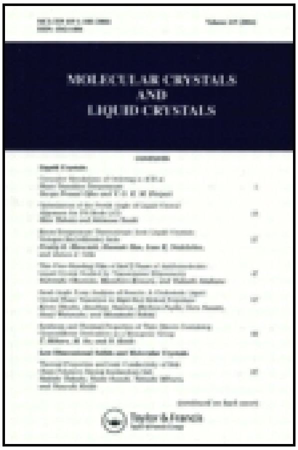

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Abstract The electrochemical behavior of the lithium / $V_2(SO_4)_3$ system has been studied with XRD observation of the intercalation/deintercalation induced structural changes. Experiments have been performed on the NASICON type rhombohedral form. The use of very slow staircase potentiodynamic cycling made able to show that the first reduction occurs in two steps very close in energy and that the system experiences an irreversible structural change if this reduction is driven to the second step, below 2.59V vs Li^0-Li^+. Then, after a specific first oxidation step at 2.8 V, the system can be cycled reversibly through two redox levels at 2.63 V and 2.59 V.

Keywords: $V_2(SO_4)_3$; lithium intercalation; potentiodynamic studies

INTRODUCTION

Rechargeable lithium batteries appear as the best power sources for future portable electronic devices since they possess high energy and power density. In this way extensive research have been undertaken since twenty years especially on oxide type materials [1].

Recently, an alternative to oxide compounds was investigated by Goodenough et al.[2,3]. It was shown that the family of materials with general formula $Li_xM_2(XO_4)_3$ (M = transition element; X = S, P, As) present very interesting electrochemical behaviors towards lithium intercalation-deintercalation. Moreover, these works demonstrated the influence of the ionicity of the chemical bonds between transition elements and oxygen anions. The more ionic these bonds the lower the corresponding redox couple energy and thus the higher the potential. A recent study [4], investigating the performances of $V_2(SO_4)_3$, brought to the fore that the V^{3+}/V^{2+} couple lies at 2.6 V vs Li^0/Li^+ in this compound. However, the electrochemical behavior of this system was investigated in a galvanostatic mode only and deserved to be more deeply characterized. Thus we put interest in both galvanostatic and potentiodynamic studies as well as in determining the structural evolution of $V_2(SO_4)_3$ during the lithium intercalation-deintercalation process.

EXPERIMENTAL

Rhombohedral $V_2(SO_4)_3$ can be prepared by digesting V_2O_3 with refluxing sulphuric acid[4]. However the $V_2(SO_4)_3$ used in this study was obtained from the reduction of vanadium pentaoxide with sulphur in stoichiometric amount, in concentrated sulphuric acid at 160 °C for 8 hours[5]. The resulting yellow powder is then washed with water and dried under vacuum at 160 °C overnight. It was controlled by X-ray diffraction to be the rhombohedral form (JCPDS card No 42-0231). $Li_2V_2(SO_4)_3$ have been obtained by chemically lithiation of $V_2(SO_4)_3$ using an excess of n-butyllithium.

Electrochemical intercalation studies were performed in a very slow stepwise potentiodynamic mode mainly, using a MacPile-II system (Bio-Logic, Claix, France). In this mode the potential scan usually was ±10mV per few hours and, for time saving, with possible curtailing of the potential level duration once the redox current is lower than a preset value (here given in equivalent galvanostatic regime). Measurements were performed on Swagelok type cells[6], with Li metal as the negative electrode and 1M $LiClO_4$ in anhydrous propylene carbonate as the electrolyte. Composite positive electrodes were made of 5 %w polyvinylidene fluoride (PVDF) and various amounts (25 or 45 %w) of acetylene black (4N, from Strem Chemicals) as electronic binder, put in suspension in cyclopentanone. The mixture was deposited on a stainless steel disk and then dried under vacuum at 80 °C.

X-ray diffraction studies of the intercalated material were performed at different levels of the first electrochemical cycle :reduction or oxidation were performed up to a given potential and then the potential was maintained until the current was close to zero, which corresponds to a quite well equilibrated sample. Owing to the moisture sensitivity of the lithiated compounds, X-ray patterns were recorded on samples taken from the cells and placed in an airtight holder closed with a Kapton window.

RESULTS AND DISCUSSION

Structure of $V_2(SO_4)_3$

$V_2(SO_4)_3$ crystallizes either in rhombohedral (R-3) or monoclinic ($P2_1/c$) structural types, isostructural with $Fe_2(SO_4)_3$[7]. However the monoclinic form could not be obtained pure and was always mixed with the rhombohedral one. In the rhombohedral form the two different VO_6 octahedra are connected via corner sharing to six SO_4 tetrahedra which share themselves each of their vertices with a VO_6 unit. This ordering of polyhedra leads to a three dimensional network with interconnected channels where lithium can migrate. Three different crystallographic sites, M1', M1" (six fold coordinated) and the larger M2 sites (height fold coordinated), are present in this structure, allowing the intercalation of up to 4 alkali cations per formula unit, from a steric point of view. The two M1' and M1" sites, almost energetically equivalent, account for 1/4 of the available sites. In the case of the isostructural Nasicon type phosphate with general formula $A_xM_2(PO_4)_3$, recent studies [8,9] showed that for A = Li and x = 1, the lithium cations reside in the M1 sites. In fact, the small size and hence the rather polarizing character of Li^+, make it more stable in M1 sites which are smaller than M2 sites. Moreover the M1' and M1" sites can be filled without any lithium in nearest neighbour position whereas lithium in M2 sites could have 2 of them in M1' or M1" separated by distances close to 3.2 Å.

Electrochemical studies

In figure 1 is shown a typical voltammogram, obtained for the first three cycles from a stepwise potentiodynamic cycling within a 3.6V to 2.0 V window (for clarity of the figure the potential window was limited to 3.0 V - 2.4 V). It appears that the reduction/intercalation occurs in two steps, denoted "A" and "B" whatever the cycle, whereas the oxidation/deintercalation is basically different on the first cycle from what it is on the following ones : upon first oxidation a single large peak is observed from 2.8V (C'1), which is drastically smaller upon second oxidation (C'2) at the benefit of a new oxidation step beginning close to 2.6 V. As we will show later on, this new step is in fact composed of two peaks B'and A', to be associated to the B and A reduction peaks respectively, the A' peak appearing as a shoulder on the high side of B'.

The A and B peaks, narrower than that of a Nernstian process, are characteristic of two-phase processes [10,11] with equilibrium potential given by the potential at which they initiate, close to 2.64 and 2.59V respectively. This is clearly seen on the shapes of the chronoamperometric responses reported on Fig.2 (left) for the A1 and B1 steps : the reduction current increases slightly when stepping from 2.64 to 2.63 V and very significantly at the next step to 2.62 V, whereas the time dependance of the current during these potential levels departs from a diffusion controlled process (Fick's law). This is the signature of crossing the characteristic potential of a two-phase equilibrium just above 2.63 V, the kinetics of the redox process beeing governed by that of the phase transformation[10]. In the same way the B reduction peak also has the shape of a phase transformation driven process, with a characteristic equilibrium potential close to 2.595 V. Surprisingly the first oxidation step occurs at 2.8 V only, again with a shape characteristic of a two-phase process (label C').

On the second cycle, both A and B reduction steps appear smaller than on first reduction, but with the same relative amplitudes as to each other. Then on second oxidation a new step is observed, initiating at about 2.60V, whereas the previous C' step appears drasticaly smaller than on first cycle. On further cycling this C' step tends to disappear in the same time as the oxidation peak beginning at 2.60 V narrows with appearance of a shoulder on its high potential side around 2.65 V. This led us to associate that oxidation step to the B reduction one and the shoulder to the A step. This was confirmed by cycling a cell with limitation of the reduction potential to 2.60 V, as reported on Fig. 2 (right). After completion of the reduction at this level the cell was set in open circuit relaxation for 10 hours before going on an oxidation sweep. Within that time the potential went close to 2.63 V with a large oxidation current immediately at the oxidizing 2.64 V level. This agrees with an equilibrium potential very close to 2.63 V. Thus the shoulder observed on the B' peak in the voltammogram is to be associated to the A reduction step. Moreover the only oxidation step then is that at 2.64 V, associated to the A1 reduction; there is no C' oxidation step at 2.8 V. This 2.8 V oxidation step is observed only one time, once a reduction has been driven down to the B level, below 2.60 V.

It should be noticed that the A step could not be isolated and characterized in galvanostatic experiment : we observed 2.59 V as open circuit equilibrium potential in galvanostatic intermittent experiments performed at C/20 regime. The A step is in fact so close to the B step, that unless the galvanostatic experiment is performed at very low regime with a potential limitation at 2.60 V, the B reduction step is always reached and it is its characteristic equilibrium potential which is measured.

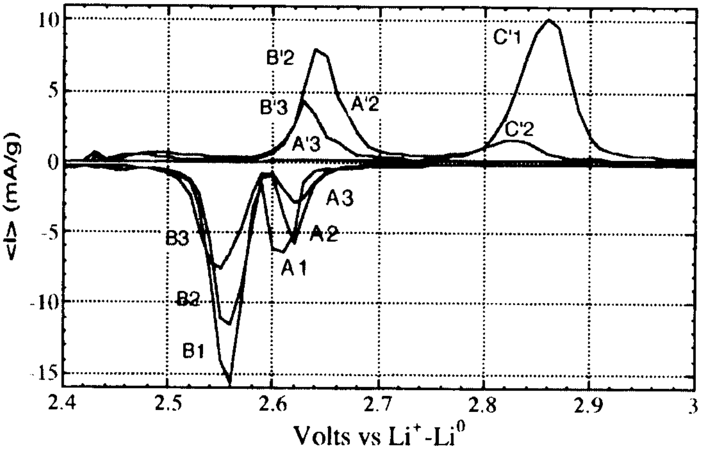

FIGURE 1 : Voltammogram obtained from potentiodynamic cycling of $V_2(SO_4)_3$ vs Li metal with ±10 mV / 1.5 h potential steps and curtailing condition of the potential level duration equivalent to a C/1000 regime. (See Color Plate I).

From the surface of the voltamogram peaks it appears that the first reduction involves 1.9 Li per formula unit for the A1 + B1 steps, which agrees with the reduction of the two vanadium from V^{3+} to V^{2+}.

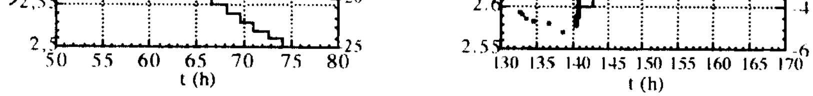

FIGURE 2. **Left** : chronoamperograms of the A1 and B1 reduction steps of fig.1, showing the specific behaviour of the current when crossing the two-phase equilibria at about 2.635 V and 2.595 V respectively. **Right** : chronoamperometric responses in a stepwise cycling (±20mV/2h, C/800 minimum regime) limited at 2.60 V on reduction, and with a 10h open circuit relaxation before oxidation (See Color Plate II).

Although this amount decreases upon cycling, the relative amplitude of the A to the A+B reduction steps is rather constant, equaling 0.25, 0.23 and 0.22 respectively from the first to the third reduction (theses results were found to be reproducible on several cells).

Structural characterization of the intercalated compounds.

In order to look at a relationship of the unusual electrochemical behavior with structural transformations upon cycling, XRD studies were performed at different levels of the redox process and cycling : after potentiostatic equilibration at 2.60 V then 2.50 V for completion of the two steps of the first reduction, and 3.0V then 2.50 V on further cycling (Fig. 3).

The first reduction step A1 leads to the pattern **b**, which appears similar to the **a** pattern of the pristine $V_2(SO_4)_3$ (we label the corresponding structure Φ_0). This absence of structural modification seems to contradict the nature of the A1 reduction step which is characterized by a well defined two phase equilibrium potential just above 2.63 V.

After completion of the B1 reduction step new lines (labeled * on the pattern **c**) are observed which unambiguously evidences the appearance of a new phase (denoted Φ_1) crystallographically different from the previous one. Lines of the initial phase Φ_0 still present in pattern **c**, **d** and **e**, evidence and agree with the fact that the cells used for XRD studies did not reached full efficiency (some grains of the material were electronically or/and ionically isolated and did not participate to the redox reactions), with only about 1 exchanged Li per formula unit instead of the expected 2. The XRD pattern of the chemically reduced sample for which the reaction was complete (pattern **c '**) confirmed the existence of this new Φ_1 phase.

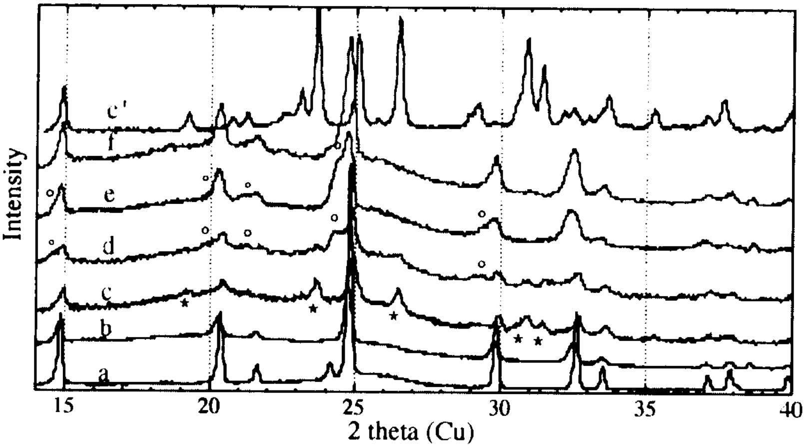

FIGURE 3. X-ray diffraction patterns of $V_2(SO_4)_3$ and $Li_xV_2(SO_4)_3$ obtained from electrochemical cycling with potentiostatic equilibration. **a**: pristine $V_2(SO_4)_3$; **b**: after step A1, and equilibration at 2.60 V; **c**, **d**, **e**: after completion of reduction steps B1, B2 and B3 respectively, with equilibration at 2.50 V; **f**: after the third oxidation and equilibration at 3.0 V; **c '**: chemically lithiated sample. (See Color Plate III).

Upon first oxidation at 3 V one recovers a pattern similar to the initial one, as will be after each forthcoming oxidation, with a small broadening of the lines only (pattern **f**), so $V_2(SO_4)_3$ seems to be fully restored. On the contrary the patterns obtained after completion of the second and third reductions down to 2.5 V (**d** and **e**, in fig. 3) are different from that obtained on first reduction. This means that the B2 reduction step leads to a phase Φ_2, different from the phase Φ_1 obtained upon complete first reduction. The new lines (^{o}) seem to correspond to that of the main lines of the pristine material with a small shift toward low angles only, suggesting that Φ_2 is crystallographically close to the starting $V_2(SO_4)_3$. In this condition, the C1' process occuring during the first cycle, could account for the oxidation of the phase Φ_1, whereas then after, the phase Φ_2 is oxidized at lower potential upon B' and A' processes (traces of Φ_1 remaining after completion of the second reduction are at the origin of the C2' process).

Thus after the first electrochemical cycling the system appears to be reversible through two redox levels which are very close in potential and both show a two-phase behavior, although only the second one apparently can be associated to a reversible structural change of the host. This behavior agrees with that of a "type II, pseudo two-phase compounds" according to the classification of intercalation compounds proposed by M. Armand[11].

CONCLUSION

The electrochemical behavior of the $Li/V_2(SO_4)_3$ system appears much more complex that can be inferred from previously published works, performed in galvanostatic mode only, from which it looked like a simple two-phase system[4]. The use of very slow stepwise potentiodynamic cycling, gave evidence for a specific behavior on the first cycle with reduction in two steps at 2.63 and 2.59 V, with 1 to 4 relative capacities,leading to the intercalation of 2 Li per formula unit and a single first oxidation/deintercalation step occuring at 2.8 V only. Then after the system cycles reversibly through the two steps observed on the first reduction, always with the 1 to 4 relative capacities. From XRD studies at various level of the reduction/oxidation cycles, it was shown that the first reduction and the forthcoming ones lead to different cristallographic phases, whereas the first step of the reduction seems not to be related to noticeable structural changes. Understanding the specific behavior of this system on the first cycle call for accurate structural studies which are planned using in-situ XRD with synchroton radiation source. Moreover expected neutron diffraction studies for different lithium compositions will help to investigate the way the site filling occurs.

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