

Water-in-Bisalt Electrolyte with Record Salt Concentration and Widened Electrochemical Stability Window

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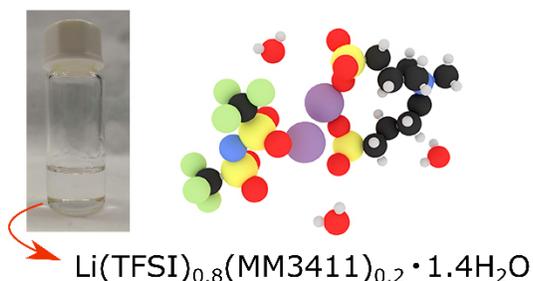
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ABSTRACT: Water-in-salt and water-in-bi-salt electrolytes have attracted much attention recently due to their expanded electrochemical stability windows. The concentration limit of such electrolytes is constrained by the solubility of the lithium salts employed, *ca.* 21 m (mol kg⁻¹) for LiTFSI (lithium bis(trifluoromethanesulfonyl)imide). By adding a second lithium salt, the total salt concentration can be increased, but the hydrogen evolution keeps limiting the application of such systems in batteries with low potential anodes. Herein we report a water-in-bi-salt electrolyte with a record salt concentration (31.4 m LiTFSI + 7.9 m Li[N(CH₃)₂((CH₂)₃SO₃)((CH₂)₄SO₃)]) in which the bulky anion completely prevents the crystallization even at such low water contents. Although the hydrogen evolution reaction is not completely suppressed, the expanded electrochemical stability window allows for low potential reactions such as aluminum-lithium alloying. The high salt concentration favors the formation of a suitable passivation layer that can be further engineered by modifying the anion structure.

TOC GRAPHICS



Aqueous highly concentrated electrolytes have attracted much attention after reports of so-called “water-in-salt” electrolytes (WiSEs) which enabled $\text{LiMn}_2\text{O}_4/\text{Mo}_6\text{S}_8$ lithium-ion battery (LIB) cells to deliver an output voltage of 2.0 V.¹ The electrochemical stability window (ESW) of this kind of systems was further expanded by adding a second Li-salt, creating “water-in-bi-salt” (WiBS) electrolytes which allowed the use of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode.^{2,3} Two main mechanisms have been suggested to be responsible for the enhanced stability of these aqueous electrolytes. The first being reduction or elimination of “free” water molecules, hence reducing their activity, and the second formation of solid electrolyte interphase (SEI) composed primarily of inorganic anion decomposition products.⁴

Very recent studies, however, suggest that the strong Lewis acidity of Li^+ promotes the hydrogen evolution reaction (HER) at the anode, especially at high salt concentrations.⁵ If the high salt concentrations of WiSEs and WiBS electrolytes do not intrinsically hamper the HER, more attention must be given to the SEI formation and its influence in the overall ESW. Indeed, several homogeneous⁶ and heterogeneous⁷ organic additives have been applied to favor the formation of a stable and hydrophobic SEI capable of blocking the HER. Also the bis(trifluoromethanesulfonyl)imide ($[\text{N}(\text{SO}_2\text{C}_2\text{F}_5)_2]^-$, TFSI) anion, ubiquitous in WiSEs and WiBS electrolytes, decomposes at the lithium metal surface creating a rudimentary SEI, but which does not support prolonged cell cycling.⁸ Nevertheless, anion decomposition is considered to be a promising route to engineer the SEIs from highly concentrated aqueous electrolytes. As a result, new anions should be explored for this kind of electrolytes, possibly also offering other advantages.

With this in mind, the standard LiTFSI salt and the previously reported LiMM3411 salt (Figure 1)⁹⁻¹¹ were combined to create a WiBS electrolyte of extremely high lithium salt concentration: 31.4 m (mol kg⁻¹) LiTFSI + 7.9 m LiMM3411. This is the first example of using a large non-fluorinated anion for WiSEs and WiBS electrolytes. So far, only large anions, such as TFSI, trifluoromethanesulfonyl (CF₃SO₃⁻, triflate or Tf), bis(pentafluoroethanesulfonyl)imide ([N(SO₂C₂F₅)₂]⁻, BETI or PFSI), and bis(fluorosulfonyl)imide (N(SO₂F)₂⁻, FSI) and its derivatives¹² have been employed. Furthermore, the combined Li-salt concentration here presented surpasses all previous WiBS electrolytes reported – up to now the record was 21 m LiTFSI + 7 m LiTf.²

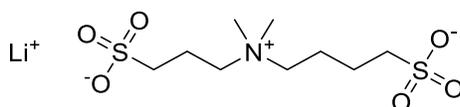


Figure 1. Chemical structure of the lithium propylsulfonate-butylsulfonate-dimethyl-amine (LiMM3411) salt.

The very low water content of the presented WiBS electrolyte, corresponding to a mere 1.4 H₂O molecules per Li⁺, was confirmed by step-wise isothermal thermogravimetric analysis; the weight loss at the end of the second isotherm at 200 °C corresponds to 8.0 wt% (Figure 2).

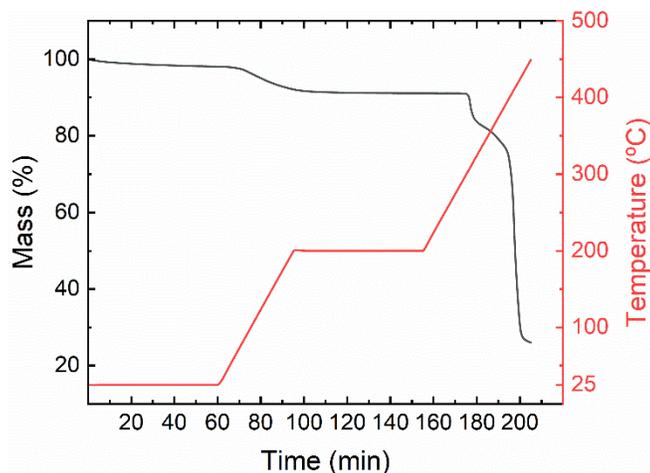


Figure 2. Step-wise isothermal thermogravimetric analysis of the WiBS electrolyte.

With a glass transition temperature of *ca.* -58°C (Figure 3a), the WiBS electrolyte is highly viscous at room temperature (without any crystallization observed for weeks). Yet, as compared to the dry system,⁹ the ionic conductivity is much higher, reaching *ca.* 0.33 mS cm^{-1} at 25°C and 2.83 mS cm^{-1} at 80°C (Figure 3b). While this still is a magnitude lower than for the standard LP30 electrolyte (12 mS cm^{-1} at 25°C),¹³ it falls in the reported range for previous WiSE and WiBS electrolytes ($< 1\text{ mS cm}^{-1}$). In all cases, the higher lithium concentration, lower flammability, lower fluorine content, and being water-based could render these electrolytes attractive in practice.

Previous reports have analyzed the temperature dependence of the ionic conductivity for WiSE and WiBS electrolytes in terms of Arrhenius^{12,14} or Vogel-Fulcher-Tammann (VFT)¹⁵ behavior. Both the “dry” system and the WiBS electrolyte presented here show clear VFT behavior (Figure 3b, Table 1). This suggests ionic mobility dominated by the segmental motion of the large and bulky anions, rather than vehicular motion or simple ion hopping. This is similar to the conduction mechanism of solid polymer electrolytes.^{16,17}

The significant decreases in both the Vogel temperature (T_0) and the apparent activation energy (E_{σ}) upon the addition of water, correlate to the lower glass transition temperature. This is also

often observed in polymer electrolytes plasticized by a low molecular weight solvent, which promotes the segmental motion and ion pair dissociation.¹⁶ It is also reassuring that the Vogel temperature from the conductivity data fitting (-100 °C) is close to the usual rule of thumb $T_g-50 = -108$ °C from the DSC data.

Borodin *et al.*¹⁴ reported a lithium transference number t_{Li^+} of *ca.* 0.7 by using pfg-NMR, much higher than for conventional electrolytes (0.2-0.4). However, it is still unclear if protons contribute to the ionic conductivity, due to that the extreme ionic concentration and association in WiSE and WiBS electrolytes might influence the water and proton dynamics.¹⁸

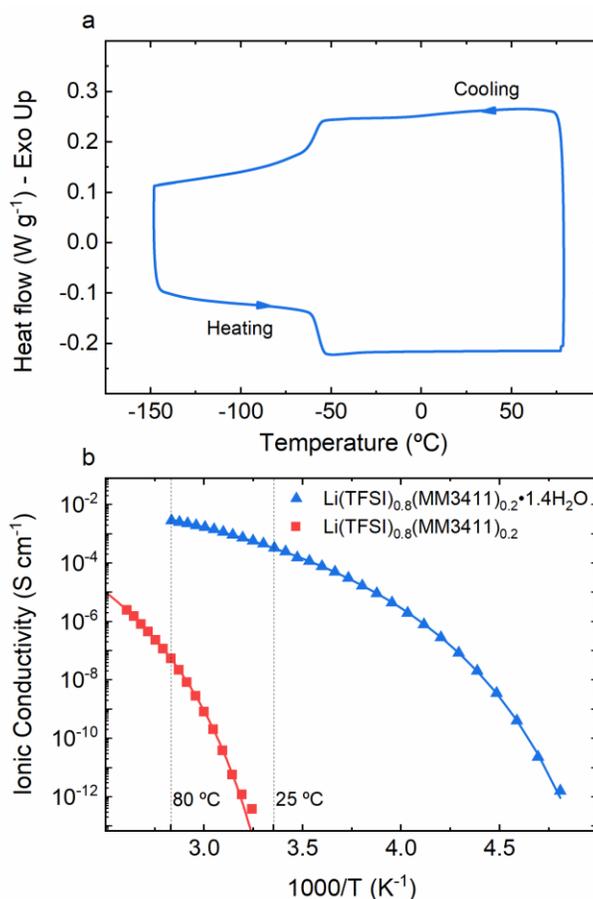


Figure 3. a) Differential scanning calorimetry (DSC) heating and cooling traces for the WiBS electrolyte and b) Arrhenius plot of ionic conductivity (heating) for the “dry” system and the WiBS electrolyte.

Table 1. VFT fitting parameters for the “dry” system and the WiBS electrolyte.

System	$\ln(A)$	E_{σ} [J/mol]	T_0 [°C]
Li(TFSD)_{0.8}(MM3411)_{0.2}	2.7 ± 0.2	195.4 ± 4.2	18.5 ± 0.9
Li(TFSD)_{0.8}(MM3411)_{0.2}•1.4H₂O	2.5 ± 0.1	116.0 ± 1.1	-100.1 ± 0.4

The stability of the WiBS electrolyte at low potentials is not enough for direct use with lithium metal as the anode. When immersing a piece of lithium metal in the WiBS electrolyte, it created a subtle bubbling. However, as the properties of the SEI layer depend greatly on its formation mechanisms,¹⁹ a slow decrease in potential at the electrode may favor the decomposition of the anions and the formation of a suitable SEI before the potential for the HER is reached.

The ESW using stainless steel (SS) working electrodes (WEs) provides an anodic oxidation limit of no less than *ca.* 5.1 V vs. Li⁺/Li^o (Figure 4), beyond, but close to, previous WiSE and WiBS electrolytes at 4.9 – 5.0 V.¹⁻³ Additional to water decomposition and anion oxidation occurs. The two small reduction peaks at 4.1 and 3.6 V are due to the reduction of the decomposition products *i.e.* adsorbed oxygen and anion oxidation by-products, produced through the oxidation process >5 V (Figure 4a, inset). This was confirmed by performing cyclic voltammetry with lower cut-off potentials *i.e.* <5 V (Figure 1S) and as expected, at cut-off potentials of 3.8 and 4.1 V, where no decomposition or oxidation occur, the reduction peaks are absent. However, a cut-off potential at 4.8 V, where the oxidative decomposition starts, a single reduction peak appears at 3.7 V, which implies the multistep nature of the decomposition process. For the cathodic reduction limit, a major peak is centered at 1.6 V, with an onset already at *ca.* 2.2 V, which corresponds to the HER on the surface of the SS WE. This is in agreement with the literature for WiSE and WiBS electrolytes.^{1,2}

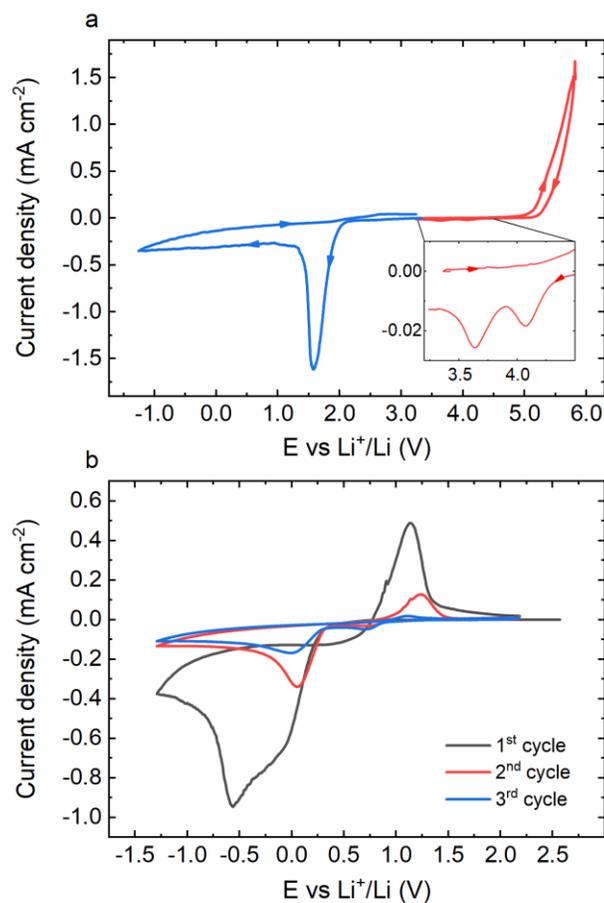


Figure 4. Electrochemical behavior of the WiBS electrolyte. (a) Cathodic and anodic stabilities of the WiBS electrolyte using a SS WE, and (b) Cycling behavior of an aluminum WE in the WiBS electrolyte.

Using an aluminum WE extended the cathodic limit as was previously reported.³ The Al electrodes used are monolithic metal films and are thus not optimized for repetitive cycling/alloying – the huge volume expansion upon lithiation cannot be accommodated. Hence, the problems of the alloying/de-alloying process observed originate mainly in the electrode, while the WiBS electrolyte fundamentally offers a wide enough electrochemical stability window to allow for the alloying reaction, as shown by the de-alloying peak at *ca.* 1 V *vs.* Li⁺/Li⁰ in the reversed direction scan.²⁰ This is the first time that such a low potential reaction has been reported

using an aqueous electrolyte. Although it is likely that Li is alloying upon reduction, we cannot attribute the intense reduction peak below 0 V vs. $\text{Li}^+/\text{Li}^\circ$ entirely to this process as the “de-alloying” peak accounts for <15% of the current consumed during reduction. The rest is believed to be due to the HER and to anion decomposition.

The subsequent cycles show a substantial decrease in the current density as the anions decompose and passivate the surface, but the created passivation layer at the WE is not sufficiently stable to sustain continuous cycling or to completely prevent the HER. However, we do believe that the mixed anion concept used here may be applied in the future to enable a stable SEI layer.

The key characteristic of the LiMM3411 salt is its capacity to effectively prevent the crystallization of LiTFSI, allowing the preparation of the present WiBS electrolytes. We have previously shown⁹ that other related anions also share this property and thus, may be applied to produce WiBS electrolytes. Even further, the basic design of this anion family allows for facile modification of its different side-chains to produce different decomposition products at the electrode surface. Hence our partly novel WiBS electrolyte chemistry opens for (stable) SEI formation and engineering at different cathodic potentials and with different compositions. This might also be a function of controlled cell cycling.⁸ Even anodes such as Sn (0.2 - 1.0 V vs. $\text{Li}^+/\text{Li}^\circ$)²¹ or graphite (0.1 - 0.2 V vs. $\text{Li}^+/\text{Li}^\circ$) might be feasible to use.

Additionally, at the very low $\text{H}_2\text{O}/\text{Li}$ ratio of 1.4, the water can be seen merely as a plasticizer to the “dry” system – in analogy with the “polymer-in-salt”²² and “IL-in-salt”²³ electrolyte concepts. Given this, we also question the “branding” and uniqueness of these aqueous electrolytes – most of the material in this kind of electrolytes is anyhow salt – and hence other plasticizing solvents, without the risk of any HER, might also be tractable.

EXPERIMENTAL METHODS

LiTFSI was bought from Solvionic (99+%) while LiMM3411 was synthesized as described elsewhere.⁹ Both salts were dried overnight under vacuum before use. The WiBS electrolyte was prepared by first mixing 412.7 mg (1.438 mmol) of LiTFSI and 111.1 g (0.3595 mmol) of LiMM3411 in 4 mL of MilliQ water and stirring until a clear solution was obtained. Second, the solution was dried at 90 °C in a vacuum oven (5×10^{-3} mbar) for at least two days obtaining a glassy solid. The water content was <0.2 wt% as determined by KF Coulometric titration. Finally, 45.3 mg of MilliQ water (2.514 mmol; 1.4 H₂O molecules per Li⁺) were added, and the product was let to homogenize at 50 °C in a closed vial to avoid evaporation.

Thermogravimetric analysis (TGA) was performed on *ca.* 10 mg of electrolyte, using aluminum crucibles and an atmosphere of nitrogen gas (22 mL/min), following the temperature ramp shown in Figure 2. Differential scanning calorimetry (DSC) measurements were carried out in sealed aluminum pans at 10 K/min using *ca.* 10 mg of electrolyte and employing an empty aluminum pan as reference.

For the ion conductivity measurements, a Teflon spacer with an inner diameter of 4 mm and 1 mm thickness was filled with sample and sandwiched between two stainless steel (SS) discs. A Novocontrol broadband dielectric spectrometer equipped with an Alpha-S high-resolution dielectric analyzer was employed in the frequency range between 10^{-2} and 10^7 Hz.

The electrochemical stability window (ESW) was determined by cyclic voltammetry (CV) (5 mV/s) in a three-electrode Swagelok cell, using SS as CE and SS or aluminum as WE. A Ag/Ag⁺ pseudo-reference electrode was prepared by electrochemically depositing a silver chloride layer on top of silver wire. The pseudo-reference electrode was calibrated against potassium ferricyanide K₃[Fe(CN)₆] as a redox standard – as ferrocene is not soluble in the WiBS electrolyte. K₃[Fe(CN)₆]

was dissolved in the prepared WiBS electrolyte (10 mmol/kg) overnight, but was not completely dissolved although the electrolyte turned yellow – and this means that the WiBS electrolyte was saturated with $\text{K}_3[\text{Fe}(\text{CN})_6]$. The redox potential was measured by differential pulse voltammetry as it is more sensitive than standard cyclic voltammetry at very low analyte concentrations. The potential of $\text{K}_3[\text{Fe}(\text{CN})_6]$ vs. the Ag/Ag^+ pseudo-reference electrode was compared to its redox potential vs. the standard Ag/AgCl reference electrode, which is shifted by *ca.* 60 mV. The electrochemical potential data were subsequently converted to the Li/Li^+ scale by adding 3.24 V.

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Notes

The authors declare no competing financial interest.

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