# Reversible and irreversible phase transformations in $Li_xCoO_2$

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Current lithium-ion battery technology uses $LiCoO_2$ as intercalation compound for the positive electrode (cathode). $LiCoO_2$ has a trigonal structure consisting of oxygen planes in ABC stacking separated by alternating layers of Li and Co in the interstial sites between them (O3 phase). Upon charge/discharge cycling, the Li content 'x' in $Li_xCoO_2$ is varied between x=1 (discharged form) and x=0.5 (charged form). In this non-stoicheometric range the lattice undergoes a series of transformations that can be described as shifts in the stacking sequence of $CoO_2$ sheets [1, 2]. The hexagonal symmetry is preserved in the newly formed phases (H1-3 and O1) and with re-intercalation of Li into the lattice the original stacking order will be taken on again. Such reversibility of slab gliding is a prerequisite for high cycle-life of the battery. O3 and H1-3 hexagonal phases were found for x=1 and x=0.72 respectively.

Among the different routes for the $LiCoO_2$ synthesis, the one involving wet chemistry such as co-precipitation of Li and Co precursors is very common. The filtered precipitates may then be dried and fired in air or in an oxygen-rich atmosphere, a process during which the low temperature (LT) (<500°C) and the high temperature (HT) (>700°C) phases are formed [3, 4]. The LT phase consists mainly of the cubic spinel $Li_2Co_2O_4$ whereas the HT phase is the hexagonal O3 phase $LiCoO_2$. The latter is preferred in practical batteries because it yields higher capacity and discharge voltage than the former one. We have followed the LT → HT transformation using a hot-stage in a TEM operated between room temperature and 770°C. Figure-1 shows the SAD evolution from the starting LT to the final HT material. While the LT phase contains diffraction spots belonging to both the spinel and hexagonal phases (Fig 1a, T=443°C, (440) parallel to $(11\bar{2}0)$) , upon heating the {440} spots became weaker and eventually dissappared at 770°C where only the O3 phase was present (Fig 1b). Upon cooling the reverse transformation didn't take place.

On the other hand, when an electrochemically delithiated sample at 4.2 V vs. Li was maintained at 75°C for 4 weeks, the original H1-3 hexagonal phase transformed to a mix of the spinel and H1-3 phase as shown in Figure-2. Similar results were observed with a heavily cycled sample at the ambient temperature where the spinel and the hexagonal phases were found to coexist. Therefore, we argue that the transformation from the hexagonal to the spinel phase is behind the capacity loss during either high temperature aging at charged state of the cathode or during extended cycling. We are currently investigating on possible transformation of the relithiated spinel phase described above to the hexagonal H1-3 or O3 phases upon thermal treatment.

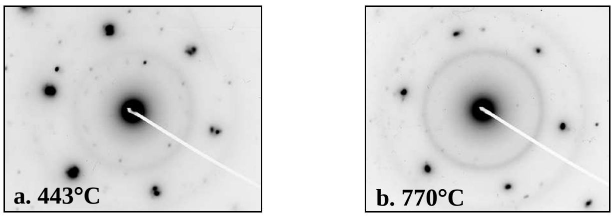

Figure 1:
Heating of LT-$LiCoO_2$. The neighbouring {440} and $\{11\bar{2}0\}$ reflexions of spinel and O3 phase in LT-$LiCoO_2$ are clearly resolved at 443°C. At 770°C only the $\{11\bar{2}0\}$ reflexions of the O3 phase are observed.

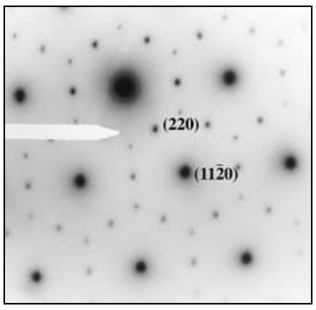

Figure 2:
Electron diffraction pattern obtained from specimen after aging at 75°C for 28 days in the charged state. Besides diffractions from the H1-3 phase contribution from the spinel phase are present.

References :

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