Journal of Solid State Chemistry **164,** 1–4 (2002)
doi:10.1006/jssc.2001.9459, available online at http://www.idealibrary.com on IDEAL®

RAPID COMMUNICATION

Anisotropic Electrical Conductivity in $LiCoO_2$ Single Crystal

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Received August 7, 2001; in revised form November 8, 2001; accepted November 16, 2001

Anisotropic temperature dependence of the electrical resistivity in $LiCoO_2$ has been first clarified using chemically and structurally characterized single crystal specimens. The resistivities both perpendicular and parallel to the *c*-axis show semiconductive behavior with large anisotropy of $\rho_c/\rho_a \approx 500$ at 300 K. The temperature dependence of in-plane resistivity suggested a variable range-hopping in the two-dimensional system. © 2002 Elsevier Science (USA)

Key Words: **lithium battery materials; intercalation compounds; electrical resistivity; two-dimensional triangular lattice; crystal growth.**

Lithium cobalt dioxide, $LiCoO_2$, has the trigonal α-$NaFeO_2$ structure. This compound is used industrially as the positive electrode material for lithium-ion rechargeable batteries. The structural, physical, and electrochemical properties for $LiCoO_2$ and $Li_{1-x}CoO_2$ $(0 < x < 1)$ have been widely investigated, after Mizushima *et al.* first reported the electrochemical deintercalation in $LiCoO_2$ (1–6). Especially, since the electrical conductivity of active materials is an important characteristic for the design of high-performance batteries, there have been a number of reports measuring the conductivity (7–15). In all of the experimental studies reported to date, sintered or pressed powder samples (7–12, 15) or the corresponding polycrystalline thin films (13, 14) are used. In an experiment using such samples, much of the information on the anisotropy is lost, and in conductivity measurements in particular, the intrinsic properties of the material are sometimes masked by those of the grain boundaries or the impurities. To clarify the anisotropic nature of the electrical conductivity of the cathode materials, well-characterized single-crystal specimens are highly desirable because one can easily expect the anisotropic conductivity in $LiCoO_2$, from a structural view point, as shown in Fig. 1. Recently, we succeeded in the growth of $LiCoO_2$ single crystals and determined the crystal structure by a single-crystal X-ray diffraction method (16). In this study, we will report the anisotropy in electrical resistivity below room temperature using single crystal specimens.

Single crystals of $LiCoO_2$ were grown by a flux method, as mentioned previously (16). The as-prepared $LiCoO_2$ powder (Cell Seed C, Nippon Chemical Industrial Co., Ltd., Japan) was mixed with Li_2O_2 (99.9%) and LiCl (99.9%) powder to form flux material in the nominal weight ratio of $LiCoO_2:Li_2O_2:LiCl = 1:4:4$. The mixture was heated to 1173 K for 10 h in a sealed gold tube, gradually cooled to 873 K at a rate of 5 K/h, and then cooled naturally. The produced single crystals were easily separated from the frozen Li–O–Cl system flux materials by rinsing the gold tube in water for several hours.

Black, hexagonal platelet single crystals of about $0.15 \times 0.15 \times 0.01$ mm^3 in average size were obtained. SEM-EDX (JEOL JSM-5400) analysis showed that the crystals were free from gold contamination from the tube. The chemical formula, analyzed by inductively coupled plasma (ICP) spectroscopy using the pulverized crystals, confirmed the stoichiometric chemical composition; the result was consistent with that of the recent structure refinement (16). X-ray Laue and precession photographs confirmed the crystal quality. The refined hexagonal lattice parameters using a four-circle diffractometer (Rigaku AFC-5S: Mo$K\alpha_1$ radiation ($\lambda = 0.70926$ Å) were $a = 2.8156(6)$ Å, $c = 14.0542(6)$ Å, and $V = 96.49(4)$ Å^3. The calculated density ($D_x = 5.055$ g/cm^3) was in good agreement with the observed value of $D_m = 5.056(1)$ g/cm^3 using a gas pycnometer (Shimadzu Accupyc 1330). These results suggest that the crystals have the stoichiometric $LiCoO_2$ composition.

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0022-4596/02 $35.00

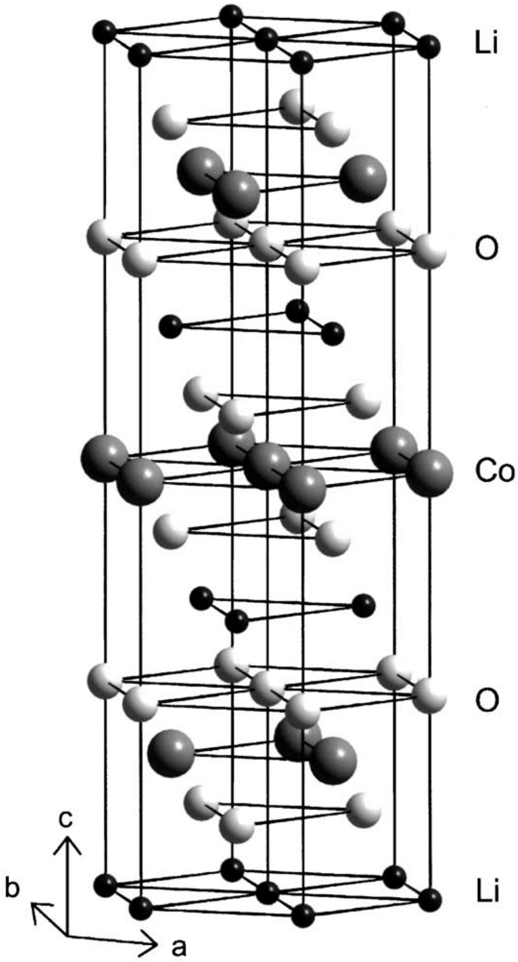

FIG. 1. Two-dimensional triangular lattice in $LiCoO_2$.

The in-plane resistivity (ρ_a) in the direction perpendicular to the c-axis was measured by the conventional direct current four-probe method from 74 K to room temperature. Single-crystal specimens measured were plane shaped with dimensions of $150 \times 200\ \mu m^2$ for the large surface and from 5 to 15 μm thick along the c-axis direction. We measured several specimens to check the reproducibility. Figure 2a shows the in-plane resistivity of $LiCoO_2$ as a linear function of temperature. $LiCoO_2$ is semiconductive, but the temperature dependence of the conductivity does not obey any activation-type behavior. Figure 2b shows the plot of the logarithm of conductivity (log σ) versus $T^{-1/3}$, where one can see a linear relation. This seems to be consistent with a variable range-hopping in the two-dimensional (2D) system. The value of ρ_a is about 5 Ω cm at room temperature, which is apparently smaller than those ($\sim 10^3$ Ω cm) reported in the literature using polycrystalline samples for $LiCoO_2$. This may be caused by a small amount of oxygen defects in the present single crystal specimens.

Out-of-plane resistivity (ρ_c) was measured by placing two gold wires on both sides of the large face of the single crystal.

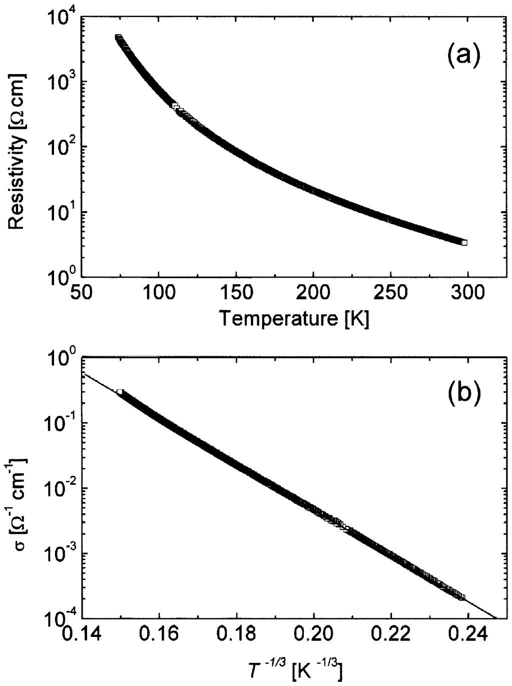

FIG. 2. Temperature dependence of the in-plane electrical resistivity of $LiCoO_2$ single crystals. (a) ρ_a versus T and (b) log σ versus $T^{-1/3}$, respectively. The solid line shows a fit to the equation for a variable range hopping in the 2D system.

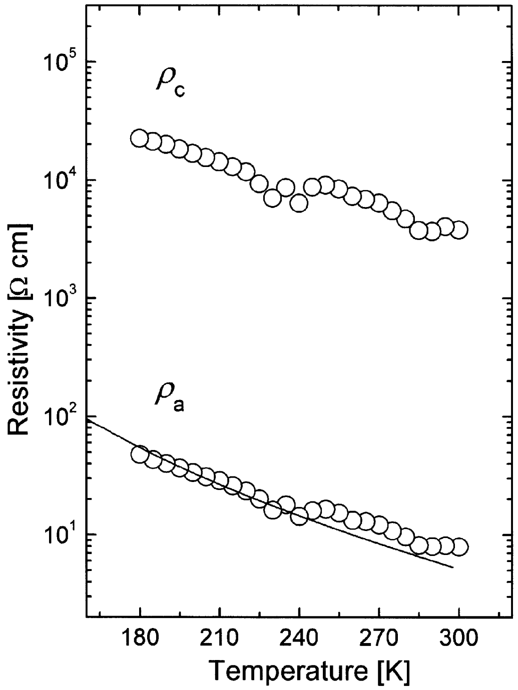

FIG. 3. Temperature dependence of the in-plane (ρ_a) and out-of-plane (ρ_c) resistivity of $LiCoO_2$ single crystals. The solid line shows the temperature dependence of in-plane resistivity measured by the conventional four-probe method and compared with the Montgomery method.

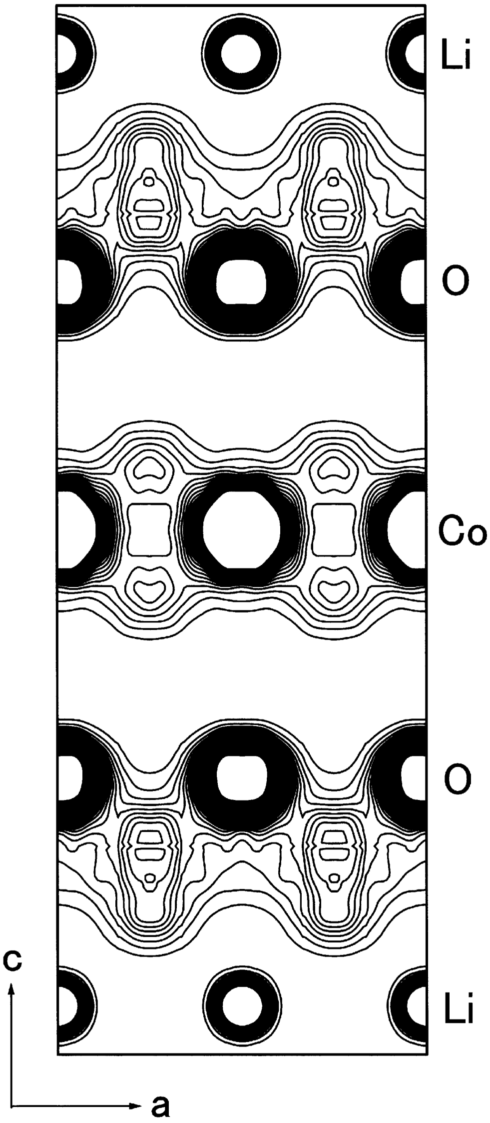

FIG. 4. The electron density distribution of $LiCoO_2$ obtained by the maximum entropy method. Contour lines are drawn from 0.0 to 4.0 at 0.1 e/Å^3 intervals.

The obtained data were analyzed using the Montgomery method (17–19). Figure 3 compares the temperature dependence of in-plane (ρ_a) and out-of-plane (ρ_c) resistivities. As shown in this figure, the temperature dependence and the magnitude of ρ_a measured by the Montgomery method (17–19) agree with the conventional four-probe method. The electrical resistivities in both directions increase with decreasing temperature, showing a semiconducting temperature dependence. The resistivities at 300 K are 8 Ω cm and 4×10^3 Ω cm for ρ_a and ρ_c, respectively. The anisotropy of the resistivity, ρ_c/ρ_a, was estimated to be about 500 at 300 K. The ratio decreases from 500 to 400 with decreasing the measurement temperature from 300 to 180 K. These values are comparable to those for $LiVO_2$ (20), $NaCo_2O_4$ (21), and $PdCoO_2$ (22) with similar two-dimensional triangular lattices. The electronic states can thus be regarded as quasi-2D, as was expected from the crystal structure (Fig. 1). In fact, the electron density distribution in $LiCoO_2$, determined by single-crystal X-ray structure analysis (16) and maximum entropy method analysis using the program MEED (23, 24), shows the strong Co–O bonds along the in-plane direction and the electron density distribution is not connected along the *c*-axis direction (Fig. 4). The details in electron density distribution analysis for $LiCoO_2$ will be published elsewhere (25).

In conclusion, the intrinsic large anisotropy in electrical conductivity of $LiCoO_2$ has been successfully revealed for the first time using chemically and structurally well-characterized single-crystal specimens. It is reported using the *in situ* electrochemical system that the conductivity of $Li_{1-x}CoO_2$ increases by several orders of magnitude when a very small amount of lithium was extracted ($x < 0.1$) (14). Recently, the insulator–metal transition upon lithium deintercalation from $LiCoO_2$ has been intensively investigated experimentally (12, 15) and theoretically (26). However, the true metallic conductivity for $Li_{1-x}CoO_2$ has not been reported to date. Further studies are in progress to confirm the metallic conductivity using the electrochemically deintercalated $Li_{0.5}CoO_2$ single crystal samples (27).

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