news & views

BATTERIES

Widening voltage windows

The energy output of aqueous batteries is largely limited by the narrow voltage window of their electrolytes. Now, a hydrate melt consisting of lithium salts is shown to expand such voltage windows, leading to a high-energy aqueous battery.

Kang Xu and Chunsheng Wang

Aqueous Li-ion batteries offer advantages in terms of safety, toxicity and cost over their non-aqueous counterparts. However, their energy density (typically less than 80 Wh kg⁻¹ based on the total mass of electrodes) is much smaller than that of the state-of-the-art non-aqueous Li-ion batteries[1] (250–400 Wh kg⁻¹). This is because the electrochemical stability window of aqueous electrolytes is much narrower than that of the non-aqueous ones. This stability window is determined by the reductive and oxidative reactions of salts, solvents or additive components in the electrolyte[2]. To ensure the reversibility (and hence rechargeability) of batteries, redox reactions of both the negative and positive electrodes must take place within such a window. In aqueous electrolytes, however, the stable operating voltage window of water is only 1.23 V, beyond which undesired water hydrolysis occurs. Expanding the operating voltage window therefore represents the core challenge in the development of practical aqueous Li-ion batteries. Recently, a highly concentrated aqueous electrolyte, dubbed water in salt, was shown to expand the voltage window to ~3.0 V on stainless steel electrodes, but the energy density remains around 100 Wh kg⁻¹ (ref. 3). Writing in *Nature Energy*, Atsuo Yamada and colleagues now report a eutectic system of organic Li salts as a new class of stable aqueous electrolytes with a voltage window larger than 3.1 V when measured on platinum (Pt) for anodic and on aluminium (Al) for cathodic limits, and demonstrate an aqueous battery with an energy density above 130 Wh kg⁻¹, competitive with non-aqueous Li-ion batteries[4].

By optimizing the mixing ratio of two organic Li salts, $LiN(SO_2CF_3)_2^-$ (LiTFSI) and $LiN(SO_2C_2F_5)_2^-$ (LiBETI), the researchers identified a room-temperature Li salt hydrate melt, $Li(TFSI)_{0.7}(BETI)_{0.3} \cdot 2H_2O$, in which the water content is minimal, and all water molecules participate in the Li⁺ hydration. This is in contrast to typical aqueous solutions where, in addition to the hydration shells, many 'free' water molecules also form hydrogen bonding networks.

The very low water molar concentration (6.30 mol kg⁻¹) and very high lithium salt concentration (27.8 mol kg⁻¹) in the hydrate melt bring about several unusual physicochemical behaviours. Firstly, despite the high viscosity, the hydrate melt possesses a high ionic conductivity of 3.0 mS cm⁻¹, because the Li⁺ movement is not affected much by the hydration effect of the water molecules. Secondly, the oxidation potential of the water molecules is increased because of the strong Coulombic bonding of the oxygen atom in the water molecule by the Li⁺, which pushes the anodic limit on the Pt electrode up to 5.05 V versus Li⁺/Li. On the other hand, the passivation of the negative electrode surface, through the formation of the interphase between the hydrate melt and the Al electrode, extends the potential window down to 1.75 V versus Li⁺/Li. The overall effect is a voltage window larger than 3.1 V. Thirdly, the water hydrolysis involving hydrogen and oxygen evolution is significantly suppressed at both the Pt
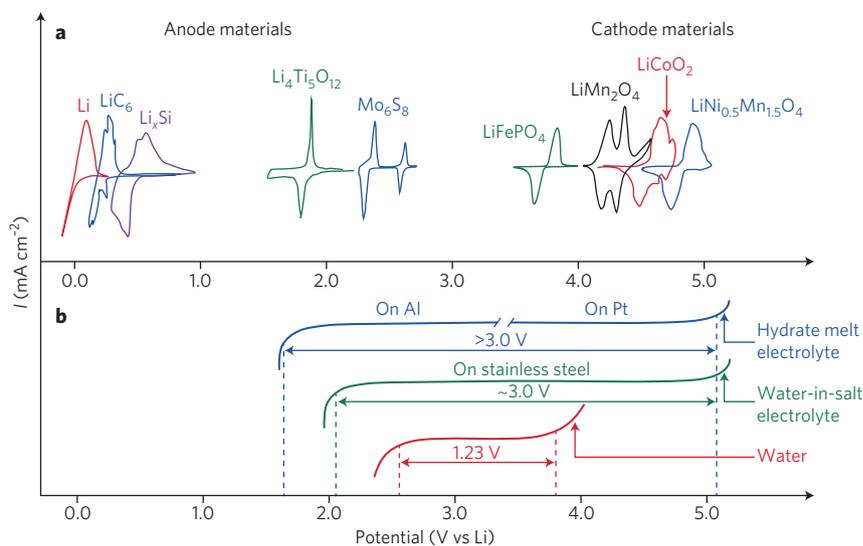

Figure 1 | Electrochemical stability windows of aqueous electrolytes and redox potentials of electrode materials. **a**, The redox potentials of major anode and cathode materials used in commercial Li-ion batteries were derived from either cyclic voltammogram (for lithium metal, Mo_6S_8, $Li_4Ti_5O_{12}$, $LiMn_2O_4$ and $LiFePO_4$) or galvanostatic experiments (for the others) and then converted to a Li⁺/Li potential scale. Note that the current density, I (mA cm⁻²), from the cyclic voltammogram carries equivalent information as the differential capacity (measured in mAh V⁻¹ g⁻¹) from the galvanostatic experiments in defining the voltage stabilities. All data is original and supplied by the authors. For Li metal, graphite and silicon anodes, we used non-aqueous electrolytes: 1.0 M $LiPF_6$ in ethylene carbonate/fluoroethylene carbonate/dimethyl carbonate (20:10:70) for silicon, and 1.2 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (30:70) for other anodes. For $Li_4Ti_5O_{12}$, Mo_6S_8, $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ cathodes, we used our own 'water-in-salt' or 'water-in-bisalt' electrolytes[3,6]. **b**, Redox reactions of water molecules at pH = 7 evolves hydrogen and oxygen at anode and cathode surfaces, respectively, giving rise to a thermodynamic stability window of 1.23 V, whereas the use of the electrolytes with highly concentrated salts (21 mol kg⁻¹ in the water-in-salt, measured on stainless steel, and 27.8 mol kg⁻¹ in the hydrate melt electrolytes, measured on Ti and Al, respectively) significantly expands windows to larger than 3.0 V.

positive and Al negative electrodes because of the absence of the 'free' water molecules.

These properties, especially the significantly expanded electrochemical stability window, make the hydrate melt an excellent aqueous electrolyte. As shown in Fig. 1, many electrode materials commonly used in Li-ion batteries can be accommodated in such a voltage window. In their work, the researchers demonstrate that the hydrate melt electrolyte allows an operation of $Li_4Ti_5O_{12}$, an energy-dense anode material at 1.75 V versus Li^+/Li, and $LiNi_{0.5}Mn_{1.5}O_4$, a high-voltage cathode material at 4.8 V versus Li^+/Li, leading to a 3.0 V aqueous Li-ion battery, which is the highest voltage aqueous battery reported to date.

They further show that coupling $Li_4Ti_5O_{12}$ with $LiCoO_2$, a cathode material that has a moderate redox potential but higher utilizable capacity, can produce a 2.3 V aqueous battery that delivers an energy density of approximately 130 Wh kg^{-1}. The hydrate melt electrolyte withstands the rigorous galvanostatic cycling, as evidenced by nearly 100% Coulombic efficiencies at both high (10C) and low (0.2C) rates. It should be mentioned that cycling at a low rate is often more challenging, because the

effect of parasitic reactions, such as water decomposition, will be more visible during the longer exposure of aqueous electrolytes to extreme potentials.

Despite the impressive performance shown in the work of Yamada and colleagues, several remaining concerns need to be addressed before this aqueous battery can be adopted in automotive and grid applications. Above all, the lithium salts used at such a high concentration are expensive, although the costs could be partially compensated in the overall production because aqueous electrolytes do not require a moisture-free production line. Furthermore, the battery packaging could be simplified, because of the safe and non-corrosive nature of aqueous solutions. Moreover, the energy density of aqueous batteries is still inferior to their non-aqueous counterparts at the cell level. In particular, the cathodic limit of the expanded voltage window still does not allow the operation of typical anode materials such as graphite, silicon or lithium metal (Fig. 1). Finally, the expanded electrochemical stability window of 3.1 V for those new aqueous electrolytes is actually not fully used, as the energy density of 130 Wh kg^{-1} is achieved with a battery voltage of only 2.3 V.

While further identification and optimization of anode–cathode couples for such aqueous electrolytes are required to achieve more competitive energy densities (>200 Wh kg^{-1}), we should remember that the first generation Li-ion battery, commercialized by Sony in the early 1990s, only achieved ~90 Wh Kg^{-1} at the cell level[5] and it has only recently been able to reach 250–400 Wh kg^{-1}, allowing it to power various technologies today. It is not yet known whether the discovery made here will eventually lead to commercial success, but the hydrate melt electrolyte offers a promising pathway forward. ❐

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