

# A Passivation Mechanism in Hydrate-melt Electrolytes for High-voltage Aqueous Lithium-ion Batteries

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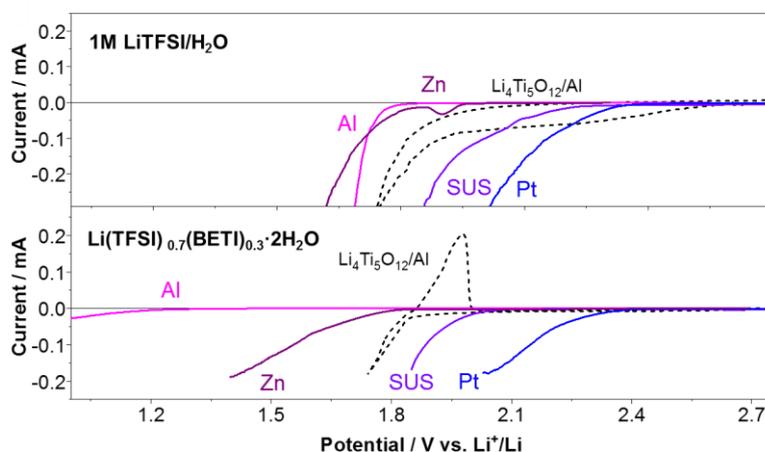
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High-voltage aqueous Li-ion batteries have been actively studied over 20 years to achieve both high energy density and ultimate safety. As part of such efforts, our group discovered a room-temperature hydrate-melt,  $\text{Li}(\text{TFSI})_{0.7}(\text{BETI})_{0.3}\cdot 2\text{H}_2\text{O}$ , as a new class of aqueous electrolyte, which enables the reversible operation of high-voltage ( $>3$  V) aqueous batteries with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  negative electrode due to its enhanced reductive stability based on the unique electrode passivation<sup>1</sup>). However, the detailed mechanism has not been fully understood yet. Herein we study the passivation mechanism from the viewpoints of the type of electrodes and the coordination state of electrolytes.

The hydrate-melt was prepared by mixing LiTFSI, LiBETI and pure water at the molar ratio of 7:3:20. From Figure 1, it is clear that the reduction stability of the hydrate melt strongly depended on the type of electrode, and an Al electrode showed the highest stability. Besides, cathodic limit (the onset for  $\text{H}_2$  evolution) on the Al electrode was extended as salt concentration was increased in the electrolyte, whereas the effect was not remarkable on a Pt electrode. To shed light on this phenomenon, the surface chemistry of Al electrodes in the hydrate-melt and dilute  $1 \text{ mol dm}^{-3}$  LiTFSI/ $\text{H}_2\text{O}$  electrolyte was analyzed via XPS and FE-SEM. The results suggest the formation of a passivation film mainly derived from the Li salt anions (TFSI and/or BETI) only in the hydrate-melt electrolyte, which may be a key factor that enhances the reductive stability through suppression of  $\text{H}_2$  evolution (reduction of water) in a kinetic way. The preferential reduction of Li-salts anions in the hydrate melt was also supported by projected density of states (PDOS) obtained with DFT-MD simulations.

## Reference

- 1) Y. Yamada et al, *Nature Energy*, **1**, 16129 (2016).



**Fig. 1** Linear sweep voltammogram ( $0.1 \text{ mV s}^{-1}$ ) of various metal electrodes (Al, Zn, stainless steel (SUS), and Pt) in  $1.0 \text{ mol dm}^{-3}$  LiTFSI/ $\text{H}_2\text{O}$  and hydrate-melt electrolytes. The dashed curves represent the cyclic voltammograms ( $0.1 \text{ mV s}^{-1}$ ) of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode on an Al current collector.