

# **Design Principles for the Cathode/Electrolyte Interfacial Phenomena in Lithium Ion Batteries**

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## **Summary**

Energy storage devices play important roles for modern human life. Among the devices, lithium ion batteries have higher performance and further enhancement of the performance is required to spread utilization of electronic vehicles and smart grid systems. In order to realize these purposes, it is necessary to understand fundamentally reactions occurring in the battery during charging/discharging process. The present work focused on the interfacial phenomena between cathode/electrolyte in lithium ion batteries. Especially, electronic and local structure at the interface and reactions at the electrode surface was investigated. The present thesis consists of six chapters, presenting correlation between surface electronic structure and the performance of lithium ion batteries, controlling the interfacial structure between cathode and electrolyte, and analyzing reactions occurring at the surface of cathode.

In chapter 1, firstly, the overview of lithium ion battery was described, and the importance of understanding mechanism of reactions occurring at electrode/electrolyte interface in lithium ion battery was presented. Secondly, the electrode/electrolyte interfacial phenomena are explained. Thirdly, methods to analyze and control the interfacial phenomena were also presented. Finally, the objective of the present thesis was described. Lithium ion battery is composed of a cathode, an anode, an electrolyte (which is in separator) and current collectors. The cathode and anode are separated by the electrolyte. In the typical  $\text{LiMO}_2/\text{graphite}$  cell, the operating principle is explained as the following. In the discharge process, lithium ions are simultaneously extracted from the graphite and solvated with

solvents in the electrolyte. The solvated-lithium ions transfer to the  $\text{LiMO}_2$  side, and then the lithium ions are simultaneously dissolved and inserted into the  $\text{LiMO}_2$ . When the  $\text{LiMO}_2$  receives the lithium ions from the electrolyte, it receives electrons from the external circuit. The interfacial reaction at the electrode/electrolyte is the starting point in the all reaction occurring in the battery, which affects largely the performance such as power density or durability. Therefore, it's important to understand the interfacial phenomena for improvement of the battery performance. Because an electrode and an electrolyte have different inner potentials each other, the gap between the two potentials is compensated around the interface. This region that potential compensation occurs is called an electrical double layer at the electrolyte side and a space charge layer at the electrode side, respectively. Because the inner potential around the electrode/electrolyte interface is different from the potential in the bulk as shown, specific phenomena occur at the interface as not seen in the bulk. However, it's difficult to investigate the interfacial phenomena because the following three conditions must be met; (1) construction of an ideal electrode/electrolyte interface (2) analytical methods with space resolution in a few nanometers (3) *in situ* analysis. Although several powerful analytical methods such as *in situ* surface X-ray diffraction or *in situ* X-ray reflectometry have been developed, the information about electronic structure at the interface is shortage. Further understanding the interfacial phenomena, a technique to investigate electronic structure of the interface is needed. There has been the large number of reports about controlling the interfacial structure by surface coatings of cathodes or electrolyte additives. It is well known that controlling the interfacial structure is effective to improve the battery performance. However, the mechanism underlying the control of the interfacial structure has not been clarified. This is because the techniques to investigate directly the interfacial structure are limited, resulting that the information about the interfacial structure is shortage, especially about the electronic structure of it. Therefore, in order to understand the mechanism of the interfacial modification, direct (*in situ*) observation of the electronic structure at the

interface must be required. Recently, two types of X-ray absorption spectroscopy (XAS) techniques have been developed to investigate the electronic structure at the electrode/electrolyte interface. The first technique is called *in situ* total-reflection fluorescence X-ray absorption spectroscopy (*in situ* TRF-XAS) and the other one is *in situ* depth-resolved X-ray absorption spectroscopy (*in situ* DR-XAS). The *in situ* TRF-XAS can investigate the electronic structure at a depth of a few nanometers from the surface of an electrode. The *in situ* DR-XAS can investigate the electronic structure and local structure from the surface to the bulk of an electrode with the depth resolution of *ca.* 3 nm. These *in situ* XAS techniques are powerful for the investigation of the electrode/electrolyte interfacial electronic structure. In the present thesis, interfacial phenomena between cathode/electrolyte are investigated by applying the *in situ* XAS techniques and various electrochemical measurements to model thin-film electrodes of LiCoO<sub>2</sub> and LiFePO<sub>4</sub>.

In chapter 2, the electronic structure at the LiCoO<sub>2</sub> and LiFePO<sub>4</sub>/electrolyte interface during electrolyte immersion and Li ion extraction/insertion was directly monitored by *in situ* TRF-XAS. The thin-films of LiCoO<sub>2</sub> and LiFePO<sub>4</sub> were prepared by using pulsed laser deposition. In the LiCoO<sub>2</sub> thin-film electrode that exhibits gradual deterioration upon subsequent lithium ion extractions and insertions (cycling), the reduction of Co ions at the electrode/electrolyte interface was observed upon immersion in an organic electrolyte, with subsequent irreversible changes after cycling. In contrast, in the LiFePO<sub>4</sub> thin-film electrode, the electronic structure at the electrode/electrolyte interface was stable and reversible upon electrolyte immersion with subsequent cycling. The reduction at the surface of LiCoO<sub>2</sub> upon electrolyte immersion indicates that a space charge layer forms on the surface. A potential gap at the LiCoO<sub>2</sub>/electrolyte interface is compensated by both of the space charge layer and an electrical double layer in the electrolyte. The surface of LiCoO<sub>2</sub> is destabilized by the formation of the space charge layer, which affects the degradation of the active material with lithium ion extractions and insertions. No reduction at the

surface of  $\text{LiFePO}_4$  upon electrolyte immersion indicates that a large space charge layer does not form on the surface. Hence, a potential gap at the  $\text{LiFePO}_4$ /electrolyte interface is compensated mainly by an electrical double layer in the electrolyte. The surface of  $\text{LiFePO}_4$  is stable due to the lack of a large potential change in the space charge layer at the surface, which is related to its reversible cycling capacity.

In chapter 3, preparing for the surface coated- $\text{LiCoO}_2$  thin-films with  $\text{MgO}$  at high temperature and room temperature by using pulsed laser deposition, the mechanism of the  $\text{MgO}$  coating on  $\text{LiCoO}_2$  was investigated via electrochemical measurements and *in situ* XAS measurements. For the  $\text{MgO}$  coated- $\text{LiCoO}_2$  at high temperature, a solid solution phase is formed on the surface of  $\text{LiCoO}_2$ . For the  $\text{MgO}$  coated- $\text{LiCoO}_2$  at room temperature, the  $\text{MgO}$  layer only covers the surface of  $\text{LiCoO}_2$  at the initial state.  $\text{MgO}$  coating at both temperatures improved the durability under high-potential cycling.  $\text{MgO}$  coating at high temperature suppresses the increase of the interfacial resistance at high potential observed in the uncoated- $\text{LiCoO}_2$ . Although  $\text{MgO}$  coating at room temperature increases the interfacial resistance at initial state, it also suppresses the increase of the interfacial resistance at high potential. *In situ* TRF-XAS observed that the reduction at the surface of the uncoated- $\text{LiCoO}_2$  thin film was inhibited by  $\text{MgO}$  coating at both temperatures. For the  $\text{MgO}$  coated- $\text{LiCoO}_2$  at high temperature, because the solid state phase makes the surface so stable that the surface is not reduced even when the space charge layer forms. For the  $\text{MgO}$  coated- $\text{LiCoO}_2$  at room temperature,  $\text{MgO}$  covering the surface plays as an insulator, preventing the electron transfer to the surface of  $\text{LiCoO}_2$ . *In situ* DR-XAS observed that  $\text{MgO}$  coating at both temperatures suppressed distortion of local structure at the surface of the uncoated- $\text{LiCoO}_2$  during charge process. The local structure at the surface of the uncoated- $\text{LiCoO}_2$  is distorted at high potential. The  $\text{MgO}$  coating at high temperature suppressed the distortion because the solid solution phase stabilized the surface structure. For the  $\text{MgO}$  coating at room temperature,  $\text{Mg}^{2+}$  ions in  $\text{MgO}$  covering the surface diffuse

into the unoccupied  $\text{Li}^+$  sites of  $\text{LiCoO}_2$  during the charge process, suppressing the distortion of the local structure at high potential. In both  $\text{MgO}$  coatings,  $\text{Mg}$  ions serve as pillars in  $\text{LiCoO}_2$  layer to improve the stability at high potential. These results provide, in detail, the mechanism underlying surface coating of a cathode that occurs at the interface on the nanometer scale under actual battery operating conditions.

In chapter 4, the effects on the electronic structure of the surface of a  $\text{LiCoO}_2$  electrode of adding vinylene carbonate (VC) to the electrolyte under battery operating conditions were investigated using *in situ* TRF-XAS. The addition of VC to the electrolyte improved the cycling performance of  $\text{LiCoO}_2$ , and suppressed the increase of the interfacial resistance with charge/discharge cycling. The addition of VC suppressed the reduction of  $\text{Co}$  ions upon electrolyte immersion. The reversibility of the electronic structure of the  $\text{LiCoO}_2$  surface during charge/discharge cycling was also significantly increased by the addition of VC to the electrolyte. The effects of the VC additive on the electronic structure can be attributed to the layer formation caused by the decomposition of VC on the  $\text{LiCoO}_2$  surface, which played an important role in mitigating the degradation of the capacity and the increase in the interfacial resistance of the  $\text{LiCoO}_2$  during charge/discharge cycles.

In chapter 5, the activation energy of nucleation and growth reactions was evaluated quantitatively by applying combination of chronoamperometry with Kolmogorov-Johnson-Mehl-Avrami analysis to  $\text{LiFePO}_4$  thin-film electrode. The activation energy of the rate constant obtained from Avrami plots for the thin-film electrode was significantly smaller than that for the composite electrode previously reported. This result means nucleation at the  $\text{LiFePO}_4$  surface is the rate-limiting step during lithium ion extraction process. For improvement of the rate performance of lithium ion battery, it is important to control the surface reaction on active materials.

In chapter 6, the results of this thesis were summarized. By using several *in situ* XAS techniques and several electrochemical measurements, it is proved that the electronic structure and local structure at surface of active materials play important roles for the performance of lithium ion battery. This thesis mainly focuses on the relationship between the interfacial structure and durability of lithium ion battery. For further improvement of the battery performance, fundamental study about interfacial phenomena based on kinetics is required, which leads to improve the rate performance of lithium ion battery.