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Preparation and characterization of (PVP + V_2O_5) cathode for battery applications

Ch.V. Subba Reddy [1], Ai-Ping Jin, Xia Han, Quan-Yao Zhu, Li-Qiang Mai, Wen Chen *

Institute of Materials Science and Engineering, Wuhan University of Technology, # 122, Lushi Road, Wuhan, Hubei 430-070, PR China

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Abstract

The cathode films of V_2O_5 xerogel modified with polyvinyl pyrrolidone (PVP) were prepared using sol-gel method. Investigations were conducted by X-ray diffractometry, Fourier transformation infrared spectroscopy, X-ray photoelectron spectroscopy and cyclic voltammetry. The results show that the H atoms in PVP are hydrogen-bonded with the O atoms of the V=O bonds of the V_2O_5 xerogel, which effectively shielded against electrostatic interactions between the V_2O_5 interlayer and Li^+ ions when the V_2O_5 xerogel is modified by the intercalation of PVP. The reversibility of insertion/extraction of Li^+ ions is greatly improved by modification of the V_2O_5 xerogel with PVP.

Keywords: V_2O_5 xerogel; PVP; Modification; Reversibility

1. Introduction

Polymer electrolytes are currently of interest owing to their advantageous and special mechanical properties, ease of fabrication of thin films of desirable sizes and suitability for electrode–electrolyte contacts in different electrochemical devices. Interest began in this field after the studies of materials based on alkali metal salts complexed with polyethylene oxide (PEO) reported by Wright and co-workers [1,2] and Armand et al. [3,4]. Polymer blend electrolytes consisting of (PVP + PVA) and alkali metal salts were reported for the purpose of electrochemical cells [5–7]. Rare reports appear in literature on the development of PVP electrolytes for solid-state batteries.

Recent research trends in the field of rechargeable lithium batteries are directed towards the development of cells with high energy density (W h/kg) and high power density [8]. To achieve a high amount of energy stored in a given mass or volume, it is usually desirable that the number of available charge carriers per mass or volume unit is as high as possible. The capacity for energy storage in a rechargeable lithium cell is mainly dependent on the cathode materials. The most studied cathode materials for lithium batteries are crystalline cobalt-, manganese- and nickel-based oxides [9]. Although these transition-metal oxides have demonstrated high positive potential and good stability toward long-term cycling for lithium insertion/extraction, relatively low discharge capacity and high cost still remain as issues to addressed.

As part of continuing efforts to improve the capacity of cathode materials, attempts to synthesize transition-metal oxides with an amorphous nature and high surface area, such as the xerogel and aerogel forms, have been made for V_2O_5 [10–14] and MnO_2 [15]. Hybridization of the layered inorganic cathode materials with electrochemically active organic polymers has been regarded as another inter-

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* Corresponding author. Tel.: +86 27 87651107; fax: +86 27 87864580 (W. Chen).

E-mail addresses: drsreddy2005@yahoo.com (Ch.V. Subba Reddy), chenw@mail.whut.edu.cn (W. Chen).

[1] Tel.: +86 27 87160129; fax: +86 27 87864580

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esting approach to improving capacity for electrochemical lithium insertion. Intercalating organic molecules into the layered inorganic host materials can produce inorganic–organic hybrid materials. Many researchers have been modified V_2O_5 with polyaniline (PANI), poly(ethylene glycol) (PEG), polypyrrole (PPY) and poly(ethylene oxide) (PEO) [16–22]. Rare reports appear in literature on modifying V_2O_5 xerogel with poly(vinyl pyrrolidone) (PVP). The intercalation of PVP is expected to enhance the mobility of Li^+ ions in the V_2O_5 xerogel interlayers and improved the reversibility of insertion/extraction of Li^+ ions. The preparation of a modified V_2O_5 xerogel film and the effect of modification with poly(vinyl pyrrolidone) on the reversibility of insertion/extraction of Li^+ ion in V_2O_5 xerogel films are investigated and discussed in the present paper.

2. Experimental

Melting V_2O_5 powder at 875 K in a ceramic crucible results in a molten liquid [23,24]. When the molten liquid is quickly poured into distilled water, a brownish V_2O_5 solution was formed. The solution viscosity is directly related to the amount of V_2O_5 powder with respect to the water volume. PVP solution was mixed with the V_2O_5 solution to form a mixed sol. The molar ratio of PVP to V_2O_5 was x:1 ($x = 0,0.5$). Indium tin oxide (ITO) conducting glass substrates were dipped into mixed sol, and then pulled out slowly. The gel formed on the glass substrate was left to dry for 48 h at room temperature. The final films were subjected to heat treatment (373 K) for 24 h in N_2 atmosphere to constant weight, which removes free water in the films [24].

The XRD patterns of the films were made with a HZG4/B-PC X-ray diffractrometer with Co Kα radiation and graphite monochrometer. Fourier transform infrared (FT-IR) absorption spectra of the films were recorded using a 60-SXB IR spectrometer with a resolution of 4 cm^{-1}. The measuring wave number range was 400–4000 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 C 1s (284.80 eV) as an internal standard, XPS spectra of Li 1s were taken from the modified V_2O_5 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 V_2O_5 xerogel film and platinum foil were used as working electrode and counter electrode, and standard calomel electrode was used as a reference electrode. All electrochemical measurements were conducted in a glove box filled with dry argon [25].

3. Results and discussion

3.1. XRD analyses

The XRD patterns of V_2O_5 xerogels both before and after modification with PVP are presented in Fig. 1. The XRD pattern of the unmodified V_2O_5 xerogel shows four peaks whose d values are 12.3803, 3.9376, 2.9402 and 1.7979 Å corresponding to diffraction by the (001), (003), (004) and (006) crystal planes, respectively [26]. No ($hk0$) and (hkl) reflections are observed in Fig. 1, confirming the turbostratic nature of the V_2O_5 slabs perpendicular to the stacking axis. The repeated distance in modified V_2O_5 xerogel film increases from 12.3803 Å to 13.283 Å. The increase of the repeat distance is thought to result from PVP being intercalated into the V_2O_5 xerogel interlayer and opening the V_2O_5 xerogel layers [27,28].

3.2. IR analyses

FT-IR spectra of V_2O_5 xerogel both before and after modification with PVP are shown in Fig. 2. There is a broad band at 3441 cm^{-1} corresponding to the O–H vibration from water [16], which confirms the presence of water in the V_2O_5 xerogel before modification with PVP. The V_2O_5 xerogel exhibits three main vibration modes in the 400–1007 cm^{-1} region. The terminal oxygen symmetric stretching mode (ν_s) of V=O and the bridge oxygen asymmetric and symmetric stretching modes (ν_{as} and ν_s) of V–O–V are at 1007, 764 and 527 cm^{-1}, respectively [17]. IR spectra after modification with PVP show characteristic intense peaks at 1166, 1293, 1375 and 1400 cm^{-1} which proves the presence of PVP and the poorly resolved peak at 3652 cm^{-1} is an indication of the presence of amorphous PVP.

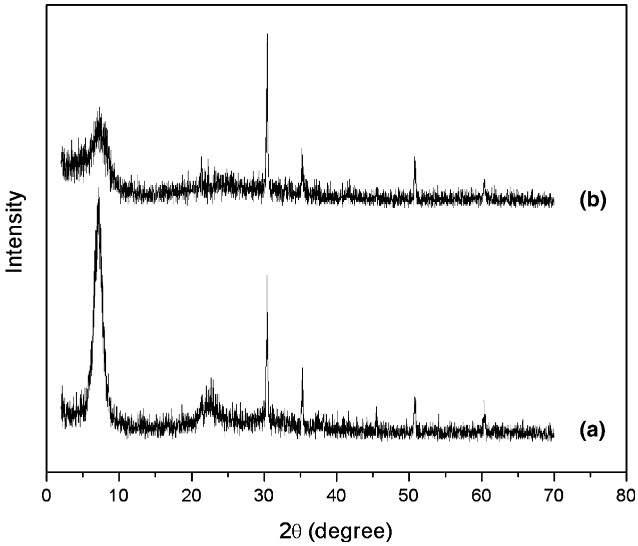

Fig. 1. XRD patterns of V_2O_5 xerogel both before (a) and after (b) modification with PVP.

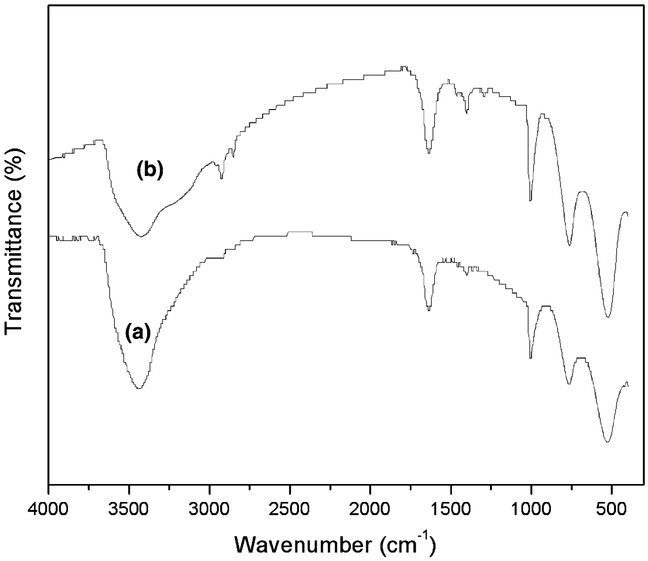

Fig. 2. IR spectra of V_2O_5 xerogel both before (a) and after (b) modification with PVP.

All the peaks change to varying extents when intercalating PVP into the V_2O_5 xerogel. The v_s(V–O–V) and v_{as}(V–O–V) modes shift to lower wave numbers. The v_{as}(V–O–V) mode shifts from 764 cm^{-1} to 754 cm^{-1} and its intensity increases. The v_s(V–O–V) mode moves from 527 cm^{-1} to 522 cm^{-1}. In contrast, the v_s(V=O) band slightly shifts to higher wavenumber, from 1007 cm^{-1} to 1012 cm^{-1}. 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 [18]. Namely, the H atoms in PVP 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 [29], which causes the strengthening of the V–O–V bond. All these observations suggest that PVP 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 good 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 Li 1s of V_2O_5 xerogel both before and after modification with PVP were recorded in the binding energy range 45–57 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 49.86, 51 and 51.55 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 [30]. The corresponding contents of these Li$^+$ species are 41.83%, 38.67% and 19.50%. After modification with PVP the intensities of Li$^+$ signals are higher than those before modification and content of Li$^+$ ions in the interlayer remarkably increased from 41.83% to 52.82%, because intercalation of PVP 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 by PVP. Also, the Li 1s core level binding energies shifted to lower values (shown in Table 1). The

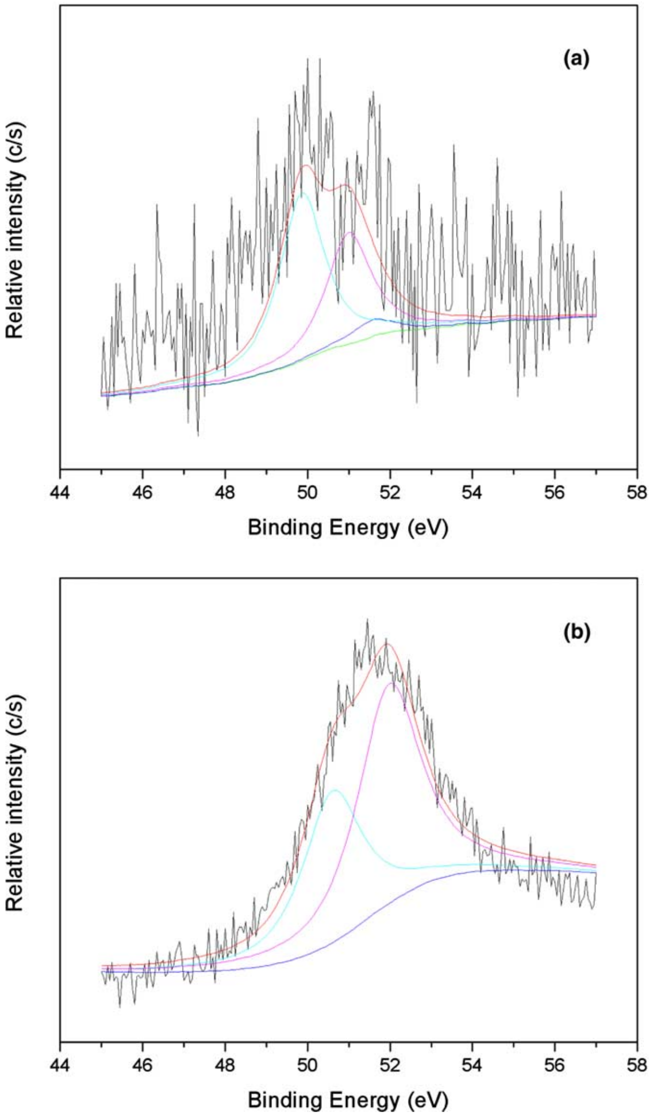

Fig. 3. XPS Li 1s core level spectra of V_2O_5 xerogel both before (a) and after (b) modification with PVP.

Table 1
Results of fitting for XPS Li 1s core level spectra

Sample	Binding energy (eV)	Content (mol%)	FWHM (eV)
V_2O_5 xerogel before PVP modification	49.86	41.83	1.30
	51.00	38.67	1.28
	51.55	19.50	1.28
V_2O_5 xerogel after PVP modification	49.60	52.82	1.30
	50.78	32.44	1.28
	51.46	15.04	1.30

decrease in the binding energy of Li 1s core level indicates a decrease of the interaction between Li^+ ions and their environment (including PVP chains and V_2O_5 layers), which is beneficial to the mobility of Li^+ ions in the interlayer of V_2O_5 [31].

3.4. CV analyses

Fig. 4 shows the cyclic voltammogram curves of V_2O_5 xerogel both before and after modification with PVP, in which the first, second, fifth, tenth, twentieth, thirtieth, fortieth and fiftieth cycle curves are plotted. The area A_i (i is the cycle times) that 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 ith cycle curve. The cycle efficiencies of different cycle times and compositions are listed in Table 2.

From Fig. 4 and Table 2, it is observed that before and after modification with PVP the second cycle efficiency Q_2 of V_2O_5 xerogel films reached to 93.5% and 92%, respectively. After modification with PVP the lower Q_2 of V_2O_5 xerogel film indicates that portion of Li^+ ions complexed by PVP chains cannot be extracted from the interlayer. Meantime, it is found that after modification with PVP the fifth and fiftieth cycles efficiencies Q_5 and Q_{50} of V_2O_5 xerogel film are 72% and 59.8%, these are higher than that of V_2O_5 xerogel film before modification with PVP (38.5%) and (16.5%), indicating that cycling stability tends to increase after several cycles. The Q_5 of V_2O_5 xerogel film before modification with PVP apparently decreases from 93.5% to 38.5%, 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 from 166 mV to 299 mV and 416 mV after the second and fifth sweeps, respectively, whereas that of modified V_2O_5 xerogel is shifted slightly from 83 mV to 200 mV and 290 mV, respectively, demonstrating the improvement of the cyclability and the cycling stability of Li^+ ion insertion/extraction upon modification with PVP. When PVP 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.

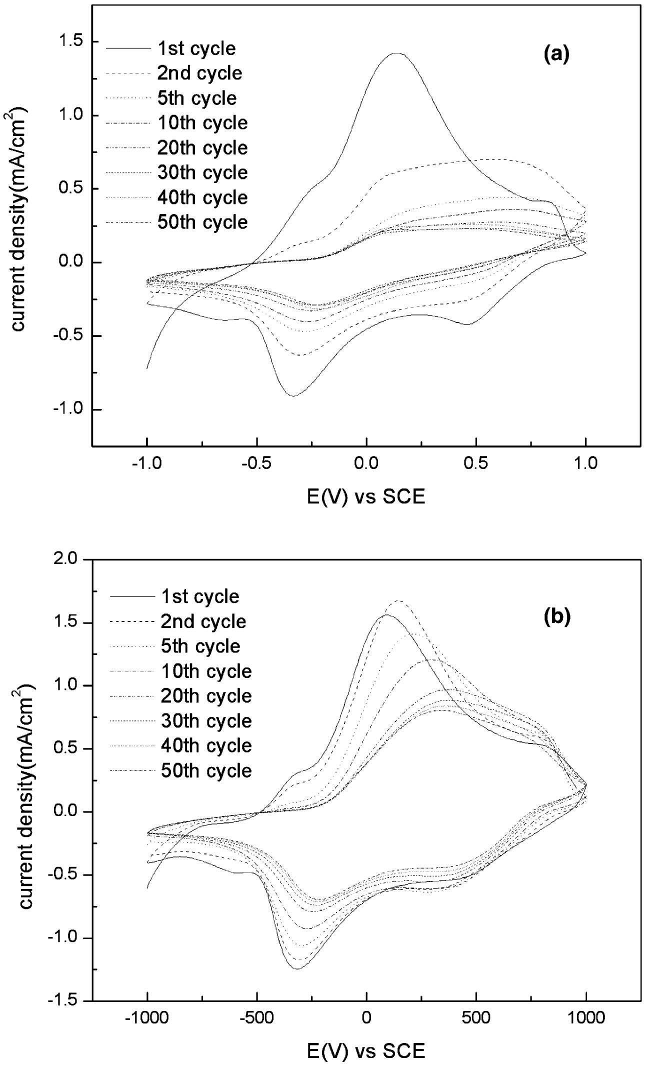

Fig. 4. Cyclic voltammetric of V_2O_5 xerogel both before (a) and after (b) modification with PVP.

Table 2
The cycle efficiency of different cycle times and compositions

Sample	Q_2 (%)	Q_5 (%)	Q_{20} (%)	Q_{50} (%)
V_2O_5 xerogel before PUP modification	93.5	38.5	33.8	16.5
V_2O_5 xerogel after PUP modification	92.0	72.0	66.9	59.8

4. Conclusions

PVP is intercalated into V_2O_5 xerogel. The intercalation is confirmed by X-ray diffraction, FT-IR, X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. The results show that the H atoms in PVP are H-bonded with the O atoms of the V=O bonds of V_2O_5 xerogel, which effectively shields the electrostatic interaction between V_2O_5 interlayer and Li^+ ions when V_2O_5 xerogel is modified with PVP. The reversibility of insertion/extraction of Li^+ ions is greatly improved with the modification by PVP in V_2O_5 xerogel.

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