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ABSTRACT
Degradation mechanism of surface coating effects at the cathode/electrolyte interface is investigated using thin-film model electrodes combined with operando X-ray absorption spectroscopy (XAS). MgO-coated LiCoO2 thin-film electrodes prepared via pulsed laser deposition at room temperature and high temperature are used as model systems. The MgO coating improves the durability of the cathode during high-potential cycling. Operando total reflection fluorescence XAS reveals that initial deterioration due to reduction of Co ions at the surface of the uncoated-LiCoO2 during charging process. The electronic and local structure changes at the electrode/electrolyte interface for two types of surface coating morphologies are discussed.

Keywords : Lithium Ion Battery, Surface Coating, Interfacial Structure, Operando Measurement

1. Introduction
Lithium-ion batteries (LIBs) are used in several applications such as mobile phones and electric vehicles, and further improvement of the battery performance is needed. For the improvement of the performance, it is necessary to control the interfacial structure between electrode and electrolyte because the electrode/electrolyte interface is the reaction site of LIBs. One of the popular methods to control the interfacial structure is to coat active materials with a metal oxide. The surface coating of the active materials enhances various aspects of battery performance such as cyclability, rate capability, and durability at high potential. However, to the best of our knowledge, the interfacial structure between the electrode and electrolyte upon surface coating is still unclear, particularly when it comes to in operando battery operations. This is because direct observation of the interfacial structure is quite difficult. Measurement techniques for the interface with spatial resolution in a nanometric scale under battery operating conditions are required.

Surface X-ray diffraction and X-ray reflectivity measurements have been reported as effective tools to probe interfacial structures under operating conditions of a battery. Although these methods are potent to probe the interface, they however cannot probe amorphous structures or even electronic structural changes. Recently we have developed operando total-reflection fluorescence X-ray absorption spectroscopy (TRF-XAS) and operando depth-resolved X-ray absorption spectroscopy (DR-XAS). TRF-XAS provides surface-sensitive information regarding the electronic structure at the electrode/electrolyte interface. DR-XAS provides information about the electronic and local structures from the surface to the bulk at a nanometric resolution. These techniques are therefore potent to probe the electronic and local structure of the active material with surface modification under battery operating condition.

This study aims on a comprehensive understanding of the surface coating mechanism. In our previous report, MgO coating on LiCoO2 forms a solid solution phase at the LiCoO2 surface, which occurs upon MgO coating at high temperatures. However, different morphologies of MgO coating layer have been reported by other research groups. In order to examine the morphology effect, we prepared two types of MgO coated-LiCoO2 thin film electrodes at room temperature and high temperature. The stability at high potential cycling was investigated by electrochemical measurements. The electronic and local structural changes under battery operating conditions were tracked via operando TRF-XAS and DR-XAS measurements. By using these data, the surface coating mechanism is discussed from the viewpoint of electronic and local structure at the electrode/electrolyte interface.

2. Experimental Methods
LiCoO2 thin films were prepared on mirror-polished platinum substrates by pulsed laser deposition (PLD). Dense LiCoO2 target with 15 wt% excess Li2O was used to compensate for Li loss during the deposition. A Nd:YAG laser (\(\lambda = 266\) nm, 10 Hz repetition rate, 200 mW of power) was used. Deposition time, oxygen partial pressure and substrate temperature were 30 min, 0.01 Pa and 600°C, respectively. After the deposition of LiCoO2, MgO was deposited onto the LiCoO2 films by PLD for 30 s at room temperature or 60 s at 700°C. Hereafter, the uncoated LiCoO2 thin film, the MgO coated LiCoO2 thin films at room temperature and the films coated at 700°C are denoted as uncoated-LCO, RT-MgO-LCO and HT-MgO-LCO, respectively.

The as-prepared thin films were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) complemented with energy dispersive X-ray spectroscopy (EDX). Electrochemical measurements were performed using three-
3. Characterization of as-prepared thin films

The as-prepared thin film electrodes were characterized by XRD, cross-sectional TEM as shown in Fig. 1. Except the diffraction peaks arising from Pt substrate, a peak at approximately 2θ = 18.9° is observed. This peak corresponds to diffraction by the (003) plane of hexagonal LiCoO₂. No other diffraction peaks were detected, validating the obtained LiCoO₂ film as a single phase oriented along the c-axis. The position of the diffraction peaks for the three thin films is almost equal, which indicates the bulk-crystal structure is unchanged upon MgO coating. The c-axis of the prepared LiCoO₂ film is tilted and not perpendicular to the substrate and the in-plane is random, meaning that the planes through which lithium ions can intercalate in LiCoO₂ face the interface. The surface morphology measured by cross-sectional TEM with EDX of the RT-MgO-LCO is shown in Fig. 1(b). The EDX scan detected a Mg containing layer of approximately 5 nm in thickness outside Co containing layer for the RT-MgO-LCO. While the HT-MgO-LCO has a Mg layer within the LiCoO₂ surface, a Mg layer covers the surface of LiCoO₂ for the RT-MgO-LCO at the initial state.

3.2 Electrochemical properties of MgO coated LiCoO₂ thin films

The MgO coating on LiCoO₂ improves the durability especially at high potentials. Figure 2 shows the cyclic voltammograms (CVs) of uncoated-LCO, RT-MgO-LCO and HT-MgO-LCO at various upper limit potentials. The main peak observed at approximately 3.9 V is attributed to the first order phase transition between two hexagonal LiCoO₂ phases. Two small peaks are observed at around 4.1 V and 4.15 V, which indicates that phase transitions occurs during lithium deintercalation. When these three thin films are cycled below 4.2 V, the shapes of the CVs show good reversibility. The peak separation is small for the uncoated-LCO and the HT-MgO-LCO, while a clear separation is observed for the RT-MgO-LCO. When the potential range is increased, the cathodic peak diminishes drastically for the uncoated-LCO as shown in Figs. 2(b) and 2(c). On the other hand, this decrement is suppressed for the RT-MgO-LCO and HT-MgO-LCO even after charging to 4.4 V. The relationship between the coulombic efficiency calculated from the CVs and the upper limit potential is shown in Fig. 2(d). The coulombic efficiency of the uncoated-LCO decreased drastically to less than 60% after charging to 4.4 V. This irreversible reaction is suppressed for the RT-MgO-LCO and the HT-MgO-LCO. These results indicate that bare LiCoO₂ is easily deteriorated at high potentials and this degradation can be suppressed through MgO coating.

The effect of MgO coating is revealed by the resistance of the interfacial reaction measured via electrochemical impedance spectroscopy (EIS). Figure 3(a) shows typical Nyquist plots for EIS measured at various potentials. The observed main arcs correspond to the resistance of the interfacial reaction between the LiCoO₂ electrode and the electrolyte. For the uncoated-LCO, the small arc observed at 4.0 V is drastically enlarged at 4.4 V. This result indicates that an inactive layer is formed on LiCoO₂ due to surface degradation. For the RT-MgO-LCO, the resistance is much greater than that of the uncoated-LCO at first. However the arc is not enlarged at 4.4 V but slightly diminishes. The interfacial resistances at each potential were estimated through the use of an equivalent circuit with the resistance in parallel with a constant-phase element [Fig. 3(b)]. Both MgO coatings inhibit the increase of the interfacial resistance at 4.4 V as observed in the uncoated-LCO. The initial resistance of the RT-MgO-LCO is much larger than those of other films because the MgO layer deposited on the LiCoO₂ surface acts as a resistive phase. Interestingly, the resistance of RT-MgO-LCO increases from 4.0 V to 4.3 V, and then decreases from 4.3 V to 4.4 V in the charging process and the subsequent discharging processes. The reason behind this phenomenon will be discussed in the latter section.

3.3 Surface-sensitive operando XAS

To investigate the interfacial chemical structure on a nanometer scale, TRF-XAS measurements were performed for the three thin films. The information obtained from TRF-XAS mainly reflects the extreme interfacial structural features between electrodes and electrolytes under battery operating conditions. Figure 4(a) shows...
surface-sensitive X-ray absorption near edge structure (XANES) spectra at the Co K-edge measured via TRF-XAS of the prepared electrodes upon electrolyte immersion. In general, the absorption edge energy of XANES corresponds to the average valence of Co ions. For the uncoated-LCO, the absorption edge of XANES is located at lower energy than that of the RT-MgO-LCO and the HT-MgO-LCO. The reduction behavior of Co ions for the uncoated-LCO immediately upon electrolyte immersion has been reported to be due to the reductive nature of organic electrolytes.15 The reduction of Co ions caused by electrolyte contact is suppressed by MgO coating as shown in Fig. 4(a). The energy at a normalized intensity of 0.5 of the XANES spectra (E0) is plotted in Fig. 4(b) as a function of the various states of charge/dischARGE for the three thin films. For the uncoated-LCO, E0 decreases immediately after electrolyte soaking and changes irreversibly during cycling between 3.8 V and 4.2 V. On the other hand, E0 of the RT-MgO-LCO and the HT-MgO-LCO show reversible valence change. These results indicate that the MgO coating enhances the stability of the surface structure under battery operating condition.

3.4 Depth-resolved analysis of local structure change

Local structural changes of LiCoO2 can be induced by the MgO coating and lithium extraction/insertion, especially around the electrode/electrolyte interface. The three thin films were investigated via DR-XAS, which can provide local structural information with a depth resolution of 3–4 nm.16 While the spectra collected at low-exit angles consist of signals only from the surface of the LiCoO2 electrode due to self-absorption of fluorescence X-ray from deeper range, the spectra collected at high-exit angles include signals from both the surface and bulk. Local structural parameters, such as the interatomic distances and the Debye-Waller (DW) factors for the Co-O bonds were calculated by EXAFS analysis. DW factor reflects static local distortions for the Co-O bonds. The calculated Co-O length and the DW factor for the Co-O bonds at various states of charge are plotted as a function of the exit angles in Fig. 5. For this EXAFS analysis, the standard error of the Co-O length is less than 0.001 nm and that of the Co-O DW factor is less than 0.002 nm. Although depth-resolved EXAFS analysis provides relatively large standard errors, one can discuss tendencies of the Co-O length and DW factor from the surface to the bulk as previously reported.17,18

The temperature of MgO coating influences the surface structure of LiCoO2. The Co-O length for the HT-MgO-LCO is longer than those of the other two thin films and is larger for low exit angles as shown in Fig. 5(a). The DW factor of the HT-MgO-LCO is larger than those for the others as shown in Fig. 5(d). This result can be explained by the formation of solid solution phase at LiCoO2 surface as reported previously.20 On the other hand, the Co-O length and the DW factor of the RT-MgO-LCO are almost similar to those of the uncoated-LCO. This result indicates that MgO layer only covers the LiCoO2 surface and does not affect the local structure of LiCoO2. The covered MgO layer for the RT-MgO-LCO impedes the interfacial reaction as observed in EIS measurement (Fig. 3).

Electrochemical lithium extraction causes rearrangement of local structure around the electrode/electrolyte interface. For the uncoated-LCO, when the cells are charged to 4.2 V, the DW factor at low exit angles increases [Fig. 5(e)], meaning that structural distortion occurs at the interface.17 When the uncoated-LCO is charged to 4.4 V, the Co-O length at low angle is almost similar to the value observed at 4.2 V. The DW factor of the uncoated-LCO also increased at 4.4 V, particularly at the surface. These results show that the local structure of LiCoO2 is deteriorated and the interfacial resistance is drastically increased.17 On the other hand, the parameter changes for the RT-MgO-LCO is similar to that of HT-MgO-LCO in which the Mg-containing solution layer in LiCoO2 surface can stabilize the electrode/electrolyte interface at high potential.20 When RT-MgO-LCO is charged, several Li+ ions become unoccupied, and Mg2+ ions at the surface can diffuse into the unoccupied Li+ sites. This process generates the solid solution phase of Mg at LiCoO2 surface. Therefore the local structure of RT-
the uncoated-LCO, the potential gap at the interface should be examined for three model thin films. LiCoO$_2$ is reported to be a semiconductor from the electrolyte to the surface, forming the space charge layer at the interface. The potential gap between the electrode and the electrolyte is mostly compensated by the space charge layer and the electrical double layer. This wide space charge layer forms a Co-$\text{Li}^{+}$ configuration in the electrolyte [Fig. 6(c)]. Considering this, the suppression of the space charge layer formation in bare LiCoO$_2$ is very stable and prevents the electron transfer to the conduction band of the LiCoO$_2$. For RT-MgO-LCO, since the space charge layer does not form at the surface, the potential gap between the electrode and the electrolyte is mostly compensated by the electrical double layer in the electrolyte and the solid solution phase formed on the LiCoO$_2$ surface is very stable. Furthermore, the capacity degradation of the uncoated-LCO occurred through potential cycling between 3.2 V and 4.0 V. This means that Mg-coating does not suppress the phase transition. As shown in Fig. 2(a), the phase transition of LiCoO$_2$ occurs at approximately 4.1 V. Although it has been reported that Mg-doping suppresses the phase transition and improves the stability of LiCoO$_2$, the peak attributed to the phase transition was still observed for the RT-MgO-LCO and HT-MgO-LCO at approximately 4.1 V. This means that Mg-coating does not suppress the phase transition. Therefore, the solid solution Mg plays an important role for suppressing the local structure deterioration.

3.5 Comprehensive model for surface coating mechanism

In this section, we summarize the surface coating mechanism based on the experimental results. For the MgO coating, our results show two types of configuration. The first is MgO layer covering the LiCoO$_2$ surface as observed for the RT-MgO-LCO. The second is a solid solution formation at LiCoO$_2$ surface as observed for the HT-MgO-LCO. At the initial state, the former configuration influences the interfacial resistance, whereby the MgO layer covering LiCoO$_2$ impedes the interfacial reaction. However, the initial deterioration observed in the uncoated-LCO can be suppressed for both cases. A schematic illustration of the electrode/electrolyte interface for the examined three model thin films is shown in Fig. 6. Co reduction observed in the uncoated-LCO indicates that the electron transfer from the electrolyte to the surface forms the space charge layer at the LiCoO$_2$ surface. LiCoO$_2$ is reported to be a semiconductor with a relatively small band gap of $\sim$1.5 eV. Electrons from the electrolyte can move to the conduction band of the LiCoO$_2$. For the uncoated-LCO, the potential gap at the interface should be compensated by the space charge layer and the electrical double layer [Fig. 6(a)]. This wide space charge layer forms a Co-reduction phase. As shown in Fig. 2(a), the phase transition of LiCoO$_2$ occurs at approximately 4.1 V. Although it has been reported that Mg-doping suppresses the phase transition and improves the stability of LiCoO$_2$, the peak attributed to the phase transition was still observed for the RT-MgO-LCO and HT-MgO-LCO at approximately 4.1 V. This means that Mg-coating does not suppress the phase transition. Furthermore, the capacity degradation of the uncoated-LCO occurred through potential cycling between 3.2 V and 4.0 V. This supports that the surface structure change of the uncoated-LCO changes upon electrolyte immersion influences the charge-discharge stability.

In contrast, the MgO coating at room temperature inhibits the reduction of the Co ions at the LiCoO$_2$ surface upon electrolyte immersion. The band gap of MgO is much larger (6.4 eV) than that of the LiCoO$_2$, preventing the electron transfer to the conduction band of the LiCoO$_2$. For RT-MgO-LCO, since the space charge layer does not form at the surface, the potential gap between the electrode and the electrolyte is mostly compensated by the electrical double layer in the electrolyte [Fig. 6(b)]. In the case of HT-MgO-LCO, the solid-solution phase formed on the LiCoO$_2$ surface is very stable because the surface structure is not deteriorated even when the space charge layer forms at the electrode side [Fig. 6(c)]. Considering this, the suppression of the space charge layer formation in bare LiCoO$_2$ layer is an effective strategy to prevent initial deterioration of active materials during battery operation.

Control of the stability of the local structure in LiCoO$_2$ is also an important strategy. For the HT-MgO-LCO, the solid solution of Mg stabilizes the interfacial structure upon cycling at high potentials. For the RT-MgO-LCO, the MgO layer only covers LiCoO$_2$ surface, leading to unfavorable increase in the interfacial resistance. However, as observed in the DR-XAS study, the local structure of
because the ionic radius of Mg$^{2+}$ is close to that of Li$^+$. Therefore a solid solution with Mg$^{2+}$ ions in the MgO can diffuse into the unoccupied Li$^+$ sites because the ionic radius of Mg$^{2+}$ is close to that of Li$^+$. This result supports the formation of a solid-solution phase when MgO coating is conducted at room temperature, the MgO layer only covers on LiCoO$_2$ thin films, whereas obtained at high exit angles reflect on more information about the bulk property.

the RT-MgO-LCO is similar to that of the HT-MgO-LCO during charging. When LiCoO$_2$ is charged, Li$^+$ sites become unoccupied, and Mg$^{2+}$ ions in the MgO can diffuse into the unoccupied Li$^+$ sites to improve the durability under high-potential cycling. The initial deterioration caused by Co reduction of the uncoated-LiCoO$_2$ thin films is inhibited by MgO coating. For the MgO coating conducted at high temperature, a solid solution phase is formed on LiCoO$_2$ surface which stabilizes the delithiated layered structure. For the MgO coating conducted at room temperature, the MgO layer only covers the surface of LiCoO$_2$ at the initial state. During the charge process, Mg$^{2+}$ ions at the surface diffuse into the unoccupied Li$^+$ sites of LiCoO$_2$. In both cases, Mg ions serve as pillars in LiCoO$_2$ layer to improve the stability at high potential.

4. Conclusion

The mechanism of the MgO coating on LiCoO$_2$ was investigated via electrochemical measurements and in operando XAS measurements. MgO coating at both room temperature and high temperature improves the durability under high-potential cycling. The initial deterioration caused by Co reduction of the uncoated-LiCoO$_2$ thin films is inhibited by MgO coating. For the MgO coating conducted at high temperature, a solid solution phase is formed on LiCoO$_2$ surface which stabilizes the delithiated layered structure. For the MgO coating conducted at room temperature, the MgO layer only covers the surface of LiCoO$_2$ at the initial state. During the charge process, Mg$^{2+}$ ions at the surface diffuse into the unoccupied Li$^+$ sites of LiCoO$_2$. In both cases, Mg ions serve as pillars in LiCoO$_2$ layer to improve the stability at high potential.

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