Short communication

Electronic structural changes of the electrochemically delithiated LiFe$_{0.5}$Co$_{0.5}$PO$_4$ cathode material studied by X-ray absorption spectroscopy☆

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ABSTRACT

In order to study the electronic structure changes of the electrochemically delithiated Li$_{1-x}$Fe$_{0.5}$Co$_{0.5}$PO$_4$ system, in situ Fe and Co K-edge XAS and ex situ P K-edge XAS have been carried out during the first charging process. The Fe and Co K-edge XAS results showed that the major charge compensation at the metal sites during charge is achieved by the oxidation of Fe^{2+} ions at lower potential plateau ($\sim$3.6 V) and the oxidation of Co^{2+} ions at higher potential plateau ($\sim$5.0 V). The gradual shift of main edge features in P K-edge XANES spectra showed that P—O bonds become less covalent during delithiation, due to the increased covalency of Fe^{3+}—O bonds via the inductive effect. From the observation of pre-edge peaks, it is concluded that the electrochemical delithiation of Li$_{1-x}$FePO$_4$ result in the hybridization of P 3p states with the metal 3d states.

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1. Introduction

The application of lithium-ion batteries has been expanded rapidly into cell phones, notebook computers, and consumer electronics. However, the more important step will be the commercialization of lithium-ion battery powered electric and hybrid electric vehicles (EV and HEV). In order to achieve this goal, materials with lower cost, longer cycling life, and better safety characteristics need to be developed. Currently, LiCoO$_2$ is the most widely used cathode material for secondary lithium batteries due to the advantages such as easy preparation and good cyclability [1–3]. Numerous studies have been carried out in searching and developing alternative non-toxic cathode materials with higher capacity, lower cost, and better safety characteristics, to replace LiCoO$_2$. Recently it has been demonstrated that LiMPO$_4$ (M = Fe, Co, Mn, and Ni) is one of the most promising alternative materials for LiCoO$_2$ [4–8]. These LiMPO$_4$ materials crystallize in an olivine structure containing Li in a framework composed of PO$_4$ tetrahedra and distorted MO$_6$ octahedra. The use of (PO$_4^{3-}$) polyanion with a strong P—O covalent bond in the olivine LiMPO$_4$ structure has been shown not only to lower the Fermi level of the transition metal redox couple to useful levels but also to improve thermal stability of Li batteries. Phosphorus plays a critical role in the performance of the LiMPO$_4$ electrode. Suitable spectroscopic studies will undoubtedly be a great help to understand this material's properties and performance. Synchrotron-based X-ray absorption spectroscopy (XAS) has been employed in order to examine the electronic and local structures of interesting atoms in various electrode materials for Li rechargeable batteries [9–13]. In this paper, we report the results of our studies on the electronic structural changes of electrochemically delithiated Li$_{1-x}$Fe$_{0.5}$Co$_{0.5}$PO$_4$ system using P, Fe, and Co K-edge XAS spectroscopy.

2. Experimental

LiFe$_{0.5}$Co$_{0.5}$PO$_4$ powder was prepared by solid-state reaction. Stoichiometric amounts of FeC$_2$O$_4$·2H$_2$O (99%, Aldrich), Co(AC)$_2$·4H$_2$O (99%, Beijing Chemicals), NH$_4$H$_2$PO$_4$ (99.5%, Beijing Chemicals) and LiF (99.99%, Beijing Chemicals) were mixed and ball-milled for 3 h [14,15]. The mixture was sintered flowing Ar–H$_2$ mixture (92:8, v/v) at 400 °C for 8 h. After cooled down to room temperature, the sample was reground and annealed at 600 °C for 24 h in the same atmosphere. Cathode specimens were prepared by mixing the LiFe$_{0.5}$Co$_{0.5}$PO$_4$ powders with 10 wt.% acetylene black and 10 wt.% PVDF (poly-vinylidene fluoride) in NMP (n-methyl pyrrolidone) solution. 1 M LiPF$_6$ in a 1:1 ethyl carbonate:dimethyl carbonate (EC:DMC) solution was used as the electrolyte. The cell

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Fig. 1. XRD pattern for the pristine LiFe$_{0.5}$Co$_{0.5}$PO$_4$ powders.
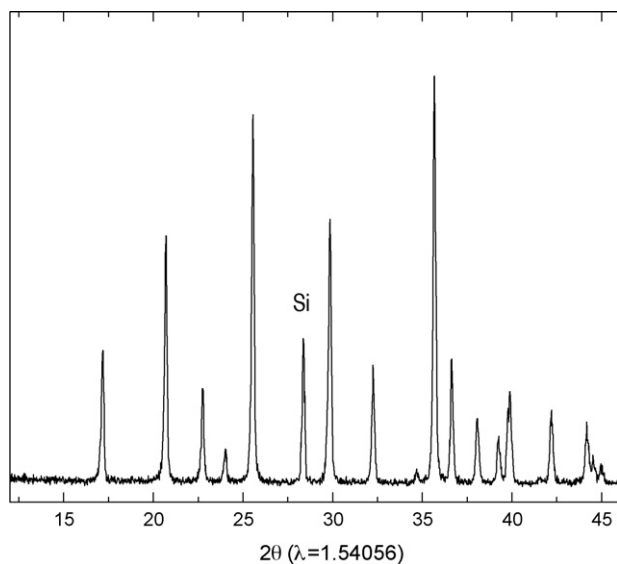
Fig. 2. First charge curve of the LiFe$_{0.5}$Co$_{0.5}$PO$_4$ electrode for in situ metal K-edge XAS experiments.

was assembled in an argon-filled glove box. The detailed design of the spectroelectrochemical cell used in the in situ XAS measurement has been described elsewhere [16]. Fe and Co K-edge XAS measurements were performed in the transmission mode at beamline X18B of the national synchrotron light source (NSLS) using a Si(1 1 1) channel cut monochromator. The monochromator was detuned to 35–45% of its original intensity to eliminate the high order harmonics. Energy calibration was carried out using the first inflection point of the spectrum of Fe metal foil as a reference (Fe K-edge = 7112 eV). Reference spectra were simultaneously collected for each in situ spectrum using Fe metal foil. The P K-edge XAS data collection was done at the NSLS using the Beamline X19A equipped with a Si(III) monochromator. With a Si(III) monochromator and collimating mirror, the resolution at the P K-edge is 0.2 eV. The XAS data were collected in fluorescence mode at ambient temperature using a solid-state passivated implanted planar silicon (PIPS) detector and a He flight path.

3. Results and discussion

Fig. 1 shows XRD pattern for the pristine LiFe$_{0.5}$Co$_{0.5}$PO$_4$ powders. All diffraction lines in the pristine LiFe$_{0.5}$Co$_{0.5}$PO$_4$ can be indexed in the orthorhombic *Pnma* space group like LiFePO$_4$ indicating the solid solution of LiFePO$_4$ and LiCoPO$_4$. [15] The lattice parameters of this triphylite LiFe$_{0.5}$Co$_{0.5}$PO$_4$ structure are $a = 10.26993$ Å, $b = 5.96685$ Å, and $c = 4.69471$ Å. In order to investigate the origin of the redox reaction on the electrochemical delithiation of Li$_{1-x}$Fe$_{0.5}$Co$_{0.5}$PO$_4$, Fe and Co K-edges XAS experiments were conducted to monitor the evolution of the electronic structure of each transition metal element under in situ conditions. The voltage profile of the cell during the first charge for experiments performed at the Fe and Co K-edges is shown in Fig. 2. The cells were charged from their open circuit potentials up to 5.16 V, at a constant current rate of $C/8$, calculated based on the theoretical capacity. The specific capacity was calculated from the elapsed time, current, and mass of the active material in the cathode, by assuming that all the current passed was applied to lithium intercalation/deintercalation reaction. Two electrochemical processes are observed, the first one occurs at a potential plateau at approximately 3.6 V and a second at a higher potential plateau of 5.0 V. More detailed electrochemical and crystal structural properties of this LiFe$_{0.5}$Co$_{0.5}$PO$_4$ electrode

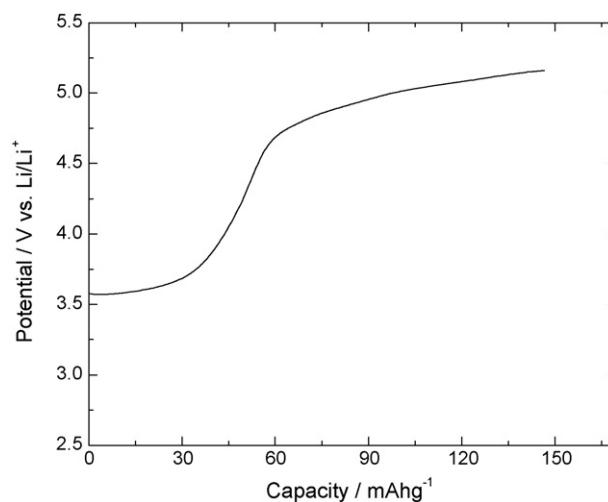have been described in the earlier report [15]. Fig. 3 shows normalized Fe and Co K-edge XANES spectra for the LiFe$_{0.5}$Co$_{0.5}$PO$_4$ electrode during charge. In the charging process of LiFe$_{0.5}$Co$_{0.5}$PO$_4$ electrode, the Fe K-edge shifts substantially to higher energies until $x = \sim0.4$ (half charged state). Spectroscopic behavior of Fe K-edge XANES for LiFe$_{0.5}$Co$_{0.5}$PO$_4$ electrode in Fig. 3 is very similar to previous Fe K-edge XAS results on LiFePO$_4$, which shows that Fe^{2+} in LiFePO$_4$ is oxidized to Fe^{3+} during the electrochemical delithiation [17,18]. However, during the same period of charging up to $x = \sim0.4$, the energy shift for Co K-edge is negligible. This indicates that charge compensation in the first half of the charging process at a potential plateau of ~3.6 V is achieved mainly via the oxidation of Fe^{2+} ions. In contrast, the Co K-edge starts to shift to higher energy values from $x = \sim0.4$ while the Fe K-edge shift from $x = \sim0.4$ to $x = \sim0.8$ (fully charged state) is very small. At high states of charge ($x > 0.4$) the Co K-edge XAS spectra of Li$_{1-x}$Fe$_{0.5}$Co$_{0.5}$PO$_4$ electrode show the similar trend to those of pure LiCoPO$_4$ during the electrochemical delithiation indicating that charge compensation in the other half of the charging process at a potential plateau of ~5.0 V is achieved mainly via the oxidation of Co^{2+} ions [19].

Fig. 4 shows normalized P K-edge XANES spectra of Li$_{1-x}$Fe$_{0.5}$Co$_{0.5}$PO$_4$ electrode as a function of x. The P K-edge XANES spectrum originates from the transition of a P 1s electron to an empty antibonding state of the anion. The main edge peak at ~2152.5 eV can be assigned to a transition of the P 1s electron into an unoccupied valence electronic state formed by the overlap of Psp^3 hybrid- and O 2p-orbitals since the PO$_4$-group has T_d-symmetry [20,21]. The white line gradually moves towards higher energy side as Li is extracted. The major charge compensation of LiFe$_{0.5}$Co$_{0.5}$PO$_4$ during Li extraction is achieved by the oxidation of Fe^{2+} and Co^{2+} ions to Fe^{3+} and Co^{3+} ions resulting in more covalent Fe—O and Co—O bonds. In the olivine LiMPO$_4$ structure, polarization of the electrons of the oxygen ions towards the phosphorus ion reduces the covalent bonding to the iron ion by the inductive effect. Likewise the increased covalency of M (=Fe, Co)—O bonds makes P—O bonds less covalent by the same inductive effect. A shift of white line to higher energy side could reflect a reduction in degree of covalency of the P—O bond altered by the presence of the more covalent M—O bond during charge.

It is notable that chemical changes beyond the first coordination sphere around the phosphorus atoms have a systematic influence on the observed XANES spectrum. No pre-edge peak was observed

in P K-edge XANES spectrum for the pristine $LiFe_{0.5}Co_{0.5}PO_4$. Upon Li deintercalation, however, pre-edge peaks start to appear in the lower energy region of the main edge. The pre-edge features of P K-edge XAS in transition metal phosphates reflect the interaction between metal 3d and P 3p states through the shared oxygen atom [20,21]. The gradual increase of pre-edge peak intensities with the Li-ion extraction at low states of charge ($x < 0.4$) shows that these pre-edge peaks are mainly due to the hybridization of P 3p states with the Fe 3d states since this is consistent with the gradual increase in oxidation state of Fe ions with the Li-ion extraction. In contrast, at high states of charge ($x > 0.4$) the peak intensity of the pre-edge shows relatively smaller change indicating that Co site is not rigorously involved in the hybridization of P 3p states with the M 3d states. It is important to note that such hybridization between P 3p and M 3d states occurs in spite of the presence of oxygen atoms that separate phosphorus ions from metal ions. Consequently, the electronic structure of orthophosphates cannot be regarded rigorously as composed of traditional ion pairs for $(Li^+)(M^{2+})–(PO_4^{3-})$

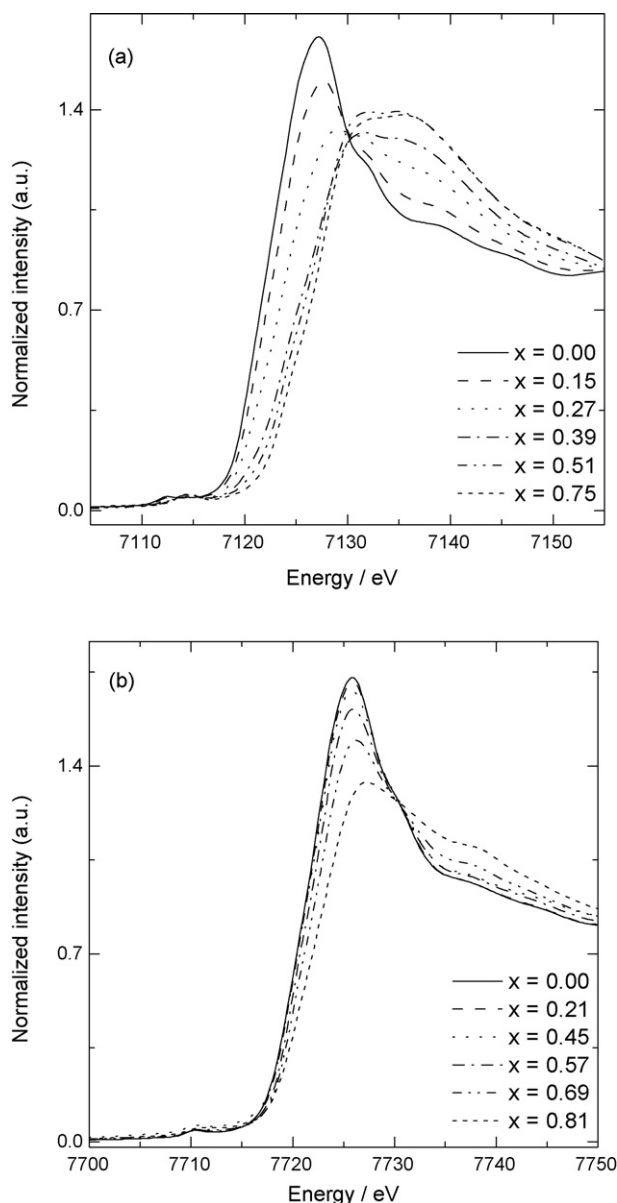**Fig. 4.** Normalized P K-edge XANES spectra of the $Li_{1-x}Fe_{0.5}Co_{0.5}PO_4$ electrode as a function of x.

and $(M^{3+})–(PO_4^{3-})$ which are charged according to their formal valence.

In summary, we have investigated the electronic structural changes of electrochemically delithiated $Li_{1-x}Fe_{0.5}Co_{0.5}PO_4$ system using in situ Fe and Co K-edge XAS and ex situ P K-edge XAS techniques, during the first charge process. From the Fe and Co K-edge XAS results, it is concluded that the major charge compensation at the metal site during delithiation is achieved by the oxidation of Fe^{2+} ions at lower potential plateau ($\sim$3.6 V) and the oxidation of Co^{2+} ions at higher potential plateau ($\sim$5.0 V). The P K-edge XAS results show that electrochemical delithiation of $Li_{1-x}Fe_{0.5}Co_{0.5}PO_4$ result in the hybridization of P 3p states with the metal 3d states.

Acknowledgment

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Fig. 3. Normalized in situ (a) Fe K-edge and (b) Co K-edge XANES spectra of the $Li_{1-x}Fe_{0.5}Co_{0.5}PO_4$ electrode during first charge.

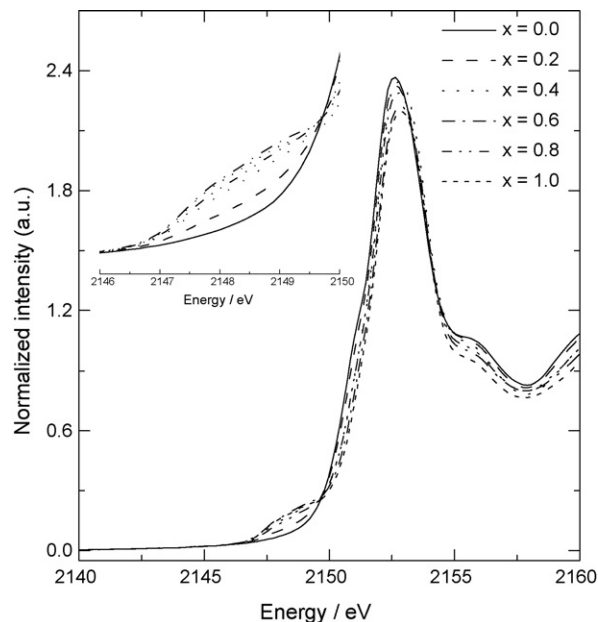[12] W.-S. Yoon, M. Balasubramanian, K.Y. Chung, X.-Q. Yang, J. McBreen, C.P. Grey, D.A. Fischer, J. Am. Chem. Soc. 127 (2005) 17479.
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