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Electrochemical Deposition and Dissolution Processes of Lithium Compound on Gold from Propylene Carbonate

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The cathodic electrolysis of propylene carbonate containing lithium perchlorate was studied by means of an in-situ quartz crystal microbalance technique. A lithium compound was deposited at about +1.5 V vs. Li/Li$^+$ and dissolved at about +4.0 V vs. Li/Li$^+$. In constant potential electrolysis at +0.9 V vs. Li/Li$^+$, the deposition process was divided into two stages. In the first stage, in which lithium carbonate was most probably deposited, an electrode reaction of ferrocene which was added to the solution was gradually retarded. In the second stage, in which some chemical reaction proceeded dominantly, the electrode reaction of ferrocene was almost completely blocked. A cathodic charge of +3.0 mC cm^{-2} was necessary for almost complete blocking.

The electrochemical deposition and dissolution of lithium is essential for a lithium secondary battery; the characteristics of the battery may suffer from the deposition of some lithium compounds in an underpotential region.[1] Indeed, it is known that a passive film develops on the surface of the lithium electrode of a lithium battery.[2] Further, the electrochemical deposition of lithium compounds is also important for intercalation of lithium into carbon.[3] Regarding these points of view, we consider here the electrochemical deposition and dissolution processes of lithium compounds on a gold electrode from propylene carbonate in the underpotential region. Although some studies concerning lithium compounds deposited onto noble-metal electrodes in an underpotential region have been reported,[4—6] none of them considered the dynamic processes of deposition and dissolution of lithium compounds.

The dynamic deposition and dissolution processes were studied in this work by means of an in-situ electrochemical quartz crystal microbalance (EQCM) technique, which permits one to measure the weight of rigid films either adsorbed or deposited onto the electrode surface, as long as the surface roughness and internal stress do not change.[7] Although there have been some studies in which the EQCM method was employed for the underpotential deposition (UPD) of several elements, such as cadmium,[8] titanium,[8] lead,[8,9] iodide,[10] and bromide,[10] the deposition of lithium compounds in the underpotential region has never been studied by means of the EQCM technique, to the best of our knowledge. Additionally, we employed ferrocene as a probe for the electric conductivity of the deposited layer. The electrochemical reaction of ferrocene in a solution is inhibited by a layer deposited on the electrode surface, if the layer is electrically insulating.

Experimental

The apparatus and procedure used in the in-situ EQCM technique have been described elsewhere.[11] 5 MHz AT-cut quartz crystals, which had been coated with gold electrodes by RF-sputtering, were employed for in-situ EQCM measurements. Chromium was used as a binder between the gold layer and the quartz crystal for better adhesion. The mass sensitivity of this quartz crystal is 17.7 ng cm^{-2} per 1 Hz. The working electrode has a piezoelectrically-active area of 0.283 cm^2 and an electrochemically-active area of 0.503 cm^2. Experiments were carried out in the three-electrode mode in propylene carbonate (battery grade) containing lithium perchlorate and/or tetraethylammonium perchlorate at ca. 20 °C. The concentration of residual water in the solution was 16 volume ppm. A silver (Ag/Ag$^+$) or lithium (Li/Li$^+$) wire was used as a reference electrode. For the results obtained with silver electrode as a reference, potentials were converted to those against the lithium electrode. The potential stability of the silver quasi-reference electrode during successive potential cycling was verified using a redox couple of ferrocene.

Results and Discussion

Electrochemical Deposition and Dissolution of Lithium Compound. Figure 1 shows typical results of the in-situ EQCM measurements performed in propylene carbonate. The initial potential was +3.00 V (vs. Li/Li$^+$). First, the potential was cycled in a 0.01 M tetraethylammonium perchlorate solution (1 M = 1 mol dm^{-3}) containing no lithium ion, in order to clarify whether lithium ion is concerned with some deposition reaction. In the 0.01 M tetraethylammonium perchlorate solution (dotted line), the cathodic current was observed at a potential below +2.5 V. Simultaneously, the resonance frequency of the quartz crystal was decreased at a potential below +2.3 V. Although a larger cathodic current was observed at a more negative potential than +1.4 V, the frequency no longer decreased. That is, the first reduction process (+2.5 to +1.4 V) was accompanied by an electrode mass increase, while the second reduction process (below +1.4 V) caused no change in the electrode mass. The direction of the potential sweep was reversed at −0.30 V, and the resonance frequency of quartz crystal returned to the initial value upon returning to the initial potential (i.e., +3.0 V). This reversible frequency change was also observed in the second and following cycles.

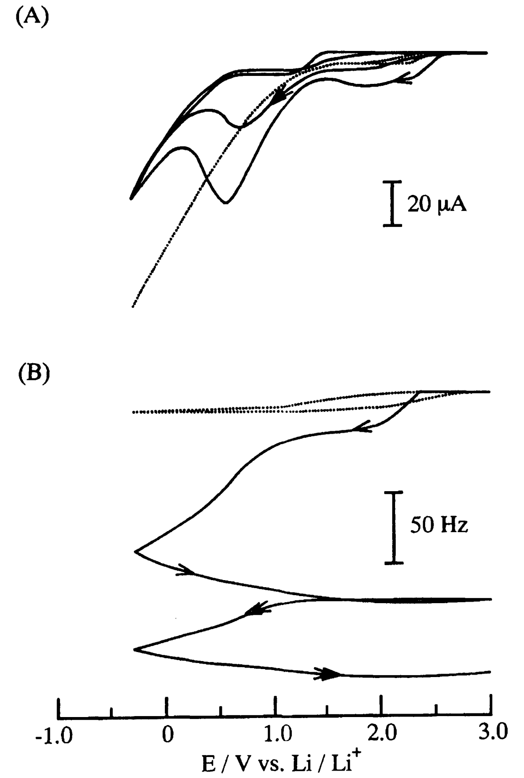

Fig. 1. (A) Cyclic voltammograms and (B) EQCM frequency responses in propylene carbonate containing 0.01 M tetraethylammonium perchlorate before (dotted curve, the first sweep) and after (solid curve, the first and second sweep) the addition of $LiClO_4$ (0.01 M). Scan rate is 20 $mV\,s^{-1}$.

In this system, a reactant may be propylene carbonate, residual oxygen, or residual water in the solution. Eggert and Heitbaum[12)] studied the electrolysis of propylene carbonate containing 0.2 M tetra-n-butylammonium tetrafluoroborate and trace amounts of water (20 ppm) at a Pt electrode by means of differential electrochemical mass spectrometry, and reported that water is reduced to generate hydrogen below +2.3 V (vs. Li/Li^+) and that propylene carbonate is reduced to generate propylene below +1.4 V. Therefore, the first and second reduction processes observed in the present study may be ascribed to water reduction and propylene carbonate reduction, respectively. The decrease in the frequency may have been caused by the adsorption of generated hydrogen gas (it is known that the adsorption of small bubbles on a quartz crystal resonator surface causes a frequency decrease[7)]) or the potential-dependent specific adsorption of some other species. In either event, a small frequency decrease is not concerned with lithium, which was not contained in the solution.

After 10 cycles of a potential sweep in the tetraethylammonium perchlorate solution, $LiClO_4$ (0.01 M) was added to the solution (solid line). A broad cathodic peak and a relatively sharp one were observed at +2.0 and +0.6 V, respectively. Both peaks were accompanied by frequency decreases. The first reduction process may be a similar reaction to that in a tetraethylammonium perchlorate solution, since the current and frequency behavior are similar. However, the second process is completely different from that in the tetraethylammonium perchlorate solution; a large frequency decrease was observed and the frequency continued to decrease, even after the direction of the potential sweep was reversed. Hence, the second process, which involved both electrochemical and chemical reactions, was accompanied by the deposition of some lithium compound onto the electrode surface.

In the second potential sweep, both the frequency decrease and the reduction current were smaller than those in the first sweep; the deposited compound retarded the overall rate of the electrochemical reaction. This suggests that the deposited compound might have been electrically resistive. Indeed, the resistivity of the deposited layer was certified by using ferrocene; this is further discussed below. Moreover, the frequency drop corresponding to the first reduction process, which was observed in the first potential sweep at around +2.2 V, was not observed in the second sweep. This indicates that the first process cannot occur on the layer deposited in the second reduction process.

Since the potential for the second process is roughly in agreement with the potential at which the underpotential deposition of lithium was observed in an acetonitrile solution by Gerischer and Wagner,[4)] or in γ-butyrolactone by Aurbach,[5)] the second reduction process may involve the underpotential deposition of lithium. If this is the case, the surface or all of the deposited lithium layer must react with propylene carbonate, residual water, or residual oxygen to form an insulating compound, since the deposited layer blocked an electrochemical reaction of ferrocene in the solution (see below). The other possible deposition reaction is the precipitation of an insoluble compound as the result of a reaction of lithium ion and the anion radical of propylene carbonate. The anion radical can be generated by electrochemical reduction of propylene carbonate, and lithium carbonate and lithium alkyl carbonates are known to be produced from lithium ion and the anion radical.[3,13,14)] These reactions are known to proceed at a potential lower than +1.5 V vs. Li/Li^+.[13)]

The dissolution process was also studied by means of the EQCM technique. The lithium compound was deposited onto the electrode surface by sweeping the potential from +3.0 V down to +0.6 V (20 $mV\,s^{-1}$); the potential was then swept between +3.0 and +4.5 V (Fig. 2). As can be seen, the frequency gradually increased and dissolution of the compound proceeded. This frequency change indicates that the three repetitious potential sweeps caused a loss of 80% of the deposited compound by weight. This dissolution process was also observed by the use of ferrocene as a probe for the electric conductivity of the deposited film (as

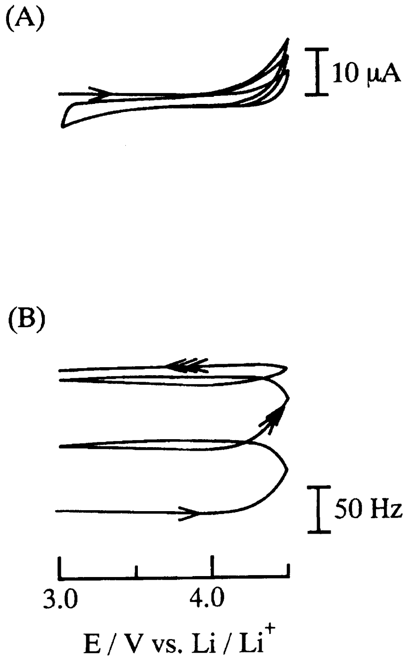

Fig. 2. (A) Cyclic voltammogram and (B) EQCM frequency response in propylene carbonate containing 0.5 M $LiClO_4$ solution obtained at the electrode on which the lithium compounds had been deposited by a potential sweep down to +0.6 V vs. Li/Li$^+$. Scan rate is 20 mV s^{-1}.

described below).

Constant Potential Electrolysis. We next performed constant-potential electrolysis in propylene carbonate containing 0.5 M $LiClO_4$. Figure 3(A) and (B) show the time-courses of the cathodic current and frequency, respectively, on a potential step from +3.0 to +0.9 V vs. Li/Li$^+$. At +0.9 V, the second reduction process occurs, as described above. From these results, the change in the resonance frequency was plotted against the amount of cathodic charge passed (Fig. 5-(C)). The curve can be divided into roughly two stages (stages 1 and 2) which have different slopes, as indicated in the figure. A different slope may mean a different apparent molecular weight of the deposited product(s).

However, it is difficult to evaluate the real mass change of a quartz crystal electrode from the resonance frequency change, since the resonance frequency is changed by many factors: not only mass, but also the internal stress,[15] surface roughness,[16] and rigidity of the deposited film.[17] Further, the deposited layer may contain a solvent and salts in itself.[18] In the present study we assumed that the film was sufficiently rigid to apply the Sauerbrey equation and that any changes in the internal stress and surface roughness were negligible.

The apparent molecular weight was thus estimated for each stage, assuming that the number of electrons per molecule deposited was one. The average value of the apparent molecular weight obtained from several independent experiments was 38.8 and 200.2 g mol^{-1} for stage 1 and 2, respectively. The value obtained for stage 1 is close to that obtained in potential-sweep experiments performed in propylene carbonate containing 0.5 M $LiClO_4$ (37.9 g mol^{-1}). Although these values for stage 1 are larger than the molecular weight of lithium (6.9), lithium hydride (8.0) or lithium hydroxide (24.0), they roughly agree with that of lithium carbonate (73.9; 36.9 per 1 mol electron). The fact that the deposited layer is not conductive (as described below) is consistent with that the layer does not consist of lithium metal. Possible reactions for the lithium carbonate deposition are[13,14]

$$2Li^+ + PC + 2e^- \rightarrow Li_2CO_3 + \text{propylene(gas)}, \quad (1)$$

where PC represents propylene carbonate, and

$$Li^+ + e^- \rightarrow Li \quad (2)$$

and

$$2Li + PC \rightarrow Li_2CO_3 + \text{propylene(gas)}. \quad (3)$$

Reaction 2 is the underpotential deposition of lithium. The estimated apparent molecular weight for a two-electron reaction (77.6 g mol^{-1}) is slightly larger than the molecular weight of lithium carbonate. This is probably due to the surface roughness or internal stress of the deposited layer, solvent and salts contained in the layer, or small babbles formed on the layer. Here, we must note that if reaction 2 proceeds in the present system, lithium hydroxide (MW=24.0) may also be deposited by a reaction with residual water,[4,5]

$$Li + H_2O \rightarrow LiOH + 1/2H_2. \quad (4)$$

As can be seen, the underpotential deposition of lithium is requisite for reaction 3 and 4. However, only a few atomic layers of lithium are expected to be deposited by the underpotential deposition, though the deposited layer is at least 19 monomolecular layers of lithium hydroxide (estimated from the frequency decrease). Therefore, lithium hydroxide may not be the dominant component in the deposited layer. Here we note that both lithium carbonate and lithium hydroxide are insoluble in propylene carbonate.

A much larger apparent molecular weight was obtained for stage 2 than in the first stage. This must be because the chemical reaction as well as electrochemical reaction occurs in the second stage. This is further discuussed below.

Electrochemical Activity of the Electrode Carrying the Deposited Layer. To examine the electric conductivity of the deposited layer, ferrocene was added to the measurement solution. Figure 4 shows cyclic voltammograms obtained in propylene carbonate containing 0.5 M $LiClO_4$ and 2 mM ferrocene. The negative limit of the sweep range was changed stepwise from +2.5 to +1.1 V. The redox responses of ferrocene were not changed as long as the negative limit

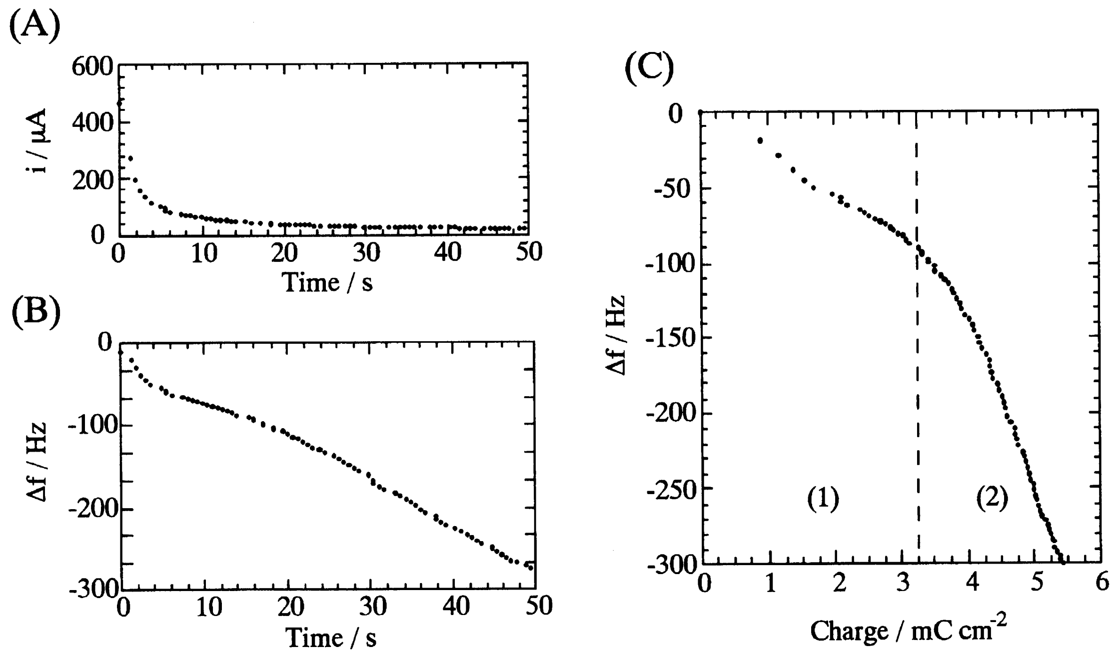

Fig. 3. (A) Typical potential-step chronoamperometric current-time curve, (B) resonance frequency change (Δf)-time curve, and (C) plot of the resonance frequency change (Δf) against the amount of cathodic charge passed for the data obtained in A and B. The electrode potential was stepped from +3.0 to +0.9 V vs. Li/Li$^+$ in propylene carbonate containing 0.5 M $LiClO_4$.

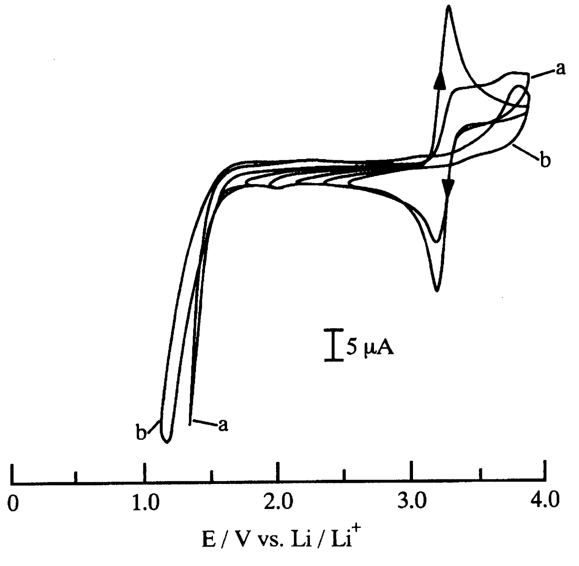

Fig. 4. Cyclic voltammograms obtained for various potential range in propylene carbonate containing 2 mM ferrocene and 0.5 M $LiClO_4$. Scan rate is 20 mV s^{-1}.

was more positive than +1.5 V. However, when the limit was +1.3 V, the responses were suppressed. These responses disappeared completely when the limit was +1.1 V. It was thus found that the electron-transfer reaction at the solution–electrode interface was blocked by the lithium compound, which was deposited on the electrode surface at a potential below +1.5 V. This potential does not contradict the potential at which a large frequency decrease was observed in the EQCM measurements (Fig. 1). These results rationalize the observation given in Fig. 1; the frequency decrease in the second potential sweep was smaller than that in the first sweep. The deposited resistive film retarded any further deposition.

In the cycles in which the blocking was observed (curves a and b in Fig. 4), a new anodic peak appeared at around +3.8 V. This irreversible peak, having no corresponding cathodic peak, should be ascribed to an oxidation reaction of the deposited film. Since this potential is broadly in agreement with the potential at which the frequency increase (i.e., mass decrease) was observed in Fig. 2, the anodic peak may correspond to the anodic dissolution of the deposited compound. Indeed, after the potential had been held at a potential more positive than +4.0 V, the redox waves for ferrocene were completely restored.

Figure 5(A) depicts redox responses of ferrocene obtained after constant potential electrolysis at +0.9 V. The cathodic charge passed during the lithium deposition was 0, +1.8, or +3.1 mC cm^{-2}. It can be seen that the anodic peak current of ferrocene decreased along with an increase in the charge passed during the deposition. Each cathodic peak is larger than each anodic peak, because the deposited lithium compound is partially oxidized and dissolved into the solution at a potential about +3.8 V, as mentioned above.

In Fig. 5(B), the anodic currents at +3.4 V in the voltammograms in Fig. 5(A), referred to as i_a^p, are plotted against the cathodic charge passed during the depo-

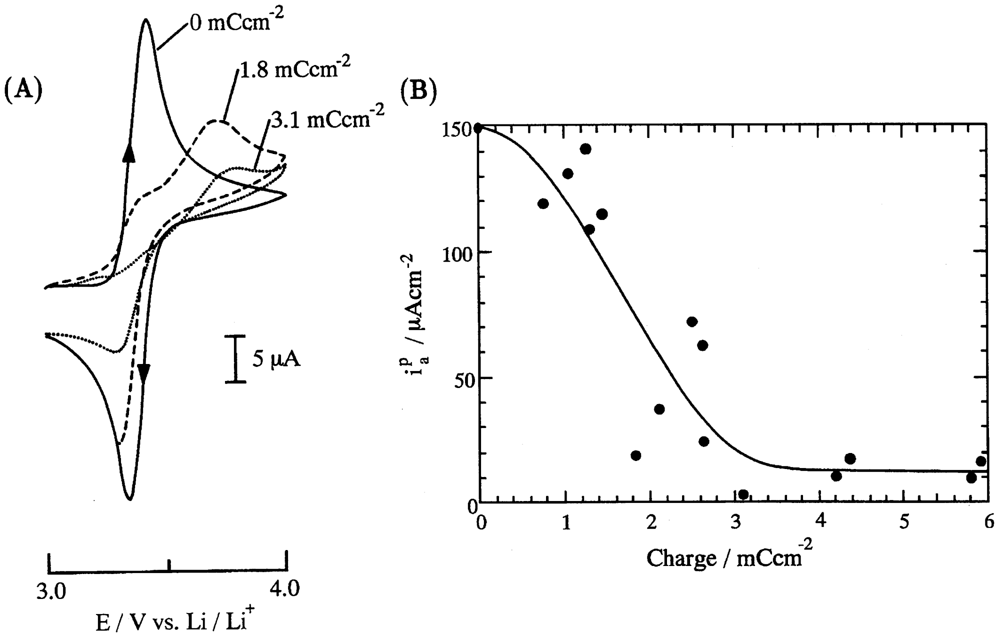

Fig. 5. (A) Cyclic voltammograms obtained in propylene carbonate containing 2 mM ferrocene and 0.5 M $LiClO_4$. The electrodes were pretreated by potentiostatic electrolysis (+0.9 V vs. Li/Li$^+$, 0, 1.8 and 3.1 mC cm^{-2}) in propylene carbonate containing 0.5 M $LiClO_4$. (B) Plot of the currents at +3.4 V during cyclic voltammetry (i_a^p) vs. the amount of cathodic charge passed during the deposition at +0.9 V.

sition at +0.9 V. The anodic current response decreased along with increasing the passed charge, and almost disappeared at ca. 3 mC cm^{-2}. Interestingly, stage 1 in Fig. 3(C) is also transferred to stage 2 at around 3 mC cm^{-2}. That is, the lithium compound, lithium carbonate most probably, is deposited during stage 1 and then the electrode surface is almost completely covered with the compound to block an electrochemical reaction to a large extent, so that a chemical reaction becomes relatively dominant in stage 2, in which the apparent molecular weight of the deposited compound(s) is thereby much larger than that in stage 1. Therefore, the chemical species deposited in stage 2 cannot be identified from the evaluated apparent molecular weight (200.2 g mol^{-1}). Identification of the chemical reaction and the species deposited in stage 2 is currently underway as a separate study. Here, we must note that a species smaller than ferrocene, such as lithium ion, may react electrochemically to some extent, even in stage 2.

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References

1) J. G. Thevenin and R. H. Muller, *J. Electrochem. Soc.*, **134**, 273 (1987).

2) a) E. Peled, *J. Electrochem. Soc.*, **126**, 2047 (1979); b) E. Peled, "Lithium Batteries," ed by J. P. Gabano, Academic Press, New York (1983).

3) Z. X. Shu, R. S. McMillan, and J. J. Murray, *J. Electrochem. Soc.*, **140**, 922 (1993).

4) a) H. Gerischer and D. Wagner, *Ber. Bunsenges. Phys. Chem.*, **92**, 1325 (1988); b) D. Wagner and H. Gerisher, *Electrochim. Acta*, **34**, 1351 (1989).

5) D. Aurbach, *J. Electrochem. Soc.*, **136**, 906 (1989).

6) J. Li, S. Pons, and J. J. Smith, *Langmuir*, **2**, 297 (1986).

7) D. Buttry and M. Ward, *Chem. Rev.*, **92**, 1355 (1992).

8) Y. Tang and T. E. Furtak, *Electrochim. Acta*, **36**, 1873 (1991).

9) M. Hepel, K. Kanige, and S. Bruckenstein, *J. Electroanal. Chem.*, **266**, 409 (1989).

10) M. R. Deakin, T. T. Li, and O. R. Melroy, *J. Electroanal. Chem.*, **243**, 343 (1988).

11) N. Yamamoto, T. Ohsaka, T. Terashima, and N. Oyama, *J. Electroanal. Chem.*, **274**, 313 (1989).

12) G. Eggert and J. Heitbaum, *Electrochim. Acta*, **31**, 1443 (1986).

13) a) D. Aurbach, M. L. Daroux, P. W. Faguy, and E. Yeager, *J. Electrochem. Soc.*, **134**, 1611 (1987); b) D. Aurbach, M. L. Daroux, P. W. Faguy, and E. Yeager, *J. Electroanal. Chem.*, **297**, 255 (1991).

14) R. Fong, U. Sacken, and J. R. Dahn, *J. Electrochem. Soc.*, **137**, 2009 (1990).

15) K. E. Heusler, A. Grzegorzewski, L. Jackel, and J. Pietrucha, *Ber. Bunsenges. Phys. Chem.*, **92**, 1218 (1988).

16) R. Beck, U. Pittermann, and K. G. Weil, *J. Electrochem. Soc.*, **139**, 453 (1992).

17) H. Muramatsu, X. Ye, and T. Ataka, *J. Electroanal. Chem.*, **347**, 247 (1993).

18) S. Bruckenstein and A. Hillman, *J. Phys. Chem.*, **95**, 10748 (1991).