NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: CRUCIAL SUPPORTING MATERIALS ADVANCEMENTS

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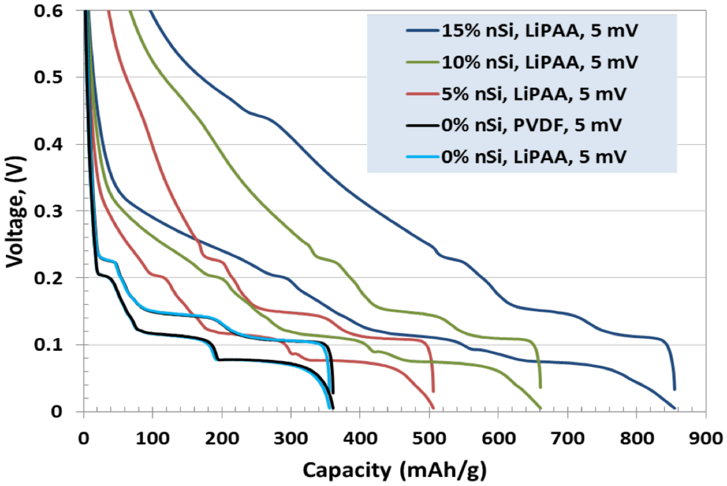
U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
2018 ANNUAL MERIT REVIEW

Silicon Deep Dive



Project ID BAT353

OVERVIEW

Timeline

- Start: October 1, 2015
  - Reset: October 1, 2017
- End: September 30, 2020
- Percent Complete: 55%

Budget

- Total project funding:
  - FY18 - $3600K
- Presentations: BAT349, BAT350, BAT351, BAT352, and BAT353

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

Partners

- Sandia National Laboratories
- Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

RELEVANCE

Objectives:

- **Stabilized SEI layer via new electrolyte additives**
- **Accommodate large volume change Si materials in the electrode via new electrode binders**
- **Compensate for the large first-cycle loss of lithium in the Si electrode via improving lithium inventory**
- **Improve overall Si electrode capacity retention to improve battery cycle life.**

Projects directly addresses performance barriers in low energy density, short cycle life, and high cost issues

- Elemental silicon can theoretically store >3500 mAh/g, but has over 300% volume change during cycling. This large volume change disrupts SEI layer. Electrolyte additives can enhance the SEI properties to withstand the large volume change during cycling.
- The large volume change also disrupts the electrode integrity during cycling leading to premature electrode failure. Functional electrode binders with higher adhesion force and advance properties provide more robust adhesion to improve electrode stabilities.
- Si composite materials such as SiO have large first cycle loss (>30%), leading to lower energy density of Si based battery. Compensating for the first cycle capacity loss during electrode and cell fabrication process can significantly improve cell energy density and cycling stabilities.

MILESTONES AND ACTIVITIES

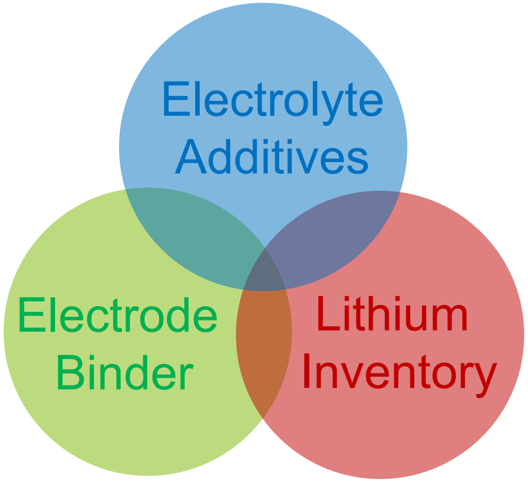
- **The program has more than twenty milestones related to the broad range of integrated activities listed below.**
- **Generally, milestones are either completed or on schedule.**

- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP) Facility; Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals.

For reviewers, a detailed list of the milestones and progress is supplied in the reviewers only slides.

APPROACH

- Use materials synthesis to develop new functional materials as critical supporting components such as electrolyte (additives), electrode binders and lithium additives for Si based batteries.
- Use advanced characterization techniques such as NMR, XRD and neutron scattering to characterize these materials.
- In collaboration with battery user facilities to fabricate electrodes and cells to accurately evaluate these materials.



APPROACH (CON)

Electrolyte Additives

- Design and synthesis of organic compounds as electrolyte additives for Si electrode.
- Use diagnostic methods and battery testing to analyze the additives in the electrochemical system.

Electrode Binders

- The lithiation effect of poly(acrylic acid) (PAA) based binders has been investigated and correlated to the cycling performance of silicon/graphite anode batteries.
- Synthetic efforts to improve the mechanical properties of the polymer binders have been conducted via modifications of the repeating units and the macrostructures.
- Use neutrons to probe the Si-PAA binder interface chemistry.
- Using emulsion polymerization to synthesize functional binder latex solution.

Lithium Inventory

- Optimize Li-source additive Li_5FeO_4 (LFO) synthesis; scale-up with MERF.
- Implement and characterize Li-source additive in positive electrode.
- Determine and understand Li loss in conjunction with diagnostic analysis.
- Conduct modeling to predict lifetime & energy density improvement by Li inventory control & optimize ratio balance.
- Use chemistry to prelithiate Si powders or electrodes.

ELECTROLYTE ADDITIVES - TOOLBOX

Design and Synthesis of bifunctional electrolyte additives for Si based electrode

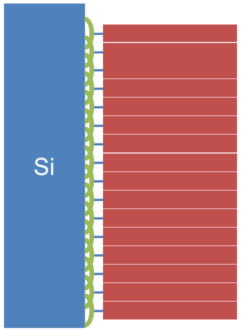
Bifunctional electrolyte additive

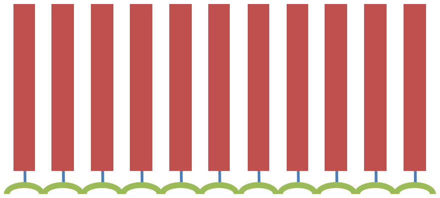
Functional group provide surface properties

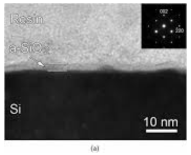
Reaction group with Si surface

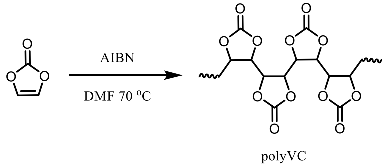
Independent polymers

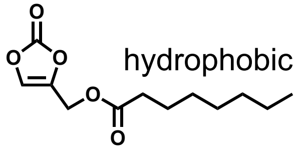
1. Materials surface coatings to protect Si particles, such as ALD.
2. Organic surface modification of the Si surfaces
3. Electrode surface coatings to protect the Si electrode, such as ALD, MLD coating
4. Electrolyte additives such as FEC, VC or siloxane compounds

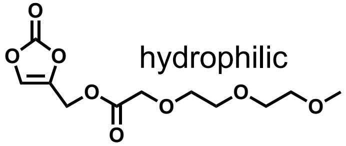












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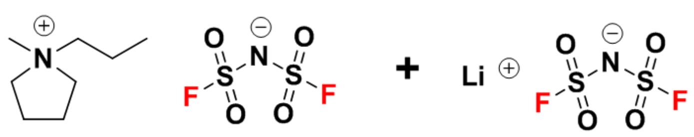
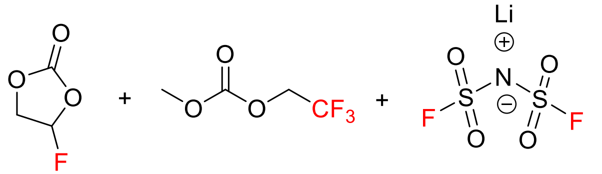
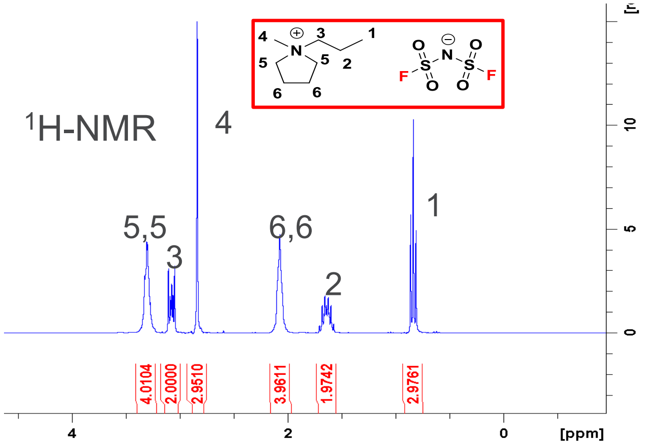
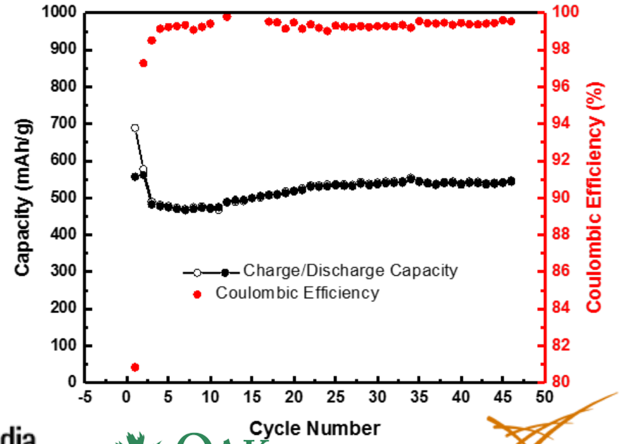
ELECTROLYTE ADDITIVES - LIFSI BASED ELECTROLYTES FOR SI ANODE

Pyrrolidinium-Based Ionic Liquids and Fluorinated Electrolytes

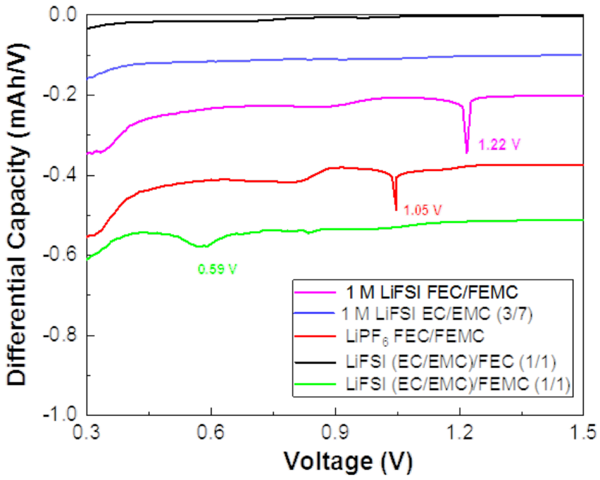








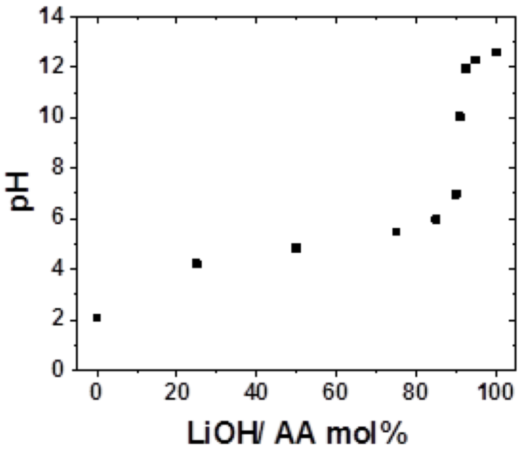
Li/Si half cell



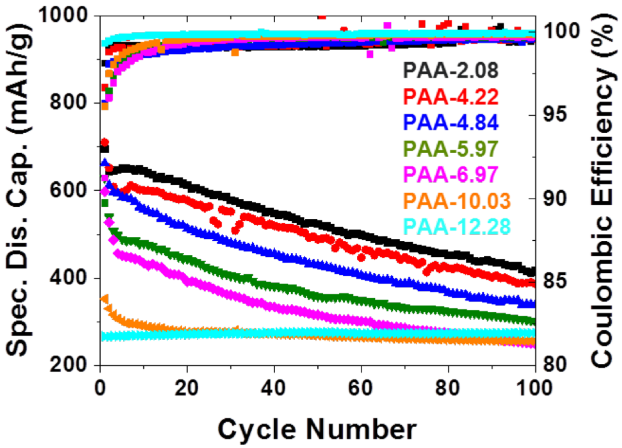
- Pyrrolidinium-FSI/LiFSI electrolyte passivates graphite anode and showed good cyclability on Si-Graphite anode.
- Gen 2 electrolyte does not passivate Si anode.
- LiFSI-based fluorinated electrolyte passivates Si anode.
- Si passivation originates from the fluorinated linear carbonate FEMC.

ELECTRODE BINDERS - LITHIATION STUDY OF PAA BINDERS

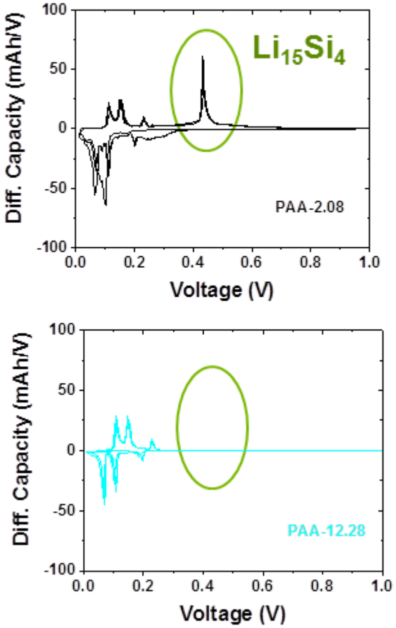
A PAA polymer with Mn of 175 KDa was titrated with LiOH in the range of 0 to 100 mol % and the resulting LiPAAs were evaluated in half cells using 15% Si-Graphite anode.



Plot of pH values vs lithiation percentage of the titrated PAA solutions (10w%)



Specific discharge capacity profiles (to the left) and coulombic efficiency profiles (to the right) of half cells using the titrated PAA samples over 100 cycles at C/3 rate;



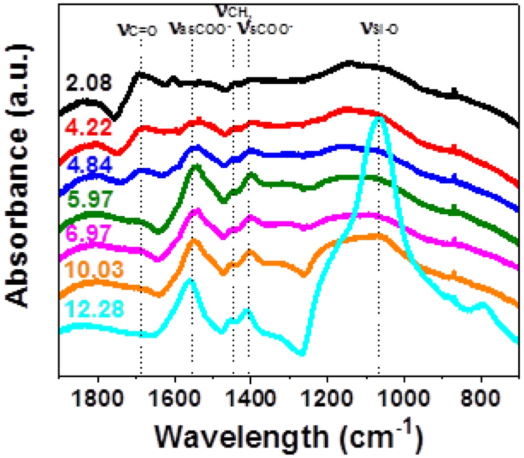
Differential capacity profiles of the formation cycles of half cells using PAA binders with pH values of 2.08 and 12.28.

Lithiation of PAA binders indeed impacted the cycling performance of silicon-graphite anodes and the half cell results indicated that less lithiation seems to afford better performance.

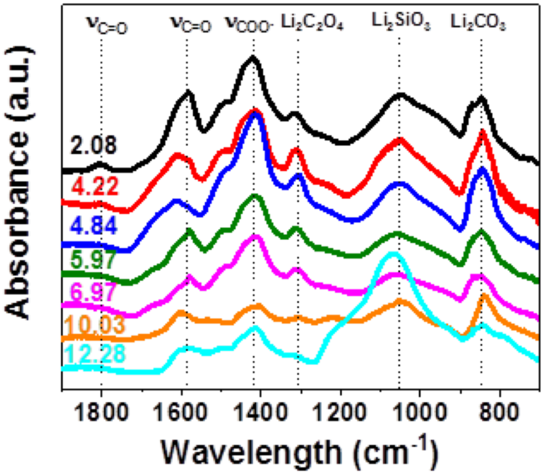
ELECTRODE BINDERS – ELECTRODE CHARACTERIZATIONS

FT-IR spectra of pristine and cycled Si-C electrodes

Pristine electrodes



Cycled electrodes

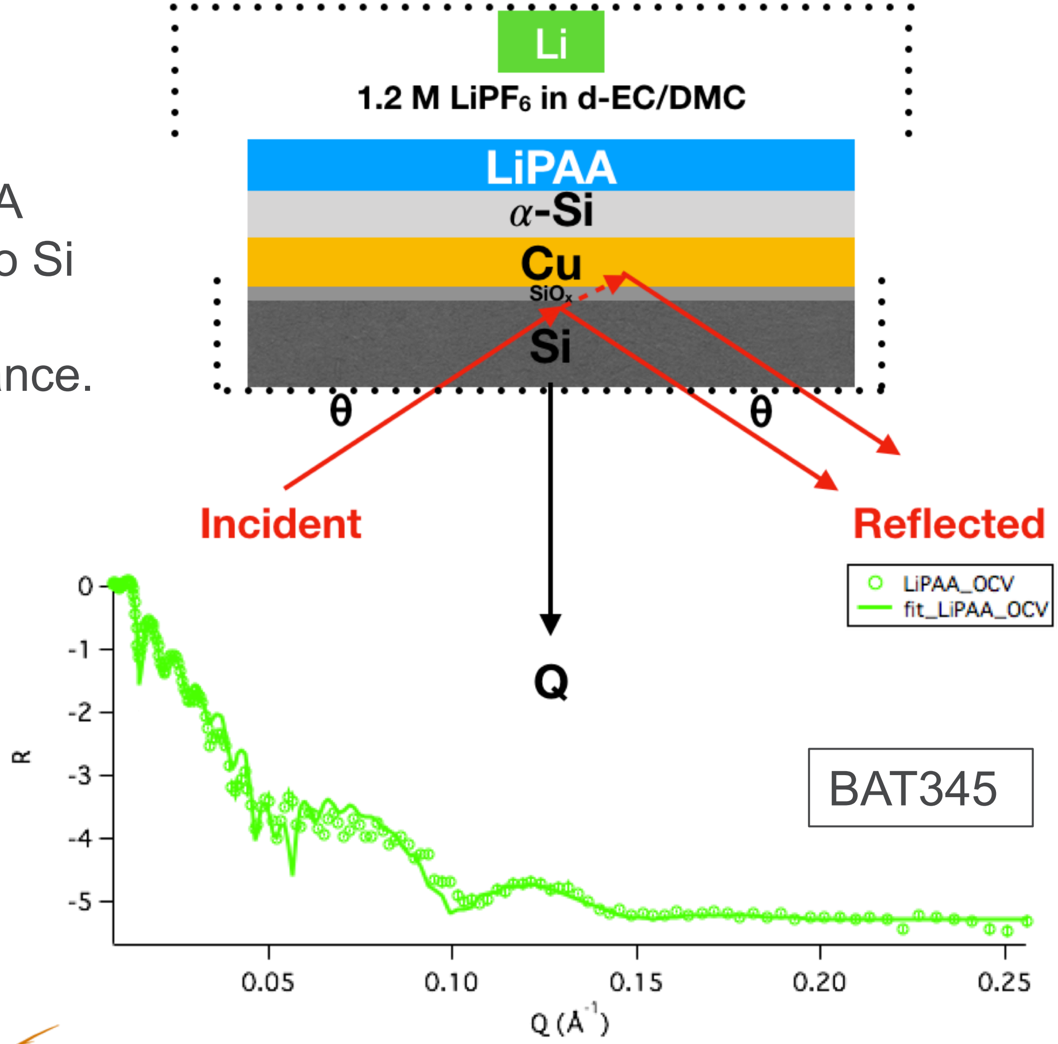


- For electrodes before cycling:
  - the low lithiation of PAA 2.08 was evidenced by the strong presence of the C=O peak around 1685 cm^{-1} and nearly no observation of lithiatiated PAA peaks.
  - As pH increases, the peaks associated with lithiated PAA at around 1562, 1453 and 1414 cm^{-1} became stronger while the C=O peak at 1685 cm^{-1} decreased.
  - When pH reached 7 and above, the peak of SiO_2 started to emerge at ~1060 cm^{-1} and became very strong when pH got to 12, indicating severe formation of SiO_2.
- For the cycled electrodes:
  - The overall peak intensity associated with PAA or lithiated PAA decreased as pH increased, indicating more severe degradation of the PAA binders.

ELECTRODE BINDERS - NEUTRON REFLECTOMETRY TO UNDERSTAND THE ROLE OF PAA/LIPAA BINDER

Neutrons are an ideal probe to understand Si-Binder interactions

Data reveals a 20 nm LiPAA or PAA binder will not let lithium diffuse into Si indicating binder thickness and homogeneity critical to Si performance. Why? And how to use?



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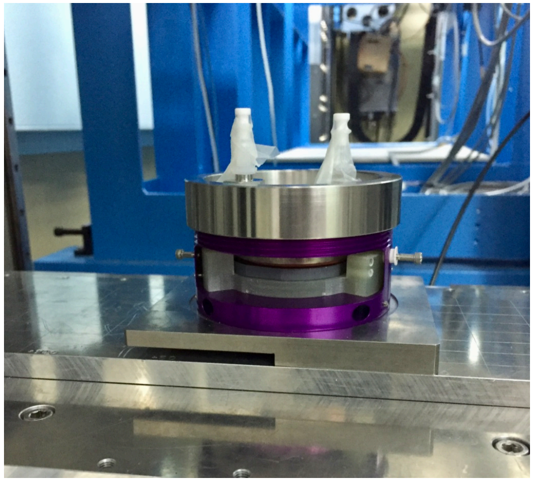
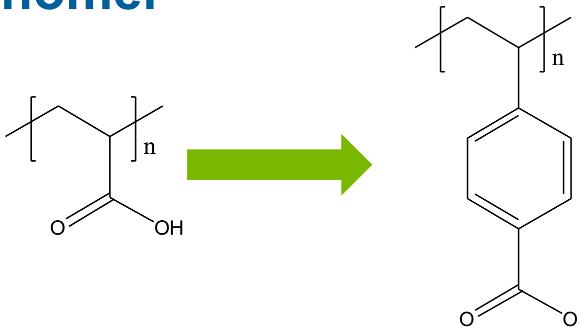


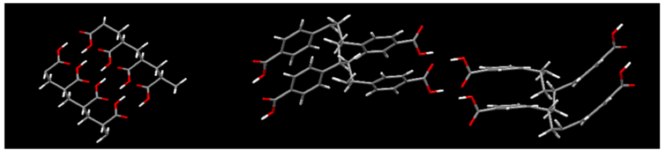
ELECTRODE BINDERS - ENGINEERING PAA BASED BINDERS: I: VIA REPEATING UNITS

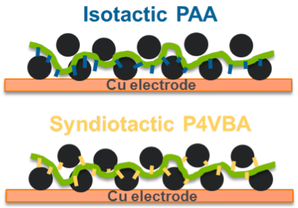
Enhance stiffness by incorporating a stiff moiety to the acrylic acid monomer



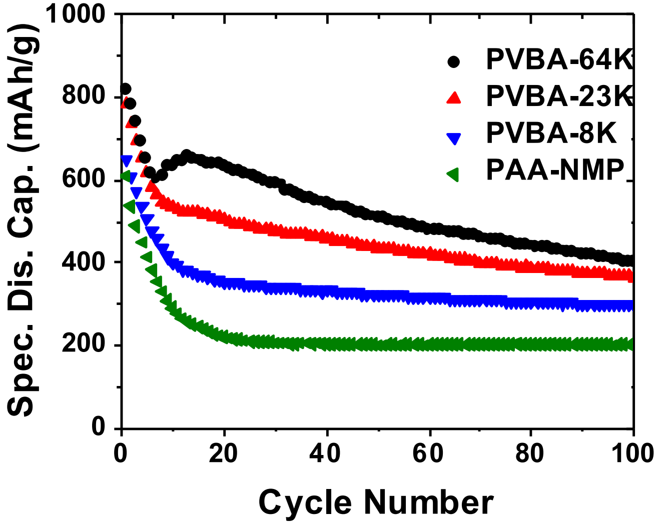
PAA

Poly 4-Vinylbenzoic acid (P4VBA)





PAA: more isotactic **P4VBA**: more syndiotactic

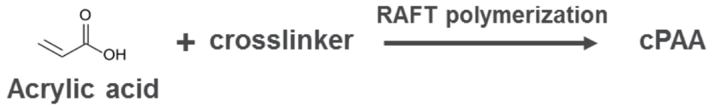


Specific discharge capacity profiles of half cells using the P4VBA binders over 100 cycles at C/3 rate;

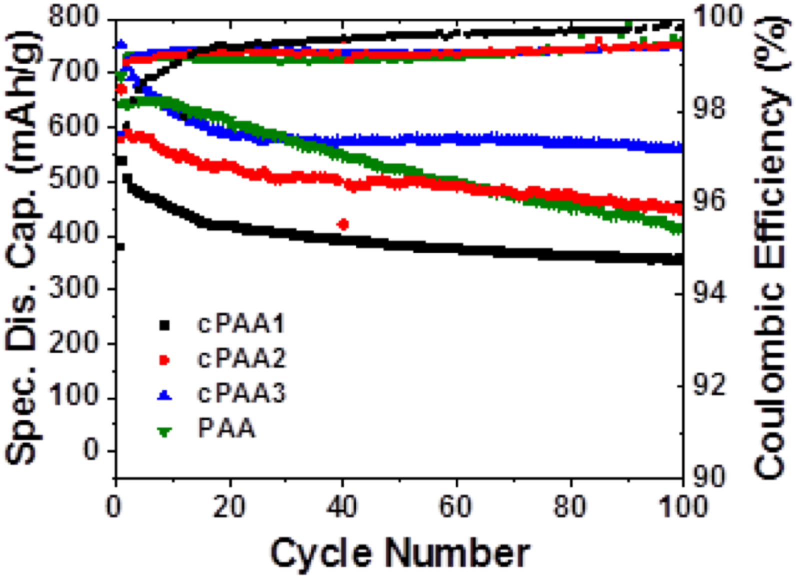
The incorporated benzene ring should help to enhance the stiffness of the flexible PAA backbone and enhance the adhesion.

ELECTRODE BINDERS - ENGINEERING PAA BASED BINDERS: II: VIA MACROSTRUCTURES

Crosslinking the PAA backbones to improve the mechanical properties



Polymer	Crosslinker mol%
cPAA1	0.05 %
cPAA2	0.1 %
cPAA3	0.2 %
PAA	N/A

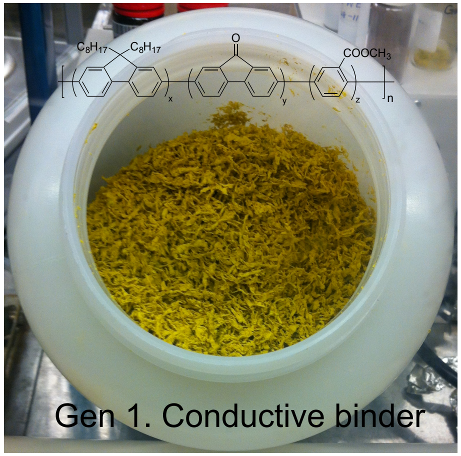


Specific discharge capacity profiles (to the left) and coulombic efficiency profiles (to the right) of half cells using the titrated PAA samples over 100 cycles at C/3 rate;

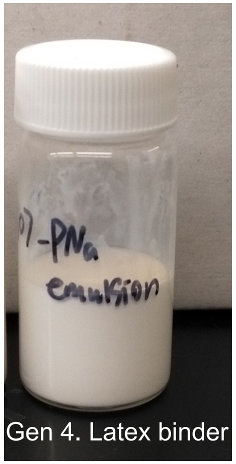
By modifying the macrostructures, cPAA binders provided strikingly better cycling performance compared to linear PAA binders.

ELECTRODE BINDERS - FUNCTIONAL LATEX BINDERS DEVELOPMENT

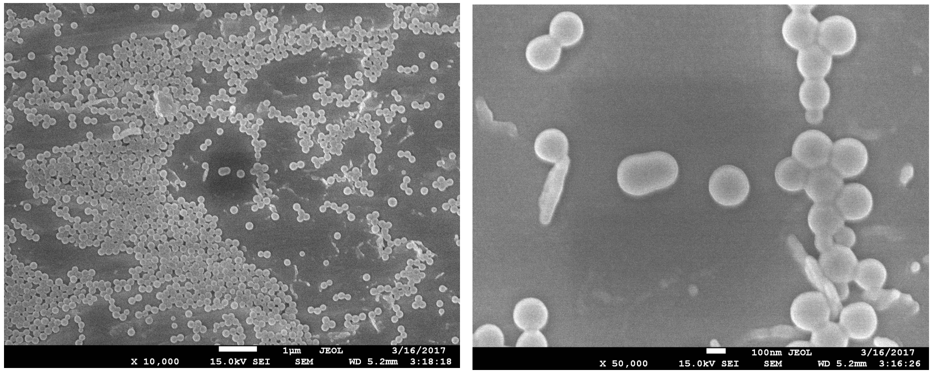
Functional conductive polymer latex binders for Si based electrode applications



Gen 1. Conductive binder

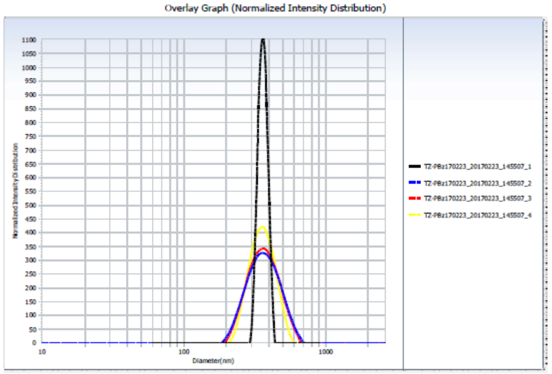


Gen 4. Latex binder



The solid content in the latex is around 25%.

Four generations of binders have been developed to address Si based materials volume expansion issues. The 4th generation binders are latex based conductive polymer emulsions, which are full compatible with current lithium-ion production process.



Particle size
300 nm

PDI
0.04

The latex has a high solid content and uniform particle size.

LITHIUM INVENTORY – MORE LITHIUM DELAYS CAPACITY LOSS – DOES NOT SOLVE PROBLEM

Impact on cycle life

BAT349

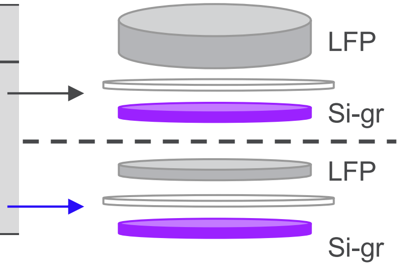
Electrochemical details

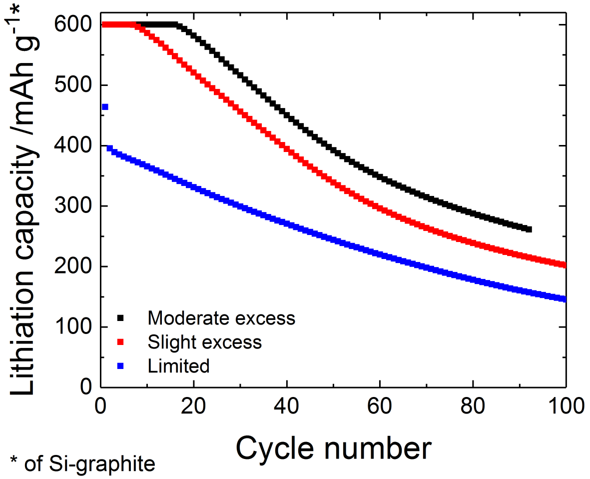
Electrode pairing	LiFePO$_4$ vs. 15% Si-graphite
Protocol	
Si-graphite lithiation	Capacity limited 600 mAh g^{-1} (or 3.455 V*)
delithiation	Voltage limited to 2.0 V

* Si-graphite at 15 mV if LFP is on 3.47 V plateau.

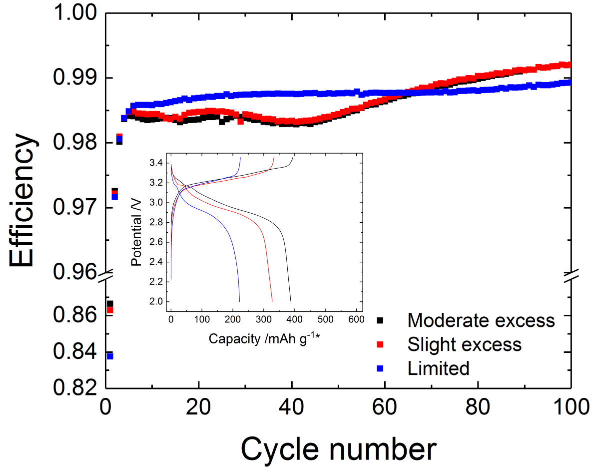
n/p ratios

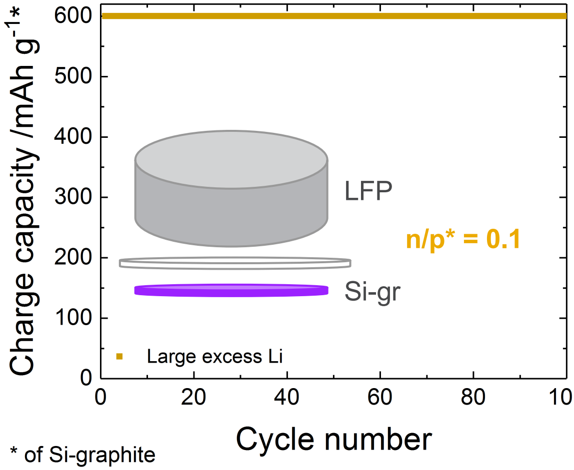
Inventory	n/p	n/p *
Moderate excess	0.95	0.70
Slight excess	1.07	0.79
Limited	1.52	1.13





* of Si-graphite



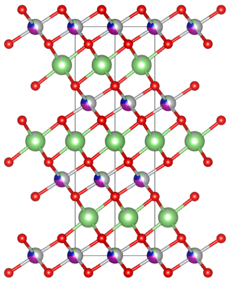


* of Si-graphite

- ☐ High capacity LFP electrode prolongs cycle life.
- ☐ Lithium inventory ***delays*** capacity fade during capacity limited cycling.

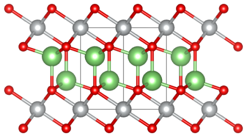
LITHIUM INVENTORY – LITHIUM ADDITION INTO CELL: NCM TYPE

New solutions: over-lithiated $Li_{1+z}Ni_{1-x-y}Co_xMn_yO_2$ for lithium introduction



$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$

R-3m



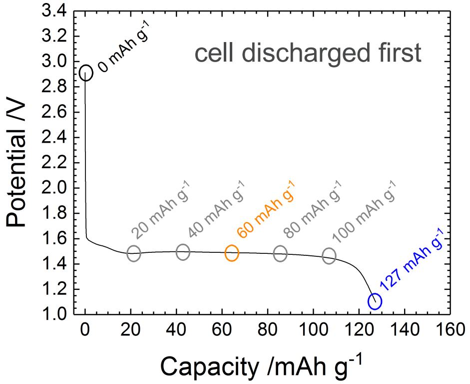
Li_2NiO_2

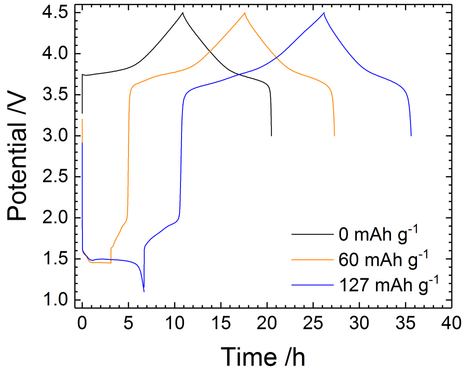
P-3m1

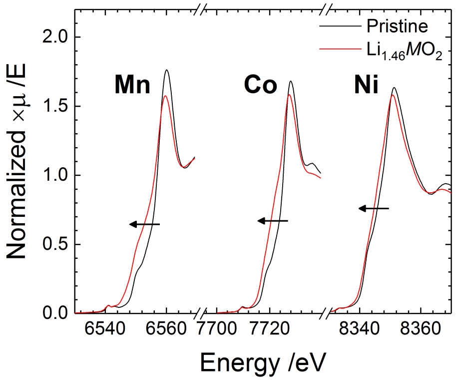
Rationale: for 20% more Li

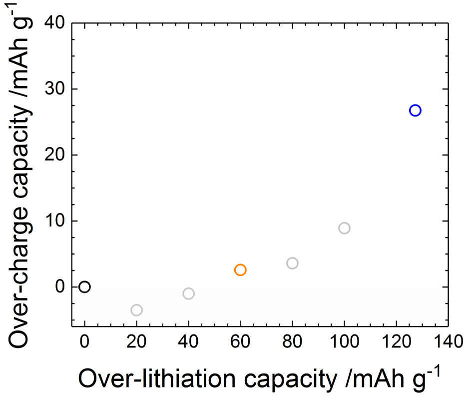
1.2x $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$
20 wt.% increase

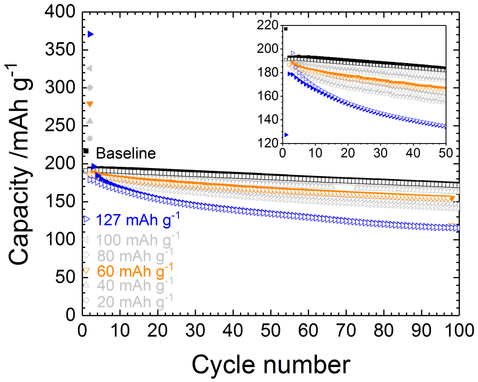
$Li_{1.2}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2$
1.44 wt.% increase











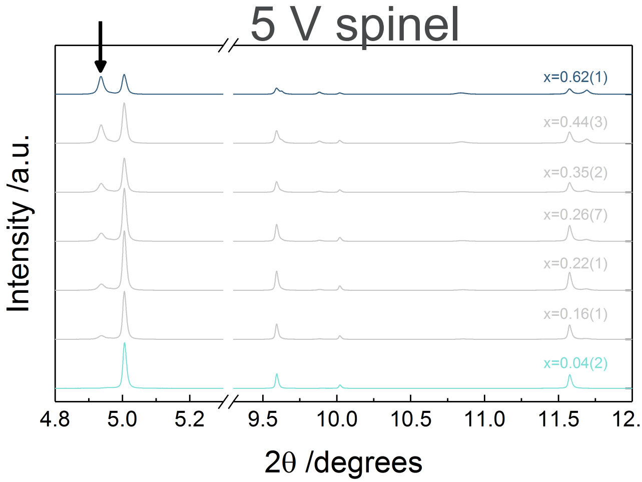
- ☐ Overlithiated NCMs may be a lithium source to address lithium inventory in Si-containing cells, although the structural hysteresis and capacity retention need to be addressed.

LITHIUM INVENTORY – LITHIUM ADDITION INTO CELL: SPINEL TYPE

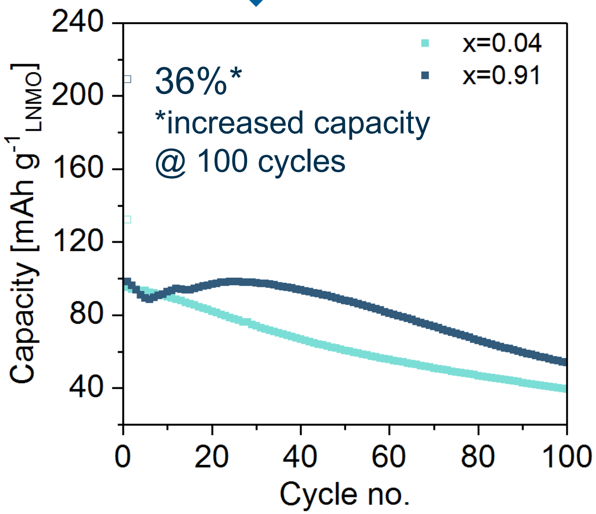
New solutions: over-lithiated 4 or 5 V spinel for lithium introduction

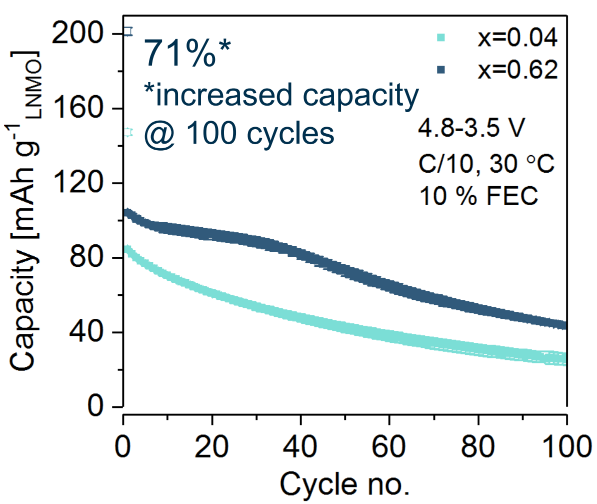
Synthesized by chemical lithiation

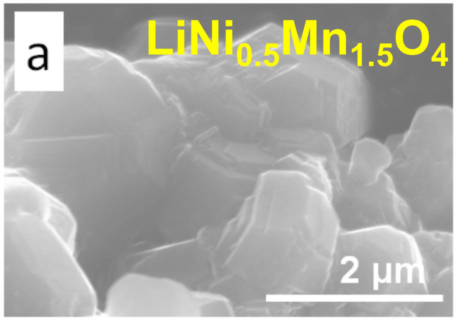
or electrochemical lithiation

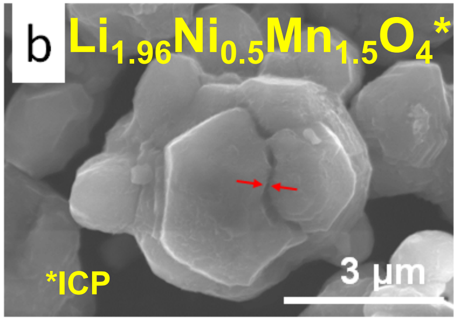


15%Si-graphite/$Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$
Full cell









- ☐ Lithiated 5 V spinels can maintain initial capacity better than parent phase – but still are starting to fade

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

Last year two poster presentations covered all the project. The two posters were each reviewed by eight reviewers. We thank the reviewers for their thoughtful comments. Selected excerpts are given below.

- Many of the reviewers' comments were generally positive.
  - "applauded the excellent, thorough approach"
  - "very ambitious program to assess advantages, disadvantages and solutions for Si anode materials"
  - "very nice intra-laboratory coordination"
- One reviewer thought we could further enhance the program by bringing in experts in mechanical stresses. We conduct limited mechanical measurements and have relied on literature to establish a stable particle size, but in general we agree more in-depth studies could improve the program.
- One reviewer suggested that our commitment to openness limits our ability to examine proprietary materials. We agree totally and recognize the limitation. However, we consider that the work we are doing is addressing the fundamental issues with silicon materials and will benefit the entire community.

REMAINING CHALLENGES AND BARRIERS

- Several key challenges remain that limit integration of silicon into graphitic negative electrodes, mostly related to the large crystallographic expansion of silicon (>300%) upon lithiation.
  - SEI stability issues, which affect cycling efficiency.
  - Electrode stability issues that include particle isolation, accommodating volume changes, and adherence.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Six National Laboratories have teamed to form this integrated effort focused on gaining insights into and advancement of silicon-based materials, electrodes, and cells.
- This effort has strong interactions with the Silicon Electrolyte Interface Stabilization (SEI-Sta) project (BAT344, BAT345, BAT346, BAT347, and BAT348).
- Paraclete Energy is suppling baseline silicon materials.

PROPOSED FUTURE RESEARCH

Electrolyte Additives

- Enrich the bifunctional electrolyte additive toolbox with more functionalities.
- Evaluate the decomposition products of the electrolytes and additives at different potentials and on the surface of Si materials.
- Establish additive-SEI structure relationships.

Electrode Binders

- More insightful characterizations of binders and electrodes to establish deeper understanding of the property/cycling relationship of PAA based binders
- Conduct mechanical properties evaluation of the PAA and its derivatives binders and further improve the mechanical properties of the binder.
- Fully characterize the performance of the water dispersion latex binder, and optimize the condition and processes for water dispersion latex based binders.
- Further explore Si surface and PAA (and derivatives) interaction through neutron experiments.

PROPOSED FUTURE RESEARCH – CON

Lithium Inventory

- Utilize prelithiation strategies to overcome and control lithium inventory issues in Si-containing cells.
- Use quantitative Li-NMR to track Li inventory as a function of state-of-charge and cycle life.
- Continue studying 15%Si-graphite/LFP cell couple with diagnostics team, and compare to 15%Si-graphite/NCM cell and 15%Si-graphite/NCM-LFO cell
  - Probe further the interactions (electrochemical and mechanical) between Si and graphite in the composite electrode.
- Continue using LFP counter/reference electrode to study capacity fade in Si-only and graphite-only systems.
- Isolate capacity fade of Si and graphite with Si-only and graphite-only electrodes versus LFP counter/reference electrode.
  - Extend Li inventory study to additional n/p ratios and vary the lithiation voltage cut-off.
- Explore over-lithiated NCM with varying transition metal ratios.
  - Consider synthetic routes to form over-lithiated NCMs.
- Pair electrochemically over-lithiated NCM with Si-graphite to determine role of Li inventory in full cell tests; continue work with 4 V and 5 V over-lithiated spinels.

SUMMARY

Electrolyte Additives

- A bifunctional electrolyte toolbox is under development. The additives have one functional group to form film on the Si surface, and the other functional group to provide desired surface properties.
- A new ionic liquid and functional electrolyte additives are developed for Si electrode, and give improved Si electrode cycling performance.

Electrode Binders

- Initial study towards understanding the property/cycling relationship of PAA based binders with Si in a composite electrode has been done, including the impact of molecular weight, lithiation, etc.
- Engineering PAA based binders are ongoing via different approaches including synthesized poly (4-vinylbenzoic acid) or P4VBA, and copolymerizing acrylic acid and crosslinkers, non-linear PAA (cPAAs) polymers. Those polymers afforded strikingly better cycling performance compared to the linear PAA binders.
- Successfully developed one class of functional aqueous dispersion of latex binders for Si based materials, and characterized the structure and performance of the binder in a Si based electrode.
- Initiated the study of functional group polymer effect on Si surface via neutron scattering method. Developed a full procedure for in situ testing and data interpretation.

SUMMARY - CON

Lithium Inventory

- Streamlined process to make phase pure Li_5FeO_4 (LFO), a pre-lithiation additive
- SiOx/NCM-LFO cells were fabricated and tested over 50 cycles with better cathode utilization and cycling over baseline non-LFO containing cells.
- $LiFePO_4$ (LFP) cathode with its stable flat voltage profile was successfully paired as an excess capacity pseudo-reference/counter electrode with 15%Si-graphite blended CAMP anode and tested.
- The 15%Si-graphite/LFP cell couple was cycled over 1000 cycles, allowing us to probe electrochemical reactions & capacity fade mechanism over long-term cycling.
- SEM and Raman spectroscopy/mapping was successfully used to compare electrode morphologies and phase changes in the 15%Si-graphite electrode over 1000 cycles.
- Pre-lithiation to compare lithium inventory were evaluated for:
  - $Li_{1+x}NCM523O_2$ over-lithiated layered phase
  - Over-lithiated 4 V spinel and 5 V spinels were tested in 15%Si-graphite full cells

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Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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