSO_4F , exhibits high Na^+ ionic conductivity, but Na withdrawal out to structure appears to be unfavorable. Other perspective type of fluorophosphates is sodium vanadium fluorophosphates, involving NaVPO_4F , $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_{1.5}\text{VOPO}_4\text{F}_{0.5}$. Their climax properties compared with other material are low cost raw materials, their safety and ability to work in high voltage. $\text{Na}_7\text{V}_4(\text{P}_2\text{O}_7)_4(\text{PO}_4)$ is sodium vanadium-based phosphate containing mixed PO_4 and P_2O_7 units. [52] The interconnected $\text{V}(\text{P}_2\text{O}_7)_4$ units created large tunnels for 3D Na^+ diffusion. Material could deliver a discharge capacity of 90 mAh g^{-1} with the working voltage plateau at 3.88 V. However $\text{Na}_7\text{V}_4(\text{P}_2\text{O}_7)\text{PO}_4$ had poor electronic conductivity, graphene oxide was doped into material to improve the rate performance and cycling stability. Full cell of hard carbon/ NaVPO_4F delivered a capacity of 80 mAh g^{-1} between 2.5 V and 4.25 V, however, after 30 cycles, only 50% of capacity could retain [53]. The low cycling performance can be improved by doping with Al or Cr into the structure.

It is remarkable that NASICON material is compatible with aqueous electrolyte in term of voltage and energy density, e.g. $\text{NaTi}_2(\text{PO}_4)_3$ / $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ full cell with high energy density of 29 Wh kg^{-1} [54]. Application in aqueous electrolyte is valuable to reduce production costs and increase safety of battery.

Cyanide and organic compound

Prussian blue and its analogues have been applied as cathode material in SIB. Their open framework could accommodate the insertion of Na^+ . Its analogue $\text{Na}_x\text{MFe}(\text{CN})_6$ have high capacity due to 2 electron reaction. However, those received low energy density when compared to other types of materials.

2.1.3. Manganese oxides

Because of large size tunnel structures for Na incorporation, manganese oxides have attracted large attention and developed to be a successful family enlisting material. In 1984, the electrochemical intercalation and deintercalation of Na_xMnO_2 bronzes (P-type and α - NaMnO_2) was studied by Mendiboure et al [55]. O'3-type $\text{Na}_{1-x}\text{MnO}_2$ has low reversible range when $x < 0.2$ and wider reversible range when $x < 0.8$. The large capacity decay was observed. However, the manganese dissolution is negligible in this case. Two polymorphs are α (O'3-type) as low temperature phase and β -type as high temperature phase, prepared at $>900^\circ\text{C}$. β - NaMnO_2 exhibited a discharge capacity of 190 mAh g^{-1} at 0.05 C and 145 mAh g^{-1} at 2 C . During the charge process, stacking fault in orthorhombic structure increases. The material has narrow active range of Na content ($0.85 - 0.96$). When lowering the amount of Na, the spinel structure, which is possible in β - LiMnO_2 , could not form due to the larger size of Na^+ .

When the sodium content is limited to 0.7, P2-type material can be formed. P2- $\text{Na}_{0.44}\text{MnO}_2$ synthesis via solid-state method is the most well known in this group, which has theoretical capacity up to 122 mAh g^{-1} between 2.0 V and 4.0 V . $\text{Na}_{0.44}\text{MnO}_2$ is also typically used in aqueous electrolyte systems.

Multiple phase transformation associates with the oxidation process, when Na content varies from $0.44 - 0.612$. The framework consists of MnO_6 octahedral and MnO_5 square-pyramidal site, interconnected by either edge-share and corner-share. Different sodium accommodations in 2 different tunnels offer high mobility of Na ions along the c-axis. The material exhibits low rate performance because of the electrostatic repulsion. One of the reasons for capacity degradation is Jahn-Teller distortion. Highly

crystalline material could promote to higher capacity retention. In this case, the de-/insertion of Na ion can be more durable and the diffusion path of Na^+ ion is reduced. Another reason for the capacity decay is volume change as can be observed in $\text{P2-Na}_{0.6}\text{MnO}_2$.

To improve the properties of material, doping other transition metal oxide to combine their advantages was reported. The role of each transition metal has been successfully defined. The substitution of Li, Ni, Co could help to suppress Mn^{3+} distortion. Doping Ni into structure could enhance the operating voltage by $\text{Ni}^{2+/4+}$ redox reaction and increases the energy density. $\text{P2-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ showed an average voltage of 3.5 V when charging to a limit of 4.5V. $\text{P2} \rightarrow \text{O2}$ phase transformation occurs at around 4.2 V, associated to a large volume change. Hence, to preserve the cycling stability, the voltage range is limited to 4.1 V. Li substitution in the metal oxide, $\text{Na}_{0.8}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ inhibited the P2-O2 phase transition and increase the capacity retention up to 91% after 50 cycles. Substitution electro-inactive ion Mg^{2+} and Zn^{2+} in the material has similar effect. Although, the presence of Mg^{2+} reduces the delivered discharge capacity, it helps to enable the occupation of Na ion in prismatic sites, retain the P2 phase of the material. Based on review literatures, integrating Ni and Co ion into NaMnO_2 structure is extensively studied for SIBs with the aim of high-voltage and long cycling cathode materials. The ratio content of transition metals needs to be considered carefully due to high cost of Ni and Co metals. Table 2.4 describes various sodium manganese oxide materials.

Table 2. 4. Discharge capacity (Q), capacity retention and working voltage of some Sodium Manganese Oxides materials with transition metal combination

Material	Electrolyte	Rate	Q	Retention/ cycles	Vol	Ref
$\text{Na}_{0.44}\text{MnO}_2$	NaClO_4 (EC/DEC)	0.5 C	100	84%/100	2.0- 3.8	[56]
$\text{P2-Na}_{0.6}\text{MnO}_2$	NaClO_4 (PC)	0.1 mA/cm^2	150	30%	2.0- 3.8	[57]

Monoclinic NaMnO_2	NaPF_6 (EC/DMC)	0.1 C	185	73%/20	2.0- 3.8	[58]
$\text{Na}_4\text{Mn}_9\text{O}_{18}$ nanowires	NaClO_4 (EC/DMC)	0.5C	128	77%/1000	2.0- 4.0	[59]
Single phase $\text{Na}_{0.44}\text{MnO}_2$	NaClO_4 (PC)	0.1 C	140	40%/1000	2.0- 3.8	[60]
$\beta\text{-NaMnO}_2$	NaPF_6 (EC/PC/DEC)	0.05 C	180	70%/100	2.0- 4.2	[61]
$\text{Na}_{0.7}\text{MnO}_2$ nanoplates	NaClO_4 (EC/PC)	0.235 C	163	74%/50	2.0- 4.0	[62]
Sphere $\text{Na}_x\text{MnO}_{2+z}$	NaClO_4 (EC/PC)	0.3 C	168	58%/150	2.0- 3.8	[63]
P2- $\text{Na}_{0.66}\text{Ni}_{0.26}\text{Zn}_{0.07}\text{Mn}_{0.67}\text{O}_2$	1M NaClO_4 PC 2%FEC	12 mA g^{-1}	132	89%/30	2.0- 4.4	[64]
O3- $\text{NaNi}_{0.32}\text{Fe}_{0.13}\text{Co}_{0.15}\text{Mn}_{0.40}\text{O}_2$	0.5 M NaPF_6 PC 2%FEC	0.2 C	192.7	85%/50	1.5- 4.3	[65]
P2- $\text{Na}_{0.4}\text{Mn}_{0.54}\text{Co}_{0.46}\text{O}_2$	NaClO_4 EC/DEC	20 mA/g	194	80%/60	1.5- 4.2	[66]
P2- $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ plates	NaClO_4 (PC/FEC)	0.1 C	86	93%/200	2.0- 4.5	[67]
P2- $\text{Na}_{0.66}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_2$	0.5 M NaPF_6 PC 2%FEC	0.1 C	162	75%/100	2.0- 4.3	[68]
P2- $\text{Na}_{0.6}\text{Mn}_{0.65}\text{Ni}_{0.25}\text{Co}_{0.1}\text{O}_2$	1M NaPF_6 EC/DMC	0.2 C	148	43.2%/150	2.1- 4.3	[69]

P3- $\text{Na}_{0.6}\text{Ni}_{0.25}\text{Mn}_{0.5}\text{Co}_{0.25}\text{O}_2$	1M NaClO_4 PC	0.1 C	118	78%/150	1.5- 3.6	[70]
P2- $\text{Na}_{0.67}\text{Mn}_{0.65}\text{Ni}_{0.2}\text{Co}_{0.15}\text{O}_2$	1M NaClO_4 PC	0.5 C (120)	132	78%/100	1.5- 4.2	[71]
P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$	NaPF_6 PC	C/10 (12)	145	82%/100	1.5- 4.3	[72]
P2-O3 mixed phases $\text{Na}_{0.67}[\text{Ni}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}]\text{O}_2$	1M NaClO_4 PC	0.1C	138	88%/100	1.5- 4.2	[73]
P2- $\text{Na}_{0.67}\text{Mn}_{0.72}\text{Ni}_{0.14}\text{Co}_{0.14}\text{O}_2$ with K ⁺ doping	NaClO_4 (EC/PC)	2.0C	141	80%/100	1.8- 4.2	[74]
Nanorod $\text{Na}[\text{Ni}_{0.61}\text{Co}_{0.12}\text{Mn}_{0.27}]\text{O}_2$	1M NaPF_6 PC/FEC 0.5M	0.5 C	160	80%/100	1.5- 4.1	[75]
P2- $\text{Na}_{0.65}\text{Ni}_{0.17}\text{Co}_{0.11}\text{Mn}_{0.72}\text{O}_2$	0.5 M NaPF_6 PC 2%FEC	12 mA g^{-1}	187	91%/100	1.5- 4.3	[76]
P2- $\text{Na}_{0.7}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{Co}_{0.1}\text{O}_2$	1M NaClO_4 EC/PC	12 mA g^{-1}	154	92%/100	1.5- 4.2	[77]
Microflake P2- $\text{Na}_{0.67}\text{Mn}_{0.65}\text{Ni}_{0.15}\text{Co}_{0.2}\text{O}_2$	NaPF_6 EC/DEC	20 mA g^{-1}	141	88%/50	2.0- 4.4	[78]

Bucky ball P2- $\text{Na}_{0.66}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_0$ $_{13}\text{O}_2$	NaClO_4 EC/DEC	1C	121	90%/150	2.0- 4.7	[79]
$\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_{2+z}$ sphere	NaClO_4 (EC/PC)	0.3 C	162	67%/150	1.5- 3.8	[63]
P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_0$ $_{66}\text{O}_2$	10 mol% NaTFSI (Pyr_{1,4}FSI)	0.1 C	225	80%/100	1.5- 4.6	[80]

Hollow spheres of $\text{Na}_x\text{MnO}_{2+z}$

Bucher et al had investigated the influence of morphology on cycle performance and concluded the preeminence of the hollow sphere over the flake [81]. The difference in cycling stability was explained by better accommodation of volume changes. Contact area of the spheres would promote the contact with added conductive carbon, which results in higher ion diffusion. The higher electrode/electrolyte interface also improves the wettability of electrolyte to active material.

The cycling stability can be further improved by Co doping. ~10% of Co was doped in material to form hollow spheres of P2- $\text{Na}_x\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ Iz Compared with initial material, Co-doping enhances Na^+ conductivity, avoid the ordering of Na^+ and gets rid of phase transformation between hexagonal and orthorhombic phase in lower voltage.

In this research, inspiring by the promising properties of the materials, hollow spheres of P2- $\text{Na}_x\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ is chosen as the applied cathode material, with the amendment of electrolyte.

2.1.4. Anode materials in sodium ion batteries

Sodium metal could be applied as anode material because of the low reduction potential. However, the use of sodium metal in practical is restricted due to the safety issues resulting from the possible dendrite formation. Compared to lithium, sodium has lower melting point (97.7°C) and high reactivity with the presence of moisture. Hence, it is important to develop the suitable anode material for SIBs.

2.1.4.1. Carbon based anode

Unlike LIBs, sodium could not intercalate with the graphite, which is the most common anode in LIBs. The insertion of Na into graphite is expected to occur below sodium plating potential. For the disorder carbon, the insertion of Na could occur at higher potential. Petroleum coke carbon was first introduced in 1993 by Doeff et al., exhibited a reversible capacity at 85 mAh g^{-1} . [82] Generally, amorphous carbon pyrolyzed from precursor at high temperature. Hard carbon (HC) could deliver a capacity close to 300 mAh g^{-1} . Hard carbon is a type of amorphous carbon, composed of graphene sheets stacking randomly. During the slurry preparation, the presence of air has no impact on the electrolyte decomposition and the surface of the material.

The main challenge of this promising anode type is the high reactivity of sodiated hard carbon with the electrolyte. In contrast to LIBs, the stable SEI layer is lacking when using NaPF_6 in EC : DEC or EC : DMC. Optimization of the electrolytes is targeted in several groups. The free additive electrolytes succeed in improvement of cycling stability are NaClO_4 in PC or NaPF_6 in EC : PC. [83-85] FEC is used as an additive to form more stable SEI layer on the HC electrode. [86]

The cycling stability and the rate performance of HC highly depend on the architecture. Therefore, hierarchical porous, [87] hollow carbon nanosphere [88] or hollow carbon nanowire [89] with structural stability could enhance the electrochemical performance, specifically rate capability. The interconnected network offers better accommodation of volume expansion and good conductivity. The low Coulombic efficiency is explained by the formation of SEI layer on the large surface of materials.

The introduction of a hetero atom (such as N, B, S and P) into a carbonaceous anode called N-doped type is beneficial for enhancing the electrochemical performance. The hetero doping atom would create a defect site on the surface to accommodate Na ion and improve surface interaction by functionalizing. For example, nitrogen doping improves the conductivity and the charge transfer processes. [90, 91] Sulfur doping into HC could provide additional reaction site for Na accommodation and enlarge the interlayer distance. [92]

2.1.4.2. Sodium alloy

Some metal, such as tin (Sn) or antimony (Sb), could form the binary alloy with Na, thus can provide capacities in SIBs. The metal alloys are attractive due to high theoretical capacity. However, the main drawbacks are pulverization and large volume expansion upon cycling. The large volume expansion is detrimental to the cycling stability. To overcome the problem, nanosizing or preparation of composite materials are prior strategies. Further research needs to be done in order to improve the cycling stability at higher rate.

2.1.4.3. Metal oxide

Titanium bases oxides such as anatase TiO_2 , layered $\text{Na}_3\text{Ti}_3\text{O}_7$ and $\text{Na}_{0.66}\text{Li}_{0.22}\text{Ti}_{0.78}\text{O}_2$ have been studied as negative electrode for SIBs. Anatase TiO_2 nanocrystal exhibited a reversible capacity of $\sim 150 \text{ mAh g}^{-1}$ and possible cycle at high rate of 2 A g^{-1} . When added C to nanoparticle materials, it offers conductivity and enable more diffusion of ion by shortening the migration length for Na insertion. Carbon coated TiO_2 microsphere enhance electrical conductivity while preventing agglomeration.

Layer $\text{Na}_2\text{Ti}_3\text{O}_7$ exhibited a plateau at 0.3 V vs. Na^+/Na , resulting a discharge capacity of 200 mAh g^{-1} in the voltage range of $0.01 - 2.5 \text{ V}$. The micro-sized $\text{Na}_2\text{Ti}_3\text{O}_7$ delivered a discharge capacity of 188 mAh g^{-1} . The nanoparticle size could improve the discharge capacity but paid off for cyclability. The auspicious of titanium-based oxide opens more room for SIB anode material.

2.2. Electrolyte

For few decades, electrochemical energy storage industrial has attracted global concern as the revolutionary of portable electric devices, electrically powered vehicle etc. In batteries industry, parallel with cathode and anode material research which are helpful to improve the stored energy of battery, electrolyte, although, is given less attention, still also an essential part due to their role to life-length, rate capability, safety, etc.

There are some basic properties needed for electrolyte, which comply for lithium-ion and sodium-ion batteries [93, 94]:

- (1) Chemical inertness and compatibility – no chemical reaction within itself and with cell components such as separator, electrodes, current collectors... during operation.
- (2) Wide electrochemical window – large separation between onset potential for oxidative and reductive decomposition.
- (3) High ionic conductivity, low viscosity and a high dielectric constant.
- (4) High thermal stability – melting point and boiling points should be outside the operating temperature range.

Beside these properties, their cost, toxicity and sustainability are factors need to be considered. However, in meantime, it is difficult to solve all these problems for any single solvent. The requirements would be optimized to choose the most suitable with special applications. The focus of this review is on non-aqueous electrolyte for sodium ion battery.

2.2.1 Sodium salts

Sodium conducting salt used in non-aqueous electrolyte is major component for providing Na^+ ion charge carries. There are properties for conducting salts that need to be considered when applying in electrolyte system: (i) the solubility in the solvent(s) (ii) the stability of anion which determines the upper limit of electrolyte stability window (ESW) (iii) the electrochemical stability when in contact with other components in battery system (iv) non-toxicity, thermal stability and other safety aspects. Up to now, the choice for sodium salts in sodium ion battery still restricts with some common anion: ClO_4^- , BF_4^- , PF_6^- , CF_3SO_3^- (Tf), and $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ (TFSI). Ponrouch et al [93] discussed these properties in a review. The most common salt in recent research is NaClO_4 . A detrimental drawback is the water content in electrolyte even after drying at 80°C . ClO_4^- is a strong oxidant. The second popular salt is NaPF_6 , however it suffers hydrolysis at moisture condition. Tf and BF_4^- result less conductive electrolyte. The same problem between Tf and TFSI is the corrosion with aluminium collectors. Another kind of salt which is not clear studied is NaFSI. NaFSI salt is less thermal stable than NaTFSI analogue, however, with the smaller size it has higher mobility than NaTFSI, results in higher conductivity in electrolyte. The basic properties of mentioned salt will be listed in table 4. It should be noted that, NaFSI and NaSO_4 are typically used in aqueous electrolyte research.

Table 2. 5. Molecular weight, melting temperature and conductivity of the most commonly Na-salts (compared with Li-salt values)

Salt	Anion chemical structure	M _w g mol ⁻¹	T _m [°C] (Li)	σ [mS cm ⁻¹] (Li)	E ^a	T- ^b	Toxic	Safety
NaClO ₄		122	468 (236)	6.4	+	-	-	-
NaBF ₄		109.8	384 (293)	(3.4)	O	O	-	O
NaPF ₆		167.9	300 (200)	7.98 (5.8)	+	-	-	-
NaTf		172.1	248 (>300)	(1.7)	+	+	-	+
NaTF SI		303.1	257 (234)	6.2 (5.1)	+	+	-	+
NaFSI		203.3	118 (130)		+	+	-	+

a: Electrochemical stability, b: Thermal stability, + high, O medium, - low

2.2.2. Organic-based electrolyte

Recently, the conventional and universally employed electrolyte is based on the combination of organic solvent, including organic carbonates (linear and cyclic), esters and ethers, salts and functional additives, same as those used for LIBs. E.g. Lithium ion battery electrolytes consists of salts LiPF₆ in the mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate organic solvent. The most important properties of organic solvent have been summarized in table 1.

Due to the high dielectric constant and large liquid temperature range, PC was first used in SIBs and LIBs. However, it causes the exfoliation for graphite layers during the co-intercalation. PC is no longer being used in LIBs. In SIBs, instead of graphene, HC is the only viable carbonaceous anode material. Hence, PC remains as main solvent for SIBs. However, when using PC as pure solvent in HC system, significant fading in capacity was observed. The main reason is attributed to continuous growth of SEI layer. In the other hand, EC is known to have positive effect on the SEI formation. However, the high melting point of EC restricts it to be used as pure solvent in electrolyte. To optimize the properties of electrolyte such as dissolution of salts, viscosity or contribution to SEI layers, co-solvents in the binary mixture are primary targeted. EC:PC (1:1 wt) were shown to have the highest thermal stability among the investigated solvents (EC:DME, EC:DMC, EC: DEC).

Table 2. 6 Properties of some common organic solvents [95]

Solvent	T _m °C	T _b °C	T _f °C	η (cP) 25 °C	ε 25 °C	SEI	Anodic stability	Safety
ethylene carbonate (EC)	36.4	248	160	1.9 (40 °C)	89.78	+	+	+
Propylene carbonate (PC)	-48.8	242	132	2.53	64.92	-	+	O
Dimethyl-carbonate (DMC)	4.6	91	18	0.59	3.107	-	O	-
Diethyl-carbonate (DEC)	-74.3	126	31	0.75	2.805	-	O	-
Ethylmethylcarbonate (EMC)	-53	110		0.65	2.958	-	O	-

Dimethoxyethane (DME)	-58	84	0	0.46	7.18	-	O	-
Diethylene glycol dimethyl ether (Diglyme)	-64	162	57	1.06	7.4	-	O	-
triethylene glycol dimethyl ether (Triglyme)	-46	216	111	3.39	7.56	-	O	-

Melting temperature T_m , the temperature T_b , the flash point T_f , the viscosity η and dielectric constant ϵ , contribution to SEI formation, the anodic stability and the total safety rating (+ high, O medium, - low)

The free energy of different electrolyte using NaClO_4 conducting salt and pure carbonates solvents or their binary mixture were calculated by Kamatha et al. [96] EC:PC was evaluated as the top formulation based on thermodynamic. Regarding to kinetic descriptors dictating rate capability and power performance, EC:DMC and EC:EMC are the best electrolyte solutions.

Safety concerns

Although organic electrolyte takes the lead with other types of electrolyte, their high volatility, high vapor pressure and flammability cause serious hazards for their application in consumer and transportation markets. Moreover, to extend the application of secondary ion batteries, future LIBs or SIBs need to have ability to operate under harsh conditions, especially drastic temperature changing. The narrow temperature range of organic based- electrolyte limits the operation temperature to around 55°C . Beside mentioned reasons, dendrite formation occurring in metal anode, especially Li and Na, is another factor responsible for battery fire and explosion [97]. Short circuit may happen when metallic alkali dendrites grows uncontrolled from the anode surface across the electrolyte and contacts opposite electrodes. In this condition, a large amount of heat generating could ignite the electrolyte to cause battery explosion.

There are some incidents reported related to battery safety. For example, in first year of services, Boeing 787 Dreamliner suffers at least 4 problems stemming from its

lithium-ion batteries. In figure 1, the incident report of overheating Samsung smartphones in the USA has been illustrated, in which regards to transportable devices' example. Introducing new nonflammable electrolytes would be an efficient solution for this issue.

Figure 2. 3. The incident reports related to Samsung Galaxy Note 7 battery in the US

The urgent of finding novel safety electrolyte for battery leads to great efforts in researching. Some nonflammable electrolytes have been introduced, however, still exists drawback to replace the dominance of carbon-based electrolyte, which could be mentioned as sulfone-based solvents, ionic liquid solvents, nitrile-based solvents. [15, 94]

2.2.3. Sulfone-Based electrolyte

Sulfone-based solvent are byproducts of petroleum industry. Their most prominent property is high anodic stability, which has the oxidation potential up to 5.5 V [98, 99]. Compared with other candidates as ionic liquid, not only having the low cost, the viscosity of sulfones is also lower. However, almost sulfone-based solvent has high melting temperature and cannot evaluate as single solvent. Sulfones is not compatible with graphite/carbon cathode to form stable SEI layer [99, 100]. Hence, mixture of sulfone-based solvent with additive (FEC) or other solvent is a method to overcome the issues. The mixture of ethyl methane sulfonate (EMS) with 2% of FEC and NaClO_4 was investigated as electrolyte for a SIB system carbon coated $\text{Fe}_3\text{O}_4/\text{NaNi}_{0.25}\text{Fe}_{0.5}\text{Mn}_{0.25}\text{O}_2$, showing a promising rate capability and cycling stability.[101] EMS electrolyte exhibits anodic stability up to 5.6 V vs. Na/Na^+ , higher than 4.5 V obtained for PC electrolyte (NaClO_4 in PC + 2% FEC). EMS electrolyte is more conductive than PC electrolyte (6.0 and 5.7 mS cm^{-1}), respectively.

2.2.4 Nitrile-Based electrolyte

The more highly attention in nitrile-based solvent is paid to dinitrile solvent than monotrile.[102-104]. They show a wide liquid range of temperature as well as a high thermal stability, high thermal flash point and high anodic potential up to 8 V vs Li^+/Li , which is applicable for high voltage batteries various kind of energy storages [15]. It is notable that the electrochemical stability of nitrile-based solvent is higher than most of other solvents, namely, carbonate organic solvent, sulfone-based solvent and even ionic liquids. However, similar to sulfone-based electrolyte, their reductive instability made them poorly compatible with lithium or graphite anodes. This issue can partially overcome by the addition of SEI promoters or additives like EC, fluoroethylene carbonate (FEC) and VC [105], EC etc.

2.2.5. Ionic-liquid (IL)-based solvent system

Ionic liquids, consist of ion and their combination, are a special kind of organic electrolyte. The class of liquid salts that have a low melting point, tend to be liquid at room temperature or lower is called room-temperature ionic liquids (RTILs). In short, RTILS in literature could be written as ionic liquid. ILs offer a viable approach to limiting the flammability and volatility of organic electrolyte. Owing to negligible volatility, low flammability, high thermal, electro-chemical stabilities and wide liquid-temperature range, ILs become a promising candidate for safe and thermal durable electrolytes in the future, hence, has been studied extensively. Unlike other type of solvent, molecular species are absent in IL electrolyte. It results in the exclusion of sponging reactions and the interaction with shuttle ions and cell components. As a result, a stable SEI formation could process with a significant improvement in coulombic efficiency and durability of battery system.

2.2.5.1. General properties of IL

The common cation of ILs are quaternary ammonium, aromatic such as imidazolium, saturated such as pyrrolidinium, piperidinium or hexyltrimethyl phosphonium, and triethylsulfonium etc. The elemental inorganic anions include halide $[\text{F}]^-$, $[\text{Cl}]^-$, $[\text{Br}]^-$,

$[I]^-$, or tetrafluoroborate $[BF_4]^-$, hexafluorophosphate $[PF_6]^-$, amide $[N(CN)_2]^-$ etc. Earlier on, fluoro-complex anion BF_4^- and PF_6^- were extensively used to obtain RTILs. Nevertheless, PF_6^- based IL are unstable against hydrolysis and highly viscous. It makes them to be unfavorable to be applied as electrolyte for energy storage systems. Moreover, BF_4^- based IL is not attractive because of the high price and strict free-water requirement. For organic anion, sulfonylamide based ILs e.g. Bis(trifluoromethylsulfonyl)imide (TFSI $^-$), bis(fluorosulphonyl)imide (FSI $^-$) are widely used because of the facility in preparation and relatively high conductivity.

The cation species in IL could be more diverse by modifying the organic framework or adding functional group, typically imidazolium, piperidinium, pyrrolidinium core structure and ether, ester functional group. By introduction of bulky group or long chain substitution, the viscosity normally increases. Thus, asymmetrical cations with short alkyl chain are more favored for battery application.

Table 2. 7. Some common ionic liquid structures [94]

Cation
$R_1 = \text{Me, Bu}$ $R_2 = \text{Me, H}$ $R_3 = \text{Me, Et, Pr, iPr, Bu}$
imidazolium		pyridinium
$R_1 = \text{Me, Et, Pr, iPr, Bu}$ $R_2 = \text{Me, Et, Pr, iPr, Bu}$
piperidinium		tetralkylammonium

<p style="text-align: center;">$R_1 = \text{Me, Et, Pr, iPr, Bu}$ $R_2 = \text{Me, Et, Pr, iPr, Bu}$</p> <p style="text-align: center;">pyrrolidinium</p>	<p style="text-align: center;">sulfonium</p> <p style="text-align: center;">phosphonium</p>
Anion	
Inorganic: halide $[\text{F}]^-$, $[\text{Cl}]^-$, $[\text{Br}]^-$, $[\text{I}]^-$; $[\text{BF}_4]^-$; $[\text{PF}_6]^-$; $[\text{AsF}_6]^+$; amide $[\text{N}(\text{CN})_2]^-$	
Organic:
<p style="text-align: center;">perfluorobutylsulfonate</p> <p style="text-align: center;">Bis(trifluoromethylsulfonyl)amide</p>	<p style="text-align: center;">triflate</p> <p style="text-align: center;">Trifluoroacetic</p> <p style="text-align: center;">Bis(fluorosulfonyl)amide</p>

Comparing with normal organic electrolyte, ILs, especially quaternary ammonium salts, have been proved to have a good electrochemical performance and can eliminate the dendritic formation. Operating voltage window is an importance property

determined when choosing electrolyte, which directly effects the safety of battery, gets rid of electrolyte decomposition. For example, Appetecchi et. al. [106] had measured electrochemical properties of N-alkyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid, proved that its voltage windows exceed 5.5 V (vs. Li^+/Li). For sodium cell, the combination of Pyr14FSI with NaTFSI salts in electrolyte system could raise up to 4.6 V (vs. Na^+/Na) [80]. However, besides unexpected irreversible reactions with electrodes, there are some remaining issue which hinder wider application of ILs: (1) High cost - compared with normal organic electrolyte due to their expensive synthesis path; (2) High viscosity, low intrinsic conductivity. Below, the intrinsic properties of ILs will be discussed in detail.

2.2.5.2. Conductivity and viscosity

In general, IL electrolyte has higher viscosity and lower ionic conductivity than organic electrolyte owing to the strong Coulombic interaction between anion and cation. The high viscosity could slow down the wetting process of electrolyte into electrodes and separators. The viscosity and conductivity of IL highly depend on the cation and anion structure. The bulky cation would lead to higher viscosity. In the other hand, the ether functional group might reduce the viscosity because of the flexibility of ether group.

The viscosity (η) and the molar conductivity (λ) are inversely proportional via Walden rule or fractional Walden rule:

$$\eta \cdot \lambda = \text{const or } \eta^\alpha \cdot \lambda = \text{const}$$

The Walden rule is applicable for pure ILs and ILs containing alkali metal cation. By adding alkali conducting salts into the IL systems, the viscosity increases, the conductivity decreases as a result of the addition Coulombic interaction. The high viscosity effects directly to diffusion coefficient, hence inversely proportional to the ionic conductivity through Stokes-Einstein and Nernst-Einstein equations, respectively.

$$D = \frac{k_B T}{6\pi r \eta} \quad (1)$$

$$\Lambda = \frac{z_c^2 e_0 F D}{k_B T} = \frac{z_c^2 N_A e_0^2 D}{k_B T} \quad (2)$$

where, D : diffusion coefficient, η : viscosity, r : effective radius (equation 1); K_B : Boltzmann constant, F : Faraday constant, N_A : Avogadro number, Λ : molar conductivity z_i : the valence of the charge carriers, e_0 : elementary charge, (equation 2). Combine (1) and (2), the molar conductivity is calculated by following equation

$$\Lambda = \frac{z_i^2 N_A e_0^2}{6\pi r \eta} \quad (3)$$

$$\text{or } \sigma = \Lambda \frac{n}{V} = \frac{z_i^2 e_0^2}{6\pi r V} \frac{N}{\eta} \quad (4)$$

where, N : the number of charge carrier in volume V . The conductivity is also proportional to the number of charge carrier N . In this equation, the number of charge carriers N are unable to define in various ionic liquid mixture.

Conductivity of ILs are normally in the range of 0.1-18 mS/cm, less than expected when consisting solely of ions. [107, 108]. It is explained by the present of ion-pair or aggregates, which neutralized some neutral precursors. The highest conductivity recorded for IL is 82 mS/cm at 170°C, belonging to allyldimethylammonium TfO [109]. ILs has [EtMeIm⁺] cation have conductivity at lever of 10 mS cm⁻¹. Meanwhile conductivities of RTILs based on pyrrolidinium or piperidinium cation are lower, at the level of 1–2 mS cm⁻¹. The conductivity of IL is much lower than the conductivity of aqueous electrolyte solutions, which is almost at a lever of around 500–700 mS/cm [110] as well as nonaqueous electrolyte at around 60 mS/cm. While for normal organic electrolyte, the highest known conductivity is at level of 3.39 cP for triglyme, the typical level of viscosity for ionic liquid is 30-50 cP.

In order to increase the conductivity of electrolyte, it is normal to increase the salt concentration inside. However, for ILs, the resulting complex ion system [Li⁺]_m[A⁺]_n[X⁻]_{m+n} when salt [Li⁺][X⁻] is diluted in [A⁺][X⁻] ionic liquid, for example with LIBs, would increase the viscosity and then reduce the conductivity [111]. The formation of strong ion-ion interaction in complex environment would lower mobility of charge carrier i.e. Na⁺ or Li⁺ [93].

Figure 2. 4. Isothermal conductivity and viscosity of $\text{Pyr}_{12}\text{O}_1\text{FTFSI}_{1-x}\text{LiFTFSI}_x$ [112]

Proved for above statement, fig. 4 represents the relationship between viscosity and conductivity with the variation of salt concentration in system electrolyte composed of Li and N-methoxyethyl-N-methylpyrrolidinium ($\text{Pyr}_{12}\text{O}_1$) cations and the (fluorosulfonyl) (trifluoromethanesulfonyl) imide (FTFSI) anion. The concentration of salts in ILs system has to be compromised to obtain the acceptable levels of conductivity and viscosity. Lower solute concentration could not be useful for the battery in high rate performance.

Temperature has a significant effect to the viscosity, conductivity and the diffusion of the ILs. The relations are described by below equation

$$D = A \exp\left(\frac{-B}{T - T_0}\right)$$

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right)$$

2.2.5.3. Transport number

Na ion transport is controlled by Na^+ conductivity by the equation: $\sigma_{\text{Na}^+} = \sigma \cdot t_{\text{Na}^+}$ where t_{Na^+} is transport number of Na^+ .

$$t_i = \frac{|z_i|c_i\mu_i}{\sum_i |z_i|c_i\mu_i} = \frac{Q_i}{\sum_i Q_i} \text{ and } \sum_i t_i = 1$$

Where μ_i is the ionic mobility, Q_i represents the charge transport by charge species i . In practically, the transport number is determined by the ratio of diffusion coefficients. However, it is only the apparent value since ILs are highly concentration systems, not infinitely diluted. It is usually derived by the initial and final states of Na symmetrical cell during polarization. Transport number t_{Na^+} values for several Na IL electrolytes

have been reported. The transport number tends to increase with the increasing of Na concentration or increasing of the temperature. The relations are described in **Figure 2.3**.

Figure 2. 5. The relations of viscosity (a), ionic conductivity (b) and Na⁺ ion transport number on Na salt concentration for IL electrolyte used in SIBs.[113] Published by The Royal Society of Chemistry.

2.2.5.4. Thermal stability

One of the main reasons for ILs becoming a promising candidate for safer electrolyte is their high thermal stability. In general, ILs are better than typical organic solvent in term of thermal stability. The main difference between molecular solvent and ILs according to Nakagawa et al. [114], when comparing LiBF₄ in *g*-butyrolactone (GBL)/EC electrolyte and methylimidazolium tetrafluoroborate (EMIBF₄) ionic liquid, is the lack of the solvent evaporation at high temperatures. The thermal decomposition of conventional electrolyte was seen from 90°C while for EMIBF₄ thermal stability measured by differential thermal analysis is around 300°C. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) are usually employed to determine the thermal decomposition temperature of ILs. It should be noted that ILs are less stable in air condition because of the presence of O₂ and H₂O facilitating the decomposition process. Hence, when using TGA method for ILs decomposition determination, the cell material, atmosphere and impurity need to be controlled. The results are highly controlled by the testing conditions.

The systematic studies on thermal stability under constant conditions are required to reveal the effect of chemical structure. Among, anion structure has major contribution to the thermal stability. By modifying the anion and keep the cation, the thermal

stability increases in the below order $[\text{OAc}]^- < [\text{Cl}]^- < [\text{Br}]^- < [\text{I}]^- < [\text{NO}_3]^- < [\text{HSO}_4]^- < [\text{Ts}]^- < [\text{BF}_4]^- < [\text{Tf}_2\text{N}]^- < [\text{TfO}]^- < [\text{PF}_6]^- < [\text{ClO}_4]^-$ (for imidazolium based ILs); $[\text{H}_2\text{PO}_4]^- < [\text{Br}]^- < [\text{DCA}]^- < [\text{NO}_3]^- < [\text{BF}_4]^- < [\text{PF}_6]^- < [\text{HSO}_4]^- = [\text{TfO}]^- < [\text{Tf}_2\text{N}]^-$. The cation core structure also contributes to the thermal property of ILs. Pyrrolidinium-based is more stable than imidazolium-based, followed by pyridinium-based and tetraalkylammonium-based ILs.

IL electrolytes containing Na conducting salts has lower decomposition temperature than the neat ILs.[56, 115] For example, when adding 1 M of NaClO_4 , NaBP_4 , NaTFSI , $\text{Na}[\text{N}(\text{CN})_2]$ into $\text{Pyr}_{1,4}\text{TFSI}$ ($\text{C}_1\text{C}_4\text{Pyrr}$), the decomposition temperature decrease from 400°C to 360°C . In the case of NaPF_6 , the onset temperature is much lower, at around 100°C . [56, 115]

The onset thermal runaway of electrolyte in the presence of electrode materials is more practical in battery application. At fully charged state of a battery, the electrodes are highly reductive/oxidative. They can cause thermal runaway under heating condition with the presence of electrolyte. However, there is a lack of studies that cover the thermal stability of whole Na-IL battery systems. IL electrolytes has wider range of operation temperature than organic electrolyte. Several reports demonstrate the performance at low temperature or room temperature. [116, 117] More importantly, unlike the conventional organic electrolyte, IL-cells could operate at elevated temperature and exhibit better performance than room temperature, exploiting the generated heat from systems or environment. [116, 118, 119]

2.2.5.5. Electrochemical stability

Application of electrolyte in electrochemical devices is governed by electrochemical reduction of cation and oxidation of anion, which set anodic and cathodic limits, respectively. Electrochemical window refers to the potential range from reduction to oxidation limits or from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the electrolyte molecular. The most common electrolyte windows are about 4.5V vs. Na/Na^+ for organic solvent. For IL electrolytes, the anodic limit could be above 5.0 vs. Na/Na^+ , which is appropriate for high energy batteries. The electrochemical stability windows of IL electrolytes are

controlled by structure of ILs combined with counter ions. BF_4^- and PF_6^- anion provide more stable electrochemical stability than TfO^- or TFSA^- anion. The stability windows of ILs had been aggregated by Greaves et al. [120] The available data illustrates a trend for electrochemical window and the anion, which follows the trend of acid. Meanwhile, when observing affect the cations, the electrochemical windows would decrease with the presence of electron-withdrawing group on the cation. In this thesis, more attempt would be made to investigate the contribution of ILs structure to ESW.

To determine the ESW of electrolyte, techniques applied are normally cyclic or linear sweep voltammetry in 2 or 3 -electrode setup. However, the stability limits comparison is sometime not reasonable because the voltammetry curves are tested with different working electrodes (GC, Pt, Au, W) and different references (e.g. Ag/Ag^+ , ferrocene, I^{3-}/I^-), which makes significant different in the value. [121] Moreover, in practical testing in LIBs or SIBs, coin cells containing Li or Na metal counter electrode are normally used. The possible large polarization on the Na/Li metal counter could derivate the anodic limit. It is explained by the formation of the SEI layers on the counter electrode during stripping/plating process. The natural of SEI layers depends on the natural of electrolyte components. Hence, it is more meaningful to investigate the ESW in the investigated systems. However, in half-cell studies, the large polarization of Na metal entangles the accuracy of target electrode evaluation.

The compatibility of Na metal with ILs should be considered in SIB system employing IL electrolyte. Na could chemically react with IL, such as $[\text{C}_2\text{C}_1\text{im}][\text{TFSA}]$ and the color transformation was observed. Na stripping/plating test could provide more details about Na metal behavior during the electrochemical process. The impact of Na salt concentration or water content on Na stripping plating had been studied. At low concentration of Na salt in $\text{C}_1\text{C}_3\text{Pyrr}$ (5% mol), higher polarization was observed in comparison with 25mol%. Interestingly, ~500ppm water in IL electrolyte has beneficial impact on lowering the interfacial resistance and the formation of ideal SEI layers. In the other study, the electrolyte having 2000 ppm water in $\text{NaFSA}-\text{C}_3\text{C}_1\text{PyrrFSA}$ has lower interfacial resistance than IL electrolyte containing 20 ppm of water.

The addition of residue water has adversely impact to ESW of IL electrolytes. The hydrolysis reaction could occur and initiate the decomposition process. Or in the other words, the presence of water might lower the kinetic of decomposition reaction. This phenomena had been detected in $[N_{3111}][TFSA]$ IL when increase the water content to 273 ppm in Pt electrode systems.

It was founded that $TFSA^-$ or FSA^- anion corrode Al current collector in organic solutions such as 1M NaTFSA-PC solution. However, the corrosion is inconspicuous in IL-based electrolyte, indicating a stable passivation film formed on Al current collectors.

Moreover, ionic liquid also can create an effective SEI layer in the electrodes during cycling. These SEI layer contribute for the excellent stability of the battery. For example, the formation of SEI layer on Si-Cu film anode in 1M lithium bis (trifluoromethylsulfonyl)imide (LiTFSI) / 1-methyl-1-propylpyrrolidinium bis(trifluoro-methylsulfonyl) imide (MPP-TFSI) was investigated [122]. The SEI layer leads to 98% capacity retention over 200 cycles. In sodium ion battery, layer cathode material $Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O_2$ when using 10% mole sodium bis(trifluoromethane-sulfonyl)imide (NaTFSI) in N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide ($Pyr_{1,4}$ FSI) could retained 80% of discharge capacity after 100 cycles [80].

2.2.5.6. Limitation of IL electrolytes

To handle IL electrolytes, there are strict requirements on IL pretreatment. The priority is controlling the water content. For hydrophobic ILs, water is removed by evacuation at elevated temperature. For hydrophilic ILs, molecular sieves could remove water effectively. However, it trades off by contamination. Purging dry gas through ILs is alternative approach for water removal.

High viscosity of IL electrolyte, especially at low temperature creates problem on impregnation into separator or porous materials. Soaking under vacuum at elevated

temperature is sometimes suggested to obtain the true performance of IL electrolytes and improve the performance.

The main drawback of IL in extensive usage is their high cost compared to commercial organic electrolytes. Lack of scale-up studies and mass synthesizes challenges industrial application. To apply in battery, high purity is required, which increases the cost further at industrial level. Compared with types of ILs, the most affordable are alkylammonium and alkylphosphonium, rather than imidazolium. Without costly fluorination requirements, FSA salts is cheaper than TFSA salts, which offers potentials in mass applications near future.

2.2.6. Ionic liquid in sodium ion battery

As mentioned previously, ILs today is an excellent choice for electrolyte in both sodium and lithium ion batteries. ILs has achieved initial success as electrolyte that outperform normal organic electrolyte, including improved cycling stability, high rate capability and electrochemical performance at elevated temperature. In this part, the performance of IL in different Na electrode materials are reviewed.

2.2.6.1. Cathode materials performance

Polyanionic compound

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ symmetrical cells with $\text{NaBF}_4\text{-C}_2\text{C}_1\text{imBF}_4$ electrolyte was the first studies in SIBs using IL electrolytes. The discharge capacity is lower than organic electrolyte but could be improved at 80°C . High viscosity of electrolyte and low conductivity of material at low temperature were reasons for the poor performance. When improving electroconductivity of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ by carbon nanofiber, using $\text{NaFSA-C}_2\text{C}_1\text{imFSA}$ the cell archives a good rate capability of 48 mAh g^{-1} at 100°C ($\sim 11.7\text{ A g}^{-1}$). Owing to high stability of materials, other IL electrolytes were investigated in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, such as $0.3\text{M NaTFSA-C}_4\text{HpyrrTFSA}$, [123] or $0.8\text{mol/kg NaFSA-C}_3\text{C}_1\text{pyrrFSA-PVdF-co-HFP gel electrolyte}$. [124]

$\text{Pyr}_{1,4}\text{TFSI}$ was studies as based IL electrolytes in $\text{NaFePO}_4/\text{Na}$ cells by Wongittharom et al. [40, 115] NaTFSI-IL with a salt concentration of 0.5M exhibited the best capacity.

The capacity could increase by increasing the temperature, suggesting the effect of conductivity and enhancement of Na^+ diffusion. Maricite NaFePO_4 half -cell in $\text{NaFSA-C}_2\text{C}_1\text{imFSA}$ electrolyte demonstrated a significant improvement in capacity from 23 mAh g^{-1} at 25°C to 107 mAh g^{-1} at 90°C . [125] The same electrolyte was applied in $\text{Na}_2\text{FeP}_2\text{O}_7$ and $\text{Na}_{1.56}\text{Fe}_{1.22}\text{P}_2\text{O}_7$ compounds. Although, a good cycling performance was obtained at high temperature, at low temperature the capacity was restricted. The electrochemical capacity of vandium-based phosphate NaVOPO_4 was investigated in 20 mol% $\text{NaFSA-C}_3\text{C}_1\text{PyrFSA}$, the reversible capacity was 60 and 101 mAh g^{-1} at 25°C and 90°C

Layer transition metal oxide

The first effort is studying the electrochemical performance of NaCrO_2 in inorganic ionic liquid NaFSA-KFSA . The electrochemical window is up to 5.2 V. At 80°C , the capacity retention obtained at 89% after 100 cycles. [126] At 90°C , the capacity retention was 98.5%. The system exhibits a discharge capacity of 63 mAh g^{-1} at a high current rate of 2000 mA g^{-1} . [127] Similarly, NaTFSA-CsTFSA , $\text{NaFSA-C}_3\text{C}_1\text{PyrFSA}$ was used as electrolyte in NaCrO_2 half cells and NaCrO_2/HC full cell system. In general, the discharge capacity improved at high temperature.

$\text{Na}_{0.44}\text{MnO}_2$ was investigated in various $\text{Pyr}_{1,4}\text{TFSI}$ based-electrolytes. $\text{NaClO}_4\text{-Pyr}_{1,4}\text{TFSI}$ was standout among IL electrolytes in term of capacity and rate performance. The capacity of cells increased with the increasing of operating temperature. However, at ambient temperature, due to high viscosity, the performance of IL systems was not comparable to organic electrolyte system. [56] Another interesting example is adding pentaglyme to sodium bis(trifluoromethanesulfonyl)amide to create solvate ionic liquid. The mixture using as electrolyte resulted a good cycling stability with $\text{Na}_{0.44}\text{MnO}_2$ electrode, with initial discharge capacity of 100 mAh g^{-1} , retained over 95% after 30 cycles [128].

The electrochemical process in IL electrolyte could be more stable than in organic electrolyte. For example, a system containing 0.45 M NaTFSI in $\text{Pyr}_{14}\text{FSI}$ and $\text{P2-Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ cathode material showed reversible P2-O2 phase transition

above 4.2 V. In addition, IL electrolyte prevented Mn dissolution at low potential. In room temperature, the cell delivered a discharge capacity of 225 mAh g⁻¹ and got 80% capacity retention over 100 cycles while with 0.5M NaPF₆ in PC, the capacity retention was only 40% [80]. Hence, ILs is appropriate electrolyte to improve the performance for sodium manganese-based oxide, even at low temperature. Due to the promising aspects, manganese-based oxide was chosen for further investigation in IL electrolytes in this thesis.

2.2.6.2. Anode materials performance

Carbon material

Currently, HC is the most popular anode material in SIBs. In contrast to cathode material performance where the stability majorly depends on the anode, the stability of cation at low voltage would determine the cycleability of IL-anode cell. In specific, the electrochemical performance of semi-graphitic HC (pyrolyzed from olive pits) in 0.5M NaTFSA-C₄C₁PyrrTFSA – 2% VEC (vinyl ethylene carbonante) outperformed the system in NaTFSA-C₄HPyrrTFSA owed to the instability of C₄HPyrr cation. Commercial HC cells employing 20mol% NaFSA-C₃C₁PyrrFSA exhibited a high capacity of 277 mAh g⁻¹ at 20 mA g⁻¹ at 90°C and 193 mAh g⁻¹ at 20 mA g⁻¹ at 25°C.

Titanium based- compound

Titanium based compounds are widely investigated owing the low cost, stability and non-toxicity. A study on anatase TiO₂ in 10% NaTFSA-C₃C₁PyrrFSA was described. At 25°C, the discharge capacity of TiO₂ at 2C was 47 mAh g⁻¹. When cycling in 20% NaFSA – C₃C₁PyrrFSA electrolyte, C coated TiO₂ form citric acid could retain 79% of initial discharge capacity after 1000 cycles. The best cycleability for negative electrode in ILs was with FeTiO₃/C electrode, with no apparent capacity fading over 2000 cycles at 90°C.

Anode alloy material NaFSA–KFSA IL mixture also tested with Sn-Cu film electrode. A stable capacity of 100–120 mAh g⁻¹ was maintained after for 1000 cycles [129]. Although many studies on anode materials in ILs have been revealed, more investigation into SEI layer should be performed to give insight into IL performances.

2.2.6.3. Benefit of IL electrolyte in SIBs

In applying IL as electrolytes, the flexibility in operating condition such as temperature and voltage window is advantageous for comprehensive studies on materials. As mentioned, in electrolyte 20%mol NaFSA-C₂C₁imFSA, Na₃V₂(PO₄)₃ delivered reversible capacities of 100.8, 78.1 and 57.6 mAh g⁻¹ at 25, -10 and -20°C. From -20°C to 90°C, the discharge capacities obtained for NaCrO₂ in the same electrolyte increased from 15 to 118 mAh g⁻¹. The deterioration in capacity in low temperature is explained by the intensification of the internal resistance. Nevertheless, the superiority of IL electrolyte at high temperature over organic electrolyte is attractive for convenient use.

When cycling Na₄Ni₃(PO₄)₂(P₂O₇)/C in NaPF₆-EC/DEC, the voltage limite is 4.9V, the Coulombic efficiency in the first cycle is only about 40%, indicating the electrolyte decomposition. Contrariwise, in 10mol% NaTFSA-C₃C₁PyrrFSA, the voltage window opens to 5.1V. The conversion of de(sodiation) in later case was improved. The results specify the prospect of IL electrolyte to replace organic electrolyte in high-voltage SIB studies.

In topical studies, IL electrolytes have been proved to be beneficial to provide a stable and robust SEI layer, as a result, improve cycling performance over a wide temperature range by a numerous of studies. SEI properties has significant implication on the performance and safety of a battery. Investigating the physical and chemical properties of SEI is essential for understanding the degradation mechanisms in batteries. Various parameters such as salt concentration, temperature or binder in used should be considered. [130-136] However, the intensive studies on SEI layer are problematic due to the limitation on characterization techniques and the sensitivity of SEI layer when exposing to the ambient conditions.

Besides HC was used in full cell configuration for SIBs, fundamental studies on materials are normally initiated from half-cell studies. However, Na electrochemical behavior was not fully explored. One of the factors is the potential polarization during the stripping/plating process, which causing the driftage on the overall potential, especially in IL electrolyte. It could be a source of error in identifying the cause of degradation and the true performance of target electrode in half-cell configurations.

Although ILs has widely applied in SIB half-cell configuration, there are only several reports of IL SIB full-cells. Notably, IL full cells outperform the organic full cells. The results are summarized in table below.

Table 2. 8. Summary of ionic liquid full-cell SIB systems

Cathode	Anode	Electrolyte	Energy/Capacity	Retention	Ref
$\text{Na}_3\text{V}_2(\text{PO}_4)_3$	HC	1M NaFSA-	368 Wh kg^{-1}	75% /100	[137]
		$\text{C}_3\text{C}_1\text{PyrrFSA}$		cycles	
		1M NaClO_4 – EC/PC		61%/100 cycles	
NaCrO_2	HC	20mol% NaFSA-	75 Wh kg^{-1} (Prismatic cell)	87%/500	[138]
		$\text{C}_3\text{C}_1\text{PyrrFSA}$		cycles	
$\text{Na}_{0.44}\text{MnO}_2$	HC	1M NaFSA-	107 mAh g^{-1} (30 mA g^{-1})	97%/200	[139]
		$\text{C}_3\text{C}_1\text{PyrrFSA}$		cycles	
		1M NaClO_4 EC/DEC	117 mAh g^{-1} (30 mA g^{-1})	88%/200 cycles	

2.3. Summary

In energy storage systems, sodium ion batteries have become a prospective alternative for LIBs owing to the high natural abundance, low toxicity, cost effectiveness and the similarity in working principles with LIBs. Among cathode materials for SIBs, layered oxides NaMO_2 are favorable candidates due to their stable structure, high discharge capacities and large operating voltages. [3, 5, 28, 140, 141] P2- sodium manganese oxides with other transition metals doping (e.g. Co, Ni, Fe, etc.) received more attention in studies for SIBs with the aim to low-cost and efficient materials.[142]

According to literature review, normal NaMnO_2 and its modifications did not provide valuable cyclability in normal organic based electrolyte. Jahn-Teller distortion, Mn dissolution and phase transformation are the main reasons for the capacity degradation of manganese oxide materials. Hollow sphere $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ has synergistic effects suppressing Jahn-Teller distortion and Na ion disordering. The hollow sphere morphology helps to reduce the structure stress by suffering the volume expansion. Inspired by the advantages, hollow sphere $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ was chosen as the target

materials in this thesis. Electrolyte modification is suggested to improve the overall performance of manganese-based materials.

Besides electrodes, electrolyte also have important contribution to the safety, the cycling performance of batteries. Organic electrolytes are widely used in SIB studies, containing NaClO₄ or NaPF₆ in carbonate organic solvent such as EC, PC or DEC. The organic electrolytes offer a good range of conductivity, low resistance SEI layers, which are appropriate for materials to extract maximum capacity. However, organic electrolytes pose a serious safety issue to the commercial application due to high volatility and flammability.

Targeting to a safe and stable energy storage system, new generations of electrolyte should be studied. Ionic liquids become a promising candidate for safe and thermal durable electrolytes in the future. The first advantages of ILs are non-volatility and non-flammability. They are thermally stable in comparison to the conventional organic electrolyte and able to operate at elevated temperature. In addition, a substantial advantage of ILs is the formation of desirable SEI layer, which is beneficial for the cycling stability of a battery. ILs has wider electrochemical stability windows than the organic electrolytes. Applying ILs in battery studies could increase the cell working voltages and help to exploit the new electrochemical performance of materials at higher potential. However, there still exist some disadvantages of ILs, including, high viscosity, low conductivity and high cost. More explicit studies on IL could give more insight into the improvement of viscosity and conductivity. The effect of ILs structure on individual properties need to be investigated. Furthermore, SEI compositions and Na interaction with ILs electrolyte should be considered in detail to explain the performance of IL-based batteries and contribute to the mass application of ILs as next generation of electrolyte for LIBs and SIBs.

2.4. References

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Chapter 3

Experimental Methodology

In this chapter, the experimental methodology, principles and analysis of characterization methods, electrochemical measurement employed in the thesis with rationale are briefly portrayed. First, for preparation the SIBs setup, synthesis procedures of based electrode materials, hollow sphere Na_xMnO_2 class with Co and Ni doping, nanowire $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ and ionic liquids are presented. Basic physical characterization techniques related to materials and electrode surfaces are X-ray diffraction (XRD), Scanning electron microscope (SEM), Inductively coupled plasma Optical emission spectroscopy (ICP-OES) and X-ray spectroscopy.

To assess the critical properties of electrolytes, conductivity, viscosity measurement, thermal stability analysis techniques are elaborated. Finally, the performance of ionic liquid electrolytes was investigated in coin cell setup. The coin-cell preparation and assembly are introduced. The principles of electrochemical measurements techniques such as cyclic/linear sweep voltammetry (CV/LSV), Galvanostatic charge/discharge cycling (GCD), electrochemical impedance spectroscopy (ESI) with technical terms are presented

3.1. Rationale for selection of Methods/Materials

In order to study on IL electrolytes for SIBs consistently, a base SIB system needs to be drawn for electrochemical investigation. Among cathode materials, P2-type materials have received substantial interest and been extensively applied in SIBs because of the stable structure and high capacity and rate capability. [1-5] P2- sodium manganese oxides with other transition metals doping (e.g. Co, Ni, Fe, etc.) received more attention in studies for SIBs with the aim to low-cost and efficient materials.[6]Exploration on electrolytes which are applicable and beneficial for P2-oxide material is essential for battery research. Hollow spherical P2- $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ (NCO) had showed the improvement for metal oxides cathodes by two strategies: Co doping and hollow-spherical morphology. However, capacity fading is still observed after long-term cycling. Altering electrolyte could boost the electrochemical stability further. It is chosen as basement cathode material in this thesis. To examine the electrochemical performance of ILs electrolyte in high voltage, the working potential range of the cathode material needs to be improved when maintaining the morphology of the base material. Ni was added into the materials by 2 methods. In the first method, Ni compound was co-precipitated together with Mn and Co compounds in the initial stage, called NaNMC. However, the significant difference in the solubility constants made the control of Ni content in final product complicated and inefficient. Hence, Ni compound was added after the formation of Mn/Co oxides, together with NaOH. The details were described in section 3.1.3 below.

Beside P2-manganese oxide, vanadium oxides show prospects in SIBs, including, significant capacity and stability at high current rates. Notably, owing to the different oxidation states of vanadium, vanadium oxides materials could be both applied as cathode or anode. To the best of author's knowledge, in SIBs studies, the system including vanadium oxides material and IL electrolyte has not been reported. Extend the investigation of IL electrolytes in vanadium oxides is valuable. In this thesis, nanowire $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \cdot 0.6 \text{H}_2\text{O}$ (NVO) was first chosen to be exploited in IL electrolyte-based half-cell. After the compatibility of material and the IL electrolyte had been proved, the electrochemical performance of full cell NCO/NVO using IL electrolyte was examined and compared to organic electrolyte-based variation. The materials' crystalline phases and morphology were characterized by X-ray diffraction

(XRD) and Scanning electron microscopy (SEM). The materials composition was determined by Inductively coupled plasma optical emission spectroscopy (ICP-OES)

First, the effect of sodium conducting salts, namely, NaClO₄, NaTFSI and NaFSI, in Pyr_{1,4}TFSI ionic liquid electrolytes in SIBs was first examined to find the most suitable salt with proper concentration for IL electrolytes and apply in the later stage of the thesis. Secondly, to implement a systematic and comparable study the effect of the nature of IL electrolyte for SIBs, including, cationic core structure, anion, presence of functional groups, on substantial parameters like thermal stability, viscosity, conductivity and ESW, a broad library of various ILs was synthesized and characterized. The focus of this study was laid on ammonium-based ILs which has different cation core structures, namely, Pyrrolidinium (Pyr), Piperidinium (Pip), Ammonium (NR₄) and Imidazolium (Im), in collaboration with TFSI/FSI anion. In addition, the introduction of different functional groups, the chemical and physical properties can be tuned almost endlessly to suit the application at hand. This section is a part of joint project, supported by the International Center for Energy Research (ICER). The IL synthesis part is credited to Dr. Pauline Fischer, Technische Universität München. A series of IL electrolytes for SIBs were prepared by adding sodium conducting salts into the pure ILs.

The important parameters, such as, viscosity, conductivity, thermal stability and ESWs of neat ILs and IL electrolytes were measured. Especially, the compatibility of Na metal with IL electrolytes, which strongly affect to the long-term performance of Na half-cells, was studied by Na stripping/plating tests in Na/Na symmetrical systems. IL electrolytes after preparation were applied in various SIBs systems, particularly, half-cells of NCO, NVO, NaNMC or full cells NCO/NVO. To understand the behaviors of different electrolytes, the electrochemical performances of the cells at various conditions were explored by basic electrochemical techniques, such as linear sweep/cyclic voltammetry (LSV/CV), galvanostatic charge discharge (GCD). Electrochemical impedance spectroscopy (EIS) was used to measure the impedance of the systems. From that, the evolution of SEI/CEI layer in the cells could be observed. After cycling, X-ray photoelectron spectroscopy (XPS) was used to study the composition of the surface layer on the electrodes.

To prove the thermal safety of IL electrolyte, thermal analysis of IL based and organic based NCO/NVO full cells was conducted by Differential scanning calorimetry (DSC) and Accelerating rate calorimetry (ARC) techniques. In addition, the performance of organic electrolyte and IL electrolyte -based cells were compared at elevated temperature.

3.1. Cathode material synthesis

3.1.1. Hollow spherical $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$

Spherical **P2- $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_{2+z}$ (NCO)** was synthesized following an already reported protocol.[7] Briefly, solutions containing 100 mmols of NH_4HCO_3 (99%, Alfa-Aesar) and 10 mmols of Co/MnSO_4 (1:9 mol ratio, Alfa-Aesar) were prepared by dissolving the required amounts of precursors separately in 700 ml of DI water. About 70 ml of pure ethanol (99.9%, Merck) was added to the solution containing sulfates. Subsequently, the NH_4HCO_3 solution was added to the solution of sulfates in water-ethanol mixture and stirred for 3 hours to obtain the co-precipitated $(\text{Mn,Co})\text{CO}_3$ which was filtered and washed repeatedly 3 times using ethanol and water and dried at 80 °C overnight. The dried carbonate precursor was calcined at 400 °C for 5h to form the oxide compound. Finally, the required amount of the oxide precursor was dispersed in a water - ethanol mixture together with NaOH (98%, Alfa-Aesar) and dried to give precursor. This precursor was subjected to calcination in 3 steps in air: first at 320 °C for 3h (heating rate of 5K/min) followed by 800 °C for 4h (heating rate of 5K/min) and finally at 610 °C for 9h (heating rate of 5K/min) before quenching to form the final product. The synthesized powder was stored in an argon-filled glovebox to minimize exposure to air.

3.1.2. $\text{Na}_{2.55}\text{V}_6\text{O}_{16}\cdot 0.6 \text{H}_2\text{O}$

$\text{Na}_{2.55}\text{V}_6\text{O}_{16}\cdot 0.6 \text{H}_2\text{O}$ was synthesized following a slightly modified procedure from Hartung *et al.*[8] 20 ml of a 0.5 M solution of vanadium pentoxide (Alfa Aesar 99.2%) were mixed with 20 ml of a 0.5 M solution of NaOH (Alfa Aesar 98%) and heated under reflux overnight. The obtained clear brownish solution was subsequently transferred to a Teflon lined stainless steel autoclave for heating at 180 °C for 48 h.

After cooling, the precipitate was filtered, washed with deionized water and dried at 80 °C overnight. The dry powder was calcined at 400 °C for 2 h in air using a box furnace.

3.1.3. Hollow spherical $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ with Ni doping

Inspired by hollow spherical $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$, Ni ion was added into the structure. The intention is increasing the average working voltage of the material and examination the behavior of IL electrolyte in higher voltage range. Two methods of introducing Ni ion into the structure were presented.

Figure 3. 1. Synthesis hollow sphere $\text{Na}_{0.6}\text{Mn}_x\text{Co}_y\text{Ni}_z\text{O}_2$ by coprecipitation method

3.1.3.1. Synthesis $\text{Na}_{0.64}\text{Mn}_{0.83}\text{Ni}_{0.06}\text{Co}_{0.1}\text{O}_2$ by co-precipitation method

Spherical $\text{Na}_{0.64}\text{Mn}_{0.83}\text{Ni}_{0.06}\text{Co}_{0.1}\text{O}_2$ was synthesized by similar procedure which already reported from our group.[9, 10] NH_4HCO_3 (Alfa Aesar, 99%) was first dissolved in DI water. After adding a small amount of absolute ethanol (10% volume of NH_4HCO_3 solution), a solution containing mixture of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 98%) and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 98%) with the following ratio 7:1:2 was added dropwise. To form $(\text{Mn}, \text{Ni}, \text{Co})\text{CO}_3$, the solution was subsequently stirred for 3h at ambient temperature. The co-precipitate was filtered, washed repeatedly by DI water and ethanol and dried at 80°C overnight. Afterward, the dried precursor was annealed in air at 400°C for 5h to form spherical oxide compound. Then, it was dispersed in a solution of NaOH (Alfa Aesar, 98%) in ethanol and DI water (ratio 1:1). The water and ethanol was slowly removed by evaporation. The residue was first calcined at 320°C for 3 hours, followed by 800°C for 4 hours and an additional step at 610°C for 9 hours. The final product was quenched to room temperature.

The material composition was characterized by ICP-OES method, as $\text{Na}_{0.64}\text{Mn}_{0.83}\text{Ni}_{0.06}\text{Co}_{0.1}\text{O}_2$, which is different with the initial ratio of Mn:Ni:Co (7:2:1). The difference in the composition of initial precursors and final compound is explained by the difference in the solubility constant of MnCO_3 , CoCO_3 and NiCO_3 ($K_{sp,\text{MnCO}_3} = 1.8 \times 10^{-11}$, $K_{sp,\text{CoCO}_3} = 1.4 \times 10^{-13}$, $K_{sp,\text{NiCO}_3} = 6.6 \times 10^{-9}$).

3.1.3.2. Synthesis $\text{Na}_{0.66}\text{Mn}_x\text{Ni}_y\text{Co}_z\text{O}_2$ by adding NiNO_3

Due to the high solubility, precipitation of NiCO_3 in the initial step is not efficient. Controlling the Ni content by co-precipitation method is impracticable. To increase efficiently Ni content in the final material, NiNO_3 was mixed with $(\text{Mn,Co})\text{O}_2$ in the later stage before calcination steps. The detail procedure was described as follows.

Figure 3. 2. Synthesis $\text{Na}_{0.6}\text{Mn}_x\text{Co}_y\text{Ni}_z\text{O}_2$ by adding NiNO_3 before calcination step

First, NH_4HCO_3 (Alfa Aesar, 99%) was first dissolved in DI water. After adding a small amount of absolute ethanol (10% volume of NH_4HCO_3 solution), a solution containing mixture of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 98%) with the following ratio 9:1 was added dropwise. The solution was subsequently stirred for 3h at ambient temperature to form the $(\text{Mn,Co})\text{CO}_3$ precipitate. The co-precipitate was filtered, washed repeatedly by DI water and ethanol and dried at 80°C overnight. Afterward, the dried precursor was annealed in air at 400°C for 5h to form spherical oxide compound. The mixture of spherical oxide compound and NiNO_3 (Sigma Aldrich, 99%) was dispersed in a solution of NaOH (Alfa Aesar, 98%) in ethanol and DI water (ratio 1:1). The water and ethanol were slowly removed by evaporation. The

residue was first calcined at 320°C for 3 hours, followed by 800°C for 4 hours and an additional step at 610°C for 9 hours. The final product was quenched to room temperature.

Table 3. 1. The proportion of (Mn,Co)O₂ and NiNO₃ initially and the ICP-OES results of final products

Sample IDs	Ratio of precursors		Initial ratio of metal ions			ICP-OES results of final products			
	(MnCo)O ₂	NiNO ₃	Mn	Co	Ni	Na	Mn	Co	Ni
S0	1	0	0.9	0.1	0	0.64	0.9	0.1	0
NO3-S3	5	1	0.76	0.08	0.17	0.7	0.8	0.08	0.11
NO3-S5	3	1	0.68	0.07	0.25	0.68	0.67	0.09	0.24
NO3-S6	2	1	0.61	0.06	0.33	0.72	0.65	0.07	0.28
NO3-S9	1.5	1	0.55	0.05	0.4	0.7	0.56	0.07	0.37

3.2. Ionic liquid electrolyte preparation.

3.2.1. Ionic liquid synthesis

Figure 3. 3. The schematic synthetic procedure of IL sythesis

Synthesis of the IL precursor salts

The synthesis of the IL precursor salts is based on quaternization reaction, following the previous report procedure. After purchase or synthesis of the tertiary ammonium precursor (NR₃), the respective functionalized alkylhalide was added dropwise to a solution of the precursor under Ar atmosphere. Then, the mixture was stirred continuously under refluxing condition for 24 to 72h. The nucleophilic substitution

Anion exchange and purification

Subsequently the strongly coordinating anion was replaced by a large and bulky, weakly coordinating anion – either bis(trifluoromethane)sulfonimide (TFSI) or bis(fluorosulfonyl)imide (FSI) – in an anion exchange reaction. In detail, a solution of LiTFSI or LiFSI (with 5% excess) in water was added to a solution of the ammonium halide precursor in water and stirred at room temperature for 24 h. Suspension was formed during the process. Then the aqueous phase was removed, the result products were centrifuged and washed 8 – 10 times with distilled water to remove LiBr and unreacted starting material. Each time, AgNO₃ was added to the washing solution by the end to exclude the halides in the products. The ILs were further purified by refluxing in dichloromethane with activated charcoal for 3 h followed by filtration. To reduce the water content to under 5 ppm the ILs are dried at 70 °C in high vacuum using an MBraun Solvent Purification for two days (first day: 10-3mbar, second day: 10-6 mbar).

Figure 3. 4. Overview of synthesized RTILs with TFSI anion unless indicated differently

3.2.2. Electrolyte preparation

In chapter 4, the effect of sodium conducting salts was examined in Pyr_{1,4}TFSI as IL solvent. A series of IL electrolytes were prepared in an argon-filled glovebox by dissolving 3 types of sodium salts namely NaClO₄ (Sigma-Aldrich, $\geq 98\%$), NaTFSI (Sigma-Aldrich, 98%), NaFSI (Nippon Shokubai) in Pyr_{1,4} TFSI (Iolitec, 99.5%) to yield a concentration of either 1M or 0.5M. The sodium salts were dried at 110°C overnight under vacuum before being transferred to the glovebox for electrolyte preparation. Electrolytes were prepared by dissolving the required amount of salt in the solvents and the solutions were continuously stirred for at least 24h before use. The water contents of IL electrolyte as determined by Karl Fischer titration are below 60 ppm.

The optimal conducting salt is NaFSI with a concentration of 0.5 M. In the following chapters, the IL electrolytes were prepared in by dissolving NaFSI (Solvionic, 97%) in the synthesized ILs or commercial Pyr_{1,4} TFSI to yield a 0.5 M solution.

For comparison with IL electrolyte, the organic electrolyte needs to be specified. First, to optimize, the organic electrolyte was prepared by dissolving either NaClO₄ (Sigma-Aldrich, $\geq 98\%$), NaTFSI (Sigma-Aldrich, 98%) or NaFSI (Nippon Shokubai) in ethylene carbonate/ propylene carbonate to yield a 1M /0.5M solution (1:1 w/w, Sigma-Aldrich). As a result, 1M NaClO₄ in EC/PC organic electrolyte was chosen for comparison.

3.3. Material characterization methods

3.3.1. X-ray diffraction-principles and analysis[11, 12]

Powder x-ray diffraction (XRD) is the most widely used method in material science. It employs the scattering of X-rays, measures the diffraction of X-rays from the atom planes to investigate and quantify the crystalline nature of materials. In detail, XRD is used to determine the crystalline content of materials; identify and quantify the crystalline phases; determine the lattice parameter and to study preferential ordering and orientation of crystallites.

X-rays are electromagnetic radiation with photo energies in the range of 100 eV – 100 keV. The wavelength used for diffraction application is in the short range of Ångstroms (10^{-10} m) or 1 keV - 120 keV of energy. X-rays are generated by x-ray tubes or synchrotron radiation. In an x-ray tube, a focused electron beam was accelerated across a high voltage field, collided with atom in the solid target. As a result, the target radiates a continuous spectrum of X-ray, termed Bremsstrahlung radiation. In case high energy electrons could eject the inner shell electrons, an electron from outer will fill the vacancy, leads to another emission of secondary X-rays. The energy of an x-ray photon is related to the wavelength value, followed by Planck equation $E = hc/\lambda$ (where h is Planck's constant, c is speed of light). For examples, Cu and Mo, as common X-ray sources, emit X-rays with the energy of 8 keV and 14 keV (correspond to 1.54 Å and 0.8 Å, respectively).

When x-ray photons collide with electrons, there could be 2 possible scattering processed: elastic scattering, when the x-ray photons do not lose the energy and inelastic scattering, when the x-rays transfer apart of energy to electrons. The condition for the reinforcement of scattered waves is that the wave scattered by the point in lattice will be in phase throughout crystal, written in Bragg's Law as $n\lambda = 2d \sin\theta$ (when d is the inner plane distance, λ is the wavelength of the x-ray, θ is the scattering angle, and n is the order of the diffraction). At other angles of incidence, the beam will vanish small because of destructive interference.

Figure 3. 5. Geometric relation of a crystal structure with atom points (B, B', B'' and B''') and incidents X-rays (A, A', A'' and A''').

For powder XRD, the material consists of polycrystals with randomly orientation. There are a variety of periodic arrays in the plane of the measurement, corresponding to different scattering peaks. As a result, diffraction pattern is recorded, containing the

unique d spacings in the crystal lattice. The information on the lattice size and unit cell could be deduced from the position of the reflection. The intensity ratio is used to define and locate the exact position and the elements in the structure. The peak shapes give the information on crystallite size and strain, etc. Diffraction pattern is considered as a “fingerprint” for specific structure.

In this thesis, the crystal structures of synthesized materials were analyzed by powder XRD using Bruker Advance D8 diffractometer with Cu $K\alpha$ radiation (40 kV and 40 mA) at 0.015° per step between 2θ from 10° to 80° . The lattice parameters were determined by Rietveld Refinement with Topas software.

3.3.2. Scanning Electron Microscope principles and analysis [13-15]

Electron microscope is a series of the techniques use an electron beam, which has higher energy or lower wavelength than visible light to resolve small samples, which cannot be resolved by visible spectrum. When electrons hit the sample, the resulting signals could give information about the specimens. The microscopy employed in this work is scanning electron microscopy (SEM). Scanning electron microscope is the most routine instrument to get a view of surface structure with high resolution and great depth of field. In a SEM column, electron gun and a series of electromagnetic lenses and apertures are arranged in order. First, electron beam is emitted from a heated filament (e.g. Tungsten) or a field emission tip, which has higher beam brightness. The electrons are accelerated by electric potential in the order of 1-400 kV. The image of the source is projected onto the condenser aperture by a condenser lens. The beam is focused by an objective lens and raster-scanned by scanning coil over the sample. When the spot size of the primary electron beam is minimized, the resolution of the instrument is improved.

Figure 3. 6. Electron - matter interactions

Figure 3. 7. The relative interaction volumes of several important secondary signals generated

When high-energy electrons strike a specimen, the electrons are scattered by interaction with the atoms in the sample. The electrons coming out are collected to produce SEM micrograph. Most of the energy is dispersed as heat. There are 2 main types of scatterings:

- Elastic scattering: The electrons bounce back out of the sample without transferring energy. The result is back scattered electron (BSE). The backscattering probability depends on the average atomic number of the material.
- Inelastic scattering: The trajectory of the electrons is slightly perturbed, the electrons transfer energy to the sample, and emission of radiations will happen. They include secondary electrons (SE), Auger electrons, characteristic X-ray radiation (EDS/XRF), visible light fluorescence, etc.

The interaction zone where electrons scatter under the sample surface are described in figure 3.7. The SEs have an energy level of few electron volts, hence escape with a depth of 5-50 nm from the surface. High energy BSEs can escape from a deeper level,

on the top 40% of interaction zone, about 50-300 nm. In term of the practicality, SEs are used to image the surface to investigate morphological and topographical characteristic, while BSEs are useful for the information of elemental composition contrast.

In this thesis, the particle morphology and the surface of the electrodes were evaluated by field-emission scanning electron microscopy (FESEM) using a JEOL 6340F SEM.

3.3.3. Inductively Coupled Plasma Optical Emission Spectroscopy principles and analysis

Inductively coupled plasma – Optical emission spectroscopy (ICP-OES) is an analysis method using high-frequency inductively couple plasma to quantify the element composition in the samples by an optical spectrometer.

A plasma is a forth state of matter, described as a domain of high energy (5000 – 7000 K), where the ion and electrons coexist in equilibrium state. In an ICP, the argon gas is supplied and passed through a touch coin, where high frequency electric current is applied. The argon gas is ionized, plasma is generated by electromagnetic field in the touch. Solution of sample is introduced into the plasma. The atoms/ions are in excited state. The electrons of atom or ion take up the energy and jump to higher energy level. Upon relaxation of “excited” electron to the ground energy level, energy is emitted as light or photon. The energy and the intensity of the emitted photons are characteristic of elements. By measuring the wavelength and the intensity of emitted lights, the specific elements are quantified. In this project, samples were prepared by dissolving around 3 mg of solid sample into a 50 ml mixture of DI water and aqua regia (~1.5 ml). After preparation, the concentration of the elements in the solution were measured by PerkinElmer® Optima™ 8300.

3.3.4. X-ray photoelectron spectroscopy principles and analysis [16-18]

X-ray photoelectron spectroscopy, also known as Electron spectroscopy for chemical analysis (ESCA), is a typical surface analysis technique which provide quantitative

and chemical state information of the characterized surface. The average depth of analysis surface is ~5 nm.

Conceptually, the atom in the surface has core electron, in which the characteristic binding energy is equal to the ionization energy. When X-ray directs to the sample surface, the energy of photon is absorbed completely by the core electron. When the energy of the photon is large enough, the core electrons would emit out the surface. XPS spectra are attained by exciting a solid surface with a monochromatic or unfilled X-ray (Al $K\alpha$ or Mg $K\alpha$), the kinetic energy E_K and emitted photoelectrons are measured and analyzed. The electron analyzer measures the photoelectrons kinetic energy. The relation between kinetic energy of photoelectron (K_E), binding energy (K_b) of core electron and energy of X-ray photon were followed by Einstein equation

$$h\nu = E_b + E_K + \varphi$$

The binding energy is characteristic information for chemical state of an element, depends on the element, the orbital of the emitted electron and the chemical environment of the atom. The binding energies and intensities (counting numbers) of the photoelectron peaks enable identification and quantification of all surface elements.

Figure 3. 8. The schematic diagram of an XPS instrument

In this project, XPS was used to characterize and analysis the surface layer of working electrodes after cycling. For sample preparation, cycled cells were opened inside an argon-filled glovebox and the electrodes extracted were washed with dimethyl carbonate (DMC) to remove residual salt and electrolyte followed by drying under vacuum to remove the DMC. To avoid exposure of the electrodes to ambient environments, a sealed glass tube was used to transfer the electrodes to the XPS instrument. There are 3 XPS instruments which were used to conduct the measurements in the thesis: Omicron EA 125 energy analyzer in conjunction with an EAC2000-125 control unit and twin anode X-ray source (Al $K\alpha$, $h\nu = 1456.6$ eV; Mg $K\alpha$, $h\nu = 1246.6$ eV) (chapter 4), PHI-5400 equipment (PHI) with an Al $K\alpha$ beam source (250 W) and a position sensitive detector (PSD) (chapter 6) and Kratos AXIS Supra equipment with automated dual anode Al/Ag beam source (chapter 7). The XPS spectra were calibrated using the standard C1s peak at 284.6 eV before being subjected to analysis.

3.4. Electrolyte characterization

3.4.1. Conductivity measurement[19-21]

Conductivity is a measure for the ability of electrolyte solution to conduct electricity. The unit of conductivity normally is S/cm. There are 2 type of measurement: contacting and inductive.

- Contacting conductivity: The sensor consists of 2 metal/graphite electrodes in contact with electrolyte solution. An alternating voltage is applied to the electrodes to produce a current through the solution. The analyzer measures the current, the resistance is calculated by Ohm law ($R = U/I$). The electrical conductance is inverse of resistance. The conductivity is calculated by multiplying the conductance by the cell constant. (Cell constant is the ratio of the know conductivity to the measured conductance)
- Inductive conductivity: The inductive sensor consists of two toroidal drive coil. The voltage is applied to the drive coil, causes an ionic current. The current induces a current in the receive coil. The current in the pickup coil is proportional to the

solution conductivity. It is suitable for measuring high conductivity or corrosive liquid.

In this project, electrochemical conductivities of electrolytes were determined in an argon-filled glovebox using a Mettler Toledo InLab 751 conductivity probe head connected to a Solartron SI1260 frequency response analyzer. The samples were placed in a small test tube inserted into a custom made, temperature-controlled steel block. A full impedance spectrum was recorded with an alternating current voltage of 0.02 V and in a frequency range between 1 Hz and 10 MHz. The Ohmic resistance of the electrolyte was determined based on the real part of the impedance where the imaginary part of the impedance is (close to) 0. The specific conductivity was determined using a cell constant of 1 cm^{-1} calibrated with 0.1 M KCl. For the temperature dependent measurements, conductivities were reported in steps of $5 \pm 0.2\text{ }^{\circ}\text{C}$.

3.4.2. Viscosity measurement [22-25]

Viscosity is described as the resistance of the material toward a shear stress, relating the viscous stress to the rate of deformation. It is noted that dynamic viscosity (or absolute viscosity) is the measurement of the fluid resistance to the flow or the force needed to make the fluid flow at a certain time. The kinematic viscosity refers to the rate of the fluid's moving when a certain force is applied. It is calculated by the ratio of dynamic viscosity to the density. The unit for dynamic viscosity in CGS system is cP (centipoise). 1 cP was defined as the viscosity of distill water at $20\text{ }^{\circ}\text{C}$. The unit of dynamic viscosity η is Pa.s (Pascal-second). $1\text{ cP} = 1\text{ mPa.S}$. The unit of kinematic viscosity in CGS system is cSt (centistokes) or St (stokes), where $1\text{ cSt} = 0.01\text{ St}$. In SI unit, $1\text{ St} = 1\text{ cm}^2/\text{s}$.

There are number types of viscometer such as U-tube viscometer (measuring the time taken for the liquid to pass through the capillary); vibrational viscometer (determining the damping (power, decay time or frequency) of an oscillating electromechanical resonator immersed in a fluid); rotational viscometers (calculating the moment of the

force required to rotate a disk at certain speed, by then the shear rate and share stress are calculated),etc.

The viscosimeter applied in this thesis is a microVISC viscometer (RheoSense) with the measuring cell B-10, powered by VROC[®] technology. The principle of rectangular slit viscosimeter is measuring the pressure drop by a pressure sensor array when the liquid flows through a slit microfluid channel. The pressure of the fluid is measured as a function of location. In comparison with conventional methods, the technology offers advantages as: small volume required, capability to characterize both Newtonian and non-Newtonian fluids, prevention of contamination and evaporation.

3.5. Thermal analysis

Thermal analysis (TA) is a group of analytical methods which investigate the changes in the properties of materials with the changes in temperature. When heating the samples, the material reactions lead to the changes in mass, phase or mechanical etc. With the increasing of the temperature, the vibration and rotation of the atomic bonds increase because of thermal energy obtained. As results, there might some changes in the state as: solid-phase transformation, glass trasition, melting. At a certain temperature, when the bonding become so weak, the samples would decompose.

Table 3. 2. Common thermal analysis techniques

Technique	Abbreviation	Measurement
Thermogravimetry analysis	TGA	Mass change
Differential scanning calorimetry	DSC	Heat flow
Differential thermal analysis	DTA	Temperature different
Accelerating Rate Calorimetry	ARC	Self-heating rate

3.5.1. Differential Scanning Calorimetry [26, 27]

Differential scanning calorimetry (DSC) is a thermal analysis technique that measure the energy changes in a sample as a function of time or temperature when heating, cooling or holding isothermally. It is a powerful technique to detect the transition that occurred in the sample such as melting, crystallization, glass transition corresponding to certain temperatures or calculate the specific heat capacity of each thermal event. The heat flow difference between the sample and a reference is monitored when the temperature of sample and reference are maintained at the same temperature.

In an DSC instrument, there are 2 separate chambers with individual heating element to control the temperature. In a thermal event, the heating element has to change the power to maintain the temperature of the sample similar to the temperature of the reference. Endothermic/exothermic event causes an increase/decrease in the power of the heating element.

Figure 3. 9. High pressure stainless-steel crucible and gold plated

Under chapter 6, DSC was used to detect the thermal events in electrolytes and the mixture of electrolyte and electrode's powder. The test was carried out using a Q10 – TA instrument with a heating rate of 10 K min^{-1} . Because of the presence of liquid in the measurement, high-pressure stainless-steel crucible and gold plate was chosen. The sample crucibles were sealed in the glove box.

3.5.2. Thermogravimetry Analysis[26, 27]

Thermogravimetric analysis (TGA) is an experimental technique, in which the mass of a sample is measured with the change of the temperature. Typically, the sample is heated in a controlled temperature program with a constant heating rate (dynamic measurement) or holding at a constant measurement. In the measurement, the sample is put inside a specific atmosphere (corrosive, oxidizing, reducing or inert).

TGA curves are plotted based on the mass change (in percentage) vs. the temperature/time. The mass changes occur at the point when the samples lose material or in thermal events. Some effects could possibly result in TGA curve mentioned as follow.

- Oxidation (decomposition) reaction with air/oxygen
- Evaporation of volatile constituents or losing water of crystallization
- Desorption/adsorption of gases/moisture
- Ferromagnetic material
- Thermal decomposition

TGA was applied to determine the decomposition temperature of pure ILs under chapter 5. The measurements were conducted on a Q5000 TGA (TA) instruments, under Argon. The heating rate is 10K min^{-1} and the offset temperature is 600°C .

3.5.3. Accelerating Rate Calorimetry[28-34]

Accelerating Rate Calorimetry is a useful technique to characterize thermal runaway reactions in chemical industry in order to develop safe working conditions and has already successfully been applied to determine safe working conditions for LIBs.[28-30] Critical parameters that are determined from an ARC-test include -i) the self-heating rate ii) the onset temperature and iii) adiabatic heat increase. Adiabatic condition is the case that no heat exchange occurs between the measuring system and its surroundings. As such, the system controls the temperature of surrounding to be equal to the temperature of the measuring chamber. In Accelerating Rate Calorimetry, temperature of the measuring chamber is increased in a small temperature step. In each step, exothermal effects (self-heat) of the samples will be sought. If presents, the temperature of the sample chamber will be tracked. Otherwise, the heating procedure will continue.

Figure 3. 10. Scheme design of the system with adiabatic scanning. Reproduced with permission. Copyright 2014 John Wiley and Sons [35]

The self-heating rate gives rise to the tendency of the sample to attain conditions of self-heating and is an indication of the speed with which thermal runaway reactions proceed. A higher heating rate indicates a more dangerous or unstable system. Similarly, a lower onset temperature means lower stability to temperature variations.

Under chapter 6, ARC was employed to investigate and compare the thermal runaway of IL electrolyte and organic electrolyte coin cells. A standard heat-wait-search procedure was applied to observe the behavior of the cells. The initial setting temperature was 100°C. A 20 min waiting-period was applied to the system at each measuring point to reach thermal equilibrium. The sample heating rate was 3 K min⁻¹. When self-heating was detected, exothermic reactions were tracked by a calorimeter under adiabatic conditions. The sensitivity of the SHR detection was 0.05 K min⁻¹.

3.6. Electrochemical measurement

3.6.1. Electrode preparation and coin-cell assembly

In order to study the behavior or electrochemical performance of electrolytes/materials, 3-electrode or 2-electrode battery systems could be used. The term “electrochemical

potential” or “voltage” is referred to the potential different between working electrode (WE) and reference electrode. Reference electrode (RE) should have an identify and stable potential. Counter electrode (CE) is used to balance the current passing to the reference electrode. Three-electrode set up was used to determine electrolyte stability windows.

In this thesis, most of the electrochemical tests were performed in 2-electrode coin cell set up. The coin cell set up is described in figure 3.11, including: bottom casing, cathode (working electrode), separator, anode (reference/counter electrode – normally Na metal), flat and wavy spacers, top casing. It should be noted that, different with 3-electrode set up, in 2-electrode system, the counter electrode is also the reference electrode. The cell potential is measured between WE and RE directly without the contribution of counter current. As a result, the overpotential could happen when the current flow through the reference electrode. In IL electrolyte, the overpotential effect is more apparent than in organic electrolyte.

For systematic comparison, the electrode preparation procedure, such as slurry preparation, coating, drying was kept constant. The electrode slurry contains active material (80 wt%), activated carbon - acetylene black (20 wt%) for better conductivity and binder - Polyvinylidene difluoride (PvDF, 20 wt%) as binder. The mixture was dispersed in N-methylpyrrolidone NMP solvent to form the homogenous slurry. After at least 8h of rigorous mixing, the slurry was pasted onto battery-grade Al foil (for NMO class materials) or Cu foil (for NVO or hard carbon) using a doctor blade with a gap of 100 μ m (in most cases). The coated electrode sheet was dried at 80 °C to remove NMP, and subsequently, electrodes with a diameter of 16 mm were obtained by punching. The punched electrode disks were rollpressed in between stainless-steel sheets of 100 μ m thickness using a roll gap of 200, 100, and 50 μ m successively. The roll-pressed electrodes were then dried at 110 °C overnight under vacuum before being taken for cell assembly in CR-2016 coin cells in an argon-filled glovebox (H_2O and O_2 < 0.1 ppm). In half-coin cell, metallic sodium (99.8%, Acros Organics) was employed as the counter and reference and glass microfiber sheets (GF/F, Whatman) was used as the separator.

3.6.2. Cyclic voltammetry/ Linear Sweep Voltammetry [36]

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are potential sweep methods, used to study the electron transfer kinetics and transport properties of electrolysis reactions. In these techniques, the applied voltage is controlled while the current response is measured. During the process, a linear sweep rate of the voltage vs. time is defined and applied for a fixed voltage range (constant dE/dt). In LSV, the potential is scanned between the initial potential (V_1) to the final potential (V_2). CV is an extension of LSV, in which after the first scan, a reverse scan direction is applied in the same potential range. The potential could be cycled multiple times between 2 switch potentials before ending at the final potential.

Figure 3. 11. Cyclic potential sweep and the resulting cyclic voltammogram in CV

The increasing of the potential (called anodic scan) is related to oxidation process. E.g. in a cathode material, this corresponds to the de-insertion of the charge carriers from the material. In the other hand, cathodic scan (or the decreasing of the potential) is accompanied by the reduction process, corresponding to the intercalation of charge carriers into cathode material. A voltammogram could be drawn from the responding current and voltage. The characteristics of voltammogram depend on the following factors:

- The electron transfer reaction(s)' rate
- The voltage sweep rate
- Electroactive species

The voltammogram of CV can supply the important information such as the potentials in which the electrochemical reactions occur, the reversibility of process, kinetic characteristic of electron transfer or diffusion coefficient. The redox potential of electroactive species is theoretically determined by Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln([R]/[O])$$

where F is Faraday constant ($96\,485\text{ C mol}^{-1}$), R is gas constant ($8.314\text{ J K}^{-1}\text{ mol}^{-1}$), n is the number of electrons transferred in the reaction, T is the temperature (in Kelvin). There are some limitation of Nernst equation as the net current flow through the electrode changing the activity of ion, the additional overpotential and the resistivity contributing to the measured potential.

The effect of the scan rate on the peak current is described by Randless-Sevick equation:

$$i_p = 2.69 \times 10^5 \text{ A n}^{3/2} D^{1/2} \nu^{1/2} C^*$$

where i_p is the peak current, A is the contact area, n is the elemental number of electrons per reaction, D is the diffusion coefficient ($\text{cm}^2\text{ s}^{-1}$), ν is the scan rate (V s^{-1}) and C^* is the bulk concentration of charge carriers. Hence, the current intensity increases with the increasing of the scan rate. It is explained by the thickness of the diffusion layers at different scan rates. In a slow scan, the diffusion layers will grow further than in a fast scan. As a result, the flux to the electrode at slow rate is smaller than it at higher scan rate. The diffusion coefficient could be determined using Cyclic voltammetry technique. In this technique, the scan rate is altered while the change of peak current is recorded. By plotting the relation between peak current and square root of scan rate, the diffusion coefficient could be calculated from contact area (A) and bulk concentration of charge carrier (C). However, it is challenged to quantify the true contact area parameter because of the porosity of active material. There are three different computation, based on geometric area of electrode, BET surface area or half of BET area. The computed coefficient is so called “apparent diffusion coefficient”. Besides, Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Impedance Spectroscopy (EIS) are other techniques to determine the diffusion coefficient, which also require the value of electrochemical active area.

Besides the charge transfer reaction on the surface of the electrodes, other processes need to be considered in battery aspects as the transfer processes inside the material, from/to the surface, adsorption, structure rearrangements, etc. CV is a routine experiment to investigate the electrochemical behavior of battery systems and was employed frequently in the thesis. To determine the stability window of ILs and IL electrolytes, LSV method was employed. All CV and LVS tests were tested using a BioLogic VMP3 potentiostat (France).

3.6.3. Galvanostatic Charge Discharge Cycling

Galvanostatic measurement is a routine electrochemical measurement to determine the behavior of battery systems. The constant charge and discharge current are applied in a limitation of defined variable, such as time or voltage. The potential response is normally measured during the galvanostatic process. Electrical capacity, which is the number of transferred electrons, is calculated by multiplying the current with time of the process. Typically, Galvanostatic curve shows the relation between the battery potential vs. time or the capacity. In the other words, GCD curve provide information about the battery capacity in the range of corresponding voltage.

In theory, the capacity of a specific material can be calculated by Faraday law: $Q = \frac{m z F}{M}$, where Q is the total charge transferred/capacity, m is the mass of the active material in electrode, z is the number of electrons transferred in each electrochemical reaction of material molecule, F is the Faraday constant ($96485 \text{ A.s mol}^{-1}$), M is molar mass of electrode material. For comparative purpose, capacity is usually normalized by the mass of the active material or the electrode surface area, called **specific capacity** (mAh g^{-1} or mAh cm^{-2}). It should be noted that the obtained capacity is usually smaller than the theoretical value.

The reversibility of electron transfer process is accessed by the **Coulombic efficiency** (CE). It is defined by the ratio of charge and discharge capacity in percentage. Low value of CE indicates the occurrence of irreversible reactions. Another important parameter of the battery system is the **capacity retention**. It is normally defined as the

ratio of discharge capacity after n cycles and the initial discharge capacity. The irrecoverable capacity is explained by the irreversible reactions in discharge process, such as decomposition of electrolyte. Capacity retention is applied to express the stability or the aging of the battery system. It is essential for comparison between battery systems.

One or multiple plateaus could be observed in GDC profile. The potential of the cell increased gradually or remains constant during a period of time current applied. In this particular potential, there are electrochemical reactions of large amount of electro active species. This potential usually corresponds with the peak position in CV curve. In this thesis, Galvanostatic charge/discharge tests were carried out on Neware battery tester system under ambient conditions

3.6.4. Electrochemical Impedance Spectroscopy[37, 38]

Electrochemical Impedance technique is an advance method to perturbative characterize the dynamic of various electrochemical process in battery system. EIS is non-destructive method, based on the perturbation of an equilibrium state, unlike other electrochemical techniques (from initial state to final state). Electrochemical impedance spectroscopy describes the response of an electrochemical system to an applied potential and alternative current (AC) with a variable frequency. The relation between current response and the potential is nonlinear. During the measurement, a small amplitude AC signal is applied with different frequency to the cell, the response current with the AC voltage is analyzed to determine the resistance, capacitance and inductance behavior. Individual process occurs at specific range of AC frequency.

The response current is usually at the same frequency but shifted in phase with the potential. The impedance of the system Z is expressed by a vector in Nyquist plot or in the form of complex number, containing the real and imaginary part. In a cell or battery systems, there are various processes which make the Nyquist plot complex. It is simplified by equivalent circuit model. The common equivalent elements are expressed in the table below.

Table 3. 3. Common equivalent elements in EIS

Equivalent element	Impedance
R (resistor)	R
C (capacitor)	$1/i\omega C$
L (inductor)	$i\omega L$
W (infinite Warburg diffusion)	$1/Y_0(i\omega)^2$
O (finite Warburg)	$\tanh (B\sqrt{i\omega}/[Y_0\sqrt{i\omega}])$
Q (constant phase element – capacitor in reality)	$\frac{1}{Y_0(i\omega)^\alpha}$

In LIBs or SIBs, several factors influencing the cell impedance could be mentioned as electrolyte resistance, electrolyte and electrode interface resistance, SEI resistance, cathode diffusion.[39, 40] First is the internal resistance of the system such as from casing, connection and electrolyte (R_Ω), observed in the high frequency range. The electron transfer between electrolyte and electrode interface is expressed as charge transfer resistance (R_{CT}), in parallel with capacitive factor of double layer capacitance. Another factor is R_{SEI} and C_{SEI} , which is arise from SEI layer. As result, in middle frequency range, semi-circles related to charge-transfer resistance and SEI layer are observed. Ion diffusion inside cathode material is stated as W factor, observed by a 45-degree tail in the low frequency range. One of the possible equivalent circuit are described in the scheme below. The value of these resistances could be obtained by using the equivalent circuit to fit the Nyquist plot. The resistance of SEI layer and charge-transfer process calculated as the diameter of semi-circle in Nyquist plot presents the effectiveness of the layer and the kinetical required for electrons to transfer in the layers. The thicker of SEI layer is, the higher of R_{SEI} obtained. By investigating the evolution of cell impedance over time or comparison between different cells, the difference in the cycling/rate performance of the cells could be explained kinetically.

3.7. References

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Chapter 4

Effect of Conducting Salts in Ionic Liquid Electrolyte for Enhanced Cyclability of Sodium Ion Battery

The electrochemical performance of IL electrolytes containing different sodium salts dissolved in 1-butyl-1-methylpyrrolidinium bis(trifluoro-methylsulfonyl)imide (Pyr_{1,4}TFSI), evaluated in a half cell configuration using spherical P2 – Na_{0.6}Co_{0.1}Mn_{0.9}O_{2+z} cathode are reported. NaFSI (0.5M) in Pyr_{1,4}TFSI shows the best electrochemical performance with a significant improvement in cycling stability (90% capacity retention/500 cycles at 50 mA g⁻¹ in a half cell) compared with conventional NaClO₄ (1M) in EC/PC electrolyte (39% retention/500 cycles). Cyclic voltammetry studies reveal that the ionic liquid electrolytes are stable up to 4.8 V vs. Na/Na⁺. When using NaFSI and NaTFSI, XPS results prove that the cathode-electrolyte interface (CEI) is comprised of components resulting from the decomposition of the TFSI anion and the deposition of Pyr_{1,4} cation. On the other hand, the CEI layer of the electrode cycled in an electrolyte containing NaClO₄ in Pyr_{1,4}TFSI follows a different pathway of TFSI decomposition and consists mainly of sodium fluoride. Similarly, plating studies were used to understand the stability of IL electrolytes in contact with metallic sodium. It was found that the excellent capacity retention for the electrolyte consisting of NaFSI salt is related to the formation of stable CEI and SEI layers.

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4.1 Introduction

Lithium-ion batteries are currently the most sought-after option for portable energy storage due to their high energy and power densities. However, it is expected that the availability of lithium sources will become a limiting factor in the future due to the projected increase in consumption resulting especially from the demand for automotive batteries. Hence it is of interest to identify alternate technologies that employ other elements.

Sources for sodium are present in abundance and have widespread availability compared to lithium.¹⁻⁵ Due to the larger mass and size of sodium ions compared to lithium ions and the lower redox potential ($E^{\circ}_{Na/Na^{+}} = -2.7$ V vs. SHE, while $E^{\circ}_{Li/Li^{+}} = -3.04$ V vs. SHE), the widespread abundance, which results in price advantages and the chemical analogy to lithium, promote sodium-ion batteries as an alternative to complement lithium ion batteries in certain applications such as stationary energy storage.^{2, 6-7}

Amongst cathode materials for sodium-ion batteries, P2-type layered transition metal oxides, composed of prismatic coordination with 2 stacking layers of MO_6 -octahedral, show better phase stability throughout electrochemical sodiation and desodiation than other layered transition metal oxides, along with a favorable compromise between cyclability and energy efficiency.^{4, 7-11} Compared to other transition metals, manganese based oxides provide a cheaper and more eco-friendly cathode material. However, the cycling stability of layered manganese oxides as cathodes material still poses a challenge, due to Jahn-Teller distortion of Mn^{3+} ion during the de/intercalation process.⁴ For example, $Na_{0.44}MnO_2$ synthesized via solid state route retains 84% of its initial capacity after 100 cycles,¹² while the retention of P2- $Na_{0.6}MnO_2$ is 30%.¹³ The effect of elemental substitutions and morphology on the cycling performance and initial capacity has been investigated in our group earlier for the layered Na_xMnO_2 .¹⁴ It was found that spherical $Na_{0.6}Co_{0.1}Mn_{0.9}O_{2+z}$, which combines the advantages offered by a hollow spherical morphology¹⁴ as well as Co-substitution had a synergistic effect.^{5, 15} Compared to un-substituted material, Co-substitution enhances Na^{+} conductivity, avoids the ordering of Na^{+} and also suppresses the undesirable phase transformation

from hexagonal to orthorhombic in lower potential range of operation (between 2.1 – 1.5 V vs. Na/Na⁺). We reported an initial capacity of 167 mAh g⁻¹ in the first cycle and about 67% of this value was retained after 150 cycles.⁵

The conventional electrolytes used in a sodium ion battery consist of sodium perchlorate dissolved in a combination of carbonate based solvents (ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) etc).¹⁶ However, NaMnO₂ and its modifications display poor cycling stability in these conventional electrolytes.^{5, 12-13, 17} To improve the cycling performance of our optimized cathodes, it was decided to evaluate the possibility of replacement of conventional carbonate based electrolytes. Room-temperature ionic liquids (ILs) are superior to conventional carbonate based electrolytes in term of their non-flammability, as well as their thermal and electrochemical stability.¹⁸⁻²⁰ There are reports of ionic liquid electrolytes improving the cycling stability of cathode materials in sodium-ion batteries. Hilder *et al.* reported the performance of P2- and O3- Na_{2/3}[Fe_{2/3}Mn_{1/3}]O₂ cathode in half cells comprising of sodium metal and an electrolyte consisting of iso-butyl phosphonium bis(fluorosulfonyl)imide at 50 °C.²¹ Chagas *et al.*²² reported the performance of an electrolyte consisting of sodium trifluoromethanesulfonimide dissolved in 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ionic liquid using Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O₂ cathode material. That system demonstrated a retention of 80% over 100 cycles compared to 40% for an electrolyte consisting of NaPF₆ dissolved in PC. The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide has also been evaluated as a solvent for an electrolyte in half cell configuration using olivine structured NaFePO₄²³⁻²⁴ or Na_{0.44}MnO₂ prepared via solid-state route.¹² According to all these reports, the ionic liquid electrolyte is able to enhance the capacity and cycling stability of cells at elevated temperature. However, the effects are described to vary with the variation of different sodium salts or concentrations.

It was thus the aim of this work to investigate the effect of using an ionic liquid electrolyte consisting of Pyr_{1,4}TFSI solvent and different sodium salts on the cycling stability of P2-Na_{0.6}Co_{0.1}Mn_{0.9}O_{2+z} (NCO) (0 ≤ z ≤ 0.25) cathode material.²⁵ The influence of NaClO₄ (NaClO₄-IL), sodium trifluoro-methanesulfonimide NaTFSI (NaTFSI-IL) and sodium bis(fluorosulfonyl)imide NaFSI (NaFSI-IL) salts, which

were dissolved to give a concentration of 0.5M in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (Pyr_{1,4}TFSI) on electrochemical performance was investigated. In order to provide fair comparison with the original reports dealing with the spherical NaMnO₂ material,^{5, 14} NaClO₄ EC/PC (NaClO₄-OR) was chosen as a reasonable benchmark for evaluating the IL based electrolytes in this study.

Besides NaClO₄, which is the most commonly reported salt in recent literature (in ca. 2/3 of the published SIB papers), NaTFSI and NaFSI appear to be attractive choices as well. They consist of the TFSI and FSI anions, which also appear in ionic liquids with high thermal stability and low-toxicity.²⁶ It should be noted that a passive layer would be formed when Na metal in contact with electrolyte. The layer formed on Na electrode could affect the performance of the reported half cells.²⁷⁻²⁹ A hypothetical explanation for the observed differences in electrochemical performance based on the analysis of the cathode-electrolyte interface using X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and sodium plating/stripping studies is presented and discussed in this work.

4.2. Experimental Section

4.2.1. Material synthesis and coin cell preparation

Spherical P2-Na_{0.6}Co_{0.1}Mn_{0.9}O_{2+z} was synthesized following an already reported protocol from our group.⁵ Briefly, solutions containing 100 mmols of NH₄HCO₃ (99%, Alfa-Aesar) and 10 mmols of Co/MnSO₄ (1:9 mol ratio, Alfa-Aesar) were prepared by dissolving the required amounts of precursors separately in 700 ml of DI water. About 70 ml of pure ethanol (99.9%, Merck) was added to the solution containing sulfates. Subsequently, the NH₄HCO₃ solution was added to the solution of sulfates in water-ethanol mixture and stirred for 3 hours to obtain the co-precipitated (Mn,Co)CO₃ which was filtered and washed repeatedly 3 times using ethanol and water and dried at 80 °C overnight. The dried carbonate precursor was calcined at 400 °C for 5h to form the oxide compound. Finally, the required amount of the oxide precursor was dispersed in a water - ethanol mixture together with NaOH (98%, Alfa-Aesar) and dried to give precursor. This precursor was subjected to calcination in 3 steps in air: first at 320 °C for 3h (heating rate of 5K/min) followed by 800 °C for 4h (heating rate of 5K/min) and

finally at 610 °C for 9h (heating rate of 5K/min) before quenching to form the final product. The synthesized powder was stored in an argon-filled glovebox to minimize exposure to air.

A series of IL electrolytes were prepared in an argon-filled glovebox by dissolving 3 types of sodium salts namely NaClO₄ (Sigma-Aldrich, ≥98%), NaTFSI (Sigma-Aldrich, 98%), NaFSI (Nippon Shokubai) in Pyr_{1,4}TFSI (Iolitec, 99.5%) to yield a concentration of 0.5M. The sodium salts were dried at 110°C overnight under vacuum before being transferred to the glovebox for electrolyte preparation. Electrolytes were prepared by dissolving the required amount of salt in the solvents and the solutions were continuously stirred for 24h before use. For comparison, the organic electrolyte was prepared by dissolving NaClO₄ (Sigma-Aldrich, ≥98%) in ethylene carbonate/propylene carbonate to yield a 1M solution (1:1 w/w, Sigma-Aldrich). The water contents of IL electrolyte as determined by Karl Fischer titration are below 60 ppm. The organic solvents have the water specification of below 50 ppm.

For the cathode composite preparation, the active material, acetylene black (Alfa Aesar, >99%) and polyvinylidene fluoride (PVdF, Arkema, Kynar HSV 900) in a weight ratio of 60:20:20 respectively were dispersed in N-methyl-2-pyrrolidone (NMP) solvent and the resulting slurry was coated on battery grade aluminum foil (Goodfellow) using a doctor blade with a gap of 100 μ. The coated electrode sheet was dried at 80°C to remove NMP and subsequently electrodes with a diameter of 16 mm were obtained by punching. The punched electrode disks were roll-pressed in between stainless-steel sheets 100 μm thick using a roll gap of 200, 100 and 50 μm successively. The roll-pressed electrodes were then dried at 110°C overnight under vacuum before being taken for cell assembly in CR-2016 coin cells in an argon-filled glovebox (H₂O and O₂ <0.1 ppm). Metallic sodium (99.8%, Acros Organics) was employed as the counter and reference and glass microfiber sheets (GF/F, Whatman) was used as separator. For sodium plating and stripping studies, symmetric cells with metallic sodium as both working and counter were used.

4.2.2. Electrochemical Measurements

All the electrochemical measurements reported in this work were performed on assembled CR-2016 coin-type half-cells. Galvanostatic charge/discharge tests at 50 mA g⁻¹ were carried out in the voltage range of 1.5 to 3.8 V vs. Na/Na⁺ on Neware battery tester system under ambient conditions. The performance at different rates (20 – 400 mA g⁻¹) was also evaluated. Cyclic voltammetry (CV) curves were recorded between 1.5 to 3.8 V vs. Na/Na⁺ using a BioLogic VMP3 potentiostat. Electrochemical impedance spectroscopy (EIS) tests were conducted on the VMP3 instrument (BioLogic, France) with channels coupled to a frequency response analyzer. The frequency range and the AC amplitude for the EIS study were 500 kHz to 1 mHz and 20 mV, respectively. The cells were charged and discharged using a current of 50 mA g⁻¹ followed by resting for 12 hours at open-circuit voltage before performing impedance measurements. Impedance measurements were carried out after 1, 30 and 500 cycles. The obtained data were fitted using standard equivalent circuit models available in the EC-lab software.

4.2.3. Physical characterization

The dynamic viscosity was measured with a microVISC viscometer (RheoSense) with the measuring cell B-10 at 23 °C. Conductivity measurements were conducted in an Argon-filled glovebox by an InLab 751 conductivity probe head (Mettler Toledo) connected to a Solartron SI1260 frequency response analyzer. The samples were placed in a test tube inserted into a temperature-controlled steel block. The frequency range and the AC amplitude for the EIS study were 10 MHz to 1 mHz and 20 mV. The high-frequency resistance at which the impedance diagram in the Nyquist plot intercepts the real axis was used to approximate the ohmic resistance of electrolytes. The specific conductivity was determined using a cell constant of 1 cm⁻¹ calibrated with 0.1 M KCl.

Surface compositional analysis of electrodes after 30 cycles was conducted by ex-situ X-ray photoelectron spectroscopy (XPS) with Omicron EA 125 energy analyzer in conjunction with an EAC2000-125 control unit. Cycled cells were opened inside an argon-filled glovebox and the electrodes extracted were washed with dimethyl carbonate (DMC) to remove residual salt and electrolyte followed by drying under

vacuum to remove the DMC. To avoid exposure of the electrodes to ambient environments, a sealed glass tube was used to transfer the electrodes into an Ar-filled glovebox which was connected to the XPS instrument. Survey spectra were recorded at a resolution of 1 eV and high-resolution spectra of Na, F, N, S, O, Cl and C core level regions were recorded at 0.1 eV resolution. 10 scanning cycles were applied. The XPS spectra were calibrated using the standard C1s peak at 284.6 eV before being subjected to analysis. The morphology of the surface electrodes before and after 30 cycles were examined by field-emission scanning electron microscopy (FESEM JEOL 7600F).

4.3. Results and Discussion

4.3.1. Electrolyte properties

Table 4. 1. Viscosity η [cP] and conductivity σ [mS/cm] of electrolytes

	NaClO ₄ -OR	NaClO ₄ -IL	NaTFSI-IL	NaFSI-IL
η [cP]	6.8	166.3	224.6	191.5
σ [mS/cm]	7.38	1.70	1.29	1.42

Table 4.1 illustrates the viscosities and conductivities of electrolytes used in this study. In general, IL electrolytes show lower conductivities and higher viscosity than the conventional organic electrolytes NaClO₄-OR. The conductivities and viscosities change with the variation of Na conducting salts. Among 3 salts, NaClO₄ has the best effect on the conductivity as well as the viscosity of the IL electrolytes. The NaTFSI-IL electrolyte has a higher conductivity than NaFSI-IL. These values are in good agreement to the measured viscosities.

4.3.2. Electrochemical studies

Figure 4. 1. Cyclic voltammogram of spherical NCO material at 0.1 mV s⁻¹ (a) in 1st cycle in different electrolytes; (b) first 10 CV cycles in NaFSI- IL; (c) first 10 CV cycles in NaClO₄-OR

Cyclic voltammetry was used to investigate the redox potentials of NCO in the different electrolytes at a scan rate of 0.1 mV s⁻¹ in the voltage range of 1.5 – 3.8 V vs. Na/Na⁺ (Figure 4.1a). The peaks observed at 2.25 V and 2.07 V vs. Na/Na⁺ in the NaClO₄-OR cells correspond to the Mn⁴⁺/Mn³⁺ redox couple (Figure 4.1b). In cells containing the NaFSI-IL electrolyte, the oxidation and reduction peaks are observed at 2.42 V and 1.85 V vs. Na/Na⁺ (Figure 4.1c) suggesting an increased polarization compared to the NaClO₄-OR. The high polarization of IL cells could be attributed to the higher viscosity of the IL electrolyte. The decrease in polarization especially during the oxidation follows the order NaFSI-IL>NaTFSI-IL>NaClO₄-IL. Besides the viscosity, the polarization trend could be explained by nature SEI/CEI layers. There is almost no fading observed for the NaFSI-IL cell (Figure 4.1c), while only minor fading is observed for the NaTFSI-IL cell and the NaClO₄-IL cell (Figure 4.S1). In contrast, fading is more pronounced in cells with NaClO₄-OR. On increasing the potential of the working electrode to 4.8 V vs. Na/Na⁺ with the NaFSI-IL cell (Figure 4.S2), an additional peak is observed at 4.4 V/4.2 V vs. Na/Na⁺ which can be attributed to the quasi-reversible P2-type to O2-type phase transition.³⁰ Again, no significant fading in peak current is observed at this increased potential limit. This suggests that this electrolyte would be suitable to evaluate cathodes that operate at higher redox potentials. For the purposes of this study though, we restricted the performance evaluation to an interval from 1.5 – 3.8 V vs. Na/Na⁺.

Figure 4. 2. (a) Cycling performance and (b) discharge profile of NCO in different electrolytes at 50 mA g⁻¹ in the voltage range of 1.5 V – 3.8 V vs. Na/Na⁺;

Figure 4.2 shows the results of galvanostatic cycling at 50 mA g⁻¹ with the respective electrolytes at room temperature in the voltage range of 1.5 – 3.8 V vs. Na/Na⁺. The discharge profiles in Figure 2b correlate well with the observed peak positions in CV discussed earlier. Cells with NaClO₄-OR exhibited a discharge capacity of 172 mAh g⁻¹ which is higher than the capacity displayed by cells containing the IL electrolytes. The first discharge capacity of the NaFSI-IL cell is 147 mAh g⁻¹, which is the highest among the IL- cells. The first discharge capacities for NaClO₄-IL cell and NaTFSI-IL cell are 136 mAh g⁻¹ and 124 mAh g⁻¹, respectively. The capacity retention of cells with NaClO₄-OR after 100 cycles and 500 cycles are 77% and 39% respectively. The NaTFSI-IL cell retains 85% and 65% after 100 and 500 cycles. For the NaClO₄-IL cell, the capacity retention after 100 cycles is 66%, after which rapid degradation is observed and only 4% of initial capacity is retained after 300 cycles. Meanwhile, the

NaFSI-IL cell shows a significant improvement retaining about 98% and 88% of the capacity after 100 cycles and 500 cycles, respectively (Figure 2a).

Regarding the coulombic efficiency (Figure 4.S3), the NaFSI-IL cell has the highest value at around 100%. The NaClO_4 -OR cell displays 98% coulombic efficiency. The coulombic efficiency of the NaTFSI-IL cell is also larger than 99% but the value varies significantly in the first 100 cycles possibly due to some irreversible side reactions during the charging process. The NaClO_4 -IL cell has the lowest coulombic efficiency of around 92% amongst the examined electrolytes. It can be concluded that the choice of sodium salts in IL electrolyte seems to have a pronounced influence on the coulombic efficiency.

To provide a more complete picture, electrolyte with a composition of 0.5 M of NaClO_4 , NaTFSI and NaFSI dissolved in a mixture of EC/PC was evaluated (Figure 4.S5). However, due to its low capacity retention, NaClO_4 in EC/PC a concentration of 1.0 M was chosen as the objective for comparison in the present study.

Figure 4. 3. Rate test performance at 5 different rates

Rate testing was performed to evaluate the performance under fast charge-discharge conditions. As can be seen in Figure 4.3, except for NaClO_4 -IL all electrolytes achieve a similar capacity of $\sim 175 \text{ mAh g}^{-1}$ at a rather slow rate of 20 mA g^{-1} . It is evident that cells with the NaClO_4 -OR display the best rate capability that is better than the different IL- cells. For example, the discharge capacity of NaClO_4 -OR cell at 400 mA g^{-1} ($\sim 2.2 \text{ C}$) is still at 100 mAh g^{-1} while it is around 50 mAh g^{-1} for the other IL

electrolytes. Among the IL electrolytes, NaFSI-IL cells again display better performance, followed by NaTFSI-IL and NaClO₄-IL. *E.g.*, the NaFSI-IL electrolyte is still able to achieve ~100 mAh g⁻¹ at 200 mA g⁻¹, corresponding to ~1.1 C. The poor rate performance of IL electrolytes can be explained by their high viscosity as well as their low conductivity when compared to OR electrolyte. In order to overcome this drawback different approaches *e.g.* addition of appropriate additives or hybrid ionic liquid/organic electrolyte have been reported in literature.³¹⁻³³

To understand the reasons for differences in rate performance, the apparent sodium-ion diffusion coefficients were determined using CV. The cells were scanned at different rates (0.1 mV s⁻¹, 0.2 mV s⁻¹, 0.5 mV s⁻¹, 1 mV s⁻¹ and 2 mV s⁻¹) and a plot of peak current versus the square root of scan rate was generated for both oxidation and reduction processes. From this plot, the slope was obtained which was used to calculate the diffusion coefficient from the Randles-Sevcik equation (eq. 1) given below.³⁴

$$i_p = (2.69 \times 10^5) A n^{3/2} D^{1/2} \nu^{1/2} C^* \text{ [eq. 4.1]}$$

where i_p is the peak current (A), A is the contact area (geometric electrode area, 2.018 cm², is used), n is the elemental number of electrons per reaction, D is the diffusion coefficient (cm² s⁻¹), ν is the scan rate (V s⁻¹), C^* is the bulk concentration of sodium (0.02102 mol cm⁻³ calculated from the unit cell volume)⁵. It is noted that the actual contact area is larger than the geometric value due to the high roughness of the surface.

Table 4. 2. Apparent diffusion coefficient value calculated for NCO cell in various electrolytes

Electrolyte	Anodic diffusion coefficient (apparent) [cm ² s ⁻¹]	Cathodic diffusion coefficient (apparent) [cm ² s ⁻¹]
NaFSI-IL	1.93 E-12	7.73 E-13
NaTFSI-IL	4.78 E-13	4.01 E-13
NaClO ₄ -IL	3.45 E-13	1.99 E-13
NaClO ₄ -OR	2.39 E-12	7.36 E-13

The diffusion coefficients in different electrolytes for anodic and cathodic processes are summarized in Table 2. In general, the diffusion coefficient in NaFSI-IL electrolyte is higher than the diffusion coefficient in NaTFSI-IL and NaClO₄-IL, and on a similar level as NaClO₄-OR, explaining the good performance of NaFSI-IL electrolyte's cell

in rate test compared with the other IL samples. However, it should be noted that the nature of SEI/CEI layers formed will also influence the rate performance.

To understand the reasons for fading better, electrochemical impedance spectroscopy (EIS) and sodium plating/stripping tests were performed. EIS would give an indication of the evolution of cell impedance with cycling while sodium plating/stripping would help in understanding the reactivity of sodium metal and the role it plays in the affecting cell performance.

Figure 4. 4. Impedance spectra of NCO after 1 cycle (a), after 30 cycles (b) and after 500 cycles (c)

Figure 4.4 shows the Nyquist plots of cells with various electrolytes after 1 cycle (Figure 4a), 30 cycles (Figure 4b) and 500 cycles (Figure 4.4c). The fitted EIS results are presented in Table S1. The cell impedance reduces from the 1st cycle to the 30th cycle for both NaTFSI-IL and NaFSI-IL samples and then increases again in the 500th cycle. On the other hand, cell impedance increases constantly from the 1st to 30th to 500th cycle for both the NaClO₄ containing electrolytes. From the 30th to 500th cycle, the cell impedance increases by about 20 times and 27 times respectively for the NaClO₄-IL and NaClO₄-OR. While for the NaFSI-IL and NaTFSI-IL samples, it increases by about 7 times and 3.5 times respectively.

The cell impedance after 500 cycles follows the trend NaClO₄-IL > NaClO₄-OR > NaTFSI-IL > NaFSI-IL which is in line with the trend observed in capacity retention (NaClO₄-IL < NaClO₄-OR < NaTFSI-IL < NaFSI-IL). The numbers are also in line with the observed rate performance with the NaClO₄-OR cell clearly displaying highest capacities at high rates of cycling (**200 mA g⁻¹ and 400 mA g⁻¹**) compared to

the other 3 electrolytes that use the IL solvent (after 30 cycles). Impedance analysis at high rates (Figure 4.S6) further confirms this trend.

The reason for the initial decrease in the cell impedance (from the 1st to the 30th cycle) for both the NaTFSI and NaFSI electrolytes could be due to the insufficient wetting of the electrode by the electrolytes (due to high viscosities (table 4.1)). With cycling, the contact area tends to increase, and this would result in reduced impedance.³⁵ Another possible explanation is the passive layer initially formed on the electrode before cycling. As cycling progresses, an ionically conducting solid electrolyte interphase (SEI) layer would form, that could possibly result in lowering the impedance in case of NaFSI-IL/NaTFSI-IL cells. Furthermore, undesirable reaction products may form at both anode/cathode causing the impedance to go up again as observed from the 30th to 500th cycle.

It is clear that the while all electrolytes result in an increased cell impedance over long-term cycling, the NaTFSI-IL and NaFSI-IL electrolytes perform relatively better compared to the NaClO₄ containing electrolytes. This suggests that the use of NaClO₄ is possibly resulting in unwanted reactions in both the IL and OR solvents.

Figure 4. 5. Potential profile vs. time during subsequent sodium stripping/plating behavior performed in symmetric Na/electrolyte/Na cell at a current rate of 0.1 mA cm⁻² and stripping/plating time of 1 h.

In an attempt to understand the impedance changes arising at the metallic sodium counter electrode, sodium plating and stripping studies were performed in symmetric Na/Electrolyte/Na cells. Coin cells were assembled and subjected to

chronopotentiometry at a current of 0.1 mA cm^{-2} . Figure 4.5 presents the potential profiles obtained from these tests. The cells employing $\text{NaClO}_4\text{-OR}$ (black) and NaFSI-IL (blue) show a stable sodium stripping/plating behavior with limiting potentials (i.e the potential at which a plateau is observed that corresponds to plating/stripping) of about 0.06 V and 0.3 V, respectively. It can be seen that this limiting potential remains fairly constant suggesting no change in polarization with cycling. This indicates that whatever layer is formed on the surface of the sodium is quite stable and allows unhindered plating and stripping of sodium in these electrolytes. On the other hand, the limiting potential of NaTFSI-IL (green) and $\text{NaClO}_4\text{-IL}$ (red) are higher (around 0.6 V) to start with and also constantly increase/vary with cycling. The limiting potential for the $\text{NaClO}_4\text{-IL}$ cell increases to almost 3V after about 120 hours while that of the NaTFSI-IL cell seems to maximize around 1.5V but seems to vary in a cyclical manner (increasing progressively for 4-5 cycles followed by a reduction). This suggests that whatever layers are formed on the surface of the sodium metal in these electrolytes, increase the polarization significantly and are probably hindering sodium plating and stripping to a much greater extent.

From the plating behavior studies, it is evident that for both NaTFSI-IL and $\text{NaClO}_4\text{-IL}$ electrolytes, changes occurring at the sodium anode seem to be a major contributor to the changes observed in cell impedance. The $\text{NaClO}_4\text{-IL}$ sample which had the highest polarization also displays the highest overall impedance (7767 Ohms). The stable performance of the NaFSI-IL cell to sodium plating/stripping suggests that most of the observed increases in cell impedance are probably occurring due to changes at the cathode. Interestingly, in the case of the $\text{NaClO}_4\text{-OR}$ electrolyte, sodium stripping and plating seems to be fairly stable suggesting that the observed impedance increases most likely are occurring due to changes taking place at the cathode.

4.3.3. Surface analysis by X-ray photoelectron spectroscopy

To understand the effect of cycling in different electrolytes on the cathode, XPS analysis was conducted to establish the nature of components formed in the cathode electrolyte interface (CEI) layer on the surface of electrodes after 30 cycles. The peaks observed in the high-resolution spectra were identified by fitting and correlation with

references.³⁶⁻⁴¹ Figure 4.S7 compares the survey spectra of the cycled NCO in the discussed IL electrolytes.

Table 4. 3. Atomic percentages of elements (excluding Mn, Co) determined from survey spectra of the pristine sample and electrode samples after 30 cycles

	C 1s	O 1s	F 1s	Na 1s	S 2p	N 1s
Pristine electrode	72.7	4.7	21.1	1.5	0	0
NaClO ₄ -OR	42.2	31.9	2.0	23.9	0	0
NaClO ₄ -IL	60.5	12.5	20.8	6.2	0	0
NaTFSI-IL	64.5	12.7	18.2	1.0	2.3	1.3
NaFSI-IL	67.5	11.6	14.6	2.0	1.3	3.0

The percentages of different elements in the various evaluated electrodes are compared to references with respect to the percentages of the elements observed in a pristine electrode (one that consists of just the active material, binder and the conducting carbon). All electrodes have been washed and dried under vacuum before analysis, so as to remove any residual salts/solvents that might modify the results of the measurements. In the following section some of the key observations are summarized:

1. Carbon and fluorine contents have decreased significantly to 42.2% and 2.0% for the NaClO₄-OR sample compared to the pristine electrode (72.7% and 21.1% respectively). The decrease in carbon and fluorine is not so significant for the electrodes tested with the IL electrolytes. Within the IL electrolytes, the carbon content increases in the order NaClO₄<NaTFSI<NaFSI while the fluorine content decreases in the order NaClO₄>NaTFSI>NaFSI. These observations suggest that the CEI layer formed in the NaClO₄-OR sample is probably deficient in carbon and fluorine containing compounds as compared to the IL samples.

2. Sodium and oxygen content have increased significantly to 23.9% and 31.9% for the NaClO₄-OR sample compared to the pristine electrode (1.5% and 4.7% respectively). Amongst the ionic liquid samples, oxygen has increased for all the samples compared to the pristine electrode. Sodium has increased significantly only for the NaClO₄-IL sample, while it has not changed much for the NaTFSI-IL and

NaFSI-IL samples. These observations suggest that the CEI layer for the NaClO₄-OR sample is probably consisting of sodium and oxygen rich compounds. To further understand the components formed, the high-resolution spectra for the various elements (Na, F, O, S and C) were analyzed. The following sections present this analysis in some detail.

4.3.3.1. CEI layer of electrodes cycled in Ionic liquid electrolytes (NaClO₄-IL, NaFSI-IL, NaTFSI-IL)

Figure 4. 6. XPS high-resolution spectrums of F 1s (a), Na 1s (b) and O 1s (c) of pristine sample and electrode samples after 30 cycles

To understand the nature of components formed on the electrode surface while cycling in ionic liquid electrolytes, first, the Na and F spectra were analyzed (Figure 4.6). From the Na 1s spectra (Figure 4.6b), two peaks are clearly discernible at 1071.9 eV and 1074.8 eV. The peak at 1071.9 eV can be assigned to the oxide material (also observed in the pristine sample). The latter peak at 1074.8 eV can be assigned to the sodium salts such as fluoride/carbonates etc.³⁹ From the F 1s spectra (Figure 4.6a), 3 distinct peaks are observed at around 684.8 eV, 688.2 eV and 689.7 eV. The most intense of these peaks is the 688.2 eV and this can be assigned to the CF₂ bond present in the binder PVdF. The higher energy peak at 689.7 eV can be attributed to the CF₃ bond found in the TFSI anion of the ionic liquid (Pyr_{1,4}TFSI) and the lower one at 684.8 eV can be assigned to sodium fluoride (NaF).^{39-40, 42} The intensity and area of the peaks assigned to sodium fluoride (NaF) from the F 1s spectra (around 684.8 eV) and the Na

1s spectra (around 1074.8 eV) increase in the order of NaTFSI $\approx$ NaFSI $<$ NaClO₄. These observations seem to indicate the presence of NaF in the CEI layer of the electrodes cycled with the ionic liquid electrolytes. It could also be deduced that the CEI layer formed on the NaClO₄-IL sample seems to be thicker than the CEI layers formed on the NaFSI-IL and NaTFSI-IL samples based on the intensity differences for the NaF peak as well as the concentrations of sodium and fluorine observed (Table 4.3).

To form NaF, F⁻ ions have to be present (the sodium ion is already present from the dissolved salts). The source of F⁻ could be a decomposition reaction of either the TFSI anion or the binder. From the curve fitting results, it was observed that the CF₃ peak at 689.7 eV (which originates from the TFSI anion) was not present for the NaClO₄-IL sample while it is clearly present in both the NaFSI-IL and NaTFSI-IL samples.

Figure 4. 7. XPS high resolution spectra of C 1s (a), S 2p (b) and N 1s (c) of pristine sample and electrode samples after 30 cycles.

Next, the high resolution spectra of C 1s, S 1s and N 1s were examined and compared to pristine spectra to obtain more information about the nature of components formed in the CEI layer.

From the N 1s spectra (Figure 7c), 3 distinct peaks can be observed at 397.0 eV, 400.1 eV and 402.1 eV for all 3 electrolytes. The peak at 400.1 eV could be assigned to

compounds such as $\text{CF}_3\text{SO}_3\text{N}^-$, $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2$, while the peak at 397 eV could be assigned to NSO_2^- , which is a fragment of the TFSI anion.⁴² The peak at 402.1 eV is attributable to the bonds formed by the nitrogen in the $\text{Pyr}_{1,4}$ cation.⁴² The peak intensity of N from anion and cation of IL in N 1s region of NaTFSI is highest, followed by NaFSI. Only trace peaks are observable in NaClO_4 - IL spectra. From the S 2p spectra (Figure 7b), only one peak at 169.7 eV is observable. The intensity, in general, is quite low compared to other elements such as C/O etc. The only source of sulfur in the systems are the TFSI/FSI anions. The trend mimics the evolution of nitrogen peaks for different IL electrolytes.

From the C 1s spectra (Figure 7a), 3 peaks are evident at ~ 284.8 eV that can be assigned to the C-C/C-H bonds which can occur in the conducting carbon additive (acetylene black) as well as the $\text{Pyr}_{1,4}$ cation, ~ 286 eV which occurs due to the carbon double bonds (sp^2 hybridized) present in both acetylene black and the PVdF binder and ~ 291 eV that belongs to the C-F bonds present in the binder and TFSI anion.^[26, 32] The peak at around 286 eV is also evident for the pristine samples. It is also clear from the C 1s spectra that the electrode cycled in NaTFSI-IL electrolyte displays a more intense 286 eV peak that is higher than the 284.8 eV peak (i.e. ratio of 286 eV vs. 284.8 eV peaks). This suggests that the $\text{Pyr}_{1,4}$ cation might be deposited on the electrode cycled using NaTFSI-IL.

The above described observations on the C 1s, N 1s and S 2p spectra seem to indicate that the CEI layer formed on an electrode cycled with NaTFSI-IL seems to consist of fragments of the $\text{Pyr}_{1,4}$ cation and TFSI anion. The electrode cycled in NaFSI-IL electrolyte also displays a similar composition. However, from the peak intensities, it seems that the CEI layer is probably thinner than the one formed on NaTFSI-IL electrodes. On the other hand, the electrodes cycled with the NaClO_4 -IL electrolyte seem to be mainly composed of NaF.

To sum up, the CEI layer of the electrodes cycled in the NaClO_4 -IL electrolyte appear to consist mainly of NaF. On the other hand, the electrodes cycled in the NaFSI-IL and NaTFSI-IL electrolytes consist mainly of organic decomposition products from the TFSI anion and $\text{Pyr}_{1,4}$ cation apart from smaller amounts of NaF. Also based on the peak intensities, it seems that the CEI layer is thickest for the electrodes cycled in

NaClO₄-IL and thinnest for NaFSI-IL. These conclusions are in good agreement with the observed cycling performances and impedance measurements.

4.3.3.2. CEI layer of electrodes cycled in conventional organic electrolyte

NaClO₄-OR

From the Na 1s spectra of the NaClO₄-OR sample, a third peak at 1071.1 eV is evident. This peak can be assigned to NaClO₄. The presence of this compound is further evident from the Cl 2p spectra (Figure 4.S8), which displays a peak at 199.2 eV that can be assigned to NaClO₄. Compared to the pristine sample, the intensity of the peak at 1071.9 eV (belonging to the sodium present in the metal oxide) is about 3 times higher (~37382 cps to 12886 cps). This suggests that apart from the sodium present in the active material, there could be other oxides of sodium that are being formed. This is again supported by the fact that both sodium and oxygen percentages increase significantly (Table 3) compared to the pristine sample. The presence of sodium chloride is also indicated from the peak at 209.1 eV in the Cl 2p spectra (Figure 4.S8). An analysis of the C 1s spectra (Figure 7a) reveals a peak at 289.5 eV, which can be assigned to sodium carbonate. This peak is not observed for any of the other samples. Further evidence for the presence of carbonate can be seen from the O 1s spectra (Figure 6c) displaying a peak at 532 eV.

To sum up, the CEI layer formed on the electrodes cycled using NaClO₄-OR electrolyte seems to consist of perchlorates, chloride, carbonates and oxides of sodium. It is already well known in the literature that inorganic compounds such as sodium fluoride, carbonates and oxides are detrimental to cycling stability.^{1, 16, 43-44} The results from cycling tests also support this observation as the NaClO₄-OR cell displays poor long-term cycling stability.

4.3.3.3. Possible pathways for the formation of observed components in IL electrolytes

It is clear that a variation in the salt dissolved in the Pyr_{1,4}TFSI ionic liquid leads to differences in the nature of components formed in the CEI layer. In this section, it is

attempted to explain potential formation pathways for these different components. The process of formation of the CEI layer occurs in a manner similar to that of the SEI layer formation (i.e. during sodium insertion into the oxide). It is known that there are 3 decomposition pathways for the TFSI anion.^{42, 45-46} They are as follows (Figure 8).

Figure 4. 8. Decomposition pathway of TFSI anion

Among these reactions, the C-S cleavage (reaction 2) was reported as less likely to occur during the decomposition process.⁴⁶ That leaves the possibilities of (reaction 1) and (reaction 3) only.

It is known that perchlorate undergoes electrochemical reduction on the electrode surface.⁴⁷⁻⁴⁸ The presence of a Cl^- peak at around 200 eV from the XPS analysis is proof that such a reaction is occurring in our case. During this reduction process, a reactive intermediate is formed that can cause a nucleophilic attack of the C-F bond.⁴⁹ The resulting F^- can easily combine with the Na^+ to form NaF , which was observed in the XPS studies. Accordingly, it appears reasonable to assume that the cleavage of TFSI anion (reaction 3) is occurring at the C-F bond in the case of the NaClO_4 -IL electrolyte.

In the case of the other 2 electrolytes NaFSI -IL and NaTFSI -IL, there is no NaClO_4 that is getting reduced and hence the mechanism described above is probably not valid. According to the XPS results, observed components such as $\text{CF}_3\text{SO}_3\text{N}^-$, $\text{CF}_3\text{SO}_2\text{N}^-\text{SO}_2$, NSO_2^- suggest that an N-S cleavage is possibly occurring (reaction 1). It is possible that these organic compounds are having a positive effect on long-term cycling.

4.4. Conclusion

In summary, the effect of various salts, namely NaTFSI , NaFSI and NaClO_4 , dissolved in $\text{Pyr}_{1,4}\text{TFSI}$ ionic liquid and used as electrolytes in sodium-ion battery has been studied with NCO as cathode material. NaFSI 0.5M in $\text{Pyr}_{1,4}\text{TFSI}$ shows excellent

cycling performance (an initial capacity of 147 mAh g⁻¹, 90% capacity retention/500 cycles at 50 mA g⁻¹). The observed fading in performance could be related to changes occurring at both the anode as well as cathode and these changes seem to be specific to each system. The nature of CEI layers formed on the cathodes were analyzed using ex-situ XPS while the reactivity of the electrolyte in contact with metallic sodium was evaluated using chronopotentiometry. The use of NaFSI salt results in the formation of thin conductive CEI layer as well as a good SEI layer that seems amenable to repeated sodium plating and stripping. This cell displays the lowest impedance after long-term cycling thus explaining the observed capacity retention. On the other hand, the use of NaClO₄ as a salt results in the formation of detrimental CEI and SEI layers which increases the cell impedance over long-term cycling thus resulting in capacity fading irrespective of the solvent used to prepare the electrolyte. We believe that the ability to form stable layers in contact with metallic sodium as well as NCO would make the NaFSI-IL system an attractive choice of electrolyte for future sodium ion batteries.

4.5. References

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4.6. Supporting information

4.6.1. Additional cycling data for the NCO half-cells with various electrolytes

Figure 4. S1. CV cycles in NaClO_4 -OR; NaFSI -IL; NaTFSI -IL; NaClO_4 -IL between 1.5V to 3.8V vs. Na/Na^+

Figure 4. S2. CV cycles in NaFSI -IL between 1.5 V to 4.8 V vs. Na/Na^+

Figure 4. S3. Discharge capacity and coulombic efficiency of NCO at 50 mA g⁻¹ from 1.5V-3.8 V vs. Na/Na⁺ in various electrolytes

Figure 4. S4. Charge – discharge charge profile of NCO at 50 mA g⁻¹ from 1.5 V–3.8 V in various electrolyte at different cycles

Figure 4.S 5. Capacity retention (%) of NCO using NaClO₄, NaFSI and NaTFSI 0.5M-OR compared with NaClO₄ 1M – OR electrolyte at 50 mA g⁻¹ from 1.5V-3.8 V vs. Na/Na⁺

4.6.2. Additional impedance spectra of NCO cells

Figure 4.S 6. Impedance spectra of NCO at OCV state after cycling at (a) 200 mA g⁻¹ and (b) 400 mA g⁻¹

Table 4. S 1 Fitting EIS results after 1 cycle, 30 cycles and 500 cycles

Salt	1 cycle		30 cycles		500 cycles	
	R _{SEI} [Ω]	R _{CT} [Ω]	R _{SEI} [Ω]	R _{CT} [Ω]	R _{SEI} [Ω]	R _{CT} [Ω]
NaClO ₄ -IL	354.3	12.4	383.3	23.9	4597	3380
NaFSI-IL	354.5	24.4	165.9	17.7	892.7	331.8
NaTFSI-IL	1183	736.3	528.7	29.2	1404	500.2
NaClO ₄ -OR	66.1	13.8	110.7	69	263.1	6358

The obtained data were fitted using the Z-fit function in EC lab software with the equivalent circuit shown in the inset of Figure 5a. R_e refers to resistance occurring from the various cell components such as spacer/ current collector/ electrolyte/separator. The resistance due to the presence of SEI (R_{SEI}) layer is usually observed at the higher frequency range while the resistance assigned to the charge transfer process (R_{ct}) is observed at medium and low frequencies. The maximum error for the fitting results is 3.5 Ω.

4.6.3. Additional XPS spectrums of NCO electrodes.

Figure 4.S 7. XPS survey spectrums of pristine electrode (black line) and electrode samples after 30 cycles in NaClO₄-OR (brown line), NaClO₄-IL electrolyte (red line), NaTFSI-IL electrolyte (green line) and NaFSI-IL electrolyte (blue line)

Figure 4.S 8. Cl 2p spectrum of NaClO₄ - OR and NaClO₄ - IL samples

4.6.4. SEM images of NCO electrodes

Figure 4.S 9. SEM images of electrodes pristine and after 30 cycles of (A) NaClO₄-OR, (B) NaFSI-IL, (C) NaTFSI-IL and (D) NaClO₄-IL electrode samples

Chapter 5

Physicochemical Characterization of Various N-based Core Structures-Room Temperature Ionic Liquids and Their Application in Sodium Ion Batteries

In this chapter, a series of novel as well as literature known N-based core structure functionalized room temperature ionic liquids (RTILs) suitable as electrolytes is presented. Special emphasis was laid on the purity of the synthesized RTILs and a consistent and uniform characterization of their physicochemical properties. Evaluation of the viscosity, conductivity, and thermal and electrochemical stabilities of pure IL and IL electrolyte resulted in clear structure–property relationships, rendering the ether functionalized RTILs most promising for application in SIBs. ILs electrolytes were first investigated electrochemically in Na/Hard carbon half-cells, Na/Na symmetrical cells. Then, examination of ether functionalized IL electrolytes in Na/Na_{0.6}Mn_{0.9}Co_{0.1}O₂ cells proved the compatibility of ether-functional group with a SIB system. Stable cycling performance was achieved with the piperidinium based RTIL IL 16 outperforming the organic electrolyte by far with a retention of 81% after 350 cycles. These results show the suitability of RTILs to enhance the performance of SIB systems and serve as a basis for the design of high-performance IL electrolytes.

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5.1. Introduction

Using a technology based on sodium as an alternative for recent lithium-ion batteries has become a promising focus of research because of its much higher abundance (ratio of reserves Li:Na = 1: 1000), [1] lower cost and easy mining of the respective minerals. [2 - 4] A further benefit of sodium ion batteries (SIBs) is based on the potential use of low weight and less expensive aluminum current collectors for both electrodes, thus leading to a further reduction of costs. [2, 5] Since Li and Na are neighboring elements in the periodic table, they share similar fundamental principles and properties. Therefore, transferring the knowledge gained for LIBs over the past two to three decades to SIBs is possible to a certain extent. [4, 6, 7] Nevertheless, the technical performance of SIBs is still far from optimal since sodium-based systems have been studied much less than Li based ones, leaving sufficient space for improvements in SIB technology. [3, 7]

In order to implement SIBs in large-scale energy storage systems, safety and long-term cycling of the system are two important challenges. [3, 7] In particular, SIB systems with conventionally applied organic electrolytes, e.g. NaClO₄ dissolved in a mixture of carbonate based solvents (ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC)), [5] pose serious safety issues due to the high flammability and volatility of the electrolytes, and the systems also suffer from poor cycling stability. [3, 8-9] Among different approaches to provide safer electrolytes, polymer electrolytes are good candidates, since they do not contain easily flammable, liquid, organic solvents. [10] Different polymer electrolytes have already been successfully tested in various studies. [11-13]

Further, ionic liquids (ILs) or room temperature ionic liquids (RTILs) have been shown to be promising alternatives to the highly volatile and flammable organic electrolytes since they exhibit several beneficial properties. [1, 5, 10] ILs are usually considered to be electrochemically and thermally stable. Further, they have an insignificant volatility, and thus a low to negligible flammability. [14 - 16] The prospect that RTILs can be tailored to meet specific requirements has promoted their application in various fields, e.g. as media for catalysis or chemical synthesis or even as catalysts themselves. [17 -

21] In particular, their high thermal and electrochemical stability combined with a good ionic conductivity renders them promising and safe alternatives to the highly flammable conventional organic electrolytes as well. [18, 22] Recent reports showed that RTILs are able to enhance the capacity and cycling stability of SIBs, underlining their suitability as promising electrolytes. [3, 6, 7, 23, 24] A further advantage of RTILs as electrolytes is the facile tunability of their physicochemical properties by modifying the anion or cation. For instance, variations of the core structures or the introduction of functional groups can have significant effects on the physicochemical properties. To date, only a few RTILs including mainly unfunctionalized imidazolium and pyrrolidinium ILs have been evaluated in SIB systems, however. [1, 2, 5] Taking lithium-based systems into account, a much broader range of RTILs has been investigated as electrolytes. [10, 22, 25] However, the evaluation of the electrochemically relevant IL properties has suffered from diverse variations of the conditions and systems in which the RTIL electrolytes were tested. Therefore, direct comparison and meaningful conclusions of the structure–property relations are hardly possible. In order to obtain comparable data and draw reliable conclusions on the structural impact of different functionalized RTILs on the physicochemical properties, a systematic and uniform approach is indispensable. Therefore, in this work, a series of novel as well as literature known RTILs with different N-based core structures, functional groups and anions is presented and examined. Focus is laid on the consistent characterization of the RTILs, especially with respect to parameters relevant for electrochemical applications like viscosity, conductivity and thermal and electrochemical stability. Based on these characteristics, the most promising RTILs were applied as electrolytes in a SIB half-cell with $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ (NMO) as the cathode material. This Co-doped NMO material was recently reported to exhibit enhanced performance compared to previously applied undoped sodium-manganese-oxides. [9] For advance comparison, series of ILs were applied in SIBs half-cells with hard carbon, which is the most common anode material for SIBs. The results were partially explained by the reactivity with the Na electrode in Na/Na symmetrical cells on long-term stripping/plating test. The results are crucial for the selection of ILs as electrolyte in SIB half-cell. Evaluation of the electrochemical performance of the selected ILs resulted in a deeper understanding of the structure–performance relationship. This knowledge can pave the way to tailored RTIL electrolyte

combinations suitable for stable and safe SIBs in the future and will help to conquer the energy challenges of the 21st century

5.2. Experimental

5.2.1. Characterization methods

Thermal stability. Thermogravimetric analysis (TGA) was carried out on a Q5000 by TA Instruments. Measurements were conducted under argon with a heating rate of 10 K min⁻¹ and an offset temperature of 600 °C. The obtained mass loss with respect to time was evaluated by the software TA Universal Analysis. T_d was defined as the temperature at the inflection point of the weight loss curve (that is, the maximum of the 1st deviation), since this a reproducible and distinct method.

Viscosity. The dynamic viscosity was measured with a microVISC viscosimeter from RheoSense with the measuring cell B-10 at 23 °C.

Conductivity. Electrochemical conductivities were determined at 23 °C in an argon-filled glovebox using a Mettler Toledo InLab 751 conductivity probe head connected to a Solartron SI1260 frequency response analyzer. The samples were placed in a small test tube inserted into a custom made, temperature-controlled steel block. A full impedance spectrum was recorded with an alternating current voltage of 0.02 V and in a frequency range between 1 Hz and 10 MHz. The Ohmic resistance of the electrolyte was determined based on the real part of the impedance where the imaginary part of the impedance is (close to) 0. The specific conductivity was determined using a cell constant of 1 cm⁻¹ calibrated with 0.1 M KCl. For the temperature dependent measurements, conductivities were reported in steps of 5 °C with a tolerance of ±0.2 °C.

Linear sweep voltammetry. LSV curves were recorded under argon using a PGSTAT302N potentiostat from Metrohm Autolab. Measurements were conducted in a three-electrode setup (sample volume: 0.2 ml, electrode distance: 3 mm) applying a glassy carbon working electrode, a Pt wire as counter electrode and a Ag/AgCl reference electrode. The respective cathodic and anodic stability limits were referenced

to the Fc/Fc^+ redox couple and defined as the potentials at the cut-off current density of 1 mA cm^{-2} in the first scan. [26]

Electrochemical measurements. Galvanostatic charge discharge tests were carried out in the voltage range from 1.5 to 3.8 V vs. Na/Na^+ on a Neware battery tester system under ambient conditions. For the determination of the diffusion coefficient, cyclic voltammetry (CV) curves were recorded using a BioLogic VMP3 potentiostat (1.5 and 3.8 V vs. Na/Na^+).

5.2.2. Synthesis and characterization of the RTILs

Synthetic procedures and characterization of the RTILs are provided in the Supporting information part 5.6.

Electrochemical investigations Coin cell preparation. The cathode material $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ was synthesized following a reported protocol. [9] The IL electrolytes were prepared in an argon-filled glovebox by dissolving NaFSI (Nippon Shokubai) in the respective RTILs 2, 8, 13 and 16 to yield a concentration of 0.5 M. The solutions were continuously stirred for at least 24 h before use. For the organic electrolyte, NaClO_4 (Sigma-Aldrich, Z98%) was dissolved in a mixture of EC/PC (1:1 w/w, Sigma-Aldrich (EC: 99%; PC: $\geq 99.7\%$)) to yield a 1 M solution.

For preparation of the electrodes, the active material was mixed with acetylene black (Alfa Aesar, 499%) and polyvinylidene fluoride (PVdF, Arkema, Kynar HSV 900) with a weight ratio of 60:20:20 in N-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich, 99%). The resulting cathode composite was coated on battery grade aluminum foil (Goodfellow) using a doctor blade with a gap of 100 mm and subsequently dried at 80°C to remove NMP. Electrodes with a diameter of 16 mm were obtained by punching. After drying at 110 $^\circ\text{C}$ under vacuum overnight, the prepared electrodes were assembled in CR2016-coin cells in an argon-filled glovebox (H_2O and $\text{O}_2 < 0.1$ ppm) with sodium metal (99.8%, Acros Organics) as anode and glass fiber (Grade GF/F – Whatman) as separator.

Galvanostatic cycling. Galvanostatic cycling tests were carried out in half cells employing NMO as the working electrode and metallic sodium as the counter/reference electrode. The cells were first charged to 3.8 V followed by discharging to 1.5 V at a rate of 50 mA g⁻¹.

Rate testing. The cells were cycled at different rates (20, 50, 100, 200, 400 mA g⁻¹) for 5 cycles each and cycled once again at 50 mA g⁻¹ at the end of the test.

Diffusion coefficient. To determine the diffusion coefficients, the cells were subjected to cyclic voltammetry at different scan rates (0.1 mV s⁻¹, 0.2 mV s⁻¹, 0.5 mV s⁻¹, 1 mV s⁻¹ and 2 mV s⁻¹). A plot of peak current versus the square root of scan rate was generated for both oxidation and reduction processes. From this plot, the slope was obtained and was used to calculate the diffusion coefficient from the Randles–Sevcik equation. [27]

5.3. Results and discussion

5.3.1. Selection of suitable RTILs as electrolytes

The selection of the cationic core structures for the evaluated RTILs was based on the respective electrochemical stabilities. For their application in battery systems, a wide electrochemical stability window (ESW) of the ILs is of great importance to prevent electrochemical decomposition of the electrolyte. Imidazolium based ILs are known for their inferior reductive as well as oxidative stability and were therefore not considered in this study. [22, 25] In contrast, piperidinium, pyrrolidinium and tetraalkylammonium based ILs have been shown to exhibit outstanding electrochemical stabilities up to 6 V, rendering them as suitable core structures for IL electrolytes. [22, 25, 28] In order to reduce the viscosity and enhance the conductivity of the RTILs, asymmetric core structures like NEt₂Me on the one hand, or ether substituents on the other hand, have been proven to be advantageous. [25, 28 - 30] When incorporating ether or other functional groups, the length of the NC-spacer between the quaternary nitrogen and the carbon attached to the functional group has a significant influence on the thermal stability of the cation. It was shown that cations with a methyl linker exhibit considerably lower thermal stabilities than their analogues with an ethyl or longer linker. [31] Therefore, all functional groups in this study were tethered to the respective nitrogen atom via an ethyl linker in order to achieve high

thermal stabilities. Another important characteristic of an electrolyte is its solid electrolyte interface (SEI) layer formation ability. To achieve good cycling stability, the formation of a stable SEI layer on both electrodes, preventing further electrolyte decomposition, is essential. [10, 25] Nitrile, allyl and ester groups are known to improve cell performance by supporting the formation of a stable SEI layer and were thus included in the present study. [25, 32-35] Additionally, ester substituents are able to improve the solubility of conducting salts when compared to the unfunctionalized analogues. [36] Regarding the anion, focus was put on the two imide anions bis(trifluoromethane)sulfonimide (TFSI) and bis(fluorosulfonyl)imide (FSI) since they are known to form RTILs and account for comparably low viscosities. FSI ILs tend to exhibit even lower viscosities and higher conductivities compared to TFSI ILs and are said to have superior SEI layer forming abilities. [29, 30] TFSI ILs on the other hand show higher thermal and electrochemical stabilities and are less cost-intensive. [22, 25]

5.3.2. Synthesis of various RTILs

All RTILs were synthesized under similar conditions according to a two-step reaction protocol starting from the respective tertiary amine (Figure 5.1) in 47 to 90% yield. In order to introduce the desired functional group, the tertiary amine was reacted with the respective alkyl halide in a nucleophilic substitution reaction. Subsequent exchange of the rather hard and strongly coordinating halide anion with a large and bulky, weakly coordinating anion, like TFSI and FSI, converts the quaternary ammonium salt to the respective RTIL. All synthesized RTILs were thoroughly purified in several washing steps followed by additional purification using activated charcoal. A water content below 5 ppm was ensured by drying the pre-dried ILs at 70 °C under ultra-high vacuum (106 mbar) for at least 24 h. The RTILs synthesized for this study are shown in Figure 5.2 (newly synthesized ILs are depicted in blue) and their respective physicochemical properties are listed in Table 5.1. For the sake of convenience, the ILs were abbreviated by numbers, as indicated in Figure 5.2. Further, Pyr, Pip, Mor and N₂₂₂/N₂₂₁ (1 = methyl, 2 = ethyl) denote the applied cationic core structures: pyrrolidinium, piperidinium, morpholinium and ammonium. Full characterization was carried out via ¹H and ¹³C NMR spectroscopy, electrospray ionization mass spectrometry (ESI MS)

and elemental analysis. The characterization data are fully consistent with the expected compositions and structures and document the high purity of each compound.

Figure 5. 1. Synthesize route and procedure applied in the RTIL synthesis

Figure 5. 2. Overview of the RTILs synthesized in this study (novel ILs depicted in blue). IL 1 and 7 were not synthesized but obtained from commercial sources and purified.

Table 5. 1. Physicochemical properties of the characterized RTILs

IL number	η^a [cP]	σ^a [mS cm ⁻¹]	T _d [°C]	E _A [V] vs. Fc/Fc ⁺	E _A [V] vs. Na/Na ⁺	E _C [V] vs. Fc/Fc ⁺	E _C [V] vs. Na/Na ⁺	ESW[V]
1	83.5	3.26	427.5	2.49	5.6	-2.65	0.46	5.14
2	63.0	5.26	408.6	2.35	5.46	-2.63	0.48	4.98
3	287.1	1.27	351.9	2.55	5.66	-2.49	0.62	5.04
4	222.4	1.68	286.0	1.19	4.3	-2.76	0.35	3.95
5	533.8	1.28	163.4	2.71	5.82	-2.20	0.91	4.91
6	43.6	7.66	271.2	2.22	5.33	-2.67	0.44	4.89
7	156.0	1.94	396.2	2.55	5.66	-2.75	0.36	5.30
8	98.2	2.92	390.3	2.39	5.5	-2.69	0.42	5.08
9	312.2	1.02	410.8	2.57	5.68	-2.46	0.65	5.03
10	156.2	1.91	345.9	2.18	5.29	-2.69	0.42	4.96
11	71.8	5.07	280.4	2.29	5.4	-2.73	0.38	5.02
12	119.7	3.81	261.2	2.08	5.19	-2.74	0.37	4.82
13	80.1	3.99	406.5	2.34	5.45	-2.58	0.53	4.92
14	291.5	1.20	346.1	2.55	5.66	-2.41	0.7	4.96
15	256.5	1.76	367.7	2.54	5.65	-2.63	0.48	5.17
16	123.4	2.64	403.7	2.32	5.43	-2.64	0.47	4.96
17	375.8	1.01	395.1	2.29	5.4	-2.67	0.44	4.96

^a Viscosities and conductivities determined at 23 °C.

5.3.3. Applied methods of characterization RTILs

The increasing amount of literature published on ionic liquids has generated an extensive quantity of data including manifold information regarding the properties of RTILs. [37] These data serve as a basis for further investigation, however, it has to be handled with great care. Most characterization techniques are highly dependent on the method and setup applied as well as the evaluation procedure, making a direct comparison between different sets of data very vague and not always reliable. A further major drawback of the reported data is the number of studies performed with impure or wet ILs, making some results dubious and somewhat hindering development in this field. [5] Therefore, exceptional emphasis was put on the purity of the RTILs and their

uniform and consistent characterization in this study. For the application of RTILs as electrolytes, viscosity, conductivity and thermal as well as electrochemical stability are crucial parameters and thus, they were evaluated for the RTILs presented herein.

5.3.3.1. Viscosities.

The comparably high viscosities of RTILs are one of the largest barriers for their application as pure electrolytes. [28] Both ion diffusion and conductivity in an electrolyte, and consequently the capacity of a battery cell, are highly dependent on the viscosity of the electrolyte. Therefore, the fundamental understanding of the factors that influence the viscosity of RTILs is of essential importance for the design and choice of suitable RTIL electrolytes. [28] The dynamic viscosity η is a physicochemical property that is largely governed by species interactions such as van der Waals interactions, hydrogen bonding, and coulombic forces. Further, flexibility and conformational freedom as well as the molecular mass and the shape of the respective ILs have been found to affect the viscosity. [28, 38, 39] It should be noted that viscosity values can vary depending on the measuring technique and setup. Considering this, all RTILs evaluated in this study were surveyed under identical conditions using one rheometer to enable a valid comparison (Table 1).

When comparing TFSI ILs containing the same cationic core structure, clear trends regarding the functional groups can be observed. The lowest viscosity was detected for the ether functionalized pyrrolidinium IL 2 (63 cP). Compared to the unfunctionalized analogue IL 1 (84 cP), the lower viscosity of the ether functionalized IL can be attributed to the increase of conformational degrees of freedom due to the higher flexibility of the ether side chain. This effect seems to outperform the stronger polar interactions resulting from the substitution of a C atom by the more electronegative O atom. [28, 29, 40] The same trend can be observed for the ammonium based TFSI ILs: IL 8 (98 cP) and IL 13 (80 cP). Both exhibit lower viscosities than IL 7 (156 cP). When moving to sulfur as the higher homologue of oxygen, the impact of the stronger van der Waals interactions contributes to the enhanced viscosity of IL 4 (222 cP) compared to IL 2 (63 cP) and IL 1 (84 cP). The viscosity is also increased considerably upon introduction of an ester functionality into the side chain:

$$\text{IL 3 (287 cP)} > \text{IL 1 (84 cP)} > \text{IL 2 (63 cP)}$$

$$\text{IL 9 (312 cP)} > \text{IL 7 (156 cP)} > \text{IL 8 (98 cP)}$$

$$\text{IL 14 (292 cP)} > \text{IL 13 (80 cP)}.$$

Stronger dipole–dipole interactions in combination with additional hydrogen bonding account for the enhanced viscosity in these cases.⁴² For the same reason, the viscosity of IL 5 (534 cP) is comparably high. In contrast to the side chain functionalization, an ether group incorporated in the cationic core results in a strong increase of viscosity. This effect is illustrated when comparing the two ILs containing a 6-membered ring: IL 16 (123 cP) and IL 17 (376 cP). Introduction of the ether bond in the 6-ring does not lead to an enhancement of the conformational degrees of freedom due to the rigid structure of the 6-ring. Rather, the strong polarization induced by the introduction of O determines the molecular interactions and therefore the viscosity. [28]

When comparing the viscosity of all ether- as well as ester-functionalized TFSI ILs, the following trend for the dependency of the viscosity on the cationic core structure can be found (from the lowest to the highest viscosity): Pyr < N₂₂₁ < N₂₂₂ < Pip < Mor. Excluding the functionalized core structure of the morpholinium IL, these trends can be explained by taking the impact of the ion shape into account. The decrease in viscosity for the ammonium ILs IL 8 (98 cP)/IL 9 (312 cP) vs. IL 13 (80 cP)/ IL 14 (292 cP), respectively, is caused by the asymmetry and smaller size of the N₂₂₁ cation. [38] [39] [41] Furthermore, for the ring structured ILs, the piperidinium core most likely accounts for a higher viscosity due to its chair conformation and high rigidity. On the other hand, the relatively low viscosity of the pyrrolidinium ILs (e.g. compared to an acyclic ammonium cation with an identical number of carbon atoms) seems to result from the quasi-flat geometry of the pyrrolidinium cation preventing any increases due to steric effects or entanglement. [42]

The TFSI anion and the FSI anion are characterized by an improved charge distribution and higher flexibility compared to other commonly applied anions, like BF₄ or PF₆, therefore accounting for comparably low viscosities. [42] For ILs with the same cation, FSI based ILs exhibit lower viscosities than their TFSI analogues, as evident from:

$$\text{IL 6 (44 cP)} < \text{IL 2 (63 cP)}$$

$$\text{IL 11 (72 cP)} < \text{IL 8 (98 cP)}$$

$$\text{IL 12 (120 cP)} < \text{IL 10 (156 cP)}.$$

This is expected, as the van der Waals interactions decrease for the smaller FSI anion compared to TFSI. [29, 40].

5.3.3.2. Conductivities.

Figure 5. 3. Correlation of conductivity and viscosity for the functionalized pyrrolidinium TFSI ILs.

The conductivity of an electrolyte is mainly governed by its viscosity, molecular weight and ion size. The higher the viscosity of the electrolyte and the larger and bulkier its components, the harder it is for ions to move past each other, resulting in lower conductivities. Figure 5.3 exemplarily shows the comparison of viscosity and conductivity for the pyrrolidinium based TFSI RTILs. The respective Walden plot is given in Figure. 5.4. A decreasing conductivity for the ILs with increasing viscosity can be observed, confirming the inverse connection between these two properties. Conductivities of around 1 mS cm^{-1} for the RTILs with high viscosities (4280 cP) up to 7.66 mS cm^{-1} for the least viscous IL (IL 6, 44 cP) were obtained.

Figure 5. 4. Walden plot for the functional pyrrolidinium TFSI ILs.

Thereby, the less viscous ILs exhibit conductivities that are more than sufficient for electrochemical applications. [43] In agreement with the viscosities, the introduction of an ether group in the IL side chain and the replacement of the TFSI anion by FSI enhance the conductivity of the respective ILs. On the other hand, comparing IL 5, IL 17 and IL 9, the conductivity values do not strictly follow the viscosity trend. This implies that besides viscosity, nature and spatial structure of the IL cation have an impact on the conductivity as well. It is worth noting that the difference in conductivity values becomes significantly smaller with increasing viscosity. When comparing the ester functionalized TFSI ILs (IL 3, 9, 14, 15), which all exhibit relatively high viscosities (257–312 cP), only a very small difference in their conductivities is noticeable (1.0–1.8 mS cm⁻¹). The same applies for IL 3 and IL 5, which show high viscosities (4280 cP) and nearly equal conductivities (~1.28 mS cm⁻¹). In contrast, a strong impact of the viscosity on the resulting conductivities (2.6–7.7 mS cm⁻¹) can be observed for the low viscous ether functionalized ILs (IL 2, 6, 8, 11, 13, and 16). This phenomenon has been reported before and suggests that the transport of ions in highly viscous salts is less dependent on the viscosity. [28] As expected, conductivities increase significantly with rising temperatures – about one order of magnitude between 20 and 80 °C – due to the decrease of viscosity and the enhanced ion movement at higher temperatures (Figure 5S.2). [4, 29, 43, 44]

Furthermore, it is well known that in contrast to aqueous media, the conductivities of ILs decrease upon addition of a conducting salt. [40, 44, 45] Such behavior is most likely caused by strong electrostatic interactions of the ions of the conducting salt with the ions of the IL resulting in an increased viscosity of the mixture. As stated in the literature, [7, 46] a non-linear decrease of conductivity with increasing NaFSI concentration was observed for IL 1, for example (Figure 5S.3). Further, Figure. 5S.4 shows the decrease of conductivity upon addition of the conducting salt NaFSI (0.5 M) for selected ILs, clearly underlining this phenomenon. In accordance with the literature, addition of the conducting salt to the ester functionalized ILs results in a smaller decrease in conductivity compared to the alkyl or ether functionalized ILs, underlining the enhanced salt dissolving properties of the ester functionalized ILs. [44]

5.3.3.3. Thermal stability.

Non-flammability and high thermal stability are key factors that render ILs as superior electrolytes in terms of safety, especially compared to the conventionally applied highly flammable organic electrolytes. [10, 24, 43] Thermal stability of the RTILs 1–17 was investigated by thermogravimetric analysis (TGA) and is defined by the decomposition temperature T_d . Since literature provides several different evaluation techniques to define the thermal stability from a TGA curve, an exact and uniform evaluation is barely possible. The common methods used to determine thermal stabilities include, e.g., a certain percentage of mass loss, the decomposition temperature T_d or the onset temperature T_{onset} . The contributions of the measurement process to the obtained results should not be underestimated as well: e.g., only the variation of the heating rate has been shown to influence the obtained results. [37] Additionally, it should be noted that two different stability types and measuring techniques have to be distinguished. The usually reported short-term thermal stability, which is also considered in this study, is accessible via ramped TGA. In contrast, several publications deal with the long-term thermal stability (accessible via isothermal TGA) and can therefore not be taken into consideration for comparison. [26]

Figure 5. 5. TGA curves for TFSI vs. FSI ILs (A), ether functionalized ILs (B) and pyrrolidinium ILs (C)

All investigated TFSI RTILs (with exception of IL 5) display high thermal stabilities with decomposition temperatures ranging from 346 °C to 428 °C (Table 1) and are therefore suitable electrolytes for safe battery systems. Figure 5.5A clearly shows that the nature of the anion has a strong impact on the thermal stability. Consistent with literature, the FSI based ILs 6, 11, and 12 exhibit significantly lower T_d values than their TFSI analogues IL 2, 8, and 10 ($\Delta_{\max} = 138$ °C) regardless of the cationic species. [37, 40, 47] Most likely, the higher susceptibility of the FSO₂ group in the FSI anion towards pyrolysis accounts for this behavior. [40, 47]

Thermal decomposition of the cation generally proceeds via the reverse Menshutkin reaction (dealkylation). Thus, usually, the loss of the alkyl chain leads to decomposition regardless of the cationic core structure. [31, 37] This is in accordance with the observation that for ILs with different core structures but same anion and functional group, only small differences in the T_d are apparent. Figure 5.5B confirms

this trend for the ether functionalized TFSI ILs 2, 8, 13, 16 and 17 where only the core structure is varied. Therefore, the cationic core structure has less impact on the thermal stabilities than the anion.

Among all evaluated RTILs, the unfunctionalized IL 1 exhibits the highest thermal stability with a T_d of 428 °C. As reported in literature, the thermal stability is slightly reduced with the introduction of an ether function in IL 2 to 409 °C. The synergistic electron-withdrawing effect of the N and O atoms renders the alkyl chain more susceptible to nucleophilic attack and therefore makes it easier to cleave. [31, 43, 48] The same behavior is observed for the ammonium salts IL 7 (396 °C) and IL 8 (390 °C). Comparison of all analyzed Pyr TFSI ILs (IL 1–5) (Figure. 5.5c) reveals further trends caused by the respective functional groups. As mentioned before, the unfunctionalized pyrrolidinium IL 1 shows the highest stability followed by the functionalized IL 2 (409 °C), IL 3 (352 °C) and IL 4 (271 °C). The lowest thermal stability was detected for IL 5 (163 °C). Its decomposition takes place in two steps, suggesting the loss of the nitrile group in the first step and dealkylation in the second step.

5.3.3.4. Electrochemical stability

Since electrolytes for electrochemical applications should be preferably resistant towards oxidation and reduction, it is of great importance to evaluate the electrochemical stability windows (ESWs) of potential electrolytes in advance of their application. [22] The latter is defined as the range between the cathodic (EC) and the anodic (EA) stability limits in which the involved anions and cations are not reduced or oxidized. [26] Stability limits of numerous ILs have already been reported in literature, however comparison of the data is difficult as the measurement conditions have a significant impact on the reported ESWs of the ILs. [26] Most importantly, the voltammetry curves are recorded using different working electrodes (e.g. glassy carbon, Pt, Au, and W) and against various references (e.g. Ag/Ag^+ , Li/Li^+ , I_3/I , and Fc/Fc^+ (Fc = ferrocene)). All these parameters have different effects on the electrochemistry of the evaluated ILs. [22, 25] The measurement set up, especially the volume of the measuring cell and the distance of the electrodes, has a significant influence on the results as well. Further, the conditions (mostly a defined current density) under which

the stability limit of the electrolyte is reached, are not clearly defined. This makes the exact determination of the ESW somewhat arbitrary. [49]

The herein reported ESWs were detected by linear sweep voltammetry (LSV) in a three-electrode setup using a glassy carbon working electrode and a Pt wire as the counter electrode. All values were referenced to the Fc/Fc^+ redox couple. The respective cathodic and anodic stability limits were defined as the potentials at the cut-off current density of $1 \text{ mA}/\text{cm}^2$ in the first scan. [26] The unfunctionalized TFSI ILs IL 1 and IL 7 exhibit very wide ESWs of 5.14 V and 5.3 V, respectively. However, most of the functionalized ILs in this study show only slightly smaller ESWs of around 5 V (4.82–5.17 V) and are therefore suitable for high voltage applications as well. [39] The functionalized RTILs are thought to outperform the unfunctionalized ILs in terms of conductivity, SEI layer formation and overall cell performance. Therefore, in some cases, their slightly lower electrochemical stability is rendered less important. Only the thioether functionalized IL 4 exhibits a narrow ESW of 3.95 V due to the high susceptibility of the thioether to oxidation and it is thus not considered as stable enough. [26, 50]

Figure 5. 6. Linear sweep voltammograms of the pyrrolidinium based RTILs (A) and the ether vs. ester functionalized RTILs (B).

In order to understand the respective overall stability ranges, measuring the accurate stabilities towards reduction (E_C) and oxidation (E_A) is crucial. According to literature, E_C is mainly affected by the nature of the cation and E_A is mainly affected by the nature of the anion. [25, 26, 40, 48, 51] Within this study, we focused on the

susceptibility of the ESW to three major factors: anion, cationic core structure and functional group of the respective ILs.

When comparing the LSV curves of the pyrrolidinium based TFSI ILs (IL 1–5) depicted in Fig. 4A, a clear influence of the functional groups on the cathodic stability limit can be observed. Whereas IL 2 (2.63 V) and IL 4 (2.76 V) show cathodic stabilities close to that of the unfunctionalized IL 1 (2.65 V), IL 5 (2.20 V) and IL 3 (2.49 V) exhibit fairly higher E_C values. The inferior cathodic stability of the latter two compounds is most likely caused by facile reduction of the ester or nitrile group, respectively. Decent cathodic stabilities for the ether functionalized ILs (around 2.64 V) and higher E_C values for the ester functionalized ILs (around 2.44 V) can be observed for the ammonium based TFSI ILs (IL 8, 9, 13, and 14) as well (Figure 5.6B). A slight dependence of the E_C on the cationic core structure is apparent when comparing ILs with a N₂₂₂ core (IL 8, 9) to their analogues with a N₂₂₁ core (IL 13, 14). A difference of 0.05 V for the ester and 0.11 V for the ether functionalized ones was detected. Comparison of the ether functionalized TFSI ILs without a functionalized core structure (IL 2, 8, 13, 16) in Figure 5.6B and Table 5.1 shows differences of about 0.1 V for the cationic core structures. This small shift in the reduction potentials is most likely due to a slight variability in the shielding of the respective nitrogen atoms, as previously reported for ammonium core structures. [52] The effect of the cationic core structure is even less pronounced for the anodic stability. As shown in Figure 5.6B, for the ether functionalized TFSI ILs (IL 2, 8, 13, 16) and the ester functionalized TFSI ILs (IL 3, 9, 14), almost no difference in the anodic stabilities can be observed for different cationic core structures with the same functional groups (ether or ester). The E_A values also differ by far less than 0.1 V. These results imply that the cationic core structure has a small effect on the cathodic stability and a negligible effect on the anodic stability. In contrast, the anodic stability is influenced significantly by functional groups independent of the cationic core structure to which they are attached. As shown in Figure. 4A, a broad anodic stability range from 1.19 V for IL 4 to 2.71 V for IL 5 can be covered. As mentioned before, the low oxidative stability of the thioether substituted IL 4 is most likely caused by the high susceptibility of the thioether to oxidation, thus causing it to be oxidized prior to the TFSI anion. [26, 50] All other cations should be more stable than the respective

FSI or TFSI anion in the investigated ILs. Therefore, the EA of these ILs should depend on the oxidation potential of the anions and not differ with the cation at first sight. However, based on the herein reported data, an influence of the cation on the anodic stability is evident. Such an impact has been reported before and is associated with a certain type of interaction and de/stabilization between the interacting ions. [22, 26, 48, 53] More investigations to clarify this observation are necessary and will be undertaken in the future. It should be noted that the anodic stability is further slightly influenced by the choice of the anion of the respective IL. In accordance to literature, the evaluated FSI ILs IL 6 (2.22 V), IL 8 (2.29 V) and IL 12 (2.08 V) show inferior anodic stabilities compared to their respective TFSI analogues IL 2. (2.35 V), IL 8 (2.39 V) and IL 10 (2.18 V) due to the better resistance of the TFSI anion towards oxidation. [40]

In general, the reported E_C as well as E_A values indicate that the electrochemical stability limits are mainly influenced by the functional group incorporated in the IL cation and less by the anion or the cationic core structures. When changed the reference to Na/Na^+ , except IL 3, the anodic stability is in the range from 5.19 V to 5.8 V vs. Na/Na^+ . It is a proof that ILs is a prominent solvent for high voltage SIBs. As shown in Figure 5S.5 and Table 5S.2 for selected ILs, the ILs are equally stable in combination with NaFSI (0.5 M), which is later applied as a conducting salt in the SIB half cells.

5.3.3.5. Evaluation of RTIL properties

Figure 5. 7. Summarized trends observed for the investigated physicochemical properties.

The main trends of the discussed physicochemical properties are summarized in Figure. 5.7 Viscosity and conductivity are in close relation and are mainly affected by the functional groups tethered to the different cationic core structures. Ester substituents enhance viscosity and therefore lower conductivity for all core structures, while ether groups have exactly the opposite influence. The nitrile group is responsible for the highest viscosity reported in this work. Allylic as well as thioether functionalization results in intermediate viscosities and conductivities. The morpholinium cation is the only core structure with a significantly disadvantageous effect on viscosity and conductivity. Lowest viscosities and therefore highest conductivities were detected for ILs with a pyrrolidinium core and FSI anion.

Thermal stability is lowered significantly for all RTILs containing the FSI anion regardless of the cation. Further, incorporation of a nitrile or thioether group results in thermally less stable ILs. The cationic core structure was found to have a negligible influence on thermal stability. Besides the electrochemically unstable thioether functionalized IL 4, all synthesized RTILs show large ESWs that mainly differ in their distinct anodic (E_A) and cathodic (E_C) stability limits.

5.3.4. Applied methods of characterization IL electrolytes

In SIB battery systems, ionic liquid coexists with sodium conducting salts. Hence, it is important to consider the physical properties of ionic liquid electrolytes with the

presence of conducting salts. In chapter 4, NaFSI had proved the superiority over other conducting salts in the electrochemical performance in IL electrolytes. In the next part, various methods were employed to characterize the electrolyte containing 0.5M NaFSI in ILs (EL). The purpose is to confirm the structure correlation trend in pure ILs when applying as electrolytes for SIBs.

5.3.4.1. Thermal stability by DSC methods

In practical, electrolyte is inside a closed system, e.g. coin cell, pouch cell or cylindrical cell, without exposure to ambient. It is significant different with TGA test when the sample is heated in a specific gas condition. Differential scanning calorimetry (DSC) method offers electrolyte samples a closer state to a battery system because samples are sealed in closed pans during the measurement. To confirm the thermal stability of IL electrolyte, DSC technique was employed. It should be noted that during the heating process, the explosion of DSC pans was observed due to the pressure increment. For a fair comparison, the onset temperature of exothermic reaction (t_{onset}) was indicated. The main trend of IL electrolytes in DSC measurement was similar with the observation of pure ILs in TGA.

Below are the main observations.

- (i) Compare between FSI⁻ and TFSI⁻ ionic liquids with the same cation (IL₆ vs IL₂, IL₁₁ vs IL₈), the t_{onset} of FSI – based EL₆ (303 °C) and EL₁₁ (314.4 °C) were lower than t_{onset} of FSI – based EL₂ (375 °C) and IL₈ (380.4 °C) (Figure 5.8A).

Figure 5. 8. DSC of (A) TFSI vs FSI based IL electrolytes; (B) Pyrrolidinium TFSI IL electrolytes; (C) Ammonium TFSI IL electrolytes; (C) Ether functionalize TFSI IL electrolytes.

(ii) The t_{onset} of ELs containing FSI-based IL in DSC measurement were much higher than t_d of corresponding ILs in TGA measurement (T_d : IL₆ 271.2 °C, IL₁₁ 280.4 °C, T_{onset} : EL₆ 303°C, EL₁₁ 314.4 °C).

(iii) In comparison between EL₁ to EL₅ of pyrrolidinium TFSI anion ILs (Figure 5.8B), similar trend of functional groups in pure ILs was observed for the corresponding ELs. Unfunctionalized EL₁ is the most thermal stable when no exothermal reaction occurred in the testing range, following by ether (EL₂

375 °C) and ester-functional group (EL₃ 368 °C). Sulfide-functionalized EL₄ decomposed exothermally in multiple steps, initiated at low temperature (275 °C). However, the heat flow was relatively humble until the second onset temperature (304 °C). Nitrile-functionalized EL₅ was the least thermal stable. From DSC results, the first decomposition step related with removal of nitrile group was endothermic reaction. Meanwhile, the second decomposition step, which also started at 304°C, was exothermic dealkylation process.

(iv) Among ammonium TFSI ELs (Figure 5.8D), although an endothermic reaction initiated from 360 °C, unfunctionalized EL₇ still showed the most thermally safety when no exothermic behavior was observed until 400 °C. Meanwhile, alkylene functionalized EL₁₀ was the least thermal stable, the onset temperature is 299.7 °C.

(v) Functional group contributed substantial to the thermal safety property of ELs. The effect of core structure is insignificant. When changing the core structure, the thermal behavior of series ether functionalized ELs was resemble ($t_{\text{onset}} \sim 380$ °C). The onset temperature of ELs having ring core structure (pyrrolidinium, piperidinium) were slightly higher than ammonium ELs.

5.3.4.2. Electrochemical stability in SIB coin cells

The ESW of pure RTILs and selected RTILs with NaFSI conducting salts had been investigated in section 5.3.3.3 by 3-electrode setup. However, in SIBs, the electrochemical potential is normally reported vs. Na/Na⁺ redox couple. Foremost studies in SIBs have been performed in Na half coin-cell system. The transferring results from 3-electrodes to 2-electrodes might be not comparable. It is essential to investigate the electrochemical stability window of IL electrolytes in the similar coin cell setup. In this part, the E_A of ionic electrolytes were examined in Na//C coin cells by LSV measurement (0.1 mV/s) and potential sweep (step 0.1 V / hours).

LSV methods

Figure 5. 9. LSV profile of (A) pyrrolidinium TFSI ELs (B) ammonium based ELs

Cathodic potential of all investigated ELs are below 0.25 V vs. Na/Na⁺. This level is smaller than working potential of majority anode materials. Anodic potential is more important because it decides upper working potential range of a battery. In high voltage battery systems, electrolyte should be carefully chosen to eliminate the irreversible electrolyte decomposition during the cycling. From LSV results, cation substitute group had the most contribution to the ESW of ELs. The E_A of conventional organic electrolyte NaClO₄ EC/PC was 4.66 V vs. Na/Na⁺. Figure 5.9A indicates LSV profiles of pyrrolidinium TFSI ELs. Sulfide functionalized EL₄ showed the smallest limiting potential of only 3.96 V vs. Na/Na⁺, which is not suitable for applying in high voltage SIBs. Other functionalized ELs had higher E_A, up to 5.0 V vs. Na/Na⁺, especially

cyanide function group was the most electrochemical stable. According to review literature, 5.0 V is an appropriate range for current high voltage SIBs. It should be noted that the E_A in 2-electrodes coin-cell studies is lower than E_A in 3 electrodes studies earlier (table 5.1). This does not result from the addition of conducting salt, but rather from the different setup used for the measurements. The presence of Na metal and NMO material in the half-cells will certainly influence the stability of the applied electrolytes. However, these stabilities cannot be compared one to one to the stabilities measured under “inert” conditions as applied for the LSV 3-electrode studies.

Among ammonium based ILs, alkenyl functional group EL₁₀ exhibited the least stability potential of 4.3 V vs. Na/Na⁺, which is lower than working potential of various high voltage electrodes. The trend of functional group in anodic stability was as follow: sulfide < alkenyl < ether < alkyl < ester. FSI anion EL showed slight inferior to TFSI analogue in the anodic stability (EL₁₁ 4.83 V < EL₈ 5.03 V).

Potential sweep in Na//C coin cell

The anodic stability of ELs could be investigated more clearly by measuring the current evolution during stepwise potential sweep. Ester functionalized TFSI ELs showed negligible current flow until 5.0 V vs. Na/Na⁺. At 5.3 V, the most leaking current up to 0.1 mA belonged to trimethylammonium core structure (EL₁₅). While triethylammonium EL₉ exhibited lowest current flow. The decomposition was more visible at 5.4 V when the current flow of ester functionalized ELs group increased significantly.

According to the potential sweep results of ether functionalized ELs, ether functional group had lower anodic stability range than ester functional group (5.1 V vs. 5.4 V, respectively). Pyrrolidinium core structure EL₂ showed the highest current flow at 5.1 V, following by ammonium core structure.

Figure 5. 10. Current vs. time profile subjected to a stepwise potential sweep of (A) Ester functionalize (B) Ether functionalize (C) other investigated ELs

The anodic stability order in ELs could be summarized as followed

Figure 5. 11. The trend of core structures and substitute groups for anodic stability limits

5.3.5. Electrochemical performance in SIB half cells

To gain insights into the electrochemical performance of the ILs in SIBs and their compatibility with the electrode materials, authentic cell tests in coin cells have to be performed. Therefore, a preselection of the most promising RTILs based on the evaluated physicochemical properties was made. From the above observations, however, it is obvious that compromises regarding the optimal physicochemical properties have to be made when it comes to such a selection. Combination of all features beneficial for an electrolyte, i.e. good viscosity/conductivity, high thermal stability and good SEI layer formation abilities, in one single IL is hard to achieve. Just to name two examples: the least viscous RTIL with the highest conductivity, IL 6, suffers from reduced thermal stability. Further, nitrile functionalization is said to enhance the SEI layer formation ability of electrolytes. [25, 32] In contrast, the nitrile group also accounts for a very high viscosity, reducing the applicability of IL 5 as a pure electrolyte. The drawbacks of the sole ILs might be overcome by combinations of ILs with different properties. However, to attain a meaningful approach, the electrochemical performance of the pure ILs has to be evaluated first. Once the performances of different RTILs are in hand, a reasonable selection for suitable combinations can be made.

5.3.5.2. The electrochemical performance in Hard carbon half cells

The series of IL electrolyte with NaFSI conducting salts were next tested in the Na half cells of hard carbon electrode to check their compatibility with the most popular anode material. HC_x represents for HC coin cell using the respective IL_x electrolyte. The cells were cycled in the voltage range from 0.0005 V to 2.0 V vs. Na/Na⁺ at the current rate of 50 mA g⁻¹. Overall, the discharge capacity of the cells employing IL electrolytes was inferior to the discharge capacity of HC cell employing organic electrolyte NaClO₄ EC/PC (~254 mAh g⁻¹ – Figure 5S.10). The electrochemical performance of HC cells could be summarized as follow:

- (i) Ester, cyanide functionalized IL cells, e.g. HC₃, HC₅, HC₉, etc., could not deliver any significant capacity. The results were explained by their high viscosity and low conductivity. Besides, when using Na as an electrode in the coin cell, the overpotential of stripping/plating process were unacceptably high, which leads to extremely low capacity. While HC₃, HC₅ were not operable from initial, HC₅ could deliver an initial discharge capacity of 73.4 mAh g⁻¹. However, the charge capacity was only below 1 mAh g⁻¹. It indicated that a passive layer had formed on the Na surface during the discharge process and Na ions struggled to strip out of the Na electrode in the discharge.
- (ii) HC₂, HC₇, HC₁₀ exhibited poor cycling performance. The observation for HC₂ was consistence with CC₂ in the previous part when the discharge capacity substantially reduced during the cycling. Similarly, HC₁₀ exhibited an initial

capacity of $\sim 130 \text{ mAh g}^{-1}$. The charge capacity obtained in the next cycle was just 25.2 mAh g^{-1} . This implies for the formation of SEI layer on the Na electrode during discharge process, which is the reason for large irreversible capacity. The SEI layer built up upon cycling, causing the dropping in the capacity. In the other hand, after the sharp decline initially, the discharge capacity of HC₇ increased gradually to the initial value. It might be explained by the recovering of the SEI layer during the cycling period. However, IL₇ is not a favorable option to apply as electrolyte directly in SIBs. It might work as additive for ordinary electrolyte.

(iii) HC₁, HC₈, HC₁₃ and HC₁₆ showed a stable electrochemical performance with no notable fading during the period of cycling. IL₁ had been proved its superiority as electrolyte for SIBs in chapter 4 by the formation of a stable SEI layer and a consistence stripping/plating behavior with minor overpotential. To explain the predominant of series ether functionalized IL₈, IL₁₃, IL₁₆, more effort would be done in the next chapter.

5.3.5.3. Na stripping plating behavior

From the observation of electrochemical performance for the series of IL electrolyte, an assumption based on the electroactivity of Na electrode to IL electrolytes was raised to explain for the substantial variance between ILs. Cycling stability of battery systems highly depend on the reversibility of reactions occurring in anode and cathode. In SIB half cells, the changing of active material electrode could be observed by various characterization methods. However, less attention was given on the reactivity of Na metal anode because the electrolytes using in almost studies were organic-based electrolyte. When the research focus moved to electrolyte development, the interaction between Na metal anode and electrolyte needs to be considered carefully. When contacting with ILs electrolyte, there might be apparent overpotential, causing the drift in the actual operational voltage.

To investigate the stripping/plating behavior of Na ion, tests were performed on symmetrical Na/Na cells in chronopotentiometry state, at a current of 0.1 mA cm^{-2} for 1 hour. The voltage limit was set at 3.0 V for safety reason. After a certain period, the flux of Na ion to the surface cannot endure the current, the potential changed rapidly to another potential value, at which another species is reduced/oxidized. The transition time τ is proportional to the diffusion coefficient by Sand equation:

$$\tau^{1/2} = \frac{\pi^{1/2} n F D^{1/2} C^*}{2 i_0}$$

Based on result stripping/plating test, IL electrolytes could be divided into 3 main groups.

- (1) ILs which the tests cannot be performed due to the sudden raising of potential to more than 3 V in a short period of time (Figure 5S.11). High overpotential implied that the dissolution of Na ion underneath the initial surface film required large kinetic energy. This includes ester functionalized IL₄, IL₉, IL₁₂, cyanide functionalized IL₅ and morpholinium IL₁₇. These ILs seem to decompose easily when putting in contact with metallic Na. There seem to be no functional SEI layer preventing further IL decomposition. The possible decomposition mechanisms were described below. These ILs are not suggested to be applied in SIB half-cells. However, when no metallic Na is used in practical, these application of these ILs are considerate. It is noteworthy that the viscosity of these ILs are higher than 270 cP.

Figure 5. 12. Suggested mechanisms of IL decomposition for ester functionalized cation morpholinium cation and alkenyl functionalize cation

- (2) The ILs had limited performance in Na stripping/plating test, e.g. IL₁₅, IL₁₀ (Figure 5S.11). More precisely, the overpotential of stripping/plating process increase steadily to out of the safety region. The increasing of polarization implied the raise in the electrode resistance or the thickness of the passive layer. IL₁₅ has ester group attached the other way around. Hence, the decomposition of IL could be a bit slower. Alkenyl functionalized IL₁₂ decomposed when an electron from the reactive Na is taken up by the double bond of the IL. These radicals are very reactive and can cause further electrolyte decomposition and/or polymerization. In the other hand, thioester IL₄ displayed high overpotential of stripping/plating. The value decreased after cycling, which indicated the decreasing of SEI resistance. The high susceptibility of the thioether to oxidation, thioether IL exhibited a comparably low electrochemical stability window. Although IL₄ decomposed fast, at least quite functional SEI seems to be build up, preventing further electrolyte decomposition and therefore stabilizing the system. IL₄ might be a good IL as quasi SEI building additive. These ILs have a quite high viscosity, they would probably never be a good electrolyte if using in neat.
- (3) The group of low viscosity ILs, e.g. IL₁, IL₂, IL₆, IL₇, IL₈, IL₁₁, IL₁₃, IL₁₆. They performed low polarization in stripping/plating profile, especially ether functionalized. Valley slope adapted after 10 cycles. The value and overall trend of the overpotential depended on the nature of the IL structures. It could be concluded that these ILs are compatible to Na electrodes in cycling and could be applied in Na half cells. However, in specific application, the reactivity of Na electrode to ILs need to be considered as a factor of capacity performance. The detail comparison of ether functionalized stripping/plating would be discussed in the chapter 7. The stripping/plating profiles of selected ILs were presented in Figure 5.S12.

5.3.5.1. Electrochemical performance in NMO half-cells

Due to their superior viscosity/conductivity properties, ether functionalized ILs are ideal starting materials for first electrochemical investigations in coin cells. Moreover, the thermally more stable TFSI based ILs were preferred over the FSI based ones, since enhanced safety is a main goal in future SIB technology. Different Na^+ -transport and SEI layer formation properties are expected when varying the cationic core structure. Taking all these considerations into account, evaluation of the electrochemical performance of the pyrrolidinium, piperidinium and ammonium ether-functionalized ILs IL 2, 8, 13 and 16 in SIB half cells was rendered most meaningful to start with. Electrolytes consisting of the selected ILs with NaFSI (0.5 M) as a conducting salt were thus prepared and applied in the coin cell studies described in the following.

Figure 5. 13. Electrochemical performance of NMO half-cell in (A) rate test, (B) long term cycling of first 350 cycles.

Galvanostatic cycling

The electrochemical performance of the selected IL based electrolytes and their compatibility with the active materials were tested by galvanostatic cycling in NMO half cells. The coin cells CC₂, CC₈, CC₁₃ and CC₁₆ with the respective electrolytes containing IL 2, 8, 13 and 16 were first charged to 3.8 V, followed by discharging to 1.5 V at a rate of 50 mA g⁻¹. For comparison, an NMO half-cell with the conventionally employed organic electrolyte EC/PC (1/1 wt%) with NaClO₄ (1 M) (CC_{Org}) was cycled under the same conditions. Cycling data for the first 350 cycles are depicted in Figure. 5.12B. Table 2 shows the initial discharge capacities, retention values and respective diffusion coefficients. The following observations can be summarized concerning the cycling behavior (Table 2):

Table 5. 2. Summary data of NMO coin cells (initial capacity, capacity retention and apparent diffusion coefficient)

Cell	Electrolyte	Cap _{in} ^c [mAh g ⁻¹]	Retention ^d [%]	D _{Na+} [cm ² s ⁻¹]
CC ₂	EL ₂ ^a	168.5	27	4.67 x 10 ⁻¹⁵
CC ₈	EL ₈ ^a	140.6	74	5.97 x 10 ⁻¹⁵
CC ₁₃	EL ₁₃ ^a	165.9	70	13.2 x 10 ⁻¹⁵
CC ₁₆	EL ₁₆ ^a	100.7	81	3.63 x 10 ⁻¹⁵
CC _{Org}	EC/PC ^b	175.5	32	23.9 x 10 ⁻¹⁵

^a Conducting salt: NaFSI (0.5 M); ^b NaClO₄ (1M) in EC/PC (1/1 wt); ^c initial capacity; ^d Capacity retention after 350 cycles

- (i) The cells with IL based electrolytes (CC₂, CC₈, CC₁₃, and CC₁₆) show inferior initial discharge capacities (100–169 mAh g⁻¹) compared to CC_{Org} (176 mAh g⁻¹), while CC₂ displays the best initial capacity (169 mA h g⁻¹) of all IL electrolytes tested.
- (ii) Three (CC₈, CC₁₃, and CC₁₆) of the four cells with IL electrolytes show significantly better capacity retention (69–81%) than CC_{Org} (32%) after 350 cycles.

- (iii) CC₁₆ shows the highest capacity retention with 81% of the initial capacity being retained after 350 cycles.
- (iv) CC₂ exhibits the worst performance – even lower than CC_{Org} – in spite of the high initial capacity.

Further, the charge–discharge curves of the respective cells are given in Figure 5S.6 and 5S.7, which show that the fading in cycling performance correlates well with voltage fading. Viscosity and conductivity of an electrolyte influence its ion transport properties and thus can have an impact on the initial capacity of the evaluated cell. Therefore, the higher viscosities and lower conductivities of ILs (Table 1) most likely account for the lower initial capacities of the cells with IL electrolytes compared to CC_{Org}. Within the cells with IL electrolytes (CC₂, CC₈, CC₁₃, and CC₁₆), the trend of the initial capacities can be correlated with the trends of the viscosity/conductivity of the respective ILs. Poor cycling stability for NMO half cells with organic electrolyte has been reported before and was mainly attributed to phase transitions in the cathode material during the charge–discharge processes. [9] However, the superior performance of the cells with IL electrolytes CC₈, CC₁₃, and CC₁₆ over CC_{Org} may be a result of multiple synergistic effects. Firstly, it is known that the formation of a stable SEI layer during the first cycles is crucial for cell durability. In contrast to organic electrolytes, IL based electrolytes have been shown to enable the formation of a more stable/conductive SEI layer in SIBs. Such a layer prevents continuous electrolyte decomposition, thus enhancing cycling stability. [24] Similarly, the dissolution of Mn³⁺ is a common reason for capacity fading of cells with organic electrolytes and it might also be reduced when employing IL electrolytes. [6] Further, capacity losses arising due to phase transition of the active material during the charge–discharge processes might be less pronounced when employing certain IL electrolytes. Since the instability of CC_{ORG} could also result from the perchlorate anion, the effect of the conducting salt on the cycling stability of NMO half-cells was studied. Therefore, half-cells containing EC/PC and different conducting salts (NaClO₄, NaFSI and NaTFSI, Figure 5.S8) were subjected to galvanostatic cycling. No major difference could be observed in the cycling stability, suggesting that the organic solvent mixture has a greater effect on stability than the conducting salt in case of the evaluated system. The exact reasons for the respective cycling stabilities – i.e. the superior performance of

CC₈, CC₁₃, and CC₁₆ and the poor performance of CC₂ and CC_{Org} – require detailed studies of the electrode materials and the nature of the surface layers formed on them. Further, the electrochemical stability of the electrolytes against sodium metal poses a possible reason for the electrolyte-dependent cycling stability and has to be considered as well. [52, 53] However, the observations made herein hint towards a beneficial effect of piperidinium-based electrolytes on cell stability. Whereas, the pyrrolidinium core seems to be less compatible with the SIB system.

Rate testing

To evaluate the performance under conditions of fast charge and discharge, rate tests with rates ranging from 20 to 400 mA g⁻¹ were performed. Taking the results from the rate test (Figure 5.12A) into account, the following observations can be made:

- (i) At the highest rate (400 mA g⁻¹), CC_{Org} shows the highest discharge capacity (86 mAh g⁻¹).
- (ii) Among the cells with IL based electrolytes, CC₁₃ has the best rate performance (68 mA h g⁻¹ at 400 mA g⁻¹), followed by CC₈ and CC₂ while CC₁₆ shows the lowest capacity. This is in accordance with the cycling behavior described above.
- (iii) CC₈, CC₁₃ and CC₁₆ are stable under high rate cycling, as revealed by the retention of capacity at 50 mA g⁻¹ after high rate cycling. This result indicates that these systems are reasonably stable against reversible sodiation at high rates and no considerable side reactions occur during cycling. [54]
- (iv) CC₂ and CC_{Org} are clearly affected by fading and are unable to retain their capacity at 50 mA g⁻¹ after high rate cycling, indicating an instability of these systems under high rate cycling.

Enhanced high rate performance of cells with organic electrolytes compared to cells with IL electrolytes has been reported before and is mainly due to the relatively high viscosity and low conductivity of the IL electrolytes. [23] For further explanation of the rate test results, apparent sodium-ion diffusion coefficients were determined using cyclic voltammetry are provided in Table 5.2. It should be noted that the given sodium-ion diffusion coefficients are only rough estimations and are not “physical quantities”, since the conditions for applicability of the Randle–Sevcik equation are not strictly

met. Among the IL electrolytes, the corresponding sodium diffusion coefficients show the highest values for IL 13 in CC₁₃ and the lowest for IL 16 in CC₁₆. The higher the viscosity of the electrolyte, the lower the ion mobility, resulting in a low diffusion coefficient and reduced capacity.

Generally, the trend obtained in the diffusion coefficient studies is consistent with the high rate test performance. At higher rates, the combined effect of Na⁺ ion transport coupled with the reduced kinetics of intercalation results in lower capacities for the cells containing IL electrolytes compared to the organic electrolyte. While, from a fast charge perspective, the numbers still have room for improvement, it should be noted that there is scope for further optimization of the electrolyte (i.e. modification of its viscosity/conductivity via additives or mixtures) and thus improving capacity at higher rates. Overall, the results are very promising for IL electrolytes. The IL based electrolytes containing IL 8, 13 and 16 exhibit a significantly better cycling performance than the conventional organic electrolyte in NMO half-cells.

5.4. Conclusion

As summary, ILs have been tested in various SIBs systems to investigate the compatibility with various types of electrode materials. Ester functionalized and cyanide functionalized did not show any capacity in hard-carbon half-cells. The inferiority was explained by their high viscosity and the occurrence of passive layer preventing the Na dissolution and deposition onto Na surface. Thioether functionalized IL₄ had a narrow ESW, which is not suggested to apply as electrolyte. Due to Na stripping/plating performance, the IL₄ electrolyte might be a good IL as quasi SEI building additive. Non-functionalized IL₁ and ether functionalize IL₈, IL₁₃, IL₁₆ displayed a stable cycling in hard-carbon half-cells. However, their obtained capacity is not comparable to organic electrolyte analogue. In NMO-half cells, together with IL₁ electrolyte mentioned in chapter 4, the IL based electrolytes containing IL 8, 13 and 16 exhibit a significantly better cycling performance than the conventional organic electrolyte in NMO half-cells. Therefore, the combination of the IL electrolytes and SIB electrodes can lead to superior charge–discharge properties in combination with high safety and stable performance of the SIB system, which is crucial for largescale

energy storage applications. [24] In order to further improve the systems and obtain more valuable information regarding the relation of the IL nature to the electrochemical performance, the remaining functionalized RTILs from Figure 5.2 have to be tested and evaluated as well. Moreover, detailed investigations based on XRD, XPS and EDX studies of the cycled NMO material have to be undertaken to explain the observed trends, enabling a tailored approach towards even better electrolytes.

5.5. References

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5.6. Supporting information

IL characterization

Figure 5. S 1. Correlation of conductivity (TFSI ILs black, FSI ILs green) and conductivity (blue) of all RTILs reported in the chapter (number on x axis represent the number of respective ILs).

Figure 5. S 2. Temperature dependence of the conductivity of selected RTILs with conducting salts (NaFSI 0.5 M)

Figure 5. S 3. Dependency of conductivity of IL₁ on the concentration of NaFSI conducting salt.

Figure 5. S 4. Comparison of conductivity of with and without conducting salt (NaFSI 0.5M) for selected ILs

Table 5. S 1 Comparison of conductivity and viscosity of IL1 with NaTFSI and NaFSI at RT

	Conductivity σ (mS/cm)	Viscosity η (cP)
IL1 + NaFSI (0.5 M)	1.61	1.52
IL1 + NaTFSI (0.5 M)	1.22	1.62

Figure 5. S 5. Linear sweep voltammograms of IL₂, IL₈, IL₁₃ and IL₁₆ with (A) and without (B) NaFSI (0.5M)

Table 5. S 2 Electrochemical stability vs. Fc/Fc⁺ for ILs 2, 8, 13, 16 with (EL) and without NaFSI 0.5M

	E _A [V]	E _C [V]	ESW [V]		E _A [V]	E _C [V]	ESW [V]
EL ₂	2.41	-2.99	5.40	IL ₂	2.34	-2.58	4.92
EL ₈	2.41	-2.78	5.19	IL ₈	2.35	-2.63	4.98
EL ₁₃	2.46	-2.91	5.37	IL ₁₃	2.32	-2.64	4.96
EL ₁₆	2.46	-2.75	5.21	IL ₁₆	2.39	-2.69	5.08

Electrochemical performances

Figure 5. S 6 Galvanostatic charge discharge profiles of CC_2 , CC_8 , CC_{13} , CC_{16} and CC_{org} (Na/NMO half-cells)

Figure 5. S 7. Comparison charge-discharge profiles of CC₂, CC₈, CC₁₃, CC₁₆ and CC_{org} at cycle 2, 10, 100 and 300 (Na/NMO half-cells)

Figure 5. S 8. Galvanostatic cycling of NMO half-cells with EC/PC electrolyte containing different conducting salts and concentration.

Figure 5. S 9. Discharge capacity of Hard carbon/Na cells employing NaClO_4 (1M) in EC/PC (HC_{Org}) and NaFSI (0.5 M) in IL_1 (HC_1) in the first 50 cycles.

Figure 5. S 10. Failed stripping/plating profiles of ionic liquid electrolytes in Na/Na symmetrical cells

Figure 5. S 11. Limited stripping/plating profiles of ionic liquid electrolytes (Na symmetrical cells).

Figure 5. S 12. Stripping/plating profile of functional IL electrolytes (Na symmetrical cells).

Analytical data of the synthesis RTILs

General remarks: Unless noted otherwise, all reactions except for the anion exchanges were carried out under argon atmosphere with standard Schlenk techniques. All chemicals were purchased from commercial sources. The amine precursors and all non-dry solvents were purified by distillation prior to use. Dry solvents were dried using an MBraun Solvent Purification System. IL 1 and 7 were purchased from Iolitec (99%) and purified and dried according to the general procedure described in the following.

NMR spectroscopy: NMR spectra were acquired on a Bruker Advance Ultrashield 400 MHz spectrometer. All ^1H and ^{13}C chemical shifts δ are reported in parts per million (ppm), with the residual solvent peak serving as internal reference. The abbreviation of the signal multiplets are as followed: s-singlet, d-doublet, t-triplet, q-quartet, mmultiplet. The coupling constant J is stated as average value in Hz.

Mass spectrometry (ESI MS): Mass spectra were acquired on a Thermo Scientific LCQ Fleet by Thermo Fischer Scientific (injection of 1 μ l of a $\sim$ 1 mg/ml sample in acetonitrile) using electron spray ionization (ESI) and a 3D-ion trap as detector.

Elemental analysis (EA): Elemental analysis was performed by the micro analytical laboratory at the Department of Chemistry of the Technische Universität München. The elements C and H and N were determined with a combustion analyzer (EURO EA-CHNS, HEKAtech).

Water content: Water content of the RTILs was determined with 2 g of the respective IL by Karl Fischer titration with a Mettler-Toledo DL39 with diaphragm and combi coulomat solution.

Synthesis of the IL precursor salts: The precursor salts for all ILs except the precursor for **IL 14 (PC 14)**, were synthesized following literature procedures 6-14 with slight modifications in the purification procedures in some cases. In general, for the quaternization reactions the respective functionalized alkylhalide is added dropwise a solution of the respective amine precursor under argon atmosphere. The resulting reaction mixture is stirred at room temperature or under reflux for 24 to 72 h. Afterwards, the crude product is obtained either by removal of the solvent under reduced pressure, or by addition of diethyl ether to the reaction mixture and subsequent filtration. The crude product is washed with diethyl ether/ethyl acetate or toluene three times followed by a further washing step with pentane. After recrystallization, quaternary ammonium halide salts are obtained as white to off white solids.

1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethane)sulfonamide (**IL 2**): Colourless liquid, 74% yield, $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 296.7 K, ppm): δ = 3.82 – 3.74 (m, 2H, OCH_2), 3.68 – 3.50 (m, 6H, NCH_2), 3.38 (s, 3H, NCH_3), 3.10 (s, 3H, OCH_3), 2.31 – 2.19 (m, 4H, $\text{PyrCH}_2\text{CH}_2$); $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz, 297.4 K, ppm) δ = 119.96 (q, CF_3), 66.5, 65.8, 63.6, 59.2, 49.0, 21.5; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_5\text{S}_2$: C 28.30 H 4.28 N 6.60 S 15.11; found: C 28.23 H 4.26 N 6.57 S 15.15; MS (ESI, MeCN): m/z = 144.09; 567.18 (calcd. for $[\text{C}_8\text{H}_{18}\text{NO}^+]$: 144.14; $[\text{C}_8\text{H}_{18}\text{NO}^+ \text{TFSI} \text{C}_8\text{H}_{18}\text{NO}^+]$: 568.18); η [cP]: 63; Td [$^\circ\text{C}$]: 408.6; σ [mS/cm]: 5.26; ESW [V]: 4.98.

1-(2-methoxy-2-oxoethyl)-1-methylpyrrolidinium bis(trifluoromethane)sulfonamide (**IL 3**): Colourless liquid, 78% yield, $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 296.6 K, ppm): $\delta = 3.82 - 3.74$ (m, 2H, OCH_2) 3.68 – 3.50 (m, 6H, NCH_2), 3.38 (s, 3H, NCH_3), 3.10 (s, 3H, OCH_3), 2.31 – 2.19 (m, 4H, $\text{PyrCH}_2\text{CH}_2$); $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz, 297.9 K, ppm) $\delta = 165.12$, 119.90, 65.99, 62.21, 53.33, 49.73, 21.58.; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{16}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$: C 27.40 H 3.68 N 6.39 S 14.63; found: C 27.33 H 3.66 N 6.36 S 14.80; MS (ESI, MeCN): $m/z = 158.02$; 595.49 (calcd. for $[\text{C}_8\text{H}_{16}\text{NO}_2^+]$: 158.12; $[\text{C}_8\text{H}_{16}\text{NO}_2^+ \text{TFSI}^- \text{C}_8\text{H}_{16}\text{NO}_2^+]$: 596.15); η [cP]: 287.1; Td [$^\circ\text{C}$]: 351.9; σ [mS/cm]: 1.27; ESW [V]: 5.04

1-methyl-1-(2-(methylthio)ethyl)pyrrolidinium bis(trifluoromethane)sulfonamide (**IL 4**): Colourless liquid, 94% yield, $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 299.2 K, ppm): $\delta = 3.65 - 3.48$ (m, 6H, NCH_2), 3.09 (s, 3H, NCH_3), 2.96 – 2.84 (m, 2H, CNCH_2), 2.37 – 2.24 (m, 4H, $\text{PyrCH}_2\text{CH}_2$). $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz, 298.5 K, ppm) $\delta = 119.02$, 64.69, 63.50, 48.14, 26.98, 21.33, 15.14; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_4\text{S}_3$: C 27.27 H 4.12 N 6.36 S 21.84; found: C 27.08 H 4.13 N 6.35 S 22.18; MS (ESI, MeCN): $m/z = 159.98$; 599.57 (calcd. for $[\text{C}_8\text{H}_{18}\text{NS}^+]$: 160.12; $[\text{C}_8\text{H}_{18}\text{NS}^+ \text{TFSI}^- \text{C}_8\text{H}_{18}\text{NS}^+]$: 600.15); η [cP]: 222.4; Td [$^\circ\text{C}$]: 286.0; σ [mS/cm]: 1.68; ESW [V]: 3.95.

1-(2-cyanoethyl)-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)amide (**IL 5**): Colourless liquid, 47 % yield, $^1\text{H-NMR}$ (CDCl_3 , 400 MHz 299.2 K, ppm): $\delta = 3.63$ (t, 3J = 7.3 Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CN}$), 3.59 – 3.38 (m, 4H, NCH_2CH_2), 3.02 (s, 3H, CH_3), 2.98 (d, 3J = 7.3 Hz, 6H), 2.27 – 2.16 (m, 4H, $\text{PyrCH}_2\text{CH}_2$); $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz, 299.7 K, ppm) $\delta = 119.89$, 116.26, 65.21, 58.84, 48.16, 21.36, 13.42; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{15}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$: C 28.64 H 3.61 N 10.02 S 15.29; found: C 28.31 H 3.62 N 9.93 S 15.42; MS (ESI, MeCN): $m/z = 139.07$; 557.90 (calcd. for $[\text{C}_8\text{H}_{15}\text{N}_2^+]$: 139.12; $[\text{C}_8\text{H}_{15}\text{N}_2^+ \text{TFSI}^- \text{C}_8\text{H}_{15}\text{N}_2^+]$: 558.16); η [cP]: 533.8; Td [$^\circ\text{C}$]: 163.4; σ [mS/cm]: 1.28; ESW [V]: 4.91.

1-(2-methoxyethyl)-1-methylpyrrolidinium bis(fluorosulfonyl)amide (**IL 6**): Light yellow liquid, 57% yield, $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 299.0 K, ppm): $\delta = 3.89 - 3.78$ (m, 2H, OCH_2), 3.73 – 3.51 (m, 6H, NCH_2), 3.43 (s, 3H, NCH_3), 3.16 (s, 3H, OCH_3), 2.39 – 2.21 (m, 4H, $\text{PyrCH}_2\text{CH}_2$); $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz, 299.7 K, ppm) $\delta = 66.51$, 65.96, 63.78, 59.33, 49.17, 21.64; elemental analysis calcd (%) for $\text{C}_8\text{H}_{18}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$: C 29.62 H 5.59 N 8.64 S 19.77; found: C 29.40 H 5.68 N 8.59 S 19.72; MS (ESI, MeCN): $m/z = 143.97$; 467.60 (calcd. for $[\text{C}_8\text{H}_{18}\text{NO}^+]$: 144.14; $[\text{C}_8\text{H}_{18}\text{NO}^+ \text{FSI}^- \text{C}_8\text{H}_{18}\text{NO}^+]$: 468.20); η [cP]: 43.6; Td [$^\circ\text{C}$]: 271.2; σ [mS/cm]: 7.66; ESW [V]: 4.89.

N,N,N-triethyl-2-methoxyethanamonium bis(trifluoromethane)sulfonamide (**IL 8**): Colourless liquid, 70% yield, ^1H -NMR (CDCl_3 , 400 MHz, 299.2 K, ppm): δ = 3.80 – 3.70 (m, 2H, OCH_2), 3.44 (dt, $2,3J$ = 7.4, 2.8 Hz, 2H, NCH_2), 3.41 – 3.31 (m, 9H, OCH_3 , NCH_2CH_3), 1.33 (t, $3J$ = 7.2 Hz, 9H, CH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 299.6 K, ppm) δ = 120.03, 65.73, 59.35, 56.93, 54.15, 7.62; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_5\text{S}_2$: C 30.00, H 5.04, N 6.36, S 14.56; found: C 30.01, H 4.94, N 6.42, S 14.37; MS (ESI, MeCN): m/z = 160.15; 599.68 (calcd. for $[\text{C}_9\text{H}_{22}\text{NO}^+]$ 160.17; $[\text{C}_9\text{H}_{22}\text{NO}^+ \text{TFSI}^- \text{C}_9\text{H}_{22}\text{NO}^+]$: 600.26); η [cP]: 98.2; Td [$^\circ\text{C}$]: 390.3; σ [mS/cm]: 2.92; ESW [V]: 5.08.

N,N,N-triethyl-2-methoxy-2-oxoethanamonium bis(trifluoromethane)sulfonamide (**IL 9**): Colourless liquid, 90% yield, ^1H -NMR (CDCl_3 , 400 MHz, 296.7 K, ppm): δ = 4.08 (s, 2H, NCH_2CO), 3.85 (s, 3H, OCH_3), 3.58 (q, $3J$ = 7.3 Hz, 6H, NCH_2CH_3), 1.37 (t, $3J$ = 7.3 Hz, 9H, NCH_2CH_3) ^{13}C -NMR (CDCl_3 , 101 MHz, 297.3 K, ppm) δ = 164.51, 119.97, 55.34, 54.89, 53.59, 7.67; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$: C 29.08 H 4.44 N 6.17 S 14.11; found: C 29.05 H 4.30 N 6.21 S 13.99; MS (ESI, MeCN): m/z = 174.06 (calcd. for $[\text{C}_9\text{H}_{20}\text{NO}_2^+]$: 174.15); η [cP]: 312.2; Td [$^\circ\text{C}$]: 410.8; σ [mS/cm]: 1.02; ESW [V]: 5.03.

N,N,N-triethylbut-2-enamonium bis(trifluoromethane)sulfonamide (**IL 10**): Colourless liquid, 88% yield, ^1H -NMR (CDCl_3 , 400 MHz, 299.7 K, ppm): δ = trans: 6.22 – 6.06 (m, 1H, CH_3CHCH), 5.52 – 5.41 (m, 1H, CH_3CHCH), 3.68 (d, $3J$ = 7.5 Hz, 2H, NCH_2CH), 3.20 (q, $3J$ = 7.3 Hz, 6H, NCH_2CH_3), 1.83 (d, $3J$ = 6.5 Hz, 3H, CHCH_3), 1.31 (t, $3J$ = 7.2 Hz, 9H, NCH_2CH_3); cis: 6.22 – 6.06 (m, 1H, CH_3CHCH), 5.52 – 5.41 (m, 1H, CH_3CHCH), 3.80 (d, $3J$ = 7.6 Hz, 2H, NCH_2CH), 3.25 (q, $3J$ = 7.3 Hz, 6H, NCH_2CH_3), 1.79 (d, $3J$ = 6.0 Hz, 3H, CHCH_3), 1.31 (t, $3J$ = 7.2 Hz, 9H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 304.2 K, ppm) δ = 141.88, 118.70, 116.06, 59.34, 52.64, 18.36, 7.41; elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$: C 33.03 H 5.08 N 6.42 S 14.69; found: C 32.85 H 5.07 N 6.46 S 14.62; MS (ESI, MeCN): m/z = 156.11; 591.96 (calcd. for $[\text{C}_{10}\text{H}_{22}\text{N}^+]$: 156.17; $[\text{C}_{10}\text{H}_{22}\text{N}^+ \text{TFSI}^- \text{C}_{10}\text{H}_{22}\text{N}^+]$: 592.27); η [cP]: 156.2; Td [$^\circ\text{C}$]: 345.9; σ [mS/cm]: 1.91; ESW [V]: 4.96.

N,N,N-triethyl-2-methoxyethanamonium bis(fluorosulfonyl)imide (**IL 11**): Light yellow liquid, 65% yield, ^1H -NMR (CDCl_3 , 400 MHz, 299.0 K, ppm): δ = 3.80 – 3.71 (m, 2H, OCH_2), 3.47 – 3.41 (m, 2H, NCH_2), 3.41 – 3.33 (m, 9H, OCH_3 , NCH_2CH_3), 1.34 (t, $3J$ = 7.2 Hz, 9H, CH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 299.5 K, ppm) δ = 65.75, 59.44, 56.95, 54.22, 7.72; elemental analysis calcd (%) for $\text{C}_9\text{H}_{22}\text{F}_2\text{N}_2\text{O}_5\text{S}_2$: C 31.76 H 6.51 N 8.23 S 18.84; found: C 31.58 H 6.53 N 8.17 S 18.58; MS (ESI, MeCN): m/z = 160.01; 499.60 (calcd. for $[\text{C}_9\text{H}_{22}\text{NO}^+]$:

160.17; $[\text{C}_9\text{H}_{22}\text{NO}^+ \text{FSI}^- \text{C}_9\text{H}_{22}\text{NO}^+]$: 500.26; η [cP]: 71.8; Td [$^{\circ}\text{C}$]: 280.4; σ [mS/cm]: 5.07; ESW [V]: 5.02.

N,N,N-triethylbut-2-enammonium bis(fluorosulfonyl)amide (**IL 12**): Colourless liquid, 62% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.7 K, ppm): δ = trans: 6.29 – 6.09 (m, 1H, CH_3CHCH), 5.58 – 5.41 (m, 1H, CH_3CHCH), 3.71 (d, $3J = 7.5$ Hz, 2H, NCH_2CH), 3.24 (q, $3J = 7.3$ Hz, 6H, NCH_2CH_3), 1.86 (d, $3J = 6.5$ Hz, 3H, CHCH_3), 1.36 (t, $3J = 7.2$ Hz, 9H, NCH_2CH_3); cis: 6.29 – 6.09 (m, 1H, CH_3CHCH), 5.58 – 5.41 (m, 1H, CH_3CHCH), 3.83 (d, $3J = 7.6$ Hz, 2H, NCH_2CH), 3.32 – 3.27 (6H, NCH_2CH_3), 1.82 (d, $3J = 7.2$ Hz, 3H, CHCH_3), 1.36 (t, $3J = 7.2$ Hz, 9H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 299.3 K, ppm) δ = 142.20, 115.97, 59.46, 52.76, 18.53, 7.57; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_4\text{S}_2$: C 35.70 H 6.59 N 8.33 S 19.06; found: C 35.76 H 6.66 N 8.31 S 19.08; MS (ESI, MeCN): m/z = 156.00; 491.56 (calcd. for $[\text{C}_{10}\text{H}_{22}\text{N}^+]$: 156.17; $[\text{C}_{10}\text{H}_{22}\text{N}^+ \text{FSI}^- \text{C}_{10}\text{H}_{22}\text{N}^+]$: 492.27); η [cP]: 119.7; Td: 261.2 [$^{\circ}\text{C}$]; σ [mS/cm]: 3.81; ESW [V]: 4.82.

N,N-diethyl-2-methoxy-N-methylethanammonium bis(trifluoromethane)sulfonimide (**IL 13**): Light yellow liquid, 89% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.0 K, ppm): δ = 3.66 (td, $2,3J = 4.5, 2.3$ Hz, 2H, OCH_2), 3.43 – 3.23 (m, 9H, NCH_2CH_3 , NCH_2 , NCH_3), 2.91 (s, 3H, OCH_3), 1.26 (t, $3J = 7.3$ Hz, 6H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 297.9 K, ppm) δ = 119.7, 65.55, 60.07, 58.84, 57.69, 47.83, 7.60; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_5\text{S}_2$: C 28.17, H 4.73, N 6.57, S 15.07; found: C 28.03, H 4.74, N 6.58, S 14.90; MS (ESI, MeCN): m/z = 146.02; 571.49 (calcd. for $[\text{C}_8\text{H}_{20}\text{NO}^+]$: 146.15; $[\text{C}_8\text{H}_{20}\text{NO}^+ \text{TFSI}^- \text{C}_8\text{H}_{20}\text{NO}^+]$: 572.23); η [cP]: 80.1; Td [$^{\circ}\text{C}$]: 406.5; σ [mS/cm]: 3.99; ESW [V]: 4.92.

N,N-diethyl-2-methoxy-N-methyl-2-oxoethanaminium bis((trifluoromethyl)sulfonyl)amide (**IL 14**): Colourless liquid, 80% yield, ^1H -NMR (CDCl_3 , 400 MHz, 298.52 K, ppm): δ = 4.13 (s, 2H, NCH_2CO), 3.84 (s, 3H, OCH_3), 3.64 (q, $3J = 7.4$ Hz, 4H, NCH_2CH_3), 3.21 (s, 3H, NCH_3), 1.39 (t, $3J = 7.4$ Hz, 6H, NCH_2CH_3); ^{13}C -NMR (CDCl_3 , 101 MHz, 301.0 K, ppm) δ = 164.57, 118.36, 58.29, 58.21, 53.56, 48.34, 8.05; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$: C 27.27 H 4.12 N 6.36 S 14.56; found: C 27.17 H 4.15 N 6.41 S 14.69; MS (ESI, MeCN): m/z = 160.02, 599.43 (calcd. for $[\text{C}_8\text{H}_{18}\text{NO}_2^+]$: 160.13; $[\text{C}_8\text{H}_{18}\text{NO}_2^+ \text{TFSI}^- \text{C}_8\text{H}_{18}\text{NO}_2^+]$: 600.18); η [cP]: 291.5; Td [$^{\circ}\text{C}$]: 346.1; σ [mS/cm]: 1.20; ESW [V]: 4.96.

2-acetoxy-N,N,N-trimethylethanammonium bis(trifluoromethane)sulfonamide (**IL 15**): Colourless liquid, 87% yield, ^1H -NMR (CD_3CN , 400 MHz, 297.8 K, ppm): δ = 4.40 (dq, $2,3J = 7.6, 2.5$ Hz, 2H, OCH_2), 3.54 (dt, $2,3J = 4.9, 2.5$ Hz, 2H, NCH_2), 3.09 (s, 3H, NCH_3), 2.05 (s, 3H, CH_3); ^{13}C -NMR (CD_3CN , 101 MHz, 298.5 K, ppm) δ = 170.88, 120.85, 65.69, 58.44,

54.67, 20.83; elemental analysis calcd (%) for $C_9H_{16}F_6N_2O_6S_2$: C 25.35 H 3.78 N 6.57 S 15.04; found: C 25.17

H 3.78 N 6.51 S 15.01; MS (ESI, MeCN): $m/z = 145.94$; 571.54 (calcd. for $[C_7H_{16}NO_2]^+$: 146.12; $[C_7H_{16}NO_2^+ TFSI^- C_7H_{16}NO_2^+]$: 572.15); η [cP]: 256.5; Td [$^{\circ}C$]: 367.7; σ [mS/cm]: 1.76; ESW [V]: 5.17.

1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethane)sulfonamide (**IL 16**): Colourless liquid, 80% yield, 1H -NMR ($CDCl_3$, 400 MHz, 299. K, ppm): $\delta = 3.78$ (t, 3J = 4.6 Hz, 2H, OCH_2), 3.53 (t, 3J = 4.6 Hz, 2H, NCH_2), 3.50 – 3.30 (m, 7H, NCH_3 , NCH_2), 3.11 (s, 3H, OCH_3), 1.89 (p, J = 6.0 Hz, 4H, $PipCH_2$), 1.76 – 1.64 (m, 2H, $PipCH_2$); ^{13}C -NMR ($CDCl_3$, 101 MHz, 307.7 K, ppm) $\delta = 121.60$, 65.75, 62.97, 62.72, 59.15, 49.31, 20.70, 20.13; elemental analysis calcd (%) for $C_{11}H_{20}F_6N_2O_5S_2$: C 30.14 H 4.60 N 6.39 S 14.63; found: C 29.98 H 4.63 N 6.41 S 14.51; MS (ESI, MeCN): $m/z = 158.13$; 595.84 (calcd. for $[C_9H_{20}NO]^+$: 158.15; $[C_9H_{20}NO^+ TFSI^- C_9H_{20}NO^+]$: 596.23); η [cP]: 123.4; Td [$^{\circ}C$]: 403.7; σ [mS/cm]: 2.64; ESW [V]: 4.96.

4-(2-methoxyethyl)-4-methylmorpholinium bis((trifluoromethyl)sulfonyl)amide (**IL 17**): Colourless liquid, 75% yield, 1H -NMR ($CDCl_3$, 400 MHz, 297.8 K, ppm): $\delta = 4.01$ (t, 3J = 4.4 Hz, 4H, $PipOCH_2$), 3.90 – 3.84 (m, 2H, OCH_2), 3.78 – 3.72 (m, 2H, $PipNCH_2$), 3.68 – 3.60 (m, 2H, $PipNCH_2$), 3.53 – 3.43 (m, 2H, NCH_2), 3.39 (s, 3H, NCH_3), 3.30 (s, 3H, OCH_3); ^{13}C -NMR ($CDCl_3$, 101 MHz, 298.9 K, ppm) $\delta = 118.33$, 65.66, 64.05, 61.50, 60.75, 59.34, 48.87; elemental analysis calcd (%) for $C_{10}H_{18}F_6N_2O_6S_2$: C 27.27 H 4.12 N 6.36 S 14.56; found: C 27.36 H 4.17 N 6.35 S 14.32; MS (ESI, MeCN): $m/z = 160.03$; 599.47 (calcd. for $[C_8H_{18}NO_2]^+$: 160.13; $[C_8H_{18}NO_2^+ TFSI^- C_8H_{18}NO_2^+]$: 600.18); η [cP]: 375.8; Td [$^{\circ}C$]: 395.1; σ [mS/cm]: 1.01; ESW [V]: 4.96

Chapter 6

Investigation of the Electrochemical and Thermal Stability of an Ionic Liquid based $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2/\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ Sodium-Ion Full-Cell

Electrolytes based on non-flammable and electrochemically and thermally stable ionic liquids (ILs) are rendered promising alternatives to the conventionally applied organic electrolytes for lithium as well as sodium ion batteries (SIBs). In this study the electrochemical performance and thermal stability of a SIB full-cell containing an IL based electrolyte is evaluated and compared to a reference system employing a conventional organic electrolyte. Compatibility of the IL electrolyte with the electrode materials $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO) and $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ (NVO) is assured by SIB half-cell studies. In NMO/NVO full-cells the IL electrolyte outperforms the organic electrolyte in terms of cycling stability and columbic efficiency, reaching a retention of 76% after 100 cycles. Studies at 75 °C show that, in contrast to the system based on the organic electrolyte, the IL-based SIB is capable of operating at elevated temperatures. Further, for the first time the superior safety of an IL-based SIB full-cell over the organic analogue is proven using Accelerating Rate Calorimetry (ARC) underlining the benefits of the IL based electrolyte.

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6.1 Introduction

Lithium ion batteries (LIBs) have emerged as a popular choice for energy storage in modern portable electronic devices and grid-scale energy storage applications. However, owing to the limited lithium reserves, the development of alternative rechargeable battery systems independent of lithium becomes necessary in a century of steadily growing energy demand. Due to the high abundance and low cost of sodium, sodium ion batteries (SIBs) are receiving growing attention.[1-3]

SIBs are especially suitable for stationary applications like large-scale energy storage systems, where energy density is not very critical. These energy storage systems are required to stabilize the intermittent energy provided by renewable energy sources such as wind-, solar- or water-power. So far, the only commercially employed sodium based technologies are Na-S and Na-NiCl₂ batteries, which require high operating temperatures (~300 °C) though.[4-7] Research is focusing on the development of economically viable SIBs with reasonable performance and cycling stability. Therefore, compatible electrode materials and electrolytes with reasonably high Na⁺ conductivity and the ability to form good electrode/electrolyte interfaces are indispensable.[5, 8] Especially during the last decade, various cathode and anode materials were tested with mostly organic electrolytes, steadily improving the performance and energy density of SIBs.[1-2, 6, 9-10] However, in contrast to the well-established LIBs, sodium ion based systems are still far from realization, further pushing the research and development of SIB electrode materials as well as electrolytes.[8, 11-13]

For a feasible and safe SIB full-cell the electrolyte as well as the electrode materials are crucial, since they directly affect the long-term cycling stability as well as the safety of the cell. Typically, electrolytes employed in SIBs are composed of a sodium ion conducting salt (e.g. NaClO₄ or NaPF₆) dissolved in a mixture of carbonate-based organic solvents such as ethylene carbonate (EC), diethyl carbonate (DEC) or propylene carbonate (PC).[5, 14] However, such organic electrolytes exhibit low thermal stability, which together with their high volatility and flammability, limits the operation temperature and safety of SIBs.[14-16] Further, these properties pose serious

safety issues if one considers that batteries, composed of individual cells, heat up during operation thus increasing the risk of thermal runaway, electrolyte fire or explosion.[14, 17-18] Due to their non-volatility and exemplarily low flammability combined with a good salt solubility, ionic liquids (ILs) have the potential to serve as alternatives to carbonate based organic electrolytes.[16, 19-20] Moreover, properties of ILs can easily be tuned and ILs have excellent thermal stabilities, wide electrochemical stability windows and good ionic conductivities making them adaptable to a wide range of operating conditions.[19, 21-26]

Different ILs have successfully been applied as solvents for electrolytes in several SIB half-cell configurations with *e.g.* NaCrO_2 [27-29] and Na_xMnO_2 [16, 30] as cathode materials. Excellent cycling stability was demonstrated for these systems. In particular, IL based electrolytes containing bis(trifluoromethylsulfonyl)imide (TFSI) and bis(fluorosulfonyl)imide (FSI) anions have been shown to be good candidates for IL-SIBs.[11-13, 31-32] The FSI anion is known to account for lower viscosities, higher conductivities and better Li^+/Na^+ migration abilities compared to the TFSI anion.[33-35] On the other hand, TFSI based ILs exhibit significantly higher thermal stabilities than their FSI based analogs and are less expensive.[35] Studies have shown that the advantages of the two anions FSI and TFSI can be combined in electrolytes containing both anions, resulting in higher oxidation stability, improved rate capacity and compromised cycling retention.[30, 36-37] Regarding the IL-cation, pyrrolidinium based ILs are known to exhibit outstanding electrochemical stabilities up to 6 V, rendering them suitable components for IL electrolytes.[19-20] Combining these beneficial properties, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($\text{Pyr}_{1,4}\text{TFSI}$) containing NaFSI (0.5 M) as conducting salt was chosen as electrolyte to enhance the safety of the SIB full-cell in the present study. $\text{Pyr}_{1,4}\text{TFSI}$ is a room temperature IL, characterized by its comparably low viscosity and high thermal stability and has been applied in several SIB half-cells.[11-13, 30-31] Further, flammability tests have shown the superior stability of $\text{Pyr}_{1,4}\text{TFSI}$ towards ignition when compared to conventionally applied organic electrolytes, underlining the suitability of $\text{Pyr}_{1,4}\text{TFSI}$ as safer electrolyte.[38]

Besides the disadvantages of flammable organic electrolytes, metallic sodium as anode material poses a safety issue in SIBs, as well. It was shown that Na-dendrite formation can lead to short cutting and thermal runaway of the cell.[3, 10] In addition, sodium's lower melting point (97.7 °C) compared to Li challenges the usage of sodium metal at elevated temperature.[1-3, 10] Hence, it is necessary to develop full-cell devices, where the anode is composed of more benign materials. Up to date, to the best of our knowledge only few SIB full-cells employing IL have been studied of which only two are able to operate at room temperature. [16, 39-41] In those studies hard carbon, which is currently the material of choice for SIBs containing organic electrolytes, was applied as anode material. However, the operating potential of hard carbon is close to that of the sodium plating potential, thus again giving rise to the possibility of dendrite formation, shorting and thermal runaways. Further, hard carbon suffers from poor rate capacity.[16, 42] To open research to further anode materials and establish a thermally safe and stable system, we present a fully functional IL SIB full-cell with an anode based on a sodium vanadium oxide. The $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \cdot 0.6 \text{H}_2\text{O}$ (NVO) recently reported by Hartung *et al.* exhibits reasonable capacities of 217 mAh g^{-1} at a current rate of 20 mA g^{-1} [43] and, in contrast to hard carbon, can easily be synthesized. Further, NVO exhibits a wide potential range enabling its application as anode as well as cathode material. Therefore, NVO is considered as reasonable alternative anode material to hard carbon and is employed in the present study. Regarding the cathode material of the presented SIB full-the P2 type cobalt substituted sodium manganese oxide $\text{P2-Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO), optimized by Bucher *et al.*, [44] was chosen since layered oxides are popular and promising cathode materials.[44-49] 10% Co substitution in $\text{Na}_{0.6}\text{MnO}_2$ was shown to be effective in tackling capacity fading occurring as a result of structural changes. With a capacity of about 180 mAh g^{-1} and an operating potential from 1.5 to 3.8 V vs. Na/Na⁺, [44] this material is an attractive choice for a SIB-cathode.

In continuation of these promising results, focus was set on the combination of both materials in an IL based SIB full-cell and the evaluation of its thermal stability. For comparison of the presented system, an analog full-cell containing EC/PC (1:1 wt%, NaClO_4 1 M) – one of the most commonly employed organic electrolytes in SIBs – is evaluated under identical conditions.[5, 14] The thermal stability of both full-cells is

investigated using Accelerating Rate Calorimetry (ARC). ARC is a useful technique to characterize thermal runaway reactions in chemical industry in order to develop safe working conditions.[15, 50-51] Studies characterizing IL based systems using ARC have already been reported. Yadong *et al*, compared the reactivity of TFSI and FSI-based ILs incorporated within a lithium charged electrode material using ARC.[50] The exothermic behavior of numerous ILs has been also studied separately by Vijayaraghavan *et al*. [21] However, to the best of our knowledge, the thermal runaway behavior of a coin cell comprised of a cathode and anode with an IL electrolyte has not been reported so far.

6.2. Experimental

6.2.1. Material preparation

$\text{Na}_{2.55}\text{V}_6\text{O}_{16}\cdot 0.6\text{H}_2\text{O}$ (NVO) was synthesized following a slightly modified procedure from Hartung *et al*. [43] 20 ml of a 0.5 M solution of vanadium pentoxide (Alfa Aesar 99.2%) were mixed with 20 ml of a 0.5 M solution of NaOH (Alfa Aesar 98%) and heated under reflux overnight. The obtained clear brownish solution was subsequently transferred to a teflon lined stainless steel autoclave for heating at 180 °C for 48 h. After cooling, the precipitate was filtered, washed with deionized water and dried at 80 °C overnight. The dry powder was calcined at 400 °C for 2 h in air using a box furnace. Spherical P2- $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO) was synthesized following a reported protocol.[44]

6.2.2. Electrolyte preparation

Preparation of all electrolytes was carried out under inert atmosphere in a glovebox with oxygen and moisture contents less than 0.1 ppm. For the IL electrolyte, EL_{IL} NaFSI (Nippon Shokubai) was dissolved in Pyr_{1,4}TFSI (IoLITEC) to yield a 0.5 M solution. Attempts to employ 1.0 M NaFSI in Pyr_{1,4}TFSI as the electrolyte did not work well, due to the electrolytes very high viscosity and the resulting low wettability of the electrode materials. The conventional organic electrolyte EL_{ORG} was prepared as a solution of 1 M NaClO₄ (Sigma-Aldrich) in an EC/PC mixture (1:1 w/w, Sigma-Aldrich).

6.2.3. Coin cell preparation

For preparation of the electrodes, NMO and NVO powders were mixed with acetylene black (AB) (Alfa Aesar, >99%) and polyvinylidene fluoride (PVdF, Arkema, Kynar HSV 900) in a weight ratio of 60:20:20 (active material:AB:PVdF) in N-methyl-2-pyrrolidone (NMP) as solvent. The resulting slurry was cast on an aluminum foil (15 μm , Goodfellow) using a 100 μm gap-doctor blade. The cast sheet was dried at 80 °C to remove NMP, roll-pressed and punched into 16mm-diameter electrodes. Subsequently, the punched electrodes were dried at 110 °C under vacuum and then taken for cell assembly. For NMO and NVO half-cells, CR-2016 coin cells were assembled using NVO / NMO as the working electrode, sodium metal (99.8%, Acros Organics) as counter electrode and Whatman glass fiber (grade GF/F) as separator. For evaluation of the full-cells, cathode (NMO) and anode (NVO) were chosen so as to obtain a mass ratio of 2.7 and then assembled in CR-2016 coin cells. The mass loading of the NMO cathode and NVO anode are 1.75 mg/cm^2 and 0.65 mg/cm^2 , respectively. The mass ratio was adjusted to reach equal sodium intercalation capacities for both materials as described in more detail in the SI. All coin cell assembly was carried out in an argon-filled glove box with oxygen and moisture contents less than 0.1 ppm.

6.2.4. Experimental methods

Cyclic voltammetry: Cyclic voltammetry was carried out in two electrode CR-2016 coin cells using a VMP3 potentiostat (BioLogic, France) with a scan rate of 0.1 mV/s to determine the operating window of the full-cells.

Galvanostatic cycling: A BT2000 battery tester (Neware, China) was used to conduct galvanostatic testing under ambient conditions and elevated temperatures (75 °C). For high temperature testing, the cells were placed inside a temperature & humidity chamber (Espec SH-241) to keep the temperature constant. For NVO and NMO half-cell studies, the cell potential range was set to 0.9 V - 4.0 V and 1.5 V - 3.8 V vs. Na/Na^+ respectively. The full-cells were tested in the applied cell voltage range of 0 - 2.8 V.

XRD: X-ray diffraction (XRD) data was collected using a Bruker D8 Advance XRD, with Cu K α radiation (40 kV and 40 mA).

XPS: To characterize the surface layer formed on the electrode during cycling, XPS measurements were performed using a PHI-5400 equipment (PHI) with an Al K α beam source (250 W) and a position-sensitive detector (PSD). NVO half-cells were opened inside an argon filled glovebox after 200 cycles. The extracted NVO-electrodes were washed with dimethyl carbonate (DMC) to remove residual electrolyte and subsequently dried under vacuum to remove the DMC. XPS measurement were carried out in an argon-filled glove box with oxygen and moisture contents less than 0.1 ppm. Electrodes were sealed in a glass tube to avoid exposure to ambient environment during transfer to the glovebox, which was connected to the XPS instrument.

Viscosity: Viscosities were determined by the frequency change of a quartz resonator (with and without IL sample) using a heatable electrochemical quartz crystal microbalance (EQCM). Both sides of the used quartz were covered with keyhole shaped Au-electrodes, which were connected to the signal output connector of a network analyzer. For measurements, the quartz was mounted into a temperature controlled teflon cell, which was sealed with SimrizTM O-rings and filled with 100 μ l of the respective IL sample, so that one of the Au-electrodes was in direct contact to the electrolyte. The admittance of the 10 MHz AT cut quartz resonators (KVG Quartz Crystal Technology) was read out with a SDR-Kits DG8SAQ vector network analyzer 3E with an in-house developed Delphi software. Before measurements, a short circuit (“thru”) calibration was carried out in the frequency range relevant for the measurements. From the frequency difference of the blank quartz and the quartz with the respective IL sample and its mass density, the respective viscosities were calculated using the Gordon-Kanazawa-Mason-Model.[52]

Conductivity: To determine the electrochemical conductivities of the electrolytes, a *Mettler Toledo* InLab 751 conductivity probe head was set up in an argon-filled glovebox and connected to a *Solartron* SI1260 frequency response analyzer. The sample test tube was inserted in a temperature-controlled steel block. Impedance spectra were recorded with an alternating current voltage of 0.02 V and in a frequency

range between 1 Hz and 10 MHz to determine the ohmic resistance of the respective electrolyte. A cell constant of 1 cm^3 calibrated with 0.1 M KCl was used to determine the specific conductivities.

ARC: Accelerating rate calorimetry was performed on NMO/NVO full-cells at the fully charged state, as this is the state where the most energy is stored in the cell. The 2016-coin cells were loaded into the device by loading them to the thermocouple. A standard heat-wait-search procedure was applied to observe the behavior of the cells.[53] The initial setting temperature was $100\text{ }^\circ\text{C}$. A 20 min waiting-period was applied to the system at each measuring point to reach thermal equilibrium. When self-heating was detected, exothermic reactions were tracked by a calorimeter under adiabatic conditions. The sensitivity of the SHR detection was 0.05 K min^{-1} . The sample heating step was 3 K per step.

DSC: Differential scanning calorimetry was carried out using a Q10 – TA instrument with a heating rate of 10 K min^{-1} . Electrodes from fully charged NMO/NVO_{IL} and NMO/NVO_{ORG} full-cells were extracted, washed with DMC, and dried under vacuum. The dried electrode powders were mixed with the respective electrolytes in 30 ml high-pressure gold-plated stainless crucibles. The sample crucibles were sealed in the glove box.

6.3. Results and Discussion

6.3.1. Electrode materials

The purity of the synthesized NVO and NMO phases was evaluated via XRD (Figure 6.S1). Both materials can be matched to the respective pure phases (ICDD card no. 01-078-2864, ICSD-50301). No contaminations or additional phases can be found underlining the high purity of the applied materials. Further details of the structures can be found in Hartung *et al.*[43] and Bucher *et al.*[44-45]

6.3.2. Electrolytes

The electrolytes' viscosity η and its conductivity σ can strongly influence the capacity, performance and stability of a cell. Therefore, these properties are of great interest in order to obtain a deeper understanding of the cell performance.[54]

Table 6. 1 Viscosity η [cP] and conductivity σ [mS cm⁻¹] of EL_{IL} and EL_{ORG} at 23 °C and 75 °C.

	η 23 °C	η 75 °C	σ 23 °C	σ 75 °C
EL _{IL}	173	34	1.5	9.4
EL _{ORG}	7.1	3.7	7.8	20

Table 6.1 shows the viscosities and conductivities of the electrolytes applied in this study: Pyr_{1,4}TFSI with NaFSI (0.5 M) (EL_{IL}) and EC/PC (1:1 wt%) with NaClO₄ (1 M) (EL_{ORG}) at 23 °C and 75 °C, respectively. Conductivity and viscosity of an electrolyte are in close relation to each other. The higher the viscosity of an electrolyte and the larger and bulkier its components, the harder it is for ions to move past each other, resulting in lower conductivities.[55] In contrast to EL_{ORG} (7.1 cP), EL_{IL} (173 cP) has a significantly higher viscosity and therefore lower conductivity at 23 °C. The increased viscosities of ILs in general compared to organic solvents mainly result from strong columbic interactions between the IL cations and anions whereas organic solvents only experience weaker dipole-dipole interactions. Moreover, in contrast to organic solvents, the addition of a conducting salt, such as NaFSI, to an IL leads to a further increase of the viscosity of the IL-salt mixture due to stronger intramolecular interactions between the ions of the IL and the ions of the conducting salt (for comparison viscosity of neat Pyr_{1,4}TFSI at 23 °C: 89 cP).[56-58] In spite of the inferior viscosity and conductivity of IL based electrolytes, superior electrochemical performance of IL based systems has been shown in several studies, underlining the suitability of IL based electrolytes for SIBs. [11-13, 16, 30-32] In accordance to literature, a significant increase in conductivity from 1.5 to 9.4 mS cm⁻¹ for EL_{IL} is observed at elevated temperatures.[59-61] The decrease of viscosity and the enhanced

ion movement at higher temperatures account for the increased conductivities at 75 °C compared to 23 °C. This effect is much more pronounced for the EL_{IL} than for the organic electrolyte, thus rendering the conductivity of the EL_{IL} less inferior at elevated temperatures.

6.3.3. NVO and NMO half-cells with EL_{IL}

To investigate the compatibility of EL_{IL} with the NVO and NMO material, studies with NVO and NMO half-cells containing EL_{IL} were performed. For a NMO/NVO SIB full-cell, sodium moves from the NVO anode to the NMO cathode during the discharge process, which corresponds to the charge process of the NVO half-cell on the one hand and the discharge process of the NMO half-cell on the other hand. Therefore, in the following discussions, the charge process is investigated for the NVO half-cells, whereas focus is set on the discharge process for the NMO half-cells.

Figure 6. 1. Cycling behavior of NVO_{IL} (red) and NVO_{ORG} (black) at 100 (a), 200 (b) and 400 (c) mA g⁻¹; insets show the charge-discharge profiles of the respective second cycles.

Figure 6.1 shows the cycling behavior and charge-discharge profile (second cycle) of the NVO half-cells containing EL_{IL} (NVO_{IL}) as well as EL_{ORG} (NVO_{ORG}) at different specific currents. The half-cells show similar charge-discharge profiles for both electrolytes. The initial charge capacities of NVO_{IL} at 100 mA g⁻¹, 200 mA g⁻¹ and 400 mA g⁻¹ are 141 mAh g⁻¹, 115 mAh g⁻¹ and 93 mAh g⁻¹, respectively. The capacities gradually increase to a maximum after around 16 cycles (to 170 mA g⁻¹, 134 mA g⁻¹, 117 mA g⁻¹ respectively) before fading is observed (Figure 6.S2). This initial increase

of the charge capacities can most likely be attributed to the wetting properties of EL_{IL}. Due to its high viscosity, EL_{IL} exhibits a lower wettability compared to EL_{ORG}, probably resulting in a decelerated Na accommodation for NVO_{IL} in the first few cycles until the surface layers stabilize and maximum wetting is attained.[62] Unlike NVO_{IL}, NVO_{ORG} displays the highest charge capacity in the first cycle right away (142 mAh g⁻¹, 157 mAh g⁻¹ and 124 mAh g⁻¹ at 100 mA g⁻¹, 200 mA g⁻¹ and 400 mA g⁻¹, respectively).

Table 6. 2. Charge capacity retentions (NVO) and discharge capacity retentions (NMO) of the tested half-cells at 150 cycles, with regard to the respective initial cycle.

	100 mA g ⁻¹	200 mA g ⁻¹	400 mA g ⁻¹
NVO_{IL}	62%	69%	100%
NVO_{ORG}	24%	19%	27%
NMO_{IL}	98%	100%	100%
NMO_{ORG}	56%	63%	66%

When comparing the retention values of the two systems, NVO_{IL} displays a remarkably improved cycling stability. As shown in Table 2, significantly enhanced retentions can be obtained for NVO_{IL} compared to NVO_{ORG} at all rates. The highest difference in retention values between NVO_{IL} and NVO_{ORG} of 73% (NVO_{IL}: 100% vs. NVO_{ORG}: 27%) is obtained after 150 cycles at 400 mA g⁻¹, underlining the enhanced performance of NVO_{IL} compared to NVO_{ORG}.

The superior performance of the NVO_{IL} cells especially at high rates is remarkable. Considering the lower conductivity and higher viscosity of EL_{IL} when compared to EL_{ORG}, the latter would be expected to exhibit higher capacities.[11-13] Intercalation/de-intercalation of Na⁺-ions from the NVO host structure seems to be facilitated in the NVO_{IL} cells, resulting in high capacity retention even at high specific current. The nature of the surface layers formed with the different electrolytes could account for the respective cycling behaviors. To get closer insights into the formed surface layers, XPS studies with the cycled electrodes were carried out. The results are presented and discussed in detail in the Supporting Information. According to the XPS data, the solid electrolyte interface (SEI) formed on the NVO material cycled with EL_{IL}

seems to be mainly composed of NaF and IL-fragments. These components are known to be more durable than carbonate fragments,[35, 63] which were the main species found on the electrodes cycled in EL_{ORG}. Therefore, the less stable SEI layer formed in the NVO_{ORG} cells is likely to be one of the causes for the inferior performance of NVO_{ORG} compared to NVO_{IL}. Further, the carbonate species, mainly formed in the SEI film of NVO_{ORG}, are considered to enhance the resistance to the ion transport through the SEI. The hindered Na⁺ ion transport and desolvation by a SEI layer with high content of carbonate species therefore probably contributes to the poor performance of the organic electrolyte cell as well.[64]

Figure 6. 2. Cycling behavior of NMO_{IL} (red) and NMO_{ORG} (black) at 100 (a), 200 (b) and 400 (c) mA g⁻¹; insets show the charge-discharge profiles of the respective second cycles.

Figure 6.2 shows the cycling behavior of the NMO half-cells containing EL_{IL} (NMO_{IL}) and EL_{ORG} (NMO_{ORG}) at different specific currents. The NMO_{IL} cells show higher discharge capacity retention and therefore superior cycling stability after 150 cycles at all rates (Table 2). However, in contrast to the NVO half-cells, which show similar charge-discharge profiles for both electrolytes, the discharge plateau at around 2.0 V for NMO_{IL} (insets Figure 6.2) are less pronounced compared to NMO_{ORG}. This is most likely due to the higher polarization caused by the higher viscosity of the IL electrolyte. Thus, the initial discharge capacities of NMO_{IL} are not comparable to the initial capacities of NMO_{ORG}. While the discharge capacity values decrease during repeated cycling for NMO_{ORG}, NMO_{IL}'s discharge capacities remain stable with small fluctuations. Importantly, no fading was observed after 150 cycles for NMO_{IL} even at high charge-discharge rates.

Due to the significantly higher viscosity and lower conductivity of EL_{IL} , the superior performance of NMO_{IL} as well as NVO_{IL} seem intriguing. It should be kept in mind that, further major factors affecting cell performance besides conductivity are e.g. the formation of SEI/CEI layers formed on the active materials as well as structural degradation of active materials. Detailed investigations clarifying the electrolyte/electrode interface phenomena will be undertaken in future studies.

In brief, NMO and NVO half-cells containing EL_{IL} show significantly improved cycling stability compared to the cells containing EL_{ORG} at all tested rates. The reasonable performance of NVO_{IL} and NMO_{IL} indicates the suitability of NMO and NVO as electrode materials for an IL-SIB full-cell based on EL_{IL} .

6.3.4. NMO/NVO full-cells

Based on the half-cell results, a full-cell composed of NMO and NVO was rendered promising. In order to reach equal sodium intercalation capacities for both materials, the mass ratio between the NMO cathode and the NVO anode was varied when cycling NMO/NVO cells with both electrolytes. The optimal mass ratio of NMO/NVO was determined to be 2.7 (Figure 6.S6). In order to determine a reasonable operating window of the full-cells, CVs of the latter were performed in different voltage ranges (Figure 6.S7). Due to the presence of irreversible reactions above 2.8 V the voltage range was set to 0 - 2.8 V.

Figure 6. 3. Charge-discharge curves (top) and cycling stabilities (bottom) of NMO/NVO_{ORG} (a, c) and NMO/NVO_{IL} (b, d) respectively (weight ratio: 2.7:1; specific current: 50 mA g^{-1}).

Galvanostatic charge-discharge tests were performed in the determined voltage range at a current rate of 50 mA g^{-1} . Figure 6.3 shows the charge-discharge profiles and cycling stabilities of the NMO/NVO_{IL} and NMO/NVO_{ORG} systems. In order to obtain data comparable with other reported IL full-cell configurations,[16, 39] the capacity values are calculated with respect to the mass of the NVO anode. Due to the relatively similar working potential of NVO and NMO, the average operating voltage for the full-cells (1.25 V) is not optimal but still acceptable and comparable to other SIB full-cell studies.[65-69] At room temperature, both full-cells show similar charge-discharge profiles at 50 mA g^{-1} (Figure 6.3 a, b). The charge-discharge curves show two pronounced plateaus for the first and second charge. However, for discharge these plateaus are less distinct. From the third charge onwards, charge as well as discharge processes become similar exhibiting only slightly pronounced plateaus.

The initial discharge capacities of NMO/NVO_{IL} and NMO/NVO_{ORG} are 125 and 117 mAh g^{-1} , respectively. After 100 cycles, NMO/NVO_{IL} retains 76% of its initial capacity, while capacity retention for NMO/NVO_{ORG} is 71%. Moreover,

NMO/NVO_{ORG} displays a slightly lower columbic efficiency (CE) compared to NMO/NVO_{IL} (98% vs. 99%). Within every cycling step, the CE is reasonably stable for NMO/NVO_{IL} while it varies significantly for NMO/NVO_{ORG} indicating some sort of instability in the latter system (Figure 6.3 c, d). Capacity fading of the full-cells can partly be caused by structural changes of the electrode materials. For NMO these can be caused e.g. by manganese dissolution or Jahn-Teller distortion. [44-45] NVO on the other hand can lose crystallinity or trap sodium in the interstitial sites during cycling.[70] Further, sodium consumption for the SEI/CEI formation will most likely contribute to fading as well.

In summary, the studied NMO/NVO full-cells exhibit reasonable discharge capacities and cycling stabilities in an output potential difference range from 0 V to 2.8 V at room temperature. NMO/NVO_{IL} shows higher capacity retention and higher CE compared to NMO/NVO_{ORG} underlining the beneficial influence of the IL electrolyte on cell stability. Compared to the best available LIB/SIB systems there certainly is room for further optimization to enhance the performance of the reported system.[42, 71-74] However, these initial results were considered firm enough to perform further investigations on coin-cell safety, as the main focus of the presented study.

For a great number of practical applications, the capability of batteries to withstand cycling at elevated temperatures is mandatory since battery packs and the devices they are applied in, can heat up during operating.[75-76] For highly temperature sensitive systems like e.g. conventional LIBs, small temperature deviations can lead to significant capacity losses, reduction of the battery life span as well as safety issues e.g. thermal runaway.[77-79] To maintain operating temperature and ensure safe working conditions application of complex and cost intensive battery temperature managements systems are thus required.[76-77, 80] In contrast, these additional efforts and costs can be avoided when applying less temperature sensitive systems.

Figure 6. 4. Charge-discharge profiles of different cycles at 50 mA g⁻¹ at 75 °C for NMO/NVO_{IL} (a) and NMO/NVO_{ORG} (b).

To test their ability to withstand cycling at elevated temperatures NMO/NVO_{IL} and NMO/NVO_{ORG} were thus subjected to galvanostatic charge-discharge tests (50 mA g⁻¹) at 75 °C in a controlled temperature and humidity chamber. The respective charge-discharge profiles of the cycling at elevated temperature are presented in Figure 6.4 and the corresponding cycling stabilities and CEs are shown in Figure 6.S8. For NMO/NVO_{ORG}, the first discharge capacity significantly increases to 244 mAh g⁻¹ at 75 °C compared to 117 mAh g⁻¹ at room temperature. However, a decomposition reaction seems to take place during the charge process as evident from the presence of the plateau at 2.7 V (Figure 6.4b). In contrast, this plateau is not apparent in the room temperature charge-discharge test for NMO/NVO_{ORG} (Figure 6.3a) and is therefore most likely the main cause for the different cycling stability of NMO/NVO_{ORG} at 75 °C. The presence of unwanted side reactions resulting in a rapid degradation of the discharge capacity is underlined by the CE values for NMO/NVO_{ORG} (Figure 6.S8b). The latter displays only 55 and 47% for the first and second cycle respectively. After 10 cycles only roughly 23 mAh g⁻¹ (10% of the initial value) are retained. These results clearly underline that the organic electrolyte cannot withstand elevated temperatures, most likely making the application of a battery thermal management system necessary to ensure stable performance and to maintain battery lifespan.[76, 81] Thermal decomposition of the SEI in LIBs with standard organic electrolytes has been reported to take place at 70 °C and is most likely the reason for the herein reported fast fading of NMO/NVO_{ORG} at 75 °C as well.[82] Moreover, it should be noted that the decomposition mechanism of the cathode electrolyte interface layer can also affect the overall cell performance.

In contrast to the organic electrolyte-based system, NMO/NVO_{IL} displays a significantly improved CE at 75 °C when compared to NMO/NVO_{ORG} (Figure 6.S8a). The efficiency of NMO/NVO_{IL} increases from 81% in the first cycle to 96% after 10 cycles. In the 40th cycle, the cell still displays an efficiency of 98% and retains roughly 70% of its initial capacity. It is thus clear, that the extent of side reactions, such as electrolyte or SEI decomposition, is not as significant as for NMO/NVO_{ORG}. While these values still have room for improvement, they serve to underline the potential of EL_{IL} and show that IL based systems are able to withstand elevated temperatures, bringing the above discussed advantages for temperature insensitive systems into account.

Figure 6. 5. Rate test performance of NMO/NVO_{IL} (red dot) and NMO/NVO_{ORG} (black dot) at room temperature (RT) and NMO/NVO_{IL} (red circle) at 75 °C.

Figure 6.5 compares the rate capability of NMO/NVO_{IL} and NMO/NVO_{ORG} at room temperature (RT) and NMO/NVO_{IL} at 75 °C. Due to the rapid degradation, which takes place in the first few cycles already (see cycling data Figure 6.4b) no meaningful data could be obtained from the rate test of NMO/NVO_{ORG} at 75 °C. Owing to the lower viscosity and thus higher conductivity of the organic electrolyte at RT (see Table 1), NMO/NVO_{ORG} shows better rate capability than NMO/NVO_{IL} at 400 mA g⁻¹ and 600 mA g⁻¹ (2 C and 3 C) in the rate test at RT. The enhanced rate performance of NMO/NVO_{IL} at elevated temperatures can mainly be attributed to the increased conductivity and reduced viscosity of EL_{IL} at 75 °C.[13, 83-84] As evident from Table 1, conductivity of EL_{IL} at 75 °C (9.4 mS/cm) is significantly higher than the conductivity of EL_{IL} (1.5 mS/cm) at RT. This observation demonstrates that

improvement of the rate performance of NMO/NVO_{IL} at RT is most likely possible by tuning the viscosity/conductivity of EL_{IL}, either by modification of the IL itself or by addition of suitable additives.

In conclusion, EL_{IL} shows significant beneficial effects over EL_{ORG} with respect to cell performance when operating the respective full-cells at RT and 75°C. NMO/NVO_{IL} outperforms NMO/NVO_{ORG} in terms of cycling stability and CE and is able to withstand cycling at elevated temperature, which is valuable for practical applications.

6.3.5. Thermal stability of the NMO/NVO full-cells

To investigate the safety of the evaluated full-cells, the thermal behavior of NMO/NVO_{IL}, NMO/NVO_{ORG} was studied by ARC. ARC is a useful technique to characterize thermal runaway reactions in chemical industry in order to develop safe working conditions and has already successfully been applied to determine safe working conditions for LIBs. Critical parameters that are determined from an ARC-test include -i) the self-heating rate ii) the onset temperature and iii) adiabatic heat increase. The self-heating rate gives rise to the tendency of the sample to attain conditions of self-heating and is an indication of the speed with which thermal runaway reactions proceed. A higher heating rate indicates a more dangerous or unstable system. Similarly, a lower onset temperature means lower stability to temperature variations.[15, 50-51] Therefore, a higher onset temperature is desirable for practical applications.

Figure 6. 6. Self-heating rate vs. temperature for NMO/NVO_{IL} (red) and NMO/NVO_{ORG} (black) (full-cells charged to 2.8 V).

Prior to the ARC measurements, cells were charged to a cut-off voltage of 2.8 V. During the ARC measurements, the samples are heated in small steps in an adiabatic calorimeter. Figure 6.6 illustrates the dependence of self-heating rate (SHR) on the samples' temperature obtained from ARC studies. First exothermal reactions are detected at around 185 °C for both cells. The SHR for NMO/NVO_{ORG} (0.19 °C min⁻¹ at 191 °C) is more than twice as high compared to NMO/NVO_{IL} (0.07 °C min⁻¹ at 189 °C). From the onset temperature at 185 °C, the NMO/NVO_{ORG} cell remains in exothermal mode until the cut-off temperature of 350 °C is reached. Beyond the peak at 191 °C the SHR falls slightly. Above 198 °C, the SHR increases significantly reaching a peak at 230 °C (2.6 °C min⁻¹) followed by a moderate decrease until 258 °C. Subsequently, SHR starts increasing again steadily from 258 °C until the cut-off temperature of 350 °C is reached. At 340 °C, the self-heating rate of the NMO/NVO_{ORG} sample is about 4 °C min⁻¹.

In contrast to NMO/NVO_{ORG}, the SHR observed for NMO/NVO_{IL} decreases rapidly after the peak at around 185 °C and is fully extinguished at around 195 °C. No significant SHR can be detected for the NMO/NVO_{IL} cell until a temperature of 270 °C. The SHR reaches a maximum at 340 °C with a heating rate of 2 °C min⁻¹. This result is in the same range as the observed onset temperatures (> 230 °C) of similar systems consisting of TFSI-based ILs and lithium-ion battery electrode materials.[50]

The high self-heating rate of the NMO/NVO_{ORG} cell indicates a strong thermal reactivity at lower temperatures for the organic electrolyte with the electrode materials, in contrast to the more stable NMO/NVO_{IL} cell. The obvious differences between the two electrolytes in this study confirm that application of EL_{IL} results in thermally significantly more stable and safer systems compared to EL_{ORG} for the applied electrode combination. The thermal stability of SIB full-cells is especially crucial since battery packs, which are composed of numerous individual cells, can heat up during cycling. Therefore, cells, which are thermally not stable enough, increase the risk for thermal runaway or even explosion of the whole system drastically.

To understand the origin of the exothermal reactions observed in the ARC and the differences in the behavior between cells containing EL_{IL} and EL_{ORG} as electrolytes, differential scanning calorimetry (DSC) was performed on the neat electrolytes as well as their combinations with the NMO and the NVO electrode materials extracted from charged full-cells.

Figure 6. 7. DSC of neat EL_{IL} and EL_{ORG} and the electrolytes in combination with the separate electrode materials NMO and NVO of charged NMO/NVO_{IL} and NMO/NVO_{ORG} respectively.

The top panel in Figure 6.7, shows the DSC results for the individual electrodes from a charged NMO/NVO_{ORG} full-cell in combination with EL_{ORG} (NMO-ORG and NVO-ORG). The bottom panel shows the behavior of individual electrodes from a charged NMO/NVO_{IL} full-cell in combination with EL_{IL} (NMO-IL and NVO-IL). Additionally, the DSC curves of the neat electrolytes (EL_{ORG} and EL_{IL}) are presented.

In case of the NMO-ORG mixture, exothermal peaks begin to form starting at 178 °C. Two main peaks are observed at 207 °C and 242 °C. These observations could explain the continuous increase of the SHR determined for NMO/NVO_{ORG} from 180 °C to 235 °C by ARC. Cathode related reactions such as SEI regrowth or the decomposition of NMO with the reduction of Mn⁴⁺, leading to oxygen gas evolution are likely the cause for this behavior. Similar reactions have been reported for LiMn₂O₄, LiCoO₂, Li[Ni_xCo_yAl_z]O₂, LiNi_xCo_yMn_zO₂. [18, 85] The NVO-ORG mixture starts to display runaway exothermal behavior around 250 °C as indicated by a steep increase in the heat flow curve, suggesting some sort of decomposition reaction. This reaction could explain the increase in SHR observed in the ARC starting at around 258 °C. The DSC of the bare EL_{ORG} (without charged cathode/anode) indicates that the onset of the decomposition reaction is at 300 °C, again supporting the observed increase in SHR at temperatures exceeding 300 °C. Further, it was observed that, the DSC pans of all three samples containing EL_{ORG} had exploded after the DSC measurements. This might be due to an increase in pressure within the sealed DSC pan as gaseous products are formed during electrolyte decomposition. In summary, the first increase in SHR in the ARC of NMO/NVO_{ORG} from 180 to 235 °C seems to result from different possible reactions in the NMO cathode – electrolyte mixture, whereas the subsequent phase from 235 °C until 340 °C seems to occur as a result of NVO anode – electrolyte and bare electrolyte related reactions. In case of the samples in combination with EL_{IL} (Figure 6.7, lower panel), the NMO-IL mixture displays a small exothermal peak at around 180 °C, which is consistent with the peak observed around 185 °C in the ARC analysis of NMO/NVO_{IL}. As stated above for the NMO-ORG mixture this exothermal behavior most likely results from NMO cathode related reactions as well. In contrast to NMO-ORG, no further peaks are observed in the DSC of the NMO-IL mixture until about 324 °C. The DSC of the bare EL_{IL} and the NVO-IL mixture do not show any peaks in the range of 200 – 250 °C either. Together, these results support the lack of any self-heating observed in the ARC measurements for NMO/NVO_{IL} in the range of 190 °C – 270 °C. The NVO-IL mixture seems stable until exothermic reactions are initiated at 250 °C. Exothermal peaks are observed at 252 °C, 281 °C and 334 °C. The peak at 281 °C in the DSC correlates well with the second set of self-heating reactions (271 °C – 293 °C) observed in the ARC analysis for NMO/NVO_{IL}. Above 290 °C, both

the NMO-IL and NVO-IL mixture seem to undergo exothermic reactions and the EL_{IL} starts reacting exothermically around 340 °C as well. These observations support the constant increase of the SHR observed for the NMO/NVO_{IL} cell beginning at 293 °C. To summarize, the first phase in the ARC measurement of the NMO/NVO_{IL} cell (180 – 190 °C) most likely arises from possible reactions in the NMO cathode – IL mixture. Subsequently, the cell does not undergo any further reactions as evidenced by a lack of reactions in the DSC for any of the samples. The second phase of self-heating reactions starting around 271 °C could be attributed to NVO anode – EL_{IL} reactions. As the temperature further increases beyond 290 °C, synergistic exothermal effects of both the NMO-IL and the NVO-IL mixtures seem to occur followed by the exothermic reaction of the bare EL_{IL}. A combination of all these processes seems to lead to the steep and continuous increase of the SHR. It should be noted that in contrast to the samples containing EL_{ORG}, the EL_{IL} samples did not explode during the DSC measurements underlining the higher stability of the IL bases systems.

To investigate any further side self-heating reactions DSC measurements were also performed with the applied separator material and the binder (PVdF) in combination with EL_{IL} and EL_{ORG}. As shown in Figure 6.S9 no exothermal contributions could be detected for these samples until the electrolytes started to decompose.

In line with the results from ARC, the DSC results clearly delineate the differences between the tested electrolytes. As evidenced by the lack of runaway reactions during heating for either the NVO-IL or NMO-IL mixtures in contrast to NVO-ORG or NMO-ORG mixtures, EL_{IL} seems to be more stable compared to systems with EL_{ORG} when in contact with either the charged anode or cathode. Additionally, bare EL_{IL} is clearly more stable compared to the bare EL_{ORG}. All these observations reinforce the safe nature of the IL-based electrolyte over the organic electrolyte in the studied systems. Further research is ongoing to shed more light on the exact nature of the reactions, the decomposition pathways and potential products.

6.4. Conclusion

The performance of the electrode materials NMO and NVO in combination with the IL based electrolyte Pyr_{1,4}TFSI with NaFSI (0.5 M) (EL_{IL}) was investigated and

compared to a reference system with the standard organic electrolyte EC/PC (1:1 wt%) with NaClO_4 (1.0 M) (EL_{ORG}).

In SIB half-cell studies with both active materials, the cells containing EL_{IL} displayed significantly better cycling stability at different rates compared to EL_{ORG} , proving the compatibility of EL_{IL} with the electrode materials.

Based on these results, NMO/NVO (ratio 2.7:1) full-cells with EL_{IL} as well as EL_{ORG} were studied. The average working voltage of the system accounts to 1.25 V leaving room for improvement. However, good cycling stability could be achieved with NMO/NVO_{IL} which retains 76% of its initial capacity after 100 cycles outperforming the organic electrolyte-based system displaying 71% retention after 100 cycles. The capability of the full-cells to withstand elevated temperatures as required for practical applications, was tested in full-cell studies at 75 °C. While NMO/NVO_{ORG} shows rapid degradation of the discharge capacity, NMO/NVO_{IL} was proven to be operable at 75 °C with a decent capacity retention of 70% after 50 cycles supporting the superior thermal stability of the IL based system – an important safety aspect.

For the first time, the superior safety of an IL-SIB compared to a SIB with organic electrolyte was proven using ARC. In the ARC test the NMO/NVO_{IL} full-cell shows a higher onset temperature as well as a lower self-heating rate than NMO/NVO_{ORG}. DSC studies on the individual components and their combinations were applied to delineate the exothermal behaviors observed in the ARC through the scanning temperature range. The lack of runaway reactions in the DSC measurements of EL_{IL} and the mixtures of EL_{IL} with the active materials reinforce the enhanced safety when applying an IL based electrolyte.

The presented results underline that the IL based SIB system tested herein is superior to the SIB based on the organic carbonate electrolyte, especially when battery safety and cycling stability are the major concerns. Further studies to identify the IL/electrode interface phenomena and to tackle electrode material related fading are in progress and will help to optimize capacity and cycling behavior of the IL full-cell.

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6.5. References

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6.6. Supporting information

XRD patterns of the electrode materials

Figure 6. S 1. XRD patterns of the synthesized NVO (a) and NMO (b) materials.

Figure 6. S2. Galvanostatic charge-discharge profiles for NVO_{IL} (a) 1st full cycle and (b) 16th cycle at 100 mA g⁻¹ (~0.5 C), 200 mA g⁻¹ (~1 C) and 400 mA g⁻¹ (~2C) respectively.

XPS discussion for NVO_{IL}

Table 6.S 1. Percentage of different elements (C, F, N, Na, S and V) detected on electrodes cycled in EL_{ORG} and EL_{IL} in comparison to the pristine sample.

Sample	C1s	F1s	N1s	Na1s	O1s	S2p	V2p
EL _{ORG}	45.39	2.91	3.68	11.52	33.74	0.43	2.34
EL _{IL}	27.05	17.36	5.71	14.81	24.88	8.03	2.15
Pristine	49.65	18.84	1.08	2.76	18.64	1.13	7.91

Sodium and oxygen content of the electrodes cycled in EL_{ORG} and EL_{IL} are higher than those of the pristine sample. These results suggest the presence of sodium and oxygen-rich compounds in the surface layers formed on the active material mixtures on the respective electrodes. The second key observation is the detection of N and S on the surface of the sample cycled in EL_{IL}. These elements can only result from the IL or the FSI anion.

Detailed scans of the individual elements were obtained and analyzed further to ascertain the differences between the SEI layers formed on the electrodes cycled in EL_{ORG} and EL_{IL}. The peaks are assigned based on NIST X-ray photoelectron spectroscopy database and literature.¹⁻⁶

¹ Howlett, P. C.; Brack, N.; Hollenkamp, A. F.; Forsyth, M.; MacFarlane, D. R., *J. Electrochem. Soc.* **2006**, *153*, 595-606.

² Sugimoto, T.; Kikuta, M.; Ishiko, E.; Kono, M.; Ishikawa, M., *J. Power Sources* **2008**, *183*, 436-440.

³ Budi, A. et al. *J. Phys. Chem. C* **2012**, *116*, 19789-19797.

⁴ Nguyen, C. C.; Woo, S.-W.; Song, S.-W., *J. Phys. Chem. C* **2012**, *116*, 14764-14771.

Figure 6. S 3. High resolution XPS spectra of the electrode samples cycled in EL_{ORG} and EL_{IL} and the pristine sample for (a) F1s region, (b) Na1s region and (c) C1s region.

The peak intensity in the Na1s region increases significantly for both cycled samples, which is in line with the increasing Na content observed from survey spectra. The origin of Na-rich compounds formed on the surface of the electrodes after long time cycling needs to be further explored by taking other elements into account as well.

In the F1s spectra of the sample cycled in EL_{IL}, the peak at 688 eV can be assigned to the CF₂ bond from the PVdF binder. The peak at 683 eV can be assigned to fluoride compounds (such as NaF). This peak cannot be found in the sample cycled in EL_{ORG}. These observations suggest the formation of sodium fluoride on the surface of electrodes cycled in EL_{IL}.

When comparing the samples' spectra in the C1s region, it is clear that there is an additional peak located at 293 eV that only appears for the sample cycled in EL_{IL}. This peak can be assigned to the CF₃ group from the TFSI anion and is clearly absent in the spectra for the pristine samples and samples cycled in EL_{ORG}. On the other hand, the samples cycled in EL_{ORG} show a peak at 289.5 eV, which cannot be found in the other samples. It can be assigned to the C in CO₃⁻ or C(=O)-O groups such as Na₂CO₃, NaOCOCH₃ or NaOCOCH₂CH₂CH₃.

⁵ Men, S.; Lovelock, K. R.; Licence, P., *Phys. Chem. Chem. Phys.* **2011**, *13*, 15244-55.

⁶ Lahiri, A.; Borisenko, N.; Borodin, A.; Olschewski, M.; Endres, F., *Phys. Chem. Chem. Phys.* **2016**, *18*, 5630-7.

Figure 6. S 4. High resolution XPS spectra of the electrode samples cycled in EL_{ORG} and EL_{IL} and the pristine sample in (a) O1s region, (b) S2p region and (c) N1s region.

The O1s spectra show a peak at 531.3 eV for both cycled samples. The peak position can be assigned to various compounds, e.g. Na₂CO₃ or SO_x. The assignment of SO_x for NVO_{IL} seems to be validated by the peak observed at 168 eV in the S2p spectra, which is only visible in the sample cycled in EL_{IL}. As already mentioned above, the TFSI/FSI⁻ anions are the only source for sulfur. In case of the sample cycled in EL_{ORG}, the peak at 531.3 eV can possibly be assigned to the oxygen in the carbonate group. This observation is again in correlation with the presence of a peak at 289.5 eV in the C1s spectra of the sample cycled in EL_{ORG}. A distinct peak at 533.2 eV in the O1s spectra of the sample cycled in EL_{ORG} could be assigned to oxygen in the ClO₄⁻ anion or in the carbonyl-group.

Further evidence for the presence of IL-components on the surface of the samples cycled in EL_{IL} can be obtained from the N1s spectra. These show peaks at 399.27 eV and 402.2 eV, which can be assigned to the nitrogen originating from the TFSI/FSI anions and/or the pyrrolidinium cation, respectively. The nitrate peak at 407.4 eV could result from IL decomposition.

In summary, the SEI layer formed on the electrodes cycled in EL_{IL} appears to mainly consist of NaF, together with the fragments of the TFSI/FSI anions and the Pyr_{1,4} cation. On the other hand, the SEI layer formed on the electrodes cycled in EL_{IL} seems to consist of perchlorates, carbonates or alkyl carbonates.

Additional cycling data for NVO and NMO half-cells

Figure 6. S 5 Galvanostatic charge-discharge profiles of fresh NMO (a) and NVO (b) half-cells from OCV state at 100 mA g^{-1}

Mass-ratio optimization for NMO/NVO full cell

Figure 6. S 6. Cyclability of NMO/NVO_{ORG} (a) and NMO/NVO_{IL} (b) applying different NMO/NVO ratios.

To assure that the amount of sodium, which the NMO cathode provides, is equal to the amount of sodium that the NVO anode can take up upon charge, the optimal NMO/NVO weight ratio was determined. The ratio was estimated based on the ratio of the initial discharge capacity of NVO vs. the initial charge capacity of NMO (determined in half-cells starting from OCV state - Figure 6.S5). To further optimize the ratio galvanostatic charge-discharge tests were performed with different ratios (2.5/1; 2.7/1 and 3.0/1) applying both electrolytes EL_{IL} and EL_{ORG}, where 2.7/1 proved to yield the best results (Figure 6.S6).

Additional cycling data for the NMO/NVO full-cells

Figure 6. S 7. CV profiles from 0 to 2.8 V (a, b) and from 0 to 3.5 V (c, d) for NMO/NVO_{ORG} (a, c) and NMO/NVO_{IL} (b, d) at 0.1 mV/s respectively.

Figure 6. S 8. Cycling stabilities and CEs of NMO/NVO_{IL} (a) and NMO/NVO_{ORG} (b) at 75 °C.

Additional DSC measurements

Figure 6. S 9. DSC curves of the separator and PVDF-binder in EL_{ORG} (upper panel) and in EL_{IL} (lower panel).

Chapter 7

Ether Functionalized Ionic liquids as Electrolyte in High-Voltage Sodium Ion Batteries

Four ether functionalize ionic liquids, Pyr_{1,201} TFSI, N_{222,201} TFSI, N_{221,201} TFSI and Pip_{1,201} TFSI in addition of 0.5M NaFSI were investigated comprehensively as electrolyte for high voltage sodium-ion battery. Investigated IL-based electrolytes show the high anodic stability, up to 5.0 V vs. Na/Na⁺, suggesting the suitability for high-voltage application. The cycling stability and rate performance in Na half-cell using P2-Na_{0.6}Mn_{0.84}Ni_{0.06}Co_{0.1}O₂ cathode material, in the potential range 1.5 V - 4.6 V are reported. At 50 mA g⁻¹, the cell employing Pyr_{1,201} TFSI shows the poor capacity retention. For other IL electrolytes, the initial discharge capacity is ~170 mAh g⁻¹ and the capacity retention is ~73% after 100 cycles. At higher rate, N_{221,201} exhibits the predominant in term of discharge capacity and retention (109 mAh g⁻¹ at 200 mA g⁻¹). XPS reveals that cathode surface after cycling is comprised of IL components and their fragments. The discrepancy in electrochemical performance is major contributed by Na interphase stability, proved by Na stripping plating test and electrochemical impedance spectroscopy of Na symmetrical cells. The results suggested the incompatibility of Pyr_{1,201} TFSI as electrolyte for sodium half-cell. N_{221,201} TFSI IL has the best electrochemical performance as a result of stable and appropriate cathode electrolyte interphase layer and Na-electrolyte interphase.

7.1 Introduction

As the growing demand of portable consumer electronics, rechargeable lithium ion batteries (LIBs) are the dominant energy storage system, due to its high energy density and power density. The reliance on LIBs poses several problems, especially limiting the resource and escalating the price of this alkali metal. Rechargeable sodium ion batteries (SIBs) have been an attractive alternative to lithium ion battery owing to cost effective and high natural abundance of sodium over lithium.¹⁻³ In the same alkali group, SIBs retain fundamental working principles from LIBs.

High voltage SIBs draw significant attention for the development of higher energy and power density. Electrolyte and cathode material are two aspects which has significant contribution to the stability of high-voltage SIB system. The electrolyte decomposition at high voltage was normally suspected as a reason for the capacity fading.⁴⁻⁵ However, organic electrolytes are known to be unstable at high voltage. Meanwhile, ionic liquids (ILs) are proved to be more thermally and electrochemically stable than other organic carbonate based solvents.⁵⁻⁹ Because of their large range of electrochemically active, IL electrolytes are more suitable for high voltage application. One of the drawbacks for IL electrolyte is their high viscosity, which reduce the viscosity and ion diffusion, hence decrease capacity of a battery cell.^{6,10} Adjusting the structure of cation and anion could directly affect the electrochemical properties of IL. The incorporation of one ether chain in the cation is effective in lowering the viscosity. The high flexibility of ether side chain is expected to reduce the Coulombic interaction between the cation and anion.¹¹⁻¹² However, this type of ILs is seldom applied as electrolyte in SIBs, as well as LIBs.

In any electrolyte, conducting salt used is considered as a major component, which determine the final performance in electrochemical process. While NaClO_4 and NaPF_6 are the most commonly used salts in organic carbonate-based electrolyte,^{6,12-14} sodium bis(fluorosulfonyl)imide (NaFSI) and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) are more viable candidates in IL electrolytes.^{6,15} Whereas TFSI anion offers higher thermal stability and electrochemical stability properties, FSI anion exhibits higher conductivity and lower viscosity than TFSI anion.¹⁶⁻²⁰ In this research, to combine both effect of these anions, we employed ether functionalized ILs with

different cation core structures and TFSI anion as solvent, NaFSI as conducting salts for series of IL electrolytes and applied them in a practical high-voltage half-cell.

The cathode material needs to be considered to implement the high-voltage system. Among various classes cathode material, layered oxides are the most sought-after option because of their potential capacity and rate capability. The P2-type materials are more structurally stable, thus, deliver higher capacity and rate capability.^{1, 3, 21-23} P2- sodium manganese oxides with other transition metals doping (e.g. Co, Ni, Fe, etc.) received more attention in studies for SIBs with the aim to low-cost and efficient materials.²⁴ E.g. Doping Co into P2-NaMnO₂ structure has synergistic effect: suppress Jahn-Teller distortion and Na⁺ ion ordering.²⁵⁻²⁷ Ni substitution, due to its high redox potential, could enhance the energy density as well as the working potential of the material.^{24, 26, 28-31} One of the main challenges for Ni-doped manganese oxide materials is the phase transformation from P2 to O2 at above 4.2 V vs. Na/Na⁺, which results in low efficiency when cycling to a higher cut-off voltage.^{29, 32-34} Another effort is devoted to improve the cycling stability is controlling the morphology by synthesis methods. For example, the hollow spheres reduce the structural stress of material as a result of the smaller changes of the unit cell volume.^{25, 35} Hollow spherical Na_{0.65}Mn_{0.9}Co_{0.1}O₂ (NaMC) material, which combined the effect of Co-doping and the morphology, showed initial capacity of 167 mAh g⁻¹ and capacity retention of 67%/150 cycles in organic electrolyte.²⁵ When cooperating with appropriate IL electrolyte, the cell retains at 90% of its initial capacity after 500 cycles.³⁶ To develop this material further for high voltage application, the hollow spherical Na_{0.64}Mn_{0.83}Ni_{0.06}Co_{0.1}O₂ (NaMNC) material with the addition Ni into the structure, having the capability to operate in the voltage range 1.5 V – 4.6 V, is proposed.

The aim of this report is to investigate the series of ether-functionalized IL electrolytes, especially for high voltage application. After physical properties, IL electrolyte voltage window were evaluated, rate test and long-term cycling test were employed in spherical NaNMC half cells. To explain the difference in the cycling performance, together with X-ray photoelectron spectroscopy (XPS) on NaNMC electrode surface, electrochemical impedance spectroscopy (EIS) and Na stripping/plating test are presented and discussed to appraise the compatibility of electrolytes with Na/NMC electrodes.

7.2. Experimental section

7.2.1. Material synthesis and coin cell preparation

Spherical NaMNC was synthesized by similar procedure which already reported from our group.³⁵⁻³⁶ NH_4HCO_3 (Alfa Aesar, 99%) was first dissolved in DI water. After adding a small amount of absolute ethanol (10% volume of NH_4HCO_3 solution), a solution containing mixture of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 98%) and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 98%) with the following ratio 7:1:2 was added dropwise. To form (Mn, Ni, Co) CO_3 , the solution was subsequently stirred for 3h at ambient temperature. The co-precipitate was filtered, washed repeatedly by DI water and ethanol and dried at 80°C overnight. Afterward, the annealing step for dried precursor was 5h at 400°C in air to form spherical oxide compound. Then, it was dispersed in a solution of NaOH (Alfa Aesar, 98%) in ethanol and DI water (ratio 1:1). The water and ethanol were slowly removed by evaporation. The calcination program is 3 hours at 320°C, 4 hours at 800°C and 9 hours at 610°C for 9 hours. The final product was quenched to room temperature. As a reference, spherical NaMC was synthesized through a similar method, excluded $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in the initial step.

Four ether-functionalized ILs with pyrrolidinium (Pyr), piperidinium (Pip), ammonium core structures were synthesized, namely, 1-(2-methoxyethyl)-1-methylpyrrolidinium **bis(trifluoromethylsulfonyl)imide** ($\text{Pyr}_{1,201}$), N,N,N-triethyl-2-methoxyethanamonium **bis(trifluoromethylsulfonyl)imide** ($\text{N}_{222,201}$), N,N-diethyl-2-methoxy-N-methylethanamonium **bis(trifluoromethylsulfonyl)imide** ($\text{N}_{221,201}$), 1-(2-methoxyethyl)-1-methyl-piperidinium **bis(trifluoromethylsulfonyl)imide** ($\text{Pip}_{1,201}$). Synthesis procedure of ILs are provided in the chapter 3 and chapter 5.

For electrolyte preparation, NaFSI (Solvionic, 97%) and NaClO_4 (Sigma Aldrich, $\geq 98\%$) were first dried at 110°C under vacuum overnight before being transferred into argon-filled glovebox. The IL electrolytes were prepared in by dissolving NaFSI in the synthesized ILs to yield a 0.5 M solution. The organic electrolyte used was a 1 M of solution NaClO_4 in the mixture of ethylene carbonate and propylene carbonate (1:1

wt %; EC, Sigma Aldrich, 99%; PC, Sigma Aldrich, $\geq 99.7\%$). The solutions were continuously stirred for 24h before use.

The composite cathodes were prepared by mixing (NaMNC or NaMC), acetylene black (Alfa Aesar, $>99\%$) and polyvinylidene fluoride (PVdF, Arkema, Kynar HSV 900) binder in a weight ratio 60:20:20, with N-methyl-2-pyrrolidone (NMP, Alfa Aesar, 99+%) solvent. The slurry was coated on an Al foil (Goodfellow, battery graded) by a doctor blade (100 μm) and dried at 80°C overnight to remove NMP. The coated sheet was then punched with a diameter of 10 mm, roll-pressed and dried at 110°C overnight under vacuum. The fabricated cathode and sodium metal anode (Sigma Aldrich) were assembled in CR-2016 coin cells in an argon-filled glovebox. Glass microfiber (Whatman, GF/F) was used as the separator. For sodium stripping plating studies, metallic sodium was used as working and counter electrode with the symmetric configuration.

7.2.2. Electrochemical measurement

The electrochemical studies were performed on assembled CR-2016 coin-cells, and a Na metal plate was used as counter and reference electrode. Galvanostatic tests were carried out in the voltage range of 1.5–4.6 V versus Na/Na⁺ on the BTS Neware battery tester system under ambient conditions. Cyclic voltammetry (CV) were performed at a scan rate of 0.1 mV s⁻¹ between the 1.5 to 4.6 V vs. Na/Na⁺, using a BioLogic VMP3 potentiostat. Electrochemical impedance spectroscopy was conducted on BioLogic VMP3 instrument with the frequency range from 1 MHz to 50 Hz and AC amplitude of 10 mV. The leakage current was measured using Biologic VMP3 instrument by Chronoamperometry technique, in which the voltage of the cells was kept at 4.6 V for 24h.

7.2.3. Physical characterization

Conductivity measurements were conducted at 23 °C in an argon-filled glovebox by an InLab 751 conductivity probe head (Mettler Toledo) connected to a Solartron SI1260 frequency response analyzer. The samples were placed in a test tube inserted into a temperature-controlled steel block. The frequency range and the ac amplitude

for the EIS study were 10 MHz to 1 mHz and 20 mV. The ohmic resistance of electrolytes were determined by the intercepts between the impedance diagram and the real axis in the Nyquist plot at high frequency. The specific conductivity was determined using a cell constant of 1 cm^{-1} calibrated with 0.1 M KCl.

The crystal structures of synthesized materials were analyzed by powder XRD using Bruker Advance D8 diffractometer with Cu K α radiation (40 kV and 40 mA) at 0.015° per step between 2θ from 10° to 80° . The lattice parameters were determined by Rietveld Refinement with Topas software. The particle morphology was evaluated by field-emission scanning electron microscopy (FESEM) using a JEOL 6340F SEM. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a PerkinElmer Optima™ 8300 to determine the elemental composition of the materials.

To characterize the surface composition of electrodes after cycling, X-ray photoelectron spectroscopy (XPS) measurement was conducted by Kratos AXIS Supra equipment with automated dual anode Al/Ag beam source. After 50 cycles, cells were opened inside the glovebox. The electrodes were extracted and wash with dimethyl carbonate (DMC) to remove the residual the electrolyte. Subsequently, the electrodes were dried under vacuum to remove DMC, loaded onto the sample holder inside glovebox before being transferred to the instrument by a sealed glass tube to avoid any exposures to ambient environment.

7.3. Results and Discussion

7.3.1. Physical characterization

Figure 7. 1. XRD pattern of NaMNC (green) and NaMC (black) samples

Figure 7. 2. SEM images of NaMC (a) and NaMNC(b)

The chemical composition of NaMNC and NaMC according to ICP-OES results are $\text{Na}_{0.6}\text{Mn}_{0.84}\text{Ni}_{0.06}\text{Co}_{0.1}\text{O}_2$ and $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$, respectively. Figure 7.1 presents XRD patterns of the as-prepared NaMNC and NaMC samples. The products have single P2 phase- layer structure (space group $\text{P6}_3/\text{mmc}$) without any impurities. The Rietveld refinement of the XRD patterns were performed by assuming the space group. The lattice parameters were found to be approximately $a=b\approx 2.87 \text{ \AA}$, $c\approx 11.2 \text{ \AA}$ (the exact values are depicted in table S1). By Ni doping, the lattice parameters slightly increased, which can be explained by the substitution of Ni^{2+} ($0.69 \text{ \AA}$) for Mn^{3+} (0.645

Å), rather than Ni^{3+} (0.56 Å). The particle size and morphology of as-prepared NaMC and NaMNC are shown in Figure 7.2. The NaMNC/NaMC sphere has a diameter of 3 to 4 μm . It should be noted that the materials' particles are hollow. The hollow properties had been proved in our previous studies. The spheres containing Ni doping have the tendency to break more than the undoped version.

The cycling property of hollow sphere NaMC had been studied when cycling to 3.8V vs. Na/Na^+ . The electrochemical properties of NaMNC were then investigated in comparison with NaMC in a higher voltage range. In this study, the voltage range was chosen from 1.5 V to 4.6 V, despite the fact that the phase transformation from P2 to O2 at 4.2V might occur. The results are presented and discussed in detail in the Supporting information. The NaMNC shows a superiority in the cycling stability and energy density when compared to NaMC material. Hence, NaMNC is more suitable for use as a cathode in a higher voltage NIBs. In the next part of this study, we decided to use NaMNC as electrode material for ether-functionalize IL electrolyte study in high-voltage application

7.3.2. Ether-functionalized ionic liquid as electrolytes

Figure 7. 3. Overview of ether-functionalized IL in this study

Table 7. 1 Conductivity of ILs electrolyte containing 0.5 M of NaTFSI

	$\text{Pyr}_{1,201}$	$\text{Pip}_{1,201}$	$\text{N}_{221,201}$	$\text{N}_{222,201}$
Conductivity (mS/cm)	2.23	1.07	1.08	1.10

Four ether-functionalized ILs with coordinating TFSI anion have been chosen as the objective electrolytes for this study. They contain different core structures in cation: pyrrolidinium, piperidinium and ammonium. In our previous study, the effect of structure into viscosity had been discussed. With the same cation core structure, ether-functionalized has lower viscosity the unfunctionalized and ester functionalized

analogues. The viscosity of the neat ILs depend on the cation core structure with the following trend: $\text{Pyp} < \text{N}_{221} < \text{N}_{222} < \text{Pip}$ ($\text{Pyr}_{1,2\text{O}1} < \text{N}_{221,2\text{O}1} < \text{N}_{222,2\text{O}1} < \text{Pip}_{1,2\text{O}1}$). The conductivity of IL electrolytes with 0.5M of NaFSI at 23°C is illustrated in Table 7.1. In a similar trend, $\text{Pyr}_{1,2\text{O}1}$ electrolyte has the highest conductivity. However, the conductivity of $\text{N}_{222,2\text{O}1}$, $\text{N}_{221,2\text{O}1}$ and $\text{Pip}_{1,2\text{O}1}$ electrolyte are in the same level.

Figure 7. 4. (a) Current evolution of Na/C cells subjected to a stepwise potential step; (b) linear sweep voltammetry of Na/C cells.

To evaluate the anodic stability limit of ILs electrolyte, the linear sweep voltammetry (LSV) was employed in a coin cell set up using carbon paper as working electrode, Na metal as counter and reference electrode. It should be noted that the coin-cell setup was used in this measurement in order to resemble the testing condition in other electrochemical studies. Figure 7.4 reports LSV test of the investigated electrolytes at a scan rate of 0.1 mV/s. EC/PC has the lowest anodic stability, starts to decompose at 4.7 V vs. Na/Na⁺. IL electrolytes are stable up to 5.0 V vs. Na/Na⁺. To give more insight into the electrochemical reactions of electrolyte with the increasing of the potential, the current evolution was measured in the same setup during a stepwise potential step, increasing 0.1 V each one hour. In general, the stepwise potential measurement results are in good agreement with the LSV data. For EC/PC, the current flows start to increase at 4.5 V and reaches to 0.08 mA cm⁻² at 4.7 V, which likely associates with the electrolyte decomposition. IL electrolytes shows quite similar electrochemical stability below 4.9V with negligible current flow. At 5.0 V, the differences between IL electrolytes become more visible when the current flow of $\text{Pyr}_{1,2\text{O}1}$ increases to 0.35 mA/cm². The discrepancy of the current evolution of IL is

most obvious from 5.1 V when the decomposition arises. Among IL electrolytes, Pyr_{1,2}O₁ has the highest current flow at 0.14 mA/cm², following by N_{222,2}O₁ at about 0.08 mA/cm². Pip_{1,2}O₁ show the best electrochemical stability because of the lowest current flow at 5.1 V and 5.2 V. Indeed, investigated IL electrolytes have better electrochemical stability than EC/PC electrolyte and are suitable for high voltage application. The ether-functionalized ionic liquid electrolytes were continuing investigated the compatibility as electrolyte in half-cell sodium ion using NaMNC cathode material for high voltage application.

Figure 7. 5.(a) Cyclic voltammetry of spherical NaMNC at 0.1 mV s⁻¹ in IL electrolytes; (b) Charge discharge profiles of NaMNC using IL electrolytes of 10th cycle at 50 mA g⁻¹; (c) Cycling performance of NaMNC in different IL electrolytes at 50 mA g⁻¹ in 100 cycles; (d) Rate test performance of NaMNC in IL electrolytes.

Figure 7.5a describes the CV of NaMNC in IL electrolyte at 0.1 mV s⁻¹ in the voltage range from 1.5 – 4.6 V. IL cells exhibit a similar profile, in which the main redox peaks are marked at 2.5 and 1.9 V, compared to the redox couple at 2.4 V/2.0 V in EC/PC cell (figure 7.5a – red line). The observed polarization in IL cells are attributed to their high viscosity and the natural of solid electrolyte interface formed on anode/cathode

(SEI/CEI layers). Among IL cells, reduction peak of Pip_{1,2O1} slightly shifts to the left. Whereas, peak intensity of Pyr_{1,2O1} cell is smaller than the others. The Galvanostatic charge discharge profiles of 10th cycle at 50 mA g⁻¹ (figure 7.5b) are well conform to the observation in CV. Pyr_{1,2O1} exhibited a discharge capacity of 106.8 mAh g⁻¹, which is the lowest between IL cells. There is a minor plateau in the discharge profile of Pip_{1,2O1}, which might be attributed to side reaction from electrolyte. The long-term cycling stability of IL cells was investigated at 50 mA g⁻¹ (Figure 7.6c). The cycling performance of IL 5 is the worst. The discharge capacity of Pyr_{1,2O1} fluctuates and generally degrades upon cycling. After 100th cycle, the capacity retained at 68 mAh g⁻¹. Meanwhile, there is no significant difference in the cyclability between N_{222,2O1}, Pip_{1,2O1} and N_{221,2O1}. The initial capacity of N_{221,2O1}, N_{222,2O1} and Pip_{1,2O1} are in the range from 164 mAh g⁻¹ to 173 mAh g⁻¹, which are on the same level of EC/PC cell. After 100 cycles, the discharge capacity of cells is around 122 mAh g⁻¹, corresponds to 73% of capacity retention. This number is slightly improved when compared to the discharge capacity of cell employing EC/PC electrolyte (Supporting information part).

The rate capability of IL cells was investigated at 20 mA g⁻¹, 50 mA g⁻¹, 100 mA g⁻¹, 200 mA g⁻¹ and 400 mA g⁻¹ (Figure 7.5d). At slow rate of 20 mA g⁻¹, the discharge capacity of IL cells does not show much difference. From the current rate of 100 mA g⁻¹, the capacity of IL cells become distinct clearly. Compared to other ILs, N_{221,2O1} displays the best rate capability, e.g. it still archives a discharge capacity of 109 mAh g⁻¹ and 74 mAh g⁻¹ at current rate of 200 and 400 mA g⁻¹, respectively. Pyr_{1,2O1} cell exhibits the lowest discharge capacity at low current rates. However, at 400 mA g⁻¹ the discharge capacity of Pyr_{1,2O1} is 62 mAh g⁻¹, higher than N_{222,2O1} and Pip_{1,2O1}. The rate performance of IL cells follows the trend N_{221,2O1} > Pyr_{1,2O1} > N_{222,2O1} > Pip_{1,2O1}. The superior of N_{221,2O1} electrolyte over the other IL electrolytes are clearly observed in long-time cycling test of Na at 200 mA g⁻¹ in the aspect of discharge capacity and cycling stability (Figure 7.S1).

Electrochemical impedance spectroscopy was employed to investigate the evolution of cell impedance, including cathode, anode and electrolyte. Figure 7.6 presents the Nyquist plot of IL cells at fresh condition (before cycling), at fully charged (4.6 V) and fully discharge (1.5V) in 1st and 50th cycle and at open circuit voltage (2.7 V) after 50 cycle. The impedance of cell corresponds to the diameter of the semi-circles of Nyquist

plot. The fitted total EIS results are exhibited in Figure 7.7. The following observations can be summarized concerning the electrochemical impedance spectroscopy.

Figure 7. 6. Impedance spectra of NaMNC cells using IL electrolytes at fresh state (a); at 4.6 V – 1st cycle (b); at 1.5 V – 1st cycle (c); at 4.6 V – 50th cycle (d); at 1.5 V – 50th cycle (e) and at OCV state after 50 cycle (f).

Figure 7. 7. Total fitted impedance evolution of Na/NaNMC cells employing different electrolytes (blue: N_{221,201}, orange: N_{222,201}, gray: Pip_{1,201}, yellow: Pyr_{1,201}) at fresh state, after

12h of resting at OCV, at 4.6 V of 1st cycle, at 1.5 V of 1st cycle, at 4.6 V of 50th cycle, at 1.5 V of 50th cycle, at OCV state after 50 cycles.

1. After assembly, the electrochemical impedance of IL cells (figure 7.6a) acquired a high value. It indicates that thick and electrical resistant layers formed passively on anode/cathode when contacting with electrolytes.
2. The Nyquist spectra shrinks at 4.6 V, that implies for the dissolution of the solid electrolyte interfaces during the charge process. Then, the formation of SEI/CEI layer is observed by the increase of the impedance at full discharge state.
3. Generally, the impedance of N_{222,2O1}, N_{221,2O1} and Pip_{1,2O1} decrease remarkable after 50 cycle when comparing to the corresponding state in 1st cycle. It could be explained by the formation of ionically conducting layers on cathode/anode, which replace the initial passive layer and lower the impedance of N_{222,2O1}, Pip_{1,2O1} and N_{221,2O1}. On the other hand, after 50 cycles, the impedance of Pyr_{1,2O1} increases remarkably, for instance by 2.5 times at OCV state. This suggests that Pyr_{1,2O1} and the resulted solid electrolyte interface might hindrance the ionic conductivity and hence, give a negative impact to the electrochemical performance.
4. Compared to other ILs cell, Pip_{1,2O1} cell has the highest impedance in the fresh state. This observation is in accordance with the poor rate capability of Pip_{1,2O1} which is mentioned earlier.

The cell impedance evolution is contributed by the change arising at the metallic sodium anode and NaNMC cathode. The study will continue by investigate alteration of surface during cycling in IL electrolyte.

7.3.3. Surface analysis by X-ray Photoelectron spectroscopy

It is known that the cathode electrolyte interface would form during charge discharge process. The natural of CEI components highly depend on the electrolyte. XPS analysis was employed to characterize the pristine electrode and the electrodes after 50 cycles of cycling using IL electrolytes. The percentage of different elements in various electrodes were summarized in Table 7.2.

Table 7. 2. Atomic percentage of elements determined from survey spectra of the pristine electrode and IL cell electrodes after 50 cycles.

	C	N	O	F	S	Ni	Na	Mn
N _{221,201}	43.12	5.95	17.73	20.01	11.22	0.55	1.43	N.A
N _{222,201}	34.86	6.8	20.96	20.01	13.38	0.59	3.41	N.A
Pip _{1,201}	37.25	6.4	20	19.3	12.93	0.49	3.63	N.A
Pyr _{1,201}	39.17	6.7	21.71	17.5	13.11	0.44	1.25	0.13
Pristine	79.59	0	6.74	11.17	0	0.23	1.99	0.28

The presence of N and S and the increment of F content in cycled electrodes were proofs for the formation of CEI layers which originate from IL and NaFSI compounds. Besides, the percentage of Mn decreased from 0.28 to 0.13 for Pyr_{1,201} sample and to non-detectable for other samples. It is explained by the coverage of CEI layer containing other atoms. In contrast to Mn, Ni content increases after 50 cycles. The intensity of high-resolution Ni spectra also enhances compared to pristine sample (Figure 7S4). It might be an indication for Ni dissolution and the formation of Ni-compound on the surface. The dissolution of Ni at high potential

Figure 7. 8. The XPS high resolution spectrum of C 1s, O 1s, N 1s, S 2p and F 1s of pristine electrode and electrode samples after 50 cycles.

From the C 1s spectra, there are additions of peaks at 285.9, 287.1 eV and 293.1 eV. The peaks at 285.9 eV can be assigned to C attached to O by single bond, which is considered as footprint of ether functionalized cation. The corresponding peak of C-O group is observed at 533.3 eV in O 1s spectra. The highest intensity peak at 287.1 eV can be attributed to C-N peak, possibly from Pyr, Pip and ammonium group or carbonyl C=O group. The presence of TFSI anion in cycled electrodes is observed by CF₃ peak at 293.1 eV and at 689.2 eV (F 1s spectra). In F 1s spectra, besides CF₃ and CF₂ peaks, the peak at around 684 eV is specified for fluoride F⁻ compounds, e.g. NaF. The formation of F⁻ compounds is initiated by the cleavage of C-F bond of CF₃ group, discussed by literature.

From N 1s spectra, to prove for the deposition of IL components on the CEI layer, two peaks are distinct at ~403 eV that can be assigned to N⁺ in Pyr, Pip or ammonium cation, at ~399.7 eV that belongs to N⁻ in TFSI or FSI anion. The decomposition of IL components could be clearly observed by other peaks in N 1s spectra. For example, NSO₂⁻, a fragment of TFSI/FSI, is found at the peak located at 398.6 eV. A small peak assigned to alkyl ammonium at 401.5 eV could be a proof for the decomposition of cation when electron attacks to protonated N. The side product of cation decomposition is C=O containing compounds, which can be seen by the increasing of peak intensity and areal ratio between C=O group and metal oxides peak (located at 531.9 eV and 530 eV). The ether group might transform to C=O group during the formation of CEI layer. Based on the intensity and the area percentage of determined peaks, the decomposition of N_{221,2O1} which containing N₂₂₁ is the least in comparison between ILs. It might be a reason for the superior performance of N_{221,2O1} throughout the tests.

Considering that the only source of S is from TFSI and FSI anion, the fragmentation of anion in IL electrolytes is evident from S 2p spectra. The highest binding energy peaks in this region at 170.25 eV and 169.12 is assigned to the S in TFSI/FSI anion. Aside from these peaks, the boards peak from 166 to 168 eV are attribute to oxidized S-containing compounds, such as SO₄, SO₃ or sulfinyl SO group. The similar trend is noted when the decomposition of IL cation and anion occurs more in the cases of N_{222,2O1}, Pyr_{1,2O1} and Pip_{1,2O1}. Based on the intensity of peaks in S and N region, the thickness of N, S and O based layer is thinner for N_{222,2O1} and Pip_{1,2O1}.

In summary, the CEI layer formed on the electrodes when cycling in ether functionalized electrolytes contains TFSl/FSI anion and IL cation. During cycling, cation decomposes to form organic products, such as alkyl ammonium or C=O containing compound. Meanwhile, the decomposition of TFSl/FSI anion would result in oxidized S-containing species. The core structure of IL contributes to the level of degradation progress of IL electrolyte. Among them, N_{221,201} which contains N₂₂₁ group seems to be the least to decompose. However, the difference in the CEI composition between N_{222,201}, Pip_{1,201} and Pyr_{1,201} is inconspicuous to explain the reason for capacity fading of Pyr_{1,201} cell. Hence, the change occurring in Na metallic electrode seems to be the major contributor to the cyclability of the cells. In the next part, more attempts will be implemented to clarify the effect of IL electrolyte on the Na electrode during cycling.

7.3.4. Sodium symmetrical cell study

To explore the kinetic hindrance regarding Na electrode and electrolyte, EIS was performed on the Na/Na symmetrical cell fresh cell, after 24 and 48 h under open circuit potential (OCP) condition and after 100 h of Na stripping and plating test (constant current of 0.1 mA cm⁻² for each 1 hour) (Figure 7.9).

Figure 7. 9. Impedance spectra of Na/Na symmetry cells at fresh condition, after 24h and 48h at open circuit potential and after 50 cycles of Na stripping/plating of (a) Pyr_{1,201}, (b) Pip_{1,201}, (c) N_{221,201} and (d) N_{222,201}.

Generally, the impedance of the cells increases after resting cells at OCP condition. It implies that a passive interface formed chemically on the Na electrode. Among them, the impedance of N_{221,201} and Pip_{1,201} seem to stabilize after 24 hours of resting. Meanwhile, the impedance of N_{222,201} expands around 2.5 times in the first 24 hours and slowly increased in the next 24 hours. In comparison with other IL cells, Pyr_{1,201} cell has the least impedance in the fresh state, that is consistent with the low conductivity value of the electrolyte. After 48h of resting, the resistance of electrode electrolyte interface (which corresponds to the diameter of the first semicircle) steady increases from $\sim 530\ \Omega$ to $\sim 1500\ \Omega$. The Na stripping and plating cycling process was then tested in Na symmetrical cells by continuously applying a constant current of $0.1\ \text{mA cm}^{-2}$ for 1 hour of charge/discharge (Figure 7.10).

Figure 7. 10. Voltage vs. time plot upon Na stripping/plating measurement performed in Na/electrolyte/Na cell at a current rate of $0.1\ \text{mA cm}^{-2}$ and stripping/plating time of 1h.

The overpotential was recorded to examine the compatibility of electrolyte against Na electrode and the evolution of electrolyte/Na electrode interface under current flow. Initially, the limiting potential follow trend of the Na symmetrical cell impedance after 48h of resting (just prior the cycling), that is $N_{221,201} < Pyr_{1,201} < Pip_{1,201} < N_{222,201}$. The cells employing N_{221,201} and Pip_{1,201} show a stable Na stripping/plating process with a

symmetric profile shape and a limiting potential from 0.29 to 0.39 V. On the other hand, the limiting overpotential of sodium stripping and plating in N_{222,2O1} electrolyte decreases and stabilize from 0.8 V to 0.5 V under 10 hours of repeated cycling. The shape of potential profile of N_{222,2O1} is unsymmetrical and elongated to the stripping (Na dissolution) process. The high overpotential region is assigned to the dissolution of Na underneath the surface layer. Thus, the SEI layered formed on Na electrode in N_{222,2O1} case requires higher kinetic energy for Na stripping. The high kinetically hindrance of SEI layer is more apparent when high current rate is applied since the rate Na deposition/dissolution now become a limiting factor. It is noteworthy that the limiting potential of Pyr_{1,2O1} cell rises rapidly to 7 V after 37 hours. Pyr_{1,2O1} electrolyte seems to be not electrochemical stable when in contact with Na electrode. When the decomposition happens, the detrimental layer would accumulate on Na electrode and cause the high overpotential for Na stripping/plating process. This might be a reason for the poor capacity retention of Na half-cell using Pyr_{1,2O1} when compare with other IL electrolytes.

After stripping/plating test the impedance of N_{222,2O1}, Pip_{1,2O1} and N_{221,2O1} reduce significantly when compared to the before testing state. It indicates that the SEI layer which formed during electrochemical progress has lower resistance than the passive layer which formed chemically initially. In the other way, the impedance of Pyr_{1,2O1} cell raise up to a level of 10⁶ Ohm, suggesting the inactivation of the cell. The result is in compliance with the high overpotential in Na stripping/plating test.

7.4. Conclusion

In summary, the electrochemical properties of a series of ether-functionalize ionic liquid electrolyte were evaluated and compared. IL electrolytes exhibits a good electrochemical stability, could stable up to 5.0 V vs. Na/Na⁺. The effect of the core structure on the anodic stability of IL electrolyte was observed in stepwise potential measurement. Although Pyr core structure affect positively on the electrolyte conductivity of the electrolyte, it has the lower anodic stability than the other IL electrolytes. Meanwhile, despite of the low conductivity, Pip IL electrolyte shows the highest anodic limitation.

IL electrolytes were applied in a high-voltage SIB half-cell using NaMNC as cathode material. The cell employing Pyr_{1,201} showed a poor cycling performance with significant capacity fading. Coin cell containing N₂₂₂, N₂₂₁ and Pip structures exhibited good capacity retention. In the rate test, N_{221,201} electrolyte containing N₂₂₁ asymmetric structure reveals the superiority when compared with other electrolytes.

The impedance of the NaNMC cells decreases after 50 cycles, except for Pyr_{1,201} electrolyte. It suggests that a detrimental layer possibly formed on cathode/anode during cycling in Pyr_{1,201} cell. The CEI layer formed on the NaNMC electrodes when cycling composes of IL components, conducting salt and their decomposition fragments. N_{221,201} was found to have the least decomposition. However, the major difference was not able to be detected.

Detail studies on the compatibility of IL electrolyte with Na electrode were taken. EIS study on the Na symmetrical cell proved that a passive layer would form chemically on the Na surface when putting in contact with IL electrolytes. The rate of the deposition depends on the nature of the ILs. In Na stripping/plating test, Pyr_{1,201} cell displayed a major increase in the limiting potential, which indicates that electrolyte decomposed and formed a detrimental layer on the Na electrode. Hence, Pyr_{1,201} is not compatible to be applied in Na half-cell.

Among the investigated ether-functionalize IL electrolyte, N_{221,201} displayed the best performance regarding the capacity retention and rate capability. A stable SEI layers would form on the NaNMC cathode and Na anode during cycling.

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7.5. Supporting information

Electrochemical performance of NaMNC and NaMC in 1M NaClO₄ EC/PC

Figure 7.S 1 (a) Cyclic voltammetry of spherical NaMNC (red) and spherical NaMC (black) at 0.1 mV s⁻¹; (b) Charge discharge profiles of NaMNC (red) and NaMC (black) of 1st cycle (solid) at 50 mA g⁻¹; (c) Cycling stability and Efficiency of NaMNC and NaMC at 50 mA g⁻¹ in 100 cycles; (d) Cycling stability of NaMNC at different current rates

Cyclic voltammetry (CV) on NaMNC and NaMC at a scan rate of 0.1 mV/s reveals the electrochemical processes during charge/discharge (Figure 7.S1a). For NaMC, the main redox couple observed at 2.3V/2.1V is attributed to Mn³⁺/Mn⁴⁺. In the NaMNC cell, the corresponding oxidation and reduction peaks locate at 2.4V and 2.0V. Hence, the presence of Ni ion in the structure could increase the polarization. The oxidation peak at around 3.5V in both cells relates to Co³⁺/Co⁴⁺ redox reaction. There is a small hump peak founded at 4.2V in NaMC cathode, which could be explained by the gliding of transition metal layer mentioned above. For NaMNC cathode, the peak couple at about 4.2, which is more intense than NaMC, corresponds to the redox reaction of Ni⁴⁺/Ni²⁺.

The Galvanostatic charge/discharge curves at 50 mA g^{-1} ($\sim 0.3 \text{ C}$) are displayed in Figure 7.S1b. The charge/discharge profiles correlate with the peak positions in CV curves. NaMNC delivered an initial capacity of 162.8 mAh g^{-1} , which is slightly higher than NaMC (158.6 mAh g^{-1}). Although they have similar profiles, the average voltage of NaMNC is slightly above the NaMC one. It leads to the remarkable difference in the first discharge energy density in Ni-doped sphere (NaMNC 450 mWh g^{-1} , NaMC 404 mWh g^{-1}). It is proved to the theory that the occupation of Ni in the material helps to increase the energy density. For long time cycling test at 50 mAh g^{-1} (Figure 7.S1c), a significant difference in the cycling stability could be seen between NaMC (white) and NaMNC (black). The Ni-doped version provided a capacity of 113 mAh g^{-1} (69.4% of retention) after 100 cycles, as compared to 65.6 mAh g^{-1} of the non-Ni. The Coulombic efficiency increases to a stable level during cycling in both cells. As can be seen from the graph, Ni substitution has a positive effect on the Coulombic efficiency of the cycling cell. After 10 cycles, the efficiency of NaMNC reaches and maintains at 99%, higher than NaMC (around 96%). When avoiding the irreversibility of electrochemical reactions during cycling, the capacity retention also improves. It is noteworthy that, unlike majority of reports for sodium manganese-based oxide, the P2-O2 phase transformation is ambiguous in material's charge discharge profiles.

Due to the better retention of NaMNC at 50 mA g^{-1} , we decided to cycle the cells at higher rates of 200 mA g^{-1} and 400 mA g^{-1} (Figure S1c). NaMNC exhibited a remarkable discharge capacity and a good capacity retention at 200 mA g^{-1} and 400 mA g^{-1} . The discharge capacities in the first cycle are 137.5 mAh g^{-1} and 130.8 mAh g^{-1} , respectively. Their capacity retentions after 100 cycles are 77% and 78%. Hence, this material is well suitable for applications requiring fast charge.

NaMNC electrode characterization

Figure 7.S 2. SEM of NaMNC electrode after 50 cycles in (a) $N_{222,201}$ electrolyte, (b) $N_{221,201}$ electrolyte, (c) $Pip_{1,201}$ electrolyte and (d) $Pyr_{1,201}$ electrolyte

Figure 7.S 3 The XPS.Survey spectra of NaMNC pristine electrode and electrode after 50 cycles in $N_{221,201}$, $N_{222,201}$, $Pip_{1,201}$ and $Pyr_{1,201}$ electrolyte (double intensity of pristine result).

Figure 7.S 4. The XPS high resolution spectrum of C 1s, O 1s, N 1s, S 2p and F 1s of pristine electrode and electrode samples after 50 cycles.

Cycling performance of NaNMC -IL half-cells

Figure 7.S 5. Cycling performance of NaNMC half-cells employing IL electrolytes.

IL synthesis

Synthesis of the IL precursor salts

The synthesis of the IL precursor salts is based on quaternization reaction, following the previous report procedure. Generally, the respective functionalized alkylhalide is added dropwise to a solution of the respective amine precursor under Ar atmosphere. Then, the mixture is stirred continuously under refluxing condition for 24 to 72h. After removing the solvent by low pressure or adding diethyl ether to the reaction mixture and filtration, the crude product is obtained. Subsequently, it was washed with diethyl ether/ethyl acetate or with toluene three times followed by a further washing with pentane. After recrystallization, quaternary ammonium halide salts are obtained.

Anion exchange and purification

A solution of LiTFSI or LiFSI (with 5% excess) in water is added to a solution of the ammonium halide precursor in water and stirred at room temperature for 24 h. Suspension is formed during the process. Then the aqueous phase is removed, the result products are centrifuged and washed 8 – 10 times with distilled water to remove LiBr and unreacted starting material. Each time, AgNO₃ is added to the washing solution by the end to exclude the halides in the products. The ILs are further purified by refluxing in dichloromethane with activated charcoal for 3 h followed by filtration. To reduce the water content to under 5 ppm the ILs are dried at 70 °C in high vacuum using an MBraun Solvent Purification for two days (first day: 10-3mbar, second day: 10-6 mbar).

The ILs characterization are reported in our previous publication *Phys.Chem.Chem.Phys.*, 2018, **20**, 29412)

Chapter 8

General Discussion and Recommendation

In this thesis, the initial objectives have been achieved by proving the ability of ionic liquid electrolyte in replacing conventional organic electrolyte in SIBs in different perspectives. First, IL electrolyte could enhance the cycling stability of SIBs by the formation of effective SEI as well as CEI layers. The dependence of physicochemical properties of IL electrolytes on the structures of IL electrolyte and the choice of sodium conducting salts had been observed and clarified. Besides DSC and TGA studies of pure ILs and IL electrolytes, for the first time, the superiority in thermal safety of IL electrolytes over organic electrolytes had been demonstrated in a SIB full-cell system. The third advantage of IL electrolyte is high electrochemical stability window. This aspect of various IL electrolytes had been evaluated throughout the thesis. High-voltage materials based on P2-hollow sphere $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ was developed and presented in Na ionic-liquid half-cell configuration. Together with the development of IL electrolyte as well as material, insight on the reaction mechanisms related to electrolytes were also concerned and mentioned. For the sake of completeness of stable and safer high-voltage SIB systems, recommendations are pursuing compatible anode materials, completing the study on high-voltage cathode materials to pair and apply in IL full-cell setups.

8.1. General discussion

Because of the high abundance and low cost of minerals, sodium ion batteries have evolved ongoingly and showed prominent properties to replace existing lithium ion batteries. Along the development of secondary batteries, safety keeps being the major cause of concern for commercial energy storage systems due to the usage of flammable organic solvent. In the thesis, ionic liquids had been proved as a compatible and efficacious electrolyte solvent to mitigate the safety issue of SIBs. The main aspects mentioned includes long-term cyclability, thermal stability, low self-heating rate and high voltage application. The testing systems are mostly sodium half coin-cells, in which sodium metal acts as an electrode. For a consistent study and comparison, the active materials applied throughout the study was based on hollow sphere P2- $\text{Na}_{0.7}\text{MnO}_2$ and its modifications. For further implementation, NVO and hard carbon half-cells were attempt with IL electrolytes to investigate the compatibility of IL electrolytes with other materials. Based on preliminary results from half-cell studies, a SIB full-cell was constructed and investigated the cycling performance under ambient and elevated condition. In this stage, the thermal superiority of IL electrolytes over conventional organic electrolytes was proved by multiple methods. In the final stage, IL electrolytes was examined on high-voltage SIB systems. Modifications of P2- $\text{Na}_{0.7}\text{MnO}_2$ were synthesized to increase the working potential and applied in various IL electrolytes. The detail outcomes are mentioned below.

8.1.1. Effect of sodium conducting salts in IL electrolytes

Besides solvents, sodium conducting salts play significant role in the physicochemical properties of electrolytes in secondary batteries. The chosen of salt in IL electrolyte could affect to final performance of the systems. There were 3 conducting salts using in this investigation. NaTFSI and NaFSI are considered as novel sodium conducting salts for SIBs because of containing similar anions with majority of advanced ILs. Meanwhile NaClO_4 is one of the most popular salts in SIB studies. The electrolytes of ionic liquid 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($\text{Pyr}_{1,4}\text{TFSI}$) with 0.5 M of these conducting salts were analyzed in a Na half-cell configuration using spherical P2 – $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ cathode. Amongst all NaFSI

(0.5M) solution shows excellent electrochemical performance with an initial discharge capacity of 147 mAh g⁻¹ and a capacity retention of 90% after 500 cycles (at 50 mA g⁻¹). Meanwhile, the initial discharge capacity of NaTFSI-IL cell is 124 mAh g⁻¹ at 50 mA g⁻¹. The cell retains 65% of discharge capacity value after 500 cycles. NaClO₄ – IL displays the first discharge capacity of 136 mAh g⁻¹ and the lowest capacity retention of 66 % after 100 cycles and 4 % after 300 cycles. At 200 mA g⁻¹, NaFSI-IL cell is still able to achieve ~100 mAh g⁻¹, while NaTFSI-IL and NaClO₄ – IL only obtain 75 mAh g⁻¹.

The impedance of Na half-cells after 30 cycles and 500 cycles follows the trend NaFSI-IL < NaTFSI – IL < NaClO₄ – IL, partially explained the results. It proposed that a thinner SEI/CEI layer formed on the cathode/anode surface during the cycling when applying NaFSI-IL electrolyte.

Figure 8. 1. Possible decomposition pathways of TFSI anion

In particular, the observed performance could be explained by the formation of CEI layer on Na_{0.6}Co_{0.1}Mn_{0.9}O₂ cathode and SEI layer on Na metal anode. When using NaFSI and NaTFSI, the decomposition of TFSI anion follows by N-S cleavage (reaction 1). The compounds are stabilizing during cycling and a thin CEI layer. NaFSI salt results a thinner SEI layer than NaTFSI. In case of NaClO₄-IL, the cleavage of TFSI anion is occurring at C-F bond. The resulting F⁻ combines with Na⁺ to form NaF. The process occurs continuously and thicken the CEI layers.

The result of Na stripping/plating in Na symmetrical cells revealed a stable polarization of Na dissolution and deposition of NaFSI – IL electrolyte and NaTFSI – IL electrolyte. The limiting potential of NaFSI-IL and NaTFSI-IL cell are 0.3 V and 1.5 V, respectively, implying a thinner SEI layer in the case of NaFSI-IL. In the meantime, the limiting potential of NaClO₄ – IL continuously increases during cycling, to almost 3 V after 120 hours, suggesting the thickening of inactivated layer on Na electrode.

The phenomenon probably hinders sodium stripping and plating, devastated the general performance of Na half-cells.

Among the investigated sodium conducting salts in specific IL solvent, NaFSI shows the best electrochemical performance by the formation of stable SEI and CEI layers. Hence, it was fixed to be conducting component in IL electrolytes along the further studies.

8.1.2. Effect of cation and anion structures of pure ILs and IL electrolytes to physicochemical properties

Figure 8. 2. Summary of structure effects to physicochemical properties of pure ILs and IL electrolytes.

The physicochemical properties of ILs are adjustable by modification of cation core structures, addition of functional groups or changing anion. A series of N-based core structure pure ILs and IL electrolyte was presented and characterized by consistent and uniform techniques. Viscosities, conductivities, thermal stabilities, electrochemical stabilizes and compatibilities with Na metal electrodes were compared and main trends had been detected as follows.

Viscosity is an important physical parameter of electrolytes, which influences the ion diffusion and conductivity in an electrolyte. In extend, the conductivity of solution is also governed by molecular weight and ion sizes. The conductivity value directly impacts to the capacity of a battery system, especially at high current rate. The lower conductivity of electrolyte, the lower capacity the battery obtains. As a prominent disadvantage, ILs are typically more viscous than conventional organic solvent. To apply IL as efficient electrolyte, this is needed to have low viscosity and conductivity. In comparison between ILs, pyrrolidinium core structure and ether-functional group have positive impact on conductivity and viscosity. Meanwhile, ester- and nitrile-functional ILs and morpholinium core structure are not suggested for electrolyte because of enhanced viscosity. The intermediate group is ILs containing allylic and thioester. Considering the effect of anion, TFSI anion is bulkier than FSI anion, resulting an impediment in conductivity and viscosity.

High thermal stability and non-flammability is one of the most propitious aspect of ILs in the objective of safer electrolyte. Generally, pure ILs and IL electrolytes (ELs) have higher onset temperature than the organic one. Compared to TFSI anion, FSI – ILs and ELs are lower thermal stable than TFSI version. Regarding to cation, nitrile functional group shows the least thermal stability, decomposition initiates at 125°C and releases heat during dealkylation process at ~300°C. In addition, alkene and sulfide functional ILs and ELs exhibits lower onset temperature than others. In contrast, the most thermal stable ILs are unfunctionalized, ether and ester functionalized ILs. The effect of core structure is trivial. The onset temperature of ELs having ring core structure (pyrrolidinium, piperidinium) were slightly higher than ammonium ELs.

Except thioether functionalized ILs, the electrochemical stability windows (ESW) of ILs are large. As electrolytes for SIBs, majority of ELs in this study have electrochemical stability up to 5 V vs. Na/Na⁺, which is suitable for high-voltage application. FSI anion EL showed slight inferior to TFSI analogue in the anodic stability. The anodic stability order in ELs could be summarized as followed.

Figure 8. 3. The trend of core structures and substitute groups for anodic stability limits

8.1.3. Effect of IL structures to electrochemical performance in various Na battery systems.

8.1.3.1. Na stripping/plating

In order to achieve good performance in a Na-half cell, the compatibility between Na metal anode and electrolyte during cycling needs to be considered carefully. The interaction including dissolution and deposition of Na metal. A good electrolyte supposes to have low and stable potential polarization with Na metal electrode during the cycling progress. Regarding to the Galvanostatic stripping/plating test in Na symmetrical cell, there are 3 types of IL electrolyte. The first type of IL electrolyte is not compatible with Na metal, resulting a thick passive layer on Na surface when contacting. The passive layer inhibits Na stripping/plating process, increases energy required for this process. The ILs in this group are mainly high viscous and low conductivity, such as cyanide, ester functionalized or morpholinium core structure. The second type is IL electrolytes, in which the polarization increases from low voltage to high voltage during the stripping/plating process, e.g. reverse ester or alkenyl functional group. Specially, thioether functionalized EL showed high overpotential of stripping/plating initially. The value decreases and stabilizes after cycling. The phenomenon suggests an application as quasi SEI building additive. The third group contains IL electrolyte that have low and stable limiting voltage during the stripping/plating test. Typically, the ILs in this group have low viscosity. These ILs are suggested applying in Na half-cells.

8.1.3.2. The electrochemical performance in Hard carbon -half cells

The electrochemical investigation was conducted on HC/Na systems employing the series of ELs. The structure of ILs significantly impact the performance of HC/Na cells.

Generally, the discharge capacity of IL electrolytes cells is not comparable with the capacity of organic electrolyte cells. In accordance with the Na stripping/plating results, ELs containing ester or cyanide functional group (which inhibit Na stripping/plating) did not obtain any capacity. In constant, ELs which showed stable cycling performance in HC/Na cells, were also in the EL groups offering good Na stripping/plating. However, the correlation between Na stripping/plating and cycling performance in HC/Na cells is not straightforward. The effect of CEI layer, Na diffusion coefficient etc., need to be considered as well.

8.1.3.3. The electrochemical performance in P2- $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ -half cells

Together with Pyr_{1,4} electrolyte (Pyr_{1,4}TFSI), the IL based electrolytes containing N_{221,2O1}, N_{222,2O1} and Pip_{1,2O1} exhibit a significant improvement in cycling performance in P2- $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ /Na half-cell. The rate performance is related to the Na diffusion coefficient as well as conductivity value. In addition, Pyr_{1,2O1}, a promising EL combined these features did not well-behave in the studied system. It might be a result from the geometry interaction between ether functional group and core structure, which leads to preferred decompositions. A substantial and rigid explanation regarding to decomposition mechanism need to be drawn in the future.

8.1.4. Electrochemical performance of IL electrolytes vs. organic electrolyte.

The cycling performance of cells employing IL electrolytes had been compared with organic electrolyte in various SIB systems. Generally, the cycling stability of IL cells could be improved by the formation of stable SEI and CEI layer on cathode and anode side during the charge/discharge process. The detail results are summarized as followed.

When evaluating in a half cell configuration using spherical P2 – $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_{2+z}$ cathode, NaFSI (0.5M) in Pyr_{1,4}TFSI shows excellent electrochemical performance with a significant improvement in cycling stability (90% capacity retention/500 cycles at 50 mA g⁻¹ in a half cell) compared with conventional NaClO₄ (1M) in EC/PC electrolyte (39% retention/500 cycles). When replacing Pyr_{1,4}TFSI by other ether

functionalized ILs, piperidinium based outperform the organic electrolyte by far with a retention of 81%/350 cycles, following by ammonium based ILs at around 70%/350 cycles. In rate test, organic electrolyte cell displays the best rate capability when comparing with IL electrolytes cells. The poor rate performance of IL electrolytes can be explained by their high viscosity as well as their low conductivity when compared to OR electrolyte. In order to overcome this drawback different approaches e.g. addition of appropriate additives or hybrid ionic liquid/organic electrolyte have been reported in literature.

The superiority of IL electrolyte over organic electrolyte was also proved when assessing the electrochemical performance of nanorod $\text{Na}_{2.55}\text{V}_6\text{O}_{16}/\text{Na}$ half-cells. Unlike $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ cell systems, NVO cells displayed comparable discharge capacities at high current (up to 400 mA g^{-1}) in both $\text{Py}_{1,4}\text{TFSI}$ electrolyte and organic electrolyte cases. The cycling stability of IL electrolyte half-cell is also far better than OR-electrolyte version.

Unlike NVO and NCO when the IL electrolytes show the advantage, considering Na/Hard carbon half-cell configuration, IL cells could not obtain similar amount of discharge capacity as OR cells. Hence, the performance of IL depends on the compatibility with material.

8.1.5. Thermal safety of IL electrolyte

ILs are non-flammable, non-volatile and thermal stable. In this thesis, the thermal stability of pure ILs and IL electrolytes were evaluated by DSC and TGA studies. Except thioether and nitrile functionalized ILs, majority of investigated IL electrolytes have the onset temperature higher than 350°C .

The thermal superiority was studied in Na full-cell $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2/\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ (NMO/NVO) configuration. In Accelerating Rate Calorimetry test the NMO/NVO_{IL} full-cell shows a higher onset temperature as well as a lower self-heating rate than NMO/NVO_{ORG}. DSC studies on the individual components and their combinations were applied to delineate the exothermal behaviors observed in the ARC through the scanning temperature range. The lack of runaway reactions in the DSC measurements

of EL_{IL} and the mixtures of EL_{IL} with the active materials reinforce the enhanced safety when applying an IL based electrolyte. In addition, NMO/NVO_{IL} could withstand and operate at elevated temperatures while NMO/NVO_{ORG} shows rapid degradation of the discharge capacity. The presented results underline that the IL based SIB system tested herein is superior to the SIB based on the organic carbonate electrolyte, especially when battery safety and cycling stability are the major concerns.

8.1.6. IL electrolytes in high-voltage application

The capability of IL electrolyte to operate at high-voltage condition was first seen in chapter 4. Considering IL electrolyte of Pyr_{1,4}TFSI and NaFSI (0.5M) in Na_{0.6}Co_{0.1}Mn_{0.9}O₂/Na cell configuration, no significant fading in peak current is observed at potential limit of 4.8 V vs. Na/Na⁺. This suggests that this IL electrolyte would be suitable to evaluate cathodes that operate at higher redox potentials.

In chapter 5, the ESW of a series of pure ILs and IL electrolytes were measured by 3-electrode setup (for pure ILs) and 2-electrode coin cell setup (for IL electrolytes). Except thioether functionalize IL, other ILs have wide ESWs. In 2-electrode coin cell, majority of investigated IL electrolyte have the anodic potential of ~ 5V vs. Na/Na⁺. The limited working potential of organic electrolyte is just ~ 4.6 V. Hence, IL electrolyte is suggested to replace organic electrolyte for high-voltage SIB systems. The detail comparison between ether functionalized IL electrolytes was discussed further in chapter 6 using Na/C configuration.

The main drawback of NCO/Na cells employing NaFSI- Pyr_{1,4}TFSI ILs is low energy density and low average working potential. The two of third discharge capacity is gained at the potential below 2.5 V. To develop this material further for high voltage application, substitution Mn by other metals which have high redox potential is a promising solution. The hollow spherical Na_{0.64}Mn_{0.83}Ni_{0.06}Co_{0.1}O₂ (NaMNC) material with the addition Ni into the structure, having the capability to operate in the voltage range 1.5 V – 4.6 V, is proposed. Series of ether functionalized IL electrolytes were applied in Na half-cell of introduced material. N,N-diethyl-2-methoxy-N-methylethanamonium bis(trifluoromethyl-sulfonyl)imide (N_{221,201}) showed the

predominance in the cycling performance over N,N,N-triethyl-2-methoxyethanamonium bis(trifluoromethylsulfonyl)imide (N_{222,201}), 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr_{1,201}) and 1-(2-methoxyethyl)-1-methyl-piperidinium bis(trifluoromethylsulfonyl)imide (Pip_{1,201}), especially at high current rate. However, the difference between N_{221,201} IL electrolyte cell and electrolyte version in cycling performance and discharge capacity was not obvious.

With the intention of developing the average working voltage further, more attempts were made on the cathode material by adding various Ni content into the original P2-Na_{0.6}Co_{0.1}Mn_{0.9}O₂. The usage of Pyr_{1,4}TFSI electrolyte in these materials is a considerable advancement that organic electrolyte. As a reconnaissance work, the detail of this will be discussed under next section.

8.2. Reconnaissance work – Developing high-voltage hollow spherical P2-Na_{0.6}Mn_xCo_yNi_z material

8.2.1. Introduction

In chapter 7, hollow spherical P2-Na_{0.64}Mn_{0.83}Ni_{0.06}Co_{0.1}O₂ had been synthesized from spherical (Mn,Ni,Co)O₂ as annealing product from the coprecipitation of (Mn,Ni,Co)CO₃. The material exhibits an excellent performance with the reversible cyclability in high voltage range from 1.5 V – 4.6 V. However, the Ni content in the product is only at 0.06, which is not significant to improve the average working potential of the material. Attempts had been made to increase the Ni content by increasing the amount of NiSO₄ precursor. However, it is not an effective method because of the loss of NiCO₃ during the coprecipitation and filtration process. The solubility constant of NiCO₃ is higher than these of MnCO₃ and CoCO₃ ($K_{sp, MnCO_3} = 2.24 \times 10^{-11}$, $K_{sp, CoCO_3} = 1.0 \times 10^{-10}$, $K_{sp, NiCO_3} = 6.6 \times 10^{-9}$). To tackle the problem, Ni ion should be introduced after the coprecipitation. In this reconnaissance work, a series of Na_{0.6}Mn_xCo_yNi_zO₂ would be synthesized via a modified procedure from coprecipitation method, called “NO₃-method”. NiNO₃ was added to the mixture of (Mn,Co)O and NaOH before calcination step. The electrochemical performance of

these materials would be investigated in organic electrolyte system and ionic liquid electrolyte system.

8.2.2. Experimental section

The procedure was adapted and modified from the reported procedure. A mixture of 10 mmol $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 98%) (molar ratio 9:1) were dissolved in 700 ml of DI water. About 70 ml of pure ethanol (99.9%, Merck) was added to the solution containing sulfates. In a separate beaker, the solution containing 100 mmol NH_4HCO_3 (Alfa Aesar, 99%) was prepared in 700 ml of DI water. Subsequently, the NH_4HCO_3 solution was added to the solution of sulfates in water-ethanol mixture. To form $(\text{Mn},\text{Co})\text{CO}_3$, the solution was subsequently stirred for 3h at ambient temperature. The co-precipitate was filtered, washed repeatedly by DI water and ethanol and dried at 80°C overnight. Afterward, the dried precursor was annealed in air at 400°C for 5h to form spherical oxide compound. Then, it was dispersed in a solution of NaOH (Alfa Aesar, 98%) and NiNO_3 (Sigma Aldrich, 99.999% trace metals basics) in ethanol and DI water (ratio 1:1) with the following ratios (Table 8.1). The water and ethanol were slowly removed by evaporation. The residue was first calcined at 320°C for 3 hours, followed by 800°C for 4 hours and an additional step at 610°C for 9 hours. The final product was quenched to room temperature.

The crystal structures of synthesized materials were analyzed by powder XRD using Bruker Advance D8 diffractometer with $\text{Cu K}\alpha$ radiation (40 kV and 40 mA) at 0.015° per step between 2θ from 10° to 80° . The lattice parameters were determined by Rietveld Refinement with Topas software. The particle morphology was evaluated by field-emission scanning electron microscopy (FESEM) using a JEOL 6340F SEM. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a PerkinElmer Optima™ 8300 to determine the elemental composition of the materials.

The composite cathodes were prepared by mixing active material, acetylene black (Alfa Aesar, >99%) and polyvinylidene fluoride (PVdF, Arkema, Kynar HSV 900) binder in a weight ratio 60:20:20, with N-methyl-2-pyrrolidone (NMP, Alfa Aesar,

99+%) solvent. The slurry was coated on an Al foil (Goodfellow, battery graded) by a doctor blade (100 μm) and dried at 80°C overnight to remove NMP. The coated sheet was then punched with a diameter of 10 mm, roll-pressed and dried at 110°C overnight under vacuum. The fabricated cathode and sodium metal anode (Sigma Aldrich) were assembled in CR-2016 coin cells in an argon-filled glovebox. Glass microfiber (Whatman, GF/F) was used as the separator. The electrolytes are NaClO_4 1M in EC/PC and NaFSI 0.5M in Pyr_{1,4} TFSI. The electrochemical studies were performed on assembled CR-2016 coin-cells, and a Na metal plate was used as counter and reference electrode. Galvanostatic tests were carried out in the voltage range of 1.5–4.2 vs. Na/Na^+ on the BTS Neware battery tester system under ambient conditions.

8.2.3. Results and Discussion

8.2.3.1. Material characterizations

Table 8. 1 Molar ratio of (Mn,Co)O and NiNO_3 in the synthesis procedure and the molar composition of Na, Mn, Co, Ni element based on ICP-OES results ($\text{Na}_a\text{Mn}_x\text{Co}_y\text{Ni}_z\text{O}_{2+w}$).

Sample ID	Precursor ratio		Composition based on ICP-OES			
	(MnCo)O	NiNO_3	Na (a)	Mn (x)	Co (y)	Ni (z)
S0	1	0	0.67	0.9	0.1	0
NO3-S3	5	1	0.7	0.8	0.08	0.11
NO3-S5	3	1	0.68	0.67	0.09	0.24
NO3-S6	2	1	0.72	0.65	0.07	0.28
NO3-S9	1.5	1	0.7	0.56	0.072	0.37

ICP-OES results were summarized in table 8.1. The Ni content was varied from 0.11 to 0.37. Hence, this method is effective to adjust the content of Ni in the product. The spherical morphology of samples was partially retained. Broken spheres were seen in the SEM. Compared to XRD pattern of original NCO (S0 sample), there are additional peaks in S3, S5, S6 and S9 samples, which are not from any impurities. The peak shifting is originated from the presence of Ni and the changing of lattice parameter. The refined lattice parameter information was presented in table 8.2.

Table 8. 2. Lattice parameter of NaMNC samples

Name	R_{wp}	R_p	χ^2	a	c
NO3-S3	2.2107	1.6516	1.9608	2.8780	11.1901
NO3-S5	2.0409	1.5459	1.6761	2.8742	11.1893
NO3-S6	1.9504	1.5117	1.5879	2.8789	11.1578
NO3-S9	2.8069	2.2102	1.1837	2.8790	11.2055

Figure 8. 4. XRD patterns of various NaMNC materials compared with $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$ materials (NCO) Figure 8. 5. SEM of NaMNC samples (NO3-S3, NO3-S5, NO3-S6 and NO3-S9 synthesized via NO3 method) and NCO ($\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$) sample.

8.2.3.2. Electrochemical performance

Figure 8. 6. CV profiles of NO3-S3, NO3-S5, NO3-S6 and NO3-S9 half-cells using NaClO₄ EC/PC (OR) electrolyte at 0.1 mV/s in the potential range from 1.5 V to 4.2 V

Na half-cells of materials in OR electrolyte was tested by cyclic voltammetry method with a scan rate of 0.1 mV/s in the potential range from 1.5 V to 4.2 V. From CV profiles, with the addition of Ni content in the materials, 2 oxidation peaks at 3.3 V and 3.7 V became more prominent with the increasing of intensity and area. Hence, additional Ni in the materials had contributed to the electrochemical process. All peaks are reversible and stable after consecutive cycles. The electrochemical behavior of materials in OR electrolyte was further investigated by GCD tests at 50 mA g⁻¹ in the same potential range. The discharge capacity, energy density, power density and average voltage were calculated and indicated in table 8.3. The average voltage was determined by the intersection of charge and discharge curve of GCD profiles.

From low to high Ni content, the average voltage increased with the increasing of Ni content. The maximum average voltage obtained was 3.0 V corresponding to $z=0.24$ onward. NO3-S5 sample showed the highest energy density at this current density. By increasing the Ni amount further (NO3-S6 and NO3-S9), the energy density slightly reduced. In the other perspective, the power density maximized at 134.23 W/kg, which corresponds to sample NO3-S9 with highest Ni content. When comparing with original

material $\text{Na}_{0.6}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_2$, this method is successful to improve the average voltage, energy density as well as power density. The amount of Ni needs to be compromised between energy density, power density and the purpose of application.

Table 8. 3. Comparison between NO3-S3, NO3-S5, NO3-S6 and NO3-S9 in first discharge capacity, energy density, power density and average voltage

Sample ID	1 st Dis Capacity (mAh g ⁻¹)	Energy density (Wh/kg)	Power density (W/kg)	Average voltage (V vs. Na/Na ⁺)
S0	149.5	351	119.98	2.25
NO3-S3	155.6	389	125.34	2.45
NO3-S5	159.75	406	127.35	3
NO3-S6	134.5	346	128.92	3
NO3-S9	130.726	351	134.25	3

Figure 8. 7. The cycling stability of NO3-S3, NO3-S5, NO3-S6 and NO3-S9 half cells employing organic electrolyte and IL electrolyte.

The long-term cycling performance were evaluated in OR electrolyte and IL electrolyte (NaFSI 0.5 M in Pyr_{1,4} TFSI) at the current rate of 50 mA g⁻¹. In OR electrolyte, materials exhibited similarity in the capacity fading. The capacity retained at 60% after 100 cycles. To improve the cycling stability of the materials, half-cells employing IL electrolytes were tested in the same conditions. The IL cells exhibited an excellent stability with no significant fading in the first 50 cycles. It should be noted that unlike the OR electrolyte samples, discharge capacity obtained in IL samples are substantially different. To explain the results, more experiments and methods should be conducted to investigate the change in materials further, such as diffusion coefficient, phase changes, etc.

8.2.3.3. Conclusion

By adding NiNO_3 with the mixture of (Mn,Co) oxide and NaOH before annealing steps, the result products shows an significant improvement in power density and energy density. With the utilization of IL electrolyte, the cycling stability of these materials in Na half-cell configuration could be enhanced. The result is promising for the development of high-voltage and long-term stable SIB system based on IL electrolyte. To complete the work and have a reasonable conclusion on the contribution of Ni ion in the material, more studies on the relation of Ni content to the material properties, electrochemical performance should be conducted in the future.

8.3. Future work and Recommendation

In this thesis, when employing IL electrolyte in SIB half-cell systems, the amelioration in cycling stability and high-voltage application had been successfully proven for the first time. Hollow sphere NaMnO_2 is considered as a good cathode material for SIBs. From the initial achievement, an IL full-cell NMO/NVO system had been introduced. Besides the comparable performance at ambient condition, in comparison with OR full-cell, the IL full-cell showed superiority in thermal safety and the capability to operate at elevated condition.

As a drawback, the working voltage of the full-cell is low, resulting in low energy density. To overcome the problem, the **first recommendation** of the author is finding other anode materials which is compatible with IL electrolytes and had lower working plateau in Na half-cell than NVO material, such as hard carbon. By pairing with NMO, this effort could enhance the average potential of full cell system. In chapter 5, the cycling stability of hard carbon in half-cell study is sufficient. However, the obtain capacity is not comparable with the value of organic electrolyte because of the high viscosity of IL electrolyte. Nano-sizing hard-carbon could be a beneficial method to increase the capacity in IL electrolyte.

The achievement of IL electrolyte in high-voltage half-cell paves the way for the intensive studies on high-voltage cathode materials. As mentioned in the literature

review, conventional organic electrolytes have low ESWs which, restrict the high-voltage studies. The **second** strategy is upgrading the working potential of hollow spherical P2-NaMn_{0.9}Co_{0.1}O₂ by other metals substitution. In section 8.2, materials based on hollow spherical P2-NaMnCoO₂ with the controlled amount of Ni had been introduced. With the addition of Ni, the average voltage, power density and energy density of materials significantly successfully improved. The materials displayed excellent cycling stability in IL electrolyte. This side project should be completed in the future to find the best compromised composition for further IL full-cell study.

After finding a good low-voltage anode and high-voltage cathode material, author suggestion is applying them with IL electrolyte in scale-up SIB. The order should be coin-cell, pouch-cell and then cylindrical-cells. Other components such as separator, binder and current collector should be considered carefully before commercialization.

List of publications

1. **Minh Phuong Do**, N. Bucher, A. Nagasubramanian, I. Markovits, T. Bingbing, P. J. Fischer, K. P. Loh, F. E. Kühn, M. Srinivasan “**Effect of Conducting Salts in Ionic Liquid Electrolytes for Enhanced Cyclability of Sodium-Ion Batteries**”, *ACS Appl. Mater. Interfaces*, 2019, 11, 23972-23981.
2. **Minh Phuong Do**, P. J. Fischer, A. Nagasubramanian, J. Geder, F. E. Kühn, M. Srinivasan, “**Investigation of the Electrochemical and Thermal Stability of an Ionic Liquid Based $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ / $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$ Sodium-Ion Full-Cell**”, *Journal of The Electrochemical Society*, 2019, 116 (6), A944-A952.
3. **Minh Phuong Do**, P. J. Fischer, R. M. Reich, A. Nagasubramanian, M. Srinivasan, F. E. Kühn “**Synthesis and physicochemical characterization of room temperature ionic liquids and their application in sodium ion batteries**”, *Phys.Chem.Chem.Phys.*, 2018, 20, 29412.
4. D. Gupta, A. Muthiah, **Minh Phuong Do**, G. Sankar, T. I. Hyde, M. P. Copley, T. Baikie, Y. Du, S. Xi, M. Srinivasan, and Z. Dong, “**Electronic and Geometric Structures of Rechargeable Lithium Manganese Sulfate $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ Cathode**”, *ACS Omega* 2019, 4, 11338-11345