

**Effects of Surface Modification by Metal Oxide on Interfacial Reactions of Lithium Cobalt Oxide Thin Film Electrode**

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**Introduction**

Lithium cobalt oxide (LiCoO<sub>2</sub>) is one of the positive electrode material most widely used in lithium-ion batteries. Although theoretical capacity of LiCoO<sub>2</sub> (0 < x < 1 in Li<sub>x</sub>CoO<sub>2</sub>) is calculated to be about 280 mAh/g, only about a half of the capacity have been utilized in commercial lithium-ion batteries because of large capacity fading after extended cycling when lithium ions are extracted over this composition (about at 4.2 V vs. Li/Li<sup>+</sup>). In recent years, it has been reported that surface modification of LiCoO<sub>2</sub> by ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, DLC, etc. can suppress this large capacity fading and give excellent capacity retention even when cycled over 4.2 V vs. Li/Li<sup>+</sup> [1-3]. However, effects of the surface modifications on interfacial reaction of LiCoO<sub>2</sub> electrode have not been clearly understood. Especially, relationships between the kinetics and stabilities of charge transfer reactions should be elucidated for the development of large-sized lithium batteries requiring both high power and high reliability.

In this work, we prepared LiCoO<sub>2</sub> thin films modified with metal oxide (MgO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, etc) by pulsed laser deposition (PLD) and studied effects of surface modification by metal oxide on interfacial reactions of LiCoO<sub>2</sub> thin film electrode.

**Experimental**

Thin films of LiCoO<sub>2</sub> were prepared by PLD. After depositing LiCoO<sub>2</sub> thin film on Pt substrate, metal oxide was deposited on LiCoO<sub>2</sub> thin film successively. Hereafter the bare LiCoO<sub>2</sub> and metal oxide modified LiCoO<sub>2</sub> thin films are referred to as B-LiCoO<sub>2</sub> and M-LiCoO<sub>2</sub>, respectively. Prepared films were characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). Electrochemical behaviors of the film electrodes were examined by cyclic voltammetry (CV) and AC impedance spectroscopy.

**Results and discussions**

There were no visible changes in XRD patterns of LiCoO<sub>2</sub> before and after the surface modifications. Moreover, In any cases, diffraction peaks from metal oxides were not observed at all. AES and XPS measurements revealed that metal oxide dispersed uniformly in the film electrode. Cyclic voltammetry measurements revealed that metal oxide modification stabilized electrochemical lithium insertion/extraction properties of LiCoO<sub>2</sub> film electrodes as have been reported.

Figure 1 shows AC impedance spectra of both the B-LiCoO<sub>2</sub> and MgO-LiCoO<sub>2</sub> at 4.0 V obtained at 303 K. Each spectrum consisted of a semicircle, which is assigned to the charge transfer resistance, in the high frequency region, followed by a straight line with a nearly vertical line in the lower frequency region (< 20 Hz). The charge transfer resistances of both the B-LiCoO<sub>2</sub> and MgO-LiCoO<sub>2</sub> were evaluated from the spectra to be 250 Ω and 750 Ω, respectively. An electrochemically inactive layer, including MgO, formed on the Mg-LiCoO<sub>2</sub> surface probably causes the larger charge transfer resistance of the MgO-LiCoO<sub>2</sub>. This larger charge transfer resistance

could explain a little broad CVs of the Mg-LiCoO<sub>2</sub> compared to those of B-LiCoO<sub>2</sub>.

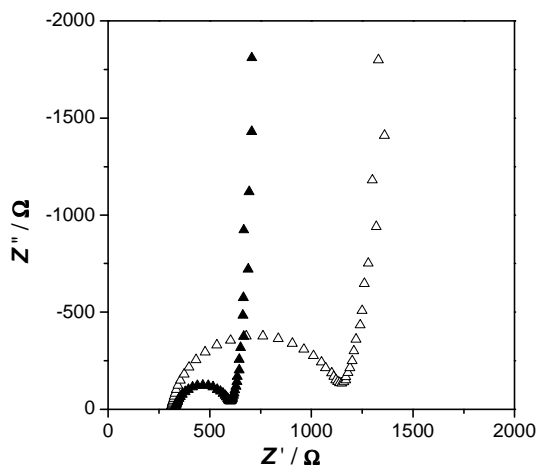
The Arrhenius plots of reciprocal charge transfer resistance multiplied by absolute temperature against reciprocal temperature are shown in figure 2. These plots could be fitted by a straight line. Activation energy of the charge transfer reaction of the MgO-LiCoO<sub>2</sub> was calculated from the slope to be 0.49 eV, which was smaller than that of the B-LiCoO<sub>2</sub>, 0.64 eV. These results clearly revealed that surface modification by metal oxide affects the kinetics of charge transfer reaction. Results of other M-LiCoO<sub>2</sub> will be discussed in the presentation.

**Acknowledgement**

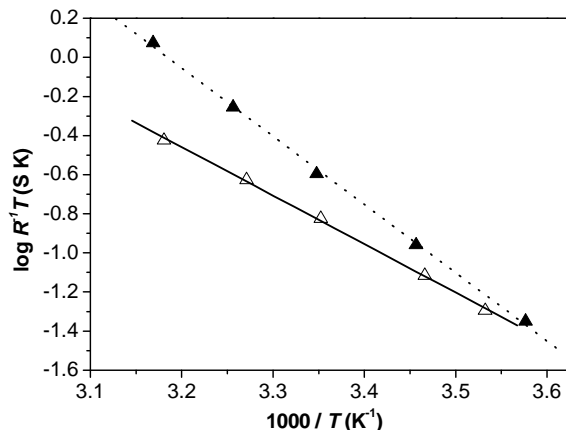
This work was supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan, and also by a Grant-in-Aid for 21 st COE program-COE for a United Approach to New Materials Science- from the Ministry of Education, Culture, Sports, Science, and Technology.

**References**

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**Figure 1.** AC impedance spectra of both a bare (closed triangles) and an MgO-modified LiCoO<sub>2</sub> (open triangles) thin film electrodes at 4.0 V.



**Figure 2.** Temperature dependency of charge transfer resistances of a bare (closed triangles) and an MgO-modified (open triangles) LiCoO<sub>2</sub> thin film electrodes at 4.0 V.