Electrochemical properties of vanadium oxide aerogels

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Abstract

Aerogels are well-known mesoporous materials whose low density and high surface area result from synthesis methods that enable the pore solvent to be removed without collapsing the solid network phase. The interconnected porosity provides both molecular accessibility and rapid mass transport via diffusion, and for these reasons transition metal oxide aerogels are gaining increased interest as intercalation electrode materials for lithium-ion batteries. The present paper reviews recent research on vanadium oxide aerogels that has been directed at establishing both their fundamental properties and unique ways of incorporating these materials into electrode structures. The experiments used to determine the fundamental electrochemical properties of vanadium oxide aerogels involve the use of a sticky-carbon electrode that is designed to both hold the material and serve as the current collector. The results show that these materials combine elements of both capacitor and battery behavior as the materials possess both high specific capacitance (>2000 F/g) and high capacity for lithium incorporation (>450 mAh/g). The unique morphology of the vanadium oxide aerogel has led us to consider alternate electrode structures because traditional methods may compromise the mesoporous, high surface area morphology. One approach has involved the incorporation of single wall carbon nanotubes as the electronically conducting network. The resulting nanocomposites effectively retain the aerogel morphology and exhibit excellent electrochemical properties. These electrodes are especially effective at high discharge rates. Another approach has involved the preparation of aerogel electrodes that possess an inverted opal structure. The fabrication route is based on combining the templating of polystyrene spheres with sol–gel synthesis and leads to materials that possess a hierarchical pore structure. This architecture is also effective at retaining high lithium capacity at high current densities.

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1. Introduction

Aerogels are composed of a three-dimensional network of nanometer-sized solid particles surrounded by a continuous macroporous and mesoporous volume. Aerogels are known for their low density and high surface area. The porosity provides both molecular accessibility and rapid mass transport via diffusion and for these reasons aerogels have been part of the heterogeneous catalytic materials field for over 50 years [1]. One would expect that such physical features would be desirable for electrochemical reactions. However, to date, relatively few aerogel systems have been investigated as electrochemical materials [2].

Aerogels differ from traditional lithium intercalation electrode materials in some significant ways. First, aerogels are nanocrystalline, if not totally amorphous materials. The solid phase in an aerogel is composed of a colloidal oxide network that is characteristically quite thin, usually on the order of 10–50 nm. One can expect that diffusion distances will be rather short compared to traditional electrode materials. The high surface area of aerogels is significant because it means that surface effects can be amplified. Thus, surface defects that may not be evident in bulk materials, can now become prominent in aerogels because of the drastic increase in surface area. Moreover, since oxides have inherently defective surfaces, the defect chemistry associated with high vacancy concentrations is likely to influence aerogel properties. Finally, the high porosity and mesoscopic pore diameters of aerogel structures enable the electrolyte to penetrate the entire aerogel particle.

Among the various aerogel systems, the most notable electrochemical results have been reported for vanadium oxide...
oxide aerogels [2]. The specific capacity for lithium is greater with V2O5 aerogels than it is with either the corresponding xerogels or crystalline V2O5 [3]. Comparisons to xerogels are especially fascinating since the differences between aerogels and xerogels are morphological (primarily porosity and surface area) and not chemical; the materials differ only by the manner in which they are dried [1,2]. Aerogel materials offer considerable promise for battery applications as prior research has shown these materials to possess a specific lithium capacity in excess of 300 mAh/g at a C/4 discharge rate [4].

Research on the electrochemical properties of V2O5 aerogels has been largely based on traditional electrode structures where one combines the aerogel with other components: carbon black conductor, polymer binder and solvent. The aerogel particles tend to agglomerate during the processing of these electrodes, which reduces their surface area and alters their pore network. Moreover, the carbon black particles aggregate and may occlude the aerogel surface. For these reasons, the electrochemical responses reported in previous studies may not represent the electrochemical properties of a high surface area aerogel, but rather the behavior of an agglomerated aerogel system.

The present paper reviews our recent research in which we have deliberately created electrode structures that preserve aerogel morphology. First, we describe experiments that establish the fundamental electrochemical properties of the V2O5 aerogel. In this work a sticky-carbon electrode provides excellent electrical contact to the submicron particles of the aerogel without altering its distinct pore-solid nanostructure. The second part of this paper describes our efforts at replacing the carbon black conducting additive with single wall carbon nanotubes. The objective with this approach was to create an electrode structure where the carbon nanotubes provide electronic conduction without blocking electrolyte access to the aerogel particles. Finally, we report on the fabrication of a novel electrode architecture, an inverted opal, that incorporates the V2O5 aerogel. The combination of macro and mesoporosity is designed to reduce the polarization associated with mass transport through the electrode.

2. Experimental

2.1. Materials synthesis

The vanadium oxide aerogels were prepared using supercritical drying (scd) and ambient drying (ambigel) methods. For both methods, an alkoxide precursor, vanadyl trisopropoxide was hydrolyzed in a water–acetone mixture. Details for preparing scd and ambigel of vanadium oxide were reported previously [5,6]. The latter approach involved drying the precursor gel using various non-polar solvents such as cyclohexane, heptane, pentane and hexane. The combination of scd and ambigel methods enabled us to prepare mesoporous vanadium oxide materials with a range of surface areas and pore volumes as shown in Table 1. When no solvent exchange occurs and the wet gel is dried in ambient, the resulting material is a xerogel.

Nanocomposites of vanadium oxide aerogel with single-walled carbon nanotubes (SWNTs) were prepared by incorporating the nanotubes as part of the sol–gel chemistry [7]. The key feature in preparing the V2O5/SWNT nanocomposite cathodes was to use a suspension of SWNTs as the source of diluting solvent (acetone) in preparing the gel. The SWNTs were received in toluene that was gradually replaced with acetone under gentle heating conditions. Although some agglomeration of SWNTs occurred upon adding acetone, the SWNTs remained suspended and did not sediment over prolonged periods of time. This suspension was combined with the requisite amounts of vanadium alkoxide precursor and water to produce a wet gel. The gelled samples were then washed repeatedly in anhydrous acetone and then solvent exchanged with cyclohexane. The cyclohexane was evaporated under ambient conditions to produce the final nanocomposite.

The process used to fabricate the V2O5 inverted opal architecture is shown schematically in Fig. 1 [8]. A suspension of polystyrene spheres (1 μm diameter) is centrifuged in a glass tube, leading to the formation of a close-packed array (Fig. 1(a)). The vanadyl trisopropoxide precursor, diluted with isopropanol, is infiltrated into the template assembly and centrifuged briefly to ensure that it penetrates the void space (Fig. 1(b)) between the spheres. The infiltrated precursor undergoes hydrolysis and condensation reactions when it is exposed to water vapor, and transforms the liquid precursor into a rigid V2O5 gel network (Fig. 1(c)). The polystyrene template is then selectively dissolved upon immersion in toluene, leaving a three-dimensional interconnected porous architecture. In the last step of this process, the V2O5 phase is converted to

| Sample/drying liquid | Surface area (m2/g) | Total pore volume (cm3/g) |
|----------------------|---------------------|--------------------------|
| V2O5, xerogel/acetone | <10                 | <0.01                    |
| V2O5, ambigel/cyclohexane | 155              | 0.87                     |
| V2O5, ambigel/heptane  | 200                 | 0.60                     |
| V2O5, ambigel/hexane   | 165                 | 0.40                     |
| V2O5, ambigel/pentane  | 185                 | 0.48                     |
| V2O5 aerogel/supercritical drying using CO2 | 280 | 0.50 |
| V2O5, ambigel/cyclohexane with SWNT (5 wt%) | 150 | 0.76 |
| V2O5, ambigel/cyclohexane with SWNT (17 wt%) | 121 | 0.6  |
| V2O5, ambigel/cyclohexane with KJB (17 wt%) | 176 | 0.85 |
an ambigel by solvent exchange with cyclohexane, followed by evaporation under ambient conditions as described above (Fig. 1(d)).

2.2. Electrode preparation and electrochemical measurements

Sticky-carbon electrodes were used to characterize the electrochemical properties of the two types of V₂O₅ aerogels [9,10]. These electrodes were prepared by mixing acetylene black with wax at a 70:30 weight ratio. The resulting electrode possesses a sticky surface for adhering a quantitative amount of aerogel powder, exposes the submicron particles to the electrolyte and provides good electrical contact to each particle. An important consideration with this electrode is that the aerogel particles are not aggregated on the electrode and the electrolyte has unrestricted access to the aerogel particles. By having ample electron, ion and solvent transport to the solid phase of the V₂O₅, it is possible to determine the intrinsic electrochemical properties of the aerogel.

The nanocomposite electrodes were prepared by mixing the V₂O₅/SWNT powder with polyvinylidene fluoride (PVDF) in cyclohexane to form a slurry which was then applied to a stainless steel mesh. The electrode material was dried under vacuum at 240 °C prior to measurement. For comparison, standard electrodes were prepared using Ketjen Black (KJB) as the conductive additive. The wt% of KJB mixed with the vanadium oxide ambigel was comparable to that of the SWNT component in the nanocomposite. The same slurry and cathode preparation method was used as described for the nanocomposite.

The electrochemical measurements were carried out in an Ar-filled glove box. For the sticky carbon and nanocomposite electrodes, a conventional three-electrode cell with lithium foil reference and counter electrodes was used. The working electrode was either (a) the sticky-carbon electrode by itself (to determine the background), (b) the sticky-carbon electrode modified with the V₂O₅ aerogel powder, (c) the V₂O₅/SWNT electrode, or (d) the V₂O₅/KJB electrode. The arrangement for the vanadium oxide inverted opal electrode was slightly different. The closed end of the glass tube used in the templating procedure was cut off and replaced with a glass slide that was coated with a conducting film of indium-tin oxide (ITO). Since the inverted opal electrode adhered very well to the ITO coated glass slide, it was possible to establish an electrically conductive contact to the bottom of the templated electrode (i.e. a current collector). The ITO coated glass was attached (via epoxy) to the bottom of the glass tube so that once the V₂O₅ inverted opal electrode was fabricated, the glass tube was filled with electrolyte and served as the electrochemical cell. In this cell as well, lithium foil was the reference and counter electrodes. The electrolyte for nearly all the experiments was 1.0 M lithium perchlorate in anhydrous propylene carbonate (PC). In some experiments involving (a) and (b), an electrolyte of 0.1 M tetrabutylammonium perchlorate (TBAP) in propylene carbonate was utilized. Galvanostatic and cyclic voltammetry experiments were carried out using a computer-controlled EG&G PAR 273 potentiostat/galvanostat.
3. Results and discussion

3.1. Microstructural characterization

Table 1 compares multipoint BET surface areas and pore volumes for the various samples investigated in this work: xerogels, scd aerogels, ambigels and electrodes composed of an ambigel with the conductive additive. Depending upon the details of the aerogel drying process, mesoporous vanadium oxide materials with surface areas ranging from \( \sim 150 \) to \( 300 \) \( \text{m}^2/\text{g} \) were synthesized (Table 1). For comparison, a low surface area vanadium oxide xerogel (\( < 10 \) \( \text{m}^2/\text{g} \)) is also listed. The total pore volumes for these materials tend to scale with the surface area. In all cases, the values are \( < 1 \) \( \text{cm}^3/\text{g} \), indicating that these aerogels are much less porous than those used for thermal insulation [2]. The addition of SWNTs to the electrode leads to a slight decrease in surface area and pore volume, although it is evident that both the V_2O_5/SWNT and the V_2O_5/KJB intercalation electrodes effectively retain the pore volume of the initial V_2O_5 aerogel.

One of the motivations for investigating nanocomposites composed of V_2O_5 aerogels and SWNTs is that the similar morphology and dimensional scale for these two components may lead to improvements in electrochemical performance. Sol–gel derived vanadium oxide exhibits a characteristic ribbon morphology [11], which aggregates into fibers that are approximately 20–30 nm wide, while the SWNTs used in this study consist of bundles of nanotubes in which the characteristic bundle diameter is on the order of 10 nm [12]. Thus, the SWNTs can provide electronic conduction in the electrode without blocking electrolyte access to the active aerogel material. Traditional composite electrodes, however, are characterized by aggregation of the carbon black particles that serve as the electronic conductor [13]. These aggregates, hundreds of nanometers in diameter, may occlude the vanadium oxide aerogel surface. The schematic shown in Fig. 2 depicts the different types of morphology for electrodes based on carbon black and SWNTs. TEM of the V_2O_5/SWNT nanocomposite (Fig. 3) is consistent with the sketch drawn in Fig. 2(b). Intimate contact is established between the two components as several aerogel fibers are intertwined with several SWNTs. The contact between the two phases occurs at the nanodimensional level and is observed at multiple points along the ribbons. With this morphology, electrolyte access to the V_2O_5 aerogel is not likely to be hindered by the SWNT phase and, as described later, these electrodes are beneficial for achieving high lithium capacity at high discharge rates.

The vanadium oxide inverted opal electrode was designed to address a very different issue than that of the nanocomposite described above. In this case, the well-defined ordered channels of the inverted opal are expected to decrease path tortuosity and reduce the polarization which arises from impeding mass transport [8].
the vanadium oxide inverted opal electrode is hierarchical in nature, consisting of an ordered network of relatively large pores produced by templating, while the walls between the pores contain an interconnected network of mesopores from the ambient drying process. With this hierarchical architecture, the macro and mesoscale porosity are linked so that electrolyte from the large pores will effectively fill the smaller ones in the ambigel walls.

3.2. Electrochemical properties of vanadium oxide aerogels

The voltammetric responses for the aerogel immobilized on the sticky-carbon electrode are shown in Fig. 6 [10]. In the LiClO$_4$/PC electrolyte, the faradic features are broad and capacitive and the intercalation peaks appear superimposed upon the capacitive response (Fig. 6(a)). The background from the sticky-carbon electrode is negligible. As one goes to higher scan rates, the aerogel responds as a capacitor (Fig. 6(b)). This capacitive response is substantially different from that which is obtained for the same V$_2$O$_5$ aerogel when it is prepared in a conventional composite electrode structure (i.e. with KJB as the conductive additive). In this case, the electrode displays the characteristic intercalation behavior for sol–gel derived V$_2$O$_5$ materials (Fig. 6(c)).

The electrochemical responses for both the scd and ambigel samples can be described in terms of both a specific capacitance (F/g) and as lithium capacity (mAh/g). The data for the various samples are shown in Table 2. Depending upon the nature of the drying process, the specific capacitance values range from 960 to over 2000 F/g. The largest specific capacitance was obtained using cyclohexane.
as the drying solvent (2150 F/g) which corresponds to nearly 1500 μF/cm². This magnitude of specific capacitance represents pseudocapacitive behavior [14], which is a very different charge storage mechanism than that which occurs with traditional intercalation materials [2].

Electrochemical measurements using the TBAP electrolyte indicate a significantly lower capacitance (Fig. 6(d)). In this case, the response for the aerogel immobilized on the sticky carbon is greater than that of the sticky carbon background, but significantly less than that obtained in the Li⁺ electrolyte. The capacitance per unit area for this sample, 45 μF/cm², is consistent with what one obtains for surface-area-normalized double-layer capacitance at smooth electrodes. The interesting part of this experiment is that it represents a control; with the larger diameter of the TBA⁺ (~9 Å), only surface adsorption of the ion is expected. Thus, as indicated in Table 2, the substantially greater voltammetric charge that occurs using the Li⁺ electrolyte (430 μF/cm²) shows the importance of ion penetration in the V₂O₅ aerogel structure.

In comparing the data in Tables 1 and 2 one notices the influence of aerogel morphology on the electrochemical properties. It is evident from the two tables that the specific capacitance does not correlate with the BET surface area for the V₂O₅ aerogels. Instead, there is a fairly linear trend between specific capacitance and pore volume for the various aerogel samples [10]. This behavior indicates the importance of pore architecture. Supercritically dried aerogels have high surface areas but moderate pore volume because there are many nano-sized pores in the sample with

| Table 2 |
|------------------|------------------|------------------|
| **Electrochemical properties of V₂O₅ aerogels prepared by supercritical and ambient drying methods** |
| Drying solvent | Specific capacitance (F/g) | Lithium capacity (mAh/g) |
|-----------------|-----------------------------|--------------------------|
| Supercritical CO₂ | 1200 | 430 | 500 |
| Ambigel–heptane | 1280 | 640 | 450 |
| Ambigel–pentane | 960 | 520 | 400 |
| Ambigel–cyclohexane | 2300 | 1480 | 650 |
| Supercritical CO₂ using TBA⁺ | 140 | 45 | 100 |
3.3. Vanadium oxide-carbon nanotube composite electrodes

Battery electrodes require the addition of an electronically conducting phase to overcome the low electronic conductivity of transition metal oxides and facilitate electrochemical reactions [16]. Typically, carbon black is added and the battery electrode is a composite consisting of micron-dimension particles. The unique morphology of vanadium oxide aerogels raises the question of whether carbon black is the best conductive additive for this system. In contrast to carbon black, which can aggregate and impede electrolyte access, carbon nanotubes possess a similar morphology and dimensional scale as the vanadium oxide ribbons that compose the aerogel. This suggested the prospect of fabricating a nanocomposite which takes advantage of the high conductivity of SWNTs and does not block the high surface area of the aerogel. Moreover, in view of the capacitor-like behavior exhibited by the aerogel using sticky-carbon electrodes, and prior work with high conductivity metal fibers [17,18], it was anticipated that the V2O5-SWNT electrodes would have good performance at high discharge rates.

A series of experiments was carried out with the objective of comparing the rate capabilities for the different composite electrodes. In these experiments, the specific discharge capacity (mAh/g) was measured as a function of specific current (mA/g) for two different V2O5-SWNT nanocomposite electrodes (9 and 17 wt%) and compared to a traditional electrode (V2O5/KJB) which had an equivalent amount of conductive additive (17 wt%). The data (Fig. 7) indicate an interesting trend. At relatively low specific current (112 mA/g, which corresponds to a discharge rate of C/5) the specific capacities for the different electrodes are approximately the same. It would seem that kinetic limitations are insignificant at this discharge rate, and that high capacity values for V2O5 aerogels (~450 mAh/g) are obtained regardless of the conductive additive used in the electrode. At slightly higher specific currents (560 mA/g), differences begin to appear with respect to the conductive additive and it is evident that the specific capacities for the V2O5/SWNT electrodes are consistently higher than that of the corresponding V2O5/KJB electrode even though they both possess the same amount of conductive additive (17 wt%). Moreover, at rates above 1120 mA/g (2C), V2O5/SWNT electrodes containing about half as many carbon nanotubes (9 wt%) exceed the performance of the V2O5/KJB that contains 17 wt% carbon black additive. At 2800 mA/g, the highest rate tested in this study, the specific capacity for the V2O5/(17 wt%)SWNT nanocomposite
cathode is approximately twice as large as the V$_2$O$_5$/(17 wt%)KJB traditional electrode. An interesting consideration with these discharge rate experiments is that there are no appreciable differences in the basic morphology for each type of electrode (Table 1). The respective pore volumes are not substantially different, which means that electrolyte access is expected to be comparable for both types of electrodes. It would seem, therefore, that the nature of the electronically conducting network and the contact developed between the conductive component and the vanadium oxide phase must be prominent factors in achieving high rate capability. We have determined that the macroscopic conductivity for electrodes prepared with carbon nanotubes as the conductive network is substantially higher (by more than four times) compared to electrodes containing the same weight fraction of the KJB additive [7]. Another contributing factor may be the nature of the contact between the two components. SWNTs may offer better electronic ‘wiring’ to the porous aerogel morphology than carbon black aggregates. The intimate contact established at multiple locations between the V$_2$O$_5$ ribbons and SWNTs at the nanometer level (Fig. 3) is undoubtedly beneficial for retaining the high capacity of the vanadium oxide aerogel at high discharge rates. It seems, therefore, that the nanostructure of the aerogel-based intercalation electrode becomes an influential factor primarily at the higher discharge rates.

### 3.4. Inverted opal electrode architecture

The electrochemical properties of V$_2$O$_5$ electrodes with the inverted opal architecture are just at the demonstration stage [8]. Voltammetric responses are similar to that shown in Fig. 6(c), with clearly defined lithium insertion and de-insertion peaks and very good reversibility. Galvanostatic results at low discharge rates confirm this behavior [8]. Thus, it is evident that the hierarchical electrode exhibits electrochemical properties representative of V$_2$O$_5$ aerogels. The more significant issue to be addressed is whether the hierarchical electrode structure leads to improvements at high discharge rates because of reduced tortuosity and lower polarization. Although only qualitative results are available at the present time, the indications are very promising. At very high discharge rates (∼5 A/g), the V$_2$O$_5$ hierarchical electrode exhibits much less polarization than aerogel electrodes at lower specific currents (∼3 A/g) that are prepared by conventional methods. Moreover, the hierarchical electrodes reported to date contain no electronically conducting additive (i.e. carbon black or SWNTs), a feature which would reduce polarization effects still further. As methods develop to incorporate such additives, it is likely that hierarchical electrode structures offer the prospect of delivering the high capacity of V$_2$O$_5$ aerogels at extremely high discharge rates.

### 4. Conclusions

Aerogels possess a novel and very desirable microstructure for electrochemical systems. Diffusion lengths are short and the mesoporous morphology enables the electrolyte to penetrate the entire aerogel particle. In determining the electrochemical properties of these materials, it is critical that this morphology be preserved. This paper has reviewed the electrochemical properties obtained with three different electrode structures. To investigate the fundamental electrochemical properties of vanadium oxide aerogels, a sticky-carbon electrode was used to hold the submicron particles of the aerogel and provide excellent electrical contact to them without altering their distinct pore-solid nanostructure. With this electrode, the electrochemical properties display a unique combination of battery-like and capacitor-like responses. These measurements underscore the importance of defects contributing to the electrochemical properties of high surface area aerogels. The second type of electrode structure, which also preserved aerogel morphology, was directed at using carbon nanotubes as the electronically conducting network in V$_2$O$_5$ aerogel electrodes. The resulting nanocomposites exhibit intimate contact between the nanotubes and the vanadium oxide ribbons that compose the aerogel. The excellent electrochemical properties obtained with this nanocomposite are particularly evident at high discharge rates. The third electrode structure, which was also intended for high discharge rates, was based on an inverted opal architecture. The resulting structure is hierarchical in nature consisting of an ordered macroporous network, from templating of polystyrene spheres, while the walls between the pores contained the characteristic mesoporous morphology of V$_2$O$_5$ aerogels. The electrochemical properties of this electrode structure are just beginning to be determined.

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