SEI Structures Dependent Li-Morphology Characterized by Cryo-TEM

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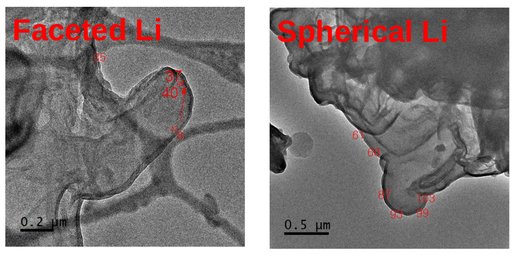
Abstract

Lithium metal batteries (LMBs) are gaining attention for promising energy-storage system by offering high energy capacities. However, LMBs face challenges in commercialization due to (1) its instability by irregular Li deposition such as Li dendrites and (2) energy density loss associated with the formation of “dead” lithium. These challenges are related to the Solid-Electrolyte Interphase (SEI) - a complex layer that forms because of interactions between lithium metal and electrolyte or salt. The SEI layer, which is formed with a thickness of several tens of nanometers, is difficult to observe because it is vulnerable to electron beam damage. The advance in cryogenic Transmission Electron Microscopy (cryo-TEM) have provided breakthrough opportunity to investigate the complex interface, minimizing electron beam damage even at high-resolution. Although many researches have employed cryo-TEM to enhance understanding of the SEI, a more holistic characterization remains necessary to unravel its intricate properties and its role in the performance limitations of LMBs. In this work, we developed an algorithm that can qualitatively analyze SEI layers in cryo-TEM images, which establishes systematic procedure for quantitative analysis of crystal composition and crystallinity within the SEI. Based on the remarkable methodology, we investigated the structural differences of the SEI formed on lithium with different morphologies (faceted Li, spherical Li) to identify the correlation between the morphology of lithium and the structure of the SEI. Also, a possible mechanism is proposed to elucidate the results, with a primary focus on how lithium deposition and its kinetics are influenced by the SEI thickness and composition.

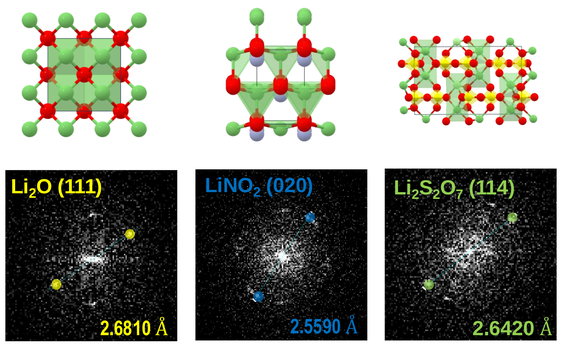
Results

Procedure: Data acquiring

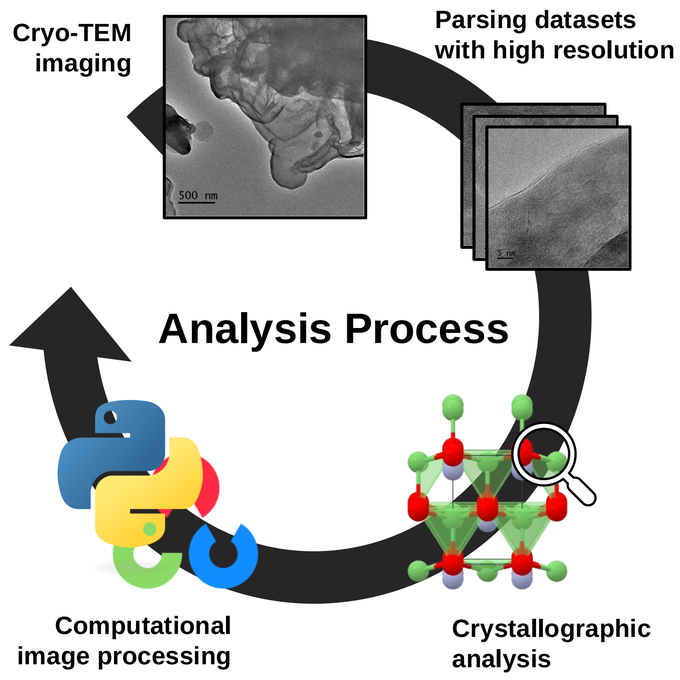
❍ Morphology of Li



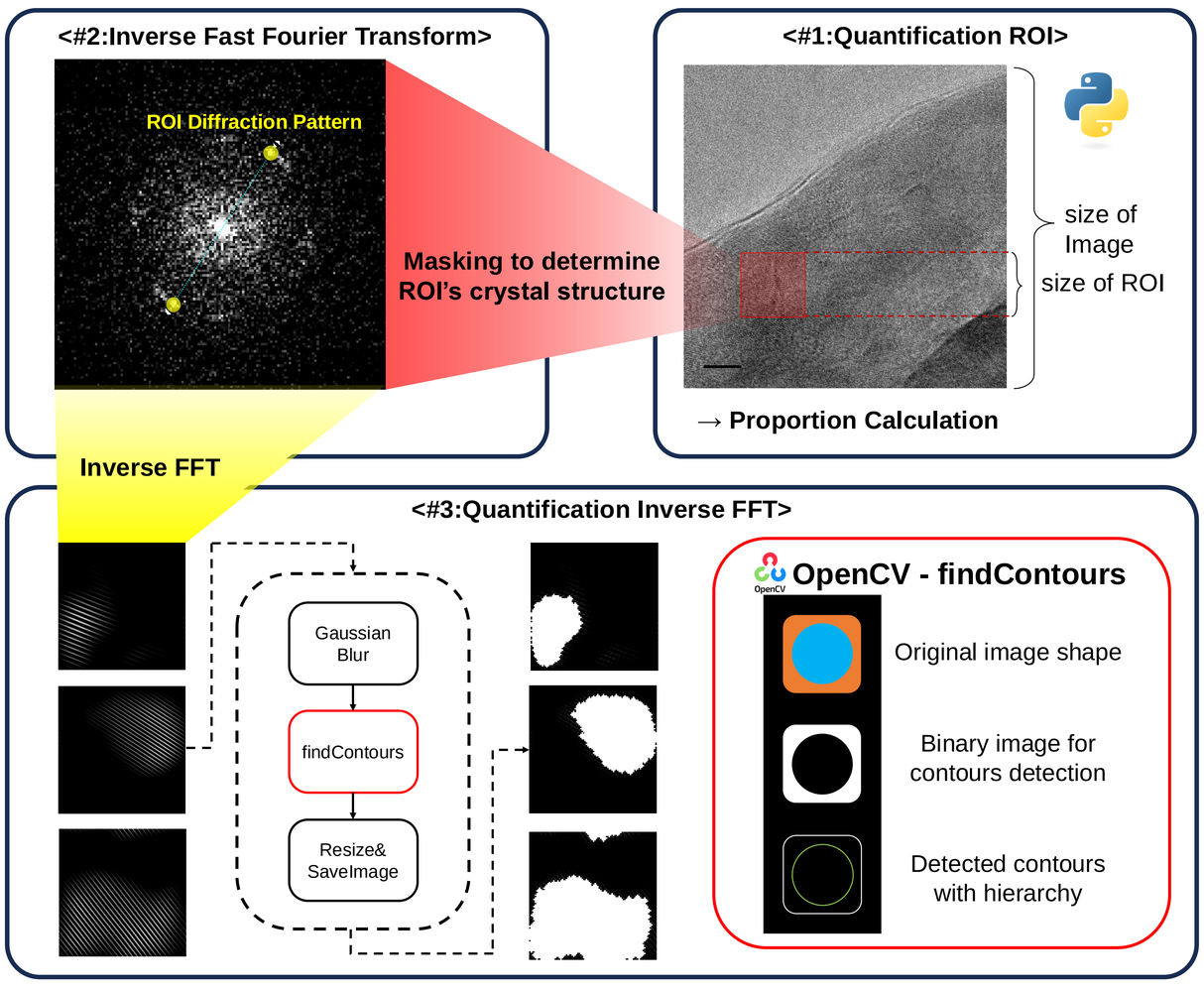
❍ Crystal & d spacing



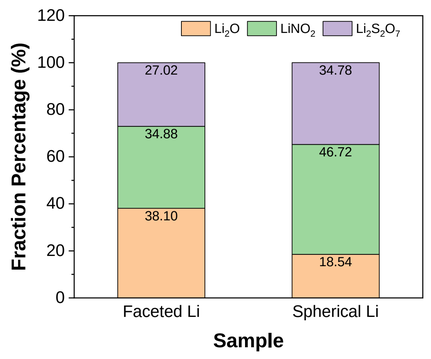
❍ Analysis Method

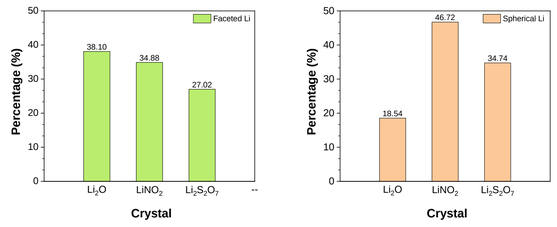


Procedure: Quantification



Quantification Result





- Faceted Li: Displayed a relatively higher proportion of **Li_2O**
- Spherical Li : Showed a comparatively higher proportion of **$LiNO_2$** and **$Li_2S_2O_7$**

Expected Mechanism

Faceted Lithium Metal

- Relatively **thin** SEI layer leads to fast Li deposition
- Crystallinity tends to be **lower**

Spherical Lithium Metal

- Relatively **thick** SEI layer leads to slow Li deposition
- Crystallinity tends to be **higher**

- Absolute amount of Li_2O is similar considering both different relative composition and different thickness of SEI layer
- Different **thickness** and **components of the SEI** show varying ionic conductivities within the SEI layer, which influence to differences in **Li deposition kinetics**

Conclusion & Suggestion

- Cryo-TEM enabled high-resolution imaging of the SEI on LMB cells, facilitating direct structural characterization at cryogenic temperatures.
- Through diffraction pattern analysis, we identified various crystalline phases within the SEI, providing insights into the diverse chemical composition of the interphase.
- Using inverse FFT and various computational algorithms, we quantified the extent of crystalline presence within the SEI, proposing a robust method for assessing crystalline distribution.
- This quantitative analysis revealed that various crystalline phases exhibit distributions in correlation with specific Li morphology and SEI morphology, underscoring the impact of formation conditions on SEI structure.
- For future work, we aim to systematically calculate crystallinity for different morphology and acquire credibility by conducting analysis with more sample with similar morphology, further conducting analysis with other instruments, such as XPS and EELS, to further elucidate SEI formation mechanism at different morphology.

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