Design and Mechanistic Understanding of the Nonaqueous Electrolyte Solvation Structure towards Optimized Interfacial Properties in Secondary Batteries

ABSTRACT

The interfacial reactions of the electrolytes at the electrode-electrolyte interface determine critical properties of the battery chemistries including the reaction reversibility, kinetic, and thermal stability etc. Rationally designing the solvation structure of the liquid electrolytes is paramount in altering their interfacial behaviors and achieving desirable battery performance. This thesis aims to provide fundamental understandings to the electrolyte solvation structure design in its correlations to the battery interphase stability and formation mechanism, interfacial desolvation kinetic, and thermal stability, providing strategies to build next-generation secondary batteries with improved energy density, wide-temperature capability, and thermal safety.

Developing high-voltage lithium metal battery (LMB) with metallic Li anode and nickel-rich metal oxide cathode is a feasible approach to enhance the battery energy density. However, inferior interfacial stabilities of conventional electrolytes towards highly reductive anode and oxidative cathode cause severe parasitic reactions. This thesis investigates the solvation structures of ether-based electrolytes and their interfacial decomposition pathways to selectively control the solid electrolyte interphase (SEI) composition. Combined theoretical and experimental studies demonstrate that lessening the coordination strength of the solvent molecules can improve the ion aggregating degrees in the solvation shell and preferentially promote the anion decomposition. Detailed surficial characterizations identify that weakly-solvating electrolytes generate robust SEIs with enriched inorganic components on anode and cathode surface, which kinetically prohibits parasitic reactions. The strategy successfully facilitates the long-term cycling of high energy LMBs. Weakening the solvent coordination ability is also identified effective to promote the desolvation kinetic and realize high battery energy retention at low temperatures.

The approach of tailoring ion-pairing behavior to achieve stabilized electrode-electrolyte interface is further validated in multivalent battery systems such as Magnesium-ion batteries (MIBs). Multivalent cations like Mg^{2+} and Zn^{2+} possess high electron density which results in strong coordination to solvent molecules and hindered desolvation process. They usually induce

large reaction overpotential and low efficiency. The methoxy-amine-based electrolytes for MIBs are selected in terms of elucidating their interfacial failure mechanism and the solvation structure-dependent reaction stabilities with Mg metal anode. The study reveals an unknown amine solvent dehydrogenation mechanism that compromises the Mg anode stability. The tight coordination between solvent amine group (-NH_2) and cation causes its direct reduction with H_2 release. The dehydrogenation products tend to diffuse into the liquid electrolyte phase, which promotes the interfacial electrolyte decay. This work also demonstrates the approach to strengthen the solvent molecule stabilities via restructuring the Mg^{2+} solvation shell. Introducing anion coordination to Mg^{2+} can effectively relief the amine-cation interaction and suppress its reduction. As the result, hundreds of stable cycling from Mg metal anode with more than 99.6 % efficiency is achieved.

Finally, the thermal stability of electrolytes featuring various solvation structures are studied in LMBs via quantitative thermal analysis and surficial characterization techniques. The thermal runaway of batteries which is known to be initiated via SEI decomposition and propagated by exothermic electrode-electrolyte reactions exhibit great dependence on the solvation structures of the liquid electrolytes. The results suggest that strong solvent-coordinating electrolytes with solvent-separated ion pair structures are prone to exothermic reduction decompositions. While the organic-rich SEI tends to decompose at low temperatures and initiate thermal runaway easily. Therefore, designing electrolytes with anion involved solvation shells that generate inorganic SEI can effectively mitigate the thermal runaway behavior. Supplementary research focusing on the thermal safety of Potassium-ion battery also indicates the critical role of SEI stability on the overall battery safety aspect, which is governed by the electrolyte composition.