Operando Investigations and High Resolution Microscopy of SEI on Metal Anodes

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Motivation and Aim

- Lithium-ion-based batteries will soon reach their limits, e.g. with respect to sustainability and the supply of raw materials. Therefore, alternative systems that use metals at the anode are investigated. Interesting examples are metals like Li, Na, K, Mg, Ca, Al
- Electroplating and dissolution of these elements depend strongly on the interface between the metal (or its carbon compound) and the electrolyte. In almost all cases a solid electrolyte interphase (SEI) forms. The electrochemical performance and reliability depend strongly on this interphase.
- These interphases/faces are often very thin and difficult to access with current methodology. Especially chemical and morphology information at high resolution are hard to obtain. Here a new method, the Helium ion microscopy (HIM), for analyzing these interphases is applied.
- Undistorted and accurate information about the SEI can only be obtained operando. Here substrate curvature and quartz microbalance measurements are going to be used.

Helium Ion Microscopy HIM

The thickness and the structure of the SEIs on sodium (and Li for comparison) are investigated with SEM and HIM.

- High resolution imaging, probe sizes < 0.5 nm
- High surface contrast due to high yield of low energy electrons

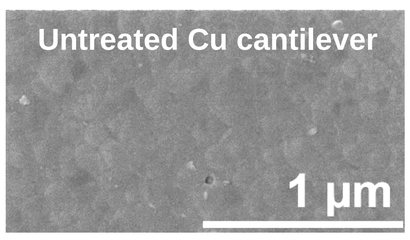
Nanofabrication:

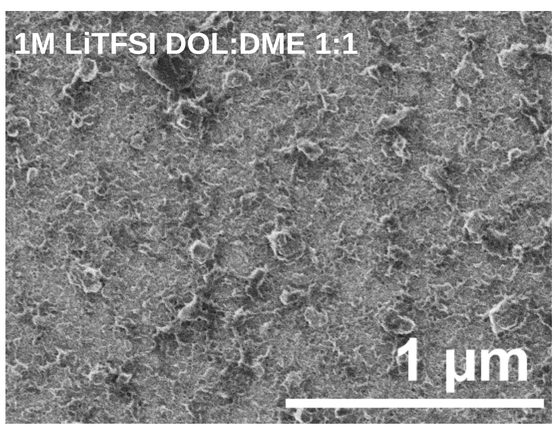
- Fabrication of sub-10 nm structures by He and Ne milling
- Gallium beam (FIB) for fast material removal
- High aspect ratio structures and cross sections

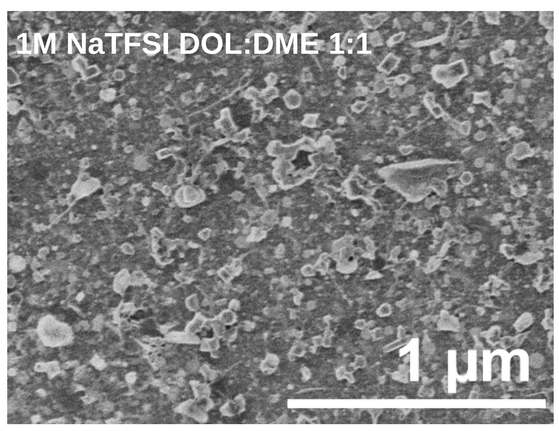
A transfer system has been adapted to allow a sample transfer without exposure to air.

Microscopic Investigations

HIM of the cantilevers used in the substrate curvature experiments





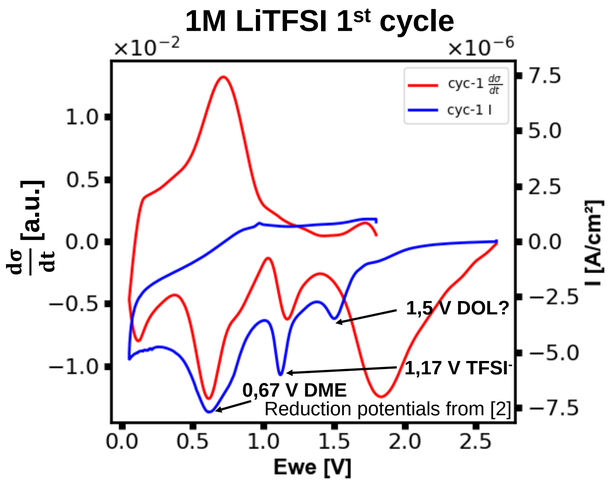


- HIM of the cantilever before and after cycling: Copper grains are covered with a thin layer and granular structures have formed on the surface.

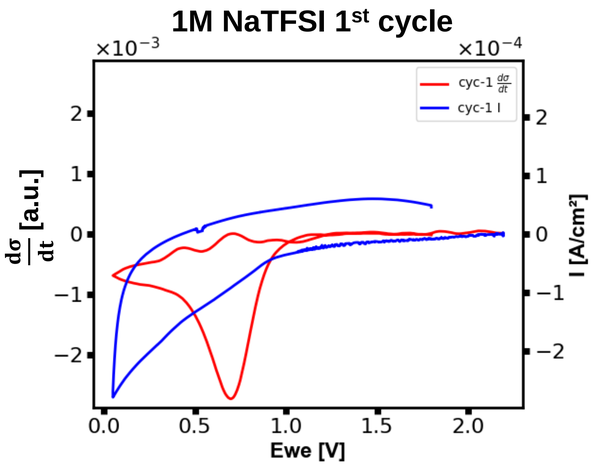
Substrate Curvature

- Very sensitive operando stress measurements of surface films
- Fractions of monolayers can be detected
- Reliable electrochemical cells exists
- Experiments with several hundreds of cycles can be performed
- Custom-built electrochemical substrate curvature systems available [1]

Mechanical Investigations

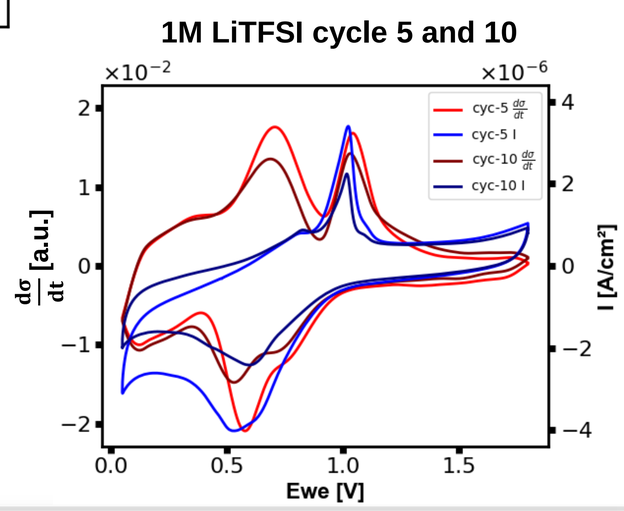


- Features found in electrochemical measurements also appear in mechanical data
- Mechanical data is highly dynamic and reveals processes not visible in electrochemical data.



- Mechanical stress exclusively originates from the metal surface (SEI) and processes in the liquid are excluded.

- Charge and stress balance counted over several cycles can be used together to assess SEI reliability.
- Stress balance over several cycles indicates unstable SEI



Fast Electrochemical Quartz Microbalance (EQCM-D)

- *Operando* electro gravimetric measurements
- Information beyond gravimetry obtained by analysis of peak width / Q-factor and resonance frequency over several overtones
- Aim: High time resolution of a few milliseconds (investigate kinetics)
- Status: Cell and electronics are under development / test

References

[1] Choi Z., D. Kramer, R. Mönig, J. Power Sources 240 (2013), 245.

[2] Zhang, C., Q. Lan, Y. Liu, J. Wu, H. Shao, H. Zhan and Y. Yang (2019), Electrochimica Acta 306: 407-419.

Summary

- Mechanical operando measurements provide further insight into the formation processes of the SEI and thus can complement electrochemical data.
- Operando measurements like substrate curvature can be used to evaluate SEI reliability and stability.
- Significant differences in the formation process of Li- and Na-interphases could be found.

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