Evidence of Bilayer Structure in V$_2$O$_5$ Xerogel

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Polarized X-ray absorption spectroscopy has been used to study the short-range structure of deposited films of V$_2$O$_5$ xerogel. The material is characterized by a layer of VO$_5$ units with the V−O apical bond perpendicular to the basal (*xy*) plane. We have focused our attention along the *z* axis. Experiments were carried out by extended X-ray absorption fine structure (EXAFS) spectroscopy in a grazing incidence geometry and showed evidence for close interactions between neighboring layers of V$_2$O$_5$. The structure is described by two sheets of V$_2$O$_5$ facing each other. Fitting of the EXAFS data has confirmed the existence of a vanadium−vanadium interaction between two different V$_2$O$_5$ layers and an oxygen bridge between them.

1. Introduction

In the past 2 decades a number of vanadium pentoxide materials have been synthesized by sol−gel chemistry[1] or hydrothermal methods.[2] This interest is related not only to the electronic and magnetic properties[3] of V$_2$O$_5$-based compounds but also to the redox electrochemistry.[4−6] There is a complex structural chemistry of vanadium oxide compounds in which the metal may adopt a wide variety of coordination geometry and various oxidation states. The structural characteristics of the V$_2$O$_5$-based compounds have been reviewed recently.[7] Large efforts in searching for new vanadium oxides for use as cathodic materials for advanced lithium batteries are still in progress.[8,9]

Here, we focus our attention on the structural properties of the V$_2$O$_5$ xerogel. Despite the large number of resolved crystalline structures of V$_2$O$_5$ related compounds, the use of X-ray diffraction (XRD) does not allow identification of the gel-based V$_2$O$_5$ structure unequivocally because of the intrinsic amorphous nature of the gel. V$_2$O$_5$ gel structure derived by analogy from the crystalline V$_2$O$_5$ has been previously reported by Livage et al.[1] A second model has been proposed by Oka et

al.[10] The former model uses a single (S) layer, while the latter involves a bilayer (B) to characterize the ribbon structure in the xerogel. Figure 1a shows the comparison between the two models. The Livage model suggests a single layered structure composed of a single slab of V$_2$O$_5$ with a corrugation step of 2.8 Å. The model by Oka is distinguished from that of Livage because of the characteristic V$_2$O$_5$ sheets facing each other at a distance of 2.8 Å. This structural type is similar to that of the layers in δ-Ag$_x$V$_2$O$_5$.[11] The debate on the structural model comes out of the observed X-ray pattern of the V$_2$O$_5$ gel that has poorly resolved components. In fact, the observed 00*l* class of reflections is explained by both models by simple Patterson analysis.[12]

To clarify this issue, we have adopted an experimental technique that allows the study of amorphous materials. X-ray absorption spectroscopy (XAS) has been successfully used in the study of a wide variety of materials and in several applications dealing with V$_2$O$_5$-based compounds.[13−21] Owing to the large asymmetry of the vanadium environment distances

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 (1) Livage, J. *Chem. Mater.* **1991**, *3*, 578.
 (2) Chirayil, T.; Zavalij, P. Y.; Whittingham, M.S. *Chem Mater.* **1998**, *10*, 2629.
 (3) Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651.
 (4) Wittingham, M. S.; Dines, M. B. *J. Electrochem. Soc.* **1997**, *144*, 1387.
 (5) Pistoia, G.; Pasquali, M.; Tocci, M.; Moshev, R. V. *J. Electrochem. Soc.* **1985**, *132*, 311.
 (6) Le, D. B.; Passerini, S.; Guo, J.; Ressler, J.; Owens, B. B.; Smyrl, W. H. *J. Electrochem. Soc.* **1996**, *143*, 2099.
 (7) Galy, J. *J. Solid State Chem.* **1992**, *100*, 229.
 (8) Coustier, F.; Hill, J.; Owens, B. B.; Passerini, S.; Smyrl, W. H. *J. Electrochem. Soc.* **1999**, *146*, 1355.
 (9) Coustier, F.; Lee, J.; Passerini, S.; Smyrl, W. H. *Solid State Ionics* **1999**, *279*, 116.
(10) Yao, T.; Oka, Y.; Yamamoto, N. *Mater. Res. Bull.* **1992**, *116*, 279.
(11) Andersson, S. *Acta Chem. Scand.* **1965**, *19*, 1371.
(12) Liu, Y. J.; Schindler, J. L.; DeGroot, D. C.; Kannewurf, C. R.; Hirpo, W.; Kanatzidis, M. G. *Chem. Mater.* **1996**, *8*, 525.
(13) Poumellec, B.; Kraizman, V.; Aifa, Y.; Cortes, R.; Novakovic, A.; Vedrinskii, R. *Phys. Rev. B* **1998**, *58*, 6133.
(14) Stizza, S.; Mancini, G.; Benfatto, M.; Natoli, C. R.; Garcia, J.; Bianconi, A. *Phys. Rev. B* **1989**, *40*, 12229.
(15) Goering, E.; Muller, O.; Klemm, M.; DenBoer, M. L.; Horn, S. *Philos. Mag. B* **1997**, *75*, 229.
(16) Stallworth, P. E.; Kostov, S.; DenBoer, M. L.; Greenbaum, S.; Lampe-Onnerud, C. *J. Appl. Phys.* **1998**, *83*, 1247.
(17) Giorgetti, M.; Passerini, S.; Smyrl, W. H.; Berrettoni, M. *Chem. Mater.* **1999**, *11*, 2257.
(18) Giorgetti, M.; Passerini, S.; Smyrl, W. H.; Mukerjee, S.; Yang, X. Q.; McBreen, J. *J. Electrochem. Soc.* **1999**, *146*, 2387.
(19) Clinton, D. E.; Tryk, D. A.; Bae, I. T.; Urbach, F. L.; Antonio, M. R.; Scherson, D. A. *J. Phys. Chem.* **1996**, *100*, 18511.
(20) Tossici, R.; Marassi, R.; Berrettoni, M.; Stizza, S.; Pistoia, G. *Solid State Ionics* **1993**, *67*, 77.
(21) Passerini, S.; Le, D. B.; Smyrl, W. H.; Berrettoni, M.; Tossici, R.; Marassi, R.; Giorgetti, M. *Solid State Ionics* **1997**, *104*, 195.
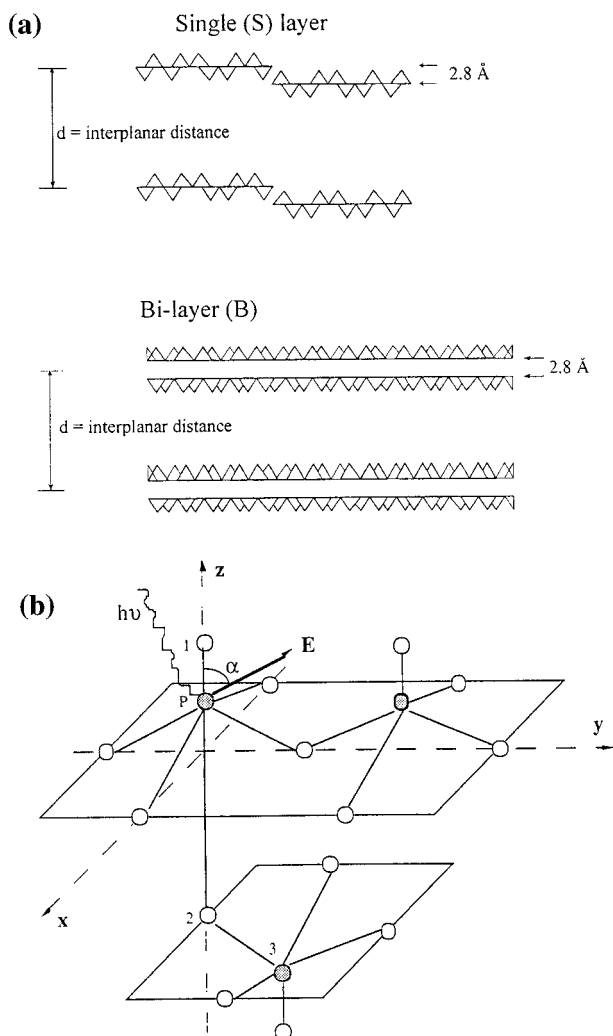
(a) Single (S) layer

2.8 Å

d = interplanar distance

Bi-layer (B)

2.8 Å

d = interplanar distance

(b)

Figure 1. Schematic picture of V$_2$O$_5$ XRG: (a) comparison of the single (S) and the bilayer (B) structural models. The basic VO$_5$ pyramid units are represented by triangles. (b) Local atomic arrangement of two adjacent VO$_5$ units interacting with a VO$_5$ from a nearly second layer: (full circles) vanadium; (open circles) oxygen. The atoms probed by the **E**∥z EXAFS spectrum are also indicated in the figure as numbers 1, 2, and 3 (P = photoabsorber).

in V$_2$O$_5$ gels, it has already been shown[13,14] that polarized absorption spectra are necessary to experimentally separate the contributions of neighboring atoms in different directions. In this paper, we probe along the z axis of a V$_2$O$_5$ xerogel sample. In particular, atomic contributions other than the apical V=O interaction will be studied to show indications of a bilayer structural arrangement in the V$_2$O$_5$ xerogel.

2. Experimental Section

A thin film of dehydrated V$_2$O$_5$ xerogel was prepared by evaporation of a 0.5 M hydrogel solution on a Mylar substrate. The evaporation was performed under dry air conditions (RH < 1%) and then under vacuum (0.1 Pa) for several days. In this way we may consider the xerogel as formed by sheets in which the vanadium pentoxide layers have a preferential orientation that is parallel to the substrate plane, i.e., the xy plane as referenced in Figure 1b. This is an approximation: The z axis of each VO$_5$ unit in the xerogel does not coincide with the macroscopic normal vector **n** of the substrate. Poumellec et al.[13] studied this issue in similar compounds by the preedge fine structure (PEFS) technique, estimating the bend of layers to be close to 12°. We will take this into account in the analysis to follow. For the sake of clarity, we consider that **n** and the z axis are parallel. Furthermore, the atomic distribution along the x and y axes is completely random, considering
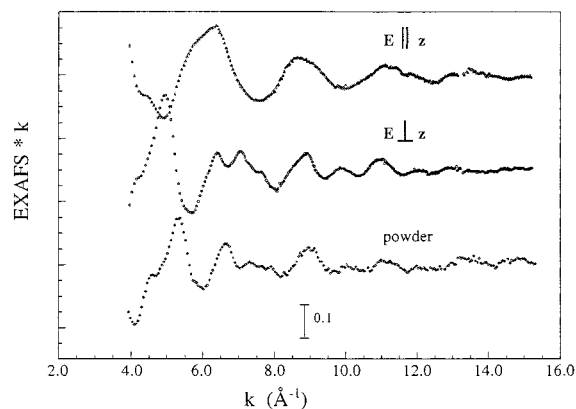

Figure 2. Experimental k-weighted EXAFS signals of an oriented V$_2$O$_5$ XRG sample at the V K-edge for two different polarization orientations. The XAS powder spectrum is shown as well.

the nature of the xerogel in which there is no definite orientation of the VO$_5$ units in the basal (xy) plane.

XAS measurements have been performed at the D21 experimental station of the LURE DCI storage ring (Orsay, France) with a positron beam of 1.85 GeV and a maximum current of 310 mA. Harmonics were rejected by using a grazing incidence mirror with a cutoff at 7.5 keV. Extended X-ray absorption fine structure (EXAFS) data have been recorded at the vanadium K-edge (5565 eV). Spectra were measured in transmission mode such that the polarization vector **E** of the incoming light was in the layer (xy) plane. The actual grazing incidence spectrum was obtained by taking the correct combination between the spectra at α = 15 and 90° (α is the angle between **E** and the z axis). Data analysis has been performed using the GNXAS package.[22,23]

3. Results and Discussion

The natural polarization property of a synchrotron radiation beam can be used to probe the structural content along different directions of an oriented sample. The dependence of the EXAFS signal on the angle between the polarization vector **E** and the position vector **r**$_j$ with respect to the photoabsorber is expressed by the relationship (for the K-edge in the plane wave approximation)

$$3|E\cdot\mathbf{r}_j|^2 = 3\cos^2\theta_j \tag{1}$$

The presence of the term $\cos^2\theta$ indicates that it is possible to discriminate between atoms in different directions by changing the beam polarization. In our case, for **E**⊥z the main contributions come from the basal plane, whereas for **E**∥z the corresponding signal has contributions from atoms along the z direction. In addition, a portion of this signal is due to atoms that are oriented at an angle that is slightly bent from the z axis. Equation 1 also indicates that there are contributions in the measured **E**∥z EXAFS spectrum from atoms that bond almost perpendicular to the z axis. However, their contribution can be estimated to be less than 3% of the total EXAFS signal because such atomic contributions belong to adjacent VO$_5$ units in which the oxygens bend about 10° from the xy plane ($\cos^2 80° \approx 3\%$). This minor contribution to the total signal does not explain any of the experimental findings.

Figure 2 shows the selected experimental EXAFS spectra for an oriented V$_2$O$_5$ xerogel sample obtained by changing the angle α. The EXAFS spectrum on a xerogel powder sample is shown as well. As may be seen, the polarization of the incoming synchrotron beam strongly affects the spectrum, clearly indicat-

(22) Filipponi, A.; Di Cicco, A.; Natoli, C. R. *Phys. Rev. B* **1995**, *52*, 15122.
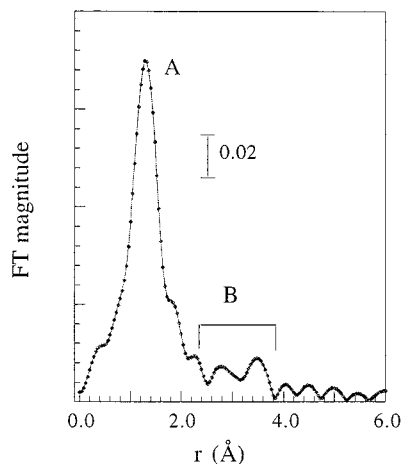(23) Filipponi, A.; Di Cicco, A. *Phys. Rev. B* **1995**, *52*, 15135.

Figure 3. Experimental FT curve of V_2O_5 XRG sample of the $E\|z$ EXAFS spectrum. The curves are obtained in the $5.5-16$ Å^{-1} k-space using a Hanning window.

ing that the VO_5 pyramids have a preferential orientation in our sample. In particular we are interested in determining the structural content of the $E\|z$ spectrum. It is evident that this signal is not dominated solely by one single main oscillation belonging to the short vanadyl oxygen perpendicular to the xy plane. The fitting procedure will explain this point further. Figure 3 shows the relative Fourier transform (FT) of the EXAFS $E\|z$ curve from Figure 2. The rather high intensity of peak A is a clear indication that it comes from a single shell contribution. However, a careful look at this FT reveals additional structure, labeled B in the figure, in the range $2.4-3.8$ Å. The intensities of the additional features are higher than the experimental noise. The main intense peak A is certainly due to the vanadyl oxygen of a VO_5 unit oriented along z. Feature B may be produced by multiple scattering (MS) effects or by other atoms shifted a few degrees from z. This experimental finding provides support for a bilayer structure of the V_2O_5 gels, and simple density considerations agree with it. The observed density of the V_2O_5 xerogel,[24] which is ~2.5 g/cm^3, is close to that of a bilayer model (2.8 g/cm^3) rather than a single layer model (1.5 g/cm^3).

To identify the structural content of the $E\|z$ EXAFS spectrum, we have fitted the experimental curve with ab initio theoretical signals based on the VO_5 unit. Figure 4A shows the fit of $E\|z$ EXAFS that is obtained when only the apical V=O interaction is used, i.e., a single layer based fit. It is evident that the experimental and theoretical curves do not match very well and that the residual is rather high. This confirms the issues pointed out in the analysis of Figures 2 and 3. To obtain a better fit, other contributions based on interaction between two layers must be included. With reference to Figure 1b, we have included the following two-atom multiple scattering signals for the $E\|z$ spectrum: (a) $\gamma^{(2)}_1$ signal due to the apical V=O$_1$ interaction; (b) a $\gamma^{(2)}_2$ signal generated by the apical V$-$O$_2$ bond; and (c) a $\gamma^{(2)}_3$ signal from V$\cdots$V$_3$ interaction generated by the vanadium of the second layer. The fitting procedure was computed with nine free parameters: three distances, three Debye$-$Waller factors, and one coordination number (CN) related to the V$\cdot\cdot$ $\cdot$V interaction. The other two parameters were E_0, which has been found to be displaced a few electronvolts with respect to the edge inflection point, and S_0^2, found to be 0.84(2).
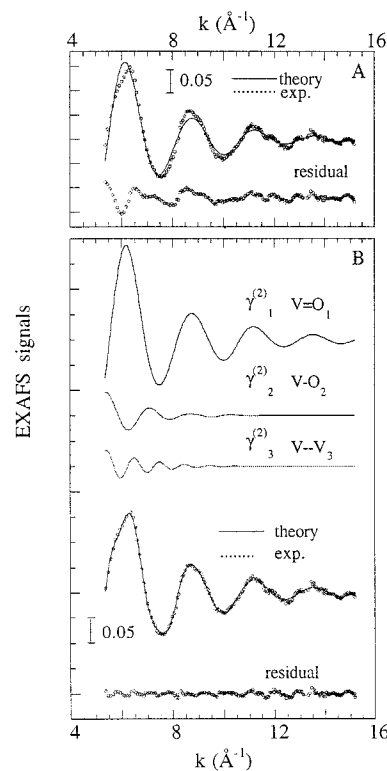
(24) Liu, Y. J.; Cowen, J. A.; Kaplan, T. A.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 1616.
(25) Filipponi, A. *J. Phys.: Condens. Matter* **1995**, *7*, 9343.

Figure 4. Details of the EXAFS analysis of the $E\|z$ EXAFS spectrum: (A) comparison between the experimental and theoretical signals based on a one-shell fit; (B) best fit. The figure shows the individual EXAFS contributions to the total theoretical signal, the comparison of the total signal with the experimental data, and the residual curve of the V K-edge EXAFS data of a V_2O_5 XRG sample.

Table 1. EXAFS Best-Fitting Results (Estimated Parameter Errors Are Indicated in Parentheses)

	1st shell/V$-$O	2nd shell V$-$O	3rd shell/V$-$V
distance/Å	1.580(2)	2.315(6)	3.53(1)
σ_2/Å$_2$	0.0035(2)	0.014(1)	0.019(3)
CN	1[a]	1[a]	3.1(6)[b]

[a] Actual coordination number. [b] Apparent coordination number from the fitting procedure. The real CNs are obtained by using the eq 1 (see text).

Figure 4B shows the single MS $\gamma^{(2)}_n$ contribution to the theoretical signal, the comparison between the experimental $E\|z$ curve with the total theoretical signal, and the residual curve. We note that all the single MS contributions are important in determining the total signal. In addition, the experimental and the total theoretical curves match very well and no other frequencies are present in the residual. The exclusion of the $\gamma^{(2)}_2$ and $\gamma^{(2)}_3$ contributions from the theoretical signal, i.e., the use of a single layer model, leads to a mismatch of the experimental and theoretical curves (as shown in the panel A). In other words, the single layer model does not explain the observed results. The evidence clearly indicates that the bilayer is the preferred structural model of the V_2O_5 gel materials.

The results of the fitting procedure are reported in Table 1 together with the estimated parameter errors, calculated by performing two-dimensional contour plots.[23,25] Because the $\gamma^{(2)}_1$ signal of the Figure 4 panel B is the more intense signal, we were able to evaluate the V=O bond distance very accurately. The value was 1.580(2) Å, which is in very good agreement with the value of 1.58 Å normally quoted for this bond length.[14] The corresponding σ^2 was found to be 0.0035 Å^2. Signal $\gamma^{(2)}_2$

refers to an oxygen atom located at 2.32 Å from the vanadium. This arises from an oxygen bridge between two layers, and it is in a direction opposite that of V=O of $\gamma^{(2)}_2$. The actual coordination number of both interactions is equal to 1, taking into account eq 1 and the slight bend of the V=O bond with respect to the basal plane. Signal $\gamma^{(2)}_3$ is due to a V···V interaction at 3.53 Å with an apparent degeneracy of 3.1. Moreover, since the angle between the electric field and the vector joining the vanadium of the $\gamma^{(2)}_3$ signal is about 35°, the real coordination number is $3.1/(3 \cos^2 35°) \approx 1.5$. Since these vanadium atoms are related to the *xy* plane of a second layer and then are not oriented in the basal plane, the corresponding signal must be averaged over all possible directions of *x* and *y* axes in the basal plane. As a result, the degeneracy of this signal should become higher than 1.5. This issue has been discussed by Stizza[14] who suggested a correction factor of 2 for the CN. In the present study, this indicates an interaction with at least three vanadium atoms belonging to the second sheet of V$_2$O$_5$ (for instance, the atom labeled 3 in Figure 1b).

4. Conclusions

The present analysis clearly indicates that there is a bilayer structure for the V$_2$O$_5$ xerogel compound. Obviously, the largest peak in the FT spectrum is the one arising from the V=O bond, but this is not involved in the argument for the bilayer. The strongest support is provided by region B in the FT or the signals $\gamma^{(2)}_2$ and $\gamma^{(2)}_3$ of Figure 4B. These were assigned to an oxygen bridge between two vanadium atoms along the *z* direction and to three vanadium atoms of a second layer, respectively. This means that there is proximity of two V$_2$O$_5$ sheets in V$_2$O$_5$ gel compounds. The model is called a bilayer structure.