

Electrochemical lithium intercalation into vanadium pentoxide xerogel film electrode

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Abstract

The lithium-ion transport in vanadium pentoxide xerogel film electrodes has been investigated by using cyclic voltammetry and electrochemical impedance spectroscopy. The oxide xerogel film electrodes were prepared by spin-coating a viscous gel on an indium tin oxide (ITO) substrate. The spin-coated xerogel films were dried under vacuum at 130 and 270 °C, respectively. The lithium intercalation into the xerogel film electrode dried at 270 °C is limited by the interfacial reaction at the electrolyte/electrode interface rather than the lithium-ion transport in the oxide electrode. On the other hand, lithium intercalation into the film electrode dried at 130 °C is largely limited by the lithium transport in the oxide film, and the chemical diffusivity of the lithium ion in the oxide film was determined to decrease from 10^{-10} to 10^{-12} $\text{cm}^2 \text{s}^{-1}$ as the electrode potential of the oxide film fell from 3.0 to 2.2 $V_{\text{Li/Li}^+}$. The transition of the diffusion-controlled intercalation to the interfacial reaction-controlled intercalation into the oxide xerogel film with decreasing drying temperature was explained in terms of the modification of the oxide lattice to a more open-structured lattice by structural modification of the oxide film by water molecules incorporated into the film. © 1997 Elsevier Science S.A.

Keywords. Lithium intercalation; Water molecule; Vanadium pentoxide xerogel films; Spin coating; Electrochemical impedance

1. Introduction

Vanadium pentoxide xerogels $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ have been studied extensively for various applications such as cathodes in rechargeable lithium batteries or in electrochromic display electrodes [1–5]. Sol-gel chemistry leads to the formation of hydrous oxide gels that can be described as nanocomposite materials [6]. They are made of water molecules trapped within the oxide. They exhibit a very open microstructure and ionic species can diffuse easily through the pores of the gel [5].

The present work is aimed at investigating the role of the water molecule in electrochemical lithium intercalation into the vanadium pentoxide xerogel ($\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) films. For this purpose, cyclic voltammograms and electrochemical impedance spectra of the vanadium oxide xerogel films dried at various temperatures were measured in 1 M LiClO_4 /propylene carbonate solution. The change in the electrochemical lithium intercalation into the oxide xerogel film with drying temperature was discussed in terms of the structural modification

of the oxide lattice by the incorporated water molecules.

2. Experimental

2.1. Specimen preparation

Vanadium pentoxide hydrosol was prepared by passing 0.1 M ammonium metavanadate (NH_4VO_3) aqueous solution through proton exchange resin (DOWEX 50W2-100), and then aged at room temperature for 20 days. During the ageing treatment the yellow-coloured hydrosol became a viscous gel with a dark red colour. Vanadium pentoxide xerogel films were prepared by spin-coating the prepared gel onto the indium tin oxide (ITO) glass substrate at a rotating speed of 3000 rpm. The spin-coated oxide xerogel films were further dried under vacuum at room temperature, 130 °C, and 270 °C for 1 h. The thickness of the spin-coated xerogel film was determined to be 160 nm by using α -step stylus (Tencor Instrument).

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2.2. Characterization of specimens

In order to identify the V–O and H–O bonds in the vanadium pentoxide xerogel film, Fourier-transform infrared (FT-IR) absorbance spectra were measured on the dried oxide xerogel films in the wave number range of 1800 to 650 cm^{-1} with a resolution of 2 cm^{-1} . The FT-IR spectra of the vanadium oxide films were obtained by the attenuated total reflectance (ATR) method. A ZnSe single crystal was used as the ATR crystal.

In order to identify the crystal structure of the vanadium pentoxide xerogel film, X-ray diffraction (XRD) patterns of the oxide xerogel films were measured in the scanning angle range of 5° – 50° ($= 2\theta$). The FT-IR spectra were obtained by using a Nicolet 520P Fourier-transform infrared spectrophotometer. The XRD patterns were recorded on an automated Rigaku powder diffractometer using Cu $K\alpha$ radiation.

2.3. Electrochemical measurements

A three-electrode electrochemical cell was employed for the electrochemical measurements. Pure lithium metal foil (Foot Mineral, USA, purity 99.9%) was used as the reference and the counter electrodes, and 1 M LiClO_4 /propylene carbonate solution served as an electrolyte. The propylene carbonate was dried for 3 days with previously activated 5 Å molecular sieves, and the LiClO_4 was dried under vacuum at 120 $^\circ\text{C}$ for 12 h.

Cyclic voltammograms were obtained with a scan rate of 1 mV s^{-1} in the potential range of 1.8 to 3.4 $\text{V}_{\text{Li}/\text{Li}^+}$. Electrochemical impedance measurements were made by applying an a.c. amplitude of 10 mV_{rms} on the equilibrium electrode potentials of 2.2 to 3.0 $\text{V}_{\text{Li}/\text{Li}^+}$ over the frequency range from 1 mHz to 100 kHz . For impedance measurements, a Solartron 1255 frequency response analyser was used in conjunction with a Solartron 1286 electrochemical interface under remote control of an IBM-compatible personal computer. All the electrochemical experiments were carried out in an argon-filled glove box (Vacuum Atmosphere Company, HE493).

3. Results and discussion

XRD patterns of the vanadium pentoxide xerogel films dried at various temperatures under vacuum are presented in Fig. 1. The diffraction peaks unchanged with drying temperature were identified as a crystalline ITO. The XRD pattern showed the character of the well-known layered structure of the vanadium pentoxide xerogel film [7]. The values of the layer spacing d calculated from the (001) peak are given above left of Fig. 1(a)–(c). The XRD patterns show that the layer spacing of the vanadium oxide xerogel film dried at room temperature decreased from 11.28 to 6.34 Å after drying at 270 $^\circ\text{C}$.

Fig. 2 presents the FT-IR spectra of the vanadium pentoxide xerogel films on ITO glass substrate, dried at different

temperatures. For comparison the IR absorbance spectrum of a crystalline V_2O_5 powder is also presented. As the drying temperature increased, the intensity of two absorbance peaks corresponding to the bending of a water molecule ($\delta_{\text{H-O}}$; 1625 and 1425 cm^{-1}) decreased, indicating the departure of

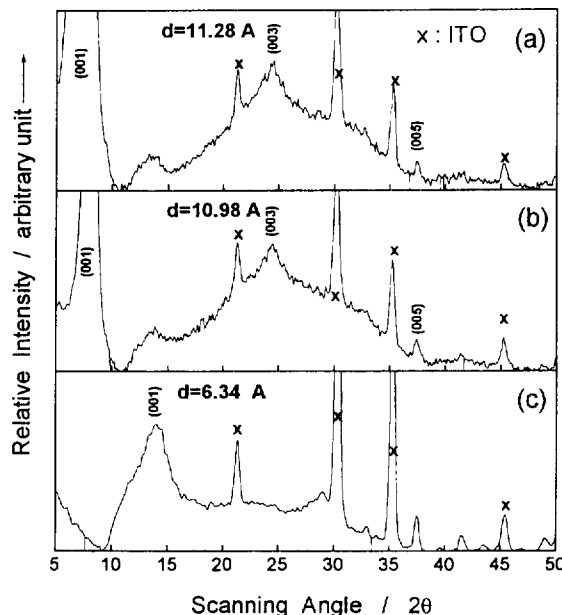


Fig. 1. XRD patterns of vanadium pentoxide xerogel films, spin-coated on indium tin oxide glass substrate: (a) dried at room temperature; (b) dried at 130 $^\circ\text{C}$, and (c) dried at 270 $^\circ\text{C}$. Drying was carried out under vacuum for 1 h.

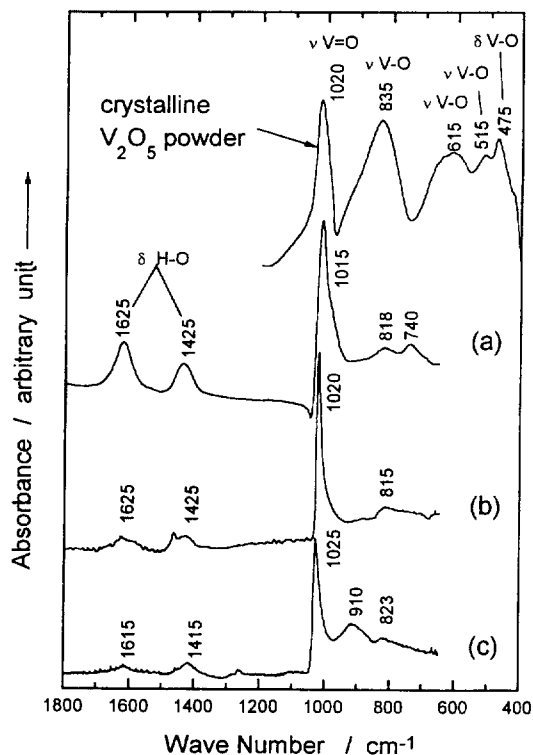


Fig. 2. Fourier-transform infrared absorption spectra of vanadium pentoxide xerogel films: (a) dried at room temperature; (b) dried at 130 $^\circ\text{C}$, and (c) dried at 270 $^\circ\text{C}$. Drying was carried out under vacuum for 1 h.

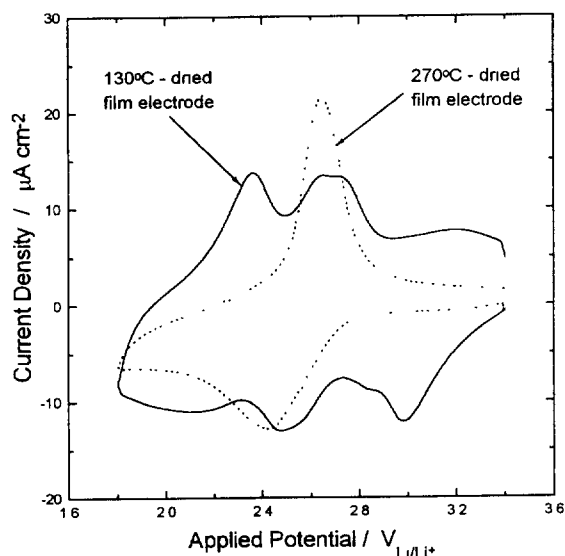


Fig. 3. Cyclic voltammograms obtained from vanadium pentoxide xerogel film electrodes in 1 M LiClO₄/propylene carbonate solution with a scan rate of 1 mV s⁻¹ (—) dried at 130 °C, and (· · ·) dried at 270 °C. Drying was carried out under vacuum for 1 h.

water molecules from the xerogel film. According to previous results obtained from vanadium pentoxide xerogel powder by Aldebert et al. [8], the vanadium pentoxide xerogel films dried at 130 and 270 °C are expected to contain 0.5 H₂O and 0.1 H₂O per V₂O₅ molecular unit, respectively.

Absorbance peaks due to V–O bonds show a blue shift with increasing drying temperature. Absorbance peak due to a double V=O bond is nearly unchanged, whereas the absorbance peaks due to single V–O bonds show a relatively large shift. This indicates that the more water molecules are released from the xerogel film, the stronger becomes the V–O bond. High intensity and narrow width of the peak for the double V=O bond as compared with the other peaks are attributed to a preferred oriented microstructure of the vanadium pentoxide xerogel film [9].

Fig. 3 shows cyclic voltammograms obtained from the vanadium pentoxide xerogel film electrodes, dried at 130 and

270 °C, in 1 M LiClO₄/propylene carbonate solution. From the xerogel film electrode dried at 130 °C, three distinctive reduction current peaks were observed at 3.0 V_{Li/Li+}, 2.5 V_{Li/Li+}, and 2.1 V_{Li/Li+} during the cathodic sweep and the corresponding oxidation current peaks were observed at 2.4 V_{Li/Li+}, 2.6 V_{Li/Li+}, and 3.2 V_{Li/Li+} during the anodic sweep, respectively. This suggests that the oxide xerogel film electrode has three kinds of distinctive sites available for lithium-ion intercalation.

The intensity of the reduction current peak around 3.0 V_{Li/Li+} was observed to be markedly reduced after the first intercalation/de-intercalation cycle, indicating the irreversible intercalation. This is due probably to the thermodynamic irreversible reaction of the intercalated lithium ion with the water molecule loosely bound to the V₂O₅ layer. Among the three coupled current peaks, the separation of peak potentials of the current peaks appearing around 2.5 V_{Li/Li+} was the smallest. This means that the current peak at 2.5 V_{Li/Li+} results due to the most reversible intercalation site. The reduction current peak at 2.1 V_{Li/Li+} is kinetically irreversible as compared with the current peak around 2.5 V_{Li/Li+}. This is due presumably to the slow lithium-ion diffusion in the oxide film electrode with relatively high lithium content. The reduction current peak is broad, whereas the corresponding oxidation current peak is sharp, suggesting the intercalation and de-intercalation being proceeded by different mechanisms.

On the other hand, cyclic voltammogram obtained from the xerogel oxide film electrode dried at 270 °C showed only one sharp current peak around 2.5 V_{Li/Li+}. The appearance of a sharper current peak for the xerogel film specimen as compared with that specimen dried at 130 °C reveals more crystalline character of the xerogel film dried at 270 °C.

In both the electrode specimens dried at 130 and 270 °C, the coupled reversible reduction and oxidation current peaks were encountered around 2.5 V_{Li/Li+}. Livage et al. [5] suggested that the lithium ion is intercalated between rather than into the V₂O₅ layers of the vanadium pentoxide xerogel, and thus the xerogel shows better reversibility as compared with crystalline V₂O₅. The coupled current peaks around 2.5

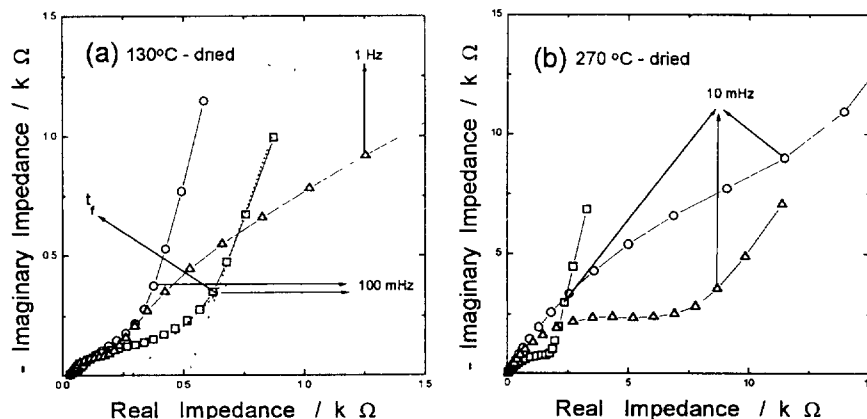


Fig. 4. Nyquist plots obtained from vanadium pentoxide xerogel film electrodes (a) dried at 130 °C and (b) dried at 270 °C in 1 M LiClO₄/propylene carbonate solution at electrode potentials of (○) 2.8 V_{Li/Li+}, (□) 2.5 V_{Li/Li+}, and (△) 2.2 V_{Li/Li+}. Drying was carried out under vacuum for 1 h. Exposed area of the electrode was 1.5 cm².

V_{Li/Li^+} are due probably to the intercalation sites between V_2O_5 layers.

Fig. 4(a) and (b) shows typical Nyquist plots obtained from the vanadium pentoxide xerogel film electrodes dried at 130 and 270 °C in 1 M $LiClO_4$ /propylene carbonate solution, respectively. The impedance spectra consist of a depressed arc in the high frequency range of 10 Hz–100 kHz, a line inclined at constant angle to the real axis in the middle frequency range of 100 mHz–10 Hz, and a capacitive line due to the accumulation of lithium at the xerogel film electrode/ITO substrate interface in the frequency range below 100 mHz. The high frequency arc is due to the charge transfer and absorption reaction at the electrolyte/xerogel film electrode interface and the inclined line in the middle frequency range is attributable to the Warburg impedance associated with lithium diffusion through the xerogel film.

It should be noted that the magnitude of the high frequency arc associated with interfacial reaction for the xerogel film electrode dried at 270 °C is much larger as compared with that dried at 130 °C. The size of the high frequency arc of the impedance spectra obtained from the xerogel film electrode dried at room temperature was similar to that measured from the 130 °C-dried xerogel film electrode. The absorption resistance for the 360 °C-dried xerogel film electrode that lost most of its water molecules was higher than the resistance for the 270 °C-dried xerogel film electrode. These results mean that the charge transfer and lithium-ion absorption reaction is more impeded at the interface between the electrolyte and xerogel film containing lower water content. From this result it is suggested that the water molecules incorporated into the xerogel film make the crystal structure of the xerogel oxide lattice disordered and thereby facilitate the lithium-ion absorption into the xerogel oxide electrode.

The value of the chemical diffusivity \tilde{D}_{Li^+} of the lithium ion in the xerogel film was determined as a function of electrode potential from Eq. (1) [10] by experimentally determining the values of f_T 's from Fig. 4(a)

$$\tilde{D}_{Li^+} = \frac{\pi f_T l^2}{1.94} \quad (1)$$

where l is the thickness of the xerogel film ($l = 160$ nm) and f_T is the frequency at which the impedance spectrum shows a transition from semi-infinite diffusion behaviour to finite-length diffusion behaviour. However, since the charge transfer and absorption resistance is so high that the Warburg impedance submerges, the f_T 's cannot be experimentally determined for the 270 °C-dried film specimen.

The determined chemical diffusivity \tilde{D}_{Li^+} of the lithium ion in the vanadium pentoxide xerogel film electrode dried at 130 °C is presented as a function of electrode potential in Fig. 5. The \tilde{D}_{Li^+} in the oxide film electrode decreased from about 1×10^{-10} to 3×10^{-12} $cm^2 s^{-1}$ at room temperature as the electrode potential decreased from 3.0 to 2.2 V_{Li/Li^+} . It should be noted that the \tilde{D}_{Li^+} in the 130 °C-dried xerogel film electrode slowly decreased in the higher electrode poten-

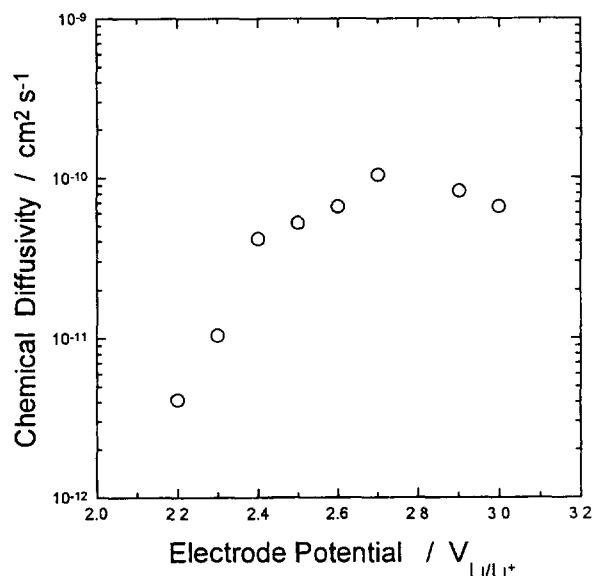


Fig. 5. Chemical diffusivity \tilde{D}_{Li^+} of the lithium ion in vanadium pentoxide xerogel film dried at 130 °C as a function of electrode potential of 2.2–3.0 V_{Li/Li^+} .

tial range, and drastically decreased near 2.4 V_{Li/Li^+} with decreasing electrode potential. The drastic fall of the \tilde{D}_{Li^+} with increasing lithium content can be accounted for in terms of the reduced fractional number of vacant lithium intercalation sites rather than the increased coulombic interaction between the intercalated lithium ion and vanadium oxide lattice.

4. Conclusions

Three different coupled reduction and oxidation current peaks appeared at the vanadium pentoxide xerogel film electrode dried at 130 °C and are characteristic of three kinds of distinctive intercalation sites in the oxide xerogel film. By contrast, only one current peak was encountered in the vanadium pentoxide xerogel dried at 270 °C, indicating that the further dehydration of the xerogel reduces the number of intercalation site in the oxide film.

From the measured impedance spectra, the resistance associated with the absorption reaction into the xerogel film electrode dried at 270 °C is much higher than that into the film electrode dried at 130 °C. From this result it is suggested that the water molecules within the oxide xerogel film modify the xerogel oxide lattice to a more open-structured lattice and thereby the lithium-ion absorption into the oxide xerogel electrode.

The chemical diffusivity \tilde{D}_{Li^+} of the lithium ion in the xerogel film electrode dried at 130 °C decreased slowly to 2.4 V_{Li/Li^+} and then drastically decreased with decreasing electrode potential. From the drastic fall of the chemical diffusivity of the lithium ion, it is suggested that the lithium ion diffusion in the oxide xerogel film is mainly limited by the fractional number of vacant lithium intercalation sites.

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