

# Effects of Native Film on Lithium for Interfacial Reactions between Lithium Metal and an Electrolyte Solution

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**Abstract**— This study examines the morphological changes for a lithium surface immersed in 1 mol dm<sup>-3</sup> LiPF<sub>6</sub> dissolved in propylene carbonate containing 1,2-dimethoxyethane as a co-solvent. A passivation film was formed on the surface of the lithium metal by electrolyte decomposition. Atomic force microscopy and electrochemical impedance spectroscopy results revealed that there were no direct correlations between the changes in the surface morphology of the lithium metal, and the resistance behavior of its passivation film.

**Index Terms**— Lithium metal, Passivation film, Native film, Atomic force microscopy

## I. INTRODUCTION

Lithium metal has a high theoretical energy density; hence, it has been extensively studied as a negative electrode material for secondary batteries, which use the oxidation-reduction reaction of lithium as an electrode reaction [1]. Recently, studies on lithium-air batteries and lithium-sulfur batteries have been progressing actively as the next-generation high-capacity secondary batteries [2,3]. Lithium metal has attracted much attention as an electrode material for lithium-ion batteries as well as for next-generation batteries. However, drawbacks exist in the form of safety and cycle life degradation due to the non-uniform precipitation/dissolution reaction of lithium. Therefore, the use of secondary batteries that contain lithium metal as a negative electrode material has not been commercialized yet.

In the case of lithium-air batteries, it has been reported that the performance of the battery is greatly improved by using an ether-based electrolyte that has a low volatility and low reactivity with oxygen ions. This is an improvement against the carbonate-based electrolyte typically used in commercialized lithium-ion batteries [4]. In the case of lithium-sulfur batteries, Sion Power has reported that the use of LiNO<sub>3</sub> salt improves the cell life by simplifying the reactions [5]. Despite such technological advances, one of the technical problems that must be resolved for the

commercialization of lithium-air batteries and lithium-sulfur batteries is to suppress the growth reaction of lithium dendrites in the lithium metal. Many studies have been conducted for such purposes. In recent years, new results indicate that the structure of the lithium dendrite can be changed to a form where lithium is covered with porosity and moss [6], and that lithium dendrite grows below the surface [7]. However, a physicochemical understanding of the generation of the lithium dendrites is still lacking.

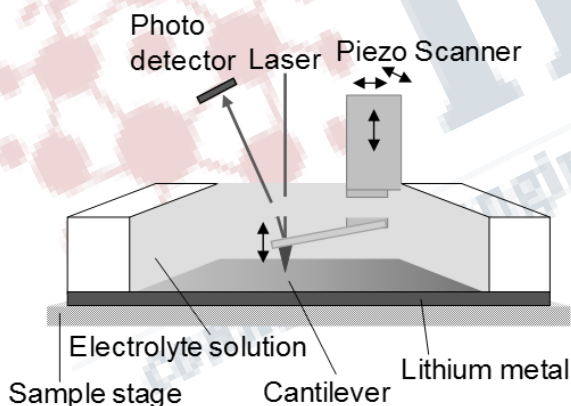
Lithium metal is thermodynamically unstable and forms a passivation film on the surface by spontaneous chemical reactions when it comes into contact with the electrolyte. Various inorganic species such as, LiF, Li<sub>2</sub>CO<sub>3</sub>, and Li<sub>2</sub>O constitute such a film, and affect the electrochemical reaction of the lithium metal [8,9]. In our previous work, we have reported the effects of structural changes of the solvated lithium ion on the generation of lithium dendrites by controlling the concentration of the co-solvent in propylene carbonate-based solutions [10]. In this study, we focus on the passivation film generated on the surface of the metallic lithium to understand the effects of solvation structures more clearly. A basic experimental analysis was carried out to study its effects on the passivation film.

## II. EXPERIMENTAL WORK

A cell, as shown in Fig. 1, was used to confirm the

surface changes in metallic lithium by atomic force microscopy (AFM). Lithium metal was used as the working electrode, and scanning was carried out at a speed of 1 line  $\text{sec}^{-1}$  in the contact mode. After immersing the electrode in the electrolyte solution, surface morphologies were measured at intervals of 1 h. An O-ring was inserted between the cell body and the working electrode to prevent leakage of the electrolyte solution. The electrolyte solutions were prepared by dissolving 1 mol  $\text{dm}^{-3}$  (M)  $\text{LiPF}_6$  in a 1:1 (by volume) mixture of propylene carbonate (PC,  $\geq 99.9\%$ ), and 1,2-dimethoxyethane (DME,  $\geq 99.9$ ) (PC + DME). All electrolytes were purchased from Enchem Co. Ltd., and were used as received. The water content in the electrolyte solution was  $<30$  ppm, as measured using a Karl-Fischer moisture titrator (Kyoto Electronics Manufacturing Co., MKC-210).

Electrochemical impedance spectroscopy (EIS) analysis was performed using a laboratory-made cell. The working electrode was lithium metal. The geometrical surface area was  $0.23 \text{ cm}^2$ . The electrochemical impedance was obtained at the open circuit potential. The impedance was measured with a potentiostat (PGZ 402, VoltaLab) over the frequency range of  $10^{-4}$ – $10^2$  kHz. The alternating amplitude was 5 mV.

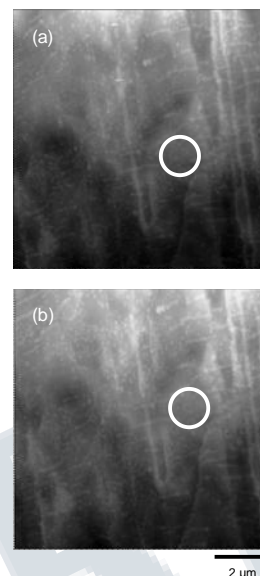


**Fig. 1 Schematic of a cell for AFM observation.**

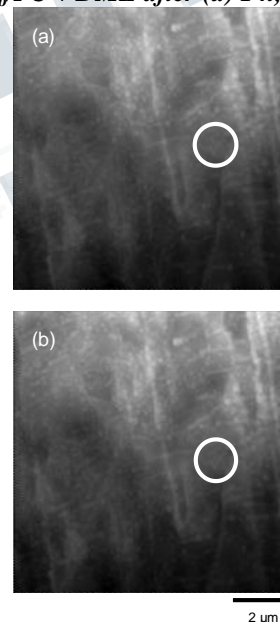
### III. RESULTS AND DISCUSSION

An inorganic film such as  $\text{LiOH}$ ,  $\text{Li}_2\text{O}$ , and  $\text{Li}_2\text{CO}_3$  is present on the surface of the lithium metal. When a non-aqueous solution of PC containing lithium ions comes into contact with the thermodynamically unstable lithium metal, a new film called a passivation film is generated. In this study, the morphological changes of the surface accompanying the passivation film were observed using

AFM.



**Fig. 2 AFM images of the lithium surface immersed in 1 M  $\text{LiPF}_6/\text{PC} + \text{DME}$  after (a) 1 h, and (b) 3 h.**



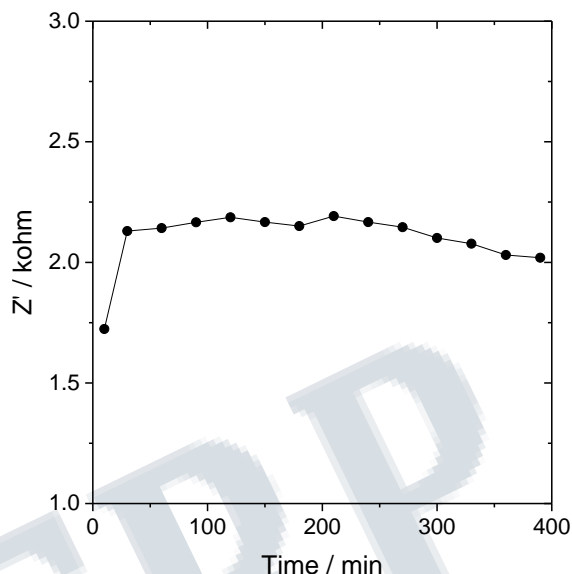
**Fig. 3 AFM images of the lithium surface immersed in 1 M  $\text{LiPF}_6/\text{PC} + \text{DME}$  after (a) 5 h, and (b) 6 h.**

The surface morphology of the lithium metal immersed in the electrolyte solution is shown in Fig. 2 and Fig. 3. In order to obtain more information on the changes of the surface morphology with time, the

surface morphology at the same position was observed for a predetermined time interval. As shown by the circles in Fig. 2, no significant change in the number and size of the surface particles was observed after 3 h. However, the trend in Fig. 3 shows that the particle size decreases with decreasing particle number after 5 h. The variations in contrast in each of the images shown in Figs. 2 and 3 allude to the difference in elevation. The lightness and darkness of the circles appear to change as time passes. However, this is not a difference in levels, rather, it is caused by the relative contrast differences in the data processing. Kanamura group analyzed the surface of the lithium metal immersed in 1 M LiPF<sub>6</sub>/PC solution by X-ray photoelectron spectroscopy [11]. In this study, the passivation film is schematically shown, and the lithium metal immersed in the electrolyte solution for a long time is interpreted as the LiF layer having thickened. The growth behavior of the lithium dendrite is also different, and the resistance of the film is also influenced. Therefore, the change in the particle size shown in Figs. 2 and 3 seems to be related to the change in LiF layer thickness.

In this study, the AFM observations were carried out in the contact mode. In the contact mode, some of the substances generated on the surface may be removed due to the physical pressure of the probe generated by continuous scanning [12]. This means that the passivation film is very firmly attached to the surface. On the other hand, the direct correlations between the morphology changes and the charge-discharge characteristics are not known at present. This is beyond the scope of this study.

An EIS analysis was performed to obtain the information on the electrical properties of the passivation film generated in the electrolyte solution. The EIS analysis was performed at intervals of 30 min based on the immersion time in the electrolytic solution. Fig. 4 shows the resistance of the passivation film of lithium generated by the contact with the electrolyte. After 30 min, the resistance rapidly increased, then remained constant, and finally gradually decreased after 200 min. The reason why the resistance increased rapidly in the early stages is presumably due to a new film being generated by the electrolyte decomposition. The decrease in the resistance after 200 min implies that the composition of the initially formed film was changing. It is also believed that this phenomenon is related to the increase in particle size as observed in Figs. 2 and 3. However, the details remain unclear.



**Fig. 4 Resistances of passivation film generated on the lithium metal in 1 M LiPF<sub>6</sub>/PC + DME as a function of immersing time.**

## CONCLUSION

A number of meaningful observations were obtained by analyzing the change in the surface morphology of lithium metal immersed in an electrolyte solution and the change in the resistance of the passivation film. It was confirmed that a stable passivation film was formed on the surface of lithium metal in the 1 M LiPF<sub>6</sub>/PC + DME. No quantitative relationship was observed between the change in the morphology of the lithium surface (number of particles and increase in size), and the magnitude of the resistance caused by a chemical decomposition of the electrolyte solution.

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