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Electrochemical and synchrotron XAS studies of lithium intercalation into vanadium pentoxide aerogels and nanocomposites

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Abstract

Vanadium pentoxide aerogels are pillared nanocomposites with exceptional stability, intercalation capacity, and reversibility. X-ray absorption spectroscopy (XAS) measurements on pristine and doped materials have revealed details of the oxidation state and local structure of the host material and of the polyvalent doping species. XANES measurements at the Cu K-edge for $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ show the atomic level reversibility of the structure upon Li^+ insertion/release cycling. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the introduction of the lithium ion cell system that avoids the problem of safety hazards of lithium metal anode batteries, non-aqueous high-energy rechargeable batteries are a significant component of portable consumer electronic products. Unfortunately, the substitution of lithiated compound anodes for lithium metal results in a large cost in terms of output voltage and specific energy. One way to offset this loss, associated with the anode, is to enhance the performance of the intercalation cathode. A second approach is to develop battery systems around other energetic materials. The present paper describes work on pillared intercalation hosts that have enhanced properties as cathode materials.

The electrochemical properties of vanadium oxide electrodes prepared by sol–gel processes have been shown to depend on the structural and morphological characteristics that are in turn quite sensitive to the method of preparation. Previous studies have demonstrated that the morphology of thin film vanadium oxide xerogels can be changed by changing the rate and mode of drying the starting hydrogel [1–3]. The resulting materials have intercalation capacities as high as 650 Ah/kg with corresponding specific energies exceeding 1600 Wh/kg. The preparation of vanadium

pentoxide via sol–gel processing has been extensively reported and a comprehensive review is available [4]. Several papers focused on the hydrogel [4–8] have led to a more complete understanding of the chemistry of the process. Formation of hydrogels involves a gelation step that proceeds through formation of decavanadic acid and subsequent polycondensation [5]. The polycondensed vanadium oxyhydroxide material that precipitates and forms the gel has the characteristic shape of ribbons. The structure of the ribbons remains controversial. Two different models have been proposed for the layered structure of gel-based V_2O_5 materials. The older one, proposed by Legendre et al. [9] was directly derived from the structure of crystalline V_2O_5 . The second model, introduced by Yao et al. [10], proposes that each V_2O_5 layer is constituted of two facing $\text{VO}_{1.5}$ sheets, further sandwiched by two layers of apical oxygens (one oxygen in each layer). The second model gives a more accurate estimation of the material density [10], and has been confirmed as the more appropriate structure by our recent studies with polarized X-ray absorption spectroscopy (XAS) measurements [11]. The incentive to improve the performance of the oxide has led us to modify the drying procedure for bulk materials. In the course of the study, it was discovered that we had pillared the oxide, and this has led to a new class of intercalation hosts.

Pillaring of vanadium pentoxide hosts by organic species was discovered in our laboratories to be effective for increasing the inherent specific energy for lithium ions [12], and for polyvalent cations such as Mg^{+2} , Al^{+3} , and

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Table 1
d-Spacing of pillared V_2O_5 nanocomposites

Solvent	d-Spacing (Å)
Acetone	12.46
1,4 Dioxane	14.20
Acetonitrile	12.11
Methyl formate	10.92
Dimethoxymethane	10.53
Acetaldehyde	13.20
Nitromethane	10.72
Propionitrile	11.63
Methyl ethyl ketone	12.45

Zn^{+2} [13]. Pillaring of the amorphous, layered host was induced by several organic compounds, i.e. acetone, 1,4-dioxane, acetonitrile, methyl formate, and others [14], and the pillaring occurred during the sol–gel processing of the vanadium pentoxide gels. A list of the pillaring agents and the interlayer distance of the pillared V_2O_5 is given in Table 1. Of the pillared composites, only the first four have been examined electrochemically, and all show an intercalation capacity of at least four Li^+/V_2O_5 . In addition, because these four materials behave in such a similar manner, it may be expected that they are a model for others in the list. Pillaring was found to be stable to repeated intercalation and release cycling of Li^+ ions [15–17] and of polyvalent ions as well [13], and the intercalation was highly reversible. In addition, there was no sacrifice of the intercalation capacity. The experimental intercalation capacity was equal to that for the unpillared material, that is up to four equivalents of Li^+ , Mg^{+2} , and Al^+ . The experimental specific energy for Li^+ was higher, however, in the pillared material. XAS studies have shown that pillaring caused profound changes, in that the intercalation charge was delocalized over the host, in contrast to the unpillared host where charge is largely associated with the vanadium cation [18–21].

In recent work, it was found that the vanadium oxide could be easily doped with a metal in the hydrogel form by reaction with a known amount of the doping metal (i.e. copper, silver, zinc, nickel and aluminum). The characterization of gel-based, copper-doped V_2O_5 materials has been reported earlier [22,23]. The materials maintain the layered structure typical of V_2O_5 , but with enhanced performance. Cathodes based on this material have a potential of around 3.7 V (versus Li) in the pristine state and are able to reversibly intercalate a large number of lithium ions ($x > 2$). This leads to experimental specific capacities exceeding 300 mAh/g at C/100 rate and specific energies exceeding 750 Wh/kg [22]. In addition, $Cu_{0.1}V_2O_5$ cathodes were able to deliver 180 mAh/g in 80 min discharges for more than 450 cycles [22] without capacity fading. Cyclic voltammetry and galvanostatic insertion of doped V_2O_5 materials indicate the reduction of the doping ion (silver or copper) to the metallic state during the lithium insertion.

2. XAS characterization of intercalation in the pillared hosts

In the present contribution, we focus on the lithium insertion mechanism of the copper-doped V_2O_5 XRG by using in situ XAS as a local structural tool. The technique is sensitive to short-range order (a few Å around the selected atom) and can be applied to disordered, amorphous and crystalline materials. Previous reports based on in situ XAS studies have given details on various topics including electrochemical interfaces [24], electrodes surface [25,26], Pt/C catalysts [27], batteries [28], and biology [29]. In the present work, the vanadium and the copper local structure arrangement could be monitored during the intercalation process, revealing the modification that occurred upon the lithium insertion and release.

Analysis of the XANES portion of the XAS spectra has been studied at the V K-edge in order to study the oxidation state of V in the lattice as a function of lithium intercalation. In our previous XAS work, we also used the EXAFS [19,21] portion of the spectra in both ex situ and in situ measurements. Lithium is too light to study by XAS techniques, so that it is not possible to determine specifics of the intercalation sites. Instead, it has been found to be advantageous to intercalate polyvalent cations with higher atomic mass so that the XAS spectra of these cations could be used to probe the nature of the intercalation sites [20,21]. In Fig. 1 is shown the XANES results of the previous studies at the V and Cu K-edges, respectively. The vanadium spectra do not change with Cu-doping, indicating that the intercalation charge is delocalized over the lattice confirming earlier work.

In the present work, the insertion mechanism and the modification of the structure have been characterized in copper-doped, unpillared V_2O_5 xerogel upon lithium insertion and release. Cathodes of the material have shown excellent electrochemical properties in terms of lithium insertion capacity both in the form of aerogels and xerogels. Up to 2.2 mol of lithium per mole of doped V_2O_5 may be reversibly inserted at reasonable rates over a few hundred of cycles (>450) with no capacity fading. The results have shown that lithium insertion in copper-doped V_2O_5 xerogel causes the reduction of the oxidation state of both copper and vanadium in the unpillared host. While the vanadium site is modified by lithium insertion as in other unpillared V_2O_5 xerogels, the copper ions are reduced to the metallic state. Under the constraint of the bi-layered structure of the host, the metallic copper forms monolayer sheets. This conclusion confirms the electrochemical result that showed metal formation reported previously for Cu- and Ag-doped V_2O_5 xerogels. Of further importance, the present work has shown that the Li^+ intercalation process is completely reversible at the atomic level. This is demonstrated in Fig. 2 where the Cu XANES results are compared for the pristine material ($Li^+/V = 0$) and for the same material after a complete cycle where metallic copper is formed and then

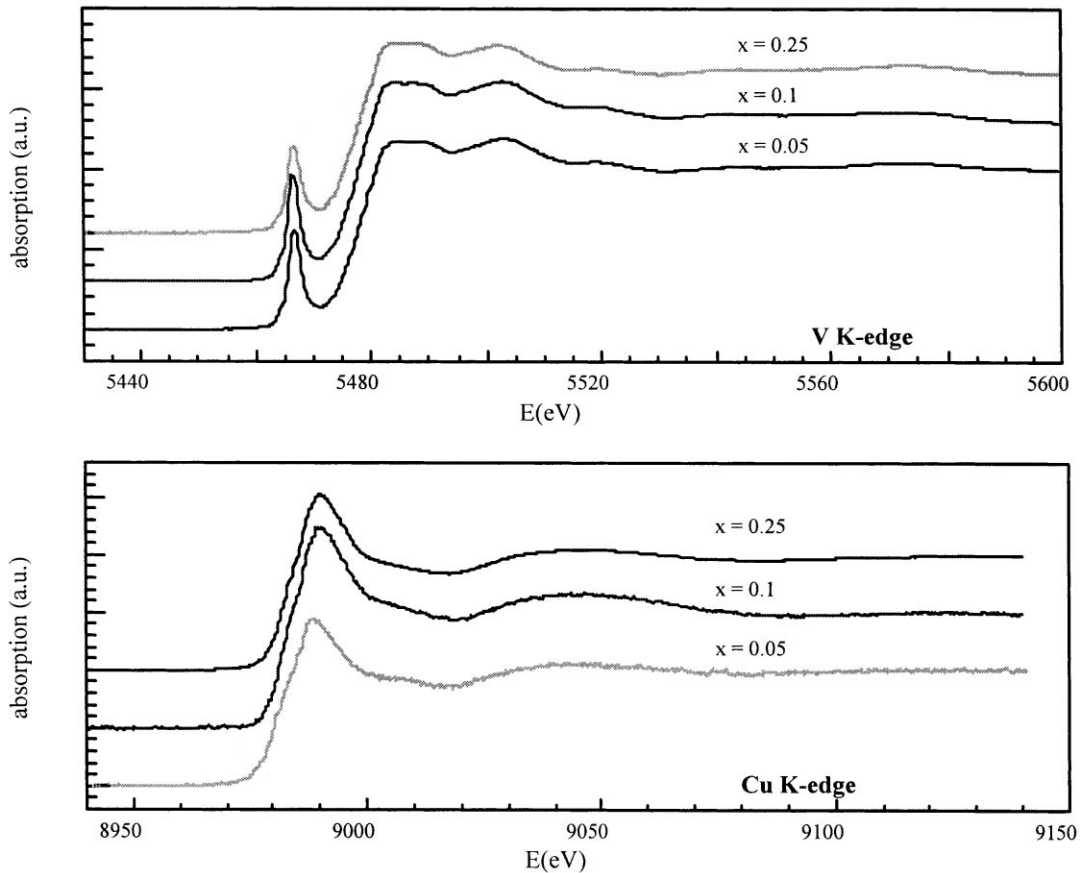


Fig. 1. XAS Characterization of Cu-doped pillared V_2O_5 at the V and Cu K-edges respectively.

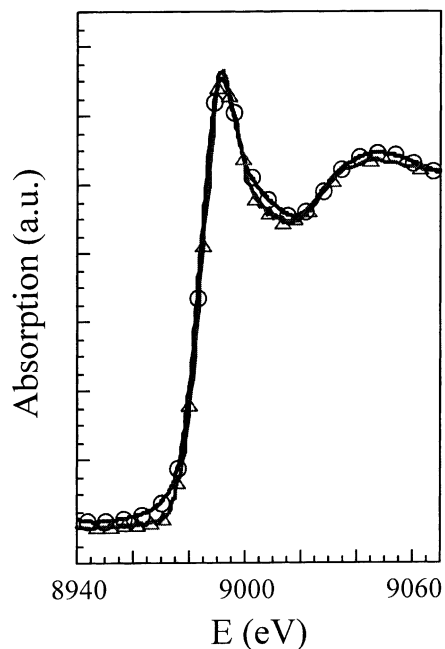


Fig. 2. Comparison of XANES Curves (Cu K-edge) for Unpillared $Cu_{0.01}V_2O_5$ XRG. (O) = pristine, (□) = after 1 Li^+ Insertion-Release Cycle.

reoxidized. Since the two curves are identical, one concludes that Cu^{+2} ions have been reinserted into the surrounding lattice at the same sites. This structural reversibility of the host at the atomic level confirms our earlier work, which reported the complete reversibility of insertion mass and charge, and host stress over multiple insertion/release cycles. Further work is planned to carry out in situ XAS measurements of pillared materials with polyvalent cation doping and with polyvalent insertion and release.

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