(1)

JSCS

13th April-2008

Dr. Iqbal M.I. Ismail
Department of Chemistry
King Abdulaziz University
P.O.Box-80203, Jeddah-21589
Kingdom of Saudi Arabia

MANUSCRIPT NO. : **0-030528-37**

TITLE: ***"Property of interface at lithium anode in contact with network polyether free chain end polymer electrolytes ".***

Dear Author(s)

The above mentioned manuscript ***has been accepted*** for Publiction in Journal of Saudi Chemical Society, Volume-**12** (1), pp .... (April – 2008).

Sincerely Yours

17/4/1429H

Prof. Hassan M.Al-Hazimi
J. Saudi Chemical Society
(Editor-in-chief)
Department of Chemistry
King Saud University
P.O.Box 2455, Riyadh-11451
Saudi Arabia
e.mail : hhazimi@Ksu.Edu.Sa

الملخص العربى

تضمن هذا البحث تحضير إلكتروليتات البوليمرات الشبكية الحاوية على سلاسل من النهايات الحرة وذلك بواسطة تفاعلات الإتحاد البيني الضوئي في وجود أملاح الليثيوم. نوعان من أملاح الليثيوم من حيث الثبات الحراري وذلك لاستطلاع المشاركات المختلفة المؤثرة على سطح التلامس بين القطب والإلكتروليت. ولقد أوضحت النتائج أن البوليمرات الشبكية احتوت على خليط من البوليمرات المشاركة من كل من أحادي وثلاثي الأكريليت المشكلة من أكسيد الإيثيلين وأكسيد البروبيلين, حيث أمكن التحكم في عدد سلاسل النهايات الحرة طبقاً لنسبة أحادي الأكريليت في المخلوط. أمكن دراسة تأثير سلاسل النهايات الحرة على الخواص الحرارية والتوصيل الكهربي الأيوني على السلوك التلامسي على قطب الليثيوم. أوضحت النتائج بأنّه في حال استخدام ملح **LiTFSI** في الالكتروليت المبلمر فإن مقلوب مقاومة التلامس المعتمد على التيار التبادلي يتناسب إلى حدٍ ما طردياً مع تركيز الملح. أوضحت الدراسة أيضاً بأنّ قيمة مقلوب مقاومة التلامس تتناقص مع زيادة سلاسل النهايات الحرة في شبكة البوليمر ، مما يوضح بأنّ عمليات ذوبانية/اتحاد الملح تتحفز بشكل كبير مع الحركة التعاونية للأيون/البوليمر. وبناءً على ذلك فإنّ نتائج المشاهدة على طبقة التلامس في سطح المعدن تعكس شيئاً من التراجع في حالة خليط البوليمر مع ملح $\mathbf{LiBF_4}$ نتيجة لعدم ثباتية هذا الملح الأمر الذي يعزز إمكانية تكون طبقة صلبة من الإلكتروليت الصلب عند نقطة التلامس.

Property of Interface at Lithium Anode in Contact with Network Polyether Free- Chain End Polymer Electrolytes

Iqbal I. Ismail

Department of Chemistry, Faculty of Science, King Abdul Aziz University,

P.O. Box 80203,

Jeddah 21589, Saudi Arabia.

Abstract

The network polymer electrolytes having various numbers of free-chain ends were critically photo-cross linked in the presence of two lithium salts namely; lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and lithium tetrafluoroborate ($LiBF_4$) have been critically investigated. Polymer network composed of mixtures of mono-acrylated (MA) and tri-acrylated (TA) copolymers of ethylene oxide and propylene oxide and the number of free-chain ends are controlled by the MA composition. The influence of the free-chain ends on the thermal property, ionic conductivity and interfacial characteristics at the lithium electrode has been discussed. In terms of thermal stability, two different types of lithium salts have been used properly to explore various contributions at electrolyte/lithium anode interface. The data revealed that, the salt LiTFSI is more stable than $LiBF_4$. The dependence of the salt concentration for the inverse of interfacial resistance (R_i), corresponding to the exchange current showed direct relationship. The R_i values of the polymer electrolyte containing LiTFSI decreased on increasing the number of free-chain ends, indicating that the dissolution/deposition process is directly accelerated by ion/polymer cooperative motion. In the $LiBF_4$/polymer mixtures at the lithium electrode interface are considered to be restrained due to the salt instability and the formation of solid electrolyte passivation layer.

Keywords: Electrical Behavior, Lithium Electrode Interface, Network Polymer Electrolyte.

Email: iismail@kau.edu.sa

1. Introduction

Recent years have seen an upsurge of interest on the investigation of interfacial phenomena using numerous techniques [1]. The majority of these efforts have been devoted to have better understanding of the chemical composition, the structure of the film, and the reported models at the lithium metal-electrolyte interface [1, 2]. The practical use of secondary Li-metal batteries is limited by the poor charge-discharge cycling efficiency and the safety problem. This recharge ability problem of the lithium metal anode batteries is correlated with the interfacial condition between a Li-metal anode and an organic electrolyte.

Most of the interfacial investigations available in the literature, involved electrochemistry and/or surface morphology studies employing lithium anode immersed in liquid aprotic solvents. However, the diagnoses at electrode/solid polymer electrolyte interfacial behavior have so far been quite limited. On the other hand, the application of polymer electrolytes to secondary lithium battery has many advantages upon liquid solvents; therefore, a better understanding at the electrode/electrolyte contact for improving the cell recharge ability represents an urgent demand. Watanabe group [3-5] has developed the polymer electrolytes having ether side chains in order to substantiate the concept of coupling of fast ionic transport and molecular motion of flexible ether side chains. The work of Kono et al. [6] has indicated that charge transfer resistance (R_{ct}) at the interface between a lithium electrode and a polymer electrolyte correlates with the dynamics of the chains in the matrix network polymer. Therefore, the molecular dynamics on interfacial resistance using polyether-based network polymer electrolytes having many free ether chain ends will be discussed in the this investigation. Thus, the network polymers having different numbers of free-chain ends will be prepared by photo-cross-linking reaction of mono-acrylated (MA) and tri-acrylated (TA) copolymer of ethylene oxide and propylene oxide as reported earlier [7]. The influence of the network polymers incorporating LiTFSI and $LiBF_4$ on the ionic conductivity (σ) and the interfacial resistance (R_i) at the interfaces between lithium electrodes and polymer electrolytes will be discussed. The concept of the coupling of fast ionic transport and fast side-chain motion on both σ and R_i will also explored.

2. Experimental

2.1. Reagents and materials:

Network polymer electrolytes having MA/TA weight ratios from 0/10 to 8/2 (total weight of MA+TA=1.0 g) together with lithium salt were prepared inside argon filled glove box (VAC, [O_2], [H_2O] <1 ppm). Proper amounts of MA, TA (produced by Dai-ichi Kogyo Seiyaku Co.) and LiTFSI (supplied by IREQ, dried at 180^{o}C under reduced pressure for 24 hours) were used. Alternatively, $LiBF_4$, (Tomiyama Chemicals, battery grade), and 2, 2-dimethoxy-2-phenyl acetophenone (Ciba Geigy, 0.05 wt% based on macro monomers) as photo initiator were dissolved in dehydrated acetonitrile (Kanto Chemical Co. Inc.) to form a homogeneous viscous solution. The viscous solution was spread between two glass plates separated by polytetrafluoroethylene spacer of 500 μm and were irradiated with UV light (250 W high pressure Hg lamp, UI-501C USHIO Electric Inc.) for 5 minutes. At room temperature, the excess of acetonitrile was removed under reduced pressure to obtain transparent and flexible polymer electrolyte films with good mechanical strength. For bulk and interfacial resistance measurements, polymer electrolyte film was cut into disk of 13 mm diameter and sandwiched between two symmetrical lithium electrodes (Honjo Metal Co.) of 200 μm thick. Finally, the whole was placed in a sealed cell and placed in a temperature controlled chamber.

2.1. Apparatus:

Differential scanning calorimetric measurements were carried out on a Seiko Instruments (DSC-220C) under nitrogen atmosphere. Impedance measurements were recorded on an AC impedance analyzer (Hewlett Packard 4192A) in the frequency range 5 - 13 MHz at 1.0 V amplitude.

3. Results and discussion

3.1. Interfacial Characteristic:

Fig. 1 shows the glass transition temperature (T_g) of network polymers complexed with lithium salts as a function of MA composition. On increasing MA composition, the values of T_g decreased indicating that the change in the mechanical property, *i.e.*, the polymer electrolyte film is getting softer with increasing of free-chain ends of MA for the expense of inflexible chain ends of TA. Therefore, the free-chain ends of MA are functioning as an internal plasticizer in the network polymer. The mechanical property of the polymer electrolyte influences the contact between the lithium electrode and polymer electrolytes, and the values of R_i. The values of T_g for the polymer electrolytes containing LiTFSI showed lower value at the entire range of MA compositions compared to that contained $LiBF_4$ in good agreement with the data reported by several laboratories [8-10]. Imide anions of large size with highly delocalized electron density and flexible structure can explain the plasticizing effect in the polymer electrolyte membrane, which depresses the increase in T_g and enhances the ionic conductivity. The dependence of the values of T_g on the lithium salt concentration is shown in Fig. 2. An increase on the values of T_g with salt concentration was noticed and is most likely attributed due to the increase in ion-polymer interaction, which decreases the mobility of polymer chains and enhances the rigidity of the polymer electrolyte system.

The time dependence of ionic conductivity of Li-salt-network polymer is shown in Fig. 3. Stable conductivity values for both salts were noticed for a period of one month of measurement time. Isothermal ionic conductivity as a function of MA composition for LiTFSI and $LiBF_4$ complexed with network polymers is shown in Fig. 4(a) and 4(b), respectively. Ionic conductivity values for LiTFSI-polymer mixtures showed a slight increase with MA composition in the electrolyte systems, while in $LiBF_4$-polymer revealed no significant change in the values of the conductivity. At network polymer of MA=0.8 the values of the ionic conductivity of complexed LiTFSI, were varied from 7×10^{-5} S cm^{-1} at 30°C and 10^{-3} S cm^{-1} at 80°C. On the other hand, the values of the ionic conductivity of complexed $LiBF_4$-polymer systems, varied from 10^{-5} S cm^{-1} at 30°C and 2×10^{-4} S cm^{-1} at 80°C. Over the range of MA compositions, LiTFSI electrolyte systems showed greater tendency towards ionic conductivity than the $LiBF_4$ systems at the corresponding temperatures. The higher ionic mobility of the $TFSI^-$ compared to that of BF_4^- may account for such trend in consistent with the thermal analysis data given in Fig. 1.

The variation of R_i with MA composition for both salts at 60°C is shown in Fig. 5(a). At constant salt concentration ([Li]/[O]=0.08), the values of R_i for $LiBF_4$-polymer electrolyte systems were scattered throughout the range of MA composition. On the other hand, LiTFSI-polymer mixtures showed clear decrease in R_i on increasing the MA content up to MA ≥0.5 reflecting the effect of wetting (contact) at the interface resulting in a decrease on the values of T_g. The values of R_i first decreases at lower values of MA composition and then reached a constant value on raising the MA content at a certain critical ratio of MA/TA. The values of σ and R_i, inversely changed with MA/TA ratio range as shown in Fig. 4(a) and Fig. 5(a), respectively. Thus, the contact effect is not a dominant factor, or its significance is limited up to some extent. However, the effect of electrode/electrolyte contact on the interfacial behavior has been adopted by a number of investigators [2, 11].

The plot of the double layer capacitance, C_{dl} as an important characterizing parameter at the interface versus MA composition is shown in Fig. 5(b). The observed increase in the C_{dl} up to MA=0.5 for LiTFSI polymer systems is fit well with the change in R_i. MA composition in the network polymers. Thus *i.e.* the number of free-chain ends, may affect the double layer structure and these may also change the interfacial charge transport process. It may also be noticed that the higher C_{dl} values for LiTFSI-polymer mixtures comparing with those for $LiBF_4$-polymer mixtures indicate a better compatibility for LiTFSI salt with lithium anode.

For several MA/TA ratios, the temperature dependence of the interfacial resistance in

Arrhenius plots is presented in Fig. 6(a) and 6(b) for LiTFSI and $LiBF_4$ electrolyte systems, respectively. A constant The value of the activation energy, E_a of LiTFSI-polymer mixtures was found equal 68±2 kJ mol^{-1}, whereas in the case of $LiBF_4$-polymer mixtures the value was in the range of 71±3 kJ mol^{-1}.The value of LiTFSI-polymer mixtures was independent of MA composition.

Time dependence of interfacial resistance (R_i) for the network polymer electrolytes complexed with LiTFSI and $LiBF_4$ over the range of salt concentrations at 60°C are shown in Fig. 7(a) and 7(b), respectively. In the case of LiTFSI, the interfacial resistances was high in the beginning and decreased on passing the time to reach constant values within 50 h and the values of R_i after stabilizing are inversely proportional to the salt concentration. On the other hand, for $LiBF_4$, the values of R_i increased with time to reach the range between 700 and 1000 ohm cm^2, and remains constant for about 500 h throughout the range of salt concentration. Moreover, after about 500 h of storing time another increase in R_i values was noticed. The thermal and thermodynamic instability for $LiBF_4$ salt may enhances the decomposition behavior of $LiBF_4$ producing LiF at the interface as reported and characterized by various techniques [12-13].

Arrhenius-type behavior of R_i values for lithium salts, at various concentrations of LiTFSI and $LiBF_4$, complexed with the network polymers is shown in Fig. 8(a) and 8(b), respectively. LiTFSI salt compositions again showed almost constant E_a values (64±3 kJ mol^{-1}), but for $LiBF_4$ complexes, higher and wider range of activation energies are calculated (82±13 kJ mol^{-1}).

The reciprocal of R_i *versus* lithium salt concentration is shown in Fig. 9. In the case of LiTFSI, the reciprocal of R_i increased linearly on increasing the ratio [Li]/ [O] up to 0.05 and leveled off, whereas in the case of $LiBF_4$ it slightly decreased with the salt concentration. The dependence of R_i on the salt concentration is quite different depending on the type of the employed lithium salt. The time dependence of R_i in the case of the polymer electrolytes complexed with LiTFSI is quite stable as seen in Fig. 7(a), while for the polymer electrolytes complexed with $LiBF_4$, the R_i increased with time (Fig.

7(b)) due to the formation of the passivation layer. The change in R_i depending on MA composition in the network polymers also confirmed that, the interfacial charge transfer process is directly affected by the polymer structure in the case of LiTFSI. Therefore, one can assume here for polymer electrolytes complexed with LiTFSI, the R_i corresponds to charge transfer resistance (R_{ct}) and the reciprocal of R_i is proportional to the exchange current density. Based on this assumption; the exchange current density increases with Li^+ concentration due to the consequent increase in its activity. This observation is in contrast with the observed increase in T_g values (Fig. 2) and associated with the stiffness of the polymer electrolyte mixtures as a function of LiTFSI concentration. The increase in the exchange current accompanied with the increase in polymer electrolyte hardness indicates that the wetting property (contact problem) is hardly contributing towards charge transfer process. The increase in the exchange current is most likely assigned to the fast ionic and polymer segments motion which functions in a cooperative fashion offsetting stiffness effect due to increase in LiTFSI concentration, and hence, enhancing lithium dissolution/deposition process. This performance turns out to saturate at some extent of LiTFSI concentration. The decomposition of $LiBF_4$, and the formation of a high ratio of LiF layer may separate the anode from the polymer electrolyte membrane causing a poor contact at the interface and decreased the exchange current.

3.2. The mechanism of electrolyte/electrode interface

Charge transfer process at the lithium electrode interface has been studied by many researchers in parallel with the improvement of lithium batteries technology; however, it is still hard to consider any of the available understanding as a unique. In the last decade Kono *et al.* [6] have reviewed and discussed in details the charge-transfer process to explain the interfacial behavior, by considering three different models namely; (a) film-free lithium interface (FLI) model; (b) solid electrolyte interface (SEI) model, and finally (c) polymer electrolyte interface (PEI) model. The experimental data have failed to explain the charge-transfer process by a single model, therefore the three models, may contribute in someway or another. However, the type of salt and/or MA composition in the polymer electrolyte directly affects the degree of contribution from either of these models.

a) FLI contribution

The FLI model assumes that the charge transfer process corresponds to the lithium dissolution/deposition reaction at the film free lithium interface. The addition of external plasticizer had well showed a reduction in R_{ct} [12]. Therefore we can consider the FLI model by explaining that the internal plasticizing effect [6] of MA is influencing the dissolution/deposition process *via* faster lithium ionic motion for network polymers complexed with LiTFSI. This hypothesis is acceptable if we assume constant values of activation energies with the increase of MA composition. Dissolution/deposition process which takes place in a reversible manner according to Sequeira *et at.* [14], implies that FLI model is predominant in the charge transfer process. The activation energies estimated in this work (~65 kJ mol^{-1}) for network polymers complexed with LiTFSI was found higher than that for lithium dissolution and deposition reactions in electrolyte solutions (42 kJ mol^{-1}). Hence, in addition to FLI contribution, other factor(s) are worthy to be fully investigated in an attempt to proper assign of the charge transfer process.

b) SEI contribution

In the SEI model, the rate-determining step for the charge transfer process is associated with the ionic transport in the passivation films at lithium electrode. The passivation film is believed to be electronically highly resistive and ionically conductive electrolytes, composing inorganic salts; Li_2CO_3, LiOH, Li_2O, and LiCl or LiF, according to the incorporated salt. In fact, the type and the growth of lithium passivation layer are affected by the presence of liquid impurities, e.g., water in the polymer electrolytes [15]. However, the observed continuous increase in the time dependence of R_i and constant E_a in the case of $LiBF_4$, indicates that not only the impurity contributes in this process. Another possibility is that; certain type of lithium salts may have the tendency of directly reacting with lithium metal. At a certain [Li]/[O] and the relatively constant value of E_a in addition to the different time dependence of charge transfer interfacial processes for the two lithium salts used in this work, are not enough evidences for salt/electrode reaction.

c) PEI contribution

In the PEI model, the charge transfer process is limited by diffusion of lithium cations through a porous non-conducting polymer or organic film, which covers the surface of lithium electrode. The issue of lithium anode stability while using liquid [16], gel [17] or solid [18] polymer electrolytes has been a matter of controversy. One may expect that, polymer structure somewhat affects Li/polymer stability, but the kind of salt has significant role in the interfacial phenomena. It may be noticed that, the magnitude of the charge transfer resistance was much more sensitive with lithium salt concentration than MA composition, especially at the initial stage. High effect from lithium salt is due to either salt decomposition ($R_i \propto [LiBF_4]$) or cooperative ion-polymer motion ($R_i \propto 1/[LiTFSI]$). This implies that the change in R_i due to variation in salt content (contributing towards SEI or FLI) is much more higher comparing with the change due to MA/TA ratio (leading to the change in PEI contribution). Hence, it may be that, the contribution of PEI model is negligible while SEI contribution is apparent as in the case of $LiBF_4$.

The reactivity of polymer network when in contact with lithium foil represents another possibility to be taken into account. The formation of lithium alkoxide species when lithium metal was allowed to immerse in tetraethylene glycol dimethyl ether in the absence of any salt was reported by Lisowska-Oleksiak [19] where the interfacial resistant increased rapidly in the first period of contact before reaching a plateau in the time dependence curve. Aurbach *et al.* [20] have confirmed the formation of ethoxide as a result of reaction of ethyl glyme, $(CH_3CH_2OCH_2)_2$, at the lithium surface employing FTIR technique. Thus, the increase in MA composition, and the consequence decrease in alkoxide compounds account for the observed decrease in R_i in the case of LiTFSI electrolytes. On the other hand, in $LiBF_4$ electrolytes, the formation of insoluble LiF offsets the effect of alkoxide compounds formation, if any, *i.e.*, limits ion/polymer interactions and/or separates the polymer from being reacted with lithium metal. The fact that, the free-chain ends (MA) are expected to be more stable than the bonded ends (TA) of the polymer toward the chemical reduction of polymer by lithium metal, the extent of alkoxide compounds formation at lithium surface will be inversely proportional with MA composition.

4. Conclusion

Network polymer electrolytes having different numbers of free-chain ends were photo cross-linked in the presence of a desired salt. Thermal and electrical behavior investigations have been carried out for polymer electrolytes containing either $LiBF_4$ or LiTFSI. Constant time dependence of ionic conductivity was recorded for both salt compositions; despite that time dependence curve for interfacial resistance at the lithium electrode was not constant for polymer-$LiBF_4$ mixtures. Contributions from three types of interfacial models are discussed in detail where SEI model is most likely apparent for network polymer electrolytes complexed with $LiBF_4$. The presence of stable salts, like LiTFSI, encourages PEI model to be predominant. The inverse of R_i is proportional to the salt concentration up to [Li]/[O]=0.05 which confirms the increase of the activity of Li^+ in the network polymers.

Acknowledgement

The author would like to thank Japan Petroleum Institute for the financial support, and Prof. M. Watanabe for the facilities provided at Yokohama National University, and King Abdul Aziz University, Jeddah, Saudi Arabia for the sabbatical leave.

References:

[1] D. Golodnitsky, G. Ardel and E. Peled, *Solid State Ionics,* **85,** 231 (1996).

[2] S.E. Sloop and M.M. Lerner, *J. Electrochem. Soc.*, **143**, 1292 (1996).

[3] M. Kono, K. Furuta, M. Watanabe, and N. Ogata, *Polym. Adv. Tech.,* **4**, 85 (1993).

[4] M. Watanabe and A. Nishimoto, *Solid State Ionics,* **79**, 306 (1995).

[5] A. Nishimoto, M. Watanabe, Y. Ikeda, and S. Kohjiya, *Electrochim. Acta,* **43**, 1177 (1998).

[6] M. Kono, E. Hayashi, and M. Watanabe, *J. Electrochem. Soc.,* **145**, 1521 (1998).

[7] I. Ismail, A. Noda, A. Nishimoto, and M. Watanabe, *Electrochim. Acta,* **46**, 1595 (2001).

[8] A. Nishimoto, K. Agehara, N. Furuya, T. Watanabe and M. Watanabe, *Macromolecules,* 32, 1541 (1999).

[9] A. Vallee, S. Besner and J. Prud'homme, *Electrochim. Acta*, **37**, 1579 (1992).

[10] D. Benrabah, D. Baril, J.-Y. Sanchez, M. Armand, and G. G. Gard, *J. Chem. Soc., Faraday Trans.,* 89, 355 (1993).

[11] A. Teyssot, M. Rosso, R. Bouchet and S. Lascaud, *Solid State Ionics,* **177**, 141 (2006).

[12] S. Shiraishi, K. Kanamura and Z. Takehara, *Langmuir*, **13,** 3542 (1997).

[13] A.N. Andersson, K. Edstrom and J.O. Thomas, *J. Power Sources*, 81-82, 8 (1999).

[14] C.A.C. Sequeira and A. Hooper, *Solid State Ionics*, **9&10**, 1131 (1983).

[15] I.M. Ismail, U. Kadiroglu, N.D. Gray and J.R. Owen, *Fall Meeting of the Electrochemical Society*, San Antonio, TX, 1996, abstract no. 63.

[16] S. Morzilli, F. Bonino and B. Scrosati, *Electrochim. Acta,* **32**, 961 (1987).

[17] F. Krok, J.R. Dygas, B. Misztal-Faraj, Z. Flojanczyk and W. Bzducha, *J. Power Sources,* **81-82**, 766 (1999).

[18] M. Watanabe, T. Endo, A. Nishimoto, K. Miura and M. Yanagida, *J. Power Sources*, **81-82**, 786 (1999).

[19] A. Lisowska-Oleksiak, *Solid State Ionics*, **119**, 205 (1999).

[20] D. Aurbach, A. Zaban, Y. Ein-Eli, I. Weissman, O. Chusid, B. Markovsky, M. Levi, E. Levi, A. Schecheter and E. Granot, *J. Power Sources,* 68, 91 (1997).

Figure Captions

Fig. 1: Variation of glass transition temperature (T_g) of network polymer electrolytes using MA composition ([Li]/[O]=0.08).

Fig. 2: Glass transition temperature (T_g) of network polymer electrolytes (MA= 0.5) as a function of lithium salt concentration.

Fig. 3: Time dependence of ionic conductivity for network polymer (MA= 0.5) complexed with lithium salt ([Li]/[O]= 0.08) at 60°C.

Fig.4: Isothermal ionic conductivity change for network polymer complexed with lithium salt (a) LiTFSI and (b) $LiBF_4$, ([Li]/[O]= 0.08), as a function of MA composition.

Fig.5: Variation of interfacial resistance, R_i, (a) and double layer capacitance, C_{dl}, (b) with MA composition in network polymer complexed with lithium salt ([Li]/[O]=0.08).

Fig. 6: Arrhenius plots of R_i for network polymer complexed with lithium salt (a) LiTFSI and (b) $LiBF_4$, ([Li]/[O]= 0.08), as a function of MA composition.

Fig.7: Time dependence of interfacial resistance for network polymer (MA= 0.5) complexed with (a) LiTFSI and (b) $LiBF_4$, at 60°C.

Fig. 8: Arrhenius plots of R_i for network polymer (MA= 0.5) complexed with (a) LiTFSI and (b) $LiBF_4$, as a function of salt concentration.

Fig. 9: Variation of reciprocal of R_i with lithium salt concentration for network polymer electrolytes (MA= 0.5) at 60°C.

Fig 1

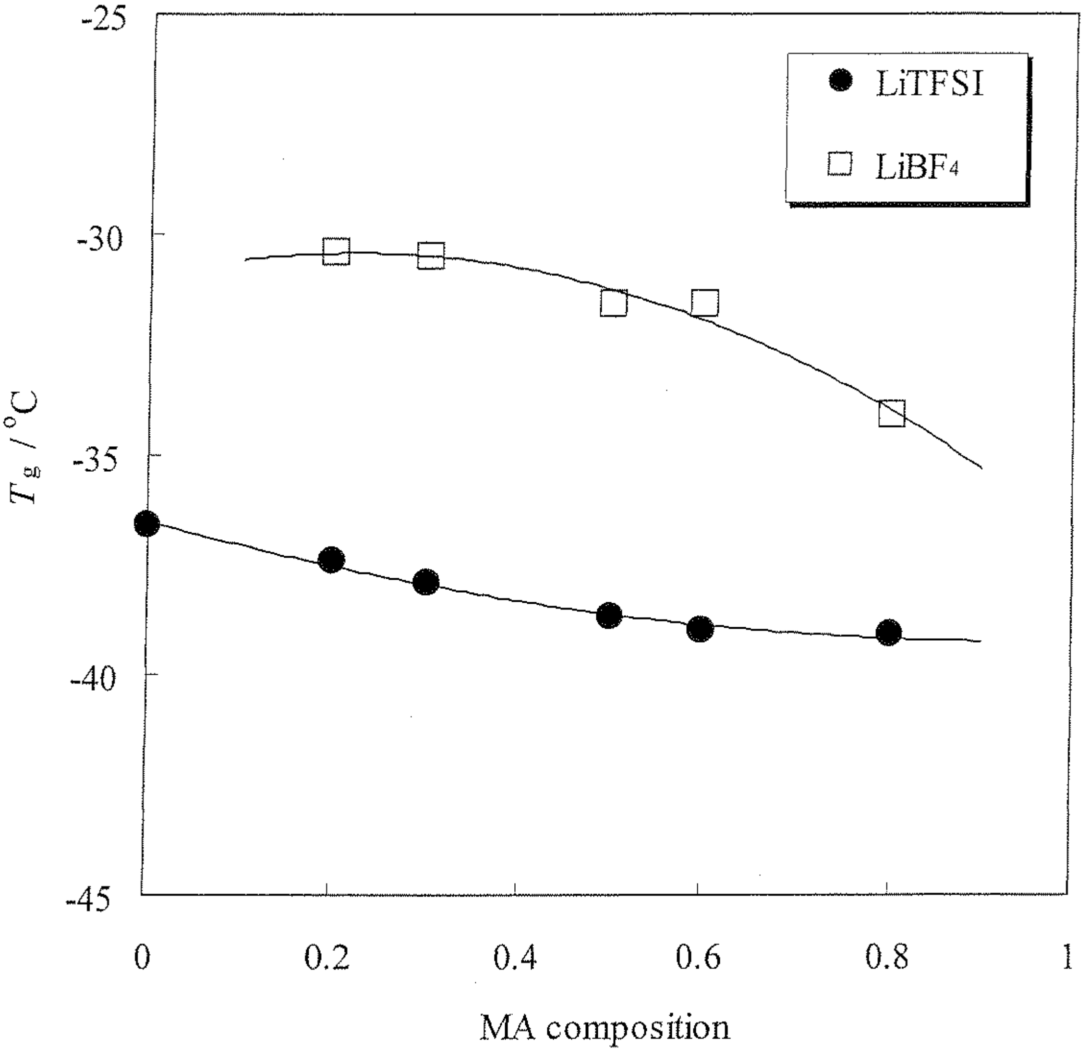


Fig 2

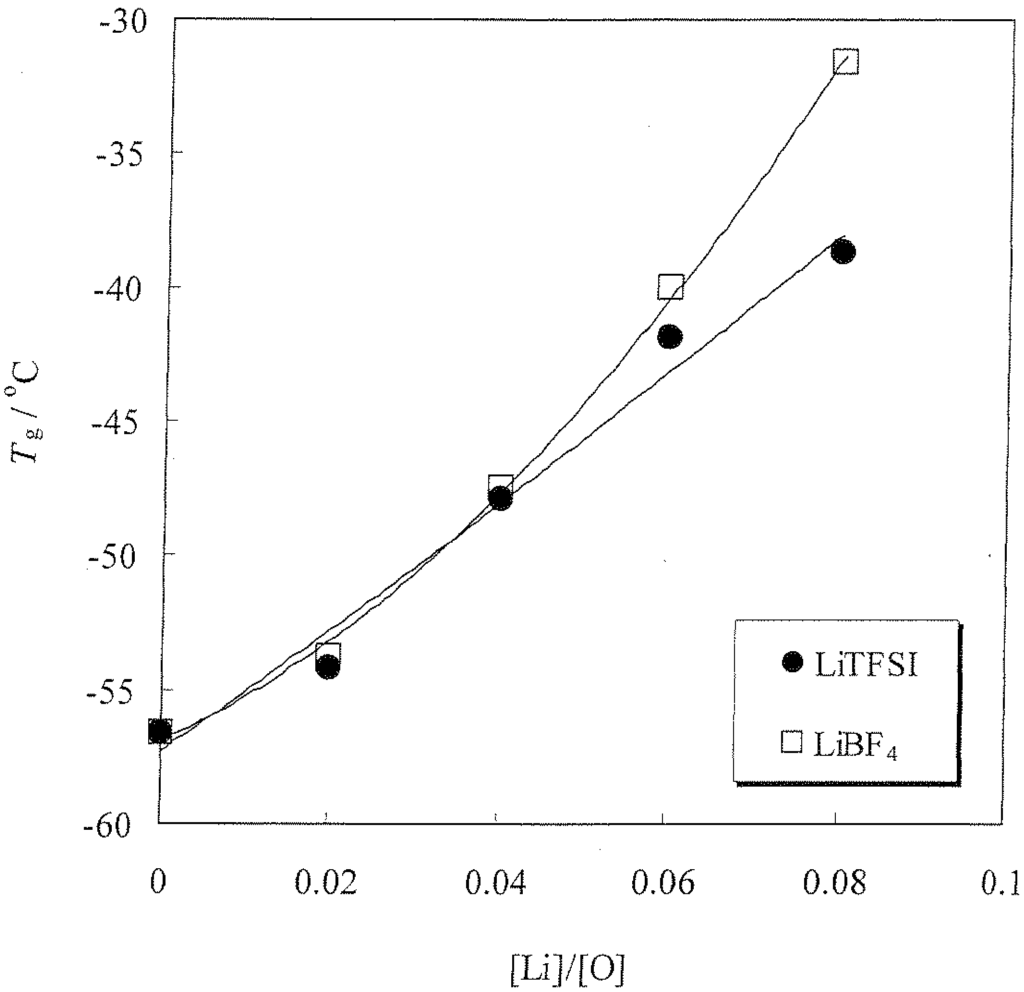
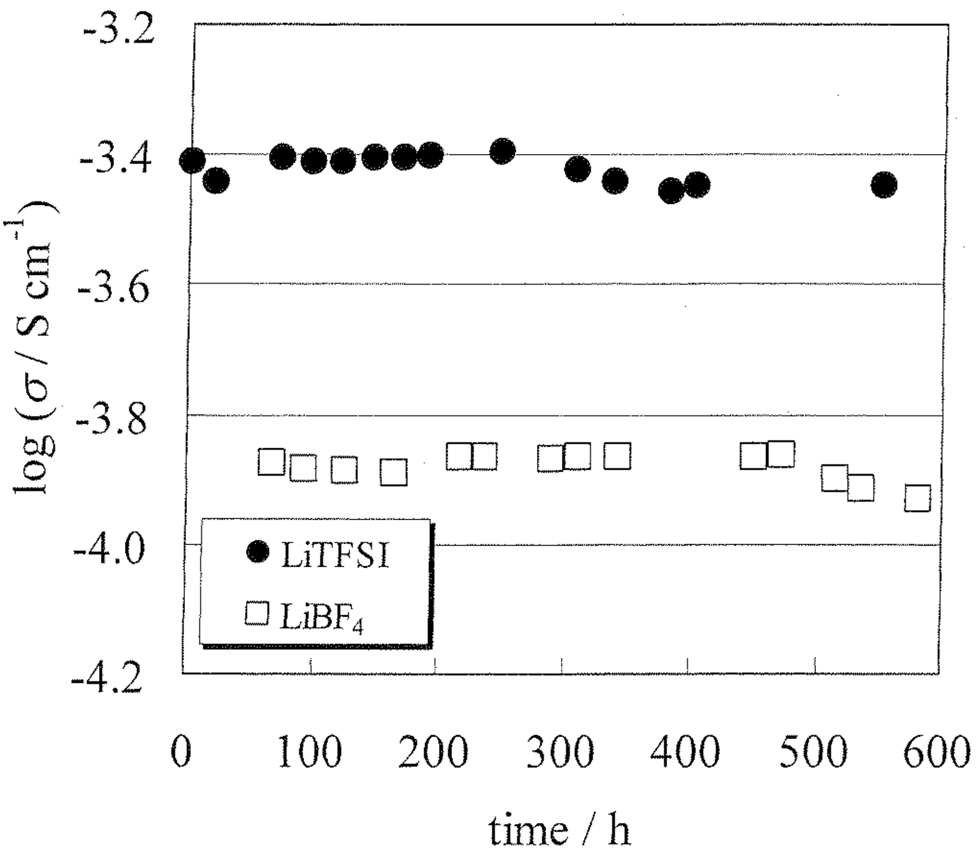
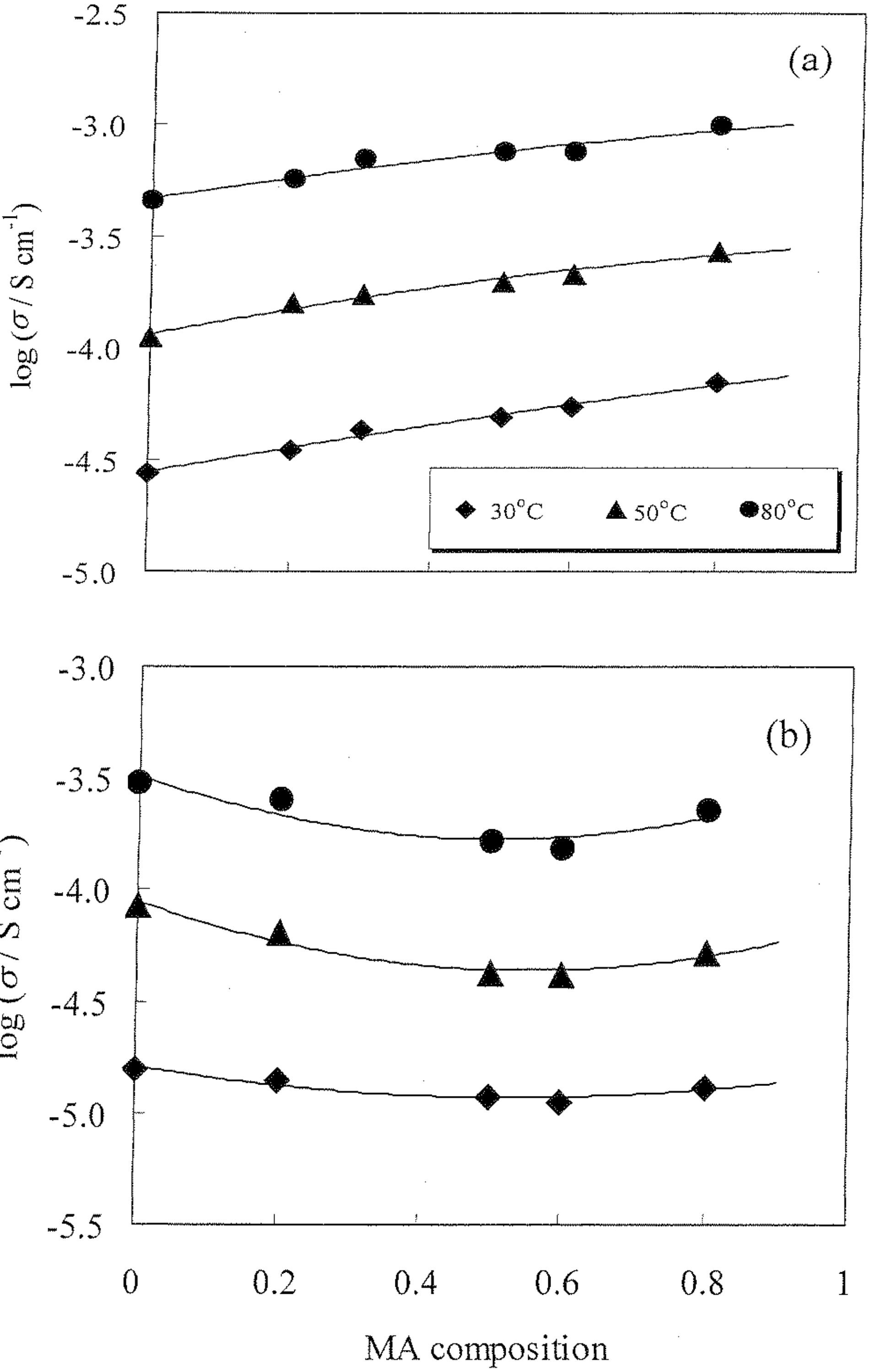


Fig 3



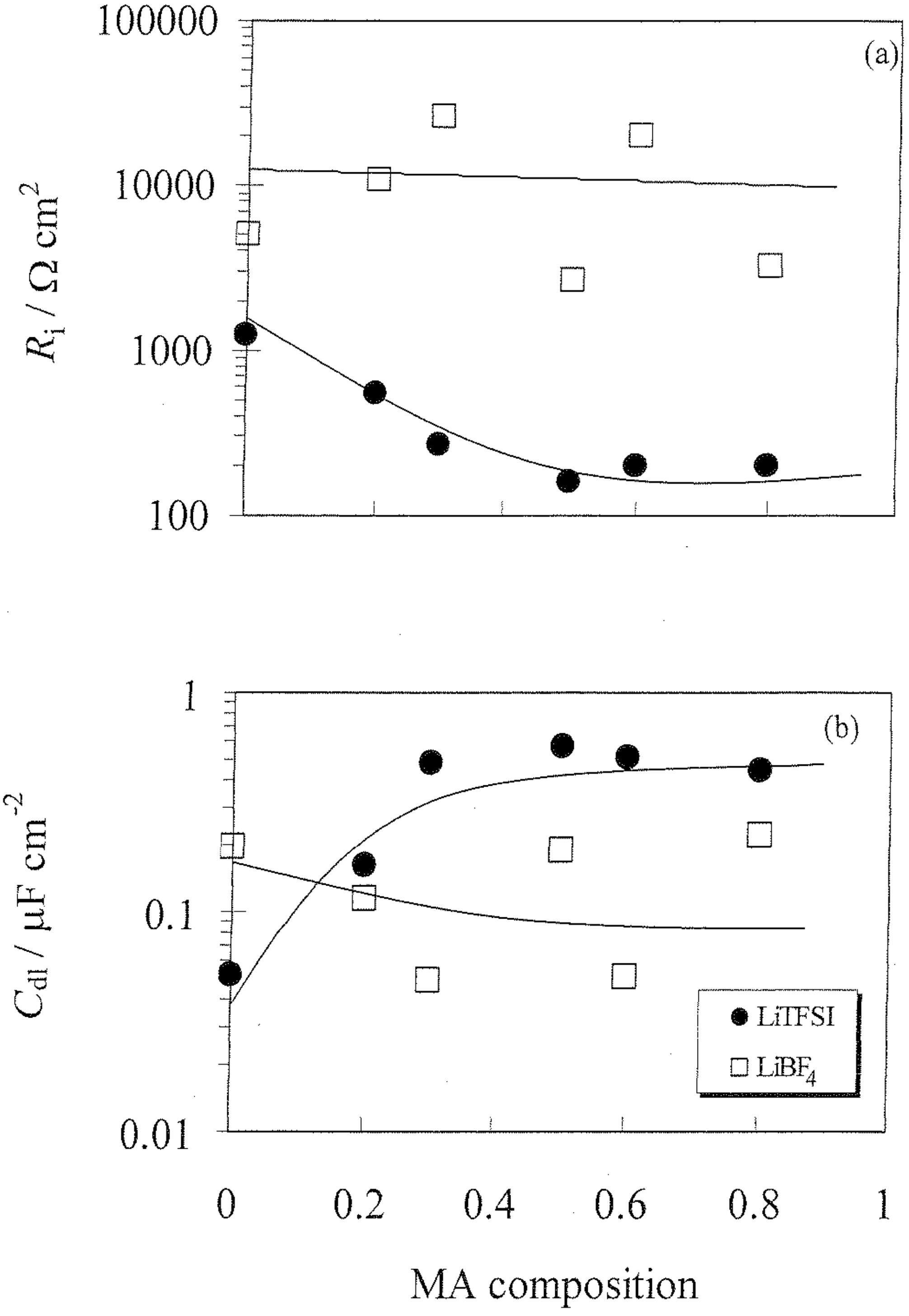
-3.2
-3.4
-3.6
-3.8
-4.0
-4.2
log (σ / S cm-1)
0
100
200
300
400
500
600
time / h
LiTFSI
LiBF4

Fig 4



(a)
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
log (σ / S cm-1)
30°C
50°C
80°C
(b)
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
log (σ / S cm-1)
0
0.2
0.4
0.6
0.8
1
MA composition

Fig 5



100000
10000
1000
100
R_i / Ω cm^2
(a)
1
0.1
0.01
C_{dl} / µF cm^{-2}
(b)
LiTFSI
$LiBF_4$
0
0.2
0.4
0.6
0.8
1
MA composition

Fig 6

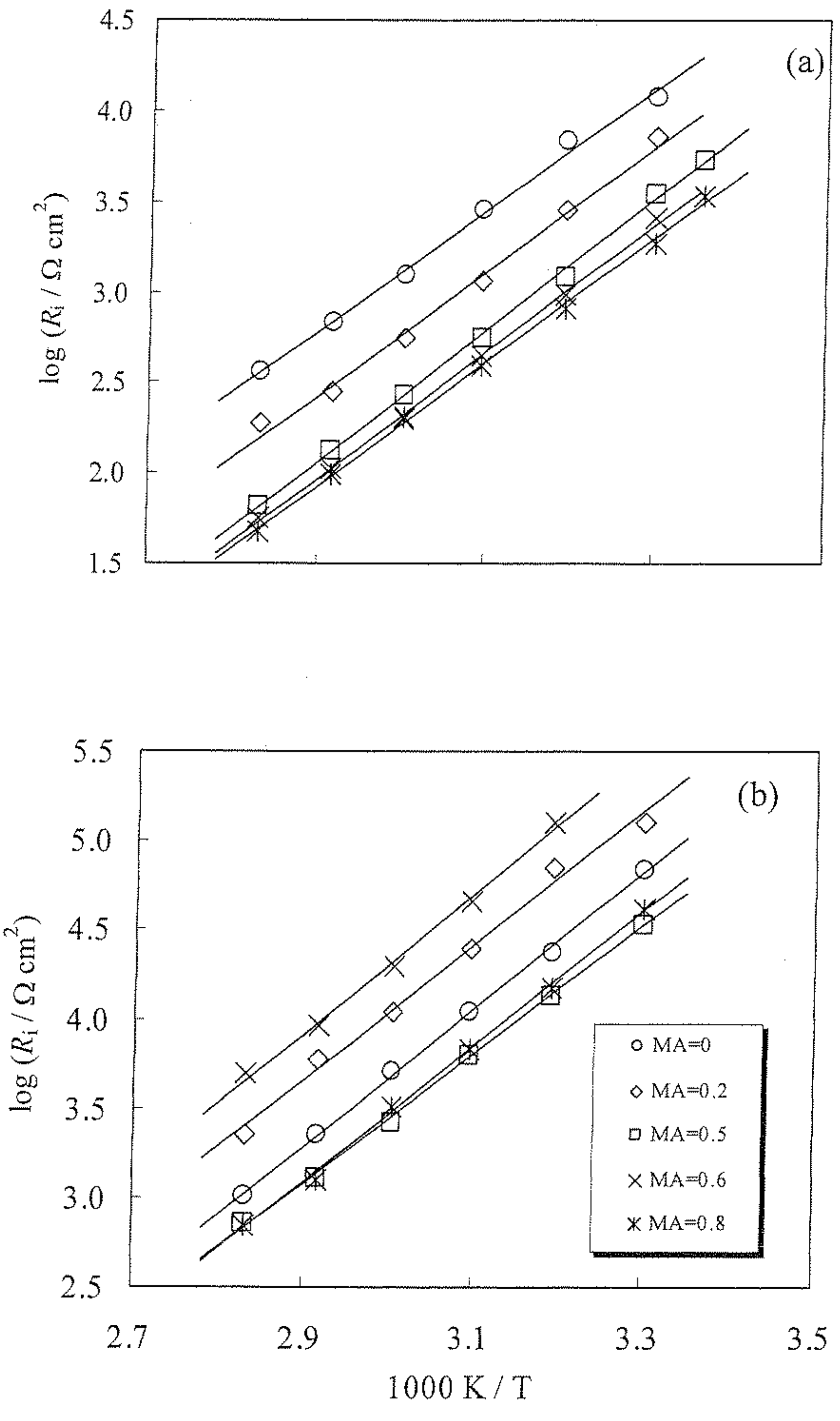
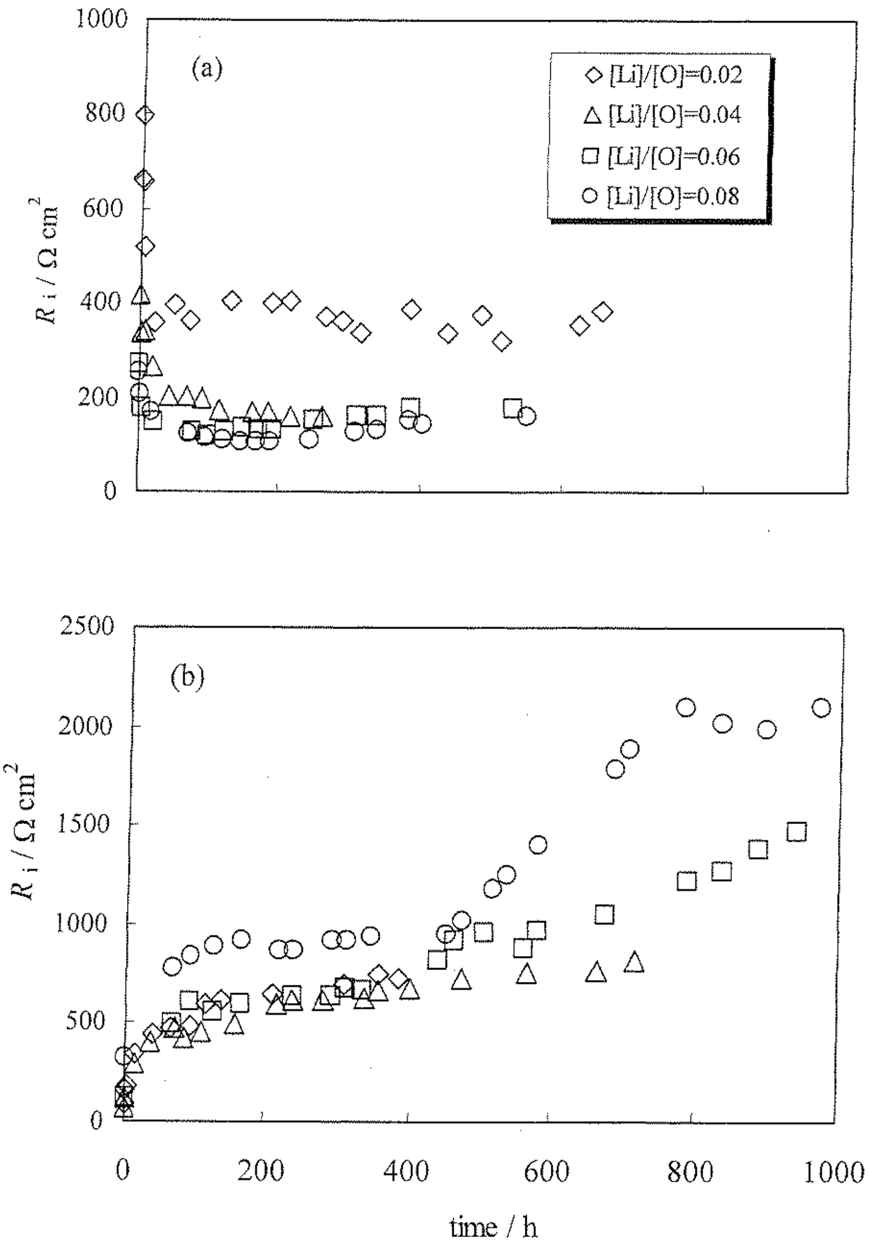
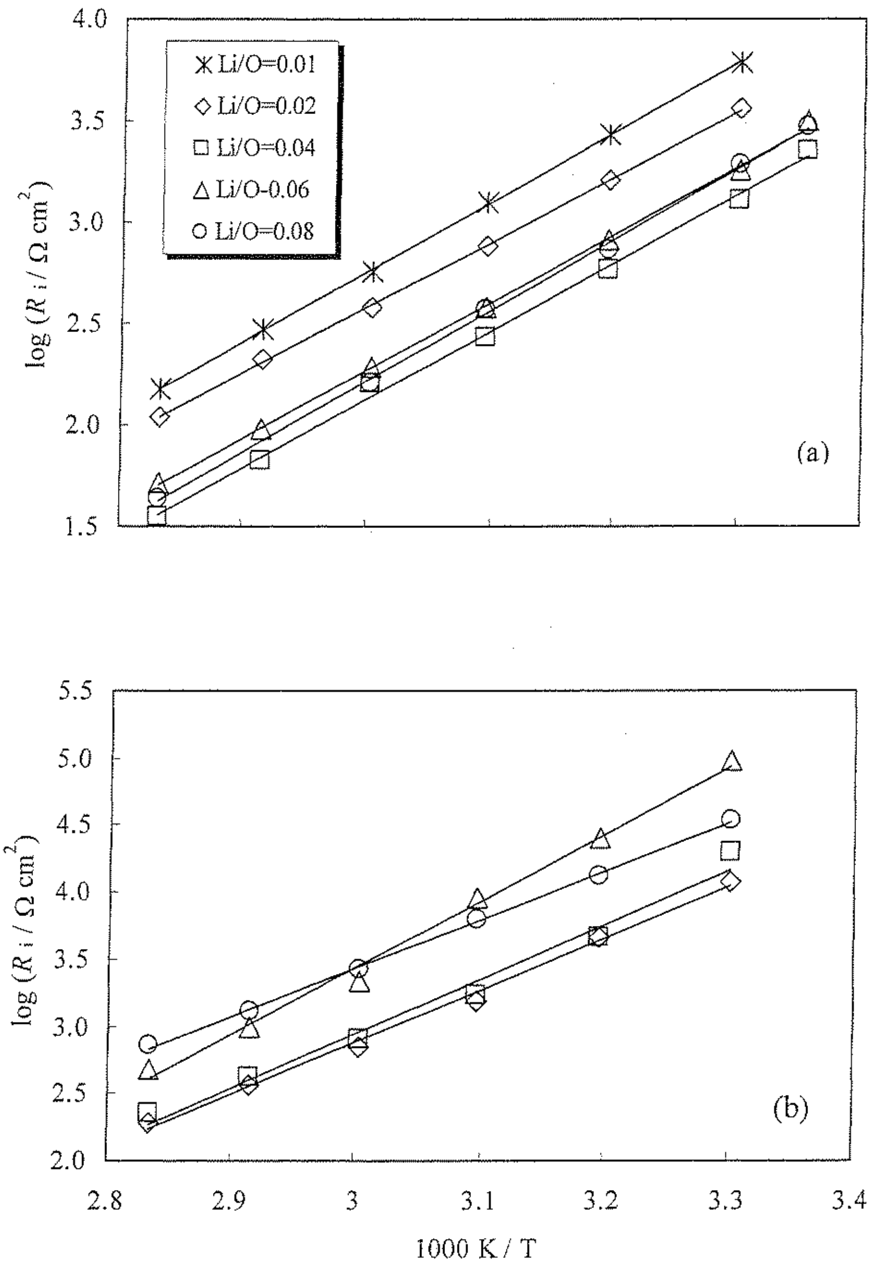

(a)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
log (R_i / Ω cm^2)
(b)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
log (R_i / Ω cm^2)
2.7
2.9
3.1
3.3
3.5
1000 K / T
MA=0
MA=0.2
MA=0.5
MA=0.6
MA=0.8

Fig 7



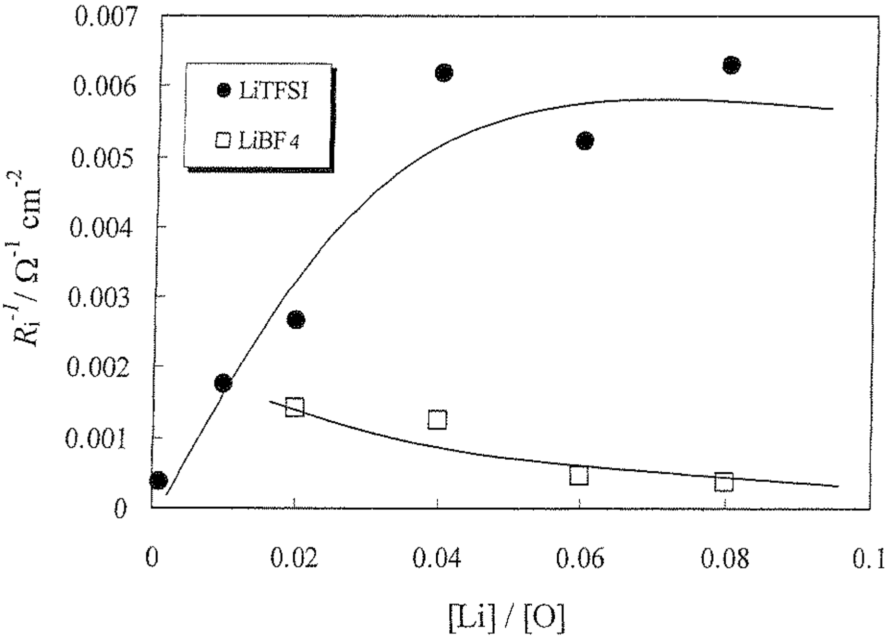
(a)
[Li]/[O]=0.02
[Li]/[O]=0.04
[Li]/[O]=0.06
[Li]/[O]=0.08
R i / Ω cm2
1000
800
600
400
200
0
(b)
R i / Ω cm2
2500
2000
1500
1000
500
0
0
200
400
600
800
1000
time / h

Fig 8



Li/O=0.01
Li/O=0.02
Li/O=0.04
Li/O-0.06
Li/O=0.08
(a)
(b)
4.0
3.5
3.0
2.5
2.0
1.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
2.8
2.9
3
3.1
3.2
3.3
3.4
log (R_i / Ω cm^2)
1000 K / T

Fig 9



0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
LiTFSI
LiBF4
R_i^{-1} / Ω^{-1} cm^{-2}
0
0.02
0.04
0.06
0.08
0.1
[Li] / [O]