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Investigations of the solid electrolyte interphace layer stained with osmium tetroxide

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Introduction

The Solid electrolyte interface (SEI)

- is an electrolyte reduction layer of several nm in thickness (compare figure 1)
- is an ionic conductor for alkali ions, but an electronic insulator [1]
- it grows during the first charge on the anode of a lithium-ion battery [1, 2]
- it was first discovered, characterized and given its name by Peled in 1979 [3]
- it is a determinant factor of battery cycle life and overall cell performance [4]
- its composition is complex [5]. The constituents are organic and inorganic lithium salts comprised of light elements (H, Li, C, O, P and F)
- low scattering contrast when using electron microscopy due to composition

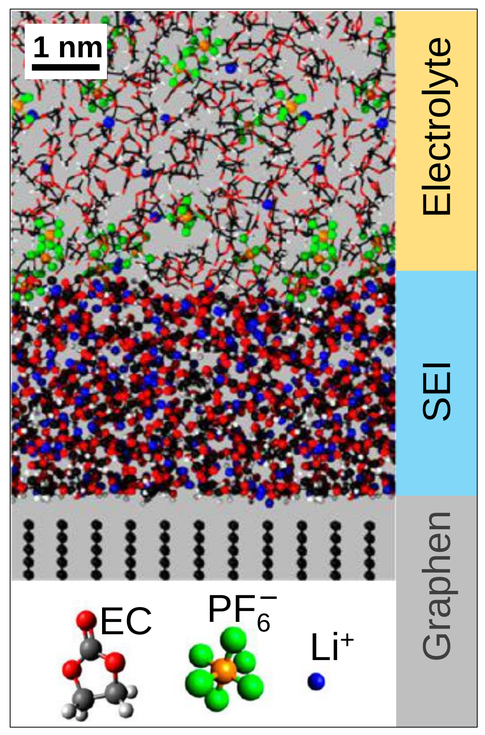

Fig. 1: Simulation of a SEI formation on a graphene anode [7].

Experiment

Mission

- increase the material contrast during transmission electron microscopy [6]
- stabilization of the SEI with respect to electron beam and air exposure [6]
- Obtaining further information of the SEI structure by selectively enhancing electron contrast

Approach

Adopting the OsO_4 staining procedure commonly used for polymer blends and biologic tissue for the use of SEI and lithium dendrite analysis in lithium ion batteries.

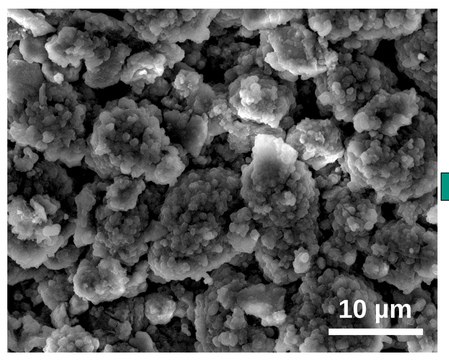

Fig. 2: SEM-BSE/SE-image of a untouched charged anode surface.

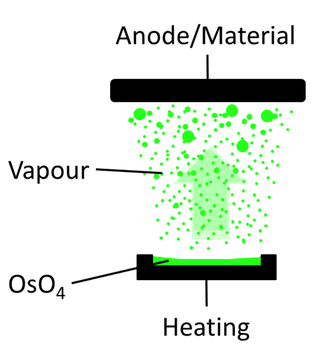

Fig. 3: Evaporation with OsO_4.

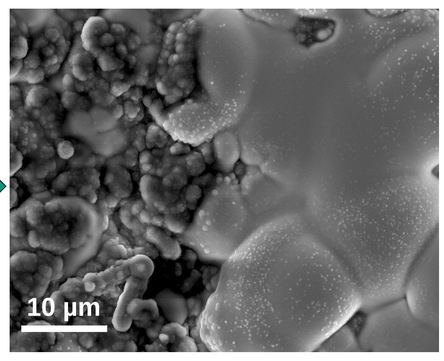

Fig. 4: SEM-BSE/SE-image of the charged anode surface evaporated with OsO_4.

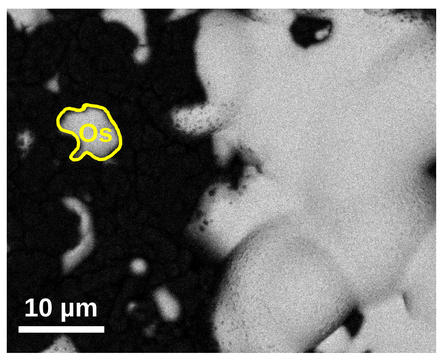

Fig. 5: SEM-EsB-image: With EDX it was verified that bright regions are Os-rich.

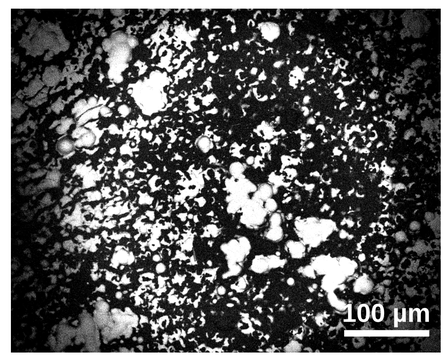

Fig. 6: SEM-EsB-image: Overview of the Os-rich regions on the surface of a charged anode.

Results

- charged/uncharged anodes were exposed to an Ar/OsO_4 atmosphere (scheme in Fig. 3) and analyzed before and after the exposure by a scanning electron microscope (SEM)
- comparison of Fig. 2 (before) and Fig. 4 (after exposure) clearly shows that OsO_4 reacts with parts of the anode's surface
- by combination of energy selected backscattering (EsB) and energy dispersive X-ray spectroscopy (EDX) it could be verified that bright fields in the EsB images correspond to osmium-rich parts on the anode surface (Fig. 5)
- thus osmium-distribution can be made directly visible by using the EsB (Fig. 6)

Outlook

Although it could be demonstrated so far that OsO_4 selectively reacts with parts of the SEI the exact reaction mechanism still remains to be elucidated to obtain further insight into the SEI structure and distribution.

Therefore, an in depth analysis of the SEI components before and after reaction with OsO4 by XPS and ToF-SIMS is planned to obtain a better understanding of the reaction mechanism and SEI structure.

References

[1] R. Fong et al., J. Electrochem. Soc. **137**, 2009-2013 (1990)
[2] R. Kanno et al., J. Electrochem. Soc. **139**, 3397-3404 (1992)
[3] E. Peled, J. Soc **126**, 2047-2051 (1979)
[4] J. Vetter et al., Journal of Power Sources **147**, 269-281 (2005)
[5] D. Aurbach et al., J. Electrochem. Soc. **142**, 2873 – 2882 (1995)
[6] M. Zier et al., 6th Lithium Battery Discussion, Electrode Materials, Meeting Abstract P029 (2013)
[7] R. Jorn et al., J. Phys. Chem. C, **117**, 3747−3761 (2013)