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The kinetics of lithium transport through vanadium pentoxide composite and film electrodes by current transient analysis

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Abstract

The kinetics of lithium transport through vanadium pentoxide composite and film electrodes have been investigated in a 1 M solution of LiClO_4 in propylene carbonate using current transient technique. In the case of the vanadium pentoxide composite electrode, all the cathodic and anodic current transients experimentally measured hardly followed the Cottrell behaviour and the relation between initial current level in current transient and applied potential step held Ohmic law. Lithium transport through the composite electrode was theoretically analysed by means of the numerical simulation of the current transient under the assumption of the ‘cell-impedance controlled’ lithium transport. The current transients theoretically calculated shared quantitatively well those experimentally measured. In contrast, all the cathodic and anodic current transients experimentally obtained from the film electrode, exhibited clearly a linear relationship between logarithmic current and logarithmic time, followed by an exponential decay. From the results, it is suggested that lithium transport through the film electrode proceeds under the ‘diffusion controlled’ lithium transport towards rough (fractal) interface. The difference in the mechanism of lithium transport between through vanadium pentoxide composite electrode and through film electrode was discussed in terms of the chemical diffusivity of lithium ion and ‘cell-impedance’ of the two electrodes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium pentoxide; Current transient; Cell-impedance; Lithium ion diffusion

1. Introduction

The electrochemical lithium intercalation into and deintercalation from lithium vanadium oxide has been studied by many researchers [1–3] because of the interest in their applications to the cathode materials for high energy density storage batteries and electrochromic display devices. Over the last two decades, many studies on the vanadium oxide as the cathode materials for secondary lithium batteries have been focussed on $\text{Li}_\delta\text{V}_2\text{O}_5$ composite and film electrodes prepared by crystalline $\text{Li}_\delta\text{V}_2\text{O}_5$ powder and amorphous $\text{Li}_\delta\text{V}_2\text{O}_5$ xerogel.

In the present work, we consider the kinetics of lithium transport through the $\text{Li}_\delta\text{V}_2\text{O}_5$ composite and film electrodes prepared from crystalline vanadium pentoxide powder and vanadium pentoxide xerogel, respectively. For this purpose, open-circuit potential transients and potentiostatic current transients were first measured on the electrode. Next, the current transients have been analysed by taking the assump-

tion that lithium intercalation and deintercalation are limited by ‘cell-impedance’ and ‘lithium ion diffusion’.

2. Experimental

Vanadium pentoxide composite electrode was prepared from vanadium pentoxide, V_2O_5 , powder (Aldrich Chemical Co., USA; purity 99.99%). The oxide powder was mixed with 30 wt.% Vulcan XC-72 carbon black and 2 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl pyrrolidone (NMP) solution. The stirred mixture was spread on 316 stainless steel ex-met. Upon the evaporation of NMP, the carbon-dispersed composite electrode specimen was dried under vacuum over 6 h.

Vanadium pentoxide xerogel was prepared by sol–gel process. Vanadium pentoxide hydrosol was synthesised by passing 0.2 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 to a viscous gel with a dark red colour. Vanadium pentoxide

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film electrode was 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 film was further dried under vacuum at 130°C for 1 h. The thickness of the spin-coated xerogel were determined to be 200 nm by using α -step stylus.

A three-electrode electrochemical cell was employed for the electrochemical experiments. Both the reference and counter electrodes were constructed from lithium foil (Foote Mineral Co., USA; purity 99.9%) and a 1 M solution of lithium perchlorate (LiClO_4) in propylene carbonate (PC) was used as the electrolyte. Galvanostatic intermittent charge–discharge experiment was conducted by using a solartron 1287 electrochemical interface (ECI). The charge and discharge currents were selected so that a change in lithium content of $\Delta\delta = 1$ for $\text{Li}_\delta\text{V}_2\text{O}_5$ composite and film electrodes would occur for 10 and 0.5 h, respectively.

Potentiostatic current transient experiment was performed by application of large potential steps 0.10–0.30 V on the $\text{Li}_\delta\text{V}_2\text{O}_5$ composite electrode and large potential steps 0.20–1.00 V on the $\text{Li}_\delta\text{V}_2\text{O}_5$ film electrode. Potentiostatic cathodic and anodic current transients were measured on the $\text{Li}_\delta\text{V}_2\text{O}_5$ composite electrode, film electrode by dropping the electrode potential 3.45 $V_{\text{Li}/\text{Li}^+}$ and 3.20 $V_{\text{Li}/\text{Li}^+}$ to a lithium injection potential and by jumping the electrode potential 3.35–3.15 $V_{\text{Li}/\text{Li}^+}$ and 3.00–2.20 $V_{\text{Li}/\text{Li}^+}$ to a lithium extraction potential, respectively. Prior to lithium intercalation/deintercalation, the electrode was maintained at the initial value of the electrode potential for a sufficiently long time to obtain a low steady-state current.

All electrochemical experiments were conducted at room temperature in a glove box (MECAPLEX GB94) filled with purified argon gas.

3. Results and discussion

3.1. Lithium transport through vanadium pentoxide composite electrode

Fig. 1 shows electrode potentials obtained from the galvanostatic intermittent charge–discharge curve of the $\text{Li}_\delta\text{V}_2\text{O}_5$ composite electrode as a function of lithium content ($1 - \delta$), in a 1 M LiClO_4 –PC solution. The electrode potential curve obtained from the discharge curve displayed two potential plateaux near 3.40 and 3.20 $V_{\text{Li}/\text{Li}^+}$, which are ascribed to the coexistence of the α - and ε - $\text{Li}_\delta\text{V}_2\text{O}_5$, and ε - and δ - $\text{Li}_\delta\text{V}_2\text{O}_5$ phases [4], respectively. Electrode potential curve obtained from the charge curve exhibited three potential plateaux near 3.41, 3.24 and 3.21 $V_{\text{Li}/\text{Li}^+}$, which proved to be caused by coexistence of the α - and ε - $\text{Li}_\delta\text{V}_2\text{O}_5$, ε - and δ - $\text{Li}_\delta\text{V}_2\text{O}_5$, and δ - and γ - $\text{Li}_\delta\text{V}_2\text{O}_5$ phases, respectively [5].

Fig. 2(a) and (b) illustrate on a logarithmic scale the cathodic and anodic current transients, respectively, experimentally measured on the $\text{Li}_\delta\text{V}_2\text{O}_5$ composite electrode in a 1 M LiClO_4 –PC solution. It should be noted that the initial

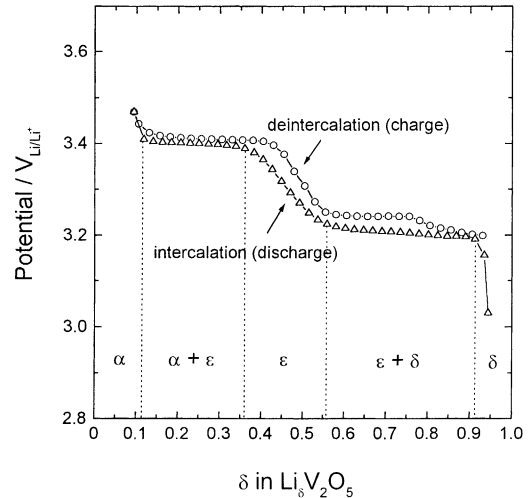


Fig. 1. The galvanostatic intermittent charge (○)–discharge (△) curve obtained from the cell of Li/1 M LiClO_4 –PC solution/ $\text{Li}_\delta\text{V}_2\text{O}_5$ composite electrode. The change in lithium content, $\Delta\delta = 1$, occurs over 10 h.

current level of all the current transients experimentally measured is smaller in value by about one order of magnitude, than that initial current level calculated from Cottrell equation [6]. Moreover, the current transients do not follow the Cottrell behaviour during the whole lithium intercalation and deintercalation.

It is also noted that all the cathodic and anodic current transients exhibited one ‘quasi-current plateau’ or two ‘quasi-current plateaux’. In addition, the initial current level on the cathodic current transient is linearly proportional to the applied potential drop, viz. initial current–potential relation follows Ohm’s law [7].

From the previous works [7,8] on the theoretical analysis of the current transients, it was suggested that both the Ohmic relationship between initial current level in current transient and applied potential step, and the ‘current plateau’ in current transient characterise the ‘cell-impedance controlled’ lithium transport through the oxide. Then, it is plausible that lithium transport through the $\text{Li}_\delta\text{V}_2\text{O}_5$ composite electrode is underlain by ‘cell-impedance’. Under the ‘cell-impedance controlled’ lithium transport, the current I by lithium ion at the electrode/electrolyte interface is determined by [7,8]

$$I = \frac{|E - E_{\text{app}}|}{R_{\text{cell}}} \quad (1)$$

where E is the electrode potential, E_{app} the applied potential (the lithium injection/extraction potential) and R_{cell} represents ‘cell-impedance’. Here, ‘cell-impedance’ means the internal cell resistance, which is mainly caused by bulk electrolyte, electrolyte/electrode interface region, and bulk electrode [9,10].

Now, we theoretically determined the current transients under the ‘cell-impedance controlled’ lithium transport [7]. Fig. 3(a) and (b) give on a logarithmic scale the cathodic and anodic current transients, respectively, obtained from the

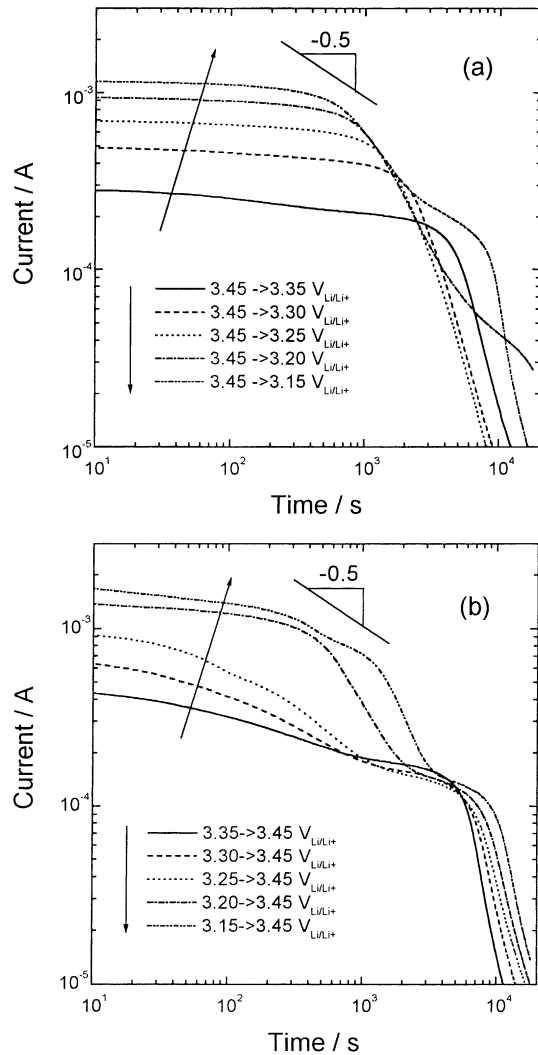


Fig. 2. (a) The cathodic current transients and (b) anodic current transients at the potential drop and potential jump, respectively, between the electrode potentials below $3.45 V_{Li/Li^+}$, experimentally obtained from the $Li_\delta V_2O_5$ composite electrode in a 1 M $LiClO_4$ -PC solution.

numerical solution to the Fick's diffusion equations. All the cathodic and anodic current transients theoretically calculated, agreed almost with those cathodic and anodic current transients experimentally measured (Fig. 2(a) and (b)) in value and shape. From the coincidence of the experimental current transients with those numerically simulated, it is suggested that lithium transport through the $Li_\delta V_2O_5$ composite electrode is purely governed by 'cell-impedance'. The slight discrepancy between the current transients theoretically calculated and experimentally measured is possibly caused by the variance of 'cell-impedance' with electrode potential [11] and size distribution of the oxide particle.

3.2. Lithium transport through vanadium pentoxide film electrode

Fig. 4 presents electrode potentials as a function of lithium content ($1 - \delta$), in a 1 M $LiClO_4$ -PC solution,

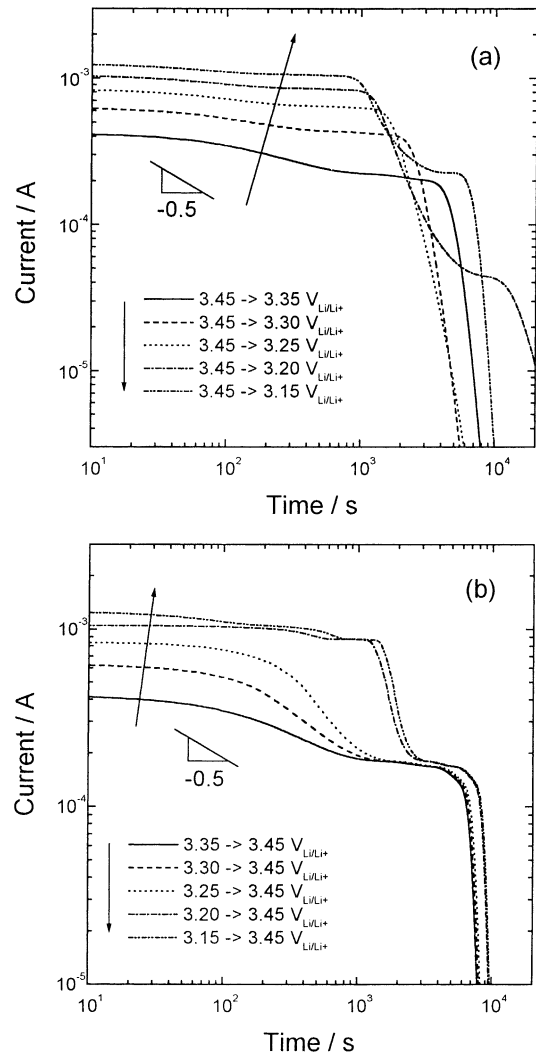


Fig. 3. (a) The cathodic current transients and (b) anodic current transients at the potential drop and potential jump, respectively, between the electrode potentials below $3.45 V_{Li/Li^+}$, theoretically determined by means of numerical analysis based upon the 'cell-impedance controlled' constraint.

obtained from the galvanostatic intermittent charge-discharge curve of the $Li_\delta V_2O_5$ film electrode prepared from vanadium pentoxide xerogel. Contrary to the $Li_\delta V_2O_5$ composite electrode (Fig. 1), the charge-discharge curve of $Li_\delta V_2O_5$ film electrode did not exhibit any potential plateau, suggesting that a single phase is maintained over a wide composition range [12].

Fig. 5(a) and (b) depict on a logarithmic scale the cathodic and anodic current transients experimentally measured on the $Li_\delta V_2O_5$ film electrode in a 1 M $LiClO_4$ -PC solution. It is worthwhile to note that the initial current level of all the current transients experimentally measured is similar in value with that initial current level calculated from the Cottrell equation [6]. Moreover, all the current transients exhibited a linear relationship between logarithmic current and logarithmic time, followed by a steep exponential decay, namely, a two-stage current transient. It is well-known [13] that the two-stage current transient signifies 'diffusion

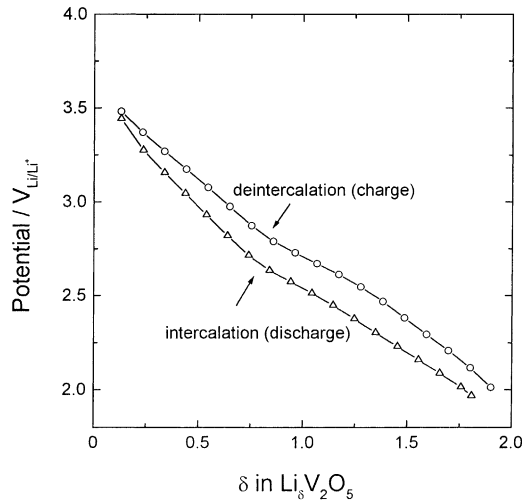


Fig. 4. The galvanostatic intermittent charge (○)–discharge (△) curve obtained from the cell of Li/1 M LiClO₄–PC solution/Li_δV₂O₅ film electrode. The change in lithium content, $\Delta\delta = 1$, occurs over 0.5 h.

controlled' lithium transport. Under the 'diffusion controlled' lithium transport, the current I by lithium ion at the electrode/electrolyte interface is determined by [14]

$$I = \left| -zFA_{\text{ea}}\tilde{D}_{\text{Li}^+} \left(\frac{\partial c}{\partial x} \right)_{x=0} \right| \quad (2)$$

where z is the valence of lithium ion, F the Faraday constant, A_{ea} the electrochemical active area, \tilde{D}_{Li^+} the chemical diffusivity of lithium ion, c the local concentration of lithium ion and x is the distance from the electrode/electrolyte interface to the electrode.

It is noted that the slope in the first stage of all the current transients negatively deviated from -0.5 . According to fractal theory, the slope in the first stage of the current transients should be changed with the roughness of the electrode surface [15]. For lithium diffusion towards fractal interface, the Cottrell equation is modified as follows:

$$I = Kt^{-(D_{\text{H}}-1)/2} \quad (3)$$

where K is the constant and D_{H} represents the fractal dimension of the interface.

The slope in the first stage of all the cathodic current transients (Fig. 5(a)) was determined to be -0.60 , which probably means that the electrode has a rough surface with $D_{\text{H}} = 2.2$ at the electrode potential $3.20 \text{ V}_{\text{Li}/\text{Li}^+}$. In the case of the anodic current transients, the slope in the first stage of the anodic current transients decreased from -0.60 to -0.75 as the initial electrode potential decreased from 3.0 to $2.2 \text{ V}_{\text{Li}/\text{Li}^+}$. This indicates that the electrode surface is more roughened with decreasing electrode potential, i.e. increasing lithium content.

The difference in the mechanism of lithium transport between through the composite electrode and film electrode

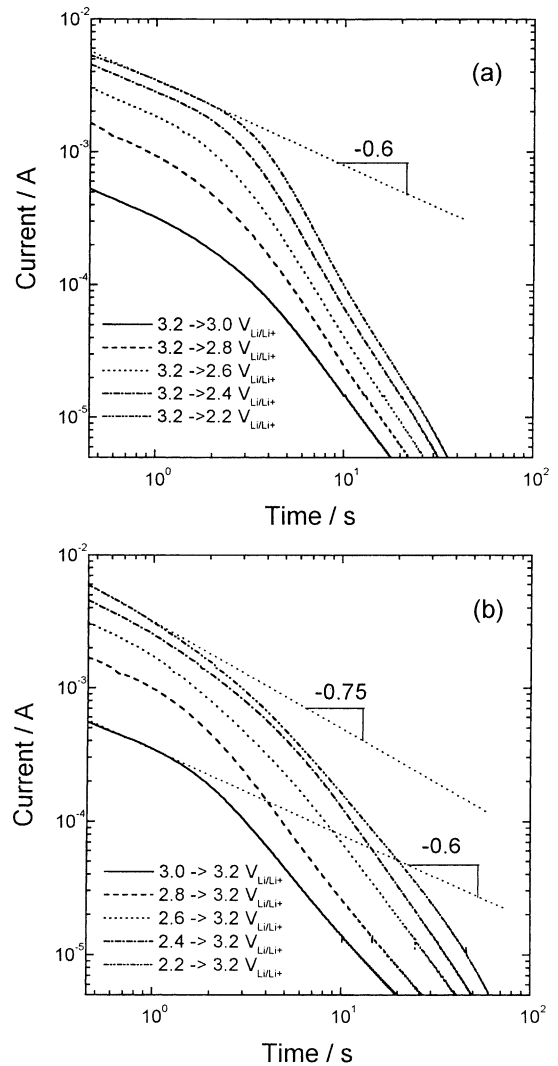


Fig. 5. (a) The cathodic current transients and (b) anodic current transients at the potential drop and potential jump, respectively, between the electrode potentials below $3.20 \text{ V}_{\text{Li}/\text{Li}^+}$, experimentally obtained from the Li_δV₂O₅ film electrode in a 1 M LiClO₄–PC solution.

can be explained as follows. In the Li_δV₂O₅ film electrode, the value of 'cell-impedance' is determined to be larger than that of Li_δV₂O₅ composite electrode by two or three times, which 'cell-impedance' is calculated from the value of iR drop in the galvanostatic intermittent charge–discharge curve. On the other hand, the chemical diffusivity \tilde{D}_{Li^+} of the lithium ion in the Li_δV₂O₅ film electrode is smaller in value than that in the Li_δV₂O₅ composite electrode by one order or two orders of magnitude [16,17]. So, the current in value at the film electrode/electrolyte interface given by $\left| -zFA_{\text{ea}}\tilde{D}_{\text{Li}^+} \left(\frac{\partial c}{\partial x} \right)_{x=0} \right|$ under 'diffusion controlled' lithium transport is plausibly below the current in value given by $|E - E_{\text{app}}|/R_{\text{cell}}$ under the 'cell-impedance controlled' lithium transport. It is thus seen that lithium transport is controlled by lithium ion diffusion through the film electrode.

4. Conclusions

In the present work, the mechanism of lithium transport through the vanadium pentoxide composite and film electrodes has been illustrated in terms of ‘cell-impedance controlled’ lithium transport and ‘diffusion controlled’ lithium transport, respectively. The results are summarised as follows:

1. In the case of vanadium pentoxide composite electrode, the experimental current transients hardly held the Cottrell behaviour during lithium intercalation/deintercalation. Moreover, the relation between the initial current level and applied potential step of the current transients obeyed Ohm’s law.
2. The current transients have been simulated as a function of applied potential under the ‘cell-impedance controlled’ constraint. The quantitative coincidence of the experimental current transients with those numerically simulated, strongly suggests that lithium transport through the vanadium pentoxide composite electrode is purely controlled by ‘cell-impedance’.
3. In the case of vanadium pentoxide film electrode, all the current transients showed a two-stage character, which means lithium transport runs under ‘diffusion controlled’ constraint. The slope in the first stage of all the current transients was determined to be in the range of -0.6 to -0.75 , indicating that lithium transport proceeds towards the rough electrode.
4. The difference in the mechanism of lithium transport between through the vanadium pentoxide composite electrode and through the film electrode can be ascribed to the difference of the chemical diffusivity between these two electrodes. Since lithium ion has much lower chemical diffusivity in the film electrode than that diffusivity in the composite electrode, the current at the film electrode/electrolyte interface given by $|-zFA_{\text{ea}}\tilde{D}_{\text{Li}^+}(\partial c/\partial x)_{x=0}|$ under ‘diffusion controlled’ lithium transport is exceeded by the current given by $|E - E_{\text{app}}|/R_{\text{cell}}$ under the ‘cell-impedance controlled’

lithium transport. Thus, ‘diffusion controlled’ constraint dominates lithium transport through the film electrode.

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