# Validation of Electrode Materials and Cell Chemistries

**Wenquan Lu (PI)**
**Q. Wu, J. Kubal, S. Trask, B. Polzin, J. W. Seo, S. B. Ha, J. Prakash, D. Dees, and A. Jansen**

**Electrochemical Energy Storage**
**Chemical Sciences and Engineering Division**
**Argonne National Laboratory**

**Vehicle Technologies**
**Annual Merit Review and Peer Evaluation**
**Washington, D.C.**
**May 13th – 17th , 2013**

Project ID: ES028

***Vehicle Technologies Program***

# Overview

## Timeline

- Start – Oct. 2012
- Finish – Oct. 2014
- Percent complete: 25%

## Barriers

- An overwhelming number of materials are being marketed by vendors for Lithium-ion batteries.
- No commercially available high energy material to meet the 40 mile PHEV application established by the Freedom CAR and Fuels Partnership.

## Budget

- Total project funding in FY2013: $550K (as part of CFF effort)
- 100% DOE

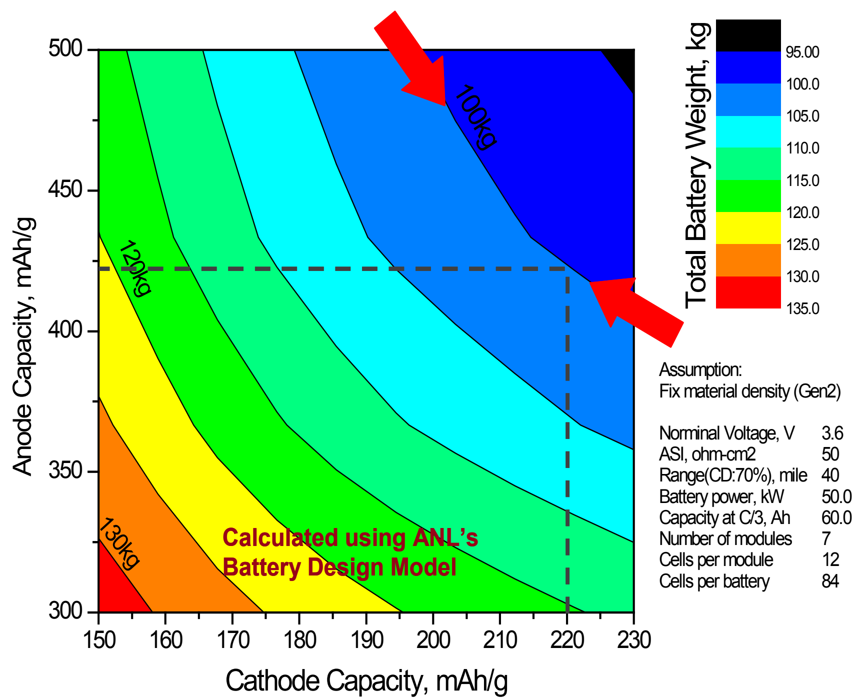
## Partners and Collaborators

- Cell Fabrication Facility (Andrew Jansen, ANL)
- Materials Engineering Research Facility (Gregory Krumdick, ANL)
- Post Test Facility (Ira Bloom, ANL)
- Prof. Prakash's group (IIT)
- Industries, Research institutes, and Universities

# Objectives

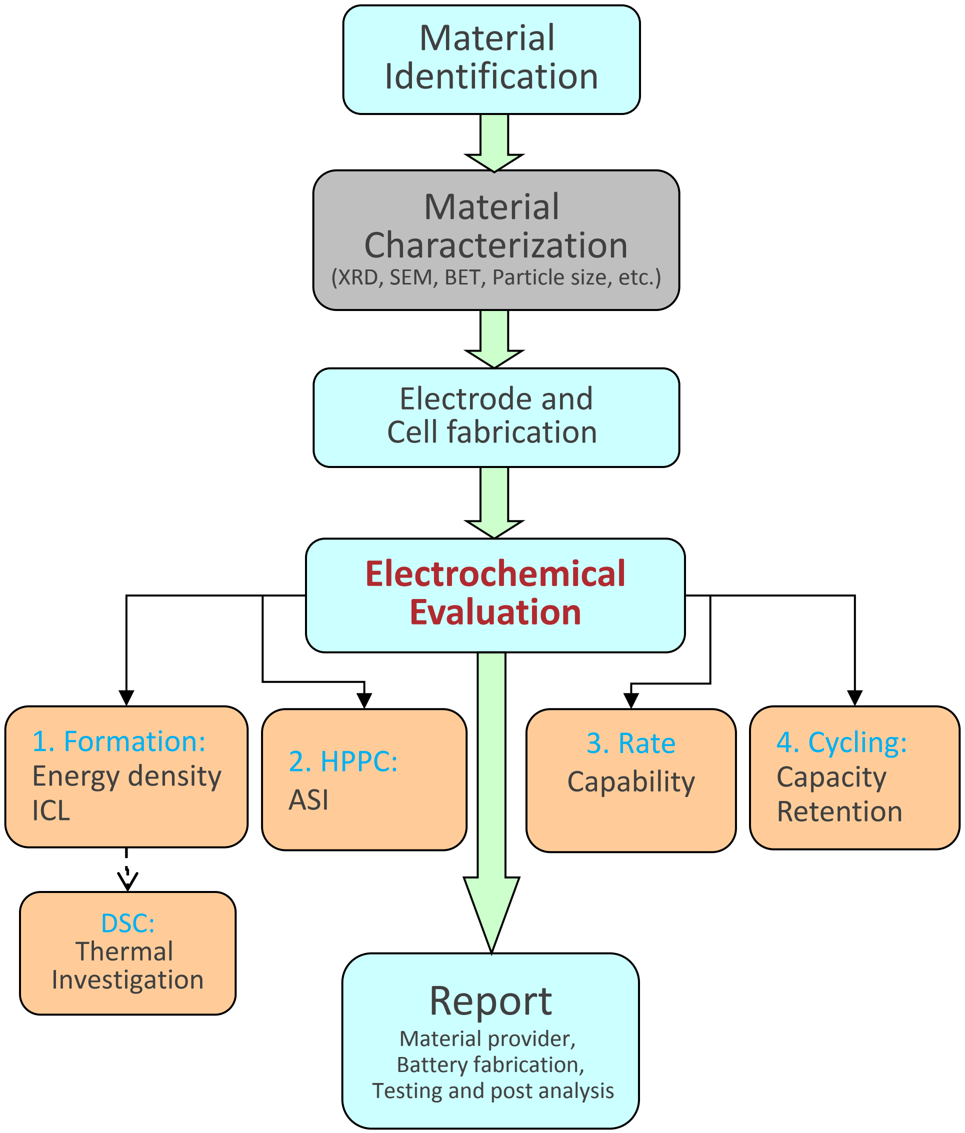
- To identify and evaluate low-cost cell chemistries that can simultaneously meet the life, performance, abuse tolerance, and cost goals for Plug-in HEV application.
- To aid the material scale up under Material engineer and research facility (MERF) and electrode library development under cell fabrication facility (CFF), respectively.

Material Requirements for PHEV40




- To enhance the understanding of advanced cell components on the electrochemical performance and safety of lithium-ion batteries.

# Approach: Test Protocol



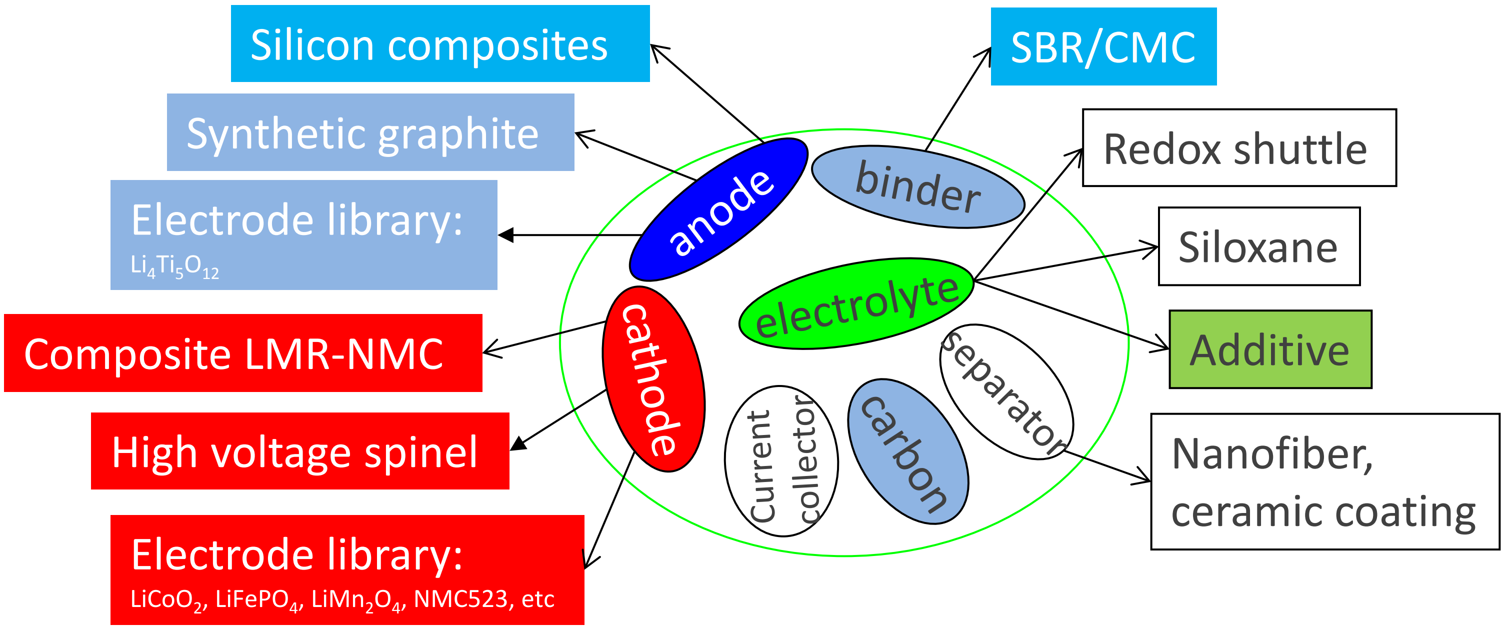

### USABC Requirements of Energy Storage Systems for PHEV

| Characteristics at EOL (End of Life) | | High Power/Energy Ratio | High Energy/Power Ratio |
|---|---|---|---|
| | | | |
| Reference Equivalent Electric Range | miles | 10 | 40 |
| Peak Pulse Discharge Power (10 sec) | kW | 45 | 38 |
| Peak Regen Pulse Power (10 sec) | kW | 30 | 25 |
| Available Energy for CD (Charge Depleting) Mode, 10 kW Rate | kWh | 3.4 | 11.6 |
| Available Energy for CS (Charge Sustaining) Mode | kWh | 0.5 | 0.3 |
| Maximum System Weight | kg | 60 | 120 |
| Maximum System Volume | Liter | 40 | 80 |

- Electrochemical evaluation of electrode couple will be the focus of this project.
- In order to conduct the electrochemical characterization of the battery chemistries for advanced battery research (ABR) program, C rate and pulse current was calculated for coin cells according to PHEV 40 requirements.

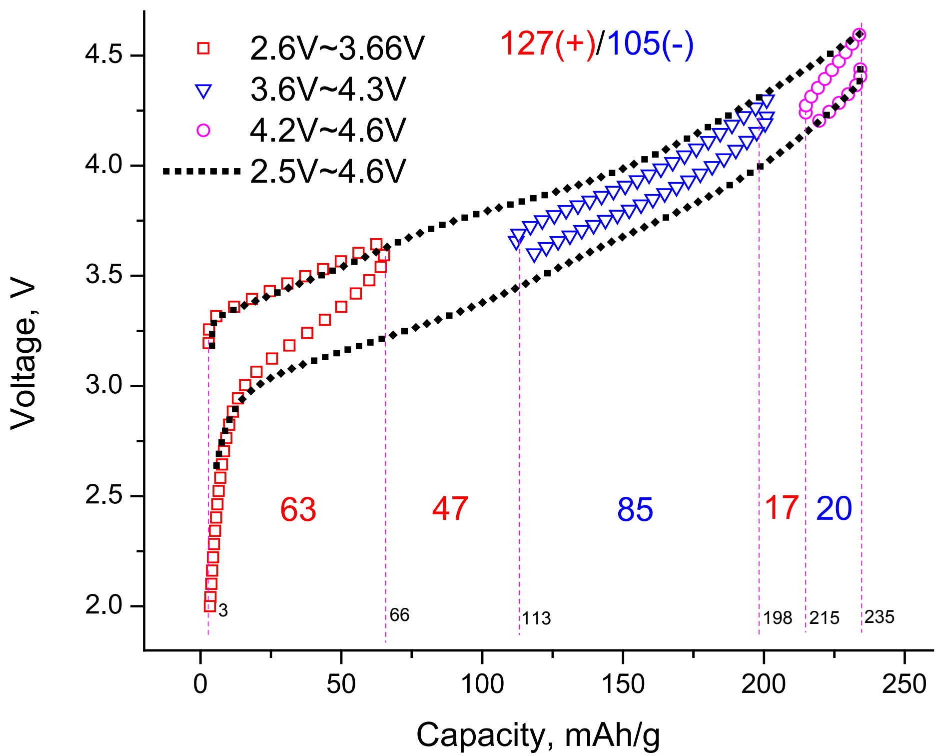
# Technical Accomplishments

- Several high energy cathode materials, composite cathode and high voltage spinel, have been identified and studied.
- Several silicon and its composite materials has been identified. The material validation work of silicon and its composite is incorporated with binder investigations.
- Other cell components, such as electrolyte and additives, conductive additive, binders, etc., have also been investigated.



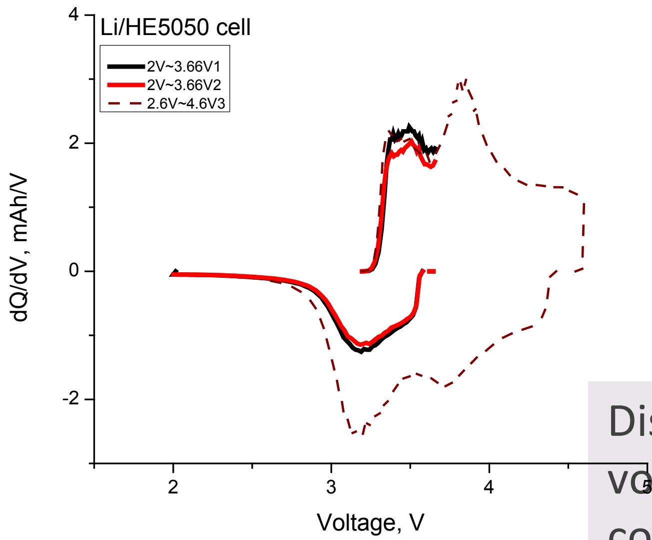
# Electrochemistry of Lithium Manganese Rich Metal Oxide (LMR-NMC)

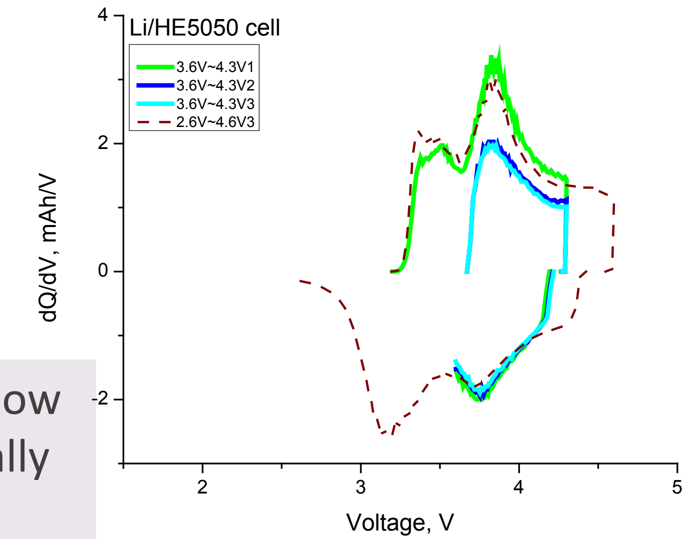
Several LMR-NMC materials have been investigated under material validation. In addition to their performance, in depth understanding of LMR-NMC was also attempted electrochemically to aid the material development.




- After formation, the electrode in half cell was cycled between three voltage windows:
  - Low: 2.0V ~ 3.66V
  - Mid: 3.6V ~ 4.3V
  - High: 4.2V ~ 4.6V
- The voltage profiles during 3rd cycle is plotted as function of specific capacity.
- Less hysteresis and reversible capacity at mid and high voltage windows.

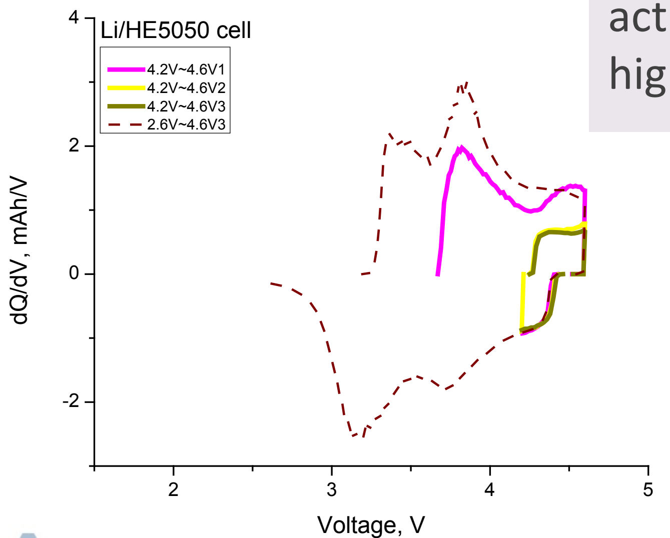
# Voltage Window Effect on Capacity Contribution

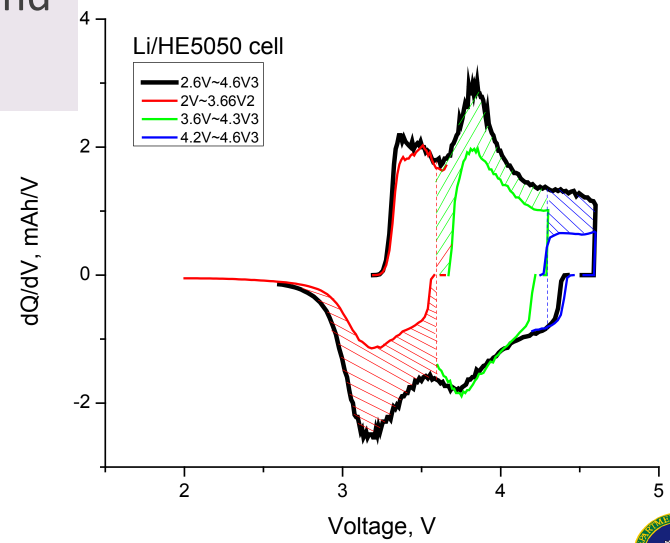



Low: 2.0V ~ 3.66V
Mid: 3.6V ~ 4.3V
High: 4.2V ~ 4.6V

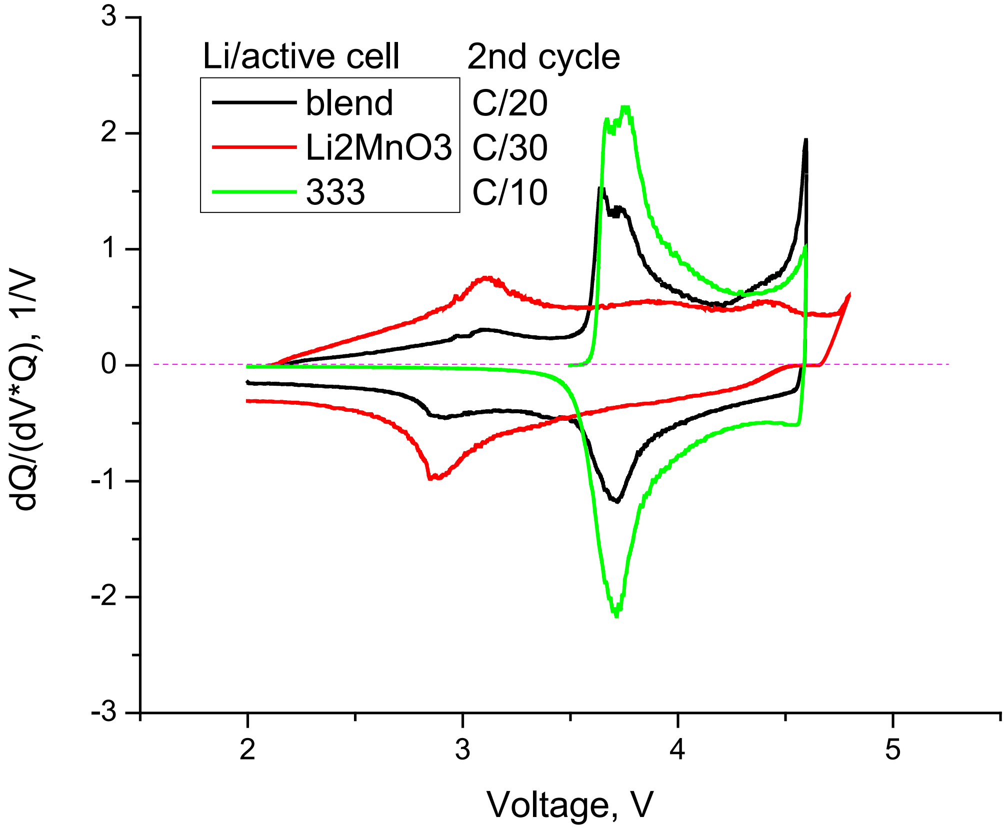
Discharge capacity in low voltage window partially comes from the activation during mid and high voltage window.

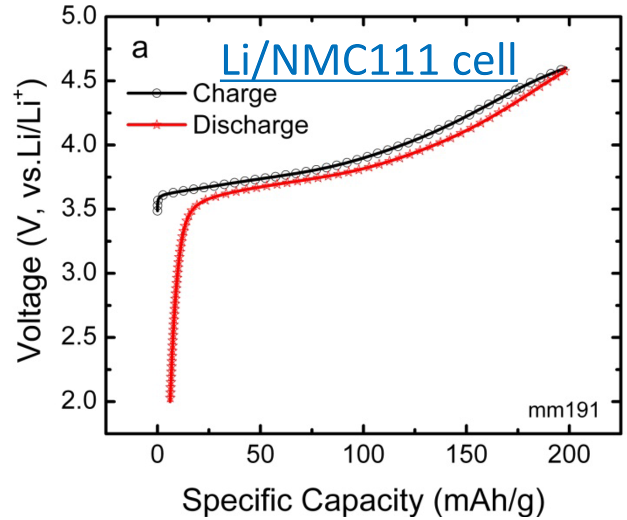


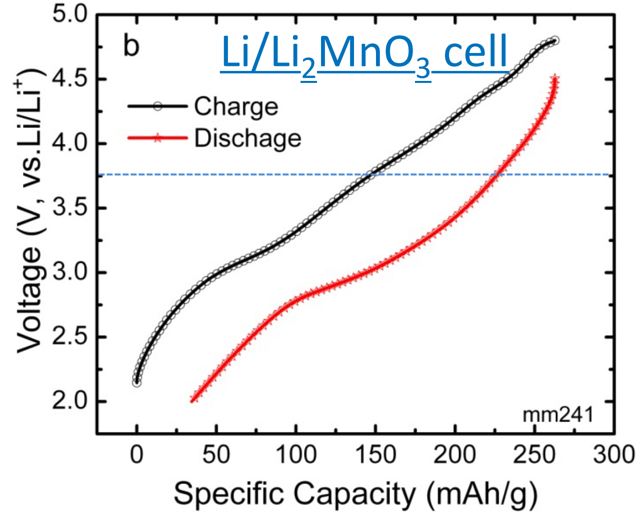



# Single Component Effect

Li/active ($Li_2MnO_3$, NMC, blend) cell



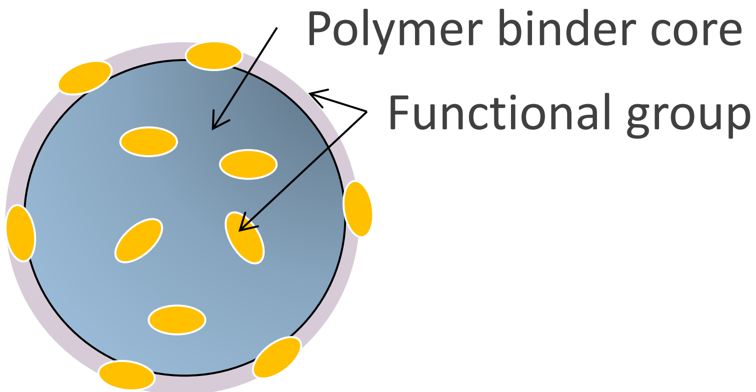




- According to the single component study, the blend of $Li_2MnO_3$ and $LiMO_2$ showed similar electrochemical performance as LMR-NMC. It is rational to speculate that the voltage fade and voltage hysteresis is caused by $Li_2MnO_3$ component.

# Aqueous Binders for Lithium Ion Battery

**Merits of aqueous binder**




Styrene-Butadiene Rubber (SBR)
Fluorine acrylic latex (FA)

**Technically**
- as electrode: high adhesion
- as battery: high capacity

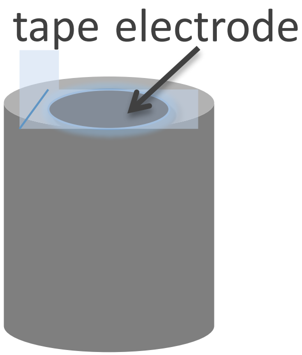
**Cost**
- Shorting drying
- Cheap material
- No recycling

**Environmentally**
- Organic solvent free

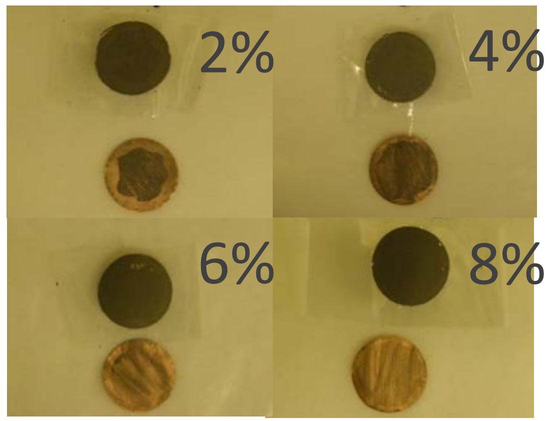
**Electrode Chemistries**

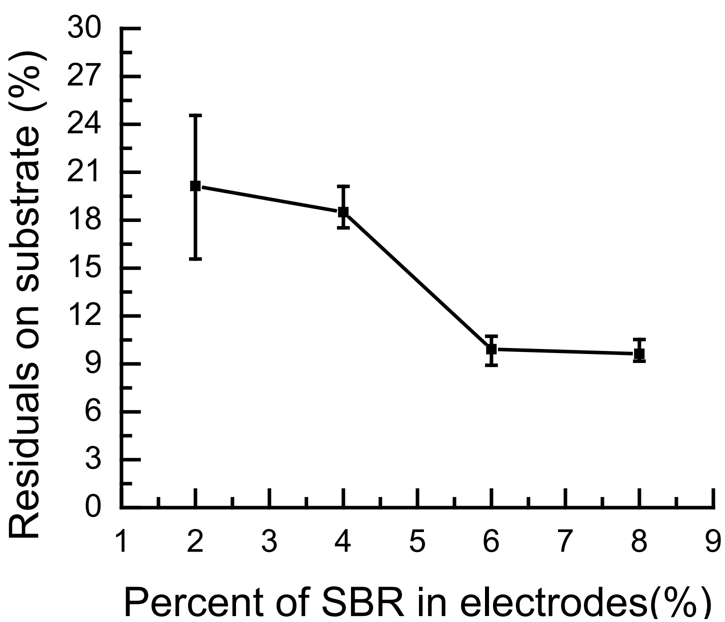
| Anode | Cathode |
|---|---|
| Graphite (A12, Phillips66 ) | LMR-NMC (HE5050, Toda) |
| SBR (TRD2001, JSR) | FA (TRD202A, JSR) |
| CMC (MAC350HC, Nippon Paper) | CMC (MAC350HC, Nippon Paper) |
| Carbon black (C45, Timcal) | Carbon black (C45, Timcal) |

# Effect of SBR on Graphite

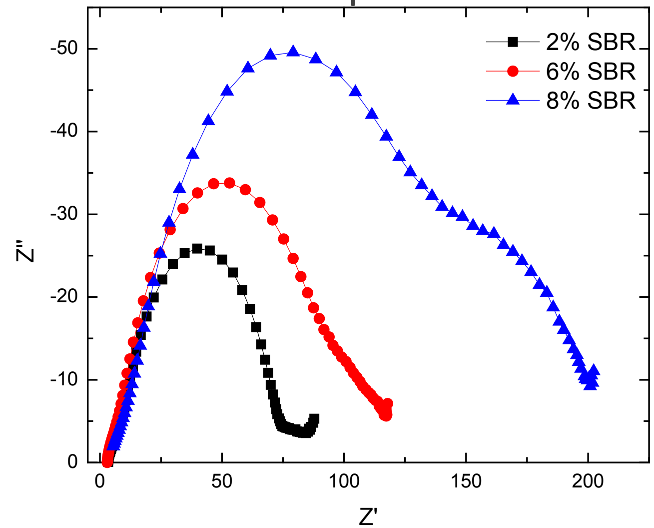



Peel test



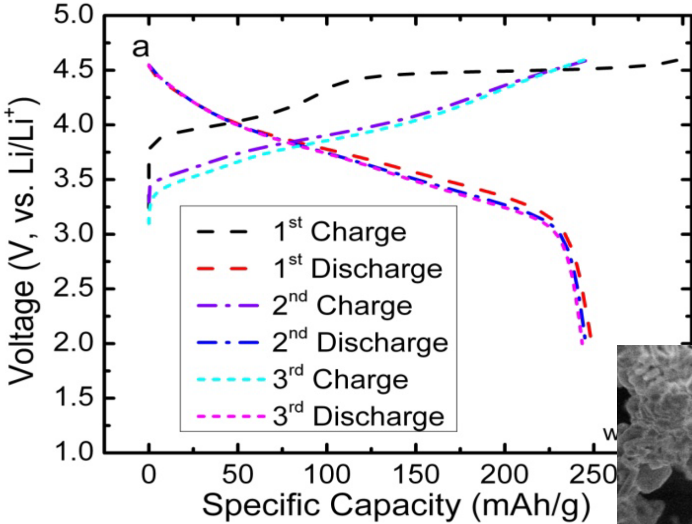



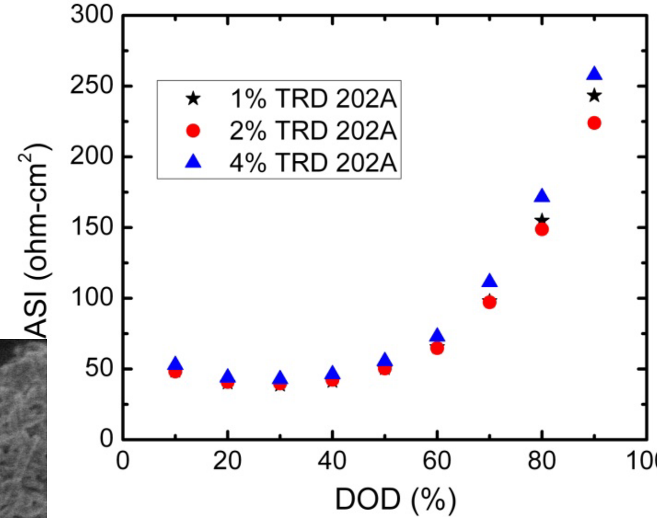

EIS spectra

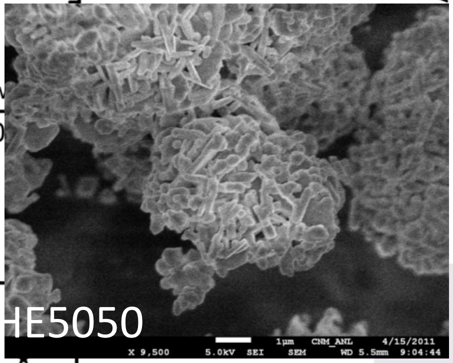


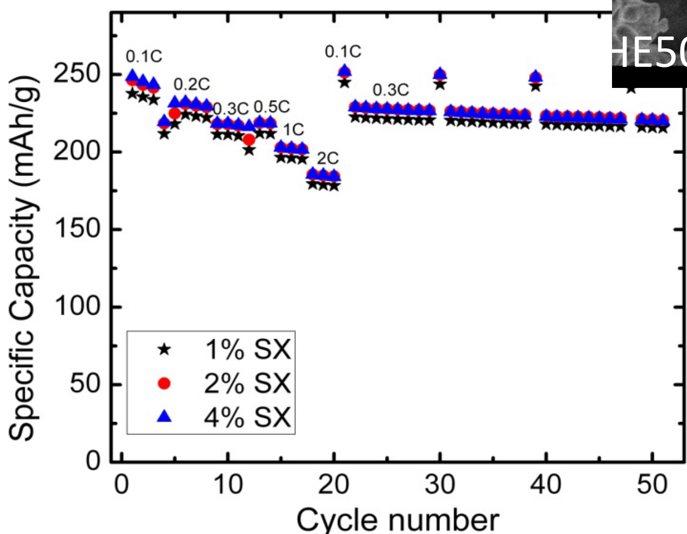

- Better adhesion and lower impedance were observed for the graphite electrode with lower SBR content, suggesting higher energy density of the cell.

# Fluorine Acrylic Latex Binder for Cathode



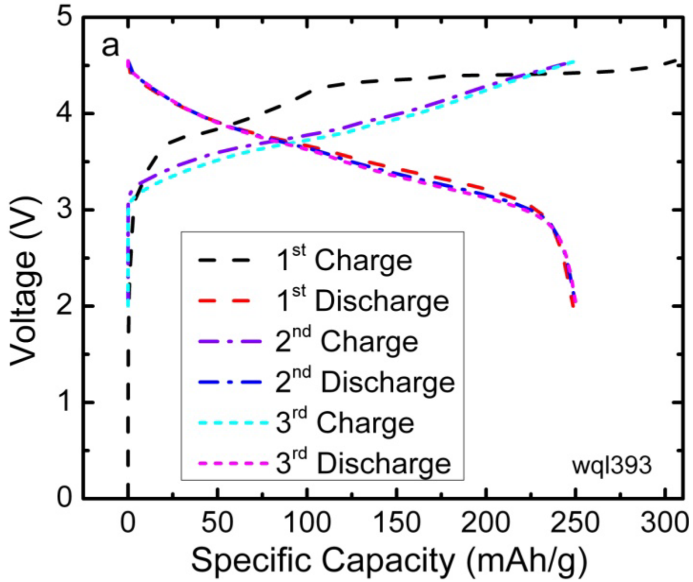




The HE5050 electrode with FA binder delivers

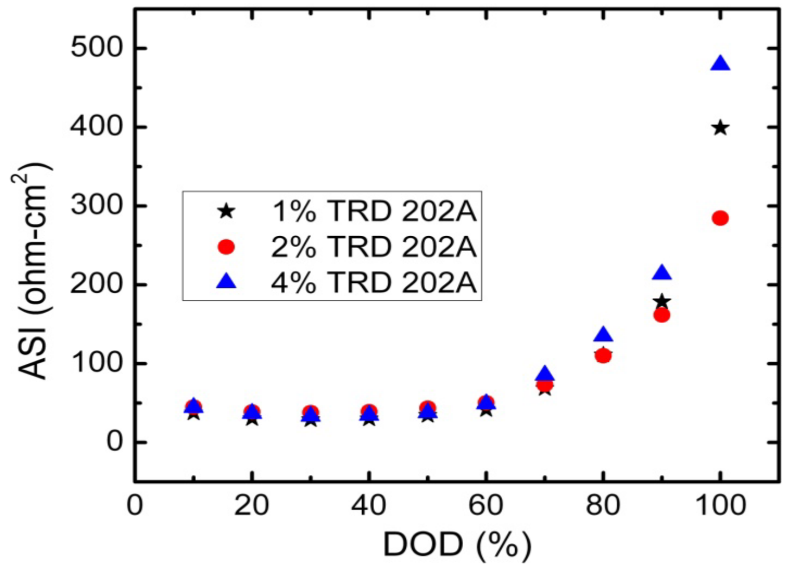
- high specific capacity 244 mAh/g,
- low Ohmic resistance <50 Ω•cm$^2$,
- excellent rate capability (> 178 mAh/g at 2C), and
- outstanding capacity retention (>87% after 50 cycles).

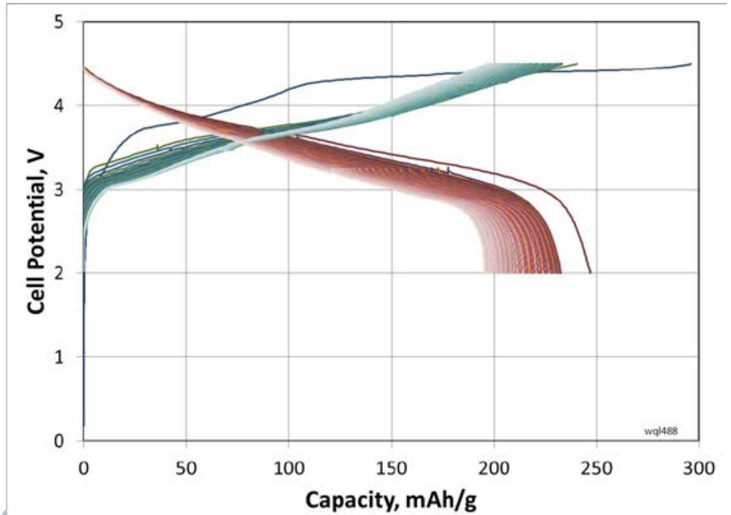
# Total Aqueous Binder Lithium Ion Battery

Formation




HPPC

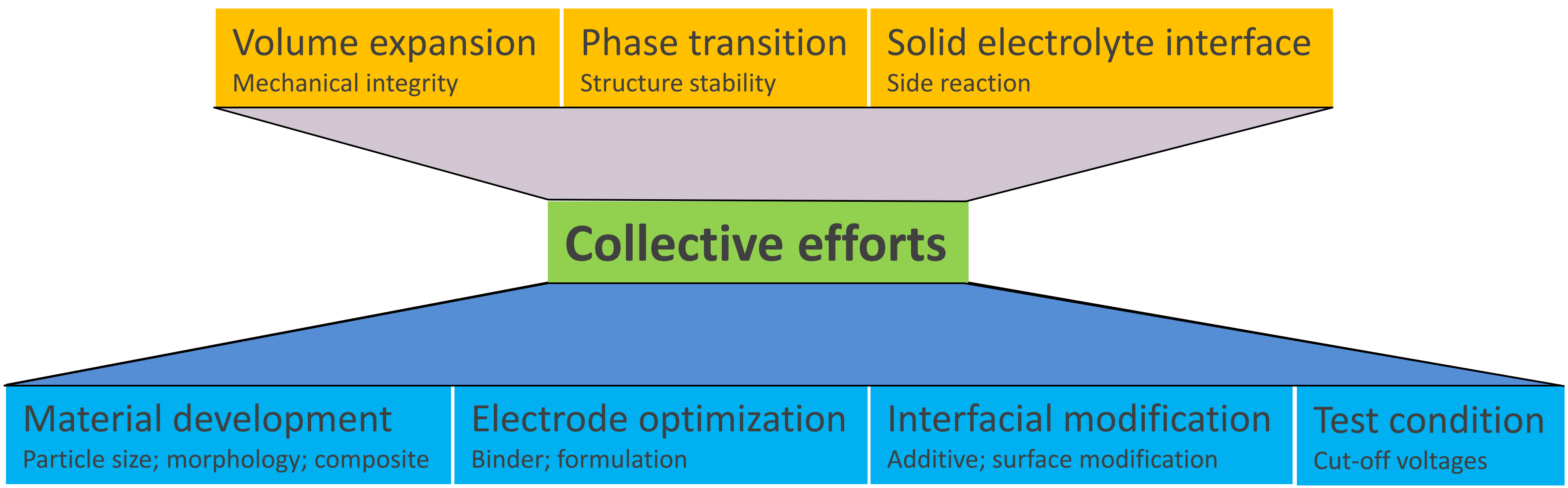



- Lithium ion battery with all aqueous binders for both anode and cathode were demonstrated.
- For graphite/LMR-NMC system, no obvious negative effect on electrochemical performance was observed.

# Silicon Electrode and Binder

- Silicon composite has a better chance to meet the energy requirements for PHEV40 due to its adjustable high capacity.
- In addition to material development, the success of silicon electrode for LIB needs collective efforts, including additive, binder, test protocol, electrode engineering.
- We has reported the additive effect last year and binder effect and electrode optimization will be the current focus.



# Silicon Electrode and Binder

Binders tested:

- Poly(vinylidenefluoride) (PVDF)
- Polyacrylic Acid (PAA)
- Na-Alginate
- Poly Amine Imide (PAI)
- carboxymethyl cellulose (CMC)
- Styrene-Butadiene Rubber (SBR)

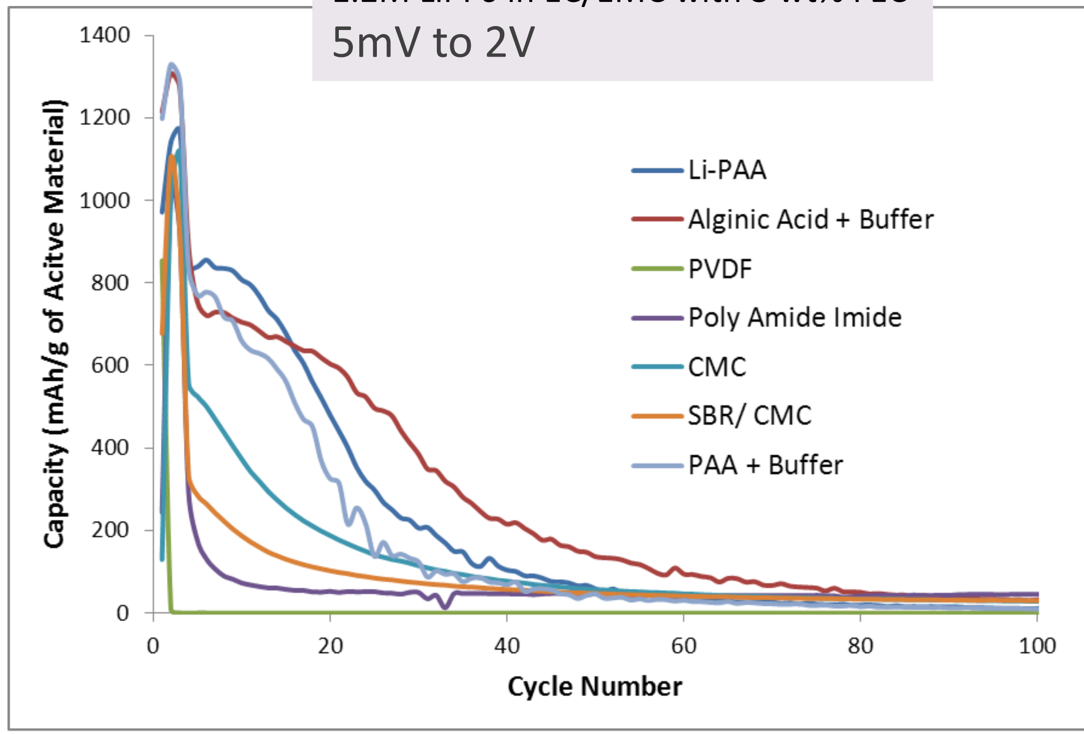
General Electrode composition

- 10% C-45
- 30% Silicon
- 45% A12 Graphite
- 15% Binder

Li/Si-C cell

1.2M $LiPF_6$ in EC/EMC with 3 wt% FEC

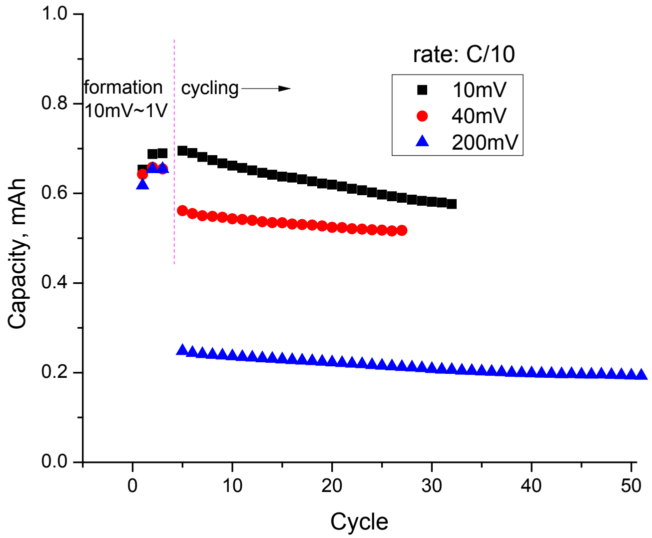
5mV to 2V

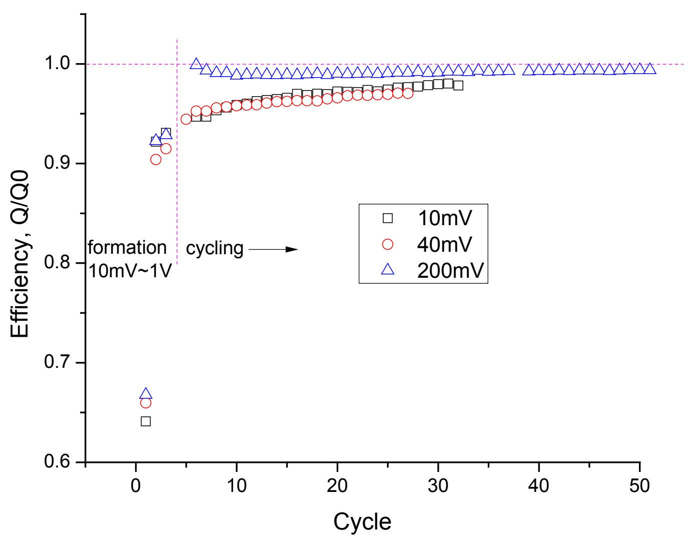



- Better cycle performances of silicon electrode were obtained when PAA and alginic acid binders were used as binder.

# Test Condition Effect on Silicon Electrode

Li/Si cell (Electrode provided by Dr. Liu, LBNL)
1.2M LiPF6 EC/EMC with 10% FEC




- Various cut off voltages was applied to the silicon electrode.
  - Lower cut-off voltage, more deliverable capacity and faster capacity fading.
  - Higher cut-off voltage, less deliverable capacity and lower capacity fading.
  - Coulombic efficiency increases with cycling.
  - Better coulombic efficiency was observed with higher cut-off voltage.

# Impact of Electrolyte on Silicon Electrode

Li/Si cell

Si/Alginic acid/Carbon = 76%/14%/10%

Citric acid buffer

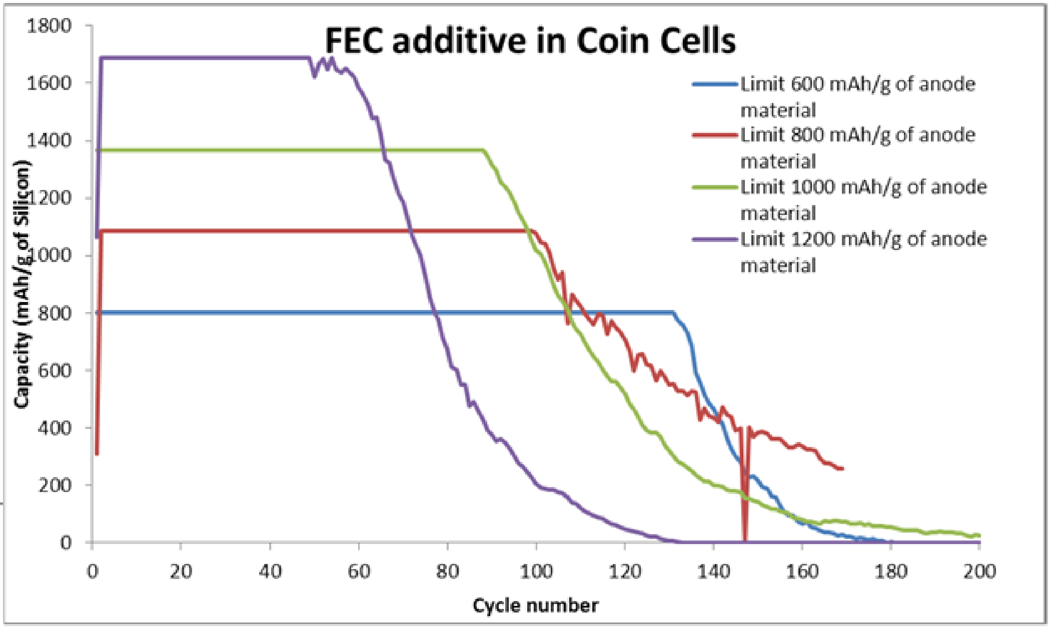
Limited capacity to various levels

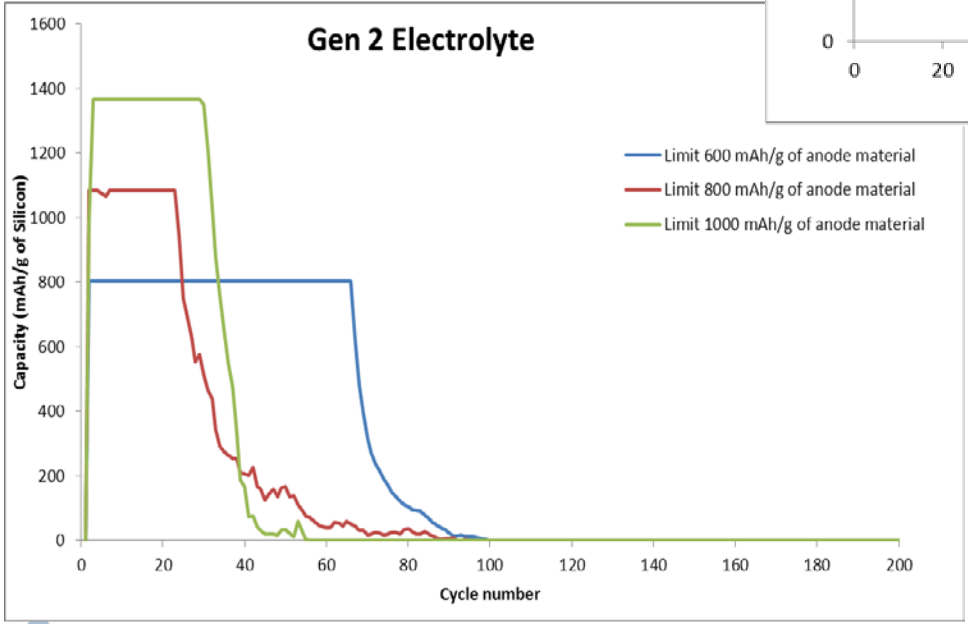
Rate: C/3 Charge/Discharge

Electrolyte:

1.2M LiPF6 EC/EMC

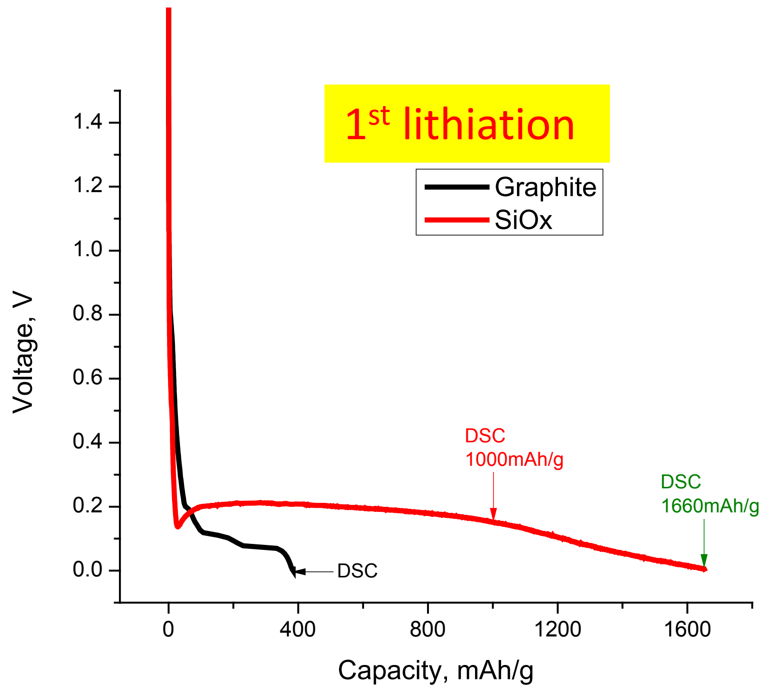
1.2M LiPF6 EC/EMC + 3% FEC

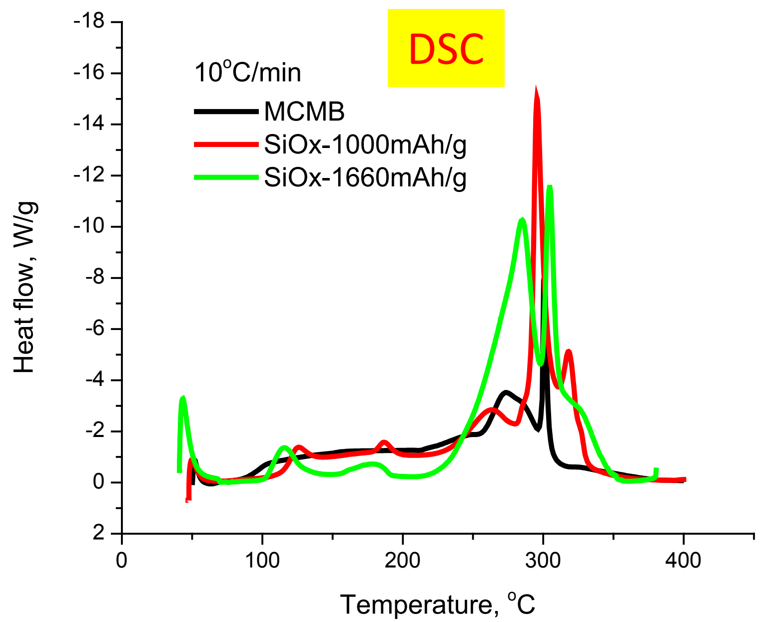



- The cycle life of silicon electrode increased 4 times by using 3% FEC as additive when 1000mAh/g specific capacity of silicon electrode was utilized.
- The better cycle life can be attributed the better SEI film formed by FEC.

# Thermal Property of Silicon Electrode




- Up to 250°C, lithiated SiOx showed similar heat flow during temperature scan with postponed on-set temperature.
- The on-set moves to lower temperature when more lithium is reacted with SiOx. In addition, the total heat generation was greater.

# Future Plan

- We will continue to evaluate the high energy density cathode materials, such as lithium manganese rich transition metal oxide (LMR-NMC), and high energy density anode materials, such as silicon/silicon composite, when they become available. For both high energy electrode materials, we will work closely with national labs and industries.
- Various electrode materials and cell chemistries will be evaluated under cell fabrication facility to help to build the electrode library.
- Materials scaled-up by Material Engineering and Research Facility (MERF) will be validated.

# Summary

- Lithium manganese rich transition metal oxide (LMR-NMC) was electrochemically charged and discharged in low, mid, and voltage windows. The differential capacity analysis indicates that the $Li_2MnO_3$ and $LiMO_2$ preserves its electrochemical features, with little off-set, in the composite. Component derived from $Li_2MnO_3$ after activation during 1$^{st}$ cycle could be responsible for the voltage hysteresis.
- The graphite/LMR-NMC cell using aqueous binders was fabricated and tested. The electrochemical performance of the cell with aqueous binders were determined to be equivalent to the cells with conventional PVDF binder.

# Summary

- Silicon and its composite was investigated as anode materials for lithium ion batteries. Binder and additive study is still in progress. The current results suggest that collective efforts, such as binder, additive, test protocol, and electrode engineering, are needed to address the challenges (cycle life and surface SEI formation).
  - Several silicon sources were identified and the evaluation process is in progress.
  - Preliminary DSC result indicated the comparable thermal stability of SiOx to graphite.
- Other cell components, such as redox shuttle, binder, separator, carbon additive have been studied and information was delivered to material supplier and internal facilities.
- Under CFF, several electrode library materials were collected and validated. Electrolyte and electrode materials from MERF were also validated.

# Contributors and Acknowledgments

- Abouimrane, Ali (ANL)
- Abraham, Daniel (ANL)
- Amine, Khalil (ANL)
- Belharouk, Ilias (ANL)
- Chen, Zonghai (ANL)
- Croy, Jason (ANL)
- Dees, Dennis (ANL)
- Dietz, Nancy (ANL)
- Gallagher, Kevin (ANL)
- Henriksen, Gary (ANL)
- Johnson, Christopher (ANL)
- Kubal, Joseph (ANL)
- Liu, Gao (LBNL)
- Liu, Bo (ANL)
- Polzin, Bryant (ANL)
- Scherson, Daniel (CWRU)
- Thackeray, Mike (ANL)
- Trask, Steve (ANL)
- Vaughey, Jack (ANL)
- Xu, Kang (ARL)
- Zhai, Dengyun (ANL)
- Zhang, John (ANL)
- Electron Microscopy Center (EMC)
- Jet Propulsion Lab

Support from David Howell and Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged.

- BTR (China)
- Cabot
- Phillips66
- Daikin Inc. (Japan)
- Dow Corning
- Dreamweaver
- Du Pont
- Electrochemical Materials
- Energy2
- Hanwha (Korea)
- JSR Micro(Japan/California)
- Kureha (Japan)
- Nanosys
- NEI corporation
- Nippon Paper (Japan)
- Porous Power Tech
- Silatronix
- Solrayo
- Solvay
- Toda Kogyo (Japan/Michigan)
- XG Sciences
- ZEON (Japan/Kentucky)