Conductivity of LiClO₄/PC-DME Solution Impregnated in LiCoO₂ Powder

Yoshimasa SUZUKI a, b, Hideshi MAKI a, b, Masaki MATSUI a, b, and Minoru MIZUHATA a, b, c

a Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan
b Center for Environmental Management, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan
* Corresponding author: mizuhata@kobe-u.ac.jp

ABSTRACT

Electrical conductivity of LiClO₄ solution in binary solvent of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) coexisting with LiCoO₂ powder was measured. Maximum value of conductivity in LiClO₄/PC-DME solution observed at ca. 1:1 of volume fraction shifted toward lower content of DME. In higher LiClO₄ concentration reached to 3 mol L⁻¹, the conductivity of LiClO₄-PC1−x-DME x increased with DME content even if LiCoO₂ was added. The results of FT-IR measurement support the results of conductivity measurement for PC solvation of the slurry sample of LiCoO₂/LiClO₄/PC-DME system.

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1. Introduction

The electrolyte solution of a lithium ion battery is required to have properties such as high conductivity, low melting point, and a wide potential window.1,2 Mixed solvents such as EC-DEC and EC-DMC, are generally used for the optimized the ionic conduction and reaction. The electrolyte solution with these solvents are stabilized by the fine powder of active materials or porous separatirs like slurry or paste. Since it is the ion transport within the positive electrode that becomes the rate-limiting step in the ion transport in the lithium ion battery, the knowledge of the conductivity in the electrolyte near solid is important. A previous study has reported that the liquid phase near the solid phase is influenced by the solid surface in the solid-liquid mixture.3-5 In this study, we measured the electrical conductivity of a sample mixed with LiCoO₂ powder and LiClO₄ solution using propylene carbonate (PC) and 1,2-dimethoxyethane (DME) as solvents (LiClO₄-PC1−x-DME x). Although a system including EC as conventional solvent might be focused, they indicate the simple decreasing of conductivity by adding low viscose solvent, therefore each effect of solvent for conductivity is not distinguish clearly. For emphasizing each solvent effect, we chose PC-DME solvent for LiClO₄ solution and investigated how the influence of each solvent property changes in the vicinity of the active material, by using a binary solvent of highly dielectric solvent; PC and low viscose solvent; DME for which the electric conductivity has a maximum value at 0.45 in DME fraction (PC:DME = 1:1 of volume ratio).3,4

2. Experimental

LiCoO₂ was dried at 200°C for 18 h in vacuo for a sample of the solid phase. A mean particle size, the specific surface area, and density are 5.1 μm, 0.91 m²g⁻¹, and 5.26 gcm⁻³ respectively. The calculated roughness factor is 4.07. A binary solvent; PC-DME was prepared by mixing thoroughly at a DME molar fraction ranged from 0 to 0.8 under dehydrated condition by molecular sieve 4A.

LiClO₄ was dried at 180°C for 20 h in vacuo and dissolved in the PC-DME solvent. Weighed powder was mixed thoroughly with LiClO₄-PC-DME solution and immediately molded into a tablet with a diameter of 20 mm under a pressure of 52 MPa for 30 min.5,6 Liquid content; φ was adjusted in φ = 5–30 vol%. All reagents except LiCoO₂ were purchased from Nacalai Tesque Inc. An AC impedance was measured using Keysight Technology 4284A for calculating the electrical conductivity of the paste sample. In order to obtain the activation energy of electric conductivity; ΔEG, electric conductivity measurement was carried out in the temperature range of 20 to 40°C. The method of calculating the activation energy from the Arrhenius or VTF equations is described in Appendix S1 in supporting information.

FT-IR spectra of the solvent and bulk solution were measured in transmission mode for the liquid film soaked by interfacial tension between KRS-5 plates as an optical window. On the other hand, for solid/liquid coexisting sample, the diffuse reflectance FT-IR spectra were obtained by JASCO FT-IR-615 spectrometer equipped with the diffuse reflectance attachment, DR-600B under dried inert atmosphere. The reference spectrum of diffuse reflectance measurement was measured for LiCoO₂ powder.

3. Results and Discussion

A dependence of the electric conductivity; σ on the molar fraction of DME in binary solvent for the LiCoO₂/ LiClO₄-PC1−x-DME x coexisting system in several liquid contents was shown in Fig. 1. In the bulk solution, the electric conductivity has a maximum value as same as the previous studies.7,8 As the liquid content decreased with the addition of LiCoO₂, the maximum point of conductivity shifted toward lower DME content. It is suggested that the effect of DME for decrease of viscosity was lost by the interaction between solid phase and DME molecules.9

Typical results of the temperature dependence of the conductivity of both liquid and paste samples in Figure S1. Variation of the electric conductivity with temperature indicated the Arrhenius-type or VTF equation-type dependency. The dependence of activation energy on the molar fraction of DME at each liquid content were shown in Fig. 2. It was confirmed that the activation energy decreased with an increase of DME content at the bulk state or φ ≥ 20 vol%. However, as LiCoO₂ powder was added and reached
the vicinity of 1800 cm$^{-1}$ of C=O with solvation is observed in similar manner. Therefore the variation moiety exists in both PC and DME unfortunately and the band shift stretching band of DME molecules by FT-IR. But the PC1 solution coexisting systems. Liquid content: 5–100 vol%. It is reasonable to conclude that the viscosity of the solution rose by the interaction between DME and the solid phase. For the resemble case of the measurement of $^1$H NMR for SiO$_2$/LiClO$_4$-PC$_{1-x}$DME$_x$ coexistent system, local viscosity of DME is more susceptible to solid than PC. Variation of $\Delta E_a$ with the liquid fraction for LiCoO$_2$/1 mol L$^{-1}$ LiClO$_4$-PC and LiCoO$_2$/1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ coexistence systems were shown Fig. S2.

It is reasonable to confirm the solvation state of –C=O–C– stretching band of DME molecules by FT-IR. But the –C=O–C– moiety exists in both PC and DME unfortunately and the band shift with solvation is observed in similar manner. Therefore the variation of C=O band existing in PC molecules only was discussed. The C=O stretching band of PC has a strong IR absorption peak in the vicinity of 1800 cm$^{-1}$ and is known to shift to the low wave number side by coordination to Li$^+$ ion.$^{11,12}$ FT-IR spectra of C=O stretching band of PC in 0–1 mol L$^{-1}$ LiClO$_4$-PC and 1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ are shown in Fig. S3. Each measured spectrum is deconvoluted using Volgt curves assigned coordinated and uncoordinated C=O stretching bands of PC molecule as shown in Fig. S3. At first, the results in the PC solvation and DME solvent effect for LiClO$_4$ solution in bulk solution and paste sample are compared in Fig. 3(a) and 3(b). As an increase of LiClO$_4$ concentration, whereas the peak shoulder caused by the absorption band at around 1790 and 1815 cm$^{-1}$ assigned to uncoordinated PC decreased, the intensity of the absorption band at 1760 cm$^{-1}$ assigned to coordinated PC increased as indicated in Table S1. It means that PC solvation was promoted in an increase of LiClO$_4$ concentration in both cases. Moreover, an increase of DME fraction in PC-DME binary solvent in 1 mol L$^{-1}$ LiClO$_4$ solution causes an increase of an absorption band at 1790 and 1815 cm$^{-1}$ in bulk system due to an increase of coordinated PC by Li coordination to DME. As reported by Matsuda et al.,$^4$ DME was considered to preferentially solvate because it has higher donor number than PC. On the other hand, the data in the liquid content is only 5 vol%, an influence of liquid phase must be observed. As DME content increases in a binary solvent in LiClO$_4$ solution, the relative intensity of the coordinated PC peak at 1760 cm$^{-1}$ further increased. From these results, in the LiCoO$_2$/1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ coexisting system, as DME interacted with the solid and solvation of Li$^+$ was predominantly proceeded to PC molecules. For the system using 3 mol L$^{-1}$ electrolyte solution, a decrease of intensity of the absorption band at 1760 cm$^{-1}$ due to PC desolvation is significant and is not impaired by the coexistence of DME in both cases as shown in Fig. S4. It is suggested that an increase of LiClO$_4$ concentration causes the decrease of interaction between DME and solid phase due to the stabilizing the DME solvation of Li$^+$ ion.

The effect of DME fraction for the electrical conductivity in various concentration of LiClO$_4$-PC$_{1-x}$DME$_x$ solution coexisting with LiCoO$_2$ powder was shown in Fig. 4. Because of a relative

![Figure 1](image1.png)

**Figure 1.** Dependence of electrical conductivities on DME content in PC-DME binary solvent for LiCoO$_2$/1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ solution coexisting systems at 25°C. Liquid content: 5–100 vol%.

![Figure 2](image2.png)

**Figure 2.** Variations of activation energy with DME content in PC-DME solvent for LiCoO$_2$/1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ solution coexisting systems. Liquid content: 5–100 vol%.

![Figure 3](image3.png)

**Figure 3.** FTIR spectra of C=O stretching band of PC in (a) 0–1 mol L$^{-1}$ LiClO$_4$-PC and 1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ solution, (b) LiCoO$_2$/0–1 mol L$^{-1}$ LiClO$_4$-PC and LiCoO$_2$/1 mol L$^{-1}$ LiClO$_4$-PC$_{1-x}$DME$_x$ coexistence systems. Liquid content: $\varphi = 5$ vol% for (b). Detector: MCT. Accumulation number: 256 times.
decrease of the influence of the solid phase in highly concentrated solution, the electrical conductivity increases with the DME content in binary solvent. The maximum point of conductivity shifted to higher DME content with the increase in the concentration of LiClO₄. Electrical conductivities with various DME content in solvent for 1–3 mol L⁻¹ LiClO₄-PC₁−ₓDMEₓ solution coexisting systems at 25°C. Liquid content: φ = 5 vol%.

4. Conclusions

The maximum point of conductivity in 1 mol⁻¹ LiClO₄/PC-DME solution observed at ca. 1:1 of volume fraction shifted toward lower content of DME and finally, the increase of electrical conductivity was not observed with an increase of DME content in the liquid content in 7.5 vol%.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00044.

References

1. K. Xu, Chem. Rev., 104, 4303 (2004).
2. D. M. Seo, S. Reiningter, M. Kutcher, K. Redmond, W. B. Euler, and B. L. Lucht, J. Phys. Chem. C, 119, 14038 (2015).
3. Y. Matsuda, M. Morita, and F. Tachiba, Bull. Chem. Soc. Jpn., 59, 1967 (1986).
4. Y. Matsuda, H. Nakashima, M. Morita, and Y. Takasu, J. Electrochem. Soc., 128, 2552 (1981).
5. H. Maki, M. Takemoto, R. Sogawa, and M. Mizuhata, Colloids Surf., A, 562, 270 (2019).
6. M. Mizuhata, G. Cha, Y. Harada, H. Kimura, A. Kajinami, and S. Deki, Proc. of Intl. Symp. on Lithium Batteries, PV99-25, pp. 463–470, The Electrical Society, Inc. (1999).
7. S. Deki, M. Mizuhata, S. Nakamura, K. Nakamura, A. Kajinami, and Y. Kanaji, J. Electrochem. Soc., 139, 996 (1992).
8. S. Deki, M. Mizuhata, S. Rakuno, A. Kajinami, and Y. Kanaji, J. Colloid Interface Sci., 168, 198 (1994).
9. N. Kunikata and M. Mizuhata, to be published.
10. M. Takemoto, H. Maki, M. Matsui, and M. Mizuhata, ECS Trans., 80, 1381 (2017).
11. J. Wang, Y. Wu, X. Xuan, and H. Wang, Spectrochim. Acta, Part A, 58, 2097 (2002).
12. M. Chapman, O. Borodin, T. Yoon, C. C. Nguyen, and B. L. Lucht, J. Phys. Chem. C, 121, 2135 (2017).