Accelerating Breakthrough Discoveries
www.wildcatdiscovery.com

Wildcat Discovery Technologies

ES219

Novel Non-Carbonate Based Electrolytes for Silicon Anodes

Dee Strand (PI)
Marissa Caldwell, Gang Cheng
Wildcat Discovery Technologies
June 17, 2014

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

Overview

Wildcat Discovery Technologies

Timeline

- Start Date: 10/01/2013
- End Date: 12/31/2015
- Percent Complete: 22%

Barriers

- Performance
  - Energy Density
- Life

Budget

- Total Funding: $1,249,723
  - DOE Share: $999,778
  - Contractor Share: $249,945
- Funding Received:
  - FY2013: $17,483
  - FY2014: $57,027 (1/1 – 3/31)
  - Total: $74,510 (thru 3/31/14)

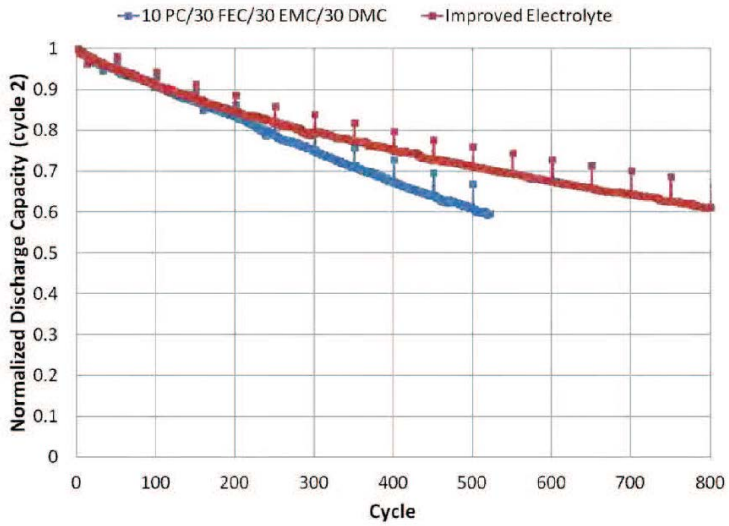
Partners

- Interactions/Collaborations
  - 3M
- Project Lead
  - Wildcat Discovery Technologies

Objectives/Relevance

Development of non-carbonate electrolyte formulations that

- form stable SEIs on 3M silicon alloy anode, enabling coulombic efficiency* > 99.9% and cycle life > 500 cycles (80% capacity) with NMC cathodes;
- have comparable ionic conductivity to carbonate formulations, enabling high power at room temperature and low temperature;
  - > 5 mS/cm ionic conductivity at 25°C;
  - > 1 mS/cm ionic conductivity at -30°C;
- are oxidatively stable to 4.6V, enabling the use of high energy NMC cathodes in the future; and
- do not increase cell costs over today's carbonate formulations.



- Silicon anodes can provide significant improvement in energy density
- Silicon anodes have low coulombic efficiency and short cycle life
- Need for electrolytes that form stable SEI on silicon surface

* Excludes 1st cycle (evaluated at Cycle > 1)

Milestones

Wildcat Discovery Technologies

Date	Milestone	Status
12/13	Assemble materials, establish baseline performance with 3M materials	COMPLETE
3/14	Develop initial additive package using non-SEI forming solvent	COMPLETE
6/14	Screen initial solvents with initial additive package	ON TRACK
9/14	Design/build interim cells for DOE	ON TRACK
12/14	GO/NO GO Performance target: NMC//Si alloy cells with cycle life > 50 cycles to 70% capacity with no EC in electrolyte formulation	ON TRACK
3/15	Identification of non-carbonate solvent lead candidates	
6/15	Formulation optimization design & execution	
9/15	Finalize non-carbonate formulations for 18650 final cells	
12/15	Assemble/test final DOE cells	

Approach/Strategy

- Stage 1
  - Develop additive package to form stable SEIs on silicon anode
  - Use PC based electrolyte which does not form SEI on its own (such as EC)
  - Initial target > 50 cycles to 70% capacity with no EC in formulation
  - Further improvements done in conjunction with solvent optimization
- Stage 2
  - Identification of non-carbonate solvents that are stable on additive-based SEI
  - Solvents also need to
    - Enable conductivity targets
    - Match current electrolyte solvents in terms of thermal stability/safety
- Stage 3
  - Formulation optimization
  - Selection of additives to ensure high voltage stability target
  - Further SEI improvements for high temperature stability
  - Cost analysis

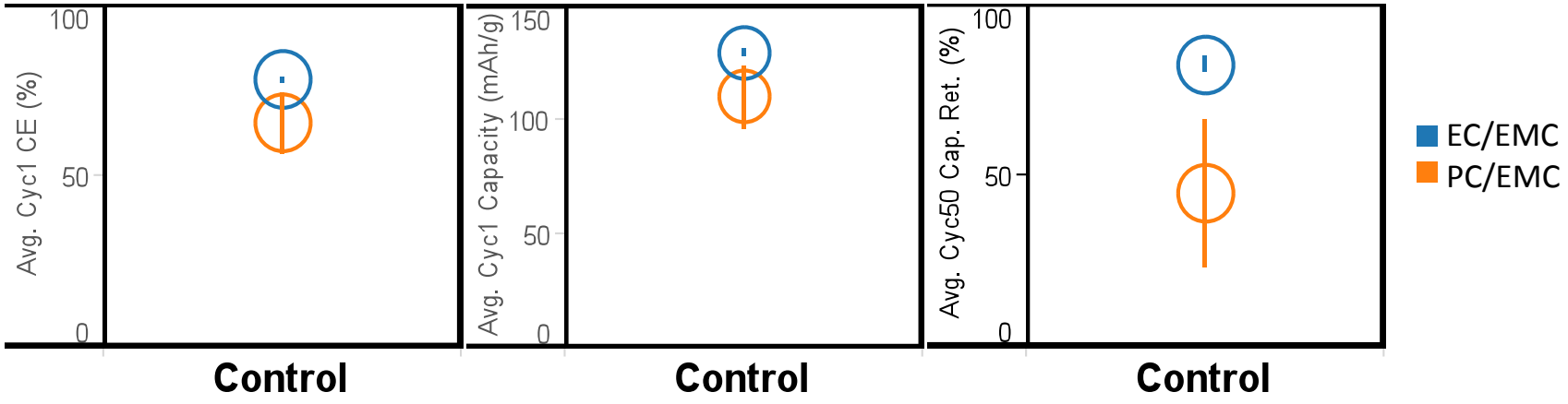
Development of Additive Package
Stable SEI

Enable New Solvents
Oxidative Stability
Ionic Conductivity
Low Temperature
Safety

Optimize Formulation
Oxidative Stability
High Temperature
Cost

Technical Accomplishments

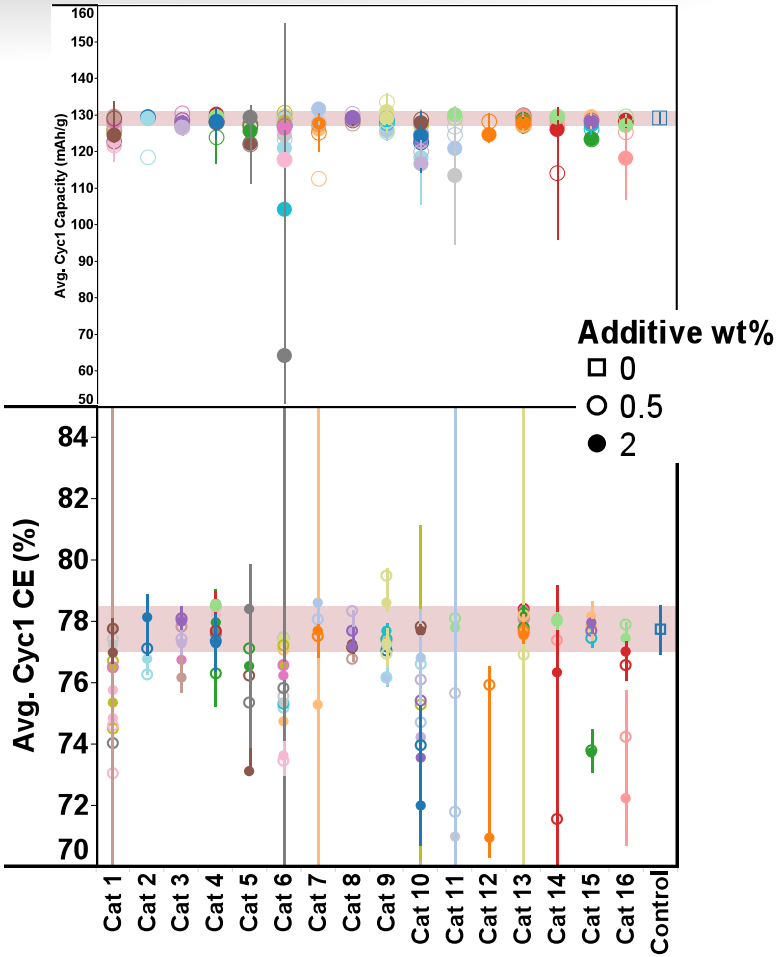
- Wildcat baseline performance established in NMC//Si alloy full cells
- EC/EMC (1/1), 1M $LiPF_6$ and PC/EMC (1/4), 1M $LiPF_6$
- PC/EMC performance significantly worse than EC/EMC
  - Expected as PC does not form good SEI
  - Initial target is EC-based performance in PC-based electrolyte



Baseline performance of EC and non-EC electrolytes established

Technical Accomplishments

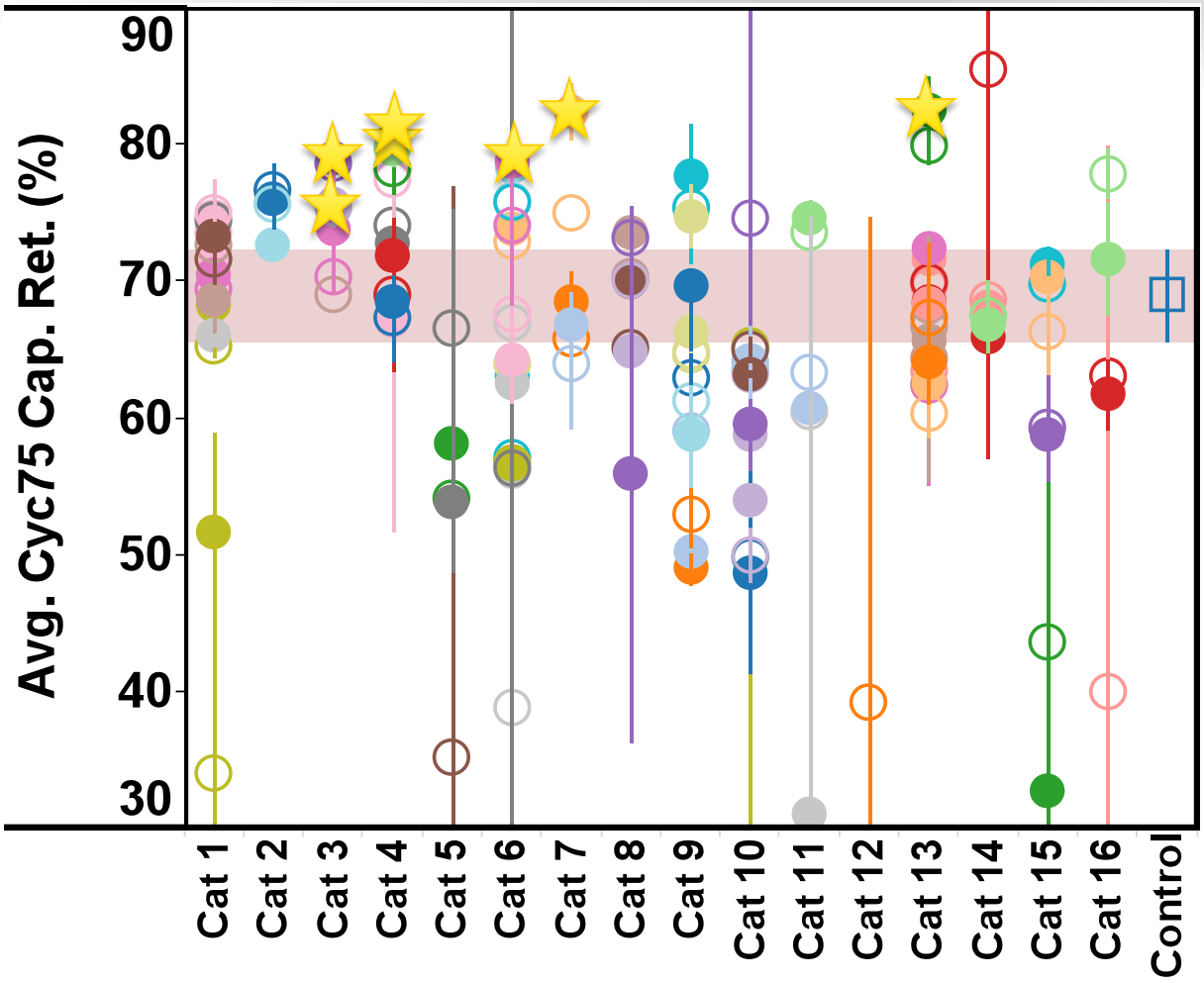
- 82 electrolyte additives tested:
  - Additives were group by category depending on structure (e.g., anhydride, boron-containing, etc.)
  - Additives tested at 0.5 and 2 weight % in base electrolyte
    - EC/EMC (1/1), 1M $LiPF_6$
  - NMC//Si alloy full cells (2.8 – 4.2V, C/5)
- Pink bands represent +/- 1σ about the mean of the baseline electrolyte with no additive



1st cycle capacity and CE maintained for many additives in EC/EMC

Technical Accomplishments

Wildcat Discovery Technologies



NMC//Si alloy
2.8 – 4.2V
EC/EMC (1/1), 1M $LiPF_6$

Additive wt%
- □ 0
- ○ 0.5
- ● 2

★ = additive with improved capacity retention on graphite

Additives with best improvement for NMC//Si alloy cells also improve NMC//graphite performance (★)

Technical Accomplishments

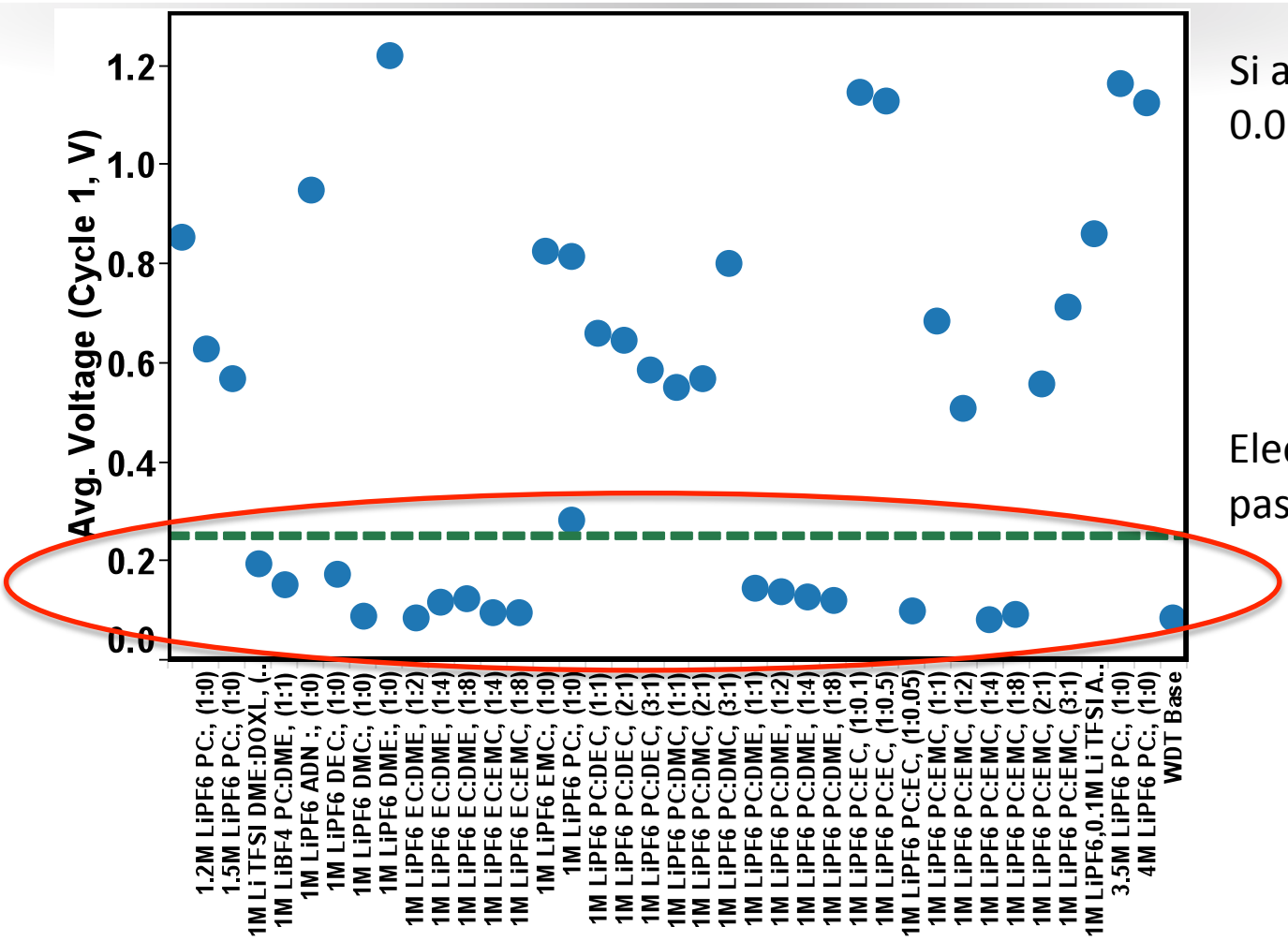
Wildcat Discovery Technologies

- Original plan to use PC as electrolyte solvent for additive screening
  - PC does not form SEI
  - Easy to observe improvements due to SEI additives
- PC causes exfoliation of graphite in anode
  - Results in ~ 0.6V plateau in discharge
- Wildcat screened non-EC electrolytes for following criteria
  - No 0.6V plateau in discharge curve
  - 1st cycle discharge capacity similar to EC-containing electrolyte
  - Cycle 10 capacity retention improved by addition of FEC

Systematic selection of non-EC containing electrolyte

Technical Accomplishments

Wildcat Discovery Technologies

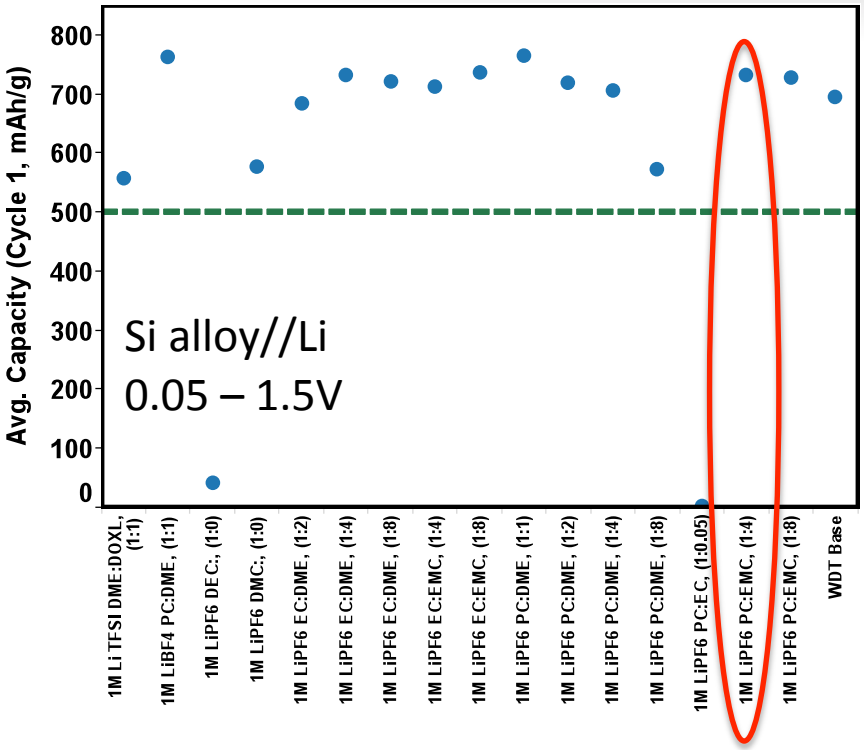


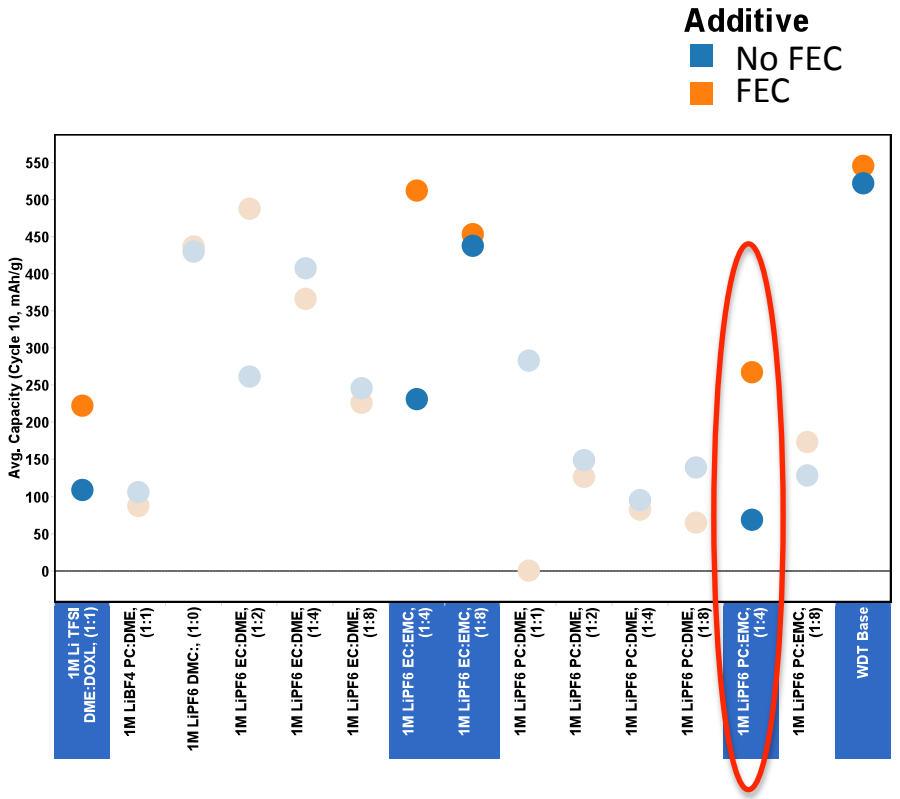
Si alloy//Li
0.05 – 1.5V

Electrolytes that pass 1st criteria

High average voltage indicative of graphite exfoliation

Technical Accomplishments

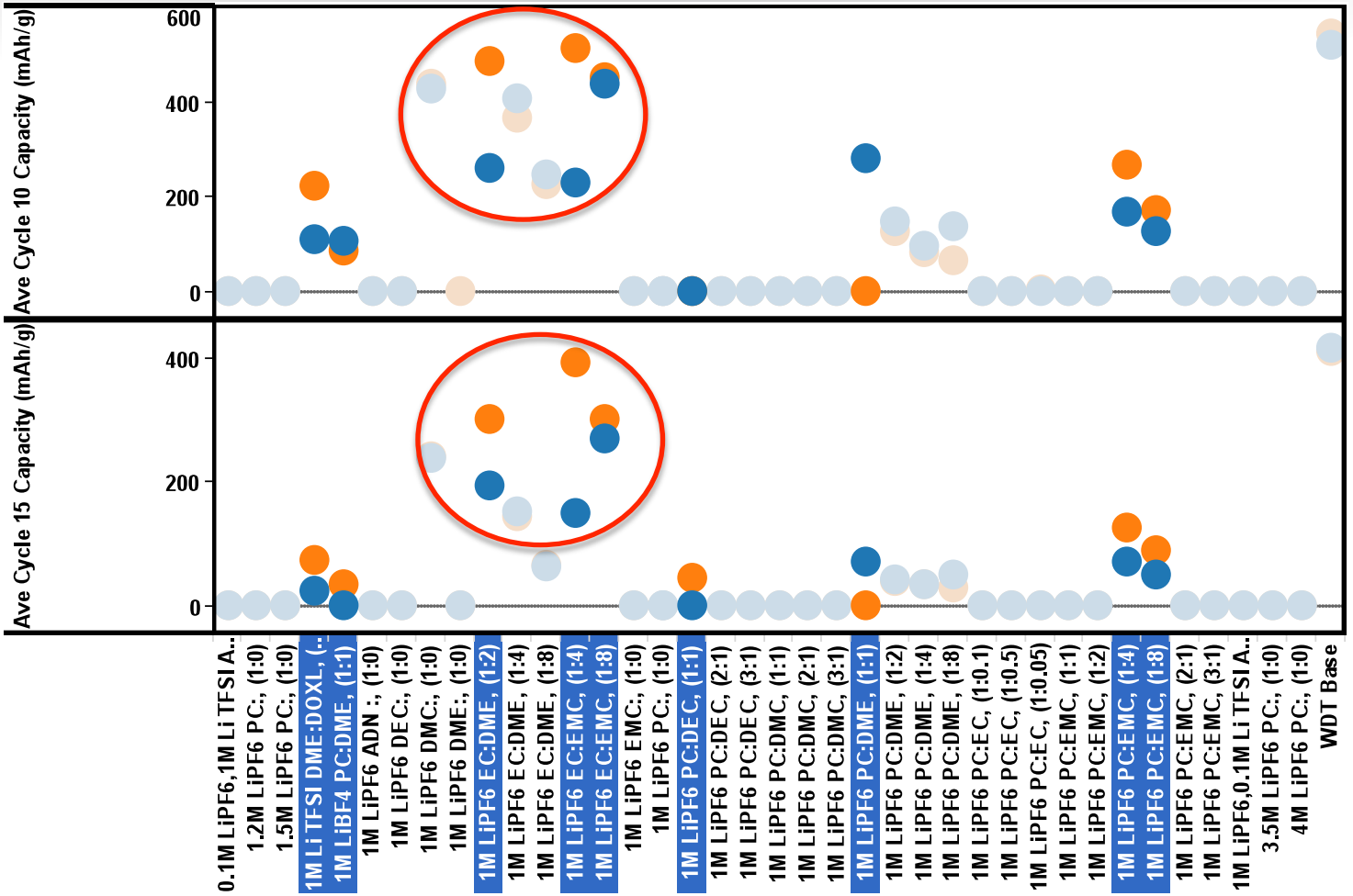




PC/EMC (1/4) 1M $LiPF_6$ chosen as non-EC baseline electrolyte

Technical Accomplishments

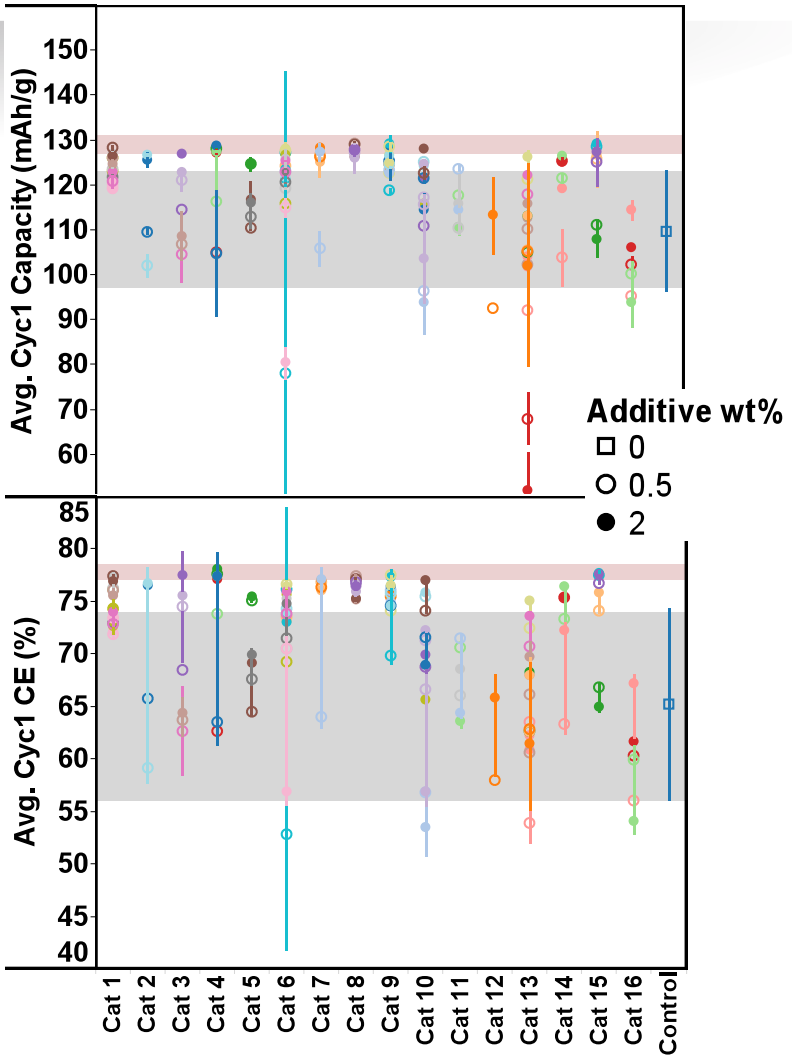
Wildcat Discovery Technologies



FEC shows largest improvement in high EC formulations

Technical Accomplishments

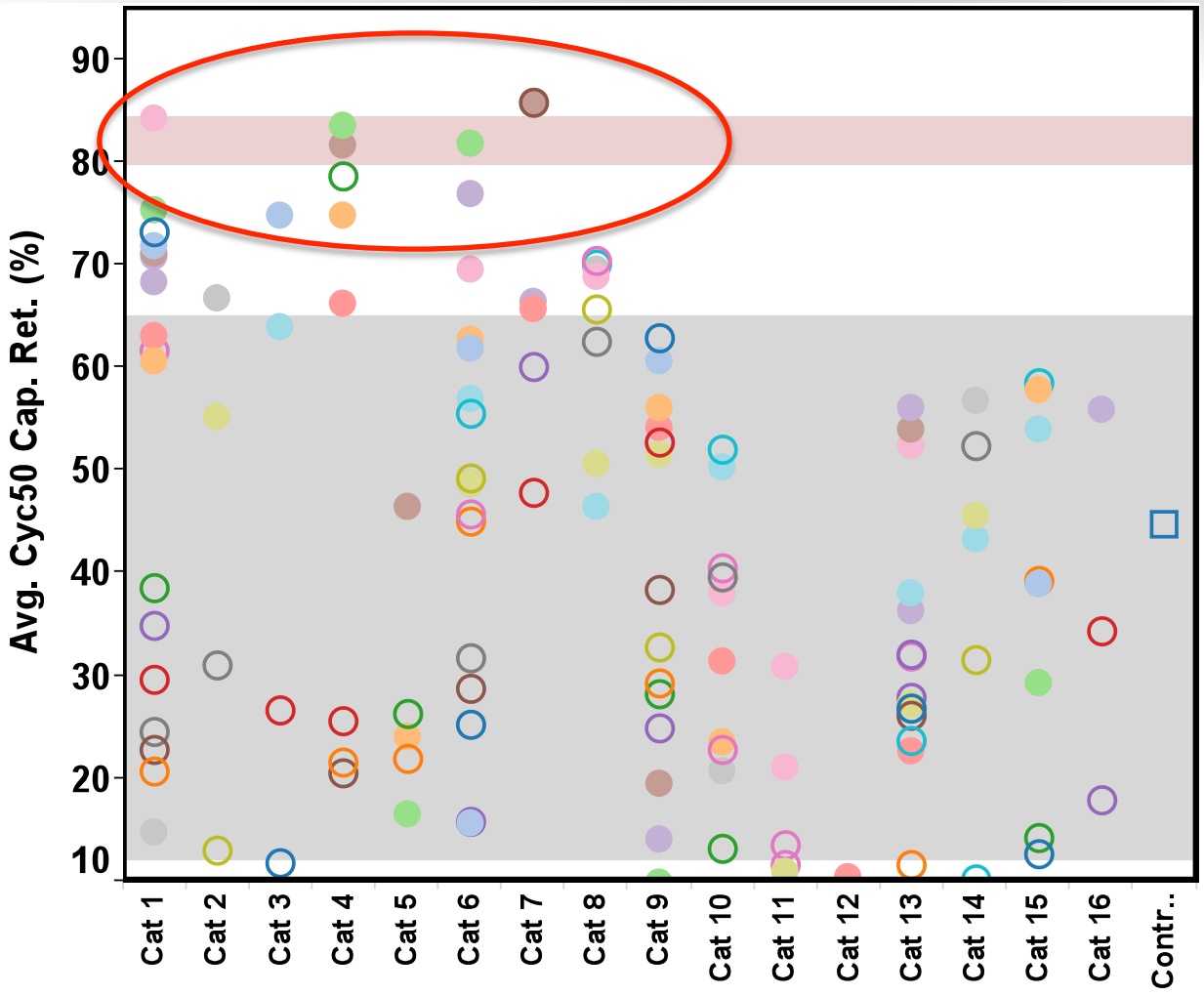
- 82 electrolyte additives tested:
  - Additives were group by category depending on structure (e.g., anhydride, boron-containing, etc.)
  - Additives tested at 0.5 and 2 weight % in base electrolyte
    - PC/EMC (1/4), 1M $LiPF_6$
  - NMC//Si alloy full cells (2.8 – 4.2V, C/5)
- Pink bands represent +/- 1σ about the mean of the EC/EMC electrolyte with no additive
- Gray bands represent +/- 1σ about the mean of the PC/EMC electrolyte with no additive



Similar 1st cycle capacity & CE obtained in non-EC containing electrolyte

Technical Accomplishments

Wildcat Discovery Technologies



NMC//Si alloy
2.8 – 4.2V
PC/EMC (1/1), 1M $LiPF_6$

Additive wt%
- □ 0
- ○ 0.5
- ● 2

"EC-like" performance in PC-based electrolyte

Collaboration with Other Institutions

Wildcat Discovery Technologies

- Collaboration with 3M
  - 3M is providing all NMC//Si alloy finished electrodes
  - 3M will design/assemble/test interim 18650 cells
- UCSD
  - Wildcat utilizes UCSD material science analytical suite

Remaining Challenges & Barriers

Wildcat Discovery Technologies

- Can SEI's formed primarily due to additives prevent reduction of non-carbonate solvents on the anode?
- How sensitive are the SEI properties to the formation process?
- Can we improve the mechanical properties of the SEI enough to withstand the volumetric changes of the anode?
  - What is the best mechanism to affect the mechanical properties?
- Can we get high power from the stable formulations?

Proposed Future Work

Wildcat Discovery Technologies

- Identification of non-carbonate solvent(s) that are electrochemically stable on both electrodes AND
  - Do not negatively affect the additive contribution to the SEI
  - Enable conductivity target
  - Are low cost
- Continued identification and development of polymeric additives to further improve SEI on the silicon anode, resulting in improved cycle life

Proposed Future Work (2014)

Wildcat Discovery Technologies

- Continued testing of novel designed additives in both EC/EMC and PC/EMC baseline electrolytes in NMC//Si alloy full cells (2Q14)
  - Additive library design of over 100 new additives complete
  - Cell build/test in progress
  - These library designs will continue throughout the course of the project
- Screening of electrochemical performance of non-carbonate solvents in NMC//Si alloy full cells (2Q14)
  - Initial testing will utilize promising additives identified in this project
  - New additives will feed into these studies
- In depth studies on combinations of promising additives and solvents (3-4Q/14)
  - Electrochemical testing
    - Formation processes
  - In situ gas measurements
  - Post-mortems

Proposed Future Work (2015)

Wildcat Discovery Technologies

- Down-select to final solvent candidates (1Q/15)
  - Complete all screens with most promising additives
- Design libraries to optimize final formulations (2Q/15)
  - Improve conductivity, low temperature performance
  - Improve high voltage stability
  - Complete fundamental studies on best materials
- Complete final 18650 design (3Q/15)
- Assemble/deliver final 18650 cells to DOE (4Q/15)

Summary

Wildcat Discovery Technologies

Relevance	• Electrolyte formulations that form stable SEI's can enable high energy density silicon anodes • High energy density solutions are critical to market adoption of EVs
Approach	• Identify electrolyte additive package that forms stable SEI in non-EC containing electrolyte • Develop non-carbonate formulations based on these additives • Engineer SEI films from additives expected to form more mechanically robust SEIs
Technical Accomplishments	• Identification of initial additives that yield "EC-like" performance in a PC-based electrolyte in NMC//Si alloy full cells
Collaborations	• 3M supplier of electrode materials
Future Work	• Identification of non-carbonate solvents to use with best performing SEI additives • Further development of SEI additives that form more mechanically robust SEI layers

Support for this work from DOE-EERE,
Office of Vehicle Technologies is gratefully acknowledged