Hybrid ionic liquid/water-in-salt electrolytes enable stable cycling of LTO/NMC811 full cells

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Abstract

Water-in-salt electrolytes have successfully expanded the electrochemical stability window of aqueous electrolytes to up to 3 V. While particularly the reductive stability of water-in-salt electrolytes can be further improved by simply increasing the salt concentration, this approach has its limitations as it leads to very viscous and hence poorly conducting solutions. An alternative strategy is the partial substitution of water by ionic liquids, which boosts the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solubility while maintaining adequate transport properties at very high salt concentrations.

Here, we study such ternary electrolytes based on LiTFSI, water, and imidazolium-type ionic liquids in terms of their thermal, electrochemical, and transport properties. We find that the LiTFSI solubility increases from 21 mol kg⁻¹ in water to up to 60 mol kg⁻¹ in the presence of these ionic liquids. Deconvolution of the different contributions to the LiTFSI solubility shows that particularly the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate acts as solubility enhancer.

The increased reductive stability of these ternary electrolytes enables stable cycling of both TiO₂ and Li₄Ti₅O₁₂ anodes. We further show that the low water content of these electrolytes also allows stable cycling of LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathodes. For instance, a TiO₂/NMC811 full cell based on such a hybrid electrolyte shows an energy density of 121 Wh kg⁻¹ on the active material level, a Coulombic efficiency of >99.7% at C/2, and retains 80% of its initial capacity after 290 cycles at this rate. Owing to the 300 mV lower redox potential of Li₄Ti₅O₁₂ compared to TiO₂, Li₄Ti₅O₁₂/NMC811 full cells reach energy densities of 141 and 150 Wh kg⁻¹ at a rate of 1C and C/2, respectively. These cells still show Coulombic efficiency of 99.4% and 99.2%, respectively, and maintain 80% of their initial capacity after 230 and 154 cycles, respectively. Considering the large number of potential lithium salt–ionic liquid combinations, we anticipate further improvements in electrolyte properties and subsequently cell performance.

Introduction

State-of-the-art lithium-ion batteries (LIBs) are based on highly flammable organic electrolytes.^{1,2} To improve the intrinsic safety of LIBs, research efforts have focused on replacing flammable organic solvents by non-flammable alternatives.^{3–5} Water as electrolyte solvent is inherently non-flammable, non-toxic, and abundant, but its narrow electrochemical stability window (ESW) of thermodynamically only 1.23 V at 25 °C has excluded it from being employed in high-voltage LIBs. In 2015, Suo et al. introduced the concept of water-in-salt (WIS) electrolytes by demonstrating a stable solution of 21 moles of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) per kilogram of water (here denoted as 21m).⁶ The high salt concentration significantly expands the ESW to 3.0 V on stainless steel electrodes while maintaining an ionic conductivity of 9.5 mS cm⁻¹ at 25 °C. This value is comparable to the conductivity of carbonate-based organic electrolytes, despite the high salt concentration. The WIS electrolyte approach has enabled the first rechargeable aqueous LIB operating at a relatively high average discharge voltage of 1.75 V by employing LiMn₂O₄ (LMO) as cathode and Mo₆S₈ as anode.⁶

The enhanced electrochemical stability of WIS electrolytes originates from a drastically reduced water content resulting in a peculiar electrolyte structure with anions being incorporated into the primary solvation shell of the Li ions.⁶ With this structure, the electrolyte is also able to form an anion-derived SEI on the anode.^{7,8} Simultaneously, TFSI anions align in the electrochemical double-layer at the cathode/electrolyte interface, establishing a water-depletion zone, resulting in particularly high oxidative stability of >4.5 V vs. Li/Li⁺.⁹

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 ca. 1.9 V vs. Li/Li⁺.⁶ At lower potentials, water molecules increasingly accumulate at the anode/electrolyte interface, facilitating HER and thus preventing the formation of a dense SEI.⁸ Combination of two highly soluble lithium salts enables even higher concentrations such as 28m, which slightly further extends the ESW of WIS electrolytes, but ultimately does not solve this cathodic challenge.¹⁰ This limitation has significant consequences as already Li₄Ti₅O₁₂ (LTO), an important anode material for LIBs, cannot be operated in such WIS electrolytes, although its average redox potential shifts to ca. 1.8 V vs. Li/Li⁺ in WIS electrolytes (Nernst shift due to the high lithium-ion concentration).¹¹

As WIS electrolytes are usually saturated solutions at room temperature, they tend to crystallize below room temperature. Some of us recently discovered that certain anions with an asymmetric chemical structure kinetically suppress this crystallization.¹² The quest for asymmetric anions has led to the introduction of the salt lithium (pentafluoroethanesulfonyl)(trifluoromethanesulfonyl)imide (LiPTFSI) to WIS electrolytes. Due to its extremely high solubility of >30m at 25 °C, LiPTFSI enables both WIS electrolytes that remain thermodynamically in the liquid state below -10 °C¹³ and the formulation of an overall 56m-concentrated monohydrate-melt electrolyte (Li(PTFSI)_{0.6}(TFSI)_{0.4} · 1 H₂O).¹⁴ The unprecedentedly high lithium concentration of the latter electrolyte further widens the ESW, enabling the use of LTO anodes. However, this electrolyte suffers from low conductivity of only 0.1 mS cm⁻¹ at 30 °C related to its high viscosity of 8555 mPa s. Hence, solely rising the lithium salt concentration has

its limitations and new approaches are needed to tackle the cathodic challenge in aqueous electrolyte research.

As a potential solution, Chen et al. reported a WIS electrolyte where half of the water molecules are substituted by acetonitrile.¹⁵ This hybrid electrolyte remains non-flammable, shows enhanced electrochemical stability, and can be operated below 0 °C. However, acetonitrile is a volatile organic solvent. Recently, addition of the 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, enabling stable cycling of a 1.74 V aqueous sodium-ion battery.¹⁶ Combining large organic cations with large organic anions typically results in salts with low melting points, i.e. ionic liquids (ILs), another class of non-flammable and non-volatile solvents. Here, we define an IL as a salt with a melting point of less than 100 °C. Following this strategy, Chen et al. reported a hybrid electrolyte containing LiTFSI, water, and the IL ethyltrimethylammonium TFSI.¹⁷ Importantly, with a concentration of 42m LiTFSI, a strongly enhanced lithium salt solubility with respect to water was observed upon addition of the IL.¹⁷ As a second benefit of the IL, the electrolyte with an overall concentration of 63m (42m LiTFSI + 21m IL) shows much better transport properties with a conductivity of 0.9 mS cm⁻¹ at 25 °C compared to classical WIS electrolytes only containing lithium salts like the 56-molal LiPTFSI/LiTFSI electrolyte introduced above.^{14,17}

Here, we prepare hybrid electrolytes based on the room temperature ionic liquids (RTILs) 1-ethyl-3-methylimidazolium TFSI (EMImTFSI) and EMIm trifluoromethanesulfonate (EMImOTf). We study the effect of addition of these RTILs to LiTFSI/H₂O solutions in terms of thermal, electrochemical, and transport properties as well as LiTFSI solubility. We show that the LiTFSI solubility increases from 21 mol kg⁻¹ in water to up to 60 mol kg⁻¹ in the presence of EMImOTf. To better understand this behavior, we deconvolute the different contributions to the increased LiTFSI solubility in the presence of these RTILs. Furthermore, we demonstrate that the enhanced LiTFSI concentration results in particularly enhanced reductive stability, translating into good compatibility with TiO₂ and LTO anodes. Finally, owing to the reduced water content, these electrolytes also support stable cycling of LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathodes.

Results and Discussion

In this study, we employ EMIm-based RTILs due to the typically lower viscosity of imidazolium-compared to, e.g., quaternary ammonium-based RTILs.¹⁸ The ability of the TFSI anion to form an SEI and its water-blocking behavior at the cathode/electrolyte interface render TFSI an ideal counter ion for ILs to be added to WIS electrolytes. For comparison, we also included electrolytes based on EMImOTf in this study. In contrast to TFSI, the smaller OTf anion is asymmetric and its higher charge density translates into stronger Coulomb interactions.¹⁹ Hence, we expect the influence of anion coordination to Li⁺ or water molecules to be more pronounced for OTf compared to TFSI. Additionally, choosing TFSI and OTf allows us to compare a hydrophobic (EMImTFSI) with a completely water-miscible hydrophilic IL (EMImOTf). We note that other cations such as of the quaternary alkyl ammonium type have higher reductive stability than EMIm with its calculated reduction potential of 0.62 V vs. Li/Li⁺.²⁰ However, we do not expect the reductive stability of EMIm to limit the ESW of IL-containing WIS electrolytes as this

potential is 2 V more negative than the thermodynamic potential of the hydrogen evolution reaction (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). Whereas 20m LiTFSI exhibits distinct crystallization 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 crystallization during the cooling scan and a glass transition (**Fig. 1a**). Interestingly, the liquidus temperature (T_L) appears to drop from 15 °C for 20m LiTFSI to –29 °C for 20/20-TFSI. However, the melting of 20/20-TFSI is hardly visible in the DSC curve due to the suppressed crystallization. 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. Indeed, 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) drops to a similar temperature of –26 °C (**Fig. 1b**) and the LiTFSI concentration can even be raised to more than 50m (T_L = 11 °C for 50/20-OTf). By increasing the RTIL content, the LiTFSI solubility at room temperature can be further increased to e.g. at least 55m and 60m for EMImTFSI and EMImOTf, respectively, for a RTIL molality of 30m, resulting in electrolytes with overall molalities of 85m and 90m.

Fig. 1: DSC curves of (a) EMImTFSI-containing aqueous LiTFSI solutions (x/y -TFSI) and (b) EMImOTf-containing aqueous LiTFSI solutions (x/y -OTf) with x being the LiTFSI molality and y being the RTIL molality with respect to water. Prior to cooling, the samples were equilibrated at 60 °C for 30 min. Cooling (thin line) and heating (thick line) curves were recorded at a scan rate of 1 °C min⁻¹. Mesocarbon microbeads (MCMBs) were added to each sample to provoke crystallization.

The reduced water content of these electrolytes in terms of their water-to-lithium molar ratio is highlighted in **Fig. 2a**, which compares this ratio for selected LiTFSI–RTIL–water hybrid electrolytes with that of 21m LiTFSI, the archetypical WIS electrolyte. 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 (in short: 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 **Fig. 2a** represent the molar fraction of the different electrolyte components. Except for the 60/30-OTf electrolyte, the molar fraction is highest for water, which is beneficial for transport properties.

The low water fraction of the 60/30-OTf electrolyte manifests itself in a rather low ionic conductivity and high viscosity of 0.4 mS cm⁻¹ and 1125 mPa s at 25 °C, respectively. Considering the overall molality of this solution of 90m, these transport properties are still surprisingly good. Temperature-dependent viscosity and conductivity data of selected LiTFSI–EMImTFSI/EMImOTf–water solutions are given in **Table 1**. For comparison, the table also contains values for 20m LiTFSI. Upon addition of RTIL, the conductivity slightly decreases from 10.4 mS cm⁻¹ (20m LiTFSI) to 6.7 mS cm⁻¹ (20/20-TFSI) at 25 °C. Taking into account the doubling of the overall salt concentration, this is only a minor drop. In contrast, the viscosity slightly decreases from 55.3 mPa s for 20m LiTFSI to 44.2 mPa s for 20/20-TFSI. We interpret this observation as a kind of plasticizer effect of the RTIL, a phenomenon that is typically observed for polymer electrolytes in which RTILs are used to increase polymer chain mobility.^{21,22} However, increasing the LiTFSI concentration further leads to much lower conductivities of e.g. 2.9 and 1.2 mS cm⁻¹ for 30/20-TFSI and 40/20-TFSI, respectively, due to stronger interactions of Li⁺ with water and anions compared to EMIm. 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.^{23–25} In light of their suitability for battery applications, we selected the following electrolytes with a conductivity of at least 1 mS cm⁻¹ at 25 °C for the subsequent experiments: 40/20-TFSI (1.2 mS cm⁻¹) and 40/20-OTf (1.4 mS cm⁻¹).

Table 1: Conductivity and viscosity data of selected electrolytes considered for this study. When only conductivity data is reported, the electrolyte is only metastable at that temperature and crystallization occurred during the viscosity experiment.

Electrolyte	$T / ^\circ\text{C}$	10	20	25	30	40	50	60
20m LiTFSI	$\sigma / \text{mS cm}^{-1}$	6.2	8.9	10.4	12.2	16.0	20.4	25.8
	$\eta / \text{mPa s}$	-	69.2	55.3	45.4	30.9	21.8	16.2
20/20-TFSI	$\sigma / \text{mS cm}^{-1}$	3.7	5.6	6.7	8.0	11.0	14.5	18.3
	$\eta / \text{mPa s}$	90.3	55.0	44.2	36.0	24.9	18.2	13.8
20/20-OTf	$\sigma / \text{mS cm}^{-1}$	3.6	5.4	6.5	7.7	10.5	13.8	17.6
	$\eta / \text{mPa s}$	96.6	60.2	48.9	40.2	28.0	20.4	15.3
40/20-TFSI	$\sigma / \text{mS cm}^{-1}$	0.49	0.93	1.2	1.6	2.5	3.8	5.3
	$\eta / \text{mPa s}$	-	407	293	216	125	78.5	51.9
40/20-OTf	$\sigma / \text{mS cm}^{-1}$	0.56	1.0	1.4	1.7	2.7	4.0	5.6
	$\eta / \text{mPa s}$	-	410	302	227	138	87.4	58.0
60/30-OTf	$\sigma / \text{mS cm}^{-1}$	0.14	0.30	0.42	0.57	1.0	1.6	2.4
	$\eta / \text{mPa s}$	-	-	1125	789	418	243	149

Fig. 2: Increased LiTFSI solubility in RTIL/water mixtures. (a) Water-to-lithium molar ratio for selected electrolytes. Numbers inside the bars represent molar fractions of the respective component. (b) Breakdown of the contributions to the LiTFSI solubility of two selected electrolytes.

To investigate the origin of the enhanced LiTFSI solubility in the presence of the RTILs, we deconvoluted the individual contributions to the LiTFSI solubility by considering the LiTFSI solubility in water and in the RTILs. For EMImTFSI, a LiTFSI solubility of 1.63m at 25 °C was reported, corresponding to a solubility of 12.8 moles of LiTFSI in 20 moles of EMImTFSI.²⁶ One kilogram of water dissolves 21 moles of LiTFSI at 23 °C.²⁷ 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 20m EMImTFSI dissolves up to 45m LiTFSI (45/20-TFSI in our notation), the difference of 11.2m, 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 0.14m at 25 °C,²⁶ corresponding to 0.7 moles of LiTFSI in 20 moles of EMImOTf. Consequently, for sample 50/20-OTf, 28.3m LiTFSI, corresponding to 57% of the LiTFSI content, cannot be rationalized by the solubility in the individual solvents. Hence, we conclude that these ILs act as solubility enhancer for LiTFSI in water. The calculations are visualized in **Fig. 2b**.

Fig. 3: Voltammograms of selected electrolytes recorded with a scan rate of 1 mV s⁻¹ on Al and glassy carbon working electrodes for cathodic and anodic scans, respectively. The measurements were conducted at 25 °C.

The increased LiTFSI concentration benefits the electrochemical stability of such hybrid electrolytes as can be seen in the linear sweep voltamgrams for 40/20-TFSI and 40/20-OTf compared to 21m LiTFSI

(**Fig. 3**). The reductive stability was examined using Al electrodes. The oxidative stability was examined using glassy carbon electrodes as they are less redox active in this potential range than, e.g., Ti or Au electrodes.²⁸ By arbitrarily defining a current density limit of $2 \mu\text{A cm}^{-2}$, the reductive stability of 40/20-TFSI, 40/20-OTf, and 21m LiTFSI equals 0.8, 1.3, and 1.5 V vs. Li/Li⁺, respectively. Note that on catalytically more active substrates (e.g. stainless steel), lower reductive stability, i.e. higher current densities, can be expected.²⁹ Regarding the oxidative stability, 40/20-TFSI also outperforms 40/20-OTf and 21m LiTFSI. By considering again a current density limit of $2 \mu\text{A cm}^{-2}$, the oxidative stability limit of 40/20-TFSI, 40/20-OTf, and 21m LiTFSI is located 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 H₂O than hydrophobic TFSI does,²⁰ which weakens the stabilizing Li⁺-H₂O 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 that suppresses the oxygen evolution reaction.⁹

Fig. 4a shows a comparison between 40/20-TFSI and 21m LiTFSI in TiO₂/NMC811 full cells with a capacity balancing of anode to cathode of $Q_n:Q_p = 1:1.3$ (considering capacities of 148 and 180 mAh g⁻¹ for TiO₂ and NMC811, respectively). The cells were cycled at a rate of C/2 based on the capacity of the negative electrode. The voltage ranges are specified in the figures. All cells were cycled at 25 °C. The enhanced electrochemical stability of 40/20-TFSI clearly translates into much better cycling stability of the cell based on this electrolyte. This cell displays a steady-state Coulombic efficiency (CE) of >99.7% and an average CE of 99.65% during the first 300 cycles compared to a maximum CE of 98% with 21m LiTFSI. The relatively low CE of the 21m LiTFSI cell 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. This cell displays an initial energy density of 121 Wh kg⁻¹ (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.¹⁰ The good cycling stability of the 40/20-TFSI cell might be related to suppression of the typical degradation modes of nickel-rich NMC like transition metal dissolution and related surface reconstruction at this very high salt concentration.³⁰ Apparently, the 21m LiTFSI electrolyte is still not concentrated enough to enable stable cycling of NMC811 as this solution still contains a small fraction of free water molecules.⁶

Importantly, the high reductive stability of the 40/20-TFSI electrolyte also allows stable cycling of niobia-coated LTO anodes (see experimental section for details). **Fig. 4b** shows cycling data for a LTO/NMC811 cell. For easy comparison with the TiO₂/NMC811 cell, balancing and cycling conditions were kept the same. For the balancing of the cell, we considered a capacity of 160 and 180 mAh g⁻¹ for LTO and NMC811, respectively. 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 higher cell voltage, resulting in a very high initial energy density for an aqueous intercalation type Li-ion battery of 150 Wh kg⁻¹. Increasing the C-rate to 1C and supplying a larger excess of cathode capacity ($Q_n:Q_p = 1:1.5$) to better compensate the lower CE compared to the TiO₂/NMC811 cell leads to much improved cell performance as shown in **Fig. 4c**.

Fig. 4: Cycling performance of various full cells containing 40/20-TFSI as the electrolyte. (a) TiO_2 /NMC811 full cell cycled at C/2. For comparison, data for a cell containing 21m LiTFSI as the electrolyte is also shown. $m(\text{TiO}_2) = 1.7$ mg. (b) LTO/NMC811 full cell cycled at C/2. $m(\text{LTO}) = 3.2$ mg. (c) LTO/NMC811 full cell cycled at 1C. $m(\text{LTO}) = 1.8$ mg. The applied current was based on the weight of the anode active material for all cells.

This cell cycles with a CE of 99.4% and retains 80% of its initial capacity after 230 cycles. The enhanced cycling stability comes at the price of a slightly lower initial energy density of 141 Wh kg^{-1} .

To further test the oxidative stability of the 40/20-TFSI electrolyte and its compatibility with LMO, we assembled an LTO/LMO full cell with a $Q_n:Q_p$ ratio of 1:1.3 (considering a capacity of 120 mAh g^{-1} for LMO) and cycled the cell at 1C (**Fig. 5a**). The cell displays an average CE of 99.4% during the first 300 cycles and retains 80% of its initial capacity after 186 cycles. Due to the lower specific capacity of LMO, the cell has a lower capacity of 59 mAh g^{-1} (based on the active mass of both electrodes) compared to 67 mAh g^{-1} for the LTO/NMC811 cell shown in **Fig. 4c**. However, the higher redox potential of LMO partially compensates for its lower capacity compared to NMC811, still translating to an energy density of 137 Wh kg^{-1} . The difference in capacity and voltage characteristics of these two cells is illustrated with the voltage profiles of the first cycles shown in **Fig. 5b**.

Fig. 5: (a) LTO/LMO full cell cycled at 1C. 40/20-TFSI was used as the electrolyte. $m(\text{LTO}) = 2.5$ mg. The applied current was based on the weight of the anode active material. (b) Voltage profiles of the 1st cycle of the LTO/NMC811 and LTO/LMO full cells cycled at 1C shown in Fig. 4c and Fig. 5a, respectively.

Conclusions

Increasing the lithium salt concentration is an effective strategy to widen the stability window of water-in-salt electrolytes and to tackle the cathodic challenge. However, when increasing the concentration beyond 30 mol kg^{-1} , the gain in stability is increasingly overcompensated by a reduction in transport properties. Binary lithium salt–ionic liquid electrolytes offer higher electrochemical stability than water-in-salt 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 high temperatures.^{31,32} 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. For the LiTFSI–EMImTFSI/EMImOTf–water electrolytes studied here, we observed a two-fold benefit of adding these ionic liquids to water-in-salt electrolytes: On the one hand, the bulky ions of these ionic liquids act as a kind of plasticizer, lowering the viscosity of highly concentrated LiTFSI–water solutions. On the other hand, the presence of these ionic liquids boosts the LiTFSI solubility. In the case of EMImOTf, the LiTFSI solubility increases to up to 60 mol kg^{-1} 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. When deconvoluting the different contributions to the LiTFSI solubility, we found large excess solubilities. Future studies should focus on the interplay between water, lithium salt, and ionic liquid to elucidate the solubility-enhancing effect of these ionic liquids.

We found that EMImTFSI-based electrolytes display higher electrochemical stability than EMImOTf-based ones. Furthermore, when limiting the LiTFSI and EMImTFSI concentrations to 40 and 20 mol kg^{-1} , respectively, the electrolyte still shows an acceptable ionic conductivity of 1.2 mS cm^{-1} at 25 °C. The high LiTFSI concentration of this electrolyte translates into improved reductive stability as demonstrated by good compatibility with TiO_2 and niobia-coated LTO anodes. In addition, the reduced water content also allows stable cycling of NMC811 cathodes. Paired with a TiO_2 anode, a TiO_2 /NMC811 full cell based on this electrolyte displays a Coulombic efficiency of >99.7% at C/2 and consequently good cycling stability

for >300 cycles compared to an efficiency of <98% and rapid capacity fading when using 21m LiTFSI as the electrolyte. For LTO/NMC811 full cells, we obtain Coulombic efficiencies of 99.2% and 99.4% at rates of 1C and C/2, 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⁻¹ on the active material level.

Further improvements of such ternary electrolytes and subsequently cell performance can be expected considering the large number of potential lithium salt–ionic liquid combinations. This approach might also invigorate the development of aqueous batteries based on other cell chemistries such as sodium-ion that have suffered from low salt solubilities.

Experimental Section

Electrolyte preparation and physicochemical characterization

LiTFSI (99.9%, Solvionic), EMImTFSI (99.9%, Solvionic), and EMImOTf (99.5%, Solvionic) were used as received and stored under an inert argon atmosphere in a glovebox (MBraun). The electrolytes were prepared by dissolving the respective amount of LiTFSI and/or RTIL in high-purity water (deionized water further purified with a Millipore Milli-Q water purification system). After preparation, the electrolytes showed a pH value between 6 and 7. pH values were determined using pH paper (Merck) with a pH range from 1 to 14. Before use, electrolytes were thoroughly degassed with Ar and stored under an inert argon atmosphere in a glovebox (MBraun).

Differential scanning calorimetry was carried out with a Netzsch STA 449 F3 simultaneous thermal analyzer. Ca. 30 mg of electrolyte sample were mixed with ca. 1 mg of mesocarbon microbeads as crystallization agent and hermetically sealed in Al pans. All measurements were carried out at a scan rate of $1\text{ }^{\circ}\text{C min}^{-1}$. The samples were equilibrated at $60\text{ }^{\circ}\text{C}$ for 30 min prior to the start of the measurement.

Ionic conductivity was determined via impedance spectroscopy (Bio-Logic MCS 10) in sealed 2-electrode cells equipped with Pt electrodes (Bio-Logic HTCC). Viscosity was determined with a Kyoto Electronics Manufacturing EMS-1000 electromagnetically spinning viscometer using 2 mm Al spheres. Sample volumes of 400 μL were used. Samples were equilibrated for 15 min at each temperature.

Electrochemical stability was determined via linear sweep voltammetry in 3-electrode configuration with a Bio-Logic VMP3 electrochemical workstation at $25\text{ }^{\circ}\text{C}$. Cathodic scans were carried out using a Swagelok T-cell with Al foil discs ($d = 12\text{ mm}$, MTI, $>99.3\%$) as working electrode, activated carbon pellets as counter electrode, and a miniature Ag/AgCl electrode (eDAQ) as reference electrode. Anodic scans were carried out in small volume glass cells (eDAQ) with a glassy carbon working electrode ($d = 1\text{ mm}$, eDAQ, type ET074), a Pt-coated Ti rod (eDAQ) as counter electrode, and a miniature Ag/AgCl electrode (eDAQ) as reference electrode. The scan rate was set to 1 mV s^{-1} .

Electrode fabrication and battery assembly

TiO_2 (Sigma Aldrich, anatase, $< 25\text{ nm}$, 99.7%) was coated with a carbon layer by dispersing the pristine powder in D-(+)-glucose dissolved in ethanol with a Ti:C ratio of 2:1. After solvent evaporation, the remaining powder was calcined in a tube furnace under Ar atmosphere at $600\text{ }^{\circ}\text{C}$ for 2 h with the heating rate set to 4 K min^{-1} .

Carbon-coated TiO_2 , LTO (Targray, type LTO-2s, $4\text{--}10\text{ }\mu\text{m}$ (D50), $\leq 8\text{ m}^2\text{ g}^{-1}$), and LMO (Targray, type SLMO03001, $17.5\text{ }\mu\text{m}$ (D50), $0.2\text{--}0.7\text{ m}^2\text{ g}^{-1}$) electrodes were prepared by dispersing the active material with PVdF binder (Arkema Kynar HSV900) and carbon black (IMERYS Graphite & Carbon C-ENERGY SUPER C65) in a mass ratio of 8:1:1 in *N*-methyl-2-pyrrolidone. NMC811 (Targray, type SNMC03001, $6.5\text{ }\mu\text{m}$ (D50), $0.5\text{ m}^2\text{ g}^{-1}$) electrodes were prepared with a mass ratio of 94:3:3 using the same binder and conductive additive. The slurry was tape casted using a doctor blade onto Al foil (TiO_2 , LTO) or Ti foil (LMO, NMC811). The electrodes were first dried for at least 2 h at $120\text{ }^{\circ}\text{C}$ in air and subsequently dried at $120\text{ }^{\circ}\text{C}$ over night under oil pump vacuum. Except for LTO, all electrodes were pressed at 1 t cm^{-2} for 30 s after punching out electrode discs with a diameter of 12 mm.

LTO electrode sheets were coated with a niobium oxide layer by atomic layer deposition (ALD) at a substrate temperature of 175 °C with argon as carrier gas at a base pressure of 19 Pa in a Fiji G2 system (Veeco Instruments). The precursors were niobium(V) ethoxide (Nb(OEt)₅) (Sigma Aldrich) and H₂O. Nb(OEt)₅ was kept at 160 °C while H₂O was unheated. The growth rate was determined by ellipsometry on Si (100) reference substrates, and linear growth was observed with a growth rate of 0.42 Å cycle⁻¹.

Two-electrode full cells were assembled using CR2032 coin cells (stainless steel) with an Al-coated negative cell casing part and a 16 mm Ti disc between positive electrode and spacer disc (1 mm). Whatman GF/D glass microfiber filters with a diameter of 15 mm were used as separators. The electrolyte volume was set to 100 µL. All cells were assembled under inert atmosphere in an argon-filled glovebox (MBraun). All cycling data was obtained at 25 °C.

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