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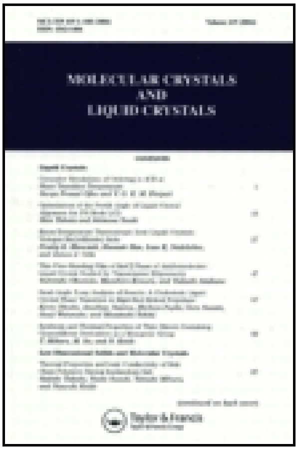

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Addition of a surfactant to increase the porosity of V_2O_5 xerogels used in lithium batteries

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Addition of a surfactant to increase the porosity of V_2O_5 xerogels used in lithium batteries

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Abstract : Addition of a surface active agent during hydrolysis of vanadium alkoxide allows to slow the gelification rate and to control the viscosity of the gel. Furthermore, after the surfactant elimination, the porosity of V_2O_5 greatly increases. Consequently, the electrochemical specific capacity and the specific energy increase. Lithium is intercaled into V_2O_5 films up to a stoichiometry of 2.5 moles Li per mole V_2O_5 ($3.5 < V$ vs $Li < 1.9$). Diffusivity coefficient of layers containing surfactant is hundred times higher than in classical V_2O_5 xerogel.

INTRODUCTION

Sol-gel method is now a common way for preparing inorganic network materials via hydrolysis and condensation reactions [1,2]. Using this method, V_2O_5 gels can be prepared by hydrolysing a vanadium alkoxide [3]. The ease of this synthesis and of processing to deposit thin layers are attractive properties. Due to the high electrophilic power of vanadium, vanadium alkoxides are very reactive towards hydrolysis and the solidification of the gel is very fast [4].

V_2O_5 xerogels are layered hosts for intercalation of lithium [5]. But they have a very low specific surface area and consequently have a low specific capacity (only 1.5 Li/ mol V_2O_5 can be intercaled).

In order to improve these two characteristics (control of viscosity and porosity), a surfactant was added to the sol without the presence of an oil phase. Porous materials are attractive because of the small distances of diffusion in the solid. The short diffusion distances allow a more rapid electrochemical insertion of ions to take place. In V_2O_5 xerogels prepared without surfactant, the specific surface areas

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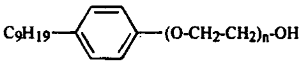
are no more than a few squares meters per gram. This limits the intercalation rate and the electrochemical properties.

In this study, V_2O_5 xerogel thin films with higher porous volumes were obtained by adding non-ionic surfactants to sol. We present in this paper, the consequences of this addition on the gel structure and on the electrochemical properties of V_2O_5 xerogels.

EXPERIMENTAL

Vanadium pentaoxide gel were prepared by hydrolysis of the vanadium alkoxide with an excess of water [6]. A non-ionic surfactant was added to the sol :



EON n

The mixture was then vigorously stirred until the required viscosity was reached. The gel structure was studied by Wide Angle X-Ray Scattering and Small Angle X-Ray Scattering.

The gel was deposited as a thin layer by dip-coating on a gold sheet. After a heat treatment at 275°C, characterisation of the surface was performed by Scanning Electron Microscopy, BET and mercury porosimetry. The final composition of the films determined by TGA was $V_2O_5 . 0.1H_2O$.

Three-electrode cells were used for electrochemical study and impedance spectroscopy. Cells were assembled in a dry box. The working electrode consisted of the thin layer V_2O_5 (2 μm) deposited on a gold sheet. Lithium was used as the reference and counter electrodes. A 1M $LiClO_4$ in PC was used as the electrolyte.

Impedance measurements were performed in the 1 MHz- 1 mHz range.

RESULTS AND DISCUSSION

The surface active agent interacts with the sol to slow the gelification process, it increases the V_2O_5 gelification time by a factor greater than 5.

WAXS studies indicated that the addition of EON2 did not modify the core structure of $V_2O_5 . 1.6H_2O$ xerogels. Surfactant affects predominantly long range interaction. Gels are assumed to be constituted by lamellar stacking of V_2O_5 ribbons. SAXS studies showed that in V_2O_5 gels, the stacking distance, d, was about 250 Å. The addition of a surfactant led to the increase of this distance; d reached 350 Å when a molar ratio EON2/alkoxide = 0.5 was added to the sol. The presence of the surfactant in the gel induces an important swelling of the structure. As a result, the xerogel is more amorphous than usual ones. The crystalline

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disorder allows the material to freely expand and compress with insertion or extraction of lithium in its structure.

The BET and porosity measurements revealed a high surface area of the xerogel containing EON2 in comparison to classical xerogel. When 25% of EON2 was added, the porous volume of the heat treated material was about 50%. Without surfactant, the specific surface area of xerogel was equal to 1 m^2/g meaning a negligible porosity of these materials. Figure 1 shows SEM micrographs of V_2O_5 xerogel thin layers with and without surfactant after a heat treatment at 290°C.

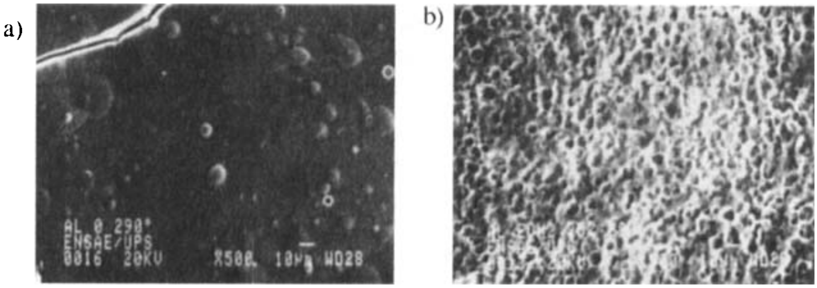

Figure 1 : SEM micrographs of V_2O_5 thin layers heat treated at 290°C, a-obtained with a gel prepared without surfactant, b-obtained with a gel prepared with 25% molar of EON2

The surface of xerogels made with EON2 presents large pores homogeneously distributed while the surface of classical V_2O_5 xerogel does not present any porosity or roughness. The mercury porosimetry measurements indicated that the size of pores is homogeneous and close to 0.1 μm (with molecular percentage of EON2 equal to 25). The pore size is a function of the quantity of surfactant added, and it increases with increasing quantity of EON2. The porosity of the xerogel was found to be limited by an incomplete departure of surfactant. TGA measurements showed that EON begins to leave at 250°C but it is totally eliminated at 400°C.

Studies of lithium intercalation in the two types of xerogels (prepared with and without EON) :

$$V_2O_5.\ 0.1H_2O + x\ Li^+ + x\ e^- \longrightarrow Li_xV_2O_5.0.1H_2O$$

were undertaken by analysis of the discharge phenomenon with current value of 5μA and Open Circuit Voltage measurements.

Figure 2 shows the voltage vs composition curves (at 18°C) for xerogels V_2O_5. $0.1H_2O$ with and without surfactant. Almost 2.8 lithium were inserted per V_2O_5 for gel prepared with addition of surfactant (25% molar) while 1.5 lithium were

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inserted for normal V_2O_5. However the values of x obtained for normal gels are smaller than those given in literature [7] : x = 1.8 for E = 2V. The difference is certainly due to our apparatus which is not really adapted for OCV experiments. But results clearly indicate that porous xerogels are better host materials than classical ones.

The stoichiometry of the insertion reaction and the composition of the intercaled materials lead to a specific capacity of 208 A.h/kg for the V_2O_5. $0.1H_2O$ xerogels prepared without surfactant and 398 A.h/kg for V_2O_5. $0.1H_2O$ xerogels made with 25 molar percents of EON2. The areas below the voltage-composition curves give the specific energies for the materials prepared with and without surfactant. At 1.9 V vs Li the experimental specific energies were 665 W.h/kg for materials with surfactant and 620 W.h/kg for xerogels without surfactant.

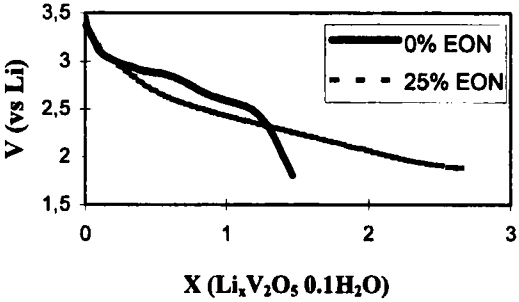

Figure 2 : Potential vs lithium composition (at 18°C) for V_2O_5. $0.1H_2O$ xerogels prepared with and without EON2.

Cyclic voltammogram of both materials (m = 1.5mg) were found to be almost identical : they present two cathodic waves at 2.9 and 2.5 V and two anodic waves at 2.7 and 3.0 V.

Impedance measurements were performed on the three electrode cell. Nyquist plots of the impedance behaviour of a xerogel prepared with 10% molar of EON2 are reported on figure 3. Part II and III of the diagram are related to the diffusion of lithium cations into the material. The straight line with a 45° angle on the real-axis corresponds to the Warburg impedance (semi-infinite diffusion). At lower frequencies, the straight line with a higher slope corresponds to a finite length diffusion process [8].

More accurate values of the chemical lithium diffusion coefficient can be obtained from the semi-infinite diffusion part. Results shown in figure 4 are deduced from this domain.

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The D_{Li} values are similar for both materials for lithium content higher than 0.15. For lower x values , D_{Li} is two orders of magnitude higher in xerogels made with surfactant.

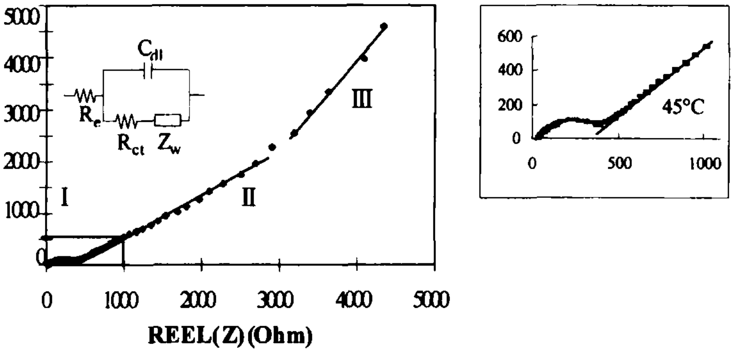

Figure 3 : Experimental impedance diagram of $Li_xV_2O_5$ 0.1H_2O in propylene carbonate-$LiClO_4$ 1M at 20°C for a lithium intercalation ratio of x = 0.25.

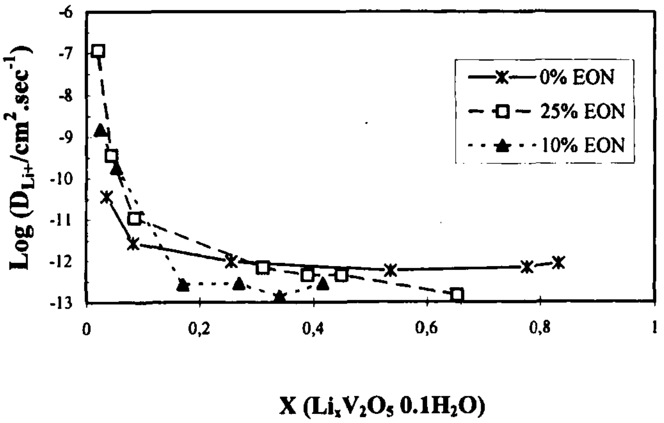

Figure 4 : Chemical diffusion coefficient (D_{Li}^+) in $Li_xV_2O_5$. 0.1H_2O as a function of x for xerogels prepared with various molar percentage of EON2.

The decrease of D_{Li} when the lithium content increases is due to the decrease of number of vacant sites [7]. Diffusion coefficient values deduced from the last part of the plot vary as those found by the other method.

CONCLUSION

Addition of a surface active agent to V_2O_5 sols makes the gel viscosity control easier. Surfactant also affects the structure in xerogels by inducing the swelling of the structure. After a heat treatment, dry materials containing surfactant present a microporosity which can be controlled by the quantity of surfactant added in the sol.

Capacity of these microporous materials is better than capacity in classical V_2O_5 xerogels. About 1 more lithium is inserted in xerogels prepared with EON2. But comparing our results with those obtained elsewhere [9], the quantity of inserted lithium is lower (2.5 instead of 4, between 3.8V and 1.9V). One reason of such difference can be due to the fact that experiments were not performed in the same conditions. For small lithium contents, the chemical diffusivity of obtained porous materials is more than a hundred time higher than in non-porous ones. Reversibility studies about materials described here should be done later.

Electrochemical properties of these porous xerogels could be improved if all the surfactant could be eliminated after heat treatment. So we are looking for a surfactant which can be more easily eliminated.

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