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# 学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　王　雨申

## 学 位 論 文 題 名

Study on The Effect of $LiNO_3$ on Solid Electrolyte Interface Structure and Electrolyte Degradation in Ether-based Low-concentration Electrolyte for Anode-free Lithium Metal Battery
（低濃度エーテル系電解液を用いた負極フリーリチウム金属電池の固体電解質界面構造および電解質劣化における $LiNO_3$ の影響に関する研究）

Rechargeable anode-free lithium metal batteries (AFLMBs) have emerged as a promising energy storage technology due to their high energy density and potential for widespread applications. However, their commercialization is mainly hindered by challenges at the electrode/electrolyte interface, particularly the formation of unstable solid electrolyte interphase (SEI) layers and complex electrolyte decomposition (E.D.) reactions. These issues are especially pronounced in low-concentration ether-based electrolytes, commonly used to address safety concerns and reduce cost.

The SEI layer, a passivation film formed on the anode surface, plays a crucial role in determining the stability and efficiency of lithium plating/stripping processes. However, its composition and morphology are highly sensitive to electrolyte components and operating conditions. Similarly, E.D. processes at the electrode/electrolyte interface can lead to the generation of by-products that compromise battery performance. These phenomena are interdependent, creating either a virtuous or a vicious cycle during charge-discharge cycling.

This thesis aims to resolve fundamental issues regarding SEI and E.D. processes by controlling the operating potential and applying *insitu* and *exsitu* techniques to monitor the potential-dependent evolution of surface species. Particular attention is given to low-concentration (<3 M) electrolytes, where these challenges are more pronounced, and to the first cycle, which lays the foundation for subsequent cycling stability. The role of $LiNO_3$ as an additive and co-salt, previously underexplored, is a central theme throughout this study. The ultimate goal is to develop strategies for improving the stability and efficiency of AFLMBs.

In Chapter 1, the background and fundamental challenges facing AFLMBs are introduced, focusing on Li nucleation and growth, SEI layers, and E.D. reactions. It reviews existing strategies for electrolyte modification and highlights gaps in current knowledge, particularly regarding the role of $LiNO_3$, which is commonly used as an inorganic additive. This chapter also emphasizes the importance of understanding interfacial phenomena from a fundamental perspective and sets the stage for the experimental and theoretical investigations presented in subsequent chapters.

In Chapter 2, the experimental framework used in this research is outlined. The pretreated Cu electrode was assembled with Li ribbon to construct the Li||Cu half-cell, resembling AFLMB anode side for a variety of electrochemical measurements. Key methodologies include advanced characterization techniques such as cyclic voltammetry (CV), quartz crystal microbalance (QCM), Fourier-transform infrared absorption spectroscopy (FT-IRAS), and surface-enhanced Raman spectroscopy (SERS). Details on instrumental setups, experimental conditions, and parameters are provided to ensure reproducibility and reliability. These methodologies enabled a detailed investigation of SEI and E.D. phenomena under various electrolyte compositions and operating conditions.

In Chapter 3, the behavior of the adsorbed layer, including native-SEI and pre-SEI, both formed on a Cu electrode surface prior to initial Li plating, was preliminarily investigated. Using tetraethylene glycol dimethyl ether (TEGDME)-based electrolytes with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and $LiNO_3$, this study examined how $LiNO_3$ influenced SEI composition and morphology. QCM and FT-IRAS analyses revealed that $LiNO_3$ accelerated the decomposition of TEGDME, promoting the formation of organic species that regulated surface roughness and composition. The study also demonstrated that $LiNO_3$ facilitated a shift in SEI composition by suppressing the formation of inorganics like $Li_2CO_3$. These findings provided insights into the role of $LiNO_3$ as either an additive or a co-salt by controlling its ratio to LiTFSI, highlighting its potential to regulate SEI layers during the pre-Li-deposition stage.

In Chapter 4, the effects of operating potential range (to 2.2 V or 3.2 V vs. $Li/Li^+$), electrolyte concentration (0.4 M or 2.0 M), and $LiNO_3$ as an additive on SEI layer structure and lithium plating/stripping efficiency were examined in details. A novel oxidative-subsequent-SEI (abbreviated as OSS) formation process was identified, which negatively impacted surface morphology and cycling stability. By adding $LiNO_3$ to compensate for the degradation caused by OSS, this study achieved significant enhancements in cycling efficiency and stability. The reason for such an enhancement was explored: at low concentrations (0.4 M), $LiNO_3$ promoted the formation of $Li_2$ O-based SEI layers, which exhibited smaller surface roughness and enhanced stability. At a relatively higher concentration (2.0 M) with $LiNO_3$ additive, the decisive SEI species shifted to LiF, further improving performance.

In Chapter 5, the investigation on E.D. mechanisms during the first Li plating/stripping cycle in 1,2-dimethoxyethane (DME)-based electrolytes was conducted. Four electrolyte systems — lithium bis(fluorosulfonyl)imide (LiFSI) and LiTFSI single salt electrolytes, LiFSI-$LiNO_3$ and LiTFSI-$LiNO_3$ dual-salt electrolytes — were compared to elucidate the role of $LiNO_3$ as a co-salt of LiFSI/LiTFSI in regulating E.D. processes. By combining multi-potential step chronoamperometry, QCM, and spectroscopic analyses, this study extracted E.D. charges and identified dominant chemical species during initial cycling. Results showed that $LiNO_3$ prevented the reduction of LiFSI and LiTFSI into smaller inorganic by-products and enhanced interactions between Li salts and the DME solvent. This promoted the substitution of functional groups within Li salts by DME fragments, increasing the charge ratio of salt-solvent interactions. These findings underscored the critical role of $LiNO_3$ in changing electrolyte decomposition reaction routes which could further influence long-term battery performance.

In Chapter 6, the key findings of this thesis are summarized and prospects for future research are given.

This study demonstrates that controlling SEI composition and morphology through electrolyte modification is a viable strategy for improving AFLMB performance. The dual role of $LiNO_3$ as an additive and co-salt is highlighted as a crucial factor in stabilizing SEI layers and mitigating Li salt decomposition. However, challenges remain, such as the gradual consumption of $LiNO_3$ during cycling and the need for more precise control over SEI formation mechanisms. Future research directions include optimizing electrolyte compositions, exploring alternative additives, and employing advanced *insitu* techniques to further elucidate interfacial phenomena.