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by

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SYNTHESIS AND PROPERTIES OF VANADIUM OXIDE AEROGEL FILMS

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The fine colloid size, high surface area and controllable density of vanadium oxide aerogels make these materials interesting candidates for lithium insertion electrodes. Thin films of vanadium oxide aerogels were prepared using an alkoxide precursor sol and supercritical drying with CO_2. Film preparation methods included spin coating of fine aerogel particles suspended in a solvent and dip coating of the precursor sol onto carbon paper substrates. The room temperature electrical conductivity of partially dehydrated materials ($V_2O_5 \cdot 0.5\ H_2O$) varies from 10^{-5} S/cm to 10^{-4} S/cm depending upon the density of the final aerogel. Potential sweep measurements indicate that the films possess good insertion capacity ($\approx$ 2 Li per V_2O_5) and can be cycled reversibly.

INTRODUCTION

Aerogels are high surface area, low density solids prepared by the sol-gel approach followed by supercritical drying of the wet gel (1). The sol-gel process has been studied extensively and the reaction chemistry for vanadium pentoxide is well known. Supercritical drying removes the liquid/vapor phase interface as the solvent is extracted, preserving the structure present in the wet gel. This process leads to surface areas as large as 1000 m^2/g and porosity greater than 99%. The aerogel field has expanded substantially in recent years and has been applied to a number of metal oxide and mixed metal oxide compositions for catalyst applications (2). Xerogels, by comparison, are materials resulting from drying of the wet gels under ambient temperature and pressure. Due to the liquid/vapor phase interface during drying under ambient conditions, shrinkage occurs as the pores collapse. Xerogels can possess surface areas up to 20 m^2/g and porosity up to 50%.

Vanadium pentoxide has been studied as an intercalation host in both crystalline and amorphous form. Crystalline V_2O_5 shows limited capacity for lithium insertion compared to its amorphous counterpart ($\approx$ 1 Li compared to 2-4 Li per V_2O_5). Papers investigating amorphous V_2O_5 have emphasized xerogel films prepared by protonation of vanadates in aqueous solutions (3). The electrochemical characterization of xerogels has received much attention due to its increased capacity over crystalline V_2O_5 (4,5).

The present paper considers the synthesis and properties of vanadium pentoxide aerogels. In aerogel form, these intercalation materials should exhibit interesting electrochemical behavior which benefit from the far greater surface area available. Shorter diffusion paths and enhanced surface reactions may also result from the unique morphology of the vanadia aerogels. There has been prior work reported on the structural and electrochemical characterization of vanadia aerogels (3,6,7). This paper extends the previous work, investigating vanadia aerogel films, new substrates and the resulting electrical and electrochemical behavior.

EXPERIMENTAL

Synthesis

The synthesis of vanadium oxide aerogels through the sol-gel route has been described previously (6). Briefly, sols of the molar ratio, $VO(OC_3H_7)_3$ / water / acetone (1 / 20 / 25), were used to prepare all vanadia aerogels in the present study. Gelation of the sol occurred within 30 seconds upon the addition of the water/acetone mixture to the vanadyl alkoxide (Gelest, Inc.) held in an ice bath. Following aging, the gel was washed with anhydrous acetone and supercritically dried with CO_2.

Gels in the shape of rods (approximately 1 cm in diameter and 5 cm in length) were used to prepare samples for conductivity measurements. The rods were cut into discs with a diamond saw to approximately 1 cm in length. The discs were then masked and sputtered with gold on each end. Two point complex impedance measurements (20 Hz to 1 MHz) were performed in flowing argon from 150°C to room temperature. The discs were held at 150°C prior to taking measurements. This heat treatment removes the continuous water layer in the interlamellar space of the V_2O_5 and produces an electronically conducting material. According to TGA results, 75% of the water is removed at 150°C, corresponding to a composition of $V_2O_5 \cdot 0.5\ H_2O$.

Several samples of vanadia aerogels were prepared with higher densities. This density variation enables one to determine the scaling relationship with respect to conductivity. To obtain higher density, the samples were exposed to laboratory air through a 1 mm diameter hole in the top of the sample container prior to washing and supercritical drying. This exposure allowed slow evaporation of some of the solvent within the wet gel, resulting in shrinkage. The partially densified gels were then washed and supercritically dried with varying degrees of shrinkage. These samples were cut and prepared for complex impedance analysis as described above. The densities of the aerogels were determined using a pycnometer vial filled with mercury.

The electrochemical behavior was determined for thin films of the vanadia aerogels. Both molybdenum coated glass slides and carbon paper (Lydall-50 Carbon Paper with polymer binder) served as substrates. In the case of the Mo coated glass, films were prepared by suspending aerogel powders in cyclopentanone (Aldrich Chemical Co.), and spin coating the solution. The film uniformly covered the slides with thicknesses between 1 μm and 4 μm as determined by scanning electron microscopy (SEM).

The second thin film approach involved dip-coating the carbon paper into the precursor sol. The coated carbon paper was then aged, washed and supercritically dried. SEM indicated that the paper had only partial coverage of the 10 μm diameter fibers. Approximately 30% of the fibers were coated and a majority of the vanadia aerogel was present as large fragments trapped between the weave of the fibers. The coated fibers contained between 2 μm and 10 μm of vanadia coating.

The electrochemical behavior or the vanadia aerogels was tested in a three electrode cell where metallic lithium served as both the counter and reference electrode, and the aerogel film acted as the working electrode. A 1 M solution of lithium perchlorate (Aldrich Chemical Co.) in propylene carbonate (Aldrich Chemical Co.) served as the electrolyte.

RESULTS AND DISCUSSION

Structural Characterization

TEM, X-ray diffraction, TGA and surface area measurements were performed on samples prepared from powders crushed from the aerogel rods. The results of these experiments have been reported previously (6,8). The vanadia aerogels possess a fibrous morphology and X-ray diffraction indicates that there is little, if any, preferred crystallographic orientation of these fibers. This behavior differs substantially from work carried out on aqueous-derived V_2O_5 xerogels (3). TGA analysis has shown that the vanadia aerogels may be described as hydrated oxides of the composition $V_2O_5 \cdot n\ H_2O$ with n = 2.0 to 2.2. BET analyses indicate these materials have surface areas in the range of 300 - 400 m^2/g.

The density of the as-prepared vanadia aerogels ranges between 0.04 g/cc and 0.1 g/cc depending upon the molar ratio of the precursors. The molar ratio used in this study consistently led to aerogels with a density of 0.1 g/cc. By allowing the wet gels to partially dry in laboratory air prior to supercritical drying, aerogels with densities as high as 0.8 g/cc were prepared. Xerogels with a density of 2.4 g/cc were made by allowing the wet gels to dry completely in air at ambient temperature and pressure.

Electrical Properties

Complex impedance measurements on monolithic vanadia aerogels were carried out on samples with densities between 0.1 g/cc and 0.8 g/cc. Standard preparation conditions (without air exposure) produced materials with a density of 0.1 g/cc which corresponds to a material with 97% porosity. The conductivity of a 0.1 g/cc vanadia aerogel was found to be 3.4×10^{-5} S/cm at 25°C. The activation energy of the 0.1 g/cc aerogel was found to be 0.23 eV. The results of the complex impedance analysis showed conductivity to be independent of frequency with all phase angles close to zero, which is indicative of conductivity being electronic in nature. These values of conductivity and activation energy are consistent with previously reported measurements (3).

The conductivities of the aerogels were found to increase with increasing density. For the series of samples with densities between 0.1 g/cc and 0.8 g/cc, the room temperature conductivity increased, reaching a value of 3.6×10^{-4} S/cm for the sample of 0.8 g/cc. The activation energy for this series of samples was 0.23 ± 0.03 eV. The xerogel sample (2.4 g/cc) was consistent with this trend; the conductivity for this material was 1.6×10^{-3} S/cm with an activation energy of 0.18 eV. Figure 1 shows the variation in room temperature conductivity with density.

Electrical conductivity is expected to vary with density because the connectivity or the number of conduction pathways within the material will change. As a result there is a scaling factor, τ, such that

$$\sigma \alpha \rho^{\tau} \qquad [1]$$

where σ is the electrical conductivity and ρ is the density. τ is related to the dimensionality, d, of the conduction pathways within the system, and also to the fractal dimensionality, d_f. In general, $\tau \approx d / 2$. Thus, for a two dimensional system, $\tau = 1.1$ and for a three dimensional system, $\tau = 1.5$.

Our results show a nearly linear relationship between the electrical conductivity and density, $\sigma \alpha \rho^{1}$. This is consistent with the two dimensional ribbon-like morphology exhibited by the vanadia aerogels at the nanometer level. By comparison, the electrical conductivity of carbon aerogels shows $\sigma \alpha \rho^{1.5}$ which is indicative of a three dimensional structure (9).

Electrochemical Behavior

The electrochemical behavior of vanadia aerogel films on Mo coated glass was reported previously (7). The open-circuit voltage (V_{oc}) of a freshly prepared cell is approximately 3.7 V. Upon sweeping the potential from 3.6 V to 1.6 V and back at 1 mV/s, the V_{oc} dropped to 3.4 V. Figure 2 shows a typical potential sweep curve of a vanadia aerogel film coated onto Mo coated glass. Integration of the curve indicates the insertion of approximately 2.0 Li per V_2O_5. Two distinct intercalation peaks were present at approximately 2.8 V and 2.4 V. This is followed by de-intercalation peaks at 2.7 V and 3.1 V. The first sweep of a cell, as shown in Figure 2, is generally characterized by a decrease in V_{oc} from 3.7 V to 3.4 V, suggesting that some lithium is inserted irreversibly at this sweep rate. This amount is less than 10% of the total lithium intercalated. Multiple sweeps of the same sample show relatively little change with the exception of the de-intercalation peak at 3.4 V shifting to slightly higher values.

The results of our potential sweep measurements show similarities to those found for vanadia xerogels prepared from the aqueous route. The electrochemical behavior of the xerogels apparently is affected by the aging time of the gel prior to spin coating the films. The amount of time necessary for aging is dependent on the concentration of the gel, and can take between one week and three months for the condensation reactions to complete(4).

Cyclic voltammetry of the aqueous derived xerogel films prepared from non-aged gels shows a single broad peak for both cathodic (3.4 V) and anodic (2.8 V) sweeps (8). Cyclic voltammetry of xerogel films prepared from aged gels have multiple peaks for both cathodic (2.6 V and 3.0 V) and anodic (2.4 V, 2.7 V and 3.1 V) sweeps (5).

Our results for vanadia aerogel films exhibit similarities to both the aged and non-aged xerogel films mentioned above. The vanadia aerogels have fairly broad peaks as do non-aged xerogels. One of the two peak potentials for the aerogel films corresponds closely to the single peaks present in the non-aged xerogels, and cathodic peaks are shifted by 0.2 V. In comparison to the aged xerogels, the aerogels have matching anodic peaks at 2.7 V and 3.1 V. However, there is an anodic peak at 2.4 V present for the aged xerogels which is not shown in the potential sweep curve for the aerogel films.

Vanadia aerogels coated onto carbon paper substrates possess similar V_{oc} behavior as that of the films on Mo coated glass. Figure 3 shows a constant current discharge of the vanadia aerogel on both types of substrates with varying current densities for the aerogels on carbon paper. The vanadia aerogel sample on the Mo coated glass with current density of 15 $\mu A/cm^2$ was comparable to the sample on carbon paper discharged at 17 $\mu A/cm^2$. These samples intercalated close to 2 Li per V_2O_5. Discharging at a higher current density of 35 $\mu A/cm^2$ significantly decreased the capacity of the aerogel on the carbon paper. Our results showing intercalation of close to 2 Li per V_2O_5 is fairly consistent with the reported values for vanadia xerogels (10). However, it is not as high as some recently reported values of 3 - 4 Li per V_2O_5 in both xerogels and aerogels (5, 11).

The discharge curves exhibit a stepwise decrease in potential indicating different energetically favorable sites within the vanadia aerogel for lithium insertion. The stepwise decrease in potential is similar to the behavior exhibited by crystalline V_2O_5. However, the steps corresponding to crystalline V_2O_5 are much more distinct and there is a large drop in potential at $x = 1$ ($Li_x V_2O_5$), which is not exhibited by the aerogel. Amorphous V_2O_5 and vanadia xerogels show a slow continuous decrease in the equilibrium potential (10). Both the amorphous macroscopic structure of the vanadia aerogels and its ordered ribbon-like structure on the nanometer level seem to play a role in determining the shape of the chronopotentiometry curves.

CONCLUSIONS

Vanadium oxide aerogels were synthesized by the sol-gel approach leading to materials of low density and high surface area. A combination of ambient and supercritical drying produced aerogels of varying density (0.1 g/cc - 0.8 g/cc). Dehydrated samples of these aerogels ($V_2O_5 \cdot 0.5\ H_20$) were analyzed by performing complex impedance measurements. Room temperature electrical conductivity of the aerogels ranged between 3.4×10^{-5} S/cm and 3.6×10^{-4} S/ cm, corresponding to a density of 0.1 g/cc and 0.8 g/cc, respectively. The series of varying density aerogel samples, along with a sol-gel derived xerogel (2.4 g/cc), were measured in order to determine the relationship of conductivity versus density. The nearly linear relationship found is indicative of the ribbon-like nanostructure present in the vanadia aerogel serving as a two-dimensional electron conduction pathway.

The electrochemical behavior of the vanadia aerogels was investigated by potential sweep and chronopotentiometry measurements. Anodic and cathodic peaks from the potential sweep measurements were comparable to those of aqueous-derived vanadia xerogel thin films. The vanadia aerogels showed good lithium insertion capacity (≈ 2 Li per V_2O_5) and little degradation upon the subsequent few sweeps. According to chronopotentiometry measurements, 2 mols of Li per V_2O_5 were inserted for films on both Mo coated glass and carbon paper substrates at a current density below 17 $\mu A/cm^2$. The insertion capacity decreased when the vanadia was discharged at 35 $\mu A/cm^2$.

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REFERENCES

1. J. Fricke and A. Emmerling, J. Am. Ceram. Soc., **75**, 2027 (1992).
2. M. Schneider and A. Baiker, Catal. Rev. - Sci. Eng., **37**, 515 (1995).
3. J. Livage, Chem. Mater., **3**, 578 (1991).
4. S. Passerini, D. Chang, X. Chu, D.B. Le and W. Smyrl, Chem. Mater., **7**, 780 (1995).
5. H.-K. Park, W.H. Smyrl and M.D. Ward, J. Electrochem. Soc., **142**, 1068 (1995).
6. F. Chaput, B. Dunn, P. Fuqua and K. Salloux, J. Non-Cryst. Solids, **188**, 11 (1995).
7. K. Salloux, F. Chaput, H.P. Wong, B. Dunn and M.W. Breiter, J. Electrochem. Soc., **142**, L191 (1995).
8. B. Katz, W. Liu, K. Salloux, F. Chaput, B. Dunn and G.C. Farrington, Solid State Ionics IV, G.-A. Nazri, J.-M. Tarascon and M. Schreiber, Editors, **369**, p.211, Proceedings of the Materials Research Society, Pittsburgh, Pennsylvania (1995).
9. X. Lu, et.al., J. Appl. Phys., **73**, 581 (1993).
11. R. Baddour, J.P. Pereira-Ramos, R. Messina and J. Perichon, J. Electroanal. Chem., **314**, 81 (1991).
10. D.B. Le, S. Passerini, A.L. Tipton, B.B. Owens and W.H. Smyrl, J. Electrochem. Soc., **142**, L102 (1995).

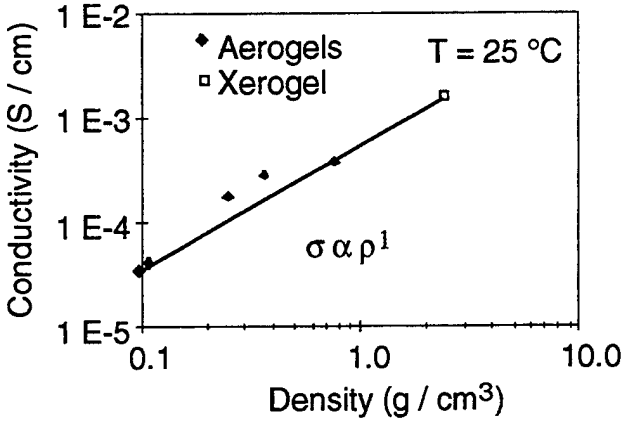

Figure 1. Electrical conductivity of vanadia aerogels as a function of density.

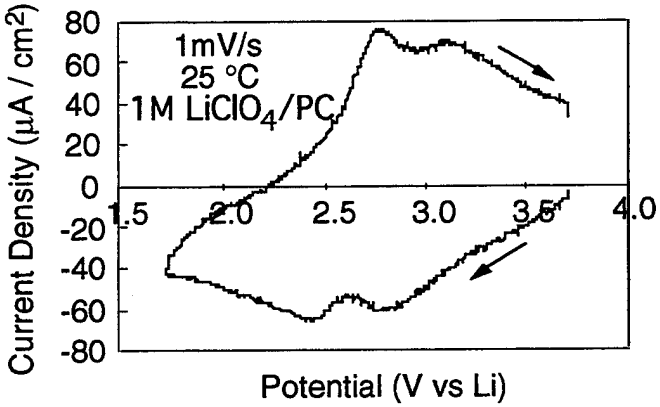

Figure 2. Potential sweep measurement of a vanadia aerogel film spin-coated onto a Mo coated glass. Integration of the curve indicates the intercalation of ≈ 2 Li per V_2O_5.

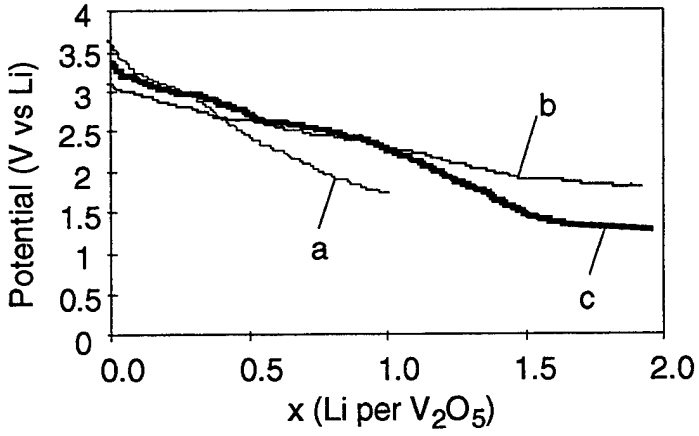

Figure 3. Constant current discharge of vanadia aerogel films on both carbon paper substrates (a,b) and Mo coated glass substrate (c). The vanadia on the glass substrate (c) was cycled at 15 μA/cm^2, and showed insertion of ≈ 2 Li per V_2O_5. Discharge of the vanadia on a carbon paper substrate discharged at 17 μA/cm^2 (b) showed similar lithium insertion capacity. A significant decrease in capacity was exhibited when the vanadia on carbon paper was cycled at 35 μA/cm^2 (a).