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Ion liquid based lithium battery electrolytes: Fundamental benefits of utilising both TFSI and FSI anions?

M. Kerner, a, b N. Plylhan, c J. Scheers d and P. Johansson a, b

Several IL based electrolytes with an imidazolium cation (EMI) have been investigated trying to elucidate a possible beneficial effect of mixing FSI and TFSI anions in terms of physico-chemical properties and especially Li+ solvation. All electrolytes are evaluated in terms of phase transitions, densities and viscosities, thermal stabilities, ionic conductivities and local structure, i.e. charge carriers. The electrolytes with up to 20% of Li-salts showed to be promising for high temperature lithium ion battery application (ca. 100°C) and a synergetic effect of having mixed anions is discernible with the LITFSI,EMIFSI electrolyte giving the best overall performance. The determination of the charge carriers revealed the SN to be ca. 2 for all analysed electrolytes, and proved the analysis of the mixed anion electrolytes to be challenging and inherently leads to an ambiguous picture of the Li+ solvation.

1. Introduction

The high specific energy density of lithium ion batteries (LIBs) makes them the battery technology of choice for many applications. 1, 2. The electrolytes of conventional LIBs, however, contain both organic volatile solvents and salts with anions prone to decompose, limiting their application to temperatures around ambient, often restricted to lower than ca. 60°C. 3. A possible alternative for high temperature LIBs “HT-LIBs” (operating > 60°C) applications are ionic liquid (IL) based electrolytes; they have a general set of properties of wide liquid range, low vapour pressure, thermally stable, and are often considered non-flammable. 4-6. In addition they can be electrochemically stable over a wide potential range and have high ionic conductivities, 5 especially at high temperatures 7.

The number of possible ILs has been estimated to be extremely large; > 10^13 or even much larger. 8, 9, which makes it possible to tailor ILs for specific applications. This variety has been made use of in electrolytes, where cations of the imidazolium (XMI), piperidinium (PIP), pyrrolidinium (Pyrin) families, etc. have been combined with anions such as bis(fluorosulfonyl)imide (FSI), bis(trifluoromethanesulfonyl)imide (TFSI) and hexafluorophosphate (PF6) 10-13. For LIBs the ILs are most often mixed with the corresponding Li-salt e.g. LITFSI. As one example utilising such electrolytes Seki et al. showed a LIB with a charge/discharge capacity of 300 mAh g^-1 at room-temperature with a LiPyr13(1-x)TFSI electrolyte. 14. In terms of cycling stability, Garcia et al. demonstrated a battery with a 1M LiTFSI in EMITFSI electrolyte outperforming a 1M LITFSI in EC:DMC electrolyte at a rate of 1C for 200 cycles. 15.

IL based electrolytes can be modified into hybrid electrolytes, by adding organic solvents, to improve the ion transport and interfacial properties, but at the risk of losing the IL safety features at higher temperatures. 16. Another trend is to add a Li-salt with a different anion than in the IL. 19, 20. Replacing TFSI by FSI, or combining the two, has been motivated by enhanced ionic conductivities and improved passivation of the aluminium current collector. 21. The primary drawback is the risk of a lower thermal stability, exemplified by the temperature for 5% weight loss of the ILs EMITFSI (374°C) and EMIFSI (225°C). 22. Lahiri et al. very recently showed a superior behaviour of a battery with an LITFSI,Pyr14(FSI)1-x electrolyte as compared to an LiPyr14(1-x)TFSI electrolyte with respect to capacity and stability. 23. Nádherná et al. successfully used LiF5,Pyr24TFSI1-x at 55°C (350-360 mAh g^-1) and Yamagata et al. LITFSI,EMIFSI1-x in a graphite half-cell at 60°C. 24. Furthermore, Yamagata et al. proposed an electrochemical double-layer structure to be created on the electrode surface instead of the in conventional electrolytes formed solid electrolyte interphase (SEI), protecting the EMI cation from decomposition, and thereby improving the cathodic stability. 25. The non-trivial nature of these double-layer structures together with their dependence not only on the electrolyte, but also on the electrode material was shown by Costa et al. 26. Another advantage of an EMIFSILIL based system was elucidated by impedance spectroscopy; Sugimoto et al. found a much lower impedance for LITFSI,EMIFSI1-x as compared to LITFSI in EC:DMC. 27. At higher temperatures, 80-120°C, the performance of IL based electrolytes seems complicated. 28-30. Yet, Matsumoto et al. reported stable cycling for different IL based electrolytes with LITFSI at 85°C. 31.

Combining the approaches above, we here investigate the physico-
chemical properties of IL based electrolytes with both FSI and TFSI aiming towards operating temperatures of ca. 100°C. EMiFSI and EMI(T)FSI are combined with ≤ 20 mol% LiTFSI or LiFSI – giving four unique sets of electrolytes. For reference purposes the neat ILs are also studied. Focus is on thermal stabilities, phase transitions, and ionic conductivities. A detailed Raman spectroscopic analysis is performed to reveal the charge carriers in the electrolytes i.e. if there is a FSI or TFSI solvation preference of the Li⁺ cation. Furthermore, the electrochemical stability window (ESW) is determined to elucidate the possible working range and hence possible suitable electrode materials.

2. Experimental

2.1 Sample preparation

The ILs 1-ethyl-3-methylimidazolium FSI, EMiFSI (99.9 %), and EMiFSI (99 %), were purchased from Solvionic and used as received. LiTFSI (99.95 %) and LiFSI (99.5 %) were purchased from Sigma-Aldrich and Suzhou Fluolyte, respectively. The Li-salts were dried for 72 h under vacuum (< 7 Pa) at 120°C and 80°C, respectively. Four families of electrolytes; LiTFSI(1-x)EMiFSI(x) and LiFSI(1-x)EMi(T)FSI(x) were prepared by direct mixing of appropriate amounts of salt and IL to reach molar fractions of x=0.1 and 0.2. Thus, in total eight electrolytes were prepared. All materials were stored and handled in an argon filled glove box (H₂O < 30 ppm, O₂ < 1 ppm). EMiFSI and its electrolytes had < 30 ppm H₂O, while EMI(T)FSI and its electrolytes had < 100 ppm H₂O, as measured by Karl Fischer titration (KF Coulometer, Metrohm).

2.2 Phase transitions and thermal stability

Differential scanning calorimetry (DSC) was performed using a Q1000 from TA instruments. ca 10 mg of sample, in a hermetically sealed aluminium pan, was cooled to -150°C before heated up to 150°C, with 5 min equilibration time at the extreme temperatures. Stepwise, faster cooling rates of 5, 10, 20, and 40°C min⁻¹ were used to suppress crystallization and promote the observation of the glass transitions, while a common heating rate of 5°C min⁻¹ was used. The points of inflection of the transitions were used to determine the glass transition temperatures, T_g, while the onset of the endothermic peaks were used to determine the melting points, T_m. Thermal gravimetric analysis (TGA) was performed using a TG 209 F1 Iris from Netzsch. An alumina crucible was loaded with ca. 10 mg of sample and placed in the sample compartment where a nitrogen flow of 100 ml min⁻¹ was applied. All samples were heated from 25°C to 500°C at a rate of 5°C min⁻¹. The decomposition temperatures (T_d) were defined as the temperature of 1% mass loss. In addition, isothermal TGA measurements were performed at 100°C and 125°C to study “long-term” stability, each temperature was maintained for 10 h.

2.3 Density and viscosity

The densities (ρ) and viscosities (η) were determined using a DMA 4500M density meter from Anton Paar with a Lovis 2000 M microviscometer module. A steel ball (Ø=1.5 mm, ρ=7.70 g cm⁻³) was used for dynamic viscosity measurements by the falling sphere method. The capillaries (Ø=1.59 or 1.8 mm) were loaded inside the glove box. The densities and viscosities were recorded in 10°C steps from 20°C to 90°C and back to 20°C. The results from the cooling runs were used for all further analysis.

2.4 Ionic conductivity

The ionic conductivities (σ) were obtained by dielectric spectroscopy in the frequency range 10⁻¹ – 10⁷ Hz with a broadband dielectric spectrometer (Concept 80, Novocontrol GmbH) with a Quattro Cryosystem temperature control unit. The sample cell, with blocking stainless steel electrodes, had an inner diameter, Ø = 13.3 mm, and a thickness, 1.04 mm, defined by a Teflon spacer. The cell was filled with sample inside the glove box and transferred to the instrument in a closed box. Starting at 20°C, the samples were heated to 150°C and then cooled to -110°C in 10°C steps, using a 30 min equilibration time before measurement at each temperature. The higher temperatures might cause minor leakage of electrolyte, but the measured volume is approximately constant. The DC conductivities were obtained from the plateaus of the frequency dependent (AC) conductivity plots for each temperature.

2.5 Ionic interactions and local coordination

Molecular level interactions were studied using a Bruker MultiRAM FT-Raman spectrometer with a Nd:YAG laser (1064 nm, 250 mW) and a spectral resolution of 2 cm⁻¹. Data were typically averaged over 1000 to 3000 scans and recorded as a function of temperature at 30, 60, 90, and 120°C. All samples were filled in an open aluminium pan and placed in a hermetically sealed Linkam FTIR600 temperature controlled stage filled with dry argon gas. For a detailed analysis of the region 680 - 790 cm⁻¹, LiₓEMi₁₋ₓFSI spectra were deconvoluted using Gaussian functions, while the LiₓEMi₁₋ₓTFSI spectra were deconvoluted using pseudo-Voigt functions (Gaussian: Lorentzian = 60:40), the latter following the procedure of Lassègues et al. 19. Solvation numbers (SN) for the lithium cations were calculated from the deconvoluted spectra in accordance with the procedure of Pitawala et al. 34; dividing the area of the band corresponding to Li⁺ coordinated anions (A_j) with the total band area (including also the contributions from “free” anions (A_j)) and the molar fraction of Li-salt (x) (eq. 1).

\[ SN = \frac{A_j / (A_j + A_0)}{x} \quad (1) \]

To support the interpretation of the experimental spectra, artificial Raman spectra were created using data from density functional theory (DFT) calculations, (B3LYP/6-311+G(d)). The conductor-like polarizable continuum model (C-PCM) was used to account for the solvent. The minimum energy conformers of both FSI and LiFSI ion-pairs, which have been discussed elsewhere 35, were geometry optimized using ACN as solvent (ε=35.7) for an improved description vs. a vacuum approach 36. Second and third derivatives of the energies with respect to nuclei displacements were calculated to verify the structures as energy minima and to obtain the vibrational modes and the Raman activities. The calculated vibrational frequencies are reported without any scaling factor. All calculations were performed with the Gaussian09 software package 38.

2.6 Electrochemical stability window
In order to determine the electrochemical stability windows (ESW) of the electrolytes, linear sweep voltammetry (LSV) was performed using a 2-electrode Swagelok cell with stainless steel as working electrode and metallic Li-foil as counter/reference electrode. A circular sheet of glass microfiber (Ø = 14 mm) was used as separator and soaked with 80 µl of the electrolyte. All cells were assembled inside the glovebox under Ar atmosphere. The LSV measurements were conducted with a scan rate of 0.5 mV s\(^{-1}\) using identical, but different, cells for the anodic scan, from open circuit voltage (OCV) up to 6 V vs. Li\(^+\)/Li\(^0\), and for the cathodic scan, from OCV down to -0.5 V vs. Li\(^+\)/Li\(^0\).

### 3. Results and Discussion

In the following we compare the physico-chemical properties of the neat ILs and the various IL based electrolytes containing either TFSI or FSI or both anions. The anions originate from both the Li-salt and the IL, why the balance between all components relative to one another can be altered. The focus is on revealing the role of each anion for basic properties; phase transitions, densities, viscosities, ionic conductivities, thermal stabilities, electrochemical stability windows, and charge carriers.

#### 3.1 Phase transitions

In order for electrolyte performance to be predictable it is necessary to avoid phase transitions in the temperature range of interest. For a HT-LIB electrolyte this would comprise both the operation temperature, here approximately 100°C, and ambient or even lower temperatures during non-operation and shelf life. Furthermore, battery cycling can alter the phases present by introducing thermal variations and non-equilibrium situations in general. A first assessment of the promise of each electrolyte is made by detailed calorimetric studies. The phases and features present are highly dependent on the thermal history, as shown for pyrrolidinium and piperidinium based electrolytes by Furlani et al. 35, why all our electrolytes were measured under the same way.

The melting (T\(_m\)) and glass transition temperatures (T\(_g\)) define the low temperature limit. Below the melting point the crystallinity severely restricts mobility and ion conduction; for totally or partially amorphous materials the same occurs below the glass transition temperature. The T\(_m\) and T\(_g\) for ILs and electrolytes are summarized in Table 1 and the DSC traces are shown in Figure 1. For the ILs, the T\(_g\) of EMIFSI is in excellent agreement with the literature 40, 41, while the T\(_m\) differ; Fredlake et al. 40 reported a similar value, but Liu et al. a T\(_m\) ca. 8°C higher 41. Deviations can arise from different measurement conditions and handling, e.g. amounts of sample or drying procedures, or different levels of purity. The T\(_m\) of EMIFSI is in excellent agreement with the literature 42. The T\(_g\) of EMIFSI was obtained only at a fast cool rate, but no T\(_m\) was observed for EMIFSI. However, an exothermal peak at ca. -35°C, corresponding to a cold crystallization, indirectly supports the prior existence of a glassy state in EMIFSI.

The phase behaviour is strongly altered upon Li-salt addition, since much stronger ion-ion interactions are introduced 43, 44. This leads to increased T\(_g\) and increased viscosity (see Figure 2), which worsen dynamics and transport properties 45, 46, but here the T\(_g\) increase only slightly: ≤ 12°C (maximum for Li\(_0.2\)EMI\(_0.8\)FSI). Based on the results of all electrolytes, the effect of the anion can be elucidated; comparing the effects of adding LiFSI and LiTFSI the latter causes a larger increase in T\(_g\). In the literature the interaction between TFSI and Li\(^+\) has been calculated to be stronger than between FSI and Li\(^+\) 43, 44, which results in a higher viscosity, hence a larger increase of T\(_g\) for samples with a larger amount of TFSI, resulting in the highest T\(_g\) of -79°C for the Li\(_0.2\)EMI\(_0.8\)TFSI electrolyte. This is somewhat remarkable given the often-mentioned plasticizing effect of TFSI 10, 47, attributed to both its sheer size and internal flexibility 48, 49. The equally flexible 50, but smaller FSI, may be just as plasticizing. The nature of the ion-ion interactions most likely plays an additional role.

Adding x=0.2 LiFSI or LiTFSI to EMIFSI result in a 20°C depressed melting points. Furthermore, all electrolytes remain liquid until ca. -22°C, in the best case until ca. -36°C, and the amount of crystalline phase basically decrease as a function of x. For LiTFSI\(_0.2\)EMIFSI\(_0.8\) it is difficult to detect the melting peak (Figure 1). There is a subtle difference between the two ILs; the EMIFSI electrolytes (x=0.2) are fully amorphous, while a low temperature melting transition remains for the corresponding electrolytes with EMIFSI.

In summary, the eight electrolytes show wide liquid ranges, increasing with Li-salt concentration. The two electrolytes with the largest liquid ranges (EMITFSI and x=0.2) only exhibit a single glass transition. These results are consistent with the literature where Paillard et al. showed a widening of the liquid range with salt content and no crystalline phase at all for Li\(_x\)Pyr\(_{14+}\)FSI electrolytes with x ≥ 0.2 51. A widening of the liquid range was also observed for mixtures of ILs containing FSI and TFSI 52, 53, but without a Li-salt. The presence of Li\(^+\) is arguably of importance, since for our mixed electrolytes, the range was not additionally widened when both FSI and TFSI were present.

#### 3.2 Density and Viscosity

The densities and viscosities are strongly dependent on the temperature and, in practice, important when the electrolyte first is to fill the porous separator. During battery operation, temperature differences can lead to mechanical stresses and worse electrode contact. The viscosity also has a strong impact on the rate of mass transport and on the wettability, affecting the rate of electrochemical reactions and general battery performance.

The densities and viscosities of the electrolytes increase with Li-salt concentration (Figure 2), suggesting an interaction between Li\(^+\) and FSI and/or TFSI. The relative increase is larger for the TFSI based electrolytes. This was suggested to be arising from the stronger interactions of TFSI with Li\(^+\) as compared to FSI as determined by ab initio calculations 43, 44. Tsuchiya et al. 54 further state that the in general higher viscosities of EMIFSI based samples are not only arising from the relatively larger TFSI, but also from stronger interactions between EMi and TFSI 43. This is also in accordance with molecular dynamics (MD) simulations of EMIFSI and EMITFSI by Borodin et al. 54. The viscosities of the electrolytes and the neat ILs were fitted by using a modified Vogel-Tammann-Fulcher (VTF) equation (eq. 2). All fits show a VTF behaviour. The VTF parameters of the best fits are summarized in Table 2.

\[
\eta = \frac{\eta_0}{\exp\left(\frac{B}{T-T_0}\right)}
\] (2)
The density of EMIFSI (RT) is in agreement with the literature \(^{55}\), while that of EMITFSI differs; Fredlake et al. \(^{40}\) report a similar value, but Liu et al. \(^{41}\) a slightly higher (by 2%, albeit using a different method) – just as for the comparison of TFSI.

The viscosities decrease exponentially and the densities linearly with temperature – the former being only ca. 10-25% at 90°C compared to the values at 20°C. The measured viscosities for the neat ILs are in excellent agreement with the literature \(^{43}\). At 90°C the IL and electrolyte viscosities are close to that of the commercial organic solvent based electrolyte LP40 at 20°C (1M LiPF\(_6\) in EC:DEC, 5.1 mPas), supporting IL based HT-LIB functionality. This is crucial, since conventional organic solvent and LiPF\(_6\) based electrolytes are not stable above ca. 60°C. \(^{1}\) Furthermore, at these elevated temperatures, the range of viscosities becomes quite narrow; 5.1-12.3 mPas, with the single largest viscosity decrease (>90%) observed for Li\(_{2}\)EMI\(_0.8\)TFSI – and in general the relative decrease in viscosity at increased temperature, is a function also of Li-salt content (Figure 2). In summary, all electrolytes have appreciably low viscosities at 90°C, but FSI seems to promote somewhat lower electrolyte viscosities than TFSI, as previously reported in the literature \(^{43, 56}\). As for mixing the two anions, no distinct advantages are apparent here.

### 3.3 Ionic Conductivities

The ion transport within any electrolyte is influenced both by the viscosity and the type of charge carriers. In IL based electrolytes the situation can happen, be quite complicated as the matrix/solvent itself is composed of cations and anions, both contributing to the measure, and the latter solvating the Li\(^+\) added as a Li-salt – a process which in general lowers the overall conductivity by creating larger complexes \(^{21, 46}\). In the here presented electrolytes, things are intrinsically even more complicated as competitive Li\(^+\) coordination can occur between FSI and TFSI. The overall highest ionic conductivity was obtained for neat EMIFSI, ca. 3x that of EMITFSI, and in acceptable agreement with provider data and the literature \(^{11, 41}\). In general, the addition of Li-salt lowers the ionic conductivity, as a direct consequence of a higher viscosity due to the interaction between Li\(^+\) and FSI and/or TFSI. The conductivities increase as a function of temperature and, at 80°C < T < 100°C, the conductivities are ≤6x those at RT and continues to increase to 150°C (end of data) for most of the electrolytes.

The anticipated decrease in ionic conductivity upon Li-salt addition is here confirmed for all but one group of electrolytes, LiTFSI\(_{2}\)EMIFSI\(_{1-x}\), where the x=0.2 electrolyte, being one of the most conductive overall, is more conductive than x=0.1 for all temperatures. The LiTFSI\(_{2}\)EMIFSI\(_{0.8}\) is also the only exception to another trend; for the same Li-salt content the conductivity increases with FSI content (Table 1). Overall, even the electrolyte with the lowest conductivity, Li\(_{2}\)EMI\(_0.8\)TFSI, has a conductivity high enough (≥10\(^{-4}\) S cm\(^{-1}\)) to be considered for battery application \(^{17}\), with the caveat that most of the conductivity likely being non-Li\(^+\) related.

At low temperatures the abrupt increases in the conductivities of EMIFSI and EMITFSI (ca. -20°C, Figure 3) agree with the melting temperatures of the ILs (Table 1). At temperatures below the glass transition the ionic conductivities also increase non-monotonically for all systems, but with much less distinct features. The conductivities were analysed in more detail by fitting the data between 90°C and close to T\(_g\) (or T\(_m\)) to a modified VTF equation (3) (Figure 3). The VTF parameters are summarized in Table 2. The Angell’s strength parameter D (B\(_s\) = D\(_{T_0}\)\(\alpha\)) is often used to classify the fragility of liquids \(^{58}\) and here all systems exhibit a D between 1.3 and 5.9, which reveals a fragile behaviour (D < 30), and hence a conductivity lower than expected for normal diffusion, due to cations and anions being coupled \(^{59}\).

\[
\sigma = \frac{A_n}{T^\gamma} \exp\left(\frac{-B_n}{T-\gamma T_0}\right)
\]

(3)

The basic data on density, viscosity, and conductivity is used to create a Walden plot for all the systems to further reveal differences in the ion association (Figure 4). The viscosity correlates to the ionic conductivity if the electrolytes follow the fractional Walden rule: \(^{59}\)

\[
A_m n^\gamma = C
\]

(4)

Here γ is a constant, 0 < γ ≤ 1, extractable from the slope of the Walden plot. The usual reference, an aqueous solution of KCl with completely dissociated ions, γ = 1, is also added. All γ’s are smaller than 1 and additionally the deviation increases with salt content. LiTFSI\(_{2}\)EMIFSI\(_{0.8}\) is an exception with almost the same γ as LiTFSI\(_{2}\)EMIFSI\(_{0.9}\) (see Table 2). Overall, the largest changes are observed for the Li\(_2\)EMI\(_0.8\)FSI electrolytes, suggesting a stronger interaction between EMI and TFSI than with FSI and an increased ion association with Li\(^+\). This agrees with both the viscosity and density data, literature data \(^{43, 44, 56}\), and is consistent with the molecular level structure suggested by NMR spectroscopy \(^{60}\), Raman spectroscopy coupled with DFT calculations, \(^{33}\) and MD simulations \(^{61, 62}\). The data for the mixed electrolytes, however, propose an advantage of having both FSI and TFSI present at a certain ratio. The LiTFSI\(_{2}\)EMIFSI\(_{0.8}\) electrolyte is among the most conductive electrolytes measured. A similar increase of the conductivity for a specific IL mixture was observed for Py\

\[\text{imid}M_{140}\text{TFSI}_{1-x}\] at -20°C. \(^{57}\) In accordance with previous IL and IL based electrolyte studies the investigated systems are classified as good ILs \(^{59, 63}\).

### 3.4 Thermal stability

For HT-LIB application the electrolyte stability at high temperatures is critical. An increased temperature often leads to increased vapour pressures and/or decomposition – why monitoring the thermal stability of the electrolyte is extremely important to secure safe operation of a HT-LIB.

In the literature the EMIFSI and EMITFSI ILs decompose at approximately 225°C and 375°C, respectively \(^{23}\). LiFSI starts to decompose >200°C \(^{21}\), but the reaction rate becomes fast only from ca. 330°C. LiTFSI has the highest stability with a decomposition at ca. 380°C \(^{64}\). Thermal stability data on electrolytes using imidazolium based ILs with a Li-salt and both anions (xFSI) have not yet been reported.
The decomposition of an IL based system can be slow, and thus the results, at lower mass loss, are thus more conservative, as obtained by dynamic TGA experiments. The decomposition of an IL based system can be slow, and thus the results, at lower mass loss, are thus more conservative, as obtained by dynamic TGA experiments.

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The Li,EMI1-xTFSI electrolytes

Starting with EMITFSI, the envelope centered at ~742 cm\(^{-1}\) is according to the literature due to two overlapping bands originating from the two conformers of the “free” TFSI anion. In addition, we found adding a minor feature at ca. 745 cm\(^{-1}\), likely due to EMI (which also has two spectrally closely spaced conformers in this region), to improve the fit considerably (Figure 6). Addition of LiTFSI leads to a new band at 747 cm\(^{-1}\), in agreement with the literature assigned to the [Li(TFSI)]\(^{+}\) complex. Deconvolution and application of eq. 1 result in an estimate of SN as a function of temperature (Figure 7). The SN decrease slightly due to many possible components; the “free” anions, both present in these electrolytes are transported as part of negatively charged [Li(TFSI)]\(^{+}\) species – which may seem awkward, but still enables functional LIBs.

The Li,EMI1-x,FSI electrolytes

The spectrum of EMIFSI shows two main features at 702 cm\(^{-1}\) and 725 cm\(^{-1}\) (Figure 8). For the deconvolution of the electrolyte spectra we apply the same EMI band as we did for the TFSI based electrolytes (744 cm\(^{-1}\)) and account for both FSI conformers (at ca. 725 and 731 cm\(^{-1}\)). We note in passing that the width of the two FSI bands (FWHM=10-20) are larger than those for TFSI (≈7), which could reveal higher dynamic disorder. The SNs obtained (Figure 7); 2.4 (x=0.1) and 2.1 (x=0.2), differ from the SN of 3 predicted by Fujii et al., but are clearly larger than for the TFSI system; 1.8 (x=0.1) and 1.9 (x=0.2). These results agree with the trend from the MD simulations of Solano et al. albeit having much larger SNs.

Electrolytes containing both TFSI and FSI

In a Raman study by Huang et al. LiFSI and LiTFSI were added to Pyr13FSI, to obtain electrolytes with mixed anions, and concluded Li\(^{+}\) to be preferentially coordinated by FSI. However, a recent NMR study of Lesch et al. proposed TFSI to be the preferred ligand of Li\(^{+}\) and forming aggregates referred to as lithium dimers (Li-TFSI-Li) in both LiTFSI,EMIFSI, and LiFSI,EMITFSI, electrolytes. These latter results agree with the computed stronger interactions predicted for Li-TFSI, as compared to Li-FSI. Yet, the overall picture is thus ambiguous.

The analysis we have made above on the nature of the charge carriers, when there is only a single anion present, is far from simple, but it benefits from a limited set of possibilities. When we use LiFSI in EMITFSI or LiTFSI in EMIFSI we expand the set of possibilities dramatically. At first sight there are three types of coordination possible: by FSI or TFSI, or a combination of both. If there is an anion preference, it should be able to elucidate this. In more detail, however, the Raman spectra will be products of bands due to many possible components; the “free” anions, both present in two conformers, totally four bands, and various complexes either of the pure or mixed types and for the latter we know neither SN nor CN. If we also account for the conformations of FSI and TFSI within the various complexes it is clear that the task of proper deconvolution becomes extremely challenging.

The manifold problems of: i) overlapping “free” and coordinated anions of various kinds and ii) the possibility for new various complexes of unknown SN and CN are a challenge. Unknown frequencies, Raman scattering cross-sections, and band-widths, makes a quantitative analysis difficult. Yet, the effect of increasing the lithium salt concentration shows an increased interaction between Li\(^{+}\) and FSI or TFSI, but the detailed coordination of Li\(^{+}\) to the anions is again, fundamentally, not possible to elucidate.

In summary, for the electrolytes with TFSI or FSI as the exclusive anions, we find that Li\(^{+}\) is solvated by approximately two TFSI, while the SN of Li\(^{+}\) with FSI is slightly higher (SN≈2.1-2.4) depending on the salt concentration. The higher SNs for FSI agree qualitatively with MD results, albeit the SN of the latter are predicted to be much larger.

The detailed solvation of Li\(^{+}\) in the mixed anion electrolytes is not clearly resolved, as Raman data does not exclude the presence of either anion in the solvation shell of Li\(^{+}\) in any of the four mixed anion electrolytes. The structures predicted from ab initio and DFT calculations, suggest a predominant coordination of Li\(^{+}\) by TFSI. Our present results show a more complex picture.

### 3.6 Electrochemical stability window

Adequate electrochemical stability of the electrolytes is crucial for their usage in LIB. Wide ESW i.e. an anodic and cathodic limit ≥ 5 V and ≤ 0 V vs. Li\(^{+}\)/Li\(^{-}\), is beneficial as it at least in principle, provides a wide selection of electrode materials possible. The voltammograms resulting from the LSV measurements are shown in Figure 10 and with respect to the anodic stability, the electrolytes with TFSI as the exclusive anion start to decompose at close to 4 V vs. Li\(^{+}\)/Li\(^{-}\). The electrolytes with TFSI as the exclusive anion are more stable (≥ 5 V vs. Li\(^{+}\)/Li\(^{-}\)). The mixed anion electrolytes all have anodic stabilities between 4.5 and 5 V vs. Li\(^{+}\)/Li\(^{-}\). Increased anodic stability with TFSI content is a clear trend. For the cathodic stability, all electrolytes are stable to potentials ca. -0.1 V vs. Li\(^{+}\)/Li\(^{-}\), but with various resulting currents – much larger in the case of FSI being the sole or dominant anion. These
observations may also be coupled to lithium plating rather than any electrochemical decomposition.  

4. Conclusions

The aim of this study was to investigate the fundamental properties of electrolytes for their possible application in high temperature, ca. 100°C, LiBs. Overall, the properties (densities, viscosities, etc.) of all systems investigated are strikingly similar, but both the amount of Li salt and the balance of FSI/TFSI affect their practical promise as battery electrolytes. The LiTFSI0.8EMIFSI0.8 electrolyte is especially promising, due to its high thermal stability in the working range and its high ionic conductivity. This might arise from a specific solvation of Li+ by TFSI and FSI, at a given Li-salt concentration, which seems to result in a synergetic advantage. The detailed Raman analysis leads to SNs of ca. 2 for all the analysed electrolytes, somewhat higher for the FSI based and lowered at higher temperatures for the TFSI based. These observations are corroborated by literature DFT, MD, and NMR results. The Raman analysis of the mixed anion electrolytes is inherently laden with ambiguities why no distinct anion coordination preference can be concluded, which infers the possibility of a TFSI/FSI mixed solvation and also various charge carriers possible. The physico-chemical properties, e.g. the exception in the trend of ionic conductivities for one of the mixed electrolytes, point towards possible general synergetic effects for mixed anion IL based electrolytes. Finally, we stress that in terms of viscosity, and hence ion transport at large, these IL based electrolytes are on par with organic based electrolytes when taking into account their foreseen operating temperatures.

Acknowledgements

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Notes and references

Figure 1: DSC heating traces of a) EMITFSI and the corresponding electrolytes with LiTFSI or LiFSI, and b) EMIFSI and the corresponding electrolytes.

Table 1: Glass transitions, melting temperatures, ionic and molar conductivities (20°C and 90°C), and decomposition temperatures for ILs and electrolytes.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ [°C]</th>
<th>$T_m$ [°C]</th>
<th>$\sigma_{20°C}$ [mS cm$^{-1}$]</th>
<th>$\sigma_{90°C}$ [mS cm$^{-1}$]</th>
<th>$\Lambda_{m,20°C}$ [S cm$^2$ mol$^{-1}$]</th>
<th>$\Lambda_{m,90°C}$ [S cm$^2$ mol$^{-1}$]</th>
<th>$T_d$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIFSI</td>
<td>-5</td>
<td>-16</td>
<td>15.3</td>
<td>60.0</td>
<td>3.08</td>
<td>12.6</td>
<td>201</td>
</tr>
<tr>
<td>Li$<em>{0.1}$EMI$</em>{0.9}$TFSI</td>
<td>-99</td>
<td>-29</td>
<td>6.6</td>
<td>27.0</td>
<td>1.27</td>
<td>5.43</td>
<td>178</td>
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<tr>
<td>Li$<em>{0.2}$EMI$</em>{0.8}$TFSI</td>
<td>-97</td>
<td>-36</td>
<td>3.7</td>
<td>13.3</td>
<td>0.61</td>
<td>2.31</td>
<td>161</td>
</tr>
<tr>
<td>LiTFSI$<em>{0.1}$EMIFSI$</em>{0.9}$</td>
<td>-99</td>
<td>-28</td>
<td>4.6</td>
<td>17.1</td>
<td>0.90</td>
<td>3.50</td>
<td>211</td>
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<td>LiTFSI$<em>{0.2}$EMIFSI$</em>{0.8}$</td>
<td>-92</td>
<td>-34</td>
<td>5.0</td>
<td>21.4</td>
<td>0.94</td>
<td>4.27</td>
<td>229</td>
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<tr>
<td>EMITFSI</td>
<td>-86</td>
<td>-18</td>
<td>5.3</td>
<td>23.5</td>
<td>1.38</td>
<td>6.39</td>
<td>302</td>
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<tr>
<td>Li$<em>{0.1}$EMI$</em>{0.9}$TFSI</td>
<td>-79</td>
<td>-22</td>
<td>2.8</td>
<td>12.9</td>
<td>0.68</td>
<td>3.32</td>
<td>288</td>
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<tr>
<td>Li$<em>{0.2}$EMI$</em>{0.8}$TFSI</td>
<td>-88</td>
<td>-24</td>
<td>3.7</td>
<td>17.4</td>
<td>0.90</td>
<td>4.41</td>
<td>213</td>
</tr>
<tr>
<td>LiTFSI$<em>{0.1}$EMITFSI$</em>{0.9}$</td>
<td>-87</td>
<td>-</td>
<td>2.6</td>
<td>13.2</td>
<td>0.58</td>
<td>3.14</td>
<td>199</td>
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<tr>
<td>LiFSI</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>LiTFSI</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>333</td>
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</table>
Table 2: VTF-parameters for the fits of the viscosities and conductivities.

<table>
<thead>
<tr>
<th>Material</th>
<th>$A_\eta$</th>
<th>$B_\eta$</th>
<th>$T_{0,\eta}$</th>
<th>$R_\eta^2$</th>
<th>$A_\sigma$</th>
<th>$B_\sigma$</th>
<th>$T_{0,\sigma}$</th>
<th>$D_\sigma$</th>
<th>$R_\sigma^2$</th>
<th>$\gamma$</th>
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<tbody>
<tr>
<td>EMIFSI</td>
<td>138</td>
<td>836</td>
<td>141</td>
<td>0.999</td>
<td>33939</td>
<td>780</td>
<td>5.86</td>
<td>133</td>
<td>0.923</td>
<td>0.969</td>
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<tr>
<td>Li$<em>{0.1}$EMI$</em>{0.9}$FSI</td>
<td>121</td>
<td>819</td>
<td>133</td>
<td>0.998</td>
<td>8107</td>
<td>545</td>
<td>3.30</td>
<td>165</td>
<td>0.940</td>
<td>0.935</td>
</tr>
<tr>
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<td>111</td>
<td>819</td>
<td>127</td>
<td>0.996</td>
<td>2308</td>
<td>396</td>
<td>2.16</td>
<td>183</td>
<td>0.925</td>
<td>0.787</td>
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<tr>
<td>LiTFSI$<em>{0.3}$EMIFSI$</em>{0.9}$</td>
<td>117</td>
<td>800</td>
<td>120</td>
<td>0.996</td>
<td>3675</td>
<td>462</td>
<td>2.68</td>
<td>172</td>
<td>0.986</td>
<td>0.844</td>
</tr>
<tr>
<td>LiTFSI$<em>{0.3}$EMIFSI$</em>{0.8}$</td>
<td>104</td>
<td>794</td>
<td>120</td>
<td>0.990</td>
<td>6012</td>
<td>512</td>
<td>2.96</td>
<td>173</td>
<td>0.987</td>
<td>0.845</td>
</tr>
<tr>
<td>EMITFSI</td>
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<td>803</td>
<td>122</td>
<td>0.997</td>
<td>7466</td>
<td>546</td>
<td>3.23</td>
<td>169</td>
<td>0.985</td>
<td>0.870</td>
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<tr>
<td>Li$<em>{0.1}$EMI$</em>{0.9}$TFSI</td>
<td>122</td>
<td>820</td>
<td>114</td>
<td>0.999</td>
<td>2701</td>
<td>412</td>
<td>2.15</td>
<td>191</td>
<td>0.997</td>
<td>0.791</td>
</tr>
<tr>
<td>Li$<em>{0.3}$EMI$</em>{0.8}$TFSI</td>
<td>114</td>
<td>837</td>
<td>105</td>
<td>0.995</td>
<td>2904</td>
<td>485</td>
<td>2.58</td>
<td>188</td>
<td>0.976</td>
<td>0.774</td>
</tr>
<tr>
<td>LiFSl$<em>{0.3}$EMITFSI$</em>{0.9}$</td>
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<td>796</td>
<td>115</td>
<td>0.986</td>
<td>4276</td>
<td>457</td>
<td>2.48</td>
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<td>0.985</td>
<td>0.840</td>
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<tr>
<td>LiFSl$<em>{0.3}$EMITFSI$</em>{0.8}$</td>
<td>90</td>
<td>760</td>
<td>102</td>
<td>0.973</td>
<td>3066</td>
<td>424</td>
<td>2.20</td>
<td>193</td>
<td>0.987</td>
<td>0.785</td>
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</tbody>
</table>

Figure 2: Densities (a) and viscosities (b) as functions of temperature. Data for an organic solvent based electrolyte LP40 (1M LiPF$_6$:EC:DEC) is added in (b). The viscosity curves (b) are the respective VTF-fits.
Figure 3: Ionic conductivities of EMIFSI (a) and EMITFSI (b) based electrolytes from 150°C to -80°C. The dotted lines are VTF-fits ($T_g$ or $T_m < T < 90°C$).

Figure 4: Walden plot for the neat ILs and the electrolytes using data between 20°C and 90°C.
Figure 5: Dynamic TGA results of the neat ILs and Li-salts (a) and isothermal TGA results of EMIFSI and LiTFSI$_{0.1}$EMIFSI$_{0.9}$ (b).

Figure 6: Deconvoluted Raman spectra of Li$_x$EMI$_{1-x}$TFSI
Figure 7: The SN of Li\(^+\) for Li\(_x\)EMI\(_{1-x}\)TFSI (x=0.1 and 0.2) as a function of temperature and for Li\(_x\)EMI\(_{1-x}\)FSI at 30°C (x=0.1 and 0.2).

Figure 8: Deconvoluted Raman spectra of Li\(_x\)EMI\(_{1-x}\)FSI.
Figure 9: The influence of LiFSI and LiTFSI on the Raman spectra of EMITFSI (a) and EMIFSI (b) at 30°C.
Figure 10: Voltammograms of the electrolytes from LSV at a scan rate of 0.5 mV s$^{-1}$ between -0.5 and 6 V using stainless steel as the working electrode and Li-foil as the counter and reference electrode.