

Solid-Electrolyte Interphase Chemistries Towards High-Performance Aqueous Zinc Metal Batteries

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Abstract: Aqueous Zn metal batteries (AZMBs) are deemed as promising technologies for electrochemical energy storage due to their high safety, low cost and high energy density. However, AZMBs still suffer from severe side reactions, including Zn dendrite formation and intrinsic hydrogen evolution reaction. In contrast to the solid-electrolyte interphase (SEI) layer that stabilizes Li/Na/K metal anodes in organic electrolytes, it is difficult to form an SEI layer on the Zn surface because of the difficulty in decomposing the salt anions within the narrow electrochemical potential window of water. A team from the University of Adelaide reports a novel pure or hybrid electrolyte with H₂O by using dimethyl methylphosphonate (DMMP) as solvent or co-solvent to construct a uniform and stable phosphate-based SEI layer (ZnP₂O₆ and Zn₃(PO₄)₂). Thus, high Coulombic efficiencies and improved capacity retentions can be obtained.

To fight against climate change hinged on the wider utilization of clean and renewable technologies, it is of great necessity to innovate batteries that store energy in a sustainable and cost-effective manner.^[1] Batteries can not only provide a significant source for power supply but also help balance the energy fluctuations between energy production and consumption. In this regard, aqueous Zn metal batteries (AZMBs) are attracting increasing attention due to their better affordability, higher safety and sustainability in comparison to the widely used Li-ion batteries.^[2] Great efforts have been dedicated to exploring high-performance cathode materials^[3] in the past decade while Zn anode research is still in its infant stage.^[2, 4-6] It has been widely accepted that the irreversibility of the Zn electrode can be ascribed to Zn dendrite growth and hydrogen evolution reaction (Figure 1a),^[7] which bring about short lifespans and poor Coulombic efficiencies.^[5, 8] Different from the solid-electrolyte interphase (SEI) layer that protects Li/Na/K metal anodes in organic electrolytes, it is quite hard to build a controllable SEI layer on the Zn surface owing to extremely electrochemical stability of salt anions in aqueous electrolytes.^[9] In spite of effectiveness of artificial SEI coatings, the processing complexity and poor adhesion to the Zn anode cannot be neglected.^[10]

To solve these issues, Guo and co-workers^[11] write in *Angewandte Chemie* to report an effective hybrid electrolyte strategy to *in-situ* generate a monolithic phosphate SEI layer on the Zn surface. This SEI layer is contributed by a fire-retardant solvent (dimethyl methylphosphonate, DMMP) and endows the Zn anode with a high electrochemical reversibility (Figure 1b). Guo and co-workers claim that the DMMP solvent with high dipole moment (3.62 D) has a high polarity to interact with valence electrons from other species and achieve electron transfer, which remarkably promotes phosphating conversion reaction that is capable of controlling the interphase chemistry and reductive

decompositions. Of note, in comparison to other organic solvents with high dipole moment (> 3D) such as propylene carbonate, acetonitrile, N,N-Dimethylformamide and dimethyl sulfoxide, the pre-cycled Zn metal in DMMP-based electrolyte presented improved cycling stabilities in 0.5 M (M: mol L⁻¹) ZnSO₄-H₂O electrolyte. Besides, DMMP displays a low viscosity of < 2 mPa s that ensures good mass transfer, a moderate dielectric constant of 22.3 that promotes the desolvation process and non-combustibility that guarantees the good safety, all of which favor good properties of the hybrid H₂O-DMMP electrolyte for AZMBs.

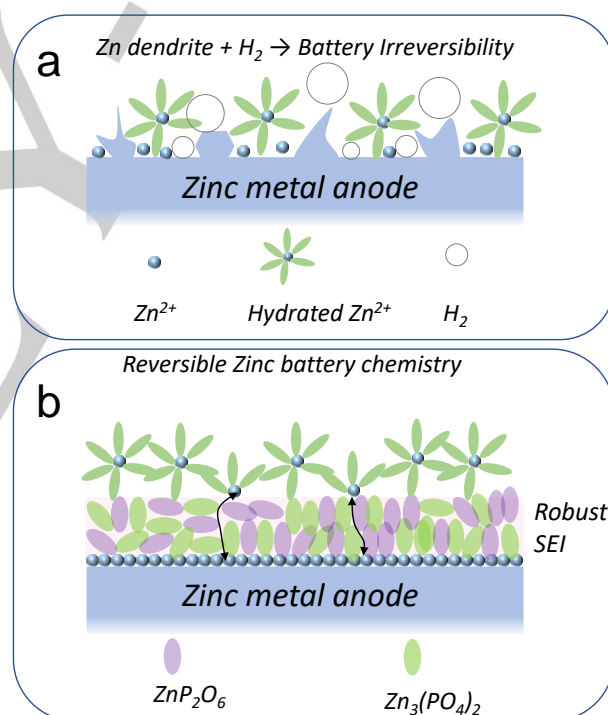


Figure 1. Schematic representation of the Zn anode chemistry a) without Solid Electrolyte Interphase (SEI), b) with SEI from dimethyl methylphosphonate (DMMP).

Guo and co-workers employ cryo-scanning transmission electron microscopy, focused ion beam and X-ray photoelectron spectroscopy to determine the SEI components of amorphous and crystallized phosphates (i.e., ZnP₂O₆ and Zn₃(PO₄)₂) with a thickness of ca. 300 nm through a facile phosphating conversion reaction from the DMMP solvent. Furthermore, molecular dynamics simulation confirms that DMMP dominates the solvation structure of Zn²⁺ in the designed DMMP-based electrolyte. The as-achieved phosphate SEI possesses fast Zn²⁺ conductivity, high interface energy, and good electronically insulating ability that blocks the contact between water and the Zn anode to inhibit

HIGHLIGHT

the hydrogen evolution reaction, all of which contribute to the suppressed Zn dendrite growth and boosted electrochemical performances.

Guo and co-workers apply this monolithic phosphate SEI concept to Zn/Cu, Zn/Zn, and Zn/V₂O₅ batteries displaying significant performance enhancement with an ultrahigh Coulombic efficiency of 99.89% and extended cycling performances over 4700 h or 4000 cycles. All these achievements are contributed by the modified interphase between the Zn anode and electrolyte due to the DMMP phosphating conversion reaction. Also, Guo and co-workers have extended the electrochemical window of the electrolyte to 3.3 V versus Zn²⁺/Zn, which is suitable to endure high-voltage operation scenarios. To increase the overall output voltage, some high-voltage cathode materials should be taken into consideration including Mn-based oxides, polyanionic compounds, Prussian blue analogues and the conversion-type iodine (I₂).^[2, 4, 8] Meanwhile, combined with other promising strategies (e.g., pulsed charging), one can anticipate that better Zn anode improvement can be obtained.^[4]

Guo and co-workers' method is effective and facile hinged on mixing an organic solvent with dilute aqueous electrolyte to *in-situ* form a uniform and robust SEI layer. This strategy addresses the concern of the absence of SEI formation from the difficult decomposition of Zn salt anions within the narrow electrochemical potential window of the dilute aqueous electrolyte. In contrast to the complex artificial SEI coating strategies, this simplicity should be paid more attention by AZMBs researchers and industrial communities for future optimization.

Overall, the generation approach of the phosphate interphase proposed by Guo and co-workers is a significant and inspiring case work for guiding future design of other better SEI layers for highly reversible zinc metal anode redox chemistries. Looking into future electrolyte engineering of AZMBs, other solvents or electrolyte additives should be developed to modify the Zn anode interphase with good electronic insulating ability, high Zn²⁺ conductivity, good adhesion ability to Zn surface, excellent anti-corrosion property and superior self-passivating behavior. The mechanical properties should also be carefully evaluated. Those solvents or additives that can decompose and react with Zn²⁺ to form uniform and controllable SEIs should be paid more attention.^[10-11]

The next-stage goals of AZMBs should focus on improving the Zn utilization in full cells at practical N/P ratios (i.e., the capacity ratio of the negative electrode to the positive electrode) of < 3 and evaluating the stability and reversibility of Zn anodes at moderate rates of ≤ 1 C under practical areal capacities of ≥ 3 mAh cm⁻² to compete with the currently used Li-ion batteries with the assistance of high-quality SEIs. In previous reports, most of cathode materials can present excellent long-term cycling stabilities at high rates of 5 C-30 C while they would display inferior cycling properties under low rates of 0.5 C-2 C. The cycling lifespan under these two circumstances can have a 10-fold difference at an analogous ratio of capacity retention.^[2] Proton de-/intercalation likely dominates and contributes to "pseudo-high Zn²⁺" capacities at high rates. Also, during Zn stripping/ plating in the aqueous electrolyte, hydrogen gas evolution can take place prior to the completion of SEI formation. The amount of hydrogen gas evolution is highly dependent on the test condition: a shorter charge-discharge period from the high rate could lead to less hydrogen gas evolution and thus a deceptively high Coulombic efficiency could be obtained, which is meaningless for practical

applications.^[10] In other words, both cathode and anode can be more realistically evaluated if AZMBs are operated at low rates of ≤ 1 C.

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Conflict of Interest

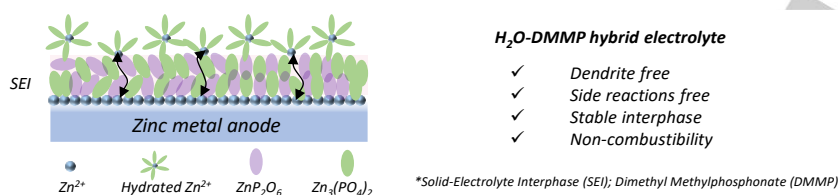
The authors declare no conflict of interest.

Keywords: Solid-electrolyte interphase • aqueous electrolyte • zinc anode • zinc metal batteries • hybrid electrolyte

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The recent work from Guo and co-workers who proposed a hybrid electrolyte strategy obtained by mixing H_2O and dimethyl methylphosphonate (DMMP) as solvents to build up a high-quality phosphate-based solid-state interphase layer is highlighted. This new solid electrolyte interphase (SEI) protects Zn metal anodes from corrosion and dendrite formation. Thus, ultrahigh Coulombic efficiencies and extended lifespan can be achieved.

Institute and/or researcher Twitter usernames: @Ericwz2333; @GuanjieHe, custom text "Solid-Electrolyte Interphase Chemistries Towards High-Performance Aqueous Zinc Metal Batteries by @Ericwz2333 and @GuanjieHe highlights a recent inspiring work on a hybrid electrolyte strategy to build up a high-quality SEI layer on the aqueous Zn anode"