Understanding of Interfacial Behavior through Tailored Electrolytes and Substrates for Metal Secondary Batteries

（金属二次電池用に改良された電解質および基板を用いた界面挙動の理解）

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Lithium (Li) and sodium (Na) metal batteries are promising candidates for energy storage system with high energy density. However, challenges such as low Coulombic efficiency, dendrite formation during deposition/dissolution, and the flammability of conventional organic electrolytes impede their widespread adoption. Ionic liquid (IL) electrolytes have garnered significant attention due to their low flammability, low volatility, and high electrochemical stability. ILs offer unique coordination structures that can improve metal deposition/dissolution processes, particularly at elevated temperatures and with optimized anionsic structures. Furthermore, high-affinity substrates combined with compatible IL electrolytes can enhance the performance of lean metal and Li metal-free secondary batteries, thereby improving energy densities. This research aims to investigate the interfacial behaviors associated with metal deposition/dissolution, focusing on the use of ILs as novel electrolytes to advance the development of high-energy-density battery systems.

Chapter 3 aims to establish a pathway for high-energy-density Na metal batteries by focusing on the practicability of Na lean-metal batteries and examining the electrochemical properties in a bis(fluorosulfonyl)amide based IL electrolyte at room and intermediate temperatures. The IL shows a higher Na deposition/dissolution efficiency than common organic electrolytes. Elevating the temperature to 90 °C increases anion coordination with Na^+, forming a robust interfacial layer for smooth deposition/dissolution. Full cells with Na metal negative and $Na_3V_2(PO_4)_3$ positive electrodes demonstrate excellent cycleability, high Coulombic efficiency (~100%), and practical energy density (280 Wh kg^{-1}).

Chapter 4 explores the impact of anions with different donor numbers on coordination structures and interfacial behaviors. Hexafluorophosphate and trifluoromethanesulfonate anions were selected to explore their effects on Li^+ ions in IL. The high donor number of trifluoromethanesulfonate shows strong coordination with Li^+ ions, optimizing the first coordination shell and reducing organic cation decomposition. This leads to a robust solid electrolyte interphase of Li metal, promoting stable Li deposition/dissolution, suppressing Li dendrite growth, and enhancing cycle life and capacity retention.

Chapter 5 introduces a highly concentrated electrolyte for Li metal-free batteries. Combining lithium bis(fluorosulfonyl)amide and trifluoromethanesulfonate salts in a pyrrolidinium-

based IL achieves a 60 mol% Li concentration and a low solvent-to-salt ratio of 0.67:1. This electrolyte enhances the Li^+ transference number and extended electrochemical window, facilitates de-coordination, and forms an anion-based solid electrolyte interface. It demonstrates stable Li deposition/dissolution and high cycling stability in Li metal-free full cells with $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ positive electrodes.

Chapter 6 develops an Al current collector using annealing and fluorination to optimize its crystal orientation and surface properties for Na deposition/dissolution. Optical characterization, electrochemical, and computational analyses showed that the fluorine-rich (100)-oriented Al substrate provides high-affinity nucleation sites, enabling uniform Na deposition and a robust solid electrolyte interphase. The Na metal-free battery features a high average Coulombic efficiency (≈98%) over 50 cycles with $Na_3V_2(PO_4)_3$ positive electrode, and IL electrolyte.

This research addresses important issues in coordination structures and interfacial behaviors in IL electrolytes. The interactions of different components in IL across various temperatures and with the incorporation of anions with different donor numbers are investigated. Additionally, a fluorinated current collector and highly Li-concentrated IL electrolyte are developed and achieved and Li (Na) metal-free cells enhance practical energy density. These efforts aim to resolve interface-related challenges during metal deposition/dissolution processes. The findings offer valuable insights and guidance for the development of high-energy-density, highly stable metal batteries, thus advancing energy storage technology.