

Phase Transformations during High-Voltage Charging of LiCoO₂ Cathodes

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The most commonly used cathode material in Li-ion batteries is LiCoO₂¹. Typically such batteries are operated at voltages up to 4.2 V, which corresponds to the removal of about 50% of the Li ions². The rhombohedral O3 structure of LiCoO₂ is maintained in this concentration range. Higher voltages would yield higher specific capacity of the battery, but lead to fast capacity fade³. The mechanism of this capacity fade is not well understood. In this study, electron diffraction techniques (selected area diffraction, SAD, and convergent-beam electron diffraction, CBED) were used to study the structural changes accompanying high-voltage charging and elucidate mechanisms of capacity fade.

Rhombohedral LiCoO₂ from Enax Co. (Tokyo, Japan) was charged to 4.7 V in an experimental battery cell. The exact experimental procedure is described elsewhere⁴. The cathode material was recovered from the electrode, washed in NMP and then in ethanol and dispersed on a lacey carbon film on a Cu TEM grid.

The SAD pattern of virgin (uncharged) LiCoO₂ in [0001] direction shows only the {11 $\bar{2}$ 0} type reflections (Fig. 1a). After charging to 4.7 V for 10 h, extra reflections halfway between the fundamental reflections of LiCoO₂ are observed for most grains (Fig. 1b). This is consistent with a phase transformation from O3 phase to the cubic spinel phase LiCo₂O₄. The reflections can be indexed as {440} and {220} of the spinel structure. For some spinel grains, an additional surface layer was observed. The SAD pattern shown in Fig. 2a, which was taken with the SAD aperture on the interface, shows the diffraction pattern typical of the spinel phase plus spot splitting in the outer area of the pattern (see arrow), indicating two different structures with slightly different lattice parameters. This could be due to coexisting spinels LiCo₂O₄ and Co₃O₄. The SAD pattern in Fig. 2b was taken with the SAD aperture mostly on the surface layer. The {440} and {220} reflections of the spinel grain are still visible. The {440} reflections are split into several spots. Additional reflections in the center of the triangles formed by the fundamental reflections are also visible. These extra spots could be due to cation order/disorder⁵. A darkfield image (Fig. 3a) taken with the inner portion of spot 1 indicated in Fig. 2b shows that this reflection originates from a surface layer on the spinel grain. Imaging with one of the central spots (Fig. 3b) of the pattern also illuminates the surface layer. It was also found that while the grain, originally LiCoO₂ and now transformed to spinel, is essentially single crystalline, the surface layer of the grain is polycrystalline and porous. This could point to a reaction of the cathode material with the electrolyte following the phase transformation, which could both contribute to the observed capacity fade.

Acknowledgements:

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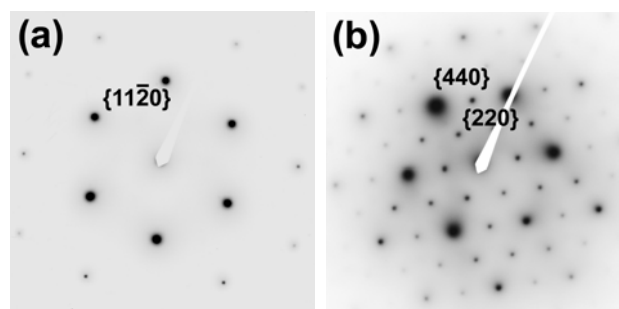


Fig. 1: SAD pattern of (a) virgin LiCoO₂ [0001] and (b) spinel Li_xCo₂O₄ [111] after 10 hours at 4.7 V

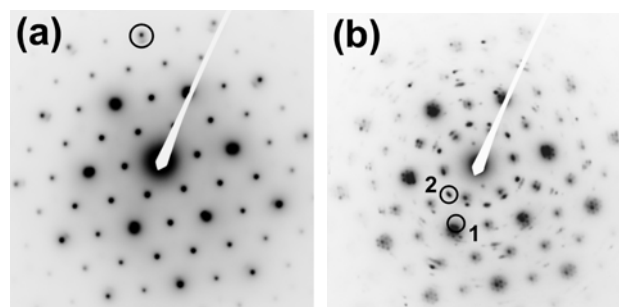


Fig. 2: SAD pattern of cathode material after 10 hours at 4.7 V showing new phases formed in a surface layer on spinel.

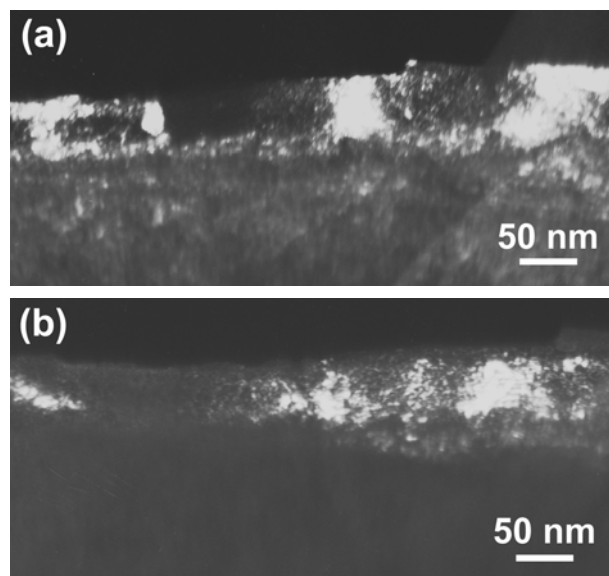


Fig. 3: TEM darkfield images of the surface layer (a) taken with spot 1 and (b) taken with spot 2 marked in Fig. 2 (b).

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