

Towards in situ X-ray diffraction on degraded lithium batteries

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Lithium-ion batteries suffer under a loss of capacity when charged and discharged hundreds of times. Due to this, the working time until a battery has to be recharged again gets shorter and shorter until it finally has to be replaced. On the cathode side of the battery, for example, structural disordering, phase transitions, metal dissolution, contact loss between particles, oxygen release, electrolyte decomposition etc. contribute to this capacity loss [1]. The aim of this study is to investigate the behaviour of the commonly used cathode material $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ at high cycle numbers by means of in situ X-ray diffraction.

For the realisation of this experiment, the cell which was developed by our group [2] had to be improved with respect to sealing. Since the electrolyte used for lithium batteries (usually a 1 M solution of LiPF_6 in EC:DMC=2:1) is very sensitive to air moisture and oxygen, the tightness of the electrochemical in situ-cell is a key point to reach high cycle numbers. This is achieved by using a Swagelok connection as cell body in which the whole battery is situated [3]. Teflon sealings also provided by the Swagelok company are used to provide satisfactory firmness of the cell. A schematic drawing of the new in situ-cell is shown in figure 1.

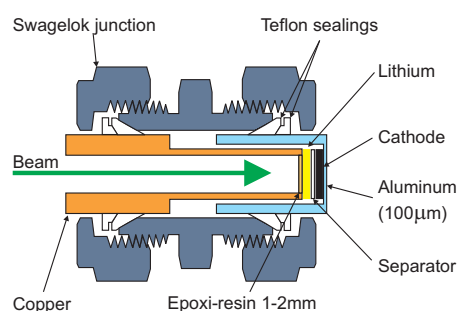


Figure 1: Schematic drawing of the in situ-cell.

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was prepared by the Pechini-method and verified to be single phase material (Spacegroup $R\bar{3}m$) with a cation disorder¹ of about 2-3%. The cathode for the in situ-diffraction experiment was prepared by mixing a certain amount of the active material (e.g. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) with carbon as conducting agent and PVDF as polymeric binder and pressing it to a pellet. The above mentioned solution of LiPF_6 and metallic lithium are used as electrolyte and anode, respectively.

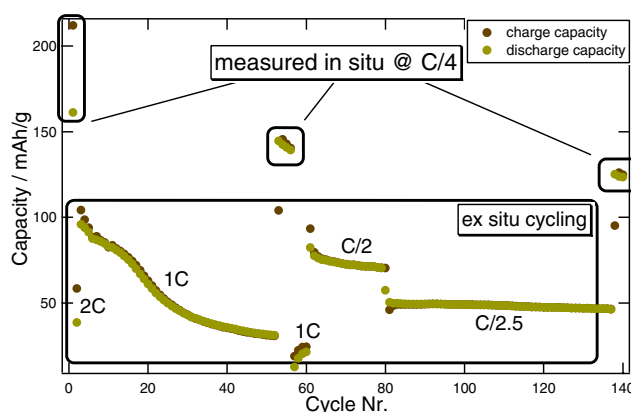


Figure 2: Cycling of the in situ-cell. The cycles during which in situ X-ray diffraction was performed (C/4) are indicated, as well as the cycles between these experiments (2C–C/2.5). The C-rates refer to the current applied to the cell for charge. 1C means that the current is chosen to charge the cell in one hour.

¹ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is a layered structure with a lithium - oxygen - 3d-cation - oxygen stacking. The migration of a 3d-cation onto a lithium layer is denoted as cation disorder.

The electrochemical cycling of the cell is shown in figure 2. During three periods in situ-diffraction was performed: During the first cycle, cycles 53-56 and cycles 138-140. Between these cycles the cell was charged and discharged in order to fatigue the cathode material. While the current rate applied for the cycles measured in situ was $C/4$ (one cycle in four hours), the current rate for the ex situ-cycling was between $2C$ and $C/2.5$. The latter was chosen to be higher in order to reach a reasonable cycle number. After 140 cycles the capacity of the cell is $\approx 90\%$ of the discharge capacity delivered by the cell during the first cycle. The diffraction experiments were carried out at beamline B2/HASYLAB[4].

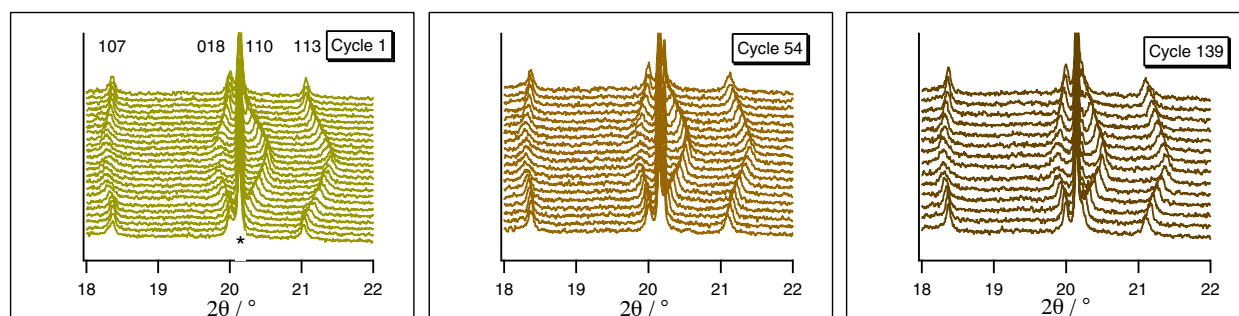


Figure 3: 2θ -sections of the X-Ray diffraction patterns recorded during cycles 1, 54 and 139. The reflection marked with * belong to the setup.

In figure 3 the diffraction patterns collected during cycling of the fresh and the fatigued cell are shown. From bottom to top the cell is first charged and afterwards discharged. During charging the (107) and (108) reflections move to lower and the (110) and (113) to higher scattering angles, respectively. This means, that during charging the lattice parameter c expands while a and b shrink. During discharge this process is reversed (more details on this point are given in[5]). This behavior of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is preserved in the cycles 54 and 139, reflecting the good reversible intercalation of lithium into the host structure. The bulk material does not show any phase transitions since no new reflections which could be attributed to a new phase can be observed. Furthermore it seems, that there are no inactive regions in the sample and though the capacity loss is not due to contact loss between particles. If after cycling the battery for a certain time some particles of the former active material (eg. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) loses contact and does not take part in the intercalation process any more, this phase would be visible as non moving reflections belonging to $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in the diffraction patterns.

Since the degradation of the battery is only slightly advanced up to ≈ 140 cycles, the next task is to get in situ-data at higher cycle numbers.

References

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