

# Developing stable, low impedance interface between metallic lithium anode and polyacrylonitrile-based polymer gel electrolyte by preliminary voltage cycling

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## Abstract

The metallic lithium anode surface facing to a gel-like polyacrylonitrile polymer electrolyte (gel-SPE) was tried to be stabilized by preliminary voltage cycling. Through voltage cycling from +0.5 to -0.5 V at a scan rate of 10 mV/s at 20°C immediately after assembling a cell having a configuration of Li/gel-SPE/Li, the cell impedance at 100 Hz was kept below 100  $\Omega$  for the cells with a gel-SPE containing LiBF<sub>4</sub> over 230 days at 20°C. The cells with a gel-SPE containing LiPF<sub>6</sub> required preliminary voltage cycling at a voltage higher than 0.5 V and at an elevated temperature of 60°C to obtain and keep a lower impedance during storage. The impedance at 10 kHz which represented the bulk resistance of gel-SPE was almost the same for both cells and constant during storage, around 15  $\Omega$ . This was confirmed in the cell of Li/gel-SPE/DMcT + polyaniline composite cathode (DMcT = 2,5-dimercapto-1,3,4-thiadiazole). The metallic lithium anode surface before and after the voltage cycling was subjected to X-ray photoelectron spectroscopy (XPS) analysis: Li<sub>2</sub>CO<sub>3</sub> disappeared and LiF–LiOH remained in the surface layer after the voltage cycling for the LiBF<sub>4</sub> gel-SPE cell while for the LiPF<sub>6</sub> gel-SPE cell, a dense and thin LiF surface layer was broken into a thicker LiF–LiOH layer. The layer consisting of mainly LiF and LiOH which was formed by preliminary voltage cycling was considered to stabilize the interface. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Polymer gel electrolyte; Polyacrylonitrile; Lithium polymer batteries; Metallic lithium anode; Ac impedance; Surface analysis

## 1. Introduction

A polyacrylonitrile-based gel-like polymer electrolyte (gel-SPE) is one of the candidates for the electrolyte of rechargeable lithium batteries [1,2]. We use this polymer electrolyte (gel-SPE) in combination with a metallic lithium anode and a composite polymer cathode consisting of a redox organic sulfur compound of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and polyaniline (PAN) in a lithium polymer secondary cell system [3,4].

We found that the ac impedance of the Li/gel-SPE/Li cell at 100 Hz during storage was lowered by preliminary polarization [5]: the cell which was subject to preliminary voltage cycling by cyclic voltammetry (CV-polarization) gave a lower stabilized value of impedance below 100  $\Omega$  during storage over 1000 h at 20°C, while the cell without

CV-polarization showed a still increasing value with storage time of over 300  $\Omega$ . We have investigated the details of the preliminary polarization effect stabilizing the Li/gel-SPE interface by analyzing the surface film compositions of metallic lithium with X-ray photoelectron spectroscopy (XPS) measurement.

## 2. Experimental

### 2.1. Materials

Metallic lithium foil 300  $\mu$ m thick was obtained from Kyokuto Kinzoku (Japan). Acrylonitrile–vinylacetate copolymers (AN/VAc, mole ratio = 97:3 or 95:5, molecular weight = ca. 400,000) were obtained from Toyobo (Japan) and were dried under vacuum at 80°C overnight. Lithium-battery-grade propylene carbonate (PC), ethylene carbonate (EC), and dimethylcarbonate (DMC) were ob-

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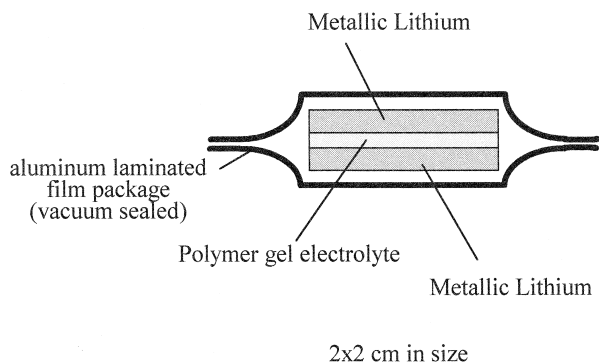


Fig. 1. Cross-sectional view of a test cell packaged with aluminum foil laminated plastics films.

tained from Tomiyama Pure Chemical Ind. (Japan). Lithium-battery-grade  $\text{LiBF}_4$  and  $\text{LiPF}_6$  were obtained from Hashimoto Kasei (Japan).

## 2.2. Preparation of gel-SPE

A gel-like polymer electrolyte was prepared by mixing AN/VAc powder and an electrolyte solution dissolving 1.7 M  $\text{LiBF}_4$  and/or  $\text{LiPF}_6$  in a mixed solvent of EC and PC or DMC; casting the milky mixture in a stainless steel pad with a glass plate lid, heating it at  $140^\circ\text{C}$  on a horizontal heat plate until it became transparent; cooling the resultant transparent viscous liquid at  $-20^\circ\text{C}$  overnight to obtain a source gel-SPE; roll-pressing the source gel-SPE at  $70^\circ\text{C}$  into a thin sheet; cooling it again at  $-20^\circ\text{C}$  overnight to obtain a self-supporting gel-SPE ca. 0.6 mm thick. This preparation was carried out in a dry argon atmosphere at a dew point below  $-40^\circ\text{C}$ .

## 2.3. Test cell assembly

Test cells were assembled also in the dry argon atmosphere. A gel-SPE cut into  $2\text{ cm} \times 2\text{ cm}$  was sandwiched

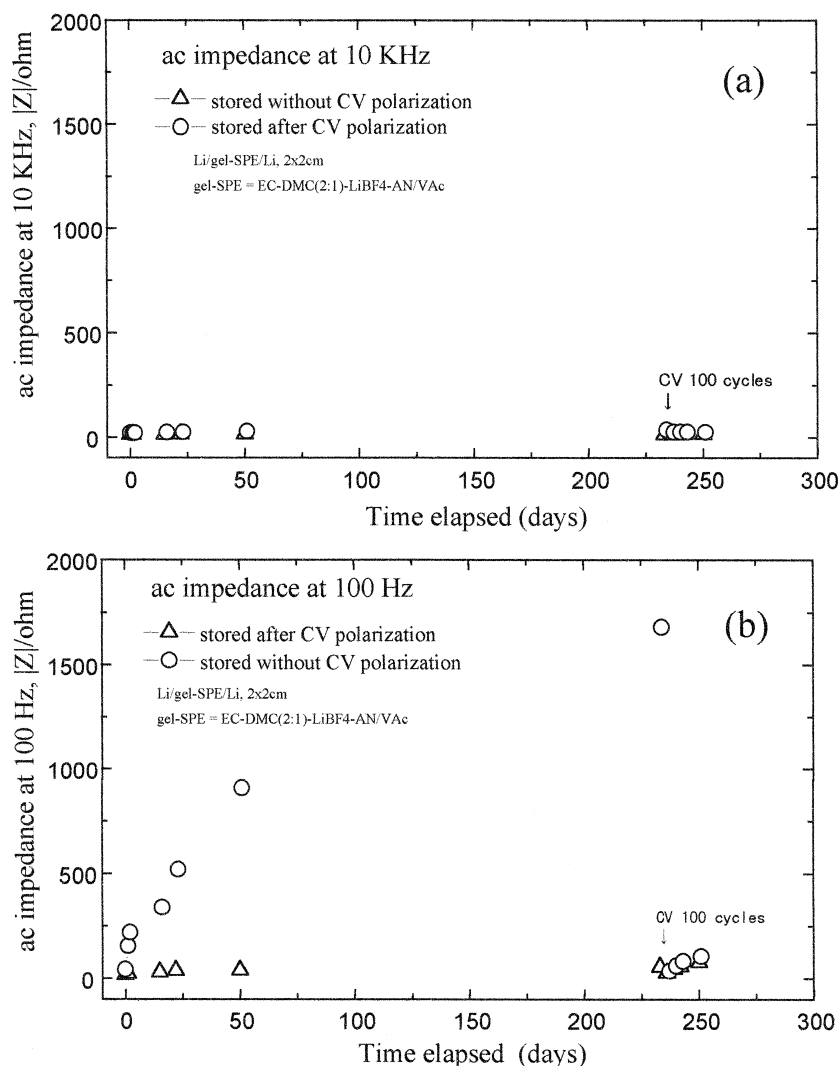


Fig. 2. Ac impedances at 10 kHz and 100 Hz of Li/gel-SPE( $\text{LiBF}_4$ )/Li cells  $2\text{ cm} \times 2\text{ cm}$  in size during  $20^\circ\text{C}$  storage with or without CV-polarization.

between metallic Li foil 2 cm × 2 cm; the whole assembly was put in a package made of an aluminum foil–polyethylene laminated film having titanium foil terminal leads; the package was heat-sealed under vacuum to obtain test cells having a construction of Li/gel-SPE/Li. The test cell (Fig. 1) was further sealed in a desiccated glass bottle on storage. A test cell 2 cm × 2 cm in size having a construction of Li/gel-SPE/DMcT + PAn packaged with the laminated film was also assembled; a gel-SPE was sandwiched between a metallic Li foil and a DMcT + PAn composite cathode film formed on a copper foil. The preparation of DMcT + PAn composite cathode film was reported previously [4].

#### 2.4. Impedance measurements and preliminary voltage cycling

Immediately after assembling cells, the test cells with LiBF<sub>4</sub>-containing gel-SPE were subjected to preliminary voltage cycling (CV-polarization) over 50 cycles in a voltage range of +0.5 to −0.5 V at a scan rate of 10 mV/s at 20°C with a Model 273 Potentiostat/Galvanostat of Princeton Applied Research. The ac impedance of the test cells with or without CV-polarization was measured with an HP4194A impedance-gain phase analyzer at a frequency of 1 MHz to 100 Hz at 20°C over 230 days. After the storage, the voltage of the cell was cycled again in ±0.5 V for 100 cycles.

For the test cells with LiPF<sub>6</sub>-containing gel-SPE, CV-polarization at 20°C did not bring any appreciable effect on the ac impedance even though the voltage range increased to ±3 V; the current decreased below 0.1 mA with cycles. The cell was cycled at an elevated temperature

of 60°C; the voltage range increased from ±0.5 V by 0.5-V steps until the current turned to increase. Once the cell got a current increasing with cycles at 60°C, it still provided a higher current of ca. 10 mA increasing with cycles even at 20°C in a voltage range of ±0.5 V.

The cell with a construction of Li/gel-SPE/DMcT + PAn was preliminary charged and discharged in a range of 4.5 to 2.0 V at a scan rate of 10 mV/s for 25 cycles at 20°C, and then stored at the same temperature. Open circuit voltage (OCV) and ac impedance were measured over 300 days.

#### 2.5. Lithium surface analysis by XPS

Two interfaces before or after CV-polarization were investigated by XPS measurement: Interface-I was Li/gel-SPE (EC-DMC-LiBF<sub>4</sub>-AN/VAc = 50:25:9:16 by mol%) and Interface-II was Li/gel-SPE (EC-PC-LiBF<sub>4</sub>-LiPF<sub>6</sub>-AN/VAc = 50:25:6:3:16 by mol%). Interface-I was polarized at 10 mV/s in a voltage range of −0.5 to +0.5 V over 50 cycles at 20°C, while Interface-II was polarized in −2.0 to +2.0 V at 60°C over ca. 20 cycles until the polarization current turned to increase. The cell with Interface-I was left for 2 h and the cell with Interface-II was left for 50 h at room temperature. They were disassembled in the dry argon atmosphere and the gel-SPE was carefully peeled off from the metallic lithium anode; a tiny specimen of the metallic lithium anode ca. 3 mm × 3 mm was mounted on an XPS stage; the depth profiles of Li 1s, O 1s, C 1s, F 1s, and N 1s of the Li surfaces were measured by Shimadzu Electron Spectrometer ESCA-850 with an energy resolution of 1.1 eV at Ag 3d<sub>5/2</sub> (Mg Kα 8 kV, 30 mA).

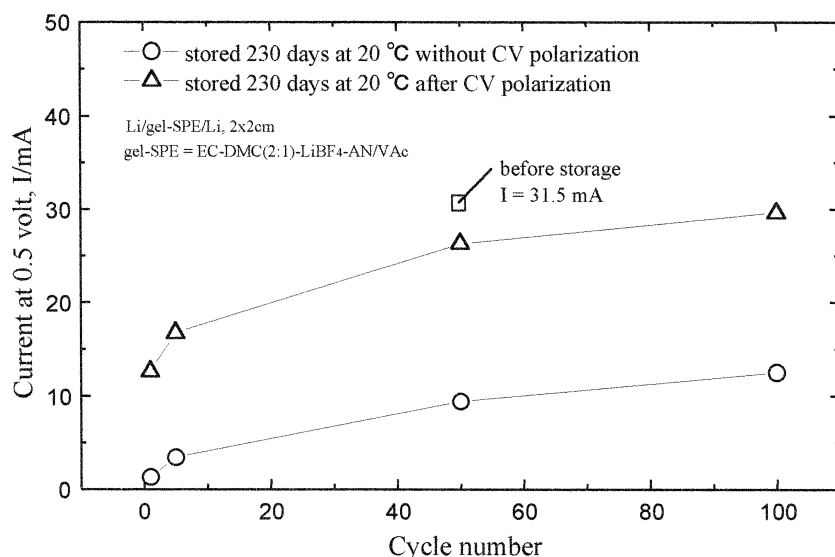


Fig. 3. CV current of Li/gel-SPE(LiBF<sub>4</sub>)/Li cells 2 cm × 2 cm in size stored at 20°C with or without CV-polarization.

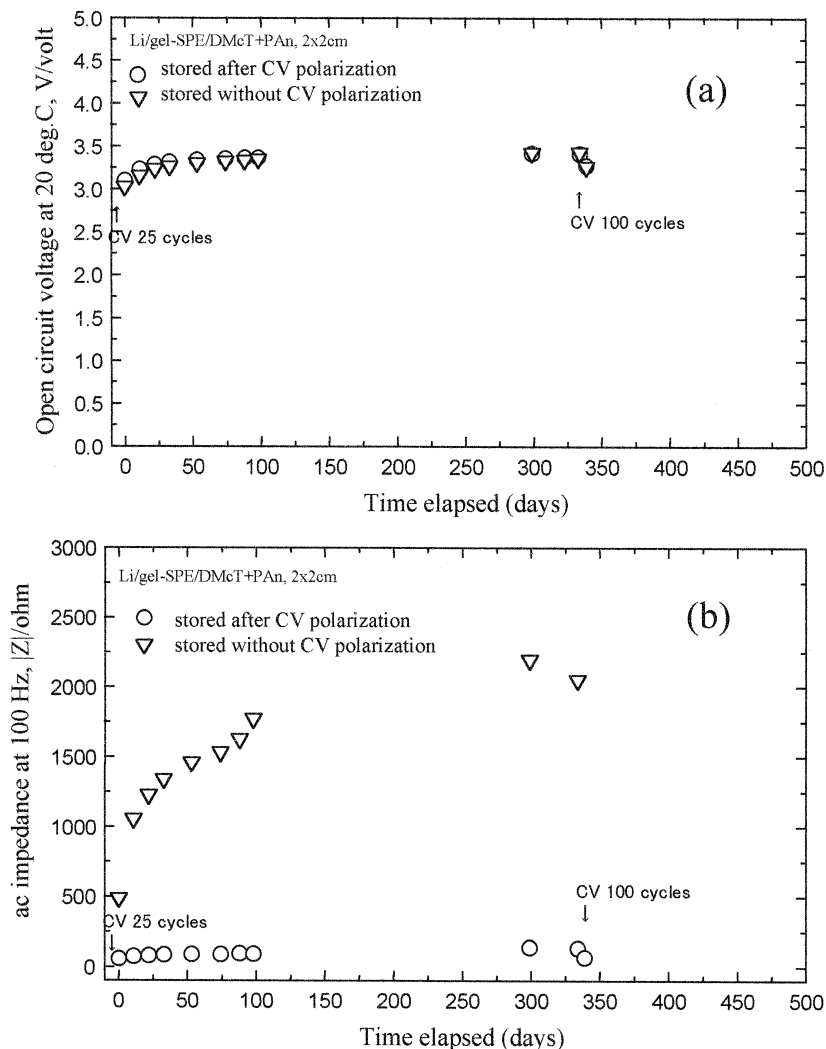


Fig. 4. Open circuit voltage and 100 Hz ac impedances of Li/gel-SPE (LiBF<sub>4</sub>)/DMcT + PAN cell during 20°C storage with or without CV-polarization.

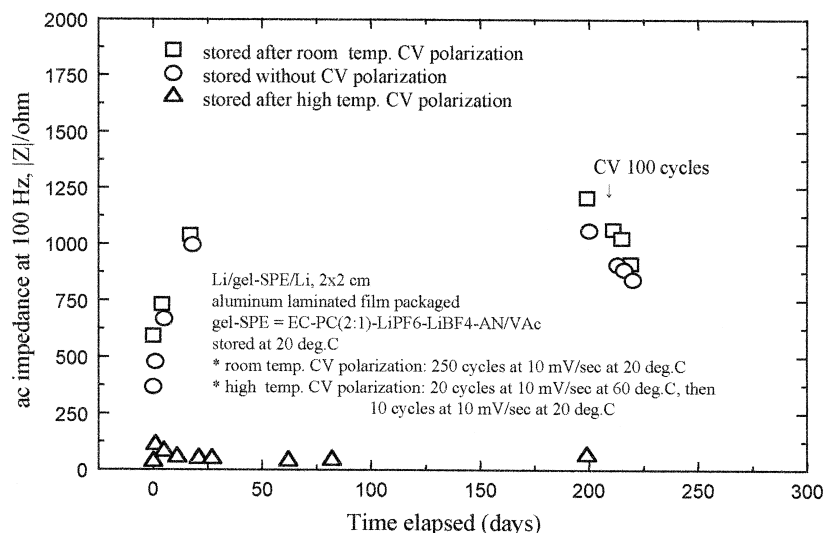


Fig. 5. Ac impedances at 100 Hz of Li/gel-SPE (LiPF<sub>6</sub>-LiBF<sub>4</sub>)/Li cells 2 cm × 2 cm in size during 20°C storage with or without CV-polarization at 20°C or 60°C.

### 3. Results and discussion

#### 3.1. Cell impedance with or without preliminary voltage cycling

Fig. 2 shows the impedances at 100 Hz and 10 kHz for the cells with Interface-I with or without preliminary CV-

polarization. As was reported in the previous work [5], the 10 kHz impedance which can be considered to reflect the bulk resistance of the gel-SPE was not influenced by CV-polarization and provided a lower constant value of around  $15 \Omega$  during storage. The 100-Hz impedance which can be considered to reflect the resistance at the metallic lithium interface was changed greatly by CV-polarization.

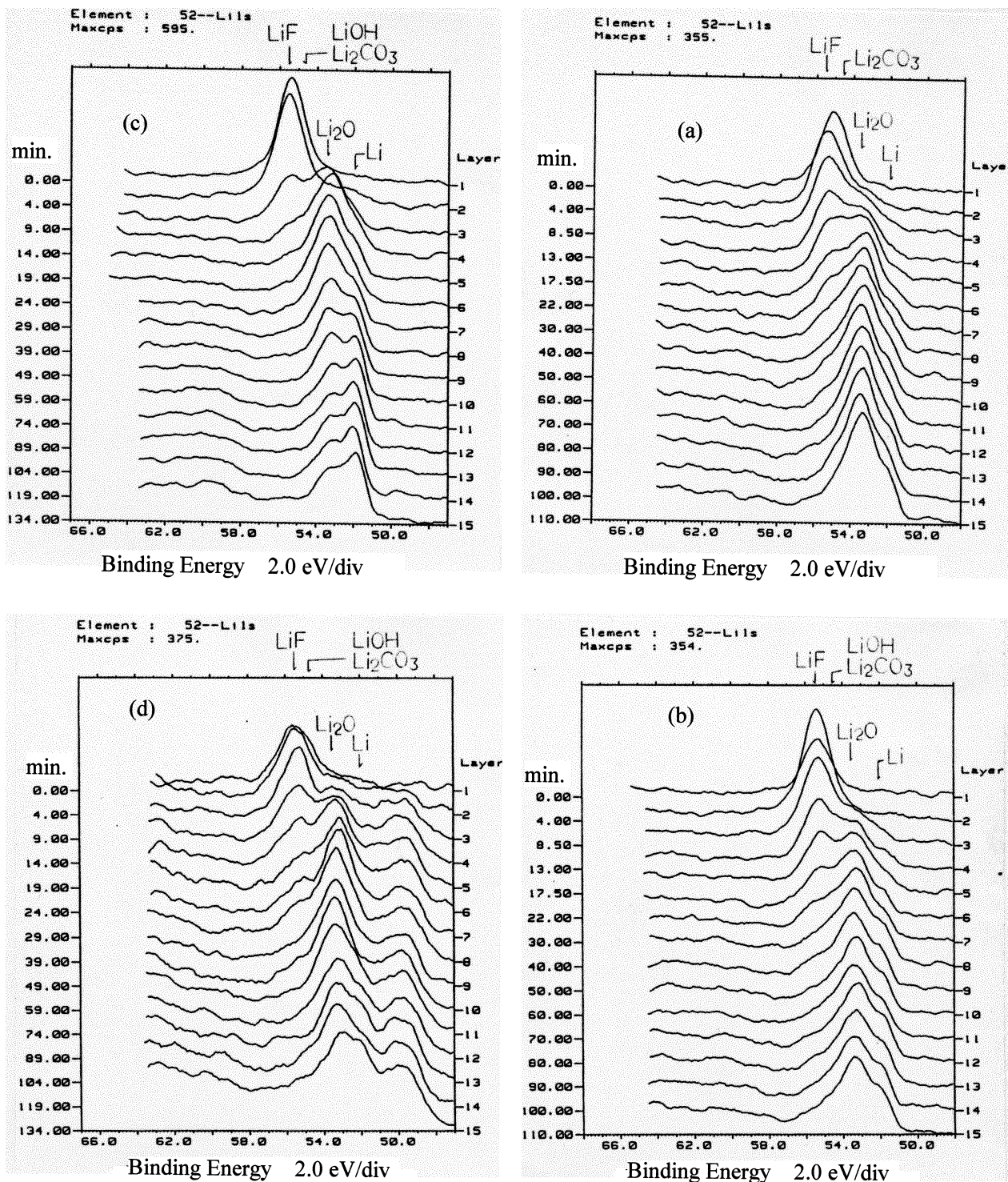


Fig. 6. XPS spectra of Li 1s on metallic lithium surface contacted to polymer gel electrolytes containing (a)  $\text{LiBF}_4$  without CV-polarization, (b)  $\text{LiBF}_4$  with CV-polarization, (c)  $\text{LiPF}_6\text{-LiBF}_4$  without CV-polarization, and (d)  $\text{LiPF}_6\text{-LiBF}_4$  with CV-polarization.

Further, even after 230 days storage, CV-polarization worked effectively; it reduced the 100 Hz impedance from ca. 1500  $\Omega$  to below 100  $\Omega$ . Fig. 3 shows the current at 0.5 V on CV-polarization; the cell with CV-polarization provided a current of 7.5 mA/cm<sup>2</sup> at 50th cycle, almost the same value with the fresh cell, while the cell without CV-polarization hardly restored the initial current even though the 100-Hz impedance almost recovered. This result indicates that CV-polarization is more effective in the earlier stage of storage.

The validity of CV-polarization was confirmed in a lithium cell system having a configuration of Li/gel-SPE/DMcT + PAn. Fig. 4 shows (a) the open circuit voltage and (b) 100-Hz impedances of the cells with or without CV-polarization. Although both cells showed an almost constant OCV of around 3.5 V over 300 days, the cell with CV-polarization provided a lower impedance, while the cell without CV-polarization gave a larger impedance of over 2000  $\Omega$ .

Interface-II with a gel-SPE containing LiPF<sub>6</sub> was found to be less sensitive to CV-polarization. The interface with a gel-SPE having a different mole ratio of LiPF<sub>6</sub>:LiBF<sub>4</sub> = 9:0, 7:2, 5:4, 3:6, or 1:8 was subjected to CV-polarization

at 20° and 60°C while the voltage range changed from  $\pm 0.5$  to  $\pm 3.0$  V. At 20°C, the CV current decreased with cycles below 0.1 mA even though the voltage range increased to  $\pm 3.0$  V. At 60°C, the CV current turned to increase with cycles, although a wider voltage range was required as the LiPF<sub>6</sub> content increased. Fig. 5 shows the 100 Hz impedance of a cell which had a gel-SPE with a LiPF<sub>6</sub>:LiBF<sub>4</sub> mole ratio of 3:6 and was stored after CV-polarization in a voltage range of  $\pm 2.0$  V at 60°C. The 100-Hz impedance was low and kept almost constant during storage.

### 3.2. Depth profiles of Li 1s, F 1s, O 1s, and C 1s of metallic lithium anode surface measured by XPS

The XPS spectra were analyzed based on the published data of binding energies [6–8], which are given in Table 1. As Takehara [9] reported for the surface structure of a metallic lithium facing to organic electrolyte solutions, Li, LiOH, Li<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub>, and LiF signals were also observed in the present study. Their peak heights were changed with etching time. Fig. 6 shows the spectra of Li1s. The depth profiles of Li 1s, C 1s, O 1s, and F 1s are given in Fig. 7.

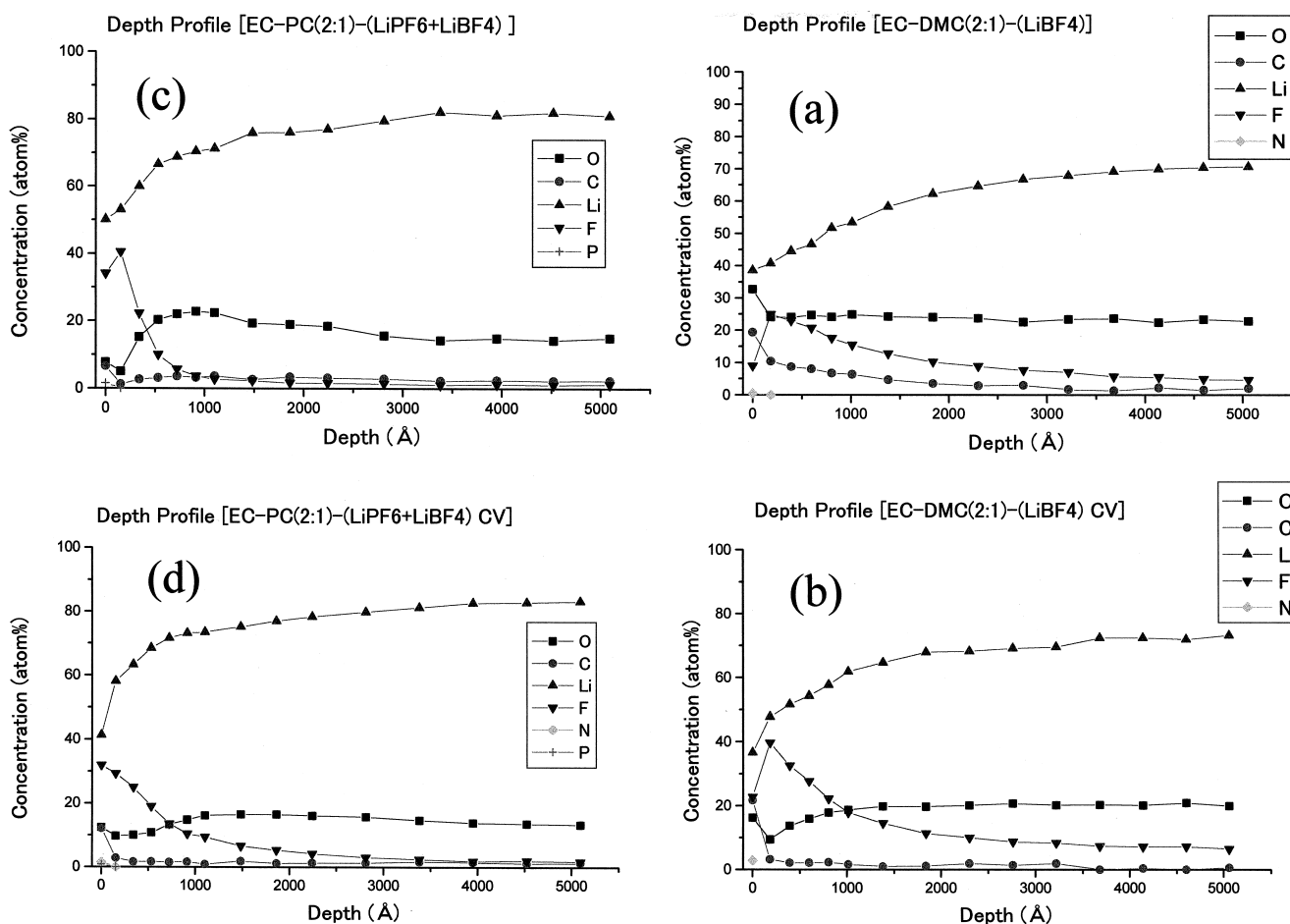


Fig. 7. XPS depth profiles of Li, C, O, F on metallic lithium surface contacted to polymer gel electrolytes containing (a) LiBF<sub>4</sub> without CV-polarization, (b) LiBF<sub>4</sub> with CV-polarization, (c) LiPF<sub>6</sub>-LiBF<sub>4</sub> without CV-polarization, and (d) LiPF<sub>6</sub>-LiBF<sub>4</sub> with CV-polarization.

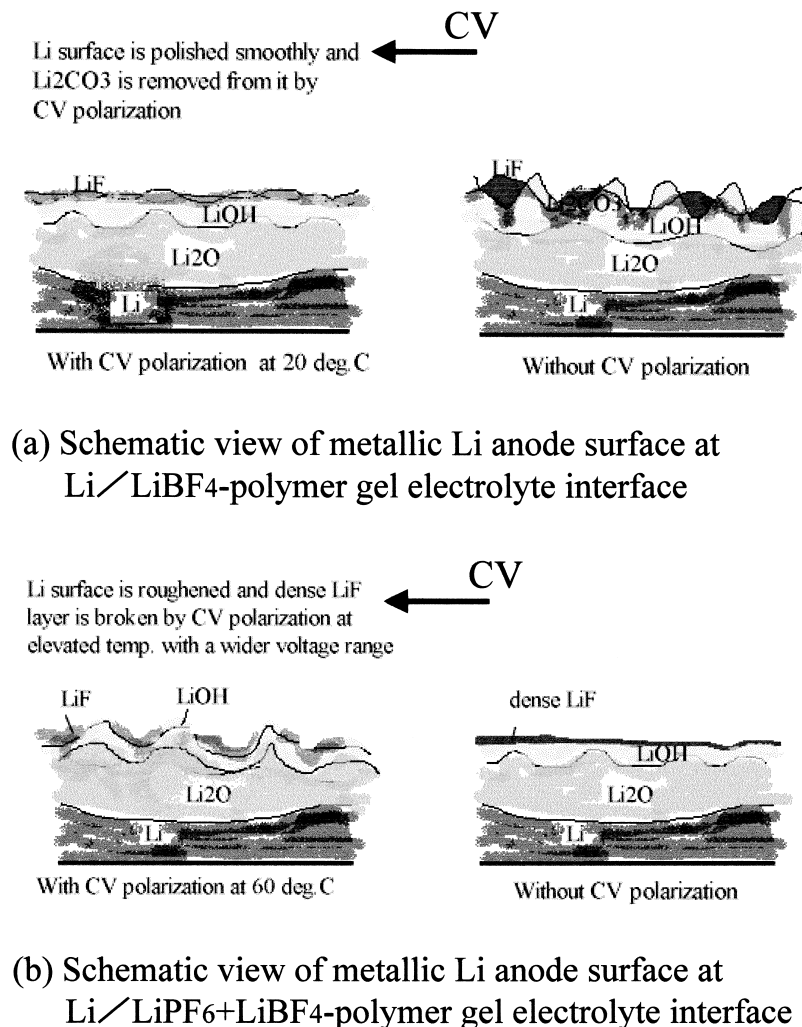


Fig. 8. Schematic illustrations of (a) lithium surfaces contacted to gel-SPE containing LiBF<sub>4</sub> and (b) lithium surfaces contacted to gel-SPE containing LiPF<sub>6</sub>-LiBF<sub>4</sub> with or without CV-polarization.

(a) is the result for Interface-I without CV-polarization, (b) is that for Interface-I with CV-polarization at 20°C, (c) for Interface-II without CV-polarization, and (d) for Interface-II with CV-polarization at 60°C. The etching rates were 46 nm (460 Å)/min for (a) and (b) and 38 nm (380 Å)/min

for (c) and (d) in terms of SiO<sub>2</sub>. The 100-Hz impedances are given in Table 2.

Carbon atom (C) assigned to Li<sub>2</sub>CO<sub>3</sub> spread deep in the metallic lithium contacted to LiBF<sub>4</sub>-containing gel-SPE, while no appreciable amount of C was detected in the metallic lithium surface contacted to LiPF<sub>6</sub> + LiBF<sub>4</sub>-containing gel-SPE. The fluorine atom (F) concentration in (a) or (b) at around zero depth is lower than that in (c) or (d). Less reactive LiBF<sub>4</sub> is considered to permit the reaction between the electrolyte and metallic lithium where Li<sub>2</sub>CO<sub>3</sub> is formed as a reaction product. More reactive

Table 1  
Binding energies of XPS spectra [6–8]

Spectra	Binding energies (eV)	Chemical species/bonding states
Li 1s	52.0	Li <sup>0</sup> (metallic Li)
	53.6	Li <sub>2</sub> O
	54.5	LiOH, Li <sub>2</sub> CO <sub>3</sub>
	55.2	LiF
C 1s	284.6	C–C, C–H, C=C
	289.5	Li <sub>2</sub> CO <sub>3</sub>
	528.2	Li <sub>2</sub> O
O 1s	528.2	Li <sub>2</sub> O
	530.8	LiOH
	531.4	Li <sub>2</sub> CO <sub>3</sub>
F 1s	685.0	LiF
	687.0	C–F

Table 2  
Impedance at 100 Hz of test cells (in Ω at 20°C)

	As assembled	After CV-polarization	Before disassembled
(a)	16	...	372
(b)	21	43	71
(c)	477	...	761
(d)	462	59	157

$\text{LiPF}_6$  reacts preferentially with metallic lithium and forms a dense LiF layer which might prevent the reaction between the electrolyte and metallic lithium. By CV-polarization, C assigned to  $\text{Li}_2\text{CO}_3$  disappeared except the very vicinity of the outmost surface and the F concentration increased as shown in Fig. 7b. This suggests that a LiF–LiOH layer free of  $\text{Li}_2\text{CO}_3$  is formed after CV-polarization. As to the metallic lithium surface contacted to  $\text{LiPF}_6 + \text{LiBF}_4$ -containing gel-SPE (Interface-II), the narrower concentration profile of F becomes broad and oxygen (O) is mixed with F by CV-polarization as shown in Fig. 7d. A dense LiF layer is considered to be broken into a rough LiF–LiOH layer.

## 4. Conclusions

### 4.1. Proposing surface structure of metallic lithium anode facing to gel-SPE

(1)  $\text{Li}_2\text{CO}_3$  which spreads into the surface layer of the Li anode surface facing to a  $\text{LiBF}_4$ -containing gel-SPE (Interface-I) is found to disappear by CV-polarization (voltage cycling) and a layer consisting of LiF and LiOH covers the Li surface as illustrated in Fig. 8a. This interface subjected to CV-polarization works electrochemically active even after 230-day storage, providing a CV current of almost the same value of  $7.5 \text{ mA/cm}^2$  at 0.5 V as a fresh interface. The LiF–LiOH layer is considered to have an action preventing direct contact between electrolyte solvent and metallic Li, preventing  $\text{Li}_2\text{CO}_3$  formation, keeping lower interfacial impedance.

(2) The lithium anode surface facing to a  $\text{LiPF}_6$ -containing gel-SPE (Interface-II) is found to have a thin surface layer rich in LiF as illustrated in Fig. 8b. The interfacial

impedance is not lowered by CV-polarization at  $20^\circ\text{C}$  even though the polarization voltage is increased over 3.0 V. The LiF layer is not easy to break by CV-polarization at  $20^\circ\text{C}$ . However, this layer is found to be collapsed by CV-polarization at an elevated temperature of  $60^\circ\text{C}$ ; a layer containing LiF and LiOH becomes predominant on the Li surface. The Interface-II also provides a lower interfacial impedance in the following storage.

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