XAFS study of $LiCo_{1-x}Fe_xO_2$ cathode for rechargeable lithium battery by laboratory XAFS spectrometer

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The change of local structure in layered-rock-salt-type iron doped lithium cobaltate $LiCo_{1-x}Fe_xO_2$ under electrochemical Li de-intercalation (charge) /re-intercalation (discharge) was studied by a laboratory type XAFS spectrometer. In Co K-XANES and Fe K-XANES of $LiCo_{0.85}Fe_{0.15}O_2$ the absorption peak shifted to higher energy by 1.5-2eV for Co K-edge and by 2-2.5eV for Fe K-edge, respectively, after the first charge. The spectra returned close to initial position and had almost original shape after the first discharge. In Co K- and Fe K-EXAFS of $LiCo_{0.85}Fe_{0.15}O_2$ during the first charge and discharge the reversible change of the local structure was observed mainly around the Co atoms although the partly irreversible change of the local structure was found around the Fe atoms. The variation of local structure occurred in similar manner for the samples with x=0.05 and 0.25. This indicates that both Co^{3+}/Co^{4+} and Fe^{3+}/Fe^{4+} redox reactions occur reversibly during the first charge and discharge.

Key words: laboratory XAFS, lithium battery, cathode material

1. Introduction

The layered-rock-salt-type lithium cobaltate $LiCoO_2$ is widely used as a cathode material of commercial rechargeable lithium battery for portable electric appliances. However, $LiCoO_2$ cathode is hardly suitable for large-scale application, for example electric vehicle because of its cost and resource problem. Because abundant transition metal substitution of cobalt is one of solutions, we have synthesized layered-rock-salt-type iron doped lithium cobaltate $LiCo_{1-x}Fe_xO_2$ (x=0-0.25) as novel cathode for rechargeable lithium battery successfully by using a low temperature hydrothermal reaction at 493-603 K (Tabuchi *et al.*, 1999). In this work XAFS study was made for as-prepared, electrochemically Li de-intercalated (charged) / re-intercalated (discharged) $LiCo_{1-x}Fe_xO_2$ at the first cycle (x=0.05, 0.15, 0.25) by using a laboratory type XAFS spectrometer in order to elucidate variation in metal valence state and local structure around metal atoms during the reaction cycle.

2. Experimental

2.1 Sample preparation

As reported elsewhere (Tabuchi *et al.*, 1999) the sample with nominal composition of $LiCo_{1-x}Fe_xO_2$ (x=0.05, 0.15, 0.25) were prepared by hydrothermal reaction between 493 and 623K from a mixture of Fe^{3+}-Co^{3+} coprecipitates and lithium hydroxides. The obtained powders were washed with distilled water for repeated times, filtered and dried at 373K to eliminate residual salts. The samples obtained were identified by powder X-ray diffractometry. The elemental analysis of metals in the obtained samples by inductive coupled plasma (ICP) emission (Li, Co, Fe) and absorption spectroscopy (Na) indicated that the cation contents of the samples were very close to those expected from the nominal composition.

The cells with a stainless steel coin-type configuration, which were constructed in an argon-filled glove box, were used for electrochemical Li de-intercalation (charge) / re-intercalation (discharge) reactions. The cathode consisted of a mixture of $LiCo_{1-x}Fe_xO_2$ sample and acetylene black with weight ratio of 5:1 and small amount of Teflon™ binder was pressed into a tablet of 15 mm under a pressure of 0.5 MPa. The separator and the electrolyte typically used were a micro porous polypropylene film and 1 M solution of $LiClO_4$ in a 50:50 mixture of ethylene carbonate (EC) and 1,2-dimethyl carbonate (DMC) (Tomiyama Pure Chemical Industries Ltd., battery Grade; less than 20 ppm water content), respectively. The electrochemical Li de-intercalation/re-intercalation reactions were carried out galvanostatically at room temperature after standing the cells overnight under zero current flow. After the electrochemical reactions, the cathodes containing $LiCo_{1-x}Fe_xO_2$ samples were sealed in a polymer films without washing and drying and used for XAFS measurement.

2.2 XAFS measurement

The Co K-XAFS and the Fe-K-XAFS of the samples were measured by transmission mode with a Laboratory type X-ray Spectrometer, EXAC-820 (Technos. Co. Lt.) (Nishihagi *et al.*, 1993). X-ray generator with a Mo rotating anode and a LaB_6 cathode was operated with a voltage of 20 kV and a current of 200 mA. The incident X-ray was monochromatized with a Ge(400) Johansson curved crystal. It is reported that resolution of XAFS spectra in this system for 3d-transition metals is comparable to that in a conventional beam line of a synchrotron radiation facility (Nishihagi et al, 1993). For Co K-XAFS measurement the intensity of the X-ray beam was measured by a sealed proportional counter filled with 25% Ar and 75% N_2 mixture gas for the incident X-ray and by a solid state detector for the transmitted X-ray, respectively. While both the intensity of the incident and transmitted X-ray beams were measured by the solid-state detector because complete cancellation of iron absorption in X-ray optics was needed. The monochromator angle was calibrated with one of Mo characteristic X-ray lines for each machine time. Cobalt powder, bis(2,4-pentadionato) cobalt(II) dihydrate, tris(2,4-pentadionato) cobalt(III) ($Co(acac)_3$), and layered-rock-salt-type $LiCoO_2$ were used as reference samples for Co K-XAFS measurement, while iron powder, iron(II) sulphate heptahydrate, tris(2,4-pentadionato)iron(III) ($Fe(acac)_3$), and layered-rock-salt-type $LiFeO_2$ (Ado *et al.*, 1997) were used as reference samples for Fe K-XAFS measurement. The stainless sample cell with Kapton™ film windows filled with a helium gas was used for the samples after the electrochemical reactions to avoid sample deterioration by water in air.

3. Results and discussion

Figure 1 and 2 show the XANES regions and their first derivative spectra of electrochemically Li de-intercalated (after the first charge) /re-intercalated (after the first discharge, *i.e.* after one electrochemical reaction cycle) $LiCo_{0.85}Fe_{0.15}O_2$ cathode compound of Co K-edge and Fe K-edge, respectively.

The comparison of the Co K-XANES showed that the peak top position of the de-intercalated sample shifted to higher energy by 1.5 - 2 eV than that of the sample before de-intercalation, which indicated that the oxidation of Co^{3+} to Co^{4+} occurred. While the peak top position and the spectra shape nearly returned to those of the sample before de-intercalation after the re-intercalation reaction (after the first discharge). This means that the reversible Li de-intercalation / re-intercalation proceeds in this electrochemical reaction system.
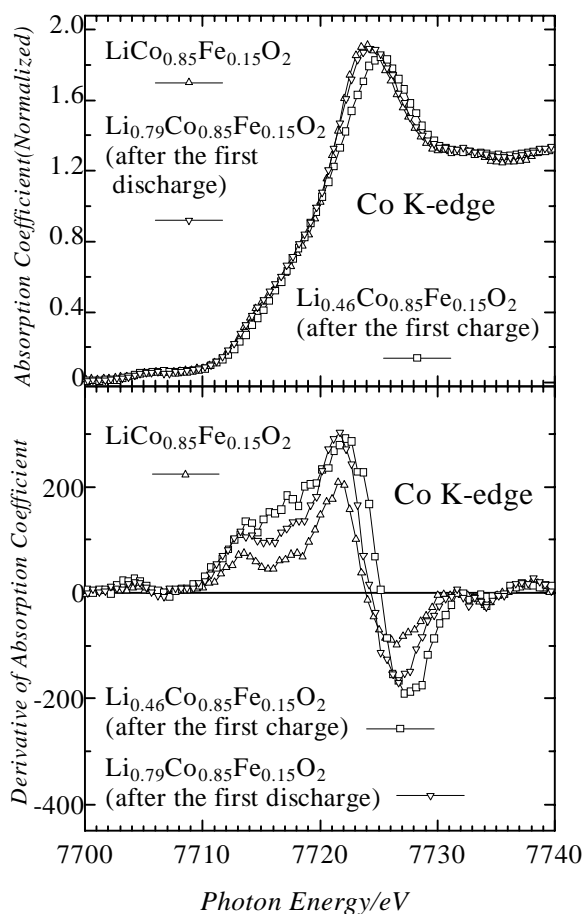
Fig. 1. The Co K-XANES regions (top) and their first derivative spectra dμ/dE (bottom) of electrochemically Li de-intercalated (after the first charge, $Li_{0.46}Co_{0.85}Fe_{0.15}O_2$) / re-intercalated (after the first discharge, $Li_{0.79}Co_{0.85}Fe_{0.15}O_2$) $LiCo_{0.85}Fe_{0.15}O_2$.

Fig. 2. The Fe K-XANES regions (top) and their first derivative spectra dμ/dE (bottom) of electrochemically Li de-intercalated (after the first charge, $Li_{0.46}Co_{0.85}Fe_{0.15}O_2$) / re-intercalated (after the first discharge, $Li_{0.79}Co_{0.85}Fe_{0.15}O_2$) $LiCo_{0.85}Fe_{0.15}O_2$.

Also the comparison of the Fe K-XANES showed that the peak top position of the de-intercalated sample shifted to higher energy by 2 - 2.5 eV than that of the sample before de-intercalation, which indicated that the oxidation of Fe^{3+} to Fe^{4+} occurred. This was supported by ^{57}Fe Mössbauer spectroscopy (Tabuchi et al., 2000).

Figure 3 and 4 show the experimentally extracted k^3-weighted Co K- and Fe K-EXAFS functions of electrochemically Li de-intercalated / re-intercalated $LiCo_{0.85}Fe_{0.15}O_2$ and their reference samples together with the calculated EXAFS functions by the feff code (Rehr *et al.*, 1991), respectively. The lattice parameters and the atomic coordinates used for feff calculation, which were obtained by the Rietvelt refinement of X-ray and Neutron powder diffraction patterns are listed in Table 1. The experimentally extracted Co K-EXAFS of $LiCo_{0.85}Fe_{0.15}O_2$ before de-intercalation is similar to that of a host material $LiCoO_2$. Also oscillation amplitude and period of the calculated Co K-EXAFS of the compound, which was based on the 'averaged crystal structure' derived from the Rietveld refinement of the X-ray powder diffraction pattern, is close to the experimental one. This means that the local structure around the Co atoms is thought be not so different from the averaged crystal structure, which would be ruled by the 'long-range-order' of the major Co and O atoms. However, the Fe K-EXAFS of the sample is fairly different from
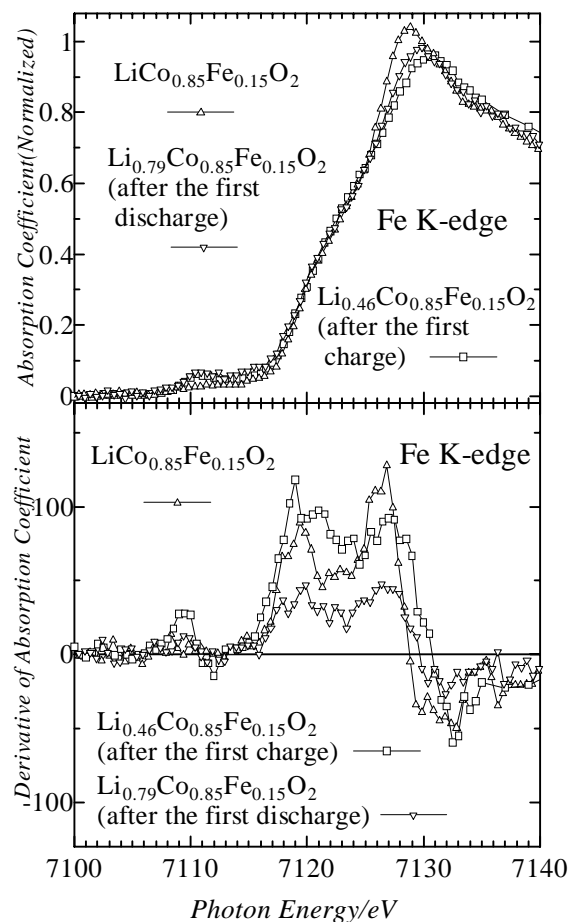
that of the other end member $LiFeO_2$. Also the calculated EXAFS does not fit well to the experimental one. This means that the local structure around the Fe atoms is considered to be far apart from the averaged crystal structure and that the unique local structure to large Fe^{3+} and its coordination symmetry would retain in the solid solution system. These results suggest the metal ion distribution model in which the major Co ions would determine the averaged crystal structure and the minor Fe ions disperse into the whole crystal lattice homogenously.

After the de-intercalation (after the first charge) the Co K-EXAFS changes slightly as expected from the averaged structure derived from the Rietveld analysis (Gummow *et al.*, 1992) while the amplitude of the Fe K-EXAFS decreases largely as compared with the calculated EXAFS. This indicates that large statistical disorder, which would cause from overlap of different kinds of local structures, would be generated especially around the Fe atom. Because only small increase of the statistical disorder is observed around the Co atoms after the de-intercalation, it is probable that some kind of 'clustering' of the Fe atoms may exist in this system.

The amplitude and period of the Co K-EXAFS almost fully recovered after the first re-intercalation (after the first discharge) while the Fe K-EXAFS partly recovered in amplitude but not in shape.
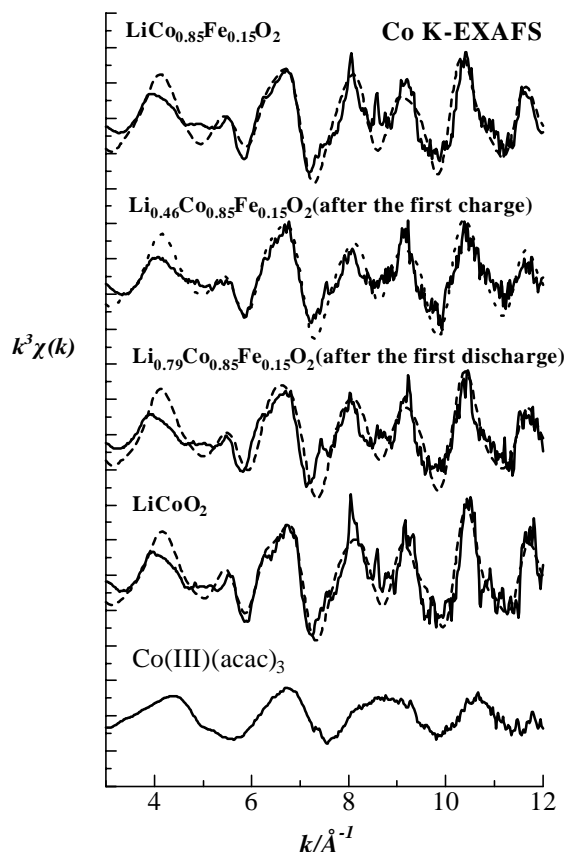
Fig. 3. The k^3-weighted Co K-EXAFS functions of electrochemically Li de-intercalated (after the first charge, $Li_{0.46}Co_{0.85}Fe_{0.15}O_2$) / re-intercalated (after the first discharge, $Li_{0.79}Co_{0.85}Fe_{0.15}O_2$) $LiCo_{0.85}Fe_{0.15}O_2$, layered-rock-salt-type $LiCoO_2$ and $Co(acac)_3$. Solid lines: Experimentally extracted EXAFS signals, Broken lines: Calculated EXAFS functions by the feff code.
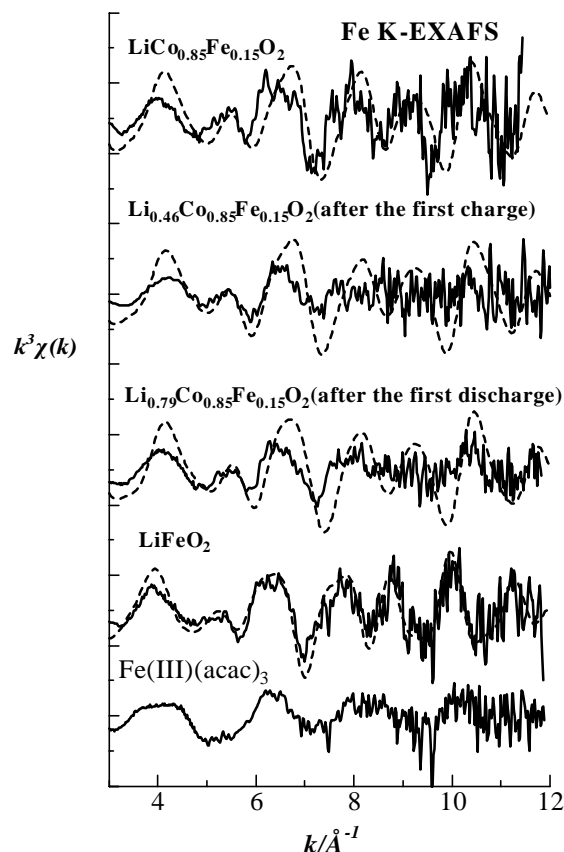

Fig. 4. The k^3-weighted Fe K-EXAFS functions of electrochemically Li de-intercalated (after the first charge, $Li_{0.46}Co_{0.85}Fe_{0.15}O_2$) / re-intercalated (after the first discharge, $Li_{0.79}Co_{0.85}Fe_{0.15}O_2$) $LiCo_{0.85}Fe_{0.15}O_2$, layered-rock-salt-type $LiFeO_2$ and $Fe(acac)_3$. Solid lines: Experimentally extracted EXAFS signals, Broken lines: Calculated EXAFS functions by the feff code.

Table 1. The list of lattice parameters and the atomic coordinates determined by the Rietvelt refinement of X-ray and Neutron powder diffraction patterns which were used for feff calculation of theoretical EXAFS functions (Rehr, 1991). All the samples have hexagonal unit cells with the space group of R3−m (No. 166). Li locates on 3a site with a coordinate of (0, 0, 0), Co and/or Fe on 3b site with a coordinate of (0, 0, 0.5), and O on 6c site with coordinate of a (0, 0, z), respectively.

Sample	a [Å]	c [Å]	Z	Ref.
$LiCoO_2$	2.815(1)	14.05(1)	0.2394(9)	1)
$LiFeO_2$	2.95427(4)	14.5275(3)	0.2420(6)	2)
$LiCo_{0.85}Fe_{0.15}O_2$	2.82970(6)	14.1419(4)	0.2399(2)	3)
$LiCo_{0.85}Fe_{0.15}O_2$ de-intercalated[a]	2.82463(11)	14.1849(11)	0.2375(3)	3)
$LiCo_{0.85}Fe_{0.15}O_2$ re-intercalated[b]	2.82339(9)	14.1555(7)	0.2385(2)	3)

[a, b] $LiCo_{0.85}Fe_{0.15}O_2$ after the first charge and discharge, respectively.
1) Orman *et al*., 1984. 2) Ado *et al*., 1997. 3) Kobayashi *et al*., 2000.

Such incomplete recovery of metal ion distribution to the initial structure of the sample before the de-intercalation would ascribed to the 'clustering' of the Fe atoms during the de-intercalation.
These phenomena were found also for the $LiCo_{1-x}Fe_xO_2$ (X=0.05 and 0.25) and were coincident with the XANES results because irreversible changes of local structure are observed especially around the Fe atoms.

Such partly reversible variation of the local structure because of tendency of the Fe ions for retaining unique coordination geometry, would be origin of the limitation of the ' rechargeablity', *i.e.*, reversibility of the charge / discharge cycle.

References

Ado K., Tabuchi M., Kobayashi H., Kageyama H., and Nakamura O., Inaba Y., Kanno R., Takagi M., and Takeda Y. (1997). *J. Electrochm. Soc.* **144**, 7, L177-L180.

Gummow R. J., Thackeray M. M., David W. L. F., and Hull, S. (1992). *Mat. Res. Bull. 27*, 327.

Kobayashi H., Shigemura H., Tabuchi M., Sakaebe H., Ado K., Kageyama H., Hirano A., Kanno R., Wakita M., Morimoto S., Nasu S. (2000). *J. Electrochem. Soc. 147*, 3, 960-969.

Nishihagi, K., Kawabata, A. & Taniguchi, K. (1993). *Jpn. J. Appl. Phys. 32-2*, 258-260.

Orman H. J. and Wiseman P. J. (1984). *Acta Cyrst. C40*, 12-14.

Rehr, J. J., Mustre de Leon J., Zabinsky S. I., and Albers R. C. (1991). *J. Am. Chem. Soc. 113*, 5135; Mustre de Leon J., Rehr J. J., Zabinsky S. I., and Albers R. S. (1991). *Phys. Rev. B44*, 4146.

Tabuchi, M., Ado, K., Kobayashi, H., Sakaebe, H., Kageyama, H., Masquelier, C., Yonemura M., Hirano, A. & Kanno, R. (1999). *J. Mater. Chem. 1999*, 9, 199-204.