Effect of modification by poly(ethylene oxide) on the reversibility of insertion/extraction of Li$^+$ ion in V$_2$O$_5$ xerogel films

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V$_2$O$_5$ xerogel films modified by poly(ethylene oxide) (PEO) were obtained *via* the sol–gel method. 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 the V$_2$O$_5$ xerogel is modified by the intercalation of PEO, the H atoms in PEO are hydrogen-bonded with the O atoms of the V=O bonds of the V$_2$O$_5$ xerogel, which effectively shielded against electrostatic interactions between the V$_2$O$_5$ interlayer and Li$^+$ ions. The reversibility of insertion/extraction of Li$^+$ ions is greatly improved by modification of the V$_2$O$_5$ xerogel with PEO.

Introduction

V$_2$O$_5$ is known to be an attractive material as a positive electrode in secondary Li batteries, with an average potential of intercalation close to 3 V *vs.* Li and a theoretical capacity of 295 mA h g^{-1}.[1–5] The latter value 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.[6] Many researchers have modified V$_2$O$_5$ with polymers such as poly(ethylene glycol) (PEG), polypropylene (PPy) and polyaniline (PAn),[7–12] but modifying V$_2$O$_5$ xerogel with poly(ethylene oxide) (PEO) has not been reported. The intercalation of PEO is expected to enhance the mobility of Li$^+$ ions in the V$_2$O$_5$ xerogel interlayers and improved the reversibility of insertion/extraction of Li$^+$ ions. The preparation of a modified V$_2$O$_5$ xerogel film and the effect of modification with poly(ethylene oxide) on the reversibility of insertion/extraction of Li$^+$ ion in V$_2$O$_5$ xerogel films are investigated and discussed in this paper.

Experimental

Materials

The layered oxide used in these experiments is V$_2$O$_5$ (99.5%). PEO was purchased from Aldrich Chemical Company Inc. with an average molecular weight of 400 000 g mol^{-1} and a melt temperature of 70 °C.

The preparation of modified V$_2$O$_5$ xerogel film

Melting V$_2$O$_5$ powder at 1073 K in a ceramic crucible results in a molten liquid.[13,14] When the molten liquid is quickly poured into distilled water, a brownish V$_2$O$_5$ sol is formed. The sol viscosity is directly related to the amount of V$_2$O$_5$ powder with respect to the water volume. PEO solution was mixed with V$_2$O$_5$ sol to form a mixed sol. The molar ratio of ethylene to V$_2$O$_5$ was x:1(x = 0, 0.5). Indium tin oxide (ITO) conducting glass substrates were dipped into the mixed sol, and then pulled out slowly. The gel formed on the substrate was left to dry for 48 h at room temperature. The as-prepared films were subjected to heat treatment (423 K) for 24 h in N$_2$ atmosphere to constant weight, which removes free water in the films.[14]

Experimental techniques

X-Ray diffraction (XRD) experiments were done on a HZG4/B-PC X-ray diffractrometer with CoK$_\alpha$ radiation and a graphite monochromator. Fourier transform infrared (FTIR) absorption spectra of V$_2$O$_5$ xerogels both before and after the modification with PEO were recorded using a 60-SXB IR spectrometer with a resolution of 4 cm^{-1}. The measured wavenumber range is 380–3200 cm^{-1}. XPS measurements were carried out by using an ESCALAB MK 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 V$_2$O$_5$ xerogel films containing Li$^+$ ions inserted by using electrochemical diffusion means. Cyclic voltammetry was performed by electrochemical methods in a non-aqueous lithium cell using 1 M LiClO$_4$ dissolved in a propylene carbonate (PC) electrolyte. The electrochemical cell was a standard three-electrode system. Indium tin oxide (ITO) conducting glass coated with the modified V$_2$O$_5$ xerogel film and platinum foil were used as working and counter electrode, and a standard calomel electrode was used as the reference electrode. All electrochemical measurements were conducted in a glove box filled with dry argon.[6]

Results and discussion

XRD analyses

The X-ray diffraction patterns of V$_2$O$_5$ xerogels both before and after modification with PEO are shown in Fig. 1. The XRD pattern of the unmodified V$_2$O$_5$ xerogel shows four peaks whose d values are 11.154, 3.659, 2.754, 2.186 Å corresponding to diffraction by the (001), (003), (004), (005) crystal planes, respectively.[15] No (hk0) and (hkl) reflections are observed in Fig. 1, confirming the turbostratic nature of the V$_2$O$_5$ slabs perpendicular to the stacking axis. The repeated distance in modified V$_2$O$_5$ xerogel film increases from 11.154 Å to 14.246 Å and the peaks of the (004), (005) crystal planes vanish. The increase of the repeat distance is thought to result from PEO being intercalated into the V$_2$O$_5$ xerogel interlayer and opening the V$_2$O$_5$ xerogel layers.[16,17] The disappearance of some peaks
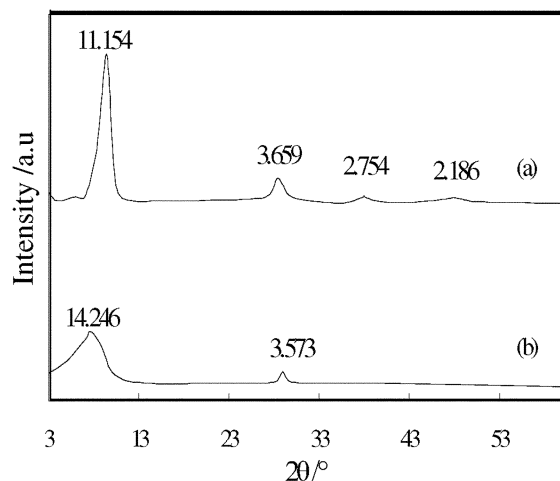
Fig. 1 X-Ray diffraction patterns of V_2O_5 xerogel both before (a) and after (b) modification with PEO.
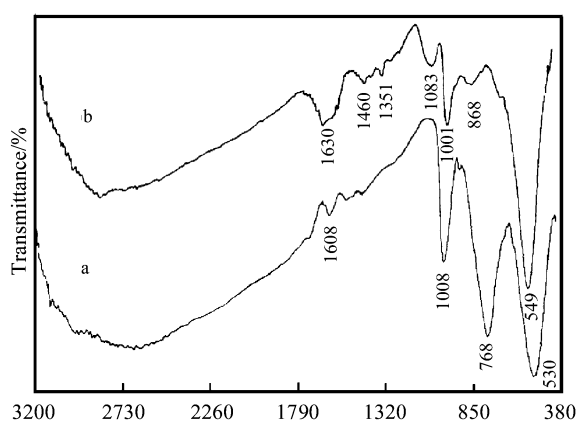

Fig. 2 FTIR spectra of V_2O_5 xerogel both before (a) and after (b) modification with PEO.

shows the reduction of the crystalline arrangement in the c-direction with intercalation of PEO into the interlayer.[18]

FT-IR spectral analyses

FT-IR spectra of V_2O_5 xerogel both before and after modification with PEO are shown in Fig. 2. There is an enormous band at 2683 cm^{-1} corresponding to the O–H vibration from water,[7] which confirms the presence of water in the V_2O_5 xerogel before modification with PEO. The V_2O_5 xerogel also exhibits three main vibration modes in the 380–1010 cm^{-1} region. The terminal oxygen symmetric stretching mode (v_s) of V=O and the bridge oxygen asymmetric and symmetric stretching modes (v_{as} and v_s) of V–O–V are at 1008, 768 and 530 cm^{-1}, respectively.[19] FT-IR spectra after modification with PEO show characteristic intense peaks at 1083, 1351 and 1460 cm^{-1} which prove the presence of PEO and the broad and poorly resolved peak at 2850 cm^{-1} is an indication of the presence of amorphous PEO, which is different from that of crystalline PEO.[20] The enormous band at 2683 cm^{-1} is not observed, confirming the disappearance of water in V_2O_5 interlayer due to the intercalation of PEO, which enables V_2O_5 xerogel modified with PEO to be used as a cathode material in secondary Li batteries. Meanwhile when intercalating PEO into the V_2O_5 xerogel, all the peaks change to varying extents. The v_s(V–O–V) and v_{as}(V–O–V) modes shift to higher wavenumbers. The v_{as}(V–O–V) mode shifts from 768 cm^{-1} to 868 cm^{-1} and its intensity decreases. The v_s(V–O–V) mode moves from 530 cm^{-1} to 549 cm^{-1}. In contrast, the v_s(V=O)

band slightly shifts to lower wavenumber, from 1008 cm^{-1} to 1001 cm^{-1}, which is in agreement with the finding reported by Harreld et al.[21] There are two types of vibration modes whose shifts indicate the nature of the modification. The shift of the v_s(V=O) mode indicates that H-bonding effects are observed in the modified hybrid V_2O_5 xerogel.[21] Namely, the H atoms in PEO are H-bonded with the O atoms of the V=O bonds of V_2O_5 xerogel. The second type of vibration mode affected by the modification is the V–O–V stretch. For the existence of H-bonds, the position of the V atom in the xerogel changes due to the lessening of the strength of the V=O bond,[22] which causes the strengthening of the V–O–V bond. All these factors suggest that PEO used as modification is intercalated in the interlayer of V_2O_5 xerogel and has relatively strong interaction with V_2O_5 xerogel, which is in agreement with the XRD results.

XPS analyses

XPS is an effective technique for the analysis of the chemical conditions of elements qualitatively and quantitatively. XPS core level spectra for Li1s of V_2O_5 xerogel both before and after modification with PEO were recorded in the binding energy range 51.00–59.00 eV for 10 detailed scans. In order to investigate a quantitative analysis of the chemical state, the spectra were deconvoluted and fitted by a VGS5000 system developed by VG Scientific Ltd. The beam was unmonochromated and argon-ion sputter etching was used to remove surface contaminants. As shown in Fig. 3, there were three different chemical states of lithium with binding energies of 54.95, 56.10 and 57.10 eV, which are ascribed to the Li$^+$ ions in the interlayer, localized by the bridge oxygen and the double bond oxygen of V_2O_5 lattice, respectively.[23] The corresponding contents of these Li$^+$ species are 52.90%, 29.03% and 18.07%. After modification with PEO the intensities of the Li$^+$ signals are higher than those before modification and the content of Li$^+$ ions in the interlayer remarkably increased from 52.90% to 70.80%, becuase intercalation of PEO removes water from the interlayer, opens the xerogel layers and increases the reversible Li insertion capacity. However, the intensities of Li$^+$ ions localized by V–O–V and V=O of V_2O_5 lattice decrease apparently (see Fig. 3) and the corresponding contents of Li$^+$ ions decrease (see Table 1), which may be due to the partial change of the structural arrangement because of modification
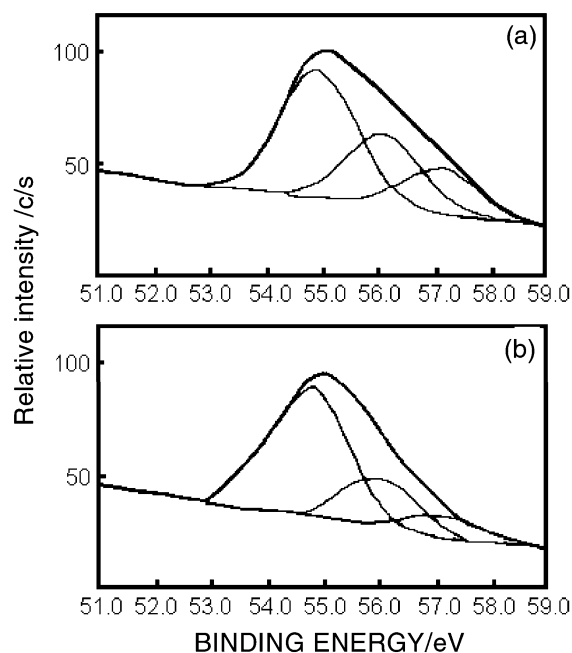

Fig. 3 XPS Li1s core level spectra of V_2O_5 xerogel both before (a) and after (b) modification with PEO.

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

Sample	Binding energy/eV	Content (mol%)	FWHM/eV
V_2O_5 xerogel before	54.95	52.90	1.60
PEO modification	56.10	29.03	1.60
	57.10	18.07	1.60
V_2O_5 xerogel after	54.85	70.80	1.60
PEO modification	55.95	26.00	1.60
	57.00	3.20	1.60

by PEO. Also, the Li1s core level binding energies shifted to lower values (shown in Table 1). The decrease in the binding energy of Li1s core level indicates a decrease of the interaction between Li$^+$ ions and their environment (including PEO chains and V_2O_5 layers), which is beneficial to the mobility of Li$^+$ ions in the interlayer of V_2O_5.[24]

Cyclic voltammetric curves

Fig. 4 shows the cyclic voltammetric curves of V_2O_5 xerogel both before and after modification with PEO, in which the first, second and fifth cycle curves are plotted. The area A_i (i is the cycle time) which is surrounded by each cycle curve represents the amount of Li$^+$ ion insertion. The cycle efficiency is calculated by using the following equation:

$$Q_i = A_i/A_1$$

where

Q_i = cycle efficiency
A_1 = the area of the first cycle curve
A_i = the area of the ith 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 V_2O_5 xerogel films before and after modification with PEO reached 95.5% and 93.0%, respectively. The
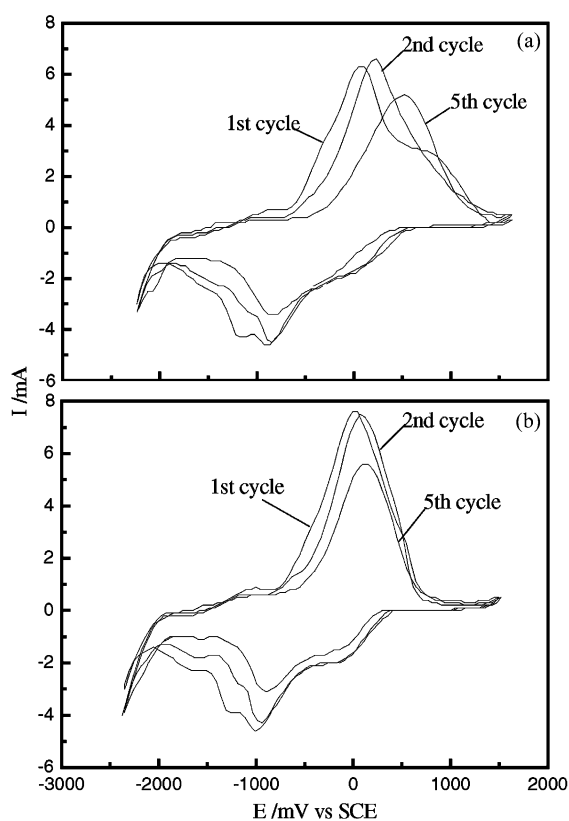

Fig. 4 Cyclic voltammetric curves of V_2O_5 xerogel both before (a) and after (b) modification with PEO.

Table 2 The cycle efficiency of different cycle times and compositions

Sample	Q_2 (%)	Q_5 (%)
V_2O_5 xerogel before PEO modification	95.5	41.7
V_2O_5 xerogel after PEO modification	93.0	70.0

lower Q_2 of V_2O_5 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 fifth cycle efficiency Q_5 of V_2O_5 xerogel film after modification with PEO was 70.0%, which is higher than that of V_2O_5 xerogel film before modification with PEO (41.7%), indicating that cycling stability tends to increase after several cycles. The Q_5 of V_2O_5 xerogel film before modification with PEO apparently decreases from 95.5% to 41.7%, primarily owing to the strong electrostatic interactions between Li$^+$ ions and oxygen atoms of the V_2O_5 lattice. It is found that the reduction and oxidation peaks shifted to higher potentials owing to the loss of crystallinity of V_2O_5 xerogel, indicating that the cyclability of Li$^+$ ion insertion/extraction is decreased after several sweeps. The potential of the oxidation peak of V_2O_5 xerogel shifts greatly from 106 mV to 232 mV and 521 mV after the second and fifth sweeps respectively, whereas that of modified V_2O_5 xerogel is shifted slightly from 45 mV to 70 mV and 148 mV respectively, demonstrating the improvement of the cyclability and the cycling stability of Li$^+$ ion insertion/extraction upon modification with PEO. When PEO is intercalated into V_2O_5 xerogel, it has relatively strong interactions with V_2O_5 layers and a complexing interaction with Li$^+$ ions, effectively shielding against electrostatic interactions between Li$^+$ ions and V_2O_5.[25] As a result, the cycling stability is improved and the reversibility of the insertion/extraction of Li$^+$ ions in the V_2O_5 interlayer is enhanced.

Acknowledgement

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