

Comparison of the Chemical and Structural Stabilities of Layered Cobalt Oxide and Nickel Oxide Cathodes

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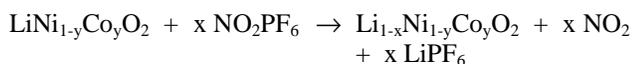
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Introduction

The exponential growth in portable electronic devices has created enormous interest in lithium-ion batteries as they offer higher energy density compared to other rechargeable systems. Currently, the commercial lithium-ion cells are made mostly with the layered LiCoO₂ cathode. However, only 50% of the theoretical capacity of LiCoO₂ could be practically utilized, which corresponds to a reversible extraction/insertion of 0.5 lithium per cobalt. With respect to increasing the energy density, the layered lithium nickel oxides with a small amount (15 %) of cobalt have become appealing as they offer a higher practical capacity of 180 mAh/g, which corresponds to a reversible extraction/insertion of 0.65 lithium per transition metal. It is not, however, clear in the literature why the LiNi_{0.85}Co_{0.15}O₂ cathodes exhibit much higher capacity compared to the analogous LiCoO₂ cathodes. Additionally, the structural stability, particularly at elevated temperatures, of LiNi_{0.85}Co_{0.15}O₂ cathodes that experience a deeper lithium extraction during the charge/discharge cycles than the analogous LiCoO₂ needs to be fully assessed. To address these issues, we have focused on a comparison of the chemical and structural stabilities of Li_{1-x}Ni_{1-y}Co_yO₂ (0 ≤ x ≤ 1 and 0 ≤ y ≤ 1) samples that were obtained by chemically extracting lithium from the parent LiNi_{1-y}Co_yO₂ samples. The chemical stability is assessed by following the variation of the oxidation state of the transition metal ions and the oxygen content with lithium content 1-x. The structural stability is assessed by examining the Li_{1-x}Ni_{1-y}Co_yO₂ samples by X-ray diffraction before and after subjecting them to mild heat.

Experimental

LiNi_{1-y}Co_yO₂ (0 ≤ y ≤ 1) samples were prepared by a sol-gel procedure for nickel-rich compositions and by solid-state reactions for cobalt-rich compositions. Chemical extraction of lithium was carried out by stirring the LiNi_{1-y}Co_yO₂ powders with an acetonitrile solution of the oxidizer NO₂PF₆ under argon atmosphere.



The Li_{1-x}Ni_{1-y}Co_yO₂ products formed were filtered and washed with acetonitrile under argon atmosphere using a Schlenk line. Structural characterizations were carried out with X-ray diffraction using Rietveld analysis. Oxidation state and oxygen contents were determined by a redox iodometric titration.¹

Results and Discussion

Figure 1 shows the variations of the average oxidation state of the transition metal ions and the oxygen content with lithium content (1-x) for the two end member systems Li_{1-x}NiO_{2-δ} (y = 0 sample) and Li_{1-x}CoO_{2-δ} (y = 1 sample). In the case of Li_{1-x}NiO_{2-δ}, the oxidation state of nickel increases proportionately with decreasing lithium content (1-x) as one would anticipate and the oxygen content remains close to 2 for the entire

value of 0 ≤ (1-x) ≤ 1. In contrast, in the case of Li_{1-x}CoO_{2-δ}, the oxidation state of cobalt increases initially to about 3.35+ at around (1-x) = 0.65 and remains constant thereafter. This results in a significant loss of oxygen at low lithium contents and the end member CoO_{2-δ} has an oxidation state of 3.34+ with δ = 0.33. The other compositions with 0 < y < 1 show behaviors intermediate between those of Li_{1-x}NiO_{2-δ} and Li_{1-x}CoO_{2-δ} and the tendency to lose oxygen increases with increasing cobalt content. The difference in the oxygen loss behavior between the Li_{1-x}NiO_{2-δ} and Li_{1-x}CoO_{2-δ} systems could be explained on the basis of the relative positions of the Co^{3+/4+}:t_{2g} and Ni^{3+/4+}:e_g bands with respect to the O²⁻:2p band. The tendency to lose oxygen limits the practical capacity of LiCoO₂ to 140 mAh/g. On the other hand, the resistance to lose oxygen allows the realization of a higher practical capacity (180 mAh/g) in LiNi_{0.85}Co_{0.15}O₂.

X-ray diffraction data show that while the nickel-rich end members Ni_{1-y}Co_yO_{2-δ} maintain the initial O3 layer structure of LiNiO₂, the cobalt-rich end members transform to a mixture of P3 and O1 structures. The transformation of the initial O3 structure to P3 and O1 structures is due to a sliding of the oxide-ion layers facilitated by the presence of significant amount of oxygen vacancies in the cobalt-rich phases. However, the nickel-rich Li_{1-x}Ni_{1-y}Co_yO_{2-δ} phases experience a decrease in c/a ratio under mild heat (T > 50 °C) due to a migration of the Ni³⁺ ions from the transition metal plane to the lithium plane as revealed by Rietveld analysis.² Interestingly, the cobalt-rich phases do not experience such a cation migration under identical conditions due to a strong octahedral site stabilization energy for Co³⁺ ions.

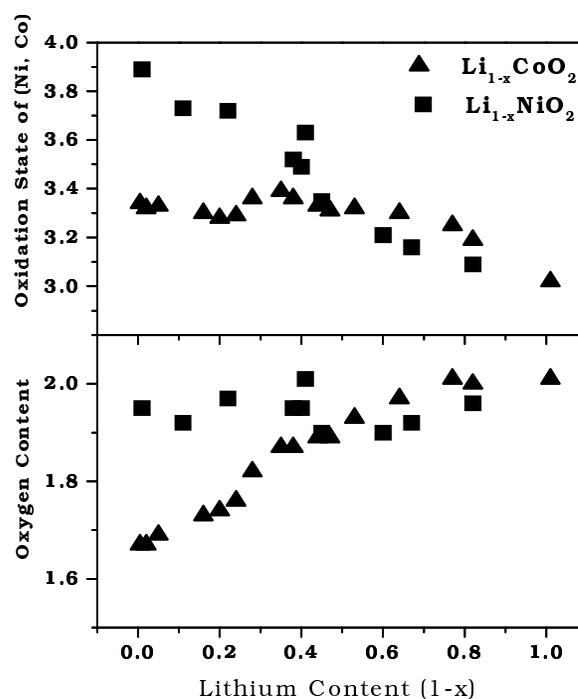


Fig. 1. Variations of the oxidation state of the transition metal ions and the oxygen content with lithium content (1-x) in Li_{1-x}NiO_{2-δ} and Li_{1-x}CoO_{2-δ}.

References

1. A. Manthiram, J. S. Swinnea, Z. T. Sui, H. Steinfink and J. B. Goodenough, *J. Amer. Chem. Soc.* **109**, 6667 (1987).
2. R. V. Chebiam, F. Prado, and A. Manthiram, *J. Electrochem. Soc.* **148**, A49-53 (2001).