Si Alloy Anode: Sudden Fade Challenge

- Project # ES256
- Electronics Materials Solutions Division
- June 10th, 2015
Capacity Fade Suddenly Accelerates with Si Alloy Anode

- Electrolyte: EC:EMC 3:7 + 10% FEC, 1M LiPF$_6$
- The capacity fade rate suddenly increased after 100 cycles with 15% Si alloy.
- Graphite alone shows no such kind of sudden fade within its typical cycle life.
FEC Plays a Critical Role to Delay the Sudden Fade

Electrolytes

- **A** - FEC:EMC:DMC:PC 3/3/3/1 0.95M LiPF$_6$, 0.05M LiBOB
- **B** - EC:EMC 3:7 + 10% FEC, 1M LiPF$_6$

Very different behavior with electrolyte composition

Conclusion: FEC delays rapid fade.
Large Amount of FEC Causes Serious Gassing

- Si alloy anode/HV LCO
- Storage at 4.35V, 85C and 3 hours
- Electrolyte:
  - Blue: 1M LiPF6 in EC/EMC (3:7) – Control
  - Red: Control+10% FEC

![Graph showing gas volume on storage (4.35V, 85C, 3 hours)]
Storage Gassing with FEC Continues After 3 Hours

• Si alloy anode/HV LCO

• Storage at 4.35V, 85C for 3 and 7 hours

• Electrolyte:
  
  Blue: 1M LiPF6 in EC/EMC (3:7) – Control
  Red: Control+10% FEC

Serious gassing issue makes high content of FEC less practical.
Sudden Fade Mechanism
Si/Electrolyte reaction – Si consumption

- Cross section SEM images of electrodes before cycling
- 3M alloy coating similar to fresh Si coating
- Both Si and 3M alloy particles are clearly observed
- EC:EMC 3:7 + 10% FEC, 1M LiPF$_6$
Si Consumption

After 100 cycles

- Cycled 3M alloy has small SEI
- Cycled Si: there are no more particles! Only reacted material

Major expansion with Si due to SEI growth
Si/Electrolyte Reaction – FEC Consumption

18650 cells

Electrolyte: FEC/EMC/DMC/PC
3/3/3/1 0.95M LiPF$_6$, 0.05M LiBOB

Cathode: HV LCO

Anode: 56 CV8/34 Graphite/10 LiPAA

Electrolyte extraction method

Jelly roll put in 10 mL CH$_2$Cl$_2$
Shaken for 10 min

Filtration

Aqueous phase with ionic species

Few drops of filtrate in 10 mL CH$_2$Cl$_2$ + 0.5 mL H$_2$O
Shaken for 5 min

After 200 cycles
Si/Electrolyte Reaction – FEC Consumption

• Significant FEC assumption

• Assuming DMC and EMC consumption negligible, ~ 60% of the initial FEC has been consumed.

• About 10% of the initial PC have been consumed.

• Two unknown peaks seem to indicate trace amount of Si containing compounds

### GC/MS Results

<table>
<thead>
<tr>
<th>Cell</th>
<th>% DMC</th>
<th>% EMC</th>
<th>% FEC</th>
<th>% PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>7866 (uncycled)</td>
<td>27.8 ± .3</td>
<td>28.0 ± .2</td>
<td>33.0 ± .4</td>
<td>11.1 ± .1</td>
</tr>
<tr>
<td>7867 (cycled)</td>
<td>37 ± 1</td>
<td>38.8 ± .2</td>
<td>11.4 ± .4</td>
<td>12.2 ± .5</td>
</tr>
</tbody>
</table>

Concentrations shown as percent of DMC+EMC+FEC+PC
Sudden Fade is Correlated With Rapid Swelling of Pouch Cells

- Pouch cells assembled by Li Fun (Hunan, China) with 3M CV7 alloy
- Approximately 5% volume expansion before sudden fade occurs
- Massive volume expansion upon sudden fade
Approach to Delay Sudden Fade
Shallow Cycling

Cathode
96% HVLCO; 2% SP; 2% PVDF

Anode
13% CV7; 75% Gr; 2% SP, 10% LiPAA

Electrolyte
5/25/35/35 FEC/EC/EMC/DMC 1M LiPF6

Cycling protocol
- 1 full cycle: 3.0 - 4.35 V, C/4; C/2
- 20 shallow cycles
  - Charge to 4.35V
  - Limited cap discharge (30% or 50% or 70%)
3M Alloy with Improved Microstructure Delays Sudden Fade

18650 Cells

Cathode
96% HVLCO; 2% SP; 2% PVDF

Anode
15% Alloy; 65% Gr; 10% KS6; 10% LiPAA

Electrolyte
30/70 EC/EMC 1M LiPF$_6$ +10% FEC
3M Electrolyte Solvent L-20446 Delays Sudden Fade

1.0M LiPF6 / EC:EMC (3:7 by wt) + 10 wt% FEC (FEC control)
1.0M LiPF6 / EC:EMC:L-20446 (1:1:1 by wt) + 10 wt% FEC
1.0M LiPF6 / EC:EMC:L-19869 (1:1:1 by wt) + 10 wt% FEC
Electrolyte with VC/EA Solvent Delays Sudden Fade

18650 Cells

Cathode
96% NMC442; 2% SP; 2% PVDF

Anode
56% CV4; 34% Gr; 10% LiPAA

Electrolyte
25/75 VC/EA (Ethyl Acetate) 1M LiPF$_6$

No sudden fade after 1000 cycles!
NMC Cathode Delays Sudden Fade Compared to LCO

18650 Cells

Cathode
HVLCO vs. NMC662

Anode
15% CV7; 65% Gr; 10% KS6, 10% LiPAA

Electrolyte
30/70 EC:EMC 1M LiPF$_6$ +10% FEC
Summary

- Repeated volume change with every cycle consumes electrolyte and leads to sudden-fade for all Si-based materials
- 3M Si-alloy has much less reaction with electrolyte
- FEC delays sudden fade, but causes too much gassing at high levels
- Changes to the electrolyte can delay or even eliminate sudden fade
- Choice of cathode can delay sudden fade