

## In situ total-reflection XAS study on LiCoO<sub>2</sub> electrode/electrolyte interface of lithium-ion batteries

Rechargeable lithium-ion batteries (LIBs) are widely used as electrical energy storage devices for technologies such as portable electronics and electric and hybrid vehicles, and they are considered to be promising power storage candidates for smart-grid electricity systems. Commercialized LIBs are composed of positive and negative electrodes separated by a liquid electrolyte containing dissociated salts, which enables lithium-ion transfer between the two electrodes. The hierarchical structure of LIBs extends over a wide scale, from greater than 1 mm to less than 1 nm, as schematically shown in Fig. 1(a). Traditionally, research in the field has focused on battery improvement through a choice of new or existing materials for the positive and negative electrodes, as the bulk properties of the electrodes primarily limit the charge capacity and power. However, the durability of LIBs is strongly dependent on side reactions that occur at the electrode/electrolyte interface, especially those at the positive electrode. Figure 1(b) shows the proposed interface structure scheme under battery operating conditions; that is, an electrical double layer in the liquid electrolyte and a space charge layer in the solid electrode form at the interface because of the potential difference between the electrode and electrolyte. The scale of this interfacial region is speculated to be on the order of a few nanometers, which shall be deemed as approximately the Debye length. This indicates that the structural and chemical information should be tracked with a resolution of a few nanometers or less to reveal the phenomena at the electrode/electrolyte

interface. However, characterization of the electrode surface at the nanoscale level under battery operating conditions remains insufficient because of a lack of suitable observation techniques.

X-ray absorption spectroscopy (XAS) is a potent and versatile technique for resolving the chemical states of lithium-ion electrode materials independent of their crystallinity. To extract the interfacial phenomena by XAS, we applied total-reflection fluorescence XAS (TRF-XAS), which integrates the fluorescence-yield XAS spectra obtained under total-reflection conditions. We utilized polycrystalline LiCoO<sub>2</sub> thin films prepared by pulsed laser deposition (PLD) as the model electrodes; they are flat at the nanometric scale and have similar structural properties to the actual composite electrode. TRF-XAS measurements were performed at **BL01B1** and **BL37XU** using a solid-state detector. Co *K*-edge XAS spectra were obtained. An original spectro-electrochemical cell, composed of a LiCoO<sub>2</sub> film on a platinum (Pt) substrate as a working electrode (WE), lithium metal as a counter electrode (CE), 1 mol·dm<sup>-3</sup> LiClO<sub>4</sub> in a 1:1 volumetric mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte, and a microporous membrane as a separator, was used for *in situ* measurement, whose schematic is illustrated in Fig. 2(a). The behavior at the top surface of the LiCoO<sub>2</sub> film and that in the bulk were comparatively studied while controlling the incident angle of the X-ray into the LiCoO<sub>2</sub> films. When the incident angle was set at 0.2° (a smaller angle than the total-reflection angle), the penetration depth was estimated to be ~3 nm (denoted as “Surface”). The bulk information was obtained by setting the incident angle at 2.2°; under this condition, the penetration depth was estimated to be greater than 50 nm (as the thickness of the LiCoO<sub>2</sub> film was *ca.* 50 nm, it was denoted as “Bulk”). Figure 2(b) shows the normalized Co *K*-edge XANES spectra obtained from the bulk and the surface before and after electrolyte soaking. The bulk XANES spectra were unchanged by electrolyte soaking. In contrast, the surface XANES spectra were significantly changed by electrolyte soaking. The energy level shifted toward a lower energy in the surface XANES spectra, which was attributable to the reduction of the Co ions at the top surface of the LiCoO<sub>2</sub> electrode in contact with the electrolyte solution. As the bulk XANES spectra were unchanged by electrolyte soaking, the reduction of the Co ions must have occurred within a depth of a few nanometers from the surface of the electrode.

Figure 3(a) shows the bulk and surface Co

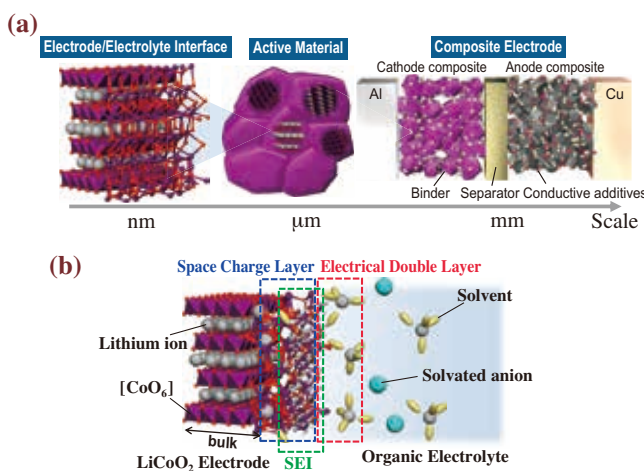


Fig. 1. (a) Schematic image of the hierarchical structure of LIBs and (b) proposed structure of the LiCoO<sub>2</sub> electrode/electrolyte nano-interface under battery operating conditions.

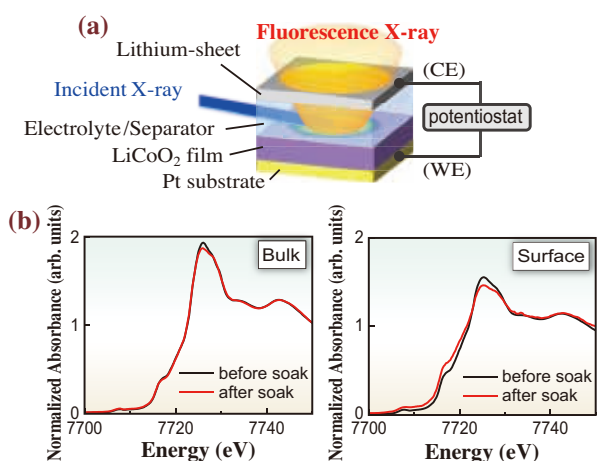


Fig. 2. (a) Schematic illustration of (two-electrode) spectroelectrochemical cell used for *in situ* TRF-XAS measurements. (b) Co *K*-edge TRF-XANES spectra of the bulk of LiCoO<sub>2</sub> film, and those at the surface before (black) and after (red) electrolyte soaking.

*K*-edge XANES spectra obtained at each state of charge under potential control conditions. The bulk XANES spectra shifted continuously toward higher (Co oxidation) and lower (Co reduction) energy levels as electrochemical charging and discharging proceeded, respectively. Figure 3(b) shows the absorption energy at the normalized intensity of 0.5 in the XANES spectra during the course of the electrochemical experiments. In the case of the bulk, the energy returns back to the original position after charge and discharge, suggesting that the LiCoO<sub>2</sub> bulk maintains its layered structure and shows good electrochemical reversibility. As the energy levels of the surface XANES spectra also changed during the charge/discharge processes, it is suggested that the surface Co species are still electrochemically active. However, the behavior at the surface is essentially irreversible, in contrast to the good reversibility in the bulk. It appears that the surface Co<sup>2+</sup> species formed during the electrolyte soaking process are oxidized during the charging, but the reduction is insufficient. Figure 3(c) shows a scheme of the proposed deterioration mechanism that occurs at the electrode/electrolyte interface in LIBs. The Co ions (Co<sup>3+</sup>) at the surface of LiCoO<sub>2</sub> are reduced to Co<sup>2+</sup> by organic electrolyte soaking. The local structure is distorted when Co<sup>3+</sup> reacts with the electrolyte and is reduced to Co<sup>2+</sup>, and this distortion propagates during the consecutive charge/discharge processes. Accordingly, the initial deterioration that starts at the surface of LiCoO<sub>2</sub> on electrolyte immersion can lead to the loss of durability that occurs during longer time scales.

In conclusion, we have succeeded in direct observation of the electronic and local structures of the LiCoO<sub>2</sub> system and their changes at the electrode/electrolyte interface during charge/discharge

processes. The Co ions are reduced at the surface of the LiCoO<sub>2</sub> electrode that is in contact with organic electrolyte solutions. Irreversible behavior was observed at the surface of LiCoO<sub>2</sub> during the first charge/discharge process. This Co reduction that occurs at the nano-interface of the electrode/electrolyte can be the initial deterioration that occurs in LIBs [1].

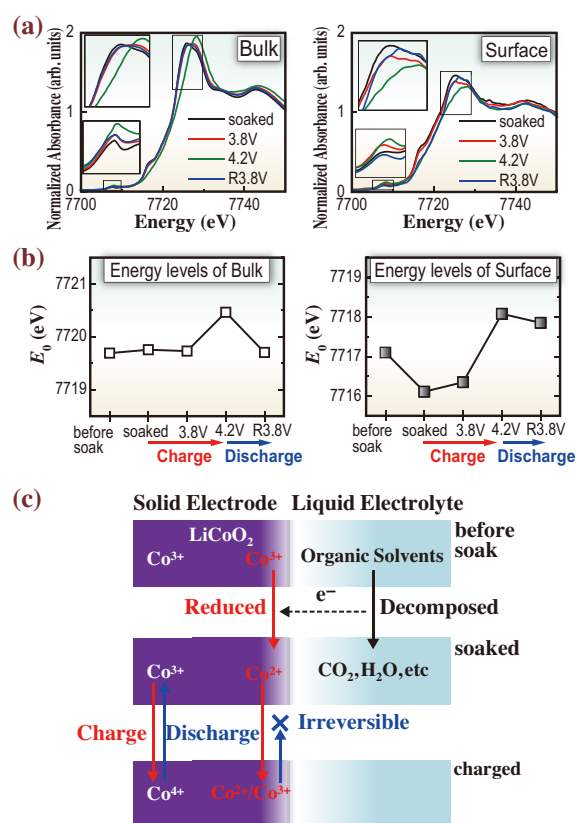


Fig. 3. (a) Co *K*-edge XANES spectra of the LiCoO<sub>2</sub> film measured at each state upon applying voltage and (b) corresponding measured absorption energy levels of the bulk and surface. (c) Schematic illustration of the proposed reaction of the initial degradation that occurs at the electrode/electrolyte nano-interface.

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## References

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