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Operando structural and chemical imaging of lithium battery interfaces

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Background incl. aims

Lithium metal is a very promising anode material to develop batteries with higher energy density due to its high specific capacity and low redox potential. However, the widespread use of lithium as anode is hindered by the safety concerns stemming from the formation of dendritic structures at the electrode-electrolyte interfaces during battery operation [1]. Hence, understanding the fundamental mechanism behind the formation of these dendritic structures is crucial for the utilization of lithium metal in producing batteries with enhanced energy density and safety. Traditional ex-situ and in-situ analysis techniques are not sufficient to understand the transient processes involved in the nucleation and growth of these dendrites. Thus, operando techniques, which allow analysis while the battery is functioning, are essential for gaining deeper insights. The primary aim of this study is to devise a methodology for capturing the nanoscale structural and chemical changes occurring at the electrode-electrolyte interface during battery operation.

Methods

Our approach utilizes a dual-beam focused ion beam-scanning electron microscope (FIB-SEM) equipped with an in-house developed magnetic sector secondary ion mass spectrometer (SIMS) for operando structural and chemical imaging [2]. Secondary electron (SE) imaging helps to visualize the structural changes and SIMS imaging depicts the chemical alterations at the battery interfaces. Here SIMS is used as it is an ideally suited technique for high-sensitivity chemical analysis and imaging of all elements, including light elements like lithium. Thus, SIMS enables unequivocal detection of the lithium rich dendrites near battery interfaces. A special operando analysis setup has been developed through which the charging-discharging of the battery can be performed inside the FIB-SEM-SIMS instrument using an external potentiostat, while maintaining the necessary sample bias conditions to allow secondary ion extraction for simultaneous SIMS analysis.

Results

Using the FIB-SEM-SIMS instrument, all solid-state symmetrical lithium cells with garnet type solid electrolyte lithium lanthanum zirconium oxide (LLZO) were analyzed both before electrochemical cycling and after short-circuit [3]. Phases with darker contrast were identified in the gallium ion induced SE images of the electrolyte after short-circuit failure, SIMS imaging showed higher lithium-ion signal in those phases (Fig. 1e,1f). Thus, the presence of lithium rich dendrites in LLZO after short-circuit was confirmed by SIMS. The development of the operando setup enables us to perform SE and SIMS imaging of the battery interfaces during cycling. Therefore, it is now possible to detect and image the progression of lithium dendrite growth at different stages of cell operation. Furthermore, this operando setup allows direct correlation between the alterations in structure and chemistry of the electrode-electrolyte interface with the evolution of interfacial resistance by combining electrochemical experiments such as impedance spectroscopy with the SEM-SIMS analysis.

Conclusion
In summary, our operando FIB-SEM-SIMS setup allows real-time observation of the nanoscale processes at the interfaces linked with dendrite growth in solid-state lithium metal batteries. This helps in acquiring a more complete understanding about the phenomenon of dendrite formation in lithium metal batteries, paving the way for development of batteries with improved safety as well as electrochemical performance.

Graphic:

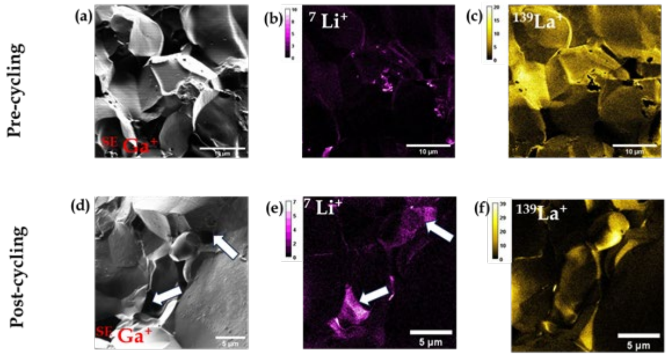

Figure 1. Gallium ion induced secondary electron image and SIMS elemental maps of $^{7}Li^{+}$ and $^{139}La^{+}$ in LLZO before cycling (1a,1b,1c) and after short-circuit (1d,1e.1f). White arrows in Fig.1d and Fig.1e indicate dendrites.

Keywords:

Operando imaging, lithium dendrites.

Reference:

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