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# Interface properties between a lithium metal electrode and a poly(ethylene oxide) based composite polymer electrolyte

Q. Li<sup>a</sup>, H.Y. Sun<sup>a,1</sup>, Y. Takeda<sup>a,\*</sup>, N. Imanishi<sup>a</sup>, J. Yang<sup>a</sup>, O. Yamamoto<sup>b</sup><sup>a</sup>Faculty of Engineering, Mie University, 1515 Kamihama, Tsu 514-8507, Japan<sup>b</sup>Genesis Research Institute, Noritake-shinmachi Nishi-ku, Nagoya 451-0061, Japan

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## Abstract

The interface resistance between a lithium metal electrode and a polymer electrolyte has been measured for composite polymer electrolytes using various ceramic fillers with poly(ethylene oxide) (PEO) and lithium salts (LiX). The interface resistance depended on the properties of added fillers and lithium salts. The PEO with LiClO<sub>4</sub> electrolyte contacted with lithium metal showed the high interfacial resistance of 1000 Ω cm<sup>2</sup> at 70°C for 25 days. In contrast, the interface resistance between lithium metal and PEO with Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N was as low as 67 Ω cm<sup>2</sup> after contacting at 80°C for 30 days. The interface stability and the lithium ion conductivity were improved by addition of a small amount of ferroelectric BaTiO<sub>3</sub> as the filler into the PEO–LiX electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Polymer electrolyte; Poly(ethylene oxide); Composite electrolyte; Lithium battery; Electrode and electrolyte interface

## 1. Introduction

Much attention has been paid to lithium ion conducting polymer and oxide heterogeneous composite electrolyte as the electrolyte in lithium polymer secondary batteries [1]. It has been successfully employed to improve the mechanical [2] and the interfacial properties [3–5] of the poly(ethylene oxide) (PEO), lithium salt (LiX), ceramic filler complex electrolytes. Furthermore, observation of conductivity enhancement following the addition of ceramic fillers have been reported [6–8]. It is quite important to control the electrode/electrolyte interface to obtain a high performance polymer lithium secondary batteries. This is indeed the requirement as regard the reactivity of the lithium metal to the polymer electrolyte. In some case, the interfacial resistance increased up to 1000 Ω cm<sup>2</sup> and stored at a high temperature for a long period [9]. The resistance value is more than one order higher than that of the polymer electrolyte. The interfacial resistance depends on the properties of the lithium salt and its concentration in PEO. Appetecchi et al. [5] have reported the interfacial resistance of lithium

metal and the PEO, LiX (X = LiCF<sub>3</sub>SO<sub>2</sub>, LiBF<sub>4</sub>), γ-LiAlO<sub>2</sub> composite electrolyte. The interfacial resistance of lithium-controlled electrolyte was 170 Ω cm<sup>2</sup> after annealing at 85°C for 2 months. The addition of γ-LiAlO<sub>2</sub> was quite effective to reduce the interfacial resistance.

It has been demonstrated in previous studies [8] that the PEO–LiClO<sub>4</sub> electrolytes have high conductivity and improved lithium metal interfacial properties with the electrolyte containing ferroelectric BaTiO<sub>3</sub> as the filler. The Li/PEO<sub>8</sub>–LiClO<sub>4</sub>–BaTiO<sub>3</sub> (10 wt.%) interfacial resistance by contacting at 70°C for 600 h was reduced to 150 from 500 Ω cm<sup>2</sup> of Li/PEO<sub>8</sub>–LiClO<sub>4</sub>. In this study, the interfacial properties of lithium metal have been examined for the PEO based polymer electrolytes with different kind of salt, LiX, using BaTiO<sub>3</sub> as the filler to provide a further support for the effect of BaTiO<sub>3</sub> on the PEO based electrolyte. In addition, the lithium ion resistance in PEO–LiX–BaTiO<sub>3</sub> has been compared with the interface resistance, where the lithium ion resistance was estimated from lithium ion transport number and the electrical resistance of the electrolyte.

## 2. Experimental

All of the polymer electrolytes described here were prepared by the solvent casting technique using tetrahydrofuran (THF) or acetonitrile (AN) as a carrier solvent. High

\* Corresponding author. Tel.: +81-59-231-9419; fax: +81-59-231-9478.  
E-mail address: takeda@chem.mie-u.ac.jp (Y. Takeda).

<sup>1</sup> Present address: Samsung Advanced Institute of Technology, Suwon, South Korea.

molecular weight ( $MW = 6 \times 10^5$ ) PEO (Aldrich Chemical) and Li salts [ $\text{LiClO}_4$  (Aldrich Chemical),  $\text{LiBF}_4$  (Aldrich Chemical),  $\text{LiPF}_6$  (Aldrich Chemical),  $\text{LiCF}_3\text{SO}_3$  (Aldrich Chemical) and  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  (Fluka Chemical)] were used as received. Barium titanate powder [Aldrich Chemical (0.6–1.2  $\mu\text{m}$ ) and Sakai Chemicals Co. (1.8, 0.5, 0.1  $\mu\text{m}$ )], rutile  $\text{TiO}_2$  (Aldrich Chemical, 1  $\mu\text{m}$ ) and  $\gamma\text{-Al}_2\text{O}_3$  (Daidou, 1  $\mu\text{m}$ ) were dried under vacuum at 100–150°C for 24 h.

Preparation of the composite electrolytes involved the dispersion of the  $\text{BaTiO}_3$  powder and of the lithium salt in THF or AN, followed by the addition of PEO. When the slurry was completely homogenized, it was heated and stirred. The slurry gradually becomes a gel. The gel was cast onto a flat polytetrafluoroethylene vessel. The solvent was allowed to evaporate slowly at 40°C for 24 h, then the sheet was held at room temperature under vacuum for 48 h. These procedures yield homogenous and mechanically stable membranes with an average thickness of 300  $\mu\text{m}$ . All of the steps in the above preparation procedures as well as the experiments were carried out in an argon atmosphere or under vacuum.

The interface resistance between composite polymer electrolyte and lithium metal electrode was evaluated by impedance response of symmetric Li/electrolyte/Li cells. The electrode area was 1.13 or 0.5  $\text{cm}^2$ . A Solatron 1260 frequency analyzer measured the impedance over a 0.01 Hz to 1 MHz frequency range with applied voltage of 5 mV.

### 3. Results and discussion

In the previous study [8], we have reported that the stability of the Li/PEO– $\text{LiClO}_4$  interface is enhanced by addition of ferroelectric oxide  $\text{BaTiO}_3$ . The characteristics of the Li/polymer electrolyte interface over storage time depend on the lithium salt in the polymer electrolyte [4,5,9]. Fig. 1 shows the change in interface resistance versus time

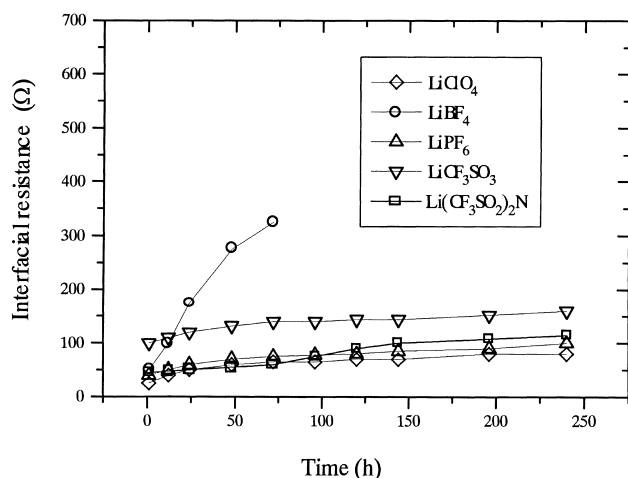


Fig. 1. Time dependence of the interfacial resistance of  $\text{Li}/(\text{PEO})_{19}\text{-LiX}$  10 wt.%  $\text{BaTiO}_3$  (0.1  $\mu\text{m}$ )/Li at 80°C (electrode area: 0.5  $\text{cm}^2$ ).

recorded at 80°C for the  $\text{PEO}_{19}\text{-LiX}$  10 wt.%  $\text{BaTiO}_3$  (0.1  $\mu\text{m}$ ) electrolyte sandwiched between two lithium electrodes. The active contact area of the lithium electrode and the electrolyte was about 0.5  $\text{cm}^2$ . Of these salts examined, the highest interface resistance is observed in  $\text{PEO-LiBF}_4\text{-BaTiO}_3$ . Krawiec et al. [9] reported the interface resistance of  $\text{Li}/(\text{PEO})_9\text{-LiBF}_4$  with nanosize  $\text{Al}_2\text{O}_3$ . The interfacial resistance in Li/electrolyte without  $\text{Al}_2\text{O}_3$  rose to 600  $\Omega\text{ cm}^2$  after stored at 70°C for 120 h. By addition of 20 wt.% nanosize  $\text{Al}_2\text{O}_3$ , the interface resistance reduced to about 100  $\Omega\text{ cm}^2$ . Borghini et al. [4], have measured the interface resistance of  $\text{Li}/(\text{PEO})_8\text{-Li}(\text{CF}_3\text{SO}_2)_2\text{N-}\gamma\text{-LiAlO}_2$ . The addition of  $\gamma\text{-LiAlO}_2$  significantly enhanced the Li/polymer electrolyte interface stability. The interface resistance at 70°C was only 100  $\Omega\text{ cm}^2$  after stored at room temperature for 5000 h. Our results show good interface stability for the polymer electrolytes with  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiClO}_4$  as the salt by addition of  $\text{BaTiO}_3$  as the filler.

Fig. 2 shows the interface resistance of a  $\text{Li}/(\text{PEO})_{19}\text{-Li}(\text{CF}_3\text{SO}_2)_2\text{N-filler}/\text{Li}$  cell. The interface of Li/polymer electrolytes with  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  is improved by the addition of 10 wt.%  $\text{Al}_2\text{O}_3$  (1  $\mu\text{m}$ ),  $\text{TiO}_2$  (1  $\mu\text{m}$ ) and  $\text{BaTiO}_3$  (0.1  $\mu\text{m}$ ). Previous studies suggested that the evaluation of interfacial resistance with time can be associated with continuous growth of a layer on the electrode surface where the passivation film is a product of the reaction of lithium with electrolyte components [3]. The passivation film formation reaction may be effected by the salt and also the moisture content in the electrolyte. The fine particle fillers are effective as a scavenger of water in the electrolyte. Therefore, the high content of fillers in the polymer composite electrolyte was more effective to stabilize the interface of Li/electrolyte. In the case of  $(\text{PEO})_8\text{-LiBF}_4\text{-Al}_2\text{O}_3$ , the stability of the electrolyte in contact with lithium varied with the content of  $\text{Al}_2\text{O}_3$  reaching the optimum for a system containing 20 wt.%  $\text{Al}_2\text{O}_3$  [9]. The  $\text{PEO-LiCF}_3\text{SO}_3\text{-}\gamma\text{-LiAlO}_2$  composite electrolyte prepared by hot pressing mixtures of the component showed a low Li/electrolyte

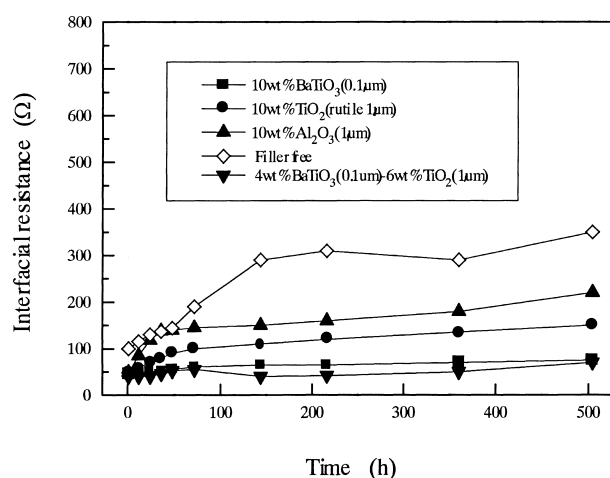


Fig. 2. Time dependence of the interfacial resistance of  $\text{Li}/(\text{PEO})_{19}\text{-Li}(\text{CF}_3\text{SO}_2)_2\text{N-filler}/\text{Li}$  at 80°C (electrode area: 0.5  $\text{cm}^2$ ).

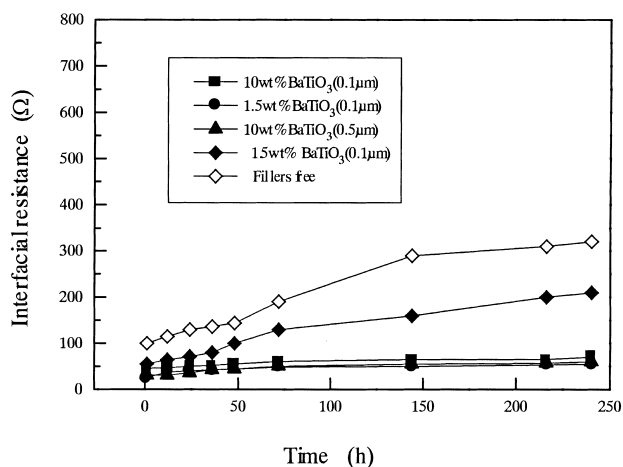


Fig. 3. Time dependence of the interfacial resistance of Li/(PEO)<sub>19</sub>-Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N-BaTiO<sub>3</sub>/Li at 80°C (electrode area: 0.5 cm<sup>2</sup>).

interface resistance [5]. This dry method eliminated the presence of any liquid impurity throughout the process. The interfacial stability in the dry composite polymer electrolyte sample was progressively increased by the addition of the ceramic filler, the highest stabilization effect being obtained for samples having 20 wt.% ceramic content.

The filler of BaTiO<sub>3</sub> showed an interesting interface stability behavior. The time dependence of the interface resistance in Li/PEO-Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N with different type of BaTiO<sub>3</sub> is shown in Fig. 3. As shown in a previous study [8], a fine particle as 0.1 μm of BaTiO<sub>3</sub> is intermediate between ferroelectric and paraelectric, and BaTiO<sub>3</sub> of particle size of 0.5 μm is ferroelectric. The polymer electrolytes with a high content of 10 wt.% BaTiO<sub>3</sub> show a low interface resistance for the both fillers of 0.1 and 0.5 μm BaTiO<sub>3</sub>. On the other hand, an addition of a small amount of 1.5 wt.% BaTiO<sub>3</sub> exhibits a different interface behavior between ferroelectric BaTiO<sub>3</sub> and paraelectric BaTiO<sub>3</sub>. The ferroelectric BaTiO<sub>3</sub> is effective to stabilize the Li/electrolyte interface by small amount of the filler. The paraelectric BaTiO<sub>3</sub> is not effective to stabilize the interface by small amount addition. The conductivity enhancement was observed by addition of 1.5 wt.% ferroelectric BaTiO<sub>3</sub> (0.5 μm) and 10 wt.% paraelectric BaTiO<sub>3</sub> (0.1 μm) at 80°C. It is not so clear to explain the interface stability enhancements by small amount addition of the ferroelectric BaTiO<sub>3</sub>, as shown in the previous study. The conductivity enhancement was explained by terms of the association tendency of anions with lithium cation and the spontaneous polarization of ferroelectric ceramic particles. It may be assumed that the addition of small amount of ferroelectric BaTiO<sub>3</sub>, may effectively scavenge impurities as water.

Fig. 4 shows the time dependence of the impedance spectra at 80°C for the cell, Li/(PEO)<sub>20</sub>-Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N 1.5 wt.% BaTiO<sub>3</sub>/Li. The bulk resistance ( $R_b$ ) of the electrolyte is the intercept on the real-axis at a high frequency, which is almost constant with time. We have observed two

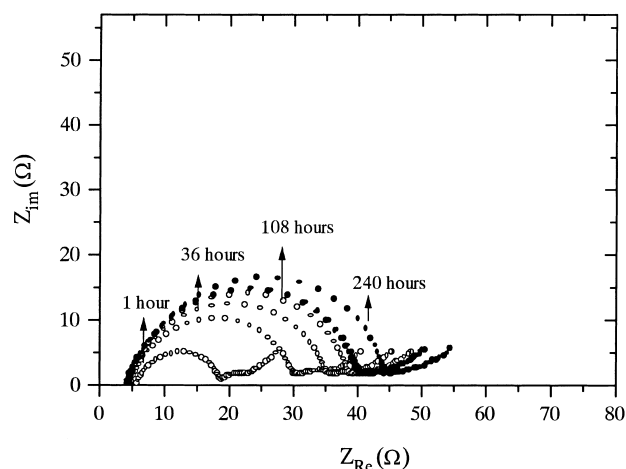


Fig. 4. Time dependence of the impedance response of Li/(PEO)<sub>20</sub>-Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N 1.5 wt.% BaTiO<sub>3</sub> (0.5 μm)/Li at 80°C (electrode area: 0.5 cm<sup>2</sup>).

semicircles. The high frequency first semicircle corresponds to the interface resistance and the second semicircles to the charge transfer process. By fitting the semicircles trend with a proper equivalent circuit [10], one can refine the analysis to obtain the value of the interfacial resistance of the films,  $R_1$  and  $R_2$ , and the charge transfer resistance  $R_{ct}$ . Fig. 5 shows time dependence of these components at 80°C. The charge transfer resistance remains at a very low value for all the duration of the test. The difference between  $R_1$  and  $R_2$  may be a small difference of the surface condition of lithium electrode.

Fig. 6 shows the Arrhenius plots of the interface resistance in the cell, Li/(PEO)<sub>20</sub>-Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N 10 wt.% BaTiO<sub>3</sub>/Li. The passivation process in these cells may basically involve a reaction between the lithium metal and lithium salt or between lithium metal and impurities. The activation

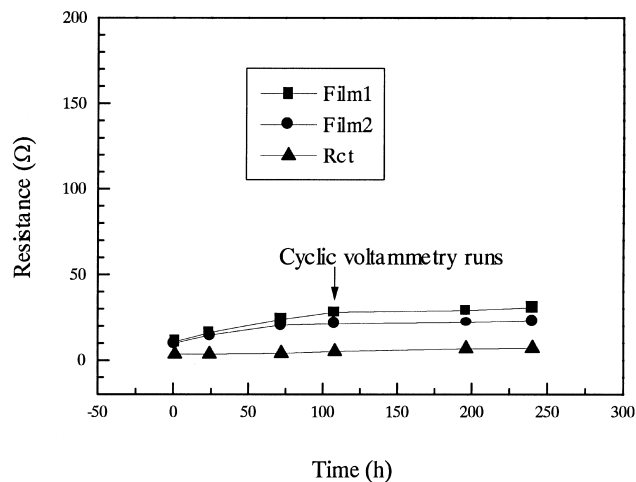
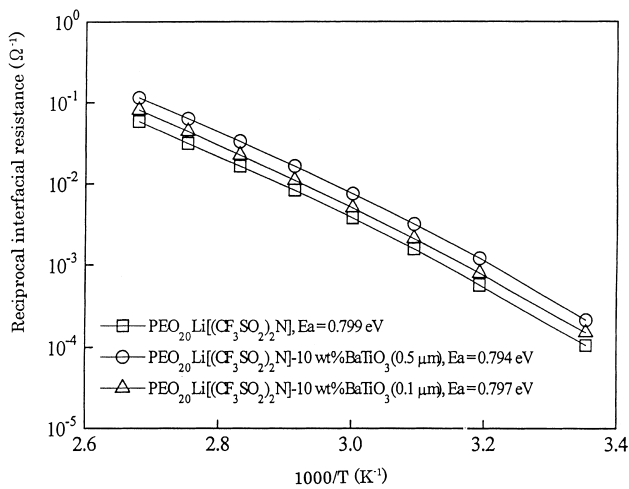


Fig. 5. Time dependence of the charge transfer resistance ( $R_{ct}$ ) and the interfacial resistance of film 1 ( $R_1$ ) and film 2 ( $R_2$ ) for the interface of Li/(PEO)<sub>20</sub>-Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N 1.5 wt.% BaTiO<sub>3</sub> (0.5 μm)/Li (electrode area: 0.5 cm<sup>2</sup>).

Table 1

Interfacial resistance of Li/PEO–LiX–filler/Li ( $R_{\text{int}}$ ) and lithium ion resistance of polymer electrolyte films of 30  $\mu\text{m}$  in thick ( $R_{\text{Li}}$ )

Electrolyte	Temperature ( $^{\circ}\text{C}$ )	$R_{\text{int}}$ ( $\Omega \text{ cm}^2$ )	$R_{\text{Li}}$ ( $\Omega \text{ cm}^2$ )
PEO <sub>8</sub> –LiClO <sub>4</sub>	70	1020 (25 days)	150
PEO <sub>8</sub> –LiClO <sub>4</sub> 5 wt.% BaTiO <sub>3</sub> (1.8 $\mu\text{m}$ )	70	380 (25 days)	17
PEO <sub>8</sub> –LiClO <sub>4</sub> 1.4 wt.% BaTiO <sub>3</sub> (0.6–1.2 $\mu\text{m}$ )	70	580 (25 days)	7
PEO <sub>12</sub> –Li(CF <sub>3</sub> SO <sub>3</sub> )	85	140 <sup>a</sup> (20 days)	64
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>3</sub> )	85	48 <sup>a</sup> (20 days)	51
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>3</sub> ) 10 wt.% LiNbO <sub>3</sub> (1–5 $\mu\text{m}$ )	85	47 <sup>a</sup> (20 days)	30
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>3</sub> ) 20 wt.% PbTiO <sub>3</sub> (0.1 $\mu\text{m}$ )	85	48 <sup>a</sup> (20 days)	37
PEO <sub>20</sub> –LiBF <sub>4</sub>	85	348 <sup>a</sup> (20 days)	17
PEO <sub>20</sub> –LiBF <sub>4</sub> 5 wt.% BaTiO <sub>3</sub> (0.5 $\mu\text{m}$ )	85	188 <sup>a</sup> (20 days)	11
PEO <sub>19</sub> –LiPF <sub>6</sub> 10 wt.% BaTiO <sub>3</sub> (0.5 $\mu\text{m}$ )	80	120 <sup>a</sup> (10 days)	150
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N	80	67 <sup>a</sup> (30 days)	52
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N 10 wt.% BaTiO <sub>3</sub> (0.5 $\mu\text{m}$ )	80	36 <sup>a</sup> (30 days)	30
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N 1.5 wt.% BaTiO <sub>3</sub> (0.5 $\mu\text{m}$ )	80	50 <sup>a</sup> (10 days)	25
PEO <sub>20</sub> –Li(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N 10 wt.% BaTiO <sub>3</sub> (0.1 $\mu\text{m}$ )	80	54 <sup>a</sup> (30 days)	25

<sup>a</sup> These cells were exposed to several cyclic voltammetry runs.Fig. 6. Arrhenius plots of the interfacial resistance in Li/(PEO)<sub>20</sub>–Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N 10 wt.% BaTiO<sub>3</sub>/Li (electrode area: 1.13 cm<sup>2</sup>).

energies for the interface resistance in Li/(PEO)<sub>20</sub>–Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N with and without BaTiO<sub>3</sub>/Li are about 0.8 eV. Hiratani et al. [11] and Fauteux [12] reported the temperature dependence of the interface resistance of Li/PEO–LiCF<sub>3</sub>SO<sub>3</sub> and estimated the activation energy for interface resistance to be 0.77 eV. Hiratani concluded that the charge transfer resistance was predominant in the interface resistance and Fauteux informed the activation energy for the contribution of the ionic conduction of the interface film. The activation energy of 0.8 eV could be compared with that of 0.70 eV for the electrical conduction of polycrystal LiF at lower temperatures [13]. We could estimate the interface film to be LiF with some impurity, because the activation energy for conduction in pure LiF is around 2 eV.

The interface resistance of Li/PEO–LiX–filler/Li depends on the characteristics of LiX and fillers, and also experimental conditions. It is difficult to allow comparison of the stability of different electrolytes versus lithium electrode

from the literatures. In this study, we have compared the interface resistance of the Li/PEO–LiX–filler/Li cell, where the electrolyte films were prepared by the same casting method and Table 1 summarizes these results. Some cells were exposed to several cyclic voltammetry runs to refresh the lithium surface. For the practical applications of these electrolytes, both the interfacial resistance and bulk resistance of the electrolyte film are important. The resistance of 30  $\mu\text{m}$  thick film are shown in Table 1. These resistances of the film were estimated from the conductivity and the lithium ion transport number [14], which was measured by the method developed by Vincent et al. [15]. The resistance of the film is less than 200  $\Omega \text{ cm}^2$  at a higher temperature. In the some electrolytes, the interfacial resistance reaches up to several hundred ohms. The lowest interface resistance was observed in the composite electrolyte PEO–Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N–BaTiO<sub>3</sub>.

#### 4. Conclusions

The time dependence of the interfacial stability of Li/PEO–LiX–BaTiO<sub>3</sub> has been examined at 80 $^{\circ}\text{C}$ . The addition of BaTiO<sub>3</sub> is quite effective to stabilize the interface. Especially, additional small amount of ferroelectric BaTiO<sub>3</sub> suppresses the reaction between lithium metal and LiX. The interfacial resistance of Li/PEO–Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N–BaTiO<sub>3</sub>/Li has maintained less than 50  $\Omega \text{ cm}^2$  and stored at 80 $^{\circ}\text{C}$  for a long period. The polymer composite is a promising electrolyte in the lithium polymer secondary batteries.

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