

Supplementary material:

Binding energy referencing for XPS in alkali metal-based battery materials research (II): Application to complex composite electrodes

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You can find here some more details of the conditions for sample preparation and special treatment. The information is sorted by the chapter number from the MS and associated with the Figures. For Li-metal foil also fit results are presented.

3.1 Reaction layers - without surface charging

Li-metal foil

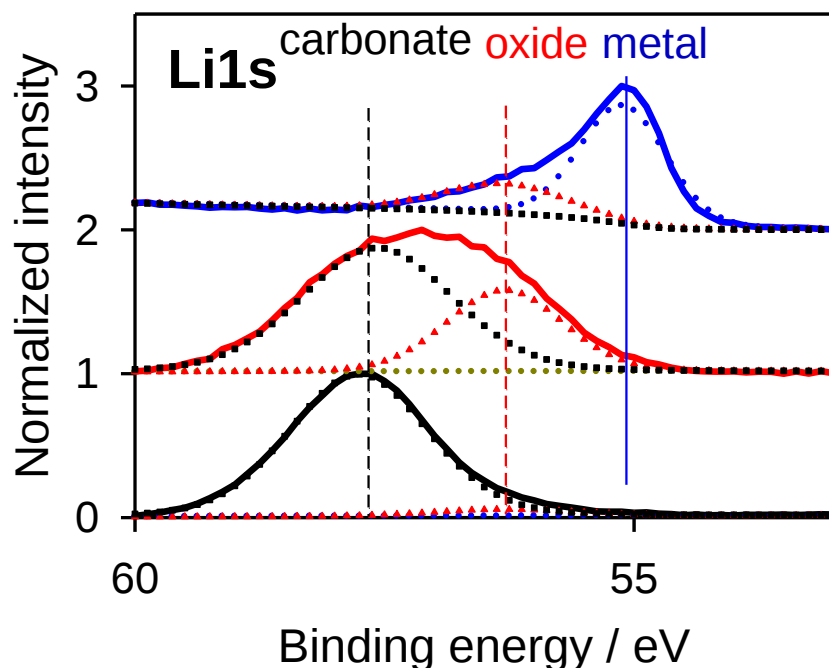
- pure Li-foil (Fig. 1)

As-delivered Li foil (Chemetall, 250 μm thickness) was simply cut into pieces in the glovebox, transferred into XPS without any treatment.

Fig. S1 demonstrate the peak fit results (Gauss-Lorentz, Shirley background subtraction) for the identification of the peak positions of Li-carbonate, -oxide and -metal in the Li-foil sample discussed in Figure 1. Due to sputtering the carbonate (black) degrades first to Li-oxide (red) and after long time sputtering (30min) Li-metal occurs (blue). The detected peak position are 57.7 / 56.3 / 55.1 eV with ± 0.1 eV uncertainty, the FWHM are 1.7 / 1.5 / 1.0 eV also ± 0.1 eV. Thus, the peak positions of carbonate and oxide are shifted by 2.2 / 2.3 eV to higher BE

with respect to the reference values for carbon reference [19], whereas Li-metal is exactly in the expected position at 55 eV.

Fig. S1: Li1s spectra of a Li-foil covered with carbonate as-delivered from the glove box and after 1 and 30 min Ar⁺ sputtering (bottom to top).

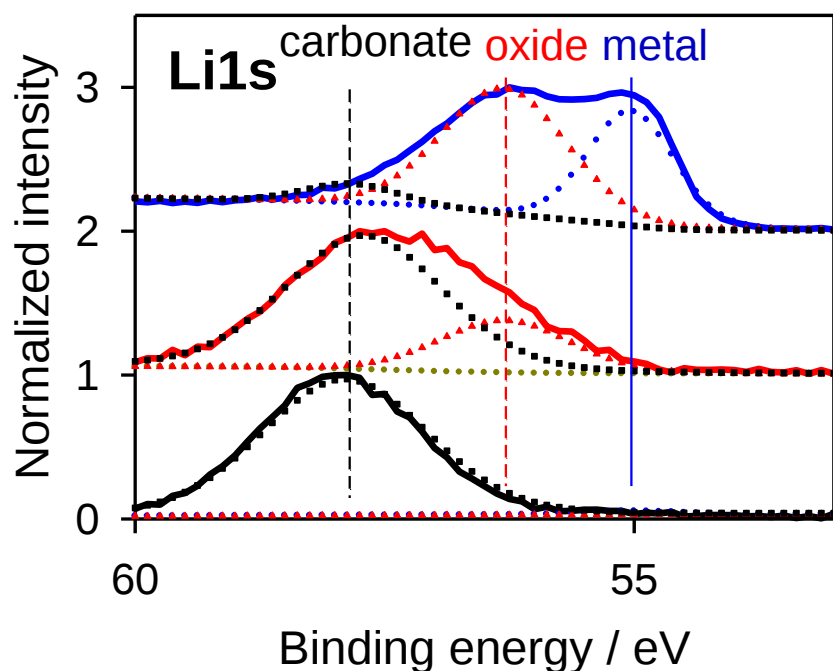


- Li-S anodes (Fig. 2)

A conventional sulfur cathode made of sulfur/Super P composite electrode (60 wt.% sulfur) was cycled between 1.8 – 2.6 V vs. Li/Li⁺ with 1 M LiTFSI/0.25 M LiNO₃ in DME/DOL (1:1) (anhydrous) as electrolyte 50 times. After disassembling, the lithium metal was briefly washed with DME, prior transfer to the XPS.

Fig. S2 demonstrates the peak fit results (Gauss-Lorentz, Shirley background subtraction) for the identification of the peak positions of Li-carbonate, oxide and -metal in the Li-electrode discussed in Figure 2. Due to sputtering the carbonate (black) degrades first to Li-oxide (red) and after longer sputtering (15 min) also Li-metal occurs (blue). The detected peak positions are 57.8 / 56.3 / 55.0 eV with ± 0.1 eV uncertainty, the FWHM are 1.9 / 1.5 / 1.0 eV also ± 0.1 eV. Thus, the peak positions of carbonate and oxide are shifted by 2.3 / 2.3 eV to higher BE with respect to the reference values for carbon reference [19], whereas Li-metal is exactly in the expected position at 55 eV.

Fig. S2: Li1s spectra of a cycled Li-electrode covered mainly with carbonate as-delivered from the glove box and after 3 and 15 min Ar⁺ sputtering (from bottom to top).



- Os-staining of Li-metal (Fig. 3)

Exposure of samples to OsO₄ vapor was performed with OsO₄ (99.8%, Merck KGaA). A special exposure device was used to allow a safe sample staining in the osmium tetroxide fume. All samples were transferred into the exposure chamber from an argon-filled box. The average exposure time was chosen between 12 h and 18 h. Afterwards the gas valves were opened and the chamber was purged with Ar. This procedure normally used also for graphite electrodes and its further electrochemical testing [29] here was used to investigate Os staining at Li metal foil. For more details including a discussion of the reaction mechanism based on the XPS results, it is referred to [29]

C-based anode material

- SEI-formation at graphite anodes (Fig. 4)

Lithium-ion pouch cells consisting of a graphite negative electrode, Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})_yO₂ (NCM) positive electrode, polymer separator and an ethylene carbonate based organic electrolyte with LiPF₆ as conducting salt were used in this study. For analysis of the SEI the pouch cells (50% state-of-charge) were opened in a glovebox and the negative electrode samples were cut out. The samples were washed with diethyl carbonate (DEC) for several times. In the antechamber, they were vacuum-dried for 1 h before transferred to the XPS. For more details, it is referred to [37].

- Hard carbon (HC) infiltrated with Na (Fig. 5)

The HC material was prepared from a mixture of 90 wt% hard carbon material (Carbotron P - Kuraray), 5 wt% MWCNT (NC7000 - Nanocyl) and 5 wt% SBR (Targray) as binder. It was deposited as a water-based slurry on Al-foil, afterwards dried at 80 °C (2 h air, 12 h vacuum) and punched to 15 mm diameter samples. The sodiation of the HC material was done in a coin cell vs. a Na metal electrode simply by short-circuiting both electrodes. The used electrolyte was a mixture of DEC and EC (6:4 vol%) with 1 M NaPF₆. Coin cell potential change was from 1.5 to 0.01 V within 48 h of the sodiation. Then the residuals of the electrolyte were washed away in a glove box using DEC/EC leaving the SEI formed during lithiation back at the surface. The samples were transferred to XPS in Ar atmosphere. For more details, it is referred to [38].

Cathode material

- LiCrMnO₄ (Fig. 6)

LiCrMnO₄ was synthesized by a modified Pechini process. Lithium, chromium, and manganese acetates were dissolved in distilled water. Afterwards, citric acid and ethylene glycol were added. The pH was adjusted with ammonia solution to 5–6. After stirring at 80 °C and slow evaporation of most of the water, the product was finally dried overnight at 120 °C and precalcined at 450 °C for 6 h. Final annealing was performed at 800 °C for 24 h. The cathode mixture consists of 80 wt.% LiCrMnO₄, 10 wt.% carbon black, and 10 wt.% PVDF pressed on an aluminum grid as usually used for electrochemical investigation. LP30 was the applied electrolyte. For Fig. 6 only the starting materials were compared to point to possible side reactions with binder and/or electrolyte. Such electrodes afterwards were used for further cycling tests to produce different charged states of LiCrMnO₄, to 4.88 and 5.2 V, respectively, and discharged to 3.2 V. For more details and the cycling results see [40, 41].

3.2 Reaction layers - with surface charging

Anode material

- LiAl- and LiAlZn- anode material (Fig. 7)

LiAl_{1-z}Zn_z alloys were prepared from the elements lithium (rod, 99.9%, Alfa Aesar, Karlsruhe, Germany), aluminum (slugs, 99.999%, Alfa Aesar), and zinc (shots, 99.99%, Alfa Aesar). All preparation steps were performed in a glovebox under argon atmosphere in a Ta crucible sealed by arc-welding. The Ta crucibles were heated to 900 °C with an induction furnace for 10 min

and were cooled down naturally. The electrode materials were prepared by mixing 80 wt% active material powder, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) and pressed onto a stainless steel grid. The electrochemical characterization was performed in Swagelok cells with the LP30 electrolyte vs. Li/Li^+ . Galvanostatic cycling with potential limitation was performed with a C/20 rate. Further details of preparation can be found in [45].

- Al-Ni-Y-based anode material (Fig. 8)

Alloys with the nominal compositions $\text{Al}_{86}\text{Ni}_8\text{Y}_6$ (and $\text{Al}_{86}\text{Ni}_8\text{La}_6$) were prepared by arc melting of Al (99.99%), Ni (99.99%), La (99.99%) and Y (99.99%). Ingots of the alloys were melt-spun (E. Bühler D-7400) at 1493 K with the help of a quartz jet nozzle and a rotating, internally water-cooled Cu wheel. The ribbons were taken as electrode as received from the melt-spinning process. They were once galvanostatically discharged/lithiated starting from 3.0 V until 0.1 V vs. Li/Li^+ in Swagelok test cell at a C/50 rate with standard LP30 electrolyte. For details it is referred to [44, 46].

- Al-Ni-Y powder (Fig. 9)

The alloy with the nominal composition $\text{Al}_{43}\text{Li}_{43}\text{Y}_6\text{Ni}_8$ (at.%) was prepared by melting the pure elements Al (Alfa Aesar, 99.999%, Karlsruhe, Germany), Li (Alfa Aesar, 99.9%, Karlsruhe, Germany), Ni (Chempur, 99.98%, Karlsruhe, Germany) and Y (Chempur, 99.9%, Karlsruhe, Germany) in sealed Ta-tubes under Ar-atmosphere in an induction furnace (Hüttinger). High-energy ball milling (Pulverisette 7 premium line, Fritsch) was applied to pulverize and amorphizise the alloy. Powders were sieved to separate a particle fraction of 20 – 45 μm diameter. Electrodes were prepared 80 wt% active material, 10 wt% carbon (Super PLi, Timcal) and 10 wt% polyvinyliden difluoride (SOLEF 1013, Solvey). The mixture was pressed onto stainless steel grids to form electrodes. Galvanostatic cycling was performed in the potential window of 0.1 to 4 V in Swagelok cells with LP30 electrolyte with C/50 for 30 full charging/discharging cycles. For the detailed preparation procedure, please read more in [46, 47].

Cathode material

- $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ cathode material (Fig. 10)

Synthesis of the $\text{Li}_3\text{Cr}_2(\text{PO}_4)_3$ powder was preformed *via* a classical solid state reaction. A precursor was produced by dissolving Li_2CO_3 (Acros, 99%), $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Acros, 99%), and $(\text{NH}_4)_2\text{HPO}_4$ (Merck, 99%) in the molar ratio of 3:4:6 in 30 wt% nitric acid. After evaporation to dryness under constant stirring at a maximum temperature of 200 °C, the residue

was calcined at 800 °C in air for 14 days in silica crucibles. 80 wt% of the as-prepared powder, 10 wt% carbon black and 10 wt% polytetrafluoroethylene (PTFE) were mixed and pressed onto an aluminium mesh. Swagelok-type cells were assembled in an argon-filled glove box using lithium foil, commercial LP30 electrolyte and a Whatman glassfiber separator. Galvanostatic cycling with potential limitation was carried in a potential window of 3 V up to 5.2 V at C/10. For more information see [17].

3.3 Reference samples - with charging

- Li-reference chemicals (Fig. 11):

The pure Li_2O , Li_2O_2 and Li_2CO_3 (Fluka (purity: p.a.), ABCR (95 %) and Aldrich (97 %)) powders were pressed in the glove box to Al grids without carbon powder and binder.

- Li_2O_2 ; treated with LiTFSI (Fig. 12):

The Li_2O_2 powder (Fluka - purity: p.a.) was pressed into an Al-grid and stored for 20 h in an electrolyte from a solution of 0.5 M LiTFSI (lithiumbis(trifluoromethansulfonyl)imid) (ABCR) in the ionic liquid PP13-TFSI (N-methyl-N-propylpiperidiniumbis(trifluoromethansulfonyl)imid) (Iolitec). Before analysis the samples were washed in acetonitril; afterwards they were transferred to the XPS system under Ar atmosphere.

References

Can be found in the main paper body.