

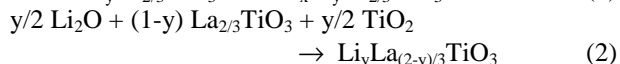
Experimental and Computational Studies on the Changes in electronic structure accompanying lithium insertion into the perovskite type oxides

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Introduction

Transition-metal oxides having lithium insertion sites are particularly interesting as the electrode material of lithium ion batteries with high-energy density. And these materials are attractive also for the good examples of the basic study of solid-state electrochemical reaction, since the host crystal structure is almost same before and after electrochemical reaction. A-site deficient perovskite type oxide, $\text{Li}_y\text{La}_{(2-y)/3}\text{TiO}_3$, is considered to be a candidate for these model compounds[1]. It stems from the fact that there are two types of lithium insertion reaction in this perovskite type compound, one is electrochemical Li^+ insertion reaction (eq.1) and the other thermal Li^+ insertion reaction (eq.2), respectively. (The latter is expressed more accurately as the substitution of Li^+ for La^{3+} in perovskite A-site.)



The reaction shown in eq.1 is classified as a redox reaction, and it is considered in conventional chemical sense that the Ti^{4+} ion is reduced to Ti^{3+} ion. On the other hand, the reaction described in eq.2 does not accompany a redox reaction, therefore the Ti^{4+} ion does not change its oxidation state.

In this study, we investigate the variation of oxidation states of each ion through the lithium insertion reaction expressed as eq.1 and eq.2 by x-ray absorption spectroscopy (XAS) measurement and *ab initio* calculation technique (the latter results will be presented at the meeting.)

Experimental

Different compositions of the $\text{Li}_y\text{La}_{(2-y)/3}\text{TiO}_3$ solid solution were prepared by conventional solid state reaction. Electrochemical lithium insertion was carried out by galvanostatic method (current density; $40\text{mA}/\text{cm}^2$) using three-electrode type cell. The XAS measurements for the La L_{III} -edge, Ti K-edge spectra were carried out by transmission mode. And that of O K-edge spectra were carried out by total-electron-yield method. For the samples after electrochemical treatment, all installation operations were performed under Ar or N_2 atmosphere.

Results and Discussion

The results of the XAS measurements for the samples of electrochemical lithium insertion are shown in figure 1. La L_{III} -edge spectra (figure 1(a)) of the XAS measurements show no marked change, and formal charges of La ions in perovskite samples are +3 because the spectra of perovskite samples were consistent with that of La_2O_3 . This indicates that the oxidation states of La ions at A-site are unchanged throughout the reaction. The Ti K-edge spectra (figure 1(b)) show two absorption peaks at the composition $x = 0$. The edge energy shifted gradually to lower energy side with composition x .

Therefore the reduction from Ti^{4+} to Ti^{3+} should occur along with electrochemical lithium insertion. Figure 1(c) shows the O K-edge spectra of the samples with composition x . Two peaks were observed at $x = 0$ in the range from 525eV to 535eV. However, the two peaks disappeared with electrochemical Li insertion, and an additional peak appeared at about 532eV. Three conceivable reasons are suggested to understand the electronic structural change in oxide ion. The interaction of (1) La - O, (2) Ti - O, and (3) Li - O. The first one would not affect the changes in electronic structure of oxide ions due to no marked change in XAS spectra (Fig.1a). Hence remaining two reasons affect the electronic structure of oxides. In order to clarify the reason for the variation of O K-edge spectra, we investigated the XAS spectra of thermally Li^+ inserted samples. The results of Ti K-edge did not show any variation with composition y , indicating Ti ions keep their formal oxidation state as +4 as expected by (eg.2). On the other hand, the O K-edge spectra changes with thermal Li^+ insertion and are similar to the spectra for the samples with electrochemical Li^+ insertion. Accordingly the origin of variation of electronic structure of oxide ions is due to the interaction between lithium ion and oxide ion, or the variation of ionicity of oxide ions.

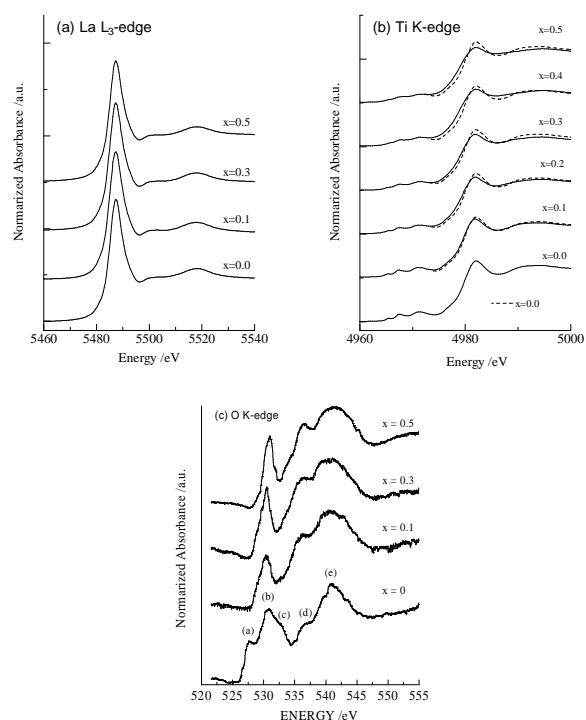


Figure 1. The variation of XAS spectra with electrochemical lithium insertion for the samples, $\text{Li}_x\text{La}_{1/3}\text{NbO}_3$. (a):La L_{III} -edge, (b):Ti K-edge, (c):O K-edge.

Acknowledgement

M.N would like to thank to Japan Society for the Promotion of Science for financial support. The La L_{III} -edge and Ti K-edge XAS experiments were performed at the Photon Factory with the approval of High Energy Accelerator Research Organization, and O K-edge XAS measurement were carried out at the UVSOR with the approval of Institute for Molecular Science.

Reference

- [1] M. Nakayama *et al.*, *J. Phys. Chem. B.*, 106, 25, 6437