Surface Layer and Morphology of Lithium Metal Electrodes

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ABSTRACT

The surface morphology of the electrodeposited lithium metal from electrolyte solutions containing electrolyte additives: fluoroethylene carbonate (FEC), vinylene carbonate (VC) and lithium bis(oxalate)borate (LiBOB), were investigated. All the film forming additive improved the surface morphology. The FEC especially shows the most uniform surface morphology compared with the other electrolyte additives and the additive-free electrolyte. The surface analyses of the lithium metal were conducted using X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The analytical study revealed that the FEC suppresses the decomposition of the PF_6^- anion, resulting in the formation of a thin stable SEI layer on the lithium metal.

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Keywords : Li Dendrite, Solid Electrolyte Interphase, Electrolyte Additives, Surface Morphology

1. Introduction

New battery chemistries so called “Beyond Li-Ion Batteries” have been getting a lot of interest during the last decade.¹ Lithium-Oxygen batteries and Lithium-Sulfur batteries are the two promising battery chemistries for high-energy applications.² Of course there still remains a lot of challenges in positive and negative electrode materials and electrolytes. Lithium metal has been considered as the ideal negative electrode material for these battery chemistries, because of its low equilibrium potential -3.04 V vs. SHE and high specific capacity $>3800\text{ mAhg}^{-1}$.³

However, rechargeable battery system using the lithium negative electrode has never been successfully commercialized due to the dendritic growth of lithium during the charging process. The lithium dendrite leads the internal short circuit of the cell resulting in the safety incidents, therefore the surface morphology control of the electrodeposited lithium is essential to utilize the lithium metal for practical battery systems.

The surface morphology of the electrodeposited lithium is basically dependent upon the kinetics of the deposition process⁴ and the preferred crystal growth mode.⁵ Especially the electrochemical reaction at the lithium-electrolyte interphase is the dominant process to determine the surface morphology. Therefore many analytical studies concerning the characterization of solid-electrolyte interphase (SEI) layer⁶ were carried out using various analytical techniques, such as FTIR,^{7–10} XPS,^{11–13} AFM^{14–17} and so forth.

In order to form the stable SEI layer, various organic and inorganic electrolyte additives were investigated. A stable SEI layer of Li_2CO_3 is formed under the presence of CO_2 resulting in the decrease of the interfacial impedance and the improvement the cycling performance. Shiraishi et al. reported that the HF could be a good film formation additive to obtain a very smooth Li surface and showed improved cycling efficiency.¹⁸ Typical film forming additives such as vinylene carbonate (VC), fluoroethylene carbonate (FEC), and ethylene sulfate (ES) developed for graphite negative electrode of lithium ion batteries, are also investigated. Mogi et al. reported that the FEC forms smooth surface morphology of electrodeposited lithium.¹⁵ The VC forms a polymeric species and

improves the cycling efficiency of lithium deposition and dissolution.^{19–21} Sano et al. added VC and ES to a room temperature ionic liquid (RTIL) electrolyte and found the improved cycling performance.²² Recently Ding et al. obtained very smooth surface morphology of the electrodeposited lithium by adding small amount of CsPF_6 .^{23,24}

Despite of these works, it is not well understood that how these additives form the SEI layers and how the SEI affects to the surface morphology of the lithium metal yet. In the present study, an ethylene carbonate (EC)-based electrolyte solution was chosen as a normal electrolyte, because the EC-based electrolyte solution forms a good SEI layer on the graphite anode. We investigated the influence of the film-forming additives FEC, VC and LiBOB in the EC-based electrolyte solution. The SEI films on the lithium negative electrode were characterized using XPS and ATR-FTIR.

2. Experimental

A commercial electrolyte solution: $1\text{ mol dm}^{-3}\text{ LiPF}_6$ EC:DEC 1:1 vol% (Kishida, battery grade) was used as the normal electrolyte solution in the present work. FEC, VC and LiBOB purchased from Kishida, were mixed into the normal electrolyte as the electrolyte additives in the argon filled glove box. The water content of the electrolyte solutions were $<10\text{ ppm}$.

Li deposition tests were conducted, using a two-electrode symmetric Swagelok cell. The distance between the two electrodes is 10.0 mm as shown in Fig. 1. Li metal electrodes were used as the

Figure 1. (Color online) A schematic representative of the 2-electrode Swagelok cell.

Figure 2. (Color online) The SEM images of the as-prepared lithium (a), the electrodeposited lithium for $1\text{ C}\cdot\text{cm}^{-2}$ (b), and the electrodeposited lithium for $10\text{ C}\cdot\text{cm}^{-2}$ (c). The magnified images of (a), (b) and (c) are (d), (e) and (f) respectively. The voltage profiles of the electrodeposition process are shown in (g): $1\text{ C}\cdot\text{cm}^{-2}$ deposition (blue) and $10\text{ C}\cdot\text{cm}^{-2}$ deposition (orange).

working electrode and the counter electrode. In order to remove the Li_2CO_3 native film, a piece of Li metal was cut off from a Li rod (Honjo metal), and sandwiched between two sheets of a polypropylene (PP). Then the Li metal was pressed to form a sheet using a stainless steel hand roller. The Li sheet was punched and layered with Ni substrate to use as the electrode.

Galvanostatic Li deposition tests were carried out with time control mode. The Li deposition amount was determined to $10\text{ C}\cdot\text{cm}^{-2}$ ($1\text{ mA}\cdot\text{cm}^{-2}$ for 10,000 sec.). After the electrodeposition of Li, the cell was disassembled and the electrode was rinsed with anhydrous DEC to remove the electrolyte salts. The rinsed electrodes were dried in vacuum for 5 minutes at room temperature. The obtained electrode was sealed in an airtight sample holder and transferred to Scanning Electron Microscope (SEM) for surface morphology observation.

The characterization of the SEI layer was conducted using XPS (ESCA-3400, Shimadzu) equipped with Mg $\text{K}\alpha$ X-ray anodes (Acceleration voltage 10 kV, Emission currents 20 mA) and argon sputtering gun. The argon sputtering of the samples were carried out to collect the depth information of SEI layer. The sample installation of the XPS measurement was carried out using a transfer vessel, which allows to insert the Li metal into the XPS chamber without exposing in air. The surface of the lithium metal was also analyzed by ATR-FTIR spectroscopy using a conventional FTIR spectrometer (Nicolet iS50R, Thermo Scientific) with a single reflection diamond ATR accessory (Golden Gate ATR, Specac). The Li metal was placed on the diamond crystal in the Ar filled glovebox and pressed with an anvil with environmental chamber to avoid the air exposure of the sample.

3. Results and Discussion

3.1 Surface morphology and SEI layer in the additive-free electrolyte solution

SEM images of the electrodeposited lithium metal negative electrodes from an additive-free electrolyte solution ($1\text{ mol}\cdot\text{dm}^{-3}$ LiPF_6 EC:DEC = 1:1 vol%), are shown in Fig. 2. During the early stage of the deposition process: $1\text{ C}\cdot\text{cm}^{-2}$, the lithium negative electrode maintained a smooth surface morphology Fig. 2(b), similar to the as-prepared one shown in Fig. 2(a). No uneven deposit is observed on the electrode even in the magnified image Fig. 2(e). On the other hand, the lithium negative electrode after the electrodeposition process for $10\text{ C}\cdot\text{cm}^{-2}$ had an uneven surface covered with aggregated lithium particles as shown in Fig. 2(c). The aggregated particles consist of round-shaped particles and rods as shown in the magnified image: Fig. 2(f). The result suggests that the roughness of the lithium negative electrodes gradually increases during the deposition process. Furthermore, the aggregated lithium particles could be the preferred site of the whisker-shaped lithium deposition, because the resistance of the fresh SEI layer on the deposited lithium is different from that of the preformed SEI layer before the electrodeposition. As a consequence, the local current density gets varied, and the dendritic lithium can easily be formed. The result suggests that the roughness of the lithium negative electrodes gradually increases during the deposition process.

Figure 2(g) shows the potential profiles of the galvanostatic electrodeposition process above, and the focused profiles for the early stage of the deposition process are shown in Fig. 2(h). In both cases, the cell voltage initially dropped down and then continuously shifted to more positive value, during the deposition process. Even

Figure 3. (Color online) The XPS spectra of lithium metal immersed in the normal electrolyte solution: $1 \text{ mol} \cdot \text{dm}^{-3}$ LiPF_6 EC:DEC 1:1 vol%. The spectrum at the top of each graph represents the surface of the sample. The following spectra were taken after the argon sputtering for each sputtering time noted at the right side of the graph.

though the minimum voltage values were slightly different, these cells showed almost same voltage profiles after the 100 sec of the initial deposition process. We assume it was probably due to the slight difference of the surface condition of the electrodes before the deposition test. However, once the lithium deposition occurs, the surface conditions of the lithium electrodes get almost equal. Consequently, these two potential profiles overlapped each other during the following deposition process. Considering the SEM images in Fig. 2, the continuous potential shift during the lithium deposition process could be owing to the increase of the surface area by the uneven lithium deposition.

Since the surface condition significantly affects to the deposition as discussed in the above section, the SEI composition on the lithium negative electrode was investigated by XPS. Figure 3 shows XPS spectra of the surface film on the Li foil immersed in the electrolyte solution: $1 \text{ mol} \cdot \text{dm}^{-3}$ LiPF_6 EC:DEC 1:1 vol%. The C 1s XPS spectra in Fig. 3(a) show that a thick layer of lithium alkyl carbonates (LiOCO_2R) is one of the main components of the SEI layer, because the two strong peaks corresponding to LiOCO_2R at 287.0 eV and C-H at 284.5 eV remained even after the argon sputtering for 40 minutes. The F 1s spectra (b) show a strong peak assigned to $\text{Li}_x\text{PO}_y\text{F}_z$ at 688.0 eV with small amount of the LiPF_6 and LiF. Contrarily to the F 1s XPS spectra, the $\text{Li}_x\text{PO}_y\text{F}_z$ mostly disappeared after 10 minutes of the argon sputtering process. It suggests that the fluorinated species mainly exist on the top of the SEI layer. The peaks corresponding to the $\text{Li}_x\text{PO}_y\text{F}_z$ are observed around 58.5 eV in the Li 1s spectra (c), and at 534.0 eV in the O 1s spectra (d) respectively. The Li 1s and the O 1s spectra also suggest that Li_2O could exist even in the bulk Li foil as an impurity phase, because the peak at 530.5 eV corresponding to Li_2O still remains even after the pure lithium metal is disposed by the argon etching process. To summarize the XPS analysis result, the SEI layer on the lithium negative electrode, mainly consists of LiOCO_2R , and some $\text{Li}_x\text{PO}_y\text{F}_z$ species are formed at the top of the lithium.

3.2 Surface morphology changes by the electrolyte additives

In order to form a stable SEI layer to eliminate the lithium dendrite formation, we investigated the effect of the electrolyte additives used as SEI former for lithium-ion batteries. Figure 4 shows the series of SEM images of the lithium metal deposited for 10 C cm^{-2} from the electrolyte solution containing 5 vol% FEC (a), (d), (g), 5 vol% of VC (b), (e), (h) and 1 wt% of LiBOB (c), (f), (i). Compared with the additive free electrolyte solution discussed in the previous section, all the electrodes maintained relatively smooth surface even after the 10 C cm^{-2} of the electrodeposition. It shows that the film-forming additives are effective to stabilize the surface morphology of the electrodeposited lithium metal. Especially the FEC maintained very uniform surface morphology like the as-prepared lithium electrode as shown in Fig. 4(a). It indicates the FEC forms a stable and uniform SEI layer, which enables the smooth deposition of lithium.

The lithium metal deposited in the electrolyte solution containing 5 vol% of VC also shows uniform morphology as shown in Fig. 4(b), (e), (h), however it partially has dendritic growth of the lithium as shown in Fig. 4(b). The magnified image showed a very unique morphology like seaweed as shown in Fig. 4(e) and (h). We assume the seaweed-like morphology is due to the mechanical properties of the SEI layer, because the electrolyte solution containing VC is known to form a rigid SEI.¹⁵ The rigid SEI layer seems to limit direction of the particle growth and initiate the in-plane 2D growth of the deposited particles, as a consequence the typical dendrite growth seems to be delayed.

An electrolyte solution containing LiBOB also showed a similar morphology to the VC. The SEM images of the lithium negative electrode deposited from the electrolyte solution containing LiBOB are shown in Fig. 4(c), (f) and (i). The solution also formed the seaweed-like lithium deposit as shown in Fig. 4(f). It indicates that the LiBOB also forms a rigid SEI layer, which delays the formation of the dendritic lithium, however we assume the SEI layer is not as hard as the SEI formed by VC, because the lithium 2D growth layer is thicker.

Figure 4. The SEM images of the lithium negative electrode after the $10\text{ C}\cdot\text{cm}^{-2}$ of electrodeposition at $1\text{ mA}\cdot\text{cm}^{-2}$ in the electrolyte solution containing the various film forming additives: 5 vol% of FEC (a), (d), (g), 5 vol% of VC (b), (e), (h) and 1 wt% of LiBOB (c), (f), (i).

Figure 5. (Color online) The XPS spectra of lithium metal immersed in the normal electrolyte solution: $1\text{ mol}\cdot\text{dm}^{-3}$ LiPF_6 EC:DEC 1:1 vol% containing 5 vol% of FEC. Same as the Fig. 2, the spectrum at the top of each graph represents the surface of the sample. The following spectra were taken after the argon sputtering for each sputtering time noted at the right side of the graph.

3.3 SEI layer in the electrolyte solutions containing additives

Since the discussions in the previous section suggested that the morphology of the deposited lithium is highly dependent upon the surface layer, a series of XPS measurements were conducted to characterize the SEI layer formed in each electrolyte.

The XPS spectra of a lithium foil immersed in the electrolyte solution containing FEC are shown in Fig. 5. The C 1s spectra in Fig. 5(a) have two main peaks corresponding to the LiOCO_2R which is similar to the C 1s XPS spectra of the additive-free electrolyte discussed in the previous section. The LiOCO_2R should

Figure 6. (Color online) The XPS spectra of lithium metal immersed in the normal electrolyte solution: $1 \text{ mol} \cdot \text{dm}^{-3}$ LiPF_6 EC:DEC 1:1 vol% containing 5 vol% of VC. The spectrum at the top of each graph represents the surface of the sample. The following spectra were taken after the argon sputtering for each sputtering time noted at the right side of the graph.

also be the main component of the SEI layer formed in the electrolyte solution containing FEC because it remains even after the 40 minutes of Ar etching process as well as the additive-free electrolyte solution. The F 1s spectra shown in Fig. 5(b) also show a peak corresponding to $\text{Li}_x\text{PO}_y\text{F}_z$, however the peak intensity was relatively weak compared with the additive-free one. It clearly shows that the decomposition of the PF_6^- anion was eliminated by the FEC. In the Li 1s spectra in Fig. 5(c), a relatively strong peak assigned to LiF was observed while a peak corresponding to $\text{Li}_x\text{PO}_y\text{F}_z$ or LiPF_6 was mostly disappeared. These results suggest that the LiF in the SEI was formed not by the decomposition of the PF_6^- anion but by the decomposition of FEC. In the O 1s spectra, the intensity of a peak assigned to $\text{Li}_x\text{PO}_y\text{F}_z$ is also weak, compared to that of the additive-free electrolyte, as a consequence, the peak corresponding to the LiOCO_2R is sharpen. The result is in good agreement with the spectra of C 1s, F 1s and Li 1s.

Thus we conclude that the FEC molecules are the direct source of the SEI layer rather than EC. The SEI formed by the FEC seem to be compact and uniform, as a consequence the decomposition of EC and PF_6^- is prevented. In addition, we assume that the suppression of the $\text{Li}_x\text{PO}_y\text{F}_z$ improves the uniform current distribution resulting in the smooth morphology of the deposited lithium.

The vinylene carbonate (VC) forms a unique SEI layer compared with FEC. Figure 6 shows the XPS spectra of lithium foil immersed in the electrolyte solution containing 5 vol% VC. A very strong peak at 287.0 eV of the C 1s spectrum and the peak at 535.5 eV in the O 1s spectrum suggests the formation of polycarbonate species at the very surface of the SEI layer. After 1 min of the argon sputtering process, a typical C 1s peak assigned to the LiOCO_2R was observed. Again the main component of the SEI layer seems to be the LiOCO_2R . The F 1s spectra shown in Fig. 6(b) have a strong peak corresponding to $\text{Li}_x\text{PO}_y\text{F}_z$. Since the peak intensity of the $\text{Li}_x\text{PO}_y\text{F}_z$ increases after 10 seconds of the argon sputtering, the typical SEI composing species such as $\text{Li}_x\text{PO}_y\text{F}_z$ and LiOCO_2R beneath the thin polycarbonate layer. The Li 1s spectra also show

that the $\text{Li}_x\text{PO}_y\text{F}_z$ and the LiOCO_2R is the main product of the SEI Fig. 6(c). In the Li 1s spectra, Li metal and Li_2O were detected after 5 minutes of the argon sputtering, suggesting that the SEI layer formed in the electrolyte containing VC is relatively thick. In addition, the O 1s spectra are in good agreement with above discussion.

The SEI layer formed in the VC containing electrolyte consists of the polycarbonate layer at the top of the surface and the thick organic and inorganic layer consists of the LiOCO_2R and the $\text{Li}_x\text{PO}_y\text{F}_z$ beneath the polycarbonate layer. The SEI components under the top polycarbonate layer are very similar to the SEI layer for the additive-free electrolyte. Thus we suspect that the EC is still the main source to form the SEI layer, considering a proposed SEI formation mechanism reported by Ushirogata et al.²⁵ Furthermore, the top polycarbonate layer probably improves the mechanical properties of the SEI layer resulting in the delay of the dendrite formation and enhancement of the in-plane 2D growth of the lithium metal.

Figure 7 shows the XPS spectra of the lithium metal immersed in the electrolyte solution containing 1 wt% LiBOB. The SEI layer formed in the LiBOB containing electrolyte also has a similar polycarbonate species to the SEI formed by VC at the top of the SEI layer as shown in Fig. 7(a). A strong peak at 287.3 eV in C 1s spectra represents the polycarbonate layer, which was also observed in the case of the VC containing electrolyte. Beneath the polycarbonate layer, LiOCO_2R and $\text{Li}_x\text{PO}_y\text{F}_z$ are observed in C1s, F1s and Li1s spectra as shown in Fig. 7(a), (b) and (c). Notably the peak intensities of the $\text{Li}_x\text{PO}_y\text{F}_z$ in the F 1s spectra were very strong at the surface of the SEI layer, however the peak intensity immediately decreased after 1 minute of the argon sputtering. It shows that the SEI layer has high content of $\text{Li}_x\text{PO}_y\text{F}_z$ but the thickness of the $\text{Li}_x\text{PO}_y\text{F}_z$ layer is thin, suggesting that the BOB⁻ anion eliminates the decomposition of the PF_6^- anion.

It is known that the BOB⁻ forms a compact SEI layer at 1.7 V vs. Li, and the SEI layer prevents the co-intercalation of propylene

Figure 7. (Color online) The XPS spectra of lithium metal immersed in the normal electrolyte solution: $1 \text{ mol} \cdot \text{dm}^{-3}$ LiPF_6 EC:DEC 1:1 vol% containing 1 wt% of LiBOB. The spectrum at the top of each graph represents the surface of the sample. The following spectra were taken after the argon sputtering for each sputtering time noted at the right side of the graph. The B 1s spectra are omitted, because no clear peak was observed in all the B 1s spectra.

carbonate (PC) into the graphite.²⁶ We think the LiBOB forms the very similar compact SEI layer, which suppresses the decomposition of the PF_6^- and the formation of $\text{Li}_x\text{PO}_y\text{F}_z$. The Li 1s and the O 1s spectra were very similar to the XPS spectra for the electrolyte solution containing VC.

Thus the electrolyte solution containing LiBOB also forms a top polycarbonate layer, which reinforces the mechanical properties of the SEI layer, resulting in the in-plane 2D growth of the lithium metal. Beneath the polycarbonate layer a thin $\text{Li}_x\text{PO}_y\text{F}_z$ layer exists and the LiOCO_2R layer forms the matrix of the SEI layer.

The ATR-FTIR spectra in Fig. 8 were in good agreement with the above discussions. Obviously the electrolyte solutions containing VC and FEC form more LiOCO_2R and Li_2CO_3 compared with the additive-free electrolyte, suggesting that the both electrolyte additives form stable SEI layer based on organic species. However, the absorption peak corresponding to the $\text{Li}_x\text{PO}_y\text{F}_z$ observed around the wavenumber 880 cm^{-1} is mostly disappeared in the case of the electrolyte solution containing FEC while the lithium metal immersed in the additive-free electrolyte solution clearly formed it. The results also suggest that the top polycarbonate layer improves the mechanical properties of the SEI layer.

3.4 The influence of the SEI layer to the surface morphologies

Overall the surface morphology of the electrodeposited lithium can be improved by using the film-forming additives. All the lithium negative electrodes deposited from the electrolyte solutions containing the electrolyte additive: FEC, VC or LiBOB showed relatively uniform morphology compared with the lithium deposited from the additive-free electrolyte. The result clearly suggests that the SEI formed by the electrolyte additives significantly affects to the morphology of the deposited lithium metal.

In the case of the electrolyte solution containing FEC showed the smoothest morphology among the electrolyte solutions used in the present work. The SEI formed by the FEC mainly consists of

LiOCO_2R . We observed the existence of the LiOCO_2R in all the cases, however the electrolyte solution containing FEC formed less $\text{Li}_x\text{PO}_y\text{F}_z$ than other film forming additives. It shows the FEC eliminates the decomposition of the PF_6^- anion. The LiOCO_2R in the SEI could show similar physical properties such as Li ion conductivity to the bulk electrolyte solution, while $\text{Li}_x\text{PO}_y\text{F}_z$ is inactive for the Li ion conduction. Therefore, we think the suppression of the $\text{Li}_x\text{PO}_y\text{F}_z$ formation is effective to make uniform current distribution. The flexibility of the SEI layer formed in the electrolyte containing FEC contributes to the uniform deposition of lithium as already reported.¹⁵

The electrolyte solutions containing, VC or LiBOB form a relatively thick SEI layer having a polycarbonate layer at the top of the SEI layer. The polycarbonate layer probably improves the mechanical properties of the SEI layer, thus the dendritic growth of lithium was also suppressed and initiated the in-plane growth of the lithium metal.

4. Conclusion

In the present paper, we investigated the relationship between the SEI layer and the surface morphology of the electrodeposited lithium. During the initial deposition process of from an additive-free electrolyte solution, the lithium negative electrode maintains a very uniform surface morphology, however once the total deposition amount increases, the lithium electrode starts to form agglomerated particles of the dendritic lithium. The electrolyte additives FEC, VC and LiBOB eliminate the dendritic growth of the lithium during the electrodeposition process, because these additives form stable SEI layer at the surface of the lithium negative electrodes.

In order to understand the role of the additives, XPS and ATR-FTIR analyses were carried out for the lithium negative electrodes immersed in the electrolyte solutions. The additive-free electrolyte solution forms an SEI layer consists of LiOCO_2R and $\text{Li}_x\text{PO}_y\text{F}_z$.

Figure 8. (Color online) The ATR-FTIR spectra for the surface as prepared lithium metal (a), the lithium metal immersed in the additive-free electrolyte solution (b), the electrolyte solution containing FEC (c) and VC (d).

Since the electrolyte containing FEC suppress the decomposition of PF_6^- anion, the FEC containing electrolyte could form a thin and uniform SEI layer resulting in the uniform lithium deposition. We also carried out further analyses of the SEI layer formed by the electrolyte additives VC and LiBOB. Both electrolyte additives form SEI layers, having a polycarbonate layer at the top of the SEI layer. The polycarbonate layer improves the mechanical properties of the SEI layer and initiates in-plane 2D growth of the lithium particles.

Here we conclude that the electrolyte additives are basically effective to eliminate the dendritic growth of the lithium. Two different types of the SEI layers were actually detected, one is thin flexible SEI by FEC and another is thick and rigid SEI formed by VC and LiBOB. Regarding the morphology of the deposited lithium, we think the thin and flexible SEI layer formed in the electrolyte containing FEC is preferable to avoid the dendritic growth of lithium. Further investigations for the electrolyte additives and the interphase are necessary for the development of the practical lithium negative electrodes.

Acknowledgment

This research was supported by Japan Science and Technology Agency PRESTO (ID: 1347486).

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