Studying electrically active defects in LiMn₂O₄

 $LiMn_2O_4$ is a cubic spinel material that is successfully used as the active cathode material in many Li ion batteries. However, the practical Li charging capacity is well below the expected theoretical value and decreases or "fades" with use, severely compromising battery performance. Our recent research studies have shown that some of the capacity problems are caused by planar defects that are present in the $LiMn_2O_4$ nanoparticles used in the electrodes. Therefore, the goal of this Master Thesis project will be to better understand the structure and properties of these planar defects. Most importantly, the electrical and ionic conductivity of the defects will be investigated using Atomic Force Microscopy (AFM), since these directly affect battery performance.



On left: SEM image of the $LiMn_2O_4$ nanoparticles.

On right: TEM image of a thin section cut from a nanoparticle using focused ion beam (FIB) machining and showing a set of parallel planar defects.



Work Plan:

The $LiMn_2O_4$ nanoparticles will be embedded in a conducting polymer and polished to prepare a cross-sectional specimen. The specimen will then be investigated in the scanning electron microscope (SEM) to locate planar defects. These will also be investigated with electron backscatter diffraction (EBSD) and energy dispersive x-ray (EDX) analysis in the SEM to probe the crystal structure and local chemical composition. Once suitable defects for further study have been identified, they will be tagged using electron beam enhanced deposition of small markers placed next to the defects.

The specimens will then be mounted into the Atomic Force Microscope (AFM) where a variety of different characterization studies will be performed. After using the topography and local friction to distinguish nanoparticles from embedding material, the electrical conductivity of the particles will be locally probed using a conducting tip to look for differences in the electrical properties of the planar defects. Scanning Kelvin Probe Microscopy (SKPM) will then be used to reveal information about work functions and trapped and mobile charges at the surface of the specimen. By the application of a macroscopic electrical voltage to the embedded nanoparticles, SKPM may help to reveal how Li motion is coupled to electrical currents.

Experimental Methods:

The following methods will be learned and used independently by the student: Scanning Electron Microscope (SEM), including EBSD and EDX; Focused Ion Beam (FIB) microscopy and machining; and Atomic Force Microscope (AFM), including methods to study local topography, electrical conductivity, and energy dissipation.

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

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