Oxygen Vacancies and Intermediate Spin Trivalent Cobalt Ions in Lithium-Overstoichiometric $LiCoO_2$

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Thermal treatments under a very wide range of oxygen pressures were used to probe the composition and defect nature of a lithium-overstoichiometric "$Li_{x_0}CoO_2$" ($x_0 > 1$) sample using X-ray powder diffraction, ^{7}Li NMR, and electrochemical tests. It was found that at 900 °C, under atmospheric and elevated oxygen pressures, the lithium-overstoichiometric sample gradually transformed to stoichiometric $LiCoO_2$ by losing excess lithium in the form of Li_2O. In addition, it was shown that the defect associated with Co^{2+} and oxygen deficiency as reported by Gorshkov et al. and Karelina et al. had a different NMR signature than that present in Li-overstoichiometric samples. Therefore, it is believed that oxygen vacancies are present but Co^{2+} ions are not present in $Li_{x_0}CoO_2$ ($x_0 > 1$). This leads to a formula $[Li]_{interslab}[Co^{III}_{1-3t}Co^{3+(IS)}_{2t}Li_t]_{slab}[O_{2-t}]$, involving an intermediate spin configuration for 2t Co^{3+} ions in a square-based pyramidal site. This new model was supported by the NMR and magnetic data of the lithium-overstoichiometric sample and its deintercalated compounds. The effect of the defect on the end-of-discharge voltage profile during cycling was also discussed.

Introduction

The properties of $LiCoO_2$, the most widely used positive electrode material for commercial Li-ion batteries, have been studied extensively [1−7] (and references therein). Its structure belongs to the trigonal system (space group R-3*m*) with a layered $\alpha-NaFeO_2$-type framework in which Co and Li planes alternate in the AB CA BC packing of the oxygen layers.[8] Li-overstoichiometry in $LiCoO_2$ was first mentioned by Carewska et al.,[9] and we addressed the question in a previous paper,[10] as briefly recalled hereafter. We observed that the ^{7}Li NMR spectra and the galvanostatic charge/discharge curves are very dependent on the Li/Co ratio used for the high-temperature synthesis. In effect, ^{7}Li MAS NMR spectra exhibit new signals in addition to the one at 0 ppm (corresponding to diamagnetic low spin Co^{3+} ions), suggesting the presence of paramagnetic cobalt ions, with unpaired electron in the e_g orbital. We also showed that the galvanostatic charge curves of batteries with "$Li_{x_0}CoO_2$" ($x_0 > 1.0$, x_0 being the actual Li/Co ratio in the material, as determined by chemical analysis) do not exhibit the two-phase domain for $0.75 \leq x \leq 0.94$ nor the trace of the monoclinic distortion at $x = 0.50$, which both occur for lithium deintercalation from stoichiometric $Li_{1.0}CoO_2$. Furthermore, our neutron diffraction study excluded the presence of lithium ions in the tetrahedral sites of the layered structure, and HRTEM experiments showed the absence of stacking faults. Thus, we hypothesized the presence of structural defects involving low spin Co^{2+} ions and a simultaneous cobalt and oxygen deficiency leading to a chemical formula close to $[Li]_{interslab}[Co_{1-t}Li_t]_{slab}[O_{2-\delta}]$ in order to account for the actual stoichiometry (determined by chemical analyses) and the global electroneutrality. High spin Co^{2+} ions were excluded because the NMR signal showed a first/second neighbor pattern characteristic of e_g single electrons. For HS Co^{2+} ions, the hole in the t_{2g} orbital would simply prevent observation of the adjacent (first neighbor) Li ions, like for localized

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Co^{4+} ions in deintercalated $LiCoO_2$,[6] and would not lead to additional signals such as those observed. The low spin configuration, however, can be considered rather unusual for octahedral divalent cobalt ions in an oxygen lattice. Still, the existence of divalent cobalt ions in this kind of material had already been hypothesized in the literature, without detail on the actual spin state and environment of these species.[9,11] Recently, Imanishi et al. performed an accurate titration of the cobalt oxidation state in various $Li_{x_0}CoO_2$ ($x_0 \geq 1.0$) samples and concluded that only Co^{3+} ions are present in the Li-overstoichiometric $Li_{x_0}CoO_2$ phases, with a solid solution limit close to $x_0 = 1.08$. Furthermore, they showed that heat-treatment under relatively high oxygen pressure (10 MPa) has no effect on the structural defects, with no observable change in either the Li NMR spectra or the shape of the galvanostatic curve.[5] Simultaneously, Gorshkov and Karelina showed that it is possible to extract oxygen from $LiCoO_2$ by a heat-treatment under reduced O_2 partial pressure ($P_{O_2} = 10^2$ Pa). On the basis of electrical and magnetic properties measurements, they concluded that Co^{2+} ions and O vacancies are predominant defects in such samples.[12,13] However, their study does not give any information as to the electrochemical behavior or the ^7Li NMR signature of these materials.

To clarify the ambiguity in whether Co^{2+} is present in the lithium-overstoichiometric samples, we here use the following three thermal treatments to probe the composition and defect nature of lithium-overstoichiometric samples monitored by X-ray powder diffraction and ^7Li NMR. First, we study the relative thermodynamic stability of stoichiometric $LiCoO_2$ and lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples by extended periods of annealing at 900 °C under atmospheric pressure oxygen flow. Second, we are interested in understanding the effect of heat-treatments under very high oxygen pressures on lithium-overstoichiometric samples. In this study, we select significantly higher temperature and oxygen pressures (100 MPa at 700 °C and 5 GPa at 900 °C) than those used by Imanishi et al.[5] to examine whether such treatments have any effect on the lithium overstoichiometry. Third, it is of interest to compare the lithium-overstoichiometric samples with the oxygen-deficient $LiCoO_{2-\delta}$ samples obtained by heat-treating $LiCoO_2$ under a reduced O_2 partial pressure, in which the presence of divalent cobalt was assumed.[12,13] We have therefore attempted to remove oxygen from $LiCoO_2$ by using titanium as getter.

Findings from these thermal treatments will be combined with magnetic data of $LiCoO_2$, lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$), and slightly deintercalated Li_xCoO_2 ($x_0 > 1$) samples. A novel defect model will be proposed which, for the first time, provides a consistent explanation of structural, magnetic and NMR data of lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$). Finally, the effect of Li-overstoichiometry on the electrochemical cycling behavior will be shown.

Experimental Section

The stoichiometric $LiCoO_2$ and lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples were prepared by heat-treating a mixture of Li_2CO_3 and Co_3O_4 with a starting Li/Co ratio of 1.0 and 1.10 under atmospheric O_2 flow at 600 °C for 12 h with two subsequent treatments at 900 °C for 24 h, respectively.[10] In agreement with the report by Imanishi et al.,[5] the $Li_{x_0}CoO_2$ sample with a starting Li/Co ratio of 1.1 had an x_0 value close to 1.08.

In the prolonged annealing experiment, the $LiCoO_2$ and $Li_{1.08}CoO_2$ samples were heat-treated in a gold crucible under atmospheric O_2 flow at 900 °C for 5 to 10 days, with a cooling rate of 2 °C/min to examine their relative thermodynamic stability.

In addition, the $Li_{1.08}CoO_2$ sample was thermally treated under two different elevated oxygen pressures, 100 MPa and 5 GPa. In the first case, the $Li_{1.08}CoO_2$ powder sample was placed into a gold tube and heated at 700 °C for 12 h with a cooling rate of 3 °C/min in a pressured reaction vessel under 100 MPa pressure of oxygen. In another experiment, a 200-mg mixture of 10% $KClO_3$ and 90% $Li_{1.08}CoO_2$ in weight was loaded into a platinum crucible and heat-treated at 900 °C for 0.5 h with a cooling rate of 75 °C/min using a belt apparatus. This equipment constitutes two anvils and one die (in tungsten carbide). Inside the die, the reaction cell includes the micro furnace (graphite) and the crucible (platinum) surrounded by a pressure-transmitting medium (pyrophyllite). The pressure is generated by a press (Remiremont) of 1000 tons.[14] $KClO_3$ is thus decomposed and produces a high oxygen pressure in the crucible. The reaction product was washed by deionized water, and the washing solution was analyzed for lithium by atomic emission spectroscopy.

Moreover, an oxygen-deficient $LiCoO_{2-\delta}$ sample was synthesized by annealing the stoichiometric $LiCoO_2$ sample under a reduced O_2 pressure. The stoichiometric $LiCoO_2$ powder was placed in an alumina crucible, the crucible was introduced into a silica tube containing metallic Ti powder, and the tube was then sealed under vacuum and heated at 800 °C for 48 h. The amount of Ti was such that the final composition of the sample would be $LiCoO_{1.95}$, should all the Ti present transform into TiO_2.

The XRD patterns of stoichiometric, lithium-overstoichiometric, and various thermally treated samples were collected using a Siemens D5000 powder diffractometer with Cu kα radiation and a graphite diffracted beam monochromator. To detect trace impurity phases, such as Co_3O_4 and Li_2CO_3, XRD patterns were also systematically recorded using an INEL CPS120 diffractometer in a Debye−Scherrer configuration with Co kα_1 radiation.

Electrochemical charge/discharge experiments were performed on $Li/LiClO_4$−PC (propylene carbonate)/Li_xCoO_2 cells at 22 °C. The positive electrode consisted of a mixture of 88 wt % active material (roughly 30 mg), 2 wt % of polytetrafluorethylene (PTFE), and 10 wt % of carbon black. The cells were assembled in an argon-filled drybox and were charged/discharged at a C/100 rate to examine the shape of the voltage profile. For cycling tests, a C/20 regime was used.

For magnetic measurements, slightly deintercalated lithium-overstoichiometric materials (removal of 0.025 and 0.05 Li per formula) were prepared using lithium cells charged at the C/1000 rate, in which the positive electrode was prepared by pressing 200 mg of $Li_{1.08}CoO_2$ powder into an 8-mm-diameter pellet under a 3 ton pressure. The deintercalated pellet samples were subsequently recovered in an argon-filled drybox, washed in dimethyl carbonate, and dried under vacuum. Magnetic susceptibility data of stoichiometric, overstoichiometric, and slightly deintercalated overstoichiometric samples were collected on a Quantum Design MPMS-5S magnetometer in the range of 5 to 340 K with a magnetic field of 5000 G.

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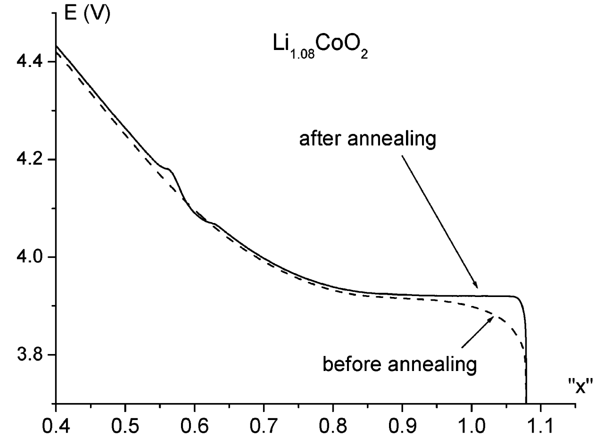

Figure 1. First galvanostatic charge of Li//Li$_x$CoO$_2$ ($x_0 = 1.08$) electrochemical cells before (dashed line) and after (solid line) 10 days annealing (J = 100 μA·cm^{-2}; m_{LiCoO_2} = 30 mg, approximately C/100). Note that the x_0 value for the 10 days annealed Li$_{x_0}$CoO$_2$ ($x_0 = 1.08$) phase is in fact close to 1 (see text).

^{7}Li MAS NMR spectra were recorded on a Bruker Avance 500 spectrometer at 193.7 MHz, with a standard 4-mm Bruker MAS probe. The samples were mixed with dry silica (typically 50% in weight) to facilitate the spinning and improve the field homogeneity, and the mixture was introduced into a 4-mm zirconia rotor in the drybox. A Hahn echo sequence [$t_{\pi/2}-\tau_1-t_{\pi}-\tau_2$] was utilized in order to facilitate the phasing of all the signals and their spinning sidebands and to ensure the observation of possibly very wide signals which would be lost during the receiver dead time in single pulse experiments. The 90° pulse duration used ($t_{\pi/2}$) was equal to 2.1 μs, and the spinning speed (ν_r) was 15 kHz. To synchronize the spin−echo with the first rotational echo, τ_1 was fixed to the rotor period $T_r = 1/\nu_r$. A spectral width of 500 kHz was used, and the recycle time D_1 = 2 s was checked to be long enough to avoid T_1 saturation effects. The isotropic shifts reported in parts per million are relative to an external sample of 1 M LiCl solution in water.

Results and Discussion

X-ray diffraction analyses showed that both as-prepared stoichiometric and lithium-overstoichiometric samples were single-phase pure, and Rietveld refinements revealed that they had nearly identical structural parameters, as reported previously.[10]

Thermodynamic Stability of LiCoO$_2$ and Li$_{x_0}$CoO$_2$ (x_0 > 1) Phases. The stoichiometric LiCoO$_2$ samples before and after an additional thermal treatment at 900 °C under atmospheric O$_2$ flow for 5 days were examined by XRD, ^{7}Li MAS NMR, and electrochemical measurements. No change was revealed in the XRD patterns, the NMR spectra, or the voltage profiles of Li/LiCoO$_2$ cells, which suggests that LiCoO$_2$ is thermodynamically stable at 900 °C in O$_2$.

Also, no changes were observed in the XRD patterns and refined structural parameters of the lithium-overstoichiometric Li$_{1.08}$CoO$_2$ sample before and after an additional thermal treatment at 900 °C under atmospheric O$_2$ pressure for 10 days. However, electrochemical measurements revealed that the Li$_{1.08}$CoO$_2$ sample transformed to a nearly stoichiometric LiCoO$_2$ under such conditions. The voltage profiles of lithium cells containing Li$_{1.08}$CoO$_2$ before and after the extended thermal treatment are shown in Figure 1. The monotonic voltage increase upon charge, characteristic of lithium-overstoichiometric samples, was changed to the presence of a 3.93 V plateau and a voltage feature at x = 0.5, characteristic of stoichiometric LiCoO$_2$ upon deintercalation.[1−3,6,10] Furthermore, the existence of a two-phase domain at 3.93 V, similar to stoichiometric LiCoO$_2$, was confirmed by XRD analyses. It should be pointed out that the lithium content of the annealed lithium overstoichoimetric Li$_{1.08}$CoO$_2$ sample was considered to be $x_0 = 1.08$ so that the monoclinic transition associated with the voltage feature does not occur at exactly $x = 0.5$ in Figure 1. In addition, it was found that the additional thermal treatment considerably suppressed the paramagnetic signals at 185, 3, −6, −16, and −40 ppm in the ^{7}Li MAS NMR spectra of the Li$_{1.08}$CoO$_2$ sample before and after the additional thermal treatment, as shown in Figure 2. The NMR spectrum of the thermally treated Li$_{1.08}$CoO$_2$ sample resembles that of stoichiometric LiCoO$_2$, which suggests that in first approximation only diamagnetic Co^{3+} ions are present. This is clearly due to the long annealing performed because the decrease in the magnitude of the additional paramagnetic signals was smaller for shorter annealing durations.

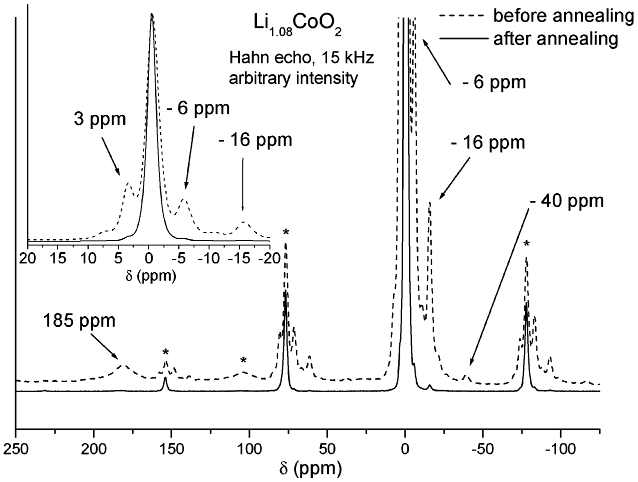

Figure 2. ^{7}Li MAS NMR spectra for the Li$_{1.08}$CoO$_2$ material before (dashed line) and after (solid line) annealing for 10 days (spinning speed = 15 kHz, * = spinning sidebands).

Both electrochemical and NMR data, therefore, indicated that lithium-overstoichiometric Li$_{x_0}$CoO$_2$ (x_0 > 1) was thermodynamically unstable and it slowly transformed to stoichiometric LiCoO$_2$ upon additional thermal treatments. It is believed that excess lithium and associated structural defects in Li$_{x_0}$CoO$_2$ (x_0 > 1) were removed in the form of Li$_2$O that was sublimated at 900 °C. Similar observations were found in Li$_{x_0}$Co$_{1-y}$Mg$_y$O$_2$ (x_0 > 1) samples upon long heat-treatments, in which a complete decomposition to LiCoO$_2$ and MgO occurred.[15]

Stability of Lithium-Overstoichiometric Li$_{x_0}$CoO$_2$ (x_0 > 1) Under Elevated Oxygen Pressures. To examine whether Co^{2+} ions are present in the Li$_{x_0}$CoO$_2$ (x_0 > 1) sample, Li$_{1.08}$CoO$_2$ was treated under two elevated oxygen pressures, 100 MPa and 5 GPa. No significant changes in either the XRD patterns or the NMR spectra were noted after treatments under 100 MPa at 700 °C.

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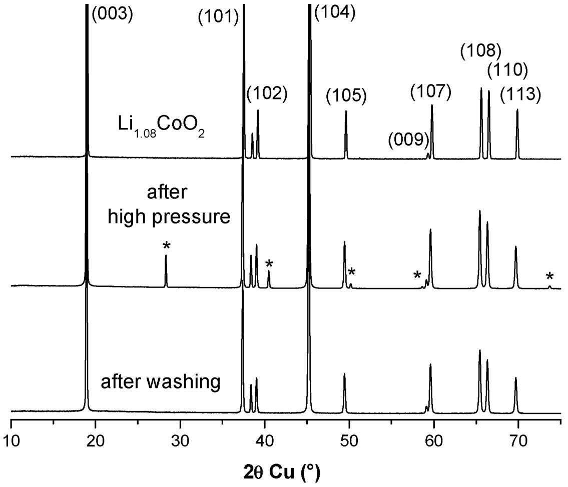

Figure 3. X-ray powder diffraction patterns of the as-prepared $Li_{1.08}CoO_2$ sample before the high-pressure experiment, the high-pressure reaction product before washing, and the same after washing. The asterisks denote KCl reflections.

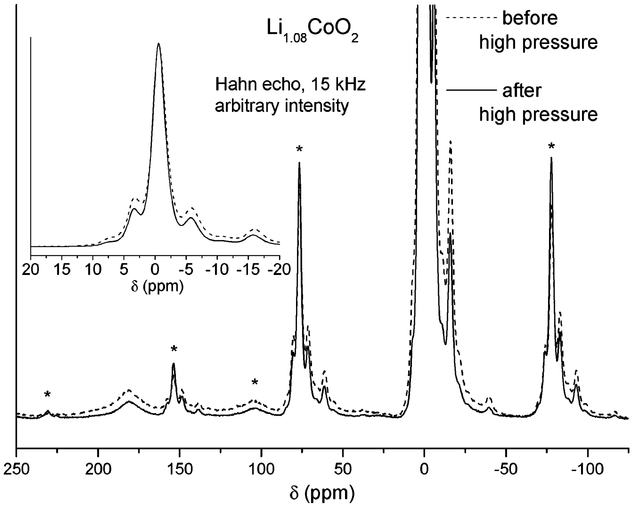

Figure 4. ^7Li MAS NMR spectra for the $Li_{1.08}CoO_2$ materials before (dashed line) and after (solid line) a 5 Gpa oxygen pressure treatment (spinning speed = 15 kHz, * = spinning sidebands).

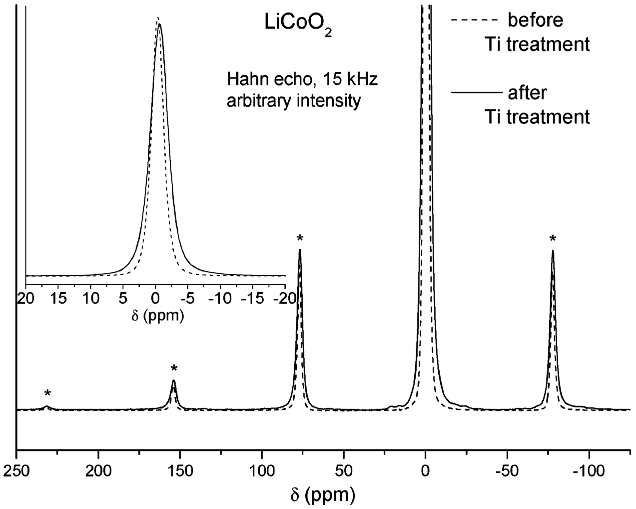

Figure 5. ^7Li MAS NMR spectra for the $LiCoO_{2-\delta}$ material compared to that of stoichiometric $LiCoO_2$ (spinning speed = 15 kHz, * = spinning sidebands).

Figure 3 shows the XRD patterns of $Li_{1.08}CoO_2$ before and after the thermal treatment under 5 GPa at 900 °C. KCl is clearly visible after the high-pressure experiment, originating from the decomposition of $KClO_3$; it was removed by washing the resulting material, with no change of the XRD pattern of the material. As shown in Figure 4, ^7Li NMR analysis revealed a significant decrease in the relative magnitude of all the paramagnetic signals in the high-pressure treated sample. This result is consistent with either of the two following hypotheses for the effect of the high oxygen pressure experiment: (i) Co^{2+} ions were initially present and were oxidized, or (ii) excess lithium ions were removed. A lithium amount corresponding to 20−30% of the excess lithium in the $Li_{1.08}CoO_2$ sample was detected in the washing solution by atomic emission spectroscopy, whereas it was checked that no significant amount of Li was detected by washing the $Li_{1.08}CoO_2$ sample itself. It is therefore believed that excess lithium in the form of Li_2O was removed under an oxygen pressure of 5 Gpa at 900 °C, similarly to what takes place during extensive heat-treatments of $Li_{x_0}CoO_2$ ($x_0 > 1$) under atmospheric oxygen pressure at 900 °C. In the high-pressure case however, the reaction occurs in a sealed crucible, so that the extracted Li can be analyzed after washing the sample. One can note that Li extraction occurs rather rapidly during the short time high-pressure experiment. Indeed, it is expected that high pressure favors this phenomenon, because it leads to a material without oxygen vacancies, and therefore with a smaller volume.

It thus appears that the paramagnetic cobalt species in the $Li_{x_0}CoO_2$ ($x_0 > 1$) samples cannot be oxidized under high oxygen pressures, which implies that they are very stable and they are most likely trivalent cobalt ions, rather than divalent ones associated to oxygen vacancies.

Stability of Stoichiometric $LiCoO_2$ Under Reduced Oxygen Pressure. A stoichiometric $LiCoO_2$ sample was treated at 900 °C in the presence of titanium, to obtain an oxygen-deficient $Li_xCoO_{2-\delta}$ material, which is expected to contain Co^{2+} ions as suggested by Gorshkov and Karelina.[12,13] The characteristics of this material were compared with those of lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$). No significant difference was found among the X-ray diffraction patterns or the refined structural parameters of stoichiometric $LiCoO_2$, $LiCoO_{2-\delta}$ obtained under reduced oxygen pressure, and lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples. The charge voltage profile of an $Li/Li_xCoO_{2-\delta}$ cell was similar to that of cells containing stoichiometric $LiCoO_2$ but different from those of lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$). In addition, the NMR spectrum of the $LiCoO_{2-\delta}$ sample resembled that of $LiCoO_2$ but for a slight increase in the line width of the central signal, as shown in Figure 5. In particular, the paramagnetic signals at 185, 3, −6, −16, and −40 ppm, characteristic of lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples, were not present in the spectrum of the oxygen deficient $LiCoO_{2-\delta}$. Therefore, it is believed that the amount of defects present in the oxygen-deficient $LiCoO_{2-\delta}$ is small, and that their nature is intrinsically different from that associated with excess lithium in $Li_{x_0}CoO_2$ ($x_0 > 1$). This result shows that, at 900 °C, it is

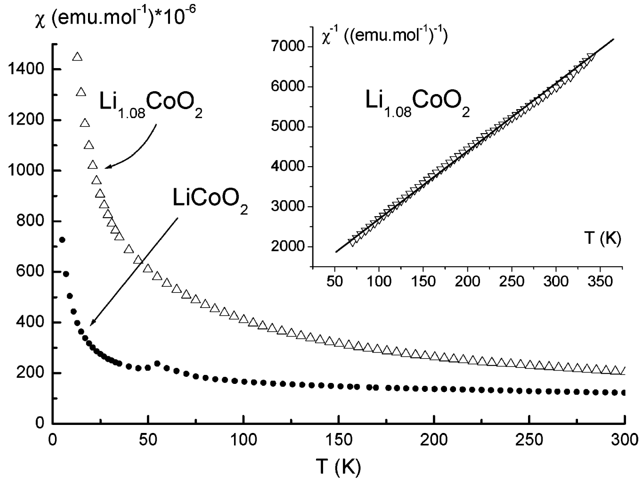

Figure 6. Thermal evolution of the molar magnetic susceptibility for the $Li_{x_0}CoO_2$ (x_0 = 1.0 and 1.08) phases. The reciprocal of the magnetic susceptibility corrected from the TIP for the $Li_{1.08}CoO_2$ phase is plotted in the inset.

very difficult to reduce the low spin trivalent Co ions in $LiCoO_2$, and therefore supports further the conclusion of the previous section that divalent cobalt ions were not present in the lithium-overstoichiometric sample.

Magnetic Measurements. The molar magnetic susceptibility data of the $LiCoO_2$ and $Li_{x_0}CoO_2$ ($x_0 > 1$) samples are plotted as a function of temperature in Figure 6. The magnetic susceptibility of $LiCoO_2$ is low and practically temperature independent, which is attributed to Van Vleck-type paramagnetism associated with diamagnetic Co^{3+} ions in the layered structure, in agreement with the report by Kikkawa et al.[16] It should be mentioned that the deviation in the magnetic susceptibility at 50 K resulted from the paramagnetism of O_2 present in the sample holder. In contrast, $Li_{1.08}CoO_2$ exhibits a typical Curie−Weiss behavior for $T > 100$ K. The magnetic susceptibility χ can then be expressed as a function of $^1/_T$:

$$\chi = \frac{C}{T} + N\alpha$$

where C is the Curie constant and $N\alpha$ is the correction that is applied to take into account the temperature independent paramagnetism (TIP) at high temperatures. The $N\alpha$ value was obtained by extrapolating χ to $^1/_T = 0$ in the plot of χ as a function of $^1/_T$. The reciprocal of the TIP-corrected magnetic susceptibility is plotted against T in the insert of Figure 6. A linear fit of all the data points above $T = 200$ K leads to a Curie constant, $C_{exp.} = 0.08$.

The molar magnetic susceptibility data of $Li_{1.08}CoO_2$ and slightly deintercalated Li_xCoO_2 ($x_0 = 1.08$) samples (removal of 0.025 and 0.05 lithium per formula) are compared in Figure 7. The reciprocal of the TIP-corrected magnetic susceptibility is plotted against T in the figure insert, in the temperature range 220−340 K from which the Curie constant was determined. Although the magnetic susceptibility values were found to increase upon initial lithium removal, it should be noted that the Curie constant decreased.

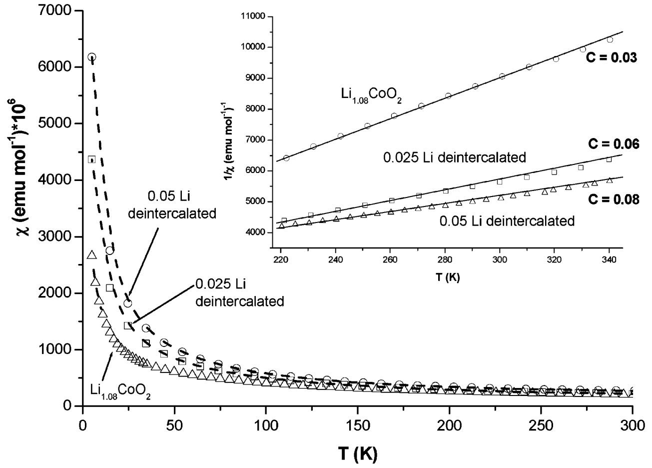

Figure 7. Molar magnetic susceptibilities of $Li_{1.08}CoO_2$ and slightly deintercalated compounds (removal of 0.025 Li (squares) and of 0.05 Li (circles)) as a function of temperature. The Curie constants of these compounds determined from the $^1/_\chi$ vs T plot, as shown in the insert, are indicated.

Proposal of an Intermediate Spin Co^{3+} Defect Model. In this study, it was shown by heat-treatments for extended periods of time that $LiCoO_2$ is thermodynamically stable with respect to $Li_{x_0}CoO_2$ ($x_0 > 1$) at 900 °C. It is believed that lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples gradually transform to stoichiometric $LiCoO_2$ by losing excess lithium in the form of Li_2O. In addition, the decrease of NMR paramagnetic signals and loss of 20%−30% excess lithium in the $Li_{1.08}CoO_2$ sample after the 5 Gpa oxygen pressure treatment at 900 °C support the fact that the defect cannot be oxidized, and is partially suppressed by loosing Li_2O, even under very high oxygen pressure. Moreover, it was found that the defect (if any) related to the existence of Co^{2+} ions due to oxygen removal from stoichiometric $LiCoO_2$ is different from that in Li-overstoichiometric $LiCoO_2$.

These results suggest the presence of only trivalent cobalt ions in $Li_{x_0}CoO_2$ ($x_0 > 1$), rather than divalent cobalt ions as proposed earlier.[10] This is consistent with recent titration results that the average cobalt oxidation state of $Li_{x_0}CoO_2$ ($x_0 > 1$) samples is +3.[5] Considering also that no extra Li was found in the tetrahedral site,[10] it is believed that the lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples have a formula $[Li]_{interslab}[Co_{1-t}Li_t]_{slab}[O_{2-t}]$, ($t = (x_0 - 1)/(x_0 + 1)$) in which all the cobalt ions are trivalent and the charge deficit associated with a Li ion in a cobalt site is compensated for by an O vacancy. It should be noted that the local environment of some cobalt ions is modified by the presence of an oxygen vacancy in the triangular lattice, as shown in Figure 8. The two neighboring cobalt ions adjacent to the oxygen vacancy are in square-based pyramids instead of octahedra, and this local environment change can induce a shift of the relative energies of the 3d orbitals. Therefore, it is proposed in this study that the trivalent cobalt ions adjacent to oxygen vacancies adopt an intermediate spin state, denoted as $Co^{3+(IS)}$, where the d_{z^2} orbital is strongly stabilized due to the oxygen vacancy, as described in Figure 8. In such a configuration, the relative position of the d_{z^2} and d_{xy} orbitals is a priori not known. The proposed scheme is discussed below, on the basis of electrochemical, ^{7}Li NMR, and

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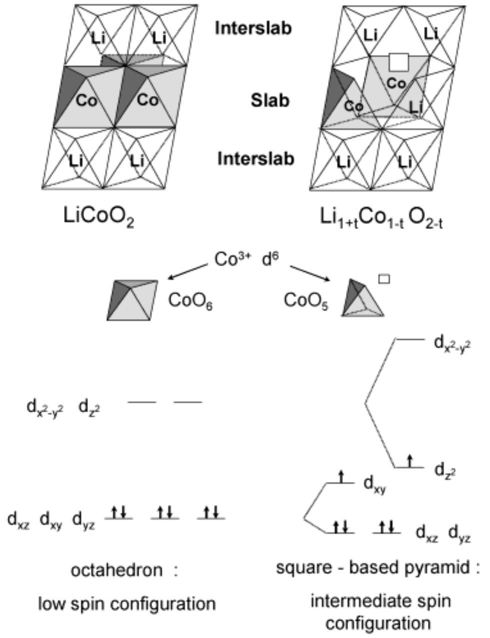

Figure 8. Schematic representation of the structural defect induced by Li substitution and the resulting electronic configuration for the neighboring Co^{3+} ions.

magnetic data for slightly deintercalated $Li_{1.08}CoO_2$. This unique electronic configuration, which has been reported previously in other cobalt oxides,[17−19] can explain the paramagnetic signals, at 185, −16, −40, 3, and −6 ppm, present in the ^7Li NMR spectra of lithium-overstoichiometric $Li_{x_0}CoO_2$ ($x_0 > 1$) samples. Although the single electron in the d_{xy} orbital could lead to a loss of observability of some neighboring Li^+ ions, similar to localized Co^{4+} ions upon initial deintercalation of stoichiometric $LiCoO_2$,[6] a transfer of hyperfine interaction leading to a 1st/2nd neighbor effect is expected from the single electron in the e_g orbital (d_{z^2}) via the oxygen opposite to the vacancy, similarly to the one observed when some Ni^{3+} ions are substituted for cobalt in $LiCoO_2$.[20,21] This would lead to the 185 ppm (first neighbor; 90° interaction via the overlap with O orbital) and −16 and −40 ppm (second neighbor; 180° interaction via the overlap with O orbital) signals. Moreover, the d_{z^2} orbital that points through the O vacancy probably leads to a weak direct transfer of hyperfine interaction with the Li^+ 2s orbital and consequently could be responsible for a slight additional positive shift of the NMR signals for some Li^+ ions, leading to the extra signals at 3 and −6 ppm. It should be mentioned that the unpaired electron associated with localized Co^{4+} ions present in deintercalated, stoichiometric Li_xCoO_2 ($0.94 \leq x \leq 1$), can occupy all three degenerate t_{2g} orbitals, which leads to the loss of NMR observation of the 6 adjacent Li ions due to the transferred hyperfine interaction.[6] In contrast, intermediate spin $Co^{3+(IS)}$ ions have only the d_{xy} orbital that contains a single electron, which results in the loss of observation of only two Li ions and allows the observation of the 90° (first neighbor) interaction associated with the d_{z^2} electron and the other adjacent Li ions.

Considering the intermediate spin $Co^{3+(IS)}$, and the low spin Co^{3+} denoted as Co^{III}, the structural model of $Li_{x_0}CoO_2$ ($x_0 > 1$) can be written as $[Li]_{interslab}[Co^{III}{}_{1-3t}Co^{3+(IS)}{}_{2t}Li_t]_{slab}[O_{2-t}]$, ($t = (x_0 - 1)/(x_0 + 1)$) in which each O vacancy is surrounded by two $Co^{3+(IS)}$, one Li^+ ion in the slab, and three Li^+ ions in the interslab space, as shown in Figure 8.

The theoretical Curie constant, $C_{th.}$, corresponding to the model, can be calculated from the $Co^{3+(IS)}$ contribution as follows:

$$C_{th.} = [n(n + 2)/8]\cdot n_{Co^{3+(IS)}}$$

where n is the number of single electrons and $n_{Co^{3+(IS)}}$ the amount of $Co^{3+(IS)}$ ions per mole in the material. This leads to a value of 0.08 for the $Li_{1.08}CoO_2$ material, written as $[Li]_{interslab}[Co^{III}{}_{0.88}Co^{3+(IS)}{}_{0.08}Li_{0.04}]_{slab}[O_{1.96}]$. This corresponds very well with the experimental Curie constant, determined as shown in Figure 6.

Figure 7 shows that the Curie constant decreases upon initial lithium removal from $Li_{1.08}CoO_2$. Besides, we reported previously that the low rate−charge curve profile of $Li_{1.08}CoO_2$ shows a step at the beginning of deintercalation.[10] These two facts suggest that the intermediate spin trivalent cobalt is oxidized before the “normal” LS Co^{3+} ions in the material. Furthermore, we also reported that the ^7Li NMR spectra of slightly deintercalated $Li_{1.08}CoO_2$ show the initial disappearance of the signals related to $Co^{3+(IS)}$ ions, which are in fact due to the d_{z^2} single electron as discussed above. Therefore, it is believed that the d_{z^2} single electron of the $Co^{3+(IS)}$ ions is removed first upon deintercalation, which is consistent with the electronic configuration scheme shown in Figure 8.

The $[Li]_{interslab}[Co_{1-t}Li_t]_{slab}[O_{2-t}]$ formula can also explain the decomposition of the lithium-overstoichiometric sample to stoichiometric $LiCoO_2$ upon prolonged annealing and the high-pressure treatment at 900 °C by the following reaction:

$$[Li]_{interslab}[Co_{1-t}Li_t]_{slab}[O_{2-t}] \rightarrow (1 - t)LiCoO_2 + tLi_2O$$

It should be noted that such a reaction requires a rearrangement of the Co−O bonds in the layered structure, which is expected at this temperature.

Electrochemical Cycling of Stoichiometric and Li-Overstoichiometric $LiCoO_2$. Finally, we wish to mention a consequence of this structural defect on the voltage profiles during cycling of lithium cells containing $Li_{x_0}CoO_2$ ($x_0 > 1$). It is known that excess Li_2CO_3, acting as a flux medium during the synthesis, increases particle sizes, which improves the battery security in the charged state.[22,23] Imanishi has also reported cycling of overstoichiometric $LiCoO_2$, stating that the increase

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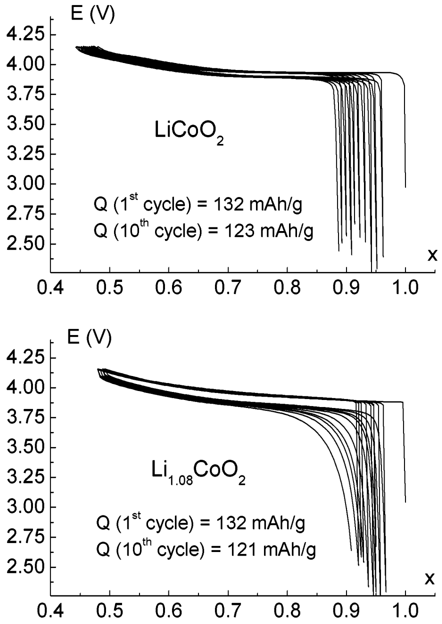

Figure 9. First 10 galvanostatic cycles of $Li/LiClO_4-PC/Li_xCoO_2$ ($x_0 = 0$ and $x_0 = 1.08$) cells, between 2.17 and 4.15 V, at the C/20 rate.

in Li/Co ratio hardly affects the capacity, and that too much doping deteriorates the performances.[5]

The voltage profiles of lithium cells containing stoichiometric and lithium-overstoichiometric samples upon the first 10 cycles are shown in Figure 9. It should be noted that the reversible capacities of these two types of cells are very similar in the first 10 cycles. However, the voltage profiles upon discharge are significantly different: the voltage drop at the end of discharge is gradual for the lithium-overstoichiometric compound in comparison to that of the stoichiometric sample, and this effect becomes more and more important as the cycle number increases. We reported previously that the insulator/metal transition upon charge is more gradual and occurs without phase separation for the overstoichiometric compound.[10] Therefore, upon intercalation, a Li-rich material must form at the surface of the particles, where the electronic conductivity gradually decreases as the metallic domains become smaller. For the stoichiometric material, two phases are present in the composition range corresponding to the end of discharge; the presence of the metallic phase seems to maintain a good overall electronic conductivity, until it disappears abruptly when the global Li content at the surface of the grain reaches 0.94. One can note that, upon charge, the polarization appears rather sharply, even more so for the Li-overstoichiometric phase, and whatever the cycle number. In that case, Li depletion at the surface of the globally insulating grain is very quick, so that the voltage increases rather rapidly. This then leads to an increase in the conductivity of the material at the surface of the grain, so that polarization stops increasing, and a steady state is reached. Thus, the consequence of the presence of the structural defect in Li-overstoichiometric $LiCoO_2$ on the cycling behavior is a more gradual voltage drop at the end of discharge, which tends to lower the reversible capacity in a fixed cycling voltage range, but may also matter for state-of-charge monitoring purposes.

Conclusion

In this paper, we propose a structural model for Li-overstoichiometric LiCoO, which takes into account all the experimental observations (X-ray and neutron diffraction,[10] chemical analyses,[10] thermal treatments under reduced and high oxygen pressure, ^{7}Li NMR, and magnetic data). The excess Li replaces some cobalt ions, and the charge is simply compensated for by oxygen vacancies. This leads to some cobalt ions being in a square-based pyramidal site with an intermediate spin configuration, leading to a formula $[Li]_{interslab}[Co^{III}_{1-3t}Co^{3+(IS)}_{2t}Li_t]_{slab}[O_{2-t}]$.

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