Abstract Summary:

Reaction distributions on LiFePO4 electrodes

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Olivine structure lithium iron phosphate (LiFePO4), which is widely used as a positive electrode material in LIBs, was examined in this study. Under charging and discharging, the material undergoes phase reactions between Li-rich Li1-\alpha FePO4 (LFP) and Li-poor Li\alpha FePO4 (FP) [1]. This system is expressed with a eutectoid-type binary phase diagram [2, 3]. In this work, we investigated the reaction distribution formation and relaxation behavior in LiFePO4 composite electrodes.

1) The Driving force for the Relaxation of Reaction Distribution in LiFePO4 Electrodes
Composite electrodes containing active materials, carbon and binder are widely used in Li-ion batteries and their morphology influences the electrochemical performance of batteries. A detailed observation of the reaction distribution in composite electrodes as well as their mechanism is important, because such distributions greatly influence the rate performance and long-life performance of Li-ion batteries. The relaxation of the reaction distribution in LiFePO4 electrodes was investigated by applying the micro XAFS technique. We herein discuss the driving force for the relaxation of reaction distribution by comparing two types of electrodes having different charge/discharge profiles.

The LiFePO4 electrode were charged under room temperature at 1C rate until the Li desorption degree approached 0.5 and 0.3, respectively. In order to observe the cross section, the dried electrodes were fabricated by a microtome. The micro XAFS measurements were performed at the beam line BL37XU at SPring-8, Japan. The beam size was 1.3 (H) x 0.8 (W) \mu m2.

Figure 1 shows the Fe K-edge X-ray absorption near edge structure (XANES) spectra of the surface and the inside of the LiFePO4 electrodes. The absorption edge energy of the surface was higher than that of the inside. This result indicates that Fe ions on the surface were more oxidized than that in the inside. This difference was not changed even after leaving 24 h in the cell. This means the distribution of the oxidation state was not relaxed. On the other hand, the behavior for LiCoO2 was different and no reaction distribution was observed after 24h. A major difference between LiFePO4 and LiCoO2 is evident in the charge/discharge potential profile. LiFePO4 cathode has an extremely flat charge/discharge potential profile [1]. This feature indicates that electrochemical potential of Li-ion in LFP is the same as that in FP. In contrast, the charge/discharge profile of LiCoO2 cathode does not exhibit a clear plateau and LiCoO2 cathode has an electrical potential gradient near a Li insertion nominal value of x=0.7 in Li\alpha CoO2 [4]. The results of this study imply that the driving force for the relaxation of the reaction distribution depends on the gradient of electrochemical potential of Li-ion.
2) Investigation of Determination Factor of Reaction Distribution in LiFePO4 Composite Electrodes

There are a number of internal resistances inherent in the composite electrode (for instance, charge transfer resistance, ionic or electronic conductivity resistance, and solid-state diffusion resistance). Since the electrode reaction occurs preferentially in regions with lower resistance, reaction distribution is happened within the composite electrode. In this work, we investigated the relationship between the reaction distribution and ionic conductivity in composite electrodes. 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 25oC at 10 C rate. 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 [5].

Average absorption energy from Fe-K edge XAFS as a function of distance from current collector for various pressed electrode is plotted in Fig. 2 (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. 2 (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.

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References

Fig. 1. Fe K-edge XANES spectra of the surface and the inside of LiFePO₄ electrodes.

Fig. 2. (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.