

Effects of Some Organic Additives on Lithium Deposition in Propylene Carbonate

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The effects of some film-forming organic additives, fluoroethylene carbonate (FEC), vinylene carbonate (VC), and ethylene sulfite (ES), on lithium deposition and dissolution were investigated in 1 M LiClO₄ dissolved in propylene carbonate (PC) as a base solution. When 5 wt % FEC was added, the cycling efficiency was improved. On the contrary, addition of 5 wt % VC or ES significantly lowered the cycling efficiency. The surface morphology of lithium deposited in each electrolyte solution was observed by *in situ* atomic force microscopy (AFM). In PC + FEC, the surface was covered with a uniform and closely packed layer of particle-like deposits of about 100-150 nm diam. The surface film seemed to be more solid in PC + VC, and inhomogeneous in PC + ES. From ac impedance measurements, it was revealed that the surface film formed in PC + FEC has a lower resistance than that in the additive-free solution, whereas that formed in PC + VC or PC + ES has a higher resistance. Large volume changes during lithium deposition and dissolution require that the surface film should be elastic (or soft) and be self-repairable when being damaged. In addition, a nonuniform current distribution is liable to cause dendrite formation, which requires that the surface film should be uniform and its resistance should be as low as possible. PC + FEC gave a surface film that satisfies all these requirements, and therefore only FEC was effective as an additive for deposition and dissolution of lithium metal. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1516770] All rights reserved.

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Lithium metal is the most attractive material for use as a negative electrode in rechargeable cells because of its high energy density. However, dendritic deposition of lithium metal during repeated charge/discharge cycles is a serious problem that is responsible for low cycling efficiencies and safety issues.¹ On lithium metal, a protective surface film, called the solid electrolyte interface (SEI), is formed, which is known to have a great influence on the morphology of deposited lithium.^{2,3} To modify and control the morphology, and physical and chemical properties of the surface film, different kinds of additives have been proposed. These include HF,⁴ CO₂, ⁵ AlI₃, ⁶ SO₂, ⁷ nitromethane, ⁷ polyethylene glycol dimethyl ether,⁸ silicone/polypropylene oxide copolymer,⁹ cetyltrimethylammonium chloride,¹⁰ ethyl trifluoroacetate,¹¹ and aromatic compounds such as benzene,¹² toluene,¹² 2-methylfuran,¹² 2-methylthiophene,¹² triazoles,¹³ dipyridyl derivatives,¹⁴ etc.

The importance of the protective surface film is a common issue to graphite negative electrodes. It has been recently reported that some film-forming additives, fluoroethylene carbonate (FEC),¹⁵ vinylene carbonate (VC),¹⁶ and ethylene sulfite (ES),¹⁷ are effective for graphite negative electrodes. In a previous study using in situ atomic force microscopy (AFM), we reported that all these additives easily decompose and leave effective surface films on graphite negative electrodes at potentials more positive than 1 V before the main solvent decomposes.¹⁸ These additives are expected to be effective not only for graphite but also for lithium metal, though there has been no report for the latter in the literature. In this report, we studied the effects of these additives on lithium deposition and dissolution. The results of charge/discharge measurements were correlated with the surface morphologies of deposited lithium observed by in situ AFM, and with the resistances of the surface films estimated by ac impedance spectroscopy.

Experimental

Nickel plates (Nilaco Co., $20 \times 20 \times 0.3$ mm) were polished with alumina powder to a mirror finish and used as substrates for

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lithium deposition and dissolution. The counter and reference electrodes were lithium metal. The base electrolyte solution was commercially available 1 mol dm⁻³ (M) lithium perchlorate (LiClO₄) dissolved in propylene carbonate (PC; Kishida Reagent Chemicals, lithium-battery grade). FEC (Kanto Denka Kogyo), VC (Aldrich), and ES (Aldrich) were added 5 wt % each to the base solution. Each solution was dried over 4A molecular sieves for weeks and was used for measurements after the water content dropped less than 30 ppm.

An electrochemical cell made of polytetrafluoroethylene (PTFE) was used for cycling tests. The geometric surface area of the working electrode was fixed at 0.8 cm^2 using an O-ring. The current density for lithium deposition and dissolution was 0.5 mA cm^{-2} . In each cycle, 0.3 C cm^{-2} of lithium was deposited and dissolved completely until the potential reached 1.5 V vs. Li⁺/Li.

AFM observation of the surface morphology of deposited lithium was carried out with a PicoSPM® system (Molecular Imaging) equipped with a PicoStat® potentiostat (Molecular Imaging). A laboratory-made fluid cell made of PTFE was set on a sample stage. The geometric surface area of the nickel substrate was fixed at 1.2 cm² using an O-ring. AFM images were obtained in the contact mode using a piezoelectric scanner with scan ranges of 7 μ m in the x- and y-directions. The microcantilever made of Si₃N₄ was scanned at 21 µm s⁻¹ to obtain AFM images. Lithium was deposited at 0.5 mA cm^{-2} . During deposition, the microcantilever was moved out of the solution because the current distribution beneath the tip would have been disturbed by its presence. After every 0.03 C cm⁻² deposition, AFM images were obtained under opencircuit conditions. In addition to the constant current deposition, cyclic voltammetry (CV) was carried out at 5 mV s^{-1} between 2.5 and 0.05 V, and AFM images after five cycles of CV were obtained in a similar manner.

AC impedance was measured with a frequency analyzer (SI 1255, Solartron) coupled with a potentiostat (model 273A, EG&G PAR) and the cell used for the cycling tests. After lithium was deposited on the nickel substrate at -0.1 V for 300 s, the impedance was measured under open-circuit conditions over the frequency range of 100 kHz to 100 mHz. The perturbation amplitude for alternating polarization was 5 mV.

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Figure 1. Cycling efficiencies for deposition and dissolution of lithium on nickel substrates in 1 M LiClO₄/PC without additive and with 5 wt % FEC, VC, and ES. The current density was 0.5 mA cm⁻². The amount of lithium deposition was 0.3 C cm⁻² in each cycle. The cutoff voltage for dissolution was 1.5 V.

All experiments were carried out at 30° C in an argon-filled glove box (Miwa Industries) with a dew point below -60° C.

Results and Discussion

Cycling efficiencies for lithium deposition and dissolution.-Lithium deposition and dissolution were carried out on nickel substrates in 1 M LiClO₄/PC solutions with and without the additives. The variations of the cycling efficiencies for lithium deposition and dissolution with cycle number are shown in Fig. 1. In the additive-free solution, the cycling efficiency was around 80% in the first cycle. However, it decreased gradually and was leveled off between 60 and 70% after the 10th cycle. The addition of 5 wt % FEC obviously improved the efficiency, i.e., the efficiency was higher than 80% up to the 30th cycle. The effects of VC and ES addition were contrary to what we expected. The efficiency decreased rapidly after the 10th cycle and became lower than 10%. It should be noted that all these additives are effective for graphite negative electrodes as mentioned earlier. However, only the addition of FEC improved the cycling efficiency for lithium deposition and dissolution in the present study. Thus, the properties required for the surface film on lithium seem to be different from that on graphite.

Morphologies of deposited lithium.—The surface morphologies of lithium deposited on nickel substrates were observed by in situ AFM to clarify the correlation between the surface morphology and the cycling efficiency. AFM images obtained in the additive-free 1 M LiClO₄ /PC are shown in Fig. 2. Figure 2a shows an image before lithium deposition. Many grooves, which were made from polishing, are seen on the nickel surface. After lithium deposition of 0.03 C cm⁻², particle-like deposits of about 100 nm diam appeared sparsely (not shown). The number of the deposits increased, and their sizes grew up with the amount of deposition. After deposition of $0.09 \text{ C} \text{ cm}^{-2}$, the sizes of particle-like deposits were not uniform over the range of 100-200 nm diam (Fig. 2b). In addition, the grooves on the nickel substrate became indistinct, which means that the surface was covered with a thin film. Some noisy lines are seen running horizontally in the image, which were made by the collisions of the microcantilever with large bulges on the surface and thus indicate that the surface was rough. In Fig. 2c, which shows an image obtained after deposition of 0.15 C cm⁻², a large deposit appeared with many noisy lines across the image. After 0.3 C cm⁻ the surface became very rough, and many agglomerates appeared on the surface (Fig. 2d). These morphology changes were similar to those obtained in lithium bis(perfluoroethylsulfonyl)imide (LiBETI)/PC at room temperature in our previous reports.^{19,20} It is



Figure 2. AFM images (7 \times 7 μ m) of the surface morphology on a nickel substrate obtained (a) before and after (b) 0.09, (c) 0.15, and (d) 0.3 C cm⁻² deposition of lithium metal in 1 M LiClO₄/PC. Lithium was deposited at 0.5 mA cm⁻².

reasonable to presume that these large agglomerates lead to the formation of dendrites during repeated deposition/dissolution cycles, which lowers the cycling efficiency.

AFM images obtained in 1 M LiClO₄/PC + 5 wt % FEC are shown in Fig. 3. Even after 0.09 C cm⁻² of lithium was deposited, the whole surface of the nickel substrate was completely covered with fine deposits as shown in Fig. 3a. The surface was very smooth and the original grooves on the substrate were invisible. Upon further deposition, the particle size increased slightly; however, almost no clear morphological changes were observed. Figure 3b shows an image obtained after deposition of 0.3 C cm⁻². The surface was still covered with a thick, closely packed layer of fine particles with no sign of large agglomerate formation. Figure 3c shows a magnified image of the 1 × 1 µm area indicated by a square in Fig. 3b. The sizes of the particles were several tens of nanometers with a uniform size distribution.

Surface morphologies after the following dissolution to 1.5 V and after another 0.3 C cm⁻² deposition are shown in Fig. 4. Surprisingly, the morphology of the precipitate layer remained almost unchanged during the dissolution and redeposition. Kanamura et al. observed the morphology of lithium deposited in LiClO₄/PC containing a trace amount of HF by scanning electron microscopy (SEM)⁴ and AFM.²¹ They reported that hemispherical deposits of about 300 nm diam were formed on deposition. During the following dissolution process, they observed the formation of holes and defects on the deposits accompanied by shrinkage of the deposits and concluded that each particle consisted of lithium metal covered with a surface film. However, this does not seem to be the case for the precipitates in Fig. 3 and 4, which showed no morphological changes during deposition and dissolution. It is therefore reasonable to consider that the particles in Fig. 3 and 4 were not lithium metal but decomposition products of the electrolyte solution. This, in turn, implies that metallic lithium was deposited uniformly underneath the precipitate layer, which suppressed dendritic deposition of



Figure 3. AFM images of the surface morphology on a nickel substrate obtained after (a) 0.09 and (b, c) 0.3 C cm^{-2} deposition of lithium metal in 1 M LiClO₄/PC containing 5 wt % FEC. Lithium was deposited at 0.5 mA cm⁻². (a, b) $6.5 \times 6.5 \mu \text{m}$; (c) $1 \times 1 \mu \text{m}$.

lithium metal and resulted in the improvement in cycling efficiency shown in Fig. 1.

The morphologies of the surface film in PC + FEC in Fig. 4 and 5 are very similar to those obtained in LiBETI/PC at elevated temperatures of 60 and 80°C in our previous studies, ^{19,20} at which temperatures the cycling efficiencies were greatly improved. In the previous studies, we concluded that the dense and uniform structure of the surface film is given by rapid decomposition of the electrolyte solution at the elevated temperatures, and such a uniform surface morphology is one of the important factors for the suppression of dendrite formation. In addition, we reported that FEC reductively



Figure 4. AFM images of the surface morphology on a nickel substrate obtained after (a, b) dissolution of lithium to 1.5 V and (c, d) the following deposition of 0.3 C cm⁻² in 1 M LiClO₄/PC containing 5 wt % FEC. The current density was 0.5 mA cm⁻². (a, c) $6.5 \times 6.5 \mu$ m; (b, d) $1 \times 1 \mu$ m.

decomposes on a graphite electrode at a higher potential (about 1.1 V) than PC is cointercalated within the graphite and decomposes (about 0.9 V).¹⁸ Thus, it seems that FEC accelerates the rate of the electrolyte decomposition and provides a surface morphology that can suppress dendrite formation.

Figure 5 shows the morphological changes observed in 1 M $\text{LiClO}_4/\text{PC} + 5$ wt % VC. After deposition of 0.09 C cm⁻² (Fig. 5a), a small amount of deposits appeared on the surface. The grooves on the substrate became indistinct, and the whole surface seemed to be covered with a very thin film of the decomposition products. However, the image was very clear and sharp when compared with that in the additive-free solution (*e.g.*, Fig. 2b) so that the film should be solid and hard. After deposition of 0.15 C cm⁻² (Fig. 5b) the size of the deposits increased to 200-500 nm diam, and they grew up to large agglomerates after deposition of 0.3 C cm⁻² (Fig. 5c). These particles are most probably lithium metal and become nuclei for lithium dendrites during repeated deposition/dissolution cycles, as was the case in the additive-free solution.

AFM images obtained in 1 M LiClO₄/PC + 5 wt % ES are shown in Fig. 6. After deposition of 0.09 C cm⁻² (Fig. 6a), the whole surface was covered with a layer of precipitates. This surface morphology was similar to that in PC + FEC in Fig. 3a. However, the precipitate layer became rough and inhomogeneous after deposition of 0.3 C cm⁻² (Fig. 6b). In some parts, large deposits, which were probably lithium metal, were observed as shown in Fig. 6c. The poor cycling efficiency in PC + ES is thus attributable to dendrite formation due to the rough and inhomogeneous structure of the precipitate layer.

CV coupled with AFM observation.—The decomposition processes of the three additives were investigated more closely by CV coupled with *in situ* AFM observation. Figure 7 shows CVs of nickel electrodes in 1 M LiClO₄ /PC with and without the additives. All voltammograms showed three peaks at about 1.1, 0.6, and 0.2 V on the first cathodic sweep, which can be assigned to reductive decomposition of electrolyte solutions to form surface films as discussed in a previous study using 1 M LiBETI/PC.²² In the second cycle in each solution, the cathodic current decreased significantly, and the peak at 1.1 V disappeared. The current further decreased with cycling number, which indicates that the surface of the nickel electrode was passivated by the surface film formed via the decomposition of the electrolyte solution. We reported that the additives, FEC, VC, and ES, reductively decompose at 1.1, 1.3, and 1.0 V,



Figure 5. AFM images (7 \times 7 μ m) of the surface morphology on a nickel substrate obtained after (a) 0.09, (b) 0.15, and (c) 0.3 C cm⁻² deposition of lithium metal in 1 M LiClO₄/PC containing 5 wt % VC. Lithium was deposited at 0.5 mA cm⁻².

respectively, on a graphite negative electrode.¹⁸ However, these peaks were not clearly observed on the nickel electrodes in the present study.

After the fifth voltammogram in Fig. 7 was obtained, the surface of the nickel electrode was observed by *in situ* AFM in each electrolyte solution. The results are shown in Fig. 8. Figure 8a shows an image obtained in the additive-free 1 M LiClO_4/PC . The image became indistinct when compared with the original surface before CV (*e.g.*, Fig. 2a). This may be due to the presence of a thin and soft film, which is slightly deformed by the microcantilever during scanning. It is clear that the surface film was formed by reductive decomposition of the electrolyte solution during the CV measurements. The grooves made from polishing were still visible; hence, the amount of deposition was not so large. In addition to the thin layer, particle-like deposits were sparsely observed on the surface. These particles were not lithium metal but decomposition products of the electrolyte solution, because observation was carried out at 2.5 V.

In PC + FEC (Fig. 8b), the image obtained was unclear, and this again indicates the presence of a thin and soft film on the surface.

Particle-like deposits are also seen in the image, but their shapes are less distinct. This implies that the particles are also made of a soft material. In contrast, a very clear and sharp image was obtained in PC + VC (Fig. 8c). The shapes of particle-like deposits were also clearly observed. These facts mean that the surface film and the particle-like deposits formed in PC + VC are much more solid than those formed in the other solutions. Particle-like deposits were hardly seen in PC + ES; however, the grooves were unclear and hence a thin film was present on the surface. From these results it can be concluded that the properties of surface films are rather different depending on the kind of additives, which affects the morphology of deposited lithium.

AC impedance measurements of deposited lithium.—Lithium metal was deposited on nickel substrates at a constant potential of -0.1 V for 300 s in 1 M LiClO₄/PC with and without the additives, and ac impedances were measured to compare the electrochemical properties of respective surface films. The results are shown in Fig. 9. Figure 9a compares the impedances over the entire frequency region. The resistances of the electrolyte solutions (~60 Ω) were



Figure 6. AFM images ($6.5 \times 6.5 \mu m$) of the surface morphology on a nickel substrate obtained after (a) 0.09 and (b, c) 0.3 C cm⁻² deposition of lithium metal in 1 M LiClO₄/PC containing 5 wt % ES. Image (b) and (c) were of different regions. Lithium was deposited at 0.5 mA cm⁻².

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Figure 7. CVs on nickel substrates in 1 M LiClO₄ /PC (a) without additive, and with 5 wt % (b) FEC, (c) VC, and (d) ES. The scan rate was 5 mV s⁻¹.



Figure 8. AFM images $(7 \times 7 \mu m)$ of the surface morphologies on nickel substrates obtained after five cycles of CV in 1 M LiClO₄/PC (a) without additive, and with 5 wt % (b) FEC, (c) VC, and (d) ES.



Figure 9. Cole-Cole plots for lithium deposited on nickel substrates in 1 M LiClO₄/PC without additive, and with 5 wt % FEC, VC, and ES. Lithium deposition was carried out at -0.1 V for 300 s.

subtracted for clarity. Two arcs are seen in each spectrum. The smaller arc in the high-frequency region appeared at 1.0 V and has been already assigned to the impedance of the surface film in a previous study.²² The larger arc in the low-frequency region appeared only after deposition of bulk lithium, and disappeared after dissolution (not shown). The arc in the low-frequency region is thus attributable to the charge-transfer reaction, though further investigation is necessary. In the present study, we compared only the arcs in the high-frequency region to discuss the electrochemical properties of the surface films. Figure 9b shows magnified spectra in the highfrequency region. In PC + FEC, the resistance of the surface film was slightly lower than that in the additive-free solution. The characteristic frequency of the arc was 3.98 kHz, which was equal to the value in the additive-free solution, which implies that the surface films formed in these two electrolyte solutions have similar electrochemical properties. In contrast, the resistances in the other two solutions, in particular in PC + VC, were higher than that in the additive-free solution. The order in the conductivity of the surface film is thus PC + FEC > PC > PC + ES > PC + VC. This order is consistent with the order for the cycling efficiency in Fig. 1; that is, the lower the resistance of the surface film, the higher the cycling efficiency obtained. A high resistance of the surface film is liable to cause a nonuniform current distribution, which accelerates the formation of dendritic lithium. Consequently, a low resistance is one of the important properties required to obtain an effective surface film on lithium metal.

Conclusions

The effects of FEC, VC, and ES as additives on the cycling efficiency for lithium deposition and dissolution were investigated. Although all the additives were reported to be effective for graphite negative electrodes, only FEC improved the cycling efficiency for lithium metal and the other two additives significantly lowered the efficiency. These results suggested that the properties required for the surface film on lithium are different from that on graphite.

In situ AFM observation revealed that deposited lithium was covered with a uniform, closely packed layer of particle-like deposits of 100-150 nm diam in PC + FEC. The surface film seemed to be more solid in PC + VC and inhomogeneous in PC + ES. Large volume changes are accompanied by lithium deposition and dissolution, which requires that the surface film should be elastic (or soft) and be self-repairable when being damaged. In addition, a nonuniform current distribution (local current concentration) easily results in dendrite formation, which requires that the surface film should be uniform and its resistance should be as low as possible. When VC was added, the surface film was very thin and solid, and its resistance was high. In PC + ES, the surface film was inhomogeneous, and its resistance was relatively high. PC + FEC gave a surface film that satisfies all the requirements, and therefore only FEC was effective as an additive on lithium metal. In contrast to lithium metal, graphite negative electrodes exhibit much smaller volume changes during charging and discharging, and are free from dendrite lithium deposition except when being overcharged. Softness and low resistivity are not severely required for the surface film, and therefore VC and ES work as effective additives for graphite negative electrodes.

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