Tuning of Molecular Water Organization in Water-in-Salt Electrolytes by Addition of Chaotropic Ionic Liquids

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ABSTRACT: Water-in-salt electrolytes (WISEs) have expanded the useful electrochemical stability of water, making the development of functional aqueous lithium-ion batteries more accessible. The implementation of additives in the formulation of WISEs can further improve the electrochemical stability of water and avoid potential lithium-ion salt solubility issues. Here, we have used Gemini-type ionic liquids to suppress water activity by designing the structure of ionic-liquid cations. The different water-organizing effects of ionic-liquid cations have been investigated and correlated to battery performance in LTO/LMO full cells. The champion device, containing the most chaotropic ionic liquid, retained at least 99% of its Coulombic efficiency after 500 charging cycles, associated with a final specific discharge capacity of 85 mA h g⁻¹. These results indicated that water-rich Li⁺ solvation shells significantly contribute to the excellent device performance and long-term stability of the LTO/LMO-based full battery cells. This work shows that the fine-tuning of the Li⁺ solvation shell and water structure by the addition of chaotropic cations represents a promising strategy for generating more stable and effective lithium-ion-containing rechargeable aqueous batteries.

INTRODUCTION

Over the past decade, rechargeable lithium-ion batteries (LIBs) have become increasingly used in vehicle electrification and grid storage markets. The high energy density and charge-cycling stability have qualified LIBs to a dominant position in current energy storage technologies. Nevertheless, the safety risks associated with the current LIB technology, predominantly owing to the high flammability and toxicity of the electrolytes employed, have highlighted the need for urgent improvements in the LIB design. Alternatives involve, for instance, completely different electrolytes, such as solid-state polymer electrolytes (SEPs), inorganic/ceramic electrolytes, or even (hybrid) metal–organic framework (MOF) electrolytes, or liquid electrolytes with different fundamental properties of the solvent used. As recently demonstrated, replacing problematic solvents with water has emerged as a promising strategy for overcoming safety issues. The main disadvantage of aqueous LIBs is the lower energy density recorded, originating from the intrinsically narrow electrochemical stability window (ESW) caused by the water present (limited to 1.23 V for pure water). This problem was initially solved by Suo et al., by increasing the concentration of the lithium-ion salt, thus pioneering the water-in-salt electrolyte (WISE) concept for aqueous LIBs. At such high concentrations of Li⁺ salt, there are not sufficient water molecules to fully solvate all ions in the electrolyte, leading to disruption of the water–water hydrogen bonding network (HBN) and predominant ion–ion interactions (ion-pair and ion-aggregate formation). This leads to a significant decrease in the thermodynamic water activity followed by a smaller amount of “free” water molecules that can aggregate into water-like entities in the electrolyte. The high concentration of anions in these systems promotes their involvement in the Li-ion coordination, and together with the low water activity, this suppresses hydrogen evolution yielding both high Coulombic efficiency and charge-cycling stability. The initial hypotheses suggested that the formation of a solid electrolyte interphase (SEI) was the main reason for the high stability of WISE-containing LIBs. However, the recent work of Ming et al. has challenged this viewpoint by “transfer experiments”, proving the importance of the thermodynamic effect (i.e., the stability of the O–H bond) on the water molecules. In this hypothesis, instead, it is the lack of water clustering that promotes Li⁺–water interactions, in turn resulting in a higher strength of the intramolecular O–H bond in the water molecules. The stronger intramolecular O–H bonds in turn...
retard the water-splitting reaction manifested by the higher electrochemical stability observed for WISEs. A slightly different viewpoint was presented in recent work by Teng and co-workers, pointing out the importance of also considering the solvation of $\text{OH}^-$ and $\text{H}^+$ with respect to the observed widening of the water ESW upon an increase of salt concentration. In essence, they emphasize that the full chemical reaction must be taken into account, not only the reactant side. In this aspect, the solvation of the products of water splitting, $\text{OH}^-$ and $\text{H}^+$, should be considered to allow a proper evaluation of the driving force for the overall reaction. In their view, the main contribution to the wider ESW of water upon increasing salt concentrations originates from the lower solvation energies of $\text{OH}^-$ and $\text{H}^+$. Notably, this effect is complementary to the hypothesis of thermodynamic effects on the $\text{O}–\text{H}$ bond strength on the reactant side.

Regardless of all the aforementioned effects, just increasing the salt content in aqueous electrolytes expands the ESW to around 2.5 V. A further increase in electrochemical stability is hampered by solubility issues with respect to the Li-ion salt. In order to overcome this issue, hybrid water-in-salt concepts have been developed. Despite higher Li-salt solubility in this type of additive-modified electrolyte, the added components themselves also influence the water activity, resulting in further enhanced electrochemical stability.

Ionic liquids (ILs) have emerged as promising additives in hybrid water-in-salt electrolytes, owing to their high electrochemical stability, nonvolatility, and nonflammability. Because of their wide application in recent decades, ILs have been considered the “green solvents of the future”. The possibility of tuning their physicochemical properties by rather straightforward modifications of the cation–anion combinations and substitution on their core molecular structures promotes them as a promising molecular design platform in different fields. The IL molecular design nature can be effectively exploited in the formulation of hybrid WISE-type LIBs as well. It is well known that ILs exhibit different tendencies to influence water HBN depending on the type and size of the constituent ions. The extensive work of Marcus and other groups has resulted in a detailed understanding of ion influence on the water structure for common ions. The ions that are prone to promote a water structure are defined as cosmotropic (structure-makers), while in contrast, chaotropic ions (structure-breakers) tend to break the intrinsic water structure characterized by extensive water–water molecule hydrogen bonding. In a search for the best strategy for anion selection in WISE architectures, Reber et al. investigated a selection of anions exhibiting different chaotropic/cosmotropic effects. It was shown that the chaotropic nature of the anion plays an important role in widening the ESW of aqueous electrolytes, with the $\text{[TFSI]}^-$ anion as a promising candidate for implementation in WISE systems. In that work, cosmotropic cations in the formulations of salt were used, causing the strengthening of the HBN. Thus, an interesting prospect would be to combine $\text{[TFSI]}^-$ with a chaotropic cation to form a cosalt that could benefit from the aforementioned effect by the $\text{[TFSI]}^-$ anion. The addition of ILs to the structure of WISEs brings another variable to light exhibited as an indirect effect of the IL cations on the molecular water organization. The cosmoptropicity and chaotropicity of ILs are, to a large extent, determined by the aromaticity of the cation ring and the type of cation substituents. Previous research has shown that aromatic imidazolium and pyridinium rings alone show a cosmoptropic tendency that is more pronounced than in ammonium, piperidinium, and pyrrolidinium cations. However, the cosmoptropicity/chaotropicity of the cations is primarily determined by the length and type of cation side chains. Short alkyl chains (–methyl, –ethyl, and –propyl) tend to promote chaotropic behavior, while a further increase of the side-chain length causes “hydrophobic hydration” and instead boosts cosmoptropicity. The water molecules around surfactant-type molecules tend to form transient clathrate-like clusters, leading to small alternation in water HBN (hydrophobic hydration). The presence of hydrophilic groups in the cation side chains promotes water organization through the formation of H-bonds. Therefore, the molecular design nature of ILs represents a useful tool for gaining a better understanding of the thermodynamic effects in WISE-type LIBs. Recently, different groups have developed cosalts of “high-entropy” aqueous electrolytes, leading to desolvation processes caused by the presence of hydrophobic cations at the electrode–electrolyte interface. However, we anticipate distinct roles for entropic and chaotropic effects in solution, with the primary focus of this article being on the latter. While the effects of chaotropic ions on the HBN and the macroscopic consequences of such interactions are still unclear, the importance of chaotropicity in the reactivity of aqueous electrolytes has clearly been demonstrated.

Recently, ILs have been used in a few formulations of hybrid WISEs for LIBs. In all those investigations, a combination of a nonflammable IL with a WISE has been proposed to both reduce the $\text{H}_2\text{O}$ activity and to improve the ionic conductivity. Chen et al. increased the solubility of $\text{Li[TFSI]}$ up to 63 m using 1-butylymethylimidazolium bis(trifluoromethanesulfonyl)imide and 1-methyl-1-propylpyrroloidimium bis(trifluoromethanesulfonyl)imide added to an aqueous $\text{Li[TFSI]}$ mixture. The influence of imidazolium-type ILs on hybrid WISEs was studied by Becker and co-workers. The addition of an IL boosted the solubility of $\text{Li[TFSI]}$ and rendered an acceptable ionic conductivity of 1.2 mS cm$^{-1}$ at 25 °C and at the same time enabled stable charge cycling of a niobia-coated $\text{LiTi}_2\text{O}_3$/NMC811 full battery cell. However, the reaction kinetics still needs improvement. The same research group formulated quaternary systems by the addition of a cosolvent in the form of succinonitrile to promote better lithium-ion mobility, resulting in promising performance of the LIBs during 250 charging cycles. In our previous work, the use of Gemini-type ionic liquids (GILs) based on pyrrolidinium and piperidinium cations was demonstrated. Pyrrolidinium cation rings interlinked with poly(ethylene glycol)-like spacers were shown to generate stable charge cycling of conventional $\text{LiTi}_2\text{O}_3$/LiMn$_2$O$_4$ (LTO/LMO for short) cells during at least 500 cycles with a specific discharge capacity of up to 80 mA h g$^{-1}$. Also, the inclusion of GILs in the architecture of the WISEs increased the ESW to $\gtrsim$3.7 V. In our present work, we have investigated the influence of chaotropic/cosmotropic cations in GILs on the molecular organization of a new generation of WISEs and their resulting performance in aqueous LIBs. The comprehensive variation of the side chains of the core pyrrolidinium ring allows systematic tuning of chaotropicity and cosmoptropicity, which was monitored by a detailed solution structure investigation of the bulk electrolytes. Most of the new systems generated show good performance in battery devices based on commercial
LTO and LMO electrode materials without the need for any additional protective coating.

**METHODS**

**Synthesis of Gemini Ionic Liquids.** The syntheses were conducted via a three-step procedure (Scheme S1). The initial phase involved alkylation of the pyrrolidine ring system with the appropriate chloroalkane analogues. An equimolar amount (0.1 mol) of pyrrolidine and chloroalkane was dissolved in acetone and mixed with solid potassium carbonate (0.2 mol). The mixture was stirred for 48–72 h at 50 °C under a protecting nitrogen atmosphere. After the removal of unreacted material and solvent, the resulting product was dried for 24 h under vacuum. The obtained N-alkylpyrrolidine (2 mol equiv) was mixed with 1 mol equivalent of bis(2-chloroethyl)ether in isopropanol. The mixture was stirred for 72 h at 80 °C under reflux. The obtained products were purified at least five times by recrystallization in acetone. The purified GILs were further dried under vacuum over P2O5 for at least 48 h. The purity of the halide-containing GILs was determined from spectral resolution of 4 cm⁻¹. A liquid-nitrogen-cooled Ge detector was employed. The effective frequency range used was 100–4000 cm⁻¹. A spectral resolution of 4 cm⁻¹ was applied.

**Viscosity and Conductivity Investigations.** The viscosities were determined by using a Brookfield CAP 2000+ viscometer. A Mettler-Toledo Seven Excellence conductometer S700 with platinum electrodes was used for the electric conductivity experiments. The analyses were performed in a Pyrex-type cell with an external thermostated water flow to maintain a constant temperature by using a Lauda thermostat. The conductivity cell constant was determined using a 0.01 M aqueous KCl standard solution, and validation was performed at all temperatures investigated.

**Raman Spectroscopy.** A BioRad FTS 6000 spectrometer with a Raman accessory was used for recording the Raman spectra. A liquid-nitrogen-cooled Ge detector was employed. The effective frequency range used was 100–4000 cm⁻¹. A spectral resolution of 4 cm⁻¹ was applied.

**Molecular Dynamics Simulations.** The molecular dynamics (MD) simulations were performed using the Tinker package, with an implemented many-body polarizable force field developed by Borodin. Three simulation cells were constructed to contain 128 molecules of Li[TFSI], 128 molecules of GIL, and 384 water molecules. All systems were initially equilibrated using an NPT ensemble at 100 °C for 10 ns, followed by 20 ns equilibration at 50 °C and an additional 20 ns at 25 °C. During NPT equilibration, the dimensions of the simulation cell were reduced to match experimental densities at 25 °C (Table S3). The obtained box size at 25 °C was used for further simulations. The production run was performed in an NVT ensemble using a Nose-Hoover thermostat set to a temperature of 25 °C. Multiple time step integration was employed with a time step of 0.5 fs for bonded interactions, a time step of 1.5 fs for all nonbonded interactions within a truncation distance of 8.0 Å, and an outer time step of 3.0 fs for all nonbonded interactions between 8.0 Å and the nonbonded truncation distance of 14 Å. Ewald summation was used for electrostatic interactions between set charges or induced dipole moments with k = 83 vectors. The reciprocal part of the Ewald model was computed at every 3.0 fs.

**Battery Assembly.** The electrodes were prepared from commercially available active materials, lithium titanate (LTO), and spinel lithium manganate (LMO). Polyvinylidene fluoride (PVDF) was used as the binder material. Before preparation of the slurry, PVDF was dissolved in N-methyl pyrrolidone forming a 5 wt % solution. The electrode slurry consisted of the active material, conductive carbon Super C65, and PVDF, mixed in a mass ratio of 8:1:1. The slurry was coated onto stainless-steel current collectors and dried for 6 h at 80 °C in air and subsequently for 6 h at 80 °C under vacuum. The

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**Table 1. Abbreviation of the Gemini Ionic Liquids Used, Along with Water Content and Synthesis Yield**

<table>
<thead>
<tr>
<th>GIL abbreviation</th>
<th>yield (%)</th>
<th>water content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C2Pyr-CO2C6H4-C2Pyr) [TFSI]2</td>
<td>94</td>
<td>8.6</td>
</tr>
<tr>
<td>(C2Pyr-CO2C6H4-C2Pyr) [TFSI]2</td>
<td>93</td>
<td>10.2</td>
</tr>
<tr>
<td>(C2Pyr-CO2C6H4-C2Pyr) [TFSI]2</td>
<td>86</td>
<td>7.9</td>
</tr>
<tr>
<td>(HOC2Pyr-CO2C6H4-HOC2Pyr) [TFSI]2</td>
<td>81</td>
<td>37.0</td>
</tr>
<tr>
<td>(HOC2Pyr-CO2C6H4-HOC2Pyr) [TFSI]2</td>
<td>84</td>
<td>25.2</td>
</tr>
<tr>
<td>(HOC2Pyr-CO2C6H4-HOC2Pyr) [TFSI]2</td>
<td>73</td>
<td>45.9</td>
</tr>
</tbody>
</table>

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**Electrolyte Preparation.** Lithium bis-(trifluoromethanesulfonyl)imide, Li[TFSI] (Sigma-Aldrich, CAS number: 90076-65-6, initial purity of 99.99%) was dried and stored under vacuum before use. The electrolytes were formulated by mixing Li[TFSI], GILs, and water in the molar ratio 1:1:3 (for all systems studied in this work). The water content of Li[TFSI] and the synthesized GILs was determined by Karl Fischer titration before the preparation of the electrolytes, and consequently, existing water was subtracted from the amount of water added to generate the target molar ratios. The added high-purity water (Millipore Mili-Q) was degassed and purged with argon before use.
electrodes were punched to a diameter of 13 mm. The mass loading of LTO was 2.4 mg (expected theoretical capacity of 175 mA h g\(^{-1}\)), while the corresponding mass of LMO was 3.0 mg (expected theoretical capacity of 148 mA h g\(^{-1}\)). Active materials and the binder were purchased from Sigma-Aldrich, while the conductive carbon was provided by MSE Suppliers. The prepared electrodes were used in coin-type LIB full cells. A CR2032 stainless-steel battery casing was used, and the electrodes were separated using a Whatman GF/D glass microfiber (d = 15 mm) sheet. The prepared electrolytes were added in a volume of 55 \(\mu\)L. All the batteries were assembled in ambient conditions and were allowed to equilibrate for 24 h prior to characterization. For the electrochemical stability window determination, a Swagelok T-cell assembly was used. The same stainless-steel current collectors as for the coin cells were used as working and counter electrodes, while an extra reference electrode was introduced consisting of a miniature Ag/AgCl electrode (eDAQ).

**Electrochemical Characterization.** Linear sweep voltammetry was performed using Swagelok T-cells with a scan rate of 0.1 mV/s and an Autolab PG12 potentiostat. Galvanostatic cycling was performed with a Neware battery station by using coin cells. The voltage window was set to 0.5–3.0 V. The current density was adjusted according to the mass of the LTO electrode. Electrochemical characterization was performed without control of the temperature. All presented data are the averages of 8 coin cells.

**Postmortem Analysis.** The cycled LTO electrodes were investigated by using FTIR spectroscopy and X-ray absorption spectroscopy (XAS). All the electrodes were carefully disassembled after cycling, and the remaining GIL-based electrolytes were removed using a mixture of propylene carbonate and dimethyl carbonate. The solvents used for washing the electrodes were subsequently evaporated at an elevated temperature under vacuum. For the XAS measurements, all of the steps were performed in an inert atmosphere. The pristine electrode was washed by using the same procedure. FTIR spectra were recorded by a Thermo Nicolet spectrophotometer by using the ATR technique on a ZnSe crystal. XAS spectra were recorded at the PEAXIS beamline, BESSY II synchrotron at the Helmholtz Zentrum Berlin. The absorption spectra of the F K-edge in the energy range 685–710 eV were recorded, and the pristine electrode data were subtracted from the obtained spectra.

### RESULTS AND DISCUSSION

According to our previous work, WISEs enriched with pyrrolidinium-based GILs offer superior results with respect to their piperidinium analogues in terms of transport properties and electrochemical performance, despite exhibiting lower electrochemical stability.\(^{36}\) Therefore, a systematic change of substituents of the pyrrolidinium GIL cations included in the WISE composition was performed in this study (Figure 1 and Table 1).

The different substituents were chosen to tune the hydrophilic character of investigated GILs, from completely hydrophobic with butyl side chains to hydrophilic GILs with hydroxyl or carboxyl groups (Figure 1). This modification also tunes their chaotropicity (structure-breaking) and cosmotropicity (structure-making), resulting in different structural organizations of the water molecules and consequently differences in the Li\(^+\) solvation shell. By including GILs with ether-containing (–C\(_2\)OC\(_2\)–) spacers, the viscosity could be minimized and the conductivity maximized. All ternary electrolyte systems were composed to have the same molar ratio of Li[TFSI], corresponding GIL, and water (1:1:3), with no initial heating in the preparation process. Equilibration at higher temperatures was avoided to prevent the risk of generating thermodynamically unstable, oversaturated electrolyte systems.\(^{15}\)

The viscosity and conductivity of the WISEs containing the different GILs were determined in the temperature range 298–323 K and the resulting data are shown in Figure 2 and Table S2. The consequence of introducing the ether-containing spacer (–C\(_2\)OC\(_2\)–) in the structure of the GIL cations is clearly observed by comparison with the analogous cations instead containing the –C\(_3\)– spacer (Figure S9 and Table S3 in the Supporting Material). The reduction in viscosity by the inclusion of the (–C\(_2\)OC\(_2\)–) spacer is in the range of 5–25%. The reduction of viscosity by introduction of the ether group in the alkyl side chain was ascribed to the increased free volume, which results from the high conformational flexibility of the ether moieties and provides more available holes for the convenience of mass transport and low viscosity. The same
trend is observed in the corresponding conductivities, where 2–15% higher conductivities were recorded for electrolytes with the \(-\text{C}_2\text{OC}_2\text{Pyr}\) spacer. Regardless of the spacer type, side-chain substitutions display a similar pattern with respect to the transport properties. Electrolytes containing \(\text{C}_2\text{OC}_2\text{Pyr}\) show the lowest viscosity (61 mPa s at 298 K) and the highest conductivity (3.4 mS cm\(^{-1}\) at 298 K). The worst electrolyte in terms of transport properties is the one containing the carboxyl end-group, \(\text{HOOCC}_2\text{Pyr}\), with a viscosity of 122 mPa s, and a conductivity of 1.6 mS cm\(^{-1}\) at 298 K. As a general pattern, the viscosity decreases in the order \(\text{HOOCC}_2\text{Pyr} > \text{HOC}_2\text{Pyr} > \text{HOC}_2\text{OC}_2\text{Pyr} > \text{C}_2\text{Pyr} > \text{C}_2\text{OC}_2\text{Pyr}\), and the same trend regarding conductivity can be observed (\(\text{HOOCC}_2\text{Pyr} < \text{HOC}_2\text{Pyr} < \text{HOC}_2\text{OC}_2\text{Pyr} < \text{C}_2\text{Pyr} < \text{C}_2\text{OC}_2\text{Pyr}\)). Overall, WISEs containing GILs with a chaotic trend (\(\text{C}_2\text{Pyr}, \text{C}_2\text{OC}_2\text{Pyr}\)) exhibit better transport properties as compared with systems with GILs that tend to promote molecular water structures.

**Solvation Structures.** In order to understand the impact of different GILs on the electrolyte performance, basic insights into the solvation structures of the bulk electrolytes were obtained by using Raman spectroscopy and molecular dynamics (MD) simulations. The most important regions of the Raman spectra for the investigated systems are the \(-\text{OH}\) stretching vibration modes of water (3300–3600 cm\(^{-1}\)) and the \([-\text{TFSI}^-\) breathing mode (740–750 cm\(^{-1}\)). Figure 3 shows normalized Raman spectra for (a) a breathing \([-\text{TFSI}^-\) mode at \(\approx750 \text{ cm}^{-1}\) and (b) water stretch vibration modes at \(\approx3500 \text{ cm}^{-1}\).

**Figure 3.** Normalized Raman spectra for (a) a breathing \([-\text{TFSI}^-\) mode at \(\approx750 \text{ cm}^{-1}\) and (b) water stretch vibration modes at \(\approx3500 \text{ cm}^{-1}\). Black: \(\text{Li}[\text{TFSI}^-];(\text{C}_2\text{Pyr}\text{C}_2\text{OC}_2\text{Pyr});\text{[TFSI]}^-;\text{H}_2\text{O}\); red: \(\text{Li}^-\text{[TFSI]}^-;(\text{C}_2\text{Pyr}\text{C}_2\text{OC}_2\text{Pyr});\text{[TFSI]}^-;\text{H}_2\text{O}\); blue: \(\text{Li}[\text{TFSI}^-];(\text{C}_2\text{OC}_2\text{Pyr}\text{C}_2\text{OC}_2\text{Pyr});\text{[TFSI]}^-;\text{H}_2\text{O}\); green: \(\text{Li}[\text{TFSI}^-];(\text{HOC}_2\text{Pyr}\text{C}_2\text{OC}_2\text{Pyr});\text{[TFSI]}^-;\text{H}_2\text{O}\); cyan: \(\text{Li}^-\text{[TFSI]}^-;((\text{HOC}_2\text{Pyr}\text{C}_2\text{OC}_2\text{Pyr});\text{[TFSI]}^-;\text{H}_2\text{O}\); magenta: \(\text{Li}^-\text{[TFSI]}^-;((\text{HOC}_2\text{Pyr}\text{C}_2\text{OC}_2\text{Pyr});\text{[TFSI]}^-;\text{H}_2\text{O}\); orange: water (intensity of the water band was divided by a factor of 5 for clarity purpose).

Raman spectra in the wavenumber region corresponding to the S–N–S vibration of the \([-\text{TFSI}^-\) is well-known that this breathing vibration is strongly influenced by the coordination environment of the anion in the WISEs. In the highly concentrated 21 m aqueous Li[\text{TFSI}^-] system, that band displays a significant blueshift to close to 750 cm\(^{-1}\), which is correlated to a strong \([\text{Li}^-\text{[TFSI]}^-\) interaction. The approach to quantify the cation–anion interaction, proposed by Suo et al., suggests that the cation–anion cluster can be linked to the wavenumber of the \([-\text{TFSI}^-\) breathing vibration. The proposed classification divides the cation–anion interactions into four groups: (I) free anion (740–743 cm\(^{-1}\)), (II) loose ion-pair (743–746 cm\(^{-1}\)), (III) intimate ion-pair (746–748 cm\(^{-1}\)), and (IV) aggregated ion-pair (748–750 cm\(^{-1}\)). In our systems, the \(\text{C}_2\text{Pyr}\)-containing electrolyte offers the lowest wavenumber (\(\approx743.6 \text{ cm}^{-1}\)). Taking the lowest wavenumber limit of the range as a point of comparison, a blueshift of \(\approx1 \text{ cm}^{-1}\) is noted for electrolytes with \(\text{C}_2\text{Pyr}\) and \(\text{C}_2\text{OC}_2\text{Pyr}\). The replacement of the terminal methyl group with –OH groups causes a significant blueshift. Electrolytes with \(\text{HOC}_2\text{Pyr}\) and \(\text{HOC}_2\text{OC}_2\text{Pyr}\) shift the Raman spectra up to 746.7 and 747.4 cm\(^{-1}\), respectively. Even if using one decimal in the wavenumbers may be overoptimistic with respect to absolute values, they serve the purpose of illustrating consistent relative Raman shifts of the analogous GIL cations. A further increase of the blueshift was noted in the presence of a carboxyl end-group in the side chain (\(748.6 \text{ cm}^{-1}\)). All the pure GILs display a Raman shift between 742 and 744 cm\(^{-1}\), suggesting weak coordination between the ionic-liquid cations and \([-\text{TFSI}^-\) (Figure S10). Based on these results, the Raman shift in water + Li[\text{TFSI}^-] + GIL systems can be assigned to the amount of \([\text{Li}^-\text{[TFSI]}^-\) interaction. Based on Suo’s classification, the formation of loose ion pairs between lithium ions and \([-\text{TFSI}^-\) is noted in the electrolytes with chaotic GILs (\(\text{C}_2\text{Pyr}, \text{C}_2\text{OC}_2\text{Pyr}, \text{C}_2\text{OC}_2\text{Pyr}\)). A more pronounced \([\text{Li}^-\text{[TFSI]}^-\) interaction is observed in \(\text{HOC}_2\text{Pyr}\)- and \(\text{HOC}_2\text{OC}_2\text{Pyr}\) and could be assigned as an intimate ion-pair formation. The largest blueshift is observed for electrolytes with the most cosmotropic GIL (\(\text{HOOCC}_2\text{Pyr}\)), which is on the borderline of aggregate ion pairs. The inclusion of GIL functional groups that promote molecular water structures correlates with a more pronounced \([\text{Li}^-\text{[TFSI]}^-\) interaction. In a typical WISE, water molecules constitute the only coordinator competitor that can displace \([-\text{TFSI}^-\) from the Li-ion solvation shell, while in our more complex systems, the indirect effects of the GIL cation may also influence the Li-ion solvation shell. Therefore, the observation of the O–H stretch vibrations in the Raman spectra of water molecules in the electrolyte systems (Figure 3b) may provide additional information about the water HBN and the availability of water molecules to coordinate \(\text{Li}^+\). The broad signal that usually can be observed in pure water or dilute aqueous solutions is close to 3500 cm\(^{-1}\) while it becomes sharper when the concentration of dissolved salt is increased. That has been explained by a disruption of the predominant water HBN, with a continuously more red-shifted and sharper band emerging at higher salt concentrations disrupting the inherent water structure. This phenomenon is noted in all highly concentrated aqueous electrolytes.

Since the GILs used in this work were designed to subtly change the HBN of water, a redshift of the O–H band should be expected as a result of reduced cosmotropicity. Electrolytes with carboxyl-substituted GIL cations show the broadest peak centered around 3547 cm\(^{-1}\), followed by –OH containing GIL cations with peaks at around 3555 cm\(^{-1}\). A large blueshift of \(\approx20 \text{ cm}^{-1}\) is observed for electrolytes with the \(\text{C}_2\text{Pyr}\) and \(\text{C}_2\text{OC}_2\text{Pyr}\) GILs, while the most prominent increase of wavenumber is observed for the ethyl-substituted GIL (\(\approx3582 \text{ cm}^{-1}\)).

The inclusion of hydrophilic groups (–COOH and –OH) in the structure of the GIL cations leads to them becoming incorporated in the HBN causing a similar shape and position of the –OH stretch band as compared with that in pure water. On the other hand, the hydrophobic groups in the \(\text{C}_2\text{Pyr}, \text{C}_2\text{Pyr}, \text{and C}_2\text{OC}_2\text{Pyr GILs disturb the HBN resulting in a significant blueshift and sharpening of the Raman bands. Thus, the obtained results for the \([-\text{TFSI}^-\) breathing vibration need to be closely correlated with the water structure effects and change in the HBN itself, as caused by the GILs. It is clear that systems based on GILs that increase the structural order of water, thus retaining the water HBN (\(\text{HOC}_2\text{Pyr}, \text{HO-}

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C$_2$OC$_2$Pyr, and HOOCC$_2$Pyr), contain fewer available water molecules that can compete with [TFSI]$^-$ for a position in the Li$^+$-ion solvation shell. Therefore, the change in the S–N–S vibration band of the [TFSI]$^-$ ion is the most prominent for these types of electrolytes, while the –OH band displays less deviation from that of pure water. On the other hand, disturbing the water structure makes water molecules more available to compete for a coordination position in the Li$^+$-ion solvation shell, thus providing [TFSI]$^-$ ions with stronger competition, and therefore, a smaller shift of S–N–S band is expected, and this is exactly what is noted for chaotrophic GILs (C$_2$Pyr, C$_3$Pyr, C$_6$OC$_2$Pyr). In spite of the above logical reasoning, the presence of –OH and –COOH groups in the structures of some GIL cations needs to be taken into account as additional Li$^+$-coordination competitors themselves. Deeper insights into the interplay between Li$^+$-coordinated competitors were revealed by molecular dynamics (MD) simulations. All the simulations were performed at 298 K, with the same molecular ratios for all electrolytes (Table S4).

The partial radial distribution functions (pRDFs) and coordination numbers (CNs) were used for the representation of the local structural environments. CNs were estimated as average coordination numbers during the simulation time using the equation:

$$\text{CN} = 4\pi \rho \int_0^{r^*} g(r)r^2 dr$$

where $\rho$ is the average density, $g(r)$ is the radial distribution function (RDF), and $r^*$ is the distance from the selected type of atom. As a better dynamic representation of the system, CN probability distribution was calculated using each time step in the simulations with a cutoff distance <4.0 Å. In typical WISE systems, the water local environment is characterized as water coordinated to a lithium ion or water solvated by other water molecules. The nature and structure of the GIL cations introduce another variable in the water organization structure that may have direct or indirect effects on the Li$^+$ solvation shell.

A “free” water organization in GIL-containing WISEs was investigated by water–water pRDFs and the corresponding CNs (Figure 4a,d). The most important feature corresponds to the first peak in the pRDFs. The most intense peak at the shortest distance ($\approx$2.9 Å) is observed for systems consisting of C$_2$Pyr and HOC$_2$Pyr. This peak is slightly shifted toward longer distances, 3.1 and 3.2 Å, for electrolytes containing HOOCC$_2$Pyr and HOOCC$_2$Pyr, respectively. The longest distances are noted for electrolytes formulated with the most chaotropic GILs, C$_3$Pyr, and C$_6$OC$_2$Pyr. Electrolytes with C$_3$Pyr display the lowest integral (i.e., CN) of the first peak appearing at a distance as long as 3.5 Å, while a more prominent peak can be observed at a similar distance for the analogous system with C$_6$OC$_2$Pyr.

By the investigation of the CN probability (Figure 4d), only systems with C$_3$Pyr and HOC$_2$Pyr show noticeable water–water clustering. In these electrolytes, around 40% of the water molecules retain some degree of structural organization corresponding to that observed in pure water. On the other hand, the presence of chaotropic GILs (C$_3$Pyr or C$_6$OC$_2$Pyr) causes an obvious disturbance in the intrinsic water structure with more than 95% of the water molecules no longer in the proximity of other water molecules. In electrolytes with the most prominent cosmotropic GILs (HOC$_2$OC$_2$Pyr and HOOCC$_2$Pyr), around 85% of the water molecules are not coordinated to any neighboring water molecules.

As a next step, the Li$^+$ solvation structure was analyzed by generating the pRDFs and CNs for Li–O(H$_2$O) (Figure 4b,e).
and Li–O(TFSI) and interactions (Figure 4c). For both types of coordination, the first peak appears at almost the same distance, regardless of which GIL is included in the system. The sharp first peak for the Li–O(TFSI) distance appears at ≈2 Å, with a significant difference in peak intensity (i.e., probability) between the electrolytes with cosmotropic and chaotropic GIL cations. The peak intensity follows the trend: HOOCC$_2$Pyr > HOC$_2$OC$_2$Pyr > HOC$_2$Pyr > C$_2$Pyr ≈ C$_2$OC$_2$Pyr > C$_2$Pyr. A similar peak position was obtained for Li–O(H$_2$O) (Figure 4b). The decrease in peak intensity in this case follows the order: C$_2$Pyr > C$_2$OC$_2$Pyr > C$_2$Pyr > HOC$_2$Pyr > HOC$_2$OC$_2$Pyr > HOOCC$_2$Pyr. The intensity of the first pRDF peak suggests that the Li$^+$–[TFSI]$^-$ interactions are the most prominent in electrolytes with cosmotropic GILs, while Li$^+$–water interactions are more pronounced when electrolytes contain chaotropic GILs.

The most straightforward comparison of Li$^+$-solvation shell structures in the presence of different GILs is obtained from the probability of the presence of CNs. Electrolytes enriched with cosmotropic GILs (HOC$_2$OC$_2$Pyr, HOC$_2$Pyr, HOOCC$_2$Pyr) are predominantly characterized by one water molecule in the solvation shell of the lithium ions, with almost 20% of lithium ions without any water in the solvation shell. With the increase of chaotropicity, CNs are gradually increasing with almost the same probability of finding 2 or 3 water molecules in the Li$^+$ solvation shell. Analogously, almost no “water-free” Li$^+$ solvation shell is observed for the most chaotropic GIL (C$_2$Pyr). The presence of [TFSI]$^-$ in the Li$^+$ solvation shell is more pronounced in all systems simulated (Figure 4c). In electrolytes with C$_2$Pyr, almost 40% of the lithium ions have 2 [TFSI]$^-$ in the solvation shell, followed by slightly more than 30% of Li$^+$ with 3 [TFSI]$^-$.

An increasing cosmotropicity of the GILs leads to a higher abundance of anions in the Li$^+$ solvation shell, which is manifested by a continuous increase in the CNs to 3 or higher. Therefore, the WISE containing C$_2$OC$_2$Pyr displays a similar probability of finding 2 or 3 anions in the Li$^+$ solvation shell, both with about 40% probability (Figure 4f). The Li$^+$ ions in electrolytes with C$_2$Pyr, HOC$_2$Pyr, and HOC$_2$OC$_2$Pyr are characterized by predominantly three anions in the Li$^+$ solvation shell, while the presence of the most cosmotropic GIL (HOOCC$_2$Pyr) increases the probability of finding even four anions in the Li$^+$ coordination shell.

In order to gain a better understanding of the overall liquid structure of GIL-enriched WISEs, the average CNs for the most probable interactions were evaluated and are presented in Figure 5. The visual interpretation of the solvation structure taken from the MD simulations from most cosmotropic and chaotropic GIL is presented in Figure S11. Upon addition of chaotic GILs (especially C$_2$Pyr and C$_2$OC$_2$Pyr), the water structure in the WISEs becomes quite disturbed, resulting in small amounts of water clusters in the systems (lowest CNs and lowest intensity of the pRDFs peaks for O(water)–O(water) interactions). Disturbance of the water structure is manifested through the breaking of water–water hydrogen bonds, making water molecules more accessible for the solvation of Li$^+$. The hydrophobic character of [TFSI]$^-$ also contributes to pushing water more toward the Li$^+$ solvation shell, inducing a higher CN for Li–O(water) in systems with C$_2$Pyr and C$_2$OC$_2$Pyr GILs. When the cosmotropicity is increased, for instance, represented by the C$_2$Pyr GIL, the water–water interaction peak in the pRDF becomes more prominent, as well as the corresponding CN, suggesting that water retains some archetypical water organization. Therefore, water molecules in these small clusters have H-bonds that need to be broken in order to contribute to Li$^+$ solvation.

Therefore, a smaller number of water molecules can contribute to Li$^+$ solvation, reducing the resulting Li-water interactions.
The inclusion of $\cdot$OH groups in the structure of HOC$_2$Pyr also helps to retain the water organization level to some extent. The water–water pRDFs peak is only slightly shifted and is of lower intensity than that for systems containing C$_2$Pyr. It is important to note that the inclusion of cosmotropic cations contributes to additional competition with respect to water coordination (hydrophilic group in the side chain). Therefore, it is not surprising to observe that a small amount of water also binds to the $\cdot$OH group of the GIL cation in the presence of the HOC$_2$Pyr. With prolongation of the side chain and increased flexibility in HOC$_2$OC$_2$Pyr, the probability of finding water molecules around the GIL cations becomes more prominent. This results in an additional decrease in water–water coordination (average CN decreases to 0.1). This effect is even more prominent in the presence of the carboxyl cation groups, which represent competitors not only for water coordination but also as potential ligands for Li-ion coordination. Owing to the presence of water-attracting groups in the structures of HOCC$_2$Pyr, HOC$_2$OC$_2$Pyr, and HOOCC$_2$Pyr, water becomes distributed among the three available environments: Li-ion, hydrophilic groups of the GIL cations and other water molecules. The higher affinity of the GIL cations with respect to water molecules leads to less accessible water for participating in Li$^+$ solvation, resulting in high Li–O(TFSI$^-$) CNs in the electrolytes containing such cations. Therefore, the electrolytes with cosmotropic GILs display [TFSI$^-$]–rich Li$^+$ solvation shells, while electrolytes with chaotropic GILs instead are characterized by Li$^+$ solvation shells rich in water.

**Electrochemical Performance.** The electrochemical stability window (ESW) for GIL-enriched WISEs was investigated by linear sweep voltammetry (LSV, Figure 6), using a previously established procedure. The presence of GILs increases the ESW as compared to non-GIL-containing WISEs by at least 1 V. The narrowest ESW (3.32 V) was recorded for the WISE containing the carboxyl-functionalized GIL, associated with both lower reductive and oxidative stability in comparison to those of the other investigated electrolytes. Other GIL-containing WISEs show similar oxidative stability but significant differences in reductive stability depending on the type of GIL present. All electrolytes with cosmotropic cations exhibit narrower ESWs, owing to a decrease in reductive stability in comparison with WISEs with chaotropic GILs. The most stable electrolyte contains the C$_2$Pyr GIL with a recorded ESW of 3.91 V. Overall, the inclusion of hydrophilic groups ($\cdot$OH and $\cdot$COOH) in the structure of the GIL cations results in a lower ESW by at least 0.2 V. Thus, the cations with a more pronounced chaotropic effect (C$_2$OC$_2$Pyr, C$_2$Pyr, C$_2$Pyr) lead to wider ESWs in the ternary-type WISEs.

In Figure 6, a small peak can be noted at $\approx$−1 V vs Ag/AgCl, and it is the most prominent in the WISE system containing HOOC$_2$C$_2$Pyr. In contrast, it is almost invisible for the electrolyte based on C$_2$Pyr. In the literature, this peak has been interpreted as essential for the formation of an anion-derived solid electrolyte interphase (SEI) at the electrode, with two possible mechanisms (reduction of “free” water, or reduction of “free” TFSI$^-$). The correlation between “free” water content in the electrolytes and the intensity of the peak at −1 V was identified by a comparison between the results from the MD simulations and the integral area from the LSV curve. A low peak intensity correlates well with high Li-water CNs, indicating the possible reduction of water molecules in these systems at −1 V vs Ag/AgCl leading to the high stability of electrolytes with more chaotropic GILs present (more water-rich Li$^+$ solvation shell). In order to investigate the battery performance of the WISE electrolytes, full cells based on Li$_4$Ti$_5$O$_{12}$ (LTO) anodes and LiMn$_2$O$_4$ (LMO) cathodes were assembled. The wide ESW of all electrolytes should ensure stable charge cycling of both electrodes (LTO $\approx$ 1.5 V vs Ag/AgCl in concentrated electrolytes, LMO $\approx$ 1.2 V vs Ag/AgCl in concentrated electrolytes). The obtained charge/discharge cycling performance of full cells in a voltage range of 0.5 to +3.0 V at 1 C rate (corresponding to 90 mA·g$^{-1}$) is shown in Figure 7. The voltage profiles of full cells, estimated with respect to the active mass of LTO at 1 C rate, for other electrolytes, are presented in the Supporting Material (Figures S12–S16). The batteries with HOOC$_2$C$_2$Pyr-based GILs showed a malfunction that possibly originates from a low reductive electrochemical stability close to that of the LTO electrode.

In terms of cycling stability, an obvious difference was observed between electrolytes containing chaotropic and cosmotropic GILs. All cells with electrolytes based on chaotropic GILs (C$_2$Pyr, C$_2$Pyr, and C$_2$OC$_2$Pyr) showed stable cycling for more than 500 cycles, while cells based on WISEs containing cosmotropic GILs instead showed a fast decline in discharge capacity. The most promising coin cells in terms of discharge capacity and Coulombic efficiency (CE) are based on C$_2$Pyr. These cells retain 99% of the CE after 500 cycles, associated with a final specific discharge capacity of 85 mAh·g$^{-1}$. The average CE over this period of cycling was 99.5%, suggesting a very high stability of the investigated electrolyte.
In terms of capacity retention, batteries based on C\textsubscript{2}Pyr GILs retain 90% of their initial discharge capacity. The second-best-performing cells were based on C\textsubscript{4}OC\textsubscript{2}Pyr, retaining just over 99% of the CE for more than 300 cycles. After 500 cycles, the cells retained 95% of the CE and 86% of its initial discharge capacity. Further decrease of chaotropicity of the GILs used in the WISEs leads to further decrease in CE and specific capacity. The batteries with electrolytes based on C\textsubscript{4}Pyr display a final 90% CE and 82% initial discharging capacity. The inclusion of cosmotropic types of cations (HOC\textsubscript{4}Pyr and HOC\textsubscript{2}OC\textsubscript{2}Pyr) caused a fast decline in the discharge capacity, leading to a decay in battery performance. The batteries with the HOC\textsubscript{2}OC\textsubscript{2}Pyr electrolyte faded away after only 100 cycles, with an almost linear decrease of the specific discharge capacity with cycle number. Slightly better performance was recorded for the formulation of WISEs with the less cosmotropic HOC\textsubscript{2}Pyr, which rendered a CE of 80% after 200 cycles, followed by a significant loss of the initial discharge capacity.

The rate performance for battery cells based on GIL-enriched WISEs is presented in Figure 6d. For each discharge rate, 10 cycles were performed starting with the slowest discharge rate that allows 2 h until the full discharge of the battery (C/2), followed by 1C, 2C, 5C, 10C, and 20C, while in the last 10 cycles, battery cells returned to a C/2 rate. The electrolytes with chaotropic GILs outperform electrolytes based on cosmotropic GILs with respect to this parameter as well. Again, batteries containing C\textsubscript{2}Pyr show the best results, being the most resilient with close to 100% of retained initial discharge capacity after changing the discharge rate from 20C back to C/2. The least viscous electrolyte, based on C\textsubscript{4}OC\textsubscript{2}Pyr, gave cells outperformed by those containing C\textsubscript{2}Pyr, suggesting that the lowest viscosity and highest conductivity in the formulation of WISEs are important factors but not the only determining factors for good rate performance. Indeed, cells based on C\textsubscript{4}OC\textsubscript{2}Pyr show better robustness at larger C-rates, as compared to those based on the more viscous C\textsubscript{2}Pyr and WISEs containing more cosmotropic GILs. However, the performance is similar to that of batteries based on C\textsubscript{2}Pyr.

The presence of carboxyl-based groups in the GIL structure results in malfunction for all batteries investigated already during the initial charging cycle involving the LTO/LMO electrode system. From the perspective of the solvation structure of the bulk electrolytes, all electrolytes with cosmotropic GILs have an anion-rich solvation shell of Li\textsuperscript{+}, with a significantly lower number of water-coordinated to the Li\textsuperscript{+} ions, as compared to electrolytes with chaotropic GILs. The presence of water-attracting groups in the GIL-cation structure clearly causes a significant amount of water molecules to be trapped within the nanodomains formed by the GIL cations, and this has consequences for the durability during battery cycling. On the other hand, electrolytes with chaotropic GIL cations have water-rich Li\textsuperscript{+} solvation shells with,

![Figure 7. Battery performance of LTO (mass loading 2.4 mg)/LMO (mass loading 3.0 mg) cells based on the GIL-containing electrolytes. (a) Specific discharge capacity, (b) Coulombic efficiency, (c) voltage profiles for the 10th cycle at 1C-rate, and (d) rate performance. Black: Li[TFSI]\textsubscript{2}; (C\textsubscript{2}Pyr–C\textsubscript{4}OC\textsubscript{2}–C\textsubscript{2}Pyr)[TFSI]\textsubscript{1.5}H\textsubscript{2}O; red: Li[TFSI]\textsubscript{1.5}:(C\textsubscript{2}Pyr–C\textsubscript{4}OC\textsubscript{2}–C\textsubscript{2}Pyr)[TFSI]\textsubscript{1.5}H\textsubscript{2}O; blue: Li[TFSI]\textsubscript{1.5}:(C\textsubscript{4}OC\textsubscript{2}Pyr–C\textsubscript{4}OC\textsubscript{2}–C\textsubscript{2}OC\textsubscript{2}Pyr)[TFSI]\textsubscript{2}H\textsubscript{2}O; green: Li[TFSI]:(HO\textsubscript{2}OC\textsubscript{OC}Pyr–C\textsubscript{4}OC\textsubscript{2}–HO\textsubscript{2}OC\textsubscript{OC}Pyr)[TFSI]\textsubscript{1}H\textsubscript{2}O; cyan: Li[TFSI]:(HO\textsubscript{2}OC\textsubscript{OC}Pyr–C\textsubscript{4}OC\textsubscript{2}–HO\textsubscript{2}OC\textsubscript{OC}Pyr)[TFSI]\textsubscript{1}H\textsubscript{2}O; magenta: Li[TFSI]:(HO\textsubscript{2}OC\textsubscript{OC}Pyr–C\textsubscript{4}OC\textsubscript{2}–HO\textsubscript{2}OC\textsubscript{OC}Pyr)[TFSI]\textsubscript{1}H\textsubscript{2}O.](Image 79x404 to 528x740)
statistically, about 1 molecule of water per lithium ion, more than electrolytes with cosmotropic GILs. The two electrolytes that combine the lowest percentage of “free” water molecules and the highest CN for the Li-ion-water interaction in the bulk electrolyte (C₅Pyr and C₆OC₅Pyr) also display the widest ESW and the best overall battery performance. However, we do take caution in correlating these findings to more quantitative kinetics interpretations. We hypothesize that the widening of the ESW and promising performance of our systems are primarily caused by the different chaotropic effects of our GIL cations. While we believe that chaotropicity is the main cause of the better performance observed in our systems, studying Li⁺ dynamics in the bulk and at the interfaces in the GIL + Li[TFSI] mixtures could provide additional insights into any entropic effects and will be studied advancing the project (preliminary results from DFT computations are included in the Supporting Information Material).

A postmortem analysis of cycled LTO electrodes was performed by FTIR spectroscopy and XAS (Figure 8). FTIR spectra show similar peaks around 1134 and 1054 cm⁻¹ for all electrodes originating from the GIL-based battery cells. These bands can be ascribed to S=O stretching or carbonyl stretching modes, suggesting the possible decomposition of [TFSI]⁻ giving rise to the formation of a sulfur-containing interphase, as has been proposed by Yamada and co-workers. A significant difference between spectra from cells containing chaotropic and cosmotropic electrolytes was observed in the range of 1570–1650 cm⁻¹. Two peaks from the electrodes being exposed to electrolytes with GILs containing −OH or −COOH substituents appear in the 1570–1650 cm⁻¹ range, while these bands are absent in WISEs containing C₅Pyr, C₆Pyr, and C₆OC₅Pyr. These peaks can be assigned to C=O, C=C, and amine bond stretching vibration modes, instead suggesting a decomposition of the GIL cations. The proposed LiF formation was followed by XAS investigations of the F K-edge. A fluorine-containing absorption peak could be observed from all electrode surfaces of successfully cycled cells, with a broader peak appearance (690–700 eV) for the electrodes exposed to electrolytes containing HOC₅Pyr and HOC₆OC₅Pyr. However, we cannot exclude the contribution from the decomposition of the remaining Li[TFSI] salt by radiation damage as has been reported previously. Therefore, the obtained results need to be verified by further experiments. An interesting feature is observed in the systems originating from cosmotropic GILs and C₆Pyr manifested by an additional peak close to 710 eV, which is characteristic of iron. This observation could suggest potential corrosion of the stainless-steel current collectors in GIL-enriched WISEs, which needs to be seriously considered in attempts to further increase Li-salt concentrations.

**CONCLUSIONS**

The current study demonstrated the possibility of influencing the electrolyte water structure by adding different GILs to WISEs. The overall conclusion is that the Li⁺ solvation shell is water-rich in WISEs containing chaotropic GILs. Instead, anion-rich Li⁺ solvation shells are predominant in WISEs enriched with cosmotropic GILs. Weak water clustering is observed in the electrolyte systems with C₅Pyr and HOC₅Pyr, while in other systems, it is absent.

The addition of GILs to the WISE systems increases the electrochemical stability to almost 4 V. The stability window is significantly increased by the addition of chaotropic GILs. Only electrolytes containing HOOCC₅Pyr were not compatible with LTO/LMO-based full battery cells. The best cells, containing C₅Pyr, retained 99% of its CE after 500 cycles, associated with a final specific discharge capacity of 85 mAh g⁻¹. Based on all results from the electrochemical characterization, we conclude that a water-rich Li⁺ solvation shell (i.e., in the presence of chaotropic GILs) significantly contributes to excellent performance and long-term stability of LTO/LMO-based full battery cells.

The fine-tuning of the Li⁺ solvation shell and water structure by the addition of chaotropic cations to the structure of ionic liquids qualifies as a promising strategy for generating more stable and effective aqueous Li-ion batteries. Since GILs offer a vast design space, we are planning to employ automated combinatorial screening methods to accelerate the identification of novel effective, secure, and environmentally friendly, water-based electrolytes.

**ASSOCIATED CONTENT**

Schematic representation of synthetic pathway; NMR, FTIR, Raman, and MS spectra of synthesized GILs; experimental results of conductivity and viscosity of GIL-enriched electrolytes; snapshots of MD simulations; and voltage profiles of each electrolyte at selected cycles along with standard deviations (PDF)

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