# Electrochemical Deposition of Uniform Lithium on an Ni Substrate in a Nonaqueous Electrolyte

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## ABSTRACT

The electrochemical deposition of lithium on an Ni substrate was conducted in propylene carbonate (PC) containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> (LiClO<sub>4</sub>/PC). The morphology of the lithium deposited on the Ni substrate had the typical dendrite form. The electrodeposition of lithium was then performed in LiClO<sub>4</sub>/PC containing  $5 \times 10^{-3}$  mol dm<sup>-3</sup> HF. The lithium deposited on the Ni substrate in this electrolyte had a hemispherical form, and irregular shapes were not observed. The color of the Ni electrode surface turned to brilliant blue during the electrodeposition of lithium. This indicates that the lithium surface is very smooth and uniform. After five discharge and charge cycles, there were no lithium dendrites on the electrode surface. From these results, it can be concluded that the addition of a small amount of HF to the electrolyte is significantly effective for the suppression to the lithium dendrite formation.

A nonaqueous battery using lithium metal is desirable for the development of electric vehicles or a load leveling system because it has high theoretical energy and power densities. Numerous studies have been performed on rechargeable nonaqueous batteries with lithium metal anodes.<sup>1-4</sup> However, the rechargeability of non-aqueous battery with the lithium metal anodes is usually very poor.<sup>5</sup> This is caused by the formation of lithium dendrites during charging process.<sup>5,6</sup>

Lithium metal is so reactive that its surface is always covered with some lithium compounds. Moreover, the lithium metal surface may react with the electrolyte to form both organic and inorganic compounds.<sup>7,8</sup> The electrochemical deposition of lithium proceeds via the migration of lithium ion through these surface films. Thus, the surface film is very important in the electrochemical deposition of lithium. Recently, we performed surface analysis using x-ray photoelectron spectroscopy (XPS).<sup>9-13</sup> We found the following reaction occurring for the lithium surface immersed in propylene carbonate,  $\gamma$ -butyrolactone, or tetrahydrofuran containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub>, LiAsF<sub>6</sub>, LiBF<sub>4</sub>, or LiPF<sub>6</sub>, when using as-received lithium whose surface is covered with Li<sub>2</sub>CO<sub>3</sub>, LiOH, and Li<sub>2</sub>O

$$\begin{split} \text{Li}_2\text{O} &+ 2\text{HA} \rightarrow 2\text{LiA} + \text{H}_2\text{O} \\ \text{Li}_2\text{CO}_3 &+ 2\text{HA} \rightarrow 2\text{LiA} + \text{H}_2\text{CO}_3 \\ \text{LiOH} &+ \text{HA} \rightarrow \text{LiA} + \text{H}_2\text{O} \end{split}$$

(HA: acid as an impurity in nonaqueous electrolyte)

Thus, the surface reaction of the as-received lithium can be explained by a simple acid-base sequence reaction in this nonaqueous electrolyte. Acids are often formed in the nonaqueous electrolyte as a decomposition product of the electrolyte salt. The concentration and kind of acid depends on the kind of salt. On the other hand, the morphology of the lithium deposited on the as-received lithium immersed in the electrolyte strongly depends on the kind of electrolyte. The electrodeposition of lithium without the dendrite formation has been often accomplished in electrolytes containing LiPF<sub>6</sub>. <sup>11</sup> The amount of HF in the electrolytes containing there salts, such as LiAsF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, and LiBF<sub>4</sub>, because LiPF<sub>6</sub> is not as stable as these. From these results, it may be suspected that HF is the key factor for the electrodeposition of lithium without the dendrite formation.

## Experimental

The galvanostatic electrodeposition of lithium on Ni substrates was performed in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> (Mitsubishi Yuka Company). Lithium foil was used as both the counter- and the reference electrodes. The electrodeposition current was 0.2 mA cm<sup>-2</sup>. The total electric charge for the electrodeposition was 1.0 C cm<sup>-2</sup>. Before the electrodeposition, the Ni substrate was polished with alumina powder (0.05 µm) to obtain a mirror surface. Then it was dipped in an ultrasonic bath to remove any remaining alumina powder. After that it was immersed in acetone and heated by a water bath for 30 min to remove any organic

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three-electrode cell was used. The electrodeposition of lithium was also conducted in propylene carbonate containing  $5 \times 10^{-3}$  mol dm<sup>-3</sup> HF and 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub>. The maximum water content of this electrolyte was determined to be 100 ppm using the Karl Fischer titration method. The morphology of lithium was observed by a scanning electron microscope. The color of the Ni electrode surface in both electrolytes was observed during the course of the lithium electrodeposition. The electrochemical deposition and dissolution cycle was per-

impurities, which might have adsorbed on its surface. A standard

formed under galvanostatic conditions in both electrolytes. The discharge and charge currents were 0.2 mA cm<sup>-2</sup>. The charging duration was 30 min. The cutoff potential for the discharge was 1.0 V vs. Li/Li<sup>+</sup>. The cycle was repeated five times.

The surface analysis on the lithium was performed with XPS. The transfer procedures for the sample were described in our previous report.<sup>9</sup> The depth profile was obtained using argon ion sputtering (2 keV, 7 to 8  $\mu$ A). All peaks in the XPS spectra were calibrated using the C 1s peak (285.0 eV) corresponding to hydrocarbons which remained in the XPS analysis chamber.

### **Results and Discussion**

Figure 1 shows the scanning electron micrograph (SEM) for lithium electrodeposited on the Ni substrate in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> (LiClO<sub>4</sub>/PC). Lithium dendrites are clearly observed. Electrodeposition in this electrolyte has been performed by many researchers.<sup>5</sup> Electrodeposition of lithium without dendrite formation has never been accomplished in LiClO<sub>4</sub>/PC.



Fig. 1. SEM of lithium deposited on an Ni substrate in propylene carbonate contaning 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub>. The electrodeposition current was 0.2 mA cm<sup>-2</sup>, and the total charge passed was 1 C cm<sup>-2</sup>.



magnification 2000



Fig. 2. SEM of lithium deposited on an Ni substrate in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> and 5  $\times$  10<sup>-3</sup> mol dm<sup>-3</sup> HF. The electrodeposition current was 0.2 mA cm<sup>-2</sup>, and the total charge passed was 1 C cm<sup>-2</sup>.

Figure 2 shows the SEM of lithium deposited on an Ni substrate in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> and 5 ×  $10^{-3}$  mol dm<sup>-3</sup> HF [LiClO<sub>4</sub>(HF)/PC]. There was no dendrite lithium on the electrode surface. The particle size for the lithium was very uniform. No irregularities were observed on the surface. This indicates that the addition of a small amount of HF is very effective in suppressing lithium dendrite formation.

In the case of LiCIO<sub>4</sub>/PC, the color of the electrode surface gradually turned to gray during the electrodeposition. This color change is due to the increasing roughness of the lithium deposits which is caused by the lithium dendrite formation. On the other hand, the color of the electrode surface turned to blue in the case of LiCIO<sub>4</sub>(HF)/PC. Probably, the color change may be caused by the interference of a visible light. This result indicates that a very uniform layer of lithium is formed by the electrodeposition of lithium in LiCIO<sub>4</sub>(HF)/PC.

The surface analysis for lithium deposited in LiCiO<sub>4</sub>(HF)/PC (the blue lithium) was performed. Figure 3 shows the XPS spectra for Li 1s, C 1s, O 1s, and F 1s for the blue surface. Figure 4 shows the depth profile for each element obtained from the integrated peak intensity and the cross section for the ionization of each element. Li 1s peaks were observed at 55.6 eV before the argon ion sputtering and at 53.7 and 52.2 eV after the argon ion sputtering. These peaks can be attributed to LiF, Li<sub>2</sub>O, and Li, respectively, according to our previous papers.<sup>9-11</sup> A peak in the XPS spectra of F 1s is assigned to LiF. From these XPS spectra, it can be seen that LiF exists on the

top surface of the lithium and Li<sub>2</sub>O is present underneath the LiF layer. The amount of fluorine element in the outer part of the surface film was larger than those of carbon and oxygen elements, as shown in Fig. 4. From this result, it can be seen that the major compound at the outer part of the surface film is LiF. A Cl 2p peak was observed at 199 eV. This peak is attributed to LiCl. The amount of LiCl was very small compared with other lithium compounds. The hydrocarbon C 1s peak was observed before the argon ion sputtering. This is mainly due to the impurities remaining in the XPS



Fig. 3. XPS spectra of (a) Li 1s, (b) Cl 2p, (c) C 1s, (d) O 1s, and (e) F 1s for the surface film of lithium deposited on an Ni substrate in propylene carbonate containing 1.0 mol dm<sup>-3</sup> Li-ClO<sub>4</sub> and  $5 \times 10^{-3}$  mol dm<sup>-3</sup> HF. The electrodeposition current was 0.2 mA cm<sup>-2</sup>, the total charge passed was 1 C cm<sup>-2</sup>. Etching time: top, 0 min; middle, 20 min; bottom, 40 min.



Fig. 4. Depth profile for each element in the surface film of lithium, as obtained from Fig. 3.



Surface Film on Deposited Lithium

Fig. 5. Schematic illustration of the surface film of lithium deposited on an Ni substrate in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> and  $5 \times 10^{-3}$  mol dm<sup>-3</sup> HF. The electrodeposition current was 0.2 mA cm<sup>-2</sup>, and the total charge passed was 1 C cm<sup>-2</sup>.



Fig. 6. Scanning electron microscope of lithium deposited on an Ni substrate after five deposition and dissolution cycles in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiClO<sub>4</sub> and  $5 \times 10^{-3}$  mol dm<sup>-3</sup> HF. The discharge and charge currents were 0.2 mA cm<sup>-2</sup>. The charging duration was 30 min. The cutoff potential for the discharge was 1.0 V vs. Li/Li<sup>+</sup>.

analysis chamber. Its peak intensity decreased after the argon ion sputtering. However, this peak was still observed after the argon ion sputtering. This indicates that a small amount of organic compounds is included in the lithium surface film. O 1s peaks were observed at 532.0 eV before the argon ion sputtering and at 528.7 eV after the argon ion sputtering. These peaks are attributed to LiOH (or Li<sub>2</sub>CO<sub>3</sub>) and Li<sub>2</sub>O, respectively. The amount of oxygen element at the inner part of the lithium surface was larger than any

other elements. The major substance at the inner part of the surface film is Li<sub>2</sub>O. From XPS analysis and observation of the lithium surface, it can be seen that the surface film of the blue lithium is very uniform. Thus, a schematic illustration of the surface state of the blue lithium can be drawn as shown in Fig. 5. The surface film on the blue lithium is very similar to that of the as-received lithium foil after being immersed in propylene carbonate containing 1.0 mol dm<sup>-3</sup> LiPF<sub>6</sub> for 3 days.<sup>9</sup> In this electrolyte, the dendrite formation of lithium is suppressed, as described in our previous report.<sup>13</sup> This electrolyte contains a larger amount of HF compared with other popular electrolytes. From these facts, it can be concluded that the suppression of lithium dendrites is due to the HF. So, the quantitative addition of HF to the electrolyte may be very effective for the suppression of lithium dendrites. If the dendrite formation of lithium was related to the current distribution caused by the variety of the surface film on lithium, the uniform surface film has the effect of making the current distribution uniform.

After five electrochemical deposition and dissolution cycles, the thickness of surface film increased, which was confirmed by XPS analysis, but the chemical compositions and structure of the surface film of the blue lithium did not change significantly. Figure 6 shows a SEM of lithium deposited on an Ni substrate after five deposition and dissolution cycles. The electrode surface is still smooth, and no dendrite growth was observed. This means that the effect of the addition of HF to the electrolyte is maintained for several electrochemical deposition and dissolution cycles.

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