

# Interfacial enhancement between lithium electrode and polymer electrolytes

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## Abstract

A protected lithium electrode was prepared by forming a protection layer on the surface of lithium metal. The protection layer was formed by ultraviolet (UV) radiation-curing of a mixture of crosslinking agent (1,6-hexanediol diacrylate), liquid electrolyte (ethylene carbonate (EC)/propylene carbonate (PC)/1 M LiClO<sub>4</sub>), and photoinitiator (methyl benzoylformate). The interfacial properties of a symmetric lithium cell containing the protected lithium electrode was better than those of the cell using a bare lithium electrode with storage. The performance of unit cells was also enhanced by the introduction of the protection layer on the surface of the lithium anode. The morphology of the solid electrolyte interphase (SEI) layer developed on the protected lithium anode during the charge–discharge runs at 1C rate was smoother at the surface and less porous.

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## 1. Introduction

Rechargeable lithium batteries with metallic lithium anodes are expected to achieve a high energy density due to a high specific capacity (3860 mAh/g) of the lithium electrode. However, the thermodynamic instability of lithium electrode in contact with most electrolytes leads to a formation of solid electrolyte interphase (SEI) layers and a dendritic growth of lithium on the electrode surface that can result in an unexpected electrochemical behavior such as capacity loss, low cycling efficiency, and poor cycleability. The SEI layer is formed on the lithium metal surface by the reaction of lithium with water trace, other impurities, organic solvent, and salt anions. It acts as an interphase between the lithium electrode and the polymer electrolyte. It is quite important to control the electrode/polymer electrolyte interface to obtain the higher energy density and the good cycling efficiency of the batteries [1]. The lithium/polymer electrolyte interface plays a fundamental role in determining cell behavior such as cycleability, cycling performance at high rate, and safety. The interfacial properties between lithium electrode and a gel polymer electrolyte can be influenced by various origins such as concentration of mobile lithium ions, degree of the reductive

reaction of liquid electrolyte, and physical adhesion of the polymer electrolyte to the lithium electrode at the interface.

Much effort has been exerted to improve the surface uniformity of the SEI layer through modification of lithium metals. The formation of a passivation layer on the lithium surface is promoted by adding agents such as CO<sub>2</sub> [2–4] or HF [5,6], and thus the dendritic lithium formation can be much suppressed. SnI and AlI<sub>3</sub> were also proposed as additives to improve the lithium rechargeability [7,8]. Another approach for controlling the passivation layer formation has been taken by forming an ultra-thin plasma polymer layer of the solid polymer electrolyte on the lithium anode surface [9]. To protect the reactive lithium metals by covering their surface with organic compounds would be one of the smart ways to prevent them from corrosion or to minimize the passivation on the lithium metal surface.

In this work, thin polymer films for protection were tried to form on the lithium electrode surface by means of the ultraviolet (UV) radiation-curing of the mixture containing a crosslinking agent, liquid electrolyte, and photoinitiator. This protection layer is aimed to enhance the physical contact between the polymer electrolyte and the lithium metal, minimize the decomposition reaction of the liquid electrolyte on the metallic lithium surface, and develop the uniform SEI layer by suppressing the formation of the lithium dendrite. The effect of the protection layer on the interfacial stability with storage was discussed. The morphology of the SEI layer

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formed on the lithium electrodes was also investigated under cycling.

## 2. Experimental

A copolymer of vinylidene fluoride and hexafluoropropylene (Kynar 2801, Atochem Co.) was dried under vacuum at 80 °C for 24 h. A liquid electrolyte of ethylene carbonate (EC)/propylene carbonate (PC) (1/1, w/w) containing 1 M LiClO<sub>4</sub> was provided by Merck and was dried with 3 Å silica molecular sieves prior to use. Kynar 2801-based bulk polymer electrolyte was prepared by solution casting of the mixture of the matrix polymer/liquid electrolyte (25/75, w/w) and tetrahydrofuran (THF) as solvent.

The UV-curable formulation consists of curable monomer, liquid electrolyte (150 wt.% based on curable monomer), and photoinitiator (2 wt.% based on curable monomer) undergoing a fast cleavage upon photolysis to generate free radicals. A curable mixed solution was poured on the lithium metal surface and uniformly spread by using Mylar film. It was irradiated with UV light for 3 min and then the protection film was formed on the lithium metal surface. The amount of the liquid electrolyte in the protection layer was 150 wt.% of the matrix polymer. Fig. 1a presents the chemical structures of the crosslinking agent, 1,6-hexanediol diacrylate and the crosslinked polymer matrix after UV-curing. Fig. 1b shows the SEM image of the cross-section of the protection layer from which a liquid electrolyte has been extracted with methanol. The thickness of the protection layer was about 10 μm. Fig. 2 shows FT-IR spectra for the

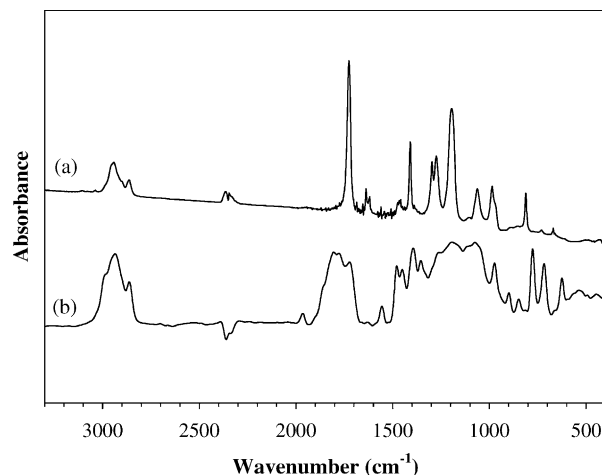


Fig. 2. FT-IR spectra for (a) 1,6-hexanediol diacrylate and (b) crosslinked protection layer after UV-curing.

chemical structure of the protection layer formed from 1,6-hexanediol diacrylate by UV-curing. There are no peaks found at  $\sim 1640$  and  $\sim 820$   $\text{cm}^{-1}$  indicating that all the double bonds in the monomer have reacted. The ionic conductivities of the protection layer and bulk polymer electrolytes were obtained from bulk resistance measured by ac impedance analysis using Solartron 1255 frequency response analyzer (FRA). The interfacial resistance of a symmetric lithium cell and the impedance of the unit cell were also measured by ac complex impedance analysis.

The unit cells were assembled by sandwiching the bulk polymer electrolyte between the cathode (LiCoO<sub>2</sub>) and the

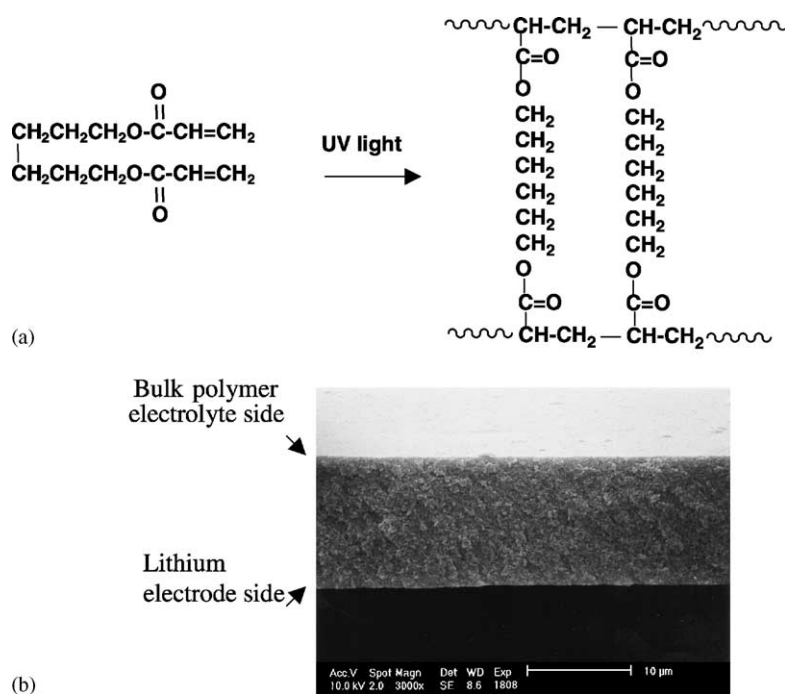


Fig. 1. Chemical structure of crosslinked polymer matrix based on 1,6-hexanediol diacrylate (a) and SEM image for the cross-section of the protection layer (b).

metallic lithium anode. The charge–discharge test of a Li/bulk polymer electrolyte/LiCoO<sub>2</sub> cell (cell size, 4 cm<sup>2</sup>) with and without the protection layer was conducted in the voltage range 3.0–4.2 V with galvanostatically-controlled equipment. The cathode was prepared by casting cathode slurry (87% LiCoO<sub>2</sub>, 7% super-P, and 6% PVdF binder by weight) on an aluminum foil. The cathode thickness was 90 μm and active mass loading corresponded to a capacity of 3 mAh/cm<sup>2</sup>. The morphology of the lithium metal surface was investigated using the Philips SEM 535M.

Before recording an infrared spectrum the sample was directly cast onto a KBr window and exposed to UV-radiation for 5 min. The FT-IR spectra were recorded in transmission on Bomem MB 102 spectrometer with a resolution of 4 cm<sup>-1</sup> in the vibration frequency range of 400–4000 cm<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Effect of the protection layer on interfacial properties under an open-circuit condition

Fig. 3 illustrates an impedance plot of the lithium symmetric cell with a time evolution. The initial interfacial resistance of the lithium symmetric cell introducing the protection layer on the surface of the lithium electrode is higher than that of the cell using a bare lithium electrode. This seems to be related to the ionic conductivities of the polymer electrolyte in contact with the lithium electrode. The ionic conductivity of the protection layer is lower than that of the bulk polymer electrolyte containing a larger amount of the liquid electrolyte as shown in Table 1. However, it is apparent from Fig. 3 that the interfacial stability of

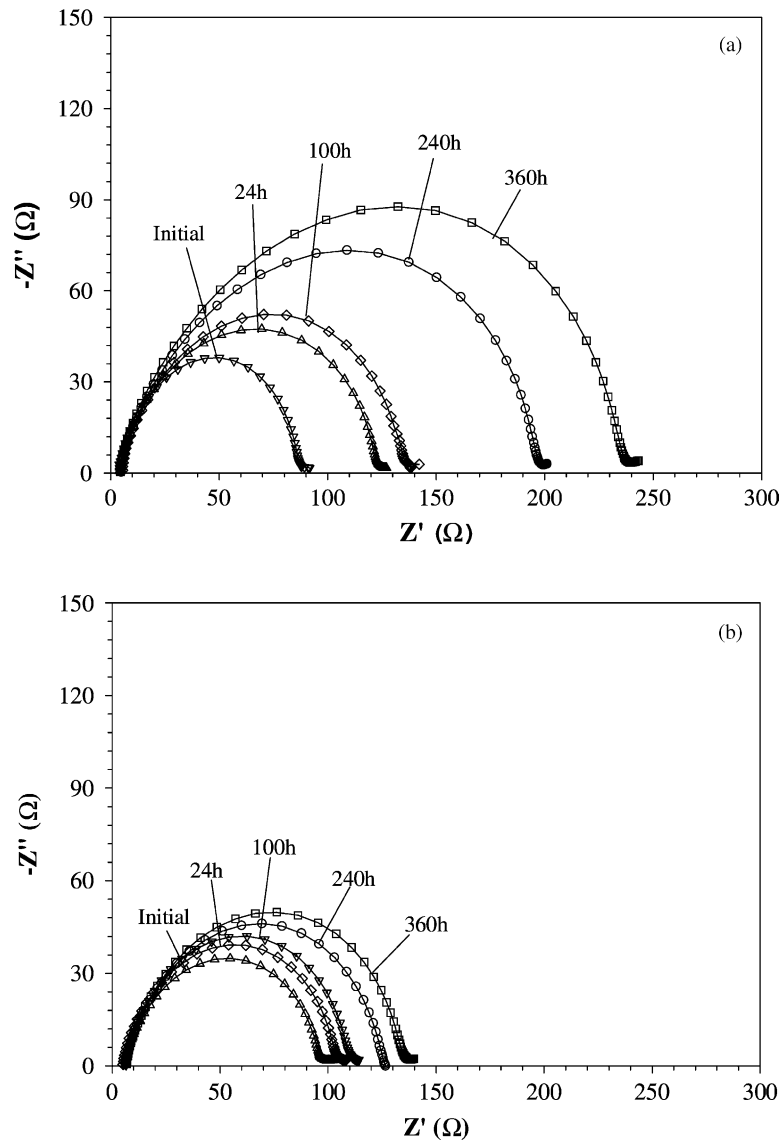


Fig. 3. Impedance spectra of the lithium symmetric cell with for (a) Li/bulk polymer electrolyte/Li and (b) Li/protection layer/bulk polymer electrolyte/protection layer/Li as a function of the storage time.

Table 1  
Composition of protection layer and bulk polymer electrolyte

	Base material	Thickness ( $\mu\text{m}$ )	$\sigma$ (S/cm)
Protection layer	Crosslinked polymer electrolyte based on 1,6-hexanediol diacrylate (150 wt.% EC/PC/1 M LiClO <sub>4</sub> )	10	$5.8 \times 10^{-4}$
Bulk polymer electrolyte	Gel polymer electrolyte based on Kynar 2801 (300 wt.% EC/PC/1 M LiClO <sub>4</sub> )	75	$2.2 \times 10^{-3}$

the gel polymer electrolyte to the lithium electrode is enhanced by the introduction of the protection layer. This result originates from the difference in the passivation behavior at the lithium metal electrode/polymer interface between the above two cases. When the bulk polymer electrolyte is in direct contact with the bare lithium electrode, a larger amount of liquid electrolyte immobilized in the bulk polymer electrolyte can induce more significant passivation at the lithium metal/bulk polymer electrolyte interface by the decomposition reaction of the plasticizer such as EC and PC or impurities. The protection layer containing a smaller amount of liquid electrolyte than the bulk polymer electrolyte could enhance the interfacial stability to the lithium metal electrode with storage.

3.2. Morphological characteristics of SEI layer formed on the lithium electrode during cycling

Fig. 4 shows the initial impedance of the unit cell with the configuration of Li/bulk polymer electrolyte/LiCoO<sub>2</sub> or Li/protection layer/bulk polymer electrolyte/LiCoO<sub>2</sub>. The initial total resistance of the unit cell based on the Li/protection layer/bulk polymer electrolyte/LiCoO<sub>2</sub> is higher

than that of the unit cell based on the Li/bulk polymer electrolyte/LiCoO<sub>2</sub>. Fig. 5a and b presents the voltage profiles during the discharge for the unit cell without and with protection layer at a different current density. The cycle test of the unit cell was carried out with a cut-off voltage of 3.0 and 4.2 V at room temperature. The discharge capacity retention of the Li/protection layer/bulk polymer electrolyte/LiCoO<sub>2</sub> cell with increasing current density is better than that of the Li/bulk polymer electrolyte/LiCoO<sub>2</sub> cell. When the protection layer was introduced on the lithium anode, the passivation is expected to reduce during the charge process due to a lower amount of the liquid electrolyte contacting with the lithium anode. The lithium ions dissolved from the lithium anode could more easily migrate through the thin

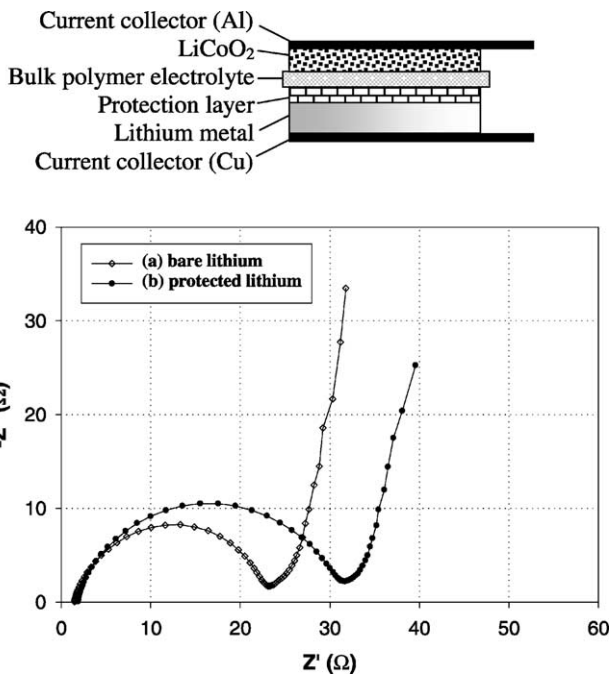


Fig. 4. Cell construction of the unit cell (upper) and initial impedance spectra of the unit cell based on (a) Li/bulk polymer electrolyte/LiCoO<sub>2</sub> and (b) Li/protection layer/bulk polymer electrolyte/LiCoO<sub>2</sub> at 25 °C (bottom).

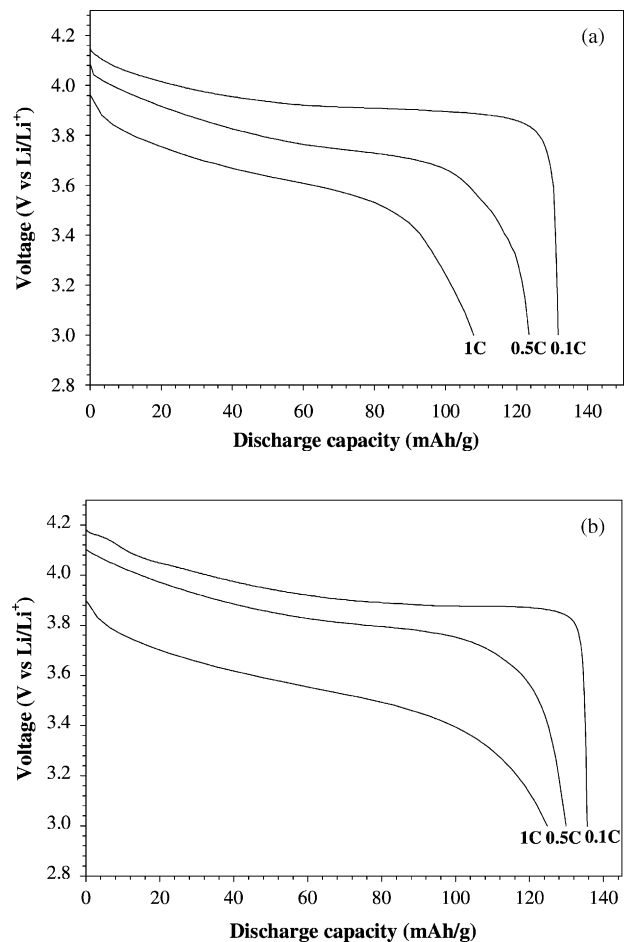


Fig. 5. Voltage profiles of the unit cell based on (a) Li/bulk polymer electrolyte/LiCoO<sub>2</sub> and (b) Li/protection layer/bulk polymer electrolyte/LiCoO<sub>2</sub> during discharge as a function of current density.

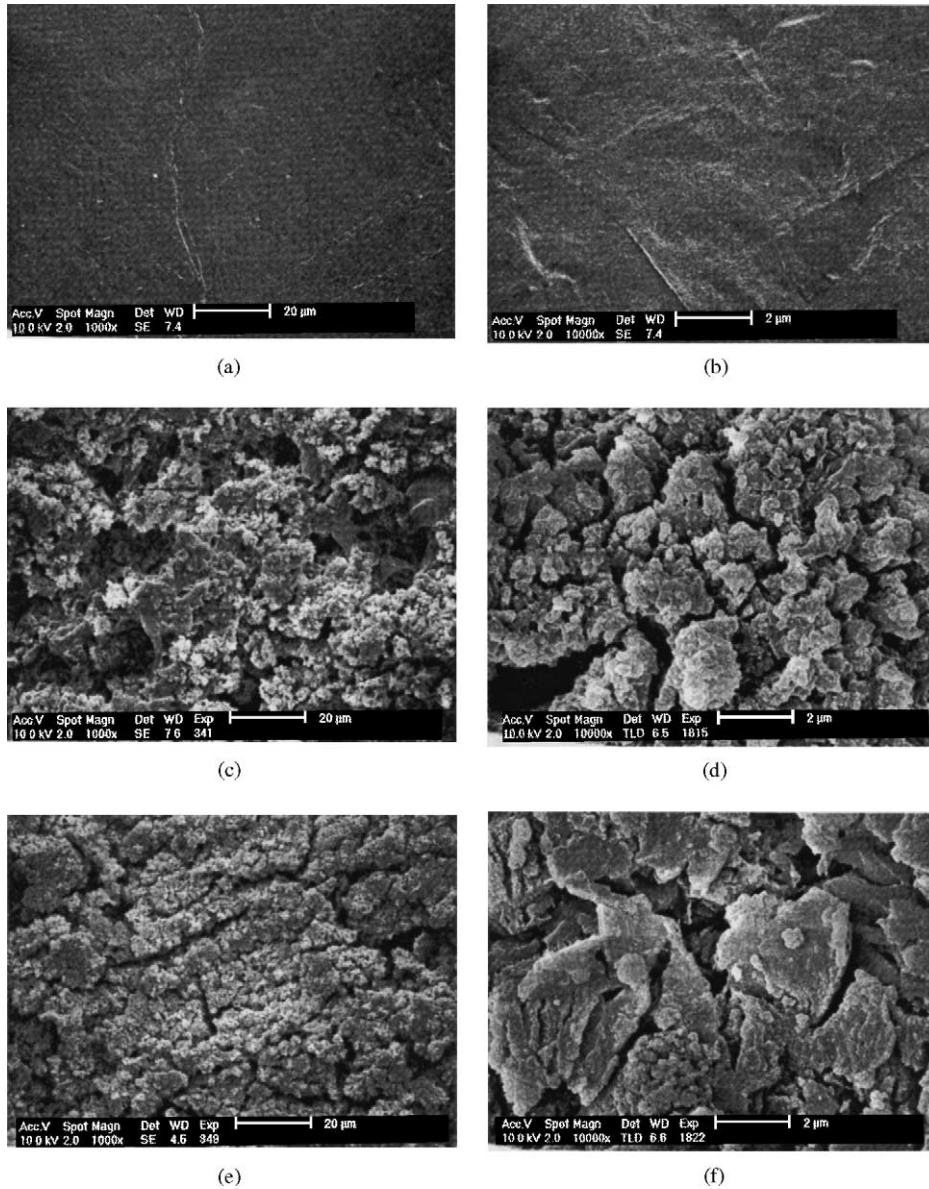


Fig. 6. SEM images for the surface of (a and b) bare lithium electrode (1000 $\times$  and 10,000 $\times$ ); (c and d) SEI layer formed on the non-protected lithium electrode (1000 $\times$  and 10,000 $\times$ ); (e and f) SEI layer formed on the protected lithium electrode (1000 $\times$  and 10,000 $\times$ ).

SEI layer formed on the protected lithium anode. Therefore, the discharge specific capacity of the unit cell with the protection layer is higher than that of the unit cell without the protection layer on cycling.

Fig. 6 shows SEM images of the surface of a bare lithium electrode and the SEI layer formed on the non-protected and the protected lithium electrodes after one cycle at 1C rate. It is seen in Fig. 6e and f that the surface of the SEI layer formed on the surface of the protected lithium electrode is relatively smooth. Since the protection layer based on the crosslinked gel polymer electrolyte is directly formed on the surface of the lithium electrode by coating, the uniform physical adhesion of the protection layer to the lithium electrode can be obtained. In general, gel polymer electrolyte films have a rough surface and thus the physical contact

with lithium electrode is non-uniform. Due to this incomplete physical contact, the SEI layer formed on the surface of non-protected lithium electrode becomes very rough at the surface and porous as shown in Fig. 6c and d. The rough surface of the SEI layer can cause the formation of the dendritic lithium with cycling and hence lead to a capacity loss of the lithium anode.

### 3.3. Correlation between cell performance and composition of the SEI layer

The discharge voltage profiles of the unit cells with and without the protection layer at a cycling rate of 3 mA/cm<sup>2</sup> are shown in Fig. 7a and b, respectively. The discharge specific capacities of the unit cell without the protection

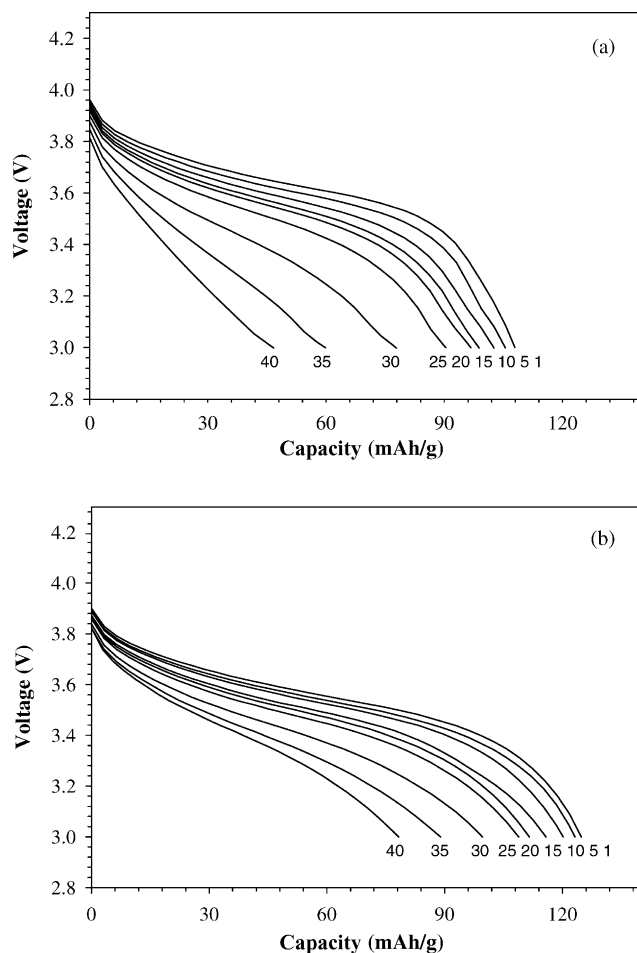


Fig. 7. The discharge voltage profiles of the unit cell based on (a) Li/bulk polymer electrolyte/LiCoO<sub>2</sub> and (b) Li/protection layer/bulk polymer electrolyte/LiCoO<sub>2</sub> during 40 cycles at 1C rate.

layer are lower than those of the symmetric lithium cell with the protection layer for the first cycle. In addition, the discharge specific capacities of the unit cell without the protection layer are sharply reduced in the subsequent cycles as shown in Fig. 7a. This means that the sufficient dissolution of lithium from the surface of the non-protected lithium anode does not occur. It is mainly attributable to the SEI layer formation by reductive decomposition of the liquid electrolyte diffusing from the bulk polymer electrolyte. The continuous decomposition of the liquid electrolyte from repeated deposition and dissolution of lithium may develop a thicker SEI layer at the lithium/polymer electrolyte interface. The thicker SEI layer might hinder the dissolution of lithium from the lithium anode or the diffusion of dissociated lithium ions through the SEI layer. However, the discharge specific capacities of the unit cell with the protection layer slowly declined with cycling as shown in Fig. 7b. From these results, it is concluded that the protection layer could prohibit the liquid electrolyte from decomposing on the surface of the lithium metal and thus a thinner SEI layer might be formed at the interface. At a relatively high cycling rate such as 1C, the introduction of the protection layer on

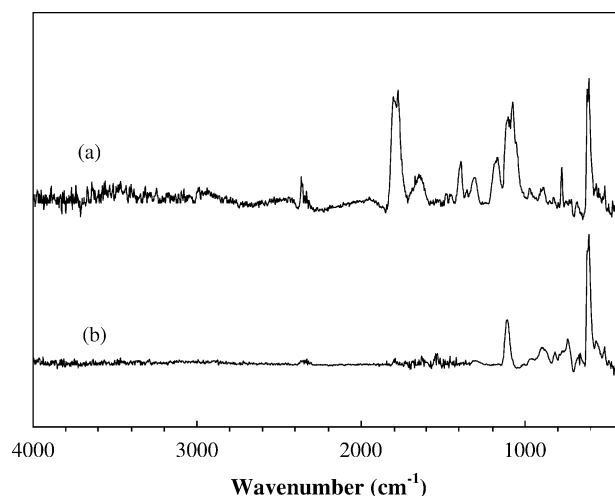


Fig. 8. FT-IR spectra of the SEI layer formed on (a) non-protected lithium anode and (b) protected lithium anode.

the lithium anode could make the deposition and the dissolution process more effective.

Fig. 8 shows FT-IR spectra of the SEI layer formed at the non-protected lithium anode and the protected lithium anode after 40 cycles at 1C rate. Irrelevant to the protection of the lithium anode, the peaks related to new compounds such as LiCl and LiClO<sub>3</sub> by the reductive decomposition of the salt anions (ClO<sub>4</sub><sup>-</sup>) appear around 600–630 cm<sup>-1</sup> as shown in Fig. 8a and b. The peaks corresponding to Li<sub>2</sub>CO<sub>3</sub> produced by the reductive decomposition of EC and PC also appear around 1520, 1450, 1100, 870, and 500 cm<sup>-1</sup>. For the SEI layer formed on the non-protected lithium anode, strong peaks of the lithium alkyl carbonates (ROCO<sub>2</sub>Li) are observed at 1650, 1308, 1070, and 821 cm<sup>-1</sup>. The peaks corresponding to EC and PC were also observed for the SEI layer formed on the non-protected lithium anode as shown in Fig. 8a. The presence of the lithium alkyl carbonates, EC, and PC, in the SEI layer means that the passivation can continuously occur by reductive reaction at the interface during cycling. However, for the SEI layer formed on the protected lithium anode, the peaks corresponding to lithium alkyl carbonates, EC and PC, are absent as shown in Fig. 8b. It is evident that for the protected lithium anode, less passivation occurs and the SEI layer mainly consists of relatively stable Li<sub>2</sub>CO<sub>3</sub> instead of lithium alkyl carbonates upon cycling. Therefore, the discharge specific capacities of the unit cell with the protection layer can be higher than that of the unit cell without the protection layer with cycling at a rate of 1C.

#### 4. Conclusions

The present study has proved that a protection layer based on the crosslinked gel polymer electrolyte is effective for minimizing the passivation caused by the decomposition reaction of the liquid electrolyte (EC/PC/1 M LiClO<sub>4</sub>) on the

surface of the lithium electrode. It was found that the electrochemical performance of the lithium metal polymer battery is enhanced by the introduction of the protection layer at the interface of the lithium anode/bulk polymer electrolyte.

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