Electrochemical studies of poly (3,4-ethylenedioxythiophene) PEDOT/VS₂ nanocomposite as a cathode material for rechargeable lithium batteries

A.Vadivel Murugan a,*, Chinnakonda S. Gopinath b, K. Vijayamohanan b,*

a Centre for Materials for Electronics Technology (C-MET), Ministry of Communications and Information Technology, Government of India, Dr. Homi Bhabha Road, Pune-411008, India
b National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India

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Abstract

Here, we demonstrate the electrochemical characterization of a new type of layered poly (3,4-ethylenedioxythiophene) PEDOT/VS₂ nanocomposite. It has been prepared via flocculation of delaminated VS₂ with subsequent in situ oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) with VS₂ as a host material in the presence of an external oxidizing agent. The interlayer spacing of VS₂ expands from 5.71 to 14.01 Å and this interlayer separation is consistent with the existence of a monolayer of PEDOT in the VS₂ framework. X-ray diffraction, XPS and TEM studies have been shown the change in interlayer separation is consistent with the existence of two phases of organic and inorganic species in the nanocomposites corresponding to the intercalation of PEDOT in the VS₂ framework. The application potential of the nanocomposite as a cathode material for rechargeable lithium batteries is also demonstrated by the electrochemical intercalation of lithium into the PEDOT/VS₂ nanocomposite, where a significant enhancement in the discharge capacity is observed (~130 mAh/g) compared to that (80 mAh/g) for pristine VS₂.

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1. Introduction

Layered transition-metal sulfides are versatile intercalation hosts which can accommodate the steric demands of a wide variety of guest species [1]. Their ability to form intercalation compounds is known to be strongly dependent on the electronic structure of dichalcogenides [2]. This may be traced to the requirement for the host structure to possess low-lying empty electronic states, as a result of redox process which accompanies the intercalation reaction. Hence, transition metals dichalcogenides of groups 4B and 5B, such as TiS₂, TaS₂, NbSe₂ readily form intercalation compounds with a wide variety of guest species [3]. In contrast, group 5B dichalcogenide materials like VS₂ undergo very limited intercalation chemistry mainly restricted to alkali metals as guest species [4]. It is surprising that VS₂ alone of these group 5B dichalcogenide compounds has not been prepared by direct combination of elements especially since VSe₂ has readily been prepared. This is specially significant, since there are only a few reports on the synthesis and characterization of VS₂ and insertion of conducting polymers in layered material despite the considerable current interest in the van der Waals
bonding of this metal chalcogenide and conducting polymer also due to the immense utility of this compounds with lithium as potential cathode electrodes in non-aqueous lithium batteries [5,6]. Recently, we have reported that the redox intercalative polymerization (RIP) of 3,4-ethylenedioxythiophene in V2O5 produces a well-ordered organo–inorganic nanocomposite with synergistic properties like enhanced electrical and Li+ ion diffusion properties [7,8]. Thus, to broaden the scope of these new hybrid materials to other layered systems, in this paper we focused our efforts on the intercalation of poly (3,4-ethylenedioxythiophene) into VS2. The primary objective is to investigate the successful entrapment of poly (3,4-ethylenedioxythiophene) chains between VS2 layers, giving rise to a novel nanoscale molecular composite by soft chemistry method of intercalation. These observations are supported by several physicochemical data and microstructure of PEDOT/VS2 nanocomposite, where the resulting nanocomposite shows improved room temperature conductivity with charge-transport and electrochemical properties compared to the polymer free VS2. The preliminary electrochemical measurement of PEDOT/VS2 nanocomposite during the initial charge–discharge cycles shows an enhanced capacity compared to that of pristine VS2. To our knowledge, this is the first study of the electrochemical Li-insertion into a PEDOT/VS2 nanocomposite, which clearly suggests that the improved capacity could be related to the presence of the conducting polymer in the interlamellar region.

2. Experimental

The LiVS2 was prepared according to previously described procedure [9], except that V2O5 was used instead of V2O3. 0.202 g of Li2VS2 was exfoliated by sonication for 0.5 h to form a colloidal suspension, to this suspension, 3,4-ethylenedioxythiophene (EDOT) monomer (4.6 mM) was added drop wise followed by 8.5 g of iron (III) chloride (FeCl3) in 10 ml water was added drop wise in to this suspension under refluxing condition for 2 h. The blue–black powder of PEDOT/VS2 nanocomposite was washed with excess of ethanol and water to remove unreacted monomer and FeCl3 [10].

The X-ray powder diffraction was carried out with a Bruker AXS D5005 instrument from 3° to 80° using Cu Kα radiation. X-ray photoemission spectra (XPS) were recorded on VG Microtech Multilab ESCA 3000 spectrometer using non-monochromatized Al Kα X-ray source (hν = 1486.6 eV). Base pressure in the analysis chamber was maintained at 10−10 Torr range. The energy resolution of the spectrometer was set at 1.0 eV with Al Kα radiation at a pass energy of 50 eV. Binding energy (BE) calibration was performed with Au 4f7/2 core level at 83.9 eV and BE of adventitious carbon (284.9 eV) was utilized for charging correction with all the samples. The error in all the BE values reported here is within ±0.1 eV. Electronic conductivity was measured on compacted pellets using a four probe conductivity method. Scanning electron microscopy (SEM) was carried out with Philips XL-30 microscope at an accelerating voltage of 20 kV after mounting samples on Al stubs with gold coatings. For TEM imaging (TEM model JEM-2010, JEOL) the powder was first dispersed in ethanol by ultrasonication, and then the suspension was drop casted once copper grid coated with carbon films and dried. 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 analyzer. The combined elemental analysis confirmed the stoichiometry of pure VS2 (V = 25.5%; S = 45.1%) as VS1.768 and nanocomposite as (C6H4O2S)0.39VS2: C, 6.92; H, 1.54; S, 48.97; V, 24.63.

The electrochemical measurements were performed using a button-type cell configuration with the help of a computer-controlled PGS201T (Tacussel) potentiostat/galvanostat system. The working electrode was prepared by mixing the PEDOT/VS2 nanocomposite powder or pristine VS2 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. The electrolyte was 1 M LiClO4 in PC and a lithium foil was used as the anode. A constant current of 0.5–0.75 mA was applied between 1.0 and 3.0 V (vs. Li+/Li) for charge–discharge experiments. Cyclic Voltammetry was conducted on similar working electrodes by scanning the potential between −1.0 and 1.0 V vs. Ag/Ag+, at 0.6 mV/s rate in 1 M LiClO4 in 1:1 mixture (by volume) of EC/DMC and a Pt foil was used as the counter electrode.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of pristine VS2 and poly (3,4-ethylenedioxythiophene) PEDOT/VS2 nanocomposite. The VS2 prepared by this method is stable in air and the compound is hexagonal (CdI2 type) with a = 3.217 Å and c = 5.712 Å as demonstrated by the powder diffraction, (Fig. 1(a)) [5]. In comparison, the X-ray diffraction pattern of composite (Fig. 1(b)) reveals the characteristic (0 0 1) peak can be observed at 2θ value decreased from 15.52 to 6.26 and subsequently increase in the interlayer distance of the pristine disulfide, VS2, from 5.712 to 14.01A, indicating substantial incorporation of organic conducting polymeric material between the layers. However, the sharp and intense peak observed at the low angle corresponding to the (0 0 1) plane of the layered well-stacked VS2 structure could be directly related to the interlayer spacing.
main features of the VS\textsubscript{2} diffraction patterns in the composites are clearly modified by the appearance of a sharp diffused scattering feature and an increase in the intensity of (001) peak. On the other hand, the $d(101)$, $d(102)$, $d(110)$ and $d(103)$ reflections of crystalline VS\textsubscript{2} are diffused after polymer intercalation (Fig. 1(b)). Thus, it is likely that these materials constitute a new PEDOT/VS\textsubscript{2} composite phase consisting of a monolayer of PEDOT chains interleaved between the VS\textsubscript{2} layers also supported by our recent report of PEDOT intercalated into vanadium pent oxide layers [7,8].

When, PEDOT and PEDOT-VS\textsubscript{2} composite material were subjected to XPS analysis and the results from vanadium 2p, oxygen 1s, sulfur 2p and carbon 1s core levels of the above samples are shown in Fig. 2. Composite materials were made into pellets and the surface was scraped in situ in the XPS spectrometer to remove any atmospheric degradation on the composite surface. The PEDOT/VS\textsubscript{2} surface analyzed prior to scraping (not shown) shows huge amount of oxidation of V and S species VOS, VO\textsubscript{x} and SO\textsubscript{x}, respectively. Although, the contamination level has decreased after thorough scraping, still quiet a large amount of oxidized species clearly indicates that the VS\textsubscript{2} could have undergone oxidation during oxidative polymerization of EDOT by using FeCl\textsubscript{3} and it may also slowly undergo atmospheric oxidation by transformation of V\textsuperscript{4+} to V\textsuperscript{5+} state. The BE observed for vanadium 2p\textsubscript{3/2} core level corresponds to V\textsubscript{2}O\textsubscript{5} type species and large amount of oxygen at 531 eV indicates that surface of VS\textsubscript{2} undergone oxidation in air. Further, S 2p core level from PEDOT/VS\textsubscript{2} shows sulfur from VS\textsubscript{2}, thiophene units and sulfur oxides at increasing BE (Fig. 2b). Carbon 1s core level from PEDOT and PEDOT-VS\textsubscript{2} shows essentially the same features, except for a shift in BE which is likely due to charge transfer between polymer and VS\textsubscript{2}.

The transmission electron microscopy (TEM) images show thick particles of VS\textsubscript{2} with micrometer order (Fig. 3(a)), whereas the nanoribbon morphology of the PEDOT/VS\textsubscript{2} nanocomposite, is illustrated in Fig. 3(b), thus suggesting that the in situ oxidative polymerization is
As can be seen from TEM images, the VS$_2$ host consists of conducting polymer nanoribbons whose order could be evaluated from the most pronounced intensity maximum in the broad X-ray diffraction pattern $d(001)$ (Fig. 1(b)). Thus, from the TEM image of the nanocomposite material, we conclude that the highly crystalline vanadium disulfide is separated by organic conducting polymer nanoribbon in this hybrid material these results also supported by our recent report [7,8].

Transition metal dichalcogenides, MX$_2$ (M = V, Ti, Ta and X = S, Se) which form layered compounds (especially groups 4B and 5B) that can act as host lattice with lithium ions are of significant interest as the basis for developing high energy density cathodes for rechargeable lithium batteries. In particular, Li$_x$VS$_2$ has been proposed as one of the attractive cathode materials in non-aqueous lithium batteries as the electrochemical insertion of Li in VS$_2$ material can be described by the following redox couple

$$x\text{Li}^+ + xe^- + \text{VS}_2 \leftrightarrow \text{Li}_x\text{VS}_2$$  \hspace{1cm} (1)

One of the most striking aspects of the Li$_x$VS$_2$ system is the occurrence of two slightly distorted phases $\alpha$ and $\beta$ [5]. This phase transition in the Li$_x$VS$_2$ appears to be related to the electronic instabilities in the VS$_2$ layers. Such instabilities could take the form of a charge density wave (CDW) [11], as observed in many MX$_2$ layered compounds including VSe$_2$ although some may be more similar to Mott-like transitions observed in vanadium oxides such as VO$_2$ [12], V$_2$O$_3$ [13], etc. as these compounds span the range from $d^1$ to $d^2$, as does Li$_x$VS$_2$ as $x$ increases from 0 to 1. When both $d^1$ and $d^2$ vanadium are present in the oxides (mixed valent), two transitions are frequently observed [5]. The occurrence of phase transitions in Li$_x$VS$_2$ from hexagonal to distorted phases suggest the possibility of suppressing these transitions by substituting other metals for V, or using macromolecules intercalated in between VS$_2$ layers, thereby introducing disorder and modifying the electronic structure of the vanadium d-band. For example, Di Savo [14,15] has reported that CDW and polytype transformation in layered compounds may be reduced by alloy formation. In particular, conducting polymers seems to be an attractive substitute because of their improved room temperature conductivity and lithium ion mobility compared to that of polymer free inorganic hosts. VS$_2$ and Li$_x$VS$_2$ are regular 1T hexagonal structures, although the compositions intermediate in lithium are distorted over most of the range. Furthermore, the nature of polymer intercalated Li$_x$VS$_2$ distortions may be somewhat different than that of Li$_x$VS$_2$ and this may give rise to interesting variants in the electrical behavior. For the case of PEDOT/VS$_2$ nanocomposites, we can write analogous electrochemical reactions after incorporating lithium ions between the layers as

$$[\text{PEDOT}^+]_{x}\text{VS}_2^{-x} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x[\text{PEDOT}]_{x}\text{VS}_2^{-x}$$

Reduction of PEDOT

$$\text{Li}_x[\text{PEDOT}]_{x}\text{VS}_2^{-x} + y\text{Li}^+ + ye^- \rightarrow \text{Li}_{x+y}[\text{PEDOT}]_{x}\text{VS}_2^{-x(y+y)}$$

Reduction of VS$_2$

Electrochemical measurements were performed based on the cell configuration of the Ag|1 M LiClO$_4$ in EC/DMC (1:1 v/v)| PEDOT/VS$_2$ nanocomposite electrode. Fig. 4 shows comparative cyclic voltammograms of (a) pristine VS$_2$ and (b) PEDOT/VS$_2$ nanocomposite, illustrating a drastic change in electrochemical properties induced by the polymer insertion. During the first cathodic scan, voltage from $-1.0$ V to $1.0$ vs. Ag|Ag$^+$, the crystalline VS$_2$ undergoes a well-known phase trans-
formation and the stabilization occurs after the fifth cycle (Fig. 4 inset). The irreversible shift in the cathodic peak from $\Delta C0 = 0.32$ V (first cathodic scan) to $\Delta C0 = 0.20$ V (third and following cathodic scans) suggests that the structural change is permanent as reported elsewhere [16–19]. Further, the weak interactions between the interlamellar layer, allow fast insertion of Li$^+$ ions between the ribbons rather than that in the crystalline vanadium disulfide [9]. In contrast, for the PEDOT/VS$_2$ hybrids, there is no sign of any irreversible structural change, however, the broad cathodic peak, resembles that of 2D inorganic layered compounds [16–19]. The broad and diffuse peak shape can, therefore, be correlated with the layer stacking derived by the polymer incorporation, as previously deduced from X-ray diffraction data.

Fig. 5 demonstrates potential vs. capacity curves for the second cycle of pristine VS$_2$, and PEDOT/VS$_2$ nanocomposite after coupling with lithium metal anode using 1M LiClO$_4$ in propylene carbonate using a constant current of 0.5 mA/cm$^2$. The potential range is from 1.0–3.0 V vs. Li and the electrode surface area is $\sim 1$ cm$^2$.

4. Conclusions

In conclusion, poly (3,4-ethylenedioxythiophene)/VS$_2$ nanocomposite formation takes place with the in situ polymerization of EDOT within the framework of capacity of Li$^+$/Li$_x$VS$_2$ cells is intimately related to the distorted intermediate phases either by reduced Li$^+$ ion mobility or by a sluggish phase nucleation. In the Li/PEDOT/VS$_2$ cells give improved capacity and cycling behavior over Li$^+$/Li$_x$VS$_2$ cells. The first cycle of a PEDOT/VS$_2$ discharge plateau show in Fig. 5 the continued presence of distorted intermediate phases is evidenced by a mild break near the middle of these curves, but their properties are apparently modified from those of Li$_x$VS$_2$ allowing easy reversibility. Cell prepared with these compositions gave good capacity and reversibility behavior as shown in Fig. 5. The lithium insertion into the pristine VS$_2$ occurs at $\sim 2.43$ V and is accompanied by the irreversible structural changes to $\beta$-Li$_x$VS$_2$ phase [11–15], leading to a transformation of curve shape in second cycle, while the open circuit voltage of this cell increases after polymer intercalation into VS$_2$ such that the OCV for PEDOT/VS$_2$ is 2.68 V and it deliver $\sim$130 mAh/g, but the pristine VS$_2$ produces 80 mAh/g on the first discharge, of which common structural feature is the separation of vanadium disulfide layers owing to the presence of interlayer molecules. It would be, hence, a plausible explanation that the disturbed layer stacking derived by the separation of layers would make structural disorders. The comparative electronic conductivity data, open circuit voltage and discharge capacity of nanocomposite and their composition are listed in Table 1. The improved performance of the hybrid material is presumably due to the larger separation between vanadium oxide layers, leading to an enhanced “bidimensionality”. In order to clarify the role of the polymer incorporation on the electrochemical performance for extended cycling. The variation of discharge capacities of VS$_2$ and PEDOT/VS$_2$ has been measured as shown in Fig. 6. PEDOT/VS$_2$ nano composite maintains capacities over 120 mAh/g for 10 cycles. This nanohybrid provides higher capacity and better cyclability than the pristine VS$_2$. The improved performances are presumably due to a higher electrical conductivity, structural disorders and enhanced bidimensionality.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interlayer spacing/Å</th>
<th>Electronic conductivity, $\sigma$/S cm$^{-1}$ (R.T)</th>
<th>Discharge capacity/mA h$^{-1}$</th>
<th>Open circuit voltage/V vs. Li$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS$_2$</td>
<td>5.69</td>
<td>$9.907 \times 10^{-2}$</td>
<td>86</td>
<td>2.43</td>
</tr>
<tr>
<td>PEDOT/VS$_2$</td>
<td>14.01</td>
<td>$3.906 \times 10^{-1}$</td>
<td>130</td>
<td>2.68</td>
</tr>
<tr>
<td>PEDOT</td>
<td>–</td>
<td>$1.248 \times 10^6$</td>
<td>78</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Fig. 6. Potential vs. specific capacity curves for the second cycle of pristine VS$_2$, and PEDOT/VS$_2$ nanocomposite after coupling with lithium metal anode using 1M LiClO$_4$ in propylene carbonate using a constant current of 0.5 mA/cm$^2$. The potential range is from 1.0–3.0 V vs. Li and the electrode surface area is $\sim 1$ cm$^2$.
VS$_2$. XRD and TEM results suggested that the incorporation of the polymer nanoribbons. These experimental data presented here suggest that the polymerization proceeds concomitantly with intercalation. Therefore, there is considerable bonding interaction between the organic and inorganic components, probably due to hydrogen bonding. The X-ray photoelectron spectrum shows the VS$_2$ surface could have undergone oxidation during oxidative polymerization of EDOT by using FeCl$_3$ and it may also slowly get atmospheric oxidation by try to transfer from of V$^{4+}$ to V$^{5+}$ state. Although, shift in binding energy of carbon which is likely due to charge transfer between polymer and VS$_2$. While the TEM results are suggests that the interlayer distance of crystalline VS$_2$ expands upon the incorporation of the polymer nanoribbons. According to electrochemical measurements, the hybrids shows reversible specific capacities up to ~130. This improvement of electrochemical performance compared with pristine VS$_2$ is attributed to higher electric conductivity and enhanced bidimensionality. The influence of intercalants on Li$^+$ diffusion rates and charge capacity in the PEDOT/VS$_2$ nanocomposite is increased relative to that for VS$_2$. The results also suggest that, the polymer nanocomposite acts as a better cathode material than the pristine VS$_2$ material by enhancing lithium diffusion.

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