

Charge-Transfer Reaction Rate of Li^+/Li Couple in Poly(ethylene glycol) Dimethyl Ether Based Electrolytes

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The exchange current densities of the Li^+/Li couple reaction in polyether based electrolytes, 0.5 M LiCF_3SO_3 /poly(ethylene glycol) dimethyl ether whose molecular weight is 500 (PEGDME500), were investigated for the studies about charge-transfer reaction rate at the electrode/electrolyte interfaces. It was found that the exchange current densities in the PEGDME500 based electrolytes decreased with increasing amounts of PEGDME1000 (molecular weight: 1000). Raman spectroscopic studies indicated that the activity of lithium ions, which is a factor for the exchange current densities, was found to be the almost constant even with the addition of PEGDME1000 in to the electrolytes. The Gibbs activation energies for the interfacial reaction were also the almost constant. Meanwhile, inversely proportional relationships between the exchange current densities and viscosities of the electrolytes were observed. Our studies elucidated that viscosity of the electrolytes was the only important factor for the charge-transfer reaction rate at polyether based electrolyte/electrode interfaces.

Introduction

Polymer electrolytes have been studied widely as an alternative electrolyte for conventional organic solution electrolytes based on organic liquid solvents, such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), for lithium ion secondary batteries.^{1–11} The great advantage of the polymer electrolytes, typically based on poly(ethylene oxide) (PEO) containing a lithium salt, is safety compared to conventional electrolytes.^{11,12} Meanwhile, low ionic conductivity and small transport number of lithium ions in polymer electrolytes are disadvantages, which are due to strong interaction between ether oxygen atoms of polymer chains and lithium ions.^{11,12} Furthermore, the strong interaction should be also a disadvantage for the charge-transfer reactions at polymer electrolyte/electrode interfaces, especially in the case of applying polymer electrolytes to lithium ion secondary batteries. However, despite many studies about characteristics of the bulk properties of polymer electrolytes,^{11,12} for example ionic conductivity and transport number of lithium ions, only a few investigations have been focused on the charge-transfer reaction rate at the interfaces from theoretical aspects.^{13,14} Therefore, it is unexplained which factor of polymer electrolytes is important for the reaction rate. Clarifying about the reaction rate at the interfaces as well as ionic conduction mechanism of the bulk should be necessary for molecular design of advanced polymer electrolytes for higher power density batteries. To our knowledge, our paper is showing for the first time a quantitative description of the factors that influenced the charge-transfer reaction at polymer electrolyte/electrode interfaces. In addition, this phenomenon should be also important for a large number of application technology, such as fuel cells, Ni-MH batteries, electrochromism, catalysis, and biochemical reactions.

In the present study, the electrokinetics of the Li^+/Li couple

reaction on lithium metal electrodes in poly(ethylene glycol) dimethyl ether (PEGDME) based electrolytes is investigated. PEGDME electrolytic solutions dissolving LiCF_3SO_3 are used as a model of polymer electrolytes, which is similar to the amorphous conducting phase in PEO with high molecular weights. To clarify the factors which influence electrokinetics in the electrolytic solutions based on PEGDME, we measured charge-transfer reaction rate at polymer electrolyte/electrode interfaces by using PEGDME, whose average molecular weight is 500 (abbreviated as PEGDME500) by adding various amounts of higher molecular weight polyether, PEGDME1000. The present paper reports that the viscosity of the polymer electrolytes is one of the important factors for the charge-transfer reaction rate at the interfaces and the phenomenon is interpreted by the Marcus microscopic theories of the charge-transfer reaction.^{15–17}

Experimental Section

Poly(ethylene glycol) dimethyl ether (average molecular weight: 500, supplied from NOF Co. Ltd.), represented as PEGDME500, was stored over activated molecular sieves in an Ar-filled glovebox (dew point: -76°C) for over 24 h before using. PEGDME1000 (average molecular weight: 1000, solid at the room temperature, NOF Co. Ltd.) and LiCF_3SO_3 (99.995%, Aldrich) were used without further purification. All experiments were carried out in an Ar-filled glovebox (dew point: -76°C). The electrolytic solutions were prepared by dissolving the optimum amounts of LiCF_3SO_3 , 0.05–1.0 mol dm^{-3} (M), in PEGDME.

For the evaluation of the charge-transfer reaction rate at the interfaces, a microelectrode technique is adopted. Microelectrodes facilitate the electrochemical analyses because of some advantages, such as minimization of the ohmic (IR) drop, suppression of the charge current, which are due to the small surface area of the electrodes, and enhancement of the transport of electroactive ions to the electrode surface due to spherical

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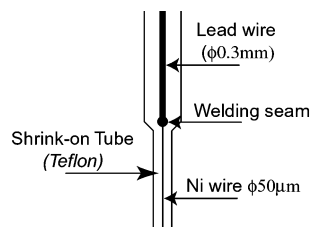


Figure 1. Schematic figures of the Ni microelectrode.

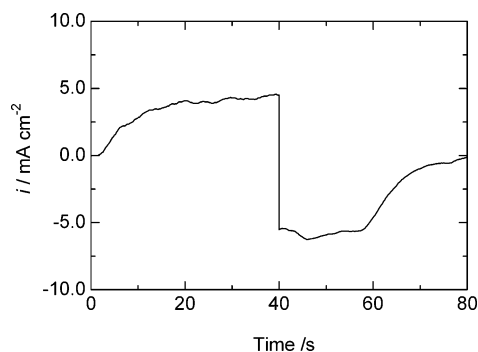


Figure 2. Chronoamperometric response of 0.5 M LiCF₃SO₃/PEGDME500 at 333 K. Potential step: 0 mV → -150 mV vs Li⁺/Li (40s) → 150 mV vs Li⁺/Li (40s).

diffusion on the electrodes.^{13,14,18–20} These advantages are especially useful for relative high resistive media like polymer electrolytes. Nickel microdisk electrodes were chosen as a working electrode for the present study and prepared with 50 μm diameter nickel wire as follows. The wire was sealed with a shrink-on tube made of Teflon, and then the end of the wire surrounded by Teflon was cut to expose the cross-section of the electrode (Figure 1). The prepared microdisk electrode was polished with 0.3 mm diameter alumina powder and polished again before every experiment. For the electrical measurements, a three electrode cell, in which the volume of the electrolyte was ca. 4 mL, was used under static conditions. Lithium foil was used as reference and counter electrodes. Electrochemical experiments were carried out using a Solartron SI 1287 electrochemical interface. The steady-state currents of the deposition and stripping of lithium on the working electrodes at various over potentials vs Li⁺/Li were measured by chronoamperometry. The temperature for electrical measurements was controlled by a block incubator, Dri-Bath Type 17600 (Thermolyne).

Raman spectroscopic studies were performed with a JASCO NRS-2100. The excitation source was an Ar⁺ laser operating at 514.5 nm, and the laser power was 10 mW. The spectral resolution was 2 cm⁻¹. The viscosity of the electrolytic solutions was measured using a viscometer, Viscomate VM-1G (Yamaichi electronics Co. Ltd.), within an incubator, ESPEC SU-240 (ESPEC Co. Ltd.).

Results and Discussion

The electrokinetics of lithium deposition and dissolution on the working microelectrode in the electrolytic solution was studied using a double potential step technique, chronoamperometry. Figure 2 shows a typical chronoamperometric curve obtained in the electrolytic solution, 0.5 M LiCF₃SO₃/PEGDME500 at 333 K. The potential was first stepped from 0 to -150 mV vs Li⁺/Li and held for 40 s for the lithium deposition on the microelectrode, and the potential was then stepped to +150 mV vs Li⁺/Li for the dissolution of the deposited lithium. During the lithium deposition, the cathodic

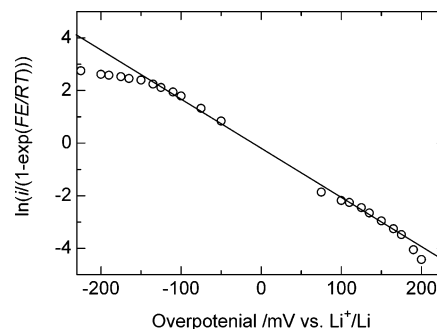


Figure 3. Allen-Hickling plots for steady-state polarization currents in 0.5 M LiCF₃SO₃/PEGDME500 at 333 K.

current increased as lithium nuclei formed and grew on the working electrode until the electrode surface was fully covered, and then the current reached a plateau, which means the steady-state current corresponding to the constant cathodic overpotential. Subsequently, after the potential was stepped to the positive value, the anodic current increased as the lithium deposited on the electrode dissolved and reached at a steady-state anodic current corresponding to the constant anodic overpotential until the surface lithium layer of the electrode was fully depleted, and then the current fell to zero. The values of the steady-state currents at various cathodic and anodic overpotentials were measured by the same procedure. All of the measured Coulombic efficiency of lithium deposition and dissolution was over 90%. This should be due to the fresh deposition and immediate dissolution of lithium on the microelectrode.

For the estimation of the exchange current densities about the Li⁺/Li couple in the electrolytic solutions, the steady-state currents (*i*) obtained at various overpotentials (*E*) by the chronoamperometry were analyzed with the following Allen-Hickling equation:

$$\ln \left[\frac{i}{1 - \exp(\{FE\}/\{RT\})} \right] = \ln i_0 - \frac{\alpha F}{RT} E \quad (1)$$

where *F* is the Faraday constant, *R* is the gas constant, *T* is an absolute temperature, α is the transfer coefficient, and *i*₀ is the exchange current density.²¹ Figure 3 shows the Allen-Hickling plots for the steady-state currents at various overpotentials in 0.5 M LiCF₃SO₃/PEGDME500 at 333 K. In the Allen-Hickling plots, a linear relationship was found in the range of overpotentials around -150 to +170 mV vs Li⁺/Li, and at numerically higher potentials, deviation from the relationship was found, which is due to the effect of mass transport limitation. The values of the exchange current density and the transfer coefficient were estimated from the intercept and slope of the Allen-Hickling plots. From the same procedure, the exchange current densities in the electrolytic solutions added with various amounts of PEGDME1000 were obtained and summarized in Figure 3. Figure 4 summarizes the estimated values of the transfer coefficient. All of the values were close to 0.5, which implies a symmetric reaction of the Li⁺/Li couple. As shown in the result, the exchange current densities decreased with increasing amounts of PEGDME1000.

The exchange current density *i*₀ can be expressed as the following equation:²¹

$$i_0 = K_r a_{\text{Li}^+}^{1-\alpha} a_{\text{Li}}^{\alpha} \quad (2)$$

where *a*_{Li⁺} is the activity of lithium ions, *a*_{Li} is the activity of lithium metal, and *K_r* is the standard rate constant, which can be expressed as the following equation (3) according to recent

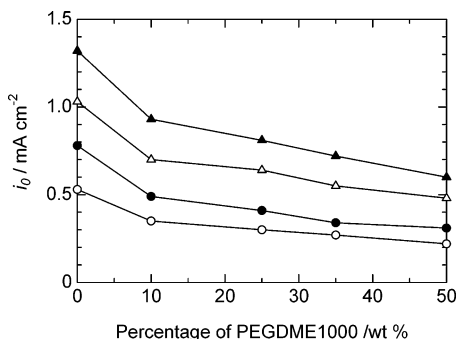


Figure 4. i_0 vs the fraction of PEGDME1000 in PEGDM500/PEGDME1000 mixed solution containing 0.5M LiCF_3SO_3 at various temperatures: \circ at 313 K, \bullet at 323 K, \triangle at 333 K, \blacktriangle at 343 K.

advanced theory revealing solvent dynamic effect on electron-transfer rates;^{15–17,22–24}

$$K_r = \frac{A}{\tau_L} \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (3)$$

where A is the preexponential factor, ΔG^* is the Gibbs activation energy of the reaction, and τ_L is the longitudinal relaxation time of the solvent. The fact that all of the obtained values of the transfer coefficient were close to 0.5 and a_{Li} is unity leads to the following equation (4) for the exchange current density:

$$i_0 = \frac{A}{\tau_L} \sqrt{a_{\text{Li}^+}} \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (4)$$

As a consequence, eq 4 indicates that the exchange current density depends on the activity of lithium ions, the Gibbs activation energy, and the longitudinal relaxation time of the solvent.

To investigate the activity of lithium ions in the electrolytic solutions, Raman spectroscopic studies were carried out. Raman spectroscopy is very useful for the investigation about the activity of lithium ions in electrolytes containing lithium salts from the spectra due to the internal vibration modes of the counteranions.^{25–27} The spectral band of the SO_3 symmetric stretching mode of CF_3SO_3^- ($\nu_s(\text{SO}_3^-)$), which is observed around 1040 cm^{-1} , was chosen for the present electrolytic solutions. Furthermore, this band consists of three components corresponding to the state of the anion as follows; the lower frequency component at $\sim 1034 \text{ cm}^{-1}$ is attributed to “free ions”, the component at $\sim 1042 \text{ cm}^{-1}$ to “ion pairs”, and the highest frequency component at $\sim 1052 \text{ cm}^{-1}$ to “multiple aggregated ions”, respectively.^{25–27} Therefore, the first component, which corresponds to a fraction of “free lithium ions”, in other words, activity of lithium ions, is very useful for the present study. The fraction of the free ions corresponds to the ratio of the area due to free ions (dissociated ions) to those of all of the components (aggregated and ion-paired as well as free ions). Figure 6 shows Raman spectra, in the region of 1000 – 1080 cm^{-1} , of $0.5\text{M LiCF}_3\text{SO}_3/\text{PEGDME500}$ with various amounts of PEGDME1000. Each spectrum was deconvoluted to three components by fitting three distinct Lorentzian curves. Figure 7 summarizes the variations for the fractions of above three kinds of ions in the electrolytic solutions at 313 and 343 K. As shown in the result, the fractions of the component corresponding to “free ions” were almost same, around 20%, even with increasing amount of PEGDME1000 at the temperature range of 313 and 343 K, indicating that activity of lithium ions was almost constant in the electrolytic solutions with various amounts of PEGDME1000. Generally, the dissociation constant of a

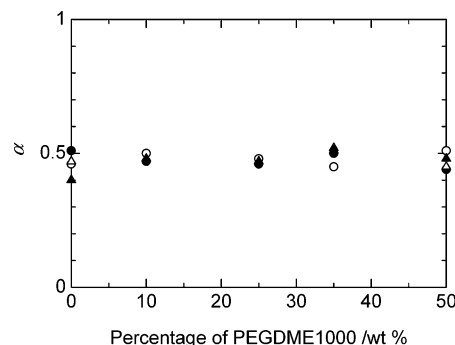


Figure 5. α vs the fraction of PEGDME1000 in PEGDM500/PEGDME1000 mixed solution containing 0.5M LiCF_3SO_3 at various temperatures: \circ at 313 K, \bullet at 323 K, \triangle at 333 K, \blacktriangle at 343 K.

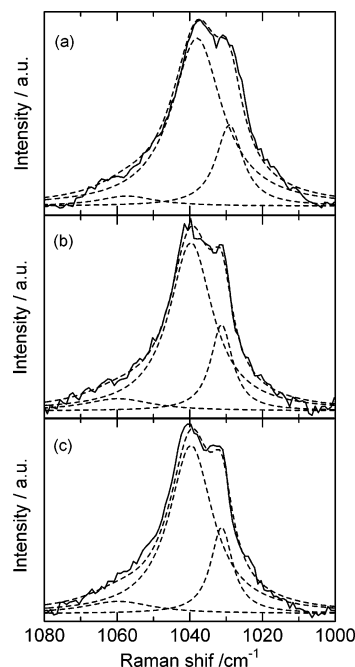


Figure 6. Raman spectra of $0.5\text{M LiCF}_3\text{SO}_3$ in the solutions at 313K: (a) PEGDME500 (100%), (b) PEGDME500 75 wt % + PEGDME1000 25 wt %, (c) PEGDME500 50 wt % + PEGDME1000 50 wt %. Solid lines: experimental data; Dotted lines: fitting results with three distinct Lorentzian curves.

lithium salt is determined with the lattice energy of the salt itself and the solvation state of ions, which is concerned with ion–solvent molecule interaction.^{11,12} When a lithium salt is added into the PEO-based matrix, the lithium ions are incorporated into the helix structures of EO chains.^{11,12} In the case of PEGDME500 and PEGDME1000, since ether oxygen acts as donor polar group, the geometry, i.e., the solvation state, of lithium ions in the PEGDME should be similar. Therefore, the ratio of free ions, i.e., the activity of the lithium ions in the electrolytic solutions, was almost constant.

The obtained exchange current densities of the electrolytic solutions at various temperatures were re-plotted in Arrhenius type in order to calculate the Gibbs activation energies of the Li^+/Li couple reaction (Figure 8). All Arrhenius plots exhibit a linear relationship between $\ln(i_0)$ and $1/T$, as shown in Figure 8, and accordingly, the values of the Gibbs activation energies were calculated from the slope of the linear relationship plots. The calculated Gibbs activation energies are summarized in Table 1.

The electrokinetics of the Li^+/Li couple reaction involves the desolvation/solvation process. Therefore, the Gibbs activation

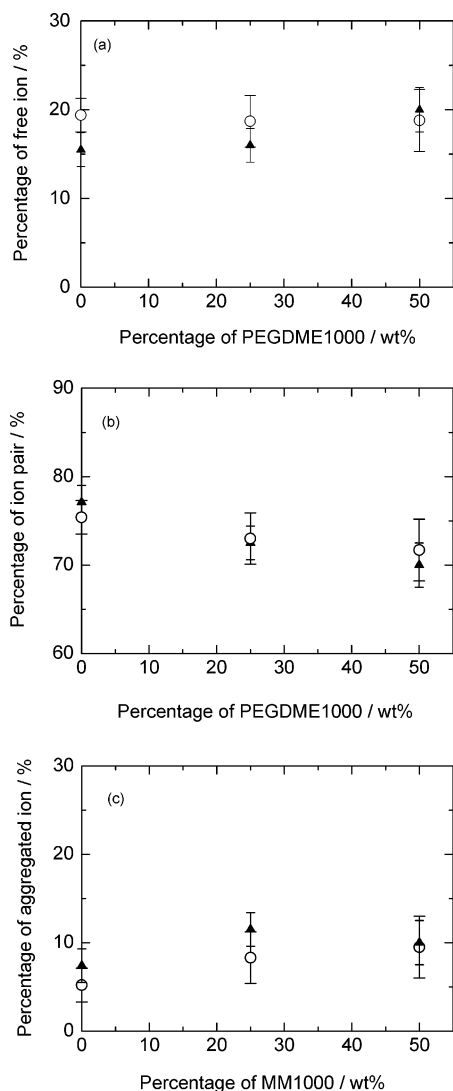


Figure 7. Fraction of (a) free ions, (b) ion-pair, and (c) aggregated ions in 0.5M LiCF₃SO₃/PEGDME500 with various amounts of PEGDME1000 at various temperatures: ○ at 313 K, ▲ at 343 K.

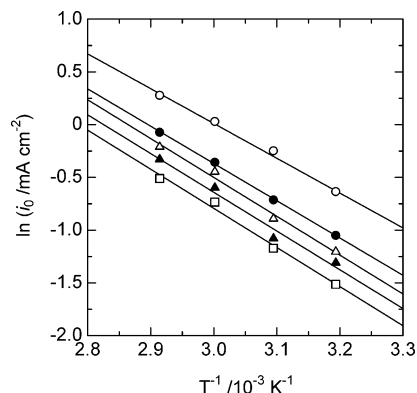


Figure 8. Arrhenius plots for the exchange current densities in 0.5M LiCF₃SO₃/PEGDME500 with various amounts of PEGDME1000: ○ PEGDME500 100%, ● PEGDME500 90 wt % + PEGDME1000 10%, △ PEGDME500 75 wt % + PEGDME1000 25 wt %, ▲ PEGDME500 65 wt % + PEGDME1000 35 wt %, □ PEGDME500 50 wt % + PEGDME1000 50 wt %.

energy may depend on the desolvation/solvation energy. In other words, the Gibbs activation energy depends on the solvation state of lithium ions in a solvent. The Gibbs activation energies were found to be around 29 kJ mol⁻¹ even with PEGDME1000

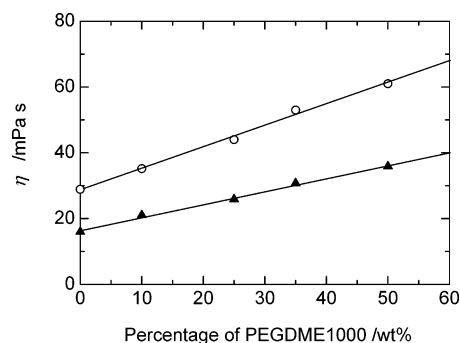


Figure 9. Viscosity of electrolytic solutions, 0.5 M LiCF₃SO₃/PEGDME500 with various amounts of PEGDME1000, at various temperatures: ○ at 313K, ▲ at 343 K.

TABLE 1: Activation Energies of Li⁺/Li Couple Reaction in 0.5 M LiCF₃SO₃/PEGDME500 with Various Amounts of PEGDME1000

amount of PEGDME1000 / wt %	$\Delta G^* / \text{kJ mol}^{-1}$
0	28.9
10	28.7
25	29.8
35	28.4
50	30.3

added into the electrolytic solutions. Such activation energy for the exchange current density of the Li⁺/Li couple in ether and/or ester based electrolytes was reported by some research groups as a range of 25–69 kJ mol⁻¹,^{13,20,28–30} which depends on the solvents and salts. As explained in the Raman spectroscopic studies, the solvation state of lithium ions in the PEGDME500 and PEGDME1000 should be similar, since lithium ions are incorporated into the helix structures of EO chains.^{11,12} Therefore, the activation energy is independent of the amounts of PEGDME1000.

The above results elucidated that the activity of lithium ions and the Gibbs activation energy do not depend on the ratio of PEGDME500/PEGDME1000 in the electrolytic solutions. On the other hand, Figure 3 clearly shows that the exchange current densities decreased with increasing amount of PEGDME1000. Equation 4 suggests that the exchange current density depends on the relaxation time of the solvents. The studies of the solvent effect on charge-transfer kinetics have elucidated that the reaction rate is concerned with the frequency of solvent reorientation at desolvation/solvation process representing solvent dynamics.^{15–17,22–24} Furthermore, this frequency is proportional inversely to the longitudinal relaxation time. As a consequence, the relaxation time can be explained as a factor for the frequency of solvent reorientation at desolvation/solvation process. In addition, the longitudinal relaxation time of the solvent, τ_L , is related to the Debye relaxation time τ_D through the following equation:^{31,32}

$$\tau_L = \tau_D \{ \epsilon_\infty / \{ \epsilon_s \} \} \quad (5)$$

where ϵ_s is the static dielectric constant and ϵ_∞ is the infinite frequency dielectric constant. Furthermore, the Debye relaxation time, τ_D , is proportional to the viscosity, η .^{32,33} Therefore, the longitudinal relaxation time of the solvent is proportional to the viscosity, η . Accordingly, the exchange current density, i_0 , is inversely proportional to the viscosity from the above relationships and the eq 4.

Figure 9 shows the relationship between the viscosities and the fraction of PEGDME1000 in the PEGDME500 based electrolytic solutions. It was found that the viscosity of the

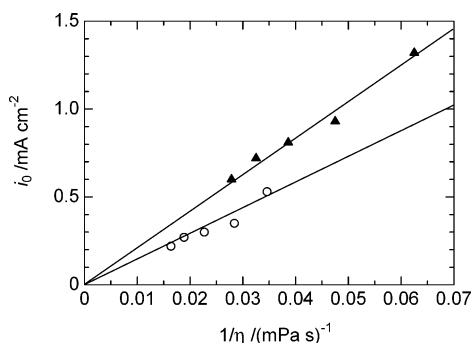


Figure 10. Exchange current densities vs inverse of viscosities of 0.5M LiCF₃SO₃/PEGDME500 with various amounts of PEGDME1000 at various temperatures: ○ at 313K, ▲ at 343 K.

solutions based on PEGDME500 increased with increasing amount of the larger molecular weight PEGDME1000. The relationships between the exchange current densities and the viscosities of the solutions were shown in Figure 10. It was exhibited that the exchange current density was inversely proportional to the viscosity. Therefore, the viscosity of a solvent is an important factor for the exchange current density of the polyether based electrolytes.

The studies in PEGDME based electrolytes about the activity of lithium ion by Raman spectroscopy, the Gibbs activation energy, and viscosity revealed that only the last factor, viscosity, of the electrolytic solution has the effect on the charge-transfer reaction rate at the electrode/electrolyte interfaces. These results imply that the difficulties of getting high rates of charge-transfer reaction at the interfaces in the case of using high viscous electrolytes, especially such as polymer electrolytes.

Conclusion

The exchange current densities of the Li⁺/Li couple reaction in the PEGDME based electrolytic solutions containing LiCF₃SO₃ were investigated using microelectrodes for the studies about the charge transfer reaction rate at the electrode/electrolyte interfaces. By using two types of PEGDME with molecular weights 500 and 1000, we investigated the influence of the factors of electrolytes on the exchange current densities. It was found that the exchange current densities in the PEGDME500 based electrolytes decreased with increasing amounts of PEGDME1000. Raman spectroscopic studies for the electrolytes revealed that the activities of lithium ions were the almost same even with the addition of PEGDME1000. The results about the Gibbs activation energies for the reaction suggested that the solvation states of lithium ions are similar in the electrolytes with PEGDME whose molecular weight range is 500–1000. Meanwhile, the viscosity of the electrolytes increased with increasing amounts of PEGDME1000. Furthermore, inversely proportional relationships between the exchange current densities and the viscosities of the electrolytes were exhibited. Therefore, the viscosity of the electrolytes is an important factor for the charge-transfer reaction rate at the polyether based electrolyte/electrode interfaces, which implies the difficulties of getting

high rates of charge transfer at the interfaces in the case of using polymer electrolytes, i.e., high viscous electrolytes.

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