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## Lithium-ion Batteries

### With only a grain of salt

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Highly concentrated electrolytes offer enhanced energy-density for aqueous batteries, but the high salt concentration presents formidable challenges for practical implementations. Now, an electrolyte is designed with a substantially reduced salt concentration while still enabling high-performance batteries.

Driven by cost, as well as concerns over toxicity and safety of organic Li-ion batteries (LIBs), aqueous LIBs were proposed as early as 1994; however, aqueous LIBs have never been commercialized due to their limited energy density<sup>1</sup>. This is because the cell potential of aqueous LIBs is limited by the thermodynamic stability window of water (1.23 V) outside of which water is electrolysed. To expand the voltage window, water-in-salt electrolytes (WiSE) – solutions in which Li-salts (often sulfonimide-based) outweighs water in mass and volume – have been proposed as an effective strategy. In these systems, a solid electrolyte interphase (SEI) forms passivating the negative electrode. The use of highly-concentrated salts (>20 mol/kg or 20 m), however, prevents their practical application<sup>2</sup>. Now, writing in Nature Energy, Chunsheng Wang and coworkers from University of Maryland demonstrate that practical LIB pouch cells can be assembled using aqueous electrolytes employing a salt concentration below 5 m<sup>3</sup>. Their approach not only alleviates the cost of using highly-

concentrated salts, but also demonstrates a new way to passivate the negative electrode, expanding the voltage window and improving the energy density.

Expanding the stability window of aqueous LIBs hinges on controlling the passivation mechanism at the negative electrode, which faces two main challenges. First, Li-salts are unable to decompose in water to form counter anions necessary for the precipitation of Li-based inorganic compounds. Second, the solubility of such Li-based inorganic products is generally greater in aqueous than in organic electrolytes, further preventing the passivation.

The peculiar solvation structure found in WiSE triggers the reactivity of sulfonimide counterions to donate fluoride anions, eventually forming a LiF-rich SEI whose solubility is low due to the common-ion effect (Fig. 1). Although theoretically elegant, the use of WiSE does not completely suppress water reduction at negative electrodes, and consequently, the batteries inherently suffer from fast self-discharge and low coulombic efficiencies (CE)<sup>4,5</sup>. Furthermore, the use of high concentrations of corrosive salts (> 20 m) is in direct contradiction with the initial goal of reducing cost and improving safety in the development of aqueous LIB batteries.

In their work, Wang and team assembled a 4.5 m LiTFSI-KOH-CO(NH<sub>2</sub>)<sub>2</sub>-H<sub>2</sub>O electrolyte utilizing a combination of different strategies previously proposed. First, the researchers used CO(NH<sub>2</sub>)<sub>2</sub>, more commonly known as urea<sup>6</sup>, as a diluent to form strong interactions with Li<sup>+</sup> and water. This diluent disrupts the hydrogen bonding network which, in diluted systems is responsible for the reactivity of water at electrochemical interfaces<sup>7</sup>. Hence, the use of urea reduces the high concentration of the LiTFSI salt typically employed in WiSE (i.e. ~20 m).

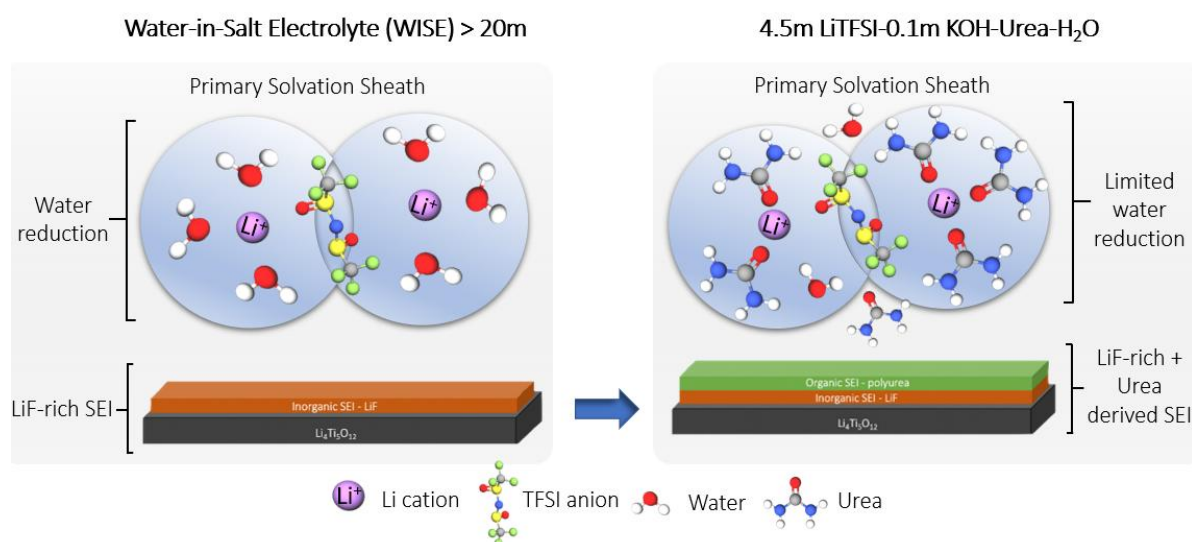
Furthermore, a urea polymerization product forms on the surface of the negative electrode, providing organic functionality to the SEI that complements LiF formed through the decomposition of TFSI anions (Fig. 1). To trigger this latter decomposition, which is normally only achieved in WISE systems for aqueous LIBs, KOH was added to catalyze TFSI degradation previously shown to be unstable in strongly alkaline conditions<sup>8</sup>. This mixed inorganic-organic SEI provides greater stability compared to the SEI formed in WISE systems, as demonstrated by electrochemical measurements.

Wang and team assessed the performance of this electrolyte using  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as positive and negative electrodes, respectively, both in the laboratory scale (that is, coin cells) as well as in a more practical format by assembling pouch cells. Using the aforementioned electrolytes, the researchers showed  $\text{LiMn}_2\text{O}_4 || \text{Li}_4\text{Ti}_5\text{O}_{12}$  full cells with a CE of ~99.9%. This performance metric represents a neat gain compared to the 99% CEs previously obtained, for instance, for  $\text{LiFePO}_4 || \text{Mo}_6\text{S}_8$  in 20 m LiTFSI (ref.<sup>5</sup>) and  $\text{LiMn}_2\text{O}_4 || \text{Li}_4\text{Ti}_5\text{O}_{12}$  using molecular crowding electrolytes.<sup>9</sup> This result is significant, because for coin cells an improvement of 99% to 99.9% CE theoretically increases the cycle life by one order of magnitude.<sup>4</sup>

Next, the Wang group assessed the performance in pouch cells with an areal capacity of 2.5 mAh/cm<sup>2</sup>, achieving a 99.87% CE and a 72% capacity retention over 500 cycles. They also examined the self-discharge rate and found a capacity decay of 18.7 % per month. This is comparable to  $\text{LiMn}_2\text{O}_4 || \text{Li}_4\text{Ti}_5\text{O}_{12}$  pouch cells with conventional organic electrolytes and commercially available Ni-MH batteries. Wang and team attribute this performance to the aforementioned stable SEI formation and inhibited water reduction.

Several roadblocks remain to be alleviated before envisioning this battery chemistry for practical usage. Despite reducing the amount of salts while improving the CE, using this complex electrolyte in fact lowers the amount of water in the system. Hence, given the values reported in this work (CE, electrode and electrolyte loadings), the concentration of water would be reduced after a limited number of cycles following the model proposed by Kühnel et al.<sup>3</sup> Such water loss could alter cell operation and its performance. To avoid this drying out of the cell, H<sub>2</sub> gas generated during self-discharge and/or cycling must be controlled so that the water concentration can be maintained.

In conclusion, this work by Wang and coworkers reports an ingenious liquid electrolyte engineering approach that improved the cell performance of aqueous batteries. No doubt that future work will focus on tackling the remaining issues in order to assess the practicality of this novel chemistry.



**Fig. 1. A typical WiSE electrolyte and the ternary urea-based electrolyte in aqueous batteries.** In WiSE, water reduction generates OH<sup>-</sup> that decomposes TFSI anions to form LiF. The solid electrolyte interface (SEI) is LiF-rich. A CE of 99% is typically achieved in WiSE-based batteries. In the urea-based aqueous electrolyte of Wang and team, the water

reduction is restricted and the decomposition of TFSI<sup>-</sup> is facilitated in presence of KOH. Meanwhile, a urea polymerization gives rise to organic products during cycling. Therefore, the SEI contains both LiF and urea-derived species. These help to reach a 99.9% CE in their pouch cell configurations.

Competing Interests: The authors declare no competing interests

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