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RAPID COMMUNICATION

Comparison of the Chemical Stability of $Li_{1-x}CoO_2$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ Cathodes

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The chemical stability of the layered $Li_{1-x}CoO_2$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ cathodes is compared by monitoring the oxygen content with lithium content $(1-x)$ in chemically delithiated samples. The $Li_{1-x}CoO_2$ system tends to lose oxygen from the lattice at deep lithium extraction while the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system does not lose oxygen at least for $(1-x) > 0.3$. This difference seems to result in a lower reversible (practical) capacity (140 mA h/g) for $LiCoO_2$ compared to that for $LiNi_{0.85}Co_{0.15}O_2$ (180 mA h/g). The loss of significant amount of oxygen leads to a sliding of oxide layers and the formation of a major P3 and a minor O1 phase for the end member $CoO_{2-\delta}$ with $\delta = 0.33$. In contrast, $Ni_{0.85}Co_{0.15}O_{2-\delta}$ with a small amount of $\delta = 0.1$ maintains the initial O3 layer structure. © 2002 Elsevier Science

1. INTRODUCTION

Lithium-ion batteries have become attractive for portable electronic devices as they offer higher energy density than other rechargeable systems (1). Most of the commercial lithium-ion cells currently use the layered $LiCoO_2$ as the cathode material. However, only 50% of the theoretical capacity of $LiCoO_2$ could be practically utilized (140 mA h/g), which limits its energy density. Additionally, cobalt is expensive and toxic. These drawbacks of $LiCoO_2$, despite its excellent performance, have prompted the development of alternate cathode hosts. In the search for alternate materials, spinel $LiMn_2O_4$ (2) and layered $LiMnO_2$ (3) have become appealing, as manganese is inexpensive and environmentally benign. Unfortunately, the manganese oxides are confronted with manganese dissolution (4) into the electrolyte and lattice distortions arising from Jahn–Teller distortion (5), which lead to capacity fade, particularly at elevated temperatures. Additionally, the layered $LiMnO_2$ suffers from structural instability and tends to transform to spinel-like phases during electrochemical cycling (6).

More recently, the layered nickel oxide with a small amount of cobalt ($LiNi_{0.85}Co_{0.15}O_2$) has drawn much attention, as it exhibits much higher capacity (180 mA h/g) (7) than the currently used $LiCoO_2$ cathode. This practical capacity corresponds to 65% of the theoretical capacity of $LiNi_{0.85}Co_{0.15}O_2$ and a reversible extraction of 0.65 lithium per transition metal ion. Additionally, nickel is slightly less expensive and less toxic than cobalt. However, it is not clear in the literature why the nickel-based $LiNi_{0.85}Co_{0.15}O_2$ exhibits much higher capacity than the analogous $LiCoO_2$ cathode. Also, the nickel oxide cathode seems to have more safety problems compared to the cobalt oxide cathode and the reason for the difference is not well established in the literature.

Recently, we investigated systematically the structural stability of $LiNi_{0.85}Co_{0.15}O_2$ cathode and compared it with that of $LiCoO_2$ cathode (8). We found that the charged $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ cathodes exhibit structural instability under mild heat ($T > 50°C$) while the charged $Li_{1-x}CoO_2$ cathodes are quite stable under similar conditions. The charged $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ cathodes show a decrease in the c/a ratio on heating above 50°C due to a migration of the nickel ions from the octahedral sites (3b sites) of the nickel plane to the octahedral sites (3a sites) of the lithium plane via the available empty tetrahedral sites. While the Ni^{3+} ions are able to undergo such a migration under mild heat, the Co^{3+} ions do not due to a strong octahedral site stabilization energy, which leads to good structural stability for the $LiCoO_2$ cathodes during the cycling process.

We present in this paper a comparison of the chemical stability of the charged $Li_{1-x}CoO_2$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ cathodes by monitoring the variations of the oxidation state of the transition metal ions and the oxygen

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content with lithium content in chemically delithiated samples. Based on the results, we also explain the differences between the two systems in practically utilizable capacity.

2. EXPERIMENTAL

$LiCoO_2$ was prepared by solid-state reaction between Li_2CO_3 and Co_3O_4 at 900°C for 24 h. $LiNi_{0.85}Co_{0.15}O_2$ was prepared by an acetic acid based sol–gel route described elsewhere (8, 9). A final firing temperature of 750°C in flowing oxygen atmosphere was used in this case. Chemical extraction of lithium from both $LiCoO_2$ and $LiNi_{0.85}Co_{0.15}O_2$ was accomplished by stirring the respective powders with various quantities of the oxidizer NO_2PF_6 (Alfa Aesar, > 99.6% purity) in acetonitrile medium (10) for two days under argon atmosphere using a Schlenk line. Typically, reactions were carried out with about 250 mg of the oxide sample and about 25 mL of acetonitrile containing NO_2PF_6. A maximum molar ratio of $LiCoO_2 : NO_2PF_6 = 1:1.5$ and $LiNi_{0.85}Co_{0.15}O_2 : NO_2PF_6 = 1:2$ was used to extract all the lithium completely. The chemical reaction occurring during this process can be given as

$$LiNi_{1-y}Co_yO_2 + x\ NO_2PF_6 \rightarrow Li_{1-x}Ni_{1-y}Co_yO_2 + x\ NO_2 + x\ LiPF_6. \quad (1)$$

The nonaqueous acetonitrile medium was employed to avoid possible incorporation of H^+ ions or H_2O molecules into the layered oxides. After the extraction reaction, the products formed were washed with acetonitrile to remove $LiPF_6$, dried under vacuum, and stored in a vacuum desiccator. In view of a literature report that the electrochemically prepared CoO_2 reacts with ambient air to give CoOOH (11), care was taken in storing the samples under vacuum and analyzing them immediately after removing them from the vacuum desiccator.

The lithium contents were determined by atomic absorption spectroscopy. The oxidation state of the transition metal ion was determined by the iodometric redox titration (12). Knowing the lithium content and the oxidation state of the transition metal ions, the oxygen content was calculated by charge neutrality principle. Structural characterization of the samples was carried by X-ray powder diffraction using Cu*K*α radiation. Rietveld refinements were carried out with the DBWS-9411 PC program (13).

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patters of the chemically delithiated $Li_{1-x}CoO_2$ samples. The samples maintain the initial O3 layer structure ($CdCl_2$ structure) for $0.35 \leq (1-x) \leq 1$. For lithium content $(1-x) < 0.35$, a second phase begins to form as indicated by the appearance of a shoulder on the right hand side of the (003) reflection centered around $2\theta = 20°$. The intensity of the new reflection increases with a further decrease in the lithium content and the end member CoO_2 consists of reflections corresponding to only the new phase. The X-ray diffraction pattern of the new phase was analyzed using the Rietveld method on the basis of several models. Models based on (i) a single O1 phase, (ii) a mixture of two O1 phases, and (iii) a mixture of an O3 and an O1 phase could not account for the X-ray data satisfactorily. On the other hand, refinement of the X-ray data on the basis of a major P3 phase with $a = 2.827(4)$ and $c = 13.445(4)$ Å and a minor O1 (CdI_2 structure) phase with $a = 2.772(2)$ and $c = 4.263(3)$ Å provided the lowest R_{wp} value of 12.62% and accounted for all the reflections. For example, the weak reflections at around $2\theta = 40°$ and 50° could be accounted only by the incorporation of a P3 phase in the refinement. The P3 structure was based on the $R3m$ space group (S.G. 160) with the cobalt ions at the 3a (0, 0, 0) site and oxide ions also at the 3a sites ($(0, 0, z)$ and $(0, 0, z')$ where z, z' are 0.5905 and 0.3764 respectively). The O1 structure was based on the $P\bar{3}m1$ space group (S.G. 164) with the cobalt ions at the 1a (0, 0, 0) site and oxide ions at the 2d sites ($(\frac{1}{3}, \frac{2}{3}, z)$, where $z = 0.248$). The formation of the P3 and O1 phases with

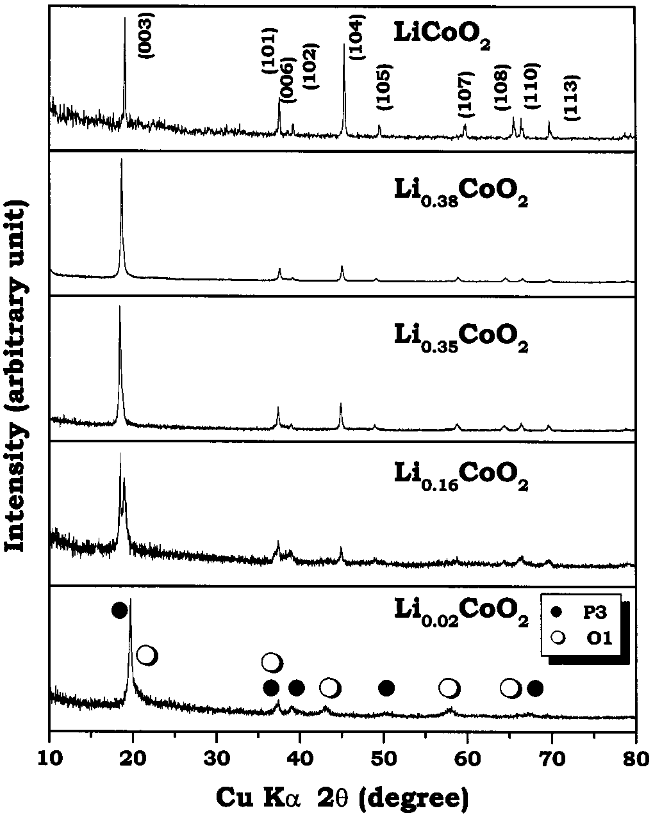

FIG. 1. X-ray diffraction patterns of chemically delithiated $Li_{1-x}CoO_2$.

oxygen stacking sequences of ABBCCA and ABAB, respectively, from the initial O3 structure having ABCABC stacking is due to the sliding of the oxide ions at low lithium content. The formation of the major P3 and minor O1 phases for the chemically prepared CoO_2 composition is in contrast to the single O1 structure (11, 14) or two O1 structures (15) reported for the electrochemically prepared CoO_2.

Figure 2 shows the X-ray patterns of the chemically delithiated $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ samples. In this case, the initial O3 structure is maintained for a wider lithium content $0.23 \leq (1-x) \leq 1$ and the new phase is formed at a lower lithium content $(1-x) < 0.23$. More importantly, the crystal structure of the end member $Ni_{0.85}Co_{0.15}O_2$ could also be refined on the basis of a single O3 structure, but with smaller lattice parameters ($a = 2.835(1)$ Å and $c = 13.573(3)$ Å) compared to the initial O3 phase. The observation of a O3 structure for the chemically prepared $Ni_{0.85}Co_{0.15}O_2$ is in agreement with that found for the electrochemically prepared NiO_2 sample (11, 14, 16, 17). However, it is in contrast to the O1 structure reported by Tarascon *et al.* (15) in a later publication. As pointed out by Tarascon *et al.* (5), the difference could be due to the differences in the degree of cation ordering. It is possible that the presence of a slight cation disorder with a small amount of transition metal ion in the lithium planes of the initial $LiNi_{0.85}Co_{0.15}O_2$ may prevent the sliding of the oxide layers and help to maintain the O3 structure.

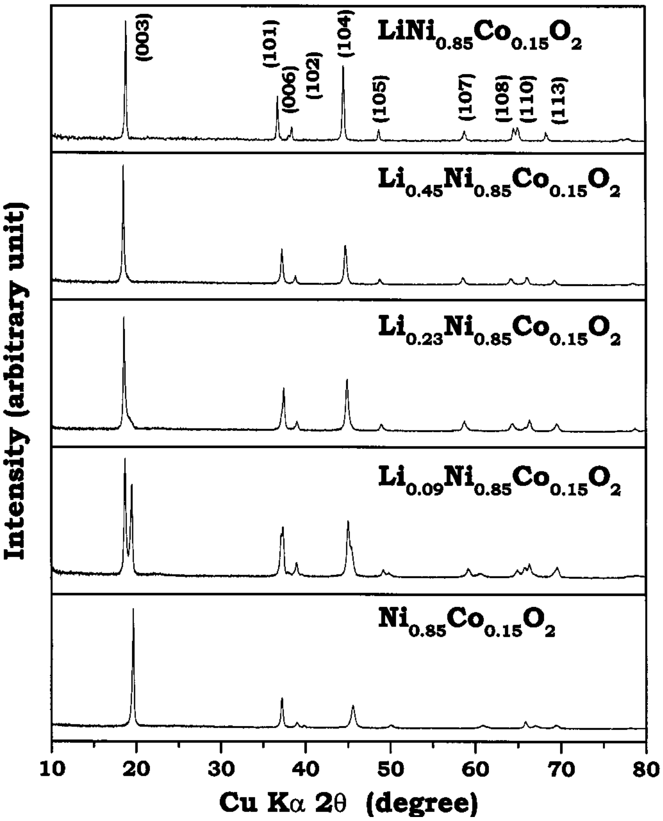

FIG. 2. X-ray diffraction patterns of chemically delithiated $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$.

With an aim to assess the chemical stability, the oxygen contents of the chemically delithiated $Li_{1-x}CoO_2$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ samples were determined by iodometric titration. The variations of the average oxidation state of the transition metal ions and the oxygen content with lithium content $(1-x)$ are compared in Fig. 3 for the two systems. While the oxidation state of (Ni, Co) in the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system increases smoothly from 3 + to 3.8 + with decreasing lithium content $(1-x)$ as one would anticipate, the oxidation state of Co in $Li_{1-x}CoO_2$ increases initially from 3 + to 3.35 + as one would anticipate, but remains almost constant around 3.35 + for $(1-x) < 0.5$. This results in a significant loss of oxygen from the lattice for $(1-x) < 0.7$ to give $Li_{1-x}CoO_{2-\delta}$ and the end member has a composition of $CoO_{1.67}$ with significant amount of oxygen vacancies. The observation of oxygen vacancies is consistent with the report by Tarascon *et al.* (15) from the structural refinement of the synchrotron X-ray data that the electrochemically prepared end member consists of a mixture of an oxygen stoichiometric phase, CoO_2, and an oxygen-deficient phase, $CoO_{1.92}$. However, the number of oxygen vacancies found in this study for the chemically synthesized $CoO_{2-\delta}$ is much larger. In contrast, the oxygen content remains close to 2 in the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system for $0.3 \leq (1-x) \leq 1$, and the system loses only a small amount of oxygen for $(1-x) < 0.3$ to give $Li_{1-x}Ni_{0.85}Co_{0.15}O_{2-\delta}$ with $\delta < 0.1$.

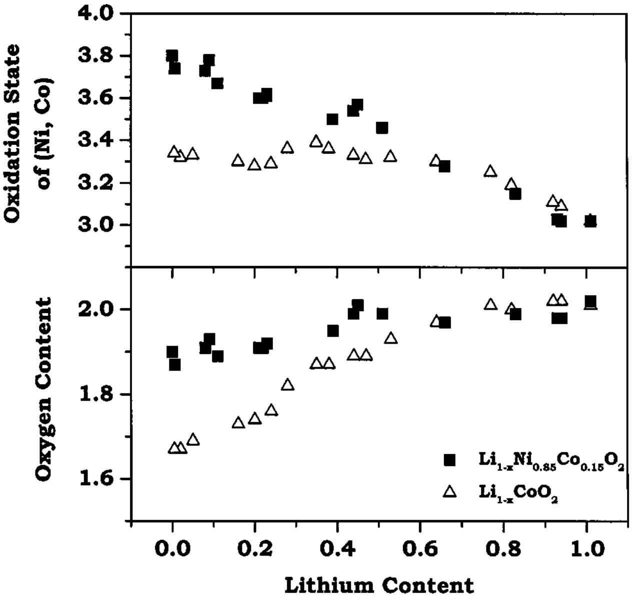

FIG. 3. Variations of the oxidation state and oxygen content with lithium content in $Li_{1-x}CoO_{2-\delta}$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_{2-\delta}$.

However, the $LiCoO_2$ cathodes are known to cycle well in lithium-ion cells for $(1-x) > 0.5$ and no oxygen loss may occur for $(1-x) > 0.5$ in electrochemical cells. The observation of the beginning of oxygen loss at a slightly higher lithium content $(1-x) \approx 0.7$ in the chemically delithiated samples could be due to a higher concentration of the powerful oxidizer NO_2PF_6 (10) used and a deeper extraction of lithium on the surface, even though the average lithium content is > 0.5. A deeper extraction of lithium on the surface may lead to the loss of oxygen from the surface, which may result in an overall oxygen content slightly less than 2 for $0.5 \leq (1-x) \leq 0.7$ in the chemically delithiated samples. We believe that the $Li_{1-x}CoO_2$ system is intrinsically prone to lose oxygen for $(1-x) < 0.5$ in lithium-ion cells and this may be the primary reason for the limited practical capacity (140 mA h/g) of this system. The loss of oxygen from the lattice can degrade the cathode and lead to capacity loss. In contrast, the absence of oxygen loss for $0.3 \leq (1-x) \leq 1$ in the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system together with the appearance of the second phase at a lower lithium content $(1-x) < 0.23$ permits the realization of a higher capacity (180 mA h/g) in this system. However, the existence of nickel ions at a higher oxidation state in the charged state due to the higher practical capacity and the absence of oxygen loss may be the cause for increased safety concerns in the nickel oxide system.

Furthermore, the formation of a significant amount of oxygen vacancies at low lithium contents in $Li_{1-x}CoO_{2-\delta}$ may be promoting the sliding of the oxide ion layers and the consequent transformation of the O3 structure to P3 and O1 structures. The P3 structure involves the presence of oxide ions directly above one another and, therefore, it is generally formed with larger cations such as Na^+ and K^+. With a given alkali metal ion, the formation of P3 structure is also favored by decreasing alkali metal content $(1-x)$ in $A_{1-x}CoO_2$ (A = alkali metal) (18). We believe, in addition to the little or no lithium content, the presence of significant amount of oxygen vacancies in $CoO_{2-\delta}$ reduces the repulsion between the oxide ions in adjacent layers and makes the formation of the P3 phase possible.

The differences between the two systems in oxygen loss behavior can be understood by considering the qualitative energy diagrams for $Li_{1-x}CoO_2$ and $Li_{1-x}NiO_2$ (Fig. 4). In the case of $LiCoO_2$ with a $Co^{3+}:3d^6$ configuration, the t_{2g} band is completely filled and the e_g band is empty. As lithium is extracted from $LiCoO_2$, the Co^{3+} ions are oxidized to Co^{4+}, which is accompanied by a removal of electrons from the t_{2g} band. Since the t_{2g} band overlaps with the top of the $O:2p$ band, deeper lithium extraction with $(1-x) < 0.5$ results in a removal of electrons from the $O:2p$ band (creation of holes) as well. The removal of significant amount of electron density from the $O:2p$ band will result in an oxidation of the O^{2-} ions and an ultimate loss of oxygen from the lattice. In contrast, the $LiNiO_2$ system with a $Ni^{3+}:3d^7$ configuration involves the removal of electrons only from the e_g band. For $LiNi_{0.85}Co_{0.15}O_2$, the electrons will be removed from the e_g band for $(1-x) > 0.15$. Since the e_g band lies well above the $O:2p$ band, this system does not lose oxygen down to a lower lithium content.

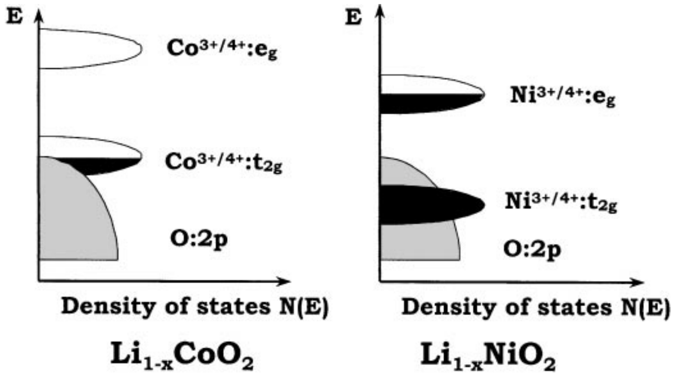

FIG. 4. Comparison of the energy diagrams of $Li_{1-x}CoO_2$ and $Li_{1-x}NiO_2$.

The band diagram for the $Li_{1-x}CoO_2$ system and the observed oxygen loss are consistent with the recent X-ray absorption spectroscopic (19) and electron energy loss spectroscopic (20) data, the electron-hole redox chemistry presented by Tarascon *et al.* (15), and the first principles calculations of Ceder *et al.* (21, 22). The spectroscopic data and theoretical calculations indicate that the holes are introduced into the $O:2p$ band rather than the $Co:3d$ band during the electrochemical extraction of lithium. Introduction of a significant number of holes into the $O:2p$ band will lead to evolution of oxygen from the lattice. However, it should be noted that in the presence of electrolytes in lithium-ion cells, neutral oxygen may not be evolved under conditions of overcharge with $(1-x) < 0.5$. Instead, the cathode may undergo a reaction with the electrolyte due to the highly oxidized nature of the deeply charged $Li_{1-x}CoO_2$ cathode. Similarly, the absence of oxygen loss for $(1-x) > 0.3$ in the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system is consistent with the recent XANES data on $Li_{1-x}NiO_2$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$. The XANES data show a continuous increase in the nickel oxidation state on charging, indicating the removal of electron density from the $Ni:e_g$ band (23, 24).

4. CONCLUSIONS

$Li_{1-x}CoO_2$ and $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ samples have been prepared successfully for $0 \leq (1-x) \leq 1$ by chemically extracting lithium with the oxidizer NO_2PF_6 in a nonaqueous medium. The $Li_{1-x}CoO_2$ system tends to lose oxygen at deep lithium extraction, which limits its practical capacity to 140 mA h/g. In contrast, the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system does not lose oxygen at least for $(1 - x) > 0.3$, which together with the maintenance of the initial O3 layer structure allows to realize a much higher practical capacity (180 mA h/g). The loss of oxygen in the $Li_{1-x}CoO_2$ system also leads to a sliding of the oxide ion layers and a transformation of the initial O3 structure to P3 and O1 structures at low lithium contents. However, the $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ system experiences a structural instability under mild heat ($T > 50°C$) due to the migration of the nickel ions to the lithium planes while the $Li_{1-x}CoO_2$ system is quite stable under similar conditions (8).

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