

Transport properties of non-aqueous lithium electrolyte coexisting with porous solid materials Montmorillonite-based electrolyte composite system

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Abstract

In order to discuss the hetero-phase effect of the coexisting solid phase on the ionic conduction in non-aqueous lithium electrolyte solution, the conductivity and transport number of ionic species in non-aqueous lithium perchlorate solution/montmorillonite clay composite system were measured using Hittorf's cell. Transport number of lithium ion rapidly increased as the clay content increased, while total conductivity gradually decreased. The calculated ionic mobility of lithium ion was constant in the liquid content range of 75–90 vol.%. The activation energy of the conductivity for both ions separately obtained from the temperature dependence of the ionic mobilities. The activation energy of lithium ion was ca. 10 kJ mol^{-1} and extremely lower than anion species. It is proved that the lithium ion transfer is promoted by the cation exchange materials using inorganic clay materials. It is suggested that the lithium ions can transfer through the inside of clay structure and anion transfer is hindered by the repulsion between anion species and clay skeleton structure.

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1. Introduction

The non-aqueous lithium electrolyte solution is a key material for the development of the secondary lithium batteries. The transport number of lithium ion has been focused because the mobility of the lithium ion in the electrolyte is the important factor of the distribution of the lithium electrolyte in the cell and the reaction rate on the electrodes in the lithium batteries. The electrolyte solution is usually supported by a separator made of fibrous or porous membranous materials between the active materials for the electrodes and most part of the electrolyte penetrated into the porous site of the separator. On the other hand, in order to improve the lithium ion transfer, numerous studies for the single ion conductors have been developed and various materials such as complex organic polymer gel [1–4], polysiloxane composite [5,6], clay minerals [7,8]. These materials are promising one to use as

lithium conductor for secondary batteries. However, even in these valuable studies, there is little research for the ionic mobility and transport number of each ionic species contained in the electrolyte because of these materials are considered and believed as “single-ion conductor” without confirmation of transport properties and the interaction and influence of the solid phase are rarely considered.

We have been studying the properties and behaviour of the lithium electrolyte solution coexisting with porous solid materials [9–12]. Previously, we established the measurement of transport number of ionic species in lithium electrolyte solution using Hittorf's cell [11,12]. The transport number of Li^+ decreases with a decrease of the liquid content for $\alpha\text{-Al}_2\text{O}_3$ powder/ $\text{LiClO}_4\text{-PC}$ solution coexisting system. Additionally, for the system using cation-exchange membrane, the ionic mobility of lithium increased due to hindrance effect to the anionic species and its back-diffusion.

In this study, we measured the transport number of Li^+ and ClO_4^- ions, and the ionic mobilities of each ion for $\text{LiClO}_4\text{-GBL}$ and $\text{LiClO}_4\text{-EC/DEC}$ solution coexisting with

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montmorillonite clay as porous solid materials and α -Al₂O₃ powder as a reference solid sample. The effect of ion exchangeable materials for ionic mobility is discussed.

2. Experimental

Natural montmorillonite (Nacalai Tesque Inc.) was treated by acid and lithium hydroxide in order to prepare the Li-montmorillonite clay as the solid phase. The original montmorillonite was immersed and stirred in 0.1 M aqueous HCl solution for 12 h and sequentially in aqueous 0.1 M LiOH or LiCl solution for 12 h. After three times of treatment of HCl and LiOH or LiCl solutions, montmorillonite has an exchangeable lithium ion, which determined by acid–base titration method and ICP quantitative analysis with SII SPS1500VR. The insertion of lithium ion was confirmed by Rigaku TTR X-ray diffractometer. As reference sample, α -Al₂O₃ powder UA-5105 gifted from Showa Denko K.K. was used which dried by calcining at 500 °C for 4 h in vacuum. The surface area of these samples was measured by BET surface area analyser Quantachrome NOVA-1000. The clay materials should be dehydrated thoroughly due to utilisation for component of non-aqueous electrolyte composite. Obtained clay was heated at 250 °C for 24 h in vacuo. The remained water in the clay sample was less than 75 ppm, which analysed by Karl Fischer titration with Mitsubishi Moisturemeter KF-07. Properties of these powders are shown in Table 1.

As the liquid electrolyte solution, LiClO₄–EC/DEC solution was used. EC and DEC solvents purchased from Nacalai Tesque Inc. were dehydrated with molecular sieves 4 Å prior to use. EC and DEC were mixed with 1:1 mol%. LiClO₄ was dried at 170 °C in vacuum for 12 h and saturated in each solvent. The concentration was determined by ICP quantitative analysis and diluted to 0.1 M.

The electrolyte and porous solid materials are mixed in a mortar in dry chamber in which dew point below –50 °C and kept in the sample chamber used for measurement of transport number.

We used Hittorf's type cell for measurement of conductivity, transport number of ionic species. The schematic drawing of the cell is shown in Fig. 1. During the measurement of the transport number using the Hittorf's cell, the composition change of the middle chamber should be avoided. At first, the powder was thoroughly mixed with the lithium electrolyte solution and put into the glass tube used as the middle

chamber with the filter at the one side end of tube, and the electrolyte solution was passed through the glass tube by the suction pump in the dry box. After the bubble from the void disappeared, the both electrode chambers were attached to the middle chamber with the filter. The volume fraction of the liquid phase; ϕ_1 , was calculated by the following equation:

$$\phi_1 = \frac{v_1}{w_s/d_s + v_1} \quad (1)$$

where v_1 , w_s , and d_s are the volume of the liquid phase, the weight of the solid phase (clay or alumina), and the density of the solid phase, respectively. The liquid content in the clay/electrolyte composite ranged from 70 to 90 vol.%.

In the Hittorf's cell, Ni wire was used as the cathode where the electrically reduced Li metal deposited and Li foil was used as the anode. The composite sample was kept into the middle chamber. The galvanostatic electrolysis was carried out for 2 h at 1 mA current with a potentiogalvanostat (Hokuto Denko HABF501). After the electrolysis, deposited Li metal on the cathode; i.e. Ni wire, and solution in the cathodic chamber and solution in the anodic chamber were collected and determined the concentrations of Li⁺ and ClO₄[–] ions by the ICP quantitative analyser and a liquid chromatogram JASCO Gulliver 1500 with anion exchange column Shodex IC I-524A. The water content of electrolyte solutions was verified to less than 70 ppm by Karl Fischer titration.

The transport number of the lithium was calculated from the following equation:

$$t_{\text{Li}^+} = 1 - \frac{(C_S - C_E)VM}{w} \quad (2)$$

where, C_S , C_E , V , M , and w are the variation of molar concentration for lithium ion in cathode cell, the volume of the electrolyte solution in the cathodic chamber, a molecular weight of the lithium, and a weight of lithium deposition on nickel wire, respectively. Obtained value is based on the results of the mass balance of cationic species; i.e., lithium, in the cathodic chamber only. The mass balances in the anodic chamber and anionic species; i.e., ClO₄[–], were measured in the similar method for the confirmation in the several measurements.

The potential probe was set between anode chamber and cathode chamber and the electrical conductivity was measured by four probe electric measurement. The potential difference was obtained with the potential probes set on the middle chamber by a digital electrometer TR8652 (Advantest Co. Ltd.). The resistance, R , and conductivity, σ , were calculated from the I – V characteristics of the electrolyte solution at 1–7 mA of the electrolytic current. Since the stable linear relationship was obtained during electrolysis for each system, the conductivity, σ , is calculated from the equation; $\sigma = C_{\text{cell}}/R$. Here, C_{cell} is the cell constant obtained from the result of conductivity for 1.0 mol l^{–1} KCl aqueous solution system.

Table 1
Properties of used clay and α -Al₂O₃ powder sample

Nature	Montmorillonite		α -Al ₂ O ₃
	LiOH ^a	LiCl ^a	
Density (g cm ^{–3})	2.29	2.64	3.88
Specific surface area (m ² g ^{–1})	86.6	113	10.0
Mean particle size (μm)	2–3	2–3	0.3
Cation exchange capacity (meq g ^{–1})	0.81	0.28	0.0

^a Treatment.

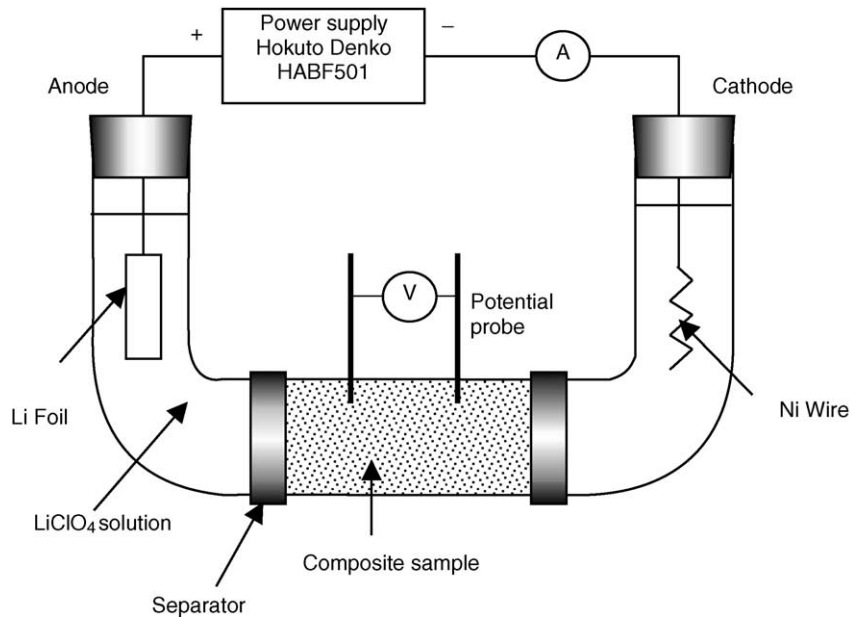


Fig. 1. Schematic drawing of the Hittorf's cell with the potential probes for the measurement of the transport number and ionic mobilities of lithium electrolyte solution.

Apparent ionic motilities, u , were calculated from these results as follows:

$$\text{for cation : } u_+ = \frac{t_+ \Lambda}{z_+ F} \quad (3a)$$

$$\text{for anion : } u_- = \frac{t_- \Lambda}{z_- F} \quad (3b)$$

where Λ , z , and F are equivalent electrical conductivity, valence of ion, and Faraday constant. The activation energies of conductivity and ionic mobility were calculated from Arrhenius-type temperature dependence.

3. Results and discussion

3.1. Transport numbers and ionic mobility of ionic species coexisting with clay and oxide powder

The variations of transport number of Li^+ ion with liquid content for the system containing clay or $\alpha\text{-Al}_2\text{O}_3$ powder and 0.1 M $\text{LiClO}_4/\text{EC-DEC}$ solution are shown in Fig. 2. The value of t_{Li^+} increases with a decrease of the liquid phase, which means the mixing with the clay, whereas the value of t_{Li^+} decreases as the liquid content decreases for the system containing $\alpha\text{-Al}_2\text{O}_3$ powder for which the electrostatic interaction between lithium ion and surface area of alumina with negative charge. As shown in Table 2, the amount of conductive species (Li^+ ion) depends on the ratio of clay/electrolyte solution. A decrease of the liquid content causes an increase of the ratio of mobile cations to the anions, and therefore the Li^+ transport number increases. Although Li^+ content in clay is 89.1% of total amount of Li^+ in the case of the sample with 75 vol.% of liquid content, the transport number of lithium

ion reached to ca. 0.95 such as single ion conductor [7,8]. It is suggested that the lithium ion can transfer through the interlayer of montmorillonite and contributes to the conduction path of ionic species. Using montmorillonite in which lithium ion interlayered by LiCl solution, the content of lithium ion is much lower than the other sample, which is prepared by LiOH . However, the transport number is sufficiently high to obtain the effect of ion-exchangeable clay up to 0.94. It is suggested that not only the lithium ion transfer is promoted by

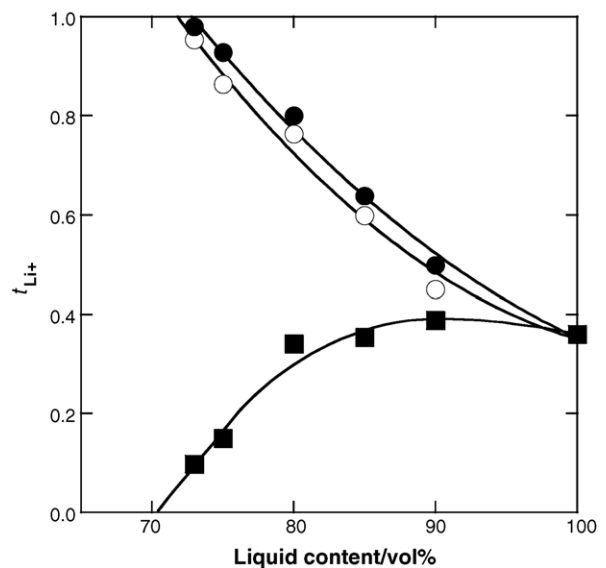


Fig. 2. Variations of transport number of Li^+ ion with the liquid content for the system containing montmorillonite or $\alpha\text{-Al}_2\text{O}_3$ powder and 0.1 M $\text{LiClO}_4\text{-EC/DEC}$ solution at 30 °C. Solid phase: (●) montmorillonite (Li^+ : 0.81 meq g^{-1}), (○) montmorillonite (Li^+ : 0.28 meq g^{-1}), and (■) $\alpha\text{-Al}_2\text{O}_3$ powder.

Table 2

Concentration for Li^+ contained in clay in middle chamber (volume: 10 ml) and the ratio of Li^+ ion existing in montmorillonite clay to total amount of Li^+ ion in the middle chamber

Liquid content (vol.%)	Treatment solution			
	LiOH (0.81 ^a)		LiCl (0.28 ^a)	
	$[\text{Li}^+]_{\text{clay}}$ (mmol)	$\text{Li}_{\text{clay}}/\text{Li}_{\text{total}}$	$[\text{Li}^+]_{\text{clay}}$ (mmol)	$\text{Li}_{\text{clay}}/\text{Li}_{\text{total}}$
90	2.05	0.695	0.82	0.476
85	3.25	0.793	1.31	0.606
80	4.61	0.852	1.86	0.699
75	6.14	0.891	2.47	0.767

^a Cation exchange capacity (meq g^{-1}).

the increase of concentration of lithium ion by ion-exchange in clay also electrostatic repulsion between clay and anion species.

The electrical conductivity of the coexisting system containing LiClO_4 electrolyte and montmorillonite or $\alpha\text{-Al}_2\text{O}_3$ powder is shown in Fig. 3. The value of electrical conductivity depends on the concentration of carrier and the morphology of the conduction path of the ionic species according to our previous studies [13,14]. In this case, since there is a difference in the specific surface area and the figure of the particles between the alumina sample and clay, it is not possible to simply compare between the results of both systems. However, the conductivities for the system using clay and alumina are comparable. The conductivity of the system containing montmorillonite treated by LiOH was similar as that of the system containing $\alpha\text{-Al}_2\text{O}_3$ powder. The effect of ion-exchange reagent; LiOH and LiCl on the conductivity is obviously observed at the liquid content

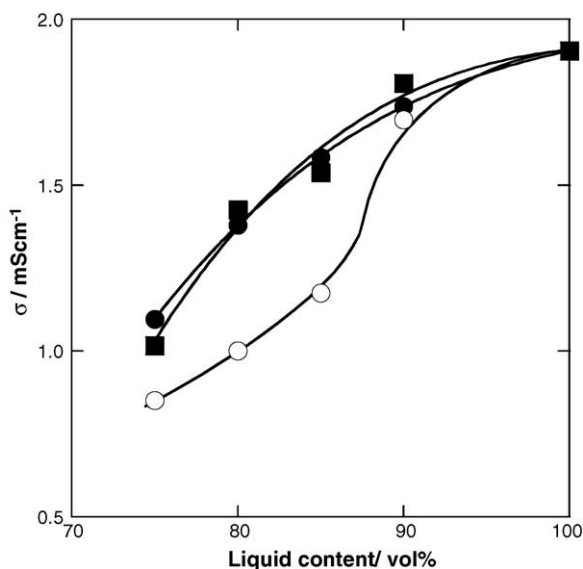


Fig. 3. Variations of electrical conductivity of the coexisting system containing montmorillonite or $\alpha\text{-Al}_2\text{O}_3$ powder and 0.1 M $\text{LiClO}_4\text{-EC/DEC}$ solution at 30 °C. Solid phase: (●) montmorillonite (Li^+ : 0.81 meq g^{-1}), (○) montmorillonite (Li^+ : 0.28 meq g^{-1}), and (■) $\alpha\text{-Al}_2\text{O}_3$ powder.

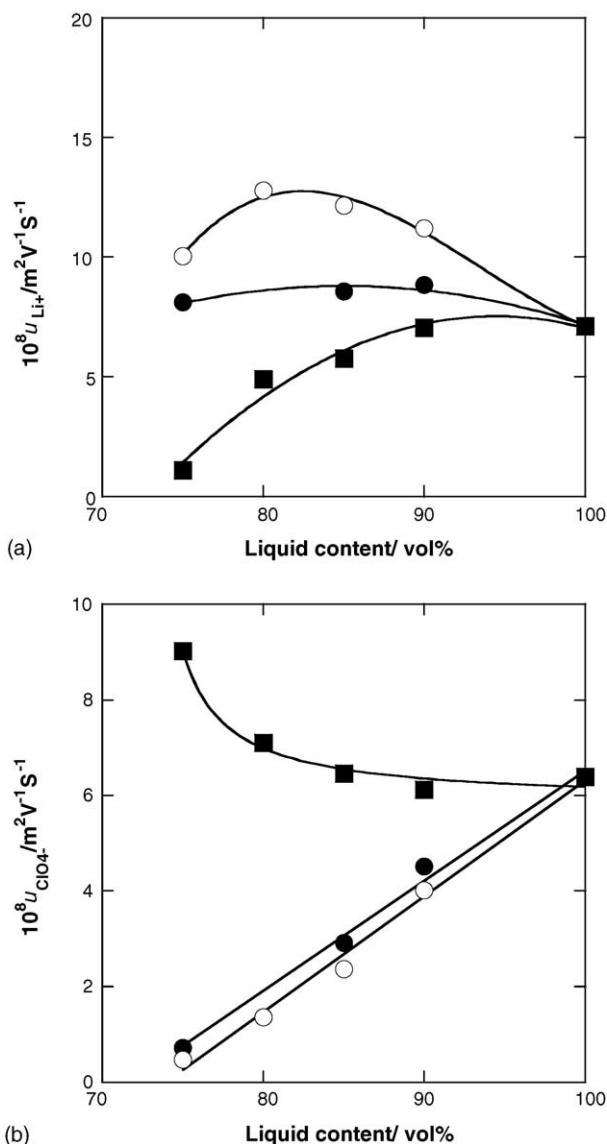


Fig. 4. Ionic mobilities of (a) Li^+ and (b) ClO_4^- ion in the system containing montmorillonite or $\alpha\text{-Al}_2\text{O}_3$ powder and 0.1 M $\text{LiClO}_4\text{-EC/DEC}$ solution at 30 °C. Solid phase: (●) montmorillonite (Li^+ : 0.81 meq g^{-1}), (○) montmorillonite (Li^+ : 0.28 meq g^{-1}), and (■) $\alpha\text{-Al}_2\text{O}_3$ powder.

range of less than 75 vol.%, at which the transport number of Li^+ ion rapidly increased and the ionic conduction might be promoted by the cationic conduction path in the layered structure.

The apparent ionic mobilities; u_{Li^+} , and $u_{\text{ClO}_4^-}$ calculated from Eq. [3] is shown in Fig. 4. It is noteworthy that the ionic mobility of Li^+ ion does not decrease with a decrease of the liquid phase and keep the value at ca. $7 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. For the system using montmorillonite treated by LiOH, the ionic mobility reached to the mostly twice values of the bulk system; $1.3 \times 10^7 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. On the other hand, the ionic mobility of ClO_4^- decreased with a decrease of the liquid content for the system containing montmorillonite. Also, there is little difference in the results between the systems using LiOH and LiCl for the treatment of montmorillonite.

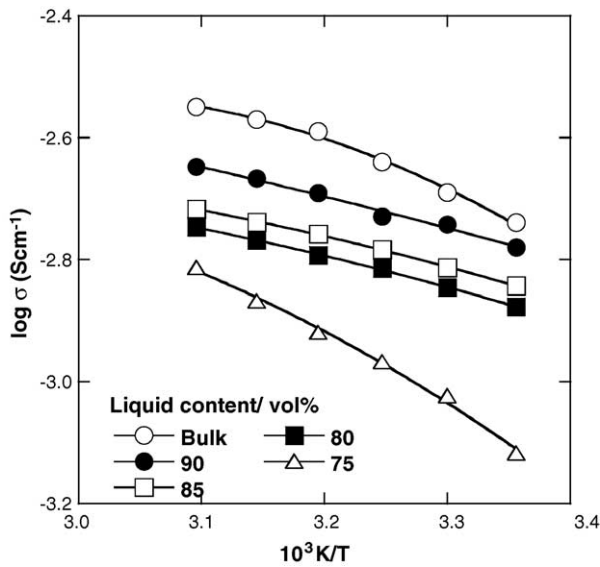


Fig. 5. Temperature dependence of the electrical conductivity of the system containing montmorillonite treated by LiOH (Li^+ : 0.81 meq g^{-1}) and 0.1 M LiClO_4 -EC/DEC solution.

It is suggested that the anionic transport rarely depends on the ion-exchange capacity of the clay, due to electrostatic repulsion force. Therefore, the composition dependence of the ionic conduction varies with the ionic mobilities of each ionic species, which independently varied with the liquid content.

3.2. Temperature dependence and the activation energy of the ionic species

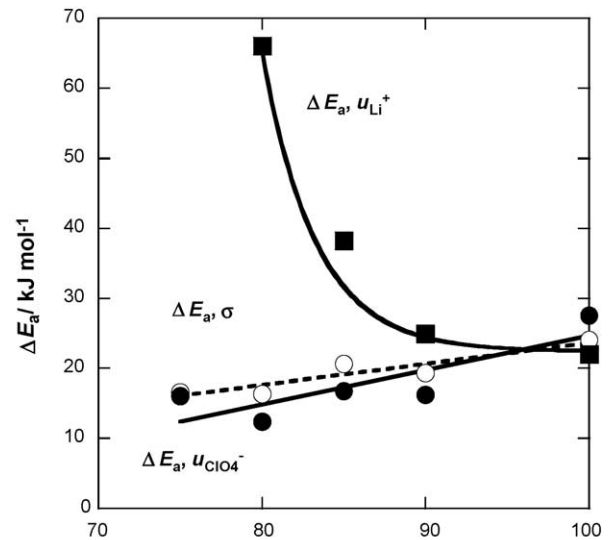
The activation energy of ionic conduction has been investigated as the ion-ion and ion-solvent interactions in electrolyte solution in solution chemistry for long period. The conductive behaviour has been also interpreted using the activation energy of conductivity as the parameter showing an influence of the surrounding materials with free volume theory using VTF or WLF type temperature dependence in the system of concentrated solution [15], lithium conductive electrolyte [16], and lithium polymer composite [17–19]. Especially, for the system of lithium electrolyte composite, the activation energy of the conduction is intensively correlated to the structural and thermochemical properties of the matrix electrolyte.

As shown in Fig. 5, the temperature dependence of electrical conductivity for the system containing montmorillonite treated by LiOH and LiClO_4 -EC/DEC solution indicated the VTF-type relationship defined as Eq. (4a). It is shown that the gradient in $\log \sigma - 1/T$ plots is not constant. Therefore, the activation energy in VTF equation is regarded as a temperature depending parameter [15,20]. The value of the activation energy of the conductivity, ΔE_a , can be calculated from the differential coefficient of the plots at 30°C .

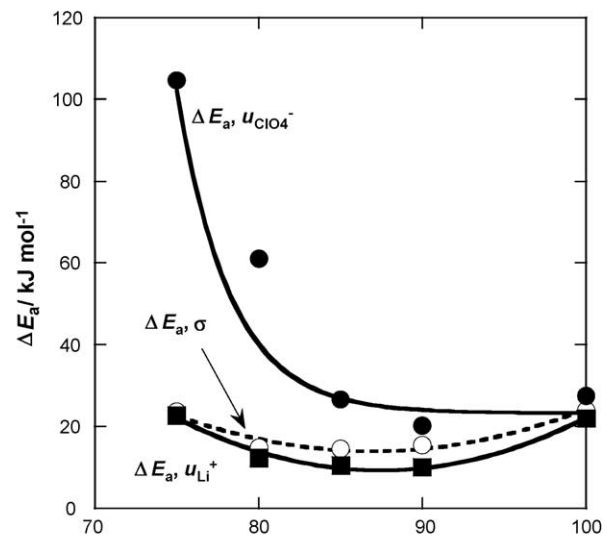
$$\sigma = AT^{-1/2} \exp[-B(T - T_0)] \quad (4a)$$

$$\begin{aligned} \Delta E_a(T)_{T=30^\circ\text{C}} &= -R \left[\frac{d(\log \sigma)}{d(1/T)} \right]_{T=30^\circ\text{C}} \\ &= -\frac{T}{2} - B \left[\frac{T}{T - T_0} \right]^2 \end{aligned} \quad (4b)$$

where R , A , B , and T_0 are a gas constant, a pre-exponential constant, a constant, and an ideal temperature at which the conductivity reached to zero. Since the ionic mobilities of both ionic species of Li^+ and ClO_4^- are obtained at the each temperature, the apparent activation energy of the ionic species, $\Delta E_{a,\text{Li}^+}$ and $\Delta E_{a,\text{ClO}_4^-}$ are also calculated in similar manner. Variations of the activation energy of the electrical



(a)



(b)

Fig. 6. Variations of the activation energy of the electrical conductivity and ionic mobilities of Li^+ and ClO_4^- ions with the liquid content coexisting with montmorillonite and $\alpha\text{-Al}_2\text{O}_3$ powder. Solid phase: (a) $\alpha\text{-Al}_2\text{O}_3$ powder, (b) montmorillonite treated by LiOH (Li^+ : 0.81 meq g^{-1}).

conductivity and ionic mobilities of Li^+ and ClO_4^- ions with the liquid content coexisting with clay or $\alpha\text{-Al}_2\text{O}_3$ powder are shown in Fig. 6. The difference of the solid phase effect is obviously indicated. In the clay system using montmorillonite treated by LiOH in which the apparent ionic mobility of Li^+ ion was kept in high value even coexisting with solid phase, the activation energy of lithium conduction is lower than that of ClO_4^- ion. Also the value of $\Delta E_{a,\text{Li}^+}$ is closed to that of whole conduction, $\Delta E_{a,\sigma}$, and reached to ca. 10 kJ mol^{-1} . It is suggested that the cationic conduction mechanism in the composite rarely vary with a content of the electrolyte solution. As shown in Fig. 2, the transport number of Li^+ ion reached to unity at the liquid content of 80 vol.%. It is suggested that the ionic conduction of lithium ion are dominant in lithium electrolyte solution/montmorillonite clay composite, because of the transport in the interlayer of the clay structure. On the other hand, in the system containing $\alpha\text{-Al}_2\text{O}_3$ powder, the activation energy of the conductivity of lithium ion rapidly increased, whereas that of ClO_4^- ion gradually decreased as the liquid content decreased. In this system, since the major carrier is ClO_4^- as shown in Fig. 2, the conduction of lithium ion does not contribute to the total conductivity. As the result of the electrostatic interaction between cation and alumina, the activation energy of Li^+ ion increased.

4. Conclusions

The conductivity and transport number of ionic species in $\text{LiClO}_4\text{-EC/DEC}$ solution/montmorillonite clay composite system were measured using Hittorf's cell. The transport number of lithium ion rapidly increased and reach to unity as the clay content increased, while total conductivity gradually decreased. The calculated ionic mobility of lithium ion was constant in the liquid content range of 75–90 vol.%. The activation energy of ionic conduction for both ions separately obtained from the temperature dependence of the ionic mobilities. The activation energy of lithium ion is ca. 10 kJ mol^{-1} and extremely lower than anion species. The lithium ions can transfer through the interlayer of clay structure and anion transfer is hindered by the repulsion between anion species and clay skeleton structure. Consequently, the lithium ion transfer is promoted by the cation exchange materials using inorganic clay materials.

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