

Study on Mechanisms of Electrochemical Reactivity in P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ as Positive Electrode Materials for Sodium-ion Rechargeable Batteries

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1 Introduction

Li-ion batteries have risen to prominence as key devices for green and sustainable energy development. Lithium batteries have potential applications for energy storage within electrical grid systems to effectively use electricity from power plants, solar cells and wind turbines. Manganese- and iron-based positive-electrode materials, such as LiMn_2O_4 and LiFePO_4 , could be used in the large-scale batteries. Manganese and iron are abundant elements in the earth's crust, but lithium is not. In contrast to lithium, sodium is an attractive charge carrier on the basis of elemental abundance. We have therefore interested to realize the Na-ion batteries^[1]. Recently, we have reported sodium iron manganese oxides, $\text{Na}_x[\text{Fe}_y\text{Mn}_{1-y}]\text{O}_2$, as the promising positive electrode materials for the rechargeable sodium batteries. P2-type $\text{Na}_{2/3}[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, consisting of only abundant elements in the earth's crust, delivers large reversible capacity (more than 180 mAh g^{-1}) with relatively good capacity retention at room temperature^[1]. In this study, We examine the charge compensation mechanisms of P2-type $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ during sodium extraction process by X-ray absorption spectroscopy (XAS).

2 Experiment

Composite positive electrodes consisted of 80 wt % $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, 10wt % acetylene black, and 10wt % polyvinylidene fluoride (PVdF), pasted on aluminum foil as a current collector. The electrolyte solution used was 1 mol dm^{-3} NaClO_4 dissolved propylene carbonate (Kishida Chemical Co. Ltd., Japan) with 2 vol.% fluorinated ethylene carbonate as an electrolyte additive. Electrochemical testing was conducted using R2032-type coin cells with Na metals as negative electrodes. The coin cells were assembled in an Ar-filled glovebox and cycled at a rate of 13 mA g^{-1} . After the electrochemical tests, composite electrodes were taken out from the cell, and the electrodes were rinsed with DMC and sealed in a water-resistant polymer film in the Ar-filled glovebox.

3 Results and Discussion

X-ray absorption near edge structure (XANES) spectra of P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ at Fe K-edge are shown in Figure 1(a). The spectrum is slightly shifted after charge to 3.8 V, but much more clear shift towards higher energy region is found at the Mn K-edge (Fig.1(c)), indicating that the charge compensation is mainly achieved by oxidation of Mn. When the $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ is charged to 4.2 V, the clear shift of Fe

K-edge absorption spectrum is observed to the higher energy region. The shift could be contributed from the complicated situations, including the changes in the local structures, e.g., sodium extraction from the Fe face-shared sites and P2/OP4 transition. Therefore, extended X-ray absorption fine structure (EXAFS) spectra during charge were further analyzed. The change in radial distribution around Fe during charge to 4.2 V is shown in Fig. 1(b). The radial distribution around Fe is not affected by charge to 3.8 V, and the interatomic distance of Fe-O remains unchanged (2.00 Å for as-prepared and 1.99 Å for 3.8 V charge). The Fe-O local environment is drastically changed after charge to 4.2 V. The intensity of the peaks for both first and second coordination shells, Fe-O and Fe-Fe(Mn), is reduced, suggesting that the distortion around Fe. The distortion also influences the neighboring Mn ions (Fig.1(d)). Thus, the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox in P2- $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ could be accessible. Note that this observation was further supported by Mössbauer spectroscopy.^[2]

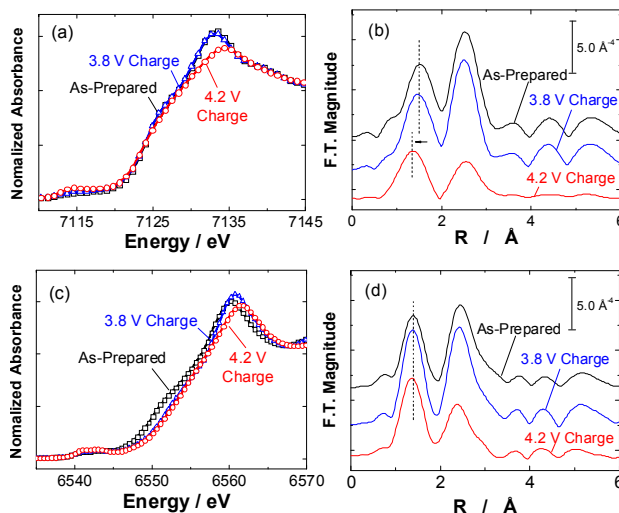


Fig. 1 XAS spectra of the P2-type $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ samples charged to 3.8 and 4.2 V; Fe K-edge XANES (a) and EXAFS (b) spectra, and Mn K-edge spectra are also shown in (c) and (d).

References

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