Accelerating Breakthrough Discoveries
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Wildcat Discovery Technologies

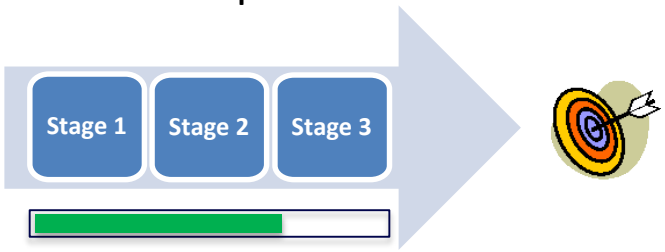
Novel Non-Carbonate Based Electrolytes for Silicon Anodes

Project ID: ES219
Dee Strand, Principal Investigator
Wildcat Discovery Technologies
2015 Annual Merit Review
June 9, 2015

Overview

Timeline

- Start Date: 10/01/2013
- End Date: 12/31/2015
- Percent Complete: 68%



Barriers

- Energy density
  - High capacity silicon anodes required to improve cell energy density
- Cycle life
  - Unstable SEI due to large volumetric changes in silicon result in poor cycle life

Budget

- Total Funding: $1,249,723
  - DOE Share: $ 999,778
  - Contractor Share $ 249,945
- Funding Received:
  - FY2013 $ 3,974
  - FY2014 $ 406,104
  - FY2015 (thru 4/10) $ 72,026

Partners

Wildcat Discovery Technologies

Lead organization: Electrolyte discovery and optimization

3M

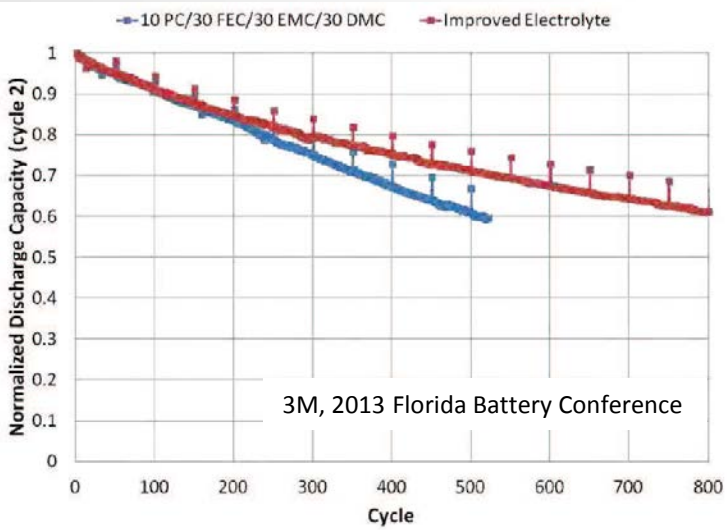
Argonne NATIONAL LABORATORY

Electrode preparation, large cell format assembly and testing

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.



Objectives (3/14 – 3/15)

- Identify best SEI additives for noncarbonate solvent evaluation
- Identify best performing noncarbonate solvents
- Begin optimization

Milestones

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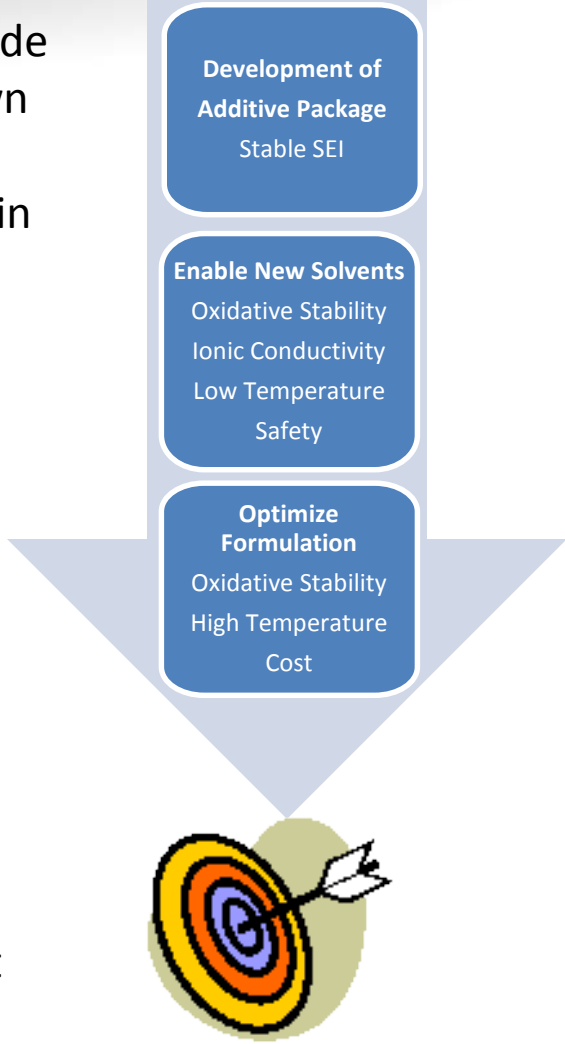
Date	Milestones and Go/No-Go Decisions	Status
06/2014	SEI additives identified with non-EC based electrolyte which performs comparably to current carbonate/FEC blends	**Complete**
12/2014	Go/No-Go Decision: Non-EC containing formulation with SEI package achieves > 50 cycles to 70% capacity in NMC full cells	**Complete/Go**
12/2014	Interim 18650 cells assembled and sent to ANL for testing	**Complete**
03/2015	Non-carbonate formulations identified which perform comparably to current carbonate/FEC blends	**Complete**
06/2015	Non-carbonate formulations identified with > 200 cycles to 80% capacity	**Complete**
09/2015	Non-carbonate formulations identified with > 500 cycles to 80% capacity	**On Track**
12/2015	Achieve project targets for ionic conductivity and voltage stability	**On Track**
12/2015	Final 18650 cells assembled and sent to ANL for testing	**On Track**

Approach

- 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)
  - Go/No-Go Decision > 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



Technical Accomplishments – Additive Approach

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Experiments:

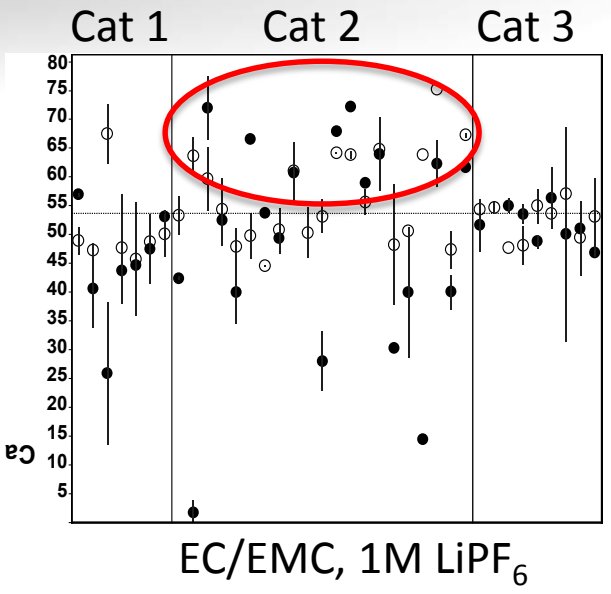
- Evaluated over 200 additives in PC/EMC and EC/EMC formulations
  - 12 chemical categories/families at multiple concentrations
  - Additives chosen based on expected effects on SEI composition/properties

Outcome:

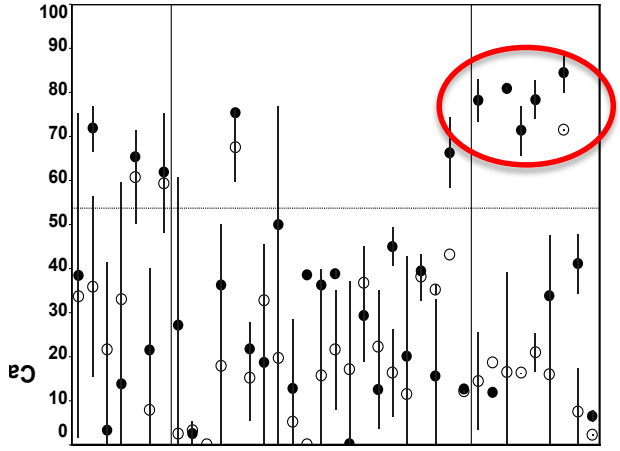
- Established working hypotheses for beneficial structures/functional groups
- Additives identified for noncarbonate solvent evaluation
- 3 patent applications filed

Next Steps:

- Synthesis and testing of new structures based on key learnings
- Combinations of additives with differing functionalities



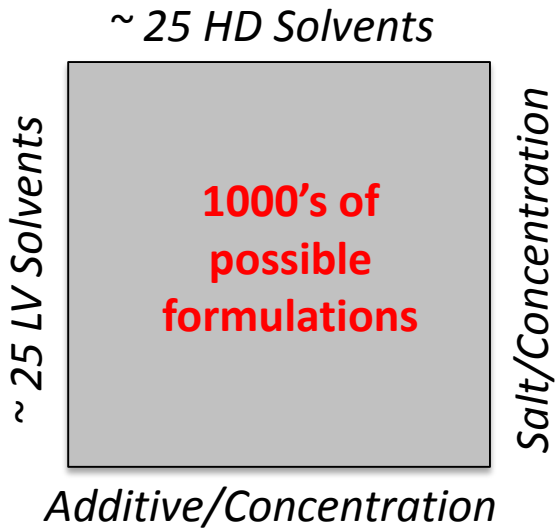
EC/EMC, 1M $LiPF_6$



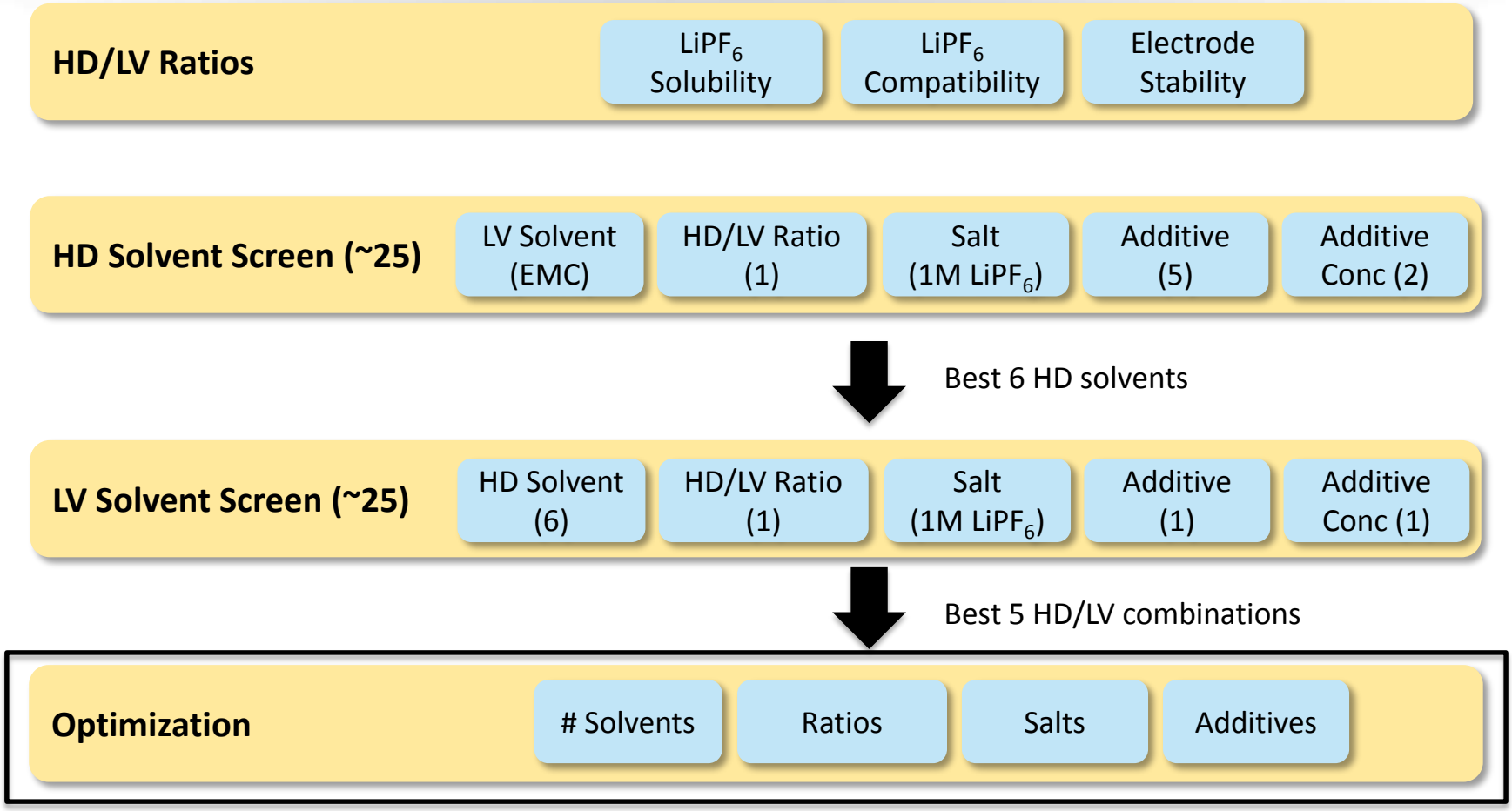
PC/EMC, 1M $LiPF_6$

Technical Accomplishments – Solvent Approach

- Oxidatively stable
- Does not participate in SEI formation (the additives are going to do that)
  - Reductively stable (aprotic)
  - Reduction potential lower than the additives
- High dielectric constant
  - Polar group in structure, necessary to dissociate salt
    - → Carbonyl C = O
    - → Nitrile C ≡ N
    - → Sulfonyl S = O
- Low viscosity
  - Asymmetry
  - Low MW
  - Low melting point
- Liquid over useful temperature range
- Others…



Technical Accomplishments – Solvent Approach



Current Stage of Project

Key Metrics:

- 1st cycle capacity/CE
- Cycle life

Technical Accomplishments – Solvent Approach

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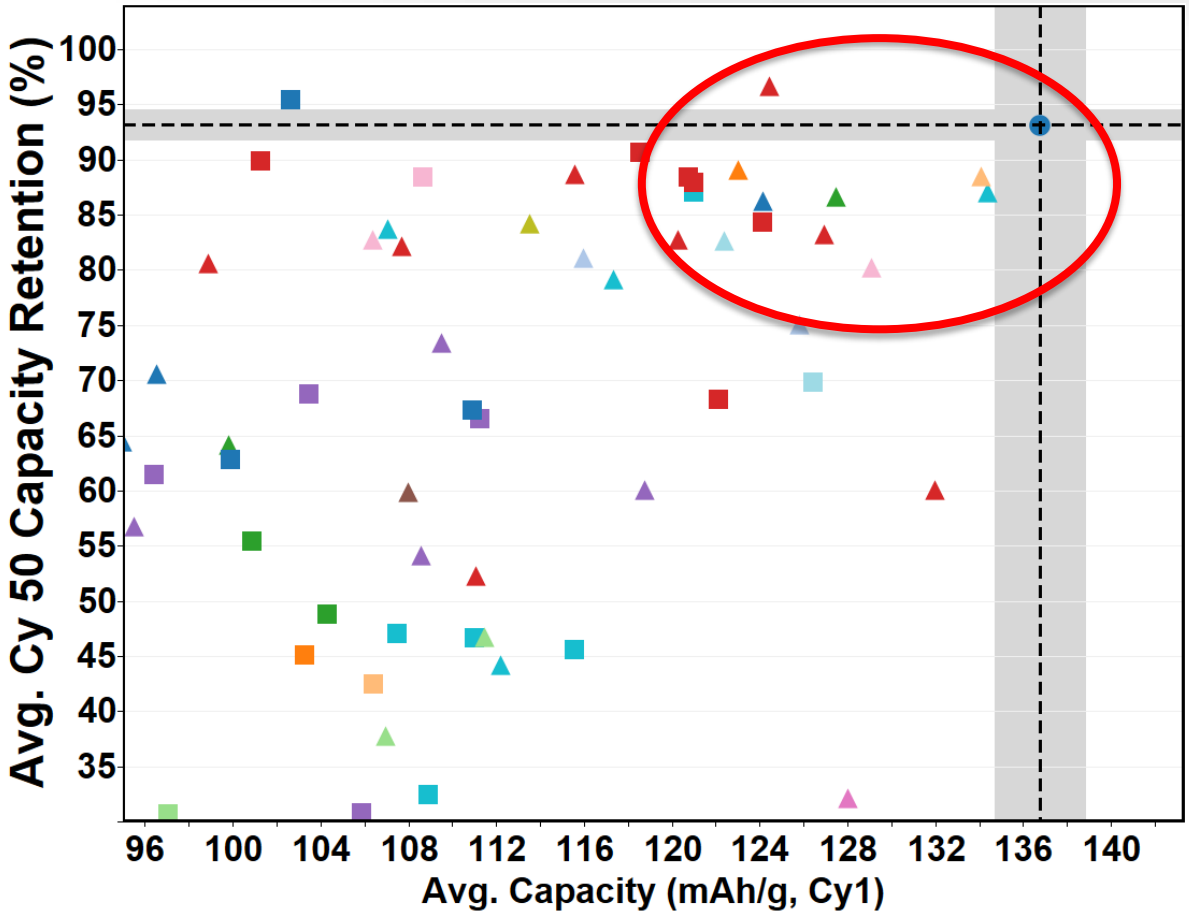
HD/EMC Combinations



NMC//Si alloy
2.8 – 4.2V
C/10

Colors: Solvent
Shapes: Additive

Control:
EC/EMC (1/2)
1M $LiPF_6$

Identified EC-free combinations similar to control

Technical Accomplishments – Solvent Approach

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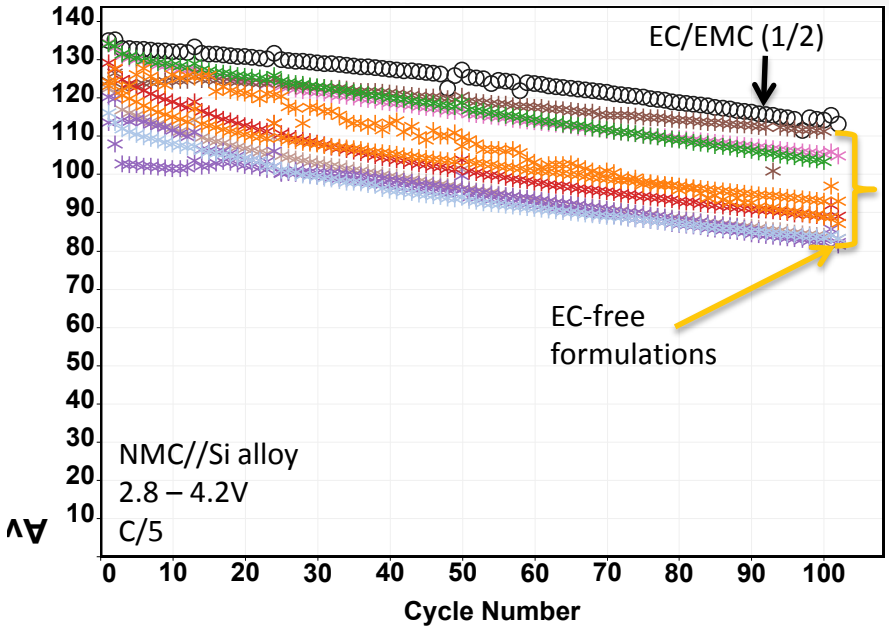
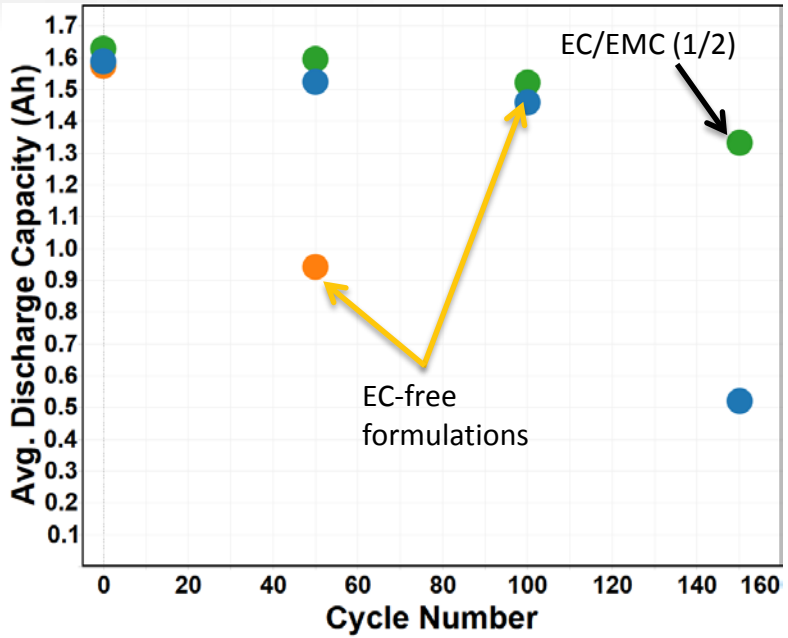
Wildcat Results



18650 Results



- 18650 cells built by 3M, tested by Argonne National Lab
- "Drop-In" new electrolyte formulations – no optimization for cell format change
- Argonne test protocol included pulse testing prior to/during cycle life (not done in Wildcat cells)

Optimization for 18650 cells is required

Technical Accomplishments – Solvent Approach

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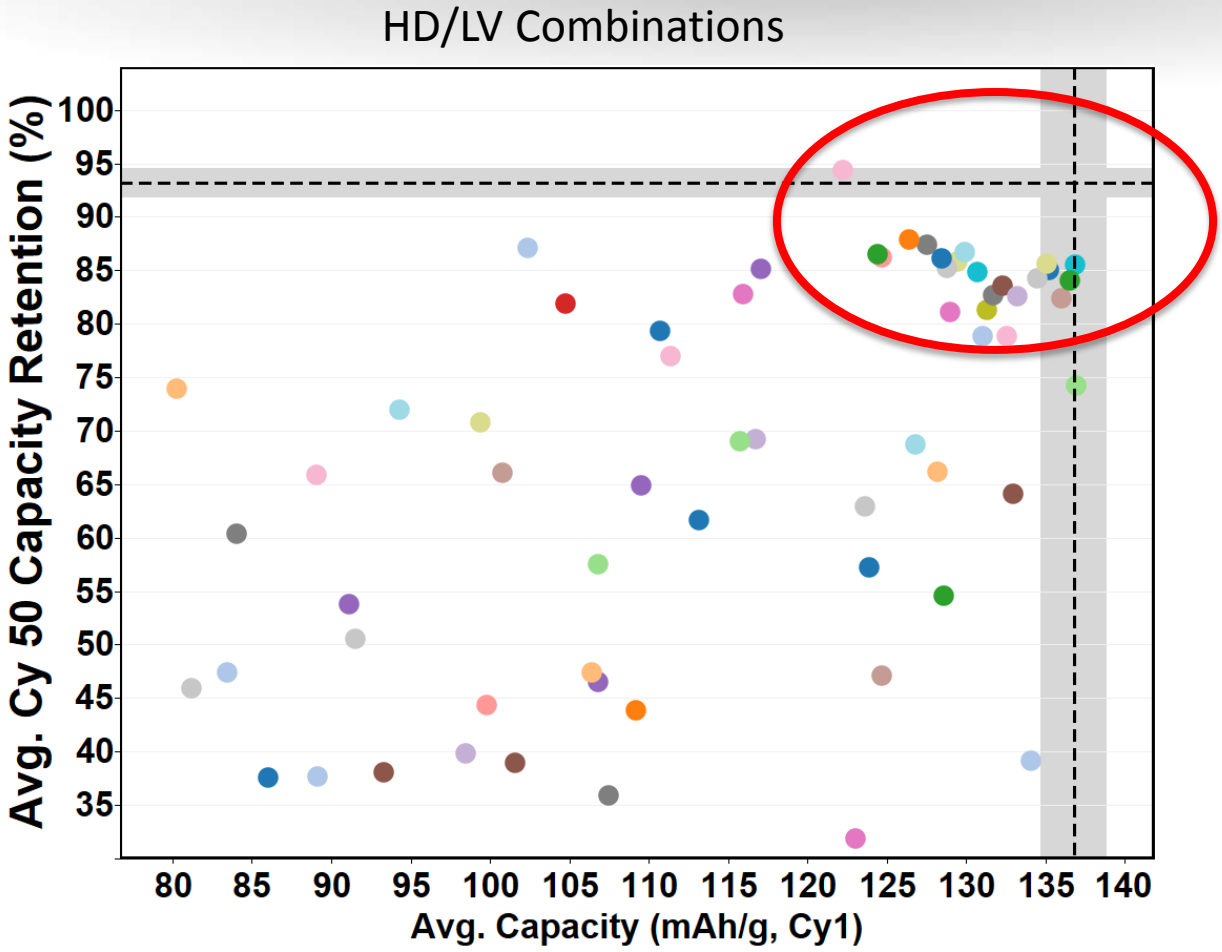

NMC//Si alloy
2.8 – 4.2V
C/10

Colors: Solvent

Control:
EC/EMC (1/2)
1M $LiPF_6$

Noncarbonate formulations similar to control at 50 cycles

Technical Accomplishments – Solvent Approach

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		LiPF6		Salt 1		Salt 2		Salt 3		Salt 4		Salt 5	
LV	HD	Cy1 Capa. mAh/g	Capa. Reten (%)	Cy1 Capa. mAh/g	Capa. Reten (%)	Cy1 Capa. mAh/g	Capa. Reten (%)	Cy1 Capa. mAh/g	Capa. Reten (%)	Cy1 Capa. mAh/g	Capa. Reten (%)	Cy1 Capa. mAh/g	Capa. Reten (%)
Control		134.2	83.6	134.2	83.6	134.2	83.6	134.2	83.6	134.2	83.6	134.2	83.6
A	1	132.4	72.0	122.4	30.3	129.4	21.7	133.1	0.47	129.1	92.1	123.8	82.4
	2	134.1	80.2	122.6	33.0	131.6	33.9	132.7	0.34	129.8	93.3	123.2	80.1
	3	122.9	71.8	80.3	41.5	131.4	53.3	128.7	1.9	125.9	89.0	122.4	82.3
B	1	124.5	78.4	31.1	59.4	125.9	26.3	134.5	76.7	127.3	15.1	131.3	88.2
	2	131.6	75.7	116.6	62.5	131.9	73.9	131.5	84.6	102.3	6.9	127.2	89.6
	4	123.1	86.9	126.1	54.2	131.1	76.0	134.0	79.8	131.9	43.0	132.9	86.3
C	5	133.8	80.8	90.6	54.5	121.6	0.1	137.7	0.1	103.6	1.2	131.8	87.7
	6	131.7	87.9	-	-	118.6	0.0	135.7	10.1	120.4	71.0	129.2	90.3
	7	136.5	84.4	-	-	118.5	86.1	135.1	87.9	133.7	62.1	129.5	83.9
D	3	134.0	86.9	122.1	66.2	121.2	90.4	135.7	88.8	133.9	81.7	130.4	88.4
E	2	135.5	85.1	-	-	130.6	81.8	127.3	80.3	134.3	91.1	125.4	86.7

Capacity Retention @ 100 cycles

New formulations require re-optimization of salt(s)

Technical Accomplishments – Solvent Approach

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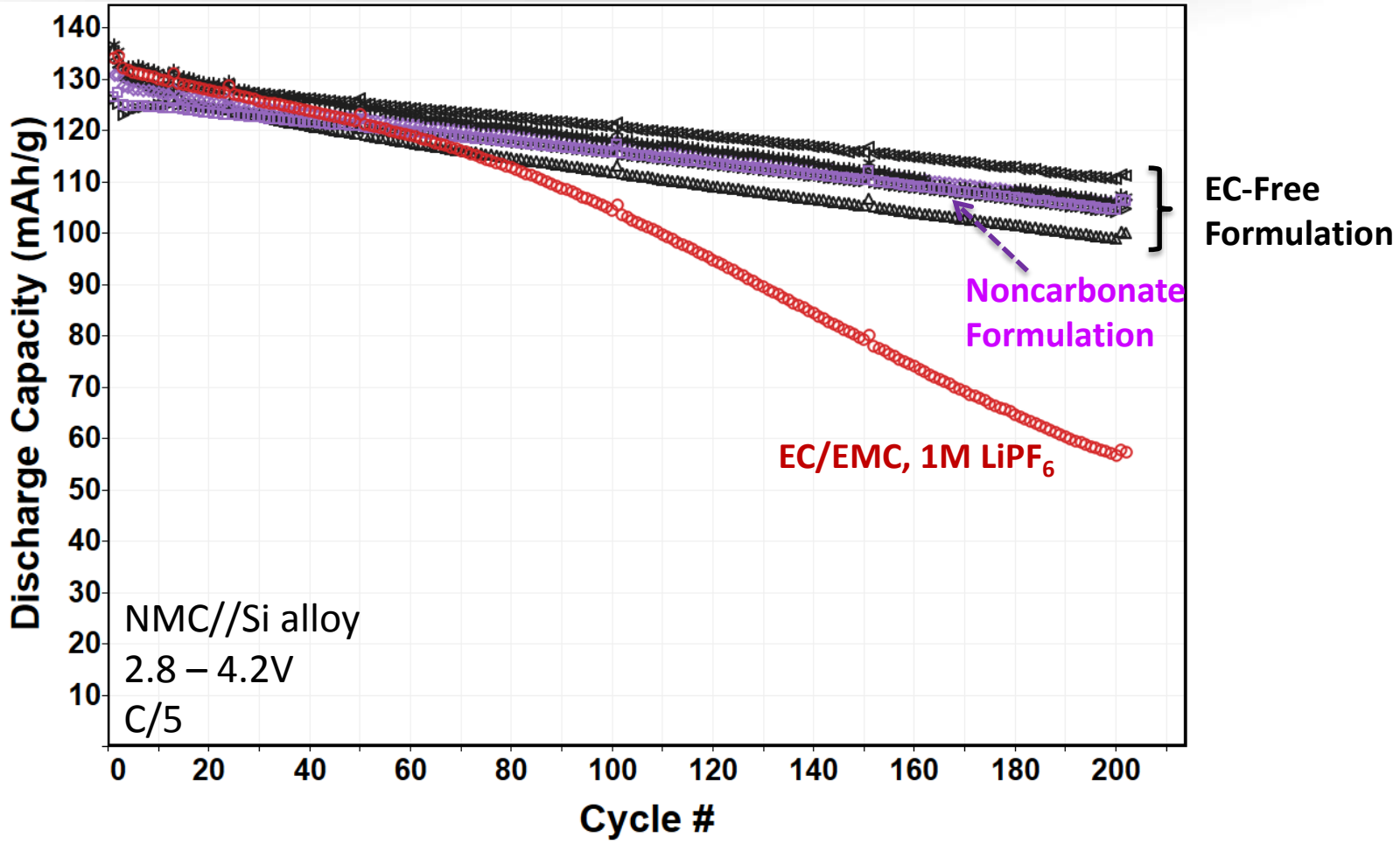


New formulations require re-optimization of salt(s)

Technical Accomplishments – Summary

Wildcat Discovery Technologies

- To date, over 5000 cells have been assembled and tested
- Beneficial additives have been identified for
  - EC-containing formulations
  - EC-free formulations
- Additives used to screen non-carbonate solvents
  - *"Head start" on additive development for traditional solvents*
  - Structure-performance relationships derived from additive screening with purchased and custom compounds
- Non-carbonate solvent formulations identified that outperform the EC-based control formulations
- Gas generation in non-carbonate formulations similar to EC-based control
- Additional testing on other Si sources in progress

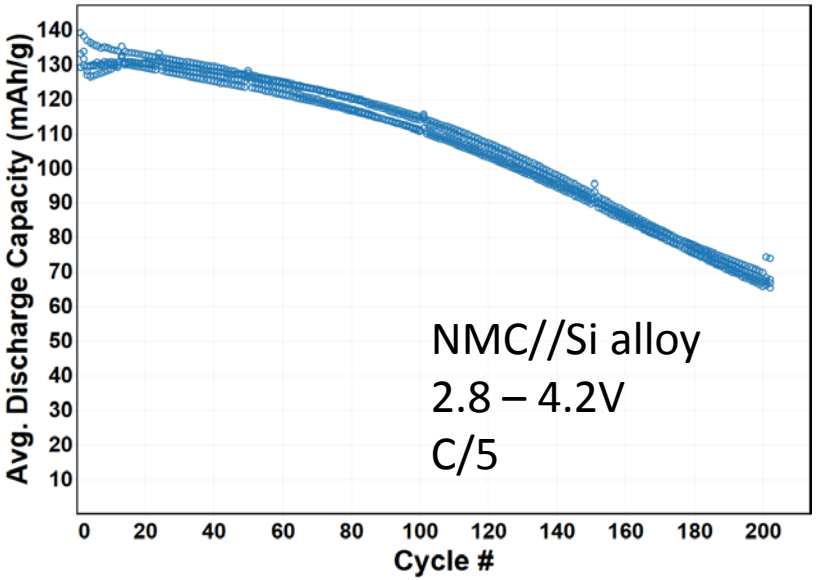
Responses to Reviewer Comments

- *Project focus on 3M silicon anode is too narrow; recommend benchmarking formulations on other materials*
  - Wildcat is currently doing testing of promising additives and noncarbonate formulations on Si//carbon composite electrodes received from Argonne National Lab
- *Recommend utilizing more analytical capability; perform post-mortem analysis to gain more understanding*
  - Wildcat plans on doing this as we down-select to the final solvent choices
- *More collaboration is recommended*
  - Now including Argonne to test 18650 cells and supply electrodes
  - Will begin analytical work at UCSD
  - In discussion with other silicon anode suppliers regarding evaluations
- *Recommend breaking out results for "best" formulations to more clearly see the progress*
  - Showed more traditional cycle life graphs on Slide 16 for best formulations in this presentation

Responses to Reviewer Comments

- *Reviewer would like more information about reproducibility of data/experiments*
  - All initial testing is done in duplicate, with averages represented on graphs
  - All promising additives/formulations are repeated
  - As we move into optimization, testing is done in triplicate or quadruplicate
- *Reviewer recommended more intimate knowledge of 18650 cell construction and testing to gain insight*
  - We plan on multiple rounds of 18650 cells with best formulations to optimize for that cell format

EC/EMC Control (quadruplicate)



Collaborations

Wildcat Discovery Technologies	Lead organization • Design of experiments/ideas • High throughput evaluation
3M	• Fabrication of electrodes (anodes and cathodes) • 18650 cell assembly and testing
Argonne NATIONAL LABORATORY	• Fabrication of electrodes (anodes and cathodes) • Supply of novel additives, salts • 18650 cell testing
University of California San Diego	• Access to analytical characterization (2015)

Remaining Challenges & Barriers

- Further improvements to cycle life (500 cycles)
- Other metrics
  - High voltage stability
  - Power/rate/conductivity
- 18650 cell optimization

Proposed Future Work

- Cycle life improvements
  - Additive optimization
  - Additive combinations
- High voltage stability
  - Formulation/solvents (expect new solvents to be stable)
  - High voltage additives
- 18650 cell optimization
  - Several rounds of cell builds
  - Optimize formulation for larger cell format
- Test vs. other silicon materials
  - In progress

Summary

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Acknowledgements

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