Alkali–Sulfur Redox Chemistry and Insights into Nonaqueous Metal–Sulfur Batteries

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Battery technology beyond lithium-based chemistry is critical to ensure low-cost and sustainable energy storage for grid and automobile applications. Recently, room-temperature sodium-sulfur (Na-S)[1, 2] and potassium-sulfur (K-S)[3, 4] batteries have attracted significant attentions in respond to the vast need in developing battery chemistry beyond lithium. We compare the *representative* voltage profiles of reported metal-S batteries, including lithium-sulfur (Li-S)[5], Na-S[1], and K-S[3] batteries. Interestingly, although the cation is the only differences in these batteries, the battery behaviors of alkali-sulfur batteries are drastically different[1-5] and the underlying mechanism responsible for the differences remain elusive. In this presentation, we will investigate the influence of cation on the sulfur redox reactions via *operando* UV–vis spectroscopy coupled with rotating-ring disk voltammetry (RRDE) approach. Here we select dimethyl sulfoxide (DMSO) as the electrolyte solvent which has high solubility of alkali metal salt from $LiClO_4$ to $RbClO_4$. These techniques offer well-defined characterizations[6, 7] to systematically reveal the differences and correlations between the Li-S and other alkali-sulfur redox reactions. We show that the larger alkali cation form a smaller solvent-ion complex due to lower coordination number, which yields an effective harder cation complex and thus hinders the formation of soft Lewis base (e.g. $S_3^{\bullet-}$). Using RRDE, we show that the smaller solvent-ion complex (e.g. K^+–$(DMSO)_n$) leads to higher diffusion coefficient of polysulfide, which explains more sever polysulfide shuttling in K-S batteries than in Li-S batteries. Detailed cation directed sulfur reaction pathways, the role of solvent –ion complex on the stability of polysulfides and the behaviors of metal sulfur batteries will be discussed.

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