X-ray photoelectron spectroscopy of osmium tetroxide stained solid electrolyte interphase on graphite electrodes

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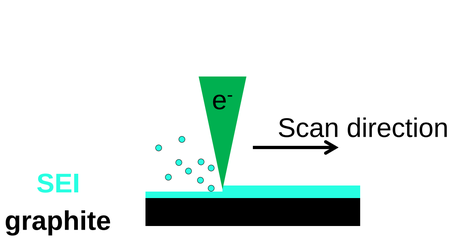
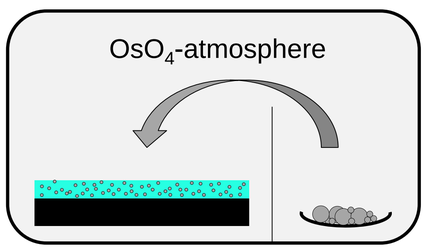
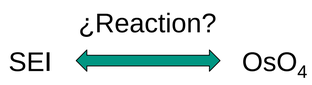
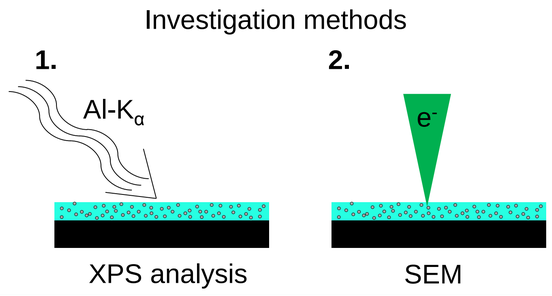
Introduction

- Aging of the solid electrolyte interphase (SEI) is one of the major degradation process in a lithium ion batteries with graphite anodes.
- The detailed structure of the SEI still remains largely unknown ➡ investigation with high resolution electron microscopy.
- Instability of the SEI in the electron beam (volatile) complicates analysis ➡ osmium tetroxide (OsO_4) staining stabilizes & enhances contrast [1].









Experiment

Sample preparation

- Electrodes were always handled and transferred under inert gas.
- Graphite electrodes were cycled with C/20 to build the SEI layer.
- As reference a sample was put into LP30 and dried without cycling.
- Samples were cut in the middle
  ➡ one half directly to XPS
  ➡ one exposed to OsO_4 - atmosphere (12 h < t < 20 h) ➡ XPS
- Samples were investigated with SEM after XPS - analysis.

XPS evaluation

- Evaluation of XPS measurements is difficult, due to the overlaps of the Li 1s with Os 4f - doublet and C 1s with Os $4d_{5/2}$ - spectra.
- At first, Os 4f – spectrum was fitted without any Li 1s peak. Then the relative intensity were kept the same for Os $4d_{5/2}$ and Os $4p_{3/2}$.
- Therafter, Li 1s peaks were added, and the Os heights were fixed, due to the very large difference of the photoionization cross section of lithium (~ 0.06) and osmium (6.96).

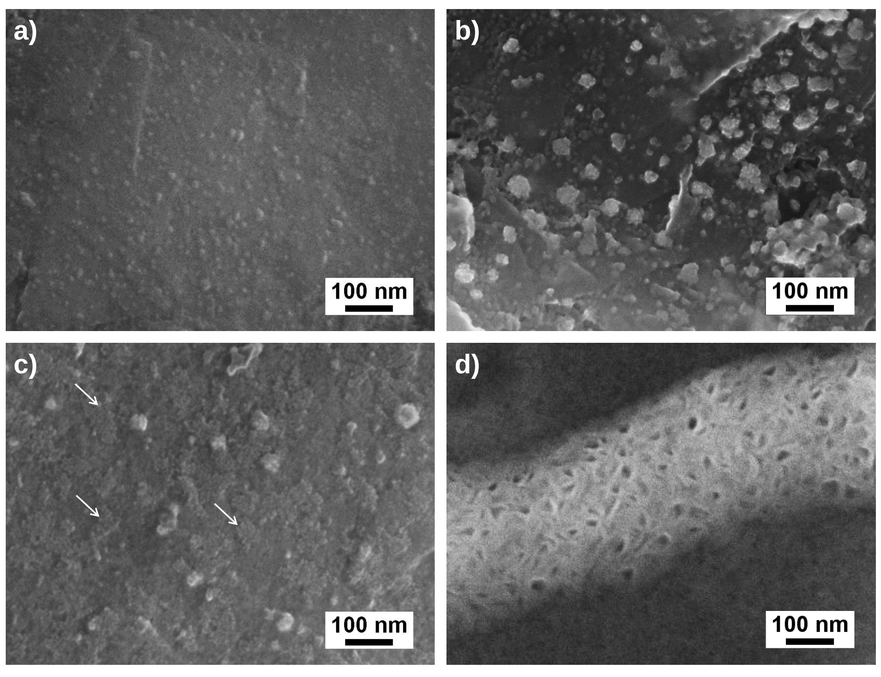


Fig. 1: SEM image of a graphite electrode with
a) dried electrolyte LP30 b) same stained with OsO_4
c) SEI from four cycles C/20 d) SEI stained with OsO_4

Results XPS

- There exists four Osmium doublets with Os $4f_{7/2}$ at 53.0 eV, 54.4 eV, 55.2 eV and 56.8 eV.
- Different binding energy for ethylene carbonate (EC) in LP30 (291.3 eV) and SEI (290.1 eV).
- After staining, the total amount of Os is about 0.2 at % for LP30 and about 4 at % in SEI
- OsO_4 does not react with EC
- After staining the SEI all the Li is bound to O as Li_2O_2 (55.0 eV, O1s 531.6 eV).
- Os seams to react with phosphorus and fluorine, causing a shift to higher binding energy.

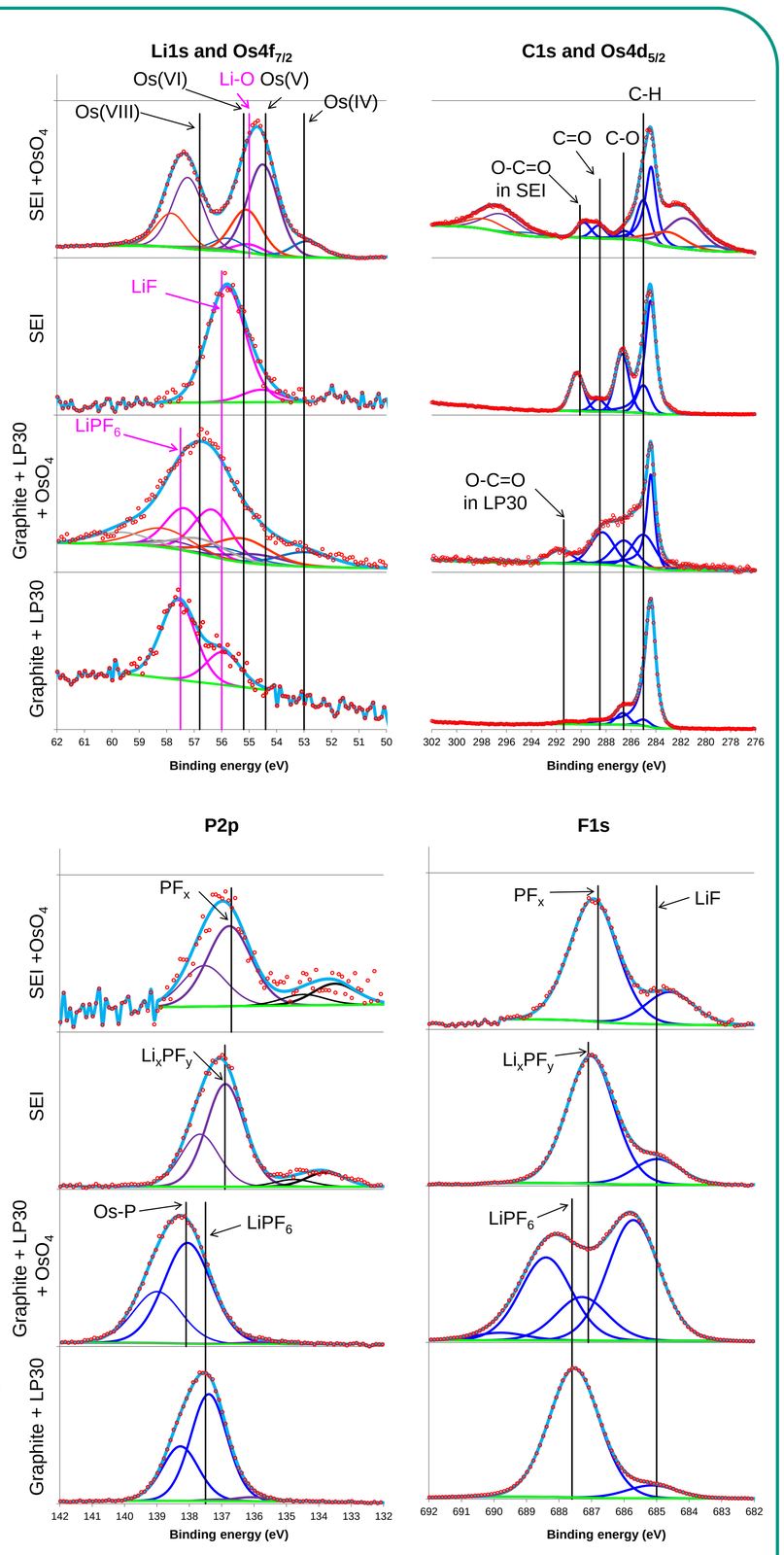
Table 1: Measured averages of four samples

	Measured value
FWHM Os $4f_{7/2}$	1.67 ± 0.24 eV
FWHM Os $4d_{5/2}$	3.32 ± 0.24 eV
ΔE (Os $4d_{5/2}$ – Os $4f_{7/2}$)	227.29 ± 0.47 eV
ΔE (Os $4p_{3/2}$ – Os $4f_{7/2}$)	419.25 ± 0.46 eV

Results SEM

- Dried LP30 (Fig. 1a)) is more stable under the electron beam than the SEI.
- There were thin layers of LP30 confirming the XPS – analysis ➡ graphite is still visible.
- LP30 is dried in small islands.
- After staining (Fig. 1b)) the size of the islands increased.

- Fig. 1 c) shows a graphite surface with SEI.
- Thin SEI - layer (marked with white arrows) is vapored away, after the first image. ➡ One can not be sure to get a real image of the SEI.
- After staining, some areas are brighter (Fig. 1d)) in the electron beam and they have a nice nano-structure.
- These structure is very stable (6 to 10 images no big change) under SEM investigation.
- EDX - measurements reveal O at % ≫ Os, P, F.
  ➡ Li_2O_2



Conclusion

- XPS – analysis point out, that OsO_4 (Os(VIII)) is reduced to Os(VI) Os(V) and Os(IV): 56.8 eV, 55.2 eV, 54.4 eV and 53.0 eV .
- The oxygen, which is released from OsO_4, mainly reacts with the lithium in the SEI to Li_2O_2 (55.0 eV, O1s 531.6 eV).
- There is found only PF_x (136.7 eV, 686.8 eV) in the stained SEI, because the whole Li is bound in Li_2O_2. The PF_x accumulates around the OsO_x.
- It can be confirmed that the stained SEI is more stable under electron beam investigations.
- SEI nano – structures could be observed on graphite surfaces by SEM.

Reference

[1] Martin Zier, Frieder Scheiba, et al., Journal of Power Sources, “Lithium dendrite and solid electrolyte interphase investigation using OsO4”, Issue 266, pp198 – 207, 2014

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