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Effect of modification by poly(ethylene-oxide) on the reversibility of Li insertion/extraction in MoO₃ nanocomposite films

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Abstract

MoO₃ xerogel films modified by poly(ethylene-oxide) (PEO) were obtained by combining ion-exchange method with sol–gel technique. Investigations were conducted by X-ray diffractometry (XRD), Fourier transformation infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. The results show that when MoO₃ xerogel is modified by the intercalation of PEO, the H atoms in PEO are H-bonded with the O atoms in the Mo=O bonds of MoO₃ xerogel, which effectively shields the electrostatic interaction between MoO₃ interlayer and Li⁺ ions. The reversibility of the insertion/extraction of Li⁺ ions is greatly improved by the modification with PEO of MoO₃ nanocomposite films.

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1. Introduction

MoO₃ is known to be an attractive material as a cathodic electrode in secondary Li batteries and electrochromic devices [1–3]. Its theoretical Li insertion capacity is difficult to attain in practice due to irreversible phase transformations in the crystalline form or irreversible Li insertion in the case of the xerogel [4]. Many researchers have modified MoO₃ with polymer such as poly(*p*-phenylene vinylene) (PPV), polyaniline (PAN), or nylon [5–7], but modifying MoO₃ xerogel with PEO has not been reported. The intercalation of PEO is expected to enhance the mobility of Li⁺ ions in MoO₃

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xerogel interlayer and improve the reversibility of insertion/extraction of Li^+ ions. The preparation of modified MoO_3 xerogel film and the effect of modification by poly(ethylene-oxide) on reversibility of insertion/extraction of Li^+ ion in MoO_3 nanocomposite films are investigated and discussed in this paper.

2. Experimental

MoO_3 sol was prepared by the ion exchange of $(\text{NH}_4)_4\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ($\geq 99.0\%$) through a proton exchange resin with particle size of 0.3–1.2 mm (from a Shanghai chemical agent company). After ion exchange, a clear light-blue MoO_3 sol (pH 2.0) was obtained. PEO with average molecular weight of 400,000 g/mol (from Aldrich) was dissolved in distilled water and the solution was mixed with MoO_3 sol. The molar ratio of ethylene to MoO_3 was $x:1$ ($x = 0, 0.5$). The composite membrane was formed in glass substrate by the dip-coating method after the mixed sol was left motionless for 2 or 3 days. The MoO_3 xerogel films were produced by heating the composite membranes for 36 h at 380°C in N_2 atmosphere.

X-ray diffraction (XRD) experiments were done on a HZG4/B-PC X-ray diffractometer with $\text{Co K}\alpha$ radiation and graphite monochromator. Fourier transform infrared (FT-IR) absorption spectra of MoO_3 xerogel both before and after the modification with PEO were recorded using a 60-SXB IR spectrometer with a resolution of 4 cm^{-1} . The measuring wavenumber range was $380\text{--}3200\text{ cm}^{-1}$. XPS measurements were carried out using an ESCALAB MK II multi-technique electron spectrometer. The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below 1×10^{-8} Pa. With the binding energy of C1s (284.80 eV) as an internal standard, XPS spectra of Li1s were taken from the modified MoO_3 xerogel films containing Li^+ ions inserted by using electrochemical diffusion means. The cyclic voltammogram (CV) was performed by electrochemical method in a non-aqueous lithium cell using 1 M LiClO_4 dissolved in propylene carbonate (PC) electrolyte. The electrochemical cell was a standard three-electrode system. Indium tin oxide (ITO) conducting glass coated with the modified MoO_3 xerogel film and platinum foil were used as working electrode and counter electrode, and standard calomel electrode as a reference electrode. All electrochemical measurements were conducted in a glove box filled with dry argon [4].

3. Results and discussion

3.1. XRD analyses

The X-ray diffraction patterns of MoO_3 xerogel both before and after modification with PEO are shown in Fig. 1. The XRD pattern of MoO_3 xerogel shows four peaks whose d values are 0.690, 0.345, 0.230 and 0.173 nm corresponding to the diffraction of (020), (040), (060) and (080) crystal planes, respectively [8]. No ($h0l$) or (hkl) reflections are observed in Fig. 1, confirming the turbostratic nature of the MoO_3 slabs perpendicular to the b -direction axis. The repeated distance in modified MoO_3 xerogel film increases from 0.690 nm for MoO_3 xerogel to 1.308 nm for MoO_3 xerogel film modified by PEO in which peaks of (060), (080) crystal planes vanish. The increase in the repeated distance is because PEO intercalates in MoO_3 xerogel interlayer and opens the MoO_3

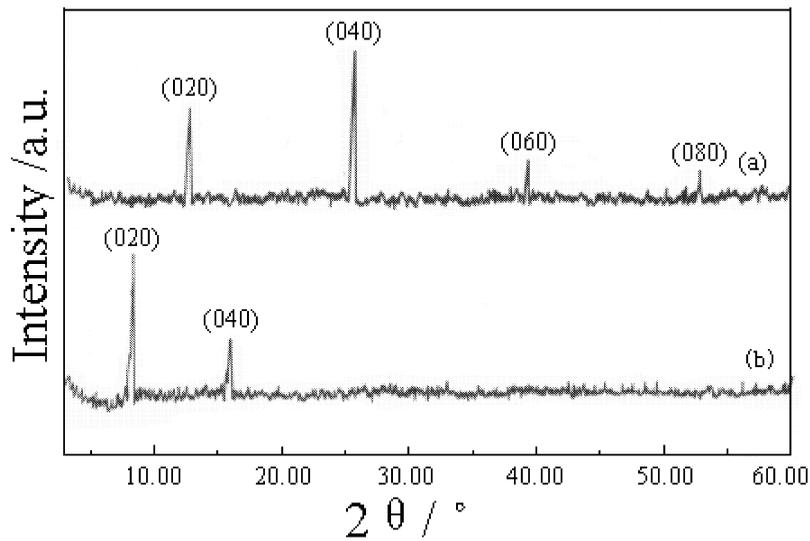


Fig. 1. X-ray diffraction patterns of MoO_3 xerogel both before (a) and after (b) the modification by PEO.

xerogel layers [9,10]. The disappearance of some peaks shows the reduction of the crystalline arrangement in the b -direction with the modification with PEO intercalating in the interlayer [11].

3.2. FT-IR spectrum analyses

FT-IR spectra of MoO_3 xerogel both before and after the modification with PEO are shown in Fig. 2. The MoO_3 xerogel exhibits three main vibration modes in the $400\text{--}1000\text{ cm}^{-1}$ range. The terminal

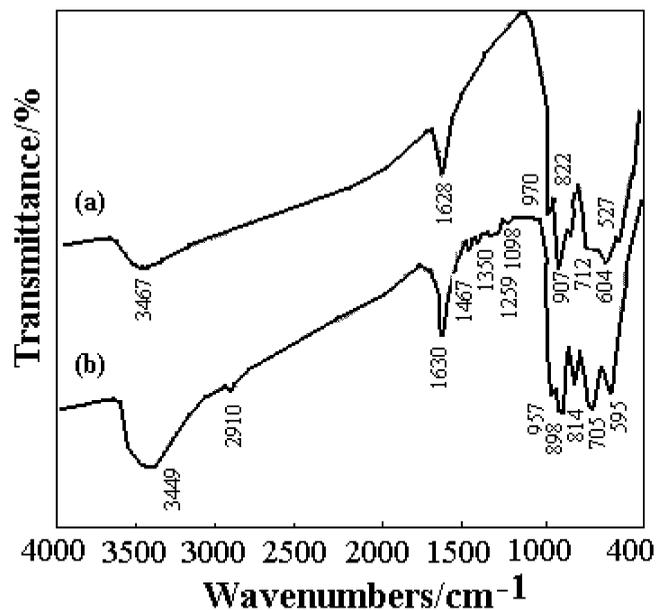


Fig. 2. FT-IR spectra of V_2O_5 xerogel both before (a) and after (b) the modification by PEO.

oxygen symmetry stretching mode (ν_s) of Mo=O, the bridge oxygen asymmetry and symmetry stretching modes (ν_{as} and ν_s) of Mo–O–Mo, are at 970, 907 and 822 cm^{-1} , respectively [4]. FT-IR spectra after modification by PEO show that the characteristic intense peaks at 1098, 1259, 1350 and 1467 cm^{-1} prove the presence of PEO and that small and poorly resolved peak at 2910 cm^{-1} is an indication for amorphous PEO, which is different from that of crystalline PEO [12]. When intercalating PEO into MoO₃ xerogel, all the vibration modes change remarkably and shift to lower wavenumber. The ν_s (Mo=O) shifts from 970 to 957 cm^{-1} , which indicates that the Mo=O...H bond is formed in the nanocomposite materials [13]. Namely, the H atoms in the PEO are H-bonded with the O atoms in the Mo=O bonds of MoO₃ xerogel. All these suggest that PEO used as modification is intercalated in the interlayer of MoO₃ xerogel and has relatively strong interaction with MoO₃ xerogel, which is in agreement with the XRD results.

3.3. XPS analyses

XPS is an effective technique to analyze chemical conditions of elements qualitatively and quantitatively. XPS core level spectra for Li1s of MoO₃ xerogel both before and after the modification with PEO were recorded in the binding energy range of 51.00–59.00 eV for ten detailed scans. In order to conduct a quantitative analysis of the chemical state, the spectra were deconvoluted and fitted by a VGS5000 system developed by VG Scientific. The beam was unmonochromated and argon-ion sputter etching was used to remove surface contaminants. As shown in Fig. 3, there were two different chemical conditions of lithium with binding energy of 55.05 and 56.00 eV, ascribed to the Li⁺ ions in the interlayer and interstitial positions (localized by the layers) of MoO₃ lattice [14], respectively. Their corresponding contents are 67.93 and 32.07%. After the intercalation of PEO, the percentage of

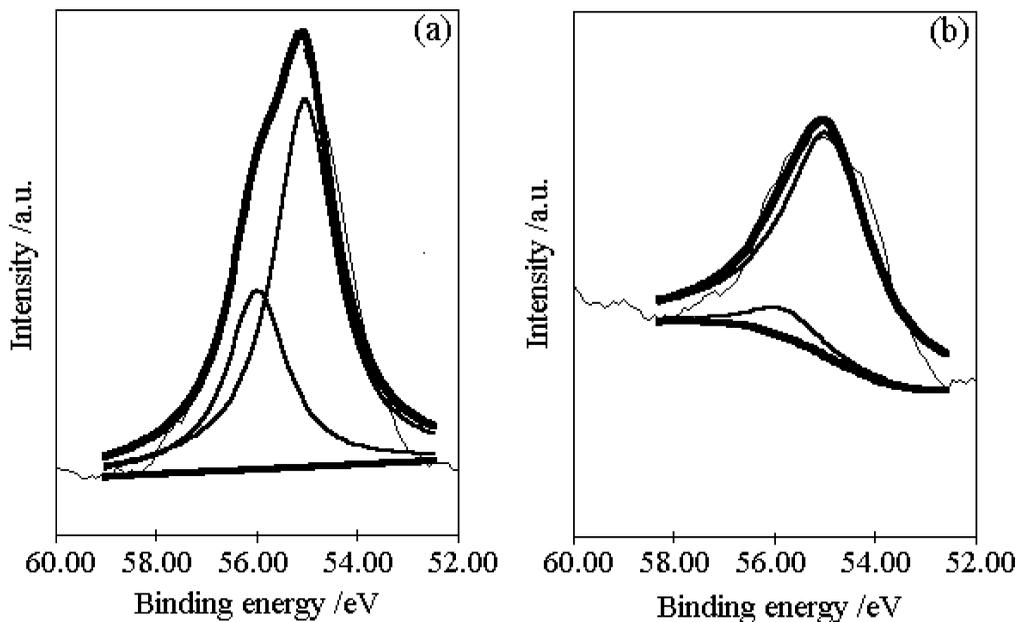


Fig. 3. XPS Li1s core level spectra of MoO₃ xerogel both before (a) and after (b) the modification by PEO.

Table 1
Results of peak fitting for XPS Li1s core level spectra

| Sample | Binding energy (eV) | Content (mol%) | FWHM (eV) |
|--|---------------------|----------------|-----------|
| MoO ₃ xerogel before PEO modification | 55.05 | 67.93 | 1.46 |
| | 56.00 | 32.07 | 1.50 |
| MoO ₃ xerogel after PEO modification | 54.95 | 91.69 | 1.46 |
| | 55.80 | 8.31 | 1.50 |

Li⁺ ions in the interlayer remarkably increased from 67.93 to 91.69%, while the percentage of ions in the interstitial positions decreased from 32.07 to 8.31%. Furthermore, the Li1s core level binding energy was shifted to lower values (Table 1). The decrease in the binding energy of the Li1s core level indicates a decrease in the interaction between Li⁺ ions and their environments (including PEO chains and MoO₃ layers) [15,16], which is beneficial for the mobility of lithium in the interlayer of MoO₃. The results are in good agreement with the following cyclic voltammogram (CV) analyses.

3.4. CV analyses

Fig. 4 shows the cyclic voltammogram curves of MoO₃ xerogel both before and after the modification with PEO, in which the first, second and seventh cycle curves are plotted. The area A_i (i is the cycle times) which is surrounded by each cycle curve represents the amount of the insertion of Li⁺ ions. The cycle efficiency is calculated by the following equation,

$$Q_i = A_i/A_1$$

where Q_i is cycle efficiency, A_1 is the area of the first cycle curve and A_i is the area of the i th cycle curve. The cycle efficiencies of different cycle times and compositions are listed in Table 2.

As can be seen in Fig. 4 and Table 2, the second cycle efficiency Q_2 of MoO₃ xerogel films before and after modification with PEO reached 89.3 and 82.8%, respectively. The lower Q_2 of MoO₃ xerogel film after modification with PEO indicates that the portion of Li⁺ ions complexed by PEO chains cannot be extracted from the interlayer. Meantime, it is found that the seventh cycle efficiency Q_7 of MoO₃ xerogel film after modification with PEO was 76.1%, which is higher than that of MoO₃ xerogel film before modification with PEO (61.3%), indicating that cycling stability tends to increase after several cycles. The Q_7 of MoO₃ xerogel film before modification with PEO apparently decreases from 89.3 to 61.3%, primarily owing to the strong electrostatic interactions between Li⁺ ions and oxygen atoms of the MoO₃ lattice. When PEO is intercalated into MoO₃ xerogel, it has a relatively strong interaction with MoO₃ layers and a complexing interaction with Li⁺ ions, effectively shielding electrostatic interaction between Li⁺ ions and MoO₃ [17]. As a result, the cycling stability is improved and the reversibility of insertion/extraction of Li⁺ ions in the MoO₃ interlayer is enhanced.

4. Conclusions

MoO₃ xerogel films modified by poly(ethylene-oxide) (PEO) were obtained by combining an ion-exchange method with sol–gel technique. Investigations were conducted by X-ray diffractometry

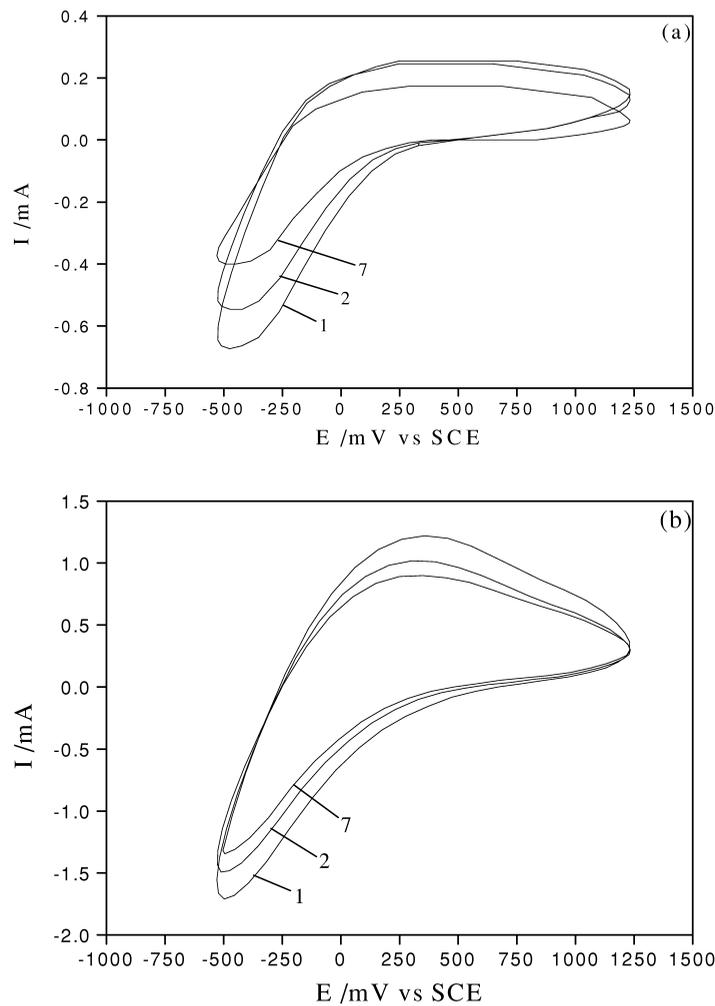


Fig. 4. Cyclic voltammogram curves of MoO_3 xerogel both before (a) and after (b) the modification by PEO.

(XRD), Fourier transformation infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. The results show that when MoO_3 xerogel is modified by PEO, the H atoms in PEO are H-bonded with the O atoms in the $\text{Mo}=\text{O}$ bonds of MoO_3 xerogel, which effectively

Table 2
The cycle efficiency of different cycle times and compositions

| Sample | Q_2 (%) | Q_5 (%) |
|--|-----------|-----------|
| MoO_3 xerogel before PEO modification | 89.3 | 61.3 |
| MoO_3 xerogel after PEO modification | 82.8 | 76.1 |

shields the electrostatic interaction between MoO_3 interlayer and Li^+ ions. The reversibility of insertion/extraction of Li^+ ions is greatly improved with the modification by PEO in MoO_3 xerogel.

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