

## X-ray absorption fine structure of $V_2O_5$ and $Li_xV_2O_5$

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(Received 4 August 1997; accepted 2 December 1997)

Vanadium *K*-edge XAFS measurements of five compounds were carried out. The compounds studied were crystalline  $V_2O_5$  and four types of  $Li_xV_2O_5$  with different insertion levels  $x$ , which show different EMFs (2.0–3.4 V). The EXAFS data analysis shows no remarkable difference in the V–O distances in the five compounds, showing that the structure of the  $VO_5$  square pyramids changes only slightly as lithium atoms are intercalated into the  $V_2O_5$ . In the XANES spectra, three peaks are observed for crystalline  $V_2O_5$  and  $Li_xV_2O_5$  (3.4 V). When the EMF is decreased, the intensity difference between the first and second peaks disappears and the third peak shifts to lower energy. The XANES data were analysed using full multiple-scattering calculations. In the calculated spectra the intensity of the first peak increases as the  $V_2O_5$  intercalates lithium atoms.

**Keywords:**  $V_2O_5$ ; X-ray absorption fine structure (XAFS); full multiple-scattering calculations.

### 1. Introduction

Vanadium pentoxide ( $V_2O_5$ ) is important as the anode material of the secondary battery (Cocciantelli *et al.*, 1991) and as an oxidation catalyst (Yoshida, 1997). Various measurements to determine the geometrical and electronic structure of the intercalation compounds  $Li_xV_2O_5$  have been performed. X-ray absorption near-edge structure (XANES) is an effective tool for the study of local structure around X-ray absorbing atoms. Many XANES spectra of these compounds have previously been measured and have given information about the geometric and electronic structures. However, these spectra have only been used as fingerprints. Therefore we have applied the short-range-order multiple-scattering calculation method (Fujikawa *et al.*, 1983; Fujikawa, 1993) to the XANES spectra of these compounds.

In this paper, by comparing the measured and calculated XANES spectra, we study the structural change in the intercalation process.

### 2. Experimental

The samples were prepared by the following method. Micro-crystallites of  $V_2O_5$  were dispersed in polyaniline using methylpyrrolidone as solvent. A layer 40  $\mu\text{m}$  in thickness was deposited onto an aluminium substrate (thickness 13  $\mu\text{m}$ ) using a wire bar. Samples prepared in this way were discharged at EMFs of 3.4, 3.2,

**Table 1**

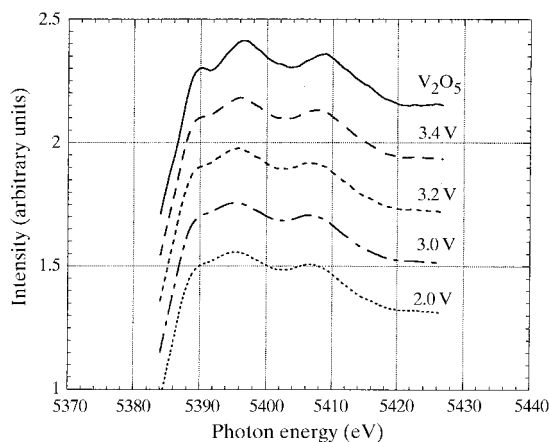
Converged structural parameters for  $Li_xV_2O_5$  with various EMFs, based on the two-distance model EXAFS analysis.

EMF (V)	$N_1$	$r_1$ ( $\text{\AA}$ )	$\sigma_1$ ( $\text{\AA}$ )	$N_2$	$r_2$ ( $\text{\AA}$ )	$\sigma_2$ ( $\text{\AA}$ )
3.4	3.6	1.769	0.005	1.1	2.013	0.003
3.2	3.3	1.773	0.005	1.3	2.026	0.003
3.0	3.3	1.775	0.006	1.4	2.026	0.003
2.0	3.4	1.777	0.004	1.4	2.037	0.003

3.0 and 2.0 V. The V *K*-edge X-ray absorption spectra were measured in transmission mode at BL-4 at Ritsumeikan University Synchrotron Radiation Center (RITS) using an Si(220) double-crystal monochromator. RITS was opened in 1996, and uses the the small ring known as AURORA, designed by Sumitomo Heavy Industries in 1989, as a light source. The electron storage ring was operated at 0.6 GeV with injection currents of 300 mA. The counting time for each data point was 1 s. The ring current was decreased by about 20 mA while an XANES measurement was performed. The distance between the source and the slit was 4.7 m, and sufficient intensity was gained to measure the range of V *K*-edge XANES. The energy and photon flux characteristics of AURORA meant that it was not necessary to take special account of the influence of harmonics in the Bragg reflected beam. The incidence and transmittance monitors were ionization chambers containing  $N_2$  and an  $N_2/\text{Ar}$  (15%) mixture, respectively. The sample was placed between the monitors in air.

### 3. Results and discussion

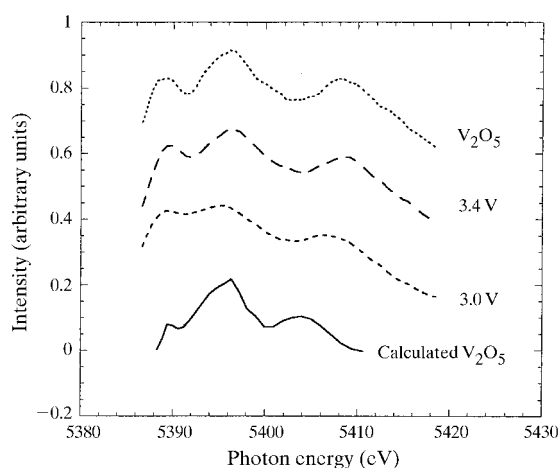
The results of the EXAFS data analysis (Tabira *et al.*, 1994) are shown in Table 1. Analysis was performed using the two-distance model under the supposition that the first peak in the radial distribution function includes contributions from the two distances (1.787 and 2.022  $\text{\AA}$ ) between the V and O atoms.  $r_1$  is the average distance from the V atom to the first shell containing four O atoms and  $r_2$  is the distance to the second shell containing one O atom. Table 1 shows that there is only a small difference between  $r_1$  and  $r_2$  in all the samples and, therefore, the structure of the  $VO_5$  polyhedra changes only slightly when the EMF is decreased from 3.4 to 2.0 V.



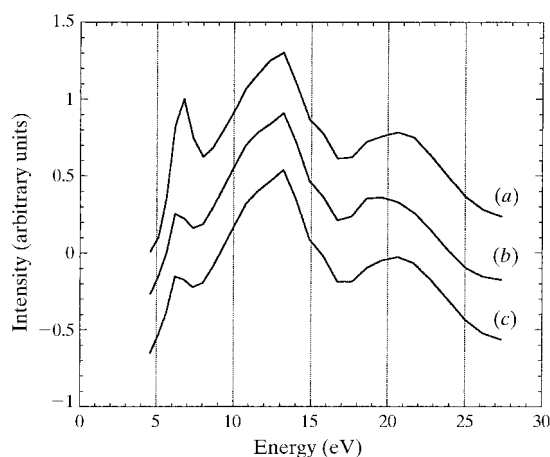
**Figure 1**  
The experimental V *K*-edge spectra for  $V_2O_5$  and  $Li_xV_2O_5$  with changes in EMF.

Fig. 1 shows the experimental XANES spectra of the intercalation compounds, compared with the spectrum of the standard  $V_2O_5$ . The spectrum of  $V_2O_5$  has three peaks, as observed in previous papers (Yoshida, 1997; Cartier *et al.*, 1990; Nabavi *et al.*, 1990). The spectrum at 3.4 V is almost the same as the spectrum of  $V_2O_5$ . As the EMF is decreased to 2.0 V, the XANES structures are smeared out and the third peak shifts to low energy. The small change in the XANES spectra with EMF is easily related to the EXAFS result that the structure of the  $VO_5$  polyhedra changes only slightly.

The calculated results for  $V_2O_5$  are compared with the experimental results as shown in Fig. 2. The experimental data in Fig. 2 are given as  $\sigma - \sigma_0$ , where  $\sigma$  and  $\sigma_0$  are the total and atomic photoabsorption cross sections; the latter is given by an arctangent function (Horsley, 1982). The geometrical parameters determined by Enjalbert & Galy (1986) are used for the present calculations, and a good convergence is obtained for a 23 atom cluster up to 4.1 Å. The phase shifts used here are calculated by the method of Pendry (1974). Two kinds of phase shift for O atoms are used; one for the nearest-neighbour O atoms and another for all other O



**Figure 2**  
The calculated V *K*-edge spectrum for  $V_2O_5$  (solid line) and the experimental data,  $\sigma - \sigma_0$ .



**Figure 3**  
The calculated V *K*-edge spectra (a) for  $Li_xV_2O_5$ , (b) for  $V_2O_5$  with slightly changed structure and (c) for pure  $V_2O_5$ .

atoms. In the cluster, there are nine O atoms with the former phase shift. The phase shifts of the absorbing atom are calculated by using the  $Z + 1$  potential to take the relaxation effect after core hole production into account.

The calculated spectrum for  $V_2O_5$  also has three peaks, and the relative intensities of the three peaks agree with the experimental result. However, the third peak is shifted to low energy by 4 eV compared with the experimental result. This disagreement may be due to charge transfer between V and O atoms.

Fig. 3(a) shows the calculated spectrum for a  $V_2O_5$  cluster with intercalated Li atoms. As described above, the EXAFS results show that the structure of the  $VO_5$  polyhedra remains almost the same. In this cluster V and O have the same coordination. We assume that the Li sites are on *c* axes through the centre of squares whose four vertices are occupied by four oxygen atoms in the basal plane on the outer side of the  $VO_5$  pyramids, and that the distance between the Li atoms on the *c* axes is 4.368 Å, the lattice constant of  $V_2O_5$ . This assumption is based on a previous paper (Cocciantelli *et al.*, 1991). There are four Li atoms in the cluster.

An increase in the first peak intensity is found for the calculated spectrum with intercalated lithium atoms, apart from which the spectrum is similar to that calculated for  $V_2O_5$  (Fig. 3c). This observation is in good agreement with the fact that the intensity of the first peak in the experimental data increases with decreasing EMF, that is, with increasing intercalation of lithium atoms. Therefore, it seems the intensity of the first peak is closely related to the amount of lithium atoms inserted into the  $V_2O_5$  layers.

The spectrum shown in Fig. 3(b) is calculated for an expanded cluster with the V–O nearest-neighbour distance increased from 1.577 to 1.627 Å. Even for such a small structural change, the third peak shifts to low energy compared with the spectrum shown in Fig 3(c) for pure  $V_2O_5$ . This result is consistent with the experimental result, *i.e.* Li intercalation can induce a small structural change slightly distorting the  $VO_5$  square-pyramidal structure.

#### 4. Conclusions

We were able to easily measure the V *K*-edge XANES spectra of complicated systems such as  $V_2O_5$  and  $Li_xV_2O_5$  using the small AURORA synchrotron radiation facility. V *K*-edge XANES spectra of  $V_2O_5$  and  $Li_xV_2O_5$  have been studied using the short-range-order multiple-scattering method. With the exception of the third-peak shift to low energy, we obtain good agreement between the calculated and experimental spectra of  $V_2O_5$ . We find that the first-peak intensity is related to the amount of Li intercalation and the third-peak shift is closely related to a small change in the  $V_2O_5$  structure.

Two of the authors (NY and KT) are grateful to Dr H. Saisho and Dr K. Ozutsumi of the Ritsumeikan Synchrotron Radiation Center for their useful advice. NY also thanks Mr K. Ohtani, Mr K. Katoh and Mr S. Nagamatsu (Chiba University) for useful discussions.

#### References

Cartier, C., Tranchant, A., Verdagner, M., Messina, R. & Dexpert, H. (1990). *Electrochim. Acta*, **35**, 889–898.

- Cocciantelli, J. M., Doumerc, J. P., Pouchard, M., Pruvssely, M. & Labat, J. (1991). *J. Power Sources*, **34**, 103–111.
- Enjalbert, B. R. & Galy, J. (1986). *Acta Cryst. C* **42**, 1467–1469.
- Fujikawa, T. (1993). *J. Phys. Soc. Jpn.*, **62**, 2155–2165.
- Fujikawa, T., Matsuura, T. & Kuroda, H. (1983). *J. Phys. Soc. Jpn.*, **52**, 905–912.
- Horsley, J. A. (1982). *J. Chem. Phys.* **76**, 1451–1458.
- Nabavi, M., Taulelle, F., Sanches, C. & Verdaguer, M. (1990). *J. Phys. Chem. Solids*, **51**, 1375–1382.
- Pendry, J. B. (1974). *Low Energy Electron Diffraction*, pp. 37–57. New York: Academic Press.
- Tabira, Y., Hara, K., Katsuragawa, T. & Tani, K. (1994). Personal communication.
- Yoshida, S. (1997). *Hyoumenkagaku*, **18**, 21–28.