Interfacial Mechanisms Understanding and Material Design for Lithium-Sulfur batteries via Integrated Computational Approaches

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Lithium-Sulfur (Li-S) batteries promise high gravimetric energy density and low cost, but its commercialization has been hindered by the rapid capacity and energy fading. In this thesis, several integrated computational models were developed to connect the electrode-electrolyte interface mechanisms with the battery discharge curves and the initial capacity loss. The new insights obtained from these models were used to design coatings on the anode, porous structures of the carbon-sulfur cathode, and the electrolyte.

On the Li anode side, the formation of an electrical insulating solid electrolyte interphase (SEI) at the anode-electrolyte interface is responsible for the initial irreversible capacity loss. Assume the electron tunneling from the electrode to the electrolyte is blocked by the SEI inorganic components at a critical thickness, based on the electronic tunneling barrier calculated from density functional theory (DFT), an analytical model was developed to connect the initial irreversible capacity loss with the anode surface area. Good agreement between the modeling prediction and experimental measurements was achieved, confirming that the initial irreversible capacity loss was due to the self-limiting electron tunneling property of the SEI.

The typical cathode is a composite with elemental sulfur embedded in a carbon matrix. During
discharging, the lithiation of sulfur involves the formation of a series of soluble long-chain Li polysulfides (Li-PSs) before the formation of the insoluble insulating Li$_2$S. In this thesis, it was found that the solvation status of Li-PS (fully, partially, or not dissolved) had a profound impact on both the ideal open circuit voltage (OCV) curves and the practical discharge voltage curves. The OCV was first predicted using DFT calculated free energies at finite temperatures along with the solvation energy, for the discharge reactions involving both insoluble crystals and dissolved Li-PS molecules. This model successfully revealed that the solvation energy stabilized the Li-PS. Thus, the formation of the fully solvated Li-PS led to the two-plateaued OCV; while the formation of non-solvated Li-PS is not favorable, so the direct transition from S to Li$_2$S led to a one-plateaued OCV. In practical cells, the solvation status of the Li-PS is highly related to the volume of the electrolyte. A mechanism based analytical model was developed to evaluate the influence of micrometer level porosity on the discharging curves by connecting the amount of electrolyte, the volume of the pores, the solubility of Li-PS in the electrolyte, and the surface area of the pores. This model was used to optimize the porosity of the carbon matrix to maximize the volumetric energy density of Li-S batteries.

The dissolved Li-PS can diffuse from the cathode to the anode, and precipitate as insulating Li$_2$S on both anode and cathode surfaces. This so-called “Li-PS shuttle problem” causes quick capacity and energy drop. The sizes of nanopore and sub-nanopore were important as they provided more precise control of the solvation status of Li-PS to prevent the Li-PS shuttling. The formation of Li-PS could be suppressed if it was only partially solvated, as suggested by the DFT calculations. Since decreasing pore size to nanometer level and increasing electrolyte concentration could both create partially solvated Li-PS, a new strategy to mitigate “Li-PS shuttle problem” based on this synergetic effect was proposed by modeling and verified by experiments.
An even more idealized structure would be sulfur filled in carbon nanotubes (CNT), with the open ring size that is only permeable to Li ions. Reactive molecular dynamics (MD) simulations showed that the DFT determined optimum open ring size could be achieved by controlling the oxidation process of CNT.

The highly concentrated electrolyte can achieve the partially solvated Li-PS, and even expand the electrochemical stability window of the electrolyte if an SEI is formed. However, its high viscosity results in very slow Li transport. Thus, a co-solvent structure was designed by adding electrolyte low viscosity and electronically stable dichloromethane (DCM) to the highly-concentrated LiTFSI in ethyl acetate (EA) solvent. The contention of the DCM was designed to obtain a unique solvation structure, where clusters of partially solvated Li\(^{+}\), TSF\(^{-}\), and EA network were surrounded by the DCM cosolvent so that the former inherited the expanded electrochemical window of the highly-concentrated salt and the latter accelerated the Li transport.

Overall, this thesis demonstrated that atomic-scale electrode-electrolyte interfacial structure, interaction, and properties can be directly connected to the cell-level discharge performance, thus modeling these connections provided an integrated approach for battery materials design.

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