

論文の内容の要旨

論文題目 Microscopic understanding of electrochemical stability of
 lithium-ion battery electrolyte using molecular simulation
 (分子シミュレーションに基づくリチウムイオン二次電池
 電解液の電気化学的安定性の微視的解明)

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Chapter 1. General introduction

In recent years, lithium-ion batteries (LIBs) are becoming more and more important and are expected to be applied to environmental problems such as temporary storage systems for renewable energy. However, the application of LIBs to large-scale energy storage systems has been postponed because of the following problems; risks of ignition due to the use of flammable organic electrolytes, the high costs associated with the use of rare elements and dry rooms, and insufficient battery performance.

The key to improve the safety and performance of LIB is a passivation film called solid electrolyte interphase (SEI). The SEI film can be formed as a result of the deposition of reduction reaction products from electrolyte components near the negative electrode interface during the initial charging. This film can suppress the successive reduction reactions of electrolyte components owing to its electronic insulation characteristic, while allowing the Li^+ conduction. Therefore, the formation of a stable SEI film is the most important factor for the LIB electrolyte. Namely, it is ideal to employ an electrolyte that can form a good SEI film. However, since the formation process and structure of SEI film is extremely intricate, the relationship between the physical properties of the individual substances in the electrolyte and the SEI film formation remains largely unknown.

In this thesis, I aimed to elucidate the microscopic mechanism of electrochemical stability of electrolytes by investigating the SEI film formation with some molecular simulations.

Chapter 2. Theoretical background

In chapter 2, an overview of computational chemistry is given. First, I introduced the representative methods of energy calculation that is basis of the molecular simulations. Next, typical

methods of molecular simulations, i.e., Monte Carlo (MC) and molecular dynamics (MD) are reviewed. Finally, the detail of mixed-MC/MD (Red Moon) method is explained.

Chapter 3. Impact of *Cis*- versus *Trans*- Configuration of Butylene Carbonate Electrolyte on Microscopic Solid Electrolyte Interphase Formation Processes in Lithium-Ion Batteries

In Chapter 3, geometric isomers, *cis*- and *trans*-2,3-butylene carbonates (*c/t*-BC) were employed as model electrolytes to elucidate the formation condition of good SEI film. Despite their similar structure and chemical properties, *t*-BC-based electrolytes have been reported to enable the reversible reaction of graphite anodes [as in ethylene carbonate (EC)], while *c*-BC-based electrolytes cause the exfoliation of graphite [as in propylene carbonate (PC)]. To understand the microscopic origin of the different electrochemical behaviors of *t*-BC and *c*-BC, we executed Red Moon simulation to elucidate the microscopic SEI film formation processes. The results revealed that the SEI film formed in *c*-BC-based electrolytes contains fewer dimerized products, which are primary components of a good SEI film; besides, the decrease in the dimerized products can cause the reduced film stability. As one of the origins of the decreased dimerization in *c*-BC, we identified the larger solvation energy of *c*-BC for the intermediate species and its smaller diffusion constant, which largely diminish the dimerization. Therefore, weakening the solvation of the intermediates is one of possible ways to stabilize the SEI film for achieving the better charge-discharge performance.

Chapter 4. First-Principles Study on the Peculiar Water Environment in a Hydrate-Melt Electrolyte

Aqueous electrolytes using water as a solvent were investigated in Chapter 4. Although aqueous electrolytes are a promising group of potential replacements for conventional organic electrolytes from the aspect of safety and low production costs, the low electrochemical stability of water and its narrow potential window have hindered the application to LIBs. Recently, an extremely concentrated aqueous electrolyte, Li-salt dihydrate melt $\text{Li}(\text{TFSI})_{0.7}(\text{BETI})_{0.3}\cdot 2\text{H}_2\text{O}$, which possesses an extremely wide potential window has been developed. Thus, unveiling the microscopic solvation structure of water molecules in the hydrate melt must provide technical clues toward further enhancing the electrochemical stability of aqueous electrolytes. To clarify the detailed liquid structure and electronic states of this unique aqueous system, first-principles molecular dynamics (FPMD) simulations were conducted. We found that water molecules in the hydrate melt exist as isolated monomers or clusters consisting of only a few (≤ 5) H_2O molecules. Both the monomers and clusters have electronic structures largely deviating from that in bulk water, where the lowest unoccupied states are higher in energy than that of the Li-salt anions, which preferentially cause anion reduction leading to formation of the stable anion-derived SEI. This clearly shows the role of characteristic electronic structure inherent to the peculiar water environment for the extraordinary

electrochemical stability of hydrate melts.

Chapter 5. First-Principles Study on the Cationic-Dependent Water Environment in Li/Na/K-Hydrate-Melt Electrolytes

In Chapter 5, aqueous electrolytes for Na and K-ion batteries were investigated. Aqueous batteries, particularly earth-abundant sodium- or potassium-based systems, are potentially safe and low-cost alternatives to nonaqueous LIBs. Recently, concentrated aqueous electrolytes with Li, Na, and K salts have been extensively studied to increase the voltage of aqueous batteries; however, their potential windows become narrower in the order of $\text{Li} > \text{Na} > \text{K}$. Here, we study the difference in the potential windows of Li-, Na-, and K-salt concentrated aqueous electrolytes (hydrate melts) by FPMD simulations. With decreasing Lewis acidity of the alkali cations ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$), the reduction of counter anions is less active, and water molecules are more aggregated. This situation is unfavorable for achieving stable anion-derived passivation on negative electrodes. Hence, the Lewis acidity of alkali cations is essential to dominate the potential windows of hydrate-melt electrolytes. On the other hand, the weaker Lewis acidic Na^+ and K^+ have an obvious advantage for better ionic transport. Namely, the electrochemical stability and ionic conductivity may be in a trade-off relationship. To achieve high electrochemical stability with higher rate capabilities in Na- or K-salt hydrate melts, it is necessary to explore new anions or additives that can prevent the H_2O aggregation.

Chapter 6. Concluding remarks

Through this thesis, I proposed the basic guideline of electrolyte design by clarifying the microscopic mechanism of the electrochemical stability based on the molecular simulations. This thesis not only showed the usefulness of molecular simulation in research of secondary battery, but also contributed to the understanding of the intricate phenomenon of SEI film formation toward more improvement of secondary batteries in the future.