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# Localized Water-In-Salt Electrolyte for Aqueous Lithium-Ion Batteries

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Abstract: Water-in-salt (WIS) electrolytes using super-concentrated organic lithium (Li) salts are of interest for aqueous Liion batteries. However, the high salt cost, high viscosity, poor wettability, and environmental hazards remain a great challenge. Herein, we present a localized water-in-salt (LWIS) electrolyte based on low-cost lithium nitrate (LiNO<sub>3</sub>) salt and 1,5-pentanediol (PD) as inert diluent. The addition of PD maintains the solvation structure of the WIS electrolyte, improves the electrolyte stability via hydrogen-bonding interactions with water and  $NO_3^-$  molecules, and reduces the total salt concentration. By in situ gelling the LWIS electrolyte with tetraethylene glycol diacrylate (TEGDA) monomer, the electrolyte stability window can be further expanded to 3.0 V. The as-developed  $Mo_6S_8$  LWIS gel electrolyte LiMn<sub>2</sub>O<sub>4</sub> (LMO) batteries delivered outstanding cycling performance with an average Coulombic efficiency of 98.53% after 250 cycles at 1 C.

#### Introduction

Rechargeable lithium (Li)-ion batteries have dominated the energy storage market from portable electronics to electric vehicles in the past two decades owing to their high energy density and long cycle life.<sup>[1]</sup> However, the prevailing application of non-aqueous electrolytes based on flammable and toxic organic solvents (e.g. carbonates and ethers) in Liion batteries has triggered severe safety hazards, including fire, explosion and harmful leakage.<sup>[2]</sup> Replacing these nonaqueous electrolytes with aqueous electrolytes not only can efficiently eliminate the safety issues of Li-ion batteries, but also reduce the battery manufacturing costs due to the nonreliance on ultra-dry assembly facilities.<sup>[3]</sup> Nonetheless, the

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electrochemical stability window (<2 V) of traditional dilute aqueous electrolytes is too narrow to support high-energy electrochemical couples, which is a major bottleneck for the development of aqueous Li-ion batteries.<sup>[4]</sup>

In 2015, water-in-salt (WIS) electrolytes were developed to unprecedentedly expand the electrochemical window of aqueous electrolytes, in which the dissolved Li salts far outnumber water molecules by both volume and mass.<sup>[5]</sup> A protective solid electrolyte interphase (SEI) was constructed on the anode surface in a 21 m (mol  $kg^{-1}_{solvent}$ ) lithium bis(trifluoromethane)sulfonimide (LiTFSI) aqueous electrolyte which exhibited a 3.0 V-wide stability window. Other organic Li salts, for example, lithium bis(pentafluoroethanesulfonyl)imide,<sup>[6]</sup> lithium trifluoromethane sulfonate<sup>[7]</sup> and lithium (trifluoromethanesulfonyl)(pentafluoroethanesulfonyl)imide,<sup>[8]</sup> have been introduced to the WIS electrolytes to further improve the saturation limitation of salts and thus further widen the electrochemical window. In addition, a cosolvent (e.g. ether<sup>[9]</sup> and carbonate<sup>[10]</sup>) was also introduced into WIS electrolyte to promote the SEI formation. However, the super-high concentration of these toxic Li salts in WIS electrolytes raises new concerns of high cost, high viscosity, poor wettability toward electrodes, and environmental hazards.<sup>[11]</sup>

To overcome above intrinsic challenges of WIS electrolytes, herein, we 1) used inexpensive and eco-friendly inorganic Li salts to replace the toxic and costly organic Li salts, and 2) lowered the electrolyte salt concentration by diluting the WIS electrolytes with an inert solvent (called a diluent) that dissolves the water but not the inorganic salt. Therefore, the diluent does not alter the salt solvation structure of WIS electrolytes forming a localized water-in-salt (LWIS) electrolyte. Since the organic diluent has a much wider electrochemical stability window than water-in-salt electrolyte, the LWIS are expected to preserve (or even enhance) the electrochemical stability of WIS electrolytes while reducing the salt concentration, decreasing the viscosity and improving the wettability. The salt/diluent configuration for LWIS electrolytes have not been reported to our best knowledge. To demonstrate the concept of LWIS, we used lithium nitrate (LiNO<sub>3</sub>) as Li salt and 1,5-pentanediol (PD) as diluent. The application of PD not only significantly lowers the total Li salt concentration of WIS electrolyte, but also reduces the water reactivity in HER/OER via hydrogen-bonding interactions between PD with water molecules and NO3<sup>-</sup> anions, thus enabling an electrochemical stability window of ca. 2.8 V (partly attributed to the formation of SEI on the anode surface). Furthermore, by in situ polymerizing of tetraethylene glycol diacrylate (TEGDA) monomer in the LWIS electrolyte, the as-prepared aqueous gel electrolyte exhibited

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an enhanced electrolyte stability of ca. 3.0 V without flammability or liquid leakage hazard. The as-developed  $Mo_6S_8$  | LWIS gel electrolyte | LiMn<sub>2</sub>O<sub>4</sub> (LMO) battery showed a high cycling stability with a 98.53 % average Coulombic efficiency at 1 C over 250 cycles. The design principles for LWIS electrolytes reported in this work will boost the future development of high-energy and low-cost aqueous Li-ion batteries.

#### **Results and Discussion**

According to the design concept of LWIS electrolytes, an ideal diluent should simultaneously possess: 1) high miscibility with water; 2) low Li salt solubility; and 3) wider chemical and electrochemical stability with electrodes during the battery operation.<sup>[12]</sup> We compared the miscibility of different solvents with water in a mass ratio 1:1. As shown in Figure 1a, diethylene carbonate (DEC), fluoroethylene carbonate (FEC) and propylene carbonate (PC) formed bi-phasic mixtures with water, while tetraethylene glycol dimethyl ether (TEGDME) formed an emulsion in water. In contrast, ethylene carbonate (EC) and PD can be well-mixed with water without phase separation (Figure 1a), and offer wider electrochemical stability window (4.2 V) than WIS (3.0 V) as shown in Figure S1, which is in the working voltage range of batteries.<sup>[13]</sup> Therefore, EC and PD can act as diluent candidates. Furthermore, the solubilities of LiTFSI as a representative organic Li salt and LiNO<sub>3</sub> as a representative inorganic Li salt in different solvents at 25°C are also presented in Figure 1 b. It should be noted that these solubility values represent the solubility limits of stable supersaturated solutions which were prepared by dissolving the Li salt at 40°C and then cooling down to 25°C. It is seen that LiTFSI delivers high solubility in both water (21 m) and organic diluents (i.e., 8.0 m in EC and 6.5 m in PD). For comparison, inorganic LiNO<sub>3</sub> salt is highly soluble in water (25 m), but has poor solubility in diluents (i.e., 0.87 m in EC and 0.75 m in PD). This solubility difference of inorganic Li salts makes them suitable candidates to develop LWIS electrolytes.<sup>[14]</sup> Moreover, we measured the solubilities of various inorganic Li salts, including lithium chloride (LiCl), lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>), lithium phosphate (Li<sub>3</sub>PO<sub>4</sub>) and lithium acetate (LiAc), in water and PD diluent. As seen from Figure 1c, although all the inorganic Li salts exhibit low solubilities of < 2 m in PD, the water solubility of LiNO<sub>3</sub> (25 m) far exceeds other Li salts (LiCl: 24.1 m; LiAc: 11.1 m; Li<sub>2</sub>SO<sub>4</sub>: 3.2 m; Li<sub>3</sub>PO<sub>4</sub>: 0.2 m). Consequently, LiNO<sub>3</sub> was chosen as the ideal Li salt to form a LWIS electrolyte. The LiNO<sub>3</sub> -based aqueous electrolytes is weakly acidic with pH values comparable to LiTFSI-based electrolytes (Figure S2).

The electrochemical stability windows of the LiNO<sub>3</sub>based LWIS and WIS electrolytes were evaluated by cyclic voltammetry (CV) in a three-electrode cell with titanium (Ti) mesh as working electrode, platinum (Pt) wire as counter electrode and Ag/AgCl as reference electrode. Figure S3 shows the first and second CV curves of the 25 m LiNO<sub>3</sub> in H<sub>2</sub>O WIS electrolyte, 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD (1:1 by mass)



LWIS electrolyte and LWIS gel electrolyte (prepared by in situ polymerizing 6 wt% TEGDA monomer in 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD electrolyte). The electrochemical window values of LWIS and LWIS gel electrolytes from the 2nd CV cycle were obviously larger than those in the 1st cycle, while the electrochemical stability windows showed almost no change during cycling in the 12.5 m and 25 m LiNO3 in H2O electrolytes. This seems to be mainly due to the SEI formation that suppresses the hydrogen evolution reaction (HER) in two LWIS aqueous electrolytes,<sup>[15]</sup> which will be discussed in the following part. The impact of dilutes (EC and PD) on electrochemical stability window of LWIS electrolytes was also investigated. Figure 2 and Figure S4 shows the 2<sup>nd</sup> linear polarization profiles of the electrolytes with and without dilute. The 10.5 m LiTFSI in H<sub>2</sub>O electrolyte exhibited a sta-

b) Solubilities of LiTFSI (blue) and LiNO<sub>3</sub> (pink) in different solvents at 25 °C. c) Solubilities of different Li salts in water (blue) and PD (pink) at 25 °C.

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**Figure 2.** a)–d) 2nd CV curves of (a) 10.5 m LiTFSI in  $H_2O$  and 10.5 m LiTFSI in  $H_2O:EC$ , b) 12.5 m LiNO<sub>3</sub> in  $H_2O$  and 12.5 m LiNO<sub>3</sub> in  $H_2O:EC$ , c) 12.5 m LiNO<sub>3</sub> in  $H_2O$  and 12.5 m LiNO<sub>3</sub> in  $H_2O:PD$ , and d) 12.5 m LiNO<sub>3</sub> in  $H_2O:PD$  and LWIS gel electrolyte couples at 0.1 mVs<sup>-1</sup>. e)–h) The corresponding hypothetical diagrams of solvation structures for the electrolytes.

bility window of 2.1 V (Figure 2a). In this electrolyte, Li ions are solvated by water molecules to form solvation sheaths, meanwhile anions are mostly excluded from these solvation sheaths (Figure 2e, left).<sup>[5,16]</sup> After adding 50 wt % EC into the solvent, the solvation structure of the electrolyte did not dramatically change, except for the appearance of EC molecules with high solubility of LiTFSI in the solvation sheaths (Figure 2e, right).<sup>[10]</sup> The 10.5 m LiTFSI in H<sub>2</sub>O: EC (1:1 by mass) electrolyte delivered a stability window of 2.3 V (Figure 2a), which is still much lower than the 3.0 V-wide window of the saturated 21 m LiTFSI in H<sub>2</sub>O electrolyte.<sup>[5]</sup> This is due to the huge amount of free water molecules outside of the solvation sheaths that trigger preferential hydrogen evolution. In sharp contrast, when EC was introduced in the 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte, the electrochemical window was dramatically widened from 1.9 V to 2.7 V (Figure 2b), which is very close to that of the saturated 25 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte (2.6 V, Figure S5). This is because in the as-developed EC-based LWIS electrolyte (i.e., 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: EC, 1:1 by mass), the EC molecules as diluent do not participate in the solvation sheaths due to the low LiNO<sub>3</sub> solubility in EC.<sup>[17]</sup> The increased LiNO<sub>3</sub>: H<sub>2</sub>O ratio in the ECbased LWIS electrolyte leads to an enlarged percentage of water molecules that are coordinated with Li<sup>+</sup>, significantly decreasing the reactivity of water molecules in HER/OER. Furthermore, NO<sub>3</sub><sup>-</sup> anions appear in the primary solvation sheaths of Li<sup>+</sup> to generate ion aggregates, reducing the water content in the primary solvation sheaths (Figure 2 f, right). Likewise, the addition of PD diluent could form a LWIS electrolyte (i.e., 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: PD, 1:1 by mass) with a similar solvation structure. However, as a protic solvent, PD can form numerous hydrogen bonds between its hydroxyl groups and the water molecules as well as NO<sub>3</sub><sup>-</sup> anions, forming polymer-like chains consisting with solvation sheaths (Figure 2g, right).<sup>[18]</sup> The reactivity of water solvent in HER/OER was thereby further reduced and the electrochemical stability window was extended to 2.9 V (Figure 2c and Figure S6). For the LWIS gel electrolyte, the fluidity of electrolyte was eliminated meanwhile additional hydrogen bonds were formed between the polymer matrix and water molecules (Figure 2h, right), thus leading to a stability window as wide as 3.0 V (Figure 2d and Figure S7). This high electrolyte stability is eligible to fulfill the requirements of the electrochemical redox couple of Mo<sub>6</sub>S<sub>8</sub> anode and LMO cathode. Therefore 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD gel electrolytes were selected for further investigation.

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Molecular dynamic (MD) simulations were conducted to investigate the solvation structures of 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD LWIS gel electrolytes, and compared it with two baseline electrolytes (12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O and 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD; Figure S8). As shown in Figure 3a, in the 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte, Li ions are mainly solvated with 4 water molecules to form a primary solvation sheath. Meanwhile, around 70% of water molecules are coordinated with Li<sup>+</sup> ions, while others interact with each other via hydrogen bonds (Figure 3d). Such a huge amount of uncoordinated water molecules triggers significant HER reaction on the anode, which severely deteriorates the performance of the batteries.<sup>[19]</sup> Moreover, most NO<sub>3</sub><sup>-</sup> ions are randomly distributed among the water molecules without any coordination with Li<sup>+</sup> ions (Figure 3a). When PD is introduced into the electrolyte, large amount of Li<sup>+</sup> ions prefer to partially share

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*Figure 3.* MD simulations of aqueous electrolytes. a)–c) Snapshots of the local structures of a) 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O, b) 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: PD, and c) LWIS gel electrolytes obtained via MD simulation after 20 ns at 298 K. d) The hydrogen bonds and the percentage of water molecules coordinated with Li<sup>+</sup> for three aqueous electrolyte samples at 20 ns.

the primary water sheaths with the neighbouring Li<sup>+</sup> ions, and the Li<sup>+</sup> primary solvation shells are aggregated together to from polymer-like chain due to the hydrogen-bonding linkage of PD (Figure 3b). In such 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: PD LWIS electrolyte, the amount of water molecules coordinated with Li<sup>+</sup> dramatically increase to 94.3%, leading to a sharp reduction of the reactivity in HER/OER for water molecules (Figure 3 d). In particular, the number of  $NO_3^-$  anions observed in each Li<sup>+</sup> primary solvation sheath rises from 0.89 to 1.55 after the introduction of PD. This reduces the water number in each Li<sup>+</sup> primary solvation sheath, which further extends the electrochemical window (Figure S5). When gelling the 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD electrolyte with TEGDA monomer, the Li<sup>+</sup>-H<sub>2</sub>O complexes delivers a longrange aggregation. It indicates that most water molecules are immobilized by localized concentrated LiNO<sub>3</sub> salt and the polymerized TEGDA matrix (Figure 3c). Furthermore, as shown in Figure 3d, the hydrogen bonds of 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O solution are ca. 1.2 per water molecule, which significantly increases to ca. 1.25 and 1.35 with the addition of PD and polymer matrix, respectively. This is mainly due to the formation of hydrogen bonds between the water molecules and  $NO_3^{-}$  anions in the electrolyte and the hydroxyl groups in the PD (Figure S9) as well as the ether groups in the polymerized TEGDA. Such water/NO<sub>3</sub><sup>-</sup>-PD and water-polymerized TEGDA interactions can disturb the water hydrogen bond network and further decrease the reactivity of water solvent in HER/OER, thereby effectively inhibiting the electrolyte decomposition.<sup>[20]</sup>

Figure 4a exhibits the polymerization mechanism of TEGDA monomer in the LWIS electrolyte. The primary radicals derived from the ultraviolet light (UV)-irradiation of 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) photoinitiator attack the C=C bonds of the monomer to generate free radicals. Subsequently, a chain growth reaction occurs through sequentially adding TEGDA monomer to the radical ends on the initiated monomer. Finally, a three-dimensional polymerized TEGDA network is constructed in LWIS electrolyte, and a gel electrolyte is thereby in situ obtained. As shown in the right of Figure 4a, the as-prepared LWIS gel electrolyte presents an appearance of a free-standing transparent film, which can maintain its integrity under the pressure of a 100 g weight (Figure S10). Figure 4b shows the Fourier-transform infrared (FTIR) spectra of the TEGDA monomer and polymer matrix of LWIS gel electrolyte. The peaks at ca. 1245 cm<sup>-1</sup> (C-O antisymmetric stretching), ca. 1450 cm<sup>-1</sup> and ca. 1390 cm<sup>-1</sup> (CH<sub>2</sub> bending) and ca. 1720 cm<sup>-1</sup> (C=O stretching) appear in the spectrum of TEGDA

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**Figure 4.** a) In situ polymerization mechanism of the TEGDA monomer in the presence of LWIS electrolyte. An optical image of an as-prepared LWIS gel electrolyte membrane is shown in the right. b) FTIR spectra of TEGDA monomer and the polymer matrix of LWIS gel electrolyte. c) Raman spectra of pure water and 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O, 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: PD and LWIS gel electrolytes. d) Ionic conductivities of 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O, 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: PD and LWIS gel electrolytes as a function of temperature. The discrete points represent the experimental data while the solid lines represent VTF fitting results. e) Flammability tests of 1 M LiPF<sub>6</sub> in EC: DEC (left) and LWIS gel (right) electrolytes.

monomer.<sup>[21]</sup> The absorption peak at ca. 1615 cm<sup>-1</sup> corresponding to stretching vibration of C=C bonds disappears after polymerization, confirming a successful in situ gelation of the LWIS gel electrolyte. Raman spectroscopy was employed to detect the O-H stretching vibration in different electrolytes. As shown in Figure 4c, the O-H stretching vibration of pure water displays a broad band centered around 3320 cm<sup>-1</sup>, which is attributed to the different hydrogen-bonding environment of water molecules.<sup>[3]</sup> The intensity of this band gradually shrinks in the spectra of 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O and 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD electrolytes, indicating that the Li<sup>+</sup>-H<sub>2</sub>O coordination breaks the hydrogen-bonding structure of water. The LWIS gel electrolyte exhibits a small hump at ca. 3480 cm<sup>-1</sup> in the Raman spectrum, which demonstrates that the free water population is dramatically diminished in this quasi-solid electrolyte. This is well-consistent with the MD simulation results in Figure 3.

The ionic conductivities of the different electrolyte samples were measured by electrochemical impedance spectroscopy (EIS) in a temperature range from 10°C to 80°C. As shown in Figure 4d and Figure S11, the plots of log  $\sigma$  versus  $T^{-1}$  present a non-linear Vogel– Tamman–Fulcher (VTF) relationship as described by the following equation:<sup>[22]</sup>

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$$\sigma = \sigma_0 T^{-\frac{1}{2}} exp(-\frac{E_a}{R(T-T_0)}) \qquad (1)$$

where  $\sigma_0$  is a pre-exponential factor,  $T_0$  is the effective glass transition temperature,  $E_{\rm a}$  is the activation energy and R is the ideal gas constant. The corresponding fitting values and ionic conductivities at 25°C are listed in Table S1. The 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O baseline electrolyte has highest ionconductivity of  $1.16 \times$ ic  $10^{-1}$  S cm<sup>-1</sup> at 25 °C, which is two-time higher than that of 25 m LiNO<sub>3</sub> in H<sub>2</sub>O WIS electrolyte  $(7.38 \times 10^{-2} \, \text{S cm}^{-1})$ . The low ionic conductivity of WIS electrolyte is mainly due to its huge viscosity which blocks ion transport (51 mPas, Figure S12). Moreover, the crystallization of LiNO3-based WIS electrolyte starts at temperature below 25°C, which leads to a sharp decline in ionic conductivity  $1.73 \times$ (from

 $10^{-2}\,S\,cm^{-1}$  at  $20\,{}^{\rm o}C$  to  $1.60\,\times$ 

10<sup>-5</sup> S cm<sup>-1</sup> at 10 °C, Figure S11). The viscosity and crystallization of LiNO<sub>3</sub>-based WIS electrolyte strongly limits its practical application in batteries. After adding 50% PD into 25 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte, the 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD LWIS electrolyte delivered a low viscosity (22 mPas), which is comparable to that of the 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte (10 mPas, Figure S12). The electrolyte crystallization was successfully inhibited in the tested temperature range attributed to the addition of PD. This results in a relatively minimal ionic conductivity change from  $1.99 \times 10^{-2} \,\mathrm{S \, cm^{-1}}$  at 20 °C to  $1.44 \times 10^{-2} \,\text{S}\,\text{cm}^{-1}$  at 10 °C (Figure 4d). After polymerization, the LWIS gel electrolyte still maintains an ionic conductivity of  $1.62 \times 10^{-2} \,\mathrm{S\,cm^{-1}}$  at 25 °C with a low  $E_a$  value of  $2.84 \times$  $10^{-2}$  eV (Figure 4d). This conductivity value is much higher than most of the organic liquid/gel electrolytes, and is sufficient to meet the requirements of Li-ion batteries.<sup>[23]</sup> The LWIS gel electrolyte also exhibits improved electronic

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insulation (Figure S13). Moreover, the thermal safety of LWIS gel electrolyte and conventional 1 M LiPF<sub>6</sub> in ethylene carbonate (EC):diethyl carbonate (DEC) (1:2 by volume) electrolyte was examined via combustion tests. The LWIS gel electrolyte could not be ignited by fire sources (Figure 4e, right and Supporting Video 1), and the weight loss was negligible after aging in open air at 25°C for 4 h (3 wt%, Figure S14). In contrast, the 1 m LiPF<sub>6</sub> in EC:DEC liquid electrolyte was highly flammable (Figure 4e, left and Supporting Video 2), and evaporated quickly at 25°C (96 wt% after 4 h, Figure S14) due to the low boiling points of the organic solvents. The superior thermal stability of the LWIS gel electrolyte facilitates safe operation of Li-ion batteries. Furthermore, the LWIS gel electrolyte can well-fill the pores of the electrodes and keep good interfacial contact with electrodes (Figure S15 and Table S2).

LWIS gel-electrolytes and baseline electrolytes were compared in full cells with  $Mo_6S_8$  anodes and LMO cathodes. CV curves of  $Mo_6S_8$  anode and LMO cathode, and electrochemical stability window are displayed in Figure 5 a. The Li intercalation/de-intercalation redox peaks at about 2.66 V and 3.68 V for  $Mo_6S_8$  and the characteristic redox peaks of LMO at 4.15 and 4.29 V<sup>[5,9]</sup> are within stability window of LWIS gelelectrolytes. However, the redox potential of the  $Mo_6S_8$  anode is lower than the HER onset potential of pure water, 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O and 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O: PD electrolytes (ca. 2.77, 2.70, and 2.27 V vs. Li/Li<sup>+</sup>, respectively, Figure 5b), which triggers water decomposition during the battery cycling and thus reduces the battery reversibility. In contrast, the LWIS gel electrolyte exhibits a 3.0 V-wide electrochemical window with a HER onset potential of 2.20 V vs. Li/Li<sup>+</sup>, enabling the successful operation of the electrochemical redox couple of  $Mo_6S_8$  anode and LMO cathode.

 $Mo_6S_8 \parallel LMO$  full cells with LWIS and LWIS gel electrolytes were cycled at 1 C (1 C =  $122 \text{ mAhg}^{-1}$ , based on the mass of the  $Mo_6S_8$  anode) between 0.5 and 2.3 V (Figure 5c). In the cells using 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O, a cut-off time set as 2 h was applied in the charge process to avoid continuous water decomposition. The cell suffered from severe HER at ca. 2 V in the charging process (the inset of Figure 5 c) due to 1.9 V stability window (Figure 5b), resulting in a low capacity of ca. 25 mAhg<sup>-1</sup> in the subsequent discharge (Figure S16a). When the salt concentration in the aqueous electrolyte was doubled to 25 m, the cell delivered an initial discharge capacity of 71 mAh  $g^{-1}$  with a Coulombic efficiency of 35%. However, the water decomposition during cycling led to a crystallization of the aqueous electrolyte (see inset of Figure S16b and Supporting Video 3), which triggered a rapid capacity fading (34 mAhg<sup>-1</sup> after 10 cycles, Figure S16b). The 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD LWIS electrolyte exhibited an improved cycling performance, compared with the saturated electrolyte in the full cell due to the suppression of electrolyte crystallization (Figure S16c). The LWIS gel electrolyte with an expanded stability window matches well with the electrode couple. As shown in Figure 5d, the cell showed a high initial discharge capacity of  $105 \text{ mAh g}^{-1}$  in the voltage between 0.5 and 2.3 V. The Coulombic efficiency gradually increased to 97.80% after 20 cycles, and maintained an average Coulom-



**Figure 5.** a) CV curves of the  $Mo_6S_8$  and LMO electrodes at  $0.1 \text{ mVs}^{-1}$  obtained with the LWIS gel electrolyte. The electrochemical window of LWIS gel electrolyte is presented for comparison. b) The electrochemical stability windows of different electrolytes and the redox voltages of  $Mo_6S_8$  anode and LMO cathode. c) Charge-discharge curves of  $Mo_6S_8 \parallel$  LMO full cells with 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte (inset) and LWIS gel electrolyte in the 25<sup>th</sup> cycle at 1 C. d) Cycling performance of  $Mo_6S_8 \mid$  LWIS gel electrolyte [LMO full cell at 1 C.

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250 cycles at 1 C (excluding the initial 20 activation cycles, whose low Coulombic efficiency could be due to the breakdown/reconstruction of SEI, irreversible proton co-intercalation in acidic electrolyte, and other complicated side reactions in the initial  $cycles^{[7,10]}$ ). The initial Coulombic efficiencv was 66.15% for the  $Mo_6S_8 \parallel$ LMO cell (Figure 5d). Considering the delithiation/lithiation Coulombic efficiency of the anode was calculated to be 74.71 % based on the CV curve of Mo<sub>6</sub>S<sub>8</sub> without influence of (Figure 5 a), HER around 8.56% of the charge capacity (i.e., the difference in Coulombic efficiency) could be attributed to the HER in the first cycle.<sup>[24]</sup> The Mo<sub>6</sub>S<sub>8</sub> | LWIS gel electrolyte | LMO full cell delivered a capacity retention of 70.0% after 250 cycles at 1 C, demonstrating an inhibited HER and stable electrolyte electrode interfaces. The ca-

bic efficiency of 98.53% over

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pacity fading could be due to the transition metal ion dissolution from cathode and other side reactions (e.g. the thickening of SEI) that consuming the limited Li inventory in the cathode. The rate performance of the cell with LWIS gel electrolyte was presented in Figure S17. The specific discharge capacity reached 103, 87, 75 and 25 mAh  $g^{-1}$  at 0.5 C, 1 C, 2 C and 5 C, respectively (Figure S17b). It is seen that the Coulombic efficiency increased with the increase of current density due to the slower side reaction kinetics at high rates (Figure S17a).<sup>[25]</sup> Moreover, the capacity retention was 97% of the initial value when the current density was reversed back to 0.5 C (Figure S17a). Therefore, this aqueous battery configuration is highly reversible and robust. The excellent electrochemical performance of the LWIS gel electrolytebased aqueous battery can be ascribed to the synergetic effect of PD diluent and TEGDA-based polymer matrix that efficiently reduces the water reactivity in HER/OER, and the formation of protective SEI layer on the anode that further inhibits the interfacial side reactions. The formation of SEI on Mo<sub>6</sub>S<sub>8</sub> anode was confirmed by XPS analysis.

Transmission electron microscopy (TEM) was employed to analyze the surface morphologies of  $Mo_6S_8$  anodes after 20 cycles in different electrolytes. When the anode was cycled in 12.5 m and 25 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte, the Mo<sub>6</sub>S<sub>8</sub> particles maintained fresh surfaces without SEI formation (Figure 6a and Figure S18a). By comparison, SEI layers with

thicknesses of ca. 4 nm and 7 nm were observed on the Mo<sub>6</sub>S<sub>8</sub> surfaces after cycling in 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD electrolyte (Figure S18b) and LWIS gel electrolyte (Figure 6b), respectively. Moreover, these SEIs exhibited a structure consisting of Li<sub>2</sub>O and Li<sub>2</sub>CO<sub>3</sub> crystalline regions dispersed in an amorphous phase (Figure 6b).<sup>[26]</sup> The SEI composition was further investigated by X-ray photoelectron spectroscopy (XPS) depth profiling. For the anode cycled in LWIS gel electrolyte, peaks at about 52.3, 54.5 and 57.2 eV in the Li 1s spectra are assigned to Li<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub> and Li<sub>3</sub>N/LiN<sub>x</sub>O<sub>y</sub> species, respectively (Figure 6e). Meanwhile, in the O 1s spectra, peaks at around 533.8, 532.2, 530.9 and 528.7 eV correspond to  $N_x O_v$ , Li<sub>2</sub>CO<sub>3</sub>, C-O and Li<sub>2</sub>O, respectively (Figure 6g).<sup>[27]</sup> This SEI composition is well consistent with the results of C1s and N 1s spectra (Figure S19).<sup>[28]</sup> Furthermore, the outer layer of the as-formed SEI is rich in Li<sub>2</sub>O, Li<sub>3</sub>N and LiN<sub>x</sub>O<sub>y</sub> while the inner layer mainly consists of Li<sub>2</sub>CO<sub>3</sub> and organic species as illustrated in as Figure 6c. Such an organic/inorganic hybrid SEI not only effectively suppresses HER, but also possesses high strength to maintain its structural integrity. Therefore, the SEI does not break upon cycling and does not expose unpassivated surfaces, thus suppressing the interfacial side reactions (i.e., HER and OER).<sup>[29]</sup> The SEI constructed in 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O:PD electrolyte (Figure S20) exhibited a similar composition compared with that in LWIS gel electrolyte. The inorganic species in SEI could be attributed



**Figure 6.** a),b) TEM images of  $Mo_6S_8$  anodes after 20 cycles in a) 12.5 m LiNO<sub>3</sub> in  $H_2O$  and b) LWIS gel electrolytes. c) Illustration of the SEI composition in the LWIS gel electrolyte. d),e) Li 1s and f),g) O 1s XPS spectra of  $Mo_6S_8$  anode after 20 cycles in d),f) 12.5 m LiNO<sub>3</sub> in  $H_2O$  and e),g) LWIS gel electrolytes.

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to the trace of dissolved N<sub>2</sub>, CO<sub>2</sub> and O<sub>2</sub> gases in PD diluent, since their solubilities in alcohols are much higher than those in water<sup>[30]</sup> and LiNO<sub>3</sub> cannot construct any robust decomposition product layer in aqueous media;<sup>[3]</sup> Meanwhile, the organic species in SEI may be related to the reduction of PDinvolved solvation shell (see Figure S6). For the Mo<sub>6</sub>S<sub>8</sub> anode cycled in 12.5 m LiNO<sub>3</sub> in H<sub>2</sub>O electrolyte, the Li 1s (Figure 6d) and O 1s (Figure 6 f) XPS spectra displayed negligible peak intensities, confirming the SEI-free morphology on this anode. This is because the main SEI components (e.g. Li<sub>2</sub>O, Li<sub>3</sub>N, Li<sub>2</sub>CO<sub>3</sub>) would quickly dissolve or hydrolyze in the water media.<sup>[31]</sup> Therefore, these species can only stably exist as solid deposits on the anode surface in LWIS electrolytes with suppressed water reactivity in HER/OER. It should be noticed that recently researchers revealed that the SEI formed in aqueous electrolytes may be unstable during long cycling and storage for real-world battery application.[11,31,32] Developing electrolyte additives and/or anode surface coating would be an attractive approach to further improve the SEI stability in the future.

## Conclusion

We reported a localized water-in-salt (LWIS) electrolyte with an electrochemical stability window of 2.9 V by using cheap inorganic LiNO<sub>3</sub> salt and 1,5-pentanediol (PD) diluent in aqueous electrolytes. The comprehensive characterizations and theoretical modelling reveal that the PD diluent not only creates a localized saturated solvation structure in the aqueous electrolyte, but also creates strong hydrogen-bonding interactions with water molecules and anions, thus significantly reducing the water reactivity in HER/OER. Furthermore, by in situ gelling the electrolyte with TEGDA monomer to form a leak-free LWIS gel electrolyte, the electrochemical window was widened to 3.0 V due to further reduction of water reactivity in HER/OER and SEI formation, which is equivalent to that of the 21 m LiTFSI WIS aqueous electrolyte, but at much lower materials cost. The asdeveloped Mo<sub>6</sub>S<sub>8</sub> | LWIS gel electrolyte | LMO full cell delivered high cycling stability over 250 cycles with 98.53% Coulombic efficiency at 1 C. The quasi-solid LWIS chemistry provides a new pathway for the development of cost-effective, safe and high-energy aqueous Li-ion batteries. Moreover, the design principles of the LWIS electrolytes can potentially be extended to a wide range of rechargeable alkali metal (e.g. sodium, potassium)-based and multivalent ion (e.g. zinc, magnesium)-based aqueous batteries for large-scale energy storage applications.

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## **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** 1,5-pentanediol · aqueous lithium ion battery · lithium nitrate · localized water-in-salt electrolyte · solid electrolyte interphase

- [1] C. Yang, J. Chen, X. Ji, T. P. Pollard, X. Lü, C.-J. Sun, S. Hou, Q. Liu, C. Liu, T. Qing, Y. Wang, *Nature* **2019**, 569, 245–250.
- [2] P. Jaumaux, J. Wu, D. Shanmukaraj, Y. Wang, D. Zhou, B. Sun, F. Kang, B. Li, M. Armand, G. Wang, *Adv. Funct. Mater.* **2021**, *31*, 2008644.
- [3] J. Zheng, G. Tan, P. Shan, T. Liu, J. Hu, Y. Feng, L. Yang, M. Zhang, Z. Chen, Y. Lin, J. Lu, *Chem* 2018, 4, 2872–2882.
- [4] a) J. Xie, Z. Liang, Y.-C. Lu, *Nat. Mater.* 2020, *19*, 1006–1011;
  b) Y. Yokoyama, T. Fukutsuka, K. Miyazaki, T. Abe, *J. Electrochem. Soc.* 2018, *165*, A3299; c) L. Coustan, K. Zaghib, D. Bélanger, *J. Power Sources* 2018, *399*, 299–303.
- [5] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938–943.
- [6] Y. Yamada, K. Usui, K. Sodeyama, S. Ko, Y. Tateyama, A. Yamada, Nat. Energy 2016, 1, 16129.
- [7] L. Suo, O. Borodin, W. Sun, X. Fan, C. Yang, F. Wang, T. Gao, Z. Ma, M. Schroeder, A. von Cresce, S. M. Russell, *Angew. Chem. Int. Ed.* **2016**, *55*, 7136–7141; *Angew. Chem.* **2016**, *128*, 7252–7257.
- [8] S. Ko, Y. Yamada, K. Miyazaki, T. Shimada, E. Watanabe, Y. Tateyama, T. Kamiya, T. Honda, J. Akikusa, A. Yamada, *Electrochem. Commun.* 2019, 104, 106488.
- [9] Y. Shang, N. Chen, Y. Li, S. Chen, J. Lai, Y. Huang, W. Qu, F. Wu, R. Chen, Adv. Mater. 2020, 32, 2004017.
- [10] F. Wang, O. Borodin, M. S. Ding, M. Gobet, J. Vatamanu, X. Fan, T. Gao, N. Eidson, Y. Liang, W. Sun, S. Greenbaum, *Joule* 2018, 2, 927–937.
- [11] L. Droguet, A. Grimaud, O. Fontaine, J. M. Tarascon, Adv. Energy Mater. 2020, 10, 2002440.
- [12] a) X. Ren, S. Chen, H. Lee, D. Mei, M. H. Engelhard, S. D. Burton, W. Zhao, J. Zheng, Q. Li, M. S. Ding, M. Schroeder, *Chem* **2018**, *4*, 1877–1892; b) Y. Yamada, J. Wang, S. Ko, E. Watanabe, A. Yamada, *Nat. Energy* **2019**, *4*, 269–280.
- [13] T. A. Barnes, J. W. Kaminski, O. Borodin, T. F. Miller III, J. Phys. Chem. C 2015, 119, 3865–3880.
- [14] X. Cao, H. Jia, W. Xu, J.-G. Zhang, J. Electrochem. Soc. 2021, 168, 010522.
- [15] C. Yang, J. Chen, T. Qing, X. Fan, W. Sun, A. von Cresce, M. S. Ding, O. Borodin, J. Vatamanu, M. A. Schroeder, N. Eidson, *Joule* 2017, 1, 122–132.
- [16] T. Liang, R. Hou, Q. Dou, H. Zhang, X. Yan, Adv. Funct. Mater. 2021, 31, 2006749.
- [17] C. Yan, Y.X. Yao, X. Chen, X. B. Cheng, X. Q. Zhang, J. Q. Huang, Q. Zhang, Angew. Chem. Int. Ed. 2018, 57, 14055– 14059; Angew. Chem. 2018, 130, 14251–14255.
- [18] a) J. Gliński, G. Chavepeyer, J.-K. Platten, *Colloids Surf. A* 2000, 162, 233–238; b) X. Chen, Q. Zhang, *Acc. Chem. Res.* 2020, 53, 1992–2002.
- [19] K. Xu, C. Wang, Nat. Energy 2016, 1, 16161.
- [20] H. Bi, X. Wang, H. Liu, Y. He, W. Wang, W. Deng, X. Ma, Y. Wang, W. Rao, Y. Chai, *Adv. Mater.* **2020**, *32*, 2000074.
- P. Jaumaux, Q. Liu, D. Zhou, X. Xu, T. Wang, Y. Wang, F. Kang,
   B. Li, G. Wang, Angew. Chem. Int. Ed. 2020, 59, 9134–9142;
   Angew. Chem. 2020, 132, 9219–9227.
- [22] D. Zhou, A. Tkacheva, X. Tang, B. Sun, D. Shanmukaraj, P. Li, F. Zhang, M. Armand, G. Wang, *Angew. Chem. Int. Ed.* 2019, 58, 6001–6006; *Angew. Chem.* 2019, 131, 6062–6067.

Angew. Chem. Int. Ed. 2021, 60, 2-11

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- [23] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, G. Wang, *Chem* 2019, 5, 2326–2352.
- [24] H.-G. Steinrück, C. Cao, G. M. Veith, M. F. Toney, J. Chem. Phys. 2020, 152, 084702.
- [25] R.-S. Kühnel, D. Reber, C. Battaglia, J. Electrochem. Soc. 2020, 167, 070544.
- [26] Y. Li, Y. Li, A. Pei, K. Yan, Y. Sun, C.-L. Wu, L.-M. Joubert, R. Chin, A. L. Koh, Y. Yu, J. Perrino, *Science* 2017, 358, 506-510.
- [27] W. Zhang, Z. Shen, S. Li, L. Fan, X. Wang, F. Chen, X. Zang, T. Wu, F. Ma, Y. Lu, *Adv. Funct. Mater.* **2020**, *30*, 2003800.
- [28] W. Qi, L. Ben, H. Yu, W. Zhao, G. Zhao, X. Huang, Prog. Nat. Sci. 2020, 30, 321–327.
- [29] X. Cao, X. Ren, L. Zou, M. H. Engelhard, W. Huang, H. Wang, B. E. Matthews, H. Lee, C. Niu, B. W. Arey, Y. Cui, *Nat. Energy* 2019, *4*, 796–805.

- [30] J. Tokunaga, J. Chem. Eng. Data 1975, 20, 41-46.
- [31] N. Dubouis, P. Lemaire, B. Mirvaux, E. Salager, M. Deschamps, A. Grimaud, *Energy Environ. Sci.* 2018, 11, 3491–3499.
- [32] R. Bouchal, Z. Li, C. Bongu, S. Le Vot, R. Berthelot, B. Rotenberg, F. Favier, S. A. Freunberger, M. Salanne, O. Fontaine, Angew. Chem. Int. Ed. 2020, 59, 15913–15917; Angew. Chem. 2020, 132, 16047–16051.

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# **Research Articles**

## Batteries

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- G. Wang\* \_\_\_\_\_

Localized Water-In-Salt Electrolyte for Aqueous Lithium-Ion Batteries



We present a localized water-in-salt gel electrolyte with low-cost and high safety for aqueous lithium-ion batteries. This electrolyte was fabricated by in situ gelling TEGDA monomer in an aqueous solution based on inexpensive LiNO<sub>3</sub> salt and PD diluent. The as-developed Mo<sub>6</sub>S<sub>8</sub> | LWIS gel | LMO batteries delivered outstanding cycling performance in with a Coulombic efficiency of 98.53 % % after 250 cycles at 1 C.