Experimental report

25/05/2022

Proposal: 5-23-740 **Council:** 10/2019

Title: Determination of Ni/Mn ordering inLiNi0.5Mn1.5O4 using operando neutron diffraction

Research area: Materials

This proposal is a new proposal

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Samples: LiNi0.5Mn1.5O4

Instrument	Requested days	Allocated days	From	To
D20	2	2	02/07/2021	05/07/2021

Abstract:

We propose to investigate the Ni/Mn ordering in LiNi0.5Mn1.5O4 cathodes as a function of the state of charge using operando neutron diffraction. Our previous work using X-ray diffraction suggests that the cation metal ordering appears in the discharged state, and disappears in the charged state for samples synthesized in the ordered form. We suspect that neutron diffraction will reveal the ordering much clearer than what X-rays are able to. The project is formed in collaboration with an industry partner who will supply the LNMO powder in an ordered and a disordered form, respectively. Pouch cells will then be made to resemble commercial cells as much as possible. Neutron diffraction will be performed directly on the cells during charging and discharging of the cells. We expect to be able to unveil the dependence of the cation metal ordering on the state of charge, as well as providing a more detailed picture of the electrode reactions.

Experimental report for 5-23-740

Objectives

We wanted to measure the structural evolution of the battery cathode material $Na_{0.7}Fe_{1/3}Mn_{2/3}O_2$ (NaFM, *P*6$_3$/*mmc*) versus Na metal using our own in operando electrochemical battery cell. The experiment originally focused on another material, $LiMn_{1.5}Ni_{0.5}O_4$, but due to the covid pandemic, this experiment was delayed and we eventually measured on $LiMn_{1.5}Ni_{0.5}O_4$ at Wombat, Opal. This experiment is part of an on-going effort to develop in operando neutron powder diffraction on novel battery materials.

Experimental

NaFM was prepared in our laboratory and mixed with conductive carbon and PVDF binder in a 80/10/10 ratio by weight. 60 mg of the composite powder was pressed into the cup of the operando cell. The cell is shown in Figure 1 along with the mounting of it at D20.

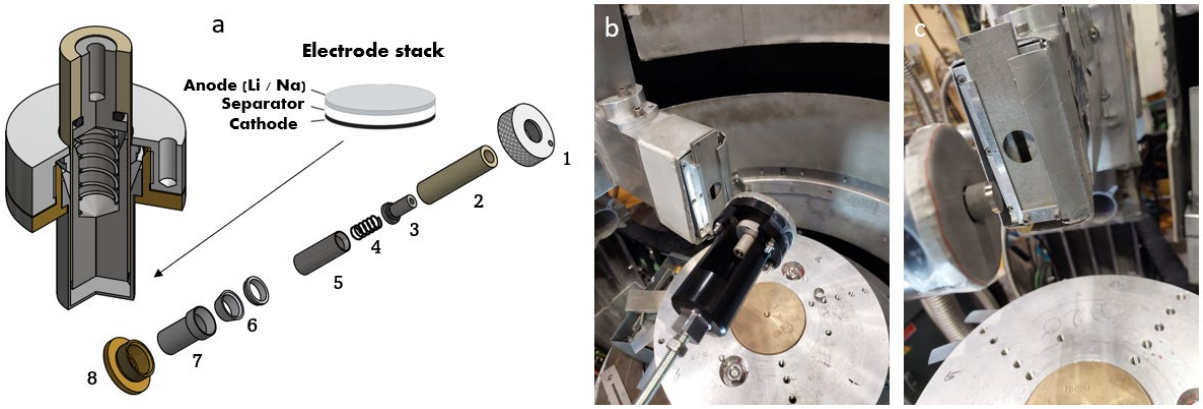

Figure 1: a) Sketch of the 12 mm in operando cell in assembled and exploded view. 1: Upper screw ring. 2: PEEK sleeve. 3: contact pin and O-ring. 4: spring. 5: TiZr anode rod. 6: Teflon gaskets. 7: TiZr cup. 8: Lower screw ring. b) Photograph of the 12 mm cell in the cell holder at D20, ILL, mounted in the horizontal position. The leads are not connected to the cell in the photograph. The beamtube is visible to the left and the curved detector array is in the background. c) Photograph of the same setup as in b) from another angle. Note that the bottom part of the cell and cell holder has been covered with cadmium foil as well as most of the cell cup. Only the part with the cathode pellet remains exposed to the neutron beam. In front of the beam tube, a 20 mm hole slit, and a 7 mm horizontal slit can be seen.

Glass fiber separator soaked in 1M $NaClO_4$ in deuterated propylene carbonate and rolled Na-metal was added in a glovebox and cell sealed. The cell was mounted at the instrument and connected to a potentiostat. Diffraction patterns were collected every 20 minutes during the charging and discharging, which was performed at a rate of C/20 charge and C/40 discharge.

Results and discussion

The obtained diffractograms are shown in Figure 2 as a function of time along with the potential curves.

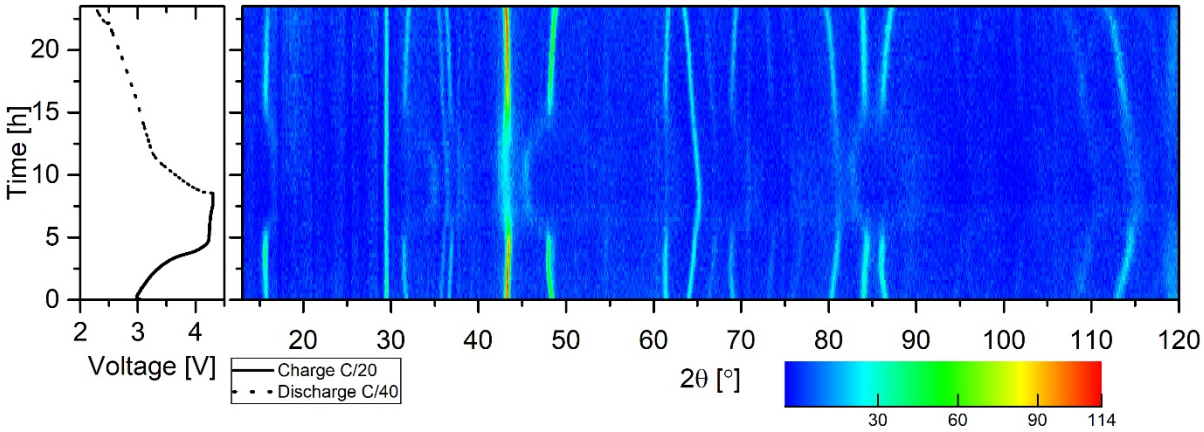

Figure 2: Stack of neutron powder diffraction patterns (intensities in arbitrary units) collected on $NaFe_{1/3}Mn_{2/3}O_2$ versus Na-metal during cell charge/discharge. The charge/discharge curves corresponding to the diffractograms are shown in the graph to the left. Measured at D20, ILL, λ = 1.54 Å.

Clear peak shifts are observed in what appears to be solid solution behavior. During the end of the charge, an amorphization occurs. This is apparently reversible on discharge. Using Topas, we managed to refine the patterns, except in the areas of very low crystallinity. The refinement results are shown in Figure 3.

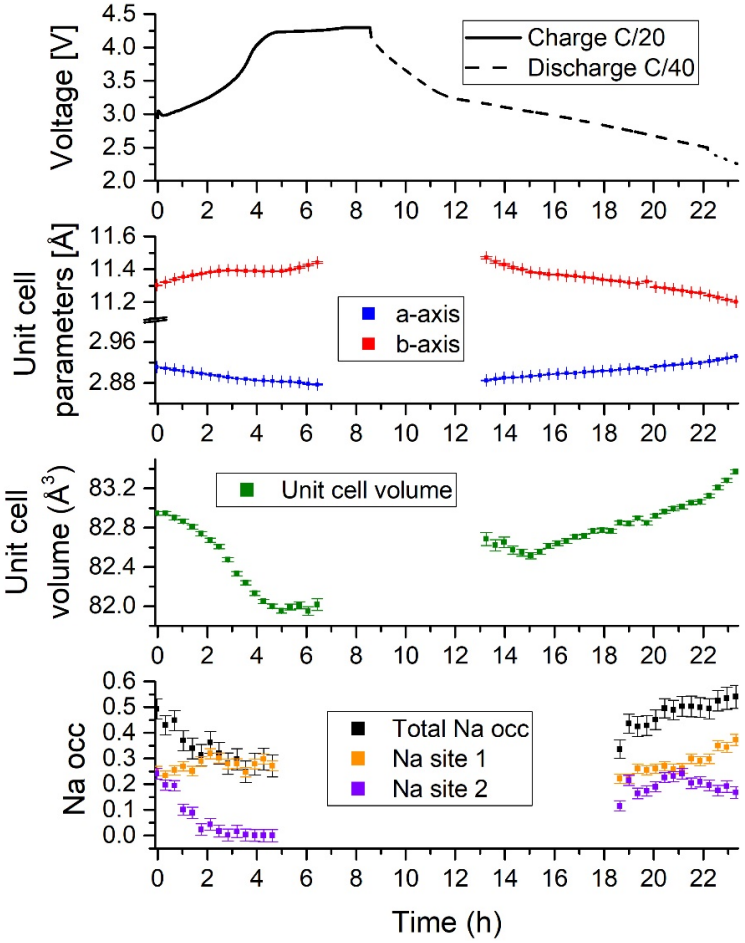

Figure 3: Results for the sequential Rietveld refinement on NaFM. a) Voltage curves for the in operando experiment. b) Unit cell parameters as a function of time. c) Unit cell volume as a function of time. d) Na-occupancies as a function of time. Occupancies for site 1, site 2 and the summed occupancy are shown. The occupancy could not be extracted very close to the disappearance of the Bragg peaks, and they were thus not refined for these diffractograms while the cell parameters were. Error bars represent one estimated standard deviation from individual refinements

From the refinement parameters, it is clear the cathode material exhibits solid solution behavior. It would appear that the unit cell recrystallizes in a volume that is significantly larger than the volume just before amorphization. From the refined Na-positions, it can be gleaned that Na is preferentially extracted from site 1 during charging. During discharge, Na is reinserted on site 1. Evidently, more than the 0.7 atoms per formula unit after synthesis can be inserted during the discharge.

Conclusion

Our experiment shows that quality diffraction patterns can be obtained for novel battery materials in operando for an active material mass as low as 48 mg. Besides cell parameters, Na-occupancies could be extracted. These results have been submitted for publication at Chemistry Methods.