

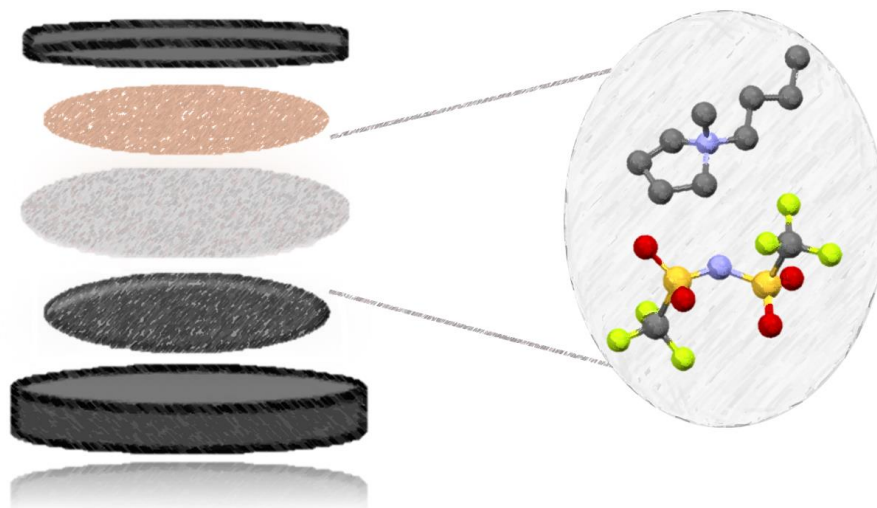


Technische Universität München
Fakultät für Chemie
Professur für Molekulare Katalyse

ROOM TEMPERATURE IONIC LIQUIDS AS ELECTROLYTES FOR SODIUM-ION BATTERIES

PAULINE J. FISCHER

DISSERTATION





Technische Universität München

Fakultät für Chemie

Professur für Molekulare Katalyse

Room Temperature Ionic Liquids as Electrolytes for Sodium-Ion Batteries

Pauline Josephine Fischer

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Vorsitzender:

Prof. Dr. Lukas Hintermann

Prüfer der Dissertation:

1. Prof. Dr. Fritz E. Kühn

2. Prof. Dr. Tom Nilges

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„Don't worry, be happy" :)

Bobby McFerrin

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KURZZUSAMMENFASSUNG

Auf Grund der hohen Verfügbarkeit und der geringen Kosten von Natrium, ist das Interesse an Natrium-Ionen-Akkumulatoren (SIBs) als Alternative zu teuren Lithium-Ionen-Akkumulatoren für Energiespeichersysteme im Großmaßstab in den letzten Jahren stetig gewachsen. Besonders für die Speicherung von Strom aus erneuerbaren Energiequellen, sind große und vor allem sichere Energiespeichersysteme nötig. Um SIBs jedoch als solche Speichersysteme zu etablieren, müssen vor allem gute Zyklierbarkeit und thermische Stabilität und Sicherheit dieser Akkumulatoren gewährleistet sein. Auf Grund ihrer guten Modifizierbarkeit, hohen thermischen Stabilität und vernachlässigbaren Brennbarkeit, werden Ionische Flüssigkeiten (ILs) als vielversprechende Elektrolyte für SIBs angesehen.

Im Rahmen dieser Arbeit wurde eine voll funktionsfähige SIB Vollzelle (Anode: $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$, Kathode: $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$), basierend auf der unfunktionalisierten IL $\text{Pyr}_{1,4}\text{TFSI}$, hergestellt. Die IL basierte Vollzelle wurde mit einem analogen Akkumulator, mit konventionellem, organischen Elektrolyten hinsichtlich ihrer elektrochemischen Leistung und thermischen Stabilität verglichen. Das IL basierte System erzielte deutlich bessere Zyklierbarkeit und Coulomb Effizienz. Des Weiteren wurde die erhöhte thermische Stabilität des IL basierten Akkumulators mittels ARC und DSC nachgewiesen und somit die förderlichen Eigenschaften des IL Elektrolyten für das SIB System weiter bestätigt.

Um den IL basierten Elektrolyten weiter zu optimieren, wurde eine Reihe von 15 funktionalisierten ILs synthetisiert und einheitlich charakterisiert. Dabei wurde besonderer Wert auf die physikochemischen und elektrochemischen Eigenschaften der funktionalisierten ILs gelegt, um deren Eignung als Elektrolyte zu ergründen. Aus den Untersuchungen konnten wichtige Tendenzen in Bezug auf die verwendeten Kationen, Anionen und funktionellen Gruppen sowie allgemeine Struktur-Eigenschaftsbeziehungen abgeleitet werden. Ether-basierte IL Elektrolyte wurden in SIB Halbzellen mit $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ als Kathode untersucht. Die resultierenden Systeme wiesen eine signifikant verbesserte Zyklierbarkeit im Vergleich zum System mit dem organischen Elektrolyten auf. Basierend auf den Ergebnissen, welche die Eignung von funktionalisierten ILs untermauern, können weitere Optimierungen des SIB Systems vorangetrieben werden.

Zusammenfassend konnte die erhöhte Zyklierbarkeit und thermische Stabilität von IL basierten Systemen - eine wichtige Grundlage für große Energiespeichersysteme - gezeigt werden. Durch die leichte Modifizierbarkeit von ILs und ihrer physikochemischen Eigenschaften bieten sich vielversprechende Möglichkeiten für weitergehende Optimierungen. Maßgeschneiderte Elektrolyte, auf Basis von IL-Mischungen, könnten die vorteilhaften Eigenschaften wie z.B. Viskosität, Leitfähigkeit und SEI Bildung einzelner ILs kombinieren um die Zyklierbarkeit und thermische Stabilität von Natrium-Ionen-Akkumulatoren weiter zu erhöhen.

ABSTRACT

Sodium-ion batteries (SIBs) have gained rising attention in the past few years particularly in large-scale energy storage systems for electricity generated from renewable energies due to the high abundance and low cost of sodium. However, in order to enable their practical application cycling stabilities have to be increased and most importantly, safety concerns related to the high volatility and flammability of conventional organic electrolytes have to be overcome. In this regard, electrolytes based on ionic liquids (ILs) are rendered promising alternatives due to their facile tunability, high thermal stability, low vapor pressure and negligible flammability.

In the context of this thesis a fully functional SIB full-cell (anode: $\text{Na}_{2.55}\text{V}_6\text{O}_{16}$, cathode: $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$) based on the unfunctionalized IL Pyr_{1,4}TFSI was assembled and compared to an analogue system containing a conventional organic electrolyte. Focus was set on the electrochemical performance and thermal stability of the respective full-cells. The IL based SIB was found to outperform the organic based analogue in terms of cycling stability and coulombic efficiency. Moreover, the thermal stability was significantly enhanced when applying the IL based electrolyte as proven by ARC and DSC studies underlining the beneficial influence of the IL electrolyte on the cycling performance and safety.

To further tune and optimize the IL electrolyte, a library of 15 functionalized ILs was synthesized and uniformly characterized regarding their physicochemical and electrochemical properties in order to estimate the suitability of the different ILs as electrolytes. Main trends with respect to the cationic core structures, anions and functional groups could be derived providing valuable information regarding structure-property relationships. Thus, the ether functionalized ILs were rendered most suitable for first electrochemical investigations in coin cells. SIB half-cell studies with $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ as cathode showed significantly enhanced cycling stability and capacity retention for most IL based systems when compared to the organic based analogue proving the suitability of functionalized IL electrolytes and serving as basis for further optimizations.

In summary, IL based systems showed enhanced cycling and thermal stability as important prerequisite for large-scale energy storage systems. Moreover, the rational tunability of IL properties based on structure-property relationships, is the fundament for further electrolyte optimizations. Tailored IL mixtures could combine beneficial properties of the single IL components, as e.g. conductivity, viscosity and surface layer formation to further enhance cyclability, capacity and thermal stability of the SIBs.

LIST OF ABBREVIATIONS

ARC	accelerating rate calorimetry
BASIL	biphasic acid scavenging utilizing ionic liquids
CEI	cathode electrolyte interphase
DEC	diethyl carbonate
DMC	dimethyl carbonate
DME	dimethoxyethane
E_a	redox energy of the anode
E_c	redox energy of the cathode
EC	ethylene carbonate
EEG	Erneuerbare-Energien-Gesetz
E_g	band gap of the electrolyte
EDX	energy-dispersive X-ray spectroscopy
EMC	ethylmethyl carbonate
ESS	energy storage systems
ESW	electrochemical stability window
FG	functional group
FR	flame retardant
FSI	bis(fluorosulfonyl)imide
GW	gigawatt
HC	hard carbon
HTR	heat-temperature-reaction
HOMO	highest occupied molecular orbital
IL	ionic liquid
Im	imidazolium
LIB	lithium-ion battery
LUMO	lowest unoccupied molecular orbital
M	molar (mol/l)
mS	milliSiemens
NMO	$\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$
NR_4	ammonium
NVO	$\text{Na}_{2.55}\text{V}_6\text{O}_{16} \times 0.6 \text{H}_2\text{O}$
OC	open circuit
PC	propylene carbonate

Pip	piperidinium
Pyr	pyrrolidinium
RES	renewable energy sources
RTIL	room temperature ionic liquid
SEI	solid electrolyte interphase
SIB	sodium-ion battery
TFSI	bis((trifluoromethyl)sulfonyl)imide
V	Volt
wt%	weight percent
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

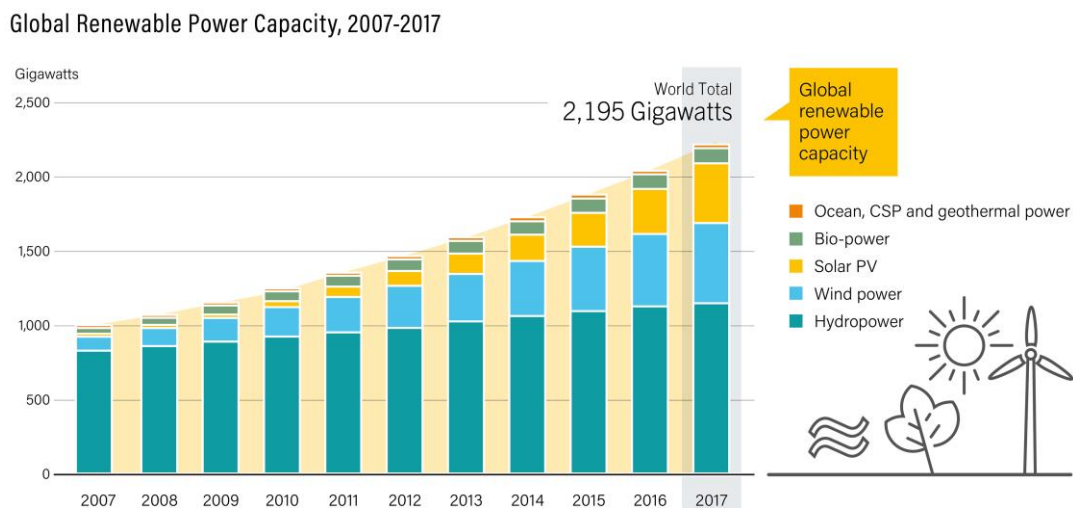
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1 INTRODUCTION

1.1 Sodium-Ion Batteries as Large-Scale Energy Storage Systems

The imminent depletion of fossil fuel resources together with the related increasing environmental problems has led to a significant rethinking in energy policy since the past two decades. In 2000 e.g., the German government announced the “Erneuerbare-Energien-Gesetz (EEG)” which is a major pillar for the energy turnaround. According to this act, 40 – 45% of the gross energy consumption should be supplied by renewable energy sources (RES) by 2025.¹ In general, the awareness of the need to reduce fossil energies has led to a rapid, worldwide development of RES comprising wind-, hydro-, solar-, geothermal- and bioenergy.¹⁻⁴ As shown in Figure 1 the total power capacity based on renewable energies is increasing steadily and has more than doubled in the decade from 2007 to 2017 reaching a world total of 2195 GW in 2017 – enough to supply approximately 26.5% of the global electricity demand.⁴



REN21 RENEWABLES 2018 GLOBAL STATUS REPORT

Figure 1: Total global power capacity based on renewable energies from 2007 to 2017. Reprinted with permission from Ref. [4].

However, with the steadily increasing exploitation of RES new problems come into account. In contrast to fossil fuel power, the energy provided by these renewable sources is intermittent and highly dependent on factors that are rather hard to control such as e.g. wind, sun or water. Thus, safe large-scale energy storage systems (ESS) are needed to stabilize and store the intermittent energy and realize its smooth and safe integration into the power grid. Energy generated during off-peak times must be shifted to meet on-peak needs to ensure a balancing of energy generation and demand. Main requirements for stationary large-scale ESS are different from those regarding transportable ESS as

applied for example in electric vehicles. Energy density is critical for the latter while long cycle life, low cost, and high safety are the most important parameters for the stationary systems.^{2,3}

A wide range of technologies for ESS is currently being investigated e.g. redox flow batteries, super capacitors, flywheels, pumped-storage hydroelectricity or Li-ion/Pb-acid/Na-S based batteries. Among these, the secondary battery technology is one of the most promising due to flexibility, high energy conversion efficiency and simple maintenance of the resulting systems. So far, lithium-ion batteries (LIBs) are pioneers in the rechargeable battery sector and definitely the technology of choice for portable applications. However, limited lithium reserves associated with high and steadily increasing costs are two major drawbacks which hinder the application of lithium based systems in large-scale ESS. Therefore, the exploration of low-cost and safe rechargeable batteries based on abundant resources is necessary. Due to the practically unlimited sodium resources and the low cost of this metal, sodium-ion batteries (SIBs) have in turn attracted great attention especially for large-scale ESS.^{2,3}

In contrast to the limited lithium resources, which are unevenly distributed (mainly in South America), sodium resources are basically unlimited (ratio of reserves: Li/Na = 1/1000)⁵ and evenly distributed due to the high abundance of sodium in the earth's crust (Figure 2).⁶ Costs^a for sodium amount to only 150 US\$/t while lithium is very expensive with 5000 US\$/t.⁵ Further, LIBs require Cu as anodic current collector since lithium alloys with the lighter and cheaper aluminum^{b,7}. Sodium on the contrary, does not alloy with aluminum, reducing costs for the anodic current collector significantly. With respect to physical and chemical properties, sodium shows similar behavior compared to lithium as its higher homologue. Moreover, sodium is the second-lightest and smallest alkali metal next to lithium with a weight of 23.0 g/mol (Li: 6.94 g/mol) and an atomic radius of 97 pm (Li: 68 pm).² Considering all mentioned aspects, SIBs are rendered as ideal alternatives to LIBs. Due to the difference in the standard electrochemical potentials (Na: 2.71 V; Li: 3.04 V)² and the relatively heavier and larger sodium atom, energy densities of SIBs will obviously not exceed those of their LIB analogues.^{2,6} However, as mentioned earlier, energy density is not a major critical parameter in the field of large-scale ESS, thus still rendering SIBs a meaningful alternative to LIBs.^{2,3,6}

^a costs for the respective carbonates

^b Cu 6755 US\$/t vs. Al 1920 US\$/t⁷

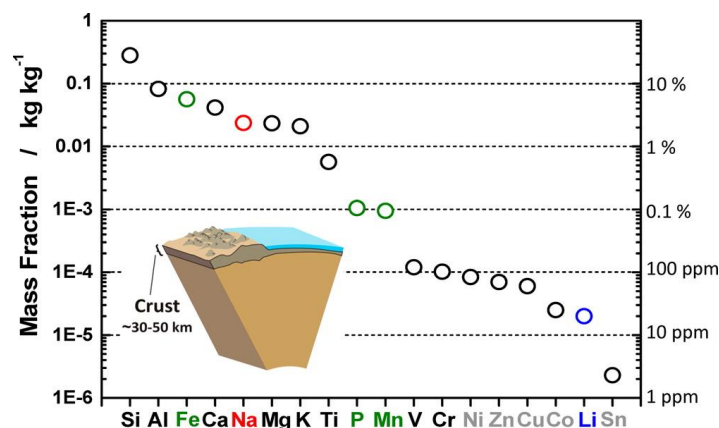


Figure 2: Elemental abundance in the earth's crust. Reprinted with permission from Ref. [6]. Copyright 2014 American Chemical Society.

Historically sodium and lithium based systems have the same origin and were investigated in parallel from the 1970s to the 1980s. However, interest in SIB systems decreased significantly after the success of LIBs and their commercial application in the 1990s. The big rush on LIBs fueled research of lithium based systems, whereas studies regarding sodium based systems almost disappeared until SIBs emerged as alternatives to LIBs for ESS especially in the last decade.^{2, 6}

1.2 Sodium Based Batteries – Setup and Function

Up to date, the only commercially employed sodium based technologies are high temperature Na/S⁸ and Na/NiCl₂⁹ batteries. The schematic setup of a Na/S battery is depicted in Figure 3 exemplarily for high temperature sodium batteries.¹⁰ In these batteries, reversible charge and discharge occur via a sodium-ion conducting alumina based solid (ceramic) electrolyte. To achieve sufficient ion conductivity, high operation temperatures of 300 – 350 °C are required since liquid sodium is used as anode. The cathode is composed of molten S/Na₂S_x or porous Ni/NiCl₂ respectively. One major advantage of these high temperature sodium batteries is their high energy efficiency (up to 90%) and high current density. However, the fact that molten sodium and sulfur are used as active materials at such high temperatures is still a severe safety issue and a tough problem for their large-scale application. In contrast, sodium-ion batteries are free of metallic sodium and operable at ambient temperature rendering these systems as safer alternatives especially for large-scale energy storage.^{2, 3, 6, 11}

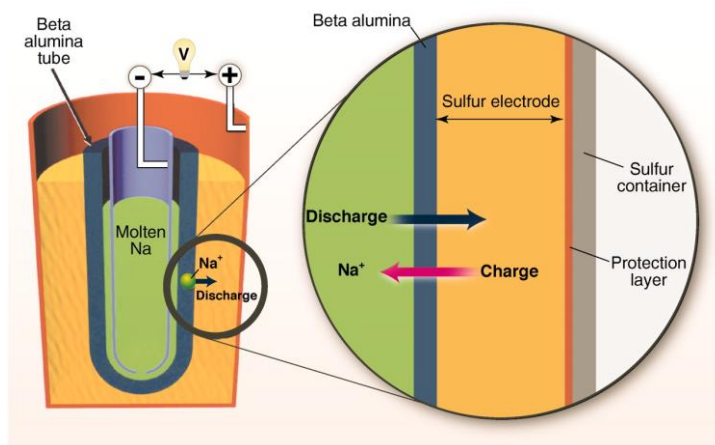


Figure 3: Schematic setup of a Na/S battery. The magnified cross section of the cell shows the direction of Na^+ transport through the alumina based solid electrolyte. Reprinted with permission from Ref. [10]. Copyright 2011 American Association for the Advancement of Science.

The schematic setup of a SIB is depicted in Figure 4. Main structural components and working principle for SIBs are essentially the same as in LIBs except that lithium-ions are replaced by sodium-ions. Thus, two sodium insertion materials serve as positive (cathode) and negative (anode) electrode respectively. The electrodes are electronically separated by the sodium-ion conducting electrolyte and the separator. During discharge, sodium-ions move from the anode to the cathode while electrons flow in the opposite direction through an external electric circuit. These processes take place vice versa during the charge process. Battery performance depends on all components, thus making optimization of electrode materials as well as the electrolyte necessary to establish a functional system.^{3,6}

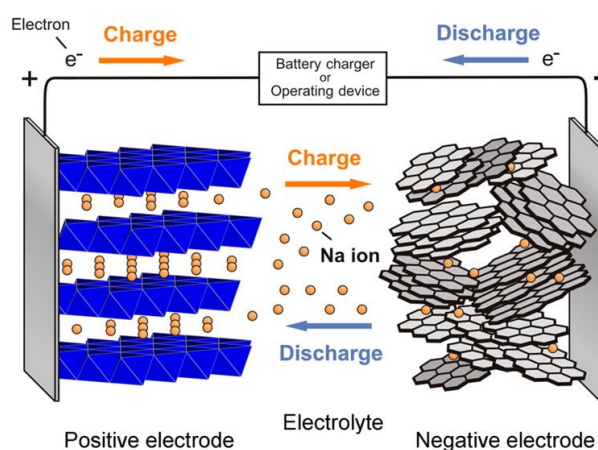


Figure 4: Schematic illustration of a SIB setup. Reprinted with permission from Ref. [6]. Copyright 2014 American Chemical Society.

Due to the conceptual similarity of SIBs to LIBs main findings derived from the extensive research performed for LIBs throughout the past decades can partly be transferred to SIBs facilitating their development. However, there are still several fundamental scientific questions regarding SIBs which require further intensive research on the SIB technology leaving vast room for improvement. For

example, the difference in transport and kinetic behaviors between sodium and lithium in analogous electrodes, as well as the sodium-ion extraction and insertion mechanism still need to be elucidated in more detail. Further, the mechanism of the formation of the interfacial layers on the electrodes and their composition and the sodium-ion transfer in the electrolyte-electrode interface and through the interfacial layers are still object of current investigations of SIB systems.² Therefore, intensive research focusing on the electrode materials as well as the electrolytes is ongoing.

1.2.1 Sodium-Ion Batteries – Cathode Materials

Up to date, several electrode materials have been proposed as cathodes or anodes for SIBs. According to their chemical composition, SIB cathode materials can roughly be grouped into five categories comprising oxides, sulfides/sulfates, phosphates, fluorides and hexacyanoferrates. Two inherent challenges SIBs have to face regarding their electrode materials are that, firstly, they often offer lower voltages compared to LIBs. Secondly, the de/intercalation of larger sodium-ions puts more strain on the crystal structures than it is the case for smaller lithium-ions.¹² Several structures have been examined to overcome these drawbacks. Among those especially layered oxides have shown promising results¹³⁻¹⁶ and thus have emerged as the most popular and extensively studied type of SIB cathodes. Layered oxides exhibit simple structures, high operating potentials and can be obtained by various synthetic techniques.^{6,11,17} Several of these materials are nanosized offering large surface areas and short diffusions paths for sodium-ions during de/sodiation upon cycling. The sodium amount deintercalated from the layered oxide materials ranges from 0.5 to 0.85.¹¹ Early contributions to layered oxide materials for SIBs of the general structure Na_xMO_2 can be traced back to the 1980s and have been made mostly by Delmas and co-workers.¹⁸⁻²⁰

In general, Na_xMO_2 compounds consist of sheets of edge sharing MO_6 octahedra (Figure 5) similar to their lithium counterparts Li_xMO_2 . The arrangement of these octahedra provides 2D transport channels between which sodium-ions can be inserted and extracted. Based on the sodium environment and the number of oxygen stacking sequences, typical Na_xMO_2 can be categorized into two main groups, i.e. P2 type and O3 type phases, following the classification proposed by Delmas *et al.*²⁰ In the O3 type the sodium-ions are located at octahedral sites between the MO_2 layers. Further, the layered structure of Na_xMO_2 is composed of three different MO_2 layers comprising an AB, CA, BC oxygen arrangement. In contrast, the P2 type phase consists of two different MO_2 layers with an AB, BA oxygen sequence building up the layered structure and sodium-ions are accommodated at the trigonal prismatic sites between these layers. The P2 type phase is empirically known to be stabilized when a sodium off-stoichiometry condition (typically $0.6 < x < 0.7$) is applied during material synthesis. The different structures of the O3 and P2 type Na_xMO_2 materials result in different electrochemical behavior of these polymorph materials. Phase transitions of both materials are generally induced when sodium is

extracted from either the O3 or the P2 type. In case of the O3 type, where sodium-ions are originally stabilized at edge sharing MO_6 octahedra, sodium-ions at prismatic sites become energetically more stable upon desodiation. Formation of the prismatic sites is achieved by movement of the MO_2 layers without M-O bond breaking when sodium is partly extracted. This phase transition results in the formation of a new phase defined as P3 type where oxygen packing is AB, BC, CA (Figure 5). The P3 type is thermodynamically stable and can be obtained directly when reaction conditions below 800 °C are applied. For example calcination at 700 °C yields P3 type $\text{Na}_{0.6}\text{Mn}_{0.65}\text{Ni}_{0.25}\text{Co}_{0.10}\text{O}_2$ whereas P2 type structures are obtained at 800, 900 and 1000 °C.²¹ When sodium is partly extracted from the P2 type Na_xMO_2 framework M_2O sheets glide to form octahedral sites. The resulting new O2 type phase contains two different MO_2 layers with a unique AB, AC oxygen arrangement and the vacancies between the layers are octahedral sites. This phase transition is accommodated by a contraction and a decrease of the inter layer distance when compared to the P2 type structure resulting in poor cycling performance. It should be noted that phase transition from P3 or O3 type to P2 type is not possible by electrochemical desodiation. Such a transformation can only be achieved when M-O bonds are broken and reformed and thus requires higher temperatures.^{6, 17}

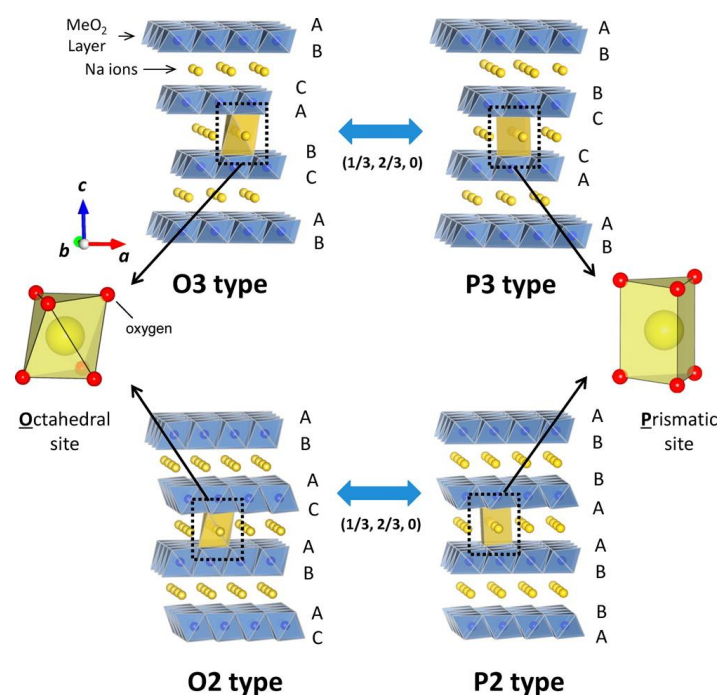


Figure 5: Classification of Na–M–O layered materials with sheets of edge-sharing MO_6 octahedra and phase transition processes induced by sodium extraction. Reprinted with permission from Ref. [6]. Copyright 2014 American Chemical Society.

The described phase transitions of O3 or P2 type materials can commonly be induced by sodium extraction from the materials during electrochemical cycling and will affect cycling performance of the respective SIB cells. For example, all O3 type Na_xMO_2 compounds undergo a O3-P3 transition after 25% sodium extraction and the irreversible phase transition of P2 type materials to O2 type at high voltages

causes structural collapse and rapid capacity degradation. To alleviate the problems accompanied with phase transitions two main strategies can be applied. On the one hand, the occurrence of transitions at high voltages can be avoided when limiting the high cut-off voltage. However, this approach may result in reduced energy density in return.²² On the other hand, different metals such as Ni, Co or Fe can be incorporated in the structure to improve cycling stability by suppressing the sodium ordering process.²³ Further, doping with electrochemically inactive elements as Mg, Al or Zn can delay structural transitions at higher voltages.^{6, 11, 17} Due to their good compromise regarding cycling stability and capacity particularly P2 type materials have received considerable interest.²³⁻²⁶ P2 type Na_xMO_2 are often composed of Mn as predominant metal, which is partially substituted by other metals such as Ni, Co or Fe with different influence on the material's performance. For example, Mn/Co based layered oxides like the spherical P2- $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ applied in the presented thesis, were found to exhibit improved cyclability compared to the undoped analogues.^{17, 27, 28} The structure of the P2 layered Na_xMnO_2 and its Co-doped analogue is depicted in Figure 6. The latter shows two possible sites for sodium intercalation which differ in their geometric coordination surrounding and are marked as Na_f and Na_e following the nomenclature introduced by Carlier *et al.*²⁹ Further, three ways of occupying the octahedral sites, i.e. Mn, Co and vacancy are depicted. It should be noted that the MO_2 layers commonly have about 1% cation vacancies as illustrated next to the MnO_6 octahedron.^{30, 31}

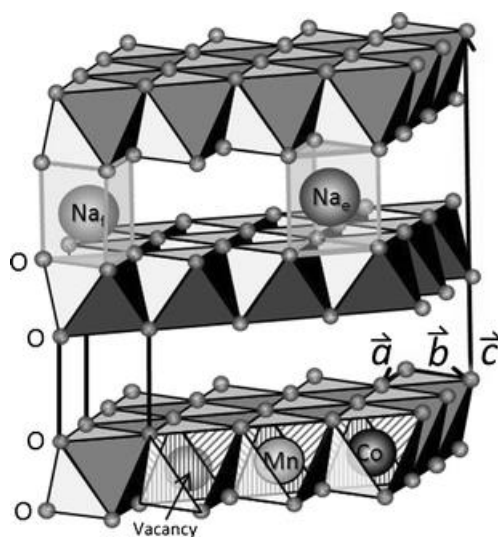


Figure 6: Structure of P2 layered Na_xMnO_2 and its Co-doped analogue showing two possible sites for Na intercalation and three different possibilities of filling the octahedral sites (vacancy, Mn, Co). Reprinted with permission from Ref. [30]. Copyright 2013 Springer-Verlag.

The influence of Co-doping and morphology optimization and the underlying structural causes for the enhanced performance of the herein applied spherical P2- $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO) compared to P2- Na_xMnO_2 were studied in detail by Bucher *et al.*²⁷ In brief, the enhanced cycling stability of the ~10% Co doped material is attributed to the following main effects: firstly, 10% Co-doping in P2- $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ suppresses a Jahn-Teller induced structural transition from the initial hexagonal

phase to an orthorhombic phase as observed for P2-Na_xMnO₂. Further, the suppression of sodium ordering processes and enhanced sodium kinetics will contribute to improved cycling stability of the Co-doped material as well. Regarding the morphology of the materials, increased cycling stability of hollow spheres as compared to flakes was attributed to reduced changes of the unit cell volume of the spheres and thus reduced structural stress.²⁷

It shall be noted, that besides the described layered metal oxides e.g. cathodes containing sulfur composites such as Cu₂S³², FeS₂³³ or NaFeSO₄F³⁴ are under investigation as well. Alternatively, metal phosphates like the sodium super ionic conductor (NASICON) Na₃V₂(PO₄)₃ have been studied in detail as SIB cathode materials.^{6,11} However, these cathode types as well as further types based on fluorides or hexacyanoferrates are not part of the presented thesis and will thus not be discussed here in detail.

1.2.2 Sodium-Ion Batteries – Anode Materials

Regarding SIB anodes early efforts involving metallic sodium as anode material suffered from dendritic growth problems giving rise to the need for alternatives. Graphite is the most commonly and widely used anode in LIB systems due to its high gravimetric and volumetric capacity. Unfortunately, it cannot be applied for SIBs due to its poor intercalation property for larger sodium-ions. Thus, several types of other carbons e.g. petroleum coke³⁵⁻³⁷, carbon microspheres³⁸ and carbon black³⁹ have been investigated as SIB anodes. In 2000 Stevens and Dahn⁴⁰ reported the electrochemically reversible sodium insertion/extraction into/from hard carbon (HC) produced from a glucose precursor leading to the intensive investigation of this material by several groups. Hard carbon generally consists of a disordered structure similar to soft carbon. However, despite the proposal of several structural models⁴¹⁻⁴⁴ the detailed structure of soft and hard carbon is still a debatable subject. Since the structure of hard carbon depends on synthetic parameters such as carbon source and carbonization temperatures it is difficult to establish a universal structural model of the material. However, as similarity of all proposed structural models hard carbon is generally composed of two domains. The first domain is comprised of carbon layers (graphene-like) the second domain consists of micropores (nanosized pores) formed between the disorderly stacked carbon layers. In contrast to graphite, hard carbon exhibits significantly better intercalation properties for sodium making reversible insertion of a much higher amount of sodium-ions into the structure possible.^{2, 6, 11} Therefore, carbon based materials and especially hard carbon are the most widely applied and investigated anode materials for SIBs. However, the operating potential of hard carbon is relatively low and close to that of the sodium plating potential. As a consequence, sodium metal is deposited on its surface during improper operation or fast charging giving rise to major safety concerns associated with possible dendrite formation, shorting and thermal runaways. Further, hard carbon suffers from poor rate capacity.^{2, 45, 46}

Thus, aside from carbonaceous materials, several alternative anode materials for SIBs are under investigation. For example, metal alloys with high theoretical capacities or titanium oxides like TiO_2 exhibiting small volume change during cycling are attractive materials. Further, organic compounds like e.g. disodium terephthalate ($\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$) and derivatives, which feature low cost and high storage capacity, are promising alternatives as well.^{2,6,11}

In the presented thesis, focus was set on a sodium vanadium oxide as a further alternative anode material to hard carbon. The $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \times 0.6 \text{ H}_2\text{O}$ (NVO) reported by Hartung *et al.*¹² exhibits reasonable capacities and, in contrast to hard carbon, can easily be synthesized. Since the material exhibits a wide potential range and sodium can be removed from the structure on the first charging process this material can operate as cathode as well as anode. Thus, NVO can be employed in a symmetrical full-cell allowing an economical production. As depicted in Figure 7 the structure of $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \times 0.6 \text{ H}_2\text{O}$ consists of V_3O_8 layers composed of VO_6 corner-sharing octahedra and edge-sharing units of V_2O_8 pyramids. Sodium ions are located in tetrahedral as well as octahedral voids in between these layers. Tetrahedrally coordinated sodium-ions are edge sharing with the VO_6 octahedra, while the octahedrally coordinated sodium-ions are edge sharing among themselves and corner sharing with the VO_6 structures. Vanadium in the plain material has an oxidation state of +5 and +4 with shares of 76% and 24% respectively as determined by X-ray photoelectron spectroscopy (XPS). Thus the average oxidation state of vanadium is < 5 .¹²

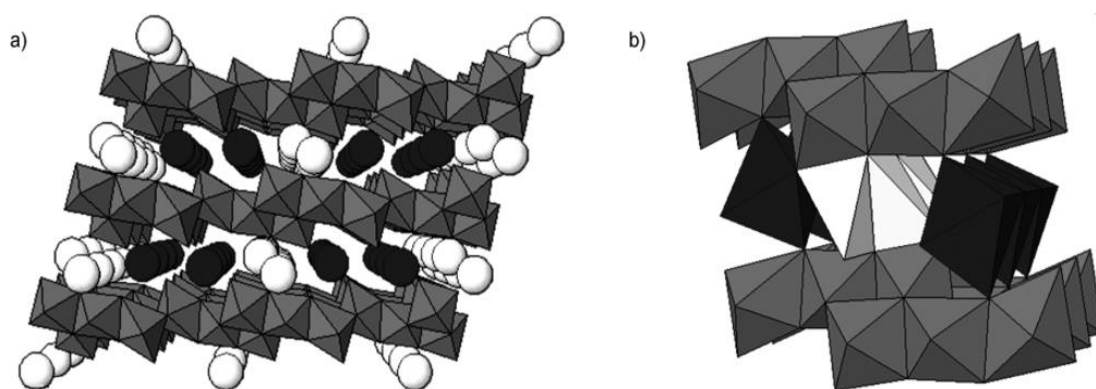


Figure 7: Structure of $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \times 0.6 \text{ H}_2\text{O}$ (black: $\text{Na}_{\text{octahedral}}$; white: $\text{Na}_{\text{tetrahedral}}$): a) structure overview; b) close-up and depiction of the octahedral/tetrahedral surrounding of Na. Reprinted with permission from Ref. [12]. Copyright 2014 Wiley-VCH Verlag.

1.2.3 Sodium-Ion Batteries – Electrolytes

Typically, electrolytes receive far less attention than the active materials (electrodes) since properties of the latter determine the system's energy density (gravimetric and volumetric) and are thus most eye-catching. However, the role of the electrolyte should not be neglected since it significantly

contributes to battery lifetime and realistically possible performance of the system in terms of practically accessible capacity, rate capability, safety etc.⁷

In contrast to well-established LIBs, where 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC) is the concordantly accepted “standard electrolyte”, the electrolyte of choice for SIBs has not been found yet. In general, electrolytes for SIBs can be classified into aqueous electrolytes and non-aqueous electrolytes. The latter comprise organic and ionic liquid based electrolytes, gel and solid electrolytes (inorganic and polymer). Ideally, an electrolyte should meet the following requirements: i) wide electrochemical stability window (ESW); ii) high ionic conductivity; iii) good chemical and electrochemical compatibility with the active materials; iv) high thermal stability; v) wide liquid range and vi) low toxicity. Apart from these intrinsic electrolyte parameters, the “controllable” surface reaction between the electrolyte and the active materials, i.e. cathode and anode, is of significant importance for a good electrolyte system as well.^{2, 5, 7, 47}

The solid electrolyte interphase (SEI) on the anode surface as well as the cathode electrolyte interphase (CEI) are built up by interfacial, electrochemical reactions between the electrolyte and the respective electrode surface. Detailed formation, composition and functioning of the interfacial layers are complex and still under investigation. It is known, that these protective solid passivation layers act as barrier between the electrolyte and the active materials and therefore prevent further electrolyte decomposition after the initial charge/discharge processes. SEI and CEI are electrically insulating yet provide sufficient ionic conductivity for battery performance. Fast and distinct buildup of functional interfacial layers is thus crucial for battery performance and can be influenced by the electrolyte itself or appropriate additives.

These passivation layers further effect the electrolyte’s electrochemical stability window (ESW). The latter is determined by the energy separation between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte components as depicted schematically in Figure 8. To exhibit good electrochemical stability, redox energies of the anode E_a and the cathode E_c should be within the ESW or band-gap (E_g) of the electrolyte. Ideally, the electrolyte should exhibit the widest possible ESW, which is quite challenging since it is in contact with strongly reducing/oxidizing electrode materials. In practice, chemical passivation of the active materials through the passivation layers (SEI/CEI) extends the thermodynamic limits of the electrolyte imposed by its HOMO and LUMO levels (Figure 8).^{5, 7}

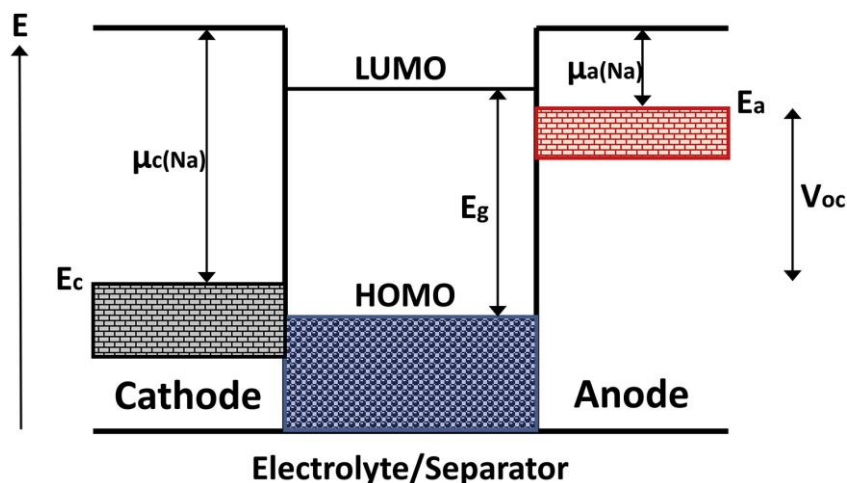


Figure 8: Schematic diagram of a SIB at open circuit (OC) showing the thermodynamic stability conditions, requiring the redox energies of the cathode (E_c) and the anode (E_a) to lie within the band gap (E_g) of the electrolyte. Reprinted with permission from Ref. [5]. Copyright 2015 Elsevier Ltd.

Considering cost as well as compatibilities with manufacturing equipment, SIBs applying organic electrolytes are said to be preferred to those applying other electrolytes. A typical electrolyte employed in SIBs is thus composed of a sodium-ion conducting salt dissolved in a mixture of flammable organic carbonate or ether solvents. Commonly used sodium salts comprise sodium perchlorate (NaClO_4), sodium hexafluorophosphate (NaPF_6), sodium bis((trifluoromethyl)sulfonyl)imide (NaTFSI), and sodium bis(fluorosulfonyl)imide (NaFSI). With respect to the organic solvents ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC) or dimethoxyethane (DME) are typically applied.⁴⁷ Numerous studies dealing with the optimization of the electrolyte have been performed especially over the last two decades.^{2, 7, 11, 47} For example Ponrouch *et al.*⁴⁸ evaluated the conductivity, viscosity, thermal and electrochemical stability of different solvents (PC, EC, DMC, DME, DEC and their mixtures) combined with three different conducting salts (NaClO_4 , NaTFSI , NaPF_6). NaClO_4 or NaPF_6 in a EC/PC mixture was thus found to be the best electrolyte when hard carbon is applied as anode.⁴⁸ However, these organic electrolytes are highly flammable and volatile, which directly results in severe safety concerns for the respective SIBs.⁴⁷ The safety issue can e.g. be overcome by applying solid state electrolytes like the $\beta\text{-Al}_2\text{O}_3$ ($\text{Na}_2\text{O} \times 11 \text{Al}_2\text{O}_3$) applied in high-temperature Na/S batteries⁸ or the sodium super ionic conductors (NASICON) based on $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 < x < 3$) which were demonstrated to have a high sodium-ion conductivity ($6 \times 10^{-4} \text{ mS/cm}$) even at room temperature.⁴⁹ Certainly, aqueous electrolytes can be taken into account as well when establishing safer electrolytes. Among various studied aqueous systems, Na_2SO_4 in deionized water is most popular but other salts as NaCl and NaNO_3 can also be used. It has to be mentioned though, that a major disadvantage of water based electrolytes is their very narrow ESW ($\sim 1.2 \text{ V}$), hindering their application in most fields.^{50,11}

However, as stated above despite intensive efforts a standard electrolyte for SIBs and especially safe SIBs has not been found so far leaving sufficient room for improvement. A further class of electrolytes which is receiving growing attention especially with regard to safer SIB systems are ionic liquid (IL) based electrolytes, which were applied in the present thesis. The properties and suitability of ILs as electrolytes for SIBs will thus be discussed in more detail in the following.

1.3 Room Temperature Ionic Liquids

1.3.1 History and Properties

Ionic liquids (ILs) - sometimes also referred to as molten salts or liquid organic salts - are generally defined as salts with a melting point below 100 °C.⁵¹ Room temperature ionic liquids (RTILs) are thus salts with a melting point below room temperature. For convenience, only the term ionic liquid/IL will be used in the following. In principal, ILs have been known in literature since Paul Walden described the first ionic liquid, namely ethylammonium nitrate, with a melting point of 12 °C in 1914.⁵² However, in the beginning only little general interest was dedicated to this new class of substances. ILs were initially mainly investigated with regard to their electrochemical properties.^{51, 53, 54} Especially in the 1970s and 1980s, ILs based on alkyl-substituted imidazolium and pyridinium cations, with halide or tetrahalogenoaluminate anions, were developed as potential electrolytes in batteries.^{55, 56} First studies dealing with the application of ILs as catalysts and solvents were published by the end of the 1980s.^{57, 58} In 1992 Wilkes *et al.*⁵⁹ obtained the first air and water stable ILs when applying tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate as anions allowing a much wider range of applications and thus leading to a significantly increased interest in this class of substances.⁵⁹ Additional interest was then dedicated to the fine tuning of ILs and their properties resulting in the development of task specific ILs initiated by Davis.^{51, 60} Figure 9 exemplarily summarizes the main developments in IL history which can be marked as “generations”.⁶¹ Since then numerous ILs have been extensively studied and applied in diverse areas, which will be outlined briefly in chapter 1.3.3 (p. 16).

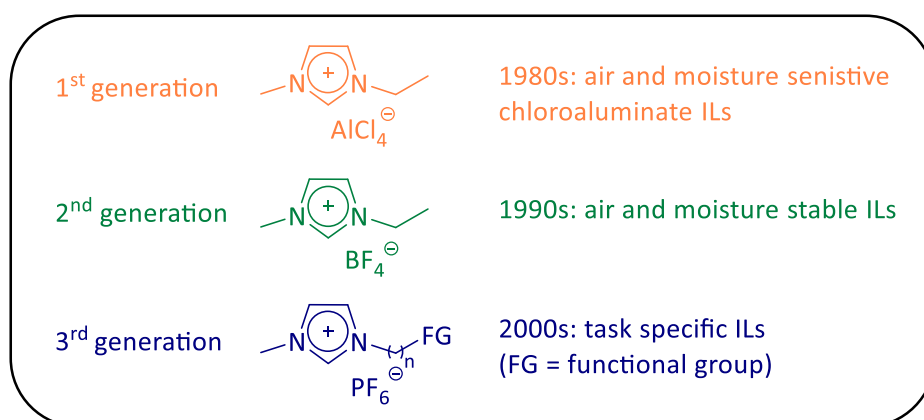


Figure 9: Overview of the main developments in “IL history”. Reproduced with permission from Ref. [61]. Copyright 2016 Elsevier B.V.

In general, ILs are usually composed of an organic cation and an inorganic, mostly polyatomic anion. In contrast to typical ionic compounds such as NaCl or KCl, which exist in the solid phase at room temperature due to strong coulombic attractions between the cation and the anion, the coulombic

interactions are significantly reduced in ILs. In case of the latter, the charge of the bulky IL cations and anions is delocalized and stabilized by e.g. the interaction with neighboring chemical groups via electronic or inductive effects resulting in the decrease of the coulombic attraction. Further, size, bulkiness and asymmetry of the large anions and cations reduces the possibility of solid crystal formation, thus lowering the melting point as well.⁶²

With regard to the cation, ILs can be based on either phosphor, sulfur or nitrogen. Since the latter is by far the most popular class of ILs, focus in this study was set on nitrogen based ILs which will thus be described in more detail. Typically, nitrogen based ILs are comprised of quaternary ammonium cations such as imidazolium (Im^+), pyrrolidinium (Pyr^+), piperidinium (Pip^+) or ammonium derivatives (NR_4^+) combined with different inorganic or organic counter ions, e.g. BF_4^- , PF_6^- , $[(\text{CN})_2\text{N}]^-$, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ (TFSI^-) or $[(\text{FSO}_2)_2\text{N}]^-$ (FSI^-) (Figure 10).^{50, 51}

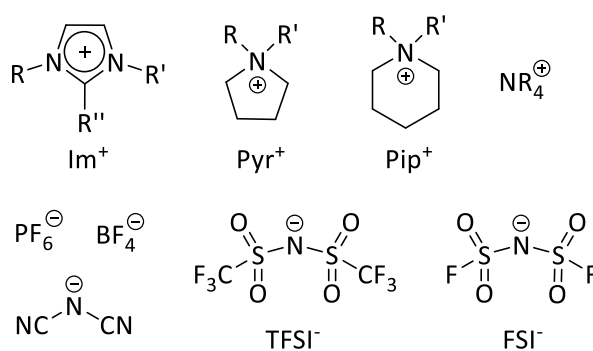


Figure 10: Commonly applied anions and cationic core structures for nitrogen based RTILs.

Due to their distinct ionic structures, ILs have unique characteristics rendering them promising for various applications. Most prominently, they all exhibit negligible vapor pressure and very low (if not negligible) flammability. Further, ILs exhibit high ion density (a few moles per liter), high polarity and a wide liquidus range (-100 – 400 °C, no evaporation or crystallization). ILs with moderate viscosity have high ionic conductivity. Moreover, ILs are chemically and electrochemically stable exhibiting wide ESWs of up to 6 V for certain cation/anion combinations, rendering them as suitable basis for electrolytes. Most importantly, properties of ILs can easily be modified by tailoring the cation as well as the anion to meet specific requirements.^{50, 62, 63}

1.3.2 Synthesis and Tailoring

The physicochemical and electrochemical properties of ILs can easily be adjusted by selecting the nature of the ionic species as well as the functional groups attached to the respective cationic core structure. Based on this concept, several ILs have been prepared steadily tuning and improving their properties.⁶²

Most nitrogen based ILs are synthesized starting from a tertiary amine as “precursor”. Depending on the desired final compound, the precursor may contain a functionalization already. ILs are then obtained in a two-step reaction protocol (Figure 11). In the first step, the tertiary amine is reacted with a functionalized alkyl halide in order to introduce the desired functional group. Reaction of the tertiary amine with the alkyl halide proceeds via a simple nucleophilic substitution reaction resulting in the quaternized ammonium compound combined with a relatively hard and strongly coordinating halide anion. Subsequent exchange of the latter by rather large, bulky and weakly coordinating anions like PF_6^- , BF_4^- , $\text{N}(\text{CN})_2^-$, TFSI^- or FSI^- converts the quaternary ammonium salt to the respective IL.^{51, 64}

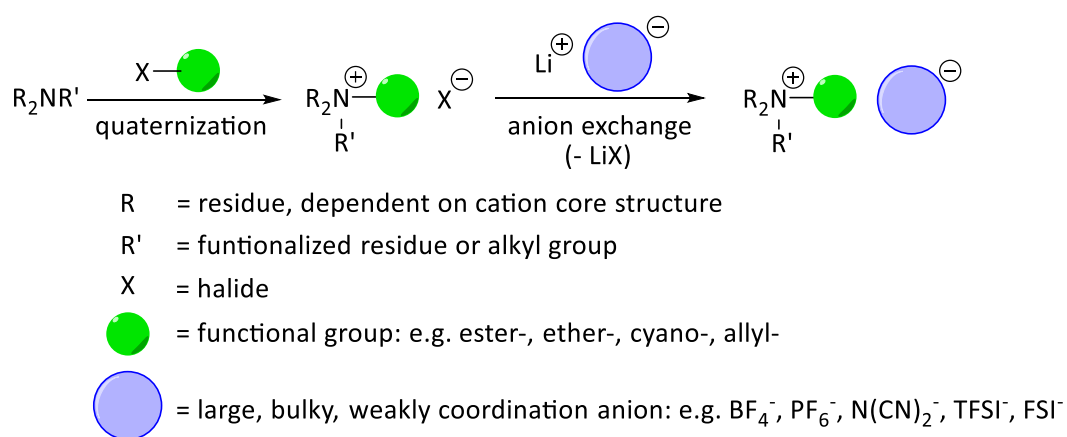


Figure 11: Schematic procedure of the synthetic route applied in the IL synthesis.

The anion as well as the cationic core structure and the functional groups attached influence the different properties of ILs. Imidazolium based ILs e.g. have been shown to be relatively easy to reduce since the proton in C2-position of the Imidazolium ring can be reduced at rather high redox potentials. In contrast, the highest electrochemical stabilities towards reduction and oxidation have been reported for ILs based on pyrrolidinium and piperidinium in combination with imide anions exhibiting ESWs of up to 6 V.^{50, 62, 65, 66} Further, the cationic core structure and particularly the anion have significant influence on the viscosity which is largely governed by intermolecular interactions such as van der Waals interactions, hydrogen bonding or coulombic forces and flexibility or conformational freedom of the ions. The viscosity of the IL in turn governs the conductivity to a large extent. The higher the viscosity of an electrolyte and the stronger the intermolecular interactions, the harder it is for ions to move past each other, resulting in lower conductivities.^{67, 68} Especially imide anions like TFSI^- or FSI^- lower the viscosity of the respective compounds. The larger size and bulkiness of the latter compared to e.g. BF_4^- or PF_6^- reduces the ionic interactions and symmetry of the chemical structures of the ILs thus lowering the melting point. Additionally, the negative charge in these imide anions is effectively delocalized by electron withdrawing groups like SO_2 , F or CF_3 via the formation of resonance structures and an inductive effect. Together, these phenomena result in significantly improved viscosity and

conductivity for ILs with imine anions.⁶² Introduction of functional groups in the cationic core structure influences the physicochemical and electrochemical properties of ILs as well. For instance, electrochemical stability of ILs in battery systems can be improved through formation of passivation layers on the electrode surfaces (as described in chapter 1.2.3 p. 9). Allylic as well as nitrile or ester substituents can support SEI/CEI formation and stabilize the layers leading to an enhanced electrochemical stability. Thus, such substituents are of great interest for ILs in electrochemical applications.^{62, 66, 69} Ester groups for example are further said to improve the solubility of conducting salts required for electrochemical applications when compared to unfunctionalized analogues providing an additional benefit.⁷⁰ Moreover, functionalization of IL cations with ether groups typically decreases the viscosity and in turn enhances the conductivity of the respective ILs. This is most likely due to reduced packing of the involved ions in the crystalline solid as well as the liquid phase.^{50, 62, 71} These findings confirm that besides adjustment of the cationic core structure and the anion, chemical substituents are suitable to tune properties of ILs. A rough overview regarding the benefits of ILs is given in Figure 12. A more in-depth understanding of the detailed structure-properties relationship would support a more efficient design of tailored ILs and is thus object of current investigations.

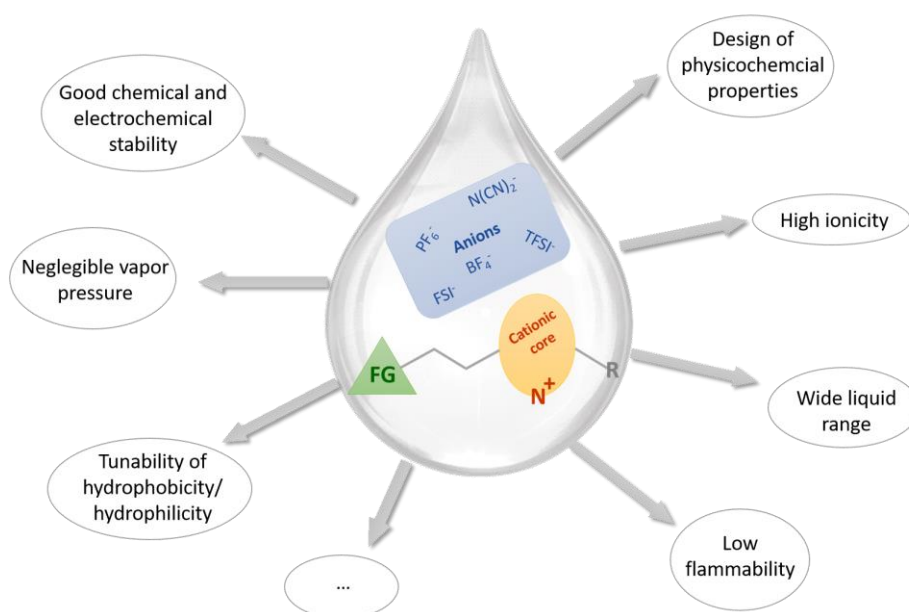


Figure 12: Overview over the tunability of ILs and their properties.

1.3.3 Overview of IL Applications

Due to their wide range of properties and easy tunability ILs are employed in several very diverse applications^{63, 64, 72-74} of which a few will be outlined exemplarily in the following.

ILs can for example be applied as reaction media for organic and biochemical reactions as alternative to conventional organic solvents. Due to their negligible vapor pressure, ILs are claimed to be “green” solvents even at high temperatures in contrast to volatile organic solvents. Further, the IL’s high ion density and polarity as well as their wide liquidus range are clearly beneficial for several reactions. For instance, the tailorable IL solvents can dissolve several organic and inorganic compounds which are insoluble in common organic solvents. With regard to biochemical reactions, a number of methods has been developed to improve the enzyme’s stability and increase its activity and enantioselectivity when applying IL solvents.⁷⁵⁻⁷⁷ Further, the possibility of biocatalyst recycling and product recovery are an important use of ILs as media for biochemical reactions.⁷⁸ The product and unconverted reactant can simply be extracted by washing with e.g. diethyl ether or hexane.

Especially the facilitated catalyst/product separation in IL based processes has promoted the application of ILs as reaction media for various two-phase catalyzed reactions. Several groups like Kühn⁷⁹⁻⁸⁴, Seddon⁸⁵⁻⁸⁷, Wasserscheid⁸⁸, Rogers^{89,90}, Dupont⁹¹ and Welton^{64,73,92,93} have investigated the potential of two-phase catalysis in ILs in detail. The fundamental knowledge gained from their research paved the way for potential applications of ILs in industry.

Regarding the industrial applications of ILs a breakthrough was achieved with the so-called BASIL™ process (Biphasic Acid Scavenging utilizing Ionic Liquids) established by BASF in 2002. This process produces alkoxyphenylphosphines, which are commonly used as photo initiator precursors. In the original process, trimethylamine was applied as acid scavenger resulting in a dense insoluble paste of triethylammonium chloride after the reaction impeding separation. Replacement of the trimethylamine by 1-methylimidazole results in the formation of the ionic liquid 1-methylimidazole chloride during the process. The latter separates out of the reaction mixture as discrete phase facilitating the whole process. The new process enabled application of much smaller reactors and increased space-time yields.^{74,89,94} Further industrial processes utilizing ILs were pursued by Degussa, SASOL, Exxon Mobile and BP to name only some of the most relevant.⁷⁴

A further field in which application of ionic liquids has attracted interest is the processing of cellulose to improve biomass processes since dissolution of cellulose in ILs was achieved in technically reasonable amounts.^{95,96} For instance, the dissolution of contaminated cellulose based materials like tissue paper waste generated in research laboratories and chemical industry and the recovery of valuable compounds like palladium and uranium by electrodeposition in ionic liquids was studied. Successful recovery of the metals and regeneration of the cellulose pulp was achieved in 1-butyl-3-methylimidazolium chloride.⁹⁷ Moreover, the good solubility of cellulose in certain ILs enables the utilization of biomass as renewable resource. Zhang *et al.* for instance demonstrated the microwave assisted direct conversion of cellulose in 1-butyl-3-methylimidazolium chloride in the presence of CrCl₃.

The product namely 4-hydroxymethylfurfural is rendered a suitable commodity for alternative polymers or liquid biofuels.⁹⁸

Due to their negligible vapor pressure, high thermal stability and good solvation properties for a variety of compounds and gases, ILs are attractive gas storage and handling media. Especially the usage of ILs to assist in separating CO₂ from other gases has become a topic of considerable interest in academic as well as industrial fields.⁶³ Several publications dealing with IL-CO₂ interactions and the application of ILs in gas separation processes have been reported underlining the significance of this growing sector.^{63, 99-101, 102}

All mentioned IL applications can be tracked back to their beneficial and tunable physico- and electrochemical properties. Especially the low volatility and flammability as well as their high chemical and especially electrochemical stability combined with their intrinsic ionic conductivity render ILs potentially ideal solvents and electrolytes for electrochemical applications as an additional quite broad field. For instance, ILs have been successfully employed in solar cells, super capacitors, actuators and of course in lithium as well as sodium based battery systems.⁶³ Since the latter application was focus of this thesis it will be elucidated in more detail in the following chapter.

1.4 ILs as Safer Electrolytes for Sodium-Ion Batteries

1.4.1 Battery Safety – Thermal Runaway

Safety problems due to thermal runaway are a severe technical and challenging scientific problem in battery research and the main hindrance for large-scale application of LIBs as well as SIBs. A safety accident in an energy storage station containing hundreds of batteries could trigger a disastrous consequence leading to huge economic losses. Therefore, improving the safety of battery storage systems is of great interest and subject of numerous present studies.⁴⁷

In principal, safety concerns of SIBs are similar to those for LIBs and tightly related to the active materials and electrolytes. There are different abuse conditions which can initiate the thermal runaway of a system such as mechanical abuse (e.g. collision), electrical abuse (e.g. short circuit, overcharge) or thermal abuse (e.g. increase in resistance due to contact loss of cell connector). In total, the eventual occurrence of an internal short circuit is the most common cause leading to thermal runaway for all abuse conditions. The mechanism of the thermal runaway of LIBs for electrical vehicles was recently reviewed by Feng *et al.*¹⁰³ The authors provide a qualitative illustration for detailed understanding of the mechanism, which can in principal be transferred to SIBs. Thus, the thermal runaway of a battery system follows a mechanism of subsequent reactions, as illustrated in Figure 13. Once the temperature rises abnormally under abuse conditions, chemical chain reactions are initiated. In detail, temperature rise of the cell under abuse triggers side reactions especially SEI decomposition. The exothermic reaction releases additional heat forming the so-called heat-temperature-reaction (HTR) loop which is the root cause for the following chain reactions comprising electrolyte and electrode decomposition, melting of the separator etc. The HTR-loop cycles at extremely high temperatures and once the separator collapses, a massive internal short circuit occurs. The electrical energy of the cell is released spontaneously, finally leading to a thermal runaway with possible electrolyte burning or explosion. Interphase decomposition and electrolyte burning are of key importance for the whole process and therefore represent the most effective parts to tackle.^{47, 103}

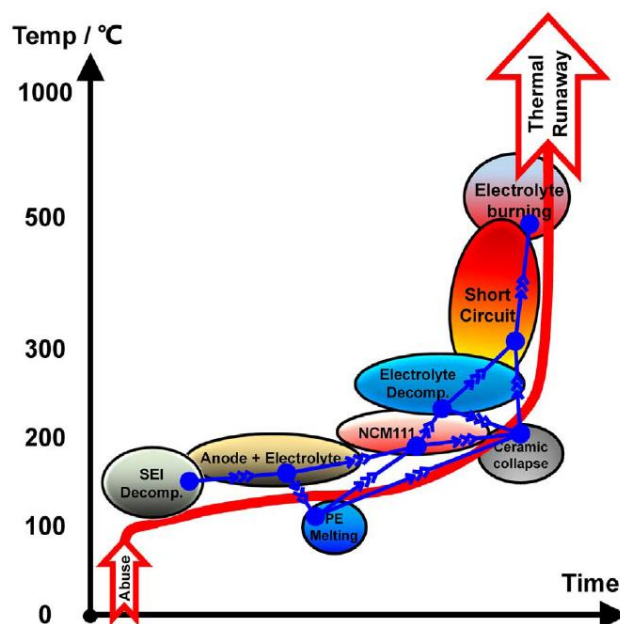


Figure 13: Schematic qualitative interpretation of the chain reactions during thermal runaway studied in detail for a LIB with $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM)/graphite electrodes, organic electrolyte and a polyethylene based ceramic coated separator. Reprinted with permission from Ref. [103]. Copyright 2018 Elsevier B.V.

Thus, research focusses on the detailed evaluation and optimization of the interphase layers on the one hand and the development of safer especially non-flammable electrolytes on the other hand when battery safety is of prime importance. Regarding the electrolytes there are different possibilities to enhance the safety of the resulting system. For organic based systems for instance, flame retardant additives (FRs) targeting the suppression of fire thus enhancing the overall thermal stability can be added. The FRs act as scavengers that trap the highly reactive, free radical species which result from thermal decomposition of the organic electrolytes inhibiting the cascade reactions leading to thermal runaway. For LIB systems especially organo-halogen and organophosphorus compounds as well as phosphazenes have been applied as FRs. However, their instability at negative potentials and the ineffectiveness to form a stable SEI layer result in decreased electrochemical performance impeding the practical application of FRs.^{47, 50}

Polymer electrolytes e.g. gel polymer electrolytes or solid electrolytes are good candidates for realizing inherently safe batteries since they do not contain easily flammable, liquid, organic solvents. Further, ILs are rendered promising alternatives for safe electrolytes. Their negligible vapor pressure and extremely low-flammability combined with high thermal stability make them ideal candidates for safer batteries. Furthermore, their high electrochemical stability, good electrode compatibility and their facile tunability are beneficial for their application as electrolytes as well.^{7, 50} Numerous ILs have been applied in various LIB systems^{7, 50, 62, 65, 66}, however research regarding IL based SIBs – which is the focus of the presented thesis – still lacks of profound studies.

1.4.2 ILs as Electrolytes in SIBs

As stated above, ILs are considered to establish safe electrolytes while still maintaining the properties of a liquid electrolyte.⁷ Main findings can be derived from the vast research performed on LIB systems^{7, 50, 62, 65, 66}, however functionality of a battery is highly dependent on the interplay of the electrolyte with the electrode materials. Thus, fundamental research regarding IL electrolytes in combination with different sodium based electrode materials is still necessary.

Prior to detailed electrochemical studies in SIB half- or full-cell configurations, evaluation of the physicochemical and electrochemical properties of the sole sodium based IL electrolytes comprised of the respective IL and the sodium conducting salt are useful and have been performed by several groups.¹⁰⁴⁻¹⁰⁸ Such studies can serve as indicators for the suitability of the tested IL/sodium salt compositions as electrolytes for SIBs. Regarding the electrochemical performance of IL electrolytes in SIB systems Nohira *et al.*¹⁰⁹ and Fukunaga *et al.*¹¹⁰ first proposed sodium conducting electrolytes based on eutectic NaTFSI/CsTFSI and NaFSI/KFSI as “intermediate-temperature ionic liquids” for SIBs in 2012. However, these “IL” electrolytes are not based on organic cations and have relatively high melting points. Thus, imidazolium and especially pyrrolidinium based ILs gained much attention as basis for SIB IL electrolytes due to their relatively low viscosity, high ionic conductivity and high chemical stability. An overview over recent studies of SIB systems applying IL based electrolytes in combinations with different electrode materials is given in Table 1. Thus, mostly unfunctionalized pyrrolidinium based ILs with imide anions (TFSI⁻ or FSI⁻) have been studied in combination with different cathode and anode materials.

In comparison to the organic based SIBs, which suffer from poor cycling stability^{27, 111, 112} in addition to the mentioned safety issues, IL based systems have been shown to exhibit significantly enhanced cycling stability.^{45, 111, 113-115} Especially for their application in large-scale ESS a good cycling stability is indispensable and thus the steady improvement of the cyclability is intense focus of current SIB electrode and electrolyte research.

Table 1: Overview over recent SIB studies with IL based electrolytes in combination with different electrode materials. Subscript numbers denote the length of the alkyl chains attached to the respective cationic core structures.

entry	IL	conducting salt	cathode	anode	main scope
1 ¹¹³	Pyr _{1,4} FSI	NaTFSI	Na _{0.45} Ni _{0.22} Co _{0.11} Mn _{0.66} O ₂	Na	Investigation of the electrochemical performance & comparison with organic electrolyte based system
2 ¹¹⁴	Pyr _{1,3} FSI	NaFSI	Na _{1.56} Fe _{1.22} P ₂ O ₇	Na	
3 ¹¹⁶	Pyr _{1,3} FSI	NaFSI	NaCrO ₂	Na	Physicochemical properties of electrolyte over wide temp range & electrochemical performance of the half-cell system
4 ¹¹⁵	Pyr _{1,4} TFSI	NaBF ₄ /NaClO ₄ / NaPF ₆ /NaN(CN) ₂	NaFePO ₄	Na	Evaluation of the effect of the type of sodium salt on the electrochemical performance of the half-cell system
5 ¹¹¹	Pyr _{1,4} TFSI	NaClO ₄ /NaTFSI/ NaPF ₆ /NaBF ₄	Na _{0.44} MnO ₂	Na	
6 ¹¹⁷	Pyr _{1,3} FSI	NaFSI	NaCrO ₂	Na	Evaluation and optimization of the effect of sodium salt concentration on cell performance & thermal stability (flammability tests)
7 ¹¹⁸	Pyr _{1,4} TFSI	NaTFSI	NaFePO ₄	Na	
8 ¹¹⁹	Im _{1,4} TFSI	NaPF ₆	Na ₃ V ₂ (PO ₄) ₃	Na	Investigation of cell performance & demonstration of the reduced flammability of the electrolyte (self-extinguish time & flammability tests) & CEI formation and composition
9 ¹²⁰	Im _{1,2} BF ₄	NaBF ₄	Na ₃ V ₂ (PO ₄) ₃	Na ₃ V ₂ (PO ₄) ₃	Proof-of-concept SIB symmetric cell assembly
10 ¹²¹	Pyr _{1,3} FSI	NaFSI	NaCrO ₂	HC	Investigation of the electrochemical performance of the SIB full-cells over a wide temp range
11 ¹²²	Pyr _{1,3} FSI	NaFSI	NaCrO ₂	HC	
12 ⁴⁵	Pyr _{1,3} FSI	NaFSI	Na _{0.44} MnO ₂	HC	Investigation of the electrochemical performance of the SIB full-cells at RT
13 ¹²³	Pyr _{1,3} FSI	NaFSI	Na ₃ V ₂ (PO ₄) ₃ /C	HC	

2 OBJECTIVE

As outlined in the introduction, sodium-ion batteries (SIBs) are gaining rising attention due to their potential application in large-scale energy storage systems coupled with relatively low cost. However, typically used organic electrolytes with high flammability and poor thermal stability have impeded further development of SIBs in large-scale energy storage due to major safety concerns and low cycling stability. Ionic liquid electrolytes are considered promising candidates to solve these issues and are thus main focus of this thesis.

As basis for this work the thermal stability of an IL based SIB full-cell is to be studied to confirm the enhanced safety of the system compared to an organic based SIB. Therefore, initially a functional IL based full-cell with a common IL electrolyte (Pyr₁₄TFSI/NaFSI) shall be developed. The thermal stability of the IL based system and a system with a conventional organic electrolyte is then to be determined applying differential scanning calorimetry (DSC) and Accelerating Rate Calorimetry (ARC). The latter is a useful technique to characterize thermal runaway reactions in chemical industry and is applied to establish safe working conditions.

In the second part of the thesis, focus is laid on the development of new IL based electrolytes for SIB systems. Up to date, nearly only unfunctionalized Pyr based IL electrolytes have been studied as outlined in chapter 1.4.2 (p 21). In order to specifically tune the properties of the IL electrolytes and the performance of the resulting SIBs, different cationic core structures, functional groups and imide based anions shall be examined. Prior to the investigation of their electrochemical performance in SIB half-cells, the physicochemical properties such as viscosity, conductivity, thermal and electrochemical stability of the functionalized ILs are to be studied in a systematic approach. Special emphasis shall be put on the uniform characterization of the ILs making the derivation of structure-properties relationships possible.

3 RESULTS – PUBLICATION SUMMARIES

This chapter summarizes the most important publications originated from this thesis. The original manuscripts can be found in the appendix (p. 46 and following).

3.1 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

Minh Phuong Do[‡], Pauline J. Fischer[‡], Arun Nagasubramanian,

Jan Geder, Fritz E. Kühn, and Madhavi Srinivasan

J. Electrochem. Soc. **2019**, *166* (6), A944-A952

This study presents a fully functional IL based SIB full-cell and proves its enhanced thermal stability compared to an organic based system via ARC and DSC studies. Pyr_{1,4}TFSI with NaFSI (0.5 M) was used as the IL based electrolyte whereas EC/PC (1:1 wt%) with NaClO₄ (1.0 M) served as the organic electrolyte as it is commonly applied in SIB studies. A popular and promising sodium manganese containing layered oxide material, $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO) was applied as cathode material. Regarding the anode, an alternative material to the widely used hard carbon was introduced – namely $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \times 0.6 \text{H}_2\text{O}$ (NVO) – since it has not been tested with IL electrolytes up to date.

Compatibility of the IL based electrolyte with the electrode materials was assured in SIB half-cell studies prior to full-cell studies. The IL based half-cells outperformed the organic based ones especially in terms of cycling stability. In continuation of these promising results the electrochemical performance of SIB full-cells comprised of NMO as cathode and NVO as anode (NMO/NVO = 2.7/1) containing the IL or the conventional organic electrolyte were investigated. With a capacity retention of 76% after 100 cycles the IL based SIB full-cell exhibits enhanced cycling stability and coulombic efficiency when compared to the organic based full cell (71% after 100 cycles). Studies at 75 °C further revealed that in contrast to the organic based system, the IL based SIB full-cell is able to withstand cycling at elevated temperatures as required for practical applications. The IL based system was able to operate with a decent capacity retention of 70% after 50 cycles whereas, the organic based SIB showed rapid degradation after only 10 cycles.

For the first time, the superior thermal stability of an IL based SIB full-cell was proven by ARC combined with DSC studies. As depicted in Figure 14 the IL based full-cell exhibits a higher onset temperature as well as a lower self-heating rate than the corresponding cell containing the organic electrolyte. In subsequent DSC studies with the neat electrolytes as well as their combinations with the electrode materials the origin of the exothermal reactions observed in the ARC was further studied. The results

reinforce the enhanced thermal stability of the IL based system as no runaway reactions could be observed in the measurements containing the IL electrolyte in contrast to the organic electrolyte.

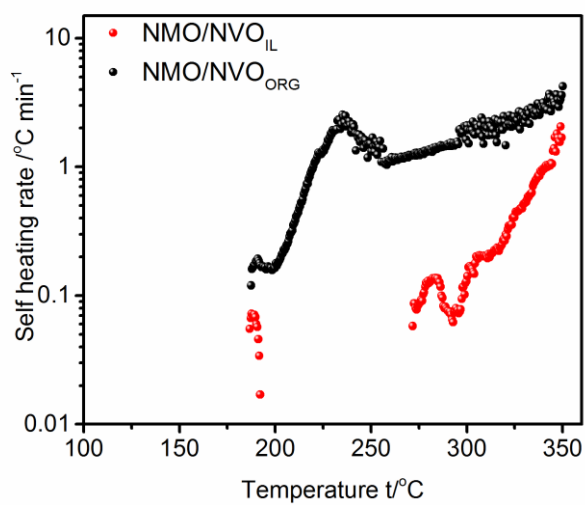


Figure 14: Self-heating rate vs. temperature for the IL based full-cell (NMO/NVO_{IL}; red) and the organic based full-cell (NMO/NVO_{ORG}; black).

3.2 Synthesis and Physicochemical Characterization of Room Temperature Ionic Liquids and their Application in Sodium-Ion Batteries

Pauline J. Fischer[‡], Minh Phuong Do[‡], Robert M. Reich, Arun Nagasubramanian,

Madhavi Srinivasan and Fritz E. Kühn

Phys. Chem. Chem. Phys. **2018**, *20*, 29412-29422

A series of 15 functionalized RTILs suitable as electrolytes was characterized regarding their physicochemical and electrochemical properties. IL cations were based on pyrrolidinium, piperidinium, morpholinium and ammonium core structures and functionalized with ether-, thioether-, ester-, allyl- and cyano-groups. To obtain ILs with preferably low viscosities, the imide anions TFSI⁻ and FSI⁻ were chosen. The ILs were synthesized in high purity and with a water content below 5 ppm. In a systematic and uniform approach, main structure-property relationships were derived regarding the physicochemical properties of the functionalized ILs. Thus, thermal stability of the examined ILs is mainly affected by the functional group tethered to the cationic core structure as well as the anion. For instance, TFSI⁻ based ILs exhibit significantly higher thermal stability than their FSI⁻ analogues. With exception of the thioether functionalized IL all synthesized ILs show wide ESWs regardless of the cation, functional group or anion incorporated. Significant influence of the functional group and the anion was observed when evaluating the viscosity and conductivity of the respective compounds. Lowest viscosities and thus highest conductivities were detected for the ether functionalized FSI⁻ ILs. Figure 15 summarizes the main trends derived from the study.

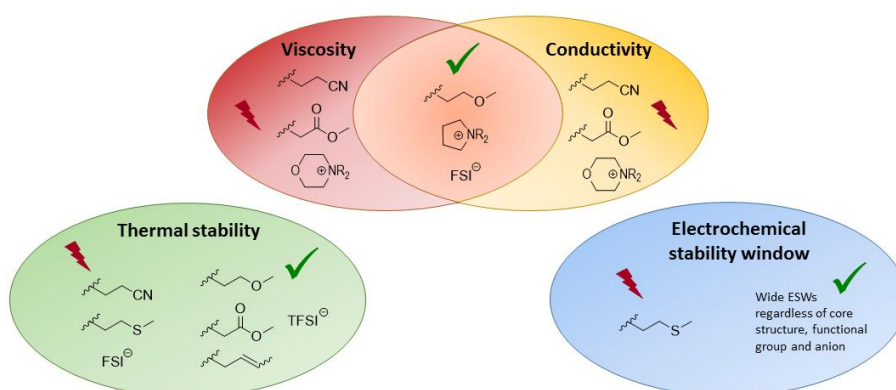


Figure 15: Schematic summary of the main trends derived for the investigated physicochemical properties of the synthesized functionalized ILs.

Moreover, electrochemical performance of the ether based ILs (IL 2, 8, 13, 16) in combination with NaFSI (0.5 M) as conducting salt was evaluated in half-cell studies with Na_{0.6}Co_{0.1}Mn_{0.9}O₂ (NMO) as cathode material and compared to the performance of the conventionally applied organic electrolyte

EC/PC (NaClO₄ 1 M). Three (IL 8, 13, 16) of the four tested IL electrolytes showed significantly enhanced cycling stability and capacity retention implying a beneficial effect of the IL electrolytes on the cell performance (Figure 16). Best cycling stability was achieved with IL 16 retaining 81 % of the initial capacity after 350 cycles. Further, rate tests performed with these three electrolytes proved that the tested systems are reasonably stable against reversible sodiation at high rates and that no considerable side reactions occur during cycling. The presented results show the suitability of functionalized ILs to enhance the performance of SIB systems and serve as a basis for the design of high performance IL based electrolytes.

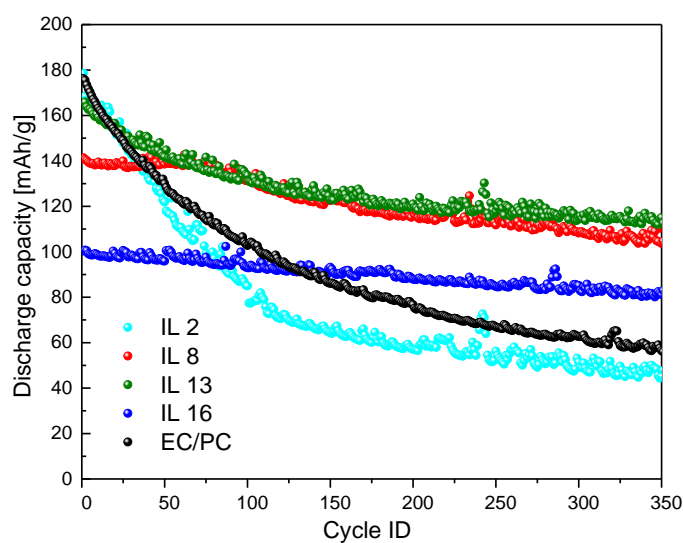


Figure 16: Long term cycling performance of the tested SIB half-cells.

4 CONCLUSION AND OUTLOOK

In this thesis, the application of room temperature ionic liquids as electrolytes for sodium-ion batteries and their effect on battery performance and especially on the thermal stability and safety of such systems was studied to enhance the applicability of SIBs as large-scale energy storage systems.

Therefore, a fully functional SIB full-cell comprised of $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ as cathode and $\text{Na}_{2.55}\text{V}_6\text{O}_{16} \times 0.6 \text{ H}_2\text{O}$ as anode with an IL based electrolyte ($\text{Pyr}_{1,4}\text{TFSI}$ with 0.5 M NaFSI) was established and compared to its analogue with a common organic electrolyte (EC/PC with 1.0 M NaClO_4). The IL based full-cell exhibits enhanced cycling stability and coulombic efficiency compared to the organic electrolyte based system at room and elevated temperature underlining beneficial effects of the IL electrolyte on cell performance. Evaluation of the thermal stability of both SIB systems applying accelerating rate calorimetry and differential scanning calorimetry proved the superior thermal stability of an IL based SIB full-cell for the first time. Thus, the presented system serves as promising basis for the development of safe energy storage systems based on SIBs where cycling stability and thermal stability are the major concerns. Closer insights into the mechanisms “at work” and the nature and composition of the electrolyte/electrode interfaces need to be obtained in future work to optimize capacity and cycling behavior of the full-cell. Studies of the thermal stability and electrochemical performance of systems containing different IL based electrolytes, e.g. with functionalized electrolytes, may help to further optimize the systems as well.

The physicochemical and electrochemical properties of 15 functionalized RTILs and their suitability as SIB electrolytes were examined in the second part of the presented thesis. Therefore, different cationic core structures, namely pyrrolidinium, piperidinium, morpholinium and ammonium were functionalized with ether-, thioether-, ester-, allyl- and cyano-groups and combined with FSI^- as well as TFSI^- as anions to tune the IL properties. In a systematic and uniform approach, the functionalized ILs were compared regarding their viscosity, conductivity, thermal and electrochemical stability resulting in clear structure-property relationships. As the ether functionalized ILs provided the best compromise of properties they were applied in initial electrochemical investigations in SIB half-cells with $\text{Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ as cathode material. Significantly enhanced performance in comparison to the half-cells based on the conventional organic electrolyte (EC/PC with 1.0 M NaClO_4) was achieved with three of the four tested ether functionalized ILs. The ether functionalized piperidinium IL showed the best cycling stability outperforming the organic electrolyte by 49% regarding capacity retention after 350 cycles. The results underline the suitability of IL electrolytes as alternatives to organic electrolytes in order to enhance SIB performance. To reveal the reasons for the respective cycling stabilities more detailed studies of the electrode materials and the surface layers formed based on X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX) should

be undertaken in the future. Additionally, the effect of other functional groups, e.g. nitrile, allyl or ester on the cell performance and on the formation of the surface layers shall be studied to further optimize cyclability and capacity of the system. Based on the acquired results, tailor-made electrolyte mixtures can be designed to combine the optimized properties of the individual IL electrolytes and thus improve the overall electrochemical performance of IL-SIB systems.

5 REPRINT PERMISSIONS

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“Synthesis and Physicochemical Characterization of Room Temperature Ionic Liquids and their Application in Sodium-Ion Batteries”

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6 BIBLIOGRAPHIC DATA OF COMPLETE PUBLICATIONS

6.1 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

Minh Phuong Do^{†a}, Pauline J. Fischer^{†b}, Arun Nagasubramanian^c, Jan Geder^d, Fritz E. Kühn^{*b} and Madhavi Srinivasan^{*a}

^a Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore 639798, Singapore.

^b Molecular Catalysis, Catalysis Research Center and Department of Chemistry, Technische Universität München, Garching 85748, Germany.

^c TUMCREATE, Singapore 138602, Singapore.

^d VDE Renewables ASIA Pte. Ltd, Singapore 138602, Singapore.

^e School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore.

[†] These authors have equally contributed to this work.

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6.2 Synthesis and Physicochemical Characterization of Room Temperature Ionic Liquids and their Application in Sodium-Ion Batteries

Pauline J. Fischer^{†a}, Minh Phuong Do^{†b}, Robert M. Reich^a, Arun Nagasubramanian^c, Madhavi Srinivasan^b and Fritz E. Kühn^{*a}

^a Molecular Catalysis, Catalysis Research Center and Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, 85747 Garching bei München, Germany.

^b School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore; Energy Research Institute at NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, 50 Nanyang Drive, Singapore 637553, Singapore.

^c TUMCREATE LTD, #10-03, CREATE Tower, 1 Create Way, Singapore – 530351.

[†] These authors have equally contributed to this work.

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8 COMPLETE LIST OF PUBLICATIONS

8.1 Journal Articles

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

M. P. Do[‡], **P. J. Fischer**[‡], A. Nagasubramanian, J. Geder, F. E. Kühn*, M. Srinivasan*

J. Electrochem. Soc. **2019**, *166* (6), A944-A952.

$\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{PPh}_3)_2$ and Ruthenium Phosphine Complexes bearing Fluoroacetate Ligands: Synthesis, Characterization and Catalytic Activity

D. Hey[‡], **P. J. Fischer**[‡], W. Baratta*, F. E. Kühn*

Dalton Trans. **2019**, *48*, 4625-4635.

Synthesis and Physicochemical Characterization of Room Temperature Ionic Liquids and their Application in Sodium Ion Batteries

P. J. Fischer[‡], M. P. Do[‡], R. M. Reich, A. Nagasubramanian, M. Srinivasan, F. E. Kühn*

Phys. Chem. Chem. Phys. **2018**, *20*, 29412-29422.

8.2 Other Articles

„Brot aus Luft“ und andere chemische Beiträge zur Welternährung

P. J. Fischer, F. E. Kühn

Chem. Unserer Zeit **2019**, *53*, 112-124.

Ultrasound application and multi-step reactions in electrodeposition of refractory metals

L. Seidl, L. Asen, G. Yesilbas, **P. J. Fischer**, F. Kühn, O. Schneider

ECS Transactions **2018**, *86* (14), 3-19.

[‡] These authors have equally contributed to this work.

8.3 Conference Contributions

Ionic Liquids as Electrolytes for Safer Sodium Ion Batteries

P. J. Fischer, M. P. Do, M. Srinivasan, F. E. Kühn

Presentation, 256th ACS National Meeting & Exposition, Boston, USA, August **2018**

Physicochemical Characterization of Room Temperature Ionic Liquids for their Application in Safer Sodium Ion Batteries

P. J. Fischer, M. P. Do, M. Srinivasan, F. E. Kühn

Poster, 8th Energy Colloquium of the Munich School of Engineering, July **2018**

Ionic Liquids as Electrolytes and Electrolyte Additives for Safer Batteries

P. J. Fischer, M. P. Do, M. Srinivasan, F. E. Kühn

Presentation, International Center for Energy Research (ICER) Workshop, Singapore, March **2017**