

Electrochemical lithium insertion into a poly(3,4-ethylenedioxythiophene)PEDOT/V₂O₅ nanocomposite

A. Vadivel Murugan^{a,*}, Chai-Won Kwon^b, Gay Campet^b, B.B. Kale^a,
Trupti Maddanimath^c, K. Vijayamohan^c

^aCentre for Materials for Electronics Technology, Ministry of Information Technology, Government of India, Panchwati, Pashan Road, Pune 411 008, India

^bInstitut de Chimie de la Matière Condensée de Bordeaux du CNRS, Chateau Brivazac, Avenue du Dr. A. Schweitzer, 33608 Pessac, France

^cPhysical and Materials Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Abstract

A nanocomposite comprised of conductive poly(3,4-ethylene dioxythiophene)PEDOT chains interleaved between the layers of crystalline V₂O₅ powder has been synthesized by direct in situ oxidation. The interlayer spacing of V₂O₅ expands from 4.32 to 13.84 Å and this interlayer separation is consistent with the existence of a monolayer of PEDOT in the V₂O₅ framework. The nanocomposite is coupled with a large-area Li foil counter electrode and a Li wire reference electrode in 1 M LiClO₄ in a mixture of ethylene and dimethylcarbonate (50/50 by volume), the discharge capacity is ≥ 300 m Ah g⁻¹ which is larger than that of pristine V₂O₅. The significant difference in capacity is explained on the basis of lithium ions insertion/de-insertion between the layers of V₂O₅. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Research on active electrode materials for rechargeable lithium batteries is intense at present [1]. Recently, electrochemically conducting polymer-based molecular nanocomposites with transition metal oxide and sulfide have been synthesized by different approaches [2–7]. Vanadium oxide has been selected as the host lattice mainly because of its well-known performance as a good cathode material for rechargeable Li-batteries. This is due to its layered structure which is immensely suitable for Li insertion [8,9]. For battery applications, the rate-limiting step is reported to be the reduction of V₂O₅ during discharge accompanied by Li⁺ insertion [10]. 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 [11,12]. For example, V₂O₅ nanotubes have been reported [13] to give 186 m Ah g⁻¹ compared with 140 m Ah g⁻¹ observed for bulk oxide. Another approach that has not been completely explored yet is to manipulate the interlayer spacing in these layered materials using various intercalants so as to enhance the rate of Li⁺ migration since it is well-known that intercalation leads to changes in the

interlayer spacing for layered materials [14–16]. Examples of such conducting polymer intercalants, e.g. polyaniline have certain limitations such as the possible presence of benzidine moieties in the polymer backbone which might yield toxic (carcinogenic) products upon degradation [17]. Consequently, it is important to develop new nanocomposites based on the (hetero) aromatic thiophene monomer, which are known to be more “eco-friendly” systems to undergo oxidative polymerization when intercalated into highly oxidizing materials such as V₂O₅. Poly(3,4-ethylene dioxythiophene), hitherto referred to as PEDOT, is one of the recently found excellent conducting polymers and has been attracting growing interest for applications in supercapacitor and lithium-ion batteries [18–21]. Hence, we have selected this to design a new nanocomposite by intercalation into a V₂O₅ host and the results indicate that the nanocomposite is highly attractive for applications such as cathodes in lithium-batteries due to several improved properties, viz. room temperature conductivity and lithium-ion transport.

To our knowledge, this is the first study of preparation and electrochemical Li-insertion using such a nanocomposite, based on the PEDOT/V₂O₅ system. We find that PEDOT/V₂O₅ nanocomposites display higher discharge capacities and greater reversibility for Li-insertion than those observed for V₂O₅ alone.

* Corresponding author. Tel.: +91-20-589-8390; fax: +91-20-589-8180.
E-mail address: vadivel12@hotmail.com (A.V. Murugan).

2. Experimental

The PEDOT/ V_2O_5 nanocomposites were prepared by the soft process of refluxing an aqueous solution which contained crystalline V_2O_5 powder and 3,4-Ethylene dioxy thiophene (EDOT) (0.02–0.08 molar ratio) under air for 12 h. After completion of the reaction, the solid was filtered off and washed repeatedly with water and acetone, and then dried at room temperature. Powder X-ray diffraction was performed (Bruker AXS D5005 using Cu $K\alpha$ radiation) to study the formation of a polymer monolayer in the V_2O_5 layer upon intercalation. Fourier transform-infra red (FT-IR) spectra were recorded on Perkin-Elmer spectrum 2000 and thermogravimetric analysis was conducted using a Shimadzu TGA-50 instrument. The room temperature conductivity measurements were made on compactions of powder in pellets form by using a standard four-probe method. Electrochemical experiments were conducted with similar pellets of the nanocomposite (70 wt.% mixed with 5 wt.% polytetrafluoro ethylene and 25 wt.% acetylene black) as the working electrode. The electrode had a geometric area of 1 cm^2 and contained $\sim 20\text{ mg}$. This was coupled to a Li foil counter electrode of larger area and a Li wire references electrode in 1 M $LiClO_4$ in a mixture of ethylene and dimethyl carbonate (50/50 by volume) to form the cell. A constant current of 15 mAh g^{-1} was applied between 2.0 and 4.2 V (versus Li^+/Li) for V_2O_5 or between 2.0 and 4.4 V for the hybrids. All charge-discharge and cyclic voltammetry measurements were performed using a compute-controlled potentiostat/galvanostat (Tacussel, PGS 201T model). The cell assemblies were carried out in an inert atmosphere of an argon filled glove box.

3. Results and discussion

3.1. FT-IR spectroscopic studies

Fig. 1 shows the FT-IR spectra of different samples of PEDOT/ V_2O_5 nanocomposites synthesized with various amounts of EDOT as presented above. The spectrum for C (EDOT/ V_2O_5 is 0.08) as a representative example, which shows the characteristic bands corresponding to PEDOT (bands in range $1049\text{--}1600\text{ cm}^{-1}$) as well as bands in lower frequency range 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.

3.2. X-ray diffraction

The powder XRD diffraction patterns (Fig. 2) of the layered structure of PEDOT/ V_2O_5 composites and crystalline V_2O_5

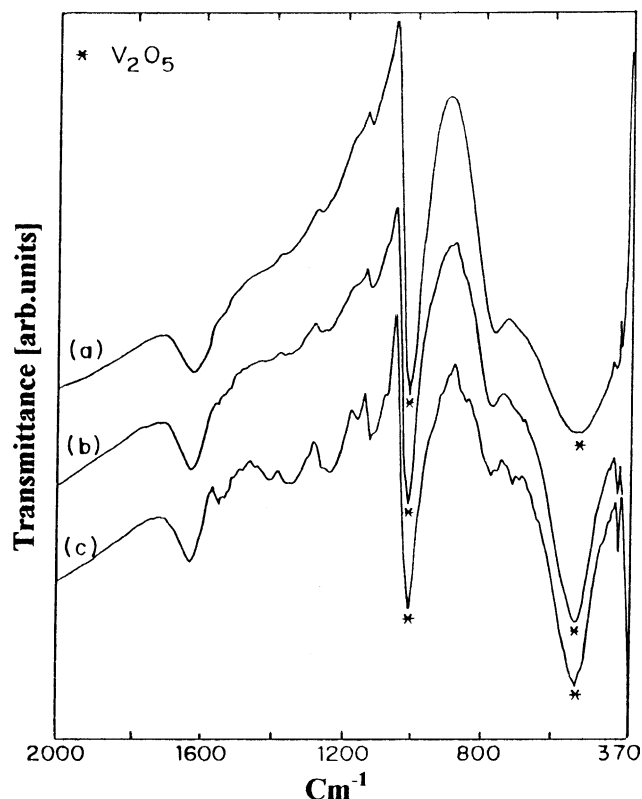


Fig. 1. FT-IR spectra of PEDOT/ V_2O_5 nanocomposites obtained with different EDOT/ V_2O_5 ratios: (a) 0.02, (b) 0.04, (c) 0.08. Peaks assigned to V_2O_5 are indicated by asterisks.

to demonstrate the subtle structural changes upon intercalation. The strongest peak observed at the low angle of 6.5° corresponding to the (001) plane of the layered V_2O_5 structure is directly related to the interlayer spacing. This interlayer spacing upon intercalation of crystalline V_2O_5 powder expands from 4.32 to 13.84 \AA . Incorporation of PEDOT in V_2O_5 and increases the interlayer spacing to form the monolayer. Both effects are advantages for the Li-insertion process.

3.3. Thermal studies

Thermal stability measurements of these materials in air show that two distinct stages are present in the thermograms and also in the differential thermal analysis (TGA-DTA) curves, as shown in Fig. 3. The first step, up to 120° C , corresponds to the removal of the reversibly bound water, whereas, the second step at $\sim 215^\circ\text{ C}$ corresponds to the loss of more strongly bound water between the layers. A weight loss is observed at 435° C in the PEDOT/ V_2O_5 composite which corresponds to the combustion of the organic polymer component, followed by a gain in mass up to 600° C , where orthorhombic V_2O_5 is formed. This mass increase is due to oxygen uptake by the V^{4+} centers in the inorganic lattices that were generated during the formation of the nanocomposites in this latter redox reaction. The 3,4-Ethylene dioxy

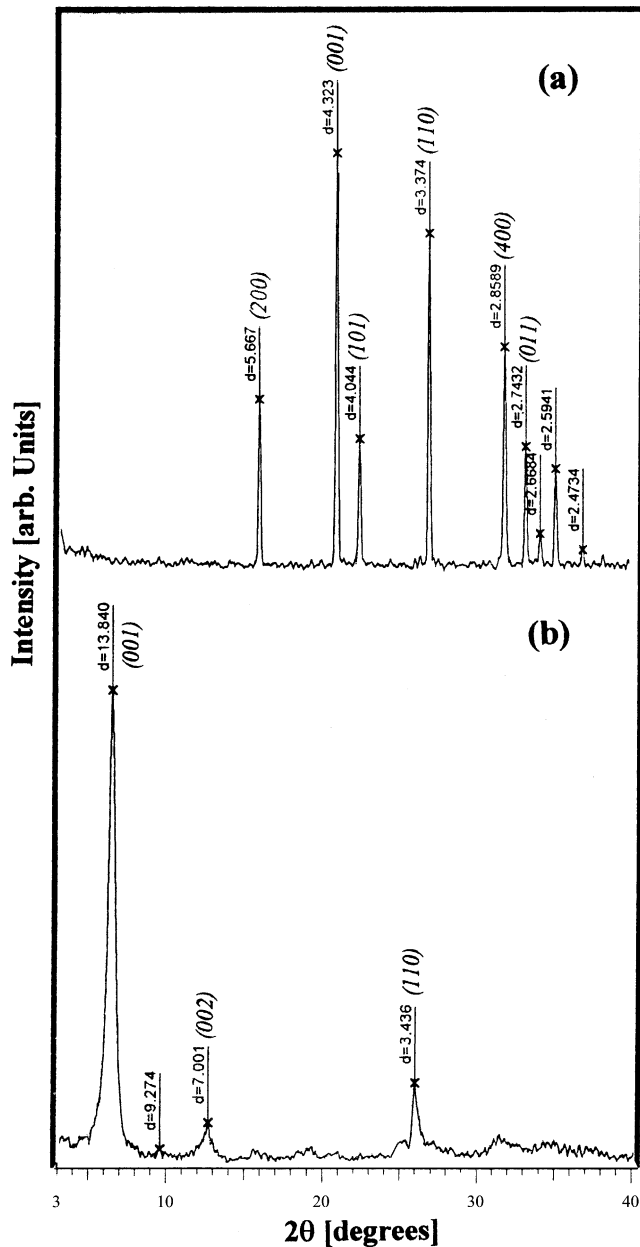


Fig. 2. Powder X-ray diffraction patterns of (a) V_2O_5 , (b) PEDOT/ V_2O_5 nanocomposite.

thiophene (EDOT) is oxidatively polymerized to poly(3,4-ethylene dioxythiophene) by sacrificial reduction of the V_2O_5 layers. Furthermore, evidence from the DTA curves also shows a large, relatively sharp exotherm at $\sim 450^\circ\text{C}$ due to the degradation of the organic PEDOT between the layers, followed by another endotherm. We attribute this endothermic peak at 650°C to oxygen uptake by the V^{4+} centers, which thus changes into V^{5+} to form V_2O_5 .

3.4. Electronic conductivity

For PEDOT/ V_2O_5 samples synthesized with different nominal EDOT/ V_2O_5 ratios, the room temperature conductivity

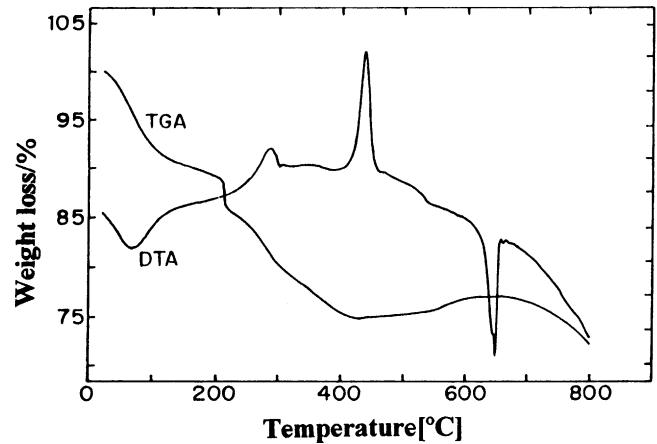


Fig. 3. TGA-DTA curves for PEDOT/ V_2O_5 composite with a ratio of 0.08.

varies from 10^{-2} to $10^{-5} \text{ S cm}^{-1}$. In this case, the increase in conductivity is probably due to a continued process of growth of the organic polymer network, as evidenced from the X-ray diffraction patterns. The electrical transport behavior of the nanocomposite 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 type of low-dimensional electronic conductors coexist at the molecular level in a dimensionally constrained environment. Two types of charge carrier can be present in these materials, namely: small polarons (electrons) associated with the d^1 (V^{4+}) centers on the vanadium oxide lattice, and massive polarons on the poly(3,4-ethylene dioxythiophene) backbone.

3.5. Electrochemical lithium insertion

For cyclic voltammetry, the voltage was cycled at a scan rate of 100 mV s^{-1} between 2.2 and 3.8 V Li reference. The cyclic voltammograms in Fig. 4 illustrate a drastic change in

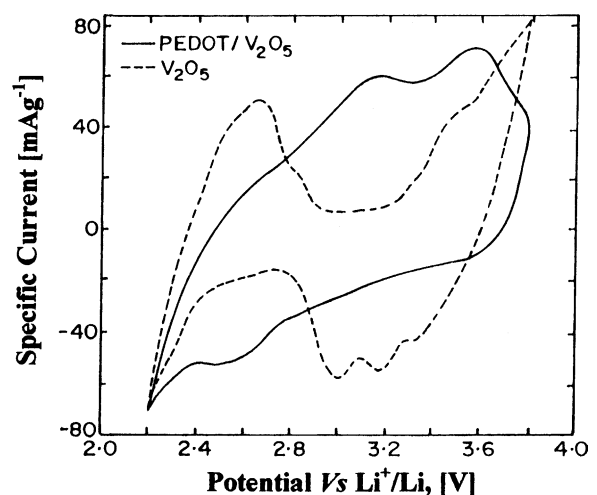


Fig. 4. Superimposed cyclic voltammograms of (a) V_2O_5 powder, and (b) PEDOT/ V_2O_5 composite coupled with Li foil counter and Li wire reference electrodes in 1 M LiClO_4/EC and DMC; scan rate 100 mV s^{-1} .

electrochemical properties induced by the polymer insertion. During the first cathodic scan, from the open-circuit voltage to 2.2 V, pristine V_2O_5 undergoes well-known phase transformations [22]. The irreversible shift of the cathodic peak from 2.65 to 2.82 V means that the structural change is irreversible, which is in agreement with reports in the literature [22]. By contrast, the voltammogram for the PEDOT/ V_2O_5 nanocomposite shows no sign for any irreversible structural change and has broad cathodic peaks. The broad and diffuse peak shape can, therefore, be correlated with the disturbed layer stacking derived by polymer incorporation, as previously deduced from X-ray diffraction data.

Potential versus capacity curves for the first two cycles down to 2.0 V (versus Li^+/Li), corresponding to uptake of ~ 2 Li per V_2O_5 unit, are presented in Fig. 5. pristine V_2O_5 shows distinctive plateau due to structural changes from α - V_2O_5 to ϵ - $Li_xV_2O_5$, then finally to the γ - $Li_xV_2O_5$ phase [22]. By contrast, the potential decreases more smoothly without

any sign of phase transformation for the hybrid samples. A similar continuous decrease in potential has been also observed for V_2O_5 xerogel, 2D- V_2O_5 and other polymer/ V_2O_5 hybrids whose common structural feature is the separation of the vanadium oxide layers due to the presence of interlayer molecules [23,24]. It should be noted that the PEDOT/ V_2O_5 nanocomposite gives a higher capacity in the first charge process than in the first discharge. This is associated with the presence of V^{4+} , which can be easily oxidized by an electrochemical method, as already observed in the case of PPY/ V_2O_5 and PTH/ V_2O_5 hybrids [23,25]. A study of the effects of the initial charge process and oxygen treatment is in progress.

A more accurate inspection of insertion voltage is accomplished by analysis of the differential capacity profiles of the first discharges (insets in Fig. 5). The sharp peaks for pristine V_2O_5 are typical signs of the phase transformations, whereas the hybrids exhibit gross peaks. The PEDOT/ V_2O_5

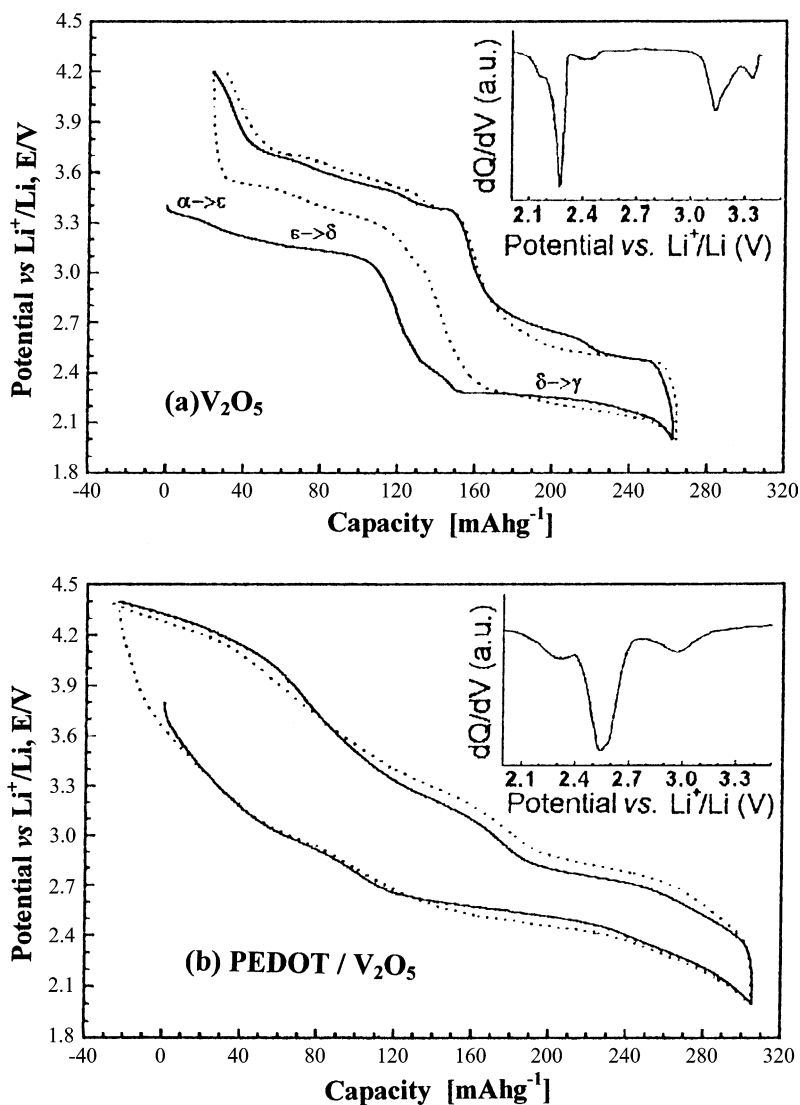


Fig. 5. Potential vs. capacity curves for first two cycles of (a) V_2O_5 and (b) PEDOT/ V_2O_5 nanocomposite, as a cathode material coupled with Li foil counter and Li wire reference electrodes in 1 M $LiClO_4/EC$ and DMC. Insets show corresponding differential profiles of first discharge.

nanocomposite shows three peaks at 2.9, 2.5 and 2.3 V analogous to PPY/V₂O₅ hybrids [23,25]. The discharge capacity of PEDOT/V₂O₅ nanocomposite is found to be ≥ 300 mAh g⁻¹ which is larger than pristine V₂O₅. The improved performances is presumably the result of the larger separation between vanadium oxide layers due to the presence of the polymer, which gives a structural stabilization. Therefore, we would like to suggest that judicious polymer incorporation into V₂O₅ is a way to improve its electrochemical properties by suppressing phase transformation and increasing the interlayer distance.

4. Conclusions

Interleaving poly(3,4-ethylene dioxythiophene) between the layers of V₂O₅ framework using a soft process of *in situ* polymerization gives a novel nanocomposite. Formation of the nanocomposite can be identified by IR fingerprints, and especially by the different interlayer spacing upon intercalation as detected by powder X-ray diffraction patterns, where a unique shift towards lower angle is observed and corresponds to monolayer formation. A PEDOT/V₂O₅ hybrid sample gives larger capacities and better reversibility than pristine V₂O₅.

The improved performance is presumably due to structural stabilization which results from incorporation of the polymer between vanadium oxide layer. The results also suggest that the polymer nanocomposite acts as a better cathode material than pristine V₂O₅ oxide material by enhancing lithium diffusion.

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