

Chemical and Structural Instabilities of LiCoO₂ Cathodes at Deep Lithium Extraction

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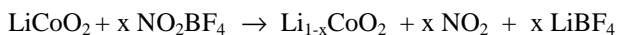
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Introduction

Presently, lithium-ion cells use the layered LiCoO₂ cathodes, but only 50% of the theoretical capacity of LiCoO₂ could be practically utilized (140 mAh/g). The reason for the limited capacity of LiCoO₂ cathodes is not fully established in the literature. We showed recently by characterizing the Li_{1-x}CoO₂ samples obtained by chemically extracting lithium from LiCoO₂ that the limited capacity could be due to the chemical instability occurring at deep charge.^{1,2} We present here a systematic investigation of the structural and chemical stabilities of Li_{1-x}CoO₂ by monitoring both the oxygen content and the crystal chemistry as a function of lithium content and the reaction time of chemical lithium extraction.

Experimental

Chemical extraction of lithium was accomplished by stirring the LiCoO₂ powder with an acetonitrile solution consisting of required amounts of the oxidizer, NO₂BF₄, for 30 minutes to 7 days under argon atmosphere:



The Li_{1-x}CoO₂ products formed were filtered, washed with acetonitrile, and characterized by X-ray diffraction using Rietveld analysis. Oxygen contents and lithium contents were determined by iodometric titration and atomic absorption spectroscopy respectively.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the Li_{1-x}CoO₂ samples obtained after a reaction time of 2 days. The initial O3 layer structure is maintained for (1-x) > 0.5 and a second phase begins to appear for (1-x) < 0.4. The amount of the second phase increases with decreasing lithium content and the end member CoO₂ consists of reflections corresponding to only the second phase. The X-ray pattern of the end member CoO₂ could be indexed on the basis of a single P3 phase. The observation of the P3 phase for the end member CoO₂ is in contrast to the O1 phase reported in the literature for the CoO₂ sample obtained by electrochemical delithiation. However, a longer reaction time of > 2 days was found to give a mixture of P3 and O1 phases as we had reported earlier.^{1,2} The formation of P3 and O1 phases from the initial O3 structure is due to a sliding of the oxide ion layers. It appears that while a faster extraction of lithium by the chemical delithiation leads to the stabilization of a metastable P3 phase, a slower extraction of lithium by the electrochemical delithiation leads to the formation of O1 phase. Nevertheless, the metastable P3 intermediate phase formed during the chemical lithium extraction transforms slowly to the O1 phase on prolonged stirring.

Figure 2 shows the variation of the oxygen content with lithium content for the samples obtained with a reaction time of 1 h. While the oxygen content remains around 2 for lithium contents (1-x) > 0.5, it decreases for (1-x) < 0.5 due to the introduction of significant amount of holes into the O:2p band. Figure 3 shows the variation of the oxygen content of the end member CoO_{2,δ} with

reaction time. The oxygen content decreases rapidly with time during the initial stages indicating chemical instability of the system. We believe the structural instability leading to the transformation of the initial O3 structure to the P3 and O1 structures is due to the loss of oxygen from the lattice caused by chemical instability and the tendency to form O-O bonds caused by the presence of large amount of holes in the O:2p band.

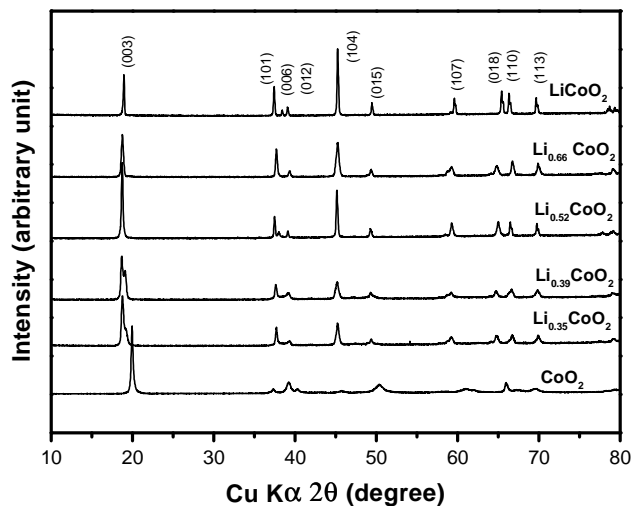


Fig.1. X-ray diffraction patterns of the Li_{1-x}CoO₂ samples obtained with a reaction time of 2 days.

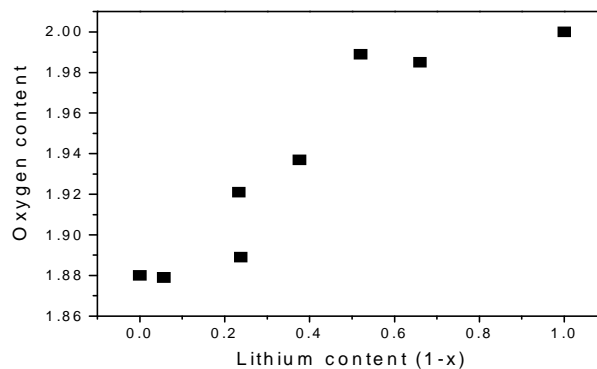


Fig. 2. Variation of oxygen content with lithium content in Li_{1-x}CoO₂ that was obtained with a reaction time of 1 h.

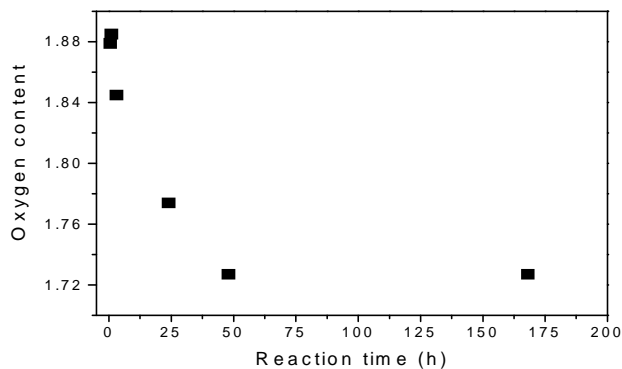


Fig. 3. Variation of oxygen content in CoO_{2,δ} with reaction time.

References

1. R. V. Ramanan, F. Prado, and A. Manthiram, *Chem. Mater.*, **13**, 2951 (2001).
2. R. V. Chebiam, A. M. Kannan, F. Prado, and A. Manthiram, *Electrochem. Commun.*, **3**, 624 (2001).