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Vanadium Oxide/Polypyrrole Aerogel Nanocomposites

by

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VANADIUM OXIDE/POLYPYRROLE AEROGEL NANOCOMPOSITES

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ABSTRACT

Vanadium pentoxide/polypyrrole aerogel (ARG) nanocomposites were prepared by hydrolysis of $\text{VO}(\text{OC}_3\text{H}_7)_3$ using pyrrole/water/acetone mixtures. Monolithic green-black gels with polypyrrole/V ratios ranging from 0.15 to 1.0 resulted from simultaneous polymerization of the pyrrole and vanadium alkoxide precursors. Supercritical drying yielded high surface (150-200 m^2/g) aerogels, of sufficient mechanical integrity to allow them to be cut without fracturing. TEM studies of the aerogels show that they are comprised of fibers similar to that of V_2O_5 ARG's, but with a much shorter chain length. Evidence from IR that the inorganic and organic components strongly interact leads us to propose that this impedes the vanadium condensation process. The result is ARG's that exhibit decreased electronic conductivity with increasing polymer content. Despite the unexpected deleterious effect of the conductive polymer on the bulk conductivity, at low polymer content, the nanocomposite materials show enhanced electrochemical properties for Li insertion compared to the pristine aerogel.

INTRODUCTION

In contrast to the well-known aqueous sol-gel route to V_2O_5 xerogels, hydrolysis of vanadium alkoxides results in rapid reaction to form monolithic V_2O_5 gels that can be supercritically dried to form aerogels. As shown by previous studies, these materials display extremely high surface areas and controllable porosity.¹ These characteristics make them extremely attractive as cathodes in rechargeable lithium batteries where kinetic limitations due to Li access and transport within the crystalline lattice pose difficulties in attaining theoretical capacities. Improved capacity for Li insertion, for example, has been observed for aerogel² and xerogel V_2O_5 ³ over that of highly crystalline V_2O_5 prepared by high temperature (HT) synthesis.

An intriguing idea is that of combining the conductive and redox properties of conjugated polymers with those of the V_2O_5 framework in its aerogel form, to maximize surface area, redox capacity and possibly introduce capacitance effects. Numerous xerogel (but not aerogel) V_2O_5 -polymer nanocomposites have been reported, including those of polyaniline⁴ and polypyrrole⁵ in which the polymer chains are interleaved between the oxide sheets. At high polymer content, these show improved conductivity compared to pristine V_2O_5 xerogels. Furthermore, our recent electrochemical studies on polyaniline-nanocomposites of HTaWO_6 ⁶ and MoO_3 have shown enhancement in lithium ion mobility.⁷ These findings have prompted us to develop methods for the synthesis of polymer/oxide aerogels, and examine their electrochemical properties.

EXPERIMENTAL

Monolithic polymer/vanadium aerogels were prepared by hydrolyzing a vanadium alkoxide solution in acetone with water/pyrrole/acetone mixtures at 0 °C. Two methods of preparation were employed. In the first method, the reaction mixture with a typical molar composition 1.0 $\text{VO}(\text{OC}_3\text{H}_7)_3$: 40 H_2O : 17 $(\text{CH}_3)_2\text{CO}$: y $\text{C}_4\text{H}_4\text{NH}$ was rapidly mixed, and immediately transferred

to a test-tube. Gelation occurred within 10-30 seconds for most samples, resulting in deep green-black gels. The ratio of pyrrole was varied from 0.15 to 1.0 moles /VO(OR)₃, and the water-acetone molar ratio was also varied extensively over a wide composition range. The second method involved the pre-oxidation of the pyrrole monomer with (NH₄)₂S₂O₈ (0.075 mole/V) prior to its reaction with the alkoxide. Upon addition of the oxidant, the pyrrole/water/acetone mixture changed from translucent to opaque dark green; after 30 minutes, polypyrrole precipitated. The solution was allowed to polymerize to different extents before it was cooled to ~0°C and added to the alkoxide (~3°C). Gelation occurred within 10 seconds.

The wet gels were aged for 4 days in capped tubes that had a 1mm hole in the cap, to allow for slow evaporation of the solvent within the wet gel. This resulted in a small amount of shrinkage (15%) and densification that strengthened the gels. After aging, the gels were removed, and immersed in acetone for a day to promote exchange of the water in the gel pores for acetone. This procedure was repeated 4 times to ensure complete exchange. The gels were transferred to the pressure vessel (Polaron E3000 Critical Point Dryer) for supercritical extraction by CO₂.¹ The resultant dark-green cylinder-shaped monoliths had dimensions of approximately 1x3 cm.

The density of the aerogels was determined using a pycnometer vial filled with Hg. Surface area measurements (N₂ absorption) were conducted on a Quantachrome Autosorb-1 system and analyzed by the BET method. The electrical conductivity of the aerogels was measured between 25 and 180 °C by the complex impedance method, similar to that reported previously.¹ Two probe measurements were performed in flowing argon on disc-shaped samples that were heat-treated at 140 °C for 24 hours, using a HP Precision LCR meter (20Hz to 1MHz). TEM was performed on a Phillips CM30. FTIR data were obtained as KBr pellets on a Nicolet FT-IR spectrometer operating between 400 cm⁻¹ to 4,000 cm⁻¹.

PPY was intercalated into the xerogel by a variation of the method reported by Kanatzidis *et al.*⁵ Powder XRD patterns of the precipitate matched those reported, with an interlayer spacing of 13.8Å. The mole fraction of polypyrrole per V₂O₅ was determined to be 0.40 by TGA.

For electrochemical studies, the aerogel was mixed with 30-85 wt % Ketjen carbon black, and 2 wt % ethylene propylene diene monomer (EPDM). The resulting composite was pressed onto a fine stainless steel grid and heated at 100 °C for 2 hours to form the electrode with a surface area of 1 cm². A 1.0 M solution of LiClO₄ in propylene carbonate served as the electrolyte. Swagelock-type cells were assembled in an argon atmosphere, and studied under galvanostatic conditions between constant voltage limits using a MAC-PILE.TM The discharge cut-off voltage was chosen based on the stability of the electrolyte previously studied with V₂O₅ (HT).⁸

RESULTS

Surface Area/morphology. The synthesis of vanadium oxide aerogels by an alkoxide based sol-gel route has been described previously. In this study, vanadium alkoxide was hydrolyzed and copolymerized with pyrrole during sol formation to form polypyrrole/vanadium oxide aerogel nanocomposites. Incorporation of the polymer resulted in fragile aerogels when the same conditions were used to age and dry the samples as those for V₂O₅ aerogels. We found that this could be compensated by partial drying of the wet gel in air under ambient conditions, which resulted in strengthening (and shrinking) of the nanocomposites. The degree of shrinkage varied between samples, resulting in densification of the gels compared to those that were not subjected to partial drying. For pure V₂O₅ aerogels, the latter exhibited average densities of 0.1 g/cc; gels subjected to a partial drying regime yielded densities in the range of 0.2 g/cc. The addition of pyrrole has little effect on aerogel density, as the [PPY]V₂O₅ ARGs (all partially dried) exhibited slightly increased densities of about 0.2 g/cc (Table 1). The nanocomposites also have surface

areas similar to those of the V_2O_5 aerogel (about 150-200 m^2/g). These values are slightly lower than the 300-400 m^2/g range reported previously prepared using different synthesis conditions.

Table 1: Properties of $[PPY]_{2y}V_2O_5$ ARG Nanocomposites

Pyrrole/V ratio (y)	ρ (g/cc)	σ (S/cm) $T=25^\circ C$	surface area(m^2/g)	Sample
0	0.1	2×10^{-4}	150	*1
0.15	0.25	a	a	*2
0.3	0.19	3×10^{-5}	a	*3
0.4	0.18	1×10^{-6}	a	*4
0.5	0.22	2×10^{-6}	a	*5
0.7	0.20	4×10^{-7}	a	*6
0.9	0.25	2×10^{-8}	a	*7
1.0	0.15	a	160	*8
0.5	0.12	1×10^{-6}		#9
1.0	0.12	2×10^{-6}	200	#10

^a not measured
* samples 1-8 prepared *without* oxidizing agent
samples 9-10 prepared *with* oxidizing agent

XRD studies showed that both V_2O_5 and $[PPY]V_2O_5$ ARG's exhibit a very low degree of crystallization compared to their respective 2D xerogel forms. TEM studies also showed a distinct difference in their fibrous morphology. Whereas the fibers for the V_2O_5 aerogel displayed a long, ribbon-like structure similar to that previously reported for vanadate xerogels,¹ those of the polymer-aerogel were much shorter in length, and were aggregated in a random fashion.

FTIR. Figure 1 shows the FTIR spectrum of the aerogel nanocomposite between 2000 and 400 cm^{-1} . The bands in the region 1600-900 cm^{-1} are diagnostic of polypyrrole, and their position and intensities show that the conductive form of the polymer is produced (Table 2). The bands exhibit

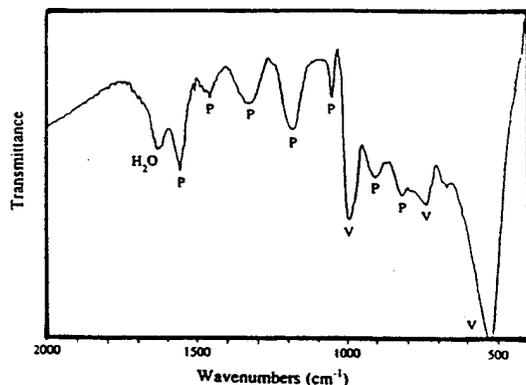


Fig.1 IR spectrum of $[PPY]_{0.5}V_2O_5$

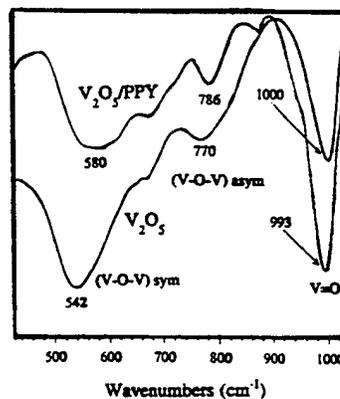


Fig. 2 IR of V_2O_5 and $[PPY]_{2.0}V_2O_5$ in the region 1000-400 cm^{-1}

shifts from those of bulk, p-doped PPY,⁹ suggesting that a substantial interaction with the V_2O_5 framework occurs. The chain length and conductivity of the PPY can be estimated from the ratio of the A'/B' bands at 1580 and 1460 cm^{-1} respectively. Studies of bulk PPY show a linear

relationship between this ratio and the log of the conductivity of the polymer.⁹ Using this data, together with the A'/B' value in the nanocomposite, ($\cong 5.0$), interpolation indicates that the PPY component appears to be relatively conductive (1 S/cm).

Table 2: FTIR Peak Positions for Polypyrrole and PPY/V₂O₅ Nanocomposites

Material	A' cm ⁻¹	B' cm ⁻¹	C' cm ⁻¹	D' cm ⁻¹	E' cm ⁻¹	F' cm ⁻¹
PPY ₅ V ₂ O ₅ ARG	1561	1461	1331	1184	1053	905
⁹ conductive PPY	1560	1480	1320	1178	1047	901
⁹ insulating PPY	1523	1440	1207	1076	1038	919
¹⁰ PPY ₄ MoO ₃	1551	1465	1321	1189	1049	906

The bands corresponding to the inorganic component are also assigned in Figure 1. Due to the presence of V-O-V moieties in the structure, two vibrational modes are expected in the 400-800 cm⁻¹ region, corresponding to the symmetric (ν_{sym}) and asymmetric (ν_{asym}) stretch. These were assigned to the bands at 542 cm⁻¹ and 772 cm⁻¹ respectively, based on our studies using ¹⁸O-labelled H₂O that will be reported elsewhere. We found that both modes shift to higher wavenumber with increasing PPY content (Figure 2). For example, in samples containing a 1:1 molar ratio of PPY:V, the ν_{sym} mode shifts up by 38 cm⁻¹ to 580 cm⁻¹, and the asymmetric mode shifts to 786 cm⁻¹. In contrast, the vanadyl stretch ($\nu_{\text{V=O}}$) which occurs at 1000 cm⁻¹ in the V₂O₅ ARG, shifts down to 993 cm⁻¹ on incorporation of the polymer, implying either increased V⁴⁺ content in the lattice or a weakening of the V=O bond. The V-O-V band "up-shift" is inconsistent with increased V⁴⁺ content: however, it could be explained by a reduced V-O-V bond length caused by weak binding of the nitrogen atom of the pyrrole ring to the sixth apical coordination site on the square-pyramidal V site. Binding of nitrogen-containing ligands with SP-coordinated V in vanadates has been observed for pyridine, for example.¹¹ This would also partially account for the down-shift of the V=O band, as the vanadyl bond would lengthen as a result of such an interaction. The major factor in the shift of the V=O band, however, is the contribution of H-bonding interactions. Spectra obtained on PPY-V₂O₅ aerogels prepared in D₂O showed a sensitivity to deuterium substitution (typically, the V=O mode shifted from 993 to 987 cm⁻¹) in contrast to the pure V₂O₅ ARG's which showed no change. These results further confirm the presence of highly interacting inorganic-organic components in these hybrid materials.

Conductivity. The samples were heat treated prior to AC impedance measurements to partially

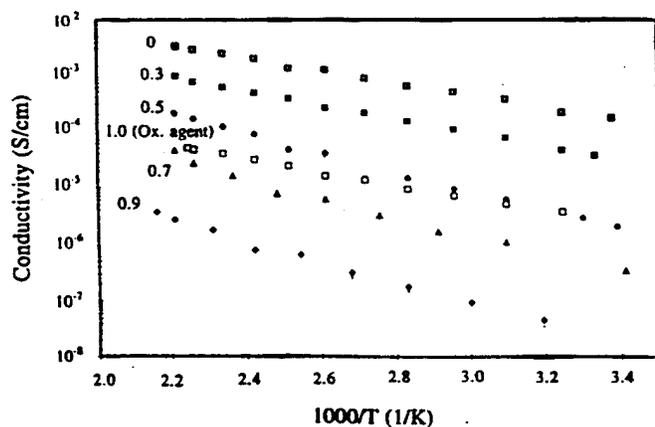
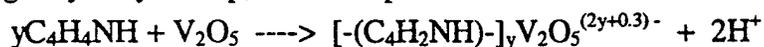


Fig. 3 Log σ vs $1000/T$ for [PPY]_{2y}V₂O₅ at varying ratios y of PPY/V (denoted on the fig.)

remove the water within the interlamellar gap of the V₂O₅. TGA of the aerogels indicated 10% mass loss at 180°C, corresponding to a composition [PPY]V₂O₅•0.6 H₂O. The conductivity of pure V₂O₅ aerogel varies linearly with respect to density. The conductivity increases by a factor of 5 when the density is increased from 0.1 to 0.25; however, the conductivity of the [PPY]V₂O₅ samples *decreases* with increasing polypyrrole content, despite the increase in density. Figure 3 shows the results of the AC

highest RT conductivity of 2×10^{-4} S/cm. The solid data points represent [PPY]V₂O₅ synthesized using Method 1. There is a dramatic reduction in conductivity as the ratio of pyrrole monomer to vanadyl alkoxide reaches 0.9. We found, however, that this could be compensated by using an external oxidizing agent. The open data points in Figure 3 represent [PPY]_{2.0}V₂O₅ samples prepared using method 2. The conductivity in this sample is increased by two orders of magnitude, although the value is still less than that of pure V₂O₅ aerogel. The reason for the decrease in conductivity with increasing polymer content is not evident at this stage, but is clearly related to the significant changes in the IR spectra of these materials, and the strong interaction of the polymer with the inorganic framework. Future studies will focus on samples with higher ratios of oxidizing agent and lower amounts of polypyrrole.

Electrochemistry. By insertion of a conductive polymer in V₂O₅, we can expect active participation of the organic component in the redox process of the cathode. Reaction of pyrrole, during the sol-gel hydrolysis step, reduces a portion of the V⁵⁺ to V⁴⁺, according to the reaction:



This takes into account the $2e^-$ /monomer oxidative polymerization of the pyrrole; and a further $0.3 e^-$ oxidation to obtain the doped polymer.¹² The reaction implies that the reducing power arises solely from the V₂O₅, although it is very likely that atmospheric oxygen plays a major role in the oxidation process, as well as oxidizing highly reduced vanadium sites. Nonetheless, incorporation of more conductive polymer in the nanocomposite results in overall less V⁵⁺ sites that are available for reduction.

Carbon black was added to the nanocomposite material to increase the electronic conductivity, which is standard practice for the formation of the positive electrode in lithium batteries. For 30% carbon black, the faradaic capacity decreases from 3.1 to 1.0 as the polypyrrole content (y) increases from 0 → 0.5 → 1.5 moles. This is accompanied by an equivalent decrease in the open-circuit voltage from 3.52V → 3.35V, consistent with increasing V⁴⁺ content. The experimental capacities are still, however, much less than the theoretical value, suggesting that there is either an electronic and/or ionic limitation. The first could be offset by increasing the carbon black fraction in the composite electrode. Electrodes prepared from [PPY]_{0.5}V₂O₅ with 85% C results in a substantial increase in capacity, showing that there is indeed an electronic limitation. The carbon black also has an intrinsic faradaic capacity characteristic of behavior that results from interfacial adsorption/desorption phenomena.¹³ Carbon aerogels and several high-surface area carbons can display this effect, which typically gives rise to capacitance on the order of 20-100 F/g. In our case, the capacitance of about 65 F/g (determined from cyclic voltammetry) accounts for approximately 40% of the response of the composite electrode.

The effect of an initial charge on subsequent electrochemical processes has different effects on the pristine vs the [PPY]V₂O₅ aerogel. During a charge, both V⁴⁺ and PPY can be oxidized; the respective electrochemical processes corresponding to the deintercalation of Li and adsorption of ClO₄⁻. For [PPY]V₂O₅, a charge to 3.8V appears to be reversible in terms of faradaic capacity, and is equivalent to a charge after beginning the cycle with a discharge (Figure 4b). Conversely, for the PPY-free V₂O₅ aerogel, an initial charge *increases* the capacity of the subsequent discharge (compared to a second discharge after beginning the cycle in discharge first) and hence changes the reduction process compared to the polymer aerogel (Figure 4a). In this case, the dx/dV (electronic density/mole) curves show a shift of the main redox process to 2.6V (vs Li) from that at 2.2V observed for the V₂O₅ ARG in charge first. This indicates that the first processes are not equivalent; with respect to either the capacity, or the Li potential sites that are occupied. Moreover, polymer/V₂O₅/C electrodes exhibit a lower degree of polarization compared

to V_2O_5/C in the same voltage range, at the same carbon content (85%). This effect, in addition to the other factors, gives rise to an increase in the faradaic capacity from 4.0 to 5.0 F/mole.

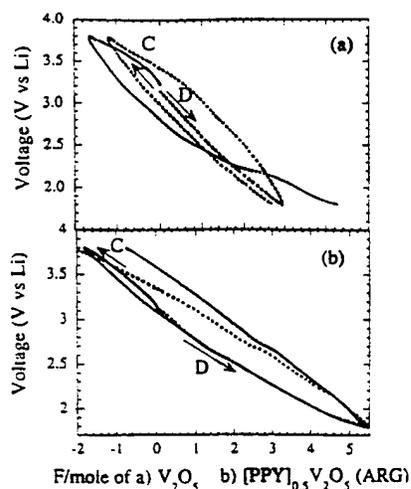


Fig. 4 Effect of a charge/discharge on the capacity of the ARG's with and without PPY in the voltage range 3.8-1.8V vs Li.

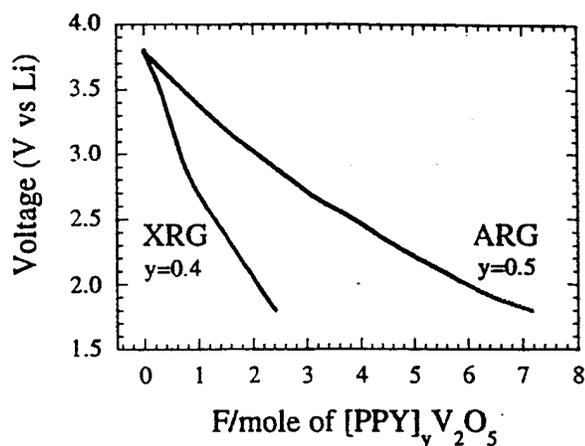


Fig. 5 Comparison of the capacity (on first discharge) of $[PPY]_yV_2O_5$ in aerogel and xerogel forms.

Furthermore, comparison of both the aero and xerogel nanocomposites (containing the same fraction of PPY, and the same percentage of carbon black) shows that both curves possess two distinct slopes (Figure 5). The aerogel electrode, however, exhibits a capacity almost 3 times greater than that of the corresponding xerogel.

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