

In Situ AFM Observation of Lithium Deposition in the Presence of Film-Forming Additives

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Lithium metal is the most attractive material for the negative electrodes in rechargeable lithium batteries because of its high energy density; however, the low cycling efficiency and the safety problems owing to its dendrite formation prevent its use in commercially available cells. Many researchers have so far studied the surface morphology of deposited lithium and the protecting surface film in various electrolyte systems.

In a previous study, we observed morphologies of lithium metal deposited on Ni substrate by *in situ* AFM [1]. Lithium was deposited smoothly and uniformly at elevated temperatures, which resulted in an improved cycling efficiency at 80°C. From these results, we concluded that rapid formation and self-repairing of the surface film improved the cycling efficiency for lithium deposition and dissolution at elevated temperatures. In the present study, we investigated the effects of additives, fluoroethylene carbonate (FEC), vinylene carbonate (VC), and ethylene sulfite (ES), which are reported as effective film-forming additives for graphite negative electrodes [2].

In situ AFM images were obtained with a PicoSPM system (Molecular Imaging). The working electrode was nickel plate polished to a mirror finish. The counter and reference electrodes were lithium metal. The electrolyte solution was 1 M LiClO₄ dissolved in propylene carbonate (PC) containing 5 wt.% of FEC (Kanto Denka Kogyo), VC (Aldrich), or ES (Aldrich). These solutions were dried over molecular sieves until the water contents decreased below 30 ppm. Lithium deposition was carried out at a constant current density of 0.5 mA cm⁻², and AFM images were obtained every 0.03 C cm⁻² deposition. All of these AFM measurements were carried out at 30°C in an argon-filled glove box.

For cycling efficiency measurements, a sealed three-electrode cell made of PTFE was used. The current densities for lithium deposition and dissolution were 0.5 mA cm⁻². In each cycle, lithium was deposited by 0.3 C cm⁻², and dissolved until the potential reached 1.5 V.

Figure 1 shows cycling efficiencies of lithium deposition and dissolution in 1 M LiClO₄ dissolved in PC containing various additives. Without additives, the cycling efficiency was initially 80% and decreased gradually to 60%. The addition of 5% of FEC improved the cycling efficiency. The cycling efficiency was kept at about 80% up to the 30th cycle. On the contrary, the addition of VC and ES lowered the cycling efficiency. In these solutions, the cycling efficiency was suddenly dropped after the 10th cycle.

Figure 2 shows AFM images of the surfaces of lithium metal deposited by 0.3 C cm⁻² on nickel substrates 1 M LiClO₄/PC with and without additives. Without additives [Fig. 2(a)] and with 5% of VC [Fig. 2(b)], the surface was rough, and large masses of deposits were observed on the surface. Such non-uniform and rough surface is responsible for the low cycling efficiency owing to dendrite formation by further lithium deposition. On the contrary, when FEC was added [Fig. 2(c)], the surface was much smoother. In a magnified image, the surface consisted of small particles of about 100 nm in

diameter, which was very similar to that observed at 80°C in the previous study [1]. The smooth and uniform surface film suppressed dendrite formation and improved the cycling efficiency as shown in Fig. 1. It is surprising that the addition of ES resulted in a smooth and uniform surface as shown in Fig. 2(d) although the cycling efficiency was poor in Fig. 1. AC impedance measurements revealed that the order of the surface film resistance was VC >> ES >> none > FEC. A high film resistance causes non-uniform current distribution, and may be another reason for dendrite formation and low cycling efficiency.

References

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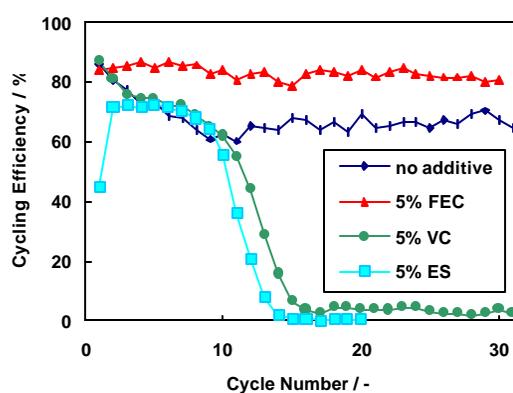


Fig. 1. Cycling efficiencies of lithium deposition-dissolution on nickel electrode in LiClO₄/PC with and without additives.

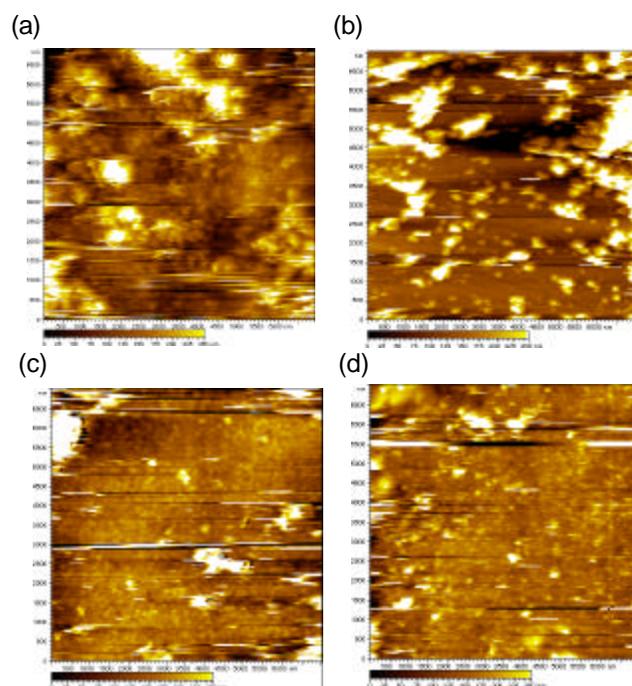


Fig. 2. AFM images (7 × 7 μm) of lithium deposited on Ni (0.3 C cm⁻²) in 1M LiClO₄/PC (a) without additives and with 5 wt.% of (b) VC, (c) FEC, and (d) ES.

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