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Chemical Extraction of Lithium from Layered $LiCoO_2$

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Chemical extraction of lithium from $LiCoO_2$ has been investigated with various oxidizing agents—Cl_2, Br_2, and I_2—and with dilute sulfuric acid. A considerable amount of lithium could be extracted with both chlorine and acid to give a final lithium content $(1 - x) \approx 0.3$ in $Li_{1-x}CoO_2$. The stronger oxidizing power of Cl_2 and the relative instability associated with the Li-extracted samples lead to the dissolution of a considerable amount of the sample during chlorine oxidation. A deeper lithium extraction with chlorine also leads to the occurrence of oxygen vacancies in $Li_{1-x}CoO_{2-\delta}$. Lithium extraction with acid proceeds predominantly by a disproportionation of Co^{3+} to Co^{2+} and Co^{4+} analogous to that in the spinel $LiMn_2O_4$ with a small degree of ion exchange of Li^+ by H^+. However, the results of both chlorine oxidation and acid treatment are strongly influenced by the nature of the initial material. An Li/Co ratio < 1 and/or a disorder between Li and Co in the initial $Li_{1-z}Co_{1+z}O_2$ result in a competition of Co extraction from Li planes with Li extraction as evidenced by the Li/Co ratio in the filtrate as well as the changes in the relative intensities of the (003) and (104) reflections. Extraction of Co from Li planes by this process might prove to be useful to obtain improved electrode materials for lithium batteries. The degree of lithium extraction that can be achieved with different oxidizing agents follows the trend in their oxidation potential. In addition, the literature data that Na can be extracted more easily from $NaCoO_2$ than Li from $LiCoO_2$ is explained on the basis of the relative energies of the $Co^{3+/4+}$ redox couple in the two compounds. © 1996 Academic Press, Inc.

1. INTRODUCTION

A few ternary oxides with the general formula $LiMO_2$ (M = V, Cr, Co, or Ni) crystallize in a layer structure (1) isotypic with α-$NaFeO_2$ (2) in which the Li^+ and M^{3+} ions are ordered on the alternate (111) planes of the rocksalt structure. These layered oxides with M = Co and Ni have become attractive candidates in recent years with respect to cathode materials (3, 4) for rechargeable lithium batteries. They offer high energy density with a mid-discharge voltage of about 4 V against a metallic lithium anode. The layered $LiCoO_2$ is intensively being pursued for commercialization of "lithium-ion" or "rocking-chair" batteries (5, 6).

Although most of the lithium could be extracted from $Li_{1-x}CoO_2$ $(0 < x < 1)$ by electrochemical oxidation (3, 4), chemical extraction of lithium from $LiCoO_2$ is somewhat difficult. This is because the most common oxidizing agents such as I_2 and Br_2 are not strong enough to oxidize Co^{3+}. While Miyazaki *et al.* (7, 8) report that it was not possible to remove any lithium from $Li_{1-x}CoO_2$ by either iodine or bromine, Mendiboure *et al.* (9) report that some lithium could be removed with bromine from an $Li_{1-x}CoO_2$ that was obtained by an ion-exchange of $Na_{0.7}CoO_2$. Recently Wizansky *et al.* (10) investigated the use of more powerful oxidizing agents such as NO_2PF_6 and MoF_6 to extract lithium from $LiCoO_2$. Although these reagents could extract a large amount of lithium, a higher oxidation potential associated with these reagents seems to lead to side reactions resulting in a partial dissolution of the oxide itself. Similar problems have also been found in the oxidation of $LiNiO_2$ with NO_2PF_6 (11).

Quite recently, extraction of lithium from $LiCoO_2$ as well as $LiCo_{1-y}M_yO_2$ (M = Mn or Ni) by treating with acid at ambient temperatures has also been investigated (12–16) analogous to the extraction of lithium from the spinel oxide $Li[Mn_2]O_4$ to obtain λ-MnO_2 (17). Although lithium could be extracted from $LiCoO_2$ by treating with acid, this method is prone to cause an ion-exchange of some Li by H. The results available in the literature on this aspect seem to vary. Although the presence of a considerable amount of protons has been reported in both $Li_{1-x-z}H_zCoO_2$ (12) and $Li_{1-x-z}H_zCo_{1-y}Mn_yO_2$ (13), another investigation by the same group (14) on $LiCo_{1-y}Ni_yO_2$ suggests the presence of protons only in the samples obtained by a low-temperature method and not in samples obtained by conventional high-temperature method. Furthermore, the mechanism of lithium extraction by acid treatment from layered compounds has not been clearly established.

Our objective is threefold: First, it is to investigate the use of chlorine gas as an oxidizing agent to extract lithium from $LiCoO_2$. The oxidation potential of chlorine (1.36 V) is slightly higher than that of bromine (1.1 V), but much

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less than that of the more powerful NO_2PF_6 (2.1 V). So one can expect the possibilities of side reactions with chlorine to be suppressed compared to that with NO_2PF_6. Synthesis of $Li_{1-x}CoO_2$ by this route and its use as a cathode can avoid the initial charging step in lithium cells. Second, we investigate systematically the extraction of lithium from $LiCoO_2$ with aqueous acid so that one can establish the mechanism of lithium extraction by acid. Specifically, does the lithium extraction occur by a disproportionation of Co^{3+} to Co^{2+} and Co^{4+} analogous to the disproportionation of Mn^{3+} to Mn^{2+} and Mn^{4+} in the spinel oxide $Li[Mn_2]O_4$? Careful wet-chemical analysis of Li and Co contents both in the filtrate and in the solid obtained after treating with acid, as well as the determination of the oxidation state of Co in $Li_{1-x}CoO_2$, can establish this point. Third, we investigate whether lithium extraction is possible from $LiCoO_2$ with a large excess of iodine or bromine. If so, does the extent of Li extraction with the three oxidizing agents—I_2, Br_2, and Cl_2—correlate with their oxidation potentials and the $Co^{3+/4+}$ redox energy in $Li_{1-x}CoO_2$?

We present in this paper our results obtained on the extraction of lithium from $LiCoO_2$ by three different oxidizing agents—chlorine, bromine, and iodine—as well as by dilute sulfuric acid. The products are characterized by X-ray powder diffraction and wet-chemical analyses for Li and Co contents and oxidation state of Co. The extent of lithium extraction achieved with the three oxidizing agents is correlated to the observed $Co^{3+/4+}$ energy in the electrochemical data. Furthermore, the extent of lithium extraction from $LiCoO_2$ is compared with the literature data on $NaCoO_2$ and the differences are explained based on the relative positions of $Co^{3+/4+}$ energy in the two compounds.

2. EXPERIMENTAL

$LiCoO_2$ was synthesized by firing a mixture of Li_2CO_3 and Co_3O_4 first at 500°C for 5 h and then at 850°C for 24 h with one intermittent grinding. An excess of about 3 at.% Li was taken in the starting mixture to compensate for any loss of lithium that may occur during the firing. This procedure gave single phase products as indicated by X-ray diffraction. Following this procedure, three batches of $LiCoO_2$ were obtained with three different cooling rates of 1°C/min, 3°C/min, and 5°C/min and are designated, respectively, as samples A, B, and C.

Lithium extraction with chlorine was carried out by continuously passing chlorine gas from a commercial cylinder through a suspension of about 500 mg of $LiCoO_2$ in 50 ml of acetonitrile for varying amounts of time ranging from 0.5 to 3 h. Lithium extraction with bromine and iodine were carried out by stirring a suspension of about 500 mg of $LiCoO_2$ in 60 ml of 0.35 N Br_2 or I_2 in acetonitrile for 65 h; these quantities correspond to a fivefold excess of Br_2 or I_2 required to remove all Li from $LiCoO_2$. After the oxidation reactions, the products were filtered, washed several times with acetonitrile and deionized water, and finally dried at 100°C in an air-oven. Lithium extraction with acid was carried out by stirring a suspension of about 500 mg of $LiCoO_2$ in 25 ml of 0.7 N H_2SO_4 (or 1000 mg in 50 ml) for varying amounts of time ranging from 2 to 48 h. The reaction product was then filtered, washed several times with deionized water, and dried at 100°C in an air-oven.

The $Li_{1-x}CoO_2$ samples obtained after lithium extraction were all characterized by X-ray powder diffraction. They were analyzed after dissolving in dilute HCl by atomic absorption spectroscopy for Li and Co contents. In addition, the filtrates in all cases were analyzed for Li and Co contents by atomic absorption spectroscopy. The average oxidation state of cobalt in the samples was determined by a redox titration. A known amount of the sample was dissolved in a slight excess of 0.08 N ferrous ammonium sulfate solution under an inert (N_2) atmosphere and the remaining ferrous ammonium sulfate was then titrated against 0.05 N potassium dichromate solution using sodium diphenylamine as an indicator (18). Cobalt content in the samples was determined by a gravimetric procedure (19). About 50 mg of the sample was dissolved by heating with dilute HCl, and the solution was brought up to 200 ml with deionized water after raising the pH to 4.5–6 with dilute NaOH. The solution was heated to boiling; about 15 ml of 3% sodium anthranilate solution was added under constant stirring and boiled for another 5 min. After cooling to room temperature, the precipitate was filtered in a sintered glass funnel, washed repeatedly with 0.15% sodium anthranilate solution in methanol, dried at 110–120°C, and weighed as cobalt anthranilate, $Co(C_7H_6O_2N)_2$. The cobalt contents were found to be 1.00 ± 0.03 in all $Li_{1-x}CoO_{2-\delta}$ samples.

3. RESULTS AND DISCUSSION

3.1. Starting Compositions, $Li_{1-\eta}Co_{1+\eta}O_2$

Wet-chemical analyses by atomic absorption spectroscopy and redox titration (Tables 1 and 2) reveal that the $Li_{1-\eta}Co_{1+\eta}O_2$ formed in the three different batches differ slightly in their Li/Co ratio (or z values). Sample A has a composition of $LiCoO_2$ ($\eta = 0$), while samples B and C have $Li_{0.99}Co_{1.01}O_2$ ($\eta = 0.01$). As the Li/Co ratio decreases below 1, the average oxidation state of cobalt decreases from 3.00.

The X-ray powder diffraction patterns of these three samples are compared in Fig. 1. All the reflections in the three patterns could be indexed on the basis of the rhombohedral layer structure of $LiCoO_2$ (20). However, the relative intensities of a few reflections vary for the three samples. For example, the relative intensity of the (003) reflection is higher than that of the (104) reflection for

TABLE 1
Wet Chemical Analysis Data of Samples Obtained by Chlorine Oxidation

Starting composition	Reaction time (h)	Li/Co ratio $(1 - x)$ in $Li_{1-x}CoO_{2-\delta}$	Oxidation state of cobalt	Oxygen content $(2 - \delta)$	Li/Co molar ratio in filtrate
$LiCoO_2$ (sample A)	0	1.00	3.01	2.01	
	1	0.37	3.45	1.91	7.03
	2	0.31	3.36	1.83	5.34
	3	0.38	3.48	1.93	1.37
$Li_{0.99}Co_{1.01}O_2$ (sample B)	0	0.98	2.97	1.99	
	0.5	0.50	3.33	1.92	15.45
	1	0.32	3.37	1.84	15.54
	2	0.23	3.42	1.82	5.56
	3	0.34	3.41	1.88	2.77

sample A, which is in accordance with that reported for the ideal, ordered $LiCoO_2$ (20). On the other hand, the relative intensity of the (003) reflection is lower than that of the (104) reflection for samples B and C. This is indicative of the presence of some Co in the Li planes and partial disorder between Li and Co (12, 13). The intensity of the (003) reflection is sensitive to the presence of Co in the Li planes and decreases with increasing Co content in the Li planes as revealed by Rietveld analysis. The differences among the three samples seem to originate from the differences in the final cooling rate and Li/Co ratio. A faster cooling rate seems to result in incomplete ordering.

Since $LiCoO_2$ has a layer structure, one needs to consider whether preferred orientation plays a role on the intensity changes. To address this problem, X-ray diffraction patterns were also recorded with side loading and top loading of the specimen on to an aluminum holder in addition to that recorded as in Fig. 1 by loading the sample onto a glass slide with amyl acetate. Although the relative intensities of the (003) and (104) reflections for a given sample vary from one method of loading to another due to preferred orientation, the intensity ratio I_{003}/I_{104} decreases from sample A to sample B or C for a given method of loading. This clearly suggests that the degree of disorder between Li and Co increases from sample A to sample B or C. Future neutron diffraction experiments might prove useful to confirm this.

Lithium extraction with acid was carried out with all the three samples (A, B, and C) to understand the influence of starting compositions as well as disorder. Lithium extraction with chlorine was carried out with samples A and B. The extraction results are discussed in the following sections.

TABLE 2
Wet Chemical Analysis Data of Samples Obtained by Acid Treatment

Starting composition	Reaction time (h)	Li/Co ratio $(1 - x - z)$ in $Li_{1-x-z}H_zCoO_2$	Oxidation state of cobalt	Hydrogen content z in $Li_{1-x-z}H_zCoO_2$	Weight of sample (mg)	Observed Li in filtrate (mg)	Calculated Li in filtrate (mg)	Observed Co in filtrate (mg)	Calculated Co in filtrate (mg)	Observed Li/Co molar ratio in filtrate
$LiCoO_2$ (sample A)	0	1.00	3.01							
	4	0.50	3.47	0.03	499.00	23.46	23.35	102.80	96.07	1.94
	8	0.43	3.52	0.05	500.30	25.68	25.44	108.16	103.06	2.04
	17	0.37	3.54	0.08	500.20	26.92	27.01	111.00	106.87	2.06
	24	0.35	3.51	0.14	499.70	27.54	27.22	111.80	101.62	2.09
	48	0.30	3.60	0.10	499.90	28.56	28.80	117.40	112.88	2.07
$Li_{0.99}Co_{1.01}O_2$ (sample B)	0	0.98	2.98							
	4	0.34	3.43	0.22	500.00	26.85	26.94	134.33	91.51	1.70
	8	0.29	3.47	0.25	509.60	30.78	28.81	164.71	96.17	1.59
	12	0.30	3.49	0.21	496.50	27.19	27.97	137.33	97.80	1.68
	18	0.26	3.57	0.18	493.10	30.88	28.99	145.67	106.02	1.80
	24	0.26	3.57	0.18	501.10	28.41	29.46	131.98	107.74	1.83
	48	0.24	3.57	0.20	496.40	27.78	29.63	145.88	106.73	1.62
$Li_{0.99}Co_{1.01}O_2$ (sample C)	0	0.98	2.93							
	4	0.49	3.31	0.20	1000.00	47.91	44.16	220.00	141.74	1.85
	12	0.42	3.27	0.31	1000.00	53.11	47.21	235.00	127.34	1.92
	24	0.43	3.33	0.24	1000.00	55.11	47.74	242.00	148.61	1.93
	48	0.28	3.29	0.44	999.20	56.07	55.07	225.00	130.92	2.12

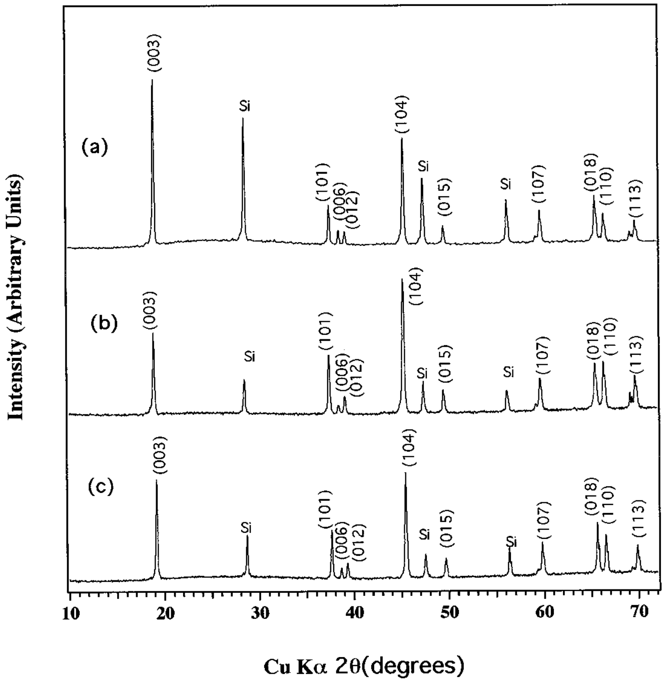

FIG. 1. X-ray powder diffraction patterns of the starting compositions, $Li_{1-\eta}Co_{1+\eta}O_2$: (a) $LiCoO_2$ obtained with a cooling rate of 1°C/min (sample A), (b) $Li_{0.99}Co_{1.01}O_2$ obtained with a cooling rate of 3°C/min (sample B), and (c) $Li_{0.99}Co_{1.01}O_2$ obtained with a cooling rate of 5°C/min (sample C).

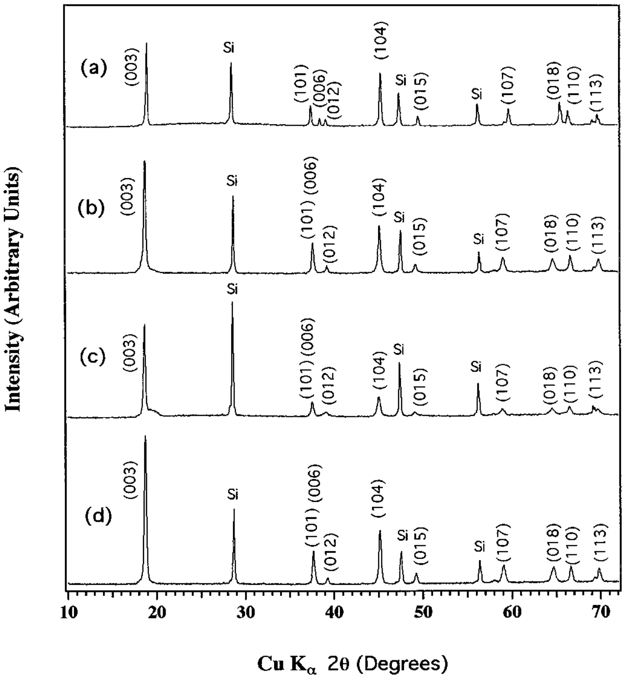

FIG. 2. X-ray powder diffraction patterns of the products obtained after oxidizing sample A with chlorine for various times: (a) before oxidation, (b) 1 h ($Li_{0.37}CoO_{1.91}$), (c) 2 h ($Li_{0.31}CoO_{1.83}$), and (d) 3 h ($Li_{0.38}CoO_{1.93}$).

3.2. Li Extraction with Chlorine

Lithium extraction from $LiCoO_2$ by oxidation with chlorine can be represented as

$$LiCoO_2 + 0.5xCl_2 \rightarrow Li_{1-x}CoO_2 + xLiCl. \qquad [1]$$

Wet-chemical analysis data of the samples obtained after oxidation with chlorine for different times are given in Table 1. The X-ray diffraction patterns of the samples are given in Figs. 2 and 3. The lithium content $(1 - x) < 1$ as well as an oxidation state of above 3+ for cobalt in the samples together with X-ray data reveal clearly that $LiCoO_2$ can be oxidized chemically with chlorine to give $Li_{1-x}CoO_2$. The data also reveals that the lithium extraction with chlorine occurs rapidly. For example, a lowest lithium content $(1 - x) = 0.23$ could be achieved with sample B in about 2 h.

The Li/Co ratios found in the filtrate after oxidation with chlorine are also given in Table 1. If the lithium extraction proceeds as in Eq. [1], then the filtrate should contain only lithium and no cobalt. The presence of a considerable amount of cobalt in the filtrate and a significant decrease in the sample mass after the oxidation reaction suggest that a dissolution of part of the cobalt from

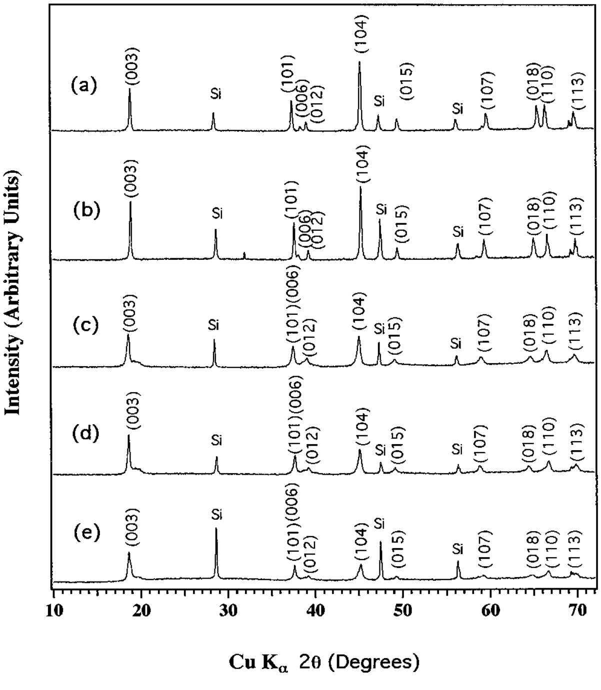

FIG. 3. X-ray powder diffraction patterns of the products obtained after oxidizing sample B with chlorine for various times: (a) before oxidation, (b) 0.5 h ($Li_{0.50}CoO_{1.92}$), (c) 1 h ($Li_{0.32}CoO_{1.84}$), (d) 2 h ($Li_{0.23}CoO_{1.82}$), and (e) 3 h ($Li_{0.34}CoO_{1.88}$).

the sample $Li_{1-x}CoO_2$ also occurs during the oxidation process. This dissolution seems to be due to the stronger oxidizing power of chlorine as well as an instability associated with the $Li_{1-x}CoO_2$ samples. The instability becomes increasingly severe with decreasing lithium content or increasing cobalt valence in the sample as indicated by a decreasing Li/Co ratio in the filtrate. Furthermore, the Li/Co ratio in the sample increases on going from 2 to 3 h of oxidation. This apparent change is due to an increasing dissolution of cobalt and a decreasing extraction of lithium as the lithium content in the sample decreases. For example, once we have reached a lowest lithium content $(1 - x) = 0.23$ in about 2 h in sample B, further reaction with chlorine results in a dissolution of more cobalt than lithium. This may result in the formation of Co vacancies at longer reaction times and future neutron diffraction studies may clarify this.

The variations of the Li/Co ratio $(1 - x)$, the average oxidation state of cobalt, and the oxygen content $(2 - \delta)$ in $Li_{1-x}CoO_{2-\delta}$ with reaction time are shown in Fig. 4 for sample B. The average oxidation state of cobalt increases initially as lithium is extracted, but becomes almost constant at longer reaction times. Also, the oxygen content decreases from 2.00 as the lithium content $(1 - x)$ in the sample decreases. This is due to the difficulty of stabilizing a higher concentration of Co^{4+} in $Li_{1-x}CoO_2$. As the Co^{4+} concentration increases, the $Co^{3+/4+}$ redox energy will approach the top of the O 2*p* energy. An overlap of the $Co^{3+/4+}$ redox couple with the O 2*p* band can result in an oxidation of O^{2-} and an evolution of oxygen. The apparent increase in the Li/Co ratio $(1 - x)$ and oxygen content $(2 - \delta)$ on going from 2 to 3 h of oxidation is due to an increasing dissolution of Co at longer reaction times, i.e., formation of Co vacancies.

The X-ray data of Figs. 2 and 3 reveal that the rhombohedral layer structure is maintained for all values of $0 \leq x \leq 0.77$ in $Li_{1-x}CoO_2$. However, the diffraction peaks broaden slightly as lithium is extracted from $LiCoO_2$, which is in accordance with what one would anticipate in "soft-chemical" methods of synthesis. Although the line broadening makes it difficult to obtain precise lattice parameters, we could clearly identify the general trend. The *a* parameters decrease with decreasing lithium content due to an increasing concentration of smaller Co^{4+}. On the other hand, the *c* parameter increases with decreasing lithium content presumably due to an increasing electrostatic repulsion between the adjacent O^{2-} layers. The opposite trends in the *a* and *c* parameters can be seen clearly, for example, by the movement of (018) and (110) reflections in the opposite directions with decreasing lithium content (Fig. 5).

It is interesting to note that the relative intensities of the (003) reflections are higher than that of the (104) reflections for all values of *x* in Fig. 2. This reveals that the ordering between the Li and Co is maintained during the lithium extraction from sample A. On the other hand, the intensity ratio between the (003) and (104) reflections vary significantly during lithium extraction from sample B (Fig. 3); i.e., the relative intensities of the (003) reflections increase and those of (104) reflections decrease as Li is extracted. With increasing extraction, the relative intensities approach a situation similar to that in sample A. This suggests that the cobalt ions present in the Li planes of sample B are extracted along with Li during the oxidation reaction; the final product with the lowest Li content $(1 - x)$ might have no cobalt in the Li planes.

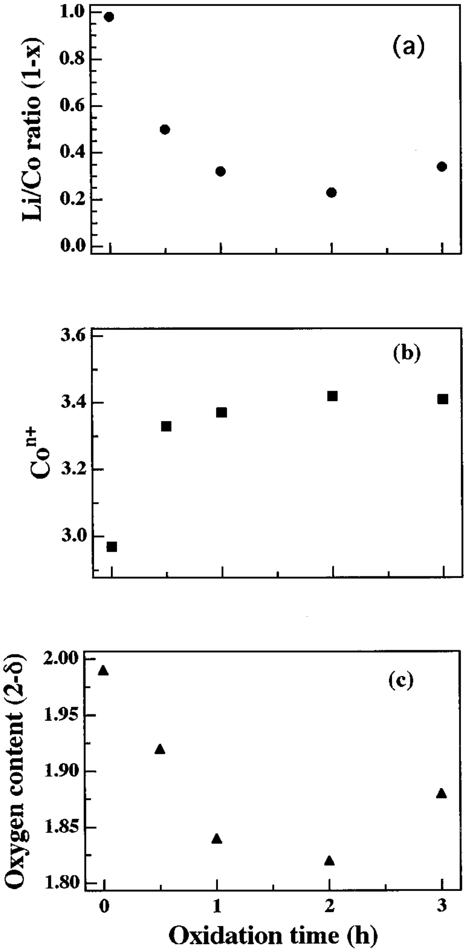

FIG. 4. Variations of (a) Li/Co ratio $(1 - x)$, (b) average oxidation state of cobalt Co^{n+}, and (c) oxygen content $(2 - \delta)$ in $Li_{1-x}CoO_{2-\delta}$ with chlorine oxidation time for sample B.

3.3. Lithium Extraction with Acid

With acid, both (i) an extraction of lithium by a disproportionation of Co^{3+} to Co^{2+} and Co^{4+} analogous to the disproportionation of Mn^{3+} to Mn^{4+} and Mn^{2+} in $LiMn_2O_4$ (17), and (ii) an ion-exchange of Li^+ by H^+ are possible:

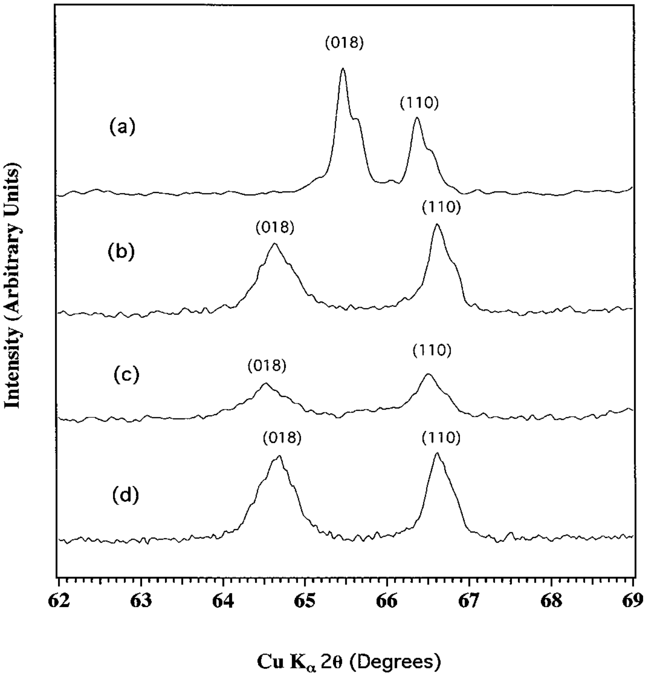

FIG. 5. Relative movements of the (018) and (110) reflections in the opposite directions showing the decrease in *a* parameter and increase in *c* parameter with chlorine oxidation time for sample A: (a) 1 h, (b) 2 h, and (c) 3 h.

$$LiCo^{3+}O_2 + 2yH_2SO_4 \rightarrow Li_{1-2y}Co^{3+}_{1-2y}Co^{4+}_{y}O_{2-2y} + yLi_2SO_4 + yCoSO_4 + 2yH_2O \quad [2]$$

$$LiCo^{3+}O_2 + 0.5zH_2SO_4 \rightarrow Li_{1-z}H_zCo^{3+}O_2 + 0.5zLi_2SO_4. \quad [3]$$

The Li_2SO_4 and $CoSO_4$ formed during the disproportionation remain in solution while the oxidized Co^{4+} remains in the solid. During ion-exchange, Li^+ in the solid is replaced by H^+ and Li_2SO_4 remains in solution.

Wet-chemical analysis data of the products obtained after extracting lithium with dilute sulfuric acid are given in Table 2 for samples A, B, and C. From the experimentally determined oxidation state of cobalt, the hydrogen contents z were calculated assuming an oxygen content of 2.00. The lithium content $(1 - x - z)$ in the sample decreases with increasing reaction time and the average oxidation state of cobalt increases with increasing lithium extraction (Fig. 6). However, the lithium extraction rate decreases with time and levels off at higher reaction times. The results clearly reveal that lithium can be extracted from $LiCoO_2$ with aqueous acids at ambient temperatures, which is in agreement with the previous literature information (12–16).

In order to establish the mechanism of lithium extraction with acid, we carefully analyzed the Li and Co contents in the filtrates in each case and the results are given in Table 2. If the lithium extraction occurs only by the disproportionation mechanism as in Eq. [2], then one would expect an Li/Co ratio of 2.00 in the filtrate. If part of the material involves an ion-exchange of Li by H, then the Li/Co ratio in the filtrate will increase above 2.00. As the degree of ion-exchange increases, the Li/Co ratio in the filtrate will increase above 2.00.

Let us first consider the results obtained with sample A that has the ideal ordered structure with an initial Li/Co ratio of 1.00. For sample A, the Li/Co ratio in the filtrates remains close to 2 suggesting that the lithium extraction occurs predominantly by disproportionation mechanism as in Eq. [2]. A slight increase above 2.00 in the Li/Co ratio in the filtrate for reaction times ≥8 h is due to the ion-exchange of a small fraction of Li by H. Furthermore, the observed amounts of lithium and cobalt in the filtrate agree closely with that calculated based on the disproportiona-

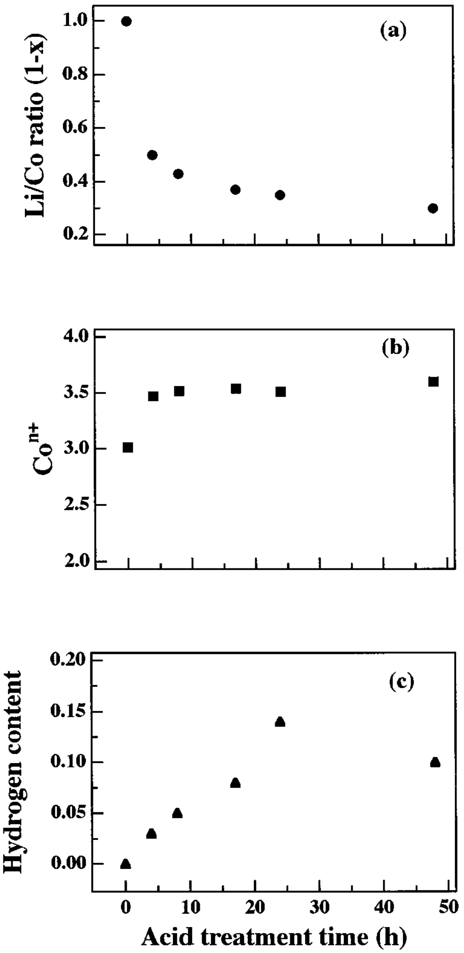

FIG. 6. Variations of (a) Li/Co ratio $(1 - x)$, (b) average oxidation state of cobalt Co^{n+}, and (c) H content z in $Li_{1-x-z}H_zCoO_2$ with acid treatment time for sample A.

tion reaction [2] and the observed degree of ion-exchange (Table 2); the details of calculations are discussed in the next paragraph. These results establish that the lithium extraction occurs by disproportionation with a small degree of ion exchange and any dissolution of the material $Li_{1-x}CoO_2$ itself in acid is small (<5%) and is negligible. A small difference between the observed and calculated amounts of Co in the filtrate could be due to the relatively larger error bar for transition metal analysis in atomic absorption spectroscopy.

The calculated values of Li and Co contents in the filtrate were obtained by the following procedure. Let us assume that lithium extraction occurs from the initial $LiCoO_2$ by a disproportionation of Co^{3+} to Co^{4+} and Co^{2+} as in reaction [2] and the solid obtained in reaction [2] undergoes an ion-exchange of Li^+ by H^+ as below:

$$\begin{aligned}&Li_{1-2y}Co^{3+}_{1-2y}Co^{4+}_{y}O_{2-2y} + 0.5\zeta H_2SO_4 \rightarrow \\ &\quad Li_{1-2y-\zeta}H_{\zeta}Co^{3+}_{1-2y}Co^{4+}_{y}O_{2-2y} + 0.5\zeta Li_2SO_4.\end{aligned} \quad [4]$$

If we wish to express the final composition as $Li_{1-x-z}H_zCoO_2$, then

$$z = 2\zeta/(2-2y) \quad [5]$$

and

$$(1-x-z) = 2(1-2y-\zeta)/(2-2y). \quad [6]$$

From Eqs. [5] and [6], expressions for y and ζ can be obtained as

$$y = x/(1+x) \quad [7]$$

and

$$\zeta = z(1-y). \quad [8]$$

The values of y and z can be calculated using Eqs. [7] and [8] and the experimental values of $(1-x-z)$ and z given in Table 2. From the values of y and ζ, the amounts of Li and Co in the filtrate can be calculated as follows:

Calculated weight of Li in filtrate by reaction [2]

$$m = \frac{(6.94)(2y)(\text{weight of sample})}{\text{molecular weight of } LiCoO_2};$$

Calculated weight of Li in filtrate by reaction [3]

$$n = \frac{(6.94)(\zeta)(\text{weight of sample})}{\text{molecular weight of } LiCoO_2};$$

Total calculated weight of lithium in filtrate =

$$(m+n);$$

Calculated weight of Co in filtrate by reaction [2]

$$p = \frac{(58.93)(y)(\text{weight of sample})}{\text{molecular weight of } LiCoO_2}.$$

The values of $(m + n)$ and p are given, respectively, as calculated Li and calculated Co in filtrate in Table 2.

Let us now consider the results obtained with samples B and C that have an initial Li/Co ratio < 1.00 and some disorder between Li and Co. We see that the results differ from that obtained with sample A. With samples B and C, the Li/Co ratio in the filtrate is generally <2.00 (Table 2) even though there is a considerable concentration of H in the final material; as the H content increases, the Li/Co ratio in filtrate can become >2 due to additional Li going in to filtrate by ion exchange. Also, the amount of cobalt in the filtrate is much higher than that calculated based on the ideal disproportionation reaction [2] and the observed degree of ion-exchange. This suggests that some amount of cobalt goes into solution by other mechanisms in addition to the ideal disproportionation reaction [2]. One possibility is an extraction of cobalt instead of lithium from the solid, which can be assisted by the disproportionation of Co^{3+} to Co^{2+} and Co^{4+}. This can become particularly feasible if some Co^{2+} is present in the solid and/or if some Co is present in the lithium planes. For example, the extraction of cobalt may compete with the extraction of lithium as the Li/Co ratio in the initial material decreases from 1 and/or as the disorder between Li and Co increases. Once the extraction of some Li from the Li planes begins, the binding of Co in the Li planes will become weaker and weaker resulting in an easier extraction of Co than that of Li. For example, extraction of Co^{2+} instead of Li^+ from $Li_{1-\eta}Co_{1+\eta}O_2$ can be represented analogously to Eq. [2] as

$$\begin{aligned}&Li_{1-\eta}Co^{3+}_{1-\eta}Co^{2+}_{2\eta}O_2 + 2yH_2SO_4 \rightarrow \\ &\quad Li_{1-\eta}Co^{3+}_{1-\eta-2y}Co^{4+}_{y}Co^{2+}_{2\eta-y}O_{2-2y} \\ &\quad + 2yCoSO_4 + 2yH_2O.\end{aligned} \quad [9]$$

A similar equation can also be written if Co^{3+} instead of Co^{2+} is extracted.

The above conclusion is supported by the fact that the relative intensities of the (003) reflections increase and those of (104) reflections decrease as Li is extracted from samples B and C similar to that in Fig. 3. But such a change in intensity does not occur with sample A and it is similar to that in Fig. 2. The *a* and *c* lattice parameters vary with lithium extraction similar to that found with chlorine oxidation.

Furthermore, the disordered samples B and C lead to a higher proton content in the final product compared to

TABLE 3
Wet Chemical Analysis Data of Samples Obtained with Different Oxidizing Agents

Starting composition	Oxidant	Reaction time (h)	Li/Co ratio $(1-x)$ in $Li_{1-x}CoO_{2-\delta}$	Oxidation state of cobalt	Oxygen content $(2-\delta)$
$LiCoO_2$ (sample A)	None	0	1.00	3.01	2.01
	I_2	65	0.91	3.09	2.00
	Br_2	65	0.47	3.47	1.97
	Cl_2	2	0.31	3.36	1.83

the ordered sample A. Our investigation clarifies some of the variations found in the recent literature data (12–16) on the acid treatment of $LiMO_2$ oxides. Although the lithium extraction proceeds by a disproportionation of M^{3+} to M^{4+} and M^{2+}, the amount of M = Co going into solution depends strongly on the initial stoichiometry (Li/Co ratio) as well as the ordering between Co and Li in the initial material. As the initial Li/Co ratio decreases below 1 and/or the disorder between Li and Co increases, the amount of cobalt in the solution increases due to a competing extraction of Co with Li from the Li planes; i.e., the Li/Co ratio in the filtrate decreases below the expected ideal value of 2.00. A competing extraction of Co with Li from the Li planes will lead to the presence of a higher concentration of Li in the solid at shorter times, which seems to result in a higher degree of ion exchange of Li^+ by H^+. The presence of H^+ in the low-temperature samples compared to the high-temperature samples of the investigation of Morales *et al.* (14) could well be due to the possible disorder in the low-temperature material.

3.4. Oxidizing Power and Degree of Lithium Extraction

Oxidation of sample A was carried out with bromine and iodine, in addition to that with chlorine, in order to correlate the degree of lithium extraction with the oxidation potentials of the reagents. Our results with the three oxidizing agents are compared in Table 3. The amount of lithium x that can be extracted to give $Li_{1-x}CoO_2$ increases from 0.09 for I_2 to 0.53 for Br_2 and to 0.69 (sample A) or 0.77 (sample B) for Cl_2. The oxidation reactions were carried out for 65 h to ensure equilibration with fivefold excess of Br_2 and I_2. In the case of Cl_2, the maximum amount of lithium that could be extracted is found to be 0.69 for sample A from Table 1 and that is listed in Table 3. As we see, the degree of lithium extraction increases with increasing oxidizing power.

In Fig. 7, the reduction potentials of the three oxidizing agents are compared with the $Co^{3+/4+}$ redox potential in $Li_{1-x}CoO_2$. The $Co^{3+/4+}$ redox potentials were obtained from the published electrochemical data of a $Li/Li_{1-x}CoO_2$ cell (3) and are expressed with respect to the normal hydrogen electrode (NHE). The reduction potential for iodine lies below the $Co^{3+/4+}$ potential in $LiCoO_2$ and iodine is not expected to extract lithium from $LiCoO_2$. However, we are able to extract 0.09 lithium with fivefold excess of I_2. A large excess of the oxidized species I_2 present under our experimental conditions may shift the reduction potential to a higher value and force the extraction of some lithium. The amounts of lithium that can be extracted with Br_2 and Cl_2 are comparable to that expected from their reduction potentials.

Finally a comparison of the $Co^{3+/4+}$ potentials in $LiCoO_2$ and $NaCoO_2$ and a correlation of them to the degree of lithium or sodium extraction with a given oxidizing agent can also be made. The $Co^{3+/4+}$ potentials obtained from the published electrochemical data of a $Na/Na_{1-x}CoO_2$ cell (7) are also given in Fig. 7. For a given value of x in $A_{1-x}CoO_2$(A = Li or Na), the $Co^{3+/4+}$ potential has a higher value in the lithium compound than in the sodium compound. A larger ionicity of the Na–O bonds seems to increase the covalency of the Co–O bonds through inductive effect and lower the $Co^{3+/4+}$ potential in $NaCoO_2$, despite a larger a lattice parameter of $NaCoO_2$ compared to that of $LiCoO_2$.

Since the $Co^{3+/4+}$ potential in $NaCoO_2$ lies below that in $LiCoO_2$, the former should be easier to oxidize than latter; i.e., with a given oxidizing agent, one should be able to extract more sodium from $NaCoO_2$ than lithium from $LiCoO_2$. Indeed, the results of Miyazaki *et al.* (7, 8) that

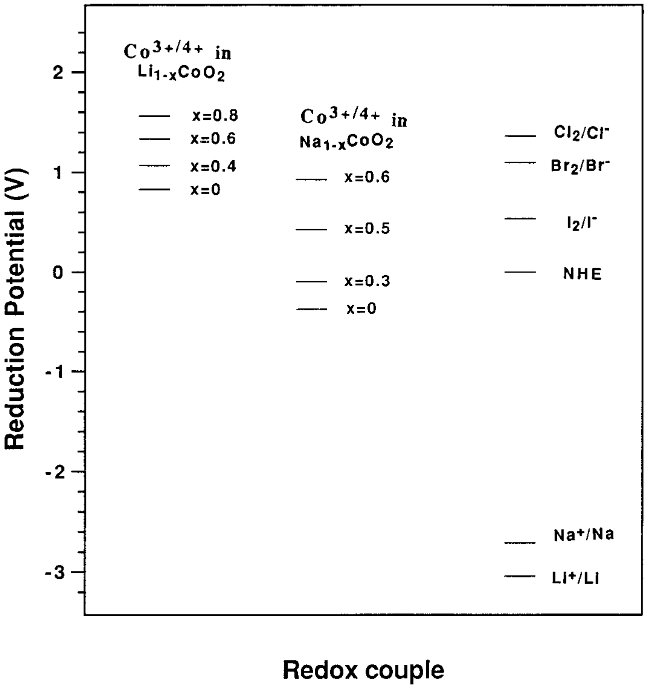

FIG. 7. Comparison of the reduction potentials of various oxidizing agents with the $Co^{3+/4+}$ redox couple in $Li_{1-x}CoO_2$ and $Na_{1-x}CoO_2$ at different values of x.

about half of the sodium can be extracted with iodine from $NaCoO_2$ while no lithium could be extracted with iodine are in accordance with this expectation.

4. CONCLUSIONS

Chemical extraction of lithium from layered $LiCoO_2$ with various oxidizing agents such as Cl_2, Br_2, and I_2, as well as with dilute sulfuric acid, has been investigated systematically. We arrive at the following conclusions:

1. The ordering between the Li^+ and Co^{3+} ions in the initial samples of $Li_{1-\eta}Co_{1+\eta}O_2$ depends strongly on the Li/Co ratio and the final cooling rate. A cooling rate of 1°C/min gives an ordered material while a cooling rate of $\geq$3°C/min introduces considerable disorder with a Li/Co ratio $<$1.00.

2. $LiCoO_2$ can be oxidized with chlorine to give $Li_{1-x}CoO_{2-\delta}$ at ambient temperatures. However, a stronger oxidizing power of Cl_2 and a relative instability associated with the Li-extracted $Li_{1-x}CoO_{2-\delta}$ leads to a dissolution of a considerable amount of sample. A deeper lithium extraction also leads to an evolution of oxygen and so to some oxygen deficiency δ in the final material $Li_{1-x}CoO_{2-\delta}$.

3. Lithium extraction with aqueous acid from $LiCoO_2$ proceeds by a disproportionation of Co^{3+} to Co^{2+} and Co^{4+} analogous to that found with the spinel $LiMn_2O_4$ (17). A Li/Co ratio $<$1, as well as a disorder between Li and Co in the initial material, leads to a competition of Co extraction with Li extraction and a relatively higher degree of ion-exchange of Li^+ by H^+.

4. Li extraction with both Cl_2 and acid results in a decrease in the *a* lattice parameter and an increase in the *c* parameter. Li extraction in both the cases also leads to a removal of any cobalt that may be present in the Li planes. This may be particularly useful to obtain improved electrode materials for rechargeable lithium batteries because any Co that is present in the Li planes of the electrode will degrade cyclability and performance. $Li_{1-x}CoO_2$ may first be prepared by chemical extraction of lithium and then used as cathode without requiring the initial charging step.

5. The amount of lithium that can be extracted with different oxidizing agents increases with increasing oxidizing power, following the trend of their oxidation potentials. Also, a relatively lower potential associated with the $Co^{3+/4+}$ couple in $Na_{1-x}CoO_2$ compared to that in $Li_{1-x}CoO_2$ makes the extraction of Na from $NaCoO_2$ easier than the extraction of Li from $LiCoO_2$.

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