Electron microscopy studies of the SEI layer and lithium plating by OsO_4-staining

Martin Zier[1], Frieder Scheiba[2], Jürgen Thomas[1], Torsten Scherer[3], Helmut Ehrenberg[2], Jürgen Eckert[1]

[1]*Leibniz Institute for Solid State and Materials Research IFW Dresden*

[2]*Karlsuhe Institute of Technology (KIT), Institute for Applied Materials (IAM)*

[3]*Karlsuhe Institute of Technology (KIT), Institute of Nanotechnology (INT)*

Fixation

Motivation

Observing SEI in electron micrsoscopy:

- ❖ lack of contrast
- ❖ lack of stability in electron beam

Already established: staining of biological tissue in order to enhance contrast and to achieve fixation

- ➢ Applied to electrodes having an SEI

Goal

- ❖ Increase visibility of SEI components in electron microscopy
- ❖ Stabilize air sensitive compounds for easier handling
- ❖ Test feasability of osmium tetroxide staining in anode materials of lihtium ion batteries

Contrast-ing

Experimental

- Sealed osmium tetroxide exposure chamber
  - Up to 12 h exposure of samples
  - Subsequent Argon flush to remove remaining OsO_4
- Standard sample preparation for electron microscope investigations

Results TEM/FIB

- Graphite electrode particles on TEM grid with lacey carbon film:

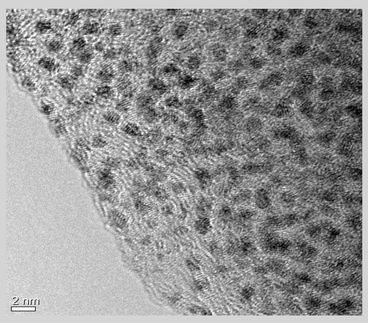


Fig: HRTEM of OsO_2 crystallites on stained graphite particle

➢ **The SEI surrounding the particle reacted with OsO_4**

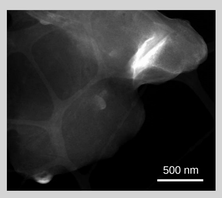


Fig: Li-rich (→ Os-rich) areas appear bright in HAADF mode

- Plated and exposed graphite electrode prepared with slice and view technique

➢ **cross sectional information**

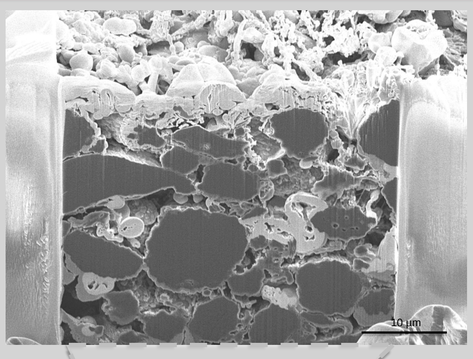


Fig: last section of slice and view.

Graphite can be clearly distinguished from dendrites

Varying elemental contrast

➢OsO_4 reaction depending on composition

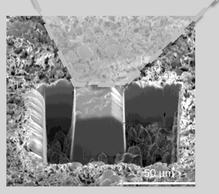
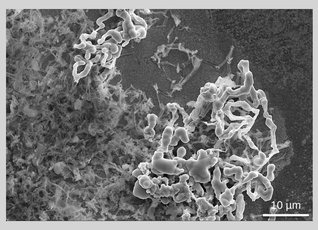
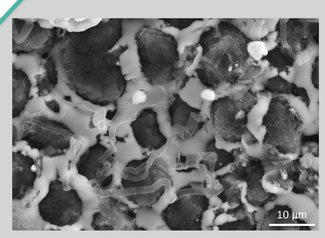


Fig: SEM of unburied electrode for slice and view (FIB)

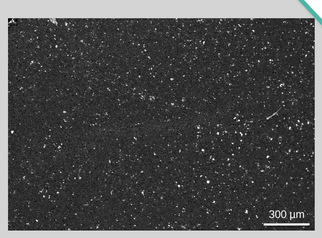
76
Os
Osmium
190.23

Results SEM/EDX





Figs: SEM images of graphite electrodes after Li-plating and subsequent OsO_4-staining



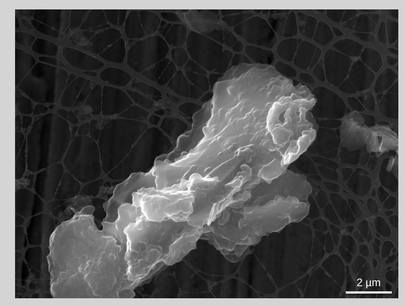
- Graphite electrodes were electrochemically forced to Lithium deposition. Two effects are observed:
  - **OsO_4 leeches the intercalated lithium from graphite if not discharged**
  - **OsO_4 stains residual Li-dendrites that have not been dissolved during discharge**
- Quantification (EDX) of residual lithium is used to estimate the amount of „dead lithium“

Results XPS/AES

- Graphite electrode particles on TEM grid with lacey carbon film
- AES probing to check for OsO_4 reaction

5 at.-% of Os found on surface

➢ **OsO4 reacts with graphite sample**



XPS investigation of stained samples, e.g.:

Li

LiOH

Li_2CO_3

➢ Osmium preferrably reacts with unsaturated bonds e.g. such as C=O and metals that are easy to oxidize, such as Li.

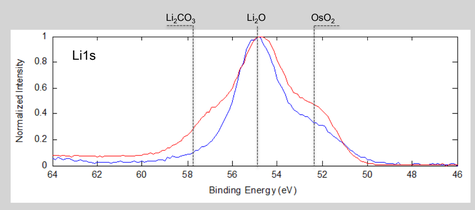


Fig: Li1s spectrum of LiOH (blue) and Li_2CO_3 (red)

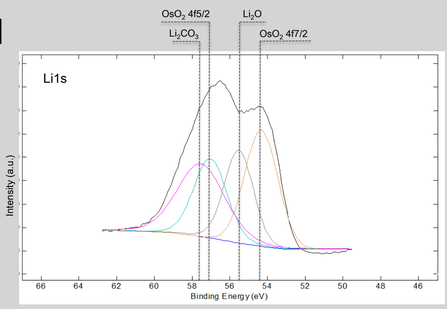


Fig: Li1s spectrum of Li-metal after exposure

➢ **staining of Li-rich and unsaturated bonds rich areas**

Detect-ion

Conclusion

- ➢ Osmium tetroxide staining of energy storage materials with low elemental contrast can be used efficiently to *improve elemental contrast* for electron microscopy.
- ➢ A *stabiliziation* of the samples can be achieved, hence allowing TEM investigation of SEI..
- ➢ Metallic lithium is oxidated preferrably by OsO_4 giving the opportunity to better investigate and *quantify lithium deposition* on graphite electrodes.

Quantifi-cation

Karlsruhe Institute of Technology

Outlook

- Deeper SEI investigation
- Further application to other lithium rich compounds (Li_2O_2)

Leibniz Institute for Solid State and Materials Research Dresden