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# Development of solid polymer lithium secondary batteries

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## Abstract

To develop a long-life secondary lithium battery using solid-state polymer electrolyte system, several factors of the polymer electrolyte were examined by using metal lithium and  $\text{LiCoO}_2$  electrodes. The lithium salts used were  $\text{LiBF}_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (abbreviated as LiTFSI) and  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  (abbreviated as LiTNSI), and the matrix polymer was cross-linked random copolymer of ethylene oxide and propylene oxide. Passivation films formed on the metal lithium surface after storage at  $60^\circ\text{C}$  were analyzed by X-ray photoelectron spectroscopy (XPS). The battery performance was found to depend significantly both on species and concentration of lithium salts. At present, our best achievement of the cycle ability for the 4 V class secondary battery was over 300 cycles at a current rate of  $C/8$  at  $60^\circ\text{C}$  by using LiTFSI. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Solid-state polymer electrolyte; Lithium secondary battery; 4 V class; Long life

## 1. Introduction

Solid polymer electrolytes have been expected to produce safe and high-energy density lithium secondary batteries to use for electric vehicles or load-conditioning devices. The first proposal was made by using polyethylene oxide (PEO) [1], and great efforts have been made to increase the ionic conductivity, but for the practical usage the ionic conductivity in the polymer electrolytes is still much lower than in organic solution or polymer gel electrolytes. Attempts to develop the high-energy density and long-life lithium batteries may be made in various laboratories, but the successful results have not been reported yet.

We have developed 4 V class lithium secondary batteries composed of the solid polymer electrolytes without organic solvent, where the electrodes are metal lithium as the negative and  $\text{LiCoO}_2$  as the positive. One of the difficult problems was that the lithium salt dissolved in polymer electrolytes participates largely in the film formation on the metal lithium surface, which brings the increase in impedance and the decrease in the cycle ability of a  $\text{LiCoO}_2/\text{Li}$  cell. Scrosati et al. investigated the surface state of lithium and the interface resistance in contacting with polymer electrolytes by ac impedance measurement [2–4]. This paper describes that the film formed on the lithium surface was

analyzed by X-ray photoelectron spectroscopy (XPS) in detail. Three lithium salts, such as  $\text{LiBF}_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (abbreviated as LiTFSI), and  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  (abbreviated as LiTNSI) were examined. Also, the salt concentration was varied to find the relation to the performance of the batteries. At present, our achievement for 10 Wh class solid polymer batteries is the cycle ability over 300 cycles at a current rate of  $C/8$  at  $60^\circ\text{C}$  by optimizing species and concentration of the salt.

## 2. Experimental procedure

The 4 V class solid polymer batteries consisted of a typical  $\text{LiCoO}_2/\text{Li}$  metal system with solid polymer electrolytes.  $\text{LiCoO}_2$  electrode was prepared by mixing ground  $\text{LiCoO}_2$ , acetylene black carbon as a conductor, and PVDF as a binder. The solid polymer electrolytes were prepared from random copolymer of ethylene oxide and propylene oxide by doping  $\text{LiBF}_4$ , LiTFSI, or LiTNSI as the lithium salt and the salt concentration was varied. To investigate reactivity between the polymer electrolytes and lithium metal, symmetrical non-blocking cells were prepared. The measurement of the cell impedance was performed by ac impedance method. The resistive component for the passivation film on the lithium surface was determined by the corresponding semicircle. The films for testing were prepared under following conditions. Metal lithium was contacted to the above polymer electrolytes and stored during 1,

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5, 15, or 30 days at 60°C. The deposit components on the lithium surface were determined by using XPS method. The measurement was performed by argon etching using a 400 W Mg lamp with 4.0 kV during 30 min. 10 Wh class solid polymer batteries were constructed by stacking the LiCoO<sub>2</sub>/Li unit cells. The cycle ability of the unit cells and 10 Wh class solid polymer batteries was obtained by the constant current charge–discharge process at C/8 at 60°C. The operating voltage was in the range of 3.0–4.1 V.

### 3. Result and discussion

The XPS analysis showed that LiF, Li<sub>2</sub>CO<sub>3</sub>, LiOH, and Li<sup>+</sup> are present on the lithium surface in all the samples. Fig. 1 shows the XPS depth profile of lithium metal of the 30 days stored sample. The deposit lithium derivatives are different depending on the lithium salt used in the polymer electrolytes. When the salt was LiBF<sub>4</sub>, LiF bonds were given by Li 1s in 56.0 eV and by F 1s in 687.6 eV, and Li<sub>2</sub>O bond was given by O 1s in 530.7 eV, respectively. And the Li–F concentration increased with the storage time. But when the salt was LiTFSI or LiTNSI, only Li<sub>2</sub>O element was observed. These results indicate that the mechanism for the deposit of lithium substances in the polymer electrolytes is similar to that in liquid electrolyte system [5]. Since LiBF<sub>4</sub> is a Lewis acid, it easily produces F<sup>−</sup> ion that reacts with the metal lithium to produce LiF. It is well known that the surface film grows more deep into the metal lithium in liquid electrolyte system [6]. But, the enhancement of the interaction between the metal lithium and the polymer electrolyte is extremely low. Two processes are assumed as the mechanism of the deposit. One is the diffusion of fluoride anion into the surface film and another is the invasion of the electrolyte including the fluorine compounds into the film. The latter process is not possible for the polymer electrolytes, since

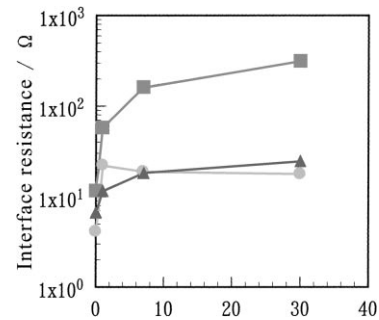


Fig. 2. Time dependence of the interface resistance of Li/Li cells using polymer electrolytes dissolved (■) LiBF<sub>4</sub>, (●) LiTFSI, and (▲) LiTNSI at 60°C; effective electrode area: 15.84 cm<sup>2</sup>.

they have the specific morphology. Therefore, the film on the metal lithium surface is considered not to grow so deep in the polymer electrolyte system.

Fig. 2 shows the change in the interface resistance depending on the storage time for the lithium symmetrical cells in the polymer electrolyte systems with various lithium salts. When the storage time became longer, the interface resistance increased especially in the LiBF<sub>4</sub> electrolyte system, while it increased little in the LiTFSI electrolyte system even after 30 days. The difference may be related to the different surface state of the lithium electrode. As confirmed by the XPS analysis, the amount of fluorine substances on the lithium surface increased according to the storage time. An important reason for the increase in the interface resistance is supposed to be the production of fluorine compounds on the lithium surface. The fluorine compounds may be formed by decomposition of the salts or by the reaction of lithium compound with the salts. The polymer electrolytes doped with LiTFSI or LiTNSI were very stable in contacting with the metal lithium electrode. The increase of the salt concentration

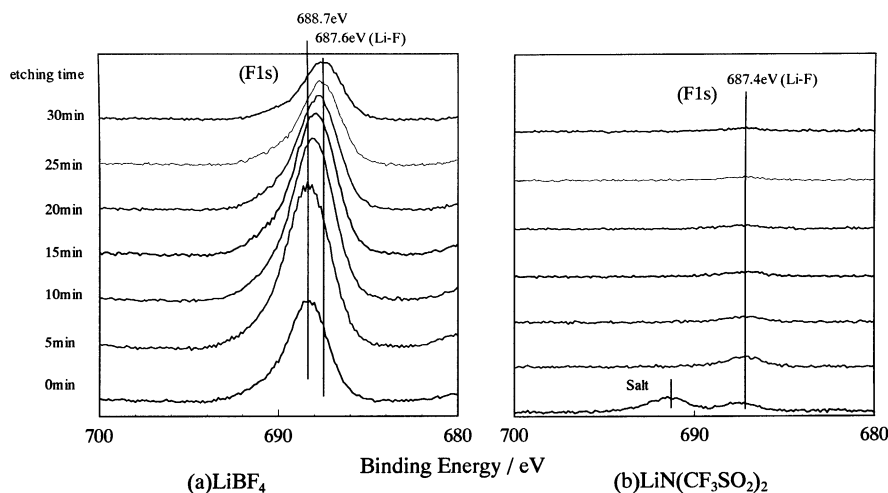


Fig. 1. X-ray photoelectron spectra of F 1s for the film formed on lithium surface in contact with polymer electrolyte dissolved in (a) LiBF<sub>4</sub> (EO/Li = 20/1), (b) LiTFSI (EO/Li = 20/1) for 30 days at 60°C after argon ion sputtering for 0, 5, 10, 15, 20, 25, and 30 min (4 kV, 0.11 A/cm<sup>2</sup>).

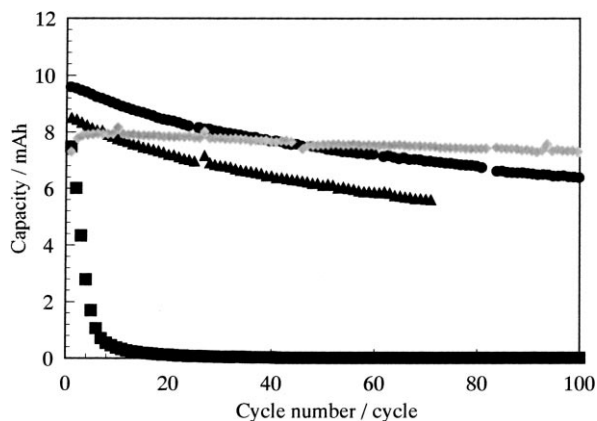


Fig. 3. Cycle ability of LiCoO<sub>2</sub>/Li cells using polymer electrolyte dissolved (■) LiBF<sub>4</sub> (EO/Li = 20/1), (●) LiTFSI (EO/Li = 20/1), (▲) LiTNSI (EO/Li = 20/1), and (◆) LiTFSI (EO/Li = 10/1) at a constant current 1 mA between 4.1 and 3.0 V at 60°C; effective electrode area: 15.84 cm<sup>2</sup>.

for TFSI did not influence the surface state and the interface resistance.

The comparison of the cycle ability of the LiCoO<sub>2</sub>/Li cell was made for the polymer electrolytes doped with the three lithium salts, and the results are shown in Fig. 3 for the 8 mAh LiCoO<sub>2</sub>/Li cell. The cycle ability in the LiTFSI electrolyte system was much better than that in the LiBF<sub>4</sub> electrolyte system. The increase in the polarization was observed for the LiBF<sub>4</sub> system compared with the LiTFSI system because of the increase in the interface resistance caused by LiF substances in the LiBF<sub>4</sub> system. The LiTFSI system was better in the cycle ability and the stability of metal surface films.

The salt concentration dependence of the cycle ability was examined for the LiTFSI system and it was found that it increased with the increase in the salt concentration from O:Li = 20:1 to O:Li = 10:1. It suggested that the number of Li<sup>+</sup> carriers increased without the ion-pair formation by higher salt concentration, or different mechanisms may be effective in the polymer electrolytes.

We developed 10 Wh class solid polymer batteries composed of the LiCoO<sub>2</sub>/Li system for the three lithium salts and the different salt concentrations. The battery was constructed by stacking up 80 sheets of a 42 mAh unit cell and packing them in an aluminum case. Our best achievement of the cycle ability was over 300 cycles for the 10 Wh class batteries at a current rate of C/8 at 60°C by using the LiTFSI with the salt concentration of O:Li = 10:1. The

performance of the batteries was shown to depend on species and concentration of the lithium salt.

#### 4. Conclusion

To develop a lithium secondary battery using a solid polymer electrolyte, we examined several factors of the polymer electrolytes in the LiCoO<sub>2</sub>/Li electrode system and found that composition and thickness of the metal lithium surface deposit depends on species and concentration of the lithium salt. The metal lithium/electrolyte interface resistance for the LiBF<sub>4</sub> electrolyte system is clearly larger than that for the LiTFSI electrolyte system under long storage at 60°C. The battery cycle ability was significantly better in the LiTFSI electrolyte system compared with the LiBF<sub>4</sub> electrolyte system, because more stable film is formed on the lithium surface in the LiTFSI electrolyte system. The battery performance was found to depend on species and concentration of the lithium salt, and our achievement of the cycle ability was over 300 cycles at a current rate of C/8 at 60°C. The strategy to develop the solid polymer lithium secondary battery having the longer life is still obscure, however the present achievement demonstrates the possibility to produce the lithium batteries composed of all the solid-state materials.

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