



Synthesis and properties of polypyrrole–vanadium oxide hybrid aerogels

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Abstract

Vanadium pentoxide/polypyrrole aerogel composites were synthesized by two sol–gel routes. The first utilized simultaneous polymerization of pyrrole and vanadyl alkoxide precursors. Hydrolysis of $\text{VO}(\text{OC}_3\text{H}_7)_3$ using pyrrole/water/acetone mixtures over a range of compositions yielded monolithic green–black gels. Supercritical drying yielded aerogels ($150\text{--}257\text{ m}^2/\text{g}$, $0.1\text{--}0.2\text{ g}/\text{cm}^3$). These polypyrrole/ V_2O_5 ‘nanocomposites’ exhibited lower electrical conductivity with increased polypyrrole content. The second method involved oxide gel formation in the presence of a dispersion of preformed colloidal polypyrrole. SEM studies of the resulting ‘microcomposites’ aerogels ($80\text{--}140\text{ m}^2/\text{g}$) show the presence of polypyrrole particles encapsulated in the fibrous V_2O_5 network. These materials exhibit conductivity equivalent to that of vanadium pentoxide. The interaction between polypyrrole and V_2O_5 in the materials was probed using infrared spectroscopy. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supercritical drying of monolithic V_2O_5 gels formed from the rapid hydrolysis of vanadium alkoxides yield aerogels that display extremely high surface areas and controllable porosity [1]. These characteristics make them attractive as cathodes in rechargeable lithium batteries where kinetic barriers due to Li access and transport within the crystalline lattice can pose limits to attaining theoretical capacities [2]. Their low electrical conductivity can be partially overcome by the incorporation of conduc-

tive carbon. Li batteries comprising electrodes of these materials demonstrate relatively high lithium insertion capacity and energy density [3–6]. Nevertheless, neither of these methods fully capitalize on the high surface area available in the materials. A potential alternative to the addition of carbon is the incorporation of a conducting polymer into the aerogel structure. Polypyrrole (PPy) is an electronically conductive polymer which has received considerable attention due to its high electrical conductivity, stability in electrochemical environments, and promise as a cathode in lithium secondary cells [7]. The support of PPy on high surface area vanadium oxide aerogels thus offers the prospect of maximizing the performance of both inorganic and organic components.

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Two synthesis strategies, leading to very different microstructures, are presented in this paper. One approach involves in situ polymerization of the pyrrole monomer during the sol–gel condensation process [8]. This method leads to a monolithic inorganic/organic hybrid aerogel in which both components are mixed at the nanometer level. For comparison, we have also investigated a homogeneous ‘microcomposite’ consisting of preformed colloidal particles of polypyrrole encapsulated within the V_2O_5 gel. Our studies show that the interaction between the inorganic and organic components has a profound effect on the resulting electrical properties of the hybrid aerogel.

2. Experimental

Vanadium pentoxide aerogels containing PPy were synthesized using two variations of the sol–gel method. In the first method, the alkoxide and pyrrole were mixed in one vial and a water/acetone mixture was prepared in a separate vial. The two vials were cooled in ice prior to mixing, after which the water/acetone mixture was stirred into the casting vial containing the alkoxide and pyrrole. The molar ratio typically used was 1:40:17: p (vanadyl alkoxide:water:acetone:pyrrole) where p was varied from 0 to 1 to modify the PPy content. Gelation occurred within 75 s without pyrrole to yield transparent dark

red gels; the pyrrole containing materials gelled within 10–30 s resulting in deep green opaque gels. Some preparations involved the pre-oxidation of the pyrrole monomer with ammonium peroxydisulfate (0.075 mol/V) prior to its reaction with the alkoxide.

Vanadium oxide/polypyrrole microcomposite aerogels were synthesized by forming the oxide gel in the presence of a dispersion of preformed PPy. Pyrrole was polymerized according to the procedure used by Myers [9], vacuum dried for 4 h at 65°C and ground into a fine powder. The desired quantity of polymer was then added to a solution of water and acetone. A relatively stable dispersion was formed by mixing the solution using an automatic stirrer at 8000 rpm. The polymer dispersion was poured into the casting vial containing the vanadyl alkoxide (1:40:18 mol, V:water:acetone), shaken quickly and allowed to gel.

The wet gels from both syntheses were aged for at least 4 days in sealed containers. The gels were then immersed in acetone for a day to promote exchange of the water in the gel pores for acetone. After four such treatments, the gels were transferred to an autoclave for supercritical extraction by CO_2 [1]. The resultant dark-green cylinder-shaped monoliths had dimensions of approximately 1 cm in diameter, several cm in length.

The density of the aerogels was determined using Hg pycnometry. BET analysis (Micromeritics) was used to measure specific surface area. FTIR data

Table 1
Comparison of physical and electrical properties for $[PPy]_p V_2O_5$ aerogels

Composition	p	ρ (g/cc)	σ $T = 25^\circ\text{C}$ (S/cm)	Surface area (m^2/g)	Oxidizing agent
V_2O_5		0.10	2×10^{-4}	150	None
PPy		1.6	1.6×10^{-2}	< 1	Ferric chloride
$[PPy]_{0.6}V_2O_5$	0.3	0.19	2×10^{-4}	184	None
$[PPy]_{0.6}V_2O_5$	0.3	–	–	257	Ammonium peroxydisulfate
$[PPy]_{1.0}V_2O_5$	0.5	0.22	2×10^{-6}	–	None
$[PPy]_{1.4}V_2O_5$	0.7	0.20	4×10^{-7}	179	None
$[PPy]_{1.8}V_2O_5$	0.9	0.25	2×10^{-8}	–	None
$[PPy]_{2.0}V_2O_5$	1.0	0.15	–	160	None
$[PPy]_{2.0}V_2O_5$	1.0	0.12	2×10^{-6}	200	Ammonium peroxydisulfate
microcomposite $[PPy]_{1.0}V_2O_5$	0.5	0.14	3×10^{-4}	–	(pre-polymerized) Ferric chloride
microcomposite $[PPy]_{2.0}V_2O_5$	1.0	0.18	3×10^{-4}	140	(pre-polymerized) Ferric chloride
microcomposite $[PPy]_{3.0}V_2O_5$	1.5	0.16	3×10^{-4}	–	(pre-polymerized) Ferric chloride
microcomposite $[PPy]_{6.0}V_2O_5$	3.0	0.19	3×10^{-4}	80	(pre-polymerized) Ferric chloride

were obtained from KCl pellets on a Nicolet FT-IR spectrometer operating between 400 cm^{-1} to 4000 cm^{-1} . Samples of V_2O_5 and $\text{PPy}_{2p}\text{V}_2\text{O}_5$ aerogels were prepared for detailed FTIR spectroscopy, using deuterium-labeled water (D_2O). Variable temperature electrical conductivity was measured (150 to 25°C) using a two-point ac impedance method in flowing argon [1].

3. Results

Vanadium alkoxide was hydrolyzed and co-polymerized with pyrrole to form $\text{PPy}/\text{V}_2\text{O}_5$ aerogel nanocomposites. Addition of pyrrole has little effect on aerogel density, as the $\text{PPy}/\text{V}_2\text{O}_5$ aerogels exhibited slightly increased densities of about 0.2 g/cm^3 (Table 1). The composition of the as-prepared aerogel nanocomposites has been determined to be $\text{PPy}_{2p}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ where $p = 0.15$ to 1.0 and $n = 2.4$ to 3.1 . A second approach involved addition of an aqueous dispersion of pre-polymerized polypyrrole to the vanadium alkoxide thus triggering hydrolysis of the alkoxide. Gelation was within 10 s thus polymer colloid particles were encapsulated in the vanadium oxide gel network.

BET analysis indicated that the surface areas of the nanocomposites prepared by simultaneous polymerization are similar to that measured for pure V_2O_5 aerogels. The $\text{PPy}_{2p}\text{V}_2\text{O}_5$ samples exhibited surface areas between 150 and $250\text{ m}^2/\text{g}$ (Table 1). Samples prepared by the dispersion method exhibited a slightly lower surface area of 80 – $140\text{ m}^2/\text{g}$ due to the presence of relatively dense polypyrrole particles within the aerogel matrix.

The TEM and SEM micrographs reveal the structural contrasts between the hybrid materials and the pristine vanadium oxide aerogel. Whereas the fibers for the V_2O_5 aerogel displayed a long, ribbon-like structure similar to that previously reported for vanadate aerogels (Fig. 1a) [1], those of the polymer-aerogel were much shorter in length, and were aggregated in a random fashion (Fig. 1b). This morphology is substantially different than that of aerogel microcomposites prepared using the dispersion method, which consisted of PPy particles encapsulated in the fibrous V_2O_5 network (Fig. 1c).

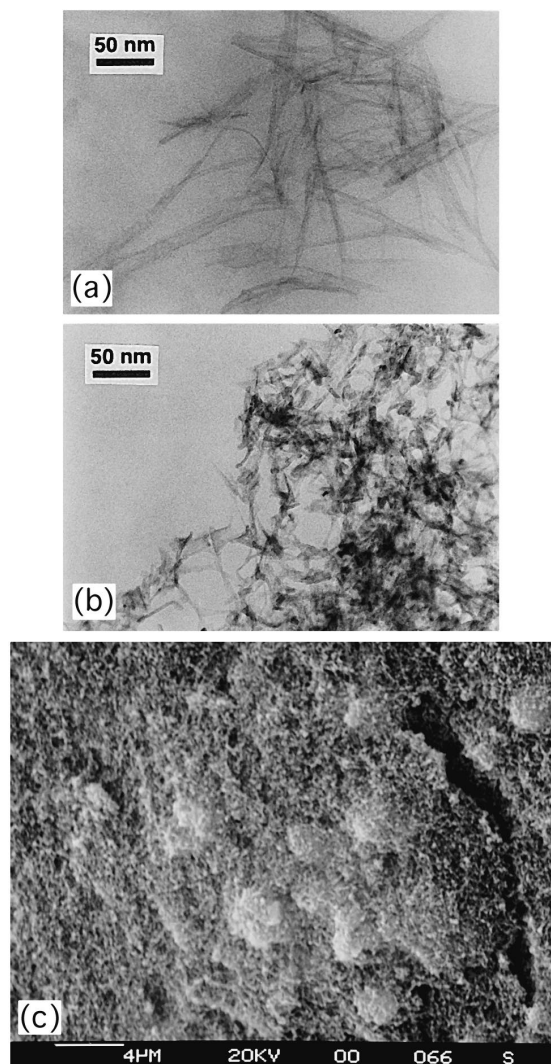


Fig. 1. TEM micrographs of (a) V_2O_5 aerogel; and (b) $[\text{PPy}]_{0.5}\text{V}_2\text{O}_5$ nanocomposite aerogel prepared by simultaneous polymerization, showing the interrupted chain growth; (c) SEM micrograph of $[\text{PPy}]_{1.0}\text{V}_2\text{O}_5$ microcomposite prepared by the dispersion method.

FTIR spectra of the aerogel nanocomposites provide insight concerning the nature of the interaction between the PPy and the V_2O_5 framework. The pristine V_2O_5 aerogel exhibits two vibrational modes in the 400 – 800 cm^{-1} range due to the symmetric stretch (ν_{sym} at 542 cm^{-1}) and the asymmetric stretch (ν_{as} at 772 cm^{-1}) of $\text{V}-\text{O}-\text{V}$ [10]. We found that both modes shift to higher wavenumber with increas-

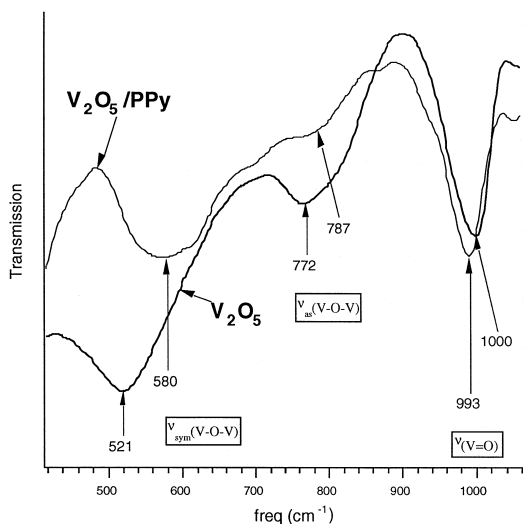


Fig. 2. FTIR spectra of V_2O_5 aerogels and V_2O_5/PPy composite aerogel showing effects of PPy intercalations upon $\nu_{sym}(V-O-V)$, $\nu_{as}(V-O-V)$ and $\nu(V=O)$. The shift in absorption of the $\nu_{sym}(V-O-V)$ mode from 542 to 521 cm^{-1} is a result of using ^{18}O -labeled water in the synthesis of the V_2O_5 aerogel sample.

ing PPy content. The ν_{sym} mode at 542 cm^{-1} in the pristine V_2O_5 sol-gel is increased to 580 cm^{-1} in samples containing 1:1 molar ratio of PPy (Fig. 2). In contrast, the vanadyl stretch ($\nu_{v=0}$) which occurs at 1000 cm^{-1} in the V_2O_5 aerogel, shifts down to 993 cm^{-1} on incorporation of the polymer.

The major factor in the shift of the $V=O$ band is the contribution of H-bonding interactions. In order to determine the nature of the H-bonding interaction between the PPy polymer and the inorganic matrix, spectra were obtained on samples prepared in D_2O . FTIR spectra of pure V_2O_5 materials show an absence of isotope shifts for the $\nu(V=O)$ mode at 1000 cm^{-1} and indicate a lack of hydrogen bonding interactions. However, this mode in $[PPy]_{1.0}V_2O_5$ aerogels downshifts to 987 cm^{-1} in the D_2O -labeled samples (Fig. 3). The development of H-bonding interactions between the V_2O_5 matrix and the polymer appears to be a principal factor for decreased $V=O$ bond strength in the nanocomposite materials. Collectively, our results therefore suggest a presence of $V=O \cdots H$ type units in the nanocomposite materials. Significantly, both the shifts in the $V-O-V$ bands, and the $V=O$ bands were not observed in the

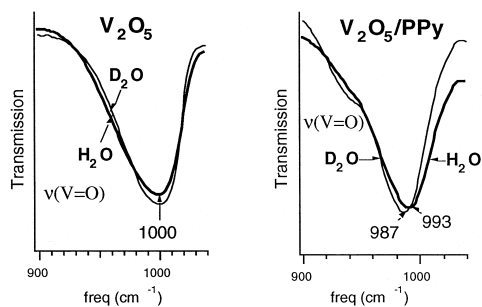


Fig. 3. FTIR spectra of (a) V_2O_5 aerogel; (b) V_2O_5/PPy composite aerogel showing effects of D_2O labeling.

microcomposite materials prepared by the dispersion method, suggesting a lack of the described interactions.

Fig. 4 shows the results of the complex impedance measurements. For the $PPy_{2p}V_2O_5$ nanocomposites, the conductivity decreases with increasing PPy content. At 25°C, the conductivity decreases by a factor of 10^4 as p increases from 0 to 0.9 (Table 1). The activation energy changes only slightly from that of pure V_2O_5 (0.23 to 0.32 eV). In contrast to this behavior, the microcomposites exhibit no change in conductivity from that of pure V_2O_5 aerogel despite the fact they contain as much as 75 mol% PPy.

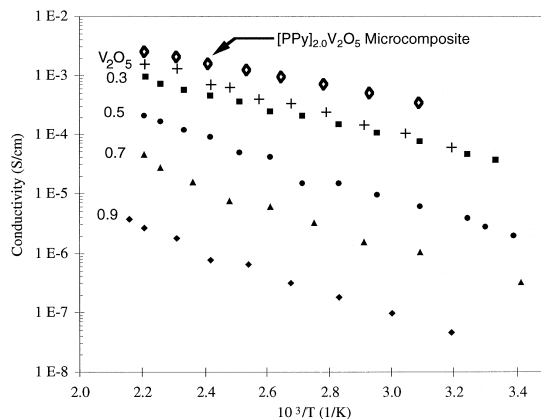


Fig. 4. Arrhenius plot of $[PPy]_{2p}V_2O_5$ aerogels where $p = 0-1$. The points represented are: pure V_2O_5 (+ data points, $p = 0$), $[PPy]_{2p}V_2O_5$ (solid data points, $p = 0.3-0.9$), and $[PPy]_{2.0}V_2O_5$ microcomposite prepared by the dispersion (open diamond data points, $p = 1.0$).

4. Discussion

TEM, conductivity and FTIR results collectively point to an intimate and strong interplay of the inorganic and organic components in the nanocomposite material, as opposed to the microcomposite material. There are two types of vibrational modes whose shifts indicate the nature of the interaction. The shifts of the $\nu(\text{V}=\text{O})$ modes indicate that increased H-bonding effects are observed in the nanocomposite material. The H-bonding upon PPy intercalation can be ascribed to interaction with the organic moiety. The second type of vibrational mode that is affected by the interaction is the V–O–V stretch. The observed upshifts of both the vibrational modes, $\nu_{\text{sym}}(\text{V}=\text{O}-\text{V})$ and $\nu_{\text{as}}(\text{V}=\text{O}-\text{V})$, on PPy incorporation is consistent with increased bond strengths of the bridging V–O–V groups in the composite. One tentative mechanism that may account for the observed increase in V–O–V bonding interaction is based on the change in coordination geometry at the metal center. The V ions in V_2O_5 adopt a square pyramidal coordination with the V atoms occupying a position slightly above the basal plane [11,12]. The distorted geometry is facilitated by the strong V=O interaction. A decrease in V=O interaction in the nanocomposite material is likely to alter the coordination geometry. A change in position of the V ions, caused by decreased axial interaction, such that it occupies a position in the VO_4 plane will result in increased in-plane bonding interactions. The V–O–V groups in the V_2O_5 -based materials lie in the plane and the strong H-bonding induced elongation of V=O bond is likely to induce structural distortions at the metal center that can account for the observed strengthening of the V–O–V bonds.

Results indicate that the interaction influences the microstructure and the electrical conductivity. In the nanocomposite systems, polymerization of the PPy network is effectively caused by a redox reaction with the inorganic component, leading to the formation of V^{4+} which in turn catalyzes the rate of the condensation of the V_2O_5 network. The latter effect is well-known for the corresponding V_2O_5 xerogels [2,13]. It is demonstrated here by the considerably shorter gelation time for the system. Thus we have a ‘double’ polymerization process that results in a homogenous composite as desired, but one in which

the rapid polymerization rate of the inorganic polymer leads to interrupted growth of the characteristic ribbon morphology of V_2O_5 , as shown in the TEM photomicrographs.

The microstructure of the inorganic/organic nanocomposite has a profound effect on the electrical conductivity. In the case of simultaneous polymerization, the truncation of this fibrous structure by interaction with the occluded PPy disrupts charge transport within the continuous V_2O_5 phase. We see a direct correlation of lower conductivity with increased PPy content. However, it is possible to increase the conductivity through the addition of an oxidizing agent (Table 1). In comparison, the dispersion method leads to isolated PPy particles encapsulated in the continuous V_2O_5 phase. In this case, the addition of PPy has no effect on the gelation rate of the V_2O_5 , enabling the characteristic V_2O_5 ribbon structure to develop. Thus, the observed conductivities are independent of PPy content and comparable to that of the pristine V_2O_5 aerogel. The expected conductivity increase upon addition of the conductive polymer was not observed because the particles were effectively isolated and did not form a continuous phase within the matrix.

5. Conclusions

Two routes were used to synthesize vanadium pentoxide/polypyrrole hybrid aerogels over a range of controlled compositions. In situ polymerization led to nanocomposites with high surface areas (150–257 m^2/g) and low densities (0.1 to 0.2 g/cc). Electrical conductivities of these hybrid aerogels were lower than that of V_2O_5 aerogels because of interaction between the organic and inorganic components. Vanadium pentoxide/polypyrrole microcomposites exhibited similar densities but somewhat lower surface areas. The microstructures of these materials consisted of polypyrrole particles isolated within the V_2O_5 aerogel matrix.

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