Synthesis and Characterization of P3-Type $CoO_{2-\delta}$

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Metastable P3-type $CoO_{2-\delta}$ oxides have been synthesized by chemically extracting lithium from the O3-type $LiCoO_2$ with an oxidizer, NO_2BF_4, in acetonitrile medium. The oxygen content values determined by a redox titration indicate that the $Li_{1-x}CoO_{2-\delta}$ system loses oxygen during lithium extraction for $1 - x < 0.5$. The oxygen content of the end member $CoO_{2-\delta}$ decreases with the lithium extraction reaction time from 1.88 for a reaction time of 1 h to 1.72 for a reaction time of 7 days, indicating chemical instability of the system. The decrease in oxygen content with reaction time is accompanied by a slow transformation of the metastable P3-type phase to the more stable O1-type phase for lithium extraction reaction times of >2 days. The formation of the P3- and O1-type $CoO_{2-\delta}$ with lower *c*-parameters from the initial O3-type $LiCoO_2$ by a gliding of the (CoO_2) sheets is attributed to the decreased charge on the oxide ions and the formation of oxygen vacancies. The P3-type $CoO_{2-\delta}$ is metallic and reverts back to the semiconducting O3-type Li_xCoO_2 upon lithium reinsertion, with the amount of lithium reinserted scaling with the oxidation state of cobalt in $CoO_{2-\delta}$.

Introduction

Metal oxides with general formula A_xMO_2 (A = alkali metal and M = transition metal) crystallize in layer structures in which the alkali-metal ions reside between the $(MO_2)_n$ sheets formed by edge-shared MO_6 octahedra. Delmas et al.[1] classified such layered compounds according to the coordination environment for the alkali-metal ion (prismatic, tetrahedral, or octahedral) and the number of MO_2 sheets per hexagonal unit cell. For example, $LiCoO_2$, which is used as a cathode material in commercial lithium ion cells, has the O3-type structure (Figure 1a) in which the Li^+ ions occupy the octahedral sites with three CoO_2 sheets per unit cell.[2] On the other hand, $Na_{0.7}CoO_2$ has the P2-type structure in which the Na^+ ions occupy prismatic sites with two CoO_2 sheets per unit cell.[3]

The layered $LiMO_2$ oxides exhibit facile lithium intercalation/deintercalation properties and have become attractive candidates as cathodes for lithium ion cells. The lithium extraction properties of such oxides at ambient temperatures provide a convenient route to access $Li_{1-x}MO_2$ ($0 \le 1 - x \le 1$) phases that are otherwise inaccessible by conventional high-temperature synthetic procedures. The $Li_{1-x}MO_2$ oxides consist of unusually high oxidation states such as $Fe^{3+/4+}$, $Co^{3+/4+}$, and $Ni^{3+/4+}$ and are unstable at high temperatures, decomposing to lower valent oxides. Such highly oxidized redox couples are characterized by a near equivalence of the metal:3d and oxygen:2p energies and can exhibit interesting electronic properties.

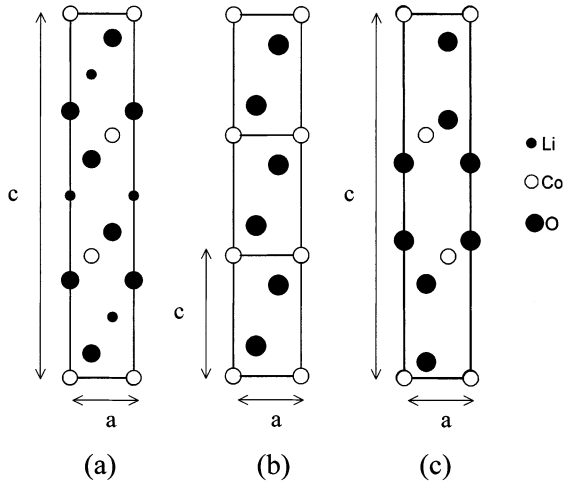

Figure 1. Crystal structures of (a) O3-type $LiCoO_2$, (b) O1-type CoO_2, and (c) P3-type CoO_2, viewed along the (100) plane.

Among the AMO_2-type compounds, both $LiCoO_2$ and $LiNiO_2$ are the most widely studied because of their use as cathodes in lithium ion batteries. These compounds have the O3-type structure with an oxygen stacking sequence of ABCABC along the *c*-axis as shown in Figure 1a. The lithium intercalation properties of these compounds have mainly been studied by electrochemical charge/discharge procedures. The electrochemical lithium extraction reactions of $LiCoO_2$ have been reported to yield the end member CoO_2 either as a single O1-type phase (Figure 1b) or as a mixture of two O1-type phases.[4−6] The O1-type structure shown in Figure 1b

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has an oxygen stacking sequence of ABABAB along the *c*-axis with a single CoO_2 sheet per unit cell.

However, the synthesis of bulk CoO_2 samples free from carbon and binder used to fabricate the electrodes for lithium cells has rarely been pursued as it is difficult to oxidize Co^{3+} to Co^{4+} by commonly used oxidizing agents such as I_2 or Br_2.[7] Several years ago, Wizansky et al.[8] showed that powerful oxidizing agents such as NO_2PF_6 can be used to oxidize Co^{3+} to Co^{4+}. Our group showed recently that bulk samples of $CoO_{2-\delta}$ free from carbon and binder can be synthesized successfully by chemically extracting lithium from $LiCoO_2$ at ambient temperatures with NO_2PF_6 in acetonitrile medium.[9,10] The $CoO_{2-\delta}$ sample obtained by such a chemical lithium extraction procedure involving the stirring of the $LiCoO_2$ powder with the oxidizer for 2−3 days was found to consist of a mixture of predominantly a P3-type phase and a small amount of O1-type phase, which is in contrast to the O1-type phases reported for the electrochemically prepared CoO_2 sample. The P3-type structure shown in Figure 1c has an oxygen stacking sequence of ABBCCA along the *c*-axis. Both the P3-type and O1-type phases can form from the parent O3-type $LiCoO_2$ phase by a gliding of the CoO_2 sheets during lithium extraction. Such a gliding of sheets involves very low reaction energies without the breaking of any Co−O bonds and, therefore, can occur at room temperature.[11]

However, the P3-type structure with a stacking sequence of ABBCCA without any alkali-metal ions between the MO_2 sheets would be expected to be unstable due to the electrostatic repulsion between the negatively charged oxide ions that lie directly one above the other across the van der Waals gap. In fact, the P3-type structure has usually been observed for predominantly covalent compounds containing small amounts of large alkali-metal ions such as K^+.[1] To our knowledge, the formation of the P3-type phase has not been reported before for MO_2 phases without any alkali-metal ions between the sheets. In our previous studies,[9,10] we could observe the P3-type $CoO_{2-\delta}$ only in a mixture consisting of P3-type and O1-type phases. We present here the synthesis of single-phase P3-type $CoO_{2-\delta}$ and its characterization by X-ray diffraction, wet-chemical analysis, and infrared spectroscopy. The investigation focuses on the influence of chemical lithium extraction time on the type of phases formed and on their chemical and structural stabilities. It also addresses why the P3-type phase is formed during chemical lithium extraction, but not during electrochemical lithium extraction.

Experimental Section

$LiCoO_2$ was synthesized by solid-state reaction between Li_2CO_3 (99.0% purity, Alfa Aesar) and Co_3O_4 (reagent grade, GFS chemicals) at 900 °C for 24 h in the air. The reaction mixture consisted of 2 atom % excess lithium to compensate for any volatilization of lithium that may occur during the high-temperature firing. Chemical extraction of lithium from $LiCoO_2$ was carried out by stirring the $LiCoO_2$ powder in an acetonitrile solution consisting of the oxidizer NO_2BF_4 (95+% purity, Aldrich) under an argon atmosphere for a specified amount of reaction time *t*:

$$LiCoO_2 + xNO_2BF_4 \rightarrow Li_{1-x}CoO_2 + xNO_2 + xLiBF_4 \quad (1)$$

Various values of lithium contents $1 - x$ in the products could be achieved by controlling the ratio of $LiCoO_2$ to NO_2BF_4 in the reaction mixture. Due to the high reactivity of NO_2BF_4 and the possibilities of its decomposition prior to use and side reactions, the experiments invariably required higher amounts of the oxidizer than would be expected on the basis of reaction 1 to achieve a specific value of lithium content $1 - x$ in $Li_{1-x}CoO_2$. For example, the end member $CoO_{2-\delta}$ without any lithium was obtained with a $LiCoO_2$:NO_2BF_4 molar ratio of 1:2. The $Li_{1-x}CoO_2$ products formed after the specified amount of reaction time were filtered, washed repeatedly with acetonitrile under an argon atmosphere to remove $LiBF_4$, and dried under vacuum at ambient temperature in a Schlenk line. After drying, the reaction flasks were opened in an argon-filled glovebox to avoid any reaction of the samples with ambient air.

Lithium reinsertion into the deintercalated $CoO_{2-\delta}$ was carried out by stirring the $CoO_{2-\delta}$ powders with an acetonitrile solution consisting of excess anhydrous LiI (99% purity, Alfa Aesar) for 3 days under argon:

$$Co^{(3+x)+}O_{2-\delta} + xLiI \rightarrow Li_xCo^{3+}O_{2-\delta} + (x/2)I_2 \quad (2)$$

To avoid reaction with ambient air, the $CoO_{2-\delta}$ powder and LiI were taken in the reaction flask inside the argon-filled glovebox, and then acetonitrile was added into the flask in the Schlenk line. After stirring, the product formed was filtered, washed repeatedly with acetonitrile under an argon atmosphere to remove I_2, and dried under vacuum at ambient temperature in the Schlenk line.

The lithium contents before and after the lithium extraction/insertion reactions were determined by atomic absorption spectroscopy. The oxidation state of cobalt and oxygen content were determined by a redox (iodometric) titration.[12] The titration was carried out by dissolving the samples in a mixture of potassium iodide and hydrochloric acid immediately after the samples were removed from the glovebox to avoid reaction with air. Crystal chemical characterizations were carried out with X-ray powder diffraction using Cu Kα radiation. The sample was covered tightly with a Mylar film to protect it from the air while the patterns were recorded. The lattice parameters were refined by the Rietveld method with the DBWS-9411 PC program.[13] Fourier transform infrared (FTIR) spectra were recorded with pellets made with KBr and the sample.

Results and Discussion

Structural Analysis. Figure 2 shows the X-ray diffraction patterns of the $Li_{1-x}CoO_2$ samples that were obtained after a reaction time of 2 days with NO_2BF_4. After the 2 days of reaction time, the initial O3-type structure is maintained for the range $0.5 \leq 1 - x \leq 1$ in $Li_{1-x}CoO_2$. At around $1 - x = 0.45$, another phase is formed as indicated by the shoulder on the right side of the strong (003) peak. This new phase grows with further lithium extraction, and in the region $0 < 1 - x \leq 0.45$, the two phases coexist. The X-ray diffraction data in the region $0 < 1 - x \leq 0.45$ could be indexed as a mixture of O3- and P3-type phases, and those of the

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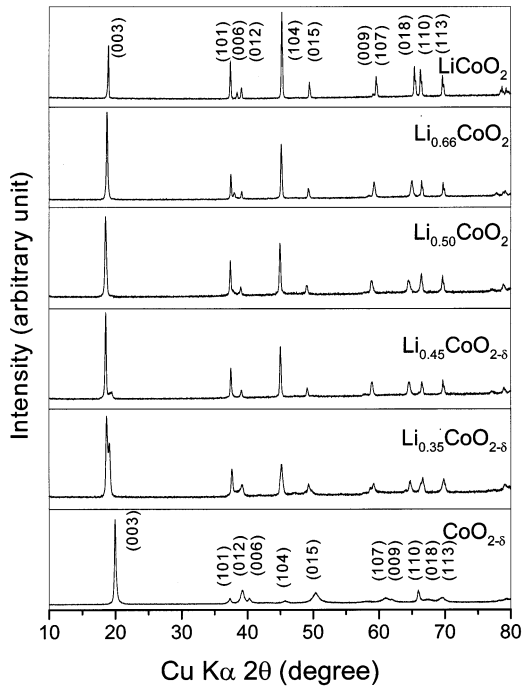

Figure 2. X-ray diffraction patterns of $Li_{1-x}CoO_2$ samples obtained by reacting $LiCoO_2$ with NO_2BF_4 for 2 days.

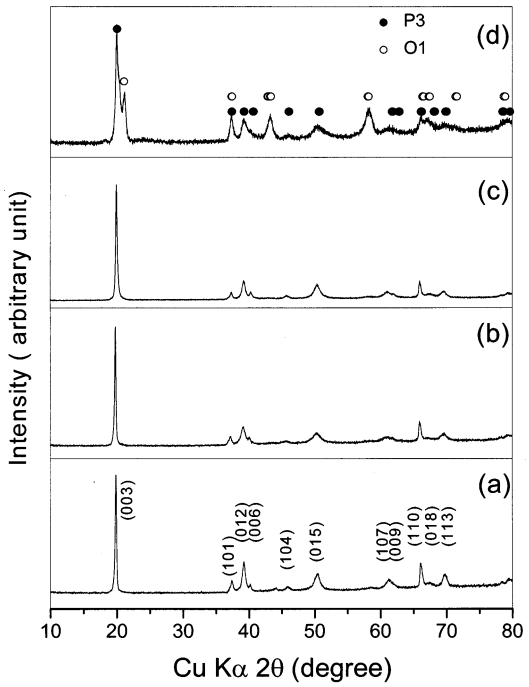

Figure 3. X-ray diffraction patterns of the end member $CoO_{2-\delta}$ obtained by reacting $LiCoO_2$ with NO_2BF_4 for (a) 1 h, (b) 3 h, (c) 2 days, and (d) 7 days. The patterns in (a)−(c) correspond to a single P3-type phase, and that in (d) corresponds to a mixture of P3-type and O1-type phases.

end member $CoO_{2-\delta}$ could be fitted on the basis of a single P3-type phase using Rietveld analysis. Moreover, the (003) reflection of the end member $CoO_{2-\delta}$ occurs at a slightly higher 2θ value than that of the new phase formed at $1 - x = 0.45$, which could be due to a small lithium solid solubility range for the P3-type phase and/or changes in the oxygen content of the P3-type phase with the overall lithium content (see later).

To see the influence of reaction time on the structure of the product formed, the end member $CoO_{2-\delta}$ was synthesized by stirring the $LiCoO_2$ powder with NO_2BF_4 (1:2 molar ratio) for various reaction times t. Interestingly, all the lithium could be chemically extracted from $LiCoO_2$ in as short as 15 min, illustrating the fast lithium extraction characteristics of the O3-type $LiCoO_2$. Figure 3 shows the X-ray diffraction patterns of $CoO_{2-\delta}$ as a function of reaction time (1 h to 1 week). The $CoO_{2-\delta}$ samples obtained with a short reaction time of ≤2 days consist of a single P3-type phase, while those obtained with a long reaction time of >3 days consist of a two-phase mixture composed of P3-type and O1-type phases. The transformation of the P3-type phase formed during shorter reaction times to the O1-type phase on prolonged reaction times indicates that the P3-type phase is metastable.

Figure 4 shows the Rietveld refinement data of the $CoO_{2-\delta}$ samples obtained with reaction times of 3 h and 7 days. The 3 h sample could be fitted as a single P3-type phase (Figure 4a) based on the $R3m$ space group (SG 160) with cobalt ions at the 3a site (0,0,0) and oxygen ions also at the 3a sites (0,0,z_{ox}) and (0,0,z_{ox}'), where $z_{ox} = 0.595(1)$ and $z_{ox}' = 0.353(1)$. This model yielded $R_{wp} = 8.63\%$ and goodness of fit $s = 2.82$ with lattice parameters $a = 2.8329(3)$ Å and $c = 13.4964(4)$ Å. The 7 day sample, on the other hand, could be fitted as a mixture of P3-type (86 mol %) and O1-type (14 mol %) phases (Figure 4b). The P3-type phase has lattice parameters of $a = 2.8239(8)$ Å and $c = 13.314(1)$ Å and

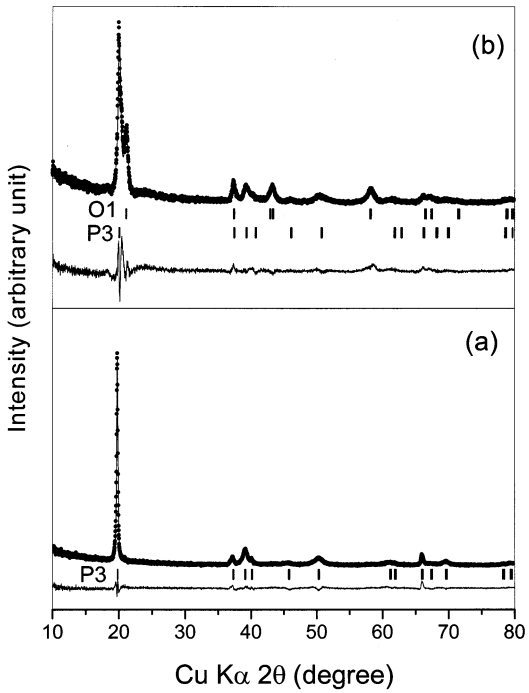

Figure 4. Rietveld refinement data of the end member $CoO_{2-\delta}$ that was obtained by reacting $LiCoO_2$ with NO_2BF_4 for (a) 3 h and (b) 7 days. Circles and lines correspond, respectively, to the observed and calculated intensities. The differences between the observed and calculated patterns and the peak positions corresponding to the P3-type and O1-type phases are also shown.

was based on the same model as above, but with $z_{ox} = 0.614(5)$ and $z_{ox}' = 0.364(4)$. The O1-type phase has lattice parameters of $a = 2.7800(8)$ Å and $c = 4.2221(9)$ Å, and was based on the $P3m1$ space group (SG 164) with cobalt ions at the 1a site (0,0,0) and oxygen ions

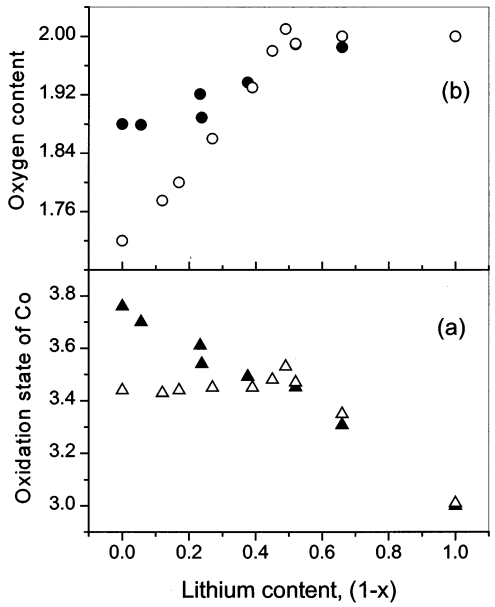

Figure 5. Variations of the (a) oxidation state of cobalt and (b) oxygen content with lithium content for the $Li_{1-x}CoO_{2-\delta}$ samples obtained after reaction times of 1 h (closed symbols) and 2 days (open symbols).

at the 2d site (1/3, 2/3, z_{ox}), where $z_{ox} = 0.257(3)$. This two-phase model for the 7 day sample yielded $R_{wp} = 11.16\%$ and goodness of fit $s = 3.56$. The slight asymmetry in the (003) reflection of the P3-type phase with a shoulder at around $2\theta = 20.32°$ between the (003) reflections of the P3- and O1-type phases in Figure 3d and the small discrepancy between the observed and calculated patterns at around $2\theta = 20°$ in Figure 4b could be due to the phase inhomegeniety or the formation of intermediate-stage phases as the P3-type phase is slowly transforming to the O1-type phase over time.

Oxygen Content Analysis. Figure 5 compares the variations of the oxidation state of cobalt and the oxygen content with lithium content $1 - x$ for the $Li_{1-x}CoO_{2-\delta}$ samples obtained with reaction times of 1 h and 2 days. For the 2 day sample, the oxidation state of cobalt increases with decreasing lithium content to about 3.5+ at around $1 - x = 0.5$ and remains constant thereafter. The constancy of the oxidation state of cobalt results in a loss of oxygen from the lattice for $1 - x < 0.5$. The 1 h sample also shows a loss of oxygen from the lattice for $1 - x < 0.5$, but the amount of oxygen lost is less compared to that found for the 2 day sample. Figure 6 shows the variation of the oxygen content in $CoO_{2-\delta}$ with the reaction time t. The oxygen content in $CoO_{2-\delta}$ decreases from 1.88 for a reaction time of 30 min to 1.72 for a reaction time of 7 days. The decrease in oxygen content with stirring (reaction) time suggests that the $CoO_{2-\delta}$ system experiences an inherent chemical instability. The end member $CoO_{1.72}$ reported here for a reaction time of ≥2 days has slightly higher oxygen content than that reported in our previous work (1.67).[9,10] The difference could be due to the differences in the oxidizers used (NO_2BF_4 vs NO_2PF_6), chemical instability of $CoO_{2-\delta}$ under stirring, and handling of the air-sensitive $CoO_{2-\delta}$.

As we pointed out in our earlier studies,[9,10] the loss of oxygen from the lattice implies an introduction of holes into the O^{2-}:2p band and a consequent oxidation

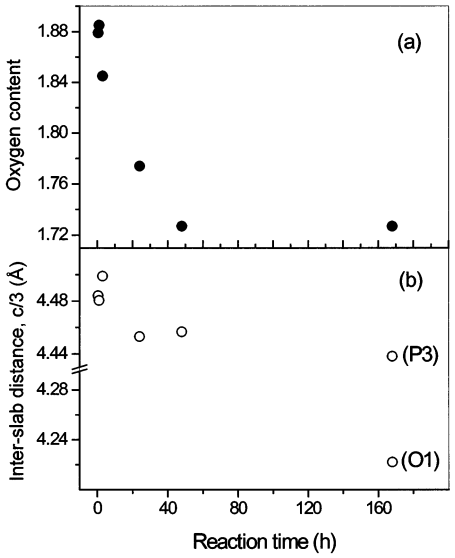

Figure 6. Variations of the (a) oxygen content and (b) interslab distance, $c/3$, with reaction time t for $CoO_{2-\delta}$.

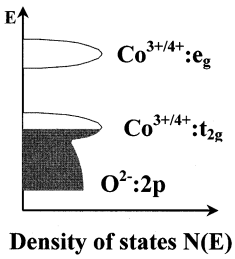

Figure 7. Qualitative energy diagram of $Li_{1-x}CoO_2$.

of the oxide ions to oxygen at deep lithium extraction. Such an oxidation of the oxide ions is due to the overlap of the $Co^{3+/4+}$:t_{2g} band with the top of the O^{2-}:2p band as shown in Figure 7. According to the band model in Figure 7, the electrons would be removed predominantly from the $Co^{3+/4+}$:t_{2g} band during the initial stages of lithium extraction, but from the O^{2-}:2p band at deep lithium extraction, resulting in an oxidation of the O^{2-} ions. This conclusion is consistent with a theoretical calculation by Van der Ven et al.[14] indicating that the average valence charge on oxygen decreases with decreasing lithium content. It is also consistent with the X-ray absorption spectroscopic[15] and electron energy loss spectroscopic data[16] indicating that holes are introduced into the O:2p band rather than into the Co:3d band during the electrochemical charging of the $LiCoO_2$ cathodes. Furthermore, the observed decrease in the c-parameter for $1 - x < 0.5$ in $Li_{1-x}CoO_2$ could also be understood to be due to the decreasing electrostatic repulsion between the oxide ions that is caused by either the decreasing valence charge on the oxide ions[14] or the oxide ion vacancies.

The participation of anions in the redox processes of transition-metal compounds has been well established

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in the case of chalcogenides.[17−20] For example, during the extraction of lithium from Li_2FeS_2, the Fe^{2+} ions are oxidized to Fe^{3+} initially, but anion pairs are formed during the later stages of lithium extraction to give $Fe^{3+}(S_2^{2-})_{0.5}S^{2-}$.[18] This is due to the overlap of the Fe^{3+}: 3d energy with the top of the S^{2-}:3p band as pointed out by Rouxel.[17−20] However, compared to the molecular disulfide ion $(S_2)^{2-}$, the peroxide ion $(O_2)^{2-}$ is relatively unstable, resulting in a loss of oxygen from the lattice and the formation of oxygen vacancies.

Figure 6 also shows the variation of the interslab distance between the $(CoO_2)_n$ sheets, which was calculated from the hexagonal lattice parameter as $c/3$, with reaction time. The interslab distance decreases with increasing reaction time or decreasing oxygen content, and the O1-type phase has a smaller interslab distance (4.222 Å) than the P3-type phases (4.45−4.50 Å). As the concentration of oxygen vacancies increases with reaction time, the electrostatic repulsion between the oxide ions across the van der Waals gap decreases, leading to a transformation of the metastable P3 structure with the oxide ions lying directly one over the other across the van der Waals gap (ABBCCA stacking) to the more stable O1 structure (ABABAB stacking). Furthermore, Van der ven et al.[14] have shown from first principle calculations that the O1-type phase is more stable by 40 meV compared to the O3-type phase for CoO_2. Similarly, Croguennec et al.[21] have recently explained the stability of the O1-type phase over the O3-type phase in the case of NiO_2 on the basis of the reduced interaction of the O:2p orbital across the van der Waals gap. Clearly, the stability of the O1-type or P3-type phase with smaller interslab distance compared to the O3-type phase for CoO_2 could be due to the decreased valence charge (or introduction of holes) on oxygen or the formation of oxygen vacancies.

Difference between Chemical and Electrochemical Lithium Extraction. As mentioned earlier, the formation of the P3-type phase for CoO_2 is observed only during chemical lithium extraction. The electrochemical lithium extraction (charging) has invariably yielded the O1-type phase.[4−6] The difference could be understood by considering the lithium extraction or charging rate in the two methods. The chemical lithium extraction experiments are carried out by adding the whole amount of the oxidizer in one step to the $LiCoO_2$ powder followed by stirring. In such a process, all the lithium ions are extracted in a very short time (<15 min), which translates into a very high charging rate (>4 C rate). In contrast, the electrochemical synthesis of CoO_2 has generally been carried out at very slow charging rates such as a 1/50 C rate.[4] Thus, the electrochemical synthesis (charging) process reported in the literature is a more equilibrated process compared to the chemical synthesis process reported in this paper. While the slow, more equilibrated electrochemical charging process leads to the formation of the equilibrium phase O1, the fast, less equilibrated chemical extraction (charging) process leads to the metastable phase P3, which eventually converts to the equilibrium phase O1 on prolonged stirring. Since both the P3-type and O1-type CoO_2 phases are formed from the parent O3-type $LiCoO_2$ by a gliding of the $(CoO_2)_n$ sheets, it is indeed possible that the charging rate can influence the rate and degree of gliding and thereby the type of phase formed. It appears that once the metastable P3-type phase is formed under very high charging rates, its transformation to the more stable O1-type phase is sluggish.

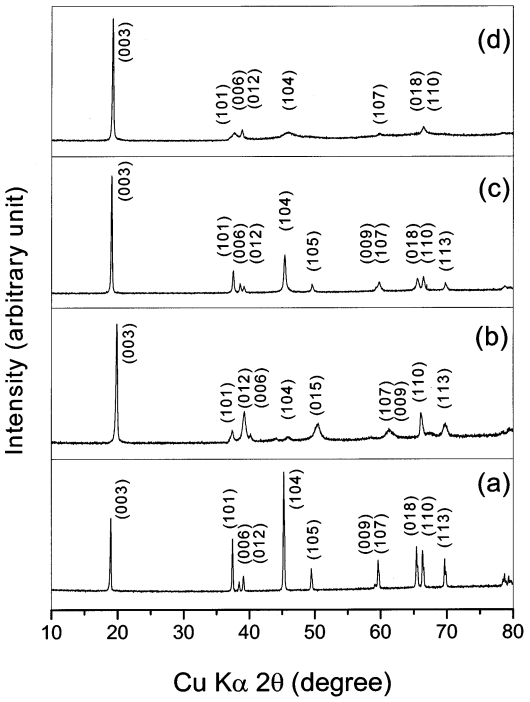

Figure 8. X-ray diffraction patterns of (a) O3-type $LiCoO_2$, (b) P3-type $CoO_{1.88}$ (obtained after a reaction time of 1 h), (c) lithium-reinserted $Li_{0.80}CoO_{1.88}$ (O3-type), and (d) lithium-reinserted $Li_{0.41}CoO_{1.72}$ (O3-type).

Lithium Reinsertion into the P3-Type $CoO_{2-\delta}$. Figure 8 compares the X-ray diffraction patterns of the O3-type $LiCoO_2$, P3-type $CoO_{2-\delta}$, and $Li_xCoO_{2-\delta}$ obtained by inserting lithium into the P3-type $CoO_{2-\delta}$. The lithium-reinserted $Li_xCoO_{2-\delta}$ sample has the O3-type structure similar to the parent $LiCoO_2$ sample as revealed by Rietveld analysis. The data indicate that the P3-type $CoO_{2-\delta}$ transforms into the O3-type $Li_xCoO_{2-\delta}$ upon lithium reinsertion. Since the $[LiO_6]$ octahedra will share not only edges but also faces with the $[CoO_6]$ octahedra in the P3 structure, the electrostatic repulsion between the Li^+ and $Co^{3+/4+}$ ions across the shared faces leads to a transformation of the P3 structure to the O3 structure, which involves only edge sharing. Similar results of the transformation of the O1-type $CoO_{2-\delta}$ to the O3-type $Li_xCoO_{2-\delta}$ were also found for the electrochemically prepared $CoO_{2-\delta}$ upon discharge (electrochemical lithium reinsertion).[4]

The P3-type $CoO_{1.88}$ sample obtained after a reaction time of 1 h with NO_2BF_4 yields O3-type $Li_{0.80}CoO_{1.88}$ with lattice parameters of a = 2.8171(1) Å and c = 14.0454(5) Å. On the other hand, the P3-type $CoO_{1.72}$ sample obtained after a reaction time of 2 days yields O3-type $Li_{0.41}CoO_{1.72}$ with lattice parameters of a = 2.811(1) and c = 14.024(2) Å. The amount of lithium

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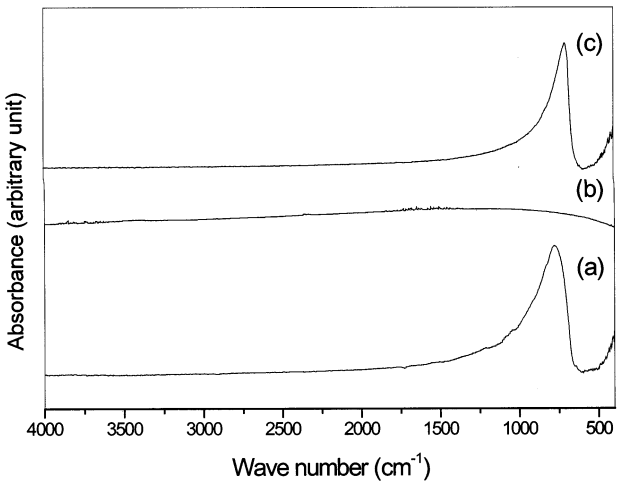

Figure 9. FTIR spectra of (a) O3-type $LiCoO_2$, (b) P3-type $CoO_{1.88}$, and (c) lithium-reinserted $Li_{0.80}CoO_{1.88}$ (O3-type).

reinserted into the two samples scales with the oxidation states of cobalt in $CoO_{2-\delta}$. On reinserting lithium into $CoO_{2-\delta}$, the oxidized $Co^{(4-2\delta)+}$ ions are reduced to Co^{3+}. Even with 500% excess LiI, the amount of reinserted lithium ions into the $CoO_{2-\delta}$ samples could not be increased further. This observation clearly confirms the presence of oxygen vacancies and an oxidation state of cobalt much less than the formally anticipated value of 4+ in $CoO_{2-\delta}$. Furthermore, while the lithium-reinserted $Li_{0.80}CoO_{1.88}$ sample shows sharp diffraction peaks (Figure 8c), the lithium-reinserted $Li_{0.41}CoO_{1.72}$ sample shows broad diffraction peaks (Figure 8d). This difference is due to a large amount of oxygen vacancies in the latter sample.

Infrared Spectra. Since it is difficult to obtain sintered specimens suitable for electrical conductivity measurements as the samples are metastable and decompose at elevated temperatures, the samples were characterized by infrared spectra to obtain a qualitative idea about the conduction behavior of the samples.[9] Figure 9 compares the Fourier transform infrared (FTIR) spectra of O3-type $LiCoO_2$, P3-type $CoO_{2-\delta}$, and lithium-reinserted O3-type $Li_xCoO_{2-\delta}$. Both the parent $LiCoO_2$ and the lithium-reinserted $Li_{0.80}CoO_{1.88}$ show characteristic absorption bands, indicating semiconducting behavior. On the other hand, $CoO_{1.88}$ does not show any absorption band, indicating metallic behavior. In the case of metallic systems, a decreased optical skin depth of the incident beam leads to a probing of only the surface of the sample and a consequent vanishing of the absorption bands. Alternatively, the free electrons of the metallic system are able to oscillate to any incident wavelength, resulting in no characteristic absorption. Additionally, the absence of any absorption band corresponding to O−H stretching around 1800 and 3400 cm^{-1} in the lithium-reinserted sample indicates that the sample does not contain any proton.[22] The absence of proton confirms the prevention of the reaction of $CoO_{2-\delta}$ with ambient air to give phases such as $H_xCoO_{2-\delta}$.

The semiconducting behavior of both the parent $LiCoO_2$ and the lithium-reinserted $Li_{0.80}CoO_{1.88}$ samples having a Co^{3+}:$3d^6$ configuration is due to the completely filled t_{2g} band. On the other hand, a partially filled t_{2g} band in the case of $CoO_{1.88}$ having a $Co^{3.76+}$:$3d^{5.24}$ configuration leads to metallic behavior. The observation of metallic behavior for $CoO_{2-\delta}$ is consistent with the literature report of a semiconductor to metallic transition for $1 - x < 0.7$ in $Li_{1-x}CoO_2$.[23]

Conclusions

Metastable P3-type $CoO_{2-\delta}$ has been synthesized by chemically extracting lithium from the O3-type $LiCoO_2$. The $CoO_{2-\delta}$ system experiences chemical instability due to an overlap of the $Co^{3+/4+}$:3d band with the top of the O^{2-}:2p band, which leads to a decrease in oxygen content with increasing lithium extraction reaction time. The metastable P3-type $CoO_{2-\delta}$ transforms slowly to the more stable O1-type phase for longer lithium extraction reaction times of >2 days. The $CoO_{2-\delta}$ phase reverts back to the O3-type $Li_xCoO_{2-\delta}$ upon lithium insertion. The $CoO_{2-\delta}$ phase is metallic due to a strong interaction between the t_{2g} orbitals across the shared edges of the CoO_6 octahedra. The formation of the P3-type $CoO_{2-\delta}$ has been observed only during chemical lithium extraction. Electrochemical lithium extraction (charging) has invariably yielded the more stable O1-type phase. The differences in the type of phases formed could be related to the differences in the charging rates involved in the two processes, the chemical lithium extraction involving a much higher charging rate than the electrochemical lithium extraction.

The overlap of the $Co^{3+/4+}$:3d band with the top of the O^{2-}:2p band also leads to a chemical instability for $1 - x < 0.5$ in $Li_{1-x}CoO_{2-\delta}$, resulting in a tendency of the system to lose oxygen from the lattice at deep lithium extraction. It is possible that such a chemical instability may play a critical role in limiting the practical capacity of the $LiCoO_2$ cathodes to a reversible extraction of 0.5 lithium ion per Co (<140 (mA h)/g).

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