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Operando Diffraction During Li Battery Operation using Neutron and Synchrotron X-Ray Radiations

Performing in situ and operando measurements on electrode materials for Li-ion and Na-ion batteries is of importance for their understanding and improvement. Electrode materials need to be studied in their environment (in situ) and in real time while they function (operando), since they normally operate in non-equilibrium conditions. Real-time experiments upon charge/discharge of the electrodes (i.e. upon lithium or sodium extraction/insertion from/into the electrodes) unveil dynamics that are not accessible by other means and allow a more complete understanding of the electrodes'functioning. The use of different probes is an important requirement for the study of such reactions. The combined use of X-Ray Powder Diffraction (XRPD), Synchrotron radiation XRPD and Neutrons Powder Diffraction (NPD) allows observing any atomic element in any crystalline electrode. However, custom setups are required to carry out operando diffraction experiments on batteries.

We recently designed an electrochemical cell manufactured with a completely neutron-transparent (Ti,Zr) alloy [1]. Used with deuterated electrolytes, the cell is able to combine good electrochemical properties and the ability to collect ND patterns operando, with good statistics and no other Bragg peaks than those of the electrode material of interest. Importantly, this allows detailed structural determinations by Rietveld refinement during operation. The cell was validated using well-known battery materials such as LiFePO4 and Li1.1Mn1.9O4 demonstrating real operando experiments conducted on the D20 high flux neutron powder diffractometer at ILL Grenoble, France. Importantly, we showed the possibility to succeed in reliable structural refinements (by the Rietveld method) and thus to observe structural modifications in details, from unit cell parameters to atomic coordinates and even site occupancy factors. We will discuss a few studies done with this setup, namely the observation of lithium extraction from different samples in the family of spinels Li1+xMn2-xO4. We performed NPD in real time on three samples (LiMn2O4, Li1.05Mn1.95O4 and Li1.10Mn1.90O4) and showed how the Li/Mn ratio influences the phase diagram of the material [2]. New insights obtained from high resolution –high flux Synchrotron X-Ray diffraction data will be presented, in particular the existence of a Li+ and Mn3+/Mn4+ ordering within the spinel-delithiated composition Li0.5Mn2O4 [3].

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