Kinetics of Li-ion Transfer at the Electrode/Electrolyte Interface and Current Rate Performance of LiCoO₂ Surface-coated with Zirconium Oxide and Aluminum Oxide

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ABSTRACT

Different oxide-based surface coatings were applied to the LiCoO₂ positive electrode material to improve its interfacial Li-ion transfer and current rate performance. Zr-oxide and Al-oxide were selected as coating materials, as the former hardly forms a solid-solution with LiCoO₂ while the latter readily does so. Zr-oxide-coated LiCoO₂ showed higher current rate performance and lower charge transfer resistance (Rct) compared to bare and Al-oxide-coated LiCoO₂. The difference in current rate performance was quantitatively explained by the different Rct. The activation energy (Ea) for the charge transfer reaction was approximately 10 kJ mol⁻¹ lower for Zr-oxide-coated LiCoO₂ than the other two. The lower Ea of the former, which suggests lower activation barriers for the elementary processes of Li-ion transfer at the electrode/electrolyte interface, lowered the Rct and increased the current rate performance. The Rct of Zr-oxide-coated LiCoO₂ decreased from the 2nd to 4th cycle, while for Al-oxide-coated LiCoO₂ it remained almost constant during the early cycles. The formation of the new electrode/electrolyte interface during the early cycles that depends on the solubility of cations in the oxide coatings into LiCoO₂ contributes to the different Rct change and Ea values.

Keywords : Positive Electrode, Electrode/Electrolyte Interface, Li-ion Transfer Kinetics, Surface Coating

1. Introduction

With increasing demand for high-energy-density Li-ion batteries, various attempts have been made to improve their positive electrodes. The formation of a surface coating on layered rock-salt active materials, such as LiCoO₂ and LiNi₀.₅Co₀.₅Mn₀.₅O₂, is an effective technique for improving the performance of the positive electrode, especially for high-voltage charge/discharge. Various kinds of coating materials have been studied for this purpose.¹⁻⁶

Some oxide coatings have been reported to improve the current rate performance as well as cycle performance of positive electrodes.⁷⁻¹⁶ Especially, these coatings could decrease the activation energy of Li-ion transfer reaction at the electrode/electrolyte interface.⁷⁻¹⁶ However, it remains unclear why these oxides, with poor electronic and ionic conductivities by themselves, could improve the current rate performance and decrease the activation energy. Therefore, it is important to clarify the kinetics of Li-ion transfer at the coated electrode/electrolyte interface, and the influence on the current rate performance.

Generally, oxide coatings are formed through calcination at high temperatures. Atoms in the coating and active materials diffuse and intermix during the calcination, and a coating phase is formed at the surface. The structure of the coating phase, which is dependent on the solubility of the cation of the coating oxide into the active material, should affect Li-ion transfer at the electrode/electrolyte interface. Recently, using in-situ X-ray scattering and thin-film electrodes of various active materials, it was found that the surface atomic arrangements of electrodes change when they are soaked in electrolyte solutions, and the surfaces are reconstructed during the initial charging.¹⁷⁻²⁰ Thus, it is the reconstructed surface through which the Li ions are transferred. Such a reconstruction process can also occur on oxide-coated active materials, depending on the as-coated surface structure.¹⁻²³ In other words, the solubility of the cations of the coating oxides can affect the surface reconstruction and Li-ion transfer at the electrode/electrolyte interface. However, there are very few studies focusing on the surface reconstruction of coated active materials and the associated kinetics of Li-ion transfer at the electrode/electrolyte interface.

In this study, we investigated in detail the kinetics of Li-ion transfer at the electrode/electrolyte interface of LiCoO₂ surface-coated with Zr-oxide or Al-oxide during early charge/discharge cycles by electrochemical impedance analysis. Because the ionic radius (ri) and valency of the Zr cation (Zr⁴⁺, ri = 0.072 nm) are different from those of Co cation in LiCoO₂ (Co³⁺, ri = 0.0545 nm), the Zr cation does not easily dissolve in LiCoO₂ to form a solid solution with LiCoO₂. On the other hand, since the ri and valency of the Al cation (Al³⁺, ri = 0.0535 nm) are similar to those of Co cation, the solubility of Al cations into LiCoO₂ is high, and Al-oxide forms a stable solid-solution with LiCoO₂ as LiAlO₂-LiCoO₂ of layered rock-salt structure (R3m symmetry).²⁴⁻²⁶ We also evaluated the charge/discharge performance of the coated LiCoO₂ at a high charge voltage of 4.5 V, and examined the current rate performance based on the result of impedance analysis. Finally, we discuss the influence of the coating oxides on the surface structural change during the early cycles, and the Li-ion transfer at the electrode/electrolyte interface.

2. Experimental

Sample preparation. – LiCoO₂ powder with a secondary particle diameter of 7 μm (Nippon Chemical Industrial) was used as the active material. Thin and uniform coatings of Zr-oxide and Al-oxide were formed using a sol-gel method.⁶⁻¹⁵,²⁷ using zirconium tetrapropoxide and aluminum isopropoxide as the respective precursors. Dipropylenglycol was used as the chelating agent for both coatings. By substituting the ligand of the precursor with...
dipropylenglycol, a uniform gel net was formed on the surface of the LiCoO₂ particles. The sol-gel-coated LiCoO₂ samples was calcined at 500°C for 2 h. Since the oxides themselves exhibit poor electronic and ionic conductivity, when they are deposited as coatings in a large amount, the Li-ion transfer resistance increases. Thus, the contents of Zr-oxide and Al-oxide were set to the lower limit at which uniform coatings can be formed (0.18 and 0.11 wt%, respectively), assuming only ZrO₂ and Al₂O₃ were present. On the basis of the specific surface area of the LiCoO₂ sample, the contents of the former and latter correspond to the sol-gel-coating thickness of 0.68 and 0.64 nm, respectively. The surface morphology of the bare and coated LiCoO₂ samples were observed using scanning electron microscopy (SEM) at an accelerating voltage of 5 kV (JEOL, JSM-6700FV).

Positive electrodes were fabricated using a mixture of 90 wt% LiCoO₂, 5 wt% acetylene black (conductive carbon), and 5 wt% polyvinylidene fluoride (binder) on aluminum foils (current collector). The thickness of the electrodes was set to 22 µm. When the electrode is thick, the influence of ionic resistance in the porous electrode becomes large. In this study, to focus on the electrode/electrolyte interface, the electrode thickness was set as thin as possible within a range not affecting the electrode fabrication. The electrodes with diameters of 14 mm were punched out and used to fabricate 2032 type coin-cells. Lithium metal foil, a polypropylene membrane, and a 1.0 mol dm⁻³ solution of LiPF₆ in ethylene carbonate+diethyl carbonate (EC+DEC; 1:2 v/v) were used as the negative electrode, the separator, and the electrolyte, respectively. The cells were assembled in a dry room with dew point of below −45°C.

Figure 1. SEM images of (a) bare LiCoO₂, (b) Zr-oxide-coated LiCoO₂, and (c) Al-oxide coated LiCoO₂.

3. Results and Discussion

Surface morphology of bare and coated LiCoO₂ – Figures 1a and 1b show surface SEM images of bare and Zr-oxide-coated LiCoO₂, respectively. Island-like grains around 10 nm in diameter (blight parts) and areas without grain deposition (i.e., the sea-like zones) were observed on the Zr-oxide-coated LiCoO₂. Because the solubility of Zr cations is poor, only a small amount of them can mix into the LiCoO₂ surface region, while the excess Zr cations are...
deposited on the surface as ZrO2 grains. In our previous study with scanning transmission electron microscopy (STEM) on Zr-oxide-coated LiNi1/3Co1/3Mn1/3O2 prepared using the same sol-gel method, the island-like grains were identified as crystals of pure ZrO2, and a compound oxide phase containing Zr, Ni, Co, and Mn (approximately 2 nm in depth) was confirmed to form on the surface of the sea-like zones. In this study, it is presumed that a compound oxide containing Zr and Co was also formed on the sea-like zones of Zr-oxide-coated LiCoO2. Since ZrO2 crystals exhibit very poor Li-ion conductivity, it is almost unlikely that Li-ions diffuse in the island-like grains. Therefore, the sea-like zones are considered to be the effective electrode/electrolyte interface where the transfer of Li ions takes place.

Figure 1c shows the SEM images of Al-oxide-coated LiCoO2. Unlike Zr-oxide, the deposited materials were not clearly visible on Al-oxide-coated LiCoO2 because Al cations easily mix into the LiCoO2 surface region. Most of Al cations exist as a solid solution with LiCoO2 in the surface region. By STEM analysis, we confirmed that a LiAlO2-LiCoO2 solid-solution phase of layered rock-salt structure was formed at the surface of Al-oxide-coated LiCoO2 prepared by the same method.

Charge/discharge performance. – Figure 2 shows the initial charge/discharge curves of bare, Zr-oxide-coated, and Al-oxide-coated LiCoO2. At a low current rate of 0.05 C, the discharge capacity (∼193 mA h g⁻¹) and discharge voltage are almost equal for the three types of LiCoO2.

Figures 3a, 3b, and 3c show charge/discharge curves at the discharge current rates of 0.2, 1, and 3 C for bare, Zr-oxide-coated, and Al-oxide-coated LiCoO2, respectively. The polarization increased with increasing current rate for all types of LiCoO2, however, it was smaller for Zr-oxide-coated LiCoO2 than for the other two. To quantitatively evaluate the cell resistance at high current rate, the direct current-internal resistance (DC-IR) was defined by the following equation:

$$DC-IR = \frac{V_{0.2C} - V_{3C}}{\Delta I}$$

where $V_{0.2C}$ and $V_{3C}$ are the voltages recorded at 3 and 1 s after the discharge started at 0.2 and 3 C, respectively, and $\Delta I$ is the difference in discharge current at 3 and 0.2 C. The values of DC-IR estimated for bare, Zr-oxide-coated, and Al-oxide-coated LiCoO2 were 25.5, 20.3, and 33.5 Ω, respectively. Here, the discharges at 0.2 and 3 C are those at the total 2nd and 4th cycles, respectively.

Figure 4 shows the charge/discharge curves at the discharge current rate of 3 C. The average discharge voltage of bare, Zr-oxide-coated, and Al-oxide-coated LiCoO2 were 3.79, 3.89, and 3.77 V, respectively. Zr-oxide-coated LiCoO2 showed higher discharge voltage than the other two. The results of Figs. 3 and 4 indicate that the current rate performance of LiCoO2 was improved with the Zr-oxide coating.

Figure 5 shows the discharge capacities and average discharge voltages during cycle test at the current rate of 1 C. The reversibilities of both were significantly increased by either Zr-oxide or Al-oxide coatings. The Zr-oxide coating improved the cycle performance as well as the current rate performance. In the region after 50 cycles, Al-oxide-coated LiCoO2 showed even better stability in discharge capacity and average discharge voltage compared to Zr-oxide-coated LiCoO2. Thus, the Al-oxide coating greatly improved the cycle performance.
Impedance analysis. — Figure 6 shows the Nyquist plots of bare LiCoO₂ measured during (a) the 1st charge, (b) the 1st discharge, and (c) the 2nd charge. A large semicircle, which indicates a large resistance, was observed at the beginning of the 1st charge (OCV = 3.94 V in Fig. 6a), and it rapidly decreased during the 1st charge/discharge. In the 2nd charge, the large semicircle disappeared, while several other semicircles with different characteristic frequencies were observed. The large semicircle and its disappearance in the 1st charge/discharge were also observed in Zr-oxide-coated and Al-oxide-coated LiCoO₂. In general, after air exposure, the surfaces of layered rock-salt materials and Li metal are contaminated with impurities such as Li₂CO₃ and/or LiOH.28,29 It has been also reported that the surface impurity phase of LiCoO₂ dissolves after soaking in the electrolyte.30 The large semicircle observed in the 1st charge/discharge is probably caused by the surface impurity phases on the LiCoO₂ and Li electrodes, which are dissolved in the electrolyte during the 1st charge/discharge. Therefore, the semicircles observed from the 2nd cycle reflect the intrinsic characteristics of Li-ion transfer at the electrode/electrolyte interface.

Figure 4. Charge/discharge curves of bare, Zr-oxide-coated, and Al-oxide-coated LiCoO₂ at discharge current rate of 3 C.

Figure 5. (a) Discharge capacities and (b) average discharge voltages during cycle-test at current rate of 1 C for bare, Zr-oxide-coated, and Al-oxide coated LiCoO₂.

Figure 6. Nyquist-plots of bare LiCoO₂ measured during (a) the 1st charge, (b) the 1st discharge, and (c) the 2nd charge. A large semicircle, which indicates a large
Figures 7a, 7b, and 7c show Nyquist plots from the 2nd to the 4th cycle (in discharge) at OCV = 4.2 V for the bare, Zr-oxide-coated, and Al-oxide-coated LiCoO₂, respectively. Multiple semicircles were observed in each plot. Figure 7d shows the Nyquist plots of bare LiCoO₂ measured during the 4th discharge. The semicircles in the low-frequency region, which have characteristic frequencies of 1.6 – 10 Hz, depend greatly on the OCV; hence, they are identified with the charge transfer resistance (R_{ct}) at the interface of the LiCoO₂ positive electrode and electrolyte. In contrast, the semicircles in the high-frequency region, which correspond to frequencies of 5 kHz, do not depend on the OCV. Instead, the considerable distortion suggests the existence of plural resistance components. These high-frequency semicircles are attributable to the resistance of the positive electrode (R_p), which results from the surface film formed on the LiCoO₂ and/or the contact resistance between the porous electrode and the current collector, and the resistance of the Li negative electrode (R_n). Each resistance was quantitatively evaluated through fitting with an equivalent circuit, as shown in Fig. 7e. In the equivalent circuit, R_{ct}, R_p, and R_n correspond to resistances in the low, middle, and high frequency regions, respectively; and R_s is the solution resistance. Figure 7f shows the Nyquist plots of the bare, Zr-oxide-coated, and Al-oxide-coated LiCoO₂ at OCV = 4.2 V during the 4th discharge. The calculated fitting lines (solid lines) show good agreement with the experimental results (symbols). Here, the lower limit frequency of the fitting was set to 0.1 Hz.

Figure 8a shows R_{ct} from the 2nd to the 4th cycle (in discharge) at OCV = 4.2 V for the three LiCoO₂ electrodes. The R_{ct} of bare LiCoO₂ increased with increasing cycle number, indicating that the electrode/electrolyte interface started to degrade from an early cycle by the high-voltage charge/discharge. In contrast, the R_{ct} of Zr-oxide-coated LiCoO₂ decreased with increasing cycle number. This
indicates that after Zr-oxide coating, Li-ion transfer at the electrode/electrolyte interface was improved during the early cycles. On the other hand, $R_{ct}$ of Al-oxide-coated LiCoO$_2$ remained almost constant from the 2nd to 4th cycle, suggesting stable electrode/electrolyte interface with cycling. This stable interface should be the cause of the superior cycle performance of Al-oxide-coated LiCoO$_2$ observed in Fig. 5. The $R_{ct}$ values (average of two cells) of Zr-oxide-coated and Al-oxide-coated LiCoO$_2$ at the 4th cycle are 2.6 and 11.6 $\Omega$, respectively. The former is considerably lower than the latter.

Figure 8b shows $R_p$ of the same samples as Fig. 8a. In all types of LiCoO$_2$, the $R_p$ values are similar and decreased monotonically with increasing cycle number.

Figures 9a and 9b plot $R_{ct}$ and $R_p$ against OCV for the bare, Zr-oxide-coated, and Al-oxide-coated LiCoO$_2$ in the 4th discharge. The $R_{ct}$ values of Zr-oxide-coated LiCoO$_2$ were lower than those of the other two in the entire range of OCV. The lower $R_{ct}$ should result in a higher discharge voltage. Meanwhile, there was no difference in the $R_p$ values among the three types of LiCoO$_2$. As described above, $R_p$ is considered to be due to the surface film resistance on the LiCoO$_2$ and/or the contact resistance between the positive electrode and the current collector. This result indicates that there is no difference in the resistances between the samples.

Figure 10a shows the average values of $R_s$, $R_n$, $R_p$, and $R_{ct}$ for the three LiCoO$_2$ electrodes at OCV = 4.5 V in the 4th discharge. There was no significant difference in the resistances among the samples, except for $R_{ct}$. The changes in $R_{ct}$ with Zr-oxide and Al-oxide coatings compared to bare LiCoO$_2$ were $-5.1$ and $+8.5\Omega$, respectively. Figure 10b shows the DC-IR values for the samples. The differences in DC-IR with Zr-oxide and Al-oxide coatings compared to bare LiCoO$_2$ were $-5.2$ and $+8.0\Omega$, respectively, similar to the differences in $R_{ct}$. From these results, the higher current rate performance of Zr-oxide-coated LiCoO$_2$ observed in Figs. 3 and 4 was attributed to its lower $R_{ct}$.

To determine the mechanism for the difference in $R_{ct}$, the temperature dependence of the impedance was measured. Figure 11a shows the logarithm of $1/R_{ct}$ plotted against the reciprocal of temperature for the three electrodes at OCV = 4.2 V in the 5th discharge. The plots show good linearity. This means that the charge transfer reaction, which controls the current rate performance, can be expressed by following Arrhenius equation:

$$\frac{1}{R_{ct}} = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

(2)

where $A$, $E_a$, $R$, and $T$ are the frequency factor, activation energy, the gas constant, and absolute temperature, respectively. This also indicates that the current rate performance is determined by $E_a$ and $A$ for charge transfer at electrode/electrolyte interface. Figure 11b shows $E_a$ of the electrodes, which was calculated from the gradients of the lines using Eq. (2). The $E_a$ of Zr-oxide-coated LiCoO$_2$ was approximately 10 kJ mol$^{-1}$ lower than those of bare and Al-oxide-coated LiCoO$_2$. Since ZrO$_2$ grains themselves exhibit poor Li-ion
conductivity, the coating decreases the number of Li-ion intercalation sites at the LiCoO$_2$ surface; in other words, $A$ in Eq. (2) decreases. Nevertheless, the $R_{ct}$ values of the Zr-oxide-coated LiCoO$_2$ was lower than those of bare and Al-oxide-coated LiCoO$_2$ as mentioned above. This is due to the lower $E_a$ of the Zr-oxide-coated LiCoO$_2$. Even in our previous studies with LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ powder and LiCoO$_2$ thin film, the Zr-oxide-coated samples had lower $E_a$ compared to the bare samples.$^{15,16}$ The effect of the Zr-oxide coating in reducing $E_a$ is probably common to layered rock-salt active materials.

An adatom model has been proposed as a mechanism of Li-ion transfer reaction at the intercalation electrode and electrolyte interface.$^{31,36,37}$ Recently, computational studies of the interface reactions in intercalation materials have also been reported.$^{38,39}$ A schematic diagram of the Li-ion transfer reaction based on them is shown in Fig. 12. The reaction from the solution phase to the solid phase is thought to proceed as follows.

1. The solvated Li$^+$ in the electrolyte adsorbs onto the electrode surface.
2. The solvated shell breaks down, which leads to partially solvated Li$^+$. 
3. The electron transfer reaction (Co$^{4+}$ + e$^-$ $\rightarrow$ Co$^{3+}$) occurs and the remaining solvent molecules desorb. 
4. The desolvated Li$^+$ is incorporated into the crystal lattice of the electrode.

In Zr-oxide coated LiCoO$_2$ in which Zr cations mixed in the surface phase, the lattice structure at the outmost surface should be different from those of bare and Al-oxide coated LiCoO$_2$. The lower $E_a$ of Zr-oxide coated LiCoO$_2$ observed in Fig. 11b suggests that it had a lower activation barrier for the lattice incorporation of Li ions. In addition, since the process (3), that is, the electron transfer and desolvation may be influenced by the electronic state of the electrode surface, it is also conceivable that this process affects the $E_a$ of Zr-oxide coated LiCoO$_2$.

Figure 13a and 13b show schematic diagrams of the surface structures of Zr-oxide-coated and Al-oxide-coated LiCoO$_2$, respectively. In the surface region of Zr-oxide-coated LiCoO$_2$, there should exist ZrO$_2$ grains and a compound oxide phase containing Zr and Co (Li-Zr-Co-O phase) as discussed in the previous section (Fig. 1). Li ions diffuse into the bulk LiCoO$_2$ through the Li-Zr-Co-O phase. The Li-Zr-Co-O phase, which cannot form a stable solid solution as a bulk, is considered relatively active. Therefore, the surface of this

![Figure 10](image1.png)

**Figure 10.** (a) $R_s$, $R_n$, $R_p$, and $R_{ct}$ (average values of two cells) for bare, Zr-oxide-coated, and Al-oxide-coated LiCoO$_2$ at OCV of 4.5 V in the 4th discharge. (b) DC-IR estimated from the rate performance for the samples.

![Figure 11](image2.png)

**Figure 11.** (a) Temperature dependence of $R_{ct}$ at OCV = 4.2 V in the 5th discharge and (b) the activation energy ($E_a$) for the bare, Zr-oxide-coated, and Al-oxide-coated LiCoO$_2$.

![Figure 12](image3.png)

**Figure 12.** Schematic diagram of Li-ion transfer at the electrode/electrolyte interface.
phase may be reconstructed in conjunction with the insertion/extraction of Li ions during the early cycles. Such reconstruction may form a new electrode/electrolyte interface where Li ions transfer. The lower \( E_a \) and \( R_{ct} \) of Zr-oxide-coated LiCoO\(_2\) should be attributed to the formation of the new interface with lower activation barrier for the lattice incorporation and/or the electron transfer and desolvation. On the other hand, the surface phase of Al-oxide-coated LiCoO\(_2\) should be highly stable, because Al-oxide can form a stable solid-solution with LiCoO\(_2\) as LiAlO\(_2\)-Li-CoO\(_2\). Therefore, there should be very little surface reconstruction, and the \( E_a \) and \( R_{ct} \) values of Al-oxide-coated LiCoO\(_2\) remain constant throughout the early cycles. This suggests that the stable and relatively higher \( R_{ct} \) and \( E_a \) of Al-oxide-coated LiCoO\(_2\) reflect the characteristics of the coated surface itself. The superior cycle performance of Al-oxide-coated LiCoO\(_2\) was attributed to the stable surface phase. By comparing the behavior of Zr-oxide- and Al-oxide-coated LiCoO\(_2\), it was suggested that the structure of the electrode/electrolyte interface formed through the early charge/discharge cycles determines the Li-ion transfer characteristics and charge/discharge performance.

4. Conclusions

The kinetics of Li-ion transfer at the electrode/electrolyte interface and the current rate performance of LiCoO\(_2\) surface-coated with Zr-oxide and Al-oxide were investigated. Zr-oxide-coated LiCoO\(_2\) showed higher current rate performance compared to bare and Al-oxide-coated LiCoO\(_2\), while Al-oxide coating greatly improved the cycle performance. The higher current rate performance of Zr-oxide-coated LiCoO\(_2\) was caused by its lower \( R_{ct} \) and \( E_a \). The lower \( E_a \) of Zr-oxide coated LiCoO\(_2\) was considered to be due to the lower activation barriers for the lattice incorporation and/or the electron transfer and desolvation. The behavior of \( R_{ct} \) during the early charge/discharge cycles suggested that the differences in \( E_a \) and \( R_{ct} \) are caused by the reconstruction of the coated surface, which further depends on the solubility of cations of the coating oxides into LiCoO\(_2\). This information about the structural change of the electrode/electrolyte interface during the early cycles is important, in terms of understanding the Li-ion transfer characteristics of surface-coated electrode materials and improving their electrochemical performances.

Figure 13. Schematic diagrams of the surface structures of (a) Zr-oxide-coated and (b) Al-oxide-coated LiCoO\(_2\).