Advanced High Energy Li-Ion Cell for PHEV and EV Applications

Jagat Singh
3M Company
June 18th, 2014

Project ID # ES210

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start Date:10/01/2013
- End Date:09/30/2015
- Percent Complete:15%

Budget

- Total Project Funding
  - DOE* Share: $3,000,043
  - Contractor Share: $774,314
- Funding Received in FY13: $0
- Funding for FY14: $494,198

**3M and the team appreciates the support and funding provided by DOE*

Barriers

- Cycle Life
- Specific Energy
- Cost

Partners

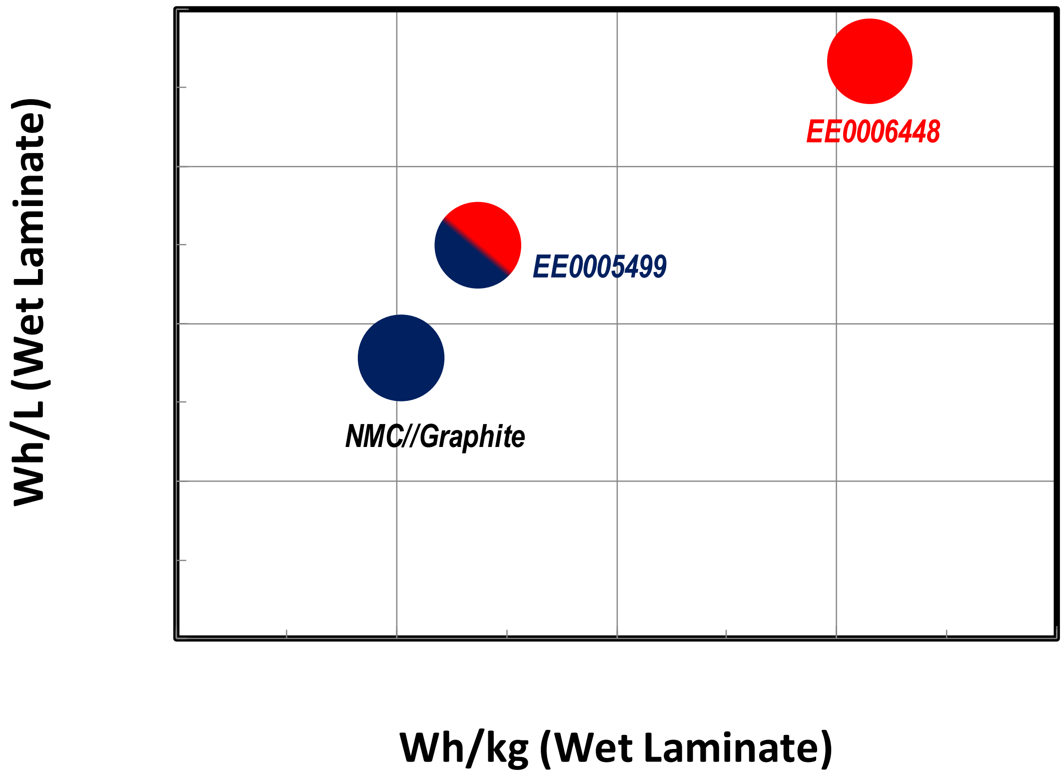
- Collaboration:
  - GM: Dr. Meng Jiang
  - Umicore: Wendy Zhou
  - Leyden: Dr. Marie Kerlau
  - ARL: Dr. Richard Jow
  - LBNL: Dr. Gao Liu
- Interaction
  - Dalhousie University
  - ANL: Deliverable Testing
- Project Lead:3M

Relevance

Objective

A collaborative team approach to leverage crucial Li-ion battery technologies and expertise to help enable

- Advanced High Energy Li-Ion Cell
- Superior Performance Envelope
  - Long Cycle Life,
  - High Power Capability,
  - Wide Operating Temperature
- Lower Cost ($/Wh)

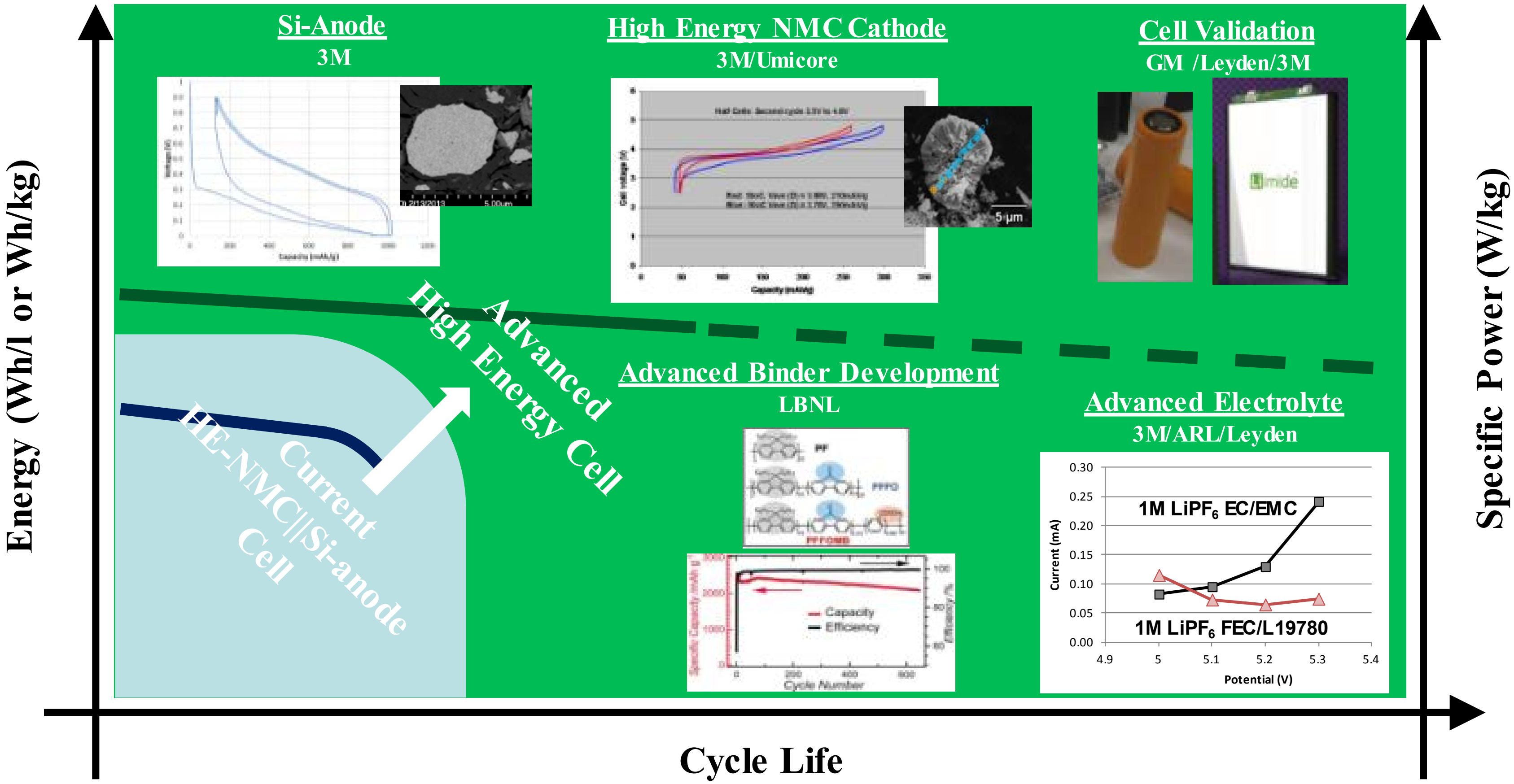


3M umicore Rechargeable Battery Materials ARL BERKELEY LAB Leyden energy GM RESEARCH & DEVELOPMENT

Milestone

Month / Year	Milestone	Status
	Phase I (Oct 1st, 2013 to Sept 30th, 2014)	
Dec / 2013	Scale up baseline anode and cathode material	✓
Jan / 2014	Sample baseline anode and cathode material powder	✓
March / 2014	Sample internally baseline electrodes and 18650 for testing	✓
April / 2014	Baseline deliverables	*WIP*
	Phase II (Oct 1st, 2014 to Sept 30th, 2015)	
Sept / 2015	Final deliverables	

Approach / Strategy



Synergistic Team Approach to Address Vital Components.

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Approach / Strategy

1. Develop Advanced Material to meet Energy Targets

Si Alloy Anode
Scalable process to develop high capacity Si alloy with stable microstructure

Binder - Si Anode
Innovative conductive binder for superior Si anode composite

Advanced Electrolyte / Additives
SEI and high voltage stability to enhance performance

High Energy NMC Cathode
Develop composition with high Wh/kg to increase cell energy

2. Characterize Performance in 18650 / Pouch Cells

Electrode Formulation Study

Tune Formation Protocol

Evaluate Dispersion, Roll to Roll Coating and Drying

Gap Analysis and Diagnostics

Energy and Life Validation

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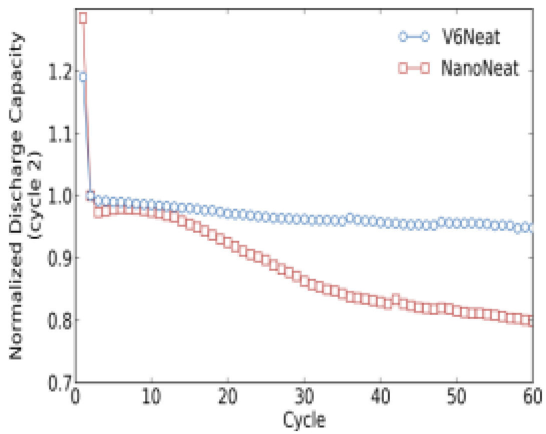
3M Si Alloy Anode Development

Baseline Material

3M Si Alloy Anode shows excellent cycling and coulombic efficiency compared to Si nano-particles



Journal of The Electrochemical Society, **161** (5) A783-A791 (2014)

Advanced Material

Develop Si alloy to target

- 20% increase in mAh/g
- 10% increase in mAh/cc
- High efficiency
- Surface stability

Si Alloy	BET (m^2/g)	1st lithiation (mAh/g)	1^{st} delithiation to 0.9V (mAh/g)	First Cycle Efficiency (%)
Candidate B	1.9	1020	910	89.2
Candidate A	4.3	1330	1160	87.0
Baseline	3.5	1050	900	85.7

Exploring Si Alloy Compositions to meet Energy Targets.

Si Alloy Anode Scale Up

- A scalable and cost effective synthesis route for Si Alloy anode manufacturing
- Full scale equipment operational in US-based manufacturing (Cottage Grove, MN)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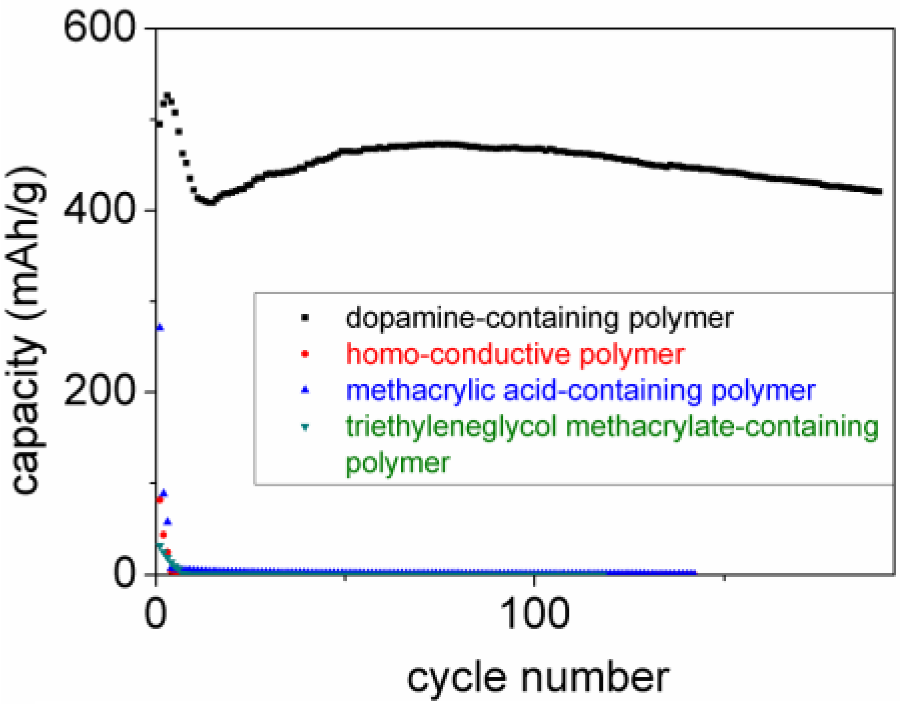
Helping to build a better battery

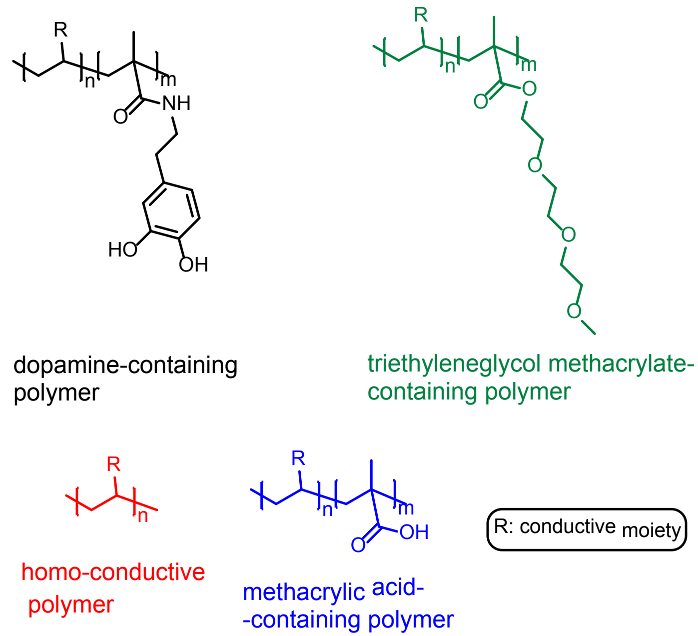
Article by: SUSAN FEYDER , Star Tribune

A 3M pilot project is making longer-lasting lithium ion batteries for consumer electronics. Next up: electric vehicle batteries.

Successfully Scaled Baseline Si Alloy Anode for Evaluation in Full Cells.

Binder Development for 3M Si Alloy Anode





10% binder, 90% 3M anode; Rate: 100 mA/g; Cut-off voltage: 0.01V~1V

Loading: 1.49 mg anode material on this 1.6 cm2 electrode

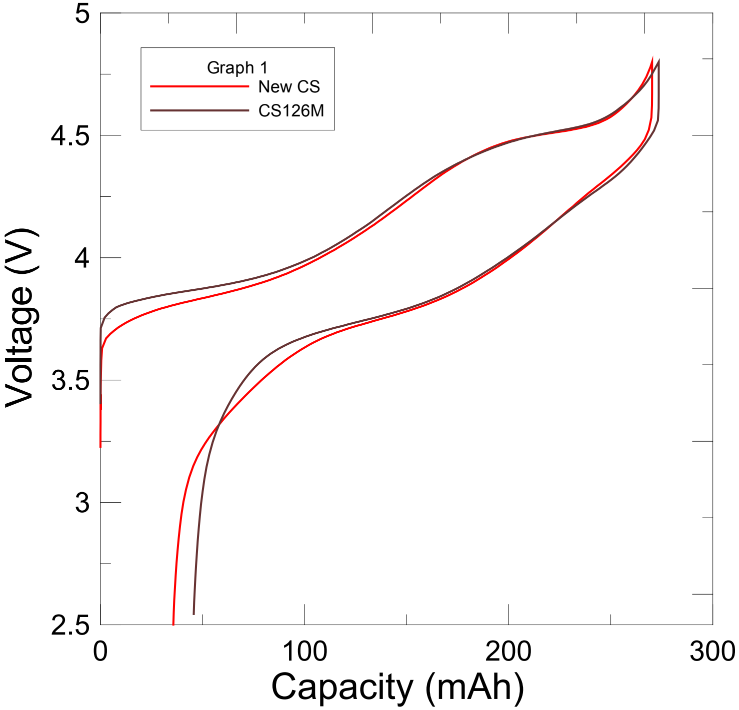
~0.9 mg anode/cm2

Electrolyte: EC/DMC/DMC=1, 10% FEC, 1M LiPF6

Observed Significant Improvement in Performance
Binder Scale Up Trials in Progress at 3M.

Technical Accomplishments and Progress

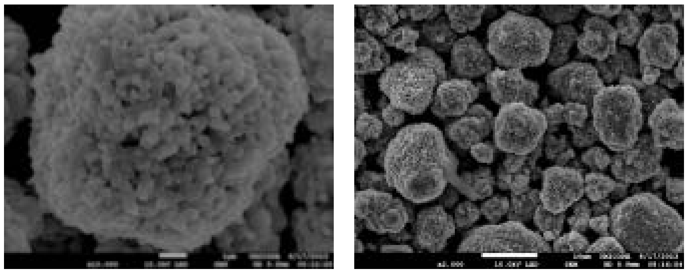
High Energy NMC Cathode Development

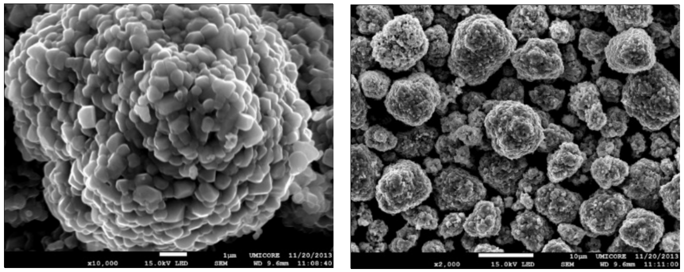


Material		CS 126M		New CS	
Lot#:		PP121113Q		PP140217H	
Electrochemical Performance		Capacity (mAh/g)	Gravimetric Energy (mWh/g)	Capacity (mAh/g)	Gravimetric Energy (mWh/g)
2.5-4.8V	1st charge (C/20)	273		271	
	1st Discharge (C/20)	227	875	233	**889**
	Irreversible loss (%)	16.7		**13.9**	
2.5-4.7V	C/2	182	687	176	653
	2C	155	564	141	507
	5C	129	443	113	388

Identified Material Composition with Reduced Irreversible Capacity. Also Exploring other Compositions.

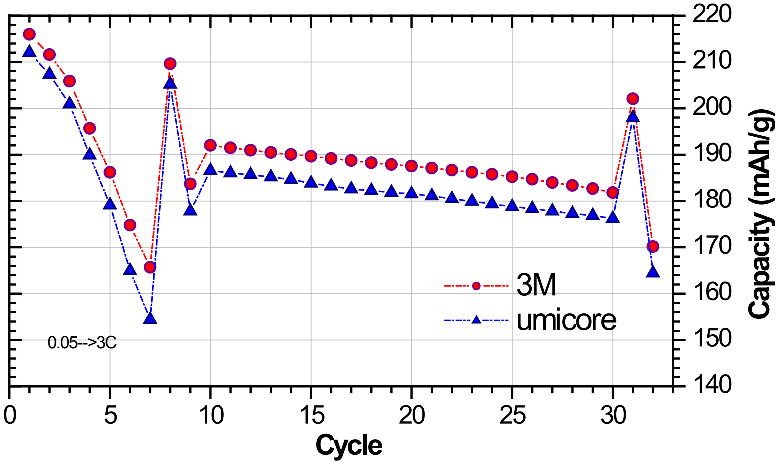
High Energy NMC Cathode Scale Up

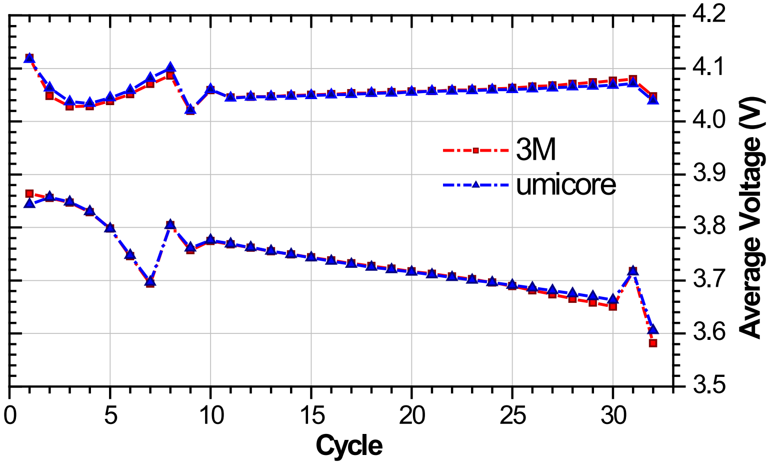




3M Design (Lab scale)
(QD1:215.98, Qirr : 14.77%)

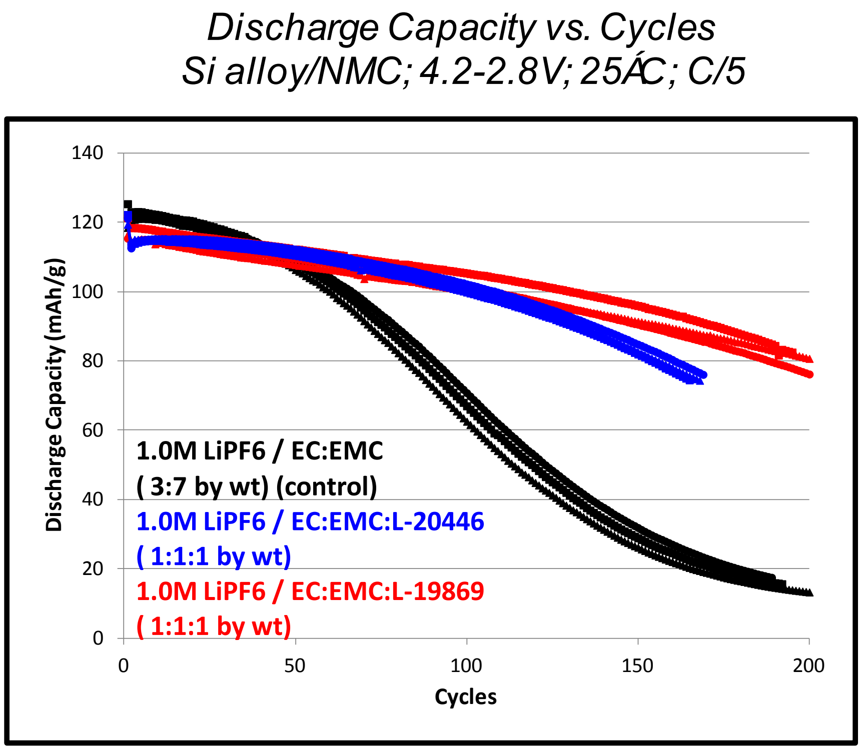
Umicore scale-up (Pilot scale)
(QD1:207.25, Qirr : 17.15%)

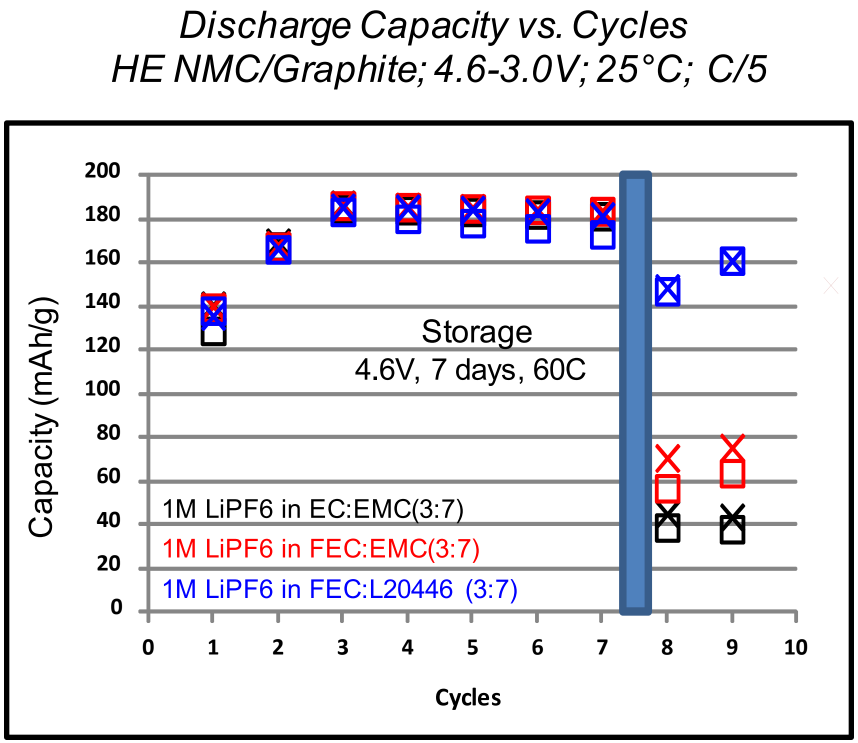




Successfully Scaled and Sampled >30 kg of Cathode Material. Process Optimization in Progress.

Electrolyte Screening (Full Cell)



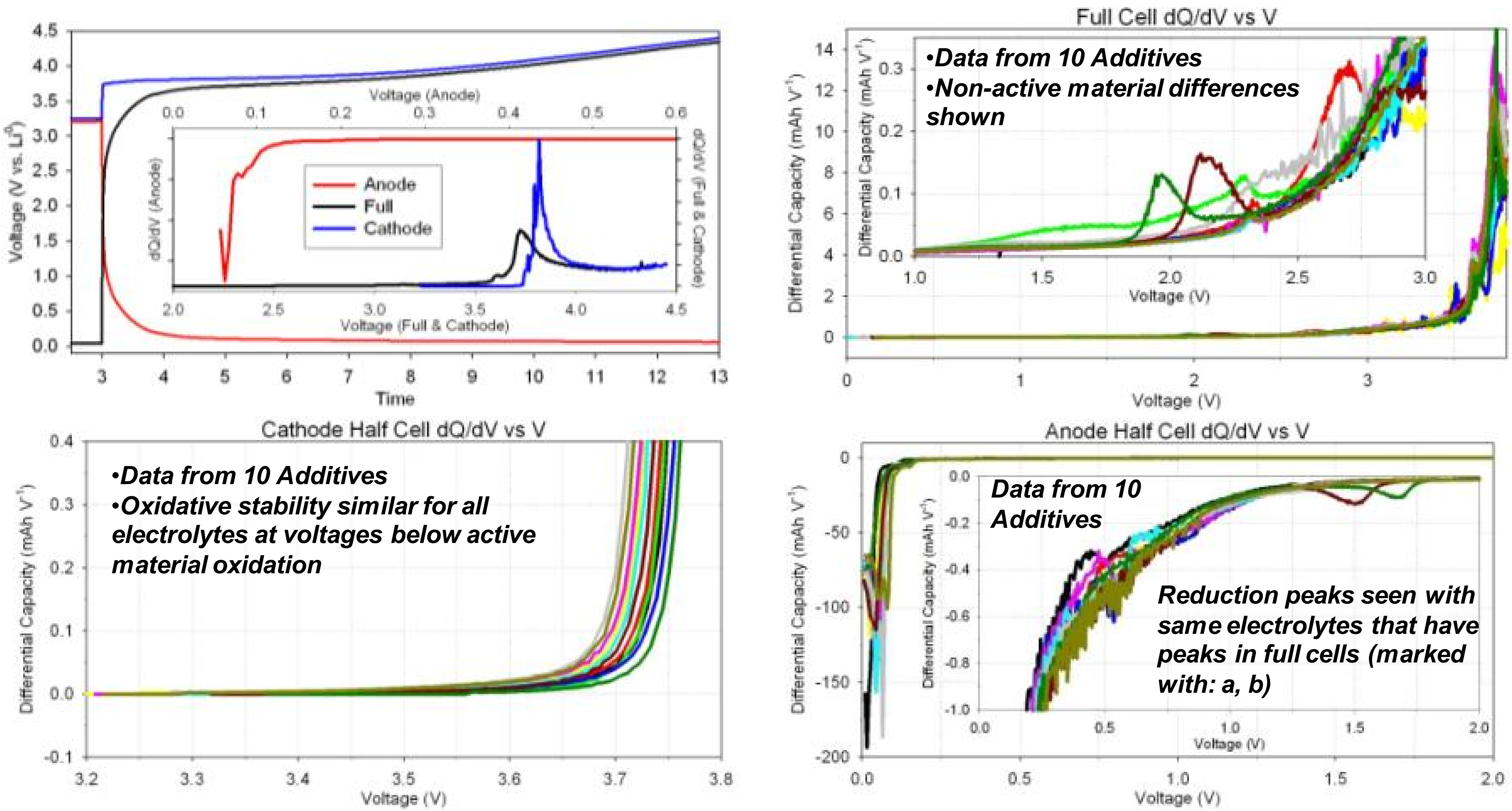


Both L-20446 and L-19869 are 3M's proprietary fluoro chemicals.

Identified Electrolytes to Help Improve Cycle Life of Si Anode and High Voltage Stability with HE NMC Cathode.

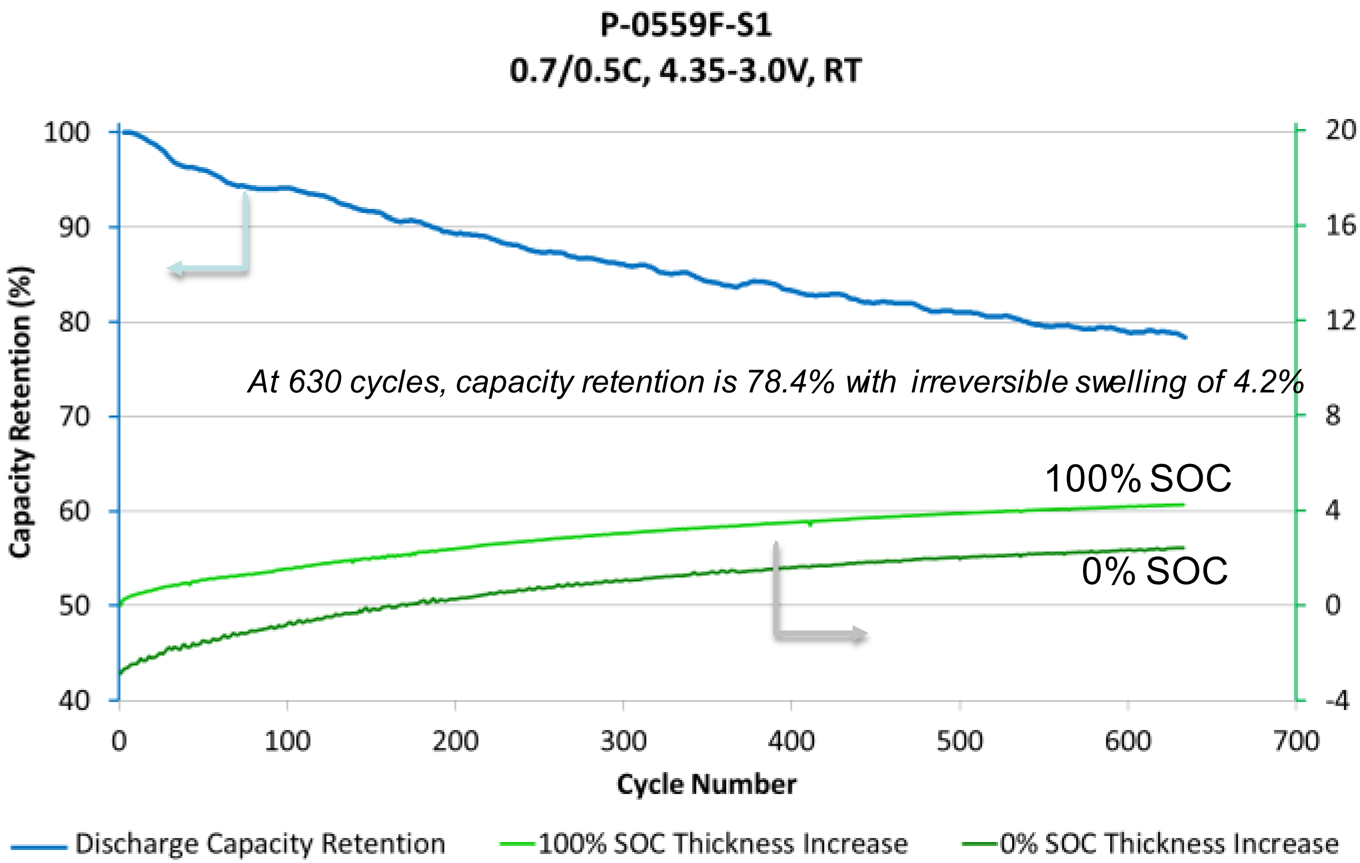
Technical Accomplishments and Progress

Electrolyte Additive Screening (3-Electrode Cell)



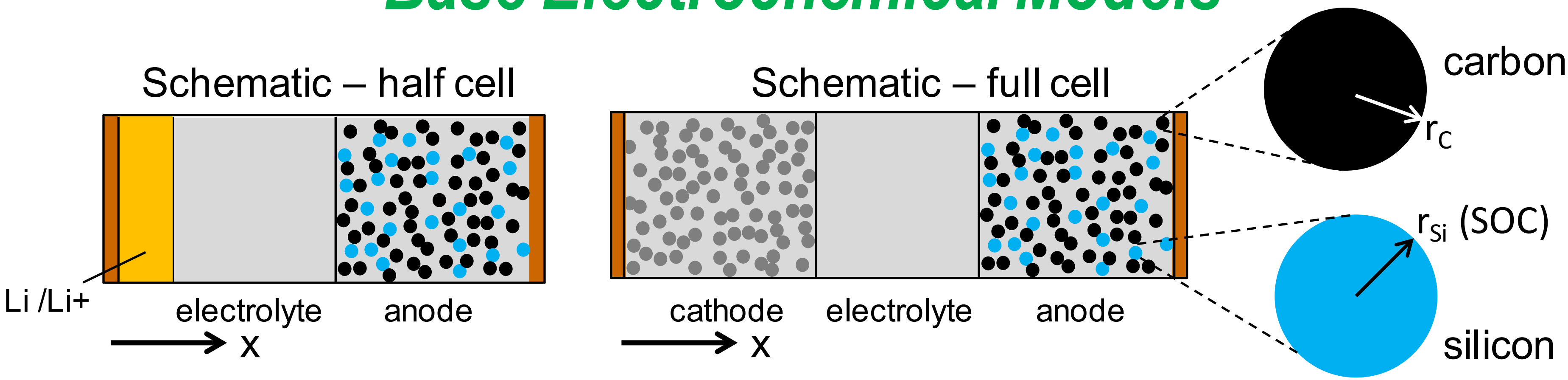
Multiple Additive Screening in Progress.

Cycle Life of 650Wh/L (C/10) Pouch Cell



Leveraging Leyden's Cell Design Methodology to Build Prototype Pouch Cells.

Base Electrochemical Models



- Newman-type Pseudo-2D model: x and r
- Ohm's law, Fick's law, and Butler-Volmer kinetics
- Model formulated in COMSOL Multiphysics®

  - **Two active material model for anode**
  - **Anode thickness and particle size depends on the state of charge**

- Half-cell model for tuning anode properties
- Full-cell model for evaluating performance

Modeling of the Electrochemical Couple in Progress.

GM RESEARCH & DEVELOPMENT

Electrochemical Model: Multiple Active Materials

Anode

Ohm's law for solid phase

$$\frac{\partial}{\partial x}\left(-K_{eff_a}^{(1)}\frac{\partial}{\partial x}\phi_a^{(1)}\right)=-\sum_{l=1}^{N}a_{a,l}i_{n_{a,l}}$$

Ohm's law for solution phase

$$\frac{\partial}{\partial x}\left(-K_{eff_a}^{(2)}\frac{\partial}{\partial x}\phi_a^{(2)}+\frac{2RT}{F}K_{eff_a}^{(2)}\left(1-t_+\right)\frac{\partial}{\partial x}\ln C_a^{(2)}\right)=\sum_{l=1}^{N}a_{a,l}i_{n_{a,l}}$$

Material balance in solution phase

$$\varepsilon_a^{(2)}\frac{\partial C_a^{(2)}}{\partial t}+\frac{\partial}{\partial x}\left(-D_{eff_a}^{(2)}\frac{\partial}{\partial x}C_a^{(2)}\right)=\frac{\left(1-t_+\right)}{F}\sum_{l=1}^{N}a_{a,l}i_{n_{a,l}}$$

Material balance in solid phase (i = 1 to N)

$$\frac{\partial C_{a,l}^{(1)}}{\partial t}+\frac{1}{r^2}\frac{\partial}{\partial r}\left(-r^2D_{a,l}^{(1)}\frac{\partial}{\partial r}C_{a,l}^{(1)}\right)=0$$

$$r=0 \qquad \frac{\partial C_{a,l}^{(1)}}{\partial r}=0$$

$$r=R_{p_{a,l}} \qquad -D_{a,l}^{(1)}\frac{\partial C_{a,l}^{(1)}}{\partial r}=j_{n_{a,l}}=\frac{i_{n_{a,l}}}{F}$$

Butler-Volmer equation for intercalation reaction (i = 1 to N)

$$i_{n_{a,l}}=i_{0_{a,l}}\left\{\exp\left(\frac{F}{2RT}\eta_{a,l}\right)-\exp\left(-\frac{F}{2RT}\eta_{a,l}\right)\right\}$$

$$i_{0_{a,l}}=k_{0_{a,l}}\sqrt{C_a^{(2)}\left(C_{\max_{a,l}}^{(1)}-C_{s_{a,l}}^{(1)}\right)C_{s_{a,l}}^{(1)}}$$

$$\eta_{a,l}=\phi_a^{(1)}-\phi_a^{(2)}-V_{0_{a,l}}$$

Electrolyte/Separator

Ohm's law for solution phase

$$\frac{\partial}{\partial x}\left(-K_{eff_e}^{(2)}\frac{\partial}{\partial x}\phi_e^{(2)}+\frac{2RT}{F}K_{eff_e}^{(2)}\left(1-t_+\right)\frac{\partial}{\partial x}\ln C_e^{(2)}\right)=0$$

Material balance in solution phase

$$\varepsilon_e^{(2)}\frac{\partial C_e^{(2)}}{\partial t}+\frac{\partial}{\partial x}\left(-D_{eff_e}^{(2)}\frac{\partial}{\partial x}C_e^{(2)}\right)=0$$

Model formulated in COMSOL®

Cathode

Ohm's law for solid phase

$$\frac{\partial}{\partial x}\left(-K_{eff_c}^{(1)}\frac{\partial}{\partial x}\phi_c^{(1)}\right)=-\sum_{l=1}^{N}a_{c,l}i_{n_{c,l}}$$

Ohm's law for solution phase

$$\frac{\partial}{\partial x}\left(-K_{eff_c}^{(2)}\frac{\partial}{\partial x}\phi_c^{(2)}+\frac{2RT}{F}K_{eff_c}^{(2)}\left(1-t_+\right)\frac{\partial}{\partial x}\ln C_c^{(2)}\right)=\sum_{l=1}^{N}a_{c,l}i_{n_{c,l}}$$

Material balance in solution phase

$$\varepsilon_c^{(2)}\frac{\partial C_c^{(2)}}{\partial t}+\frac{\partial}{\partial x}\left(-D_{eff_c}^{(2)}\frac{\partial}{\partial x}C_c^{(2)}\right)=\frac{\left(1-t_+\right)}{F}\sum_{l=1}^{N}a_{c,l}i_{n_{c,l}}$$

Material balance in solid phase (i = 1 to N)

$$\frac{\partial C_{c,l}^{(1)}}{\partial t}+\frac{1}{r^2}\frac{\partial}{\partial r}\left(-r^2D_{c,l}^{(1)}\frac{\partial}{\partial r}C_{c,l}^{(1)}\right)=0$$

$$r=0 \qquad \frac{\partial C_{c,l}^{(1)}}{\partial r}=0$$

$$r=R_{p_{c,l}} \qquad -D_{c,l}^{(1)}\frac{\partial C_{c,l}^{(1)}}{\partial r}=j_{n_{c,l}}=\frac{i_{n_{c,l}}}{F}$$

Butler-Volmer equation for intercalation reaction (i = 1 to N)

$$i_{n_{c,l}}=i_{0_{c,l}}\left\{\exp\left(\frac{F}{2RT}\eta_{c,l}\right)-\exp\left(-\frac{F}{2RT}\eta_{c,l}\right)\right\}$$

$$i_{0_{c,l}}=k_{0_{c,l}}\sqrt{C_c^{(2)}\left(C_{\max_{c,l}}^{(1)}-C_{s_{c,l}}^{(1)}\right)C_{s_{c,l}}^{(1)}}$$

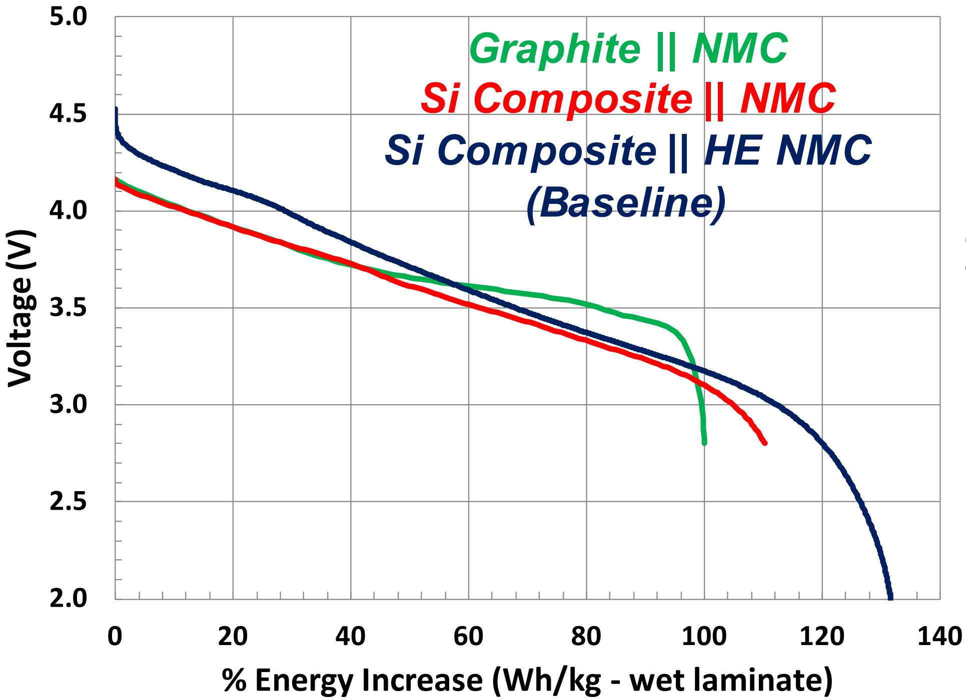
$$\eta_{c,l}=\phi_c^{(1)}-\phi_c^{(2)}-V_{0_{c,l}}$$

- Superscripts *(1)* and *(2)* refer to solid and solution phases, respectively.
- Subscripts *a*, *e* and *c* refer to anode, electrolyte/separator and cathode regions, respectively.
- **Subscript *i* (= 1 to N) refers to different active materials**

Technical Accomplishments and Progress

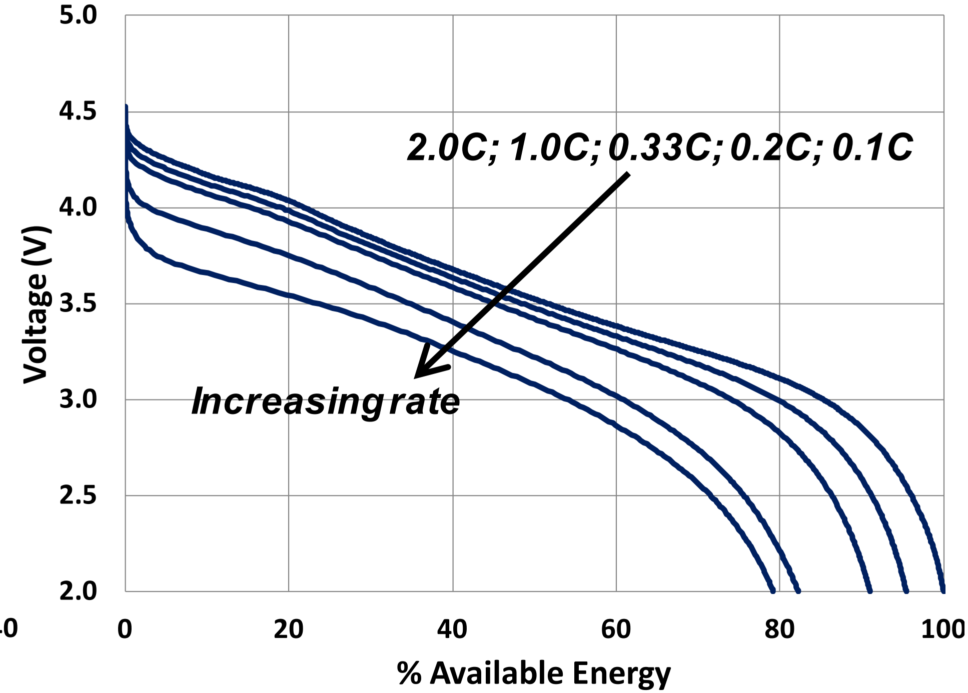
Baseline Cell Design

Energy Comparison



Rate Test (Si || HE NMC)

Normalized to 0.1C



Baseline Design Shows Energy Improvement and Good Rate Capability.

Responses to Previous Year Reviewers' Comments

- *N/A*
- *Project Awarded Fall 2013*

Collaboration and Coordination

- **3M**
  - Sample Electrodes (ARL, Leyden, GM), Si Alloy Anode Powder (Leyden, GM, LBNL), High Energy NMC Cathode Powder (Leyden, GM) and Cells (GM).
- **ARL**
  - Develop and Sample Electrolyte and Additives (3M, Leyden).
- **GM**
  - Evaluate, Analyze and Diagnose Cells (3M, Leyden).
- **LBNL**
  - Optimize and Evaluate Binder Chemistry for Si Alloy Anode (3M).
  - Binder Scale up (3M) for Testing in 18650 and Pouch Cells.
- **Leyden Energy**
  - Optimize Composite Electrodes and Pouch Cells. Sample Cells (GM, 3M).
- **Umicore**
  - Optimize Process and Scale Up Cathode Material. Sample Materials (3M).

Remaining Challenges / Barriers

- **Si Alloy Anode**
  - Full Cell Capacity Retention and Expansion over Life
- **Binder: Si Alloy Anode**
  - Binder characterization in 18650 / Pouch Cells
- **High Energy NMC Cathode**
  - Voltage Stability over Life
- **Electrolyte and Additive**
  - High Voltage Stability with Cathode
  - Stable SEI formation with Anode
- **Material Production**
  - Process Optimization
- **18650 / Pouch cell**
  - Energy (Wh/kg and Wh/l)
  - Performance over Life

Proposed Future Work

- **Si Alloy Anode**
  - Develop and Down Select Anode Composition and Particle Morphology
- **Binder: Si Alloy Anode**
  - Optimize Binder Chemistry for Si Alloy Anode
- **HE NMC Cathode Material**
  - Develop and Down Select Cathode Composition and Particle Morphology
- **Electrolyte and Additives**
  - Identify Materials to Improve Active Material Performance
- **Material Production**
  - Scale up Materials in Commercially Viable Processes
- **18650 / Pouch Cell**
  - Optimize Cell Design and Electrode Formulation and Processing.
  - Benchmark and Optimize Cell Performance

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Summary

- **Initiated Collaborative Team R&D**
  - Anode and Cathode material development
  - Binder development at LBNL on 3M Si Alloy Anode
  - Cell modeling and preliminary cell testing at GM
  - Electrolyte and Additive screening at ARL
  - Preliminary cell assembly activities at Leyden
- **Successful Scaled up Baseline Active Materials**
  - High Energy NMC
  - Si Alloy Anode
- **Initiated Full Cell Testing of Baseline Materials**
  - Started Characterization cycles at 3M and GM
- **Initiated Pouch Cell Optimization at Leyden**
  - Formation optimization
  - Electrolyte Study