

***in situ* Total-Reflection Fluorescence X-ray
Absorption Spectroscopic Study on Stability at
LiFePO₄/ Electrolyte Interface**

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Introduction

Lithium-ion batteries (LIBs) have been used as power sources for mobile devices such as cell phones and mobile PCs because of their large energy densities. In order to enhance LIB performance, it is very important to understand the electrode/electrolyte interface reactions because these reactions greatly affect the cyclability and power density of LIB. However, the mechanisms of such interface reactions have not yet been fully understood due to the difficulty of their direct observation for the reactions at nanoscale. Our group has directly observed the interface reactions of a thin-film model electrode of LiCoO₂ by *in-situ* total-reflection fluorescence X-ray absorption spectroscopy (*in-situ* TRF-XAS) [1, 2]. As a result, we clarified that irreversible change occurred at the surface of LiCoO₂ during the charge/discharge process: the change is related to the degradation of LiCoO₂ electrode.

LiFePO₄ shows higher cyclability in terms of capacity during the charge/discharge process than LiCoO₂ [3]. A higher degree of reversibility of the electronic states at the surface of LiFePO₄ is expected during the charge/discharge process. In this work, we have investigated the reversibility of the surface of a LiFePO₄ thin-film electrode by using *in-situ* TRF-XAS.

Experiments

LiFePO₄ thin-film was prepared on Au polycrystalline substrate (773K) by pulsed layer deposition (PLD) in Ar (0.0001 Pa). *In-situ* TRF-XAS measurements were performed at the BL28XU at SPring-8, JASRI, Japan using a home-made cell with a counter electrode of Li foil. In order to exclude the effect of the impurities and unstable phases in the LiFePO₄ [4] on the electrochemical behavior, *in-situ* TRF-XAS measurements were conducted on the LiFePO₄ thin-film after obtaining one cycle of cyclic voltammogram (CV). The separator (CELGARD®3501) was immersed with 1 mol dm⁻³ LiClO₄ in a 1:1 volumetric mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

Results and Discussion

Figure 1 shows the CV of the LiFePO₄ thin-film. A couple of anodic and cathodic peaks, which are characteristic of LiFePO₄ [3], were observed at 3.47 and 3.37 V, respectively. During the charge/discharge process, *in-situ* TRF-XAS spectra were measured by setting the sample angle (0.13°) to detect fluorescence X-ray from the surface region (about 3 nm) [1]. After electrolyte, the Fe-K edge XANES spectrum of LiFePO₄ did not shift. This result indicates that the surface does not react with the electrolyte. In the case of LiCoO₂, Co³⁺ on the surface is reduced by electrolyte soaking [1]. The difference between the surface XANES spectra of LiFePO₄ and LiCoO₂ indicates that LiFePO₄ surface is more stable than

LiCoO₂ surface in a reduction atmosphere. The stability of LiFePO₄ was also confirmed by annealing LiFePO₄ and LiCoO₂ each powder at 973 K for 10 h in 3% H₂ gas + 97% Ar gas. After treatment, LiFePO₄ remained unchanged, but LiCoO₂ was reduced to form Li₆CoO₄ and CoO.

In the charge process, the Fe-K edge XANES spectra of LiFePO₄ surface exhibited a shift towards higher energy region thereby indicating that the Fe in the LiFePO₄ surface was oxidized. When the discharge was proceeded, the XANES spectra shifted towards the lower energy region thereby indicating that the Fe in the LiFePO₄ surface was reduced. The XANES spectra before and after the charge/discharge process were well reversed; this reversal was not observed for LiCoO₂ [1]. This result indicates that the surface of LiFePO₄ is more stable than LiCoO₂ (Fig. 2).

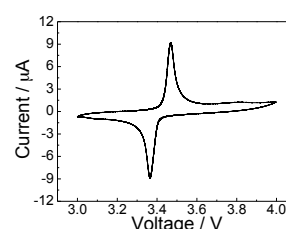


Fig. 1. CV of the LiFePO₄ thin-film at 0.1 mV·s⁻¹.

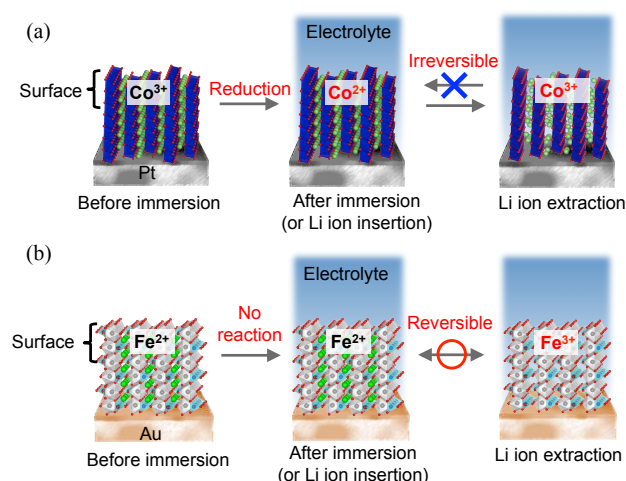


Fig. 2. Schematic illustrations of changes in electronic structures at (a) LiCoO₂/ electrolyte and (b) LiFePO₄/ electrolyte interfaces as a result of electrolyte immersion and Li-ion extraction/insertion.

Conclusions

By using *in-situ* TRF-XAS, we have observed the reversible nature of the electronic states of LiFePO₄ surface during charge/discharge process.

Acknowledgments

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