Tuning the Solvation Structure in Aqueous Zinc Batteries to Maximize Zn-Ion Intercalation and Optimize Dendrite-Free Zinc Plating

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ABSTRACT: Aqueous zinc batteries are recognized to suffer from H⁺/Zn²⁺ coinsertion in the cathode, but few approaches have been reported to suppress deleterious H⁺ intercalation. Herein, we realize this goal by tuning the solvation structure, using LiV₂(PO₄)₃ (LVP) as a model cathode. Phase conversion of LVP induced by H⁺ intercalation is observed in 4 m Zn(OTf)₂, whereas dominant Zn²⁺ insertion is confirmed in a ZnCl₂ water-in-salt electrolyte (WiSE). This disparity is ascribed to the complete absence of free water and a strong Zn²⁺–H₂O interaction in the latter that interrupts the H₂O hydrogen bonding network, thus suppressing H⁺ intercalation. On the basis of this strategy, a novel PEG-based hybrid electrolyte is designed to replace the corrosive ZnCl₂ WiSE. This system exhibits an optimized Zn²⁺ solvation sheath with a similar low free water content, showing not only much better suppression of H⁺ intercalation but also highly reversible Zn plating/stripping with a CE of ~99.7% over 150 cycles.

Owing to the high electrodeposition potential of Zn²⁺ (~0.76 V vs SHE), the high theoretical volumetric capacity of the Zn anode (~850 mAh mL⁻¹) and the advantages of low-cost, high-safety, and eco-friendly operation, aqueous zinc metal batteries (AZMBs) are becoming one of the most attractive technologies for large-scale stationary energy storage.¹⁻³ Much work has focused on developing cathode materials for AZMBs, including MnO₂,⁴ Zn₀.₂₅V₂O₅·nH₂O,⁵ and many others. However, recent studies have found that the high electrochemical capacity of these metal oxides is not solely due to Zn²⁺ insertion/extraction but also relies on H⁺ (de)intercalation.⁶⁻¹¹ Proton intercalation results in the formation of layered double-hydroxide salts (LDH, for example, ZnₙSO₄(OH)₆·5H₂O) on the surface of metal oxides,⁸⁻¹⁰ which aids the reversible and stable operation of metal oxides due to its unique buffering mechanism.⁹ On the other hand, the LDH forms an insulating layer on the oxide surface that detaches from the electrode over time, leading to loss of active material. Proton intercalation has now been generally accepted as a common phenomenon for metal oxides in AZMBs. Studies involving polyanion compounds similarly showed that either H⁺ (or Na⁺) insertion occurs along with Zn²⁺ intercalation.¹²⁻¹⁴ For example, by analyzing the differential capacity curves (dQ/dV) of layered VOPO₄·xH₂O cathode in different electrolytes, Sun et al. found that H⁺ intercalation played a dominant role in an electrolyte comprised of 5 m ZnCl₂/0.8 m H₃PO₄.¹³ Not surprisingly, on increasing the concentration of ZnCl₂ to 10⁻¹³ m, Zn²⁺ was suggested to dominate the intercalation process based on the higher peak intensity of the Zn contribution in the dQ/dV curve. The factors responsible for Zn²⁺ versus H⁺ intercalation (aside from concentration) were not investigated in this study. Monoclinic LiV₂(PO₄)₃ was reported to be a superior host for AZMBs and can be cycled at an exceptionally high rate of 60 C.¹⁵ As the high charge density of Zn²⁺ would likely result in limits to solid-state diffusion at this current density and significant structural distortion in monoclinic V₂(PO₄)₃,¹⁶ a fundamen-
tally different mechanism based on H+ intercalation rather than exclusive Zn2+ insertion has been proposed to account for this high-rate performance. Recently, an approach to favor Zn2+ intercalation was reported for a VPO4F host lattice based on a hybrid electrolyte (water + propylene carbonate); however, proton intercalation still could not be fully suppressed. A multiphase mixture with overall composition of Zn0.3H0.7VPO4F was formed on discharge, but the implicit existence of a more highly zincated phase could not be quantified.14

Herein, we demonstrate that solvation-structure engineering of aqueous Zn electrolytes (AZEs) is an effective method to suppress H+ intercalation and realize dominant Zn2+ intercalation. To establish proof-of-concept, we chose LiV2(PO4)3 (LVP) as the cathode platform and compared its electrochemistry in two previously reported electrolytes, 4 m (molality, mol/kg) Zn(OTf)2 and 29 m ZnCl2 "water-in-salt" electrolytes (WiSE), as well as a newly designed hybrid electrolyte developed by incorporating polyethylene glycol 400 (PEG 400) and water as a cosolvent with Zn(OTf)2 as the salt. Importantly, we explore the H-bonding network, free water fraction, Zn2+-solvation structure and their roles in Zn2+ vs H+ intercalation in all three electrolyte systems, using experimental and computational methods to understand why the PEG-based hybrid electrolyte exhibits the least H+ intercalation and the most dominant Zn2+ intercalation.

The synthesized LiV2(PO4)3 (Li3VP)—carbon composite consists of approximately 1 μm aggregate crystallites that are enclosed by conductive carbon (Figure S1). The ~8.75% carbon content was confirmed by thermogravimetric analysis (TGA), as shown in Figure S2. LiV2(PO4)3 (LVP) electrodes were prepared by charging Li3VP electrodes to 1.85 V (vs Zn2+/Zn) in 4 m Zn(OTf)2, where two Li+ per formula unit of Li3VP was successfully extracted. Rietveld refinement of the powder X-ray diffraction (XRD) pattern indicates that all LVP reflections are well indexed to a monoclinic LVP phase with a space group of P21/c. A unit cell volume contraction of 7.3% upon two Li+ extraction is in close accord with the reported value (Tables S1 and S2).17

The electrochemistry of LVP in 4 m Zn(OTf)2 was compared to 29 m ZnCl2 WiSE electrolytes at a 1 C rate (discharge/charge of 1 Zn2+ in 1 h). Very different electrochemical behavior was observed. As shown in Figure 1a, in 4 m Zn(OTf)2 a new discharge plateau below 0.5 V accompanies the increase in capacity and becomes more dominant as the cycle number rises, suggesting a phase conversion process (Figure 1b). That process is especially evident in the differential capacity curve (Figure S3a). The new lower-voltage plateau was also identified by Wang et al. for a spray-dried LVP cathode,15 but its origin was not disclosed. It should be noted that this low-voltage discharge plateau (0.5 V vs Zn) is also seen in VOx-based cathode materials, indicating H+ intercalation and the formation of LDHs.8−10 In contrast, no lower-voltage plateau was observed in ZnCl2 WiSE, only a minor activation-like process (Figures 1c, d and S3b). Strikingly different from the high maximum capacity of 200 mAh g−1 exhibited in 4 m Zn(OTf)2, a more realistic discharge capacity of about 90 mAh g−1 was recorded at the 60th cycle in ZnCl2 WiSE after the initial activation process. LVP also shows poor cycling stability in 4 m Zn(OTf)2 with only 61% capacity retained after cycling at a rate of 1 C for 200 cycles (Figure 1b), whereas very good cycling stability with a high capacity retention of about 88% in ZnCl2 WiSE was observed at the same rate for 500 cycles (Figure 1d). Such contrasting electrochemistry is also exhibited at higher current densities, as shown in Figure S4.

The abnormal electrochemistry observed in 4 m Zn(OTf)2 can be attributed to the decomposition of LVP and the formation of hydrated vanadium oxides (VOx) phases based on our X-ray diffraction (XRD) studies. The XRD patterns in Figure 2a show that monoclinic LVP gradually disappears in 4
Zn(OTf)₂ as the cycle number increases. Simultaneously, two new reflections assigned to hydrated VOₓ phases appear, and finally become the major components of the active material (Figure S5). The morphology of the LVP electrodes during this phase conversion process was determined by SEM (Figure 2b). The well-crystallized particles gradually decompose and exhibit severe loss of crystallinity on cycling. EDX mapping also reveals a gradually decreasing P:V ratio (Figure S6a), further supporting the formation of hydrated VOₓ phases. In contrast, the structure of LVP was better maintained in ZnCl₂ WiSE as cycling progressed (Figure 2a), although two small new peaks corresponding to hydrated VOₓ appear over a period of 20 cycles. Figures 2b and S6b shows that the morphology and P:V ratio of LVP electrodes only change slightly in ZnCl₂ WiSE, where clear and distinguishable crystalline particles are preserved upon cycling.

To explore whether hydrated VOₓ phases result from vanadium dissolution of LVP or H⁺ uptake, LVP electrodes were soaked in 4 m Zn(OTf)₂, ZnCl₂ WiSE, and with the addition of 0.2 m H₃PO₄ to both electrolytes. Figure 2c shows the XRD patterns of LVP electrodes that were soaked in the above four electrolytes for 24 h. The intensity and position of the LVP reflections compared to the pristine material remain unchanged in 4 m Zn(OTf)₂, indicating insignificant vanadium dissolution. However, a major change in the XRD pattern was observed for the electrode soaked in ZnCl₂ WiSE for 24 h,
which we ascribe to ion-exchange of Li⁺ for Zn²⁺ owing to a similar ionic radius and the ultrahigh Zn concentration. With the addition of 0.2 m H₃PO₄, this ion exchange process is partially suppressed. While the LVP phase completely disappears in 4 m Zn(OTf)₂ + 0.2 m H₃PO₄, two new distinct and characteristic peaks of hydrated VO₃出现. This XRD pattern is almost the same as that of fully charged LVP after 20 cycles at C/5 in 4 m Zn(OTf)₂ (Figure S7), suggesting H⁺ uptake is responsible for generating these hydrated VO₃ phases.

Dominant Zn²⁺ intercalation of LVP in ZnCl₂ WiSE was confirmed by Rietveld refinement of the XRD pattern of fully discharged LVP (at a C/40 rate). As shown in Figure 3a and Table S3, two independent phases with different amounts of intercalated Zn²⁺ coexist: 59 wt % of a Zn-rich phase (Zn₀.₃⁴Li₀.₆₆V₂(PO₄)₃) and 41 wt % of a Zn-deficient phase (Zn₀.₃₃Li₀.₆₇V₂(PO₄)₃). The average fraction of inserted Zn²⁺ was 0.61 per formula unit, corresponding to an electrochemical capacity of 83 mAh g⁻¹.

The electrochemistry observed for LVP in 4 m Zn(OTf)₂ can be ascribed to the decomposition of active materials induced by H⁺ intercalation, which likely produces hydrated vanadium oxides as discussed above. This H⁺ intercalation process can be largely suppressed by using ZnCl₂ WiSE, resulting in dominant and reversible Zn²⁺(de)intercalation electrochemistry. Suppression of H⁺ intercalation is due to an interrupted H₂O hydrogen bonding network and the existence of only a small fraction of free water molecules in ZnCl₂—WiSE as we show below via molecular dynamics (MD) simulations. A systematic study on a similar ZnCl₂—WiSE has been carried out by Ji et al.¹⁹,²⁰ Their studies, using FTIR spectroscopy, revealed a decreased O—H symmetric stretch (3200 cm⁻¹) and an increased asymmetric stretch (3400 cm⁻¹) on increasing the concentration of ZnCl₂ from 5 to 30 m, suggestive of a strong Zn²⁺—water interaction that triggers interruption of H₂O hydrogen bonding network.

Further analysis of our simulations reveals that the fraction of free water is only 16% in 70PEG, compared to 47% in 4 m Zn(OTf)₂ (3.3, Figures 4a and S12), reducing the amount of water available to react at the cathode surface. The Zn²⁺—H₂O coordination distance is similar in all three electrolytes (Figure S13), indicating that the strong Zn²⁺—H₂O interactions previously observed in ZnCl₂ WiSE are operative in 70PEG as well. Nonetheless, while ZnCl₂ is low-cost, it is also corrosive at high concentrations. As an alternative approach to reducing H₂O activity, we designed a novel hybrid AZE by using a high concentration of polyethylene glycol 400 (PEG 400) as a crowding agent to form a PEG/H₂O cosolvent. Increased PEG content in 2 m Zn(OTf)₂ (∼2.2 M) lowers the conductivity and increases the viscosity as expected (Figure S10). Nonetheless, σL is still 0.7 mS cm⁻¹ even at 70 wt % PEG (denoted as 70PEG, see Methods), comparable to that of ZnCl₂—WiSE.¹⁹ FTIR spectra suggest a strengthened O—H bond owing to the strong H-bonding network between PEG and H₂O (Figure S11), which is anticipated to be less favorable to cleavage at the cathode interface in an electrochemical cell.

We propose that H⁺ intercalation at the cathode interface can be effectively suppressed owing to this decreased H₂O activity. Indeed, analysis of the Zn²⁺ solvation structure obtained from MD simulations of the bulk electrolyte shows that the Zn²⁺—H₂O coordination number in 70PEG (2.3) is lower than in 4 m Zn(OTf)₂ (3.3, Figures 4a and S12), significantly decreasing from 10 m ZnCl₂ to 30 m ZnCl₂.²⁰

Further analysis of our simulations reveals that the fraction of free water is only 16% in 70PEG, compared to 47% in 4 m Zn(OTf)₂ and 0% in ZnCl₂—WiSE (Figure 4c, Table S4), presumably resulting in very low water activity. Examination of the structure of the 70PEG shows that PEG400 molecules aggregate to form PEG-rich regions which absorb water but exclude ions (Figures 4b, d and S14). This finding is consistent with experimental studies, which have shown that PEG aggregates in aqueous solution, forming internally hydrated helical structures that result from the balance of hydrophobic and hydrophilic moieties on the molecule.¹⁹ In 70PEG, this internal hydration reduces the free water content and hinders H₂O molecules from transporting to the cathode interface. Thus, we attribute the reduced H⁺ intercalation in ZnCl₂—WiSE and 70PEG to the low availability and reactivity of water molecules.

Proof of concept was realized by evaluating Zn plating/stripping behavior for the hybrid AZE in Ti/Zn asymmetric cells, where a very high Coulombic efficiency of around 99.7%...
is achieved for 70PEG at a current density of 1 mA cm$^{-2}$ (1 mAh cm$^{-2}$ capacity), as shown in Figure 5a, b. In contrast, 0PEG cells suffer from extensive dendrite formation under the same operating conditions and failed after three cycles (Figure S15). A Zn||Zn symmetric cell with 70PEG also functions steadily with a capacity of 1 mAh cm$^{-2}$ over more than 1800 h (>450 cycles), with a denser and more oriented Zn deposition morphology (Figures S16 and S17). Such dendrite-free Zn plating/stripping is consistent with previous work based on a very low weight ratio of PEG or PEO (<1 wt %) in water, where the adsorption of PEG polymer on the electrode surface was proposed to result in more uniform Zn deposition. In addition, the electrochemical stability window is expanded to 2.75 V in 70PEG (vs 2.32 V in 0PEG) owing to the reduced water activity (Figure S18).

The 70PEG electrolyte is as efficient for suppressing H$^+$ intercalation as ZnCl$_2$ WiSE in LVP||Zn full cells (Figure S19). Compared to the second discharge capacity of 115 mAh g$^{-1}$ (~0.85 Zn$^{2+}$) in ZnCl$_2$ WiSE, a similar capacity of 112 mAh g$^{-1}$ (~0.82 Zn$^{2+}$) is obtained at C/40 in 70PEG (Figure S19). Analysis of the electrode by EDX shows a composition of 0.83 Zn$^{2+}$ per formula unit, suggesting almost all the capacity is contributed by Zn$^{2+}$ intercalation (compared with only 70% in ZnCl$_2$ WiSE). XRD patterns of these two discharged samples are quite similar (Figure S5c); however, the presence of at least three zincated phases lead to a poor Rietveld fit owing to the significant overlap of peaks in these similar structures. Galvanostatic intermittent titration technique (GITT) studies in LVP/70PEG (Figure Sd) yielded an average diffusion coefficient of $\sim 10^{-13} - 10^{-16}$ cm$^2$ s$^{-1}$ that is about $10^2 - 10^3$ lower than previously reported, presumably owing to the lack of significant contribution from H$^+$-ion diffusion. Protons are anticipated to be much more mobile due to their small ionic radius and monovalent property. However, direct comparison with LVP/4 m Zn(OTf)$_2$ could not be obtained due to severe phase transformation resulting from very high degrees of proton intercalation at such a low rate of C/40, where endless discharging was observed (Figure S20). Long-term Zn$^{2+}$ cycling behavior of LVP in PEG was also evaluated at higher rates (Figure 5e). After an initial activation process, LVP can be cycled steadily with a capacity retention of 83.5% after 100 cycles at C/5 and 74.5% after 300 cycles at C/2. Compared to the evolution of the charge/discharge curves upon cycling cells in 4 m Zn(OTf)$_2$, only a slight change can be observed in 70PEG (Figure S21). The absence of a voltage plateau below 0.5 V also indicates the suppression of H$^+$ intercalation.

In summary, our studies of 4 m Zn(OTf)$_2$, 29 m ZnCl$_2$ WiSE, and 2 m Zn(OTf)$_2$ PEG-based hybrid electrolyte on Zn$^{2+}$ versus H$^+$ insertion/extraction of an LVP cathode, reveal the effect of solvation structure and H$_2$O hydrogen bonding network on H$^+$ intercalation. Proton cointercalation verified in 4 m Zn(OTf)$_2$ is suppressed in ZnCl$_2$ WiSE by the interrupted hydrogen bonding network induced by a strong Zn$^{2+}$--H$_2$O interaction and few free H$_2$O molecules, resulting in dominant Zn$^{2+}$ intercalation that is confirmed quantitatively by Rietveld refinement and EDX. A reduced free water content and further optimized solvation structure was identified in a 2 m Zn(OTf)$_2$ and 70PEG.
PEG-based hybrid electrolyte, where 70PEG shows excellent reversibility and stability for Zn plating/stripping and much better suppression of H\(^+\) intercalation due to the strong interaction between PEG and H\(_2\)O. The excellent ultra low-rate electrochemical performance (C/40) of LVP in 70PEG also suggests the hybrid electrolyte outperforms the conven-
tional low-concentration aqueous electrolyte to realize dominant Zn$^{2+}$ intercalation. Our work demonstrates that tuning the solvation structure and building strong interactions between H$_2$O and PEG to interrupt the H$_2$O hydrogen bonding network is an effective strategy to suppress detrimental H$^+$ intercalation, maximize Zn$^{2+}$ intercalation, and achieve highly reversible Zn utilization.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02514.

Experimental methods, electrochemical measurements, Rietveld refinements, and lattice parameters (PDF)

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**Author Contributions**

C.L. and L.F.N. designed this study. C.L. synthesized the materials, carried out the characterization and all the electrochemical measurements. R.K. and K.A.P. performed molecular dynamics simulations. L.Z. helped with the Rietveld refinements. A.S. helped to perform the GITT measurement. C.L. and L.F.N. wrote the manuscript with contributions from R.K. and K.A.P.

**Notes**

The authors declare no competing financial interest.

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