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Li-insertion into thin monolithic V_2O_5 films electrodes characterized by a variety of electroanalytical techniques

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Abstract

Slow-scan rate cyclic voltammetry (SSCV), potentiostatic intermittent titration (PITT) and electrochemical impedance spectroscopy (EIS) have been simultaneously applied to study Li-ion intercalation into V_2O_5 films prepared by vacuum-deposition on Pt foils. The most prominent feature of their electrochemical behavior relates to sharp minima on D versus E plots, which are observed in the vicinity of very narrow cyclic voltammetric peaks. This was explained in the framework of a lattice-gas model with very high, attractive electron-ion interactions during Li-ion intercalation into the V_2O_5 electrode, as was already described for similar processes in graphite and some transition metal oxides: Li_xCoO_2 , Li_xNiO_2 , $Li_xCo_yNi_{1-y}O_2$ and $Li_xMn_2O_4$. Referring to the impedance spectra of the V_2O_5 electrodes, we show good agreement between the data obtained by the different techniques in the related time (or frequency) domains. This relates to both the differential intercalation capacity, C_{int} (low-frequency domain), and the chemical diffusion coefficient D (medium-frequency domain). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rechargeable lithium batteries; V_2O_5 electrodes; Impedance spectroscopy; Chemical diffusion coefficient of Li-ions

1. Introduction

Commercialization of rechargeable Li-ion batteries during recent years has stimulated interest in the elucidation of the mechanisms of Li intercalation into transition metal oxides, which function usually as the active mass in composite cathodes for Li-ion batteries. Although electroanalytical characterization of these composite cathodes (which contain conductive additives and binder in addition to the active mass) can be semi-quantitatively carried out, much more direct and precise information is expected to be obtained with pure oxide materials in the form of thin films. Vacuum-deposited V_2O_5 films, well crystallized by annealing at about 400°C, present an almost ideal model system for the elucidation of Li-intercalation mechanisms using, simultaneously, slow-scan rate cyclic voltammetry (SSCV), potentiostatic intermittent titration (PITT), electrochemical impedance spectroscopy (EIS) [1,2], as well as in situ conductometry [3]. The main objective of this paper is to show that an approach based on the finite-space diffusion model results in reliable and self-consistent calculation of

the chemical diffusion coefficient of Li-ions in thin V_2O_5 electrodes by both PITT and EIS.

2. Experimental

V_2O_5 films were thermally evaporated onto Pt foils using a vacuum thermal evaporating system (STES model, VST Service LTP, Israel). The target used was V_2O_5 powder (Aldrich 99.99%). The thermal deposition rate was 0.1–0.2 Å s⁻¹. After deposition, the Pt foil covered with V_2O_5 film was annealed at 400°C in air for 1 h, and was then allowed to cool down to room temperature. The film's thickness was monitored using quartz-crystal microbalance (QCMB). V_2O_5 films, 1600 and 3600 Å thick, with a geometric surface area of 1.7 and 1.8 cm², respectively, were used in this study. The film structure and morphology was characterized by XRD [1] and AFM [3].

A three-electrode polyethylene cell with a parallel plate configuration was used for the electrochemical measurements. A Pt foil covered with a V_2O_5 film served as a working electrode, whereas two Li foils were used as reference and counter electrodes. The electrochemical measurements were carried out in 1 M LiClO₄ + propylene carbonate (PC) solutions. An EG&G model 273 potentiostat

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was used for the SSCV and PITT measurements. Other details regarding the various measurements were already provided [1–3].

3. Results and discussion

In Fig. 1 we compare two plots: potential dependence of the differential intercalation capacity (obtained from a slow-scan rate cyclic voltammetric curve: $C_{\text{int}}(E) = I(E)v^{-1}$, $v = 0.2 \text{ mV s}^{-1}$), and the chemical diffusion coefficient D versus potential for as-prepared V_2O_5 film. In the most simple case of one-dimensional solid-state diffusion, D is inversely proportional to the diffusion time constant τ .

$$D = \frac{l^2}{\tau} \quad (1)$$

where l denoting the characteristic diffusion length. Here, we identify l with the film's thickness.

According to the finite-space diffusion model developed specifically for analyzing PITT measurements [4], the diffusion time constant τ is defined by the following equation [4,5].

$$\begin{aligned} \tau &= \left(\frac{Q_m \Delta X}{\pi^{1/2} I t^{1/2}} \right)^2 = \left(\frac{Q_m (\Delta X / \Delta E)}{(\pi^{1/2} I t^{1/2}) / \Delta E} \right)^2 \\ &= \left(\frac{C_{\text{int}}}{(\pi^{1/2} I t^{1/2}) / \Delta E} \right)^2 \quad \text{at } t \ll \tau \end{aligned} \quad (2)$$

where Q_m denotes the total intercalation charge of the electrode, $X(E)$ the intercalation level (and hence, ΔX is the change in X during a specific potential step), $I t^{1/2}$ the Cottrell slope obtained from the linear portion of the I versus $t^{1/2}$ curve for each potential step.

The potentiostatic titrations were performed during the electrode discharge, and thus the two minima in the D versus E curve (Fig. 1) correspond almost precisely to the cathodic

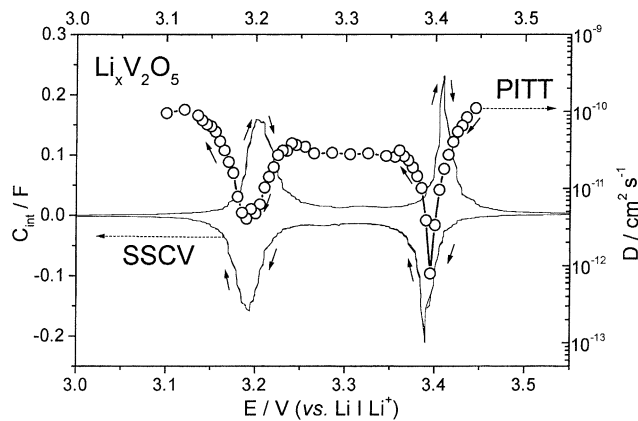


Fig. 1. Plots of the differential intercalation capacity, C_{int} ($v = 0.2 \text{ mV s}^{-1}$) and the chemical diffusion coefficient of Li-ions, D vs. potential for a 1600 \AA thick $\text{Li}_x\text{V}_2\text{O}_5$ electrode.

peaks of C_{int} . There is also a similarity in the half-peak widths of the related C_{int} and D versus E curves. These highly resolved data, which can scarcely be obtained with the composite electrodes in a similar time domain, are appropriate for theoretical modeling using the lattice-gas approach. The above correlation is due to highly attractive electron-ion interactions during Li-intercalation into the V_2O_5 film. Above a critical value of the attraction constant (which appears as a parameter in the intercalation isotherm chosen for describing the intercalation reaction and reflects attractive interactions among Li-insertion sites), the electrochemical insertion process is expected to proceed in the form of a first order phase transition. Crystallographic studies of Li-insertion into V_2O_5 correlate with this prediction, which results from the model based on the electroanalytical response of these electrodes.

Since SSCV and PITT mainly reflect the processes occurring in the long and medium-time domains, we have also applied EIS in order to obtain a general view of the various relaxation steps that belong to the entire intercalation process, as presented in Fig. 2. This figure shows as an example, the Nyquist plot of the $\text{Li}_x\text{V}_2\text{O}_5$ electrode (1600 \AA thick) measured during Li-intercalation in the vicinity of the SSCV peak at 3.4 V (versus Li/Li^+).

The low-frequency (long-time) domain of the spectra is represented by a sloping capacitive line, which is very similar in shape for spectra measured at different potentials. The main difference in the very low frequency part of spectra measured at different potentials (mHz domain) relates to the $-Z''$ values obtained at $\omega \rightarrow 0$. For instance, the following values of $-Z''$ were obtained at 2 mHz for spectra measured at $3.44, 3.42, 3.41, 3.40, 3.39, 3.38$ and 3.37 V (versus Li/Li^+): $7522, 2234, 833, 525, 1852, 3420$ and 4900Ω , respectively. The Z'' values, which are reciprocals of C_{int} (i.e. $Z'' = -(\omega C_{\text{int}})^{-1}$ at $\omega \rightarrow 0$), reflect a deep minimum centered at ca. 3.4 V (versus Li/Li^+). Hence,

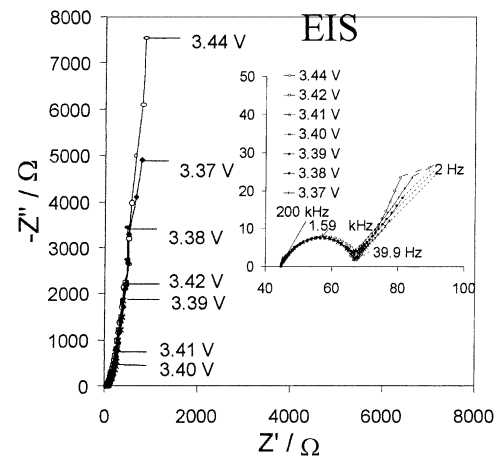


Fig. 2. Typical Nyquist plots for a thin $\text{Li}_x\text{V}_2\text{O}_5$ electrode measured in the vicinity of the SSCV peak centered at 3.4 V (vs. Li/Li^+). The high-frequency domain of the spectra is presented as the insert in the figure.

we show a good correlation between C_{int} measured by SSCV (Fig. 1) and C_{int} calculated from EIS, which appears as a pronounced peak at 3.4 V (versus Li/Li⁺). This good correlation between the results obtained for C_{int} by SSCV and EIS is the proof of their reliability and the high resolution of the EIS data.

The high-frequency domain of the impedance spectra (which cannot be reflected by SSCV) presents a slightly depressed semicircle, as shown in the insert of Fig. 2. We identify this semicircle with surface layers, which cover the V₂O₅ electrodes, and can be attributed to acid–base reactions between the oxide and acidic solution species.

This depressed semicircle can be simulated by Voigt-type analogs of three $R||C$ circuits in series [1]. Such an analog may reflect the expected situation on the electrode's surface, where a multilayered surface film covers the metal oxide. Such a film has at least two interfaces, solution/film and metal oxide/film. Hence, the three $R||C$ circuits in series required to obtain the best fit between the equivalent circuit analog and the impedance spectra, may reflect different resistances to Li-ion migration and interfacial charge transfers, coupled with film and interfacial capacitances. It is significant that the optimized simulation provided values around a few $\mu\text{F cm}^{-2}$ for two of the capacitors in the 'Voigt'-type analog, while the third capacitor was in the order of few tens of $\mu\text{F cm}^{-2}$ [1]. The low C values of the order of a few $\mu\text{F cm}^{-2}$ are typical for capacitances of surface films formed on Li [6], lithiated carbons [7], or Li_xMO_y [8,9] electrodes, which comprise thin layers of Li salts, while the higher C value (related to the third $R||C$ circuit) is typical of interfacial capacitance (e.g. surface film/vanadium oxide interface).

The insert of Fig. 2 shows that a 'Warburg-type' element (straight line at 45°) appears in the medium frequency domain of the spectra. Thus, it was important to check the reliability of the values of D obtained by PITT by the use of a finite-space diffusion model (Eq. (2)), by their comparison with the values of D obtained from the Warburg slope. Application of a finite-space diffusion model for the quantitative treatment of the impedance data in the medium-frequency domain results in τ depending on the Warburg slope, $A_w = \Delta\text{Re}/\Delta\omega^{-1/2} = \Delta\text{Im}/\Delta\omega^{-1/2}$ (ΔRe and ΔIm are the differences of the real and imaginary components of the impedance, respectively, corresponding to a finite variation in the angular frequency of the alternative current, $\Delta\omega$), and the differential capacity $C_{\text{int}} = Q_m dX/dE$, as follows [5,10].

$$\tau = 2 \left(\frac{Q_m A_w dX}{dE} \right)^2 \quad (3)$$

Eqs. (1) and (3) allow calculation of D as a function of E for each combination of $A_w(E)$ and $C_{\text{int}}(E)$. Fig. 3 compares D versus E relationships obtained for the thin electrodes (1600 Å) using both PITT and EIS. This figure demonstrates a good fit between the two curves, which seems to reflect the

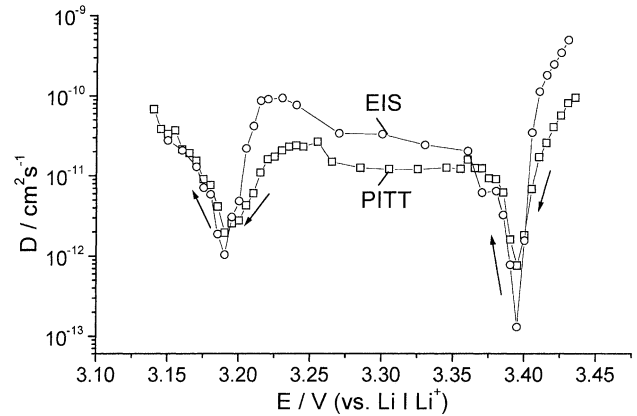


Fig. 3. Comparison between D vs. E plots of 1600 Å thick Li_xV₂O₅ electrodes obtained by EIS and PITT.

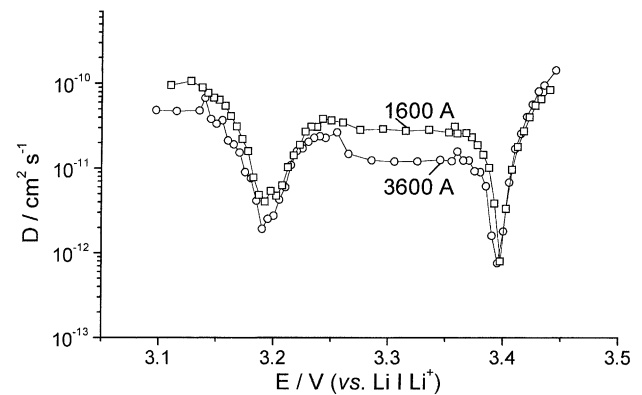


Fig. 4. Comparison between D vs. E curves for the 1600 and the 3600 Å thick Li_xV₂O₅ electrodes, calculated according to a finite space diffusion model.

reliability of the data obtained by both methods and the related calculations.

Finally, the applicability of a finite-space diffusion model can be verified by observing the characteristic diffusion time τ as a function of the film thickness l . If the model is applicable, τ should be proportional to the square of the film thickness, thus D is expected to be independent of l . Fig. 4 demonstrates that within the range of experimental error, there is good agreement between the D versus E curves obtained for 1600 and 3600 Å thick V₂O₅ electrodes.

4. Conclusion

SSCV, PITT and EIS were applied in a single study in order to explore Li-ion intercalation into a thin V₂O₅ electrode. The plots of C_{int} and D versus potential obtained from the different methods correlate very well, and were practically independent of the technique used. Applicability of the finite-space diffusion model for the description of

Li-intercalation into V_2O_5 was strictly checked for electrodes of two different thicknesses (1600 and 3600 Å). The shape of the plots of C_{int} and D versus potential is consistent with a lattice-gas approach, assuming highly attractive interactions among the Li-intercalation sites during Li-insertion into this material.

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