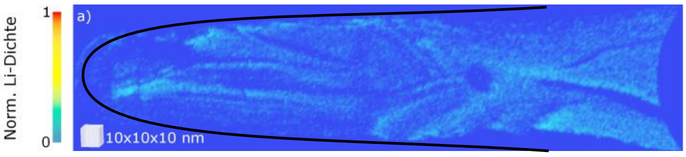
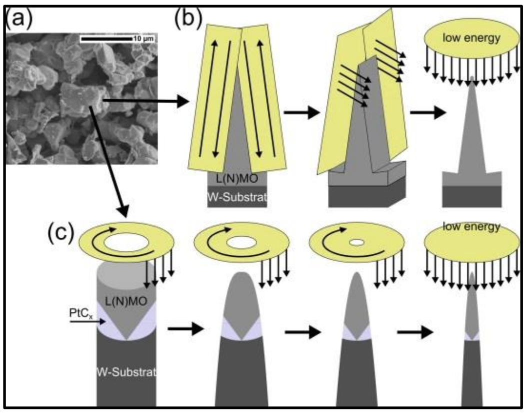
In-Situ De-Lithiation and Atom Probe Tomography of $LiFePO_4$

Information about Li positions and mobilities in battery electrode material is of great importance for understanding and optimizing battery performance. Due to its low atomic number only very few methods are able to reliably detect Li, making Atom Probe Tomography (APT) an extremely important method since it can deliver atomic scale information about Li. Recent APT studies on $LiMn_2O_4$, an active cathode material for Li ion batteries, have revealed that the reduction in battery performance due to capacity fade may be due to an extremely sensitive dependence of the Li mobility on the Li concentration. This results in the formation of isolated pockets of Li which cannot be easily moved in and out of the cathode material during battery charging/discharging. The goal of this Master Thesis project is to test how general this behavior is by using APT to investigate the mobility of Li in $LiFePO_4$, a second important battery cathode material.



(Above) Atom Probe Tomography (APT) reconstruction of a $LiMn_2O_4$ crystal showing heterogeneously distributed Li after in-situ removal of Li through the crystal surface (indicated schematically by the solid line) using field evaporation. (Right) Schamatic of two methods used to prepare the nanoscale tips needed for APT using FIB machining,



Work Plan:

Micron-sized particles of $LiFePO_4$ will be shaped into the nanoscale tips needed for ATP analysis using focused ion beam (FIB) machining (see right Figure). The tip specimens will then be investigated with Transmission Electron Microscopy (TEM) to confirm that they have the desired shape (with tip radius of curvature ca. 10 nm) and to identify any existing crystalline defects or other features. A specimen will then be mounted into the ATP where Li ions are field evaporated from the tip, without removing Fe, P or O atoms. Because Li is mobile at room temperature, it is depleted by both lattice and surface diffusion from the crystal. Afterwards, the specimen is cooled down to 30K where the Li should be immobile and laser-assisted field evaporation and time-of-flight mass spectrometry can be used to determine the positions of the Fe, P, O, and Li atoms in the near-tip region of the specimen with atomic scale resolution. The goal will be to generate three-dimensional, atomic-resolution distributions of the atoms in the $LiFePO_4$ tip (such as shown above for Li in $LiMn_2O_4$) and thereby to learn something about the dynamics of de-lithiation in this material.

Experimental Methods:

The following methods will be learned and used independently by the student: Atom Probe Tomography (APT) measurement and reconstruction; Focused Ion Beam (FIB) microscopy and machining; and conventional Transmission Electron Microscopy (TEM).

The Master Thesis may be written in either English or German.

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