ESRF

Experiment title:

In situ high energy synchrotron X-ray diffraction: Electrochemical reactions and state-of-charge mapping of lithium batteries during charge/discharge.

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Report:

Lithium batteries have a large potential for use in electrical vehicles, but several challenges must be tackled before large scale introduction of electrical vehicles is possible including increasing the energy and power densities, improving safety and reducing the price. Improved materials and an increased fundamental understanding of the electrochemical reactions and microstructural changes taking place during operation are needed. The aim of the present study was to use high energy diffraction to obtain time resolved information about the chemical and structural changes taking place in commercial lithium batteries during charge/discharge at operating conditions.

Experimental details

The commercial batteries (From Amita Technologies) were mounted on a rotatable *xyz* translation stage. The batteries are approximately 130x98x7.5 mm in size and are built up as stack of parallel connected battery cells. The batteries were connected to a charging/discharging device, ALC 8000-Plus, and aligned with the stacking direction parallel to the X-ray beam. A Frelon2K detector with a pixel size of ~47x48 µm was placed ~633 mm from the battery. Powder diffraction data were collected during charging/discharging of the batteries using a wavelength of 0.12492 Å and exposure times of 1-5 s. Two types of experiments were performed. A mapping experiment where an area of the battery across the two current collectors was monitored by moving the battery during charging/discharging and a single point experiment where the battery was kept at a certain position during charging/discharging. The batteries were oscillated ±2° during the exposure in the single point experiments to increase the number of grains in diffraction conditions. This resulted in a time-resolution of 8.4 s per scan (exposure time + data readout time) for the single point experiments and 8.5 s per scan for the mapping experiments. The data were converted to one-dimensional powder pattern using the program FIT2D.

Results

Figure 1 shows *in situ* XRPD patterns collected in a single point of a $LiCo_xNi_yMn_zO$-based battery during a charge-discharge-charge cycle. The powder diffraction patterns reveal the transformations in the cathode and anode materials during charging and discharging. Lithium ions migrate from the cathode material into the graphitic anode material during charging of the battery. The lithium ions intercalate the layered graphite structure and form lithiated graphite phases. Figure 1b shows that the intercalation process proceeds via a non-stoichiometric Li_xC phase to stoichiometric LiC_{12} and LiC_6 phases. Figure 2a shows integrated peak intensities of the 00*1* reflections of LiC_6, LiC_{12} and Li_xC phases demonstrating that the LiC_6 and LiC_{12} coexist in the charged battery and that the Li_xC is the only graphitic phase present in the discharged battery. Figure 2b shows the *d*-spacing of the 002 reflection of the Li_xC phase. The discharged battery has a *d*-spacing of ~3.37 Å which is comparable to that of pure graphite (~3.35 Å).

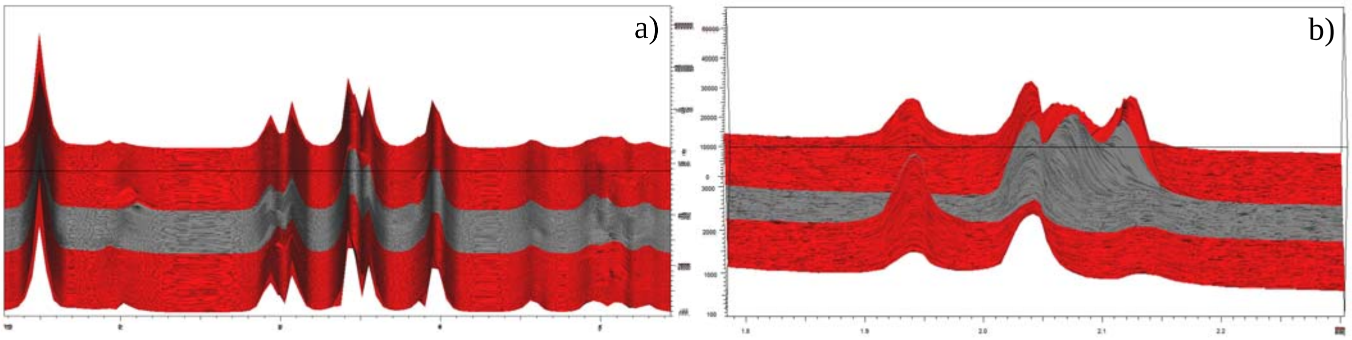

Figure 1. a) *In situ* XRPD patterns of a commercial $LiCo_xNi_yMn_zO$ battery collected during a charge (red)-discharge (grey)-charge (red) cycle. b) A magnified section of the region around the 00*1* reflections of LiC_6, LiC_{12} and Li_xC phases.

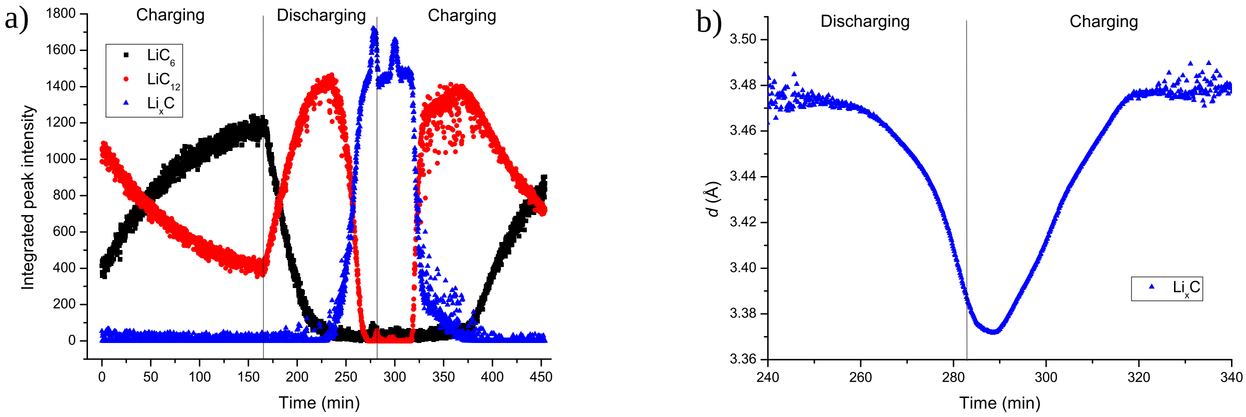

Figure 2. a) Integrated peak intensity of 00*1* reflections of LiC_6, LiC_{12} and Li_xC. b) *d*-spacing of the 002 reflection of the Li_xC phase during discharging and charging.

Figure 3a shows *in situ* XRPD patterns of a mapping experiment of a commercial $LiFePO_4$ battery where the battery was translated laterally in 51 steps of 1 mm across the two current collectors during charging and discharging. The figure reveals the phase transformations caused by the migration of the lithium ions. Figure 3b shows the normalized integrated intensities of the 002 diffraction peaks of the $FePO_4$ and $LiFePO_4$ phases demonstrating that a two-phase transformation is occurring in the cathode material where $LiFePO_4$ is formed by intercalation of lithium into the $FePO_4$ structure during the discharging of the battery and *vice versa* during charging.

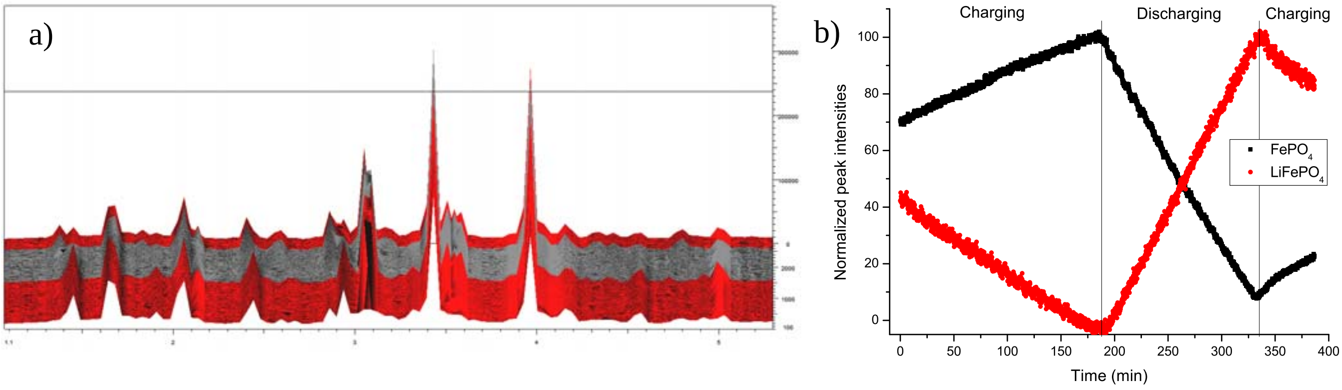

Figure 3. a) *In situ* XRPD patterns of a commercial $LiFePO_4$ battery collected during charge (red) and discharge (grey). b) Normalized integrated peak intensities of the 200 reflections of the $FePO_4$ and $LiFePO_4$ phases.