The Carbon-Electrolyte Interface at High Cathodic Voltages

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Outline

• Introduction
• Carbon materials, properties
• Results
  – Electrochemical characterization (galvanostatic cycling, cyclic voltammetry)
  – In-situ XRD
• Potential route for mitigation of structural damage
• Summary
Carbon conductive additives in Li-ion batteries

Positive electrode: \( \text{LiMO}_2 \rightleftharpoons \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \)

Negative electrode: \( \text{C}_6 + x\text{Li}^+ + xe^- \rightleftharpoons \text{Li}_x\text{C}_6 \)

Total cell reaction: \( \text{LiMO}_2 + \text{C}_6 \rightleftharpoons \text{Li}_{1-x}\text{MO}_2 + \text{Li}_x\text{C}_6 \)
Anion intercalation

salts: LiPF$_6$, LiBF$_4$, LiF…

Li-ion hybrid capacitor

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At high voltages: Electrolyte oxidation and anion intercalation

- Loss of conductive network, loss of contact to active material
- Structural/mechanical stability, loss of adherence to current collector
At high voltages

- Exfoliation due to co-intercalation or mechanical stress of decomposition products\(^5\)
- Exfoliation depends on crystallinity of carbon\(^6,7\)


- Preferential oxidation of EC\(^1,2\)
- No film, but decomposition products integrated in surface region\(^3\)


- Oxygen surface groups\(^4\)

Materials

KS6 graphite powder
Particle size ~ 3 μm, IMERYS

AO-2, multilayer graphene (graphitic) Graphenesupermarket
Particle size 0.15-3 μm

Super P Li, carbon black
Particle size ~ 40-60 nm IMERYS

Gold coated cast of Super P Li
## Material properties

<table>
<thead>
<tr>
<th></th>
<th>KS6 graphite</th>
<th>AO-2 ‘graphitic’</th>
<th>Super P Li (carbon black)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle size</strong>¹</td>
<td>3 µm (d50)</td>
<td>0.15-3 µm</td>
<td>40-60 nm</td>
</tr>
<tr>
<td><strong>Surface area (N₂ ads) [m²/g]</strong></td>
<td>22.4</td>
<td><strong>57.8</strong></td>
<td><strong>64.9</strong></td>
</tr>
<tr>
<td><strong>d002 [Å]</strong></td>
<td>3.357</td>
<td>3.357</td>
<td>3.532</td>
</tr>
<tr>
<td><strong>Lc [Å]</strong></td>
<td>649</td>
<td>539</td>
<td>30</td>
</tr>
</tbody>
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¹From suppliers
Galvanostatic cycling

1 M LiPF6 3:7 EC:DMC

KS6 graphite

SuperP Li

AO-2

High 1st cycle ICL for all materials
- Correlates to surface area of edge planes

Cycling program 3.0 – 5.0 V vs. Li+/Li
Voltage profile during galvanostatic cycling

KS6 graphite

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**In-situ XRD, KS6 (graphite)**

Staged intercalation, stage index between 3 and 4

2x10mA/g
2x20 mA/g

9.6 % increase in d002
In-situ XRD, AO-2

2x10mA/g
2x20 mA/g

8.4 % increase in d002
XRD patterns at 5V vs cycle

KS6

AO-2
Cyclic voltammetry, cut-off voltage = 4.7 V
0.1 mV/s

KS6

AO-2

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Cyclic voltammetry, cut-off voltage = 5 V

KS6

AO-2
Cyclic voltammetry, Super P Li, cut-off voltage = 5.5 V
Addition of anion receptor, Tris (hexafluoroisopropyle) borate THFIPB (AR)

- Borate with fluorinated functional groups
- Reduced ion-pairing in electrolyte
- Improved SEI stability of graphite anode demonstrated

\[ \text{PF}_6^- + \text{THFIPB} \rightarrow \text{THFIPB} - \text{F}^- + \text{PF}_5 \]

Increased release of PF$_5$ and PF$_3$O observed$^1$

$^1$OEMS performed at PSI
Experiments performed at PSI.
CV, KS6

CV, AO-2

wo AR (0.025 M)

with AR (0.025 M)
Cyclic voltammogram, cathodic, SLP30 graphite

AR25 = 0.025 M AR
AR75 = 0.075 M AR
Effect of AR on graphite anode

200 cycles at 1 C, total charge (above), galvanostatic charge (below)
SUMMARY

• Anion intercalation occurs from around 4.6 V for graphitic materials

• Irreversible capacity loss correlates with edge plane surface area

• Growth of film from electrolyte decomposition products prevents anion intercalation

• Structural damage caused by anion intercalation is observed for graphitic materials (by in-situ XRD)

• Structural damage occurs during first cycle

• Chemical surface film formation, for example by addition of an anion receptor, possibly involving oxygen surface groups, may prevent structural damage.
Thank you for your attention!!

NTNU and PSI are acknowledged for the support
SFG44 in 1.2M $\text{LiPF}_6$-PC:DMC

**wo AR (0.025 M)**

**with AR (0.025 M)**
Cyclic voltammetry, KS6 and AO-2

Reduction of current upon multiple cycles

Shift in cathodic peak (de-intercalation peak) after cycling
1st charge/discharge

Graphene AO-2

KS6
- initial: 3.358
- 1st charge: 3.679
- 1st discharge: 3.365

Graphene AO-2
- initial: 3.357
- 1st charge: 3.639
- 1st discharge: 3.358
Galvanostatic cycling, AO-2 (multilayer graphene)
Carbon conductive additives

Cyclic voltammetry, 1M LiPF6 3:7 EMC:DMC
Potential range: 3.0 – 5.5 V vs. Li⁺/Li, 0.1 mVs⁻¹
Comparison KS6 and AO-2

Initial

KS6

Final

AO-2

Increase in d002 from initial to 4th discharge:

<table>
<thead>
<tr>
<th>Material</th>
<th>Increase (%)</th>
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<tbody>
<tr>
<td>KS6</td>
<td>0.20 %</td>
</tr>
<tr>
<td>Graphene AO-2</td>
<td>0.05 %</td>
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