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Perspective—Electrolyte Design for Aqueous Batteries: From Ultra-High Concentration to Low Concentration ?

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High voltage aqueous Li-ion batteries have the potential for sustainable large-scale energy storage due to their intrinsic advantages of safety, low cost, as well as environmental friendliness. "Water-in-salt" electrolytes have significantly enhanced the energy density of aqueous Li-ion batteries by extending the aqueous electrolyte stability window to 3.0 V. However, the cathodic limit and salt concentration need to be reduced, enabling to operate low cost $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells. In addition, gravimetric energy density of LiMn $_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$, self-discharge rate, and operation temperature range remain rarely studied. This perspective aims to briefly summarize the opportunity and challenges of aqueous batteries for practical applications. © 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ ac5ba9]

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To address the climate crisis and achieve net-zero emissions, advanced batteries are required for electric vehicles, and large-scale energy storage. Conventional non-aqueous Li-ion batteries possess relatively high energy densities, however, suffer from the safety issues largely originating from the flammable organic electrolytes. To make Li-ion batteries intrinsically safe, the flammable organic electrolytes can be replaced by aqueous electrolytes with water as the non-flammable solvent. In addition, water is totally non-toxic, and the cost of water and water-soluble lithium salts is relatively low. In these regards, aqueous Li-ion batteries with high safety, lowcost, and environment-friendly is a promising choice towards the gigawatts of energy storage coming over the next decades. However, the narrow electrochemical stability window (ESW: ≤ 1.5 V) of the aqueous electrolyte is a long-standing barrier for achieving a high energy density of aqueous Li-ion batteries.² Our recent invention of "Water-in-salt" (WIS) electrolytes significantly expanded the ESW to as high as 3 V by forming a robust solidelectrolyte interface (SEI),³ which provide the opportunity to develop high energy and safe aqueous Li-ion batteries. However, the cathodic limit of 1.9 V (vs Li) for WIS electrolyte is still not low enough for using the high-capacity anode (such as Li₄Ti₅O₁₂). Besides, the cost and energy density of WIS electrolyte-based Li-ion batteries still cannot complete with organic electrolyte Li-ion batteries. Extensive research has been conducted to extend the cathodic limit at a reduced salt concentration by introducing additives into WIS. In addition, some critical parameters of aqueous pouch cells such as self-discharge, gassing and fast charging capability were also investigated.4

This perspective seeks to summarize the recent advances and challenges of aqueous electrolytes for high-voltage Li-ion batteries. First, we reviewed the expanding process of electrochemical stability window through changing the salt concentration from "salt-in-water," to "water-in-salt" and then come back to "salt-in-water." Then we discussed the design principle of "salt-in-water" electrolyte for high energy aqueous Li-ion batteries. Finally, we provide a critical outlook for pushing aqueous batteries into practical applications.

Current Status

The success of high energy organic electrolyte Li-ion batteries is partially attributed to the formation of solid electrolyte interphase (SEI) on graphite anodes, which significantly extended the stability window of organic electrolyte from 3.0 V to 4.2 V.⁵ However, it is very challenging to form a SEI on the anode in salt-in-water electrolytes because the water reduction potential is much higher than that of salt and the reduction of water produces gas rather than solid phase. However, when the LiTFSI salt concentration increase to the water-in-salt state (21 m), the salt can be reduced to form a robust SEI under catalytic of OH⁻ formed by water reduction,⁶ expending the electrochemical stability window to 3.0 V. To further extend the electrochemical stability window, Yamada et al.⁷ mixed two lithium salts of LiTFSI and LiBETI to form a hydrate-melt electrolyte, further increasing of salt concentration to 27.7 m. Meanwhile, Wang and co-workers investigated 28 m "water-inbisalt" electrolyte,⁸ consisting of 21 m LiTFSI and 7 m LiOTf, making TiO₂ anode possible. Afterward, 40 m mixed cation electrolytes,⁹ 55.5 m lithium-salt monohydrate,¹⁰ and 63 m ionicliquid electrolytes¹¹ were successfully developed following the same logic. However, the cathodic limit of the aqueous electrolytes only slightly extends to 1.75 V even when the concentration increases to 63 m.¹¹ It is highly possible that the SEI cannot block the solvated water, and the gas from water reduction disrupted the SEI. The water-in-salt electrolyte concept also extended to other aqueous batteries,^{12,13} including monovalent Na^{+}/K^{+} -ion, and $Zn^{2+}/Mg^{2+}/Al^{3+}$ multivalent batteries. Unfortunately, the high salt concentration itself drives up the cost of the electrolytes. According to the cost comparison of various high-concentration electrolytes,¹ there is clearly an urgent need for the development of low concentration, high voltage aqueous electrolytes.

To further extend the electrochemical stability window (ESW) and performance at a reduced cost,¹⁵ SEI formation agent solvents were introduced into WIS electrolytes. Lu et al.¹⁶ added PEG organic solvent into WIS achieving a wide ESW of 3.2 V at a low salt concentration of 2 m. Suo et al.¹⁷ introduced CO₂ into WIS electrolyte to promote the formation of Li2CO3-rich SEI in 5 m LiTFSI-CO₂-H₂O electrolyte. We reported a 4.5 m ternary eutectic LiTFSI-KOH-CO(NH₂)₂-H₂O electrolyte enabling 2.5 mAh cm⁻² LiMn₂O₄||Li₄Ti₅O₁₂ full cell to achieve excellent cycle life with a record CE of ~99.9% and low self-discharge rate.¹⁸ Electrochemical stability window roadmap of aqueous electrolytes by changing the salt concentration from salt-in-water to water-in-salt, and back to salt-in-water electrolyte is presented in Fig. 1. The advance in the expansion of electrochemical stability window is attributed to the deep understanding of the solvation structure and interface chemistry through advanced characterizations together with first-principles calculations.¹⁹ The long cycle life and high rate performances of high voltage aqueous batteries reported in the literature demonstrated a high possibility for commercialization of high energy aqueous batteries. To bridge the gap between academic research and practical applications, in this perspective, we addressed three critical requirements for commercial aqueous batteries.



Figure 1. Aqueous electrolytes roadmap from salt-in-water to water-in-salt, and back to salt-in-water electrolyte (Source: Web of Science, Clarivate Analytics). Refs. 2, 3,7–11,16–18.

Future Needs and Prospects

Gravimetric energy density at the cell-level.—To make the aqueous batteries competitive with non-aqueous batteries, gravimetric energy density is the most important parameter for realistic aqueous cells. Most of the current works intuitively focus on pushing the limit of ESW of aqueous electrolyte to achieve a high cell voltage and thus a high energy density.²⁰ However, when cyclic voltammetry is employed for ESW measurement, the current collector, a low CV scan rate (<1.0 mV s⁻¹), and a low cut-off current density should be properly chosen to give a more accurate assessment of the ESW.²¹ In addition, the gravimetric energy density calculation is normally only based on the total mass of active materials. By taking the amount of inactive materials into consideration, the areal capacity loading (capacity loading per unit area), the electrolyte quantity, and the positive/negative capacity (P/N) ratio are critical for the practical energy density of realistic cells.

Firstly, electrodes with high areal capacity (≥ 1.5 mAh cm⁻²) are required to achieve a reasonable cell energy density. At a low areal capacity of <0.5 mAh cm⁻², the aqueous cell can achieve a high rate performance and long cycle life in the super concentrated aqueous electrolytes with a high viscosity, low ionic conductivity and poor wettability. In such cases, increasing of areal capacity leads to much more severe polarization, lower utilization of active materials, and poor rate performance. Therefore, the areal capacity of the aqueous cells highly depends on the ionic conductivity, viscosity, and simplified electrolytes. Based wettability of the on LiMn₂O₄||Li₄Ti₅O₁₂ pouch cells, we calculated the energy density at the different areal capacities. As shown in Fig. 2a, a significant 10% surge in cell-level energy density from 98 to 107 Wh kg⁻¹ at a lean electrolyte of 3 g $A^{-1}h^{-1}$ is expected by increasing the areal capacity from 0.5 to 1.5 mAh cm⁻². Upon further increasing the areal capacity from 1.5 to 2.5 mAh cm^{-2^{-2}}, a small increase of 2% in energy density is estimated. This indicates that the areal capacity of 1.5 and 2.5 mAh $\rm cm^{-2}$ are the optimal values that benefit the higher energy density for the specific LiMn₂O₄||Li₄Ti₅O₁₂ system.

Secondly, the amounts of electrolytes also play a vital role in determining the energy density at the cell level. For a given areal capacity loading of 2.5 mAhcm², the specific energy densities of LiMn₂O₄||Li₄Ti₅O₁₂ pouch cells are 132, 124, and 117 Wh/kg for electrolyte usage of 1.5, 2.0, 2.5 g A⁻¹h⁻¹ (Fig. 2a), respectively. This suggests that lean electrolyte is required to achieve a high energy density. However, a large amount of electrolyte (typically > 5 g A⁻¹h⁻¹) was used in the reported aqueous batteries. So far, it is still challenging to reduce the aqueous electrolyte quantity owing to the decomposition of the aqueous electrolytes. Continuous efforts are needed to use the lean electrolyte by improving the wettability between electrolytes and electrolyte density, and so on. Also bearing in

mind that the electrolyte quantity greatly affects other cell properties such as self-discharge which will be discussed in detail in the next section.

Thirdly, the deviation of the ideal P/N ratio of 1, either high P/N ratio or low P/N ratio, results in a significant reduction in specific energy density. Note that the energy densities in Fig. 2a are calculated for the perfect capacity match between the LiMn₂O₄ cathode and Li₄Ti₅O₁₂ anode (P/N ratio = 1). In regard to realistic aqueous batteries, the limited ESW of aqueous electrolyte suffers from side reactions, and the formation of SEI will consume the Li from the cathode. Common strategies to compensate for the lithium loss such as employing a P/N ratio large than 1.0, or adding Li-rich second materials (Li₂O reported in non-aqueous batteries) in the cathodes will unavoidably decrease the energy density.²² Another possible solution is using Li-rich cathodes (Li_{1.5}Mn₂O₄) without increasing the P/N ratio and without sacrificing energy density.¹⁷

To sum up, a more stringent evaluation of energy density at the cell level is suggested to allow more accurate assessment and comparison. Key factors like areal capacity loading, electrolyte quantity, and P/N ratio need to be optimized to achieve high energy density for realistic cells.

Self-discharge.—Self-discharge is the Achilles' heel of aqueous batteries, and has been rarely studied. The self-discharge occurs when one and/or both electrodes is not within the electrochemical stability window of the electrolyte, or a shuttle reaction between anode and cathode occurs. In high voltage aqueous electrolytes, the formation of SEI suppresses the H₂O reduction. the self-discharge behaviors are clearly correlated with SEI stability, which is critical to suppress H₂ gas generation, and reduce safety hazards.²³ Tarascon et al.⁴ performed operando gas monitoring of Mo₆S₈||LiFePO₄ full cell using online electrochemical mass spectrometry (OEMS) and found a continuous formation of gaseous hydrogen and severe selfdischarge in a flood electrolyte since the formed SEI can be partially dissolved into aqueous electrolytes when electrolyte quantity is large. While no visible gas generation is observed for 2 m molecular crowding electrolyte using the same OEMS method due to the low solubility of SEI compound and a small amount of aqueous electrolyte.¹⁶ Therefore, the formation of SEI that has low solubility in aqueous electrolytes and the use of lean electrolytes can significantly reduce the self-discharge of aqueous Li-ion batteries. Thus, the self-discharge experiments should be conducted and compared by maintaining the same amount of electrolyte as normal non-aqueous batteries if possible. The SEI stability is also highly affected by the operation temperature. Simply taking LiF as an example, the solubility of LiF in water increases from 0.13 to 0.14 wt% when the temperature increases from 25 to 50 °C.²⁴ Not even to mention the easy breakdown of SEI accompanied by diverse side reactions triggered at elevated temperatures. There is no wonder that



Figure 2. (a) The projected energy density of the LiMn₂O₄||Li₄Ti₅O₁₂ pouch cell at different electrode areal capacities and electrolyte amounts (2.0; 2.5; and 3.0 h/Ah). The projected energy density was calculated by consideration of cathode active materials, anode active materials, binder, conductive carbon, current collector, electrolyte, and package materials. Detailed parameters can be found in the previous report.¹⁸ (b) Critical factors to make practical aqueous batteries possible.

the self-discharge process is exacerbated at 50 °C. To deep understanding of the self-discharge mechanism in aqueous electrolytes, in situ techniques (Raman, or FTIR) is highly required.

The SEI stability in aqueous electrolytes also affects the true cycle life and Coulombic efficiency (CE). When the SEI is not stable, the side reaction depends on the reaction times. The true cycle life and CE in aqueous electrolytes should be measured at a low current. A high CE can be achieved by applying a very high current for a short time with a high capacity. For aqueous batteries, the minimum discharge time should be 1.0 h.

Operation temperature range.—Another key parameter that is often overlooked is the operation temperature range. Practical cells should be able to operate at wide temperature ranges, from subzero to as high as 60 °C. At a high temperature, Li-ion conductivity increased and viscosity reduced which favors rate performance. However, the side reaction between electrode materials and electrolytes is also enhanced the SEI stability is reduced. For example, Li₄Ti₅O₁₂ in the presence of carbon was found to have extreme reactivity towards electrolytes at high temperatures such as 60 °C.² The manganese dissolution into the aqueous electrolyte is accelerated at high temperature,²⁶ limiting the cyclability of LiMn₂O₄ electrodes. An increase of the operating temperature of aqueous batteries is generally accompanied by lower CE caused by side reactions and SEI instability. Intrinsically, the high temperature makes the original SEI unstable, which has already been discussed in the self-discharge section.

In the case of subzero temperature, the insufficient ionic conductivity and freezing of electrolytes are generally considered as the main limitations. It is easy to understand that the Li⁺ diffusion would become sluggish within electrodes under low temperatures. Besides the poor kinetic problem, possible crystallization is another concern for the aqueous electrolyte of ultra-high concentration even though the freezing point of electrolytes are depressed at high salt concentration. Introducing acetonitrile with a low freezing point as a co-solvent is a nice try to enable low-temperature operation.²⁷ Depressing the freezing point via eutectic effect (DMSO-H₂O) is another effective strategy to develop low-temperature aqueous batteries.²⁸

Overall, the aforementioned three key parameters (gravimetric energy density at the cell level, self-discharge, and operation temperature range) are interwoven and dynamically interact with each other (Fig. 2b). In designing aqueous electrolytes for practical application, we need to combine and compromise them into one single cell. It is important to consider the battery as a whole system, system thinking of balancing the interwoven and interactive parameters can direct us towards better batteries.

Conclusions

Electrolyte design is critical to developing advanced Li-ion aqueous batteries with superior performances. In addition to the fundamental understanding of the solvation structure of the electrolytes and interfacial chemistries, we emphasize that practical conditions including gravimetric energy density at the cell level, self-discharge property, and operation temperature range cannot be overlooked when considering aqueous batteries into large-scale applications.

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