Kinetic Characterization of the Electrochemical Intercalation of Lithium Ions into Graphite Electrodes

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Lithium intercalated graphites have taken the place of metallic lithium as anodes for secondary lithium batteries. Controlling the anode-electrolyte interface has been a major technical challenge in the development of lithium-ion battery technologies. The interfacial characteristics can be greatly affected by the kinetics of intercalation. However, the kinetics of the electrochemical intercalation of lithium into graphites has not been well analyzed yet. Very few kinetic and interfacial parameters have been reported. In this work, the electrochemical impedance spectroscopy, constant charge step, and galvanostatic pulse polarization techniques were applied to study the kinetics of the intercalation and deintercalation processes of graphite electrodes in a few important lithium battery electrolyte solutions. Based on the proposed equivalent circuit model, we determined the kinetic and interfacial parameters of the intercalation and deintercalation processes. The measured intercalation charge-transfer resistance, exchange current densities, and intercalation capacitance range between 11 and 28 Ω cm^2, 1.0 and 2.3 mA/cm^2, and 1.0 and 2.0 μF/cm^2, respectively, depending on the electrolyte solution compositions. The dependence of these kinetic and interfacial parameters on solvent composition, electrolyte concentration, storage time, and intercalated state is discussed. In addition, the transfer coefficients have been determined. The results suggest that the intercalation/deintercalation process is electrochemically reversible.
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Rechargeable lithium-ion batteries have been commercialized recently.[1] The typical lithium-ion battery is made up of a carbon-based negative electrode, a Li$^+$-transition metal-oxide positive electrode, and a nonaqueous electrolyte which serves as an ionic path between electrodes and separates the two materials. The electrolyte may be a single organic solvent or a mixture of organic solvents.[2] A lithium salt added to the solution provides Li$^+$ ions that diffuse back and forth between electrodes during charge and discharge. Among the many types of carbon anodes reported, graphite appears to be the most desirable candidate due to its high host capacity and low electrode potential relative to Li metal,[3,4] hence we concentrate on the study of well-ordered graphite electrodes.

The formation and characterization of the lithium-graphite intercalation compounds have been studied by Ohzuku *et al.*[5] The mechanisms of capacity fading in lithiated graphite electrodes have been intensively investigated in recent years.[1,4,6-9] Several investigations dealing with the relation between the electrochemical intercalation of lithium and the crystal structure of carbonaceous materials have been reported by Dahn *et al.*,[10] Jiang *et al.*,[3] and Marquez *et al.*[2] However, the kinetics of the electrochemical intercalation of lithium into graphites has not been well analyzed yet. Despite the importance of electrochemical kinetics in determining the power densities of lithium batteries, very few researchers addressed the reaction kinetics.[11,12] Takami *et al.*[11] reported the polarization resistance of lithium ions intercalation into various carbon fibers (heated at different temperatures) and artificial graphite (Lonza, SFG44) in 1 M LiPF$_6$-ethylene carbonate/propylene carbonate (EC/PC, 1:1) and 1 M LiPF$_6$-ethylene carbonate-diethylene carbonate(EC/DEC, 1:1) electrolyte solutions, respectively, using an ac impedance technique. A few words deserve to be mentioned. Since Takami *et al.*[11] modeled the film-covered carbon/electrolyte interface simply with one equivalent circuit containing the polarization resistance in parallel with the corresponding capacitance and derived the value of the polarization resistance from the diameter of the semicircle in the impedance spectrum, the reported polarization resistance thus consisted of the charge-transfer resistance and the film resistance. The kinetics of the intercalation of lithium into graphite anodes is affected by the passivating film, and the film may grow during the measurements. Therefore, the polarization resistance is not equal to the charge-transfer resistance, unless the film resistance is negligible. It is necessary to reduce the film effect to the lowest degree possible in order to reveal the intrinsic kinetic characteristics. In this work, we attempted such a study using nonstationary methods. The duration of each measurement is sufficiently short (a few milliseconds). Piao *et al.*[12] determined the exchange current densities of lithium ions intercalating into graphite electrodes in PC-EC mixed solutions with LiClO$_4$ as an electrolyte by ac impedance techniques. It should be noted that these researchers[11,12] did not publish kinetic and interfacial data on the deintercalation processes which are relevant to the study of irreversible capacities of graphite electrodes.

In contrast to lithium metal anode rechargeable batteries, the lithium-ion batteries are limited by anode capacity. Therefore, controlling the anode-electrolyte interface has been a major technical challenge in the development of lithium-ion battery technologies. The interfacial characteristics can be greatly affected by the kinetics of intercalation. It is now commonly understood that in lithium-ion batteries containing organic electrolytes, the stabilization of lithiated graphite electrodes is insured by the formation of stable passivating surface layers.[4,8,9] The actual morphology, as well as the composition, of the solid electrolyte interphase is very complex and changes with time and with electrolyte composition. Understanding the influence of solvents, electrolytes, and the composition of the graphite anodes on the kinetics of intercalation is essential to further characterizing the fundamental physical and chemical features that control interfacial phenomena. In the present work, the ac impedance, galvanostatic pulse polarization,[13] and constant charge step[14] methods have been used to study the kinetics of the electrochemical intercalation and deintercalation processes of lithium into well-ordered graphite electrodes in a few selected electrolyte solutions. The experimentally determined kinetics and interfacial parameters such as charge-transfer resistance, exchange current density, transfer coefficient, and intercalation capacitance are presented. The effects of the electrolyte composition, stored time, and intercalation level on these measured kinetic and interfacial parameters are also discussed.

Experimental

The electrochemical intercalation-deintercalation investigation for the synthetic graphite (Aldrich) was carried out using a specially designed three-electrode hermetically sealed glass cell. The cell consisted of a porous graphite electrode supported by a copper foil (with a geometric area of 1 cm^2 and a weight of 32 mg graphite), a lithium rod on a nickel wire reference electrode, and a lithium foil on a nickel wire counter electrode. EC, DEC, and PC were obtained

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from Riedel-deHae. These solvents were stored over 4 Å molecular sieves. $LiPF_6$, $LiClO_4$, and $LiBF_4$ were obtained from Aldrich.

Graphite electrodes were made by mixing a slurry containing 10 weight percent (wt %) polyvinylidene fluoride binder (Aldrich) and 90 wt % graphite powder in a *N*-methyl-2-pyrrolidinone solution (Aldrich). The slurry was then coated on a copper foil current collector. Finally, the porous structures obtained were dried in a vacuum oven at 120°C for 24 h. All cells were assembled in a glove box (Mbraun master 130). The moisture and oxygen levels were less than 5 and 20 ppm, respectively.

The galvanostatic pulse polarization,[13] constant charge step,[14] and ac impedance techniques were used to investigate the kinetic characteristics of lithium intercalation and deintercalation reactions. For the charge-transfer resistance measurements by means of the galvanostatic pulse polarization technique, pulses were typically of 1.0-6.0 mA/cm² amplitudes and 8 ms duration. For the capacitance measurements using the constant charge-step method, amplitudes typically were 0.10-0.25 mA/cm² and duration 10 μs. All experiments were carried out at 26 ± 1°C.

Results and Discussion

The charge-transfer resistance.—A typical complex impedance plot at a graphite electrode in its intercalated state is shown in Fig. 1a in which a depressed semicircle in the high-frequency region and a straight line with an angle close to 45° to the real axis at low frequencies dominate the plot. The depressed semicircle can be approximately characterized by two partially overlapped semicircles (Fig. 1a), indicating the existence of two time constants in the high-frequency region. The depressed semicircle can be interpreted as resulting from the charge-transfer process and the passivating film formed on the graphite.[9,11] The small semicircle is considered to be related to the formation of a passive film on the graphite surface. The large semicircle is assigned to the charge-transfer reaction of Li intercalation into graphite. The process of lithium ions in graphite is considerably slower than in an electrolyte solution.[11] Thus the 45° slope linear portion at low frequencies is attributed to semi-infinite diffusion conditions for the diffusion of lithium ions in graphite. The semicircles in the impedance spectrum were not clearly separated; therefore, the elementary processes could not be properly analyzed individually. As a first-order approximation of the real situation, we modeled the film-covered graphite/electrolyte interface as a simple equivalent circuit consisting of two parallel circuits in series
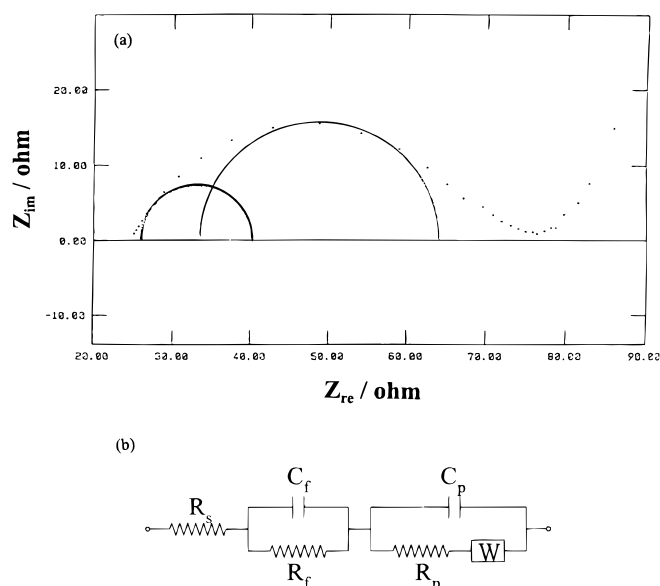
(Fig. 1b). Therein, R_p represents the charge-transfer resistance. The parameters C_p is the capacitance corresponding to R_p. R_p is in series with the Warburg impedance W. R_f and C_f are the film resistance and film capacitance, respectively. The overall interfacial resistance R_t can be estimated by means of the galvanostatic pulse polarization technique based on the relationship $R_t = (\partial\eta/\partial i)_{\eta=0}$.[13] The overall interfacial resistance (R_t) consists of the charge-transfer resistance (R_p) and the resistance associated with the film (R_f). It is essentially equal to R_p because R_f is proportional to the thickness of film that is extremely thin for each experimental run (time duration a few milliseconds only).

Figures 2 and 3 show the variation of R_p with concentration of various electrolytes in EC/DEC (1:1) and PC, respectively, during the charge of graphite anodes at 26°C. The EC/DEC ratios appearing in this paper are all volume ratios. The measured values of the charge-transfer resistance in various solutions are as follows: 13.0 Ω cm² (1 M $LiPF_6$), 14.5 Ω cm² (1 M $LiClO_4$), and 18.0 Ω cm² (1 M $LiBF_4$), all in the EC/DEC (1:1) mixed solvents; 17.0 Ω cm² (1 M $LiPF_6$), 20.0 Ω cm² (1 M $LiClO_4$), and 23.0 Ω cm² (1 M $LiBF_4$), all in the PC solvent. The reported values are as follows: 8 Ω cm² for the graphitized carbon fiber electrodes (heated at 3000°C) in 1 M $LiPF_6$-EC/PC (1:1) solutions,[11] 6 Ω cm² (independent of cycle number) for the graphitized carbon fiber anodes (heated at 3000°C) in 1 M $LiPF_6$-EC/DEC (1:1) solutions,[15] 6-13 Ω cm² (depending on the lithium content of the graphite electrode) for the artificial graphite (Lonza, SFG44) in 1 M $LiPF_6$-EC/DEC (1:1) solutions,[11] 6-80 Ω cm² (depending on cycle number) for the graphite electrode (Lonza, SFG15) in 1 M $LiPF_6$-EC/DEC (1:1) solutions,[15] and 11-19 Ω cm² (depending on the level of preintercalation) for the graphite electrode in 1 M $LiClO_4$-PC/EC (1:1) solutions.[12] Our results are comparable with those of the reported data which were determined using ac impedance measurements. As can be seen from Fig. 2 and 3 the charge-transfer resistance decreases monotonical with electrolyte concentration. Furthermore, the decrease slows down beyond about 1.0 M concentration. We also see that the solutions with a $LiPF_6$ electrolyte always have the lowest charge-transfer resistance at each of the concentrations studied compared to $LiClO_4$- and $LiBF_4$-based solutions, with the $LiBF_4$-containing solutions having the highest charge-transfer resistance. The results that the charge-transfer resistance of graphite electrodes in the
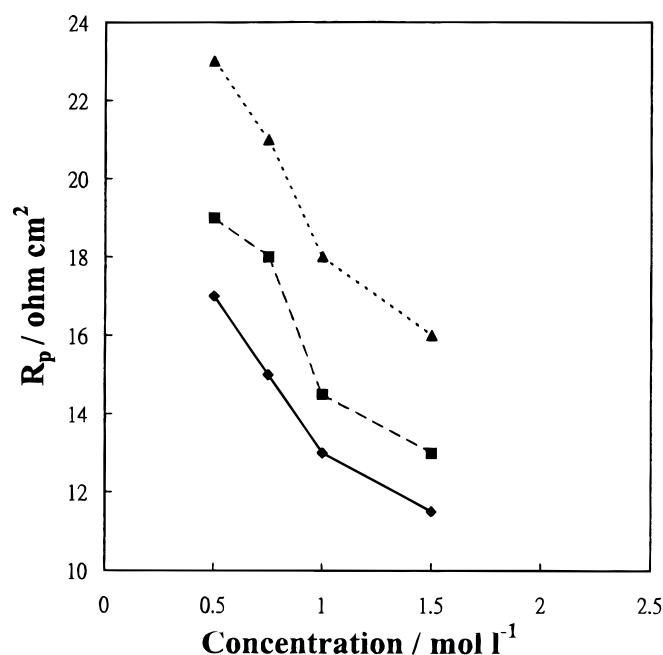

Figure 1. (a) Impedance diagram of the graphite electrode in a 1 M $LiPF_6$-EC/DEC (1:1) system at an *X* value of 0.1 in Li_xC_6 at an open-circuit potential of 0.2 V at 26°C; (b) an equivalent circuit for our graphite electrodes.

Figure 2. Variation of R_p with the concentration of various electrolytes for the graphite electrode in EC/DEC (1:1) solutions: (◆) $LiPF_6$, (■) $LiClO_4$, (▲) $LiBF_4$.
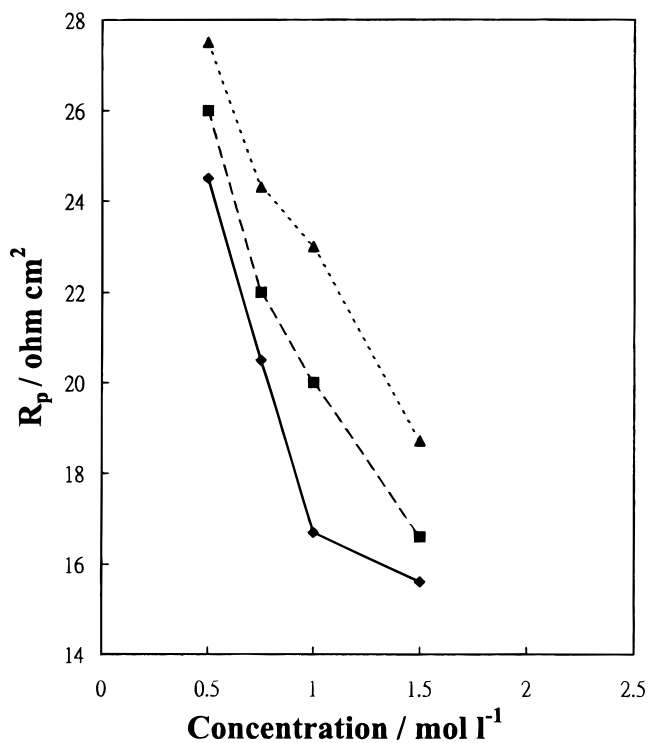
Figure 3. Variation of R_p with the concentration of various electrolytes for the graphite electrode in PC: (◆) $LiPF_6$, (■) $LiClO_4$, (▲) $LiBF_4$.

LiPF$_6$ solutions is lower than that in the LiClO$_4$ solutions are consistent with the available data for relevant systems reported in the literature.[11,12,15] The present results clearly show that the charge-transfer resistance is dependent on the Li salt used.

The performance of the Li_xC_6 anodes in organic liquid electrolyte systems depends strongly on the surface chemistry developed on the carbon.[16] It is interesting to investigate to what extent the solvent systems affect the kinetics, which is closely related to the surface chemistry developed on the carbon during lithium intercalation processes. Figure 4 presents the charge-transfer resistance of lithium intercalation into graphite electrodes in LiPF$_6$-containing solutions with different solvents. A consistent, monotonic impact of the solvent on the charge-transfer resistance was observed. Solutions with a PC solvent have the highest polarization resistance. In all EC/DEC mixture solutions, at a high EC content, the charge-transfer resistance is the lowest and at a lower EC content, the charge-transfer resistance has higher values. The difference in the behavior of graphite electrodes in the three salt solutions reflects the effect of solvents on the surface films of the electrodes.

Exploring the interfacial resistance of graphite electrodes during prolonged storage in nonaqueous electrolyte solutions may help to provide guidelines for commercialization of lithium-ion batteries with graphite anodes. Figure 5 compares the charge-transfer resistance of graphite electrodes prepared and stored in LiPF$_6$ 1 M solutions of different solvent compositions. The charge-transfer resistance is highly dependent on the solvent used. The charge-transfer resistance of graphite in PC solutions is much higher than that measured in EC-DEC solutions and increases severely after storage. In contrast, the charge-transfer resistance shows no pronounced change for graphite electrodes in different EC-DEC mixture solvents during prolonged experiments, but in the EC-DEC mixtures, as the EC content was higher, the charge-transfer resistance was slightly lower. The behavior observed in PC solutions is in agreement with those reported in the literature: PC reacts with graphite causing structural degradation. The results of these experiments (Fig. 4 and 5) indicate that mixtures of ethylene and diethyl carbonates are suitable solvent systems for lithium-ion batteries in which the anode is a graphite-lithium intercalation compound.
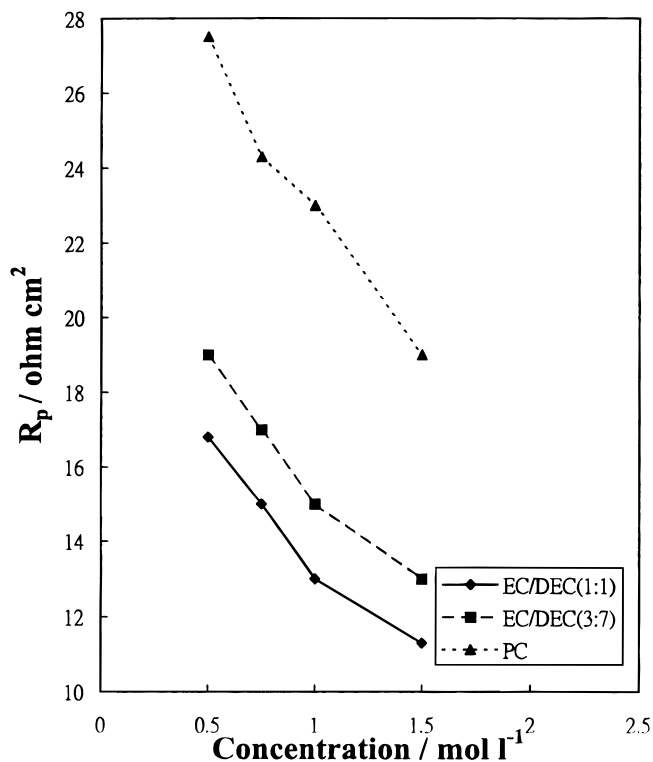

Figure 4. The polarization resistance of lithium intercalation into the graphite electrode in LiPF$_6$-containing solutions of various solvents as indicated.

Figure 6 compares the charge-transfer resistance of graphite electrodes which were intercalated or deintercalated galvanostatically during experiments. It is clear that the charge-transfer resistance of graphite electrodes during intercalation is higher than that of the same electrodes during deintercalation. Experimentally, the interlay-
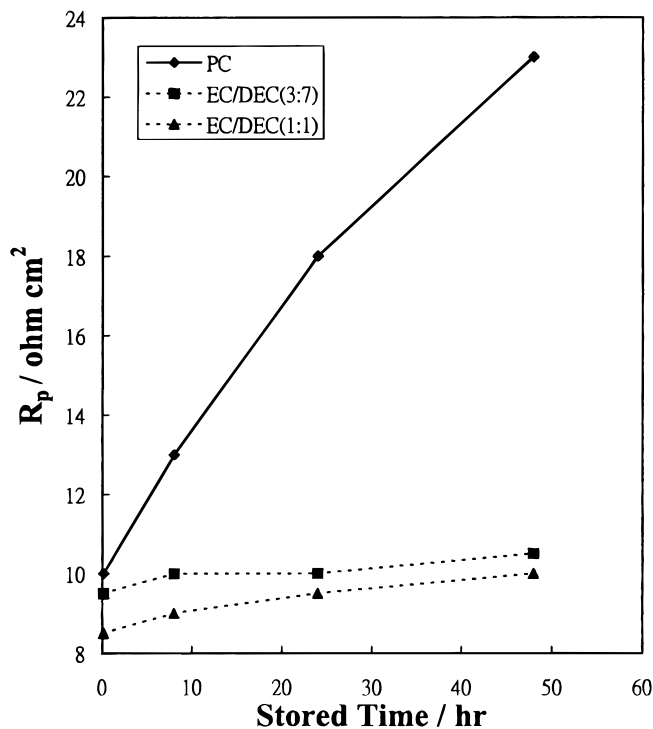

Figure 5. The polarization resistance for the graphite electrode prepared and stored in LiPF$_6$ 1 M solutions in single PC and EC-DEC mixtures.
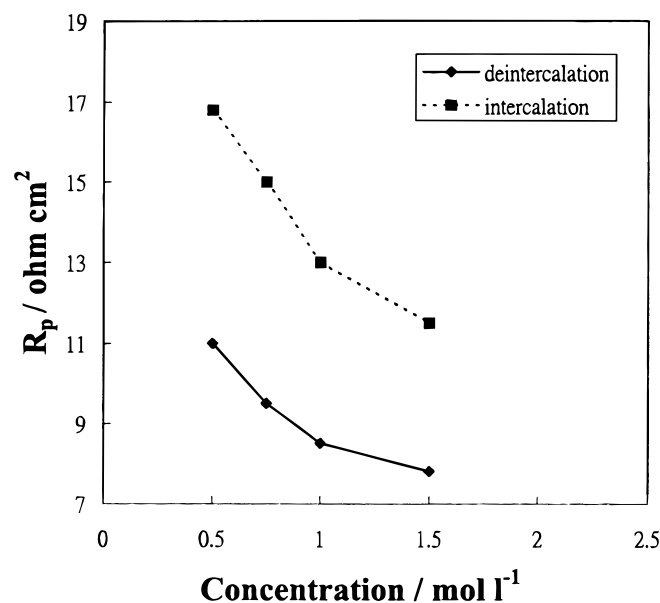
Figure 6. Polarization resistance *vs*. LiPF$_6$ electrolyte concentration for the graphite electrode intercalated/deintercalated with Li in EC/DEC (1:1) solutions.

er spacing of graphite is found to increase about 10% due to the electrochemical intercalation of lithium into graphite.[3] The expanded structure thus facilitates the deintercalation of lithium out of graphite electrodes. The behavior of graphite electrodes in LiClO$_4$ solutions is similar to that found in LiPF$_6$ solutions.

Judging from the experimental results reported by Jiang *et al*.[3] bare lithium ions appear to be the only species involved in the intercalation and deintercalation processes, as shown in Eq. 1

$$C_6 + x\text{Li}^+ + x\text{e} \rightarrow \text{Li}_x\text{C}_6 \qquad [1]$$

Figure 7 shows the charge-transfer resistance of graphite electrodes in the 1 M LiPF$_6$-EC/DEC (1:1) electrolyte during intercalation/ deintercalation as a function of *x* in Li$_x$C$_6$. The charge-transfer resistance, as shown in Fig. 7, shows a relatively small variation with *x*. The common trend is that the charge-transfer resistance (R_p) decreased slightly with increasing lithium content of the graphite electrode. The features and values shown in Fig. 7 are in agreement with those reported for the intercalation of lithium ions into the artificial graphite electrode in 1 M LiPF$_6$-EC/DEC (1:1) solutions.[11] It should be noted that different features have been reported in the literature.[11,12] The graphitized carbon fibers heated at 2300 and 3000°C showed a relatively small decrease with *x* in 1 M LiPF$_6$-EC/PC (1:1) solutions.[11] The values of R_p were reported to increase with an increase in the *x* value with some scattered points for the graphite sheet in a 1 M LiClO$_4$-PC/EC (1:1) electrolyte.[12] The present results and those reported in the literature suggest that the relation between R_p and *x* depends on the graphite types and the electrolyte composition. This deserves further study in order to identify the exact mechanism.

The exchange current density.—The most significant feature of graphite as a host is its amphoteric character: either electron donors or acceptors can be accommodated within the carbon layers, the charge balance being realized through the formation of macroanions C$_n^-$ or macrocations C$_n^+$.[17] An electrochemical approach to the charge-transfer phenomenon which describes the formation of C$_6^-$ considers C$_6^-$ as a result of the carbon reduction from the intercalation of a lithium cation as represented by

$$6C + \text{Li}^+ + \text{e} \rightarrow \text{C}_6^-\text{Li}^+ \qquad [2]$$

This indicates that after insertion, the lithium still retains a significant positive charge as evidenced by X-ray photoelectron spectro-
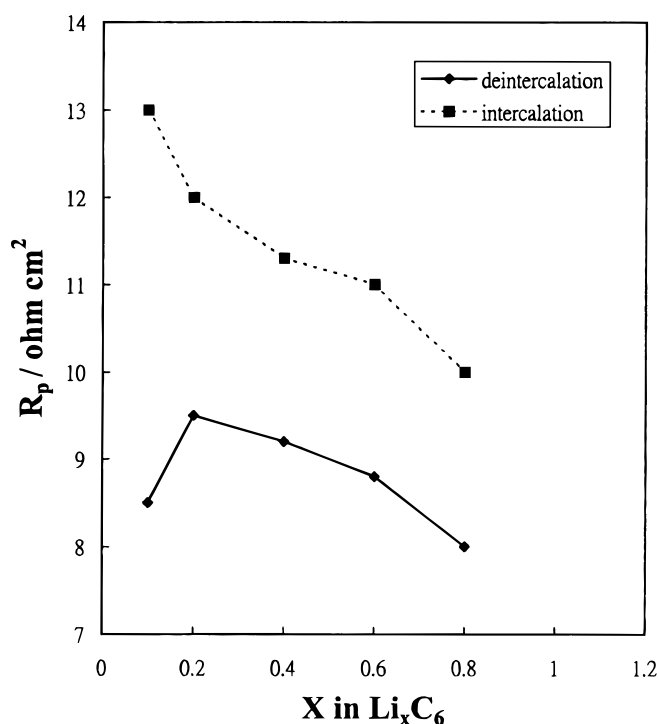

Figure 7. Variation of the polarization resistance with *X* in Li$_x$C$_6$ for the graphite electrode in 1 M LiPF$_6$-EC/DEC (1:1) solutions.

scopy analysis,[18] and the carbons originally constituting the host site take on a negative charge.

Experimentally, the exchange current density i_0 for Reaction 2 is given by the relationship $i_0 = RT/nFR_p$. The determined exchange current densities range between 1.1 and 2.1 mA/cm^2 depending on the electrolyte types and concentrations. The exchange current density data for lithium ions intercalation into the graphite electrode in 1 M LiClO$_4$-EC/DEC (1:1) solutions are close to those reported in the literature (1 M LiClO$_4$-PC/EC (1:1) solutions).[12] The measured i_0 values of the present work are based on the apparent geometrical area. Therefore, our exchange current densities are higher than those reported by Verbrugge and Koch[19] who take into account the specific surface and electrode thickness. The transfer coefficient β (= 1 − α) with respect to Li$^+$ can be determined from the dependence of i_0 on C$_{\text{Li}^+}$. Figure 8 shows the typical results in EC/DEC (3:7) mixture systems. The straight lines represent the data according to least squares analysis. For the majority of cases, an average value for the charge-transfer coefficient of 0.35 is obtained for the intercalation and deintercalation processes. The present results suggest that the electron transfer is reasonably reversibly in the electrolyte systems studied. Similar results have been obtained for electrolyte systems with different EC/DEC ratios. One thing merits mention. Similar conclusion that the intercalation/deintercalation process is electrochemically reversible has been reported by Fong *et al*.[6] They studied the electrochemical behavior of Li/graphite cells with 1 M LiAsF$_6$-PC/EC and 1 M LiAsF$_6$-PC systems at 21°C and reported that though the PC decomposition reaction results in the formation of passive films on the graphite electrode surface, reversible Li intercalation still takes place on the film-covered graphite surface even after the surface is passivated.

The values of the exchange current densities determined at various states of charging are presented in Fig. 9. It can be seen that increasing the intercalation level caused the exchange current density to increase slightly because it is weakly dependent on lithium content during charge and discharge of the graphite electrode. A similar trend was reported for the case of PAN-based carbon in 0.5 M LiPF$_6$-PC solutions.[19]

The capacitance.—In the constant charge-step measurement the injected charge causes the potential of the electrode to deviate from

its original value E_i to a value E_f. The response $\Delta E(t)$ of the circuit of Fig. 1b is given by

$$\Delta E(t) = \frac{\Delta q}{C_p} \exp\left(-\frac{t}{R_p C_p}\right) + \frac{\Delta q}{C_f} \exp\left(-\frac{t}{R_f C_f}\right) \qquad [3]$$

Since the time duration is very short (a few microseconds) and R_f is also very small (much smaller than R_p), the capacitance C_p can be determined experimentally via the relationship $C_p = \Delta q/\Delta E$, where $\Delta q = I\Delta t$, $\Delta E = E_f$-E_i, and I is the applied current during a sufficient short-duration Δt. Figure 10 shows the measured C_p as a function of electrolyte concentration. While we found no reported capacitance data for lithium ions intercalation into the graphite electrode in the literature, there are reports about the ac impedance diagrams of the artificial graphite electrodes in 1 M LiPF$_6$-EC/DEC (1:1) solutions at various intercalation levels determined by ac impedance methods.[11] Our

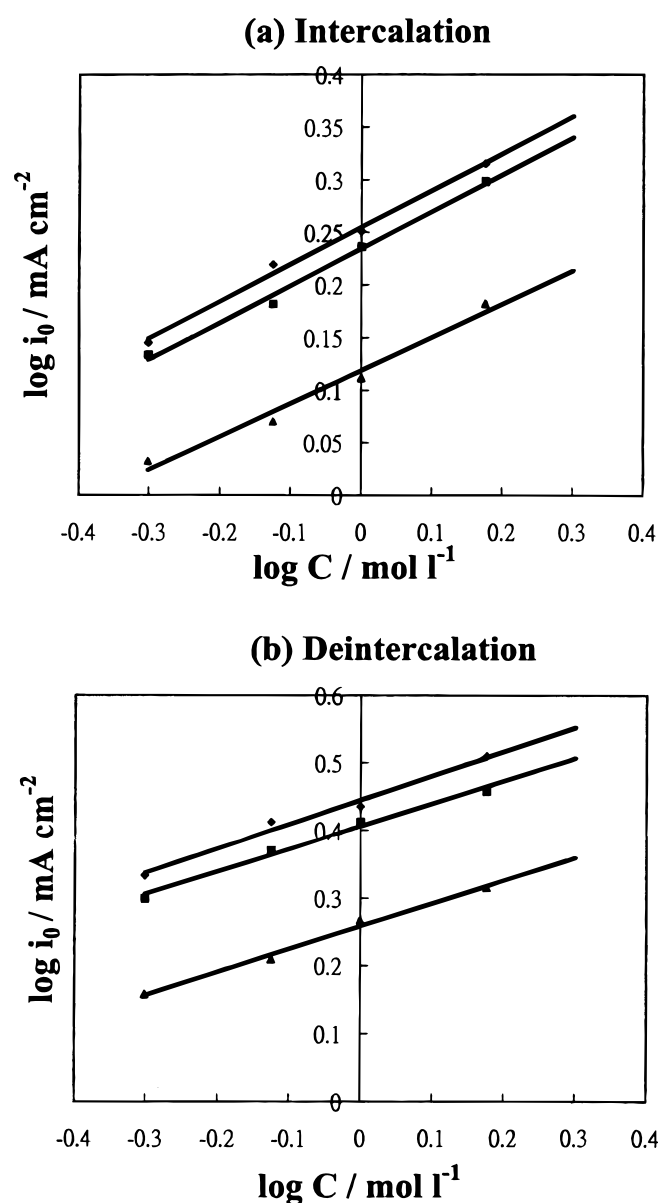## (a) Intercalation

(b) Deintercalation

Figure 8. Exchange current density-electrolyte concentration plot for the graphite electrode in EC/DEC (3:7) mixture with different electrolytes. (a) Intercalation: LiPF$_6$ (◆), $y = 0.3503x + 0.2546$; LiClO$_4$ (■), $y = 0.3512x + 0.2345$; LiBF$_4$ (▲), $y = 0.315x + 0.1186$. (b) Deintercalation: LiPF$_6$ (◆), $y = 3568x + 0.4447$; LiClO$_4$ (■), $y = 0.3345x + 0.4059$; LiBF$_4$ (▲), $y = 0.3404x + 0.2581$. $y = \log i_0$, $x = \log C$.
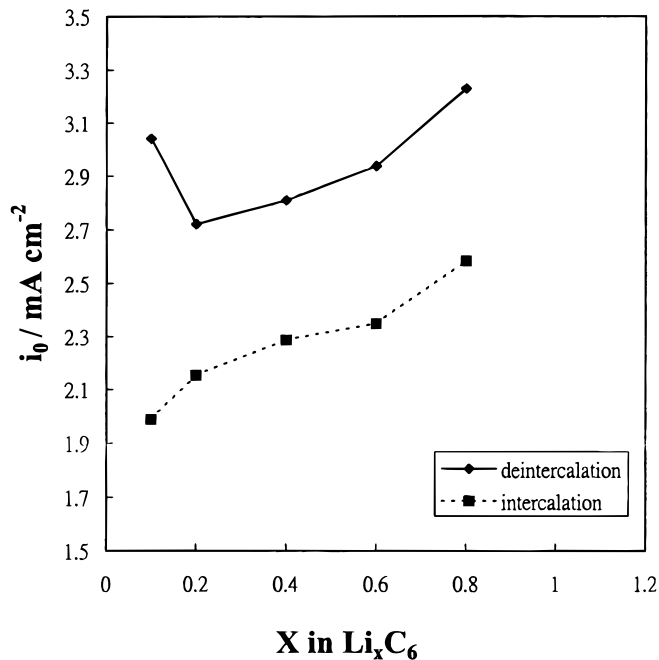

Figure 9. Exchange current density for the graphite electrode as a function of X in 1 M LiPF$_6$-EC/DEC (1:1) solutions.

measured capacitance values in 1 M LiPF$_6$-EC/DEC (1:1) solutions are comparable with the data estimated from the ac impedance diagrams of Takami and co-workers.[11] Figure 10 also shows that the capacitance increased very slightly with increases in electrolyte concentration. Figure 11 represents the capacitance of graphite electrodes in LiPF$_6$-containing solutions of different solvent compositions. The data indicate clearly the dependence of the capacitance on the solvent
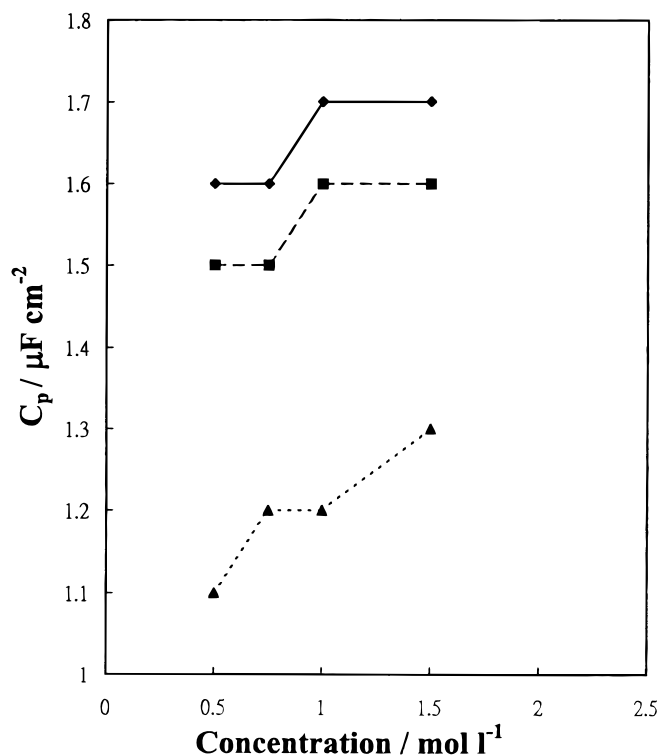

Figure 10. Variation of C_p with electrolyte concentration for the graphite electrode in EC/DEC (3:7) solutions: (◆) LiPF$_6$, (■) LiClO$_4$, (▲) LiBF$_4$.
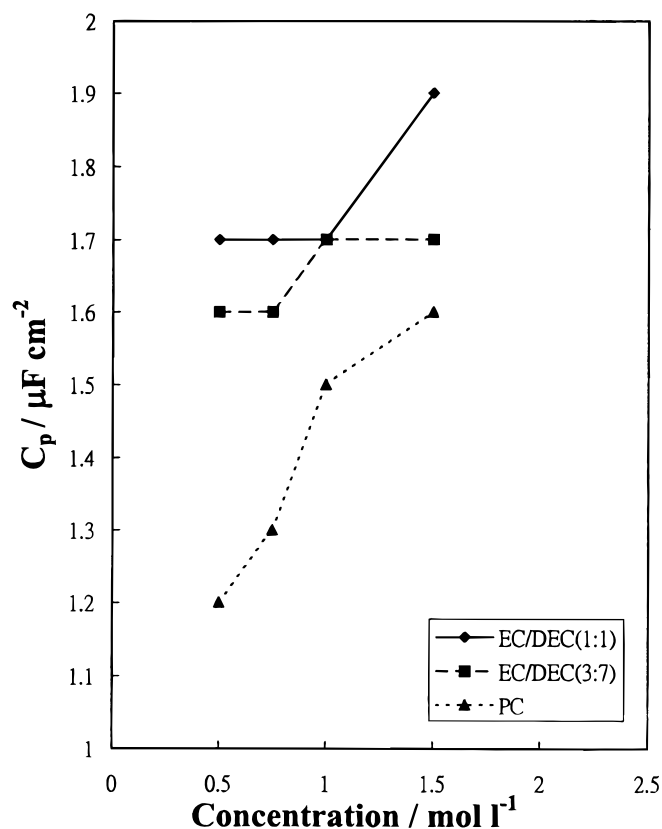
Figure 11. The capacitance of the graphite electrode in $LiPF_6$-containing solutions of various solvent mixtures.

Figure 12. Capacitance dependence on Li intercalation level in the graphite electrode in 1 M $LiPF_6$-EC/DEC (1:1) solutions at room temperature.

composition. These results imply that the electrolyte, as well as the solvent, does influence the interfacial structure of the systems.

In order to gain insight into changes at the surfaces of graphite electrodes during the intercalation and deintercalation processes, a series of measurements were performed to determine the dependence of the capacitance on the intercalation level in graphite electrode. The typical corresponding C_p/x dependence is shown in Fig. 12. The capacitance increased slightly with increasing intercalation level during charge and discharge and, at any intercalated state, the capacitance was larger during deintercalation processes.

Conclusions

The kinetic characteristics of graphite electrodes in $LiPF_6$-, $LiBF_4$-, and $LiClO_4$-containing solutions have been studied using electrochemical impedance spectroscopy in conjunction with the constant charge-step and galvanostatic pulse polarization techniques. The solvents used were single PC and EC-DEC mixtures. The Cole-Cole plot shows that two partially overlapped semicircles in the high-frequency region and a straight line in the low-frequency region dominate the plot. The charge-transfer resistance, exchange current density, transfer coefficient, and intercalation capacitance have been determined experimentally from the galvanostatic pulse polarization and constant charge-step measurements. The charge-transfer resistance and capacitance depend on the types of salt, as well as solvent, used. The intercalation level and the solution composition also affect the kinetic and interfacial parameters. The charge-transfer resistance of graphite in $LiBF_4$ is much higher than that measured in $LiPF_6$ or $LiClO_4$ solutions in the same solvent system. The charge-transfer resistance of graphite in PC solvent increases remarkably after storage. The charge-transfer resistance decreases slightly with intercalation level as opposed to the capacitance case. The transfer coefficient for the intercalation and deinter-
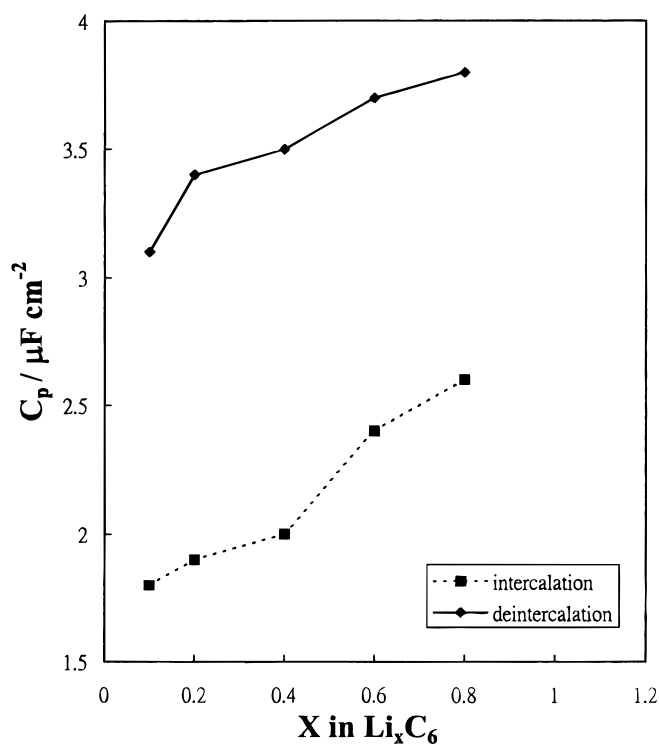
calation processes was about 0.35, indicating that the electron transfer process is electrochemically reversible. The experimental results also indicate that ethylene and diethyl carbonates mixtures are suitable solvent systems for Li-ion batteries with graphite electrodes.

References

1. P. Arora, R. E. White, and M. Doyle, *J. Electrochem. Soc.*, **145**, 3647 (1998).
2. A. Marquez, A. Vargas, and P. B. Balbuena, *J. Electrochem. Soc.*, **145**, 3328 (1998).
3. Z. Jiang, M. Alamgir, and K. M. Abraham, *J. Electrochem. Soc.*, **142**, 333 (1995).
4. D. Aurbach, M. D. Levi, E. Levi, H. Teller, B. Markovsky, G. Salitra, U. Heider, and L. Heider, *J. Electrochem. Soc.*, **145**, 3024 (1998).
5. T. Ohzuku, Y. Iwakoshi, and K. Sawai, *J. Electrochem. Soc.*, **140**, 2940 (1993).
6. R. Fong, U. von Sacken, and J. R. Dahn, *J. Electrochem. Soc.*, **137**, 2009 (1990).
7. Z. X. Shu, R. S. McMillan, and J. J. Murray, *J. Electrochem. Soc.*, **140**, 922 (1993).
8. E. Peled, D. Golodnitsky, C. Menachem, and D. Bar-Tow, *J. Electrochem. Soc.*, **145**, 3482 (1998).
9. E. Barsoukov, J. H. Kim, C. O. Yoon, and H. Lee, *J. Electrochem. Soc.*, **145**, 2711 (1998).
10. J. R. Dahn, K. Sleigh, H. Shi, J. N. Reimers, Q. Zhong, and B. M. Way, *Electrochim. Acta*, **38**, 1179 (1993).
11. N. Takami, A. Satoh, M. Hara, and T. Ohsaki, *J. Electrochem. Soc.*, **142**, 371 (1995).
12. T. Piao, S-M. Park, C-H. Doh, and S-I. Moon, *J. Electrochem. Soc.*, **146**, 2794 (1999).
13. Y. Geronov, F. Schwager, and R. H. Muller, *J. Electrochem. Soc.*, **129**, 1422 (1982).
14. A. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 270, John Wiley & Sons, New York (1980).
15. N. Takami, A. Satoh, M. Hara, and T. Ohsaki, *J. Electrochem. Soc.*, **142**, 2565 (1995).
16. D. Aurbach, A. Zaban, A. Schechter, Y. Ein-Eli, E. Zinigrad, and B. Markovsky, *J. Electrochem. Soc.*, **142**, 2873 (1995).
17. R. Yazami, in *Lithium Batteries: New Materials, Developments and Perspectives*, G. Pistoia, Editor, Chap. 2, Elsevier Science B.V., Amsterdam (1994).
18. M. W. Verbrugge and B. J. Koch, *J. Electrochem. Soc.*, **143**, 600 (1996).
19. M. W. Verbrugge and B. J. Koch, *J. Electrochem. Soc.*, **146**, 833 (1999).