



	Experiment title: In situ XRS study of operational Li ion battery chemistry	Experiment number: HC-732
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Report:

We performed an experiment to study the in-situ chemistry in an operational Li ion battery on ID20 using the imaging-capable x-ray Raman spectroscopy station. The sample was a large-angle scattering compatible developmental cell (Fig. 1). We used cathode electrodes that were cast with powders of two different compositions. First composition was $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ (by mass 80% active material, 10% PVDF binder, and 10% carbon black as a conductive additive). Second cathode was $\text{LiCr}_{0.02}\text{Zn}_{0.02}\text{Ni}_{0.48}\text{Mn}_{1.48}\text{O}_4$. The electrodes were circular disks with diameter 7 mm and active mass 0.85 mg. Capacities were estimated to be 120 mAh/g and the cell capacity thus 100 uAh. The anode was pure Li metal. The electrolyte solution was a mixture of EC:DMC with LiPF_6 . The electrolyte filled a 5 mm gap between the anode and the cathode, and the x-rays passed onto the cathode, scattered off by and the electrolyte, and exited the cell to the spectrometer through this gap.

Photon energies used in the experiment were 10 keV and 13 keV (utilising Si660 and Si880 analyzer crystal reflections, respectively). 13 keV was estimated to be more efficient energy for the experiment owing to a) higher penetration through the electrolyte solution, cell walls, and into the cathode; as well as owing to b) expected smaller amount of beam damage to the cell and the liquid electrolyte. However the energy resolution and flux at 13 keV are necessarily worse than at 10 keV; for which reason both options were attempted. We unfocused the beam to 600 μm (H) x 400 μm (V) in order to illuminate a macroscopic region of

the cell for XRS imaging purposes, as well as in order to reduce radiation damage. We used a Si(311) channel cut in order to reach energy resolutions below 1 eV.

Cells were charged with 50 uA constant current up to a desired voltage in the battery cycle and kept there until current dropped to 5% of the initial value (constant current/constant voltage). Starting with a 3.5V increasing the voltage to ~4.5V Mn^{3+} is expected to change to Mn^{4+} , after which at higher voltages Ni changes from $\text{Ni}^{2+} \gg \text{Ni}^{3+} \gg \text{Ni}^{4+}$. We measured Ni and Mn L edge XRS spectra as well as Li K edge spectra of the combined electrolyte+cathode ensemble. Thanks to the imaging capability we could record the spectra of both separately but simultaneously.

We performed preliminary tests of the electrolyte stability, using pure EC:DMC solution in the ID20 beam in a glass capillary, during an inhouse beamtime well prior to the experiment. However, a number of unforeseen challenges were found in the experiment. The liquid electrolyte was much less stable in the x-ray beam of ID20 than was expected by the results of the aforementioned tests. The reason could be that the heavily absorbing cathode emits photoelectrons that are detrimental to the solution's stability. In ~1h the electrolyte evaporated, causing problems to charge/discharge the cell in situ. It was discovered that Mn $K\beta$ fluorescence (energy 6.490 keV) was reflected directly by our Si(660)/Si(880) analyzers via their Si(440) harmonic (that spots the energy 6.457 keV) onto the detector. This background was discriminated as efficiently as possible using a Cr foil as a filter for the scattered radiation, and raising the Medipix detector low-energy threshold. Despite of these, the otherwise strong XRS spectra had a background/signal ratio of the order of 10, reducing the data quality. Recorded spectra of Ni and Mn in cell voltage of 4.74 are shown in Fig. 2. More detailed data analysis is in progress but the project would benefit greatly of an improved setup that has modifications to address the above issues.

Below: Figure 1. Cell principle and a direct tomography image from the cell.

Right: Figure 2. Example of spectra of Mn L and Ni L edges obtained from the cathode in this cell.

