SEI formation studied by combined *operando* EIS and EQCM-D

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Electrolyte is reduced on the surface of the anode during cycling of a Li-ion cell. Solid reaction products form the solid electrolyte interphase (SEI) and hinder further electrochemical decomposition by blocking electron transport. While this process is required for a functioning cell, it is also leading to several key problems such as irreversible loss of specific charge and an increase of electrode impedance.
Investigations of electrode-electrolyte interphases in Li-ion batteries are challenging due to complex formation/dissolution mechanisms and the inherent instability of interphase components outside of the cell. In this work we examine mass accumulation at the interface *operando* by using an electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D). We furthermore study the effect of anode layer formation on Li-ion diffusion and therefore cell performance by combining EQCM-D with simultaneous electrochemical impedance spectroscopy (EIS).
EQCM model cells typically feature – in comparison to commercial batteries – a relatively high electrolyte volume to electrode surface area ratio, because of the required free liquid volume in contact with the QCM sensor and the comparatively low QCM electrode mass loadings allowed [1]. In order to minimize the electrolyte volume to electrode surface area ratio we short circuit an additional high surface area working electrode with the QCM sensor and cycle both against the counter electrode. Isolated EIS measurements of the QCM electrode furthermore require the addition of a reference electrode in the cell. Figure 1 displays the four-electrode setup developed in this study.
We demonstrate how electrolyte decomposition products precipitate and dissolve on the anode surface depending on the electrode potential during cycling of a cell and analyze its effects on anode impedance. Various model electrodes such as gold, carbon or copper can be used as anode materials. The effect of electrolyte additives such as vinylene carbonate (VC) on SEI formation and anode impedance will be discussed.
In conclusion the unique combination of *operando* EQCM-D and EIS gives new insights into formation and dissolution of the electrode-electrolyte interphase at the anode and its impact on cell performance.

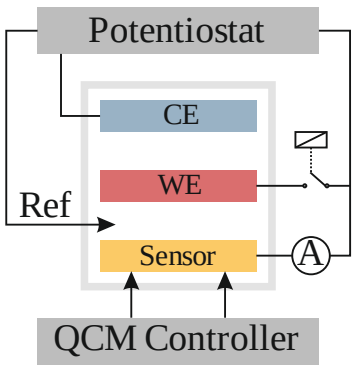

Figure 1: Four-electrode cell for combined operando EIS and EQCM-D.

Reference:
[1] V. Dargel, N. Shpigel, S. Sigalov, P. Nayak, M.D. Levi, L. Daikhin, D. Aurbach, Nat. Commun., 8 (2017) 1389.