In-Situ and Operando Neutron Powder Diffraction on Li-ion batteries at the ILL

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The structure and purity of Li-ion batteries have long been classically characterised ex-situ by neutron powder diffraction. More recently, great efforts have been made to provide scientists with a tool to study Li-ion batteries operando, in order to gain a better insight into the processes involved during charging and discharging. Several electrochemical cells have been developed in different facilities [1]

At the ILL, we have designed our own custom-made electrochemical cell to respond to some specific requirements #ILLBAT1 [2]. We have shown that this cell can function properly electrochemically, while at the same time, allowing the acquisition of high quality Neutron Powder Diffraction (NPD) patterns for Rietveld structural refinement. The next step was to develop of similar electrochemical cells for operando studies on all solid-state lithium batteries. This cell #ILLBAT2 has a similar design as the original one, the main difference being that it can be used at non-ambient temperatures (either high or low). Then ILLBAT#4 and ILLBAT#5 are cells designed to work on ASSB as ILLBAT#2, but its specificity is that it will be possible to maintain a high pressure on the sample while measuring. First experiments on $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532)[3] and $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)[4] has been performed to understand the ASSB system NMC|LPSClBr|LiIn showing the appearance of a new phase upon extraction of Li ion during the cycling. Finally, a cylindrical cell is available that allows a double coated electrode to be loaded with 5 g of sample, similar to commercial batteries[5]. All made of TiZr alloys.

NPD operando experiments are not just about electrochemistry: the study of chemical reactions in real time can give unparalleled insight into the evolution of intermediate species and provide guidance for optimising reaction conditions during synthesis. Powder diffraction has been shown to be an effective tool for resolving the structural evolution that takes place during heating in the study of cathode materials in solid-state synthesis reactions. [6] Another recent example is the study of the LNMO spinel phase equilibrium during synthesis using in situ temperature controlled SXRPD and NPD techniques. We studied how the composition and synthesis conditions affect a particular material, $LiNi_{0.5-x}Mn_{1.5+x}O_4$ (LNMO), used in the positive electrodes of batteries. By adjusting the ratio of manganese and nickel in the material, we discovered that adding a small excess of manganese significantly enhances battery performance, increasing its capacity and efficiency and we have shown that during synthesis, the structure and composition evolve, sometimes forming additional phases, which also affect the material's properties. [7]

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