

Mechanistic analysis of degradation phenomena considering electrode–electrolyte interfaces

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Lithium-ion batteries (LIBs) store and release energy through electrochemical reactions associated with Li-ion transport between the positive and negative electrodes. Electrolyte decomposition at the negative electrode and dissolution of the Al current collector at the positive electrode significantly affect battery performance and lifetime. These phenomena are governed by the electric double-layer structure formed at the electrode-electrolyte interface. However, direct observation of interfacial reactions is difficult, making the development of reliable simulation techniques essential for battery research and development.

In this study, we applied the ESM-RISM method, which represents the electrolyte using a continuum approximation, to investigate electrode-electrolyte interfaces. An original parameterization scheme was developed to reproduce electrolyte structures and interfacial properties obtained from first-principles calculations. By leveraging the Fugaku supercomputer for large-scale parallel calculations, analysis times were reduced from several years to approximately two months while maintaining high predictive reliability.

The validity of the method was verified through comparison with in situ infrared spectroscopy measurements. The simulations successfully reproduced concentration changes in solvent molecules and Li-ion coordination structures during charging and showed good agreement with experimental observations. The method also enables quantitative analysis of three-dimensional molecular configurations and concentration distributions near interfaces, providing insights that are difficult to obtain experimentally.

As a practical application, we investigated Al dissolution from the positive-electrode current collector. Simulations predicted the dependence of the Al dissolution potential on the mixing ratio of Salt A and Salt B at a fixed total salt concentration of 1.4 M. Increasing the proportion of Salt A improved power performance but lowered the Al dissolution potential, revealing a trade-off between battery performance and resistance to Al dissolution. The optimal composition was predicted to be Salt A:Salt B = 0.9:0.5 M at an upper operating voltage of 4.3 V, which was subsequently validated experimentally.

Furthermore, visualization of interfacial structural changes revealed that Al dissolution is strongly influenced by local ion distributions and the formation of stable solvation structures around dissolved Al species. These results demonstrate that interfacial simulations can provide mechanistic insights into electrode-electrolyte reactions and enable efficient electrolyte design. The proposed approach significantly reduces development time and is expected to accelerate the development of high-performance, long-life LIBs.

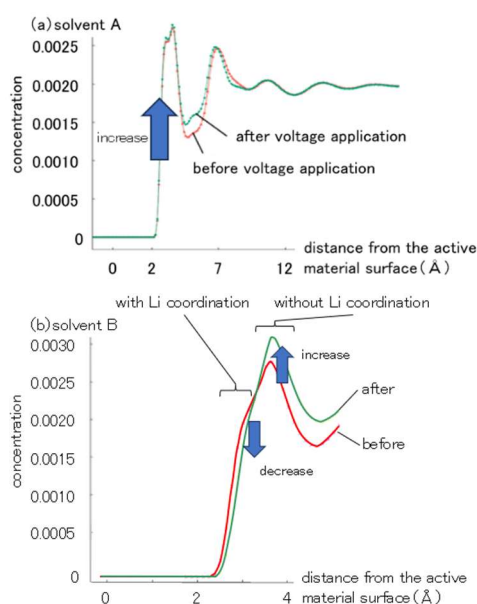


Fig.1 Calculation results

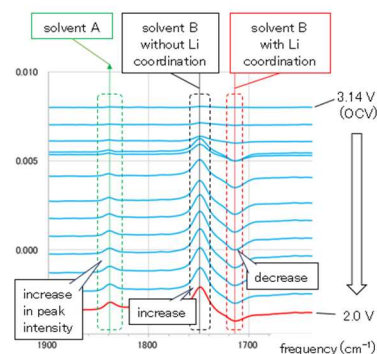


Fig.2 Experimental results

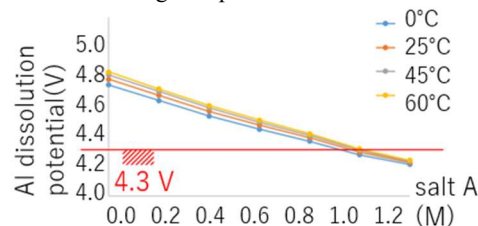


Fig.3 Al dissolution potential with varying mixed salt ratios