Application of the microelectrode technique to the kinetic study of lithium deposition/dissolution and alloying in organic solutions

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Abstract

The kinetic study on lithium deposition/dissolution has been carried out in 0.1–1 M LiClO$_4$/PC solutions using the microelectrode technique. The concentration dependence of the kinetic parameters for lithium deposition/dissolution and the diffusion coefficient of the lithium ion were evaluated under the condition of suppressed electrolyte decomposition by applying a fast scan rate in cyclic voltammetry. The diffusion coefficient of the lithium ion was evaluated to be 3.99×10^{-6} cm^2/s at 27 °C, independent of the salt concentration. The exchange current density for lithium deposition/dissolution was 0.81 mA/cm^2 in 0.1 M LiClO$_4$/PC solution, and increased with increasing salt concentration. © 1997 Published by Elsevier Science S.A.

Keywords: Kinetic study; Concentration dependence, Diffusion coefficient, Lithium deposition/dissolution; Organic solvents

1. Introduction

The cycle life of rechargeable lithium batteries, especially with high energy density, is often limited by the dendritic deposition of lithium [1–3]. This is believed to result from the high activity of freshly deposited lithium which leads to the reaction of lithium with the organic solvent. Therefore, a well-understanding of the interphase behavior of the organic solution/lithium interphase and the application of the alternatives of metallic lithium anode such as lithium alloys become important factors in improving the cycling characteristics of lithium rechargeable batteries.

Previous studies on the electrochemical behavior of organic solutions were performed by using the macroelectrode technique [4,5]. Due to the very low conductivity of the organic solutions, it is inevitable to address the iR drop effect to the measurement results. To solve this problem, the microelectrode technique is very striking because of its dramatic improvements in decreased sensitivity of the effect of solution resistivity and increased temporal resolution [6]. This enables us to measure the electrochemical behavior under the condition of very small concentrations of the electrolyte.

In a previous paper, we reported the temperature dependence of the kinetic parameters for lithium deposition/dissolution and lithium-ion diffusion by using the microelectrode technique in 1 M LiClO$_4$/PC and PC + EC solutions under the condition of the suppressed solvent decomposition at high scan rate of cyclic voltammetry (CV) measurements [7]. The present investigation aimed at the effect of the lithium-ion concentration on the kinetics of the lithium electrode reaction in 0–1 M LiClO$_4$/PC solution using the microelectrode technique.

2. Experimental

1 M LiClO$_4$/PC solution and pure PC solvent were received with a water content of <20 ppm from Mitsubishi Chemical. The LiClO$_4$ concentration was controlled by blending the pure PC solvent and 1 M LiClO$_4$/PC solution in a glove box under dried argon gas. Atomic absorption analysis was used to verify the salt concentration. The solutions and Li reference electrode were sealed into glass ampoules in stock, and led into an electrochemical cell just before the experiment was starting. The electrochemical measurement was carried out in a three-electrode configuration. A Pt coil served as the counter electrode. All potentials are referred to Li/Li$^+$ (1 M) electrode. A Pt (diameter 30 μm) microelectrode was constructed by sealing a Pt wire into a Pyrex glass tube. Details of the experimental setups were reported elsewhere [7].

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The electrochemical measurement was performed by a computer-controlled elctrochemical system (Cypress Systems, Model CS-1090). The water content in the solution was checked by the Karl–Fischer titration (Mitsubishi, Model CA-06).

3. Results and discussion

3.1. Lithium-ion diffusion

Cyclic voltammograms of the Pt microelectrode (diameter 30 μm) are shown in Fig. 1 for the PC solution with LiClO$_4$ concentration ranging from 0.1 to 1 M at 27 °C. The potential was initially set to + 1.2 V where no appreciable current was yielded, then scanned to − 0.8 V and reversed to + 1.5 V at scan rate of 1 V/s. The characteristic sigmoid curves for microelectrode were observed, indicating that the solvent decomposition was retarded due to a short exposure duration of the lithium surface at high scan rate [7]. The limiting current density corresponding to the lithium deposition increased with the increasing concentration. Furthermore, it was found that the value of the limiting current density kept constant at the scan rate larger than 0.5 V/s, suggesting that the pseudosteady-state conditions prevailed.

Fig. 2 shows the plot of the limiting current density versus the LiClO$_4$ concentration. A well-defined straight line was observed. According to the theory of the microelectrode technique [6], the limiting current density is proportional to the LiClO$_4$ concentration as expressed in Eq. (1) so that it is reasonable to obtain a straight line in the i_L–C plot
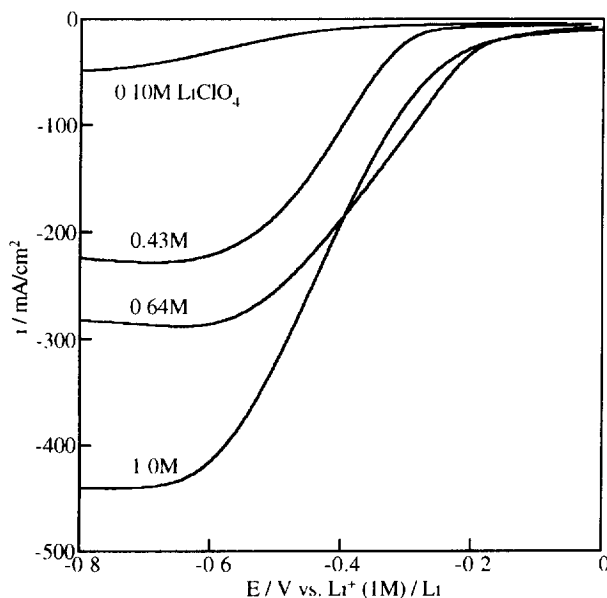
$$i_L = \frac{4nFDC}{r\pi(1 - t_+)}$$
(1)

Fig. 1. Limiting current density at the Pt microelectrode (diameter 30 μm) in PC solution containing different concentrations of LiClO$_4$ at 27 °C, scan rate 1 V/s.
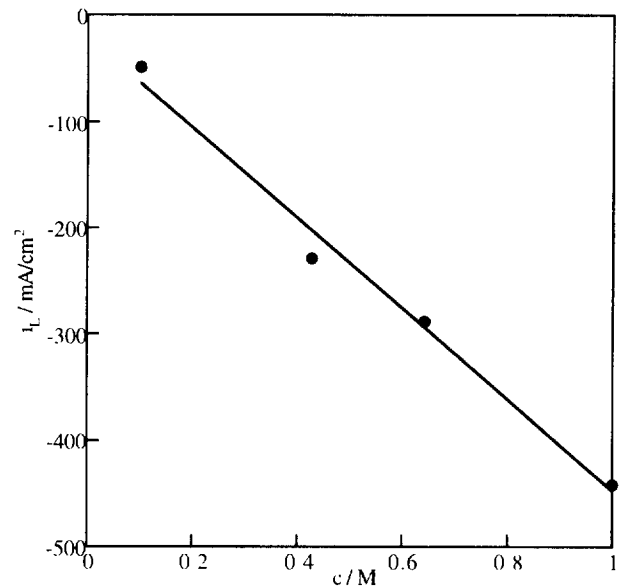

Fig. 2. Limiting current density i_L vs concentration C obtained from Fig. 1.

where i_L is the limiting current density, n the electron number, F the Faraday constant, D the diffusion coefficient of lithium ion, C the bulk concentration of lithium ion, r the radius of Pt microdisk electrode, t_+ the transference number of the lithium ion. By assuming the transference number of lithium ion to be 0.3 [8] and independent of the temperature, the diffusion coefficient of the lithium ion was evaluated to be 3.99×10^{-6} cm^2/s at 27 °C.

3.2. Kinetic parameters for lithium deposition/dissolution

In order to get further insight into the mechanism of lithium electrode reaction, the effect of the lithium-ion concentration on the kinetic parameters for lithium deposition/dissolution was evaluated. Fig. 3 shows CV for the Pt microelectrode in 1 M LiClO$_4$/PC solution at 23 °C at 1 V/s, where the potential was reversed at − 0.4 V to maintain the lithium deposition/dissolution process in the charge-transfer control. In the forward scan, the current of lithium deposition grew up from − 0.3 V, indicating that the nucleation overpotential of − 0.3 V was needed. Therefore, the Allen–Hickling relation may be used to evaluate the kinetic parameters of lithium deposition/dissolution by using the i–E response at the reversed scan [9]

$$\log\frac{i}{\exp\left(\dfrac{nF}{RT}\eta\right) - 1} = \log i_0 - \frac{(1 - \alpha)nF}{2.3RT}\eta$$
(2)

where i denotes the current density, R the gas constant, T the absolute temperature, h the overpotential for lithium electrode reaction, i_0 the exchange current density, α the anodic transfer coefficient. Thus the Allen–Hickling plots were constructed as a function of the LiClO$_4$ concentration and the result was shown in Fig. 4. The straight lines were observed at the potential ranging from − 0.1 to + 0.3 V. The values of the
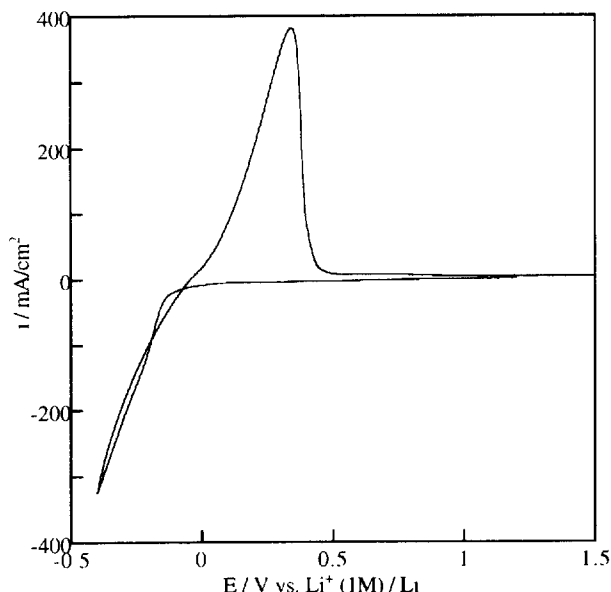
Fig. 3. Cyclic voltammogram at the Pt microelectrode (diameter 30 μm) in 1 M LiClO₄/PC solution at 23 °C; scan rate: 1 V/s.
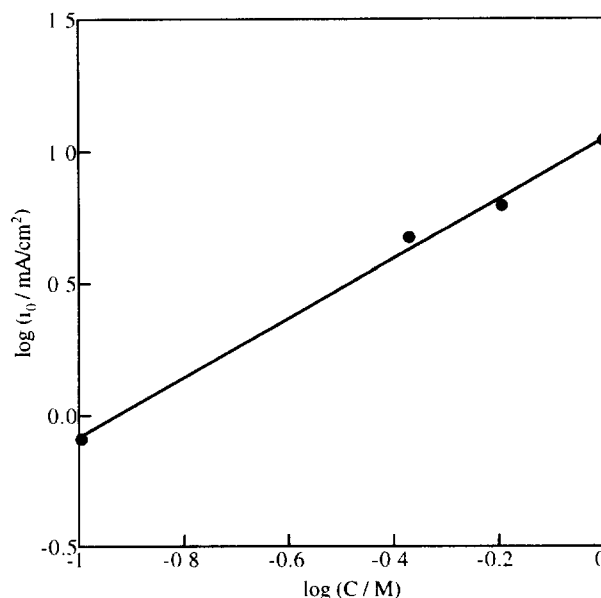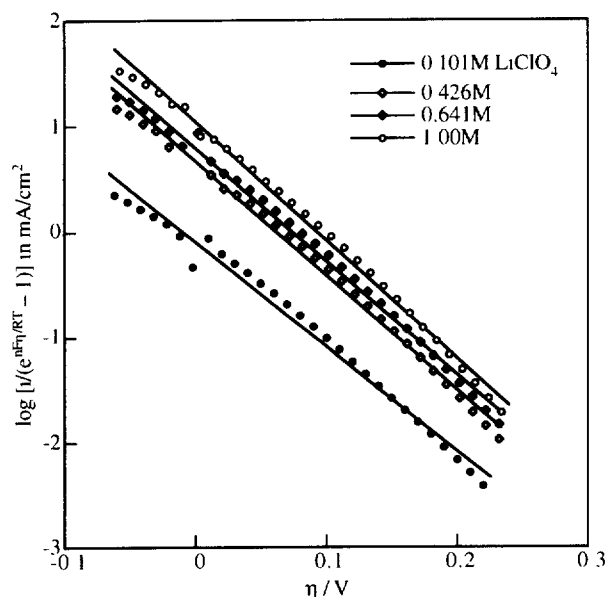

Fig. 5. Log i_0 vs. log C obtained from Table 1.

Fig 4 Allen-Hickling plots for lithium dissolution as obtained from Fig. 3.

Table 1
Kinetic parameters for lithium deposition/dissolution at Pt (30 μm in dia.) microelectrode in PC solution containing different concentration of LiClO₄

C/M	0.10	0.43	0.64	1.0
i_0/mA/cm²	0.81	4.72	6.24	10.3
α	0.42	0.36	0.37	0.34

exchange current density and the transfer coefficient were evaluated from the intercepts at $\eta = 0$ and the slope of the straight lines; the results are summarized in Table 1. It was noted that the values of the transfer coefficient were 0.34–0.42, no appreciable difference with the LiClO₄ concentration was observed.

To examine the relation of the exchange current density and the LiClO₄ concentration, a logarithmic plot of the exchange current density versus the LiClO₄ concentration was constructed, as shown in Fig. 5. The linearity was fairly good and the slope was found to be 1. According to the kinetic theory of the charge-transfer process, the following equation must be fulfiled [9]

$$i_0 = nFk^0 C^\alpha C_{Li}^{1-\alpha} \tag{3}$$

where k^0 is the standard rate constant, and C_{Li} the concentration of the deposited lithium. In this equation, C_{Li} is 1 (pure metal) so that the reaction order of C should be equal to α. However, the α value obtained from Allen–Hickling plots was 0.34–0.42 but the actual reaction order of the lithium-ion concentration was 1.0. In fact, this difference has been reported by Scarr [4] and Meibuhr [5] for the same electrode/solution system. There was no clear explanation of this difference effect; it may be possible to attribute this difference to the influence of the activity coefficient and the double-layer effect which were involved in Eq. (3). Especially, the double-layer effect may give the most plausible explanation that the charge distribution at the diffusion double layer may reduce the potential difference at the reaction zone at the electrolyte/electrode interface, and this reduces the i_0 values by so called Frumkin effect.

By supposing the transfer coefficient to be 1, the standard rate constant was estimated to be 1.84×10^{-4} cm/s from the intercept at $\eta = 0$ of the straight line in Fig. 5.

4. Conclusions

The kinetic study on lithium deposition/dissolution was carried out in 0.1–1 M LiClO₄/PC solutions by using the microelectrode technique.

The lithium-ion diffusion coefficient was found to be 3.99×10^{-6} cm^2/s at 27 °C, which was independent of the $LiClO_4$ concentration ranging from 0.1 M to 1 M.

The values of transfer coefficient a were evaluated to be 0.34–0.42 from Allen–Hickling plot. On the other hand, the exchange current density linearly increased with increasing $LiClO_4$ concentration and the calculated a value was 1.0. This difference may be attributed to the double-layer effect, the so-called Frumkin effect.

Acknowledgements

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