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Lithium electrochemical intercalation in β-$VOSO_4$

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Abstract

A new low-temperature route for β-$VOSO_4$ synthesis is proposed, involving reduction in sulphuric acid in the presence of sulphur. Lithium intercalation has been performed on this material, both chemically and electrochemically and the compounds have been characterized by XRD as well as IR and Raman spectroscopy. From potentio-dynamic and galvano-static electrochemical studies it is shown that intercalation occurs in two steps, firstly with a structural change at 2.84 V vs. Li metal, then in a solid solution domain. The process appears partly reversible and the system is shown to present a good cycling behavior on almost 0.6 e^- per transition metal. From these results it appears that the energy of redox transition metal couples involving VO^{2+} structural units in octahedral coordination is between those observed in oxides and in $M_2(XO_4)_3$ (X = S, P, As) compounds, respectively. © 1997 Elsevier Science S.A.

Keywords: Synthesis of β-$VOSO_4$; Lithium intercalation; Electrode material; VO^{2+} structural unit

1. Introduction

For 20 years, a lot of research has been carried out on materials for lithium batteries. High energy density and working voltage are an answer to the rapid advance of miniaturization, such as portable technologies. However, the use of a Li metal anode as a negative electrode generates safety and rechargeability problems. As a result, there is great interest in 'rocking chair' batteries where the Li anode is replaced by a Li-intercalation compound. But such batteries call for positive electrodes with high working potential for compensating the potential of the negative electrode, significantly above that of lithium metal.

Apart from the working potential, the main parameters that need to be optimized for these electrode materials are the specific capacity and the cyclability. Another parameter to be taken into account is the cost of the initial products and of the synthesis process.

Oxide compounds like $LiMn_2O_4$, $LiNiO_2$ and $LiCoO_2$ have stimulated a great deal of interest since the commercialization of two rocking-chair cells with carbon negative electrode: $LiNiO_2$//C and $LiCoO_2$//C [1,2].

Recent studies in order to lower the synthesis temperature of Li-Mn-O spinel materials [3-5] showed that samples prepared at low temperature exhibit better cyclability but lower capacity than those synthesized at high temperature. In addition Co and Ni are problematic in terms of availability, cost and toxicity.

Recently, Goodenough et al. [6,7] investigated new electrode materials with the general formula $Li_xM_2(XO_4)_3$ (X = S, P, As). These studies demon-

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strated the influence of the ionicity of chemical bonds between transition elements and oxygen anions. The more ionic these bonds, the lower the intercalation energy. Accordingly, the potential of a redox couple in a given coordination shell is lower in the oxide form than it would be by substituting the oxygen anion by a more electro-attractive anionic structural unit.

However these anionic units tend to isolate the transition elements and consequently to lower the electronic conductivity. This seems to be partly responsible for slower intercalation kinetics in these materials than in transition metal oxides. Thus it appears interesting to study new host materials between oxides and oxo-compounds, where transition elements are surrounded by O^{2-} and $(XO_4)^{n-}$ (X = S, P) simultaneously.

In this paper a new synthetic method for β-$VOSO_4$ and electrochemical and structural studies of the lithium intercalation compound are presented.

2. Experimental

β-$VOSO_4$ is usually prepared by dehydration of the vanadyl sulphate hydrate above 280°C.

The β-$VOSO_4$ used in this study was synthesized through an original route, which is the reduction of vanadium pentaoxide with sulphur in stoichiometric amounts, in concentrated sulphuric acid at 140°C for a few hours. The resulting powder is then washed with water and dried under vacuum at 160°C overnight. It was shown by X-ray diffraction to be anhydrous β-$VOSO_4$ (JCPDS No. 19-1400).

Of the above two methods, the new one we propose is more interesting in term of energy cost since the temperature of synthesis is lower. Moreover, it leads to micronic particles which is better for intercalation from a kinetic point of view.

A chemically lithiated sample was prepared using the *n*-butyllithium route. The reaction was carried out in a flask under dry argon at ambient temperature with continuous stirring for 10 days. The product was then washed several times with hexane and dried under vacuum.

Electrochemical intercalation studies were performed in both potentio-dynamic and galvano-static modes using a MacPile sytem (Bio-Logic, Claix, France) and Swagelok type cells [8], with Li metal as the negative electrode and 1 M $LiClO_4$ in anhydrous propylene carbonate as the electrolyte. Composite positive electrodes were made of 5% wt. of polyvinylidene fluoride (PVDF) and various amounts of acetylene black (4 N, from Strem Chemicals) as electronic binder, in suspension in cyclopentanone. The resulting mixture was then deposited on a stainless steel disk and then dried under vacuum at 80°C. For basic studies, mainly performed with potentio-dynamic methods, we used 45% wt. acetylene black in order to insure complete electronic connection of every grain of the active material, whereas 25% wt. only was used for studies undertaken in galvano-static mode in order to check the cycling behavior of the material in conditions close to practical ones.

X-Ray diffraction studies (λ_{Cu} = 1.5418 Å) of the intercalated material were performed at different levels of the first electrochemical cycle and for clarity the range in 2Θ was limited to 30°. Reduction was performed down to a given potential and then the potential was maintained until the reduction current was close to zero, which gives well equilibrated samples. Owing to the moisture sensitivity of the lithiated compounds, X-ray patterns were recorded from samples taken from the cells and placed in an airtight sample holder closed with a Kapton® window.

Infrared spectra of pristine and chemically lithiated β-$VOSO_4$, as mulls in Nujol, were recorded on a Perkin–Elmer 983 spectrometer with a CsI window.

3. Results and discussion

3.1. Structure of β-$VOSO_4$

β-$VOSO_4$ is orthorhombic, space group Pnma [9]. This form presents an open three-dimensional network with interconnected channels where the alkali cations can easily migrate (Fig. 1).

Along the *a* axis, distorted vanadium oxygen octahedra are connected by opposite corners to form chains. These polyhedra are pairwise twisted along the *b* axis, with alternating angles of 50.95° and 125.98°, and connected by SO_4 tetrahedra via corner sharing. Each sulphate group is linked to two other chains of VO_6 octahedra.

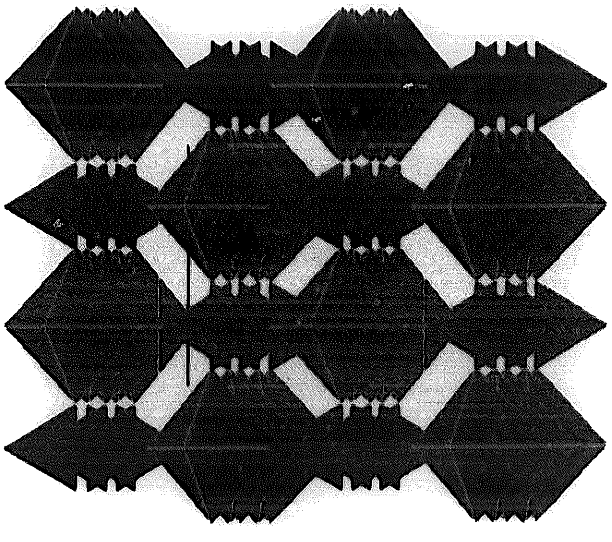

Fig. 1. Structure of β-$VOSO_4$, along (100) plane

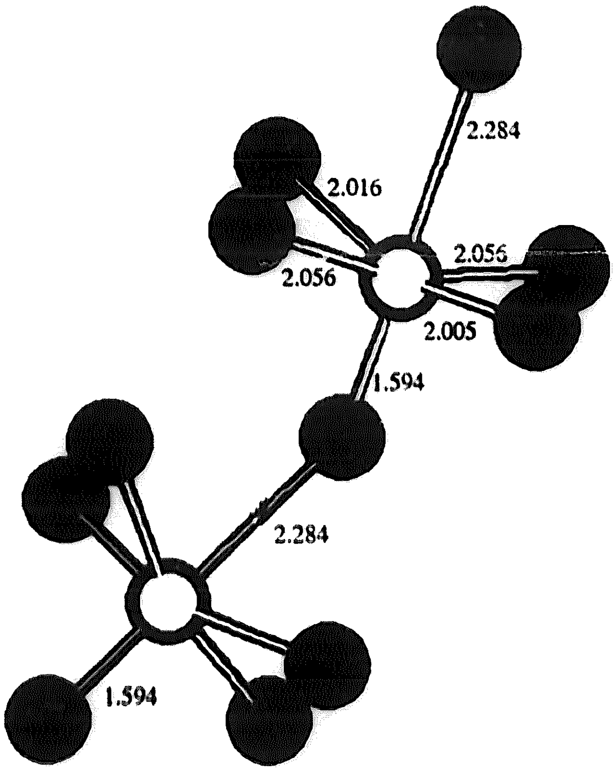

Fig. 2. VO_6 polyhedra in β-$VOSO_4$ (distances are given in Å).

As shown in Fig. 2, these VO_6 octahedra appear strongly distorted along the chain direction. Vanadium ion is displaced from the center of the octahedron, leading to a short Vanadyl bond. This is supported by IR spectroscopy [10] and was confirmed in a Raman study we undertook.

The IR spectrum of our β-$VOSO_4$ shows the vibration band characteristic of a VO^{2+} structural unit at 945 cm^{-1} (Fig. 3A). This vibration is found to be at 925 cm^{-1} in the Raman spectra. The slight shift between IR and Raman line position confirms the presence of a center of symmetry in the unit cell.

3.2. Electrochemical intercalation studies

Fig. 4 shows a typical incremental capacity curve, ΔQ(V), obtained for the first cycles from a stepwise potentio-dynamic cycling with ± 10 mV steps every 3 h within a 2.4–3.1 V potential window.

It appears that the redox process occurs in two steps, denoted 'A' and 'B'. Although upon first reduction the two steps are not well resolved, the A incremental capacity peak is characteristic of a biphasic process (narrower than the Nernst broadening). The intercept of its initial slope with the x axis which appears at 2.77 V on the first reduction and then tends towards 2.80 V on further cycles corresponds to potential characteristic of the equilibrium two-phase potential plateaus in a coulometric titration curve.

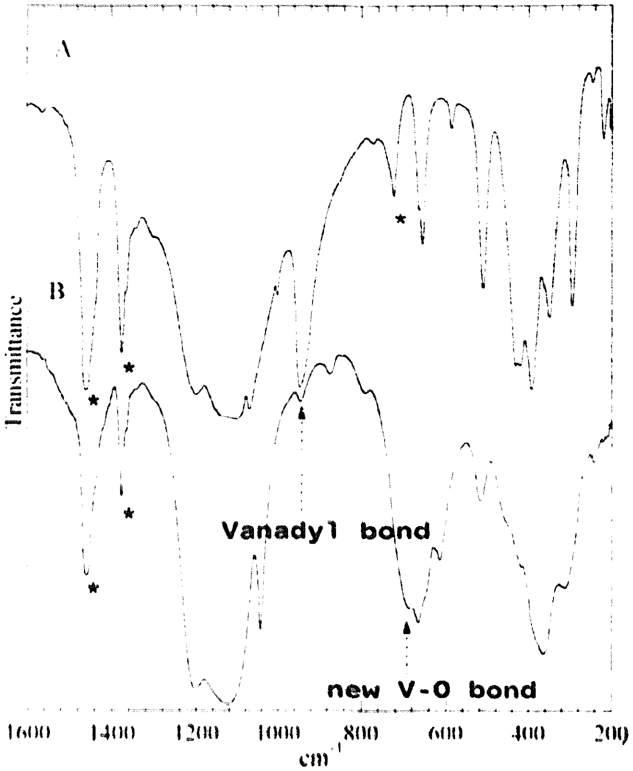

Fig. 3. IR spectra of β-$VOSO_4$ (A) and Li_xVOSO_4 (B) (* for Nujol bands).

Accordingly a two-phase step is observed on oxidation with a characteristic potential of 2.84 V (A' peak).

B reduction peaks are associated to the broad B' oxidation step centred at 2.62 V These broad and almost unshifted redox peaks correspond to a monophasic redox process.

Thus lithium intercalation-deintercalation occurs in

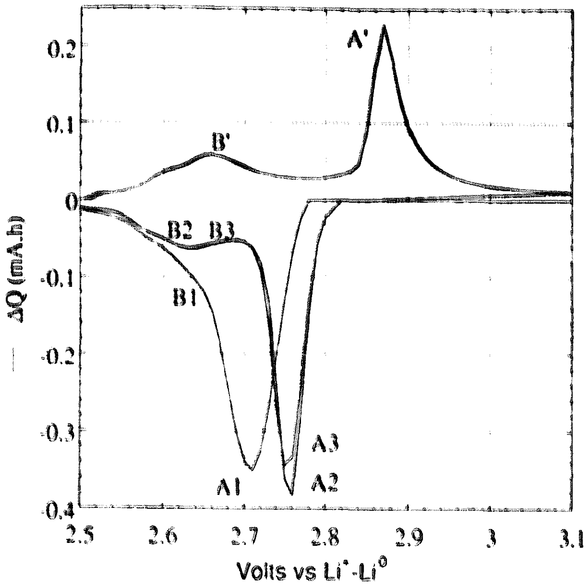

Fig. 4. Voltammogram of incremental capacity obtained from potentiodynamic cycling of Li_xVOSO_4 vs. Li with ± 10 mV/3 h steps.

two steps: first with a two-phase process with some hysteresis and then in a single phase, solid solution domain. Hysteresis of the phase transformation (A–A′ shift) decreases on the second cycle but stabilizes at 40 mV. The process appears reversible apart from some loss of capacity in the A step between the first and second reduction (decrease of its surface). The fact that the A2–A3 peaks are thinner than the A1 peak indicates that the system reacts with a faster kinetics toward lithium intercalation after the first cycle.

Fig. 5 shows the cycling behavior of this system from a galvano-static study at a rate of C/20 (current corresponding to flowing the nominal capacity in 20 h) in the 2.2–3.7 V potential limits. The two steps of the lithium intercalation appear here as a voltage plateau for the two-phase A step and then, for the B step, as a continuous decrease of the potential with the intercalated amount of lithium.

With 90% total efficiency on first reduction, a very good reversibility of the lithium intercalation–deintercalation process is clearly observed after the first cycle, but involving 0.55 Li/formula unit only (i.e. a reversible capacity of 90 mAh g^{-1}).

The decrease of the hysteresis upon cycling is also observed in this galvano-static experiment, with an increase of the voltage plateau from 2.74 to 2.78 V.

The cycling behavior of this system has also been recorded at higher rates: C/2 and C/10 in reduction with same C/10 oxidation rate. The capacity recovered on discharge is reported against the number of cycles in Fig. 6. One can assume that the electrochemical behavior is strongly kinetically dependent: in fact the capacity increases from 74 mAh g^{-1} to 84 mAh g^{-1} when slowing the reduction current to a C/10 regime.

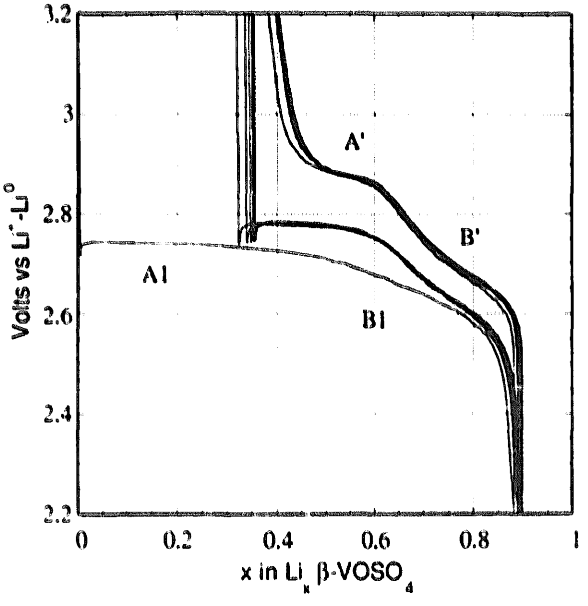

Fig. 5. Potential composition curve for β-VOSO$_4$-Li obtained from galvanostatic cycling at a nominal C/20 regime.

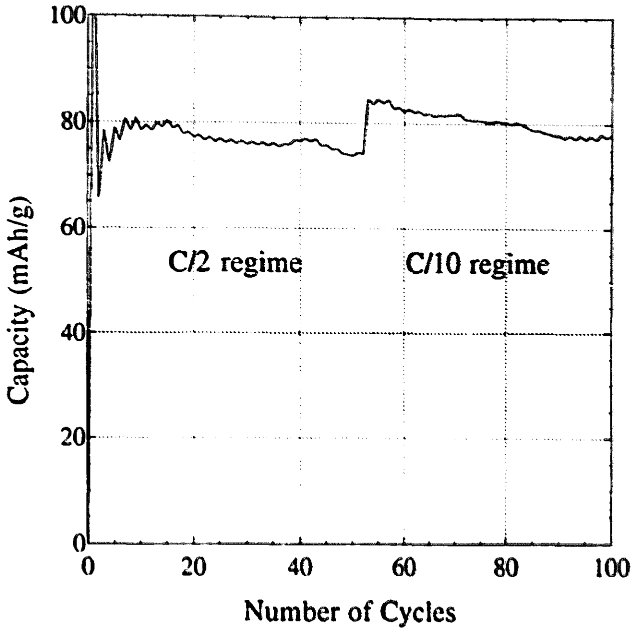

Fig. 6. Cycling behavior of the Li/β-VOSO$_4$ system at successive reduction regime: C/2 and C/10, with a constant C/10 oxydation regime.

3.3. Structural characterization of the intercalated compounds

In order to determine the structural evolution of β-VOSO$_4$ on lithium intercalation, XRD studies were performed at several redox levels after potentio-static equilibration: at 2.74 V for completion of the first reduction step, 2.40 V for complete first reduction and 3.2 V for complete reoxidation. Corresponding patterns are reported in Fig. 7.

New lines associated to the second phase, ΦII, created in the first reduction step clearly appear on diffractogram *b* at 18.3° and 24.1°, whereas lines at 19°, 25.2° and 28.5° almost completely disappear. Further lithium intercalation then leads to the pattern *c*, similar to *b* with a small shift of lines towards low angle only. This confirms that the second B step of the lithium intercalation, down to 2.4 V, occurs in a single-phase solid-solution process, with some expansion of the ΦII lattice parameters only. Finally, on recharge to 3.2 V (after step A′), β-VOSO$_4$ is almost fully restored: diffractogram *d* shows phases I and II pointing out that lithium deintercalation process is not finished. Moreover the observed broadening of the lines probably reflects an amorphization of phase I which could be at the origin of the increased kinetics on the next cycles.

In order to characterize the new intercalated phase, IR and Raman spectra were taken of a chemically

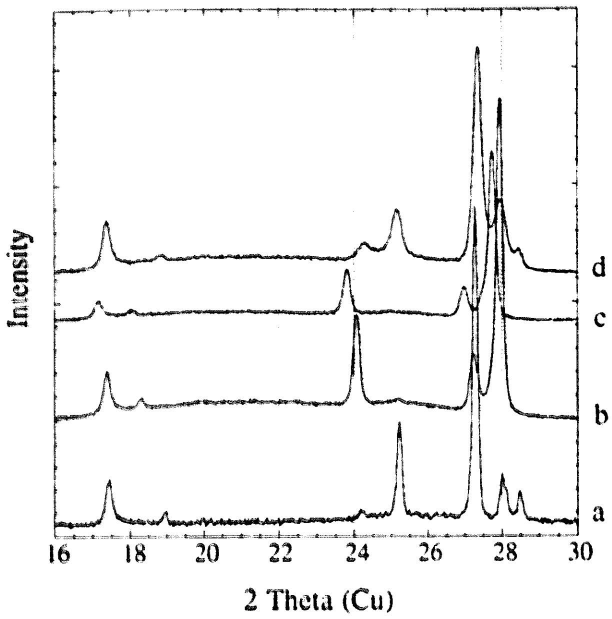

Fig. 7. X-ray diffraction patterns of $VOSO_4$ and Li_xVOSO_4 obtained from electrochemical intercalation. (a) Pristine β-$VOSO_4$; (b) after reduction step A1, and equilibration at 2.74 V; (c) after reduction step B1, and equilibration at 2.40 V; (d) after first oxidation step A′ and equilibration at 3.2 V.

lithiated Li_xVOSO_4 instead of an electrochemically prepared sample for experimental reasons (Fig. 3B). The as obtained product was found by XRD to be isostructural with electrochemically intercalated compounds. The x value was determined by coulometric titrations at approx. $x = 0.9$. Only a slight vibration band is observed in the vanadyl region corresponding to less than 2% of remaining VO^{2+} unit whereas a new one attributed to a V-O bond of 2.0 ± 0.1 Å is found at 690 cm^{-1}. The corresponding band is found at 494 cm^{-1} in the Raman spectra of Li_xVOSO_4. These two values are close to the one found in the -O-V-O-V-O- chains of the $V_2O_7^{3-}$ structural unit. In this condition, during the phase transformation, the vanadyl unit stretches out, reflecting the lithium intercalation process.

Intercalation of lithium in β-$VOSO_4$ leads to the reduction of V^{4+} to V^{3+}. The characteristic equilibrium potential is found to be 2.84 V (initial potential of the A′ oxidation peak). Trying to map the energy position of the V^{4+}/V^{3+} redox couple vs. the nature of the anionic environment, this value nevertheless cannot be compared to what it could be in a sulphate as this V^{4+}/V^{3+} couple has never been observed in such materials. But it was shown recently [11] that the V^{3+}/V^{2+} redox couple in $V_2(SO_4)_3$ lies at 2.50 V and the authors established the separation between V^{4+}/V^{3+} and V^{3+}/V^{2+} redox couples to be 2.0 V.

As a result, compared to sulphate materials the energy of the V^{4+}/V^{3+} couple in β-$VOSO_4$ is higher. This may be related to the short vanadyl bond involved in this structure which is strongly covalent.

Otherwise, sulphate counter cations weaken the V-O bonds belonging to the (100) plane and then raise the potential of the V^{4+}/V^{3+} couple in comparison to what it is in oxides. In this manner the V^{4+}/V^{3+} couple is close to 2.1 V in the $Li/Li_{2+x}V_2O_5$ system.

4. Conclusion

β-$VOSO_4$ was synthesized by a new route at lower temperature than by the usual one, and led to micronic particles. The electrochemical behavior of the as-obtained material vs. Li was investigated for the first time. Lithium intercalation occurs in two successive steps, firstly with a structural change, then in a solid-solution process. This is supported by XRD studies and the new phase, whose structure has not yet been determined, has been characterized by IR and Raman spectroscopies.

The β-$VOSO_4$-Li system presents quite a large irreversibility on the first cycle (involving approx. 0.4 $e^- V^{-1}$ in the first reduction step), but then shows a very good reversibility upon further cycling. Chemical bonding considerations lead to the conclusion that the use of covalent VO^{2+} structural unit is a good mean to place the redox couple energy of a given transition element in an octahedral coordination, between that observed in oxides and in $M_2(XO_4)_3$ (X = S, P, As) compounds.

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