The hydrotropic effect of ionic liquids in water-in-salt electrolytes

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Abstract: Water-in-salt electrolytes have successfully expanded the electrochemical stability window of aqueous electrolytes beyond 2 V. Further improvements in stability can be achieved by partially substituting water with either classical organic solvents or ionic liquids. Here, we study ternary electrolytes composed of LiTFSI, water, and imidazolium ionic liquids. We find that the LiTFSI solubility strongly increases from 21 mol/kg in water to up to 60 mol/kg in the presence of ionic liquid. The solution structure is investigated with Raman and NMR spectroscopy and the enhanced LiTFSI solubility is found to originate from a hydrotropic effect of the ionic liquids. The increased reductive stability of the ternary electrolytes enables stable cycling of an aqueous lithium-ion battery with an energy density of 150 Wh/kg on the active material level based on commercially relevant Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and LiNi\textsubscript{0.8}Mn\textsubscript{0.1}Co\textsubscript{0.1}O\textsubscript{2} electrode materials.

Introduction

Water-in-salt (WIS) electrolytes are a class of liquid electrolytes for lithium-ion batteries that combine the non-flammability of traditional aqueous electrolytes with a wide electrochemical stability window of ≥2.5 V.[1-3] The archetypal WIS electrolyte is composed of 21 mol of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in one kilogram of water (21 mol/kg, here denoted as 21m).[4] At such a high concentration, WIS electrolytes have a very different electrolyte structure than traditional much less concentrated electrolytes.[4] A molality of 21m translates into a water-to-lithium ratio of only 2.65. This scarcity of water leads to the incorporation of TFSI anions into the primary solvation shell of the cations.[5,6] Strong Li+-TFSI interactions lower the reductive stability of the anion and enable the formation of an anion-derived solid-electrolyte interphase (SEI) on the negative electrode at modest potentials.[5,6] Simultaneously, the high oxidative stability of WIS electrolytes of >4.5 V vs. Li/Li\textsuperscript{+} results at least in part from a water-depletion zone created by the alignment of TFSI anions in the electrolyte double-layer at the cathode/electrolyte interface.[7] However, despite convincing evidence for the formation of an anode SEI in WIS electrolytes, effective suppression of the hydrogen evolution reaction (HER) is limited to potentials above 1.9 V vs. Li/Li\textsuperscript{+}.[1] At lower potentials, water molecules increasingly accumulate at the anode/electrolyte interface,[7] facilitating HER and thus preventing the formation of a dense SEI.[6] This so-called cathodic challenge has significant consequences as already Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (LTO), an important anode material for lithium-ion batteries, cannot be operated in such WIS electrolytes although its average redox potential shifts to ca. 1.8 V vs. Li/Li\textsuperscript{+} in WIS electrolytes due to the high lithium-ion concentration (Nernst shift).[2]

By employing eutectic mixtures of various lithium salts, the water content can be further reduced and higher reductive stabilities can be achieved.[5,8,9] However, solely increasing the lithium salt concentration produces highly viscous solutions with low ionic conductivity.[5] An alternative strategy was reported by Chen et al.: By substituting half of the water molecules with acetonitrile, a hybrid electrolyte is formed that remains non-flammable and shows enhanced reductive stability leading to compatibility with LTO anodes.[10] Alternatively, the addition of an electrochemically inert organic salt (tetraethylammonium trifluoromethanesulfonate) to a sodium-based WIS electrolyte has shown to be an effective strategy to further reduce the water content.[11] Combining large organic cations with large organic anions typically results in salts with low melting points, i.e. ionic liquids, another class of non-flammable and non-volatile solvents. Following this strategy, a hybrid electrolyte containing LiTFSI, water, and the ionic liquid ethyltrimethylammonium TFSI was reported.[12] Importantly, with a concentration of 42m LiTFSI, a strongly enhanced lithium salt solubility with respect to water was observed upon addition of the ionic liquid.[12]

To investigate the origin of the enhanced LiTFSI solubility in the presence of ionic liquids, we prepare hybrid WIS electrolytes based on the room temperature ionic liquids (RTILs) 1-ethyl-3-methylimidazolium TFSI (EMImTFSI) and EMIm trifluoromethanesulfonate (EMImOTf). We show that the LiTFSI solubility increases from 21m in water to up to 55m in the presence of 30m EMImTFSI and up to 60m in the presence of 30m EMImOTf. We investigate the solution structure of selected electrolytes by means of Raman and NMR spectroscopy and relate the enhanced LiTFSI solubility to a hydrotropic effect of the RTILs. Briefly, a hydrotrope is a solubility-enhancing compound that does not act through micelle formation.[12] Taking advantage of the reduced water content and an extended electrochemical...
such a low DSC curve of 20/20-TFSI due to the suppressed crystallization.

However, we do not expect the reductive stability of hydrophobic EMImTFSI, the quaternary alkyl ammonium type, to be as high as EMIm with its calculated reduction potential of 0.62 V vs. Li/Li+. Additionally, choosing TFSI and OTf allows us to compare a hydrophobic (EMImTFSI) with a completely water-miscible hydrophilic RTIL (EMImOTf). Other cations, e.g., of the quaternary alkyl ammonium type, have higher reductive stability than EMIm with its calculated reduction potential of 0.62 V vs. Li/Li+. However, we do not expect the reductive stability of EMIm to limit the electrochemical stability window of RTIL-containing WIS electrolytes as this potential is 2 V more negative than the thermodynamic potential of the HER at neutral pH (2.6 V vs. Li/Li+). In the following, all molalities for RTIL-containing WIS electrolytes are reported with respect to water (moles of lithium salt/RTIL per kilogram of water).

To study the effect of EMImTFSI and EMImOTf on the LiTFSI solubility in WIS electrolytes, we investigated the thermal behavior of multiple LiTFSI–RTIL–water ternary mixtures via differential scanning calorimetry (DSC). The individual electrolyte compositions are reported in Table S1 of the Supporting Information (SI). Whereas 20m LiTFSI exhibits distinct crystalization and melting events, addition of 20m EMImTFSI (sample denoted as 20/20-TFSI with TFSI referring to the anion of the RTIL) results in suppressed crystalization during the cooling scan and a glass transition at ~87 °C (Figure S1 a). Interestingly, the liquidus temperature (T_L), marking the transition to a fully liquid state, appears to drop from 15 °C for 20m LiTFSI to ~29 °C for 20/20-TFSI. However, melting is hardly visible in the DSC curve of 20/20-TFSI due to the suppressed crystalization. Such a low T_L indicates that the solution is not saturated at room temperature, i.e., the LiTFSI and/or EMImTFSI concentration could be increased while retaining a T_L below room temperature. In fact, when fixing the EMImTFSI molality at 20m, the LiTFSI concentration can be more than doubled to 45m while T_L increases to 23 °C. For hydrophilic EMImOTf instead of hydrophobic EMImTFSI, the T_L of the equivalent solution (20/20-OTf) likewise drops to ~26 °C (Figure S1 b) and the LiTFSI concentration can even be increased to more than 50m (T_L = 11 °C for 50/20-OTf). By increasing the RTIL molality to 30m, the LiTFSI solubility at room temperature can be further increased to at least 55m and 60m for EMImTFSI and EMImOTf, respectively, resulting in electrolytes with total molalities of 85m and 90m.

The reduced water content of these electrolytes in terms of their water-to-lithium molar ratio is highlighted in Figure 1 a, which compares this ratio for selected LiTFSI–RTIL–water hybrid electrolytes with that of 21m LiTFSI. The number of available water molecules per lithium ion shrinks from 2.65 in 21m LiTFSI to 1.39 in a solution containing 40m LiTFSI and 20m RTIL (sample 40/20). Pushing the LiTFSI content to its solubility limit reduces the ratio further to 1.23 for 45/20-TFSI and to 1.11 for 50/20-OTf. For 60/30-OTf, the water-to-lithium ratio equals 0.93. Hence, this solution contains more lithium ions than water molecules. The numbers inside the bars shown in Figure 1 a represent the molar fraction of the different electrolyte components. Except for the 60/30-OTf electrolyte, water still has the highest molar fraction among all components, which is beneficial for transport properties.

Indeed, the low water fraction of the 60/30-OTf electrolyte results in a rather low ionic conductivity of 0.4 mS/cm and a high viscosity of 1125 mPa s at 25 °C. However, considering the overall molality of this solution of 90m, these transport properties are still surprisingly good. For comparison, a lower conductivity of 0.1 mS/cm and a higher viscosity of 8555 mPa s at 30 °C were reported for a 55m WIS electrolyte based on a combination of LiTFSI and lithium (pentfluoroethanesulfonylimide) (LiPTFSI). [9] Temperature-dependent viscosity and conductivity data of selected LiTFSI–RTIL–water solutions are given in Table S2. For comparison, the table also contains data for 20m LiTFSI. Upon addition of RTIL, the conductivity at 25 °C drops from 10.4 mS/cm (20m LiTFSI) to 6.7 mS/cm (20/20-TFSI) while the viscosity slightly decreases from 55.3 mPa s (20m LiTFSI) to 44.2 mPa s (20/20-TFSI). We interpret the lower viscosity as plasticizer effect of the RTIL, a phenomenon that is typically observed for polymer electrolytes in which RTILs are used to increase polymer chain mobility. [17,18] However, increasing the LiTFSI concentration further leads to even lower conductivities of, e.g., 2.9 and 1.2 mS/cm for 30/20-TFSI and 40/20-TFSI, respectively. We find the same trend for EMImOTf-containing electrolytes, which correlates well with the behavior of binary lithium salt-ionic liquid electrolytes that show decreasing ionic conductivities upon increasing lithium molar fractions. [19–21] In light of their suitability for battery applications, we selected the following electrolytes with conductivities of at least 1.0 mS/cm at 25 °C for the subsequent experiments: 40/20-TFSI (1.2 mS/cm) and 40/20-OTf (1.4 mS/cm).
To investigate the enhanced LiTFSI solubility in the presence of the RTILs, we deconvolute the individual contributions to the LiTFSI solubility by considering the LiTFSI solubility in water and in the RTILs. For EMImTFSI, a LiTFSI solubility of 1.63 m at 25 °C was reported, corresponding to 12.8 moles of LiTFSI dissolved in 20 moles of EMImTFSI.[22] One kilogram of water dissolves 21 moles of LiTFSI at 23 °C.[23] Hence, a solution containing one kilogram of water and 20 moles of EMImTFSI should hypothetically dissolve 33.8 moles of LiTFSI. As a solution containing 20 m EMImTFSI dissolves up to 45 m LiTFSI (sample 45/20-TFSI), the difference of 11.2 m, corresponding to 25% of the LiTFSI content, remains unexplained by the solubility in the individual solvents. LiTFSI has been reported to have an even lower solubility in EMImOTf of only 0.14 m at 25 °C,[22] corresponding to 0.7 moles of LiTFSI in 20 moles of EMImOTf. Consequently, for the sample 50/20-OTf, 28.3 m LiTFSI, corresponding to 57% of the LiTFSI content, cannot be rationalized by the solubility in the individual solvents. Hence, we conclude that these RTILs act as solubility enhancer for LiTFSI in water. The results of the calculations are visualized in Figure 1.b. The composition range in which excess LiTFSI solubility relative to the weighted sum of the LiTFSI solubilities in H2O and RTIL is found is highlighted in red in the ternary phase diagrams shown in Figure 1.c (LiTFSI–EMImOTf–H2O) and 1.d (LiTFSI–EMImTFSI–H2O). Blue bullets indicate that the mixture is a single-phase liquid at 25 °C and red crosses mark electrolytes that are not in a fully liquid state at 25 °C as they either crystallize at ≥25 °C upon cooling from 60 °C (the temperature at which we prepared the samples) or do not form a homogeneous liquid even at 60 °C. The dashed line marks the calculated LiTFSI solubility limit for a given H2O/RTIL mixture that results in a single-phase liquid based on the LiTFSI solubilities in water and RTIL at 25 °C. Compositions with a higher fraction of LiTFSI than this line are considered for the excess-solubility regime. We find a similar maximum LiTFSI fraction of ca. 0.4 in a ternary mixture for both RTILs. Likewise, the excess solubility is highest for an RTIL fraction between 0.20–0.25 in both cases. However, excess solubility is limited to compositions with an RTIL fraction of less than ca. 0.35 for EMImOTf while also compositions with a higher EMImTFSI fraction display excess LiTFSI solubility. This finding corresponds well to the much higher LiTFSI solubility of EMImTFSI compared to EMImOTf.

To elucidate the origin of the excess solubility of LiTFSI, we studied the effect of EMImTFSI/EMImOTf addition on the solution...
structure of highly concentrated aqueous LiTFSI solutions via Raman and NMR spectroscopy. EMim-containing RTILs typically show strong hydrogen-bonding (H-bonding) between anions and the hydrogen atom located between the two nitrogen atoms of EMim (H2, numbering of positions shown in the inset of Figure 2 a), which allows to spectroscopically identify changes in the solution structure.[24] Hydrogen bonding causes a prolongation of the C–H bond and a reduction of electron density at the proton, resulting both in a bond vibration at lower wavenumbers in vibrational spectroscopy and a high-frequency shift of the H2 proton in 1H NMR.[24,25] Figure 2 a shows the 1H NMR chemical shift region of the imidazolium ring protons (full spectra shown in Figure S2). The chemical shift at position H2 decreases in the shift region of the imidazolium ring protons (full spectra shown in Figure S2). The chemical shift at position H2 decreases in the order EMImOTf > EMImTFSI > 20/20-OTf > 20/20-TFSI > 40/20-TFSI. The 1H NMR chemical shifts of the other aromatic protons (positions H4 and H5) show the same trend, albeit to a lower extent, which we attribute to less pronounced H-bonding of H4 and H5 with anions/solvent molecules, which has previously been observed with IR spectroscopy.[26] Our findings indicate weaker H-bonding of the EMim cation in the hybrid electrolytes compared to the ionic liquids. We interpret this finding as dissociation of the ionic liquids, i.e., the average distance between EMim and TFSI/OTf increases when the ionic liquids are added to water-in-salt electrolytes.

Complementary to NMR we carried out Raman spectroscopy (Figure S3 a). We prepared a concentration series with a constant molality of 20m EMimOTf and varying LiTFSI molalities ranging from 0 to 40m. EMimOTf was chosen for this series because it is completely water miscible, unlike hydrophobic EMimTFSI, which allows the preparation of a lithium-free solution of EMimOTf in water. The bands between 2800 and 3115 cm$^{-1}$ are related to symmetric and asymmetric stretching vibrations of aliphatic C–H bonds[24] and the band with a peak maximum at ca. 3180 cm$^{-1}$ is assigned to symmetric stretching vibrations of the C–H bonds of the imidazolium ring.[27] The latter band displays the largest shift upon changing the composition of the electrolyte in this wavenumber region as the ring protons and especially H2 are the ones forming hydrogen bonds. Comparison of the peak maximum of this band for neat EMimOTf and 20m EMimOTF (see inset of Figure S3 a) reveals that the presence of water alone has only a minor influence on H-bonding of EMim, i.e., the RTIL remains associated. In contrast, the presence of 10m LiTFSI already causes a pronounced blue shift of this band, i.e., the RTIL dissociates upon LiTFSI addition to the RTIL–water solution. Upon further addition of LiTFSI, the peak maximum shifts slightly further to higher wavenumbers, indicating increasing dissociation of the RTIL with increasing LiTFSI content. The dissociation of the RTILs in the hybrid electrolytes provides additional anions that can participate in the coordination of Li$^+$.

The coordination of TFSI to Li$^+$ can be analyzed via the intense Raman band of TFSI at ca. 740–750 cm$^{-1}$ that is highly sensitive to the TFSI coordination environment. This band is a superposition of several bond vibrations and is also called breathing mode as it is related to the expansion and contraction of the whole TFSI anion.[28] While *free* TFSI displays this band at ca. 740 cm$^{-1}$, coordination to Li$^+$ causes a shift to higher wavenumbers.[29,30] Figure 2 b shows the spectral region of the TFSI breathing mode for selected electrolytes. For EMimTFSI with its only weakly coordinated EMim cations, the band appears at 742 cm$^{-1}$. In contrast, 20m LiTFSI with its strong interaction between TFSI and Li$^+$ displays the band at 749 cm$^{-1}$. Upon addition of EMimTFSI, the band red shifts to 746 cm$^{-1}$ (sample 20/20-TFSI), indicating weaker TFSI–Li$^+$ interactions compared to 20m LiTFSI. When further increasing the LiTFSI concentration (sample 40/20-TFSI), the band reverses to a higher wavenumber of 750 cm$^{-1}$, even slightly exceeding the value for 20m LiTFSI. Apparently, at this concentration, the TFSI anions are again as strongly coordinated as in 20m LiTFSI. We also probed Li$^+$–TFSI interactions via $^{19}$F NMR spectroscopy but could not derive unambiguous conclusions from this experiment. For completeness, the data is shown in Figure S4 and discussed separately in the SI.

To validate the trend seen in Figure 2 b, we analyze again the LiTFSI–EMimOTf–water concentration series introduced above. The OTf anion exhibits a Raman band related to the TFSI breathing mode at slightly higher wavenumbers, namely the symmetrical deformation vibration of the trifluoromethyl group $\delta_s$(CF$_3$).[31] Upon coordination to Li$^+$, $\delta_s$(CF$_3$) of OTf also undergoes a blue shift.[32] The upper row of Figure S3 b shows Raman spectra for this concentration series in the wavenumber region corresponding to the breathing mode of TFSI and $\delta_s$(CF$_3$) of OTf. In line with the results for the EMimTFSI-containing solutions, only for 40/20-OTf the peak maxima of these two bands appear at very similar wavenumbers as for 20m LiTFSI and 20m LiOTf (shown in the lower row of Figure S3 b). 30/20-OTf, 20/20-OTf, and 10/20-OTf show, in this order, increasing red shifts compared to the 20m Li salt electrolytes for both the breathing mode of TFSI and $\delta_s$(CF$_3$) of OTf (see again upper row). Judging from the position of these two Raman bands, the coordination environment of the anions in 10/20-OTf even approaches the situation in the neat RTILs. We conclude again that the presence of RTILs in WIS electrolytes weakens Li$^+$–TFSI/OTf interactions.

Weakening ion-ion interactions and a change in the composition of the solvation shell may also influence the electron density of Li$^+$. Figure 2 c displays the 1H NMR spectra of 20m LiTFSI, 20/20-TFSI, and 40/20-TFSI. 20/20-TFSI shows a slight high-frequency shift compared to 20m LiTFSI (~0.52 vs. ~0.59 ppm, respectively). In contrast, 40/20-TFSI (~0.89 ppm) shows a more shifted 1H NMR signal compared to 20m LiTFSI. The increased electron density around Li$^+$ for the latter sample can be rationalized by the incorporation of additional anions into the primary solvation shell of Li$^+$. An anion-rich solvation shell of lithium ions in LiTFSI–EMimTFSI–H$_2$O hybrid electrolytes was also recently reported by Dou et al. by using computational methods complemented by NMR spectroscopy.[33] The high-frequency 1H chemical shift observed for 20/20-TFSI relative to 20m LiTFSI indicates overall weaker interactions between Li$^+$ and TFSI, supporting the observations in Figure 2 b and S3 b.

The surplus of anions in the primary Li$^+$ solvation shell might also affect Li$^+$–H$_2$O interactions. Dubois et al. showed that the 1H chemical shift of water steadily decreases from 4.6 ppm for 1m LiTFSI to 3.4 ppm for 20m LiTFSI and explained their findings by a disruption of the H-bond network with increasing LiTFSI concentration.[9] Due to the dependence of the H-bond network between water molecules on the water concentration, it is illustrative to consider the molar water concentration of the electrolytes. By using the densities reported in Table S1, we converted molality (moles of salt per kilogram of water) into molarity (moles of water per liter of solution). The water concentration of the hybrid electrolytes is significantly lower compared to 20m LiTFSI: We calculate 4.1, 6.1, and 4.6 mol/L for 20m LiTFSI, 20/20-TFSI, and 40/20-TFSI, respectively. Figure
2 d displays the $^1$H NMR chemical shift region of water. For 20m LiTFSI, the chemical shift of the water protons is 3.35 ppm. For 40/20-TFSI, a slight shielding to 3.25 ppm was detected. In contrast, we find a slightly higher chemical shift of 3.40 ppm for 20/20-TFSI. The chemical shift for the 40/20-TFSI electrolyte continues the trend observed by Dubouis et al.\textsuperscript{[6]} However, although 20/20-TFSI has a significantly lower water concentration than 20m LiTFSI, we measure a slightly higher chemical shift for its water protons, which indicates a slightly less disrupted H-bond network. We interpret this observation as weaker Li$^+\cdot$H$_2$O interactions caused by the presence of EMImTFSI in 20/20-TFSI.

Weaker interactions between the electrolyte species upon RTIL addition is also reflected in a lower density of 20/20-TFSI (1.60 g/mL at 25 °C) compared 20m LiTFSI (1.72 g/mL). When further increasing the LiTFSI concentration, the density recovers to a value of 1.69 g/mL for 40/20-TFSI, reflecting stronger interactions between the electrolyte species.

$^{17}$O NMR can serve as a direct probe for interactions between Li$^+$ and solvent molecules.\textsuperscript{[1,33]} For example, in non-aqueous electrolytes coordination to Li$^+$ leads to a low-frequency shift (shielding) for the carbonyl oxygen atoms.\textsuperscript{[33]} In aqueous systems, the resonance of water in $^{17}$O NMR experiences a high-frequency shift upon increased H-bonding (e.g., transition of water vapor to liquid water).\textsuperscript{[34]} Increasing the LiTFSI concentration (reducing the water concentration) results in a weakening of the H-bond network and consequently in a shielding of the oxygen nuclei of water.\textsuperscript{[1]} Figure 2 e shows natural abundance $^{17}$O NMR spectra for water, 20m LiTFSI, 20/20-TFSI, and 40/20-TFSI. Relative to water, the concentrated solutions of 20m LiTFSI, 20/20-TFSI, and 40/20-TFSI show a peak maximum at $\approx$13.3, $\approx$16.7, and $\approx$36.6 ppm, respectively, and increasing line broadening with increasing concentration of the electrolyte. The stronger shielding of the oxygen nuclei with increasing salt molality continues the trend observed by Suo et al.\textsuperscript{[3]} However, we emphasize again to consider the water concentration rather than the salt molality. Despite its significantly lower water concentration, 20/20-TFSI only exhibits a relatively small difference in the chemical shift when compared to 20m LiTFSI. This finding suggests again weaker Li$^+\cdot$H$_2$O interactions in the presence of EMImTFSI (20/20-TFSI) and supports the conclusion drawn from $^1$H NMR and Raman spectroscopy. The very high shielding in 40/20-TFSI originates from the low water concentration and presumably strong Li$^+\cdot$H$_2$O interactions, and consequently, much less hydrogen bonds between water molecules. We speculate that almost all water molecules are likely involved in Li$^+$ coordination at this concentration.

**Figure 2.** Spectroscopic investigation of the solution structure of selected electrolytes: a) $^1$H NMR spectra. b) Normalized Raman spectra in the wavenumber region corresponding to the breathing mode of TFSI. c), d), e) $^7$Li, $^1$H, $^{17}$O NMR spectra, respectively.

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Further information about ion-water interactions can be obtained from the energy distribution of the O-H stretching vibrations of water (Figure S5). Pure water shows a very broad Raman signal in the wavenumber region from 3000 to 3600 cm$^{-1}$ due to the various H-bonding environments in water.\[35\] In contrast, the H-bond network of water is disrupted at high salt concentration, which can be seen by a peak narrowing and a blue shift of the maximum to $\sim$3550 cm$^{-1}$ for 20m LiTFSI. The water environment in the hybrid electrolytes (20/20-TFSI and 40/20-TFSI) appears not to be significantly altered by the presence of EMImTFSI when compared to 20m LiTFSI. The only notable difference is a further peak narrowing with increasing salt concentration, which we ascribe to the reduced water content and consequently a narrower distribution of water bonding environments.\[2\]

Summarizing the results of the spectroscopic analysis, the water-miscible RTIL EMImOTf as well as the hydrophobic RTIL EMImTFSI both dissociate in aqueous LiTFSI solutions. As a consequence of the surplus of anions that can coordinate Li$^+$, we find both weaker Li$^+\cdots$H$_2$O and Li$^+\cdots$TFSI interactions relative to 20m LiTFSI in a solution containing equal amounts of LiTFSI and EMImTFSI (sample 20/20-TFSI). Considering the competition between H$_2$O and OTf/TFSI anions for Li$^+$ coordination, we conclude that anions partially replace H$_2$O in the primary solvation shell of Li$^+$ when providing additional anions through RTIL addition. The less tightly bound water and the additional (and weaker interacting) anions in such solutions are then available to coordinate/solvate additional Li$^+$, overall increasing the LiTFSI solubility. When approaching the LiTFSI solubility limit in these hybrid electrolytes, the strength of the Li$^+\cdots$TFSI interaction eventually reaches a similar level as in 20m LiTFSI, which is also a nearly saturated solution at room temperature.

Entropy gains upon RTIL addition might also play a non-negligible role in enhancing the LiTFSI solubility particularly in the case of EMImOTf, for which two additional types of ions are added to the solution. Indeed, slightly higher LiTFSI solubilities are achieved in the presence of EMImOTf compared to EMImTFSI as discussed above. A detailed thermodynamic study should be conducted to quantify the entropy and enthalpy contributions to the enhanced solubility.

Our experimental observations are in good agreement with recent reports about the ability of RTILs to enhance the solubility of poorly water-soluble organic drugs and bio-molecules in aqueous media.\[36\] Following the classification of solubility enhancers by Kunz et al. into surfactants, co-solubilizers, and hydrotropes,\[13\] we conclude that particularly the RTIL EMImOTf acts as hydrotrope for LiTFSI in water. We come to this conclusion by excluding the other two options: i) Surfactants act through micelle formation, which has not been observed for both OTf and TFSI anions as well as EMIm cations. Imidazolium cations only form micelles with longer alkyl chains (larger than hexyl).\[37\] ii) A key difference between co-solubilizers and hydrotropes is enhanced aggregation of the solubilizing agent in the presence of the solute, here LiTFSI, only in the case of hydrotropes.\[13\] Considering that EMImOTf only dissociates in water in the presence of LiTFSI and that the OTf anions strongly interact with Li$^+$, which could be considered as a kind of aggregation, we conclude that EMImOTf should be classified as hydrotrope for LiTFSI.

The increased LiTFSI concentration benefits the electrochemical stability of such hybrid electrolytes as can be clearly seen in the linear sweep voltammograms of 40/20-TFSI compared to 21m LiTFSI (Figure 3). The reductive stability was examined using aluminum working electrodes and the oxidative stability was probed on glassy carbon working electrodes as they are less redox active in this potential range than, e.g., Ti or Au electrodes.\[38\] In order to be able to quantify the reductive/oxidative stability, we defined a current density of $\pm$2 $\mu$A/cm$^2$ as stability limit (dashed lines in Figure 3).\[39\] This yields reductive stabilities of 0.8 V (40/20-TFSI), 1.3 V (40/20-OTf), and 1.5 V vs. Li/Li$^+$ (21m LiTFSI). Note that on catalytically more active substrates (e.g. stainless steel), lower reductive stability, i.e., higher current densities, can be expected.\[39\] Oxidative stability limits of 40/20-TFSI, 40/20-OTf, and 21m LiTFSI were determined at 4.7, 4.0, and 4.1 V vs. Li/Li$^+$, respectively. The lower electrochemical stability observed for 40/20-OTf compared to 40/20-TFSI can be understood by considering that hydrophilic OTf anions interact more strongly with H$_2$O than hydrophobic TFSI anions,\[40\] which weakens the stabilizing Li$^+\cdots$H$_2$O interaction. In addition, molecular dynamics simulations revealed that TFSI but not OTf anions preferentially adsorb at the cathode/electrolyte interphase in WIS electrolytes, forming a water-depletion zone suppressing the oxygen evolution reaction.\[7\] Consequently, 40/20-TFSI was chosen for further galvanostatic cycling tests.

We chose TiO$_2$ and LTO anodes to test the reductive stability of the 40/20-TFSI electrolyte during battery cycling. Since the average redox potentials of TiO$_2$ and LTO of 2.1 and 1.8 V vs Li/Li$^+$ are well below the HER onset potential at neutral pH of 2.6
V vs Li/Li⁺, we applied protective coatings on the anode materials to suppress hydrogen formation. For TiO₂, a carbon coating is sufficient to obtain good passivation. However, in our experience this approach is insufficient for LTO with its ca. 300 mV more negative redox potential. Therefore, we developed a niobium oxide coating that we applied via atomic layer deposition (for details see experimental section in SI). As we used a niobium(V) precursor, we expect the composition to be close to Nb₂O₅. Nb₂O₅ is a Li-ion intercalation material with fast Li-ion mobility and low volume changes, similar to LTO. In combination with its low electronic conductivity, Nb₂O₅ is a promising coating candidate to suppress reductive side reactions like HER. The NbOₓ coating does not contribute significantly to the anode capacity due to its limited amount relative to LTO.

Capitalizing on the reduced water content of 40/20-TFSI, we chose NMC811 as cathode material, which is typically not compatible with aqueous electrolytes due to the high surface reactivity of, especially delithiated, NMC811. Already storage of NMC811 under ambient conditions can lead to reactions with H₂O and CO₂ and loss of performance.

The cycling performance of TiO₂/NMC811 full cells containing 40/20-TFSI or 21m LiTFSI as the electrolyte is shown in Figure 4 a. The anode to cathode capacity ratio was set to Qₐn : Qₖ = 1:1.5 (considering capacities of 148 and 180 mAh/g for TiO₂ and NMC811, respectively). The cells were cycled between 0.5 and 2.45 V at a rate of C/2 based on the capacity of the negative electrode. The enhanced electrochemical stability of 40/20-TFSI compared to 21m LiTFSI clearly translates into much better cycling stability. A steady-state CE of >99.7% and an average CE of 99.65% during the first 300 cycles were determined for the cell containing 40/20-TFSI. On the contrary, the cell with 21m LiTFSI only reaches a maximum CE of 98%, which leads to rapid capacity fading after 50 cycles when the excess Li ions of the cathode are consumed. In contrast, the 40/20-TFSI cell still retains 80% of its initial capacity after 290 cycles (Figure 4 a). This cell displays an initial energy density of 121 Wh/kg (based on the weight of the active materials of both electrodes), among the highest energy densities reported for an aqueous Li-ion battery with a TiO₂ anode. The good cycling stability of the 40/20-TFSI cell is expected to be related to suppression of typical degradation modes of nickel-rich NMC such as transition metal dissolution and related surface reconstruction at this very high salt concentration. Apparently, the small amount of free water molecules still present in 21m LiTFSI prevents stable cycling of NMC811.

Importantly, the high reducible stability of the 40/20-TFSI electrolyte also allows stable cycling of Nb₂O₅-coated LTO anodes. Figure 4 b shows cycling data for a LTO/NMC811 cell. For better comparison with the TiO₂/NMC811 cell, balancing and C-rate remained unchanged. We considered a capacity of 160 and 180 mAh/g for LTO and NMC811, respectively, for the cell balancing. The more challenging, i.e., more negative, redox potential of LTO results in a lower CE of 99.2%, which also translates into faster capacity decay. However, the energy density of the cell benefits from the lower redox potential of LTO, resulting in a very high initial energy density of 150 Wh/kg (active material level), among the highest values for an aqueous intercalation type lithium-ion battery. Increasing the C-rate to 1C and supplying a larger excess of cathode capacity (Qₐn : Qₖ = 1:1.5) to better compensate the lower CE compared to the TiO₂/NMC811 cell results in much improved cycling stability as shown in Figure 4 c.

We also assembled LTO/LiMn₂O₄ (LMO) full cells to further investigate the oxidative stability of the 40/20-TFSI electrolyte. The results are shown and discussed separately in the SI (Figure S6).

Figure 4. Cycling performance of various full cells prepared with 40/20-TFSI as the electrolyte. a) TiO₂/NMC811 full cell cycled at C/2. For comparison, data for a cell containing 21m LiTFSI as the electrolyte is also shown. m(TiO₂) = 1.7 mg. b) LTO/NMC811 full cell cycled at C/2. m(LTO) = 3.2 mg. c) LTO/NMC811 full cell cycled at 1C. m(LTO) = 1.8 mg. The applied current was based on the weight of the anode active material for all cells.

Conclusion

Increasing the lithium salt concentration is an effective strategy to widen the stability window of WIS electrolytes and to tackle the cathodic challenge. However, when increasing the concentration beyond 30 mol/kg, the gain in stability is increasingly overcompensated by a reduction in transport properties. Binary lithium salt–ionic liquid electrolytes offer higher electrochemical stability than WIS electrolytes but suffer from high viscosities and particularly from low lithium-ion conductivities, even at high lithium molar fractions, that limit their practical use to elevated temperatures. Ternary lithium salt–ionic liquid–water mixtures provide a better compromise between stability and conductivity compared to binary lithium salt–water and lithium salt–ionic liquid electrolytes. Finally, addition of non-volatile ionic liquids further improves the safety of water-in-salt electrolytes by reducing the water content and hence the potential for hydrogen formation.

For the LITFSI–ionic liquid–water electrolytes studied here, we observe a two-fold benefit of adding these ionic liquids to water-in-salt electrolytes: i) The bulky ions of the ionic liquids act as a plasticizer, lowering the viscosity of highly concentrated LITFSI–water solutions, similar to the plasticizing effect of RTILs in polymer electrolytes; ii) The presence of the ionic liquids boosts the LITFSI solubility. In the case of EMImOTf, the LITFSI solubility increases to up to 60 mol/kg with respect to water. These extremely high values cannot be explained by the sum of the LITFSI solubilities in water and in the ionic liquid itself as we find particularly in the case of EMImOTf large excess solubility.
when deconvoluting the different contributions to the LiTFSI solubility. Raman and NMR spectroscopy results indicate that the ions of EMImTFSI and EMImOTf dissociate in the presence of LiTFSI in water. The additional anions of the ionic liquid plus water replaced by anions in the solvation shell of Li⁺ are then available to solvate additional Li⁺, increasing the LiTFSI solubility. We conclude that particularly EMImOTf can be considered as a special type of hydrotrope for LiTFSI in water.[13]

We find that EMImTFSI-based electrolytes display higher electrochemical stability than EMImOTf-based ones. Furthermore, when setting the LiTFSI and EMImTFSI concentrations to 40 and 20 mol%, respectively, the electrolyte still shows an acceptable ionic conductivity of 1.2 mS/cm at 25 °C. The high LiTFSI concentration of this electrolyte translates into improved reductive stability as demonstrated by good compatibility with TiO₂ and niobia-coated LTO anodes. For the first time, the reduced water content also allows stable cycling of NMC811 cathodes in aqueous electrolytes. Paired with a TiO₂ cathode and LTO/NMC811, the reduced water content also allows stable cycling of NMC811/LTO/NMC811 systems. For the first time, the reduced water content also allows stable cycling of NMC811/LTO/NMC811 full cells, we obtain Coulombic efficiencies of 99.4% and 99.2% at rates of 1C and 2C, respectively. Due to the high capacity of NMC811, LTO/NMC811 full cells incorporating the hybrid electrolyte also display very high energy density for aqueous intercalation-type batteries of up to 150 Wh/kg on the active material level.

Further improvements of such ternary electrolytes and subsequently cell performance can be expected considering the large number of potential combinations of lithium salts and ionic liquids. This approach might also invigorate the development of highly concentrated electrolytes including and beyond aqueous electrolytes.

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Ionic liquids boost the LiTFSI solubility in water from 21 to 60 mol/kg. Excess lithium salt solubility arises from a hydrotropic effect of the ionic liquids. This approach improves particularly the reductive stability of water-in-salt electrolytes, enabling stable cycling of commercially relevant LTO/NMC811 full cells.