

Modification of lithium/electrolyte interface by plasma polymerization of 1,1-difluoroethene

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Abstract

Surface of lithium electrodes was covered by an ultra-thin and uniform solid polymer electrolyte layer conductive for lithium ion which was prepared from 1,1-difluoroethene by plasma polymerization. The solid polymer electrolyte showed room temperature conductivity of $3 \times 10^{-8} \text{ S cm}^{-1}$. Lithium was deposited (1 C cm^{-2}) on the surface-modified lithium electrode in 1 M LiClO_4 /propylene carbonate. Scanning electron microscopy observation suggests that dendritic growth of lithium was suppressed on the lithium electrodes surface modified by the ultra-thin solid polymer electrolyte.

Introduction

Much effort has been devoted to produce lithium secondary batteries for these several years and some kinds of secondary Li batteries are produced and commercialized. However, such batteries do not have a sufficient cycle life [1, 2]. Some problems remain to be solved for the development of secondary Li batteries of high performance, and one of the most important of them is to suppress the dendritic crystal growth during battery charging [3-5]. Although the dendritic growth mechanism in deposition of metals has been investigated for a long time, it is not clear yet. The dendritic growth of Li reduces not only the cycle life, but also the battery capacity and the safety. Lithium alloys [6, 7] and Li-carbon [8, 9] have attracted much attention as anode materials of secondary Li batteries which do not present any dendritic Li growth.

Recently, Takehara *et al.* [10] have revealed the formation of films of high electric resistivity between polymer electrolyte and Li. Aurbach *et al.* [11-13] reported a similar film formation on the interface between liquid electrolytes and Li. It is very difficult to suppress the film formation on the Li surface because of high reactivity of Li. A nonuniform film formation is considered to cause the dendritic growth [3]. In this communication, it is aimed to control the film formation on the lithium surface. A stable uniform film conductive for Li cation may suppress the dendritic growth as it is in the case of an electrolyte solution using LiAsF_6 , which is considered to form a stable film on Li conductive for Li cation and enables, therefore, a uniform deposition of Li [14]. In this work, a stable thin polymer film was formed on the Li by plasma polymerization. As a starting monomer for a plasma polymer, 1,1-difluoroethene, was selected since poly(1,1-difluoroethene) is known to give an ionic conductivity by complexing with Li salts, although its conductivity is low [15].

Experimental

Surface modification of lithium electrodes by plasma polymerization

A schematic diagram of the process for modification of Li electrodes by an ultra-thin solid polymer electrolyte layer is shown in Fig. 1.

Commercially-available Li films are usually covered with some Li compounds such as, e.g., Li oxide, Li carbonate, Li hydrate [16]. After this layer being removed by Ar sputtering for 90 min to remove the native film from the Li surface, an ultra-thin plasma polymer layer (0.6 μm) of solid polymer electrolyte was deposited on the Li surface immediately after sputtering in the same reactor.

Materials

1,1-Difluoroethene (DFE) (SCM Chemicals, extra pure grade) and 1 M Li perchlorate/propylene carbonate (Mitsubishi Petrochemical Company, battery grade) were used without further purification.

Plasma treatment

A schematic diagram of the apparatus for plasma treatment is shown in Fig. 2. The system for plasma treatment consists of a glass reactor equipped with a pair of stainless steel SUS-304 inner disk electrodes (diameter: 8 cm, gap: 6 cm), two gas inlet lines, a Pirani gauge, an ionization vacuum gauge, and an RF power supply (13.56 MHz) with an impedance matching network. This reactor was connected to a pumping system consisting of a diffusion pump and a rotary pump. Glass plate deposited with Au and Li metal plate were used as substrates. The substrate Li was placed on the RF power electrode for Ar sputtering in the beginning. After sputtering, the substrate was moved on the substrate holder located between two inner electrodes for plasma polymerization.

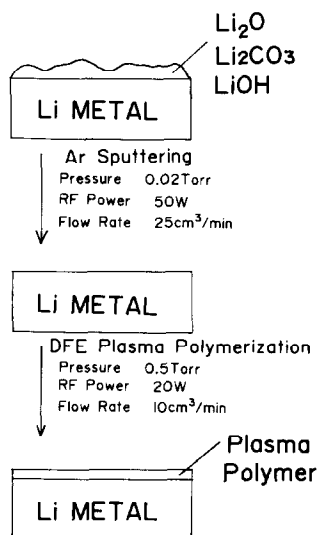


Fig. 1. Procedure for lithium surface modification by an ultra-thin solid polymer electrolyte film.

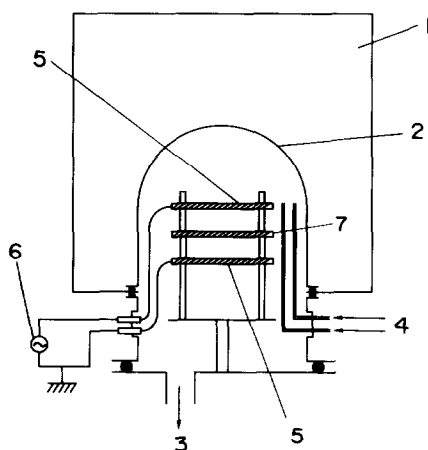


Fig. 2. Schematic diagram of an apparatus for plasma surface treatment: 1: vacuum dry box, 2: glass bell-jar, 3: pumping system, 4: gas inlets, 5: parallel electrodes, 6: 13.56 MHz power generator with matching network, and 7: substrate holder.

In order to prepare an ultra-thin fluorinated solid polymer electrolyte layer on the Li surface, 1,1-difluoroethene was selected as a monomer of plasma polymerization. The thin layer is required to have Li ion conductivity for use in Li batteries. Tsunemi *et al.* [15] reported that poly(1,1-difluoroethene)-LiClO₄ complex showed an ionic conductivity of $4 \times 10^{-7} \text{ S cm}^{-1}$ at room temperature.

The reactor was pumped to a pressure lower than 10^{-4} Pa before the plasma treatment. The system was set at a constant pressure by controlling a throttle valve connecting to the vacuum pump. The Li substrate was sputtered with an Ar plasma at a flow rate of $25 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$, pressure of 2.7 Pa and RF power of 50 W for 90 min. Plasma polymerization was performed at monomer flow rate of $10 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$ pressure of 67 Pa and RF power of 20 W for 10 min.

Measuring techniques

The surface and cross-sectional morphology of the plasma polymer layer formed on Au/glass was observed with a scanning electron microscope (SEM) (JEOL JSM-20). The plasma polymer was characterized by Fourier-transform infrared spectroscopy (FT-IR) (Shimadzu FTIR-4100) using a reflection method and by electron spectroscopy for chemical analysis (ESCA) (Shimadzu ESCA-850). Static contact angle of the surface of the plasma polymer was measured using a contact angle meter (Kyowa International Science model CA-A).

Lithium disks (0.57 cm^2) deposited with the thin plasma polymer layer served as a working electrode. Lithium metal was used both as reference electrode and counter electrodes. 1 M Li perchlorate/propylene carbonate was used as electrolyte. The ohmic resistance of the plasma-polymerized solid polymer electrolyte film formed on the Li electrode when immersed in 1 M Li perchlorate/propylene carbonate was determined from a.c. impedance measurements carried out over the frequency range of 2×10^2 – 2×10^4 Hz using a vector impedance meter (Iwatsu SM-2100 A). Lithium was deposited from 1 M Li perchlorate/propylene carbonate on the surface-modified Li electrode (1 C cm^{-2}). The deposited Li was observed by SEM after rinsing with petroleum ether to remove Li perchlorate and propylene carbonate.

Results and discussion

Characterization of plasma-polymerized 1,1-difluoroethene

Plasma-polymerized 1,1-difluoroethene was a colourless, transparent solid. The rate of polymer deposition determined from substrate weight change was $2.2 \times 10^{-4} \text{ g cm}^{-2} \text{ h}^{-1}$.

A FT-IR spectrum of plasma-polymerized 1,1-difluoroethene is shown in Fig. 3. The spectrum exhibits absorption peaks at 2950 cm^{-1} (C–H vibration), 1750 cm^{-1} (C=O stretching vibration), and 1260 and 1150 cm^{-1} (C–F vibration). As compared with IR spectrum of 1,1-difluoroethene, the characteristic peak for an olefin group was completely absent and the peak strength of C–H vibration was decreased. On the other hand, a new small peak ascribed to C=O was observed for the plasma-polymerized 1,1-difluoroethene. These facts indicate that cleavage of the olefin double bond and removal of hydrogen atom have taken place during the plasma polymerization process. The C=O group was considered to be introduced by the reaction of radical sites remaining on the plasma polymer film with oxygen and/or water after exposure to air.

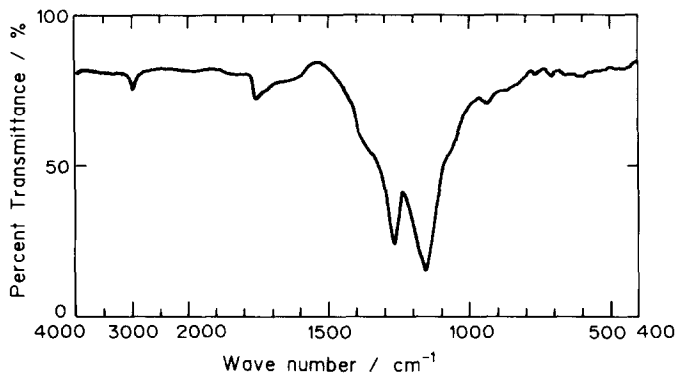


Fig. 3. FT-IR spectrum of plasma-polymerized 1,1-difluoroethene; flow rate of 1,1-difluoroethene: $10 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$; RF power: 20 W, and polymerization pressure: 67 Pa.

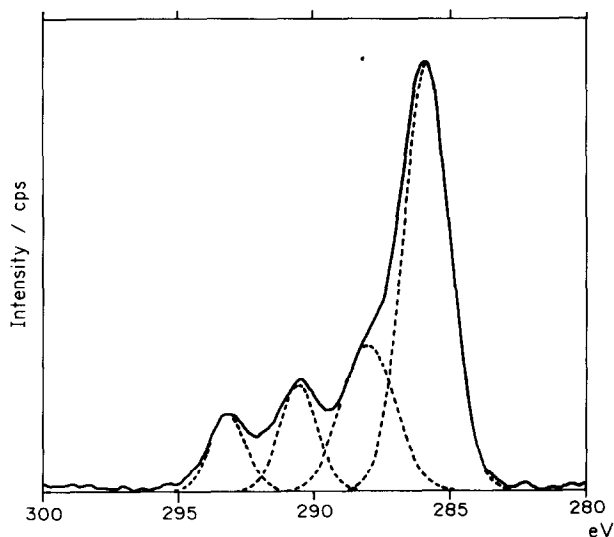


Fig. 4. ESCA C_{1s} spectrum of plasma-polymerized 1,1-difluoroethene; flow rate of 1,1-difluoroethene: $10 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$; RF power: 20 W, and polymerization pressure: 67 Pa.

Figure 4 shows ESCA C_{1s} spectrum of the plasma polymer. The spectrum can be deconvoluted into four components centered at ~ 294 , 292 , 288 , 286 eV which are assigned to CF_3 , CF_2 , C=O or $-\text{CF}-$, and C-CF_n sites, respectively [17]. The existence of CF_3 , CF_2 indicates that removal of hydrogen atom has taken place during the plasma polymerization process. This result is in agreement with the FT-IR observation of Fig. 3. The fluorine:carbon atomic ratio of the plasma polymer obtained by ESCA measurements is indicated in Table 1. The F:C ratio is 0.66 and is lower than that of monomer (F:C ratio=1). This result indicates that not only C-H bond but also C-F bond were cleaved during plasma polymerization. This means that a cross-linking reaction proceeded during the plasma polymerization.

Contact-angle measurements of the plasma polymer surface were conducted using a series of hydrocarbon liquids with different surface tensions. The critical surface

TABLE 1

F/C ratio of 1,1-difluoroethene and plasma-polymerized 1,1-difluoroethene

Compound	F/C atomic ratio
Plasma-polymerized 1,1-difluoroethene	0.66
1,1-Difluoroethene (monomer)	1

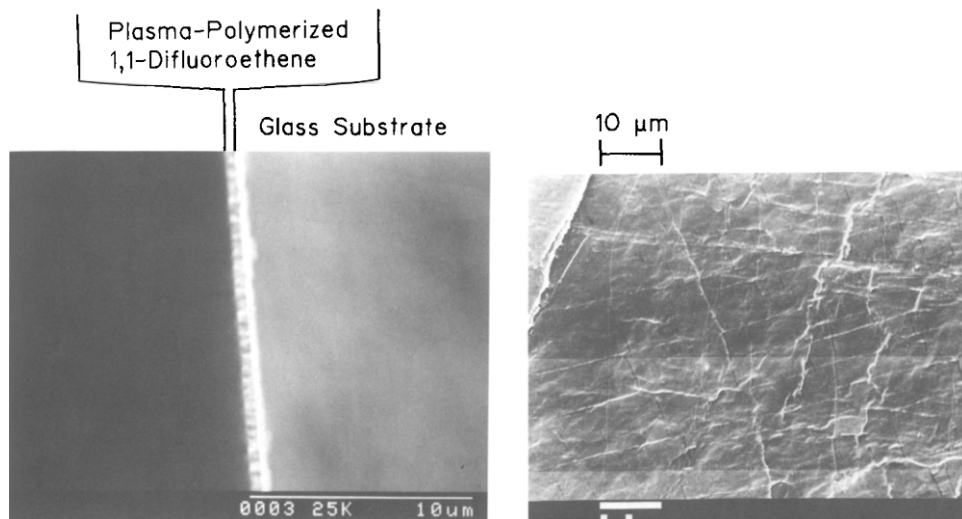


Fig. 5. Scanning electron micrograph of a cross section of plasma-polymerized 1,1-difluoroethene; flow rate of 1,1-difluoroethene: $10 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$; RF power: 20 W, and polymerization pressure: 67 Pa.

Fig. 6. Scanning electron micrograph of an untreated lithium surface.

energy was obtained from the Zisman method, cited in ref. 18. The critical surface energy of the plasma polymer was 20 dyn cm^{-1} as shown in the Table which falls between values of poly(tetrafluoroethene) $(-(\text{CF}_2-\text{CF}_2)_n-)$, 18.5 dyn cm^{-1} , and poly(trifluoroethene) $(-(\text{CF}_2-\text{CFH})_n-$, 22 dyn cm^{-1} .

Figure 5, which shows a typical cross-sectional view of the plasma polymer, indicates that the film was about $0.6 \mu\text{m}$ thick, free from pinholes, and, on the scale of SEM observation, of uniform thickness.

Ionic conductivity of the plasma-polymerized solid polymer electrolyte layer from 1,1-difluoroethene

The ionic conductivity of the plasma-polymerized solid polymer electrolyte layer on the Li electrode, when immersed in 1 M Li perchlorate/propylene carbonate solution, was measured by a complex impedance method. Incorporation of the solvent (propylene carbonate) into the solid polymer electrolyte is considered to be not so remarkable because of the low critical surface energy of the surface of the plasma polymer layer

as shown in the Table. A distinguishable arc attributed to the bulk resistance of the plasma-polymerized solid polymer electrolyte was observed on the complex impedance plots. The ionic conductivity of the solid polymer electrolyte was calculated from the plots, which was $3 \times 10^{-8} \text{ S cm}^{-1}$ at room temperature, and is one order of magnitude lower than the value reported for of poly(1,1-difluoroethene)/LiClO₄ ($4 \times 10^{-7} \text{ S cm}^{-1}$) [15]. The low ionic conductivity might be attributed to the cross-linking structure of the plasma polymer and hydrogen removal from the polymer.

Lithium deposition on the surface-modified lithium electrode and its morphologies

Figure 6 shows an SEM micrograph of an untreated Li surface. The surface was fairly smooth except that some sharp edges are observed on the surface.

SEM pictures of the surface after Li deposition (1 C cm^{-2} , 0.5 mA cm^{-2}) from 1 M Li perchlorate/propylene carbonate on (a) an untreated Li electrodes and (b) a Li electrode covered with plasma-polymerized 1,1-difluoroethene are shown in Figs. 7(a) and 7(b).

Figure 7 shows that the coating by the plasma-polymerized solid polymer electrolyte layer changes significantly the morphology of Li deposits. The Li deposited on the untreated electrode is of a needle-like dendritic structure and has many bottlenecks which are apt to lead to the formation of electrochemically-nonactive Li [3]. On the other hand, the Li deposited on the electrode covered with the solid polymer electrolyte was not needle-like but moss-like and smooth and flat.

Figure 8 shows SEM micrographs of the Li deposits under conditions similar to those for Fig. 7, except that the depositing current was much smaller than those for Fig. 7. The morphology of Li deposits is remarkably different between Figs. 8(a) and 8(b). While Li was deposited on an untreated Li electrode in moss-like form, the presence of thin solid polymer electrolyte layer on Li electrode leads to the flat and smooth deposits and suppressed the dendritic deposition of Li. In conclusion, a morphology of Li deposits is much smoother than indicated in the SEM figure when the thin solid polymer electrolyte layer covers the Li electrode.

Although the reason of a change in the morphology of Li deposits is not yet clear, the following may be possible. Usually, Li films are easily covered with nonuniform

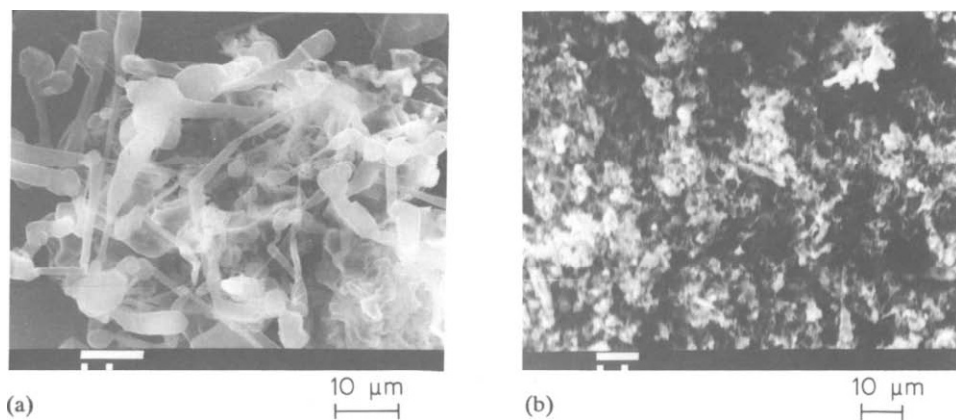


Fig. 7. Scanning electron micrograph of the lithium electrode surface after deposition of lithium (1 C cm^{-2} , 0.5 mA cm^{-2}) in 1 M lithium perchlorate/propylene carbonate: (a) untreated lithium surface, and (b) lithium surface covered with plasma-polymerized 1,1-difluoroethene.

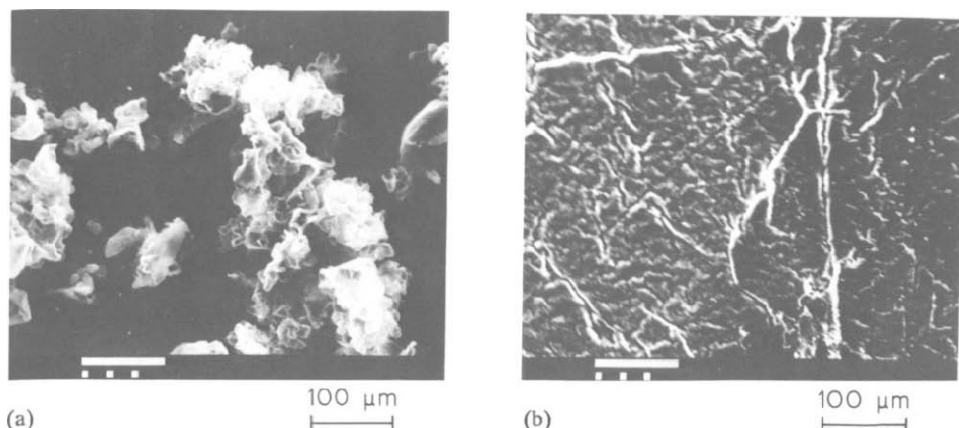


Fig. 8. Scanning electron micrographs of the lithium electrode surface after deposition of lithium (1 C cm^{-2} , 0.01 mA cm^{-2}) in 1 M lithium perchlorate/propylene carbonate solution: (a) untreated lithium surface, and (b) lithium surface covered with plasma-polymerized 1,1-difluoroethene.

Li-compound layer, which causes nonuniform Li deposits like dendrites. In this work, a uniform solid polymer electrolyte layer was artificially deposited on the Li surface instead of the nonuniform native surface layer. Furthermore, the low surface energy of deposited plasma polymer (20 dyn cm^{-1}) may contribute to suppress the growth of dendrites. The surface energy influences the growth of bulges of dendritic deposit. High surface tension caused by the low surface energy of the electrolyte may suppress the bulge growth and keep its size at a certain value [19].

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