

## $V_2O_4S$ – a new transition metal oxysulfide as positive for lithium batteries

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### Abstract

In an attempt to combine the advantages of both oxides and sulfides in their use as positives in lithium batteries, we are investigating the electrochemical performances of new transition metal oxysulfides. A new amorphous vanadium oxysulfide can be prepared by room temperature reaction between aqueous solutions of a vanadyl salt and sodium sulfide. Chemical analysis and thermogravimetric analysis (TGA) experiments are consistent with the formula  $V_2O_4S \cdot 2H_2O$  and show complete dehydration at 150 °C. Electrochemical tests have been performed on lithium button cells containing the dried vanadium oxysulfide as positive. The open-circuit voltage (OCV) curve shows a lower potential than for the parent  $V_2O_5$  compound but a low polarization is observed for the cell containing  $V_2O_4S$ . The cells can be cycled between 1.5 and 4.0 V with one lithium per vanadium atom, the mean voltage being 2.4 V, at regimes C/12 and C/24. This behaviour corresponds to a capacity of 270.9 A h/kg and an energy of 650 W h/kg. To date, 21 cycles have been performed with a capacity loss lower than 10%.

### Introduction

For more than twenty years, many low dimensional compounds have been tentatively used as intercalation positives in lithium batteries. This electrochemical application comes from their unique ability to reversibly intercalate Li. Besides graphite, various transition metal compounds have been considered for this purpose. They can be divided into two main groups, oxides and sulfides. Batteries built with sulfides generally have very good reversibility along with a rather low voltage [1]. On the contrary, oxides provide much higher cell voltages but have a lower reversibility [2]. This different behaviour can be related to the higher ionicity of the oxides as compared with the sulfides. In the frame of our research concerning new positives for Li batteries, transition metal oxysulfides have been considered in order to combine the above described characteristics of both groups. It immediately appeared that very few transition metal oxysulfides were known. Only zirconium [3] and hafnium [4] derivatives have been characterized, both of which have closed structures inappropriate for Li intercalation. Amorphous phases of molybdenum oxysulfides have been reported, and used as positives in Li batteries. These molybdenum oxysulfides,  $MoOS_2$  and  $MoO_2S$ , have been synthesized by thermal decomposition at 300 °C of ammonium oxythiomolybdates [5]. A titanium derivative has also been prepared as thin film by sputtering [6]. When utilized in Li

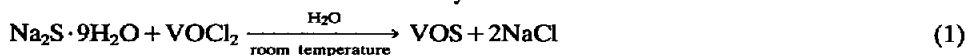
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batteries, these amorphous phases show promising characteristics both in voltage and cycling capabilities [6, 7], verifying the above hypotheses. Nevertheless, due to their amorphous character, little is known about their structure and there is no proof that they are actually single-phase oxysulfides with a mixed transition metal coordination of oxygen and sulfur ions and not simply a mixture, even at a microscopic level, of oxides and sulfides. In our laboratory, we are interested in investigating transition metal oxysulfides as positives for Li battery application. This paper presents the synthesis, characterization and electrochemical properties of a new vanadium oxysulfide,  $V_2O_4S$ .

### Synthesis and characterization

Because of the large electronegativity difference between oxygen and sulfur, soft chemistry techniques were used to obtain a mixed coordination of the transition metal atom. The new phase was prepared by reacting, at room temperature, hydrated sodium sulfide dissolved in water with a vanadyl salt. The envisioned reaction was:



A grey powder is immediately formed upon addition of  $VOCl_2$ . This suspension was stirred for 24 h, filtered and washed three times with large amounts of water. No sodium is detected in the obtained powder by flame spectroscopy analysis, showing that sodium chloride and unreacted sodium sulfide have been completely removed by washing. Powder X-ray diffraction shows that the product is completely amorphous. Energy dispersed X-ray analysis, in a scanning electron microscope, gives as V:S atomic ratio close to 2 and, in addition, indicates a good sample homogeneity. Complete chemical analysis shows the analysed weight fraction of 45.67%, 11.22% and 43.08% for vanadium, sulfur and oxygen, respectively. The sum of these weight fractions is very close to 100% indicating the absence of other elements in noticeable proportion, excepting a very light one as hydrogen. These values are to be compared with those calculated for the composition  $V_2O_6S$ , i.e., 44.23%, 13.92% and 41.76%, respectively. The high anionic:cationic atom ratio led to some uncertainty about the success of the reaction. The possible presence of the sulfate group  $SO_4^{2-}$  could not be ignored (sulfates are a common product observed in high-temperature reactions). However, infrared spectroscopy and sulfate analysis with barium chloride did not support the presence of  $SO_4^{2-}$  in the product. Infrared spectroscopy detects the presence of water in the phase, explaining the above mentioned high anion:cation ratio, the formula being more accurately written  $V_2O_{6-x}S \cdot xH_2O$ . TGA experiments were performed to confirm the above formula, determine the amount of water and study the thermal behaviour of the phase. The TGA curve is presented in Fig. 1 and two distinct weight losses are observed. The first weight loss at lower temperature corresponds to evolved  $H_2O$  and shows 2 equivalents of  $H_2O$  per  $V_2O_6S$ , hence a formula  $V_2O_4S \cdot 2H_2O$ . The second weight loss corresponds to decomposition of  $V_2O_4S$  to the oxide  $VO_2$  with concurrent sulfur loss. The weight loss in this region is consistent with V:S ratio of 2.

The  $V_2O_4S$  formulation for the new phase suggests a direct relation with  $V_2O_5$ , by substituting one oxygen atom by a sulfur one. Nevertheless, it is surprising that the synthesis reaction would involve a redox process allowing the oxidation of vanadium from its pristine oxidation state (IV) in the vanadyl salt to the oxidation state (V) encountered in  $V_2O_5$ . Preliminary physical characterizations are more in favour of a

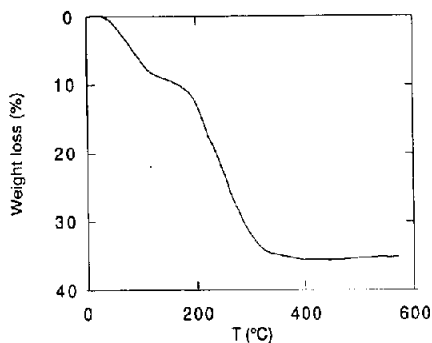


Fig. 1. Thermogravimetric analysis (TGA) for the obtained phase,  $V_2O_4S \cdot 2H_2O$  under argon flow. The heating rate is  $2^\circ C/min$ . The first weight loss ( $T < 150^\circ C$ ) corresponds to evolved  $H_2O$ . The second weight loss corresponds to sulfur loss and decomposition of  $V_2O_4S$  to  $VO_2$ .

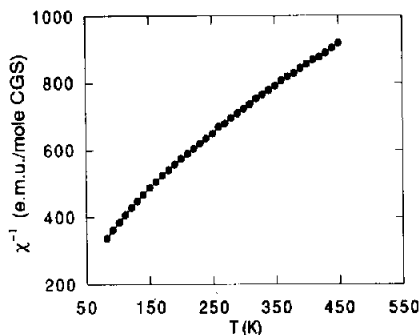


Fig. 2. Inverse molar magnetic susceptibility variations vs. temperature. The curvature can be interpreted as the sum of a temperature-independent paramagnetism and a Curie-Weiss temperature-dependent paramagnetism from which a  $1.53 \mu B$  magnetic moment can be calculated.

vanadium (IV) in the new phase. If vanadium were in the (V) oxidation state, diamagnetic or temperature independent paramagnetism would be observed. Electron paramagnetic resonance (EPR) experiments show a broad and intense paramagnetic signal attributable to a vanadium (IV). Magnetic susceptibility measurements (Fig. 2) can be interpreted as the sum of a temperature-independent paramagnetism ( $X_{TIP}$ ) and a Curie-Weiss paramagnetism. From these data an experimental magnetic moment of  $1.53 \mu B$  can be deduced ( $X_{TIP} = 457 \times 10^{-3} \text{ emu/mol cgs}$ ), in a good agreement with the theoretical value of  $1.73 \mu B$  calculated for a vanadium (IV).

### Electrochemical properties

Electrochemical tests have been performed with button cells on anhydrous  $V_2O_4S$  and with the automated battery test system Autebat. The positive is a polytetrafluoroethylene (PTFE)-bonded electrode containing 7.5 wt.% of graphite 7.5 wt.% of carbon black and 5 wt.% of PTFE, the electrolyte being a 1 M solution of  $LiClO_4$  in propylene carbonate (PC). The positive electrode is dried under vacuum at  $150^\circ C$  for 24 h, before introducing it into the cell. Figure 3 compares OCV curves obtained for the new phase and the well-known  $V_2O_5$ . Due to the lower vanadium oxidation state and the partial sulfurization of the vanadium environment, the observed equilibrium potential is lower for  $V_2O_4S$  than for  $V_2O_5$ . It is interesting to note that the OCV curve for the new phase is smooth, without important breaks, up to the composition  $Li_2V_2O_4S$ , the voltage being constantly maintained above 2 V. For the current density of  $50 \mu A/cm^2$ , the cell polarization remains lower than 150 mV for the entire composition range.

Cycling capabilities have been tested with various current densities between  $50 \mu A$  and  $1 \text{ mA/cm}^2$ . Thus far, approximately 40 cycles have been performed at  $1 \text{ mA/cm}^2$  between 1.5 and 4.0 V, corresponding to a cycling rate of C/12. Identical results obtained with a current density of  $500 \mu A/cm^2$  are presented in Fig. 4 showing cycling for about one Li per vanadium, with a slight displacement to low Li content

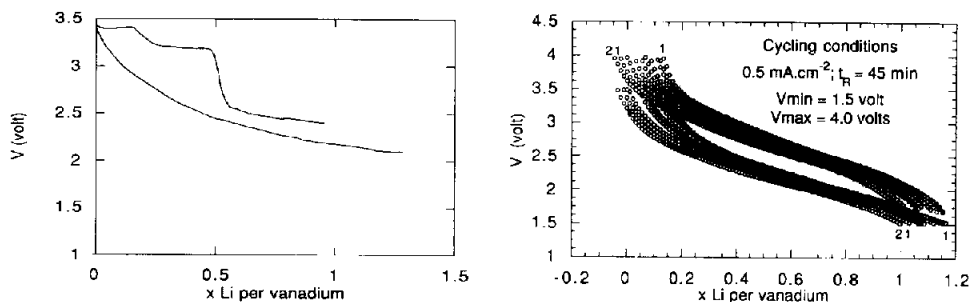


Fig. 3. Compared open-circuit voltage (OCV) curves for  $V_2O_5$  (upper) and  $V_2O_4S$  (lower). Experiments have been done with button cells under a discharge current of  $50 \mu A$ ; the relaxation time was four times the discharge time.

Fig. 4. Cycling curves of lithium button cells whose positive is made of a PTFE-bonded  $V_2O_4S$ .

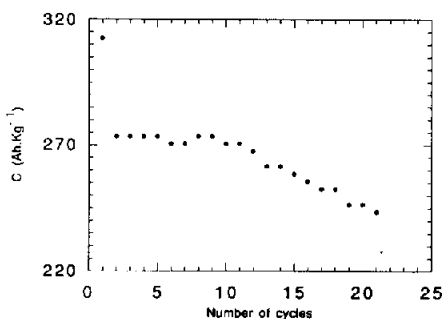


Fig. 5. Variation of the capacity of the lithium button cells whose positive is made of a PTFE-bonded  $V_2O_4S$ , during cycling. The capacity loss is 8% after 21 cycles.

during cycling. The mean voltage is 2.4 V and, for 1 F per vanadium atom, a capacity of 270.9 A h/kg and an energy of 650 W h/kg are calculated, considering only the positive weight. The capacity is not largely affected by cycling, and a loss of only 8% is observed for the first 21 cycles (Fig. 5).

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