Experimental report

22/02/2020

Proposal: **5-23-735** **Council:** 4/2019

Title: Investigation of battery materialsby operando neutron diffraction

Research area: Materials

This proposal is a new proposal

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Samples: LiFePO4
LiV2(PO4)3
LiNi0.33Mn0.33Co0.33O2

Instrument	Requested days	Allocated days	From	To
D20	3	1	14/10/2019	15/10/2019

Abstract:

We propose to use operando neutron diffraction to obtain details about the Li-sublattice in the Li-ion cathode material Li3V2(PO4)3. We have studied the material with operando synchrotron X-ray diffraction where we discovered that the material behaves differently than what has previously been discovered by ex-situ diffraction. The phase evolution of the material is highly dependent on the number of Li-ions extracted during charging of the material due to ordering of the Li-ions. Information about the Li-sublattice is very difficult to obtain by X-ray diffraction, however, due to the very low scattering strength of lithium. Neutron diffraction is ideal in this regard, and is expected to yield valuable information about the Li-sublattice, the nature of which seems to dictate the phase evolution of the material. Due to our experience with operando X-ray diffraction, we wish to also use operando neutron diffraction to investigate the material under realistic conditions.

In this test experiment we wanted to investigate the possibility of using an operando neutron diffraction cell designed by us for measurements of battery materials. Our test cathode material of choice was $LiNi_{0.5}Mn_{1.5}O_2$ (LNMO), which was supplied to us by our industry partner, Haldor Topsøe A/S.

Test measurements on three different sample of LNMO using wave lengths of 1.30 and 2.41Å were performed to get an idea of the data quality. We decided on 1.30Å with a take-off angle of 42°. The difference between the three LNMO sample is the ordering of the Ni and Mn metal ions. The samples consisted of an ordered ($P4_332$), a disordered (*Fd*-3*m)*, and a mixture. Below is shown the diffractograms:

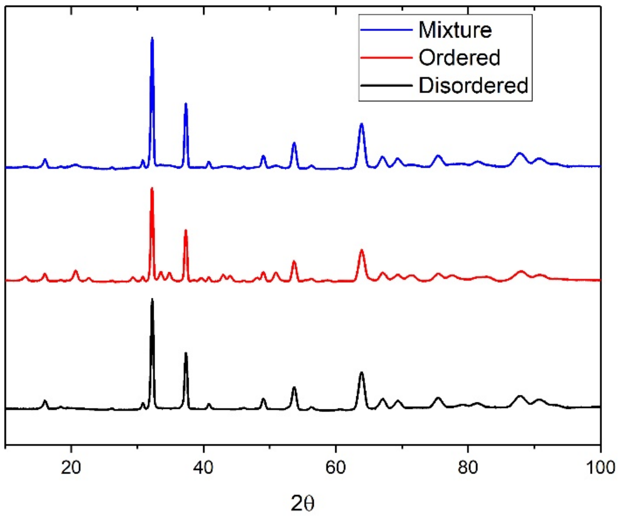

Figure 1: Neutron powder diffractograms of the three samples with differing degree of ordering.

Extra peaks from the metal ion ordering is clearly seen for the ordered sample. A 60mg pellet of the mixed sample was placed in the operando cell, and electrolyte and Li-metal foil were added. Photographs of the operando cell is shown below:

Figure 2: Photographs of the assembled and disassembled operando cell.

Without connecting the cell to the potentionstat, a 30-minute scan was performed to compare with the earlier ex-situ measurements. The comparison is shown below:

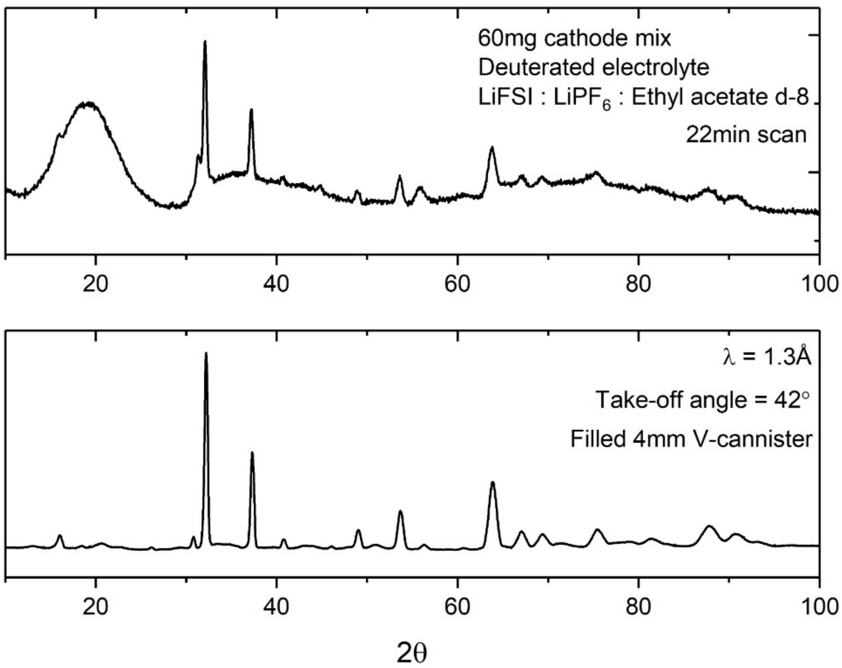

Figure 3: Comparison of the diffractogram of 60mg LNMO in the assembled operando cell (top) and on the pure powder (bottom).

Despite a large background, mainly from the electrolyte, the Bragg peaks are still clearly visible. We then wanted to charge the battery while simultaneously measuring diffractograms in 30 minute scans. Unfortunately, the wetting of the cathode pellet by the electrolyte turned out to be insufficient, and the electrochemical performance failed:

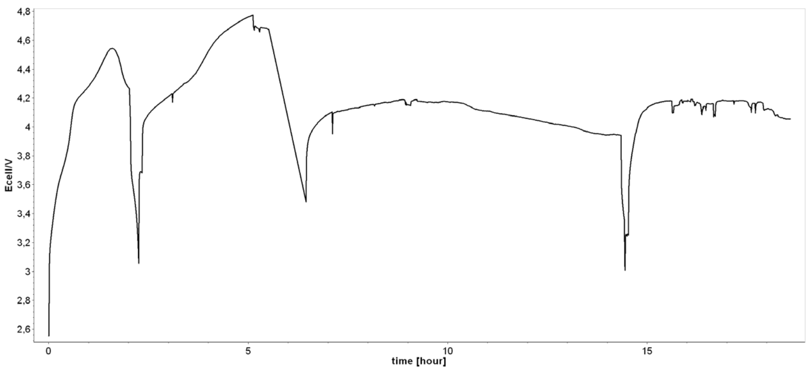

Figure 4: The noisy voltage curve during the operando experiment.

We were therefore not able to perform a successful operando experiment, as we only had a single day available. We have beamtime in April 2020, where we expect to have a much better electrochemistry. We have already performed a large number of adjustments and improvements to the measurement procedure. We will also bring cells with a larger diameter, as it seems that this increase will not reduce the resolution too much. This will allow us to use more material, which will improve the diffraction quality even further. An example of the improved electrochemistry can be seen below:

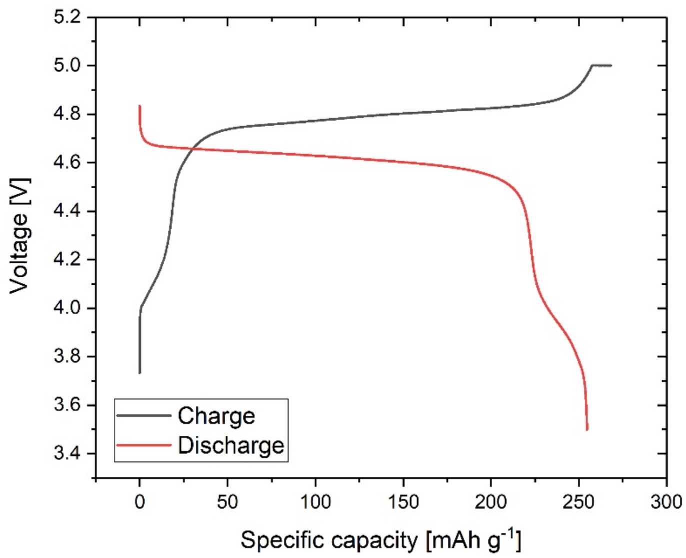

Figure 5: An example of the much-improved electrochemistry in the operando cell. Obtained in our laboratory after the beamtime.

Conclusion:

The diffraction capabilities of the operando cell were satisfactory. All Bragg peaks were visible in the assembled cell. Due to poor electrode wetting, the electrochemistry failed. The operando experiment was thus not possible. Improvements to the setup is expected to ensure a successful operando experiment for another beamtime at D20 in April 2020.