Aqueous-hydrotrope hybrid electrolytes with minimized water activity

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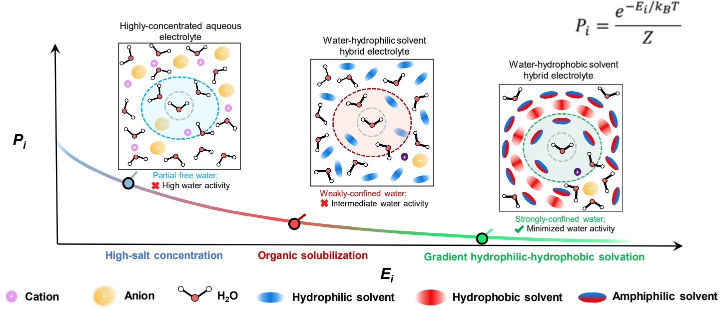
Introduction

- Aqueous Zn-metal batteries (AZMBs) are promising candidates for sustainable, grid-scale energy storage.
- The narrow working temperature range and limited electrochemical stability window of aqueous electrolytes pose two major concerns impeding practical deployment of AZMBs, both can be brought down to the high water activity in conventional aqueous-based electrolytes.
- Here, we propose a guideline that minimizes water activity by reducing the free water probability (***P***$_i$), which is realized through manipulating the water structure energy (***E***$_i$) in electrolyte.

$$P_i = \frac{e^{-E_i/k_BT}}{Z}$$



Methodology

- We introduce the "water confinement" in aqueous electrolytes via confining water molecules in a gradient hydrophilic-hydrophobic solvation sheath.
- Such structure is enforced by introducing a hydrotropes to bridge the immiscibility of aqueous electrolytes with the most hydrophobic and nonpolar hydrofluoroethers (HFEs), enabling a maximal water-water separation.
- “Hydrotrope-induced solubilization” with 2,2,2-trifluoroethanol (TFEA) hydrotrobe and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (TTE) hydrophobe enforces the hydrotrope structuring in the ternary mixture, thereby partitioning water from immiscible species through differential affinity to the hydrophilic and hydrophobic segments.

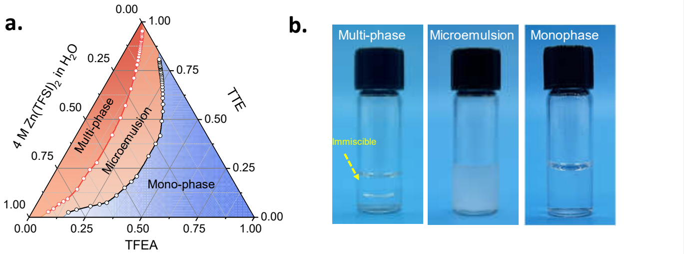


Fig. a. Ternary phase diagram of the Zn(TFSI)$_2$ in H_2O-*x* TFEA-*y* TTE ternary mixture. **b.** Optical photos of Zn(TFSI)$_2$ in H_2O-*x* TFEA-*y* TTE mixture at multi-phase, microemulsion and mono-phase states.

- Molecular-dynamics snapshots reveal an effective disruption of the long-range connected water network in the aqueous–hydrotrope electrolyte.
- Radial distribution function analysis indicates the accumulation of TFEA and TTE at distances of ~1.95 and ~2.46 Å from water, respectively, demonstrating the formation of the gradient TFEA-TTE layer around H_2O molecules.

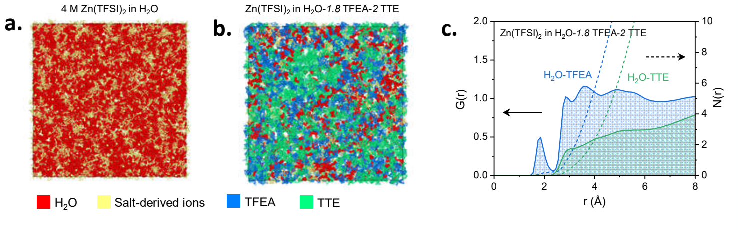


Fig. MD simulation of the **a.** 4 M Zn(TFSI)$_2$ in H_2O and **b.** Zn(TFSI)$_2$ in H_2O-*1.8* TFEA-*2* TTE electrolytes, with a focus on the water solvation structure. **c**, G(r) and N(r) of the H_2O-TFEA and H_2O-TTE pairs in the Zn(TFSI)$_2$ in H_2O-*1.8* TFEA-*2* TTE electrolyte.

Objectives

- Focusing on the water solvation sheath, we define three kinds of water: (i) free water: equivalent to one water molecule being surrounded by four other water molecules; (ii) weakly-confined water: equivalent to one water molecule being surrounded by ≥2 to <4 water, the ratio of water would be [0.5-1.0). (iii) strongly-confined water: equivalent to one water molecule being surrounded by ≥0 to <2 water, the ratio of water would be [0-0.5)
- The addition of the TTE molecules leads to a consistently decreasing ratio of free water, and increasing percentage of strongly-confined water.
- These statistical results show that, compared to adding salts, the cosolvents incorporation more effectively produces strongly-confined water.

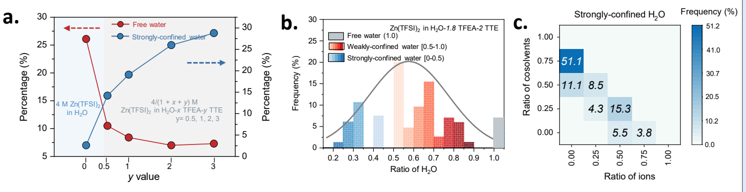
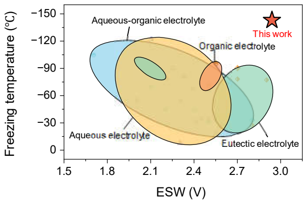


Fig. a. Summary on the percentage of free water and strongly-confined water in the Zn(TFSI)$_2$ in H_2O-*x* TFEA-*y* TTE electrolytes. **b.** Normal distribution of the frequency in line with the ratio of water in the Zn(TFSI)$_2$ in H_2O-*1.8* TFEA-*2* TTE electrolyte. **c.** Frequency analysis of the constituents surrounding the strongly-confined water.

Research accomplishments

- Wide electrochemical stability window .
- Wide operation temperature range.
- Stabilized Zn/electrolyte interphase.
- High Zn reversibility and utility.
- Wide-temperature cycling in coin/pouch cells.



- With the aqueous-hydrotrope electrolyte, the electrochemical stability window is expanded to 2.94 V, with freezing temperature dropping to -143 ℃.
- The unique water solvation around the Zn^{2+} cations contributes to an anion-derived SEI with suppressed water decomposition on Zn surface.
- Zn reversibility of 99.92% is realized for 4000 cycles. The Zn||$VOPO_4·2H_2O$ full cell can operate over a wide temperature range from -80 to 60 ℃. The Zn ||$VOPO_4·2H_2O$ pouch cell sustains over 500 cycles under RT and -60 ℃.

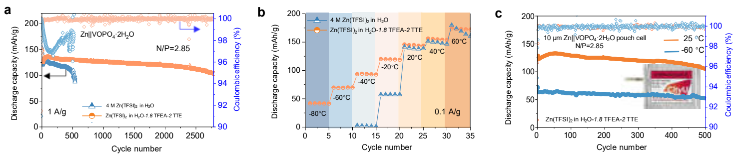


Fig. a. Cycling performance of Zn||$VOPO_4·2H_2O$ at 1 A/g. **b.** Discharge capacities of Zn|| $VOPO_4·2H_2O$ cells at different temperatures. **c.** Cycling performance of Zn||$VOPO_4·2H_2O$ pouch cells with the Zn(TFSI)$_2$ in H_2O-*1.8* TFEA-*2* TTE electrolyte.

Outlooks

- The protocol for realizing gradient water solvation in the aqueous-hydrotrope hybrid electrolyte goes beyond the specific hydrotrope (fluorinated alcohol)/hydrophobe (hydrofluoroether) pair used here, providing a generalizable route that allows substitution of functionally equivalent pairs to achieve low water activity.
- The design principle could be extended to electrolytes based on other mono- and multi-valent cations, which could guide the electrolyte design to enable wide-temperature aqueous batteries at low salt concentrations.
- Future efforts would aim to conduct machine-learning or high-throughput data mining to explore more efficient and cost-effective hydrophobe/hydrotrope pairs. Techno-economic assessment of electrolyte formulations are expected that considers raw-material pricing, synthesis scalability, solvent recovery, and supply-chain availability to guide cost optimization for grid storage.