Investigation of Determination Factor of Reaction Distribution in LiFePO₄ Composite Electrodes

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1. Introduction

Composite electrodes containing active materials, carbon and binder are widely used in Li-ion batteries and their morphology influences the electrochemical performance of batteries. There are a number of internal resistances inherent in the composite electrode (for instance, charge transfer resistance, ionic or electronic conductivity resistance, solid state diffusion resistance, *etc.*). Since the electrode reaction occurs preferentially in regions with lower resistance, reaction distribution is happened within the composite electrode. A detailed observation of the reaction distribution in composite electrodes as well as their mechanism is crucially important, since such distributions greatly influence the rate performance and long-life performance of Li-ion batteries. Although some researchers have studied the distribution model from the theoretical aspect [1, 2], there are very few reports made to directly observe the reaction distribution of composite electrodes [3-6]. In this work, we investigated the relationship between the reaction distribution and ionic conductivity in composite electrodes.

2. Experimental

LiFePO₄-based composite electrodes were densified at various pressures to control their porosity. These electrodes were assembled in electrochemical flat cells with lithium metal as the counter electrode. The LiFePO₄ electrodes were discharged under 25°C at 10 C rate. As soon as the electrodes were discharged, they were removed from the button cells, rinsed in dimethyl carbonate (DMC) and dried. In order to observe the cross section view, the dried electrodes were fabricated by a microtome. 2D-imaging XAFS measurements were performed at the beam line BL-4 at Ritsumeikan SR center, Japan. The beam size was 4 (H) x 4 (W) mm². Fe *K*-edge XAS spectra of the LiFePO₄ electrodes were collected in transmission mode. The ionic conductivity in composite electrodes is measured with the previously reported 6-probe method [7].

3. Result and Discussion

Average absorption energy from Fe-K edge XAFS as a function of distance from current collector for various pressed electrode is plotted in Fig. 1 (a). As the LiFePO₄ electrode is discharged, the absorption energy edge of the Fe-Kedge X-ray absorption spectra decreases. When the porosities of the electrodes were less than 44% the absorption energy was higher at the top surface of the electrode than at the bottom. However, when the porosity of the electrode was 57% and 48 %, the energy was nearly constant in the vertical direction. These results imply that the reaction distribution is happened in lower porosity composite electrodes.

The ionic conductivity in composite electrodes is shown in Fig. 1 (b). When the porosities of the electrodes are less than 47%, the ionic conductivity decreased. The decreased ionic conductivity causes the preferential reaction at the electrode surface. When the porosity is higher, however, the ionic conductivity is high. This results in the uniform discharge reaction at all depths in composite electrodes.
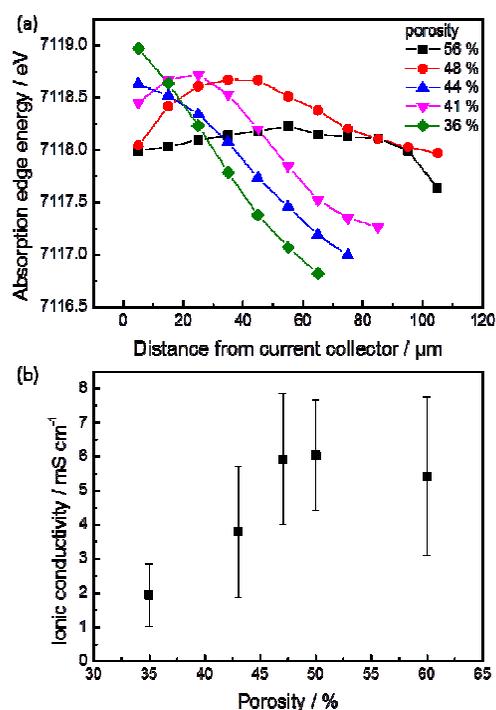

Fig.1 (a) Average absorption energy as a function of distance from current collector measured by the 2D-XAFS of various porosity composite electrode. (b) Effective ionic conductivity of various porosity composite electrode.

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