JOURNAL OF Materials CHEMISTRY

Synthesis and characterization of a new organo–inorganic poly(3,4-ethylene dioxythiophene) PEDOT/V_2O_5 nanocomposite by intercalation

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Received 19th January 2001, Accepted 19th June 2001
First published as an Advance Article on the web 31st August 2001

We have developed a novel nanocomposite material, PEDOT/V_2O_5 by inserting poly(3,4-ethylene dioxythiophene) PEDOT in V_2O_5 layers using oxidative polymerization/intercalation in air. A systematic study of the synthesis of the nanocomposites by direct *in situ* reaction of 3,4-ethylene dioxythiophene (EDOT) with V_2O_5 fine powder shows that upon intercalation, the interlayer spacing of V_2O_5 expands in two stages, *i.e.*, first from 4.32 to 13.84 Å and further to 19.04 Å. The interlayer separation is consistent with the existence of two phases in the PEDOT/V_2O_5 system corresponding to the intercalation of one and two monolayers of PEDOT, respectively, in the V_2O_5 framework. The unique properties of the organo–inorganic composites are investigated by electronic conductivity measurements, X-ray diffraction, FTIR spectroscopy, thermogravimetric analysis and SEM. The application potential of these composites as cathode materials in rechargeable lithium batteries is also demonstrated by the electrochemical intercalation of lithium into the PEDOT/V_2O_5 nanocomposites, where an enhancement in the discharge capacity (240 mA h g^{-1}) is observed compared to that (140 mA h g^{-1}) observed for V_2O_5.

Introduction

Recently, soft chemistry ("*Chimie douce*") has been shown to be an effective method for the preparation of conducting polymer based nanocomposites for several applications such as light emitting diodes, supercapacitors, chemical sensors, and nonlinear optics.[1–4] The low temperature processing of such nanocomposites is especially relevant in the area of rechargeable lithium batteries where the composition and structure can be modulated to obtain many advantages such as the formation of amorphous matrices to facilitate lithium ion transport, flexibility with respect to fabrication, high energy density, good cycle life, *etc.*[5–8] Although the early studies on two-dimensional or layered oxides/sulfides of transition metals primarily involved the intercalation of simple, small molecules or ions into van der Waals gaps, later several new classes of these materials were developed based on the extension of these concepts, including the incorporation of macromolecular species.[9,10] In particular, the insertion of conjugated polymers has been examined extensively over the past few years.[11–23] One approach is based on the oxidation of the polymer backbone (p-doping), where the method provides materials that are highly conductive, and poses fascinating questions as to the change in their properties upon intercalation. For example, the degree to which the polymer–polymer interactions in the bulk are affected by the polymer host is not clear and questions related to how the polymer–host interactions sequester the polymer chains affecting either the polymer conformation, chain length, and/or bulk electron-transport properties are not fully elucidated. In addition, there is also the possibility of electron or hole transfer between the polymer and the inorganic component especially if the latter is a transition metal oxide with conductive properties.[24] More significantly, the application of either conjugated polymers[25] or transition metal oxides[26] individually as positive electrodes in rechargeable lithium batteries also suggests that when these polymer/oxide materials are blended together at a "nanoscale" level new properties are possible due to synergistic effects.

During the past several years many conducting polymers have been inserted into layered transition metal oxides to form nanocomposites. For example, Kanatzidis, Gomez-Romero, and their co-workers have inserted polyaniline, one of the few conducting polymers that is completely air stable in the p-doped form into V_2O_5 to form a nanocomposite.[27–30] Unfortunately, owing to the possible presence of benzidine moieties in the polymer backbone, the application of these systems is limited since they might yield toxic (carcinogenic) products upon degradation.[31] Numerous industrial and academic groups have considered alternatives to polyaniline including the (hetero) aromatic polypyrrole and polythiophene, two more "environment friendly" systems.[32] In this context it may be better to use poly(3,4-ethylene dioxythiophene) (PEDOT), one of the recently found excellent conducting polymers, as it has been reported to exhibit greatly enhanced stability compared to polypyrrole and polyaniline.[33,34] Indeed, it appears to be one of the most stable conducting polymers currently available[35] and has been attracting growing interest for applications in supercapacitors[36,37] and lithium ion batteries.[38–40]

In this communication we report the successful preparation of PEDOT/V_2O_5 nanocomposites by a soft method of intercalation, where the resulting nanocomposite shows improved room temperature conductivity and enhanced lithium ion mobility compared to the polymer free vanadium oxide. The primary objective is to characterize the redox intercalation reaction of EDOT with V_2O_5 powder and the subsequent

DOI: 10.1039/b100714i

polymerization chemistry associated with this system to demonstrate the existence of two phases in the PEDOT/V_2O_5 system corresponding to the intercalation of one or two monolayers of PEDOT into V_2O_5. These observations are supported by several physicochemical data and the microstructure of PEDOT/V_2O_5 nanocomposites, attributed in part, to the polymer propping open the inorganic layers, effectively reducing electrostatic and steric effects which hinder lithium diffusion through the material. Preliminary measurements on the PEDOT/V_2O_5 nanocomposite system during few initial charge–discharge cycles show an excellent capacity of 240 mA h g^{-1} compared to 140 mA h g^{-1} observed for V_2O_5, after coupling these nanocomposites as cathodes with a lithium metal anode using 1 M $LiClO_4$ in a mixed electrolyte of ethylene carbonate and dimethyl carbonate. To our knowledge, this is the first study of electrochemical Li-insertion into a PEDOT/vanadium oxide nanocomposite, which shows that the improved capacity is related to the presence of the conducting polymer in the interlamellar region.

Experimental

Materials

Vanadium pentoxide (99%), lithium metal foil (99.9%), $LiClO_4$ (99.99%) and dimethyl carbonate (DMC, 99%), purchased from Aldrich were used without further purification. Ethylene dioxythiophene (Bayer AG Germany) was distilled under vacuum prior to use; ethylene carbonate (EC, Prolabo 99%), Chevron Carbon black and PTFE (Teflon) binder were used as received. All the experiments were conducted with double distilled water.

Characterization

Fourier transform infrared (FTIR) spectra were recorded from pressed KBr pellets using a Perkin-Elmer spectrum-2000 FTIR spectrometer. The X-ray powder diffraction studies were carried out with a Bruker AXS D5005 instrument in the range 3–80° using Cu-Kα radiation. Thermogravimetric analysis (TGA/DTA) was performed with a Shimadzu TGA-50 thermal analysis system using dry oxygen as a carrier gas. The TGA experiments were conducted from room temperature to 800 °C at a linear heating rate of 10 °C min^{-1}. Electronic conductivity measurements were made on compactions of powder in pellet form by using a four probe conductivity method, while scanning electron microscopy (SEM) images were taken on a Philips XL-30 microscope after mounting samples on Al stubs with gold coatings. The electrochemical measurements were performed using a computer controlled Tacussel, PGS 201T model, potentiostat/galvanostat. Elemental analysis was carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer 1000) and using a CE-Instruments-EA 1110 CHNS-O Analyser.

Synthesis of PEDOT/V_2O_5 nanocomposites

Insertion of PEDOT into V_2O_5 by a soft process in aqueous medium was carried out by dissolving a given amount of EDOT in double distilled water and refluxing this with crystalline vanadium pentoxide for 12 h. The molar ratio of EDOT/V_2O_5 was varied from 0.02 to 0.6 in five different compositions. After completion of the reaction, the solid was filtered off and washed repeatedly with water and acetone until the initial light yellow color in the filtrate was totally absent, and the bluish black powder was dried in air. The vanadium content was determined by applying ICP-OES analysis to the sample solution that was prepared by placing the composite powder in a concentrated sulfuric acid solution to dissolve the V_2O_5 in the composite, followed by dilution with water and filtration to remove the dispersed polymer. Elemental analysis of nanocomposites: $(C_6H_4O_2S)_{0.02}{\cdot}V_2O_5$ **A**: C, 0.84%; H, 1.15%; S, 0.17%; V, 44.53%. $(C_6H_4O_2S)_{0.04}{\cdot}V_2O_5$ **B**: C, 1.35%; H, 1.48%; S, 0.28%; V, 43.67%. $(C_6H_4O_2S)_{0.08}{\cdot}V_2O_5$ **C**: C, 2.12%; H, 1.61%; S, 1.09%; V, 39.15%. $(C_6H_4O_2S)_{0.40}{\cdot}V_2O_5$ **D**: C, 6.92%; H, 1.54%; S, 3.77%; V, 34.36%. $(C_6H_4O_2S)_{0.60}$ V_2O_5 **E**: C, 9.01%; H, 1.07%; S, 4.86%; V, 33.66%.

Electrochemical measurements

Electrochemical measurements were carried out using composite cathodes, prepared by mixing the PEDOT/V_2O_5 nanocomposite powder with carbon black and PTFE binder (70 : 25 : 5 by weight), followed by compaction and drying under a primary vacuum for 3 h at 80 °C. This composite cathode was coupled with a lithium foil anode in 1 M $LiClO_4$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (50/50 by volume) to form the electrochemical cell. All charge–discharge measurements were performed in galvanostatic mode using a computer controlled potentiostat/galvanostat. All manipulations of air sensitive materials as well as the cell assemblies were carried out in an inert atmosphere of an argon filled glove box.

Results and discussion

The intercalation of EDOT in V_2O_5 powder is a redox reaction in which EDOT is oxidatively polymerized, concomitantly reducing vanadium during the refluxing conditions to form a relatively quasi-crystalline layered material, and is associated with a dramatic color change to dark blue. Generally if the solvent containing EDOT is able to swell the V_2O_5 powder, the intercalation reaction is observed to be fast whilst there was no swelling (or intercalation) if V_2O_5 was refluxed with neat EDOT. Water is reported to be a good solvent for the completion of polymeric intercalation in oxide layers, in comparison with organic solvents;[29] water molecules can be expelled from the slightly hydrophobic intragallery space during intercalation, allowing more polymer to be inserted. The composites obtained from the reaction between EDOT and V_2O_5 in aqueous medium showed good lamellar order, as judged by the following physicochemical characterization techniques.

X-Ray diffraction and SEM studies

Fig. 1 shows a comparison of the powder XRD patterns for the series of PEDOT/V_2O_5 composites and V_2O_5 to demonstrate the subtle structural changes upon intercalation. The strongest peak observed at low angle corresponding to the (001) plane of the layered V_2O_5 structure is directly related to the interlayer spacing. The main features of the V_2O_5 diffraction pattern in the composites are clearly modified by the appearance of a sharp diffuse scattering feature and an increase in the intensity of the (001) peak. Within the series of nanocomposites, a clear change in the position of the peak takes place, which indicates differences between samples. Samples **A**–**C** with EDOT/V_2O_5 ratios of 0.02–0.08 show the (001) peak at 2θ 6.6–6.4°, which corresponds to an interlayer spacing of 13.84–14.02 Å, respectively, *cf.* the interlayer spacing of V_2O_5 of 4.32 Å. More interestingly, this peak in the patterns for **D** and **E** has shifted to lower angle, 5.0 to 4.5°, corresponding to an interlayer spacing of 17.8 and 19.04 Å, respectively, which is substantially larger than that found for the samples **A**–**C**.

This behavior is summarized in Fig. 2 (also see inset), where the evolution of the *c* parameter is shown in relation to the nominal EDOT/V_2O_5 ratio used in the preparation of each sample. There are two regions with qualitatively different features, which confirm the existence of phases with distinct structures. This suggests that PEDOT intercalation occurs in

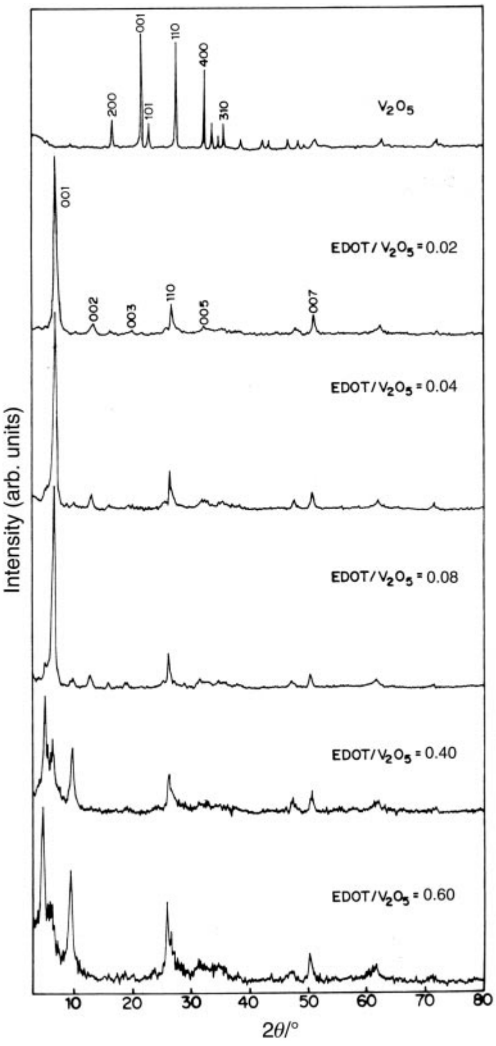
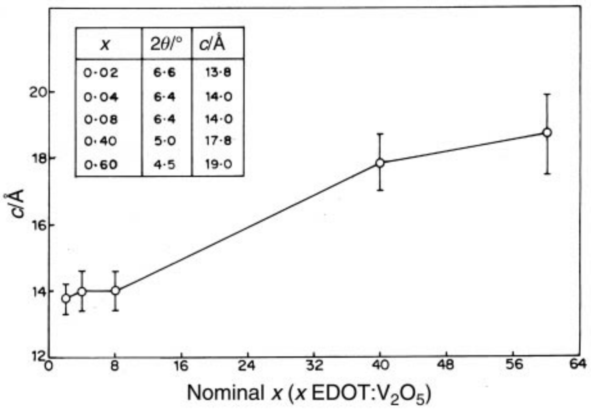


Fig. 1 Powder X-ray diffraction patterns of V_2O_5 powder and PEDOT/V_2O_5 nanocomposites **A**–**E** synthesized with different ratios of EDOT/V_2O_5.

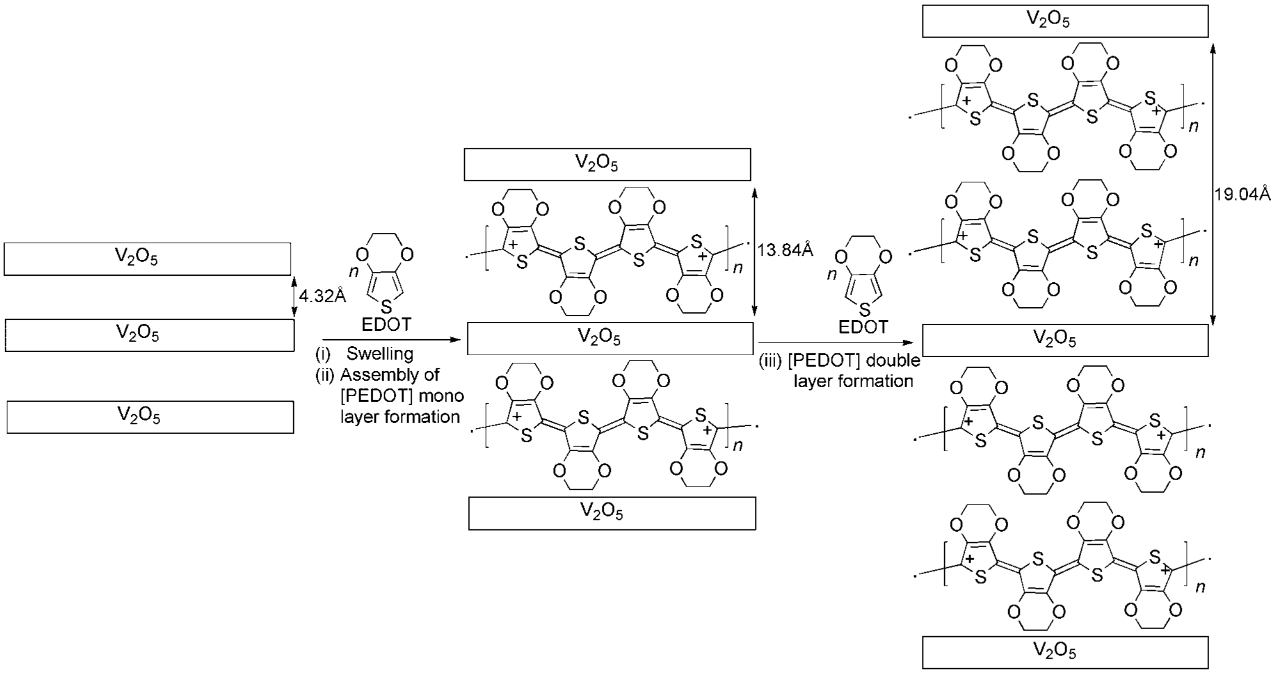


x	2θ/°	c/Å
0·02	6·6	13·8
0·04	6·4	14·0
0·08	6·4	14·0
0·40	5·0	17·8
0·60	4·5	19·0

Fig. 2 Plot of interlayer spacing in V_2O_5 (*c* parameter in Å, calculated from the position of 001 peaks) *vs.* the EDOT/V_2O_5 ratio as derived from Fig. 1.

two steps, leading to the formation of two correspondingly different phases. The first one represents an expansion from 4.32 to 13.84 Å and can be explained by monolayer formation of PEDOT. On the other hand, the formation of the second phase, associated with an additional expansion of the *c* parameter to 19.04 Å indicates double the amount of PEDOT between layers per V_2O_5 unit as reported recently for the PANI/V_2O_5 system.[30] Thus it is likely that these materials constitute a new PEDOT/V_2O_5 composite phase consisting of a double layer of PEDOT chains intercalated within the V_2O_5 interlayer spacing. (see Scheme 1)

SEM micrographs of V_2O_5 and a synthesized PEDOT/V_2O_5 composite are illustrated in Fig. 3. It is apparent that PEDOT/V_2O_5 composites form a continuous and relatively homogeneous matrix with a clearly lamellar morphology. It is evident that the incorporation of PEDOT into the V_2O_5 leads to morphological changes in agreement with the results of XRD patterns, but these can be seen only at high resolution. More significantly, the SEM micrographs also suggest that there is no bulk deposition of polymer on the surface of the micro-crystallites.



Scheme 1 Schematic diagram of the swelling and assembly process of monolayer and double-layer formation of PEDOT into the V_2O_5 layers during preparation of the nanocomposites.

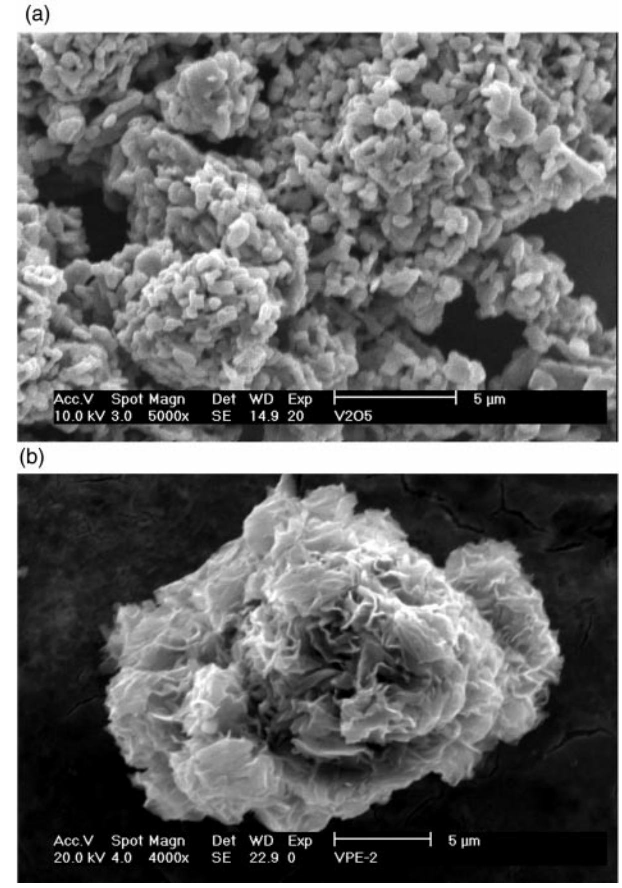


Fig. 3 SEM micrographs of (a) V_2O_5 and (b) PEDOT/V_2O_5 nanocomposite **C** synthesized with EDOT/$V_2O_5 = 0.08$.

FTIR spectroscopic studies

Fig. 4 shows the FTIR spectra of different samples of PEDOT/V_2O_5 nanocomposites synthesized with various amounts of EDOT as described above. The spectrum for **C** (EDOT/$V_2O_5 = 0.08$), is discussed as a representative example, which presents the characteristic bands corresponding to PEDOT (bands in the range 1049–1600 cm^{-1}) as well as bands at lower frequencies assigned to V_2O_5 (523 and 759 cm^{-1} for V–O–V stretching modes and 1003 cm^{-1} for V=O stretching). The changes in position and shape of the vibrational peaks of the vanadium oxide framework are also significant. The V=O peak shifts from 990 to 1003 cm^{-1} while the V–O–V vibrational peaks shift from 852 and 530 cm^{-1} to 758 and 523 cm^{-1}, respectively. These changes are attributed to the greater number of V^{4+} centers present in the nanocomposite. The mechanism of this remarkable all-solid-state intra-lamellar polymerization is presumed to be coupled to the ability of vanadium centers[41] to activate oxygen. Therefore, vanadium oxide plays a direct role in this redox event, which is consistent with its ability to catalyze several oxidation reactions of organic molecules.[42] The qualitative differences between spectra of **D** and **E** relative to nanocomposites **A**–**C** relate to bands at 1218 and 1105 cm^{-1} owing to the presence of excess PEDOT in these two samples.

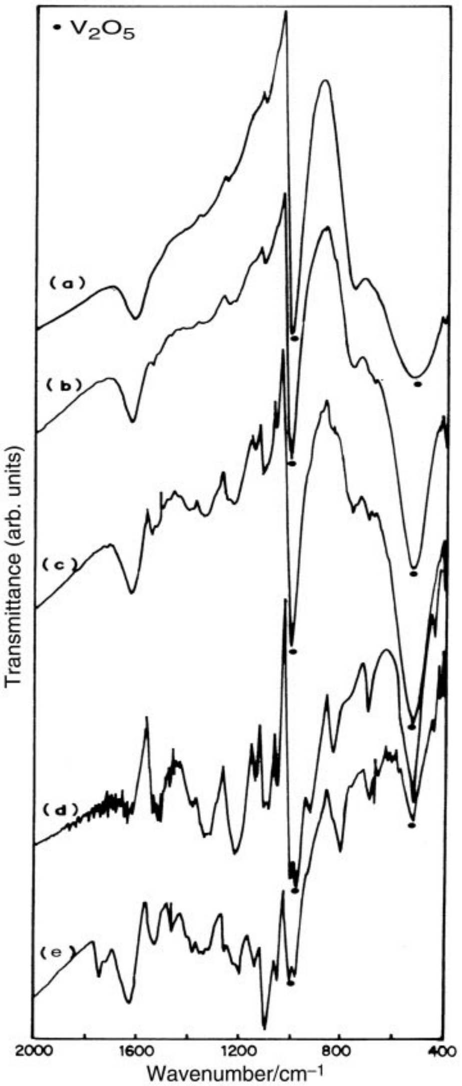


Fig. 4 FTIR spectra of the PEDOT/V_2O_5 nanocomposites **A**–**E** obtained with different EDOT/V_2O_5 ratios; (a) 0.02, (b) 0.04, (c) 0.08, (d) 0.40, (e) 0.60; peaks assigned to V_2O_5 are indicated by filled circles.

Thermogravimetric analysis

The thermal stability of these materials in air was examined by TGA experiments. Two distinct stages were observed in the thermogravimetry and differential thermal analysis (TGA–DTA) curves as shown in Fig. 5. The first step, up to 120 °C, corresponds to the removal of the reversibly bound water, whereas the second step at ~215 °C corresponds to the loss of more strongly bound water between the layers. This is followed by a continuous weight loss up to ~420 °C which can be attributed to the combustion of the organic polymer component, in agreement with the exothermic peak in the DTA curve. A subsequent mass gain up to 650 °C can be attributed to the formation of orthorhombic V_2O_5. Crystallization of this phase was evidenced from the DTA curve which showed a relatively sharp endotherm peak at 650 °C. These results suggest that the insertion and polymerization of the 3,4-ethylene dioxythiophene (EDOT) monomer is accompanied by 'sacrificial' reduction of the V_2O_5 layers.

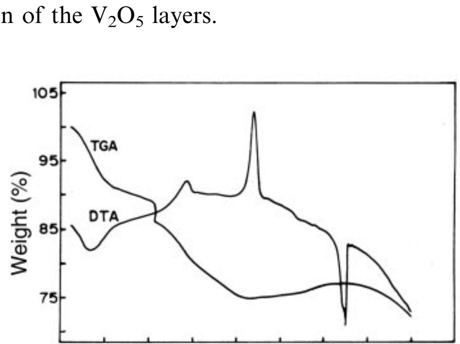


Fig. 5 TGA–DTA curves of PEDOT/V_2O_5 composite **C** (ratio of 0.08), as a representative example.

Table 1 Comparison of room temperature conductivity, interlayer spacing and open circuit voltage with EDOT/V_2O_5 ratio in composites **A**–**E**

	Nanocomposite	EDOT : V_2O_5 ratio	Interlayer spacing/Å	Electronic conductivity, σ/S cm^{-1}	Open circuit voltage^a/V
1.	V_2O_5		4.32	8.78×10^{-5}	3.43
2.	**A**	0.02	13.84	2.92×10^{-3}	3.74
3.	**B**	0.04	14.00	6.97×10^{-3}	3.76
4.	**C**	0.08	14.02	3.84×10^{-2}	3.77
5.	**D**	0.40	17.80	9.82×10^{-2}	3.62
6.	**E**	0.60	19.04	1.01×10^{-1}	3.61

^{a}The open circuit voltage is obtained from the charge–discharge measurements of V_2O_5 and PEDOT/V_2O_5 nanocomposites synthesized from EDOT/V_2O_5 (ratio 0.02–0.6), as a cathode material by coupling with a lithium metal anode using 1 M $LiClO_4$ in a mixed electrolyte of ethylene carbonate and dimethyl carbonate.

Electronic conductivity

The electrical transport behavior of nanocomposites can be understood by considering the insertion of poly(3,4-ethylene dioxythiophene) in V_2O_5 powder as a composite system in which two different types of low-dimensional electronic conductors coexist at the molecular level in a dimensionally constrained environment. Two types of charge carriers can be present in these materials, small polarons (electrons) associated with the d^1 (V^{4+}) centers on the vanadium oxide lattice, and large polarons on the poly(3,4-ethylene dioxythiophene) backbone. The actual nature of charge transport would depend on the relative mobility of these two different types of carriers as demonstrated by the fact that the electronic conductivity of PEDOT/V_2O_5 is 10^4 times higher than that of pristine V_2O_5. In all samples, the conductivity is almost exclusively electronic under our experimental conditions, and increases with temperature as has been observed in most intercalated compounds and conjugated polymers.[12–42] For similar PEDOT/V_2O_5 samples synthesized with different nominal EDOT/V_2O_5 ratios, the room temperature conductivity varies from 10^{-1} to 10^{-5} S cm^{-1}. In this case the increase in conductivity is probably due to a continued process of growth of the organic polymer network. The conductivity increases as the length of polymer chain increases from **A**–**E** although the exact mechanism may be complex (see Table 1)

Electrochemical lithium insertion

Vanadium oxide host lattice has been proposed as a good cathode material in secondary Li-batteries, mainly due to its layered structure which is highly suitable for Li-insertion.[43,44] For battery applications, the rate limiting step is reported to be the reduction of V_2O_5 material during discharge accompanied by Li^+ insertion.[45] One common strategy to achieve higher efficiency and lithium uptake is to use high surface area materials, so that the distance over which Li^+ must diffuse through the host material is minimized.[46–50] For example, V_2O_5 nanotubes have been recently reported to give rise to a discharge capacity of 186 mA h g^{-1} compared to 140 mA h g^{-1} observed for the bulk oxide.[51] Another approach that has not been completely explored yet is to manipulate the interlayer spacing in these layered materials by using various intercalants so as to enhance the rate of Li^+ migration (it is well-known that intercalation leads to changes in the interlayer spacing for layered materials).[52,53] Examples of such intercalants include pyrrole and aniline, which are known to oxidatively polymerize when intercalated into highly oxidizing materials such as V_2O_5.[15–23] The electrochemical insertion of Li in V_2O_5 material can be described by the redox couple of eqn. (1).

$$x\mathrm{Li}^+ + x\mathrm{e}^- + \mathrm{V_2O_5} \leftrightarrow \mathrm{Li}_x\mathrm{V_2O_5} \qquad (1)$$

For PEDOT/V_2O_5 nanocomposites, we can write analogous electrochemical reactions [eqns. (2) and (3)] after incorporating lithium ions between the layers

$$[\mathrm{PEDOT}^+]_x\mathrm{V_2O_5^{x-}} + x\mathrm{Li}^+ + x\mathrm{e}^- \xleftrightarrow{\text{Reduction of PEDOT}} \mathrm{Li}_x[\mathrm{PEDOT}]_x\mathrm{V_2O_5^{x-}} \qquad (2)$$

$$\mathrm{Li}_x[\mathrm{PEDOT}]_x\mathrm{V_2O_5^{x-}} + y\mathrm{Li}^+ + y\mathrm{e}^- \xleftrightarrow{\text{Reduction of } \mathrm{V_2O_5^{x-}}} \mathrm{Li}_{x+y}[\mathrm{PEDOT}]_x\mathrm{V_2O_5}^{-(x+y)} \qquad (3)$$

The open-circuit voltage (OCV) of the composites when coupled with a lithium metal anode is found to be a function of the PEODT/V_2O_5 ratio and clearly all nanocomposites give higher OCV values (3.61–3.77) than that observed (3.43) for pure V_2O_5 (Table 1). The discharge process of the Li/V_2O_5 cell seems to be thermodynamically more favorable as the deviation from open circuit voltage is less for a given current density. However, the discharge capacity is found to be significantly enhanced (240 mA h $g_{\mathrm{composite}}{}^{-1}$ for PEDOT/V_2O_5 nanocomposites compared to 140 mA h g^{-1} for pure V_2O_5) under similar experimental conditions. A typical example is illustrated in Fig. 6 showing the charge–discharge behavior of pure V_2O_5 and a representative example of a nanocomposite, **A** (EDOT/V_2O_5 ratio of 0.02). Better reversibility for the composite is also suggested by the reduced overpotentials reflected in both charge and discharge curves. This indicates that the effect of PEDOT intercalated into the V_2O_5 framework in enhancing the discharge capacity of V_2O_5 material can be attributed to the changes in the interlayer spacing due to more facile lithium ion diffusion.

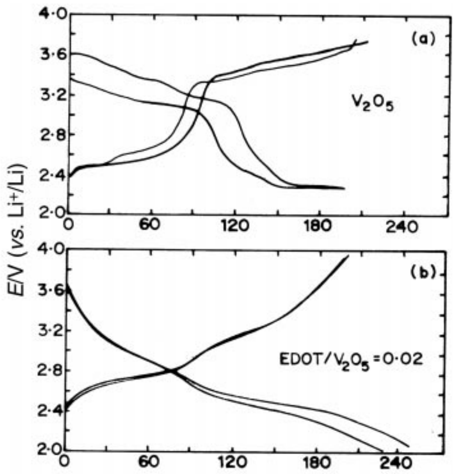


Fig. 6 Typical charge–discharge curves of (a) V_2O_5 and (b) PEDOT/V_2O_5 nanocomposite **A** (EDOT/V_2O_5 ratio of 0.02), as a cathode material by coupling with a lithium metal anode using 1 M $LiClO_4$ in a mixed electrolyte of ethylene carbonate and dimethyl carbonate using a constant current density of 15 mA g^{-1} (electrode surface area is ~1 cm^2).

Conclusions

We have found a novel method of interleaving poly(3,4-ethylene dioxythiophene) between the layers of V_2O_5 using a soft process of intercalation. The reaction takes place with the *in situ* polymerization of EDOT within the framework of V_2O_5 with different nominal EDOT/V_2O_5 ratios to give two distinct phases. These two phases can be distinguished by their different interlayer spacings as detected from powder X-ray diffraction patterns. The fact that two distinct phases rather than a continuum of compositions are obtained in this system suggest the existence of a significant interaction between the host and guest beyond simple insertion into van der Waals gaps and is closer to the formation of true compounds. The experimental data presented here suggest that polymerization proceeds concomitantly with intercalation. The polymer chains appear fixed in the interlamellar space, and the ring flips observed in the bulk form of PEDOT are frozen in these materials. Therefore, there is considerable bonding interaction between the organic and inorganic components, probably due to hydrogen bonding. We observed that the influence of intercalants on Li^+ diffusion rates and charge capacity in the PEDOT/V_2O_5 nanocomposite was increased relative to V_2O_5. The results also suggest that the polymer nanocomposites act as better cathode materials than the pristine V_2O_5 oxide material by enhancing lithium diffusion.

Acknowledgements

A. V. M. would like to thank Dr B. K. Das (Executive Director, C-MET) and gratefully acknowledge to Messrs Bayer AG, Germany, Mr S. D. Joshi (Bayer India Ltd. Mumbai) and Dr Tanay Seth for SEM analysis, Mr S. K. Apte for FTIR analysis, Mr P. Sasidharan, Mr S. N. Potty for XRD analysis and Mrs S. D. Adyanthaya (NCL) for thermogravimetric analysis.

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