Irreversible conductivity change of $Li_{1-x}CoO_2$ on electrochemical lithium insertion/extraction, desirable for battery applications

Matsuhiko Nishizawa, Satoru Yamamura, Takashi Itoh and Isamu Uchida*†

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aramaki-aoba, Aoba-ku, Sendai, 980-8579, Japan

Electrical conductivity of a sputter-deposited $LiCoO_2$ thin film was studied *in situ* during electrochemical lithium extraction/insertion, revealing that the metallic behavior of $Li_{1-x}CoO_2$ induced by the initial lithium extraction did not revert to its original insulating state in the following successive reduction/oxidation cycles.

$LiCoO_2$ is one of the most promising cathode active materials for lithium secondary batteries, and the battery system based on the $LiCoO_2$/carbon couple has been used commercially in many types of electronic equipment.[1–8] 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 upon taking the electrode out of the electrochemical cell; *i.e. ex situ* characterization.[9–11] In contrast, work in our laboratory has shown that the interdigitated microarray (IDA) electrode is a powerful tool for studying the dynamic changes in the DC conductivity of electroactive films *in situ*.[12–17] We recently reported that the conductivity of $Li_{1-x}CoO_2$ increased by several orders of magnitude when a very small amount of lithium was extracted ($x < 0.1$),[16] as was predicted theoretically.[1,9] Such a drastic conductivity change requires that care must be taken when using $LiCoO_2$ as a battery active material. Since our previous work was on a composite film consisting of $LiCoO_2$ powders mixed with poly(vinylidene fluoride) and acetylene black, we could not treat the measured conductivity as that of $LiCoO_2$ itself.[16] Therefore, in this study we prepared a fine $LiCoO_2$ film by sputtering onto IDA electrodes to obtain more precise and reproducible results. It was found that the metallic behavior of $Li_{1-x}CoO_2$ induced by the initial lithium extraction (charge) did not revert to its original insulating state in the following reduction/oxidation cycles, indicating that this electrode material maintains its high conductivity during the successive use of secondary batteries.

The IDA electrode was fabricated by photolithography with a sputter-deposited Pt film on a thermally oxidized silicon wafer,[12–16] to have two sets of comb-type Pt arrays; each array has 50 band-electrode elements of 10 μm wide, 2.4 mm long and 0.1 μm thick, separated by 10 μm from its adjacent elements. A $LiCoO_2$ film of 0.2 μm thickness was deposited onto the IDA electrode by RF-sputtering and annealed in air at 700 °C for 15 min. Each peak in the X-ray diffraction spectrum of the annealed film was assigned to $LiCoO_2$. During the sputtering of the $LiCoO_2$ films, the IDA substrate was masked to limit the exposed area to a 0.2 cm × 0.3 cm rectangle. Each electrochemical measurement was conducted in a glove box filled with dried Ar, by using propylene carbonate (PC) containing 1 M $LiClO_4$ as the electrolyte solution. Lithium foils were used as the reference and counter electrodes. The *in situ* conductivity measurements were carried out, as previously,[15,16] using a bipotentiostat to maintain a 5 mV potential difference between the two working electrodes. The specific conductivity of the film was calculated from the ohmic current flowing through the film under the 5 mV bias voltage.[14,15] Note, however, that our measurement is a two-point probe method and that the film is thicker than the Pt film electrodes, therefore it is still dangerous to discuss the obtained conductivity as an absolute value. Rather, this method is suited to the study of dynamic, relative changes in the conductivity taking place with redox reactions.[12–14]

Fig. 1 shows cyclic voltammograms (CVs, solid lines) and *in situ* potential–conductivity profiles (dashed lines), which were measured simultaneously. The results for the first and the sixth cycles are presented. During the initial extraction of lithium, the conductivity of the film increased by more than four orders of magnitude and saturated around the main CV peak at 3.9 V, as observed for the $Li_{1-x}CoO_2$ composite film.[16] The saturated conductivity was not varied even upon expansion of the potential range up to 4.2 V ($x \approx 0.5$ in $Li_{1-x}CoO_2$). The drastic conductivity change which appeared before the CV peak is known to be the metal–insulator transition (MIT) resulting from the possible direct overlap of cobalt t_{2g} orbitals across a shared octahedral edge.[1,9] It was found here that the increased conductivity did not revert to the initial low value in the following reduction process, and that the conductivity value remained within the same order of magnitude during the successive charging/discharging cycles. This conductivity profile hysteresis was not removed even upon reduction of the potential scan rate to 10 μV s^{-1}. Fig. 2 shows the conductivity measured under open-circuit conditions to examine the above potentiodynamic results. A known amount of charge was induced using a galvanostat (typically, 150 μC with 0.1 μA), and then the rest potential and conductivity of the $Li_{1-x}CoO_2$ film were measured after more than 2 h. The correlation between the rest potential and the conductivity, shown in Fig. 2(*a*), was essentially the same as the result obtained by potentiodynamic measurements; the initial insulating state was not reproduced. Fig. 2(*b*) represents the conductivity changes as a function of *x*, calculated using the apparent volume of the film and the density of a single crystal of $LiCoO_2$. Although the

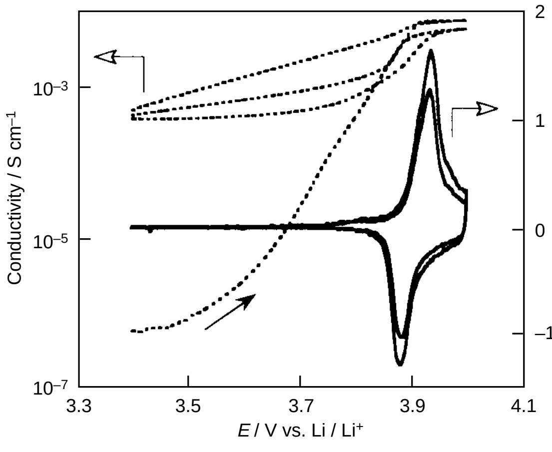

Fig. 1 Cyclic voltammograms (solid lines) and potential–conductivity profiles (dashed lines) of a $LiCoO_2$ film (0.2 μm thickness) sputter-deposited onto a Pt IDA electrode, taken in 1 M $LiClO_4$/PC at a scan rate of 0.1 mV s^{-1}. The bias voltage set between arrays was 5 mV. The first and the sixth cycles are presented.

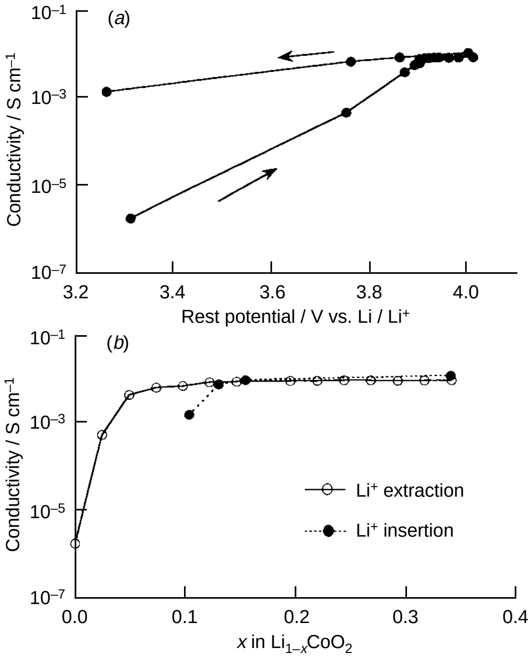

Fig. 2 The variations of the conductivity of a $LiCoO_2$ film during the first extraction/insertion of lithium as functions of (*a*) the rest potential and (*b*) x in $Li_{1-x}CoO_2$, taken in 1 M $LiClO_4$/PC with a bias voltage of 5 mV

calculated x values are not strictly accurate because of the polycrystallinity of the film and some side reactions, it was roughly confirmed that the MIT was induced by extraction of a very small amount of lithium (less than 10%) and the conductivity of the film could not revert to the initial insulating state due to the difficulty in reinserting this small amount of lithium. There are many reports showing similar irreversible capacities for the first charge/discharge cycle.[2,6–8] Crystallographic irreversibility may be the reason for this hysteresis because of the fact that a structural transformation occurs around $x = 0.1$ in $Li_{1-x}CoO_2$; within the composition range $0 < x < 0.1$, a single hexagonal phase exists, whereas within the range $0.1 < x < 0.22$, two hexagonal phases coexist.[1,6,7] Furthermore, electrochemical processes accompanied by growth of insulating phases are kinetically unfavorable in general, as seen for conducting polymers such as polyaniline.[18] Anyway, the insulating nature of $LiCoO_2$, which may be serious for battery applications, was found not to be regained within the time scale of battery applications.

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Notes and References

† E-mail: uchida@est.che.tohoku.ac.jp

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