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Scanning Probe Microscopy for the Evaluation of Thin Film Sputtered Cathode Libraries

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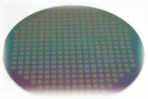
Sputtered libraries for battery cathode evaluation

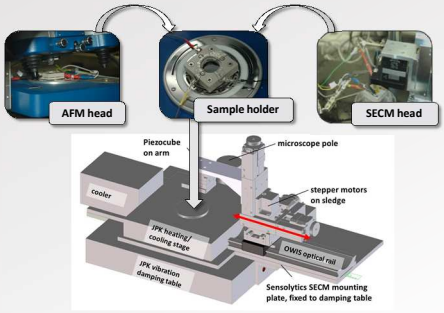
Combinatorial thin film sputtering by PVD allows to create material libraries with tunable thickness and composition[1].
Aim of this work is to investigate these libraries with spatially resolved techniques, i.e. Atomic Force Microscopy (AFM) for topological information and Scanning Electrochemical Microscopy (SECM) for local electrochemical activity.

Our glove box for laterally resolved electrochemistry



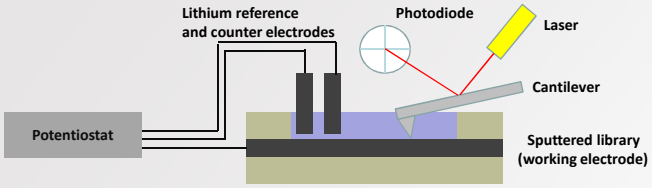
A sputtered thin film library

Combined AFM/ SECM system in a glove box



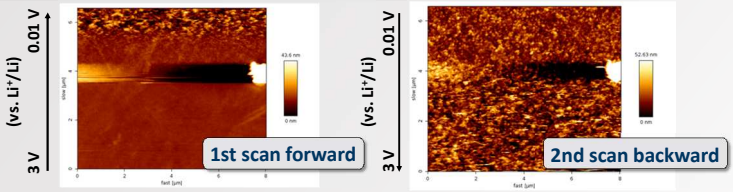
AFM and SECM yield complementary information. To combine both, a common sample holder has been designed, which creates an electrolyte filled cell including lithium reference and counter electrode. The AFM and SECM probe heads can be successively placed on top of the sample via a sliding rail.

Work principle of in-situ AFM



A laser beam is deflected from a sharp tip cantilever and registered on a multi array photodiode. During a surface scan, topological features will force the cantilever to bend. The signal change on the photodiode is then used to calculate a 3D image of the sample.
Contacting the sample as working electrode, changes in the topology (e.g. volume change during de/intercalation) can be visualized in-situ.

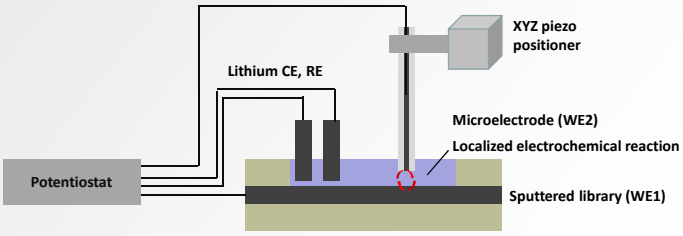
in-situ AFM Volume change during de/intercalation



Electrochemical SEI formation on glassy carbon during in-situ AFM scan

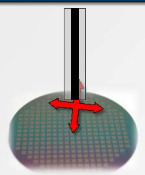
As proof-of-principle, the AFM tip was scanned over a glassy carbon electrode during Solid Electrolyte Interphase (SEI) formation. The potential was decreased from 3 V to 0.01 V (vs. Li^+/Li) during progressive AFM scan from bottom to top (left image). The formerly flat glassy carbon surface changes morphology below 1 V, which is maintaned in the AFM back scan during the reversed electrochemical sweep from 0.01 V to 3 V.

Work principle of SECM

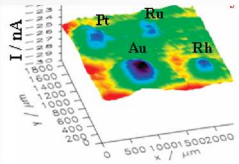


Instead of an cantilever, SECM uses a small spectator electrode as the scanning probe. Changes in the electrochemical activity (e.g. rate of lithium release) will be detected as current in the microelectrode and result in a map of electrochemical activity.

Kinetics of lithium de/intercalation of a LIB cathode library



Thin film sputtered cathode library



Example of locally resolved electrochemical activity[2]

SECM imaging has already been developed for the evaluation of catalyst libraries for oxygen reduction reaction[2]. An imaging mode for electrochemical activity of lithium ion batteries materials (e.g. the system Li_xFePO_4) is currently under development.

Outlook

A microscopy platform for AFM and SECM mapping has been set up in the protective environment of a glove box. Scans with model materials have shown that the AFM system is ready for in-situ mappings. The SECM imaging modes are currently under development. Combining both techniques, findings from electrochemical evaluation can be directly related to topological changes.

References
[1] M. D. Fleischauer, T. D. Hatchard, A. Bonakdarpour, J. R. Dahn, Combinatorial investigations of advanced Li-ion rechargeable battery electrode materials, Meas. Sci. Technol. (2005) 212
[2] X. Chen, K. Eckhard, M. Zhou, M. Bron, W. Schuhmann; Anal. Chem. (2009), 81, 7597–7603

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