UV-cured Gel Polymer Electrolytes with Improved Stability for Advanced Aqueous Li-Ion Batteries

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UV-cured Gel Polymer Electrolytes with Improved Stability for Advanced Aqueous Li-Ion Batteries

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We report the development of a new class of "water-in-salt" electrolytes based on UV photopolymerized acrylic polymers. Incorporation of "water-in-bisalt" in a polymer matrix reduces water activity, expands the electrochemical stability window to 4.1 V, and dramatically improves cycle life in full cells with lithium titanate anodes compared to liquid water-based electrolytes.

Li-ion batteries (LIBs) have emerged as the energy storage vehicle of choice for portable electronics, electric vehicles, and grid storage due to their high energy and power density and long cycle life. Today's LIBs rely on organic electrolytes that can support the high voltage window required for the cell chemistry. These electrolytes, however, contain flammable, toxic and highly reactive salts and organic solvents[1] that, in combination with oxygen-rich cathodes, result in safety concerns and limitations in cell manufacturing, operation, and form factor.

Significant research has been focused on addressing these challenges by replacing organic electrolytes with safer alternatives. Solid-state (polymer or inorganic) electrolytes do not use solvents, but, despite significant progress to increase their room temperature ionic conductivity,[2-3] challenges with interfaces with porous electrodes and cost still remain. Ionic liquids are very stable and non-flammable, but they suffer from high viscosity, lower ionic conductivity, synthetic complexity, and incompatibility with graphitic anodes.[4-5]

Using water to replace the organic solvents in the electrolytes is an intuitive solution due to its safety, solvency toward salts, and conductivity. Aqueous electrolytes for LIBs have long been proposed.[6] The narrow electrochemical stability window of water (~1.2 V) limits the voltage and energy density of aqueous LIBs to < 2 V and < 70 Wh/kg, respectively.[7-8] Recent breakthroughs in the development of concentrated aqueous electrolytes, termed as "water-in-salt" and "water-in-bisalt" (WiS and WiBS) have been reported. Addition of one or more Li-salts at high molality (> 21m) changes the water solvation and suppresses its electrochemical activity, expanding the stability window to 3.0 V.[9-10] Similar concepts have also been reported for hydrate melt aqueous electrolytes.[11] Though combining WiBS with novel anode passivation films has resulted in proof-of-concept 4.0 V cells,[12] the cathodic limit of the WiBS is still too high for passivation-free anodes, limiting their practical use to only a few, non-commercially used anodes.[13]

Here, we overcome the limitations of the liquid WiBS through the development of stable WiBS-based aqueous gel polymer electrolytes (GPEs) made via UV-mediated polymerization of water-soluble acrylates in the presence of WiBS. While UV GPEs have been previously reported for LIBs,[2, 14-19] this is the first report of UV GPEs with WiBS, along with a rational design for monomer selection and evaluation to improve ionic conductivity, mechanical properties, and electrochemical stability of both GPEs and batteries. For the first time, we show that $Li_4Ti_5O_{12}$ (LTO), a low-cost and widely used anode in today's market, can be reliably used for > 100 cycles in a WiBS GPE LIB full cell, with coulombic efficiencies exceeding those of other concentrated aqueous liquid electrolytes at comparable C-rates and active material loadings.[11] This marks a significant advancement toward transitioning this new class of supersaturated aqueous gel polymer electrolytes from proof-of-concept to practical applications.

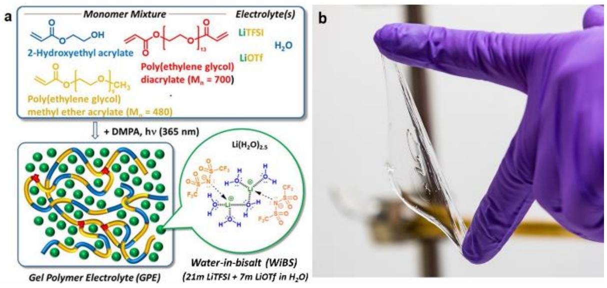

Fig. 1: a) Schematic of the UV cured GPE; b) image of one such GPE after curing

Fig. 1 shows the design approach for our aqueous GPEs. All formulations use a fixed concentration of 28m WiBS containing 21m Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 7m lithium trifluoromethanesulfonate (LiOTf) in H_2O.[10] Acrylate chemistry was selected due to its simplicity in rapidly

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forming robust polymers. Monomer selection was inspired by our previous work,[13] where it was found that hydroxyl group rich polymers further coordinate with free water and expand the electrochemical stability window. As such, 2-hydroxyethyl acrylate (HEA) was selected as the initial monomer. To modulate the polymer tack and flexibility, and to elucidate the effect of hydroxyl groups on performance, poly(ethylene glycol) methyl ether acrylate (MPEGA) evaluated as a comonomer. Poly(ethylene glycol) diacrylate (PEGDA) was selected as the cross-linker. All monomers were low molecular weight, low viscosity starting materials that allow for good wetting of the porous electrodes.

A detailed investigation was conducted to optimize GPE formulations. This started by mixing varying weight ratios of the WiBS stock solution and the monomer mixture, wherein the monomer mixture contained varying HEA and MPEGA contents, with cross-linker in the range of 1-3 wt%. Upon addition of a photoinitiator and UV irradiation at 365 nm, free-standing, dimensionally stable films are made (Fig. 1b). Based on the ability to cross-link mixtures at that PEGDA content, it was determined that a 75 wt% WiBS, 25 wt% polymer ratio was optimal for the fabrication of mechanically stable GPE films having the highest room temperature ionic conductivity. At lower WiBS contents, ionic conductivity decreases substantially. Conversely, adding WiBS yields more conductive, yet less robust films. While increasing cross-linker is expected to mitigate this effect, it was not explicitly studied in this work, due to the lower WiBS electrochemical stability.

With 75% WiBS in the GPE, the monomer formulation was narrowed down through a thorough evaluation of ionic conductivity, mechanical properties, glass transition, and cell performance. Fig. S1 in the ESI shows the room temperature ionic conductivity for GPEs made using HEA only, equal ratios of HEA/MPEGA, and 89% MPEGA, 9% HEA (at 75% WiBS, MPEGA only films could not be cross-linked). The highest ionic conductivity of 0.6 mS cm^{-1} is observed for the latter composition. This finding was supported by Dynamic Mechanical Analysis (DMA) characterization, wherein the axial adhesion stress vs strain was studied. The DMA results (Fig. S2) show that a high MPEGA content produces GPEs with higher stretchability, consistent with higher Li-ion mobility. Differential Scanning Calorimetry (DSC) analysis (Fig. S3) shows distinct glass transition temperatures for the polymer-only samples, which disappear with the addition of WiBS, due to hydroplasticization, the increase in free volume by water. Thermal stability was confirmed by thermogravimetric analysis (Fig. S4) that shows water retention up to ~175°C, with polymer decomposition at higher temperatures (>330°C).

At this MPEGA/HEA/PEGDA (89/9/2) formulation (termed W-GPE (**W**iBS-**GPE**)), we attempted to further increase the GPE stability by leveraging the high solubility of LiTFSI in the monomer to increase the Li salt content. Thus a second GPE formulation consisting of 25 wt% of this polymer, 58 wt% of the stock WiBS, and 17wt% extra LiTFSI was also evaluated, referred to as C-W-GPE (**C**oncentrated-**W**iBS-**GPE**). Though it exhibits slightly lower ionic conductivity due to the higher salt content, it was evaluated alongside W-GPE to elucidate the effects of water content. Fourier-transform infrared spectroscopy data (Fig. S5) show that the synthesized GPEs exhibit similar shifts for the H_2O peaks as the WiBS, validating that the mechanism is similar to that reported for the WiBS.

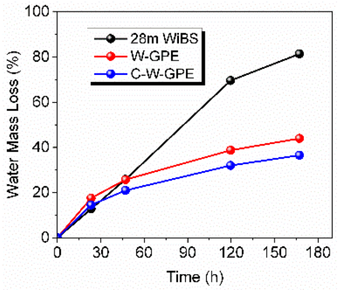

Fig. 2: Normalized water mass loss for the liquid and GPE formulations at room temperature

Fig. 2 shows the normalized water mass loss for the WiBS, W-GPE, and C-W-GPE after 167 hours of exposure in an argon-filled glove box (H_2O content < 4 ppm). Formulation details for these electrolytes are summarized in Table S1. The starting mass was 2 g with identical exposure area – cross-section of glass vial. The starting water content for the WiBS, W-GPE, and C-W-GPE was 12.3%, 9.2%, and 7.2% respectively. While WiBS retained more water during the first 23 hours (roughly 13%, vs 18% and 15% of water loss for W-GPE and C-W-GPE, respectively), both polymer formulations retained more water thereafter. After 167 hours, the WiBS had lost roughly 81% of the initial water content, while W-GPE and C-W-GPE had lost 44% and 37% respectively, maintaining their structural integrity as shown in Fig. S6.

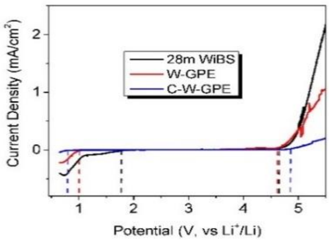

Fig. 3: Electrochemical stability window for the liquid and cross-linked water-in-bisalt electrolyte formulations

The capability of the cross-linked polymer formulations to retain water translates to an expanded electrochemical stability window (Fig. 3). The WiBS exhibits a cathodic stability limit of 1.8 V (vs. Li^+/Li). Incorporation of the WiBS in a cross-linked polymer in a 3:1 ratio improves cathodic stability, suppressing reduction down to 1.1 V. Addition of LiTFSI to the mixture further lowers the gas evolution potential[11] to 0.8 V. The oxidation potential for the WiBS and W-GPE is similar at ~ 4.8 V, resulting in overall stability windows of 3 V and 3.7 V, respectively. For the C-W-GPE, the anodic limit is expanded to ~4.9 V, resulting in the widest window among all three formulations at 4.1 V. This expanded stability in the cross-linked polymer formulation marks a substantial improvement over both the liquid WiBS,[10] and the WiBS-based polyvinyl alcohol (PVA) GPE reported in our previous work,[13] where the PVA content was 10% by weight. The improved electrochemical stability (Fig. 3) and water retention properties (Fig. 2) of the current crosslinked GPE systems result from the combination of the reduced water content and strong coordination of water by the high level of ether groups in the polymer network.

The improved cathodic stability enables our GPEs to be used in LIB cells with practical anodes such as LTO, which exhibits a Li^+ intercalation potential of 1.55 V. Fig. 4 shows the 1st and 2nd charge/discharge cycles for LTO/$LiFePO_4$ (LFP) full cells with 28m WiBS, W-GPE, and C-W-GPE. LFP was chosen due to its lower intercalation potential and high stability, in order to eliminate any cathode effects. A glass fiber separator was used in all three cases with equal amount of electrolyte. The tests were performed using constant current/constant voltage (CC/CV) charge at 0.1 C, holding the potential at 2.4 V until 0.05 C was reached. Discharge was done at 0.1 C. This slow rate is essential to better understand the effect of formulation on cell performance, as side reactions are more evident at slow rates.[11] Fig. 4 shows a significant difference between the liquid WiBS and the GPEs. The 1st cycle coulombic efficiency for the WiBS was only 43.6%, with a capacity of 104 mAh g^{-1} (per LTO active mass). In the 2nd cycle, the capacity decreased further (~80 mAh g^{-1}), and the efficiency remained low at 58.4%. Conversely, the W-GPE exhibited a high capacity of ~151 mAh g^{-1} with a first cycle efficiency of 81%. In the 2nd cycle, the capacity dropped slightly while the efficiency increased to 94.9%. The performance was slightly improved for the concentrated C-W-GPE, with starting capacity of 152.5 mAh g^{-1}, and efficiency of 82.9% that increased to 95.5% in the 2nd cycle. Fig. S7 shows the first 10 cycles for three such cells, further highlighting the substantial improvement resulting from the UV cured GPEs. It should be noted that, in addition to achieving this performance in a full cell (i.e. with only slightly excess cathode as in a commercial cell), the areal capacity of the LTO electrodes is ~0.8 mAh/cm^2. This is an impressive finding since it shows that GPE mixtures can penetrate into moderately thick electrodes, achieving nearly 100% active material utilization, enabling the potential for practical aqueous LIBs.

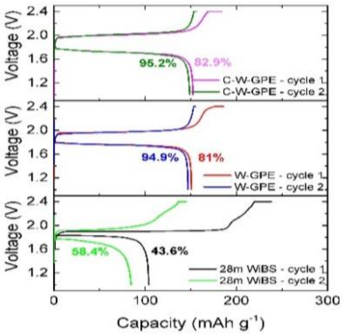

Fig. 4: 1st and 2nd cycle comparison for liquid WiBS and GPEs in LTO/LFP full cells

The plots in Fig. 4 suggest that the cell impedance is higher when GPEs are used. This is primarily attributed to the lower ionic conductivity of the GPEs compared to 28m WiBS (6.5 mS cm^{-1} [10]). Generally, the ionic conductivity of the GPEs decreases with reduced water content. W-GPE exhibits a room temperature value of 0.6 mS cm^{-1}, whereas the C-W-GPE has 0.23 mS cm^{-1}. For the cells in Fig. 4, the separator adds to the cell overpotential, as it slightly increases electrolyte resistance (Fig. S8). The ionic conductivity was characterized for all GPEs in the -20°C to 60°C range as shown in Fig. S9. Below 0°C, the GPE behaviour is typical of "frozen electrolytes", as reported by Abraham et al.[20]

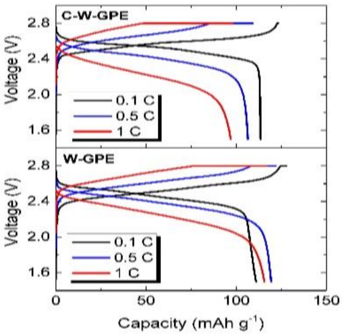

Fig. 5: 5th cycle at 0.1 C, 0.5 C, 1 C for the two GPEs

The GPE performance was characterized for rate capability and cycle life in full LTO/LMO cells with a LTO areal capacity of 0.4 mAh/cm^2. These cells were assembled without a separator, and GPEs cured on both electrodes (Methods section of the ESI) to a total thickness of ~100-150 µm (Fig. S10). Rate capability was done in 5 cycle increments from 0.1 C to 3 C using CC/CV as described earlier. Fig. 5 shows the 5th cycle for 0.1 C, 0.5 C, and 1 C. The capacity is comparable for both GPEs at low C-rates. Interestingly, the capacity for W-GPE increases from 111 mAh g^{-1} at 0.1 C to ~120 mAh g^{-1} at 0.5 C and ~115 mAh g^{-1} and 1C, respectively. This suggests improved wetting/contact area over time in the W-GPE case. This is further supported if the entire cycle is evaluated (Fig. S11, ESI). The capacity difference between LTO/LFP:LTO/LMO cells is due to calendering variation of in-house fabricated and production-grade LTO and LMO.

Another interesting observation from Fig. S11a is that the 1st cycle efficiency in the LTO/LMO cells without separator is lower compared to the LTO/LFP cells of Fig. 4. This is attributed to a combination of three effects, which affect side reaction rate: a) the presence of the separator; b) the electrode composition (loading and carbon black amount); and c) the amount of electrolyte. In both cases, the C-W-GPE is more tolerant to electrode/electrolyte variations, suggesting that despite lower ionic conductivity, it may provide a better option for stable operation. At 0.25 C, without separator, the C-W-GPE cycle for >100 cycles with >70% capacity retention in a LTO/LMO full cell (Fig. 6).

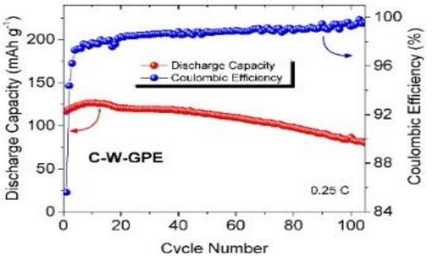

Fig. 6: Cycle life of C-W-GPE in LTO/LMO full cell at 0.25 C

The WiBS GPE cell safety is highlighted in Fig. S12 and video SV1 in the ESI. Not only are WiBS GPEs non-flammable, but they are also non-combustible, as evident when UV-cured GPEs with/without water are exposed to flame. This safety, along with the exceptional mechanical stability of the UV films, allows fabrication of damage-tolerant flexible batteries with vastly improved operational features compared to our prior work (Fig. S13 and videos SV2 to SV4). Flexible batteries were fabricated in entirely ambient laboratory conditions, without need for a glove box or dry room. The flexible cells had no packaging and the edges were completely exposed to air. Fig. 7a shows these cells can be fully cycled in open air, with minimal open circuit voltage drop for 30 hours. When exposing the cell to a torch during operation (video SV4), the flame does not propagate. In fact, the cell operated after the charred portion was cut off for ~100 hours, recovering from incidental-transient short circuit, until testing was manually stopped. These operational capabilities are a notable improvement over our prior work,[13] where PVA-based GPEs were not dimensionally stable enough to support open air operation with such remarkable stability.

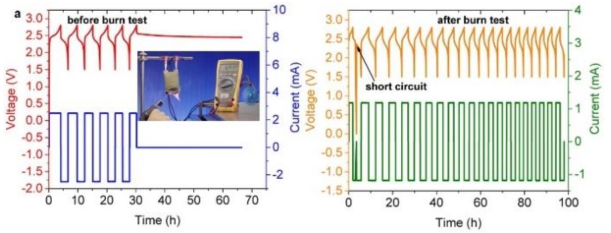

Fig. 7: a) a flexible battery, operating in open air with no packaging, is subjected to a burn test while powering a fan; b) battery continued to work for nearly 100 hours after burning, recovering from an incidental short circuit

Conclusions

In summary, we have demonstrated a novel fabrication method for “water-in-bisalt” based gel polymer electrolytes based on a UV curing process. Integration of WiBS in a polymer expands the electrochemical stability window due to reduced water as well as improved retention of free water that is coordinated by the polymer. For the first time, LTO can be reliably cycled with a concentrated aqueous electrolyte in a full cell with high efficiency. The flexible, tacky, and dimensionally stable nature of the GPEs enables flexible batteries that can be built and operated in open-air, exhibiting remarkable tolerance to abuse conditions. Our work significantly advances the state-of-the-art in aqueous LIBs , thus forming the foundation of the next-generation, safe and robust energy storage technology.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Graphical Abstract

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We report UV-photopolymerized “water-in-bisalt” electrolytes that expland the electrochemical stability window, improving “water-in-bisalt” cycle life in lithium titanate full cells