Spin-Coated V_2O_5 Xerogel Thin Films. 1. Microstructure and Morphology

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Vanadium pentoxide xerogel films spin-coated on nickel/silicon substrates have shown high electrochemical performance. In fact, more than 3 equiv of lithium V_2O_5 unit can be reversibly inserted between 3.5 and 1.6 V in aprotic electrolytes. The high insertion capacity coupled with the inexpensive and well-known preparation procedure make the material interesting for thin-film lithium battery and electrochromic device applications. In the present paper we report the characterization of such thin films based on X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), quartz crystal microbalance, optical, and electronic conductivity measurements. The spin-coated films are highly amorphous, with a small amount of ribbon stacking that is randomly oriented. The disorder is caused by the joint effect of high shear and rapid drying during spin coating.

Introduction

Thin films used for specific functions have become increasingly more widespread in the past few decades. Film deposition techniques are diverse and range from high-energy, physical deposition methods to low-energy methods that are more common. The high-energy techniques include evaporation, sputtering, and ion beam methods that have been developed for microelectronics and data storage applications, for example. The low-energy methods include dip coating, brush coating, multilayer roll coating, spray coating, screen printing, and spin coating. These latter techniques are used to apply protective or decorative films or to form tailored films of materials that cannot survive the high-energy conditions used in the former deposition methods. Recent interest in ceramic films derived from sol–gel processing has led to the adoption of the low-energy methods for film formation, with subsequent processing at high temperatures, for example, to yield materials with enhanced properties.

Electrochemically functional films (electroactive films) are used for devices such as batteries, fuel cells, electrochromic displays, catalysts, and sensors. The techniques that have been used to form the electroactive films usually influence their appearance, behavior, and performance, and the methods used to form them include all of those listed above. With the development of sol–gel processing for ceramic films, it has become clear that the same approach could prove beneficial for electroactive films as well, especially intercalation hosts based on oxides. Livage and colleagues have pioneered much of the work for sol–gel synthesis of intercalation hosts, and that work has been summarized for V_2O_5 in a recent review.[2] Other chemical systems are also cited in that review. Much of the previous work on sol–gel derived electroactive films has been focused on materials formed by slow evaporation of the solvent from the hydrogel precursor, e.g., dip coating. As we will show below, the properties of V_2O_5 films are altered by changing the evaporation rate and shear during deposition. Spin coated films have superior electrochemical properties, as reported earlier,[1,3] and more complete characterization will be published elsewhere.[4] We find in particular that the insertion capacity of spin-coated films is *double* that of dip-coated films. In these previous studies, it was found that there is no change of properties of spin-coated films after 1000 cycles between 3.5 and 1.8 V, and there is completely reversible electrochemical behavior.[5] The reasons for the superior electrochemical behavior are associated with the microstructural characteristics of the deposited materials, and we wish to report some aspects of the microstructure here.

The formation of thin films from sol–gel precursors has been reviewed recently by Brinker et al.[6] They discuss both spin-coating and dip-coating techniques. Spin coating has been practiced successfully for many years in microlithography, where the interest is to make thin films that are uniform in thickness over lateral dimensions of 15 cm or more. Bornside et al.[7] analyzed the fluid mechanics of film deposition by the spin-coating technique. It was found that the most important processes in the spin-coating operation are the "spin off" and evaporation stages. In spin off, liquid is removed by the centrifugal forces of spinning, and continuous evaporation of liquid occurs to deposit the

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solid film material. High shear forces in the liquid are important in determining the rate of removal of the liquid and in determining the uniformity of the final films. Uniform films are expected within a certain range of operation (e.g., uniform solvent evaporation from the film surface), if the precursor solutions are Newtonian liquids. In this case, the thickness of the deposited film decreases approximately as $\Omega^{-2/3}$, where Ω is the angular velocity of the spinning disk substrate. Brinker et al.[6] have noted however that many sol–gel solutions are "shear thinning" (i.e., non-Newtonian), so that the lower shear rate near the center causes the viscosity to be higher there and the film to be thicker. We find that the V_2O_5 hydrogels used in the present study yield spin-coated films which are thicker near the center of rotation, consistent with their shear-dependent viscosities.[2] Away from the center, however, the films are quite uniform in thickness over lateral dimensions of several centimeters. It is the uniform films deposited in the latter regions that have superior electrochemical properties and that are the subject of the present paper.

Considerable effort has been devoted recently to vanadium pentoxide xerogel as a lithium ion insertion compound for rechargeable lithium batteries or electrochromic devices because it can be prepared through the sol–gel process. Vanadium pentoxide xerogels are obtained by drying the precursor gel, the latter being prepared by processes such as pouring molten V_2O_5 into water, by the reaction of vanadium oxide with hydrogen peroxide, and by proton exchange of metal metavanadate solutions. All the processes yield solutions of decavanadic acid, which then undergoes transformation by self-assembly of ribbons of V_2O_5. Tetravalent vanadium appears to play a role in the self-assembly process, and is present to the extent of up to 4% in most of the decavanadic acid solutions.[2] The ribbons are typically 1.1 nm thick, 10 nm wide, and 100 nm long, having been formed from smaller fibrils.[2] The ribbons also self-align in solution with other ribbons to form large rod and coil aggregates as the sol matures to the gel state.

There are several reports on V_2O_5 xerogel (XRG) powder[8] or as a thin film deposited via dip coating on an appropriate substrate[9,10] dried in air[8,9] or under vacuum.[12,13] However, the only previous reports on spin-coated films are those from our laboratory[1,3] which focused on electrochemical properties.

In the present paper, we will report properties of spin-coated films of V_2O_5 XRG determined by mass and thickness measurements and by electronic conductivity, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical measurements. It will be shown that the spin-coated films have microstructural characteristics that are considerably different from films formed by dip coating. The spin coating films are amorphous, and the local ribbons are more randomly oriented than dip-coated analogues.

Experimental Section

Vanadium pentoxide xerogel thin films were prepared by spin coating. The starting aqueous V_2O_5 gel was prepared according to the ion-exchange procedure described elsewhere.[2] Briefly, a solution of 0.2 M sodium metavanadate (Aldrich, 98%) was run through a column loaded with a proton exchange resin (Dowex 50 WX_2 50–100 mesh), producing a pale yellow solution of decavanadic acid that was then immediately filtered using a 0.45 μm nylon membrane to avoid particle contamination from the resin. Upon aging, the solution turned dark red due to the spontaneous polycondensation of the acid.[2] The gelation time changes from a few minutes at high concentrations to weeks or months at low concentrations.

The gels were aged at least for two months, time in which the gelation process goes to completion at this concentration,[12] before spin coating onto a substrate. Identical results were obtained for gels aged for 1 week, but those studies are less complete and will be discussed in later publications. Because the evaporation rate of the solvent (water) is enhanced by the rotation, sample air drying usually required only a few minutes (1–5 min) except for very thick samples for which 30–45 min were necessary. The resulting sc-V_2O_5 XRG films contained 1.6–1.8 mol of water/mol V_2O_5.[8] Additional water was removed from the samples by vacuum drying (30 mTorr or less) for 12 h. Water removal was measured by the use of a quartz crystal microbalance. The final composition of the spin-coated films was $V_2O_5{\cdot}0.5\ H_2O$.

Depending on the characterization technique, various substrates such as nickel-coated silicon wafers, glass, or fused silica slides were used. The use of metallic nickel, not stable in contact with V_2O_5 hydrogel (strong oxidizer in acidic solution), is allowed by the slow kinetics of the oxidation process. The corrosion rate of nickel, measured in our laboratory using the optical fiber micromirror technique,[14] was found to be lower than 1 Å/h. With such slow kinetics, no substantial change of the vanadium oxidation state of the films was induced during the very short period of time required to obtain dry samples (a few minutes in most of the cases). There is no reaction between nickel and the film in the dry state. In addition, we have found identical electrochemical behavior for V_2O_5 films spin coated on gold and nickel substrates. When needed, crystalline V_2O_5 was easily prepared by heating the spin coated films at 400 °C (in air) for several hours.

Mass and Thickness Measurements. The mass of the samples was determined by using both a mechanical microbalance and a quartz crystal microbalance. In the first case, the substrates were nickel-coated silicon wafers, while in the latter, quartz crystals coated on both sides with nickel were used.

Thickness measurements obtained using the usual profilometer technique were not reproducible because the spin-coated V_2O_5 films were soft and porous. This problem was solved by breaking the substrate with the attached spin-coated film and obtaining the thickness of the film by looking at the cross section using scanning electron microscopy (SEM).

Electronic Conductivity Measurements. The electronic conductivity of air-dried and vacuum-dried sc-V_2O_5 films was measured by complex impedance analysis using a Solartron 1260 impedance analyzer and dc characterization with the use of a Solartron 1286 potentiostat. Two different cell geometries were used which allowed us to measure the conductivity in the coplanar and perpendicular directions to the substrate.

X-ray Diffraction. XRD spectra were collected for sc-V_2O_5 XRG films deposited onto nickel-coated silicon wafers using a Siemens D500 X-ray diffractometer with Cu Kα (1.5418 Å) radiation. The sample chamber was furnished with a heating unit that provided XRD measurements at different temperatures. In some cases, to avoid water absorption from the

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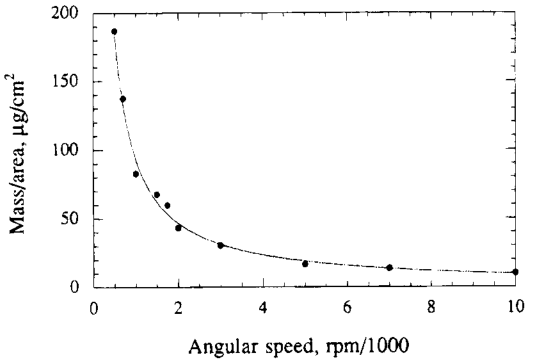

Figure 1. Mass of sc-V_2O_5 XRG thin films as a function of the rotation speed determined by the use of a quartz crystal microbalance. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

Table 1. Mass per Area, Thickness, Density and Drying Time for Thin-Film V_2O_5 Xerogel Samples Spin Coated at Different Rotational Speed[a]

rotational speed, rpm	mass/area, µg/cm² (±0.1)	thickness, Å (±100)	density, g/cm³ (±0.05)	drying time, s
500	187.0	10400	1.8	1140
700	137.0	6400	2.1	720
1000	82.7	4000	2.1	480
1500	67.6	3000	2.3	300
1750	59.7	2700	2.2	180
2000	36.9			120
3000	30.7	1275	2.4	90
5000	16.6			45
7000	13.7			30
10000	10.3			20

[a] Weight measured by QCM. Thickness measured by SEM cross section.

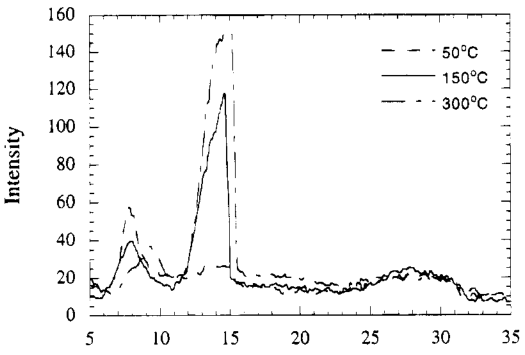

Figure 2. XRD patterns of sc-V_2O_5 XRG on Ni/Si substrate heated at different temperature: (a) room temperature, (b) 150 °C, and (c) 300 °C. Rotation speed: 1750 rpm. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

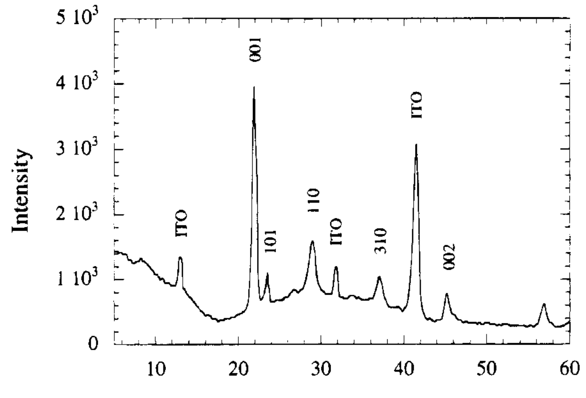

Figure 3. XRD patterns of sc-V_2O_5 XRG on ITO/glass substrate recrystallized by heating, in air, at 450 °C. Rotation speed: 1750 rpm. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

atmosphere, the samples were sealed in a polyethylene bag almost transparent to X-rays.

SEM and TEM Analysis. A JEOL-JSM-840 was used to characterize the surface morphology of the sc-V_2O_5 XRG films deposited on nickel-coated silicon wafers. Cross-sectional micrographs were also obtained.

TEM micrographs were collected using a CM 30 Philips microscope. sc-V_2O_5 xerogel films on copper grids were obtained with the normal procedure described above simply by mounting the grid onto a silicon wafer.

Optical Measurements. Transmittance of the sc-V_2O_5 XRG films in the UV and visible regions (0.4–0.9 µm) were measured using a Varian Lambda 9 double-beam spectrophotometer. Fused silica slides were used as the substrate for the samples as well as the reference in the spectrophotometric measurements.

Results and Discussion

The amount of V_2O_5 xerogel spin coated onto the substrate changes substantially with the rotation speed used as shown in Figure 1. The shape of the curve indicates an inverse dependence of the mass per area of spin-coated V_2O_5 XRG on the rotation speed. Consequently, the thickness of the coated films changes similarly. The resulting density of the material varies between 1.8 and 2.4 g/cm³. A summary of these results is presented in Table 1. The average value of the film density is comparable to that published by other researchers[9] for films deposited by dip coating and other methods.

XRD analysis was performed to characterize the thin spin-coated film structure. In Figures 2 and 3 the X-ray diffraction patterns of $V_2O_5{\cdot}nH_2O$ air dried at different temperatures are shown. Curve a (sample dried at room temperature) corresponds to the diffraction of the (001) plane that is perpendicular to the ribbon stacking direction. The correlated basal spacing of 11.4 Å, in agreement with the value published by other authors,[8,9] indicates the presence of one intraribbon monolayer of water ($n = 1.8$). Upon heating the sample and removing water, the first peak moved to a higher angle, suggesting the lowering of the basal distance.[2,9] A broad peak structure ($2\theta \approx 25°-32°$) and a broad peak ($2\theta \approx 15°$) appeared at 150 °C ($n = 0.5$, curve b), and the latter became predominant at 300 °C (curve c) where the amount of water in the material was reduced to 0.15 mol/vanadium atom ($n = 0.3$). On comparison with the V_2O_5 powder XRD pattern, it is seen that the peak can be associated with the (200) plane of the orthorhombic structure of V_2O_5 while the (110), (310), and (400) lines are in the broad peak structure region. Further removal of water (temperature higher than 350 °C) caused crystallization of the spin coated thin film. According to previous work[14,15] and to the XRD pattern shown in Figure 3, the so-formed V_2O_5 crystallites are preferentially oriented with the (00*l*) plane oriented parallel to the substrate as indicated by the strong intensity of the peak at $2\theta = 20.25°$. (It is useful to note that the

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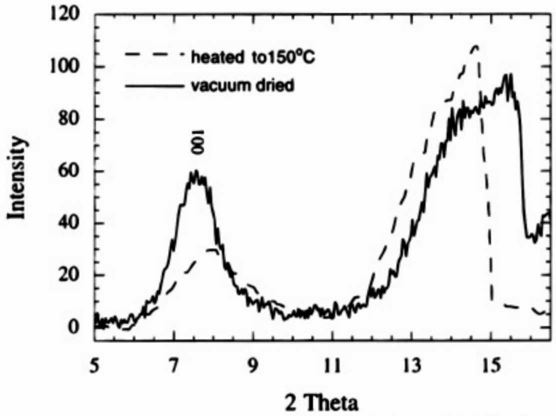

Figure 4. XRD patterns of sc-V_2O_5 XRG on Ni/Si substrate (a) vacuum dried and (b) heated at 150 °C. Rotation speed: 1750 rpm. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

removal of the last water molecules causes a collapse of the stacked ribbon structure. The basal distance decreases from 8.8 to 4.37 Å.)

A first, simple conclusion about the structure of sc-V_2O_5 xerogel is obtained by the comparison of the X-ray spectra shown in Figure 2 (curve a) and Figure 3. Although the mass of vanadium oxide is almost the same in both samples, the intensity of the peaks is much higher in the recrystallized material. This clearly indicates that the spin-coated films are dominantly amorphous.

More important is the effect of the high shear and the quick evaporation of the solvent during the spin coating that generates a more chaotic structure in sc-V_2O_5 XRG than in dip-coated V_2O_5 XRG. The action of the high shear is to disrupt the self-alignment of ribbons in the gel, and the rapid evaporation prevents any subsequent reorganization. In fact, thin films of the latter material have strong anisotropy due to the stacking of ribbons parallel to the substrate. In dip-coated films, only the (00*l*) set of diffraction is evidenced by X-ray reflection measurements, while the (*hk*0) diffraction is evidenced by X-ray transmission.[2,8] Removal of the intraribbon water layer ($n = 1.8-$ to $n = 0.5$) causes the shift to higher angle (lower basal distance) of the (00*l*) peaks but does not affect the 2D structure of the ribbons.[8] The strong anisotropy and unchanging 2D structure were not found in XRD patterns of sc-V_2O_5 XRG. In fact, the peak related to the (200) plane and the broad peak structure ($2\theta \approx 25°-32°$), shown after removal of the intraribbon water layer by heating or vacuum drying (Figure 4), clearly indicate the presence of some V_2O_5 ribbons whose stacking direction is *parallel* to the substrate rather than perpendicular to it as is the case for dip-coated films. Electronic resistance measurements support the proposed chaotic morphology of spin coated thin films. Only a factor of 80 is found for the ratio of the electronic conductivity measured in a configuration parallel (7.8×10^{-4} S/cm) or perpendicular (0.95×10^{-5} S/cm) to the substrate. The ratio is smaller than that found for dip-coated V_2O_5,[17,18] where the ratio was 4 orders of magnitude, confirming that sc-V_2O_5 XRG thin films are not as anisotropic as dip-coated films.

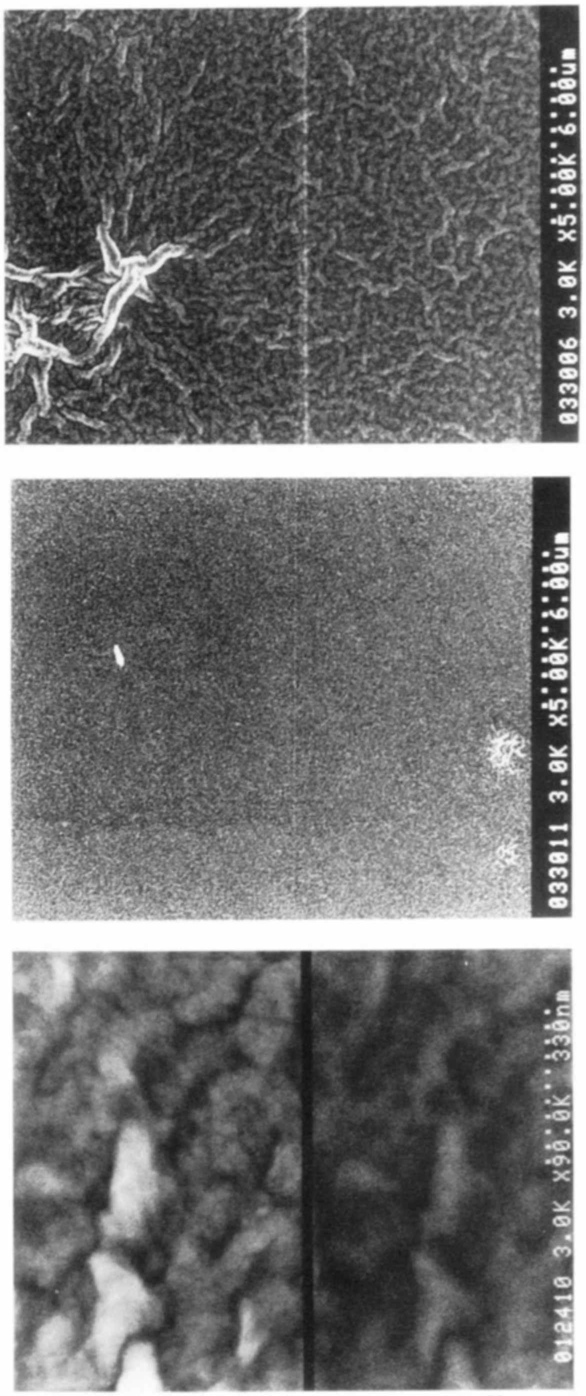

Figure 5. SEM micrographs of sc-V_2O_5 XRG thin films coated on Ni/Si substrates. Rotation speed: (a, top) 500 rpm, (b, middle) and (c, bottom) 3000 rpm. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

The morphology of the samples is strongly influenced by the deposition technique. The rotation of the substrate affected the film formation from the aqueous V_2O_5 gel in two different ways: the application of a centrifugal force and the modification in the solvent evaporation rate. Both effects increased with rotational speed. For example, a film coated at 10 000 rpm needed only a few seconds to remove excess water (see Table 1) while 5 and 45 min were required to obtain visibly dry solid films at 1500 and 500 rpm, respectively. As the rotation speed increased, there were dramatic changes in the V_2O_5 XRG film surface morphology as shown by SEM micrographs reported in Figure 5. A low-speed spin-coated film (500 rpm in Figure 5d) showed features that

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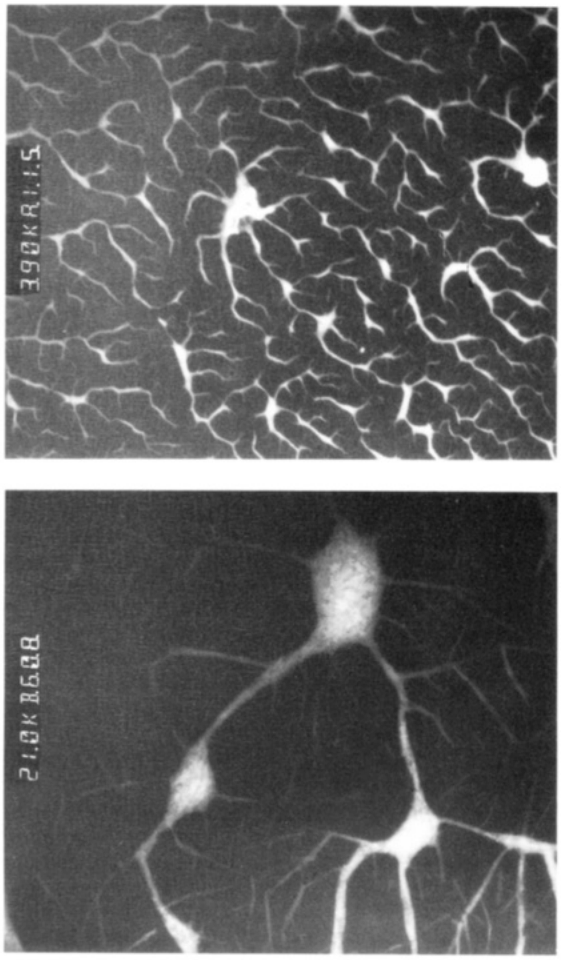

Figure 6. TEM micrographs of sc-V_2O_5 XRG on copper grid at different magnification. Rotation speed: 1750 rpm. Gel aging more: 2 months. Starting solution: 0.2 M sodium metavanadate.

could be associated with bundles of rods or coils on the surface that are also present, although more pronounced, in dip coated films.[12,19] The features almost disappeared in a film coated at 3000 rpm (see Figure 5b) that shows a uniform surface. Nevertheless, a higher magnification SEM picture of the latter (Figure 5c) still showed the presence of agglomerates but they were smaller. We suppose that the spindlelike rod structure of the precursor V_2O_5 hydrogel is strongly affected by the high shear applied to the gel during the spin-coating process, and this leads, particularly at high rotational speeds, to a more amorphous structure in spin-coated films.

TEM analysis performed on V_2O_5 xerogel spin coated on a copper grid (Figure 6d) showed the presence of single ribbons, fibrils, and agglomerates. Single ribbons were approximately 10 nm wide and 200 nm long, values that are in agreement with previous results.[2] Agglomerates and fibrils seem to be linked to form a network as shown by a low magnification micrograph (Figure 6b). The features appeared to be oriented in the direction of the centrifugal force generated by the rotation of the substrate during spin coating.

The optical properties of the material in the visible range have also been investigated. Figure 7 shows the transmittance versus wavelength (0.4–0.9 μm) of sc-V_2O_5 XRG thin films as a function of the rotation speed while the influence of the heat treatment on the optical properties is reported in Figure 8, for a film deposited at 1750 rpm. The transmittance is seen to decrease sharply at small wavelengths for all samples, which is consistent with a semiconductor bandgap of about 2.2–2.4 eV.[20,21] Two features deserve special attention: (i) some adsorption peaks are seen in the spectra of thicker samples (Figure 7); (ii) the transmittance decay at low wavelength, which can be correlated with the bandgap, is found to occur at higher wavelength for the heat-treated (recrystallized) sample (Figure 8).

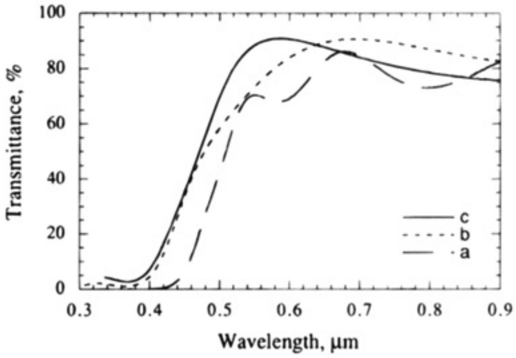

Figure 7. Transmittance versus wavelength of sc-V_2O_5 XRG thin films coated on fused silica as a function of the rotation speed. (a) 500 rpm, (b) 1000 rpm, and (c) 1750 rpm. All the values are referred to as bare fused silica slide. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

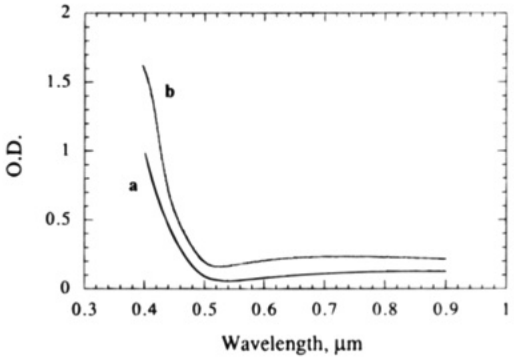

Figure 8. Optical density as a function of wavelength of sc-V_2O_5 XRG thin film as made (a) and after recrystallization at 450 °C in air (b). All the evaluate are referred to a bare fused silica slide. Rotation speed: 3000 rpm. Gel aging time: 2 months. Starting solution: 0.2 M sodium metavanadate.

A blue shift of the bandgap has been found in noncrystalline vanadium oxide materials such as low-temperature sputtered V_2O_5 thin films[16,20] and vanadium-based glasses.[22] It has been suggested that the blue shift is caused by the presence of tetravalent vanadium ions in an amorphous environment. Both these factors are present in our sc-V_2O_5 XRG thin films. The tetravalent vanadium, proposed as initiator for the polymerization of decavanadic acid,[2,23] was found by TGA measurements to be present in the hydrogel used in this

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work to the extent of 3.8% (similar to published results reviewed by Livage[2]) while the poor crystallinity is evidenced by the XRD measurements. We suggest that both factors, tetravalent vanadium in an amorphous structure, are also the cause of the bandgap blue shift occurring in our sc-V_2O_5 XRG thin films.

The adsorption bands at $\lambda > 0.5$ μm shift as the thickness of the films changes. Thinner samples show a broad band at wavelengths higher than 0.9 μm, while two bands at 0.58 and 0.8 μm are found for the thicker ones. The 1000 rpm sample had an intermediate behavior, showing a shoulder around 0.55 μm and a peak which grows in at higher wavelengths. All these features have been associated with oxygen vacancies or tetravalent and trivalent vanadium in non stoichiometric sputtered V_2O_5.[16,20,22] The bands at 0.58, 0.9, and 1.1 μm are associated with the presence of intragap states (from self impurities) and in mixed-valence polyvanadic acid gels[11] (bands at 0.63, 0.71, 0.79, 1.41, and 1.51 μm associated to d−d transitions and intervalence transfer between V^{V} and V^{IV} ions). At present we are not able to fully interpret the difference in the optical spectra, and more work is in progress in our laboratory. We can only suggest that, because the properties of the material at the interfaces (the external interface and the internal region in contact with the substrate) are different from that in the bulk,[10] the thickness can play an important role in the properties of the sc-V_2O_5 XRG thin films.

Conclusion

The easy preparation of sc-V_2O_5 XRG together with its favorable properties makes this material promising for use as a cathode in thin-film solid-state lithium batteries. The shear forces exerted on the sample during the coating procedure give air dried $V_2O_5 \cdot 1.8H_2O$ thin films (0.04−1.0 μm) in a few minutes that are highly disordered. This is due to the joint effect of the quick evaporation of the solvent and the shear applied during fast spin coating (>1500 rpm) from the V_2O_5 hydrogel. The large aggregates present in the gel phase are disrupted by the shear force. The organization of ribbons in ordered stacks with a stacking direction perpendicular to the substrate, that is largely the effect of slow water removal (e.g., dip-coated films), is prevented by the fast drying. The morphology of the final dry material is strongly affected. The reduced extent of ribbon stacking is reflected in a very poor crystallinity. Furthermore, the few stacks formed or already present in the gel phase cannot reorganize and remain randomly distributed with a small amount of stacking with the ribbon plane perpendicular to the substrate. The result is that sc-V_2O_5 xerogel thin films are largely isotropic and homogeneous with macroscopically smooth surfaces. Nevertheless, microscopically rough surfaces are revealed by SEM analysis. These features, respectively indicating high surface area and favorable morphology for lithium diffusion, explain the high lithium insertion capacity reported previously.[1,3]

The low optical absorption in the visible region suggests that one may use sc-V_2O_5 XRG thin films as a source sink for lithium ions in lithium-based electrochromic devices. Furthermore, by heat treatment at 400 °C under air, spin-coated films can be easily transformed into crystalline V_2O_5 layers by a less expensive route than the alternative sputtering techniques.

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