

# In situ atomic force microscopy observation of lithium deposition at an elevated temperature

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## Abstract

Lithium deposition was carried out on a Ni substrate in a 1 M solution of lithium bis(perfluoroethylsulfonyl)imide (LiBETI) dissolved in propylene carbonate(PC) at room temperature and at an elevated temperature of 80°C. The morphologies of lithium deposits were compared using in situ atomic force microscopy. The cycling efficiency for lithium deposition and dissolution at 80°C was higher than that at room temperature in 1 M LiBETI/PC. Large masses of deposits were observed after lithium deposition at room temperature. However, the surface of lithium deposited at 80°C was smooth and uniform throughout lithium deposition and dissolution. It was shown that temperature is one of the important factors that affect the cycling efficiency. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lithium metal; Atomic force microscopy; Surface film; Elevated temperature; Cycling efficiency

## 1. Introduction

Lithium metal is the most attractive material for the negative electrode in rechargeable lithium batteries because of its high energy density. However, the low cycling efficiency and the safety problems owing to dendrite formation prevent the use of lithium metal in commercially available cells [1]. Many researchers have so far studied the surface morphology of deposited lithium in various electrolyte systems by scanning electron microscopy (SEM) [1–4] and atomic force microscopy (AFM) [5–7]. It was reported that dendrite formation was suppressed and the cycling efficiency of lithium was improved to nearly 100% when dry solid polymers were used as electrolytes [8]. Such dry polymer electrolytes are usually used at elevated temperatures around 80°C; hence, the elevated temperatures may affect the morphologies of lithium deposits. However, there are few researches about the effects of temperature on the morphology of lithium deposited in liquid electrolytes, except for reports on the surface film formed at low temperatures [9,10]. In the present study, the morphologies of lithium deposited on nickel substrate in a propylene carbonate (PC) solution was examined at room temperature and at an elevated temperature by in situ AFM.

## 2. Experimental

In situ AFM images were obtained with a PicoSPM system (Molecular Imaging). The cell was made of polytetrafluoroethylene (PTFE), and set on a heating sample stage. The temperature of the cell was kept at 80°C with a temperature controller (Model 330, Lake Shore). The electrolyte solution used was a 1 M solution of lithium bis(perfluoroethylsulfonyl)imide ( $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ , LiBETI, 3 M) dissolved in PC. The water content of the solution was less than 30 ppm. The working electrode was nickel plate polished to a mirror finish, and the surface area in contact with the electrolyte solution was 1.4 cm<sup>2</sup>. The counter and reference electrodes were lithium metal. Cyclic voltammetry (CV) was performed using the AFM cell. The scan rate was 5 mV/s, and the scan range was 2.5–0 V versus Li/Li<sup>+</sup>. After each cycle of CV, the temperature of the cell was cooled down to 33°C, and AFM images were obtained at 33°C to avoid the lens for laser beam from being fogged up. In addition to CV, lithium deposition was carried out at a constant current density of 0.5 mA cm<sup>-2</sup>, and AFM images were obtained every 0.03 C cm<sup>-2</sup> deposition. During each CV cycle or lithium deposition, the cantilever was moved out of the solution because the current flow beneath the tip is disturbed by its presence. All of these AFM measurements were carried out in an argon-filled glove box (MDB-1B, Miwa) with a dew point lower than –60°C.

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For cycling efficiency measurements, a sealed three-electrode cell made of PTFE was used. The cell was assembled in an argon-filled glove box, and the measurements were performed in an electric oven kept at 80°C. The current densities for lithium deposition and dissolution were 0.5 mA cm<sup>-2</sup>. In each cycle, lithium was deposited by 0.3 C cm<sup>-2</sup>, and dissolved until the potential reached 1.5 V.

### 3. Results and discussion

#### 3.1. Cycling efficiency

Fig. 1 shows the cycling efficiencies for deposition and dissolution of lithium metal in LiBETI/PC at room temperature and 80°C. At room temperature, the efficiency was initially in the range of 60–70%, and dropped rapidly after 15 cycles. However, relatively high efficiencies (~75%) were obtained up to the 30th cycle at 80°C. These results show that the cycling efficiency of lithium deposition and dissolution in liquid electrolytes is improved by elevating temperature, as was reported in solid polymer electrolytes.

#### 3.2. Cyclic voltammetry coupled with AFM observation

Cyclic voltammograms obtained at room temperature and 80°C in 1 M LiBETI/PC are shown in Fig. 2(a) and (b), respectively. At room temperature (Fig. 2(a)), the cathodic current rose at 1.1 V, and major cathodic peaks were observed at 0.9, 0.5, and 0.2 V. The peak currents gradually decreased in the subsequent cycles. Although each peak in these CV's are not specified, these peaks are mainly attributable to the reductive decomposition of the electrolyte solution and surface film formation. At 80°C (Fig. 2(b)), the cathodic current began to flow at a more positive potential, approximately 2 V. Major cathodic peaks were observed at 1.2, 0.7, 0.5, and 0.4 V at 80°C. The peak currents in the first cycle at 80°C were much larger than those at room temperature. In the subsequent cycles, the peak currents decreased significantly, and were comparable with those

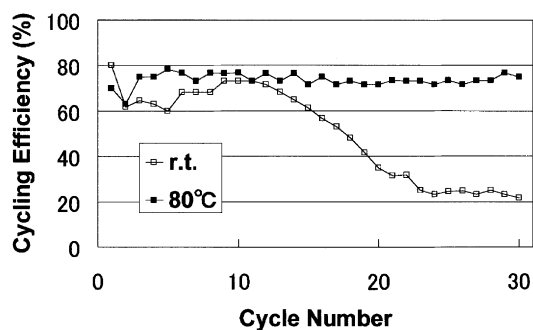


Fig. 1. Cycling efficiencies of lithium on nickel substrate in 1 M LiBETI/PC at room temperature (□) and at 80°C (■). Lithium deposition was carried out to 0.3 C cm<sup>-2</sup> at 0.5 mA cm<sup>-2</sup>. The cutoff voltage for dissolution was 1.5 V.

at room temperature. These facts indicate that reductive electrolyte decomposition and passivation of the nickel surface are fast at 80°C.

The surface morphological change of Ni was observed by *in situ* AFM after each cycle of CV. AFM images after five cycles of CV at room temperature and 80°C are shown in Fig. 2(c) and (d), respectively. The morphology after one cycle at room temperature (not shown) did not change clearly from that before CV, and grooves on the Ni substrate, caused by polishing, were still visible. After five cycles (Fig. 2(c)), particles of 50–150 nm in diameter appeared sparsely on the surface, and the grooves became indistinct. On the other hand, the surface was covered with many particles even after one cycle at 80°C (not shown). The particle size was about 200 nm, which was larger than that of the particles deposited at room temperature. It should be noted that the potential was scanned between 2.5 and 0 V. Hence, the observed particles were not lithium deposits, but surface film formed by reductive decomposition of the electrolyte solution. Grooves from polishing were only marginally visible after one cycle, which showed that the surface film was rapidly formed at 80°C. After five cycles at 80°C (Fig. 2(d)), the number of the particles increased and the grooves were not seen on the surface. We observed other areas, and confirmed that there was a uniform covering of the particles.

#### 3.3. Morphology changes during constant current lithium deposition

Lithium was deposited on Ni substrate at a constant current density of 0.5 mA cm<sup>-2</sup> at room temperature and 80°C, and the surface morphology was observed by *in situ* AFM every 0.03 C cm<sup>-2</sup> deposition. Fig. 3 shows AFM images obtained after lithium deposition. After the first 0.03 C cm<sup>-2</sup> deposition at room temperature, there was little morphological change of the Ni substrate before deposition, and grooves on the Ni were seen clearly on the surface. After 0.09 C cm<sup>-2</sup> deposition, particles of 200–400 nm in diameter appeared, and they became larger with increasing amount of lithium deposition. Fig. 3(a) shows an AFM image obtained after 0.3 C cm<sup>-2</sup> deposition at room temperature. Large masses of deposits were observed at 0.3 C cm<sup>-2</sup>. The image was noisy because the surface was very rough.

At 80°C, the whole surface of Ni was uniformly covered with particle-like deposits even after 0.03 C cm<sup>-2</sup> deposition (Fig. 3(b)). The surface morphology had hardly changed with increasing amount of deposition. Fig. 3(c) shows an AFM image obtained after 0.3 C cm<sup>-2</sup> deposition. It should be noticed that the surface morphology on lithium deposits in Fig. 3(b) and (c) is quite similar to that after the CV measurements at 80°C in Fig. 2(d). After 0.3 C cm<sup>-2</sup> deposition, the deposited lithium was dissolved at 80°C, and AFM observation was carried out. Fig. 3(d) shows an AFM image after dissolution. The morphology of the surface did not change from that of deposited lithium shown in Fig. 3(c).

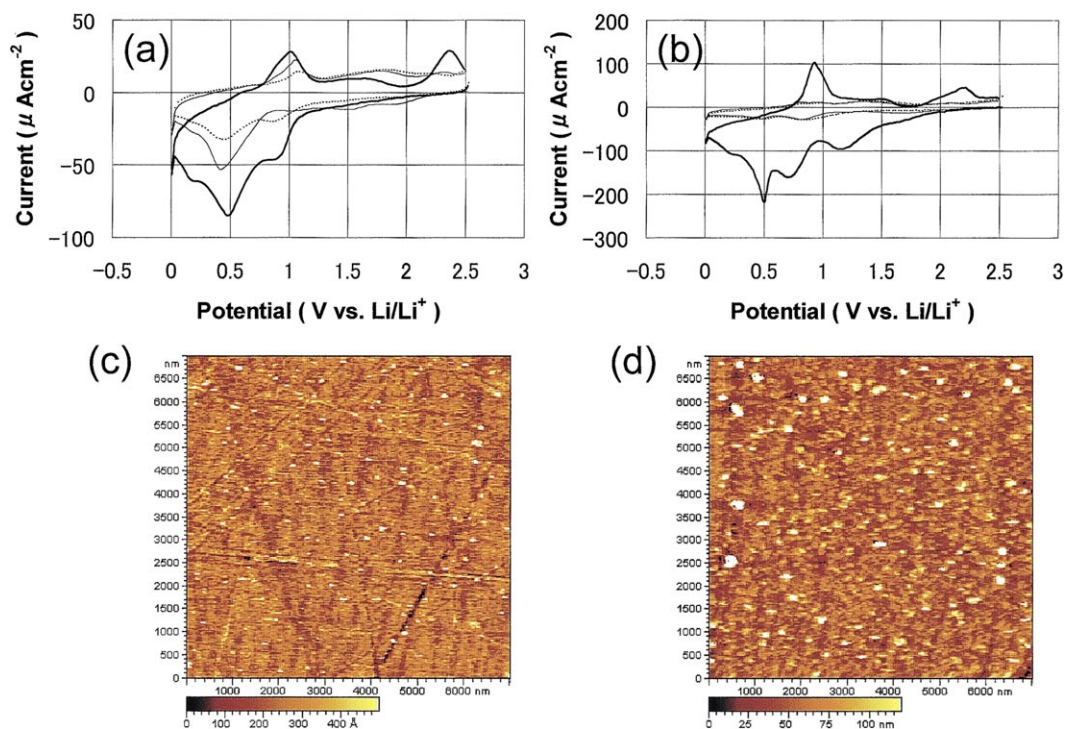


Fig. 2. (a and b) Cyclic voltammograms and (c and d) AFM images ( $7\ \mu\text{m} \times 7\ \mu\text{m}$ ) obtained after five cycles of Ni electrode in 1 M LiBETI/PC at (a, c) room temperature and (b and d) 80°C. Scan rate was 5 mV/s. Bold solid lines: 1st cycle; solid lines: 2nd cycle; dashed lines: 5th cycle.

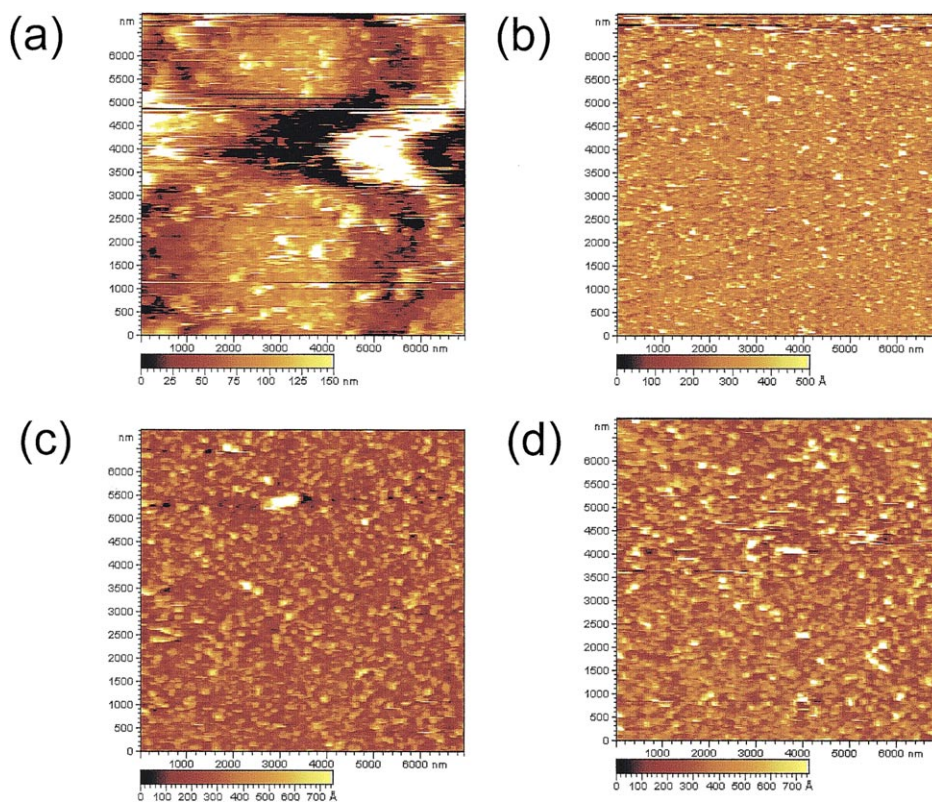


Fig. 3. AFM images ( $7\ \mu\text{m} \times 7\ \mu\text{m}$ ) of lithium after deposited at  $0.5\ \text{mA cm}^{-2}$  by (a)  $0.3\ \text{C cm}^{-2}$  at room temperature, (b)  $0.03\ \text{C cm}^{-2}$  at 80°C, (c)  $0.3\ \text{C cm}^{-2}$  at 80°C, and (d) after dissolution at 80°C in 1 M LiBETI/PC.

Because the cutoff potential was set at 1.5 V, the AFM images obtained after dissolution showed the morphology of the residue of the surface film formed on lithium. Consequently, the morphology of the surface, which was formed in the earliest step of lithium deposition by reductive decomposition of the electrolyte, was maintained all through the deposition and dissolution of lithium at 80°C. This fact suggests that a flat and uniform layer of lithium metal was deposited beneath the surface film. As shown by the results of the CV and AFM measurements, reductive decomposition and surface film formation were much faster at 80°C, which gave a uniform surface film in the earliest step of lithium deposition. In addition, cracks and flaws in the surface film formed during lithium deposition would be repaired quickly. Such rapid formation and self-repairing of the surface film would favor the deposition of flat and smooth lithium, which resulted in the improvement of the cycling efficiency at 80°C.

#### 4. Conclusions

The cycling efficiency at 80°C was higher than that at room temperature in 1 M LiBETI/PC, which showed that temperature was one of the important factors that affect the cycling efficiency. Large masses of deposits were observed

after lithium deposition at room temperature. However, the surface of lithium deposited at 80°C was smooth and uniform throughout the deposition and dissolution. At 80°C, reductive decomposition of the electrolyte solution was so fast that the whole surface was covered with a stable surface film in the earliest step of lithium deposition. It was concluded that rapid formation and self-repairing of the surface film improved the cycling efficiency for lithium deposition and dissolution in 1 M LiBETI/PC at 80°C.

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