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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

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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 coulombic 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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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. NaCrO₂²⁷⁻²⁹ and Na_xMnO₂^{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 (BMPTFSI) 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. BMPTFSI 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 BMPTFSI toward ignition when compared to conventionally applied organic electrolytes, underlining the suitability of BMPTFSI 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 electrolytes 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

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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-based 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-cell 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.

Experimental

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 $\text{P2-Na}_{0.6}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (NMO) was synthesized following a reported protocol.⁴⁴

Electrolyte preparation.—Preparation of all electrolytes was carried out under inert atmosphere in a glove box with oxygen and moisture contents less than 0.1 ppm. For the IL electrolyte, EL_{IL} NaFSI (Nippon Shokubai) was dissolved in BMPTFSI (IoLitec) to yield a 0.5 M solution. Attempts to employ 1.0 M NaFSI in BMPTFSI 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 NaClO_4 (Sigma-Aldrich) in an EC/PC mixture (1:1 w/w, Sigma-Aldrich).

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 ($15 \mu\text{m}$, Goodfellow) using a $100 \mu\text{m}$ gap-doctor blade. The cast sheet was dried at 80°C to remove NMP, roll-pressed and punched into 16 mm-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 were 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.

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 glove box 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 measurements 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 glove box, 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 $100 \mu\text{l}$ 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 glove box and connected to a Solartron SI1260 frequency response analyzer. The sample test tube

Table I. 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

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 cm³ 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°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 rate was 3 K min⁻¹.

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.

Results and Discussion

Electrode materials.—The purity of the synthesized NVO and NMO phases was evaluated via XRD (Figure 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}

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 I shows the viscosities and conductivities of the electrolytes applied in this study: BMPTFSI 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 BMPTFSI 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

Table II. 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%

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.

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 1 shows the cycling behavior and charge-discharge profiles (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 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).

When comparing the retention values of the two systems, NVO_{IL} displays a remarkably improved cycling stability. As shown in Table II, 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

Figure 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.

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 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 II). 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 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}.

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 S6). In order to determine a reasonable operating window of the full-cells, CVs of the latter were performed in different voltage ranges (Figure S7). Due to the presence of irreversible reactions above 2.8 V the voltage range was set to 0–2.8 V.

Galvanostatic charge-discharge tests were performed in the determined voltage range at a current rate of 50 mA g⁻¹. Figure 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

Figure 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 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).

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 (Figures 3a, 3b). 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 coulombic 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 (Figures 3c, 3d). 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 management systems are thus required.^{76,77,80} In contrast, these additional efforts and costs can be avoided when applying less temperature sensitive systems.

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 4 and the corresponding cycling stabilities and CEs are shown in Figure 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 4b). In contrast, this plateau is not apparent in the room temperature charge-discharge test for NMO/NVO_{ORG} (Figure 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 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

Figure 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).

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 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 previously discussed advantages for temperature insensitive systems into account.

Figure 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 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 I), 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 I, 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.

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.

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 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} ($0.19^\circ\text{C min}^{-1}$ at 191°C) is more than twice as high compared to NMO/NVO_{IL} ($0.07^\circ\text{C min}^{-1}$ 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 ($2.6^\circ\text{C min}^{-1}$) 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

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

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.

The top panel in Figure 7, shows the DSC results for the individual electrodes from a charged NMO/NVO_{ORG} full-cell in combination

Figure 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.

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 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 exothermally 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 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 of 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.

Conclusions

The performance of the electrode materials NMO and NVO in combination with the IL based electrolyte BMPTFSI 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 NaClO₄ (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-based SIB compared to a SIB with an 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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