A bilayer insertion of poly(oxyethylene-oxyethylene) into vanadium pentoxide xerogel: Preparation, characterization and insertion mechanism

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Abstract

We report a method for inserting poly(oxyethylene-oxyethylene) (POMOE) and LiCF3SO3-POMOE (Li-POMOE) complex into V2O5nH2O xerogel at room temperature leading to a bilayer arrangement of the POMOE-chains within the gallery spaces. This could be a significant step towards developing improved electrolyte/cathode materials for lithium/Li-ion batteries. A series of intercalates were prepared to study the effect of changing the polymer concentration on the interlayer expansion of the layered host, and to determine the optimal insertion ratio. An insertion reaction mechanism is proposed. A hydrogen-bonding network between the polymer and the V2O5 framework contributes significantly to the formation of the nanocomposites. The nanocomposites showed reversible color change from red to green when subjected to electrical stimuli, thus making them good candidates for electrochromic devices. The materials were characterized by powder X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, Fourier transform infrared spectroscopy, and impedance spectrosopy.

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1. Introduction

Intercalation chemistry provides an excellent route to combine the properties of two materials, which cannot be obtained through other methods such as organic or solid-state syntheses. Traditionally the term “intercalation” in chemistry was used to refer to a process in which a guest species (e.g. Li+) ion can be reversibly inserted into a host structure such as CoO2. However, nowadays the term intercalation has been expanded to include irreversible insertion of a guest species (e.g. polymers) into hosts with layered structures [1]. Therefore, the terms intercalation and insertion will be used interchangeably in this article. One feature of an intercalation reaction is that the guest and host experience some degree of perturbation along a spectrum, from subtle to extreme, in their geometric, chemical, electronic, and optical properties [1]. Vanadium pentoxide xerogel (V2O5nH2O) is a host material that continues to receive researchers’ attention. This is because V2O5nH2O nanocomposites have various applications such as in electrochemical energy storage devices [2,3], biosensors [4], and electrochromic devices [5]. Most of the current research on V2O5nH2O xerogel nanocomposites is devoted to developing materials that can be used in rechargeable batteries to address the ever increasing demands for renewable and portable electrical energy.

V2O5nH2O xerogel is a good candidate for developing nanocomposites because of its versatile intercalation properties. This is because the V2O5 ribbons in the xerogel are linked together via hydrogen bonded water molecules. Thus, the basal distance in the xerogel is quite large and interactions between the ribbons are much weaker compared to crystalline V2O5 [6]. Intercalation may occur via dipole-dipole interaction, ion-exchange, acid–base, coordination, and redox reactions enabling the system to accept both neutral and charged guest species [7,8]. V2O5nH2O has also shown promising redox reactions that can be utilized in lithium ion batteries. For example, Passerini et al. demonstrated that V2O5nH2O could be used as a cathode material that reversibly intercalates more than 3 equivalents of lithium [9]. However, the presence of intercalated water molecules in V2O5·nH2O is of considerable concern because of the parasitic reaction of water with the anode for lithium based batteries [10]. Therefore, replacing water molecules with ionically conducting polymers would improve the safety of lithium batteries employing vanadium oxide cathodes. Inclusion of ionically conducting polymers would also maintain the structural integrity of the vanadium oxide framework and promote facile movement of Li+ through the interlayer spaces.

Organic compounds, which can conduct alkali ions, have been under intense investigation since first reported over four decades ago by Fenton et al. [11]. In 1978 Armand et al. [12] were the first to propose that organic compounds such as polyethylene oxide (PEO) could be used as polymer electrolytes in electrochemical devices. Since then, PEO and its derivatives have been subjected to intense research to make Armand’s dream a reality. Derivatives of PEO such as poly(oxyethylene-oxyethylene) (POMOE) [13] have been developed because PEO is a semi-crystalline material, which limits its ionic conduction at room temperature. The optimum room
temperature ionic conductivity of POMOE complexes with lithium trifluoromethanesulfonate (LiCF<sub>3</sub>SO<sub>3</sub>) at the ratio [O]/[Li<sup>+</sup>] = 25 was reported to be 5 × 10<sup>−3</sup> S cm<sup>−1</sup> which is higher than PEO complexes with LiCF<sub>3</sub>SO<sub>3</sub> under the same conditions [13].

The insertion of ionically conductive polymers into layered structures is meant to improve their mechanical stability, so that they can be used as solid electrolytes and/or as cathodes in solid-polymer-batteries. Kanatzidis et al. [14] were the first to insert PEO into V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O xerogel. Shriver’s group [15] reported on the insertion of POMOE into V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O, a process that involved heating and gave a monolayer loading of the polymer. They reported that the nanocomposite showed high electronic conductivity parallel to the films while conduction pathways perpendicular to the films appeared to be virtually closed. They also noted that variations of the lithium triflate concentration affected the electronic conductivity, however, no predictable trends were observed. POMOE has also been intercalated into other layered systems such as hectorite [16], molybdenum diselenide [17], tin disulfide [18], graphite oxide [19], and molybdenum disulfide [20].

The focus of this article is to report a method for intercalating POMOE and LiCF<sub>3</sub>SO<sub>3</sub>-POMOE complex into V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O xerogel at room temperature resulting in a bilayer loading of the polymer chains. The procedure used in this work is an improved and more efficient modification of the methods reported by the Kanatzidis’ group [14,21], Ruiz-Hitzky et al., [22] and Guerra et al. [23] for intercalating PEO into V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O. Therefore, the method can be extended to the insertion of PEO and other derivatives into V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O. The significance of this method is that the hybrid materials can be obtained within 30 min and they have higher polymer content compared to previous methods, thus potentially increasing their ability to intercalate more Li-ions. The nanocomposites could potentially show enhanced performance in Li-ion battery applications. In this article, the lithium salt (LiCF<sub>3</sub>SO<sub>3</sub>) and a complex of POMOE with LiCF<sub>3</sub>SO<sub>3</sub> will be abbreviated as LiX (X = CF<sub>3</sub>SO<sub>3</sub>) and Li-POMOE, respectively. The nanocomposites will be abbreviated as V<sub>2</sub>O<sub>5</sub>-POMOE and V<sub>2</sub>O<sub>5</sub>-Li-POMOE followed by the mole ratio used e.g. V<sub>2</sub>O<sub>5</sub>-POMOE 1:1.

2. Experimental

2.1. Materials

Sodium metavanadate, purchased from Fluka and Dowex 50 W-X8, 20–50 mesh resin, purchased from Baker were used as received. Poly(ethylene glycol) (PEG 400), purchased from Aldrich was dried over 3 Å molecular sieves under nitrogen. Dichloromethane, purchased from Caledon was dried by refluxing over calcium hydride under nitrogen. The dichloromethane was freshly distilled before use. Potassium hydroxide 85%, purchased from Aldrich was ground to a fine powder before use.

2.2. V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O xerogel synthesis

The synthesis of V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O xerogel was adapted from the literature [23]. In this experiment, sodium metavanadate (4.0 g, 0.033 mol) was dissolved in deionized water (150 mL). The resulting colorless solution was then passed through an acidic ion exchange column (510 meq capacity) made from Dowex 50 W-X8, 20–50 mesh resin. The collected eluate, (200 mL), was the yellow –brown polyvanadic acid (HVO<sub>3</sub>). The excess water was evaporated from the HVO<sub>3</sub> at room temperature for 2 weeks and the solution polymerized to the dark-red xerogel (V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O). The V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O solution was used without further dilution in the intercalation reactions.

2.3. POMOE Synthesis

POMOE was synthesized as reported in the literature [13]. Potassium hydroxide (50.0 g, 0.891 mol) powder was introduced into a three neck flask connected to a mechanical stirrer under nitrogen purge from a Schlenk line. Dichloromethane (283.5 g, 180.0 mL) was syringed into the reaction vessel. Polyethylene glycol 400 (PEG 400) (49.3 g, 50.0 mL) was added slowly by means of a dropping funnel to the reaction mixture. The reaction vessel was protected from direct light with aluminum foil. After three days, the excess potassium hydroxide was washed off the thick rubbery product. The thick rubbery product was dissolved in water (500 mL) and purified via dialysis for several days. After dialysis, the solution was filtered to remove any suspended particles, and was then freeze-dried. A clear colorless rubbery mass of the polymer was obtained. The yield was over 90%.

A Li-POMOE complex was prepared using the optimum ionic conductivity ratio of [EO]/[Li<sup>+</sup>] = 25 as reported in literature [13].

2.4. Nanocomposite synthesis

The nanocomposites were prepared by adding POMOE or Li-POMOE dissolved in methanol into an aqueous solution of V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O and stirring magnetically for 30 min at room temperature in air. In a typical experiment of mole ratio 1:1, 7.8 mL of the xerogel (95.9 mg, 4.44 × 10<sup>−4</sup> mol) was mixed with the POMOE solution in methanol (2.00 mL, 1.47 × 10<sup>−4</sup> mol). The following mole ratios were prepared 1.0:5, 1.1, 1.2, 1.3, and 1.4. The mole ratios were calculated based on moles of V<sub>2</sub>O<sub>5</sub>1.9H<sub>2</sub>O and moles of POMOE’s repeat unit. From here on the nanocomposites will be referred to as V<sub>2</sub>O<sub>5</sub>-POMOE followed by the mole ratio (e.g. V<sub>2</sub>O<sub>5</sub>-POMOE 1:3 for the mole ratio of one to three).

To confirm that the polymer chains were actually inserted into V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O and not just the solvent, a control sample was prepared and characterized. The control sample was prepared by adding methanol (5.0 mL) (the solvent used for dissolving POMOE) into an aqueous solution of the V<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O gel (10.0 mL), followed by stirring for 30 minutes. From here on the control sample will be denoted as V<sub>2</sub>O<sub>5</sub>MeOH.

2.5. Materials characterization

Powder X-ray diffraction studies were carried out on a Bruker AXS DB Advance X-ray diffractometer equipped with a graphite monochromator, variable divergence slit, variable anti-scatter slit, and a scintillation detector. Cu (Kα) radiation (λ = 1.5406 Å) was used. Samples were prepared at room temperature in air as dry thin films on a glass or silicon substrate.

The thermal properties of the samples were investigated using TA instruments. Thermogravimetric analysis (TGA) was performed on a Q500 in dry air or nitrogen purge using a heating rate of 10 °C/min up to 680 °C, which is 10 °C below the melting point of pristine vanadium pentoxide. Differential scanning calorimetry (DSC) was performed on a Q100 under dry nitrogen purge using heating and cooling rates of 10 °C/min and 5 °C/min, respectively. The samples were freeze-dried using a Virtis Benchtop 3.3/Vacu-Freeze dryer and stored overnight in a desiccator prior to analysis. The dry samples were sealed into aluminum pans for DSC analysis. The TGA and DSC data were processed using the TA Universal Analysis 2000 software.

Fourier transform infrared (FTIR) spectroscopy was recorded on a Bruker Equinox 55 series spectrometer over the range 4000–400 cm<sup>−1</sup>. The resolution of the instrument was 0.5 cm<sup>−1</sup> and 64 scans were used. The samples were dispersed in KBr, and pressed into pellets.

The conductivities of the samples were determined by alternating current impedance spectroscopy, using a Solartron 1250 frequency response analyzer and a home-built accessory circuit. The amplitude of the sign wave perturbation was 50 mV rms, and a frequency range of 10 kHz to 0.01 Hz was used. The samples were run as cast films on rectangular glass substrates. Silver paste was placed on the two ends of the films as electrodes. The distance between electrodes was measured with calipers for each sample, and ranged from 4.5 to 11.5 mm.
Sample widths were in the 8 to 11 mm range. Film thicknesses were estimated from SEM images and ranged from 7 to 60 μm. Prior to the conductivity measurements, samples were held in vacuum for at least 20 hours at room temperature to remove any moisture and adsorbed volatile materials. Conductivity measurements were also made in vacuum. The current flow was along the film, parallel to the substrate.

To determine the morphology and thickness of the nanocomposite cast films used for conductivity measurements, the glass slides were cleaved to expose a cross-section of the film. Samples were sputter-coated with a 30 nm palladium-gold film, and examined with a Hitachi TM 3000 scanning electron microscope.

### 3. Results and discussion

#### 3.1. Powder X-ray diffraction (XRD)

Powder X-ray diffraction was used to confirm the successful insertion of POMOE into V$_2$O$_5$nH$_2$O and the identity of the as synthesized V$_2$O$_5$nH$_2$O xerogel. The nanocomposites showed complete insertion of the polymer into the gallery spaces based on the absence of pristine V$_2$O$_5$nH$_2$O diffraction peaks. The X-ray diffraction patterns for V$_2$O$_5$nH$_2$O, V$_2$O$_5$MeOH and V$_2$O$_5$POMOE 1:1 are shown in Fig. 1. Fig. 1 curve c shows the X-ray diffraction pattern for the nanocomposite with mole ratio 1:1. The diffraction pattern shows a d-space increase to 20.6 Å, which corresponds to an interlayer expansion of 8.7 Å with respect to V$_2$O$_5$nH$_2$O (d = 11.9 Å). Other nanocomposites showed similar trends and are summarized in Table 1.

The interlayer spacing for the as prepared V$_2$O$_5$nH$_2$O film was 11.9 Å, closely comparable to other literature reports (lit. n = 1.8, d = 11.5 Å, in this work n = 1.9, d = 11.9 Å). The X-ray diffraction of the nanocomposites shows only (00 l) reflections, which is indicative of highly oriented materials. From Table 1 it is clear that there is no significant increase in d-spacing as the amount of POMOE is increased. This indicates that the average net expansion of 8.7 Å corresponds to the optimum loading of POMOE into the V$_2$O$_5$nH$_2$O xerogel. Here is how this observation relates to other work in the literature. Kloster et al. using water as solvent inserted POMOE into V$_2$O$_5$nH$_2$O xerogel with an interlayer expansion of 8.7 Å and a bilayer conformation was proposed. With all of the above evidence and arguments the average interlayer expansion of 8.7 Å observed here was assigned to a bilayer conformation of the POMOE-chains within the V$_2$O$_5$ ribbons. A schematic lamellar representation of the nanocomposites is shown in Fig. 2.

The difference between the monolayer loading reported by the Shriver’s group and the bilayer arrangement reported in this work could be due to two factors. The first factor was the solvent used. While Shriver’s group used water, we used methanol as the solvent. The second factor could be the ageing period of V$_2$O$_5$nH$_2$O xerogel. In our case, we used a two week aged V$_2$O$_5$nH$_2$O (dark red) without any dilution.

<table>
<thead>
<tr>
<th>Material</th>
<th>Observed d-spacing (Å)</th>
<th>Expansion Δd-spacing (Å)</th>
<th>Peak widths at half height (2θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_5$nH$_2$O</td>
<td>11.9</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>V$_2$O$_5$MeOH</td>
<td>14.5</td>
<td>2.6</td>
<td>0.88</td>
</tr>
<tr>
<td>V$_2$O$_5$POMOE 1:0.5</td>
<td>20.2</td>
<td>8.3</td>
<td>0.67</td>
</tr>
<tr>
<td>V$_2$O$_5$POMOE 1:1</td>
<td>20.6</td>
<td>8.7</td>
<td>0.70</td>
</tr>
<tr>
<td>V$_2$O$_5$POMOE 1:2</td>
<td>20.6</td>
<td>8.7</td>
<td>0.76</td>
</tr>
<tr>
<td>V$_2$O$_5$POMOE 1:3</td>
<td>20.5</td>
<td>8.6</td>
<td>0.88</td>
</tr>
<tr>
<td>V$_2$O$_5$POMOE 1:4</td>
<td>20.6</td>
<td>8.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Since POMOE is a derivative of PEO, this interpretation was consistent with Kanatzidis et al.’s work on the insertion of PEO into V$_2$O$_5$nH$_2$O. In fact, Kanatzidis et al. were the first to report on the insertion of PEO into V$_2$O$_5$nH$_2$O with a d-spacing increase of 4.5 Å [14]. Later, Kanatzidis et al. [21] and Guerra et al. [23] using aqueous solutions of PEO with slow evaporation of water were able to report an interlayer expansion of 8 Å or higher and they suggested a bilayer loading of the PEO-chains within the V$_2$O$_5$ framework. Guerra et al. also observed that the interlayer expansion was independent of the molecular weight of the PEO. 1-D electron density (ED) calculations performed by Kanatzidis et al. provide supporting evidence for a bilayer loading of the PEO-chains in the V$_2$O$_5$ framework [21]. Kanatzidis et al. calculated ED maps along the c axis and reported that a bilayer loading of PEO-chains fully extended (i.e. zigzag conformation) parallel to each other was the most likely conformation for an interlayer expansion of about 8 Å. Similarly, insertion of POMOE into tin disulfide [18] was reported with an interlayer expansion of 8.7 Å and a bilayer conformation was proposed. With all of the above evidence and arguments the average interlayer expansion of 8.7 Å observed here was assigned to a bilayer conformation of the POMOE-chains within the V$_2$O$_5$ ribbons. A schematic lamellar representation of the nanocomposites is shown in Fig. 2.

![Fig. 1. XRD for a) V$_2$O$_5$nH$_2$O, b) V$_2$O$_5$MeOH, and c) V$_2$O$_5$POMOE 1:1.](image-url)
The intercalation mechanism and the success of the reaction can be explained based on the following findings. Ruiz-Hitzky et al. [22] reported that the presence of water in the reaction assures a well controlled swelling of the V2O5 layers, allowing the penetration of the polymer chains. The absence of water strongly limits the insertion process, whereas the absence of organic solvents provokes a complete colloidal dispersion of the vanadium pentoxide, thereby destroying the ribbons and making it difficult to obtain well-defined intercalated phases. Based on this report we decided to use V2O5nH2O gel without allowing it to dry completely to ensure its homogeneity and the presence of water in the reaction mixture. The polymer was dissolved in methanol to ensure the presence of organic solvent in the reaction. Another advantage of using methanol is that it can be easily removed to facilitate the drying process of the nanocomposite films. The intercalation mechanism can be summarized as shown in Fig. 3.

During the insertion process, the V2O5nH2O ribbons are swelled by methanol allowing penetration of the POMOE chains and methanol molecules (Fig. 3A). Then, as the methanol is removed or evaporated the hydrogen atoms of POMOE combines with oxygen atoms (V=O) of V2O5nH2O ribbons leading to the formation of hydrogen bonds (Fig. 3B). The formation of hydrogen bonds was confirmed by the presence of an infrared band at 3445 cm⁻¹ in the IR spectrum of the intercalated product. When the excess solvent is removed by slow evaporation of the cast solution, the vanadium oxide ribbons oriented in the ab plane coated with POMOE chains on both sides re-stack, resulting in a bilayer loading of the polymer chains (Fig. 3C). The observation that even higher polymer ratios yield a re-stack, resulting in a bilayer loading of the polymer chains.

Slow evaporation of the cast solution, the vanadium oxide ribbons and making it difficult to obtain well-defined intercalated phases. Based on this report we decided to use V2O5nH2O gel without allowing it to dry completely to ensure its homogeneity and the presence of water in the reaction mixture. The polymer was dissolved in methanol to ensure the presence of organic solvent in the reaction. Another advantage of using methanol is that it can be easily removed to facilitate the drying process of the nanocomposite films. The intercalation mechanism can be summarized as shown in Fig. 3.

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Thermogravimetric analysis was used to further characterize the materials. Fig. 4 shows the thermogram in air for POMOE, V2O5POMOE 1:1, and V2O5POMOE 1:4. Pure POMOE (Fig. 4 curve a) is stable up to 298 °C, thereafter decomposing completely in a single weight loss step of 98.9%. The small weight loss below 100 °C of the nanocomposites is assumed to come from the adsorbed solvent or the moisture content of the samples. Therefore, V2O5POMOE 1:1 (Fig. 4 curve b) is stable up to 173 °C, and then decomposed in a one-step weight loss of 41.8%, providing a constant weight percentage residue of 45.6%. On the other hand, V2O5POMOE 1:4 (Fig. 4 curve c) showed two major weight loss steps of 54.3% and 13.8% between 100 °C to 253 °C and between 390 °C to 440 °C, respectively. The first weight loss is due to the inserted polymer and the second weight loss corresponds to the externally lying polymer.

It is worthy to note that the nanocomposites decompose at lower temperatures compared to pure POMOE. The lower decomposition temperatures indicates that the presence of the V2O5 in the nanocomposites catalysed the thermal decomposition of the polymer. This interpretation is supported by the observation that with higher V2O5 ratio (such as in V2O5-POMOE 1:1) the decomposition is faster leading to a sharp drop in weight loss as shown in Fig. 4 curve b.

For comparison, the decomposition profile of V2O5nH2O in both air and nitrogen, as well as that of V2O5-POMOE 1:1 in air are shown in Fig. 5. It was found that the weight loss due to evaporation of water from V2O5nH2O (Fig. 5 curve a and b) is independent of the atmosphere used. This is strong evidence that the weight loss was due to an evaporation process and therefore, was not facilitated through an oxidation reaction.

Fig. 5 curve a and b, shows a two-step weight loss process. The initial weight loss step corresponds to the evaporation of adsorbed and loosely bound water molecules from the xerogel. The second weight loss step corresponds to the removal of coordinated and/or strongly bound water molecules to the vanadium centers. From the TGA data, the amount of loosely bound water (H2Olo) and tightly bound water (H2Otb) were calculated. The exact composition of vanadium pentoxide xerogel could, in fact, be written as V2O5(H2O)1.6(H2O)0.3. However, for convenience the loosely bound and tightly bound water are combined together and the chemical formula is written as V2O5(H2O)1.9.

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A complete list of the decomposition profile of the nanocomposites is shown in Table 2. It is clear (from Table 2) that increasing the amount of POMOE decreased the residue percentage. This is expected because increasing the amount of POMOE decreases the concentration of V2O5nH2O from which the residue is derived. The thermal stability of the nanocomposites increases from around 186 °C to around 253 °C as the mole ratio of POMOE is increased from 0.5 to 4, respectively. This is due to reduced catalytic combustion effect of V2O5 at higher polymer ratio.

The stoichiometric compositions of the nanocomposites were calculated from the decomposition profiles. The weight loss steps are grouped into four stages: stage I (<120 °C), stage II (121–390 °C), stage III (391–500 °C) and residue (>500 °C) as stage IV. In stage I solvent/water is removed. Stage I is observed in all nanocomposites, as well as in the control sample (V2O5MeOH). Stage II corresponds to the decomposition of the inserted polymer. Stage III, which is present
in samples with higher polymer content (>1:3), is assigned to the externally lying POMOE-chains around V2O5 ribbons. Increasing the polymer mole ratio from 1:3 to 1:4 increases the stage III weight loss percentage by 4%. The reported stoichiometric ratios (in Table 2) for the samples showing stage II and III (V2O5/POMOE 1:1 and 1:4) represent a combined POMOE ratio. The residue phase (yellow in colour) was identified by XRD to be orthorhombic V2O5. Table 2 provides a complete list of the calculated stoichiometric ratios. Although the composition ratios (by TGA) of the nanocomposites show lower polymer ratio than the experimental mole ratios used, the trends are very consistent with each other.

3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used to investigate any phase transitions occurring in the nanocomposites. The nanocomposites exhibit a glass transition temperature (Tg), crystallization temperature (Tc), melting temperature (Tm) and a blending temperature (Te). Fig. 6 shows the thermal transitions for V2O5/POMOE 1:1 and V2O5/POMOE 1:4. A cold crystallization is observed for the nanocomposites with mole ratio 1:1 (Fig. 6 curve b) which is absent in nanocomposites with higher molar ratios. Other nanocomposites showed features similar to V2O5/POMOE 1:4 (Fig. 6 curve a) but with changes in the peak positions. The thermal transitions are summarized in Table 3.

The glass transition temperature (in Table 3) was found to be lower in the nanocomposites in comparison to pure POMOE, and the glass transition temperature decreases with increasing amount of the polymer. The DSC spectrum for nanocomposite with mole ratio (1:0.5) is reproducible, but inconsistent with the trends observed in the other samples. Possible interpretation of this observation is that in the mole ratio 1:0.5 all the polymer chains are inserted within the layered structure forming a rigid nanocomposite. The nanocomposites with higher molar ratios contain excess (un-intercalated) polymer, which contributes to the lowering of the glass transition temperature. The melting temperature of the nanocomposites was lower than that of pure POMOE, and the melting point increases with increasing amount of the polymer. The melting heat of fusion (ΔfusH) is also shown to increase with increasing POMOE content and the values approach that of the pure polymer, 47 Jg⁻¹.

All nanocomposites show an exothermic phase transition after 110 °C. This phase transition is referred to as the blending temperature (Te) i.e. the transition when the POMOE-chains thermally blend with V2O5nH2O ribbons. This interpretation was based on the fact that the Te is below the major decomposition temperatures, which is above 173 °C for all nanocomposites, and the materials obtained just above the Te are mechanically stable films. Fig. 6 shows sharp endothermic peaks with well-defined baselines after the glass transition temperatures, which confirms the presence of the polymer in the nanocomposites in comparison to the control samples. The DSC control samples were a cast film of V2O5nH2O, freeze-dried V2O5nH2O, and freeze-dried V2O5MeOH and their spectra are shown in Fig. 7.

Fig. 7 curve a and curve b show two broad endothermic overlapping peaks for the freeze-dried and the cast film of V2O5nH2O, respectively. The broad peaks indicate the evaporation of the solvent/volatiles from the samples. The first peak corresponds to the removal of the strongly bound water molecules i.e., in V2O5nH2O, while the second peak corresponds to the removal of the strongly bound water molecules. It is important to note that for highly oriented samples (the cast films), the peaks are observed at higher temperatures compared to the randomly oriented (freeze-dried) samples. Therefore, higher orientation was associated to a compact packing of water molecules within the layers, hence needing more energy to evaporate from the samples. On
Table 2
Summary of TGAs for POMOE, V₂O₅nH₂O, and V₂O₅POMOE nanocomposites in air.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mole ratios</th>
<th>TGA stoichiometry</th>
<th>Decompositions in air</th>
<th>Weight (%)</th>
<th>Temp. (°C)</th>
<th>Residue (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POMOE</td>
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<td>98.9</td>
<td>299</td>
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<tr>
<td>V₂O₅nH₂O</td>
<td>V₂O₅(H₂O)ₙ</td>
<td></td>
<td></td>
<td>10.3, 2.5</td>
<td>49, (321, 364)</td>
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<tr>
<td>V₂O₅MeOH</td>
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<td>V₂O₅POMOE</td>
<td>V₂O₅(POMOE)ₙ₉ (H₂O)ₙ₉</td>
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<td>186</td>
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<td>(1:0.5)</td>
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<td>V₂O₅POMOE</td>
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<td>41.8</td>
<td>173</td>
<td>45.6</td>
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<td>(1:1)</td>
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<tr>
<td>V₂O₅POMOE</td>
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<td></td>
<td>54.9</td>
<td>181</td>
<td>29.6</td>
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<td>(1:2)</td>
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<tr>
<td>V₂O₅POMOE</td>
<td>V₂O₅(POMOE)₁₃ (H₂O)₁₃</td>
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<td></td>
<td>53.8, 10.1</td>
<td>223, 416</td>
<td>21.3</td>
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<td>(1:3)</td>
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<tr>
<td>V₂O₅POMOE</td>
<td>V₂O₅(POMOE)₁₁ (H₂O)₁₁</td>
<td></td>
<td></td>
<td>54.3, 13.8</td>
<td>253, 440</td>
<td>18.7</td>
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</table>

*The temperature values were taken from the maximum peak of the derivative plot. Where the derivative peaks were not well resolved (due to overlapping weight loss steps), the temperature values of the peaks are enclosed in brackets.

The other hand, the DSC of V₂O₅MeOH (Fig. 7 curve c) shows only one endothermic peak, which corresponds to the loss of methanol molecules. Fig. 7 curve c also indicates that when methanol is added to V₂O₅nH₂O it displaces the interlayer water molecules. This conclusion is supported by thermogravimetric analysis, Fig. 5 curve c, which shows a one step weight loss process. X-ray diffraction also provides evidence, which shows an interlayer expansion of 2.6 Å due to the insertion of methanol.

The disparity in the decomposition temperatures between the DSC and TGA is due to the difference in the experimental set up. In TGA, the samples were placed on a platinum holder under direct gas (air or nitrogen) purge, whereas in DSC, the samples were sealed in aluminum cells and the measurements were performed under a nitrogen atmosphere.

3.4. Fourier transform infrared (FTIR)

Infrared spectroscopy was further used to characterize the nanocomposites. The IR spectra of the nanocomposite exhibited similar features. The absorption bands for POMOE, V₂O₅nH₂O, and V₂O₅POMOE 1:2 and the major bond group assignments [22,23] are summarized in Table 4. The nanocomposites show all the diagnostic bands for POMOE and V₂O₅nH₂O diagnostic bands in the nanocomposites indicate non-significant structural disruptions to the polymer chains and V₂O₅ ribbons upon intercalation. Therefore, the vibration shifts observed in the nanocomposites suggest a distortion in coordination geometry due to steric interactions between the confined polymer and the V₂O₅ framework [21,23].

3.5. Impedance spectroscopy

The conductivities of the nanocomposites were calculated from complex impedance data. The impedance experiment involved applying an AC voltage to the sample and measuring the real (Re Z) and imaginary (−Im Z) parts, of the resulting current. Complex plane plots of the impedance were single semicircles for all nanocomposite samples (Fig. 8), similar to plots for a simple parallel RC circuit. This indicates that the dominant mode of charge transport is electron conduction [24]. (Ion conduction may also occur, but if so it plays a relatively insignificant role).

The impedance was real at low frequencies, corresponding to the resistance R of the electrically conducting sample, with C being the POMOE and V₂O₅nH₂O. Mechanical stability was demonstrated by the formation of free standing films. The cast films can be easily peeled off the glass substrates by dipping in water (the peeling was facilitated by the use of soap water).

It is also interesting to note that the C–H stretching vibration peak in pure POMOE occurs at 2870 cm⁻¹. However, this peak is split into two vibrations (2912 cm⁻¹ and 2876 cm⁻¹), when the polymer is inserted into the layered structure, consistent with the polymer being in a constrained environment. The V=O and C—O—C stretching vibrations overlap in the region (1010–1115) cm⁻¹. The presence of POMOE and V₂O₅nH₂O diagnostic bands in the nanocomposites indicates non-significant structural disruptions to the polymer chains and V₂O₅ ribbons upon intercalation.
cable capacitance in parallel with it. This resistance and the sample dimensions were then used to calculate conductivity. For comparison, Fig. 8B shows impedance data for Li-POMOE, which is an ionic conductor. The diagonal spur on the right is due to blocking electrode behaviour at low frequencies.

The electrical conductivity results for V$_2$O$_5$nH$_2$O and nanocomposite samples are shown in Fig. 9. The straight lines on this graph of log $\sigma$ as a function of inverse temperature are indicative of a thermally-activated conduction process, described by an equation of the form

$$\sigma(T) = \sigma_0 e^{-E/kT}$$

where $\sigma_0$ is the pre-exponential constant and $E$ is the activation energy or band gap for conduction (semiconductor band gap).

The activation energies were estimated from the slopes of the curves and the values are shown in Fig. 9. The activation energy, $E$, for the V$_2$O$_5$nH$_2$O film was $\approx 0.17$ eV, close to what was reported by Livage [25] (0.2 to 0.4 eV) and De et al. [26] (0.13 eV). The activation energies for nanocomposites with and without LiX were practically equal ($\approx 0.22$ eV and 0.23 eV, respectively). It is interesting to note that the polymer ratio used did not affect the activation energy, but affected the conductivity values. Increasing the amount of POMOE lowered the electrical conductivity of the nanocomposites. The decreased electronic conductivity with increasing amount of POMOE indicates that the charge-transport channels are closed. This would be due to stronger hydrogen-bonding within the nanocomposites, as well as the electrical insulating property of POMOE. Although there were large uncertainties in the conductivity values, primarily due to non-uniform film thickness, the data show the temperature dependences clearly, and demonstrate the general trend that conductivity drops as the amount of POMOE increases.

The nanocomposite samples all showed conductivity behavior characteristic of electrical semiconductors. It was expected that by doping the nanocomposites with lithium salts, ions might replace electrons as the dominant charge carriers. That change would make these nanocomposites suitable for use as solid electrolytes in lithium ion batteries. However, the electrical conductivity was still large enough that the ionic conductivity could not be detected by our measurement technique. Studies are underway to investigate the effect of changing the LiX ratio.

A unique colour change was observed for some of these nanocomposites. The cause of this color change is not well understood, but it may be influencing the conductivity properties of these materials. For example, before impedance testing, V$_2$O$_5$POMOE cast films were red. Applying the silver paint electrodes, and/or exposing the samples to vacuum, did not cause any colour change. However, when the samples were removed from the vacuum chamber immediately after impedance measurements they were observed to be completely green. The colour change from red to green is a result of applying ac voltage (50 mV rms) and current during impedance measurement. After leaving the samples exposed to air on the laboratory bench for a few days, the colour changed back to red. However, it was noticed that the portion of the sample which was trapped underneath the silver electrodes remained green. This is likely because the trapped portion did not have direct exposure to air. These colour change phenomena indicate that chemical reactions occurred in the sample. Exactly what reactions occurred, and the possible role played by silver from the electrodes, is not yet known. A possible explanation

<table>
<thead>
<tr>
<th>Sample</th>
<th>IR band (cm$^{-1}$)</th>
<th>Major bond group assignments</th>
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<tr>
<td>POMOE</td>
<td>2870</td>
<td>C–H stretch</td>
</tr>
<tr>
<td></td>
<td>1113</td>
<td>C–O–C stretch</td>
</tr>
<tr>
<td></td>
<td>949</td>
<td>CH$_2$ rocking</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>CH$_2$ rocking</td>
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<tr>
<td>V$_2$O$_5$nH$_2$O</td>
<td>1616</td>
<td>H–O–H stretch</td>
</tr>
<tr>
<td></td>
<td>999</td>
<td>V=O stretch</td>
</tr>
<tr>
<td></td>
<td>707</td>
<td>V–O–V stretch</td>
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<tr>
<td>Nano composites (V$_2$O$_5$POMOE 1:2)</td>
<td>3445</td>
<td>O–H stretch</td>
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<td></td>
<td>2912</td>
<td>C–H stretch</td>
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<tr>
<td></td>
<td>2876</td>
<td>C–H stretch</td>
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<td></td>
<td>1108</td>
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<td></td>
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<td>CH$_2$ rocking</td>
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<tr>
<td></td>
<td>751</td>
<td>V–O–V stretch</td>
</tr>
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</table>

Table 4
A summary of major FTIR bands for POMOE, V$_2$O$_5$nH$_2$O and V$_2$O$_5$POMOE 1:2.

Fig. 8. A: Typical complex plots for nanocomposites a) V$_2$O$_5$Li-POMOE 1:1 and b) V$_2$O$_5$-POMOE 1:2. The temperature was 310 K. B: Complex plot for Li-POMOE at 300 K.

Fig. 9. Conductivity-temperature relationship for V$_2$O$_5$nH$_2$O and for nanocomposites with and without LiX. To avoid clutter, error bars are shown for only a few representative points. Uncertainties for other points are similar.
is suggested by the fact that the green colour corroborates with work done by Livage’s group [25]. Livage reported that uniform and adherent films had been deposited onto electroconductive glasses (ITO) by electrolysing colloidal V2O5 aqueous solutions. Colour changes were seen on thicker films which turned reversibly from orange on anodic polarization to green on cathodic polarization. Therefore, the colour change observed in our samples is a strong evidence of a redox reaction which means that the ionic and electronic conductivity of the nanocomposites may have been altered. It was noticed that dipping V2O5-POMOE films in water changed their colour to green, but was irreversible to red colour even after several days. It has been reported that electrical conductivity of V2O5nH2O increases as the amount of V4+ increase and ionic conductivity increases with increasing humidity due to fast proton conduction [27].

Figs. 10 and 11 show SEM images of cleaved cast films that had previously been used for conductivity measurements. Fig. 10 is a sample of V2O5 Li-POMOE 1:1. Note the strongly layered morphology of the film, evident in the cross-section, the non-uniform film thickness, and the rippled top surface. The dark region at the bottom of the figure is the glass substrate. Samples of V2O5 Li-POMOE 1:1 and V2O5 Li-POMOE 1:2 showed similar morphology, although the layering was less pronounced in the latter sample.

Fig. 11 shows a cleaved cast film of V2O5 Li-POMOE 1:2. In comparison to the other samples, this film is less compact, and its thickness is more non-uniform. The reasons for these differences would be due to lower concentration of the layered structure which provides the rigidity to the morphology of the nanocomposites. Similarly, the presence of the LiX matrix would be contributing to the non-uniform thickness morphology. The presence of voids in the film may be a reason why this sample had the lowest conductivity of all the nanocomposites in Fig. 9.

4. Conclusions

In summary, a versatile method for inserting POMOE and Li-POMOE into V2O5nH2O at room temperature resulting into a bilayer polymer loading has been demonstrated. The optimal insertion mole ratio for V2O5nH2O to POMOE was determined to be 1:1. This is because 1:1 is the lowest mole ratio resulting into the maximum interlayer expansion of 8.7 Å. The bilayer loading of POMOE-chains is a significant finding because it may mean that Li-ions are more mobile in bilayer V2O5-POMOE in comparison to the monolayer materials reported before, increasing the prospect of the nanocomposites being used as cathode materials in lithium ion batteries.

The ionic conductivity of the nanocomposites could not be determined by the method used, due to the high electronic conductivity. The next challenge is to study the effect of using different lithium salts because the additional matrix from the salt could be influencing the ionic conductivity, as well. For example, LiI would be a good candidate because it has been reported to produce V2O5Li-PEO with the elimination of iodine gas hence avoiding the anion matrix in the nanocomposites [14]. The ionic conductivity of the nanocomposites may also be improved by using completely amorphous polymers such as poly[bis-(2-methoxyethoxyethoxy)phosphazene] (MEEP). Although POMOE had been reported as amorphous, subsequent study [28], and our work show that it is not 100% amorphous. Currently we are working on the insertion of MEEP into V2O5nH2O xerogel using the same method.

A intercalation reaction mechanism is proposed. This mechanism can apply to PEO and other derivatives. Hydrogen bonding is thought to play a key role in the formation of the nanocomposites leading to improved mechanical stability of pure POMOE and pristine V2O5nH2O films upon intercalation.

Acknowledgments

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References