

Preparation of Polyethylene Oxide/Li_xV_{2-δ}O_{4-δ} Nanocomposites

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ABSTRACT: Polyethylene oxide (PEO)/Li_xV_{2-δ}O_{4-δ} nanocomposites were prepared in aqueous solution. Characterization of the nanocomposites using thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), powder X-ray diffraction (XRD), and Fourier transform infrared spectrum (FTIR) shows that polymer chains intercalate inorganic host lamella and exhibit lattice expansion along the stacking direction of 4.2 Å. A possible model for the structure of the nanocomposite is also provided. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2162–2166, 2001

Key words: polyethylene oxide; vanadium oxide; nanocomposite

INTRODUCTION

Recently, there has been considerable interest in constructing alternating layers of organic polymers and inorganic sheet structures in nanoscale. These materials can be described, as intercalation compounds of polymers within a layered host, or as nanocomposites of two solid phases. The main reason for the present investigation is the requirement for novel electronic anisotropic materials, better-performing battery cathode materials, functionalized structural materials, and polymer/inorganic surface interaction.¹

Polyethylene oxide (PEO) is a particularly important polymer that has the simplest structure of water-soluble polymers; it has been used in the study of polymer/layered inorganic host nanocomposites

because it can act as a solid solvent for salt, facilitating ion mobility in the solid state.² The layered inorganic hosts studied include layered silicates^{3,4} (e.g., montmorillonite, hectorite), transition metal oxides (e.g., V₂O₅,^{5,6} MoO₃,^{7–9}), transition dichalcogenides (e.g., MoS₂,^{10,11} TiS₂¹²), phosphorus trichalcogenides¹³ (e.g., CdPS₃, MnPS₃).

Li_xV_{2-δ}O_{4-δ} is a kind of new layered lithium vanadium oxide prepared by hydrothermal method.¹⁴ It has a simple tetragonal structure, and the vanadium oxide sheets are planar; all vanadium oxides have identical coordination. These vanadium oxides can reversibly intercalate lithium ions, making them viable candidates for the cathode of high-energy density lithium batteries. To improve the ion mobility in this new vanadium oxide, PEO can most likely be intercalated into host lamella, since it has a layered structure similar to that of other transition metal oxides, such as MoO₃ and V₂O₅.

The most common methods of preparing polymer/inorganic nanocomposites are (1) *in situ* polymerization of small precursors that are first

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incorporated by a topotactic mechanism; (2) the exfoliation of a layered inorganic structures, adsorption of a polymer onto the exposed surfaces from solution, and subsequent flocculation of nanocomposites; (3) melt intercalation where a polymer is heated above the melting temperature or flow temperature; and (4) the use of a polymer as a template for growth of the inorganic layers.

In this study, a new polymer/inorganic nanocomposite (PEO/Li_xV_{2-δ}O_{4-δ}) was first prepared by intercalating macromolecule in aqueous solution directly, which is proved by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Fourier transform infrared spectrum (FTIR). The influence of different PEO molecular weight and loading on host interlayer spacing is also described.

EXPERIMENTAL

Materials

Lithium vanadium oxide was synthesized as reported previously.¹⁴ V₂O₅ powder was mixed with 25% N(CH₃)₄OH and LiOH crystals in the ratio of 1:2:1, respectively. This mixture was then acidified with 3 M HNO₃ to pH values of 2–5. The resulting solution was transferred to a Teflon-lined autoclave, sealed, and reacted hydrothermally for 2 days at 200°C. The resulting greenish black crystals of a new layered vanadium oxide were formed. The lithium vanadium oxide was then filtered and dried in air. Commercial-grade PEO ($M_r = 3 \times 10^5$, 1×10^5) was used for reactions. All other reagents and solvents were of analytical reagent grade and were used without further purification.

Synthesis of Nanocomposites

The PEO/Li_xV_{2-δ}O_{4-δ} nanocomposites were prepared as follows: The Li_xV_{2-δ}O_{4-δ} was exfoliated in degassed water by 10 min of sonication to form a suspension with a concentration of 5 g/L⁻¹. The suspension was added to aqueous PEO solution and was stirred at certain temperature under nitrogen for about 10 h. The colloid was centrifuged. The resulting mixture was cast into a film by evaporation by water at room temperature on a flat surface without further washing.

Measurements

Powder XRD patterns were carried out on D/Max-3 using Cu-Kα radiation (1.5415 Å) at

3–35°C, and a scanning speed of 2°C/min⁻¹ was chosen. TGA was performed with a TGA 1000M instrument under a flow rate of 20 mL/min⁻¹; the heating rate was 10°C/min⁻¹. DSC was carried out by a DSC-SP instrument under N₂ flow at a rate of 20 mL/min⁻¹; the heating rate was also 10°C/min⁻¹. Elemental analysis was performed on an ICP/IRIS Advantage instrument. FTIR spectra were recorded on samples pressed into a KBr disk containing 0.5 wt % samples, using a Nicolet 510P FTIR spectrometer. A spectrum of pure KBr was collected for background correction.

RESULTS AND DISCUSSION

The quantity of elements in all samples was determined by TGA and direct elemental analysis. Li_xV_{2-δ}O_{4-δ} consists of 1.29% Li and 49.17% V, which gives a Li-to-V ratio of 0.2:1, less than the ratio described in the literature.¹⁴ This ratio was determined to be 0.08:1 in PEO/Li_xV_{2-δ}O_{4-δ} nanocomposites. TGA showed the amount of PEO of various samples. The lower amount of lithium element in PEO/Li_xV_{2-δ}O_{4-δ} nanocomposites is most likely attributable to the fact that much of it was removed by solution and some was replaced by intercalated PEO molecules.

Because of the lamellar structure of the ordered intercalation, XRD is a powerful technique to monitor the formation and structure of these nanocomposites. Figure 1 shows the XRD pattern of Li_xV_{2-δ}O_{4-δ} and PEO (3×10^5)₃/Li_xV_{2-δ}O_{4-δ} nanocomposites, respectively. From Figure 1, it is obvious that the interlayer *d*-spacing of Li_xV_{2-δ}O_{4-δ} increases from 7.7 Å to 11.9 Å with Δd of 4.2 Å after PEO intercalation, which means that PEO molecules were intercalated into Li_xV_{2-δ}O_{4-δ} and expanded lattice *d*-spacing with 4.2 Å. This value is similar to the net interlayer distance of V₂O₅ *n*H₂O intercalated by PEO and indicates a straight-chain conformation for PEO (rather than helix).⁶

For the different molecular weights of PEO used, the intercalation peaks appear at similar position in the X-ray data, which indicate that the molecular weight of PEO has little influence on the lamellar repeat distance of the host. In addition, a series of PEO (3×10^5)_{*x*}/Li_xV_{2-δ}O_{4-δ} nanocomposites intercalates with $0 < x \leq 7$ were prepared. XRD shows that the phase with $x = 1$ has an interlayer spacing of 10.8 Å. This value increases to 11.7 Å at $x = 2$; as x increases, the interlayer distance remains nearly constant until

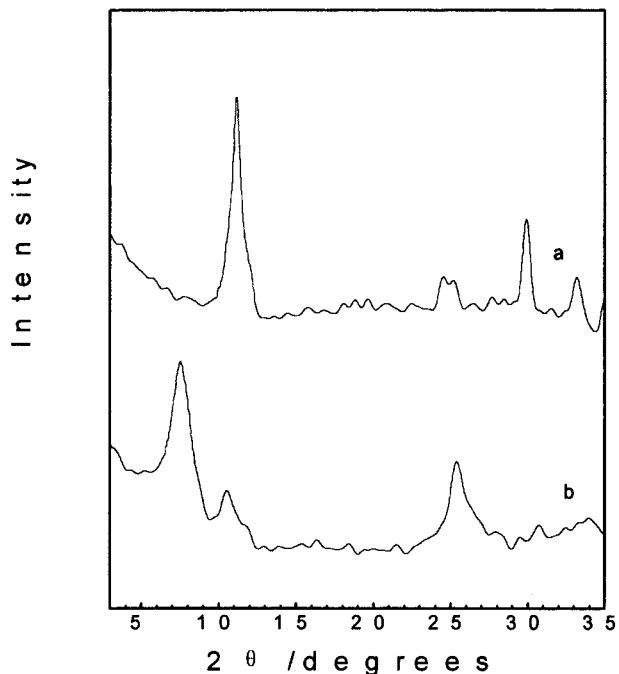


Figure 1 Powder X-ray diffraction data (Cu-K α , room temperature) for oriented film of (a) $\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$; (b) $\text{PEO} (3 \times 10^5)_3/\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$ nanocomposites.

$x = 4$. Despite the large amounts of PEO that could be intercalated in the $\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$, the lamellar repeat distance of the host did not change greatly, indicating that a large amount of polymer exists outside the layers as a separate phase. With the continued increase of x , the interlayer distance increases to 14.1 Å at $x = 7.0$ (Fig. 2). However, the stacking regularity primarily decreases with such high polymer loading according to the peak width at half-height.

Further evidence for PEO intercalation is provided by DSC studies. Figure 3 compares the DSC curves of pure PEO (3×10^5) and $\text{PEO} (3 \times 10^5)_3/\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$ nanocomposites. It is obvious that a pure sample gives a distinct endotherm, corresponding to the melt transition of crystalline PEO, but the endotherm peak is reduced for $\text{PEO}/\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$ nanocomposites, since some polymer chains are intercalated; crystallinity is then restricted as a result of intercalation. The endothermic peak does not vanish completely because a small fraction of unintercalated crystalline polymer is adsorbed on the external surfaces of the inorganic host. The endothermic peak at $\sim 30^\circ\text{C}$ is related to $\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$ instead of PEO.

As further evidence for PEO intercalation, FTIR spectroscopy of $\text{PEO} (3 \times 10^5)_3/\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$

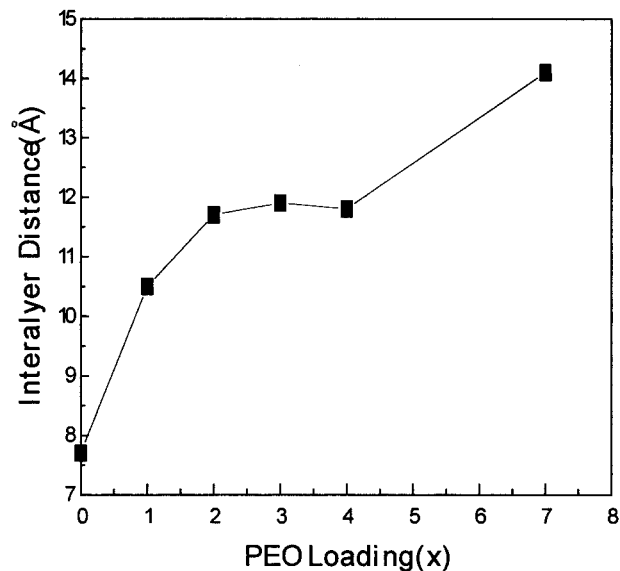


Figure 2 Variation of interlayer spacing as a function of polymer loading in $\text{PEO} (3 \times 10^5)_x/\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$ nanocomposites.

nanocomposite was provided (Fig. 4). The broad and intense $\text{V}_{\text{CH}}(\text{CH}_2)$ band centered at 2888 cm^{-1} in pure PEO is resolved into two small bands in the nanocomposite at 2920 cm^{-1} and 2850 cm^{-1} , similar to that observed for other PEO nanocomposites.¹⁵ This has been ascribed to

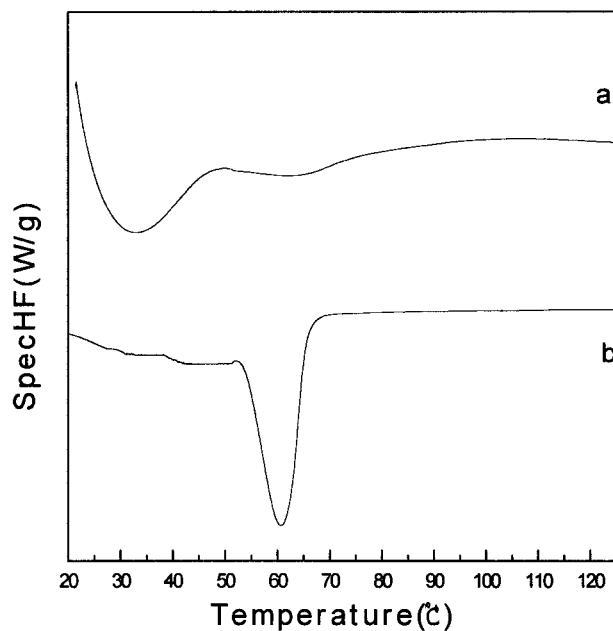


Figure 3 DSC curves of samples (a) $\text{PEO} (3 \times 10^5)_3/\text{Li}_x\text{V}_{2-\delta}\text{O}_{4-\delta}$ nanocomposite; (b) $\text{PEO} (3 \times 10^5)$.

a strong interaction between the oxygen atoms of the PEO chain and the interlayer cation. As compared with bulk PEO, another major difference is in the positions of the mid-infrared (IR) band of the intercalated PEO. The CH₂ deformation in this region is sensitive to the PEO chain structure and can, in principle, be used to help distinguish the possible conformation of PEO between host layers—helix (TTG)₇, Zig-Zag type I (T₅GT₅G) and Zig-Zag type II (TG₂TG₅). Among them, helical PEO has the structure in which the O—CH₂—CH₂—O has an all-gauche conformation.¹⁶ The bands observed at 852 cm⁻¹ and 951 cm⁻¹ in the intercalated compound are characteristic of O—CH₂—CH₂—O in the gauche conformation and may be assigned to a rocking vibrational mode of the CH₂ group. The intercalated compound shows an additional set of bands at 1310 cm⁻¹, 1408 cm⁻¹, 1352 cm⁻¹. Bands at these positions have been observed in the Zig-Zag type I PEO—HgCl₂ complex¹⁷ and consequently interpreted similarly; 1310 cm⁻¹ band is assigned to V_{CH}(CH₂) of a *trans*-O—CH₂—CH₂—O conformation. The strong band at 1115 cm⁻¹ in pure modes is known to shift to lower frequencies at 998 cm⁻¹ in the PEO/Li_xV_{2-δ}O_{4-δ} nanocomposite. The significant low-frequency shift in FTIR spectrum is also an indication of very strong interaction of the oxygens of the PEO chain with either the Li⁺, the host Li_xV_{2-δ}O_{4-δ} lattice, or both.

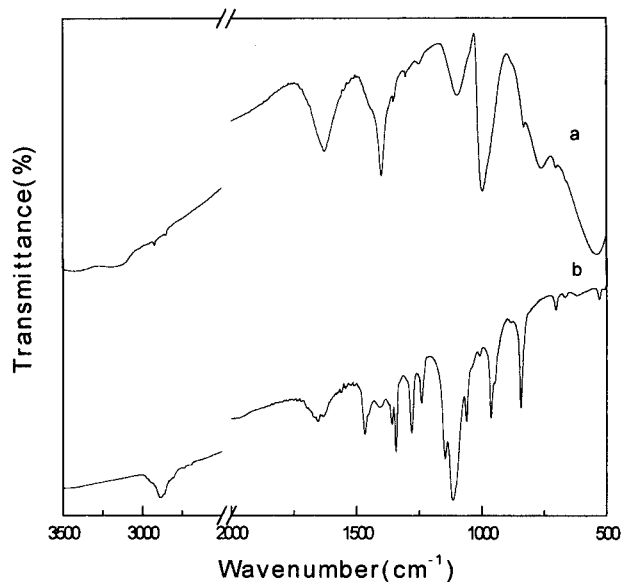


Figure 4 Fourier transform infrared spectrum of (a) PEO(3×10^5)/Li_xV_{2-δ}O_{4-δ} nanocomposite; (b) PEO(3×10^5).

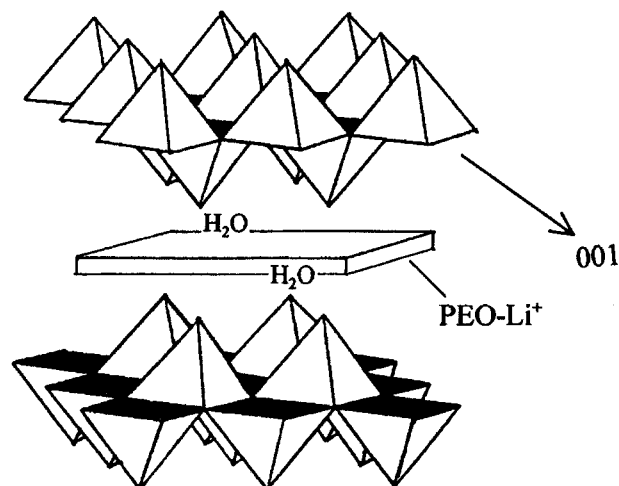


Figure 5 Schematic diagrams of the proposed structure of the PEO/Li_xV_{2-δ}O_{4-δ} nanocomposite (the view of the plane perpendicular to the Li_xV_{2-δ}O_{4-δ} sheets—001).

This investigation shows that PEO molecules were intercalated into Li_xV_{2-δ}O_{4-δ}. Although the result so far is not about to provide direct evidence for the structure of the intercalated PEO, it is possible to rule out certain possibilities. Lattice expansion distance and FTIR spectrum analysis make it possible that there is only one layer chain exists between lattice lamella (Fig. 5). The accurate structure mode requires further study, which is currently in progress.

CONCLUSIONS

This experiment indicates that PEO molecules were intercalated into Li_xV_{2-δ}O_{4-δ} layers and exhibited lattice expansion. It is suggested that the PEO between hosts has Zig-Zag type I conformation and that its crystallinity is restricted.

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