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A Study of Electrochemical Kinetics of Lithium Ion in Organic Electrolytes

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Abstract–Limiting current densities equivalent to the transport-controlling step of lithium ions in organic electrolytes were measured by using a rotating disk electrode (RDE). The diffusion coefficients of lithium ion in the electrolyte of PC/LiClO$_4$, EC : DEC/LiPF$_6$ and EC : DMC/LiPF$_6$ were determined by the limiting current density data according to the Levich equation. The diffusion coefficients increased in the order of PC/LiClO$_4$<EC : DEC/LiPF$_6$<EC : DMC/LiPF$_6$ with respect to molar concentration of lithium salt. The maximum value of diffusivity was 1.39×10^{-5}cm^2/s for 1 M LiPF$_6$ in EC : DMC=1 : 1. Exchange current densities and transfer coefficients of each electrolyte were determined according to the Butler-Volmer equation.

Key words: Lithium Ion Batteries, RDE, Electrolyte, Limiting Current Density, Diffusion Coefficient

INTRODUCTION

In the last decade many studies have been performed to develop secondary lithium batteries [Blomgren, 1993; Dominey, 1994; Nam et al., 2001]. Recent development and applications of lithium ion batteries (LIB), of which the anode is a carbon-lithium intercalation compound and the cathode is lithiated metal oxide, are being commercialized rapidly. Despite significant achievements in LIB, mass transport data of lithium ion in bulk phase of the organic electrolytes are limited as compared with the practical aspects of researches such as development of the electrode materials, enhancement of the cycle efficiency [Langenhuizen, 1998]. In particular, basic data for ethylene carbonate (EC)-based mixed electrolytes are insufficient, in spite of the fact that EC-electrolyte systems are applied to commercial lithium ion batteries. The mass transport of lithium ion in the electrolytes gives an effect on the performance of batteries, because lithium ion batteries have porous electrodes and a separator to be immersed in the electrolyte. Therefore, it is necessary to obtain data of the transferent properties (viscosity and mass diffusivity) of lithium ions in organic electrolytes and the kinetic parameters for the optimal design of lithium batteries.

Propylene carbonate (PC), which forms a stable protective insulating layer-solid electrolyte interphase (SEI) on lithium electrode, has been applied to lithium primary batteries [Blomgren, 1993]. Therefore, the basic data of PC-based electrolytes have been well established. But lithium secondary batteries demand more complex functions of SEI with carbon electrode. Recent results show that EC-based electrolyte systems are suitable to LIB because these are more highly conductive and slightly lower viscous than PC-systems and exhibit good SEI characteristics with carbon anode. Many studies are reported focusing on the high ionic conductivity or interface analysis for various EC-based mixed solvent electrolyte systems with various compositions [Ishikawa et al., 1994; Naoi et al., 1996; Zhang et al., 1996; Kanamura et al., 1997]. Specially, Ein-Eli et al. [1996, 1997] and Aurbach et al. [1995, 1996] have published a series of considerable researches about the passive film of lithium batteries in different organic electrolytes.

Since high permittivity solvents (HPS) such as PC and EC have a high viscosity that hinders the mass transport of solutes, these solvents are mixed with low viscosity solvents (LVS) such as dimethoxy ethane (DME), dimethyl carbonate (DMC), diethyl carbonate (DEC) [Matsuda et al., 1986]. This is because the solid phase of EC at room temperature EC is usually blended with these solvents. As the solute providing lithium ion, inorganic salts such as LiPF$_6$, LiAsF$_6$, etc. are mainly used, lithium perchlorate tends not to be used for commercial batteries but in the laboratory.

The aim of this experiment was to investigate the mass transferent properties of lithium ion in organic electrolyte for secondary lithium batteries by finding limiting current densities of electrodeposition of lithium ($Li^+ + e^- \Rightarrow Li$) on the rotating disk electrode (RDE), which is suitable for studying the mass transport of a salt in electrolytes [Quickenden and Jiang, 1984; Uceda et al., 1990; Lee et al., 2000]. In addition, electrochemical parameters such as exchange current density and electrochemical transfer coefficient of each electrolyte were determined according to the Butler-Volmer equation.

EXPERIMENTAL

Propylene carbonate (PC, Aldrich, 99%), ethylene carbonate (EC, Aldrich, 99%), diethyl carbonate (DEC, Aldrich, 99%), and dimethyl carbonate (DMC, Aldrich, 99%) were used for solvent of electrolytes. These organic solvents were distilled under reduced pressure prior to use. LiClO$_4$ (Aldrich, 99.99%) was dried at 120 °C for 24 h under vacuum and LiPF$_6$ (Aldrich, 99.99%) was used as received. The following electrolytes for electrochemical tests were prepared:

0.1, 0.5, 0.75, 1.0 M LiClO$_4$ in PC (PC/*x*M LiClO$_4$)
0.1, 0.5, 0.75, 1.0 M LiPF$_6$ in 1 : 1 mixture (wt%) of EC and DEC (EC : DEC=1 : 1/*x*M LiPF$_6$)
0.1, 0.5, 0.75, 1.0 M LiPF$_6$ in 1 : 1 mixture (wt%) of EC and DMC (EC : DMC=1 : 1/*x*M LiPF$_6$)

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$LiClO_4$ in PC is the most popular salt for laboratory tests, and the latter two electrolytes are used for commercial lithium ion batteries. The system of PC/$LiClO_4$ was tested for comparison with other data [Verbrugge and Koch, 1994] and EC-based electrolytes. Electrochemical experiments were performed by using three-electrode half cell (Teflon body) with a luggin capillary for reference electrode of lithium metal [Jung et al., 1998]. This capillary was directed to the underside of the disk and separated from it by a distance of 3 mm without hindering convection of electrolyte. It was known that even in the most dilute solution used, this distance could be varied from 1 to 10 mm without detectable effect on Levich plots [Quickenden and Jiang, 1984]. Lithium foil was used as the counter electrode. RDE (dia.=0.3 cm) was changeable SUS (304) substrate in Teflon holder. Before each electrochemical experiment the RDE surface was polished with fine alumina powders (0.3 μm) to obtain a mirror surface and rinsed with DEC or DMC. The RDE was placed axially in the middle of the cell unit. The shaft of the RDE was connected to the BAS (RDE-1, BAS Co.) rotator system. The preparation of electrolytes, cell assembly and electrochemical tests were carried out under high purity argon atmosphere in a glove box (J-924A, JISCO). Argon gas was dried twice by anhydrous $CaSO_4$ on inlet line and forced convection through molecular sieve-packed column in the glove box. The RDE system was connected to the potentiostat (Zahner, IM6 Model) with electrical shield lines sealed through the wall of the glove box.

Low rotation speed of RDE was selected to preserve laminar flow condition of the electrolyte in the cell with small diameter (2 cm). The RPM of the RDE was maintained at 30, 60, 90, 120, 150, and 180. Linear voltage sweep experiments were performed to obtain the steady state current responses and then constant limiting current plateau by controlling voltage sweep rate. All experiments were performed at 25 °C. At that temperature kinematic viscosities of each electrolyte, which are included in the Levich equation, were determined by using a pycnometer and Ostwald viscometer.

RESULTS AND DISSCUSSION

Fig. 1 shows densities and kinematic viscosities of the electrolytes depending on lithium salt concentration at 25 °C. For both PC- and EC-based systems, the density increased linearly as the solute (lithium salt) increased. It is shown that both EC-based electrolytes have almost the same gradient because the solute in those solvents (EC : DEC=1 : 1, EC : DMC=1 : 1) is the same ($LiPF_6$). Upon an equal salt concentration, the densities increased in the order of EC : DEC=1 : 1/$LiPF_6$<PC/$LiClO_4$<EC : DMC=1 : 1/$LiPF_6$. The density and viscosity of pure DEC and pure DMC are 0.98 g/cm^3 and 0.75 cP for DEC and 1.071 g/cm^3 and 0.59 cP for DMC at 25 °C, respectively [Dominey, 1994]. From these values, it can be expected that the EC : DEC system has a low density and EC : DMC system has a low viscosity. Fig. 1 (b) shows the viscosities increased in the order of EC : DMC=1 : 1/$LiPF_6$<EC : DEC=1 : 1/$LiPF_6$<PC/$LiClO_4$, which is correlated with an increase in the viscosity of LVS. The viscosity of each electrolyte increased with the salt concentration due to increasing of ion association. Electrolytes of low density can reduce the weight of batteries and a low viscosity one provides a high ionic conductivity. In addition, EC has relatively higher permittivity (ε=89.6) than PC (ε=64.4) [1,5], so that EC-based electrolyte systems in the presence of LVS have the higher ionic conductivity than PC-based ones [Aurbach et al., 1995, 1996].

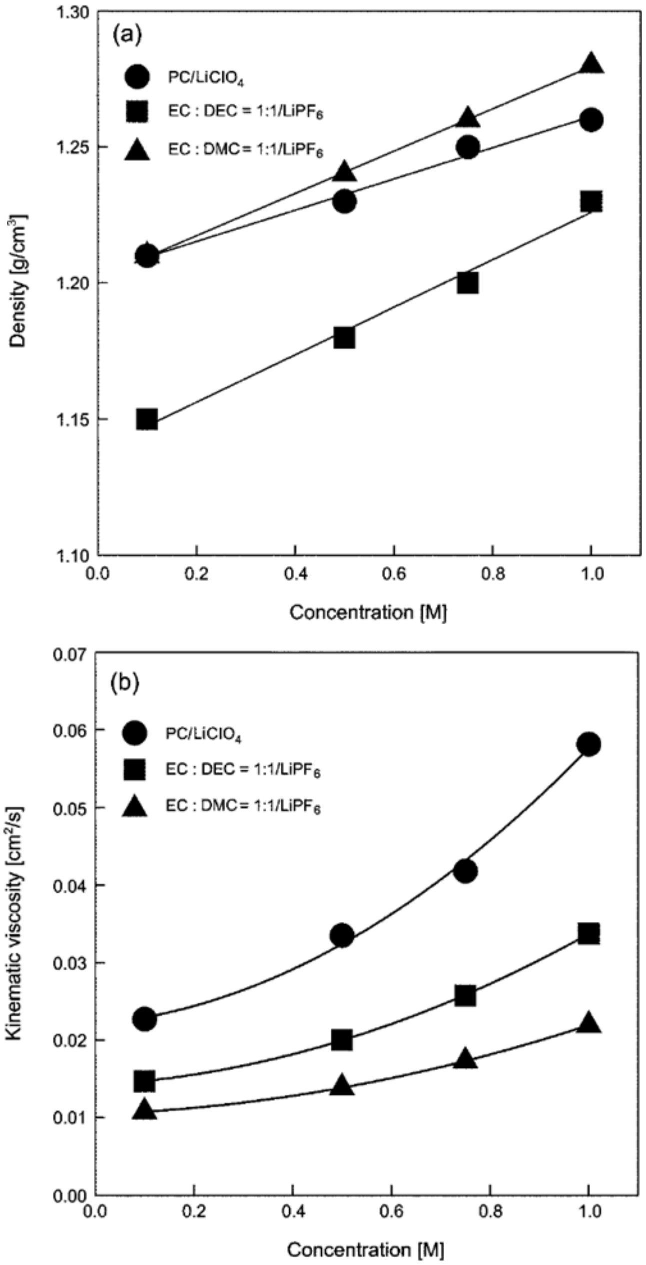

Fig. 1. Variation of the density and kinematic viscosity of electrolytes with the lithium salt concentration at 298 K: (a) density and (b) kinematic viscosity.

Fig. 2 shows *i-E* curves of (a) 1 M $LiClO_4$ in PC, (b) 0.5, 1 M $LiPF_6$ in EC : DEC=1 : 1, and (c) 1 M $LiPF_6$ in EC : DMC=1 : 1 at different rotation speeds of the working electrode. Lithium deposition in PC/$LiClO_4$ began at a high negative overpotential (−150 mV vs. Li/Li$^+$) with an abruptly rising current, and low current was observed on the overpotential range prior to the increase as shown in Fig. 2(a). Such a high overpotential was probably required due to the resistive passivation film that was formed on the surface of working electrode as the scan started. It is estimated that the passivation film suppressed current after the scan started and reduction of electrolyte caused small cathodic current near zero overpoten-

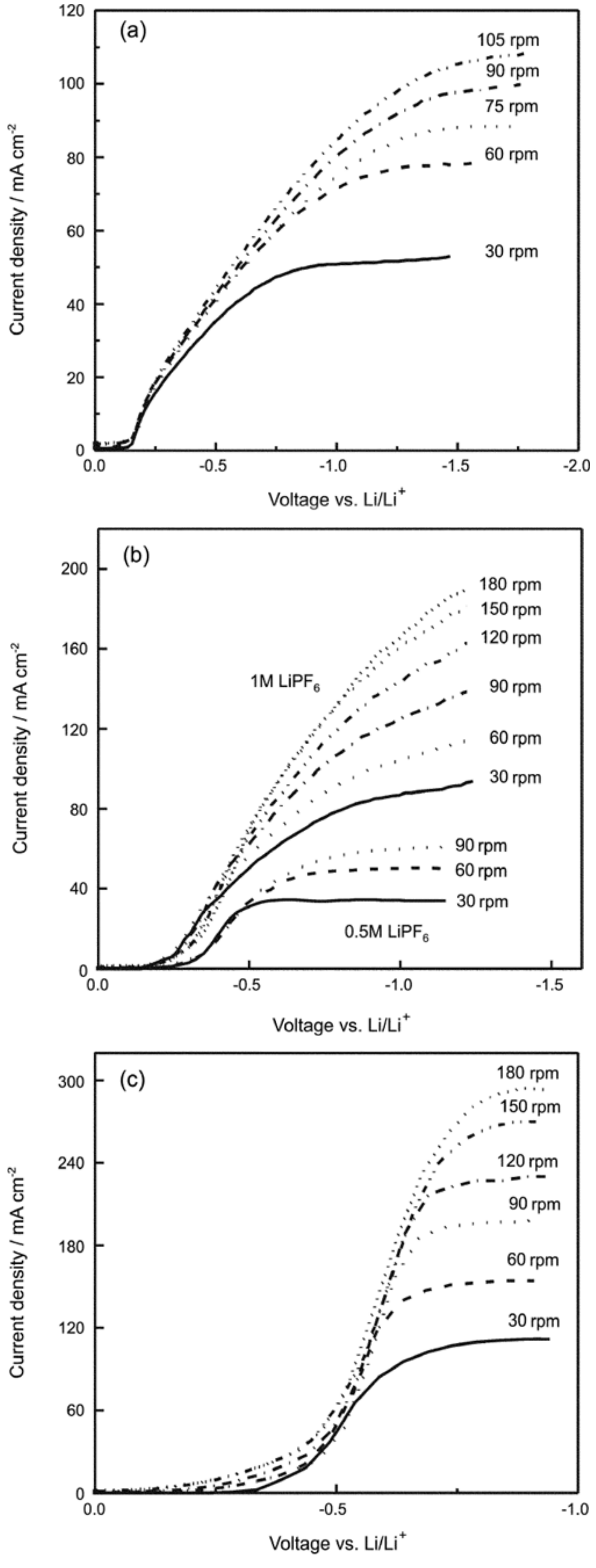

Fig. 2. Linear sweep voltammetry results depending on rpm of disk electrode: (a) 1 M LiClO$_4$ in PC, (b) 0.5 M, 1 M LiPF$_6$ in EC : DEC=1 : 1, and (c) 1 M LiPF$_6$ in EC : DMC=1 : 1.

tial. The other salt concentration samples of PC systems exhibited a similar behavior. The overpotential at which current reaches its limiting current moved to more negative over a wide potential range from −0.8 to −1.6 V vs. Li/Li$^+$ by increasing the rotation speed of the working electrode and salt concentration. The explanation of this is that lithium deposition in PC/LiClO$_4$ is mainly controlled by diffusion of the solute (lithium ion) through its high viscous solvent. Current response of EC-based electrolytes showed a continuous increase as shown in Fig. 2(b) and (c), as compared with the abrupt rise observed in PC/LiClO$_4$. At the start of lithium deposition the current increased steadily but a rapid increase of current was observed at about −0.3~−0.5 vs. Li/Li$^+$. In the case of EC : DMC=1 : 1/LiPF$_6$ the current reached most rapidly a plateau at −0.6~−0.8 V vs. Li/Li$^+$ and exhibited small negative shifting of overpotential for limiting current with raising the rotation speed as shown in Fig. 2(c). The limiting current density of this sample was higher than the other two samples at the same condition. The *i-E* curves of EC : DEC=1 : 1/LiPF$_6$ showed a medium behavior of other two samples. The current increased steadily at low potential and then reached the limiting current showing a wide negative shifting of overpotential near −0.5~−1.0 V vs. Li/Li$^+$ with respect to RPM of the electrode and solute concentration. In the case of 1 M LiPF$_6$ in EC : DEC=1 : 1, a distinct limiting current plateau was not observed but current increased continuously in comparison with 0.5 M LiPF$_6$ in EC : DEC =1 : 1 as shown in Fig. 2(b). It is known that the system, which is controlled by reaction (electrodeposition) as well as diffusion, exhibits no distinct plateau but the continuous increase of current density in the RDE experiment. The system with a presence of plateau (limiting current density) is analyzed as below.

In the RDE experiments, the diffusion coefficient can be obtained from the simple (mass diffusion only controlled) Levich equation:

$$I_l=0.620nFAD^{2/3}\nu^{-1/6}c\omega^{1/2} \tag{1}$$

where I_l is the disk electrode current, n is the number of electron transferred in the elementary reaction step, F is the Faraday constant, A is the disk electrode area (cm^2), D is the diffusion coefficient (cm^2/s) of species charged at the disk electrode, c is its bulk concentration of a solute in electrolyte, ν is the kinematic viscosity of electrolyte (cm^2/s), and ω is the angular velocity of the disk electrode (rads/s). The usual procedure is to determine D from the slope of a plot of I_l vs. $\omega^{1/2}$ which according to Eq. (1) should be a straight line passing through the origin. For the mixed control system including diffusion and reaction of lithium deposition that is deviated from linearity, the modified Levich equation is used to obtain D [Uceda et al., 1990]. The modified equation contains a term I_k, the disk electrode current which would be observed if mass transport limitation were negligible, and the disc current, I, is expressed as:

$$1/I=1/I_k+1/(0.620nFAD^{2/3}\nu^{-1/6}c\omega^{1/2}) \tag{2}$$

where the symbols are the same as defined for Eq. (1). It follows from Eq. (2) that if 1/I is plotted vs. $\omega^{-1/2}$, I_k and D are determined from the intercept and slope, respectively.

The values of the limiting current densities for lithium deposition from *i-E* curves were plotted vs. the square root of the rotating speed according to the simple Levich equation in Fig. 3. Plots show the good linearity and extrapolation of lines passing through the origin as predicted by the simple Levich equation for a simple diffusion-

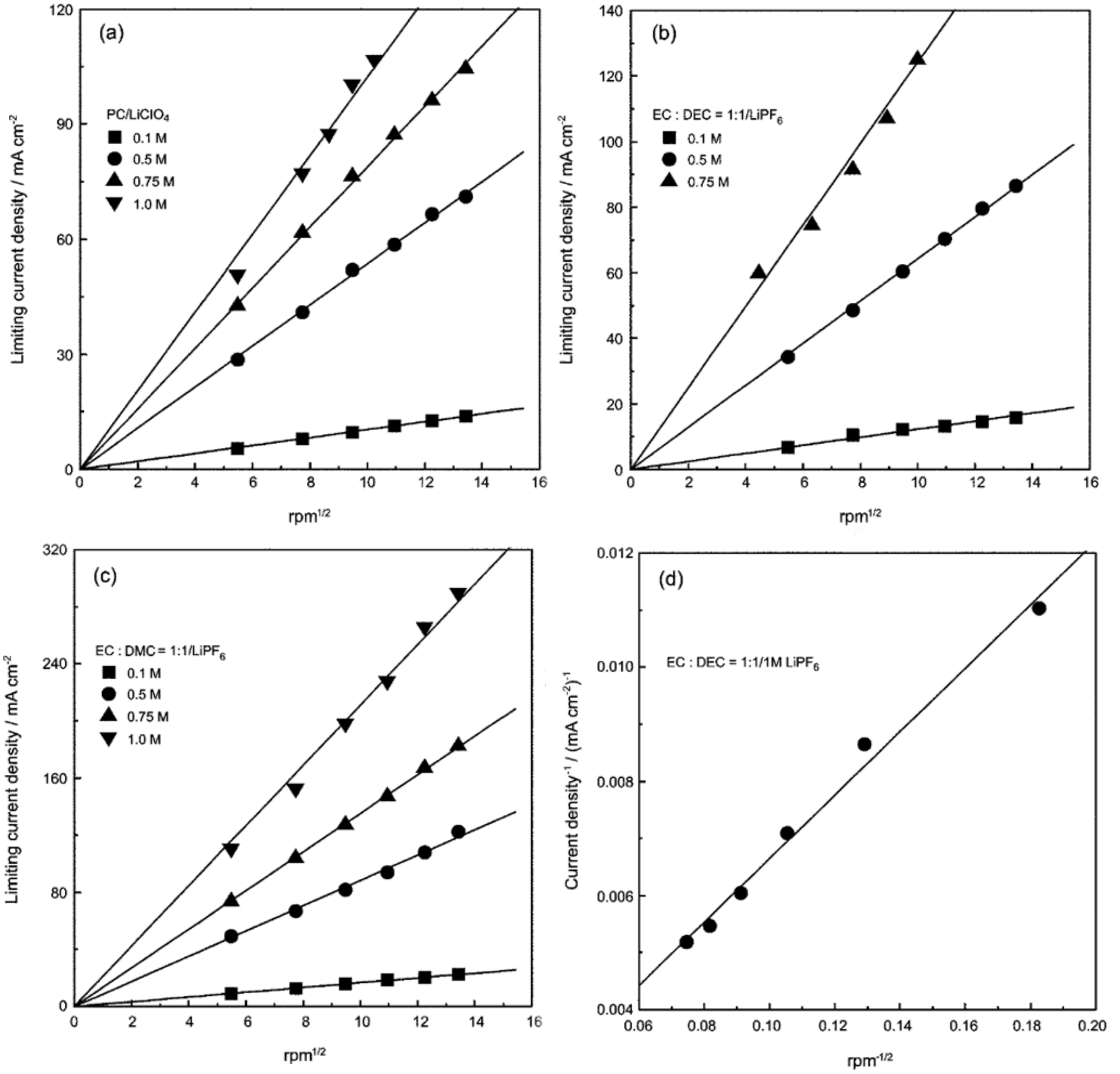

Fig. 3. Plots of limiting current density and rotation speed according to the simple (a-c) and mixed control Levich equation (d) for electrolytes with different lithium salt concentration; (a) $LiClO_4$ in PC, (b) $LiPF_6$ in EC : DEC=1 : 1, (c) $LiPF_6$ in EC : DEC=1 : 1, and (d) 1 M $LiPF_6$ in EC : DEC=1 : 1.

controlled processes except the case of 1 M $LiPF_6$ in EC : DEC= 1 : 1, where a sharp limiting current plateau cannot be observed as shown in Fig. 2(b). In this case all limiting current values were chosen at 1.2 V vs Li/Li^+, and then applied to Eq. (2) to obtain the kinetic parameters. The reciprocal of current vs. the reciprocal of the square root of angular velocity showed a good linearity as shown in Fig. 3(d) for the EC : DEC=1 : 1/1 M $LiPF_6$ electrolyte. From the plots of Levich and the modified Levich equation in Fig. 3, diffusion coefficients were calculated by using Eqs. (1) and (2), respectively. These values were plotted in Fig. 4. The diffusion coefficients increased in the order of PC/$LiClO_4$<EC : DEC=1 : 1/$LiPF_6$<EC : DMC=1 : 1/$LiPF_6$. The maximum value was 1.39×10^{-5} cm^2/s for 1 M $LiPF_6$ in EC : DMC=1 : 1. This sequence is well correlated with a decrease in the viscosity of the electrolytes. The diffusion coefficient of PC/$LiClO_4$ electrolyte system was almost constant and a relatively smaller value than the other electrolytes due to its high viscosity. That value was about 5.5×10^{-6} cm^2/s for 1 M $LiClO_4$ in PC which is a good agreement with the result from microelectrode experiments by Verbrugge et al. [1994]. The diffusion coefficient of EC-based electrolytes increased with increasing solute concentration in spite of the increasing of viscosity. This sequence is in contrast to the previous result, inversely proportional to viscosity with respect to each sample. The result was probably due to the nature of the dissolved substance (e.g., solvation, complex formation) [Blint, 1997; Cazzanelli et al., 1997]. It is well known that activities (or activity coefficient) of many aqueous electrolytes exhibit a

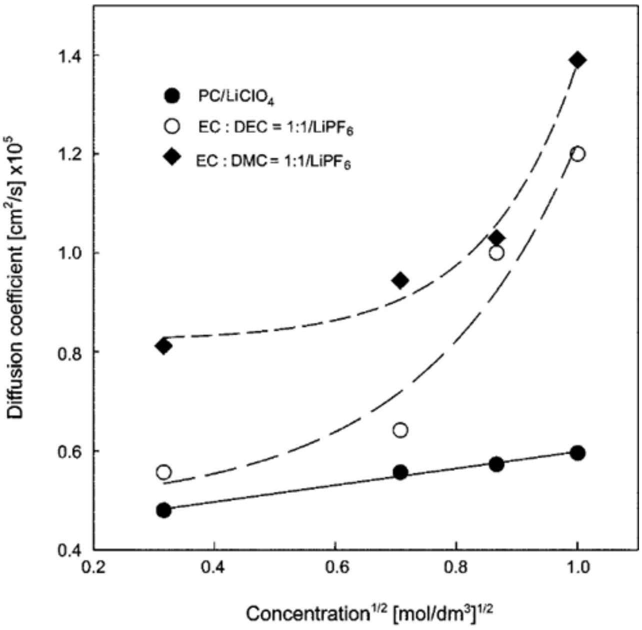

Fig. 4. Variation of the diffusion coefficients, D, of lithium ion in electrolytes with the lithium salt concentration at 298 K.

minimum and increase as the salt concentration increases [Bockris and Reddy, 1973]. This increase is mainly due to the ion-solvent interaction (hydration). As the strong hydration between ion and solvent decreases the free solvents, which are not trapped by ion, effective concentration ([solute]/[free solvent]) of ion increases with the salt concentration so that the activity increases [Horvarth, 1985]. In addition, the repulsive short-range hard core contribution at high concentration may increase the activity [Bockris and Reddy, 1973]. Therefore, the diffusion coefficient of the solute in aqueous electrolyte showed a minimum and increasing behavior, even a maximum behavior at its extremely high concentration in spite of high viscosity. It is impossible to anticipate the diffusion coefficient of electrolyte with respect to the salt concentration by its viscosity only. For the organic electrolytes, PC and EC have almost similar values of permittivity and polarity to those of water or even higher. In the case of organic electrolyte systems, the lithium ion solvation by the organic solvent affects the ionic radii, free solvent concentration, electrochemical conductivity and mass transport as shown in the aqueous electrolytes. From the result it is expected that the solvation effect in the organic electrolyte probably compensates for the increase of viscosity with increasing salt concentration. In the system of EC-based mixed electrolytes, lithium ion is probably coordinated by EC in preference to the acyclic carbonate (DEC, DMC) because of its high polarity and slightly higher donor number (DN, 16.4 for EC, 15.1 for DEC and DMC). It is considered that the strong solvation complex of lithium ion with EC, of which high permittivity reduces the ion association effect, diffuses in low viscous medium of DEC or DMC. In addition, the increment of viscosity for EC-based electrolyte with increasing concentration was relatively smaller than the corresponding PC-based one in the previous result of Fig. 1. Relatively lower viscosity, different solvation complex, and low dipole moment (solvent-solvent interaction) according to mixing of LVS are responsible for the enhancement of the diffusion of lithium ion in EC-based electrolyte system. However, there is no clear explanation for diffusion of lithium ion in organic solvent.

The experimental results are also applied to the Stokes Einstein equation:

$$D\mu/T=K/6\pi r \tag{3}$$

where μ is viscosity, K is Boltzmann constant, and r is ionic radii. The left term of the equation is ca. 3.37×10^{-10} dyne/K for 0.1 M $LiPF_6$ in two EC-based samples; the mean value of ionic radii was calculated to be 2.1×10^{-8} cm. This equation has the limitation that it is only suitable for the system of a bigger size of solute than that of solvent with continuum phase assumption, and mainly applied to experiments with respect to temperature, in which the system diffusion coefficient decreases generally with increasing viscosity [Cussler, 1984]. The ionic radii calculated here are comparable to a strong degree of solvation for high polarity of EC.

The exchange current density i_o and transfer coefficient a for the lithium electrodeposition were evaluated by the following current-overpotential relation based on the Butler-Volmer equation according to mass transport in the Tafel region. The results are summarized in Table 1 by applying least square regression of Eq. (4) to the data:

$$\frac{i}{i_o}=\left(1-\frac{i}{i_{l,c}}\right)e^{-\alpha nF\eta/RT} \tag{4}$$

where i is current density, i_o is exchange current density, $i_{l,c}$ is cathodic limiting current, α is transfer coefficient, η is overpotential, F is Faraday constant, R is gas constant and T is temperature. Fig. 5 shows the result of regression with good agreement of fitting, and the exchange current densities and transfer coefficients for three electrolyte systems were determined. The exchange current density and the transfer coefficient of 1 M $LiClO_4$ in PC were 10.3 mA/cm² and 0.20 at 25 °C, respectively, which is in good agreement with the result of the microelectrode (10.3 mA/cm², 0.29, 23 °C, 1 M $LiClO_4$

Table 1. Exchange current densities and transfer coefficients of test electrolytes (298 K)

Concentration [M]	PC/LiClO₄		EC : DEC=1 : 1/LiPF₆		EC : DMC=1 : 1/LiPF₆	
	i_o*	α**	i_o	α	i_o	α
0.1	0.565	0.38	0.141	0.48	0.141	0.44
0.5	4.42	0.34	1.13	0.51	0.565	0.50
0.75	7.21	0.23	1.27	0.27	0.0375	0.53
1.0	10.3	0.20	3.54	0.21	0.0943	0.51

*Exchange current density [mA/cm²]
**Transfer coefficient

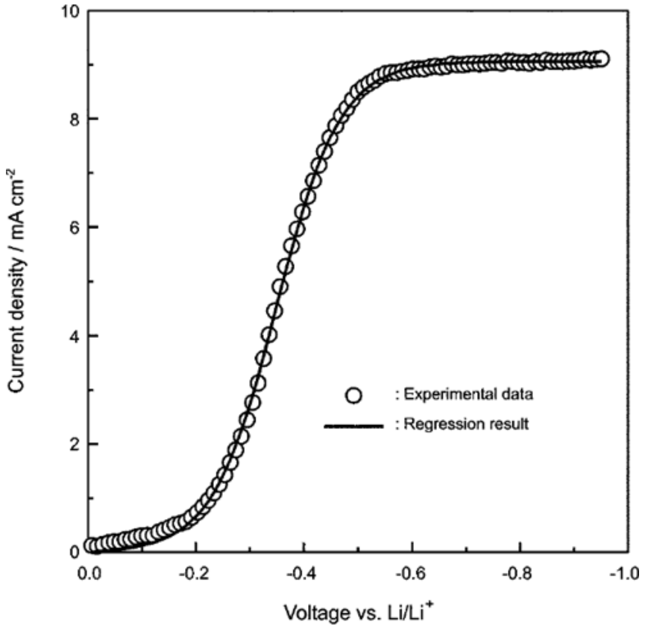

Fig. 5. Regression result for electrochemical parameters (exchange current density and transfer coefficient) in the case of 0.1 M LiPF$_6$ in EC : DMC=1 : 1.

in PC) [Wang et al., 1996]. The transfer coefficients of EC-based electrolytes were nearly 0.5 with good symmetrical characteristics. In general, it is known that the transfer coefficient should be 0.5 if the reactant is strongly solvated [Verbrugge and Koch, 1994]. The result aagrees with the result of ionic radii from the Stokes-Einstein equation. These electrolytes showed smaller exchange current density (10^0-10^{-2} mA/cm^2) than that of PC-based electrolyte.

CONCLUSIONS

The rotating disk electrode was suitable for studying the effect of mass transport of lithium salt in organic solvents on Li electrodeposition process. The diffusion coefficients were obtained by the simple Levich equation except the case of 1 M LiPF$_6$ in EC : DEC=1 : 1. In the latter case the effect of charge transfer reaction was increased in high solute concentration; therefore, the modified Levich equation was applied. The maximum value of diffusivity was 1.39×10^{-5} cm^2/s for 1 M LiPF$_6$ in EC : DMC=1 : 1. EC-based mixed electrolytes show lower viscosity and higher diffusion coefficient than PC-based electrolytes. The effect of viscosity and solvation plays an important role in mass transport of lithium ion in these electrolytes. This result suggests that the EC-based mixed electrolytes with low viscosity, low density, high limiting current density and high diffusion coefficient are suitable for commercial lithium ion batteries. Electrochemical kinetic parameters such as exchange current densities and transfer coefficients for electrodeposition of lithium in PC/LiClO$_4$, EC : DEC=1 : 1/LiPF$_6$ and EC : DMC=1 : 1/ LiPF$_6$ electrolyte system were obtained. In the case of EC : DEC= 1 : 1/1 M LiPF6, i_o and were 3.54 mA/cm^2, 0.21, respectively.

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