

In-situ XRD investigation of insertion and extraction mechanisms of Lithium in nanostructured gold thin films

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Currently lithium ion batteries (LIBs) have applications in a wide range of consumer electronics. The requirements of future electromobility and other high power applications in capacity, stability, safety, and lifetime call for considerable improvements of the performance. For achieving substantial advances towards this goal a fundamental atomic-scale insight into the mechanisms during charging and discharging will be highly beneficial. Applying in-situ techniques is often inevitable due to the high reactivity and since also metastable phases are in some cases involved [1,2]. Beyond the classical carbon based anode materials currently metals and silicon are investigated. In these materials Li can be stored by forming Li alloys. The related uptake capability for Li is here considerably higher than for carbon based electrodes [3]. However charging results in a high volume change of these materials leading to new problems due to the high stress induced. The consequence is partial cracking of the electrode materials, loss of contact to the current collector material and a relatively quick capacity loss. One approach to address these problems is to nanostructure the active material. Morphologies like thin films or nanowires offer more space and freedom to compensate the volume changes during battery cycling.

We investigated the electrochemically driven insertion and extraction of Li by in-situ X-ray diffraction employing high-energy synchrotron radiation. In addition to Au single crystals, thin-film Au electrodes were prepared by PVD on copper substrates. For X-ray diffraction studies the Au model system offers a high diffraction cross section. Moreover different crystalline AuLi alloy phases including frequent reports about metastable phases have been observed so far which can be addressed by XRD.

For our measurements we used as electrolyte a 0.3 M solution of the Li salt LiTFSI in the ionic liquid 1-Butyl-1-methyl-pyrrolidinium-bis(trifluoromethane)sulfonylimide (Pyr₁₄TFSI). The Au film was polarized galvanostatically at a rate of 2,5C. During the lithiation of the electrode a set of new diffraction peaks (denoted as phase 1 in the following) arose in addition to the peaks of Au and Cu (Fig. 1,2). After reversing the current direction and a short period in time the intensity passes a maximum and decreases (Fig. 2). A second new phase (phase 2) was observed indicated by a different set of peaks {Fig. 1}. Phase 2 passes a maximum of intensity when intensity of phase 1 has slumped to around 33% of its maximum intensity. Then also phase 2 is dissolved. At the end of the cycle both phases have disappeared {Fig. 2}. During the emerging of phase 1 the signal of the substrate Au goes down. In addition, no shift of peak positions nor any upcoming of a shoulder were

observable as it would be expected for formation of Au Li solid solution. Together it can be said, that phase 1 is formed consuming the crystalline Au material. Phase 1 dissolves via the intermediate formation of phase 2 and the initial Au structure develops into an amorphous state. X-ray diffraction has proven a valuable tool to get to a more detailed image of the structural changes inside the gold film during reaction with Li. The occurrence of metastable Au phases [1,2] enables an instructive comparison with results from theoretical structure simulation.

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[2] P. Bach, A. Seemayer, U. Rütt, O. Gutowski, F. U. Renner, in preparation

[3] M. N. Obrovac, L. Christensen, D. Ba Le, J. R. Dahn, Alloy Design for Lithium-Ion Battery Anodes, *Journal of The Electrochemical Society* 154, A849-A855 (2007)

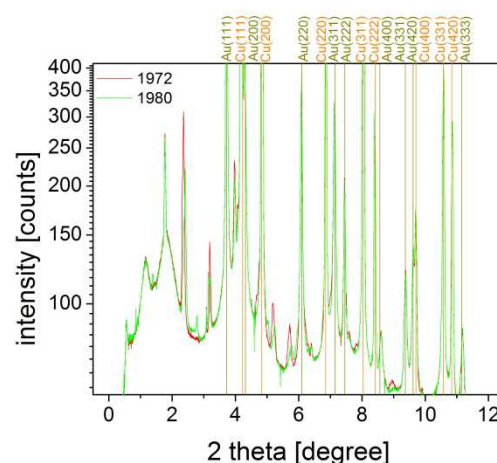


Fig. 1: Diffractograms of different stages during the charge discharge cycle of the Au model electrode. In the red one phase 1 is present, in the green one phase 2

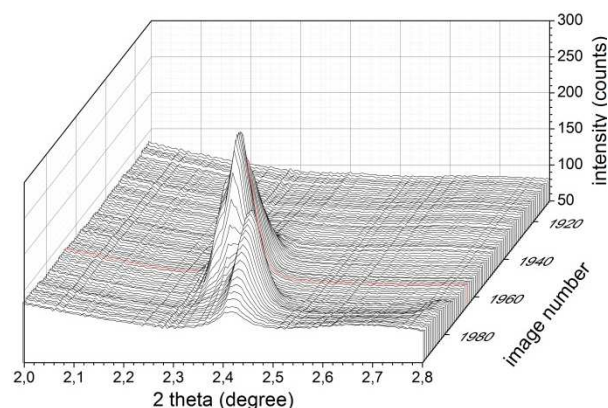


Fig. 2: Course of intensity in a certain angle range. The higher peak stems from phase 1 the lower one from phase 2. The red line marks the end of the end of electrochemical Li loading.