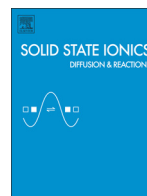




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Evaluation of the effective reaction zone in a composite cathode for lithium ion batteries

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ABSTRACT

Reaction distribution in the composite electrode of LiCoO₂, an acetylene black and an organic binder was evaluated by two-dimensional X-ray absorption spectroscopy (XAS). The valence change of Co ion in LiCoO₂ due to the Li de-intercalation during charging was evaluated as the change of the absorption energy of Co K-edge. To demonstrate the reaction distribution due to ionic transportation in the composite cathode, a composite electrode laminated by an aluminum foil and a polyimide film was fabricated in this study. After charging, clear shifts of the absorption energy was observed. The reaction distribution was evaluated by evaluating the peak top energy of Co K-edge as a function of the distance from the edge of the laminated cathode. Two-dimensional mapping of the reaction distribution revealed that the electrochemically active area expands about 700 μm from the edge of the electrode under the charging condition of 0.2 C. This is consistent with a result of electrochemical charging test showing only 42% of the theoretical capacity with the current rate of 0.2 C.

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1. Introduction

Recently, Li ion batteries are being used in large scale applications such as distributed power sources and electric vehicles as well as conventional mobile devices. High rate characteristics become important for large scale applications because of the strong demand on high power output and rapid charging [1–4]. However, the present composite cathodes show insufficient performance and stability under high rate charging/discharging conditions [2–4]. Loss of the capacity and insufficient output are caused by the non-uniform electrochemical reaction in the porous electrode caused by the slow reaction process. Possible rate controlling processes are generally considered as electronic transfer at the current collector/conductive aids and/or conductive aids/active material interfaces, charge transfer at the surface of the active material, ionic transfer in the liquid electrolyte and ionic/electronic transfer in the active material [5–7]. While the composite cathode shows large capacity loss under high rate charge/discharge, a single particle of active materials showed excellent rate capability [8–10]. According to these works, the rate controlling processes for the single particles are charge transfer at the surface of the active material and ion/electron diffusion in the active material. These processes can't be the rate controlling process for a composite electrode, because the rate controlling process for the composite electrode should be a process which can be neglected

in a single particle but significant in a composite electrode. Strong candidate is an ionic transportation through the liquid electrolyte filled in the complex pore network in the composite electrode. While ionic transport is negligible for a single particle active material, this must be a significant process for a composite electrode which has complex three-dimensional network structure. The sluggish ionic transportation may inactivate the inside of the composite electrode electrochemically. In such a case, only the active material in the electrochemically active region, near the surface of the composite electrode, can contribute to the charge and discharge. The formation of the reaction distribution degrades the output characteristics and the practical capacity of the battery. Additionally, the degradation due to charge/discharge cycles progresses in the electrochemically active region because the electrode reaction takes place only in the active region. Therefore, it is important to clarify and to understand factors that cause the reaction distribution and how the reaction progresses in a composite electrode during charge/discharge.

In this work, in order to examine the effect of the limited ionic transportation through a liquid electrolyte on the reaction distribution in a porous composite cathode, we prepared a composite electrode schematically illustrated in Fig. 1. As shown in this figure, thin composite cathode layer was laminated by an aluminum foil and a polyimide film to limit the ionic transportation in the planar direction of the composite electrode. Hereafter, we call this composite electrode as a “laminated electrode”. In this laminated electrode, if the ionic transportation through the liquid electrolyte in the composite electrode controls the rate of the

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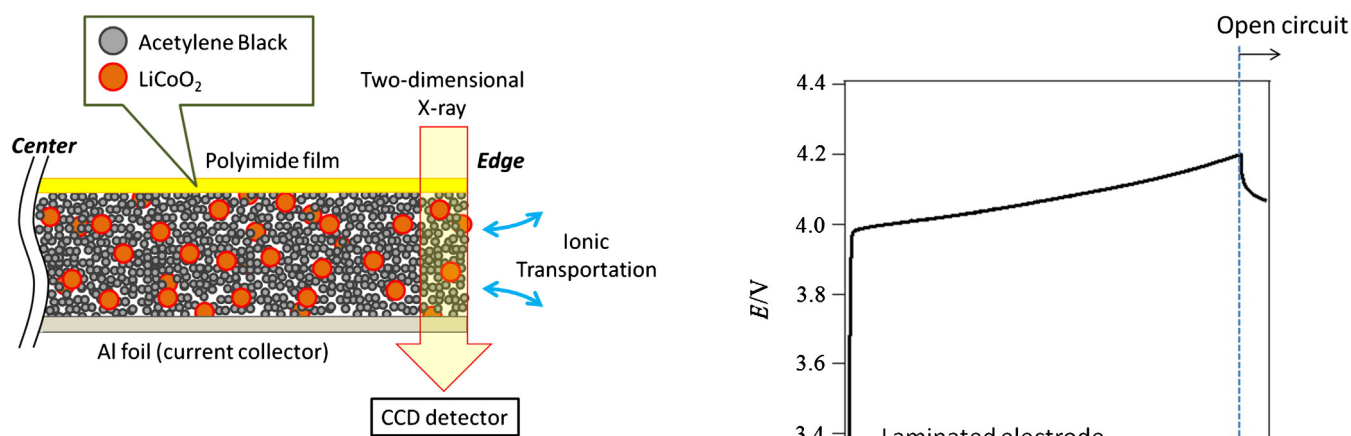


Fig. 1. Schematic illustration of the laminated electrode used in this work. An area near the edge of the laminated electrode was observed by two-dimensional XAS after charging.

reaction, the reaction distribution will be formed along in-plane direction, from the edge of the cathode to the center, because ions are supplied or released only through the edge of the cathode. The reaction distribution in the laminated electrode was evaluated by observing the valence change of Co ion in LiCoO_2 due to the de-intercalation of Li by X-ray absorption spectroscopy (XAS).

2. Experimental

To prepare the composite cathode slurry, LiCoO_2 (supplied by Nichia Co.) of $6\ \mu\text{m}$ in the average diameter, acetylene black (Denka-Black, Denki Kagaku Kogyo Kabushiki Kaisha) and organic binder PVDF (KF Polymer L#1120, Kureha Co.) were mixed by the weight ratio of 75:15:10. 1-methyl-2-pyrrolidone (Wako Pure Chemical Industry, Ltd.) was added to the mixed powder. The mixture was stirred at 2200 rpm for 2 min by an agitation equipment (NRJ-250, Thinky Co.). The slurry was uniformly spread on an aluminum foil by a tape casting technique. A polyimide film (UBE Industries, Ltd.) was put on the spread slurry to set an insulating layer for the liquid electrolyte. The laminated cathode was dried in an oven at about 353 K for 24 h and in another 24 h in vacuum. The thickness of the composite cathode layer was about $50\ \mu\text{m}$. Finally, the laminated cathode was cut into $10 \times 10\ \text{mm}$. The electrochemical cell was fabricated with an Li metal (Honjo Metal Co., Ltd.) as an anode, EC-DMC with $1\ \text{mol L}^{-1}$ of LiPF_6 (EC:DMC = 1:1 in volume, Kishida Chemical Co., Ltd.) as an electrolyte, a polymer separator (Cell-Gard #2500, Polypore International, Inc.) and the laminated cathode. The laminated cathode was charged by the current rate of 0.2 C before the XAS measurement. The cut-off voltage was 4.2 V vs. Li^+/Li .

As soon as the charging process was completed, the laminated cathode was taken from the electrochemical cell. The XAS measurements were carried out at the Co *K*-edge by a transmission mode using a synchrotron radiation beam at the beam line BL28XU in SPring-8, Japan. The intensity of the transmission X-ray was recorded by a CCD detector placed behind a phosphor screen. The spatial resolution of this technique was confirmed by the observation of the standard patterned specimen (XRESO-100, NTT Adv. Tech. Co.) and it was found out that the resolution was about a few μm . Similar 2D XAS measurement by the PILATUS and the two-dimensional CMOS sensor detectors have been reported [11,12]. The intensity of incident X-ray without specimen was used as I_0 . As references, the fully-charged and fully-discharged composite cathodes were prepared by charging to 4.2 V and 3.2 V vs. Li^+/Li , respectively.

3. Results and discussion

Fig. 2 shows a charging curve of the laminated cathode with the charging rate of 0.2 C. It took about 120 min to reach to the cut-off

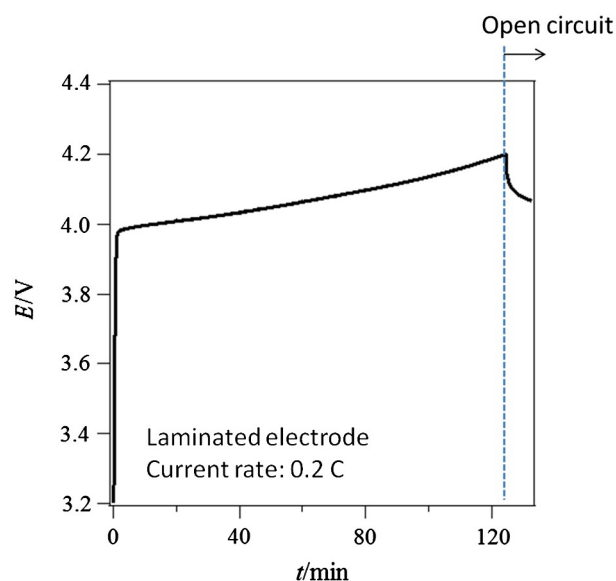


Fig. 2. Charging curve of the laminated electrode at the current rate of 0.2 C.

voltage of 4.2 V. The sum of the electric charge was $52\ \text{mAhg}^{-1}$, which was about 42% of the theoretical capacity for the whole composite cathode. This indicates that the laminated cathode cannot be fully charged under the current rate condition of 0.2 C. Because ions are supplied/released only through the edge of the laminated cathode, it is supposed that Li intercalation/de-intercalation of the active material preferentially takes place near the edge of the laminated cathode. If this is the case, active materials at the edge react firstly and the reaction area gradually expands to the central part of the laminated electrode.

X-ray absorption spectra at the Co *K*-edge of LiCoO_2 in fully charged and discharged states are shown in Fig. 3. During charging, Li ions are extracted from LiCoO_2 and consequently the valence of Co ions increases. As shown in Fig. 3, the shift of the peak top position to the higher energy and the disappearance of a small peak in the pre-edge region were observed as LiCoO_2 was charged. These are consistent with the earlier report about the XAS spectra of partially delithiated Li_xCoO_2 [13]. Since the most apparent change in the XAS spectra was the shift of the peak top position, the degree of the charge is discussed by the peak top position in the following discussion. X-ray absorption spectra observed at five different positions from the edge of the laminated cathode are also shown in Fig. 3. The XAS spectra in Fig. 3 were obtained from the area of $12 \times 60\ \mu\text{m}$. The obtained XAS spectra gradually changed depending on the position from the edge. XAS spectra obtained near the edge of the limited electrode was similar to those of the fully-charged cathode. On the other hand, the XAS spectra observed at the central part ($1000\ \mu\text{m}$ away from the edge) was almost the same to those of fully-discharged cathode. At 200–800 μm away from the edge, the shape of the spectra was transformed gradually from the shape of fully-charged to that of fully-discharged state. These indicated that the extraction of the Li from the active material took place preferentially near the edge of the laminated electrode and the active materials in the central part of the laminated cathode were not almost charged. In other words, the electrochemical reaction did not occur uniformly in the laminated electrode because of the limited ionic transportation. This was qualitatively consistent with the result of charging test that the cell voltage reached the cut-off voltage before whole active materials were fully-charged, as shown in Fig. 2.

In order to demonstrate the reaction distribution due to the ionic transportation more clearly and visually, a two-dimensional image of the reaction in the composite LiCoO_2 electrode was prepared. First, a part of the observed area (about $600 \times 1400\ \mu\text{m}$) was divided into 90×210 arrays. The size of an array was about $6.5\ \mu\text{m}$ square which is

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