

Reshaping Electrolyte Solvation Structure for High-Energy Aqueous Batteries

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A highlight on reshaping aqueous electrolyte solvation structure for high-energy batteries is provided. Firstly, the recent key design routes for regulating solvation structure to widen electrochemical stability window (ESW) of aqueous electrolyte are briefly summarized. Then, the groundbreaking work of Wang et al. on reshaping electrolyte structure using urea as the diluent is elaborated. Finally, the significance of Wang's work is highlighted.

Aqueous electrolytes are emerging as a promising replacement for flammable and toxic organic systems due to their superior safety, environmental friendliness, and low cost.^[1–3] However, a rather narrow electrochemical stability window (ESW, 1.23 V) restricted by the inherent thermodynamic oxidation potential (oxygen evolution reaction: OER) and reduction potential (hydrogen evolution reaction: HER) generally leads to low-voltages of aqueous energy storage devices, thus limiting the energy densities.^[4,5] Moreover, the solid electrolyte interphase (SEI) as usually found in non-aqueous batteries is absent in conventional aqueous electrolytes, making it impossible to prevent water electrolysis and widen the ESW above the thermodynamic value.^[6] Thus, the limitation of low voltage (<1.5 V) and low-energy density (<70 Wh kg⁻¹) impedes the grid-scale applications of most aqueous batteries.^[7] Although some efficient strategies including the electrode design and introduction of extra redox activity that is competitive with HER or OER can increase the cell voltage beyond 1.5 V,^[8,9] there is still a huge gap between aqueous batteries and organic systems that typically operate above 3.0 V.

In recent years, increasing studies revealed that regulating the electrolyte salt, solvent, and additives can reshape aqueous electrolyte structure, which offers an opportunity to eliminate the above restrictions and concerns raised by the ESW.^[6] In particular, metal-ion (e.g., Li⁺) solvation structure in aqueous electrolytes can significantly affect the number and activity of free H₂O. For traditional dilute electrolytes, sufficient free water molecules with high-electrochemical activity are distributed around the metal ions well hydrated in the primary solvation sheath, responsible for the generally observed OER/HER.^[10] In 2015, Suo et al. changed this conventional structure by increasing the salt concentration to form a 21 m (mol kg_{solvent}⁻¹) “water-in-salt” (WIS)

electrolyte.^[10] The novel electrolyte exhibits a anion-containing Li⁺ solvation structure, where there is little free water with other water molecules bonded, thus reducing the water activity and regulating the redox potentials. Interestingly, in such an electrolyte, the preferential anion reduction generates a dense SEI on anode instead of HER, which further isolates the interfacial H₂O and expands ESW up to ~3.0 V. Despite this breakthrough, retained H₂O molecules within the Li⁺ solvation sheath are inevitably reduced

under lower potentials of <1.9 V versus Li⁺/Li.^[11] Therefore, further efforts have also been devoted to reduce H₂O molecules in the Li-ion solvation by co-salt strategy, for instance, constructing 28 m “water-in-bisalt” (21 m LiTFSI and 7 m LiOTf) electrolyte with 1.83 V (vs Li⁺/Li) cathodic stability limits, and 63 m “water-in-hybrid-salt” (42 m LiTFSI + 21 m Me₃EtN·TFSI) with the cathodic stability limits to 1.75 V (vs Li⁺/Li).^[12,13] However, WIS electrolytes still suffer from several drawbacks, such as 1) the obviously increased viscosity and cost compromise the merit of aqueous electrolytes; 2) the possible salt precipitation at sub-zero temperatures severely restricts the application scenarios.^[14]

To resolve this challenge, Suo et al. creatively introduced CO₂ as an additive that could generate interfacial SEI phase in dilute LiTFSI electrolyte and designed a CO₂-SIW (salt-in-water) electrolyte (5 m LiTFSI–H₂O with CO₂).^[15] This electrolyte not only inherits the high ionic conductivity and low viscosity of conventional dilute electrolytes but also demonstrates excellent low-temperature tolerance (maintaining good fluidity at –40 °C). In particular, the SEI derived from the reduction of the TFSI–CO₂ complex in diluent electrolyte enables a wide ESW equivalent to WIS electrolyte (realizing ~2.0 V voltage plateau for the LiMn₂O₄/Mo₆S₈ full cell), thus reducing the cost of using massive LiTFSI. In a word, benefiting from the interaction between CO₂ and TFSI⁻, an interphase is formed at a relatively low salt concentration, highlighting that adjusting electrolyte structure can manipulate interface chemistry and thus boost the energy density of aqueous batteries.

Very recently, Wang et al. reported a more advanced strategy in designing high-voltage and high-energy aqueous batteries.^[16] By simply utilizing CO(NH₂)₂ as a low-cost diluent, a non-flammable ternary eutectic dilute electrolyte (4.5 m LiTFSI–KOH–CO(NH₂)₂–H₂O) with wider ESW of >3.3 V was designed (Figure 1a). The most significant benefits of this new electrolyte are the reduced viscosity and cost compared to WIS electrolytes. Moreover, CO(NH₂)₂ as both the donor and acceptor of hydrogen bonds (HBs), can lead to the generation of strong HBs among C=O, N–H and O–H; the interactions are even stronger than that among water molecules or between Li⁺ and H₂O. Thus, CO(NH₂)₂ exhibits a greater ability to stabilize the H₂O and further decreases the number of H₂O in the primary Li⁺ solvation shell from 2.6 in 21 m LiTFSI WIS to 0.7 (subly substitutes the H₂O site), greatly changing the solvation structure of the diluent electrolyte (Figure 1b).

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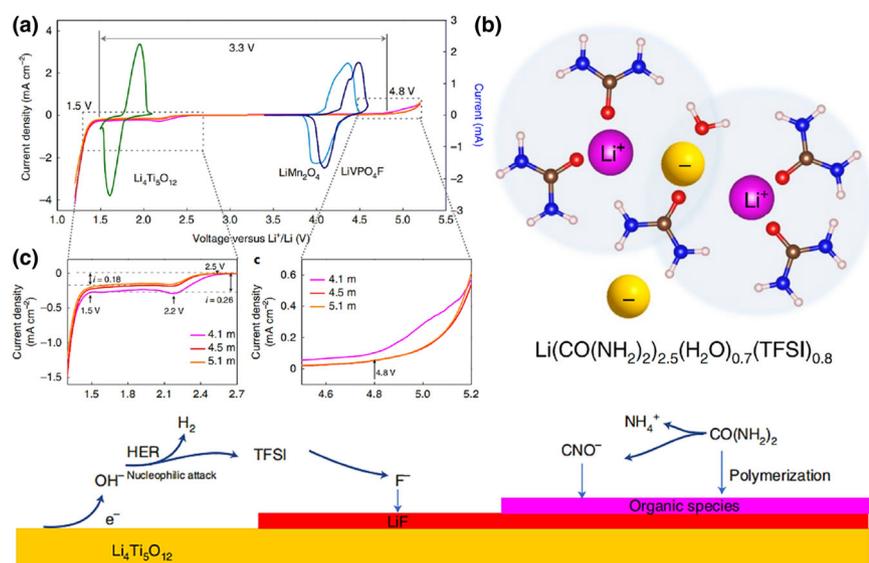


Figure 1. a) Overall ESW of the electrolytes with different LiTFSI concentrations. The enlarged view of the regions outlined in the linear sweep voltammetry curves and the redox currents of various active electrodes in 4.5 m electrolytes are also included. Schematic illustration of b) the Li^+ primary solvation sheath in the 4.5 m electrolyte and c) the formation mechanism of the robust SEI on anode.^[16] Copyright 2022, Springer Nature.

In addition, as shown in Figure 1c, with the introduction of a small amount of KOH, catalytic decomposition of TFSI^- at a high potential is achieved, which together with the electrochemical polymerization of $\text{CO}(\text{NH}_2)_2$ at a low potential cooperatively constructs a robust SEI on the surface of the anode. The redesign of solvation structure with extremely few water molecules in the solvation sheath and generation of smart SEI push the hydrogen evolution to 1.5 V versus Li^+/Li and thus result in 3.3 V ESW. Furthermore, thanks to the regulated solvation structure and low salt concentration, the ternary eutectic electrolyte also demonstrates extra merits including low freezing temperature of -60°C and high thermal stability of 225°C . With this novel electrolyte, full cells using LiMn_2O_4 and LiVPO_4F cathodes against $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have demonstrated impressive energy density of 103 and 123 Wh kg^{-1} , respectively.

In summary, Wang et al. demonstrated the groundbreaking advance in designing a dilute aqueous electrolyte with ESW larger than 3.3 V, representing a significant step forward in aqueous energy storage research. This work uncovered the importance of complex interactions between electrolyte components in reshaping solvation structure and provided a new direction for the development of novel aqueous electrolytes. Simply mixing HB donor-acceptor $\text{CO}(\text{NH}_2)_2$ and aqueous solution to reshape electrolyte structure opens up an opportunity to replace traditional organic electrolytes for developing a wide spectrum of low-cost, safe and high-energy aqueous electrochemical energy storage devices that can even operate in wide temperature range. Ultimately, depending on constantly improving upon aqueous electrolytes, the

low-cost, high-security, and high-performance energy storage techniques will be implemented in large scale in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aqueous electrolyte structure, $\text{CO}(\text{NH}_2)_2$, electrochemical stability window, energy density

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