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Electrochemical synthesis and properties of CoO₂, the *x*=0 phase of the *A*ₓCoO₂ systems (*A*=Li,Na)

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Single-phase bulk samples of the "exotic" CoO_2, the $x=0$ phase of the A_xCoO_2 systems (A =Li,Na), were successfully synthesized through electrochemical deintercalation of Li from pristine $LiCoO_2$ samples. The samples of pure CoO_2 were found to be essentially oxygen stoichiometric and possess a hexagonal structure consisting of stacked triangular-lattice CoO_2 layers only. The magnetism of CoO_2 is featured with a temperature-independent susceptibility of the magnitude of 10^{-3} emu/mol Oe, being essentially identical to that of a Li-doped phase, $Li_{0.12}CoO_2$. It is most likely that the CoO_2 phase is a Pauli-paramagnetic metal with itinerant electrons. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828525]

The layered cobalt oxide systems, A_xCoO_2 (A=Li,Na), have attracted increased attention due to recent discoveries of various unconventional transport and magnetic properties. Namely, among the members of the systems, Na_xCoO_2 exhibits a superb thermoelectric property about $x=0.7$,[1,2] a spin-density-wave excitation at $x=0.75$,[3] a charge ordering at $x=0.50$,[4] and superconductivity about $x=0.35$ with a hydrated form.[5] The crystals of A_xCoO_2 consist of alternate stacking of a CoO_2 layer and a single atomic layer of A ions. The CoO_2 layer contains a two-dimensinal triangular cobalt lattice with possible magnetic frustrations (due to the geometry) that may be underlying aforementioned unconventional electronic states.

As mentioned above, the physical properties sensitively depend on the concentration of A ions. It is thus important to establish the electronic phase diagrams for the A_xCoO_2 systems with respect to x. Nevertheless, properties have remained unclear in the low x regime, i.e., $x<0.25$, due to the difficulty in sample syntheses. In particular, it is worth synthesizing the $x=0$ phase of the A_xCoO_2 systems, i.e., pure CoO_2, since it can be regarded as the parent of these systems.

Synthesis of CoO_2 samples was previously reported,[6,7] but the sample purity was insufficient for the accurate determination of physical properties. Here we report the synthesis and the properties of pure CoO_2 bulk samples.

Bulk samples of pure CoO_2 phase were synthesized through electrochemical deintercalation of Li from pristine $LiCoO_2$ samples. The $LiCoO_2$ samples were prepared by a conventional solid-state reaction technique. A mixture of Li_2CO_3 and Co_3O_4 with the ratio of Li/Co=1:1 was calcined (600 °C) and then sintered (900 °C) in flowing O_2 gas. Electrochemical oxidation was carried out with a constant current (i.e., galvanometric) setup utilizing an airtight flat cell filled with a nonaqueous electrolyte. The electrochemical cell consisted of an as-synthesized $LiCoO_2$ pellet and an aluminum metal disk as the cathode and anode, respectively. No auxiliary agents (e.g., acetylene black and Teflon powder) were added to the bulk pellet to avoid any magnetic noise sources. Since high-valent cobalt oxides tend to experience chemical instability when exposed to atmospheric moisture, sample handling and characterization were carefully made in an inert gas atmosphere. Details of experimental procedures are given elsewhere.[8]

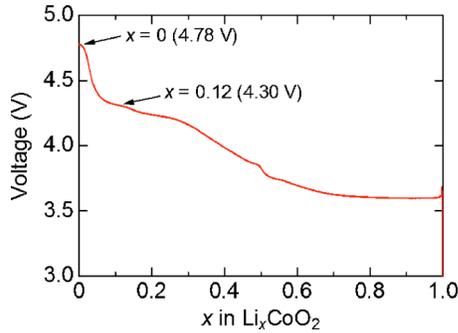a)Electronic mail: t-mot@msl.titech.ac.jp.

FIG. 1. (Color online) Change in voltage for the Li_xCoO_2/Al electrochemical cell as Li is deintercalated from $LiCoO_2$. The Li content (x) of Li_xCoO_2 is calculated based on Faraday's law.

Single-phase CoO_2 samples were successfully obtained through the aforementioned electrochemical synthesis technique. Figure 1 shows a typical voltage versus x plot for the Li_xCoO_2/Al cell. The x values were estimated through theoretical calculations based on Faraday's law with an assumption that the full amount of electricity was used for the Li deintercalation reaction. The cell voltage gradually increased with decreasing x in Li_xCoO_2 and finally reached +4.78 V at $x = 0.0$. As x decreased below ≈ 0.1, the cell voltage increased rapidly to indicate the completion of lithium extraction.[6] The actual Li content (x) of the resultant CoO_2 sample was determined by means of inductively coupled plasma atomic emission spcotroscopy to be below the detection limit of the apparatus, i.e., smaller than 0.01. This ensures that our CoO_2 samples are indeed the $x = 0$ end member of the Li_xCoO_2 system.

In Fig. 2, x-ray powder diffraction patterns for the pristine $LiCoO_2$ and the CoO_2 samples are shown. The pattern for $LiCoO_2$ was readily refined based on space group R-$3m$ with the lattice parameters $a = 2.814$ Å and $c = 14.05$ Å, being in good agreement with those previously reported.[6,9] For CoO_2, on the other hand, diffraction peaks were indexed based on space group P-$3m1$ with the lattice parameters a
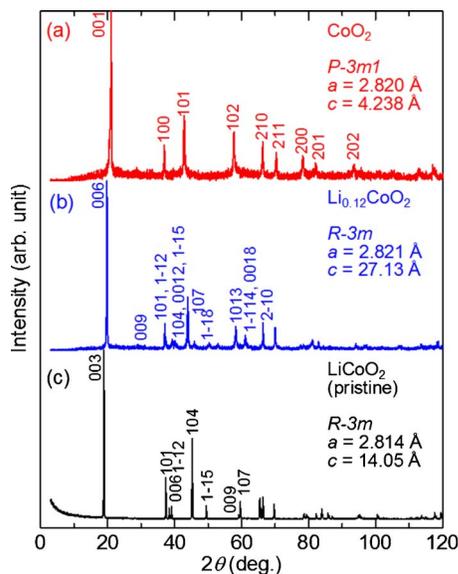

FIG. 2. (Color online) X-ray powder diffraction patterns for (a) CoO_2, (b) $Li_{0.12}CoO_2$, and (c) $LiCoO_2$ samples.

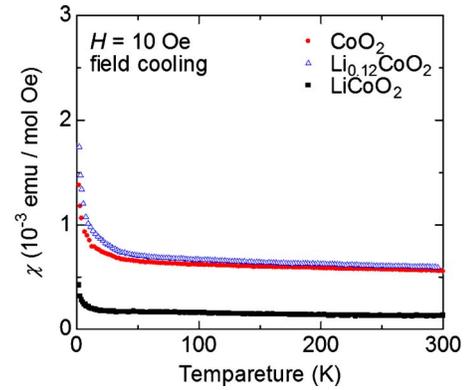

FIG. 3. (Color online) Temperature dependence of magnetic susceptibility (χ) for the samples of CoO_2 (red circles) $Li_{0.12}CoO_2$ (blue triangles), and $LiCoO_2$ (black squares).

$= 2.820$ Å and $c = 4.238$ Å. The $LiCoO_2$ phase crystallizes in the so-called $O3$-type structure, in which Li ions occupy the octahedral site with three CoO_2 layers per unit cell, while the CoO_2 phase possesses an $O1$-type structure consisting of a single CoO_2 layer only per unit cell. Oxygen-content analysis was performed based on hydrogen reduction experiments in a 5% H_2/Ar gas flow with a thermobalance. The oxygen content of the sample was determined to be $CoO_{1.98\pm0.02}$. Thus, the resultant CoO_2 sample is essentially oxygen stoichiometric, implying that the highest formal valence of cobalt is realized, i.e., $V_{Co} \approx +4.0$.

In the cell voltage versus x curve shown in Fig. 1, one may notice that there appears a narrow plateau at about $x = 0.12$ prior to the rapid increase in voltage, suggesting the existence of another stable phase neighboring on the $x = 0$ end member. We thus synthesized a Li_xCoO_2 sample precisely controlling the electric charge setting at $x = 0.12$. It is found that the $x = 0.12$ sample is indeed of single phase possessing a hexagonal structure with the lattice parameters $a = 2.821$ Å and $c = 27.13$ Å (Fig. 2). The crystal of the $x = 0.12$ phase is reported to consist of alternate stacking of a Li-intercalated $O3$-type block (as in $LiCoO_2$) and a Li-free $O1$-type block (as in CoO_2), leading to a six-CoO_2-layer unit cell that is called "H1-3."[10,11] Note that $Li_{0.12}CoO_2$ ($V_{Co} = +3.88$) may correspond to an electron-doped phase of CoO_2 ($V_{Co} = +4$).

Magnetic susceptibility (χ) measurements were performed with a superconducting quantum interference device magnetometer (MPMS-XL, Quantum Design). The χ vs T plots for the $LiCoO_2$ (pristine), $Li_{0.12}CoO_2$, and CoO_2 samples are given in Fig. 3. The χ value for the $LiCoO_2$ sample is small in magnitude and little dependent on temperature due to the nonmagnetic nature of low-spin Co^{III}. Surprisingly, the CoO_2 and $Li_{0.12}CoO_2$ samples also exhibit temperature-independent susceptibility in the temperature range between 50 and 300 K. The susceptibility data for CoO_2 are in good agreement with those reported by de Vaulx *et al.*,[7] although their sample contains a large amount of secondary phases. The χ vs T plots were fitted with the following formula: $\chi = \chi_0 + C/(T-\Theta)$, where χ_0, C, and Θ denote the constant susceptibility, the Curie constant, and the Weiss temperature, respectively. Fitted values for χ_0, C, and Θ are

TABLE I. The χ_0, C, and Θ values for the $LiCoO_2$, $Li_{0.12}CoO_2$, and CoO_2 samples. These values were determined based on least-squares calculations for the χ vs T plots (Fig. 3).

x in Li_xCoO_2	χ_0 (10^{-4} emu/mol Oe)	C (10^{-3} emu K/mol Oe)	Θ (K)
0.0	5.68	4.01	−3.3
0.12	6.00	5.48	−3.1
1.0	1.34	0.89	−1.6

summarized in Table I. The C value for the CoO_2 sample yields an effective magnetic moment (μ_{eff}) of $0.18\mu_B$/Co site, being much smaller than the theoretical spin-only value of low-spin Co^{IV} ($S=1/2$), i.e., $1.73\mu_B$/Co site. Thus, any localized spin model is unlikely.

We conclude that (1) the magnetism of CoO_2 is featured with a temperature-independent susceptibility with a relatively large value for χ_0 and that (2) the upturn behavior at low temperatures likely originates from an extrinsic cause, e.g., lattice defects. A possible (and the most conservative) explanation for this is that the CoO_2 phase is a Pauli-paramagnetic metal with itinerant electrons. Assuming that the difference in magnitude of χ_0 between CoO_2 and $LiCoO_2$ corresponds to the Pauli-paramagnetic contribution, the density of states at the Fermi level, $D(\varepsilon_F)$, is calculated at 13 electrons/eV. This value is three times larger than the theoretical value: $D(\varepsilon_F) \approx 4$ electrons/eV for nonmagnetic CoO_2 according to local densly approtimation calculations.[12]

It is worthwhile to compare the magnetic property of "electron-doped" $Li_{0.12}CoO_2$ to that of the parent phase, CoO_2. Our magnetic data (Fig. 3) demonstrate that the χ-T curve for $Li_{0.12}CoO_2$ is essentially identical to that for CoO_2, indicating that $Li_{0.12}CoO_2$ is also a Pauli paramagnet of the same magnetic origin as CoO_2. Thus, the $x=0$ composition is *not* a singular point in the electronic phase diagram of the A_xCoO_2 systems. The situation is in sharp contrast to the case of high-T_c superconductive copper oxides in which the parent material is a Mott insulator. The present study implies that any theoretical approaches starting from a Mott insulator

may not be appropriate for discussion of the metallic state in A_xCoO_2.

In summary, synthesis and properties of CoO_2, the $x=0$ phase of the A_xCoO_2 systems ($A=Li, Na$), were reported. Single-phase bulk samples of CoO_2 were successfully obtained through electrochemical deintercalation of Li from pristine $LiCoO_2$. The magnetism of CoO_2 is featured with a temperature-independent susceptibility with a relatively large value, being essentially identical to that of a Li-doped phase, $Li_{0.12}CoO_2$, This suggests that the CoO_2 phase is a Pauli-paramagnetic metal with itinerant electrons.

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