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The kinetics of lithium transport through $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode by theoretical analysis of current transient and cyclic voltammogram

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Abstract

Lithium transport through lithium cobalt dioxide thin film electrode prepared by rf-magnetron sputtering was investigated in a 1 M solution of LiClO_4 in propylene carbonate (PC) by means of analysis of current transient and cyclic voltammogram. All the experimental current transients in shape deviated markedly from the Cottrell behaviour, and the cathodic current transients intersected the corresponding anodic current transients each other. Moreover, the relation between initial current level and applied potential step followed Ohmic law. The current transient was simulated as a function of applied potential by means of the numerical analysis underlain by the ‘cell-impedance controlled’ lithium transport. The numerically simulated current transients coincided quantitatively almost with those current transients experimentally determined. The cyclic voltammograms theoretically obtained at various scan rates under the assumption of the ‘cell-impedance controlled’ lithium transport, were also quantitatively in good agreement with those cyclic voltammograms experimentally measured. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium cobalt dioxide; Current transient; Cyclic voltammogram; Cell-impedance

1. Introduction

Transition metal oxides have been widely studied over the last two decades as the electrode materials for rechargeable lithium battery [1–4]. Among these LiCoO_2 is used, in spite of its relatively high cost, as the cathode material for almost all rechargeable lithium batteries commercially available today owing to its favourable electrochemical performances and ease of manufacture.

The kinetics of lithium transport through the oxide electrode has been a main interest to whom wants to realise a high power application. Most researchers on lithium transport kinetics have analysed their kinetic data under the assumption that lithium diffusion through the oxide was a rate-determining step of the lithium intercalation process.

In earlier studies from our laboratory, however, it has been found that the Cottrell relation between current and time was not satisfied at current transients measured on the carbon-dispersed transition metal oxide composite electrodes, and from the experimental and theoretical current transients, it

has been suggested [5–8] that the internal cell resistance crucially determines current transient in value and shape. Nevertheless, the electrochemical response obtained from the composite electrode should be greatly distorted owing to such constituents of the composite electrode as organic binder and conductive additive [9]. So, the rigorous kinetic study requires the use of binder- and carbon-free pure electrode.

In this respect, this work discussed lithium transport through the sputter deposited $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode with respect to the ‘cell-impedance controlled’ lithium transport. For this purpose, open-circuit potential transient, potentiostatic current transient, and cyclic voltammogram were measured on the film electrode. The current transient and cyclic voltammogram have been simulated by taking the assumption that the rate of lithium intercalation/deintercalation is limited by ‘cell-impedance’ to compare with those experimentally determined.

2. Experimental

A LiCoO_2 disc (99.9% purity, 75 mm diameter, Kojundo Chem. Lab. Co., Ltd., Japan) and Ar gas (99.999% purity)

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were used as target material and sputter gas, respectively. LiCoO₂ film was deposited on 400 nm thick Pt current collector on alumina substrate at room temperature with an rf power 200 W and an Ar gas pressure of 1.4 Pa by using a conventional rf magnetron sputtering system (CemeCoat Model CC300, Germany). The flow rate of Ar gas was adjusted by the mass flow control system (Sierra Instrument Model 202C-PE, USA).

After deposition, the electrode was heated in air at a rate of 5°C min⁻¹ and held 700°C for 3 h, then cooled at a rate of 5°C min⁻¹. X-ray diffraction (XRD) pattern was recorded on an automated Rigaku diffractometer using Cu K α radiation. The thickness of the LiCoO₂ film was measured with alpha-step stylus (Tencor Instrument, USA).

A three-electrode electrochemical cell was employed for the electrochemical measurements. The reference and counter electrodes were constructed from lithium foil (Foote Mineral Co., USA, 99.99% purity), and a 1 M LiClO₄ propylene carbonate (PC) solution was used as the electrolyte. The electrode exposed to electrolyte amounted to 1 cm².

Open circuit potential transients were obtained by charging/discharging the cell in steps of 0.14 μ Ah cm⁻². The charging/discharging current was selected so that a change in lithium content of $\Delta\delta = 1$ for Li_{1- δ} CoO₂ would occur for 1 h. The current transient experiment was performed by application of large potential steps 0.05–0.15 V. The current transients were measured on the film electrode by dropping/jumping one potential to the other lithium injection/extraction potentials. Cyclic voltammograms were obtained from the film electrode with various scan rates of 0.5–5 mV s⁻¹ in the potential range of 3.5–4.2 V_{Li/Li+}. All the electrochemical measurements were performed at 25°C in a glove box (MECAPLEX GB94, Switzerland) filled with purified Ar gas.

3. Results and discussion

Fig. 1a and b show the XRD pattern of LiCoO₂ powder which was used as the target material for rf-magnetron sputtering, and that pattern of sputter deposited LiCoO₂ thin film, respectively. All diffraction patterns in Fig. 1a can be indexed by assuming the structure to be a hexagonal lattice of the α -NaFeO₂ type. From the comparison between two patterns of Fig. 1a and b, it can be seen that the principal diffraction peaks of the sputter deposited film (asterisk (*)) in Fig. 1b correspond to the peaks in the LiCoO₂ powder.

It is noted that the (1 0 1) and (1 0 4) reflections were detected to predominantly appear in Fig. 1b, whereas no (0 0 3) reflection was detected within the accuracy of the measurement, suggesting the preference of the grains for (1 0 1) and (1 0 4) orientations [10]. This means the majority of the grains in the LiCoO₂ thin film have their (1 0 1) and (1 0 4) planes parallel to the substrate. This situation is very favourable to lithium ion diffusion through the layered path of the oxide.

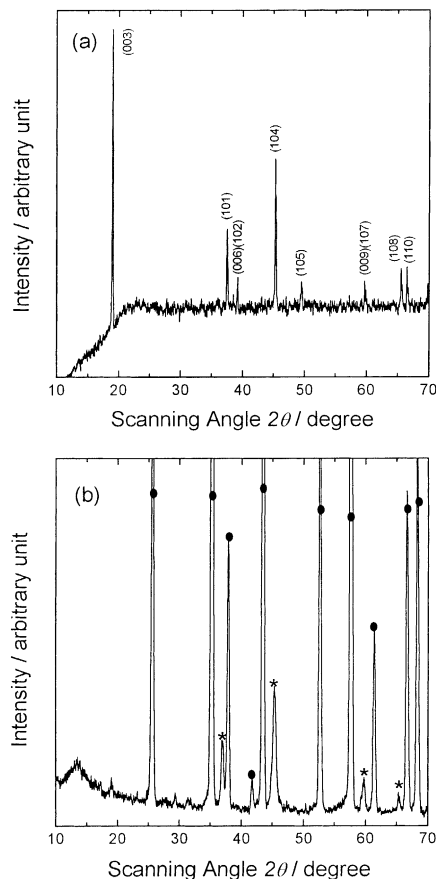


Fig. 1. The X-ray diffraction patterns of (a) the LiCoO₂ powder which was used as the target material and (b) the sputter deposited LiCoO₂ thin film. The peaks due to the substrate are indicated in the figure by a solid circle (●).

Fig. 2 gives the electrode potentials obtained from the intermittent galvanostatic charge/discharge curve of the Li_{1- δ} CoO₂ thin film electrode in a 1 M LiClO₄-PC solution as a function of intercalated lithium content. The electrode potential curve was characterised by a wide potential plateau at 3.91 V_{Li/Li+}, and two inflexion points at ca. 4.06 and 4.17 V_{Li/Li+}. The former potential plateau is attributed to the coexistence of two hexagonal phases of slightly different lattice parameters. And the latter inflexion points are assigned to the order/disorder phase transition [11].

Fig. 3a presents on a logarithmic scale the cathodic and anodic current transients, experimentally obtained from the Li_{1- δ} CoO₂ thin film electrode with a thickness of 140 nm in a 1 M LiClO₄-PC solution at the potential drop and potential jump, respectively. The current transients did not give any transition time at which semi-infinite diffusion behaviour of lithium ion changes to finite-length diffusion behaviour, and never followed the linear relationship between logarithmic current and logarithmic time (the Cottrell behaviour) during the whole intercalation/deintercalation.

It should be noted that the initial current level I_{ini} in current transient is linearly proportional to the applied potential drop ΔE as can be seen in Fig. 3b. This means

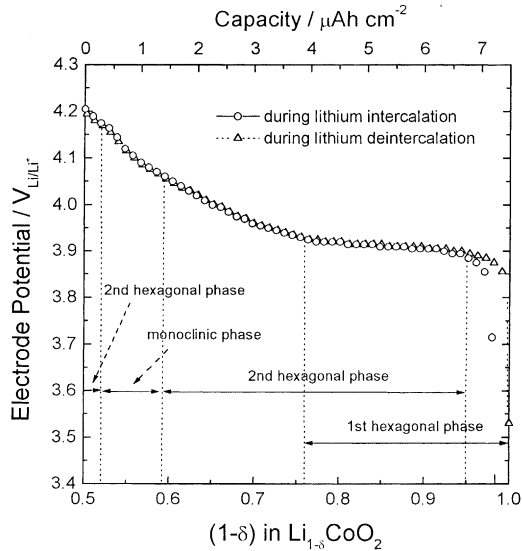


Fig. 2. The electrode potential obtained from the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode with a thickness of 140 nm in a 1 M $\text{LiClO}_4\text{-PC}$ solution as a function of lithium content $(1-\delta)$ during lithium intercalation (\circ) and deintercalation (\triangle).

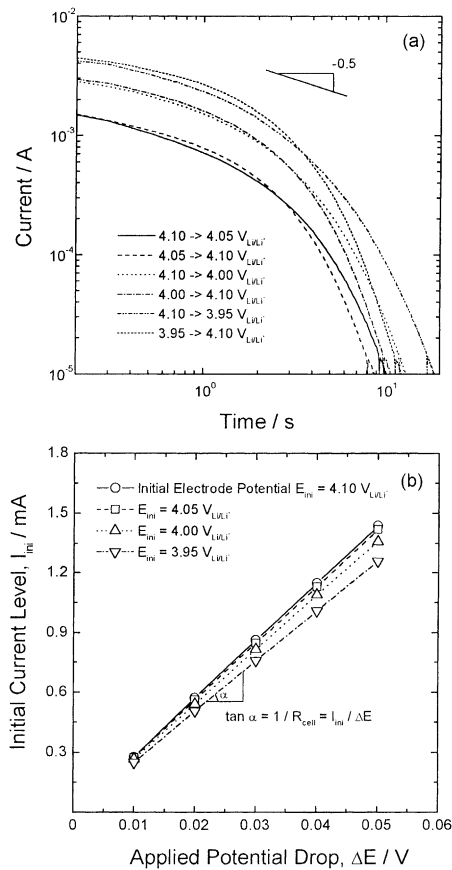


Fig. 3. (a) The cathodic and anodic current transients experimentally obtained from the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode with a thickness of 140 nm in a 1 M $\text{LiClO}_4\text{-PC}$ solution at the potential drop and potential jump, respectively, and (b) the plot of initial current level I_{ini} against applied potential drop ΔE at the initial electrode potentials E_{ini} of 4.10, 4.05, 4.00 and 3.95 $\text{V}_{\text{Li}/\text{Li}^+}$.

that the current–potential relation obeys Ohm’s law during lithium intercalation/deintercalation in the electrode potential between 4.10 and 3.95 $\text{V}_{\text{Li}/\text{Li}^+}$. This Ohmic relationship is observed in the electrode potential ranging between 4.20 and 3.80 $\text{V}_{\text{Li}/\text{Li}^+}$ from the plot of initial current level against applied potential step [12].

It is also noticeable that the cathodic current transients at the potential steps of 4.10–4.05, 4.10–4.00 and 4.10–3.95 $\text{V}_{\text{Li}/\text{Li}^+}$ intersected those anodic current transients of 4.05–4.10, 4.00–4.10 and 3.95–4.10 $\text{V}_{\text{Li}/\text{Li}^+}$ each other, respectively. In the previous works on transition metal oxide composite electrodes [5,7], a mutual intersection of the anodic and cathodic current transients has been discussed in terms of the concavity of the electrode potential curve and the ‘apparent’ (not ‘real’) potentiostatic boundary condition at the electrode/electrolyte interface. In that work, it has been suggested that the intersection of the current transients should be ascribed to the ‘cell-impedance controlled’ lithium transport.

Under the circumstances, we theoretically determined the current transient under the assumption of the ‘cell-impedance controlled’ lithium transport. The numerical procedure can be found elsewhere [5–8].

Fig. 4 depicts on a logarithmic scale the cathodic and anodic current transients at the potential drop and jump, respectively, determined from the numerical solution to the Fick’s diffusion equations under the assumption of ‘cell-impedance controlled’ lithium transport. The theoretical current transients (Fig. 4) shared almost exactly those experimental current transients (Fig. 3a) in value and shape.

From the quantitative coincidence of theoretical current transient with experimental current transient, it is reasonable to conclude that lithium transport through the $\text{Li}_{1-\delta}\text{CoO}_2$ film electrode in a 1 M $\text{LiClO}_4\text{-PC}$ solution is purely governed by the ‘cell-impedance controlled’ constraint during

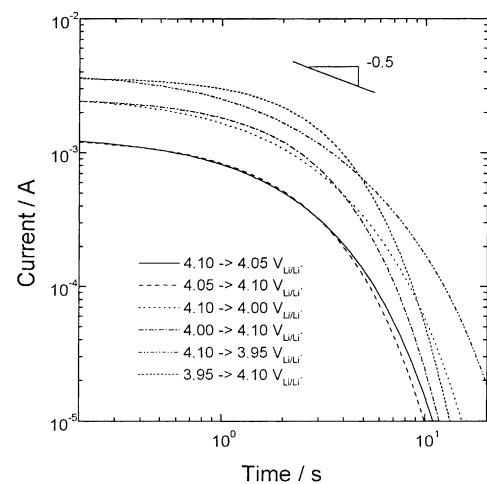


Fig. 4. The cathodic and anodic current transients at the potential drop and potential jump, respectively, theoretically determined by means of the numerical analysis based upon the ‘cell-impedance controlled’ lithium transport.

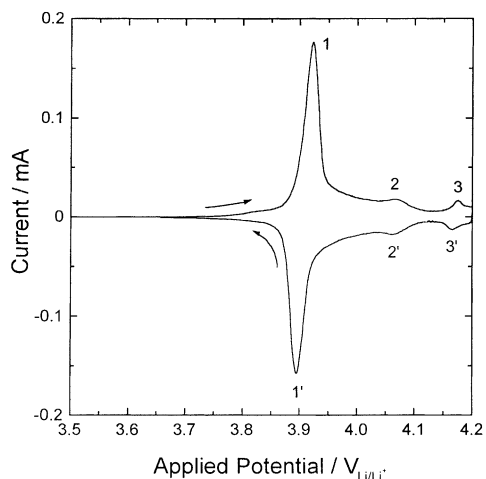


Fig. 5. The cyclic voltammogram experimentally obtained from the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode in a 1 M $\text{LiClO}_4\text{-PC}$ solution at a scan rate of 0.5 mV s^{-1} .

the whole intercalation/deintercalation time, not by the 'diffusion controlled' constraint. This teaches us the following: the equations used for determining the chemical diffusivity of lithium in the electrode were derived under the assumption that lithium intercalation/deintercalation is rate-controlled by lithium ion diffusion through the electrode. Thus, those equations are not appropriate to provide a reliable value of lithium diffusivity in the $\text{Li}_{1-\delta}\text{CoO}_2$ film electrode in a 1 M $\text{LiClO}_4\text{-PC}$ solution.

Now, we extend the kinetic investigation of lithium transport through the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode to the case of potential scanning. Fig. 5 illustrates the cyclic voltammogram experimentally obtained from the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode with a thickness of 140 nm in a 1 M $\text{LiClO}_4\text{-PC}$ solution at a scan rate of 0.5 mV s^{-1} . The cyclic voltammogram clearly showed three sets of well-defined current peaks, i.e. the first set (3.922, 3.894), the second set (4.065, 4.060), and the third set (4.174, 4.164). The first set is due to lithium deintercalation from and intercalation into the intercalation sites. The second and third sets prove to be caused by the order/disorder phase transition [11].

It is noted that the anodic peak current (1) was larger than the cathodic peak current (1') and that the shape of the anodic and cathodic current peaks was asymmetric. The higher the scan rate was, the larger appeared the difference between the anodic and cathodic peak currents and the more appeared the departure from the symmetry of the anodic and cathodic peaks in shape on the cyclic voltammogram (Fig. 6a).

It was also observed that the anodic peak current was linearly proportional not to the square root of the scan rate [13], but to the scan rate to the power of ca. 0.7. The relation was extended to above the scan rate of 100 mV s^{-1} [14]. As far as we know, there is no literature available that gives any clear explanation for these anomalous cyclic voltammetric behaviours.

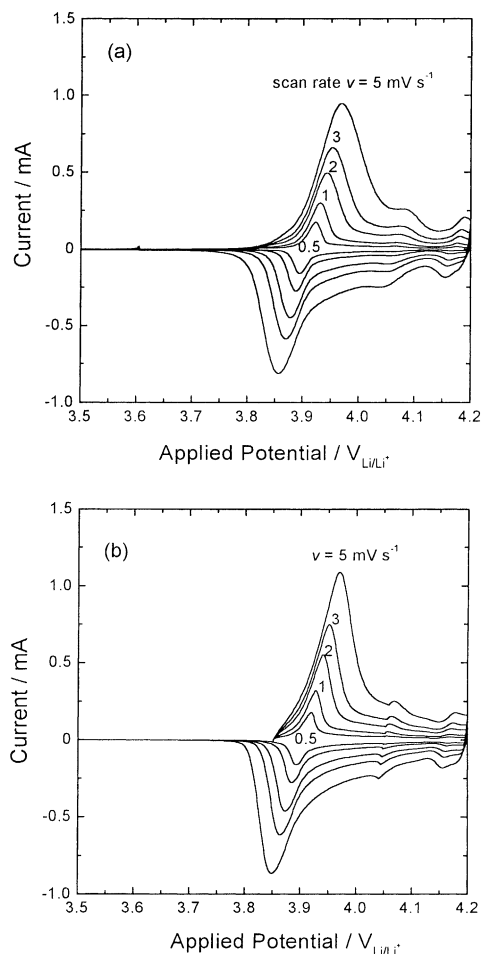


Fig. 6. The cyclic voltammograms at various scan rates 0.5 to 5 mV s^{-1} (a) experimentally obtained from the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film electrode with a thickness of 140 nm in a 1 M $\text{LiClO}_4\text{-PC}$ solution, and (b) theoretically determined by means of the numerical analysis based upon the 'cell-impedance controlled' lithium transport.

From the analysis of the current transient, we have concluded that lithium transport through the film electrode is purely governed by 'cell-impedance controlled' constraint during potential stepping. Then, it is likely that the rate of lithium intercalation/deintercalation, i.e. current, should be limited by 'cell-impedance' during potential scanning as well.

So, we theoretically determined the cyclic voltammogram under the assumption of the 'cell-impedance controlled' lithium transport. The resulting cyclic voltammograms are illustrated in Fig. 6b. The theoretical cyclic voltammograms (Fig. 6b) coincided quantitatively with those experimentally determined (Fig. 6a).

As a matter of fact, the low cathodic peak current compared to the anodic peak current, the asymmetry between anodic and cathodic peaks, and the proportionality of the anodic peak current to the scan rate to the power of ca. 0.7 were fairly well observed to be maintained in Fig. 6b. This result strongly indicates that lithium transport through the $\text{Li}_{1-\delta}\text{CoO}_2$ thin film proceeds under the 'cell-impedance

controlled' constraint during potential stepping and potential scanning alike.

4. Conclusions

In the present work, lithium transport through the sputter deposited $\text{Li}_{1-\delta}\text{CoO}_2$ thin film has been investigated by means of analysis of current transient and cyclic voltammogram. The results are summarised as follows.

1. The experimental current transients hardly followed the Cottrell behaviour during lithium intercalation/deintercalation, and the cathodic current transients intersected the corresponding anodic current transients each other. The relation between initial current level and applied potential step of the current transients held Ohm's law.
2. The current transients have been simulated under the assumption of the 'cell-impedance controlled' lithium transport. The quantitative coincidence of the experimental current transient with those numerically determined, strongly suggests that lithium transport through the $\text{Li}_{1-\delta}\text{CoO}_2$ film electrode is purely governed by 'cell-impedance' during potential stepping.
3. The cyclic voltammograms theoretically determined by taking the assumption of the 'cell-impedance controlled' lithium transport, agreed quantitatively well with those experimentally determined, indicating that lithium transport is rate-controlled by 'cell-impedance' during potential scanning.

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