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Structural, physical and electrochemical characteristics of a vanadium oxysulfide, a cathode material for lithium batteries

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Abstract

A vanadium oxysulfide is obtained by a reaction between water solutions of a vanadyl salt and sodium sulfide at room temperature. After drying under mild conditions, the formulation of this phase is $V_2O_3S \cdot 3H_2O$. Thermogravimetric analyses show that it is not possible to remove completely water without losing sulfur. This is in agreement with proton nuclear magnetic resonance experiments which prove that water molecules are tightly bonded to vanadium. Magnetic susceptibility and X-ray absorption spectroscopy measurements allow to define the oxidation states of vanadium and sulfur, (IV) and (-II) respectively. From extended X-ray absorption fine structure spectroscopy at the vanadium K edge and infrared spectroscopy, the local structure around vanadium can be defined as a distorted octahedron, with a vanadyl bond and an opposite sulfur atom. Magnetic susceptibility and X-ray absorption spectroscopy measurements on chemically lithiated compounds show a complex charge transfer from lithium to the host structure upon lithium intercalation. If it appears that vanadium atoms are reduced, a possible role of sulfur atoms in the redox process has to be considered. Cycling tests of lithium batteries whose positive consists of oxysulfide are promising with 70 cycles under a regime of *C*/8, without noticeable loss in capacity of 120 Ah/kg.

Keywords: Lithium batteries; Cathode materials; Vanadium oxysulfide

1. Introduction

In the frame of the quest for performing lithium batteries, new materials are still considered in order to improve both capacity and cycling capabilities. If the transition metal oxides are presently viewed as the more promising candidates as positives for such batteries, it can be also interesting to obtain transition metal oxysulfides which can make a good compromise between oxides and sulfides. Very few examples of such compounds are known, especially if we consider phases with an open structure favourable for lithium insertion. Poorly crystallized molybdenum [1,2] and titanium [3] oxysulfides have been obtained and tested as positives in lithium batteries. Both of them give good reversibility and mean voltage intermediate between those generally observed for oxides and sulfides. They have been prepared under mild synthesis conditions which probably allow to stabilize a mixed oxygen and sulfur environment for the transition metal. By using a soft chemistry reaction we were able to prepare a new vanadium oxysulfide by an ion condensation reaction [4,5]. In this paper we first establish its formulation, from various physical measurements, and its local structure, deduced from infrared, nuclear magnetic resonance (NMR) and extended X-ray absorption fine structure (EXAFS) spectroscopies. Some of these techniques have been used on chemically intercalated compounds, in order to define the nature of the redox process involved during the reaction with lithium. Finally, we give some electrochemical characteristics of button cells whose positive has been built with this vanadium oxysulfide.

2. Synthesis and characterization

In previous papers [4,5], it has been shown that vanadium oxysulfide is prepared by a reaction between water solutions of vanadyl salts ($VOCl_2 \cdot 2H_2O$ or $VOSO_4 \cdot 5H_2O$) and hydrated sodium sulfide, $Na_2S \cdot 9H_2O$ at room temperature. A gray precipitate is immediately obtained and the reaction is completed in about 24 h upon mechanical stirring. The absence of noticeable features on X-ray diffraction (XRD) pat-

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terns, even for long time exposures, confirms the amorphous nature of the new phase. Energy dispersive analysis of X-rays (EDAX) performed in a scanning electron microscope (SEM) indicates a mean V/S atomic ratio of 2 with a very small dispersion for various samples and different parts of them. This is confirmed by a chemical analysis (excluding hydrogen), on a phase dried at 100 °C for 24 h under atmospheric pressure, which gives a formula V_2O_6S. By a simple comparison with $VOSO_4 \cdot 5H_2O$, infrared spectroscopy experiments attribute the unexpectedly large amount of oxygen to the presence of water molecules. At the same time, they show that the new phase contains a vanadyl group but no sulfate groups.

Magnetic susceptibility measurements show clearly a temperature-dependent paramagnetic behaviour with a curve of the χ^{-1} versus T variation which can be analysed as superimposed temperature-independent paramagnetism (χ_{TIP}) and Curie–Weiss paramagnetism [5] attributed to vanadium at the oxidation state (IV). Electron paramagnetic resonance (EPR) spectroscopy measurements, which show a large signal at room temperature with $g = 1.97$, are in good agreement with this oxidation state. It is known that the positions of various singularities at the XAS edges are very sensitive to the oxidation state (pre-peak, main edge, first peak, etc.). The main vanadium K edge of the vanadium oxysulfide is found at the same position as that of $VOSO_4 \cdot 5H_2O$, confirming the oxidation state(IV) for vanadium. A similar study performed at the sulfur K edge with various reference compounds proves the anionic nature of sulfur with the probable oxidation state(-II). Taking into account these oxidation states, the formula of the new phase may be written $V_2^{(IV)}O_3^{(-II)}S^{(-II)} \cdot yH_2O$.

An EXAFS study at the vanadium K edge [5] and infrared spectroscopy show that the vanadium first coordination shell is made of five oxygen and one sulfur atoms. One oxygen forms a vanadyl bond ($d_{V\text{-}O} = 1.58$ Å) and the four others describe a square plan ($d_{V\text{-}O} = 2.02$ Å). The sulfur atom is found at a distance of 2.23 Å; this is in good agreement with the expected vanadium–sulfur distance for the considered oxidation states and environment. Fig. 1 gives the scheme of the vanadium first coordination shell. The vanadium–vanadium distance, deduced from the EXAFS spectra (3.14 Å, very close to the one observed in V_2O_5), and the very low number of vanadium atoms at this distance ($N \approx 2$) indicate that these groups probably form chains by sharing O–O edges, in such a way as to find vanadium atoms alternatively above and below the chains.

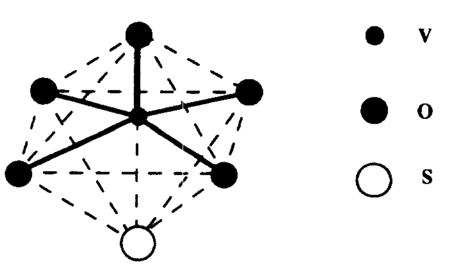

Fig. 1. Schematic representation of the vanadium environment in the oxysulfide $V_2O_3S \cdot 3H_2O$.

TGA experiments performed under argon flow on the compound obtained at room temperature and before any thermal treatment, show two distinct weight losses. A mass spectrometry analysis of the evolved gases proves that the first loss, below 120 °C, corresponds mainly to water (attributable to adsorbed molecules) and the second one, between 120 and 300 °C, to remaining water and sulfur. The final plateau corresponds to VO_2. The water content and the nature of these water molecules depend largely on the heat treatment of the rough powder and it is easy to imagine that they will influence deeply the electrochemical performances of batteries built with the new phase. Various drying processes have been then tested. Adsorbed water can be removed either by heating at 120 °C at ambient pressure or by drying at 70 °C under dynamic vacuum. Lyophilisation can also be used to dry the compound. In any case, it is impossible to remove completely water without losing sulfur. For example, drying under dynamic vacuum at temperatures higher than 70 °C induces a sulfur loss evidenced by a large increase of the V/S atomic ratio. This tends to indicate that a fraction of water stabilizes the phase.

A proton NMR study confirms this fact. Mainly two types of line width may be observed depending on the way water molecules are bonded to vanadium atoms. If water is only adsorbed, the corresponding spin–spin relaxation time $T2$ is rather long (100 μs), and the line is sharp. On the contrary, if oxygen is bonded directly to the vanadium atom, $T2$ is very short (6 μs) and the line is broad. An interesting evolution in the line shape is observed, depending on the procedure used to dry the phase. The general tendency is that the fewer water molecules in the phase, the more tightly they are bonded to vanadium.

3. Redox process upon lithium intercalation

A series of lithium intercalated compounds have been prepared for $x = 0.38$, 0.76, 0.97, 1.16, 1.56 and 1.93 in $Li_xV_2O_3S \cdot 3H_2O$, by applying the *n*-butyllithium technique to an oxysulfide dried at 70 °C under vacuum. Due to their hygroscopic character, all these phases have been handled in nitrogen- or argon-filled glove box and specially conditioned for physical measurements.

Magnetic susceptibility has been measured between 5 and 300 K. The reciprocal magnetic susceptibility variations versus temperature present the same type of curve as the one encountered for the pristine material and evidence a progressive increase of the susceptibility in agreement with a larger number of unpaired d electrons on vanadium atoms (Fig. 2). The data have been analysed as superimposed χ_{TIP} and Curie–Weiss paramagnetism. The variations of the deduced magnetic moment and χ_{TIP} versus the lithium content are plotted in Fig. 3. The general tendency corresponds to an increase of the temperature independent paramagnetism and of the magnetic moment, upon intercalation. The variations are not very regular but they all indicate a reduction of vanadium atoms, by increasing the amount of either the delocalized electrons responsible of the TIP or the localized ones which induce the magnetic moment.

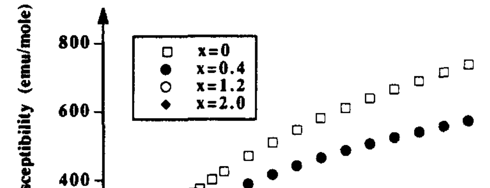

Fig. 2. Variation of the reciprocal molar magnetic susceptibility vs. temperature for some phases in the $Li_xV_2O_3S \cdot 3H_2O$ system.

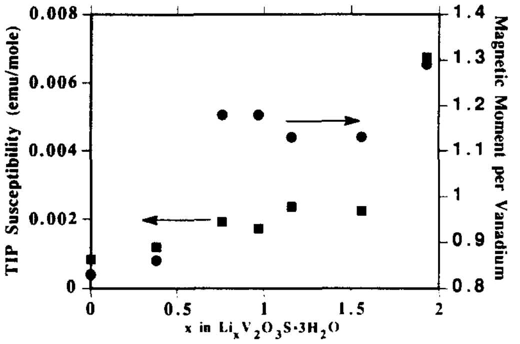

Fig. 3. Variation of the temperature independent paramagnetism (TIP) susceptibility and the magnetic moment per vanadium atom (in Bohr magneton) vs. x in $Li_xV_2O_3S \cdot 3H_2O$.

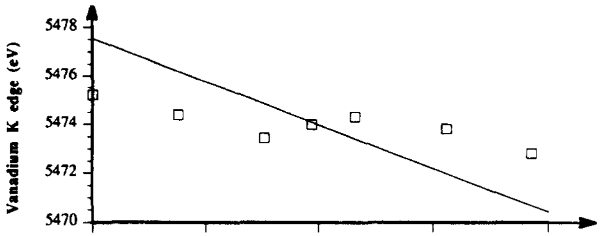

Fig. 4. Variation of the XAS vanadium K edge position vs. x in the $Li_xV_2O_3S \cdot 3H_2O$ system. The full line corresponds to the expected variation from Ref. [6].

It is well known that the X-ray absorption spectra near the edge are mainly related to the electronic structure of absorbing atoms and are sensitive to the crystal field and the electronic population. This has been especially observed for various vanadium derivatives [6] and lithium intercalated vanadium oxyde $Li_xV_2O_5$ [7]. The X-ray absorption spectra of the lithium intercalated vanadium oxysulfides have been collected at the vanadium K edge, using the DCI synchrotron storage ring at LURE (Orsay, France). Upon lithium intercalation, only small displacements towards lower energies can be observed, which can be interpreted as a reduction of vanadium. The edge position, determined by the first derivative, versus the lithium content is plotted in Fig. 4. Such a variation is in complete agreement with the reduction of vanadium. The amplitude of the edge displacement is lower than expected from previous studies upon the relation between the edge position and the vanadium oxidation state [6], especially for a lithium/vanadium ratio greater than 0.5. The characteristics of the pre-edge peak can be compared with the results obtained on the $Li_xV_2O_5$ system [7]. We may observe a slight displacement towards lower energies and a broadening, upon lithium intercalation. For $x < 1$, these phenomena have a very comparable amplitude in both systems with a shift of 0.3 and 0.36 eV and a broadening of 0.8 eV and 0.65 eV, for $Li_{0.9}V_2O_5$ and $Li_{0.97}V_2O_3S \cdot 3H_2O$, respectively. For higher lithium contents, almost no extra change can be detected on the vanadium oxysulfide intercalates, when the evolution is going on for the V_2O_5 derivatives. This different behaviour suggests the occurrence of another redox centre which could imply sulfur atoms. Further experiments at the sulfur K edge are currently under way.

4. Lithium batteries testing

The new compound, dried under vacuum at 70 °C, has been tested in lithium cells. The positive is made of a mixture of the oxysulfide (80 wt.%), graphite (7.5 wt.%), carbon black (7.5 wt.%) and Teflon (5 wt.%). It is incorporated in a button cell whose negative is lithium and its electrolyte a solution of 1 M $LiClO_4$ in propylene carbonate. As expected for a partially sulfur-substituted oxide, the open-circuit voltage is lower than in the parent vanadium oxide V_2O_5 with a mean value of 2.6 V compared with 3.3 V, but higher than generally observed in the sulfides [4]. The behaviour in cycling conditions is very promising. Up to now, the batteries were cycled 70 times, between 3.6 and 1.5 V, under a regime of $C/8$ (current density of 1 mA/cm^2), with about 0.5 lithium atom per vanadium corresponding

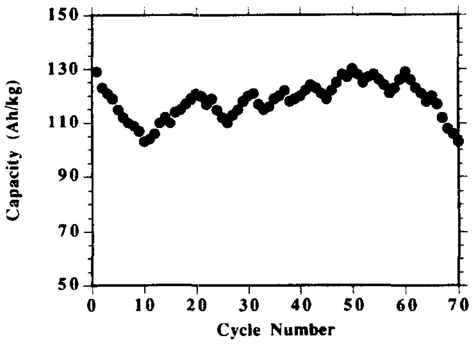

Fig. 5. Capacity of lithium batteries whose positive is oxysulfide vs. cycle number.

to a capacity and an energy of 120 Ah/kg and 300 Wh/kg, respectively. Under this regime, a slight displacement (0.1 lithium per vanadium) of the cycling curves can be observed towards higher lithium content. Nevertheless, this is done without noticeable loss in capacity (Fig. 5).

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