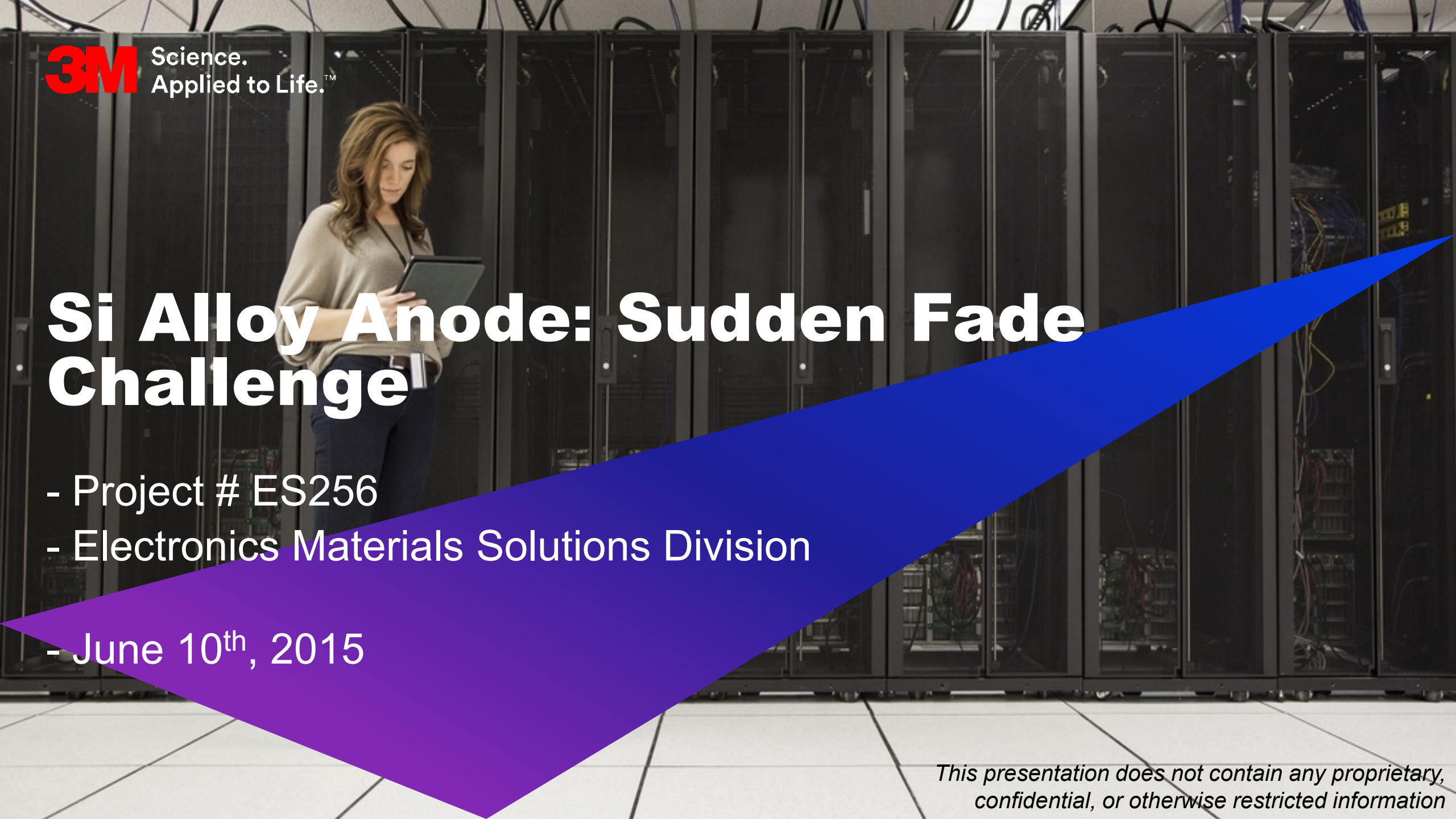

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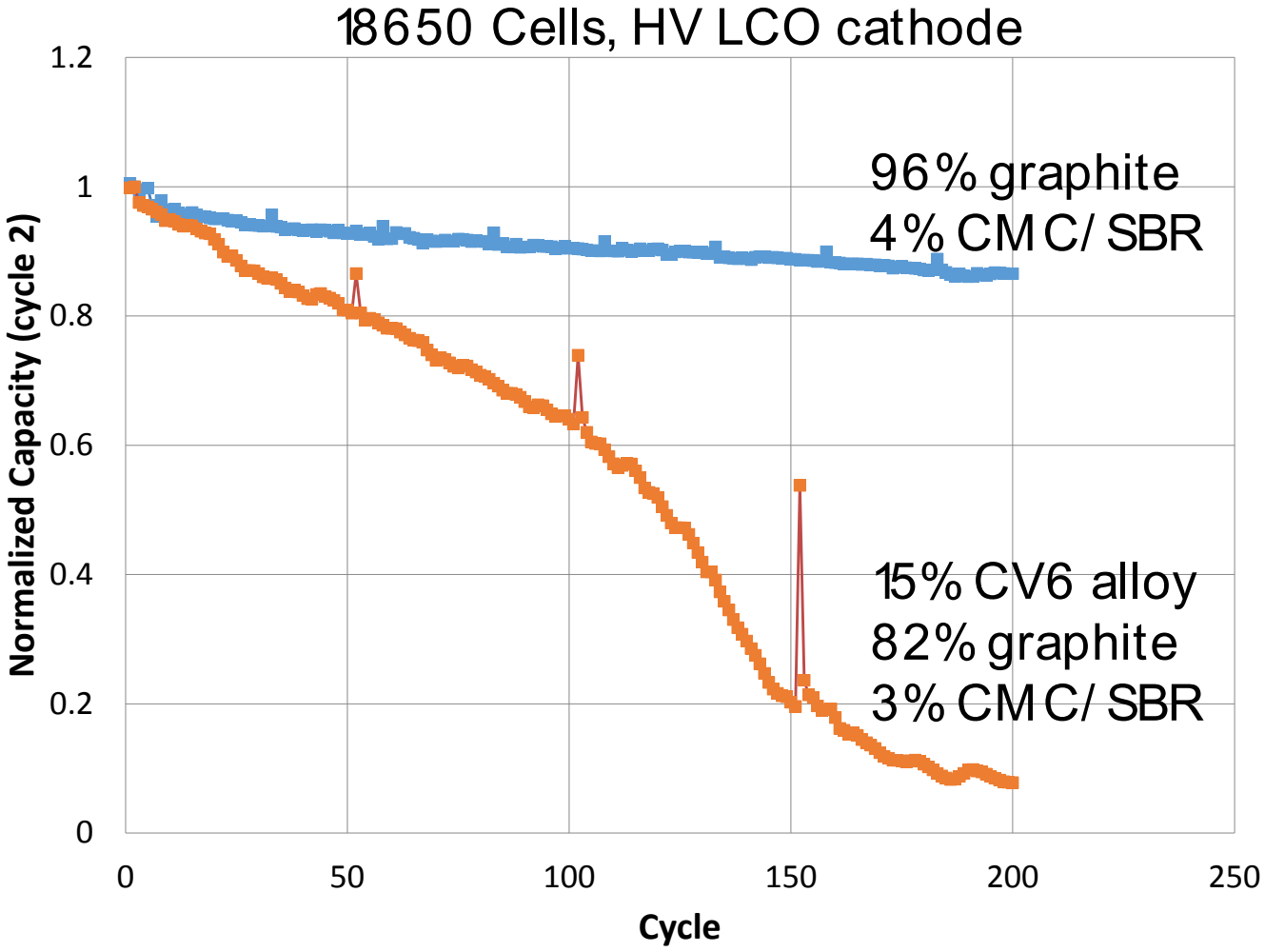
Si Alloy Anode: Sudden Fade Challenge

- 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



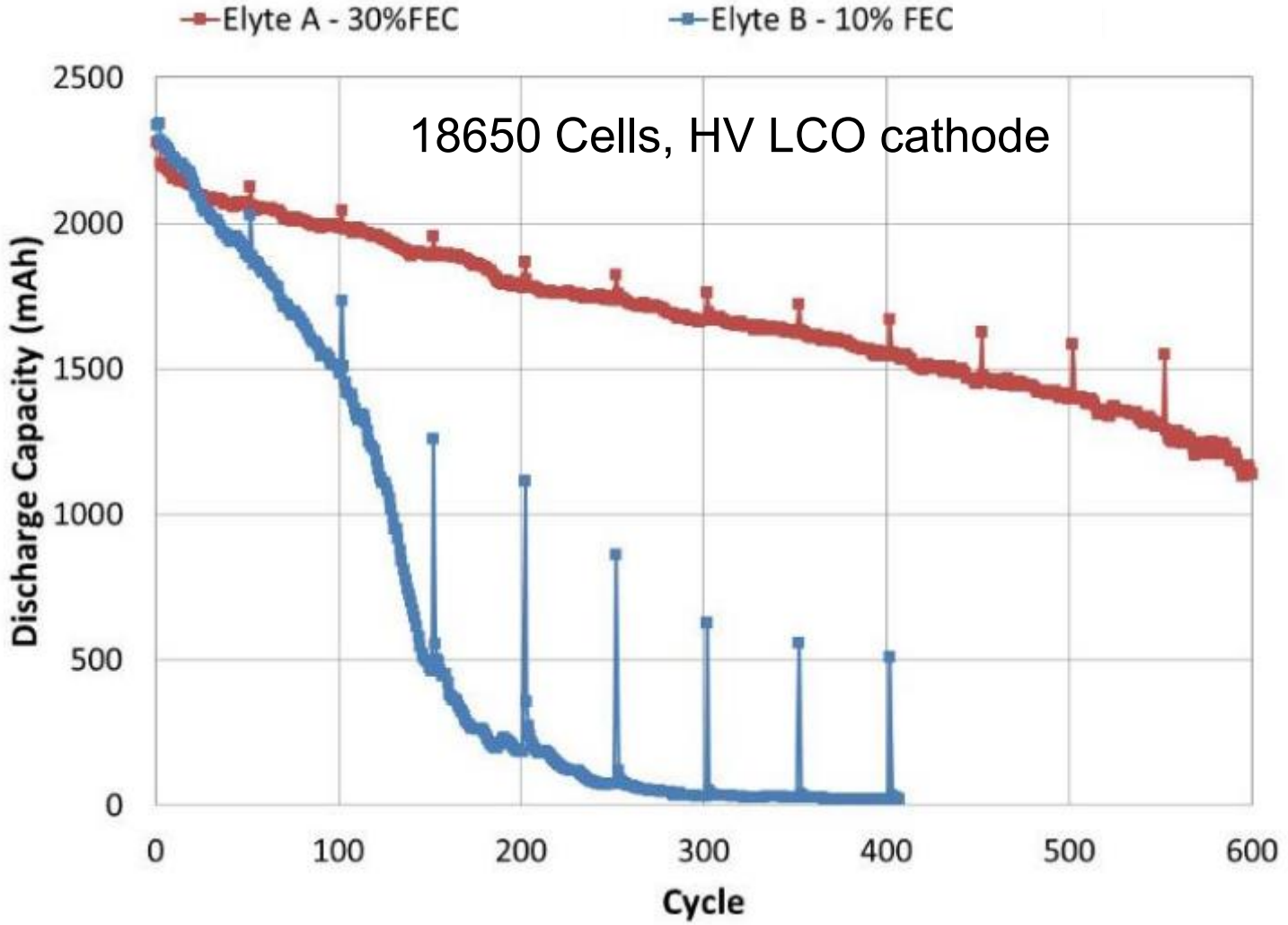
FEC Plays a Critical Role to Delay the Sudden Fade

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

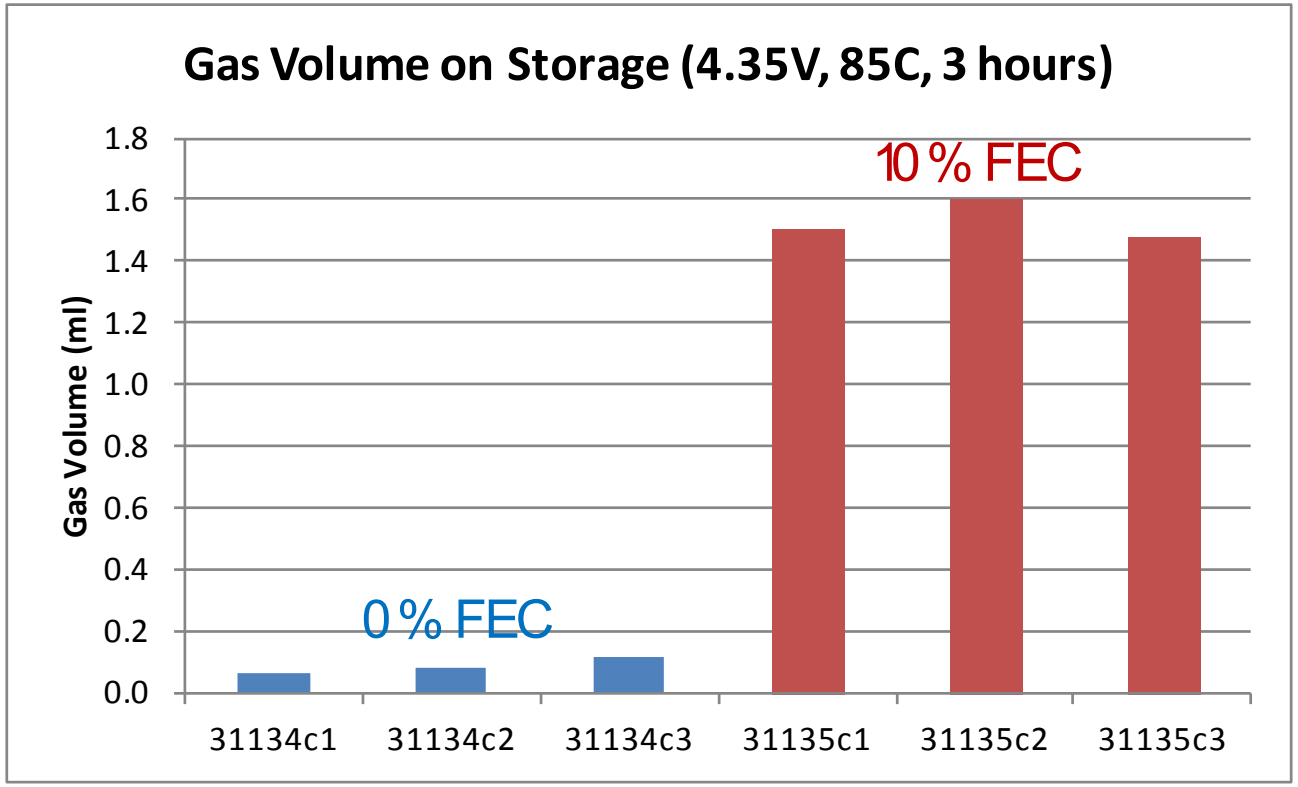
Conclusion: FEC delays rapid fade.



Large Amount of FEC Causes Serious Gassing

- Si alloy anode/HV LCO
- Storage at 4.35V, 85C and 3 hours
- Electrolyte:

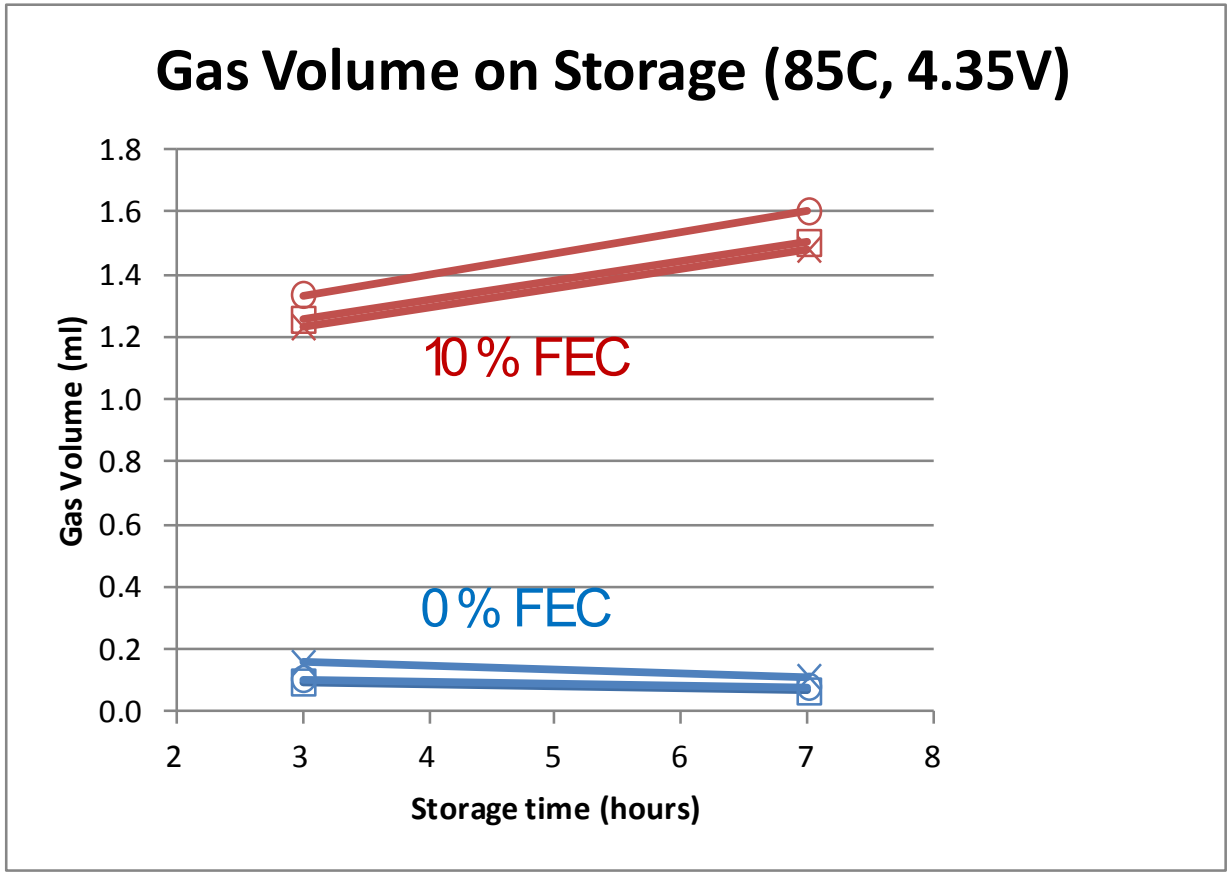
  Blue: 1M LiPF6 in EC/EMC (3:7) – Control
  Red: Control+10% FEC



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

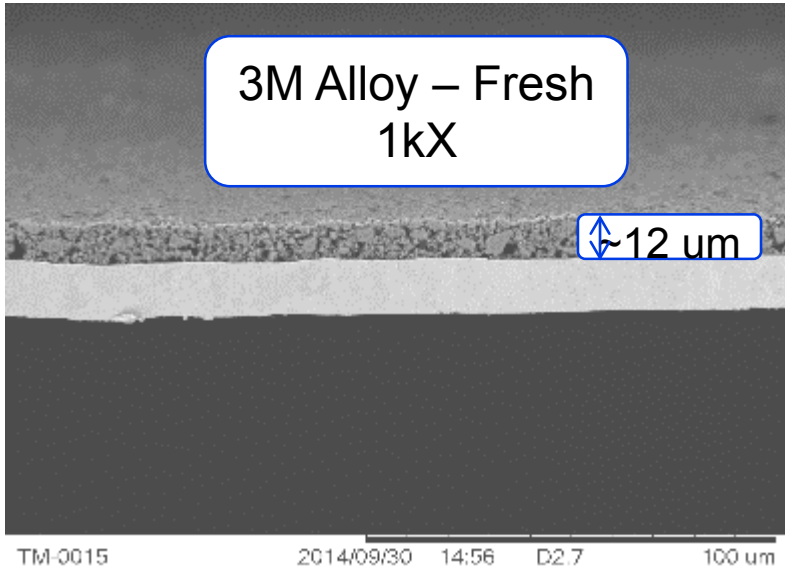


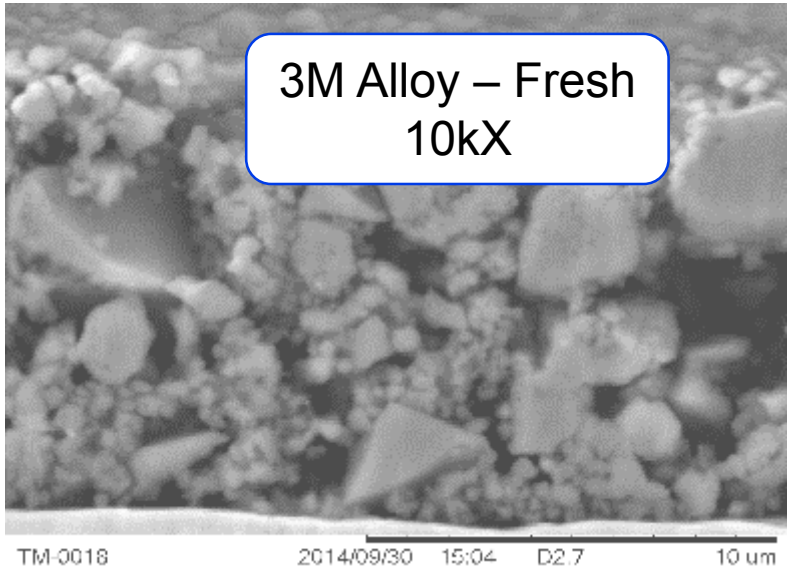
Serious gassing issue makes high content of FEC less practical.

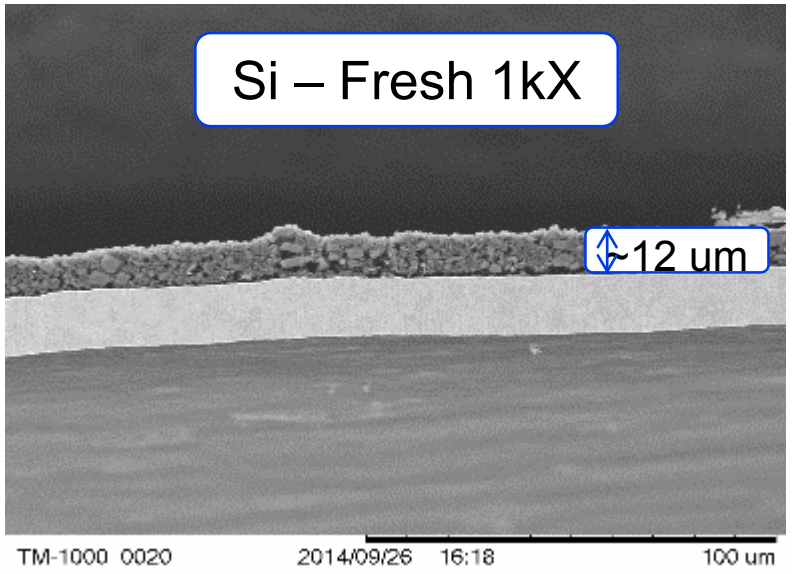
Sudden Fade Mechanism

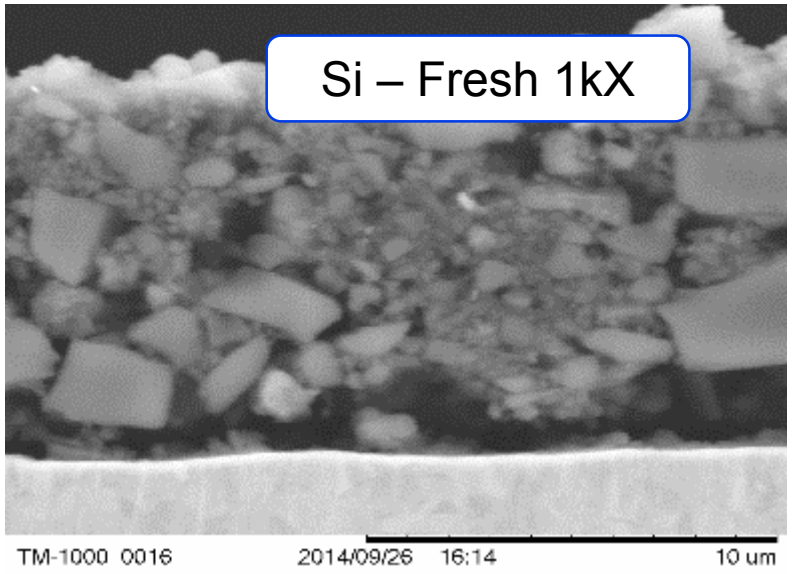
Si/Electrolyte reaction – Si consumption

- 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 $LiPF_6$







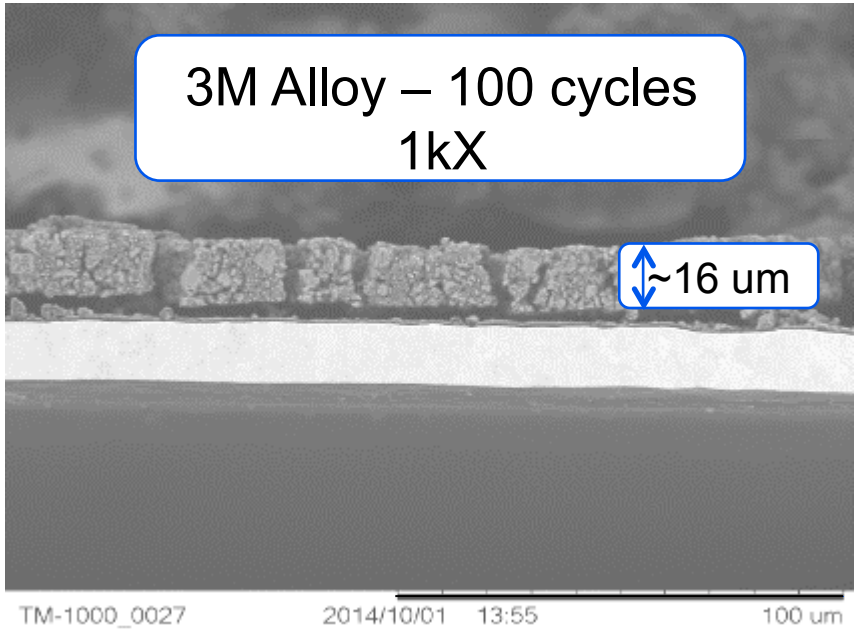


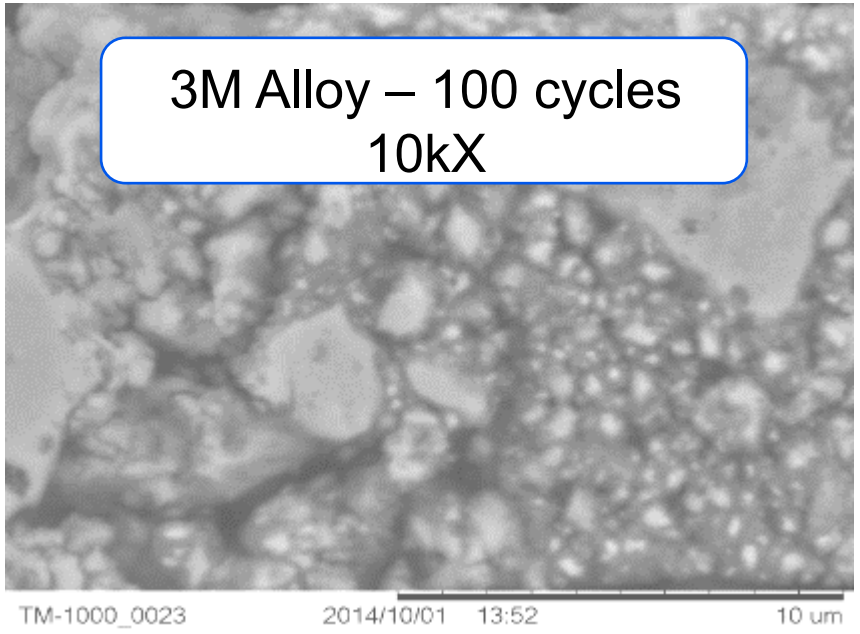
Si Consumption

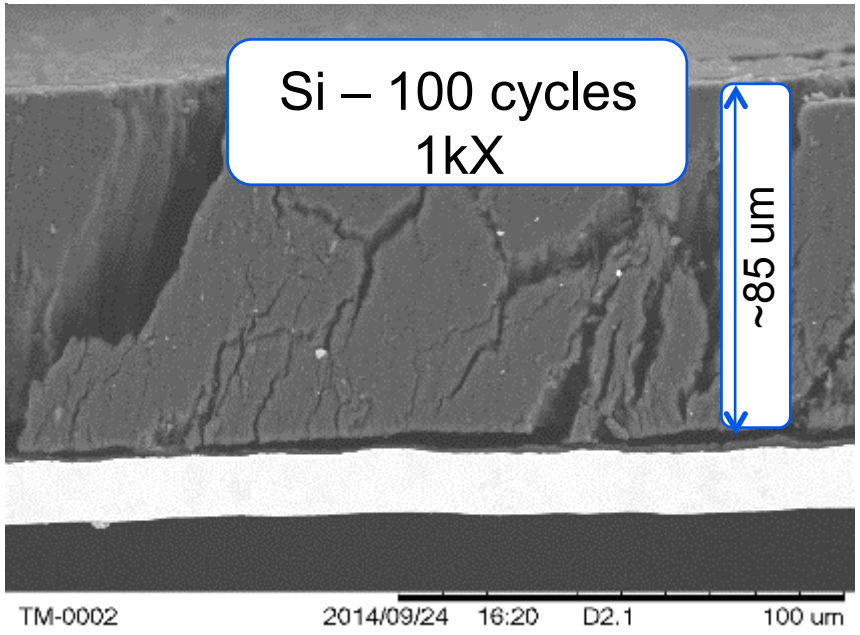
After 100 cycles

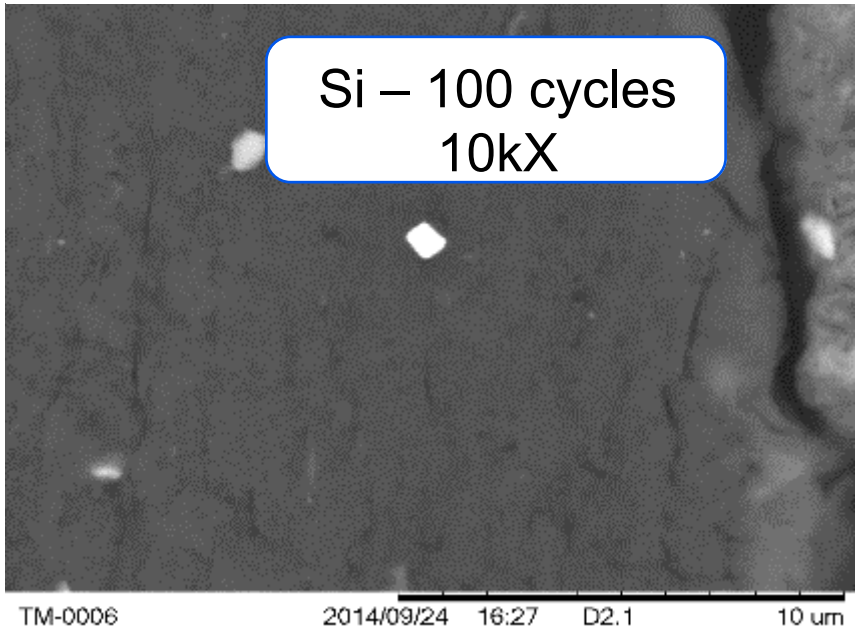
- Cycled 3M alloy has small SEI
- Cycled Si : there are no more particles! Only reacted material

Major expansion with Si due to SEI growth









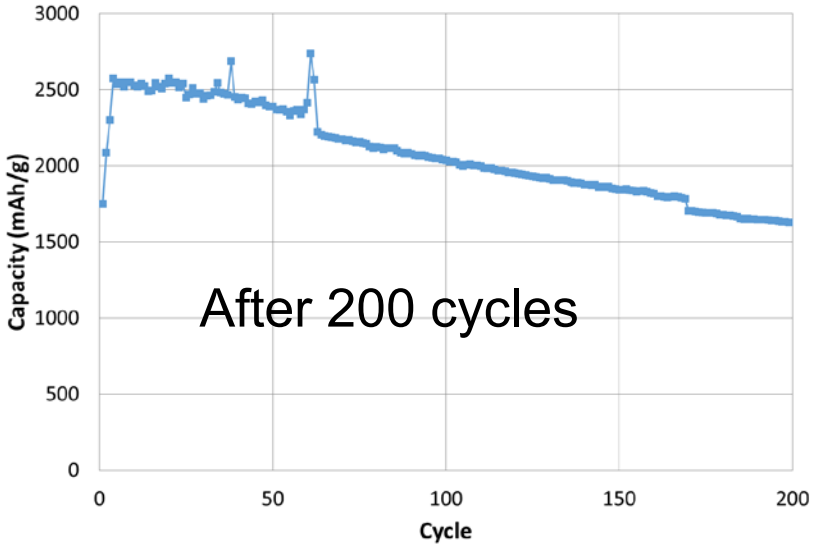
Si/Electrolyte Reaction – FEC Consumption

18650 cells

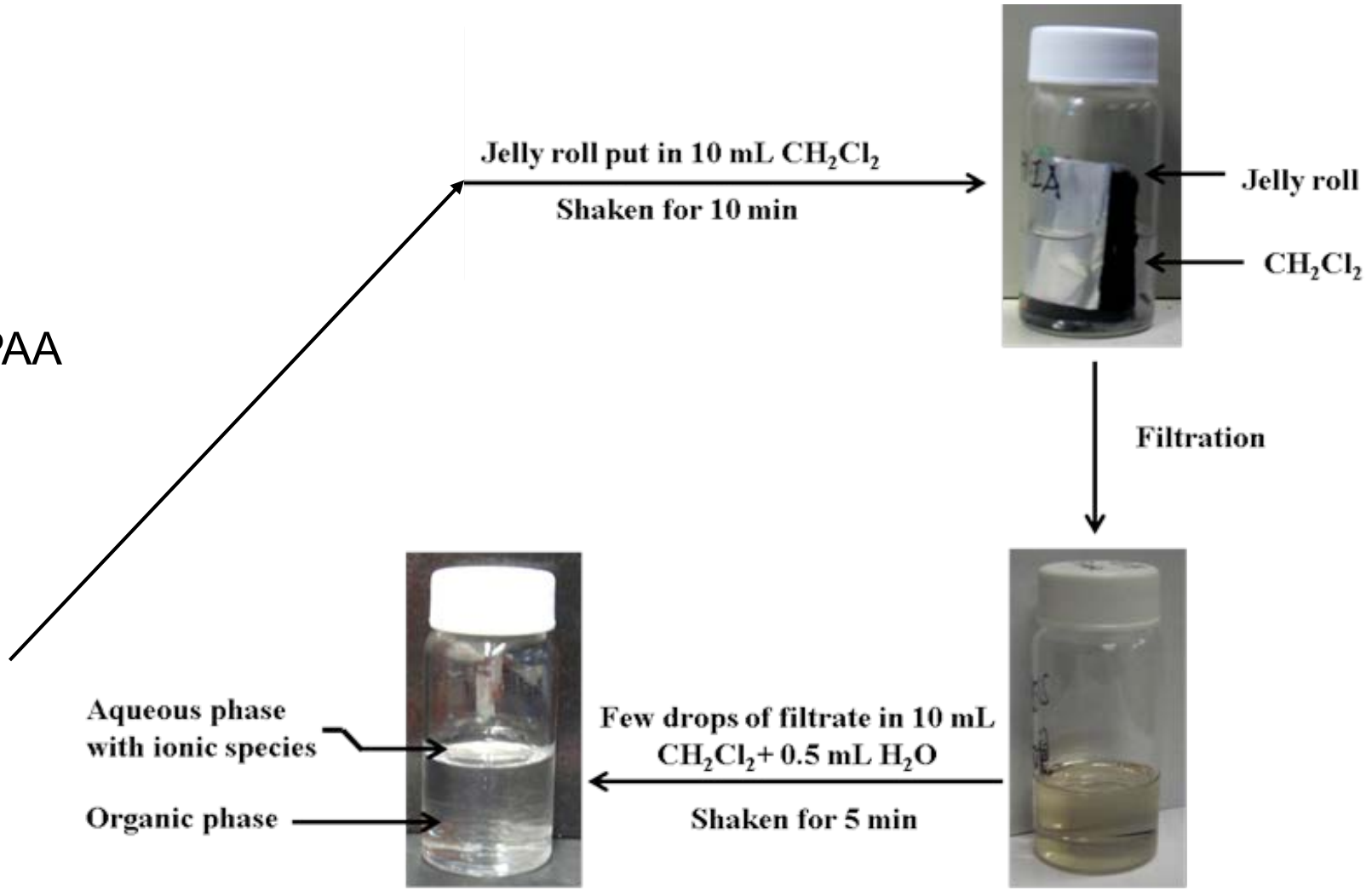
Electrolyte: FEC/EMC/DMC/PC
3/3/3/1 0.95M $LiPF_6$, 0.05M LiBOB

Cathode: HV LCO

Anode: 56 CV8/34 Graphite/10 LiPAA

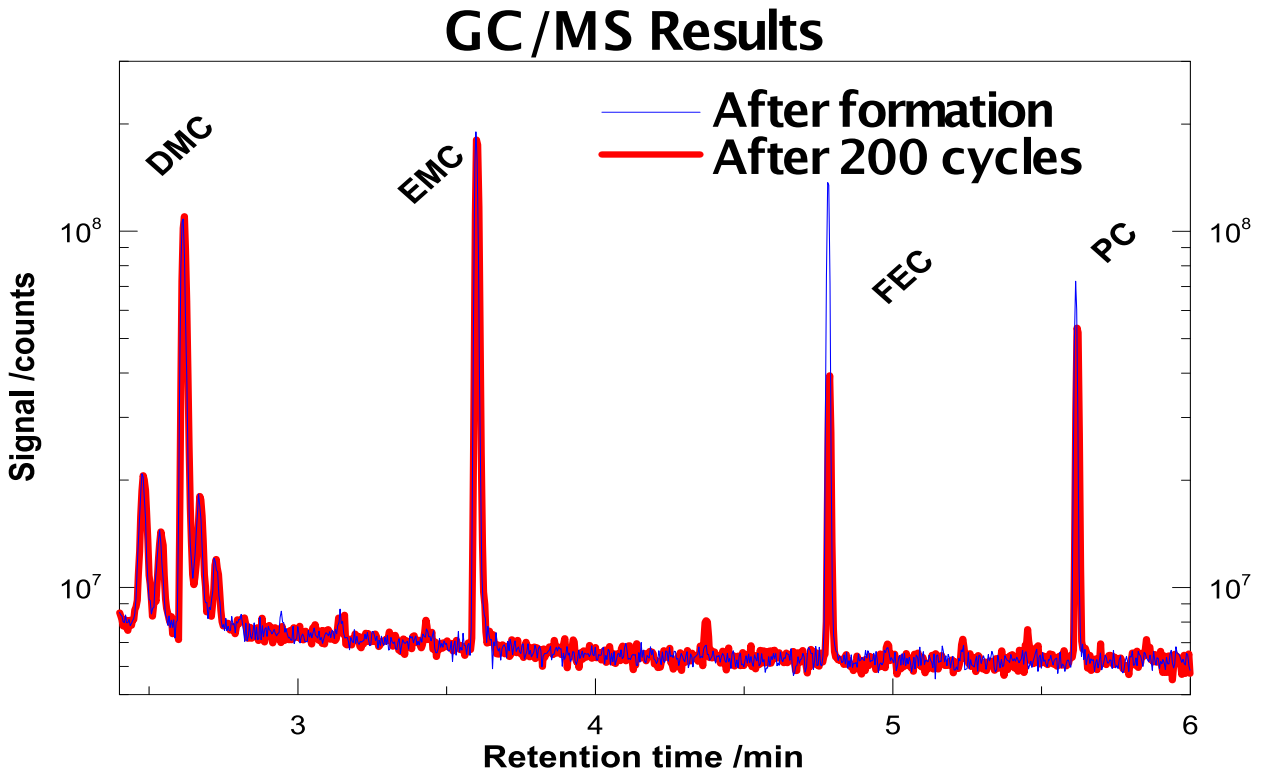


Electrolyte extraction method



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 seems to indicate trace amount of Si containing compounds

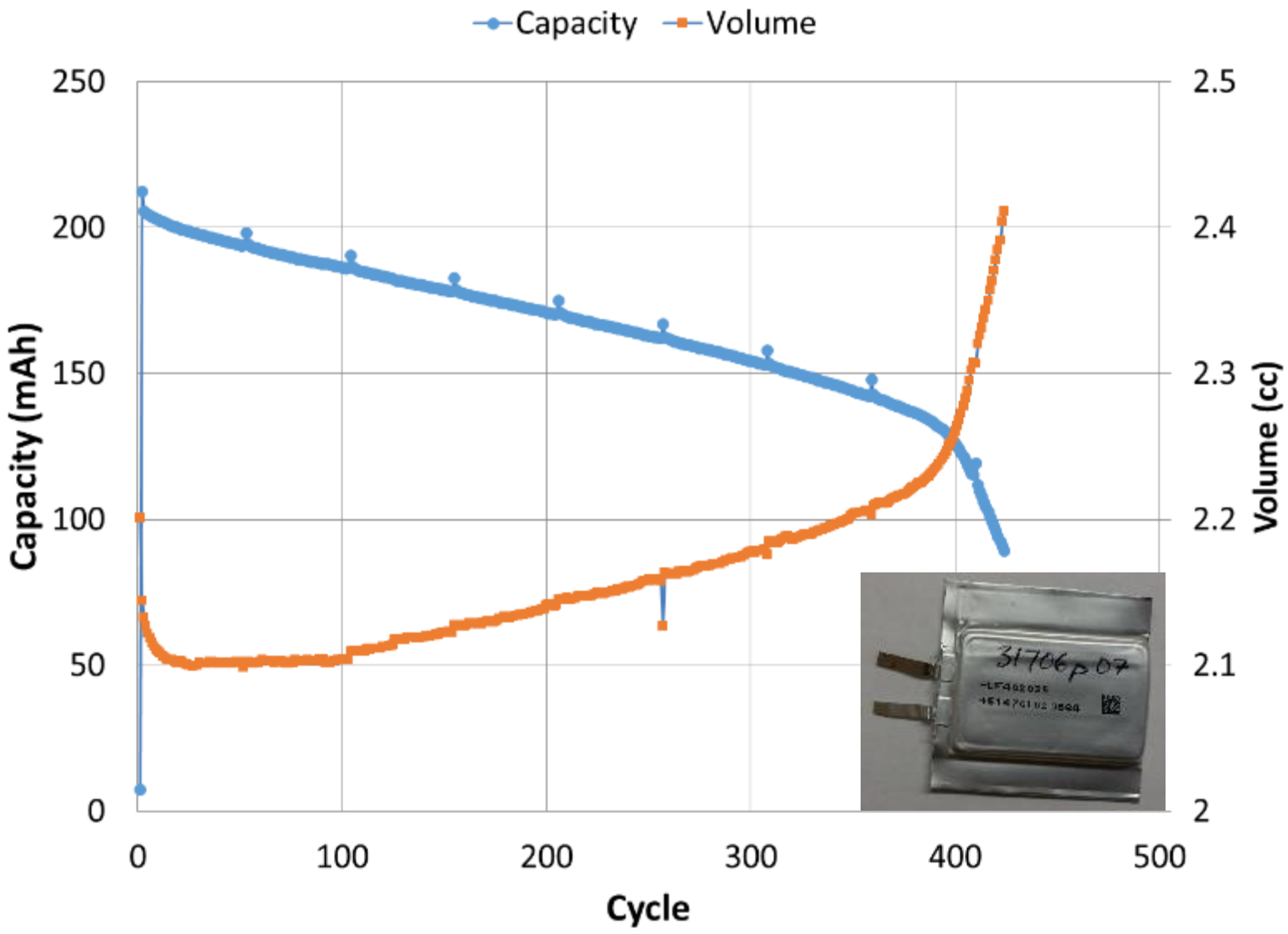


Cell	% DMC	% EMC	% FEC	% PC
7866 (uncycled)	27.8 ± .3	28.0 ± .2	33.0 ± 0.4	11.1 ± 0.1
7867 (cycled)	37 ± 1	38.8 ± 0.2	11.4 ± 0.4	12.2 ± 0.5

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

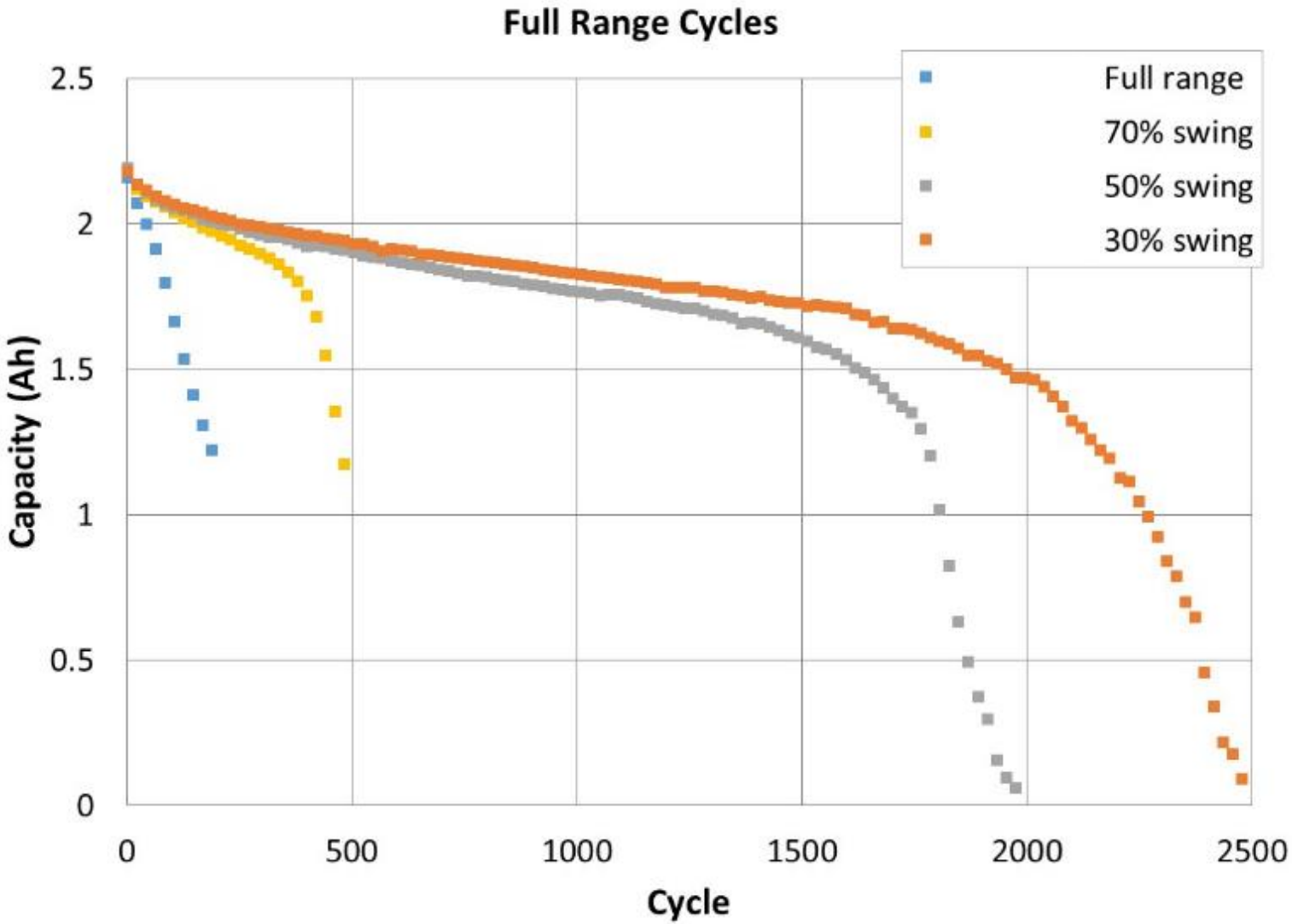
Cathode
96% HVLCO; 2% SP; 2% PVDF

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

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

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%)



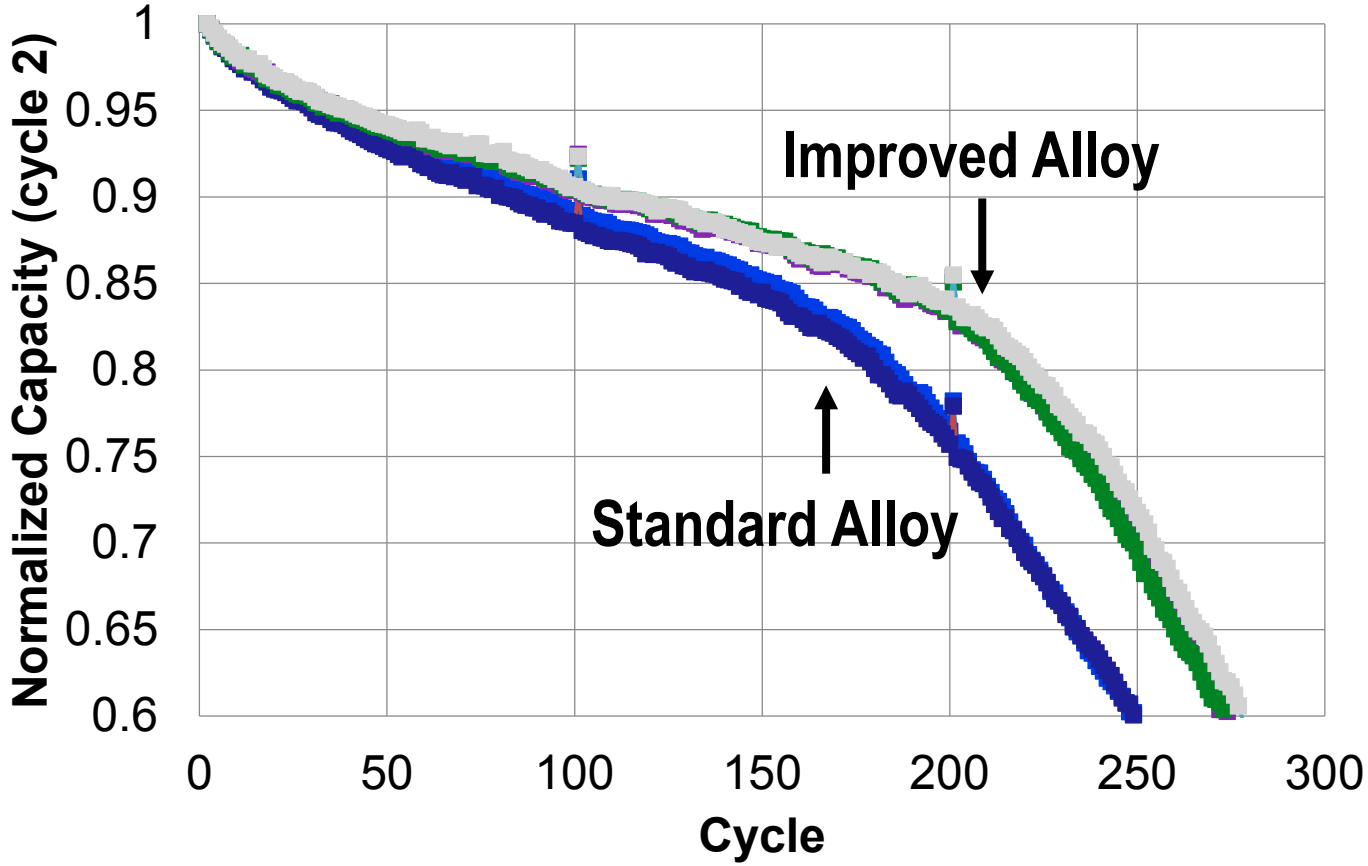
3M Alloy with Improved Microstructure Delays Sudden Fade

18650 Cells

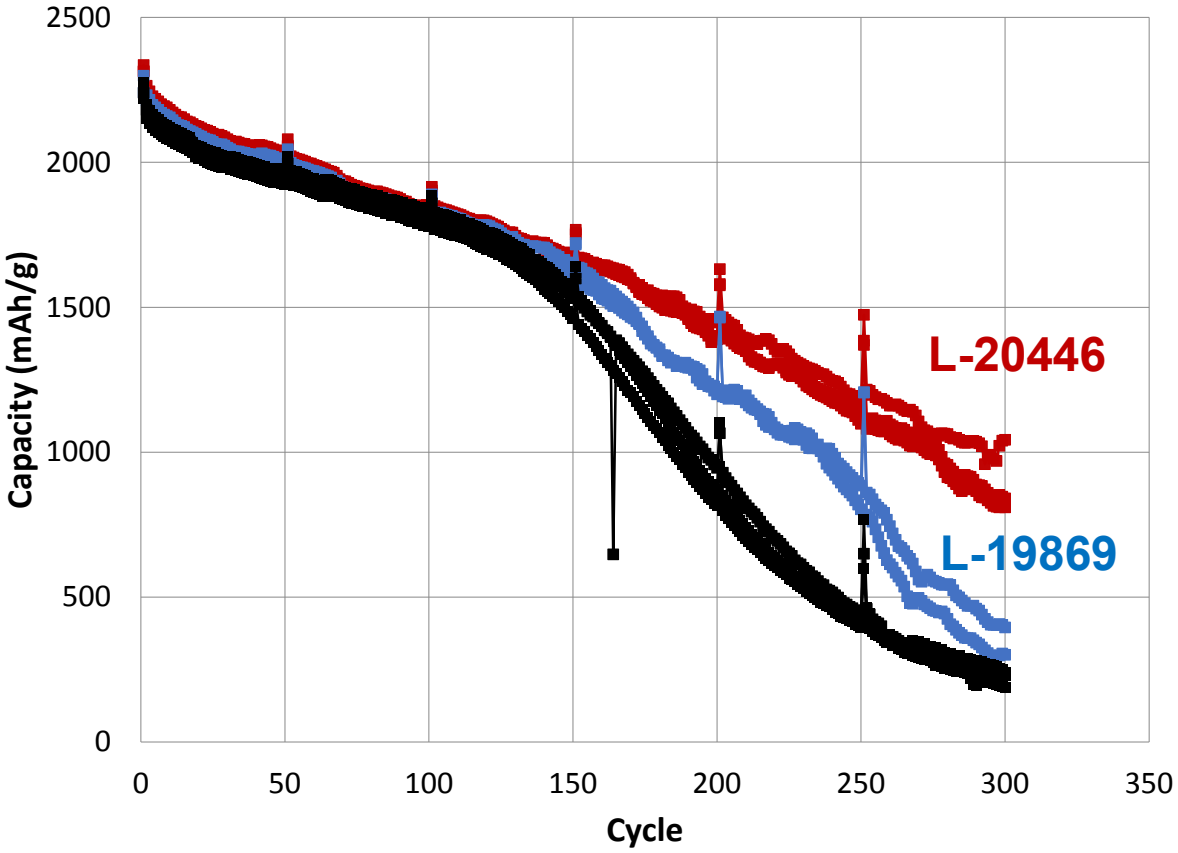
Cathode
96% HVLCO; 2% SP; 2% PVDF

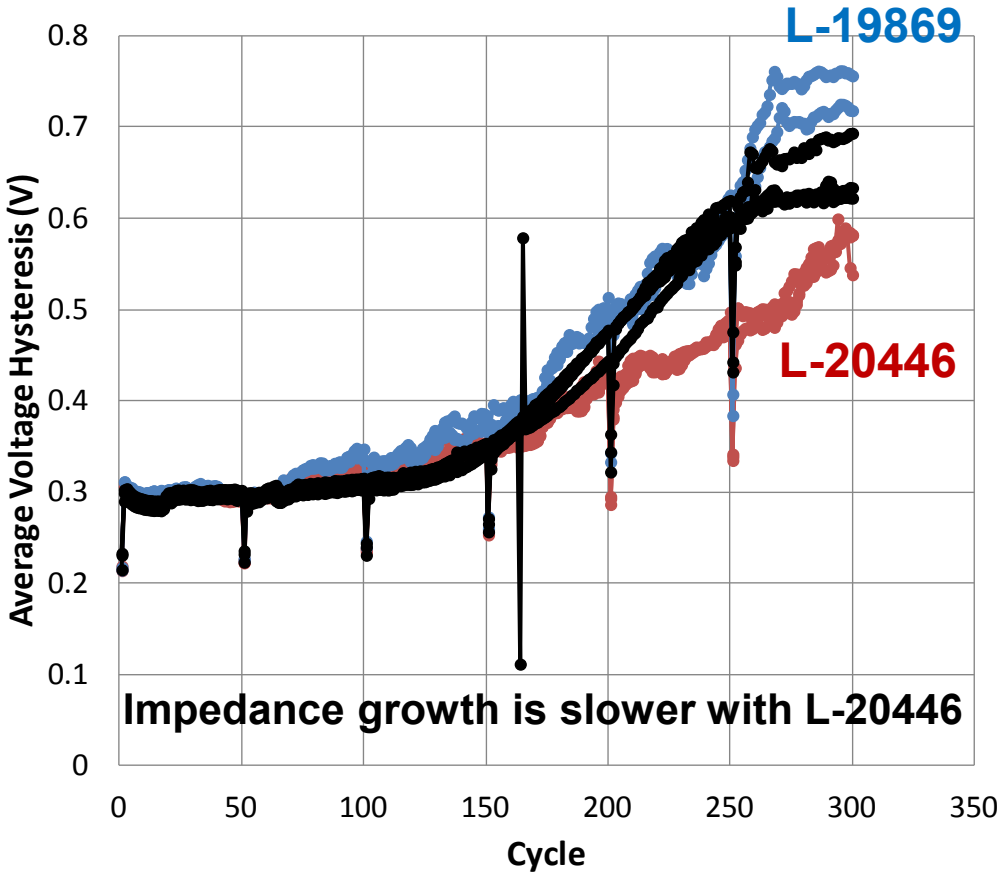
Anode
15% Alloy; 65% Gr; 10% KS6;
10% LiPAA

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

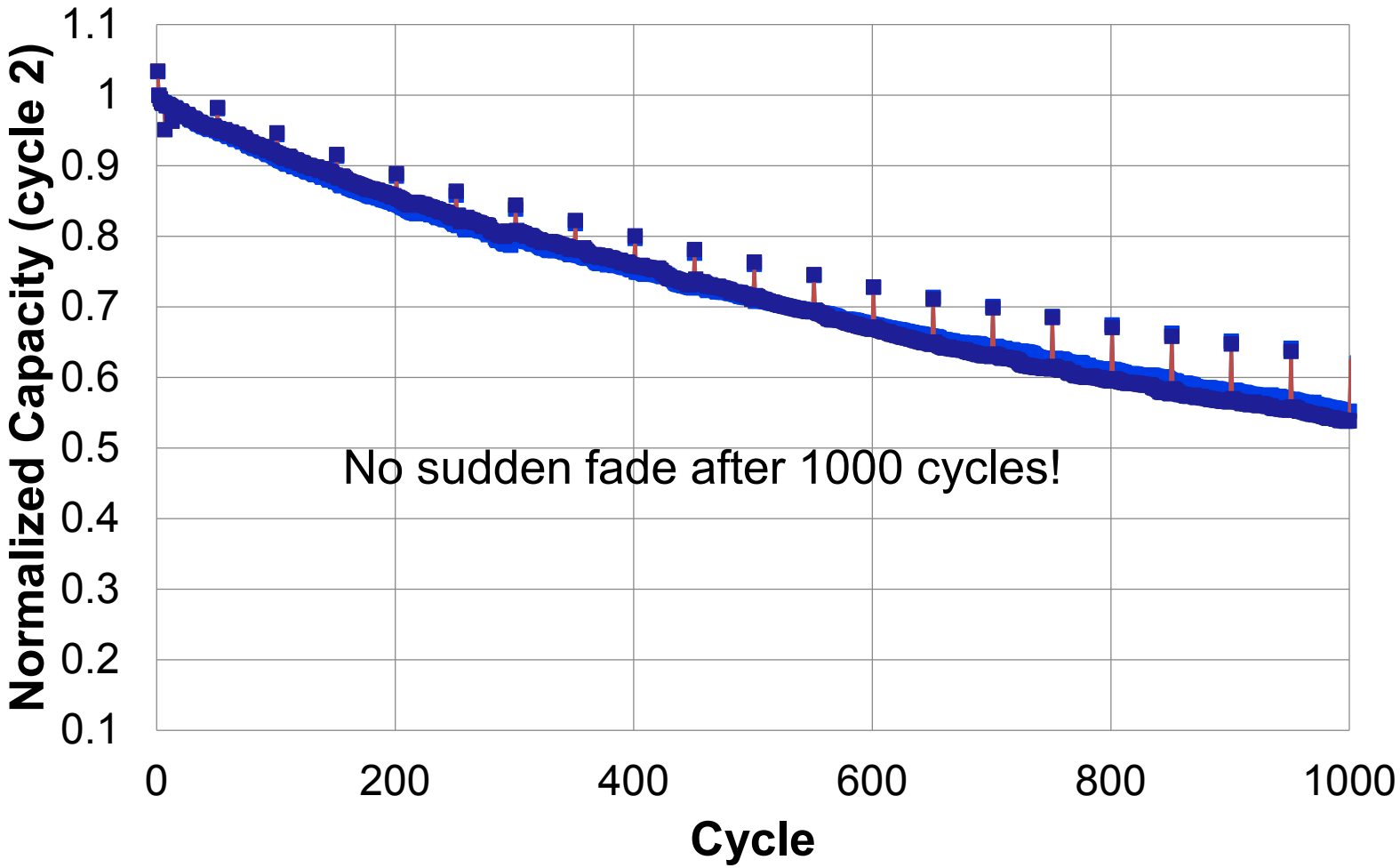
Electrolyte with VC/EA Solvent Delays Sudden Fade

18650 Cells

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

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

Electrolyte
25/75 VC/EA (Ethyl Acetate) 1M $LiPF_6$



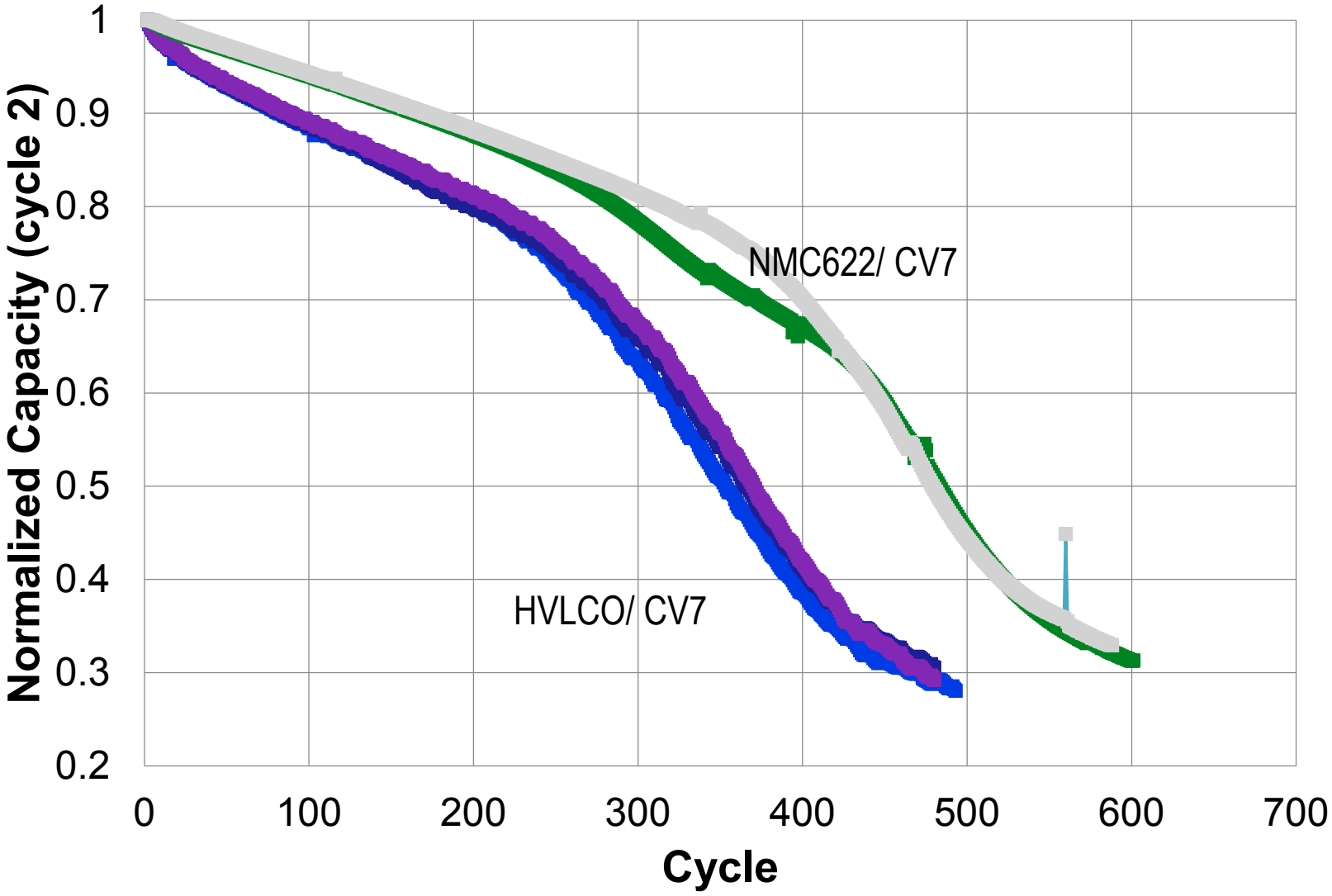
NMC Cathode Delays Sudden Fade Compared to LCO

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