New approach to evaluate and visualize the EASA of carbon electrodes using OsO_4

Lukas Pfaffmann[1], Dr. Frieder Scheiba[1], Prof. Dr. Helmut Ehrenberg[1]

[1] Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), 76344 Eggenstein-Leopoldshafen, Germany

Introduction

- In graphite Li can diffuse only parallel to graphene layers or through grain boundaries [1] (Fig. 1a).
- Li-intercalation only at the edge sites in the graphite where graphene layers end.
  → Only a fraction of the surface is active for lithium intercalation.
- This area is generally addressed by the concept of the Electrochemical Active Surface Area (EASA) [2].
- The higher the relative amount of EASA in graphite electrodes, the more reactive is the graphite electrode [3].

Difficulty: EASA does not differ optically to the rest of the surface of a graphite particle.
In this work: First time visualization of the EASA by means of Scanning Electron Microscopy (SEM).

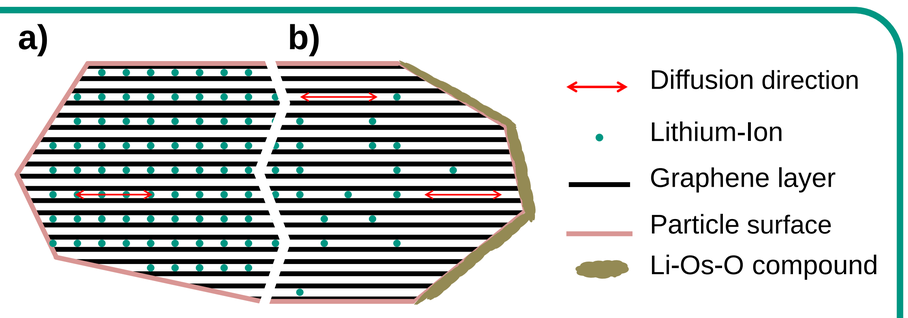

Fig. 1: Sketch of a graphite particle a) before and b) after the osmium tetroxide staining. EASA is covered with a Li-Os-O compound after staining.

Experiment

Ambition

- Work out a visualization method of the EASA by mans of SEM.
- Determination of EASA amount in different carbon anode materials.

Approach

- Adopting the OsO_4 staining procedure commonly used for polymer blends and biologic tissue for EASA analysis in lithium ion batteries.
- Lithium shows a strong reaction with OsO_4 [4] which is also expected for lithiated graphite.
- Li should extracted and diffuses to the particle's surface forming solid Li-Os-O compounds.
- Li-Os-O can be visualized by SEM and therefore allows a visual inspection of the EASA.

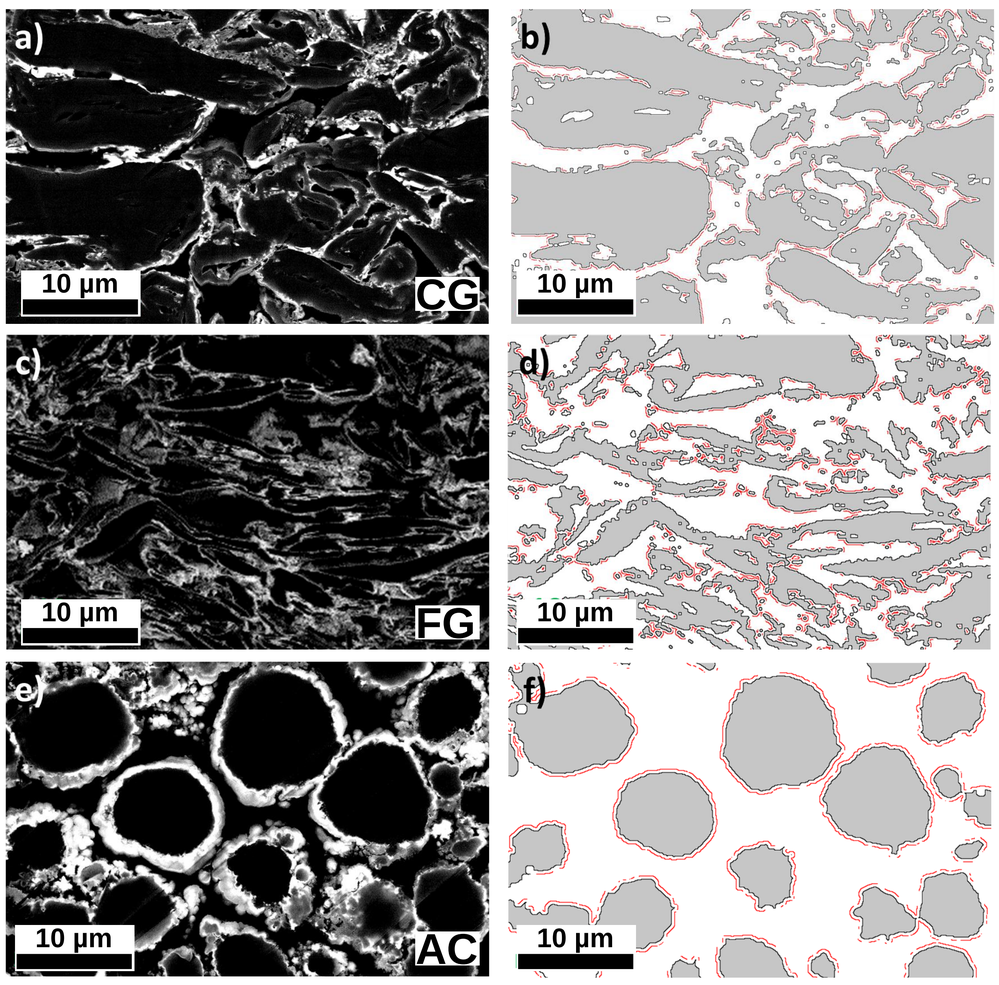

Fig. 3: a), c) and e): AsB-image section of cross-sections. The Li-Os-O compound appears as bright regions.
b), d) and f): Processed AsB-images. Grain-boundaries are markedby black and EASA by red lines, respectively. The grain area is filled out with grey.

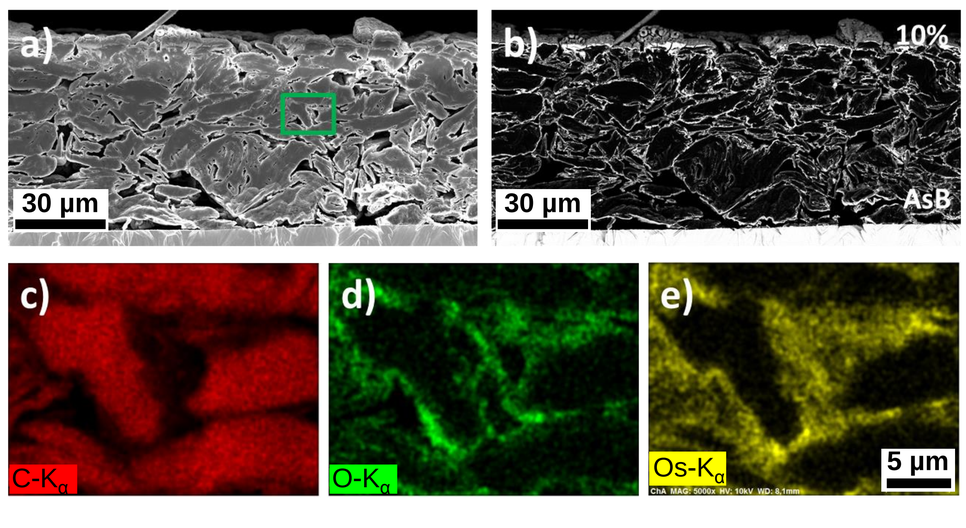

Fig. 2:
a): SEM InLens-image of a 155 x 59 µm² wide anode cross-section of the CG sample with a SOC of 10%.
b): corresponding AsB-image.
c-e): show the EDX maps of the green marked region in a). Thus the bright regions in b) correspond to the Li-Os-O compound.

Experimental

- Investigation of three different anodes: Coarse Graphite (CG) with 20 µm particle size, Fine Graphite (FG) with 9 µm particle size and Amorphous Carbon (AC).
- Using two State Of Charge (SOC): 5% and 10 %.
- After the exposure Ar-Ion-milling cross-section were prepared and analyzed by a SEM.
- Angle selective Backscattering (AsB) and energy dispersive X-ray spectroscopy (EDX) confirmed that bright areas in AsB-images correspond to osmium-rich parts on the anode surface (cf. Fig. 2).
- Porosity was obtained by both, ratio of grain area in processed AsB-images (grey Fig. 3) to cross-section area and ratio of material (graphite or amorphous carbon) density in relation to the anode's mass and volume.

Results

- AsB-images clearly show that Li-Os-O compound is at some parts of the anode's surface (cf. Fig 3).
  → Li can be extracted of electrodes by OsO_4.
  → EASA of the particles can be made visible by using the AsB detector.
- To count Li-Os-O compound among the EASA, it should be thicker than 100 nm (→ 3 image pixels). Samples with an SOC of 10 % showed better results.
- The EASA of a graphite electrode is one third of the grain area, whether big or small particles (cf. Table 1).
- AC shows an EASA twice as large as graphite electrodes.
- The porosity obtained by SEM image contrast coincides with the porosity obtained by density considerations.

Table 1: Results of the three investigated anodes.

Anode	EASA	Porosity by SEM contrast	Porosity by material density
Coarse Graphite (CG)	37 %	34 %	36 %
Fine Graphite (FG)	35 %	54 %	52 %
Amorphous Carbon (AC)	72 %	46 %	38 %

Conclusion and Outlook

It was demonstrated that the reaction of lithiated graphite with OsO_4 is suitable to visualize the EASA by means of electron microscopy. AsB-images could be evaluated to get a quantitative approximation of the EASA.

The reaction of OsO_4 with certain Solid Electrolyte Interphase (SEI) components may also help to gain a deeper understanding of the SEI structure. Therefore, XPS analysis of OsO_4 reaction products with SEI components are underway to facilitate the interpretation of how SEI layers reacted with OsO_4.

References

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