in situ AFM Observation of Surface Film Formation on Graphite Negative-electrodes of Lithium Ion Batteries

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SEI Formation on HOPG Basal Plane Based on AFM Observation

Initial intercalation of Li$^+$ (initial charge)

- Hill-like structure
- Blister

- Li$^+$ 0.06 nm
- EC molecule
- $\downarrow 0.335$ nm
- ca. 1.0 V (vs. Li/Li$^+$)
- Intercalation of solvated Li$^+$ beneath the surface
- ca. 0.8 V
- Decomposition of solvated Li$^+$ between graphite layers
- Below 0.65 V
- Decomposition of solvents on the surface

Precipitate layer

Charge/discharge characteristics in 1 M LiClO₄ / PC + 3 wt % additives

VC, FEC, ES form stable surface film

Charge/discharge characteristics: VC > FEC ~ ES
Thickness of the precipitate layers formed during 1st cycle / PC + 3 wt % additives

Basal plane PC, LiClO₄ Additives

Thickness of precipitate layer: VC < FEC < ES
**Reduction potential of Additives in PC**

- **Surface film (SEI) formation**
  - 1.35 V: VC 8 nm
- ** Suppress PC co-intercalation**
  - 1.15 V: FEC 20 nm
  - 1.05 V: ES 30 nm
- **PC co-intercalation and exfoliation**
  - 0.90 V

**Potential (V vs. Li⁺/Li)**
Effect of Li Salts on Electrochemical Performances and Surface Films

The larger the discharge capacity is, the smaller the resistance of surface film is.
Electrochemical performances should be related with the composition of surface film.

After 60th cycle

Fig. 3. Specific capacity versus cycle number of Si/C/DC in different single electrolytes.

- The larger the discharge capacity is, the smaller the resistance of surface film is.
- Electrochemical performances should be related with the composition of surface film.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>( R_s ) (( \Omega ))</th>
<th>( R_f ) (( \Omega ))</th>
<th>( R_{ct} ) (( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPF(_6)</td>
<td>7.9</td>
<td>8.4</td>
<td>49.1</td>
</tr>
<tr>
<td>VC-containing LiPF(_6)</td>
<td>6.1</td>
<td>5.5</td>
<td>23.1</td>
</tr>
<tr>
<td>LiClO(_4)</td>
<td>15.1</td>
<td>48.0</td>
<td>52.5</td>
</tr>
<tr>
<td>LiBOB</td>
<td>7.8</td>
<td>85.9</td>
<td>189.1</td>
</tr>
<tr>
<td>LiBF(_4)</td>
<td>16.0</td>
<td>167.6</td>
<td>244.5</td>
</tr>
</tbody>
</table>

Influences of Graphite Planes on Surface Films

Carbonates were contained in surface films formed on the basal plane, while they were not formed on the edge plane.

AFM cell and HOPG

Ar-filled glove box

Probe

RE (Li foil)

CE (Li foil)

WE (HOPG)

Teflon cell

Electrolyte

Graphite (HOPG)

Li+ Solvent

SEI Graphite

Basal plane

Step edge
Contents

1) 1 mol dm$^{-3}$ LiClO$_4$ in EC+DEC without additives
2) 1 mol dm$^{-3}$ LiClO$_4$ in EC+DEC with additives
3) 1 mol dm$^{-3}$ LiClO$_4$ in PC with additives
4) 1 mol dm$^{-3}$ LiPF$_6$ in EC+DEC without additives

Effect of film-forming additives
Effect of solvents
Effect of Li salts

Additives used in this study:
- VC
- VEC
- FEC
AFM Observations of the HOPG Edge plane

LiClO₄ EC+DEC No Add.

Edge plane

Before CV

Fine particles
(Projections, ca. 0.1 µm)

Particle-like precipitates of 0.3-3.0 µm
(Decomposition products of electrolytes)


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Repeated scanning probe to scrape off the surface film in contact-mode AFM

Electrode potential: 3 V

Precipitate layers (ca. 0.3-3 μm)

AFM Probe

Precipitate layers were removed, and projections remained at the surface even after scraping by repeated scans.

HOPG edge plane

Projections small (ca. 0.1 μm)

1st AFM probe scan

5th AFM probe scan

10th AFM probe scan

20th AFM probe scan

LiClO₄ EC+DEC No Add.

No change in further scans

Role of Remaining Surface Layer as SEI

LiClO$_4$ EC+DEC No Add.

AFM image after the 2nd CV

2nd CV
0-3.0 V, 0.5 mV s$^{-1}$

No Change: work as SEI
Re-deposition of precipitate layers
$\rightarrow$ Further decomposition of electrolyte

Surface film was not uniform in-plane.
Effect of the Additives on Surface Film Formation

Reductive decomposition potentials of additives (over ca. 1.1 V) are higher than that of EC (below about 0.8 V).
AFM observations of the HOPG (edge plane)

Direct decomposition products of VC (ca. 0.2-2 μm)

Similar changes in the surface morphology were observed in EC+DEC-based electrolyte containing VEC and FEC, and PC-based electrolyte containing 3 kind of additives.
Scraping-off of Precipitate Layers in EC-based Electrolyte with 2% VC

Electrode potential: 3 V

Decomposition products of VC (ca. 0.2-2 μm)

The fine particles almost disappeared after the 10th scan, while coarse particles larger than ca. 1 μm remained even after the 30th scan.
Scraping the Precipitate Layers in PC-based Electrolyte with 2% VC

Electrode potential: 3 V

A depression formed during AFM observation in potential cycling between 3.0 and 0 V.
(After 12 times scanning for AFM observation)

The number of probe scanning required to remove the precipitate layer formed in PC-based electrolytes was much larger than that needed for EC+DEC-based electrolytes containing additives. More stable or thicker film is formed in PC.
Effect of VC Addition on Effective Surface Film Formation

Few precipitate layers were deposited at the 2nd CV.
Remaining surface layer protected electrolyte decomposition in the 2nd CV.
(Let’s see that the thickness was unchanged after the 2nd CV.)
Comparison of Thickness of the Precipitate Layers

<table>
<thead>
<tr>
<th></th>
<th>1 mol dm⁻³ LiClO₄</th>
<th>No additive</th>
<th>VC</th>
<th>VEC</th>
<th>FEC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>EC+DEC without additive</td>
<td>1st cycle</td>
<td>56 ± 8 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd cycle</td>
<td>66 ± 3 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC+DEC with additives</td>
<td>1st cycle</td>
<td>18 ± 1 nm</td>
<td>19 ± 2 nm</td>
<td>26 ± 1 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd cycle</td>
<td>21 ± 4 nm</td>
<td>19 ± 2 nm</td>
<td>29 ± 3 nm</td>
<td></td>
</tr>
<tr>
<td>PC with additives</td>
<td>1st cycle</td>
<td>11 ± 1 nm</td>
<td>12 ± 0 nm</td>
<td>17 ± 3 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd cycle</td>
<td>13 ± 3 nm</td>
<td>11 ± 1 nm</td>
<td>16 ± 3 nm</td>
<td></td>
</tr>
</tbody>
</table>

Repeated AFM scanning (times) needed to remove the precipitate layers

- The number of AFM scanning required to remove the surface films increased with decrease in the thickness of them.

- Film-forming additives can form a thin, dense, and solid surface film in PC-based electrolyte solutions, compared to EC+DEC-based electrolytes.

*Basal plane: 47 ± 4 nm (1st cyc.) → 77 ± 5 nm (2nd cyc.,+30 nm)
Short Summary (LiClO₄, Edge Plane)

1. Surface film formed in EC-based electrolyte without additives was not uniform in-plane; functional distribution existed.
2. The additives (VC, VEC, and FEC) to EC-based systems lead to form thinner and uniform surface film.
3. The additives to PC-based systems form thin, dense, and solid films.
Contents

1) 1 mol dm$^{-3}$ LiClO$_4$ in EC+DEC without additives
2) 1 mol dm$^{-3}$ LiClO$_4$ in EC+DEC with additives
3) 1 mol dm$^{-3}$ LiClO$_4$ in PC with additives
4) 1 mol dm$^{-3}$ LiPF$_6$ in EC+DEC without additives

Effect of film-forming additives
Effect of solvents
Effect of Li salts

Additives used in this study:
- VC
- VEC
- FEC

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Influences of Li Salts on Surface Crystallinity

To elucidate the degradation mechanism of graphite in LiPF$_6$-based electrolytes.

- AFM: changes in the surface morphology
- XPS and FT-IR: composition of surface film
- Raman: surface crystallinity / structural degradation

Basal plane

Surface destruction is remarkable

D band (1330 cm$^{-1}$)  G band (1580 cm$^{-1}$)  D' band (1620 cm$^{-1}$)

Intensity (arb. unit)
AFM Observations of the HOPG basal plane at 3 V

No morphological change was observed even after 12 hours, which indicate that the HOPG basal plane was quite inert and neither deposition nor intercalation took place at 3 V.
AFM Observations during the First Cathodic Scan

Basal plane

- Pits are formed (1.75 V)
  - Size: 124 nm in diameter
  - Depth: 2.2 nm (7 graphite layers)

- Particle Formation (<1.5 V)
  (smaller than 200 nm)

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AFM Observations during the First Cathodic Scan (Basal plane)

Some deposits are newly formed.

Deposits adhered strongly and were not scraped off by prove.
AFM Observations during Potential Step

Potential stepping (step by step)
OCV (1 h) → 2.0 V (5 h) → 1.75 V (5 h) → 1.5 V (13 h) → 1.25 V (5 h) → 1.0 V (5 h)

Basal plane

LiPF₆
EC+DEC
No Add.
Composition of Fine Particles (XPS)

- LiPF$_6$
- No Add.

Main Components
- LiF
- Phosphate
- \( (LiPO_3, Li_4P_2O_7, P_2O_5, (LiF)_x(LiPO_3)_{1-x} \)

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XPS and FT-IR results revealed that surface film formed in LiPF$_6$-based electrolyte are consisted of LiF and phosphate (P$_2$O$_5$, (LiF)$_x$(LiPO$_3$)$_{1-x}$, (F$_2$)$_x$(LiPO$_3$)$_{1-x}$).

Short Summary (LiPF$_6$, Basal Plane)

1. Pits and fine particles were formed at 1.75 and 1.5 V, respectively.

2. Destruction of graphite layer was occurred below about 1.1 V.

3. Main composition of the fine particles formed at around 1.5 V was LiF and phosphate (PO$_n$, (LiF)$_x$(LiPO$_3$)$_{1-x}$, (F$_2$)$_x$(LiPO$_3$)$_{1-x}$).

\[ \downarrow 0.335 \text{ nm} \rightarrow \text{Formation and growth of fine particle} \rightarrow \text{Destruction of graphite layer} \]

\[ \text{ca. 1.75 V (vs. Li/Li$^+$)} \rightarrow \text{ca. 1.5 V} \rightarrow \text{Below 1.1 V} \]
Summary

1. VC and VEC form surface films more effectively than FEC.

2. Thin, dense, and solid surface film is formed in the electrolyte in the order of PC-based electrolyte with additives > EC+DEC-based electrolyte with additives > EC+DEC-based electrolyte without additives.

3. Changes in the surface morphology of the HOPG basal plane in LiPF$_6$-based electrolyte occurred at higher potential region, which the intercalation/de-intercalation of lithium ion did not take place.
   1.75 V : Pit formation
   1.5 V  : Fine particle formation
   1.1 V  : Destruction of graphite layers
Acknowledgement

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Thank you for your attention