Cell Analysis, Modeling, and Prototyping (CAMP) Facility Research Activities

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Argonne National Laboratory

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Washington, D.C.

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

Timeline

- Start: October 1, 2014
- Finish: September 30, 2017

Budget

- $2,000 K for FY15
  - 100% DOE-ABR

Barriers

- Need a high energy density battery for Plug-in Electric Vehicle (PEV) use that is safe, cost-effective, has long cycle life, and meets or exceeds DOE/USABC goals.
  - Independent validation analysis of newly developed battery materials are needed in cell formats with at least 0.2 Ah before larger scale industrial commitment

Partners

- Lawrence Berkeley National Lab
- Oak Ridge National Lab
- Sandia National Lab
- Argonne Facilities: MERF, EADL, CNM & PTF
- Illinois Institute of Technology (Jai Prakash)
- See Industrial list at end
Relevance/Objectives

- Transition new high energy battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats (xx3450 pouch & 18650 cells).

4 mAh Coin Cells \( \times 100 \) 400 mAh CAMP Zone \( \times 100 \) 40 Ah PHEV/EV

- Researchers are often not able to provide the quantities of novel materials needed to make a full size PEV cell to demonstrate the merits of their discoveries. The CAMP Facility is ideally sized to explore new materials with quantities as small as 50 grams for active materials, and even less for electrode/electrolyte additives.
Approach

- Researchers submit materials with promising energy density
- Small hand-coated electrodes are made
- Coin cells are made and tested
- Larger material samples are obtained (MERF, partnerships, etc.)
- Longer lengths of electrode are made from scaled materials
- Pouch cell or 18650s are made and tested
- Extensive diagnostics and electrochemical modeling on promising technologies
<table>
<thead>
<tr>
<th>Milestone</th>
<th>Planned End Date</th>
<th>Milestone Type</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recommend optimal concentration of VC and FEC electrolyte additives in silicon//LMR-NMC cell system</td>
<td>12/31/2014</td>
<td>Progress Measure</td>
<td>Complete</td>
</tr>
<tr>
<td>Assess electrochemical performance of coatings on LMR-NMC particles deposited under various conditions</td>
<td>3/31/2015</td>
<td>Progress Measure</td>
<td>Complete</td>
</tr>
<tr>
<td>Report on optimal PAA binder system for silicon-graphite electrode with goal of 3 mAh/cm²</td>
<td>6/30/2015</td>
<td>Progress Measure</td>
<td>On-going</td>
</tr>
<tr>
<td>Submit final report on advanced battery materials validated in FY15 and summary of Electrode Library activity</td>
<td>9/30/2015</td>
<td>Progress Measure</td>
<td>On-going</td>
</tr>
<tr>
<td>Fabricate Final Deliverable pouch cells for ABR-Amine FOA Award</td>
<td>9/30/2015</td>
<td>Milestone</td>
<td>On-going</td>
</tr>
<tr>
<td>Fabricate pouch cell build with silicon anode and LMR-NMC cathode</td>
<td>9/30/2015</td>
<td>Milestone</td>
<td>On-going</td>
</tr>
<tr>
<td>Advance development of electrochemical models focusing on silicon-graphite negative electrodes and LMR-NMC positive electrode</td>
<td>9/30/2015</td>
<td>Progress Measure</td>
<td>On-going</td>
</tr>
</tbody>
</table>
Technical Accomplishments (more discussed in ES028)

- Developed mechanically robust silicon-graphite electrode with 4 mAh/cm²
- Optimized binder system for silicon-graphite cells using LiPAA
- Investigated FEC and VC electrolyte additives for silicon-graphite electrodes
- Explored silicon content and voltage window of silicon-graphite electrodes
- Measured electrode swelling as a function of SOC for silicon-based cells
- Initiated study of silicon-graphite cells with Argonne’s Post-Test-Facility
- Applied and tested Al₂O₃ coating on LMR-NMC cathode particles
- Supplied numerous baseline electrodes for High-Energy High-Voltage Project
- Assisted High-Energy High-Voltage Project in developing assembly and testing protocols
- Fabricating interim pouch cell build for DOE-EERE Award-Amine (high energy couple)
- Fabricated pouch cell builds for DOE-EERE Award-Zhang (high voltage electrolyte)
- Fabricated and tested NASA-JPL baseline and coated LMR-NMC electrodes in pouch cells
- Supplied numerous electrodes via Electrode Library and expanded its offerings
- Explored new applications for conductive binder from LBNL with Argonne’s MERF
- Held numerous discussions with materials suppliers regarding their materials
- Conducted study on impact of electrode thickness on cell performance
- Working with PPG Industries in CRADA on novel aqueous cathode binder
- Expanded electrochemical model for interfacial impedance and bulk transport
Making a Physically Robust, Uniform, and Flexible Silicon-Graphite Electrode with > 3 mAh/cm²

- **The Challenge**
  - Develop a physically robust, uniform, flexible, and high performance silicon-graphite electrode as a drop-in replacement of a graphite-only electrode for lithium-ion batteries.

- **The Approach**
  - Use Argonne’s Cell Analysis, Modeling, and Prototyping (CAMP) Facility’s pilot scale equipment to engineer and evaluate slurry and electrode development bearing silicon and graphite.
  - Identify:
    1. Viable and industrially available silicon powders
    2. Compatible graphite
    3. Compatible binders enabling improved cycle life
    4. Effective mixing methods

- **The Result**
  - A step forward in achieving a practical, physically robust, uniform, flexible, and high performance silicon-graphite electrode with > 3 mAh/cm² that can be used for pouch cell evaluation and included in the Electrode Library.

Photo image of the silicon-graphite electrode (3.7 mAh/cm²) passing a 3 mm diameter pin test without visible cracking or adhesion issues.

*SEM micrographs from Argonne’s Post Test Facility (PTF)*

*SEM micrograph Si powder (NanoAmor) and graphite (Mag-E) laminate (CAMP Electrode A-A006)*
## Selection of Viable and Industrially-Available Silicon and Compatible Graphite

<table>
<thead>
<tr>
<th>Silicon Sources</th>
<th>Alfa Aesar (1-5 µm)</th>
<th>NanoAmor (130 nm)</th>
<th>NanoAmor (50-70 nm)</th>
<th>American Elements (50 nm)</th>
<th>American Elements (150 nm)</th>
<th>American Elements (1 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*SEM Micrograph</td>
<td><img src="image1" alt="SEM Micrograph" /></td>
<td><img src="image2" alt="SEM Micrograph" /></td>
<td><img src="image3" alt="SEM Micrograph" /></td>
<td><img src="image4" alt="SEM Micrograph" /></td>
<td><img src="image5" alt="SEM Micrograph" /></td>
<td><img src="image6" alt="SEM Micrograph" /></td>
</tr>
</tbody>
</table>

Various silicon powders have been investigated for cycling performance. For this study, commercial availability, cost per gram, and various silicon particle sizes available were taken into consideration for choosing a powder to develop a robust electrode. Nanostructured and Amorphous Materials Inc. (NanoAmor) (50-70 nm) showed promising electrode processing and cycling performance.

<table>
<thead>
<tr>
<th>Graphite Sources</th>
<th>Phillips 66 CPreme® A12</th>
<th>Timcal SFG-6L</th>
<th>Superior Graphite SLC1520P</th>
<th>Kureha Hard Carbon S(F)</th>
<th>Gelon MCMB G15</th>
<th>Hitachi Mag-E</th>
</tr>
</thead>
<tbody>
<tr>
<td>*SEM Micrograph</td>
<td><img src="image7" alt="SEM Micrograph" /></td>
<td><img src="image8" alt="SEM Micrograph" /></td>
<td><img src="image9" alt="SEM Micrograph" /></td>
<td><img src="image10" alt="SEM Micrograph" /></td>
<td><img src="image11" alt="SEM Micrograph" /></td>
<td><img src="image12" alt="SEM Micrograph" /></td>
</tr>
</tbody>
</table>

Various graphite materials were evaluated for slurry making, coating ability, and resulting electrode integrity to identify an ideal pairing with silicon. The graphite type had a significant impact on electrode preparation, processing, and cycling performance. Mag-E performed well for the silicon and binder systems explored.

*SEM micrographs courtesy of Argonne's Post Test Facility (PTF)
## Compatible Binders Enabling Improved Cycle Life & Effective Mixing Methods

<table>
<thead>
<tr>
<th>Binder</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alginic acid</td>
<td>• High degree of cyclability</td>
<td>• Binder solutions have short shelf life</td>
</tr>
<tr>
<td></td>
<td>• Relatively Cheap</td>
<td>• Brittle laminates</td>
</tr>
<tr>
<td></td>
<td>• Easy to mix</td>
<td></td>
</tr>
<tr>
<td>Li-PAA/ PAA</td>
<td>• High degree of cyclability</td>
<td>• Not compatible with every type of graphite</td>
</tr>
<tr>
<td></td>
<td>• Uniform mixing and coating</td>
<td>• Laminates can be brittle</td>
</tr>
<tr>
<td>CMC</td>
<td>• High degree of cyclability</td>
<td>• Concentration of a useable CMC binder solution is ~1%; laminates have a low loading</td>
</tr>
<tr>
<td></td>
<td>• Cheap</td>
<td></td>
</tr>
<tr>
<td>PAI</td>
<td>• Uniform mixing and coating</td>
<td>• Elevated temperatures needed for curing binder</td>
</tr>
<tr>
<td></td>
<td>• Can cycle well with silicon if cured correctly</td>
<td>• More work needed for optimum drying procedure</td>
</tr>
<tr>
<td>PVDF</td>
<td>• Uniform mixing and coating</td>
<td>• Does not cycle well in silicon systems</td>
</tr>
</tbody>
</table>

Utilized various mixing methods to improve slurry quality and electrode coating.

Implemented new mixing equipment and processing steps to minimize silicon agglomeration and produce a homogeneous slurry/coating:
- Use pre-mixing steps with silicon + H₂O only or with binder + carbon black
- The Retsch planetary ball mill produced the best silicon dispersion
Silicon-Graphite Electrode Developed with Adequate Performance for Baseline Purposes

**A-A006(-):** made by CAMP (NanoAmorSi_MagE Graph)

**Negative Electrode:**
- 73 wt% Hitachi MAGE Graphite
- 15 wt% Nano&Amor Silicon (50-70nm)
- 2 wt% C45 (Timcal)
- 10 wt% Li-PAA binder (LiOH titrate)
- 2.94 mg/cm² loading density - coating
- 2.646 mg/cm² loading density - active MagE, Si, C45
- 1.18 g/cm³ total coating density
- 42.4% electrode porosity
- 25-µm-thick composite coating
- 10-µm-thick Cu current collector

Included in CAMP Facility’s Electrode Library

**Technical Accomplishments and Progress**

DOE-EERE-Vehicle Technologies Program
Silicon Content has Significant Impact on Voltage Profile

The Si component increases electrode capacity as expected. This, however, results in voltage hysteresis and slow electrode kinetics. Strong correlation between plateaus in Si-Gr and Gr electrodes. Use of LiPAA as binder does not change graphite capacity or voltage profile.
Over-discharging Silicon-Graphite Cells May Lead to SEI Breakdown

GITT: 0.0142 mAh/cm² pulse, 150 m rest, 100X, Ch & Disch, 2.5-4.1V, 30°C

When full cell is discharged to 2.5V, the negative electrode voltage exceeds 0.8 V vs. Li/Li+, which may increase the likelihood of SEI breakdown and gas generation.

15 wt.% Si + Graphite/NCM523

Suggestion – Improve SEI stability through use of electrolyte additives and raise discharge cutoff voltage

DOE-EERE-Vehicle Technologies Program
FEC Addition Enhances Cycle Life More than VC, but Coulombic Efficiency is Still Too Low

Discharge capacity retention after 100 cycles & Coulombic Efficiency
FEC: Fluorinated Ethylene Carbonate
VC: Vinylene Carbonate
15 wt.% Si + Graphite/ NCM523
Gen2 = 1.2 M LiPF₆ in EC:EMC (3:7 wt)

- Very small differences in measured capacity retention at low and high cycling currents indicates that cell impedance rise is minimal and not a major contributor to capacity fade.
Despite Creation of Mechanically Robust Silicon-Graphite Electrode and FEC Addition, Cycle Life Severely Limited

Addition of FEC may increase LiF on anode and cathode. Work on-going in Argonne’s Post Test Facility.
Ex situ Measurement of Electrode Swelling at Select SOC

Disassemble silicon-based cells at various SOC

- DMC rinse
- Air Dry (~1 minute)
- 5 measurement points per electrode (BL, BR, TL, TR, Mid.)

Technical Accomplishments and Progress

DOE-EERE-Vehicle Technologies Program
**Technical Accomplishments and Progress**

**Swelling Must be Accounted for in Electrode Design**

### Graphite Coating Thickness % Rise vs. Dry Cell

<table>
<thead>
<tr>
<th>SOC [%]</th>
<th>Graphite % Rise (based on dry cell)</th>
<th>Si-Graphene % Rise (based on dry cell)</th>
<th>Si (130nm) % Rise (based on dry cell)</th>
<th>Si Alloy % Rise (based on dry cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>33</td>
<td>+11</td>
<td>+21</td>
<td>+39</td>
<td>+15</td>
</tr>
<tr>
<td>66</td>
<td>+9</td>
<td>+38</td>
<td>+41</td>
<td>+18</td>
</tr>
<tr>
<td>100</td>
<td>+26</td>
<td>+51</td>
<td>+61</td>
<td>+25</td>
</tr>
</tbody>
</table>

*Dry & Soaked Thickness:

- Graphite: +0%
- Si-Graphene: +0%
- Si (130nm): +0%
- Si Alloy: +0%

After Formation:

- Graphite: +11%
- Si-Graphene: +21%
- Si (130nm): +39%
- Si Alloy: +15%

---

**Active Materials**

<table>
<thead>
<tr>
<th>Active Materials</th>
<th>Material Capacity, mAh/g</th>
<th>Vol. Electrode Capacity at 0% SOC, mAh/cm³</th>
<th>Vol. Electrode Capacity at 100% SOC, mAh/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>~350</td>
<td>390</td>
<td>340</td>
</tr>
<tr>
<td>Si (130nm) + Graphite</td>
<td>~600</td>
<td>400</td>
<td>330</td>
</tr>
<tr>
<td>Si Alloy + Graphite</td>
<td>~450</td>
<td>550</td>
<td>510</td>
</tr>
<tr>
<td>Si-Graphene + Graphite</td>
<td>~600</td>
<td>515</td>
<td>415</td>
</tr>
<tr>
<td>NCM523</td>
<td>~160</td>
<td>395</td>
<td>395</td>
</tr>
</tbody>
</table>

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*Cathode and separator showed negligible change*

*Electrode soaked in electrolyte (4 days) showed no change in thickness vs. dry fresh electrode*.

DOE-EERE-Vehicle Technologies Program
Electrochemical Modeling

- Differential and algebraic equations describing transport, thermodynamic, and kinetic phenomena are solved to determine current, potential, and concentration distributions
  - Volume-averaged continuum transport equations
  - Complex solid electrolyte interphase structure
  - Range of active materials studied
  - Conducted multi-dimensional, multi-scale, and transient simulations

- 2015 activities focused on CAMP facility efforts. Some activities integrated with High-Energy High-Voltage project and BatPaC project efforts.
  - Modeling NCM-523 electrodes. Analyzing electrochemical performance and characterization studies to create a model parameter set for baseline electrodes.
  - Early model development on silicon-graphite composite electrodes. Evaluating existing silicon material models to incorporate into graphite electrode model.
  - Current distribution and edge effects in lithium-ion cells. Examined impact of oversized electrode and electrode alignment in test cells.
  - Thick electrode modeling studies. Studying electrode performance and life limitations associated with electrodes thicker than 100µm.
Measuring Rate Capability as a Function of Electrode Loading - Towards Thick Electrodes

Areal capacity, mAh/cm²

\[ Q_{\text{rate,max}} = \gamma Q_v L_{\text{conc}} = \gamma \left[ \frac{Q_v \left( \frac{\varepsilon}{\tau} \right) Dc_{\varepsilon} v_{\gamma} F t_d}{(1-t^\circ_+)} \right] \]

\[ L_{\text{conc}} = \sqrt{\frac{\left( \frac{\varepsilon}{\tau} \right) Dc_{\varepsilon} v_{\gamma} F t_d}{(1-t^\circ_+)} \frac{t_d}{Q_v}} \]

- Full-cell, single-layer 14 cm² pouch-cells (Graphite/NMC622)

<table>
<thead>
<tr>
<th>Required Continuous C-rate</th>
<th>Design capacity, mAh/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/5</td>
<td>4.8</td>
</tr>
<tr>
<td>C/3</td>
<td>3.8</td>
</tr>
<tr>
<td>C/2</td>
<td>3.1</td>
</tr>
<tr>
<td>1C</td>
<td>2.1</td>
</tr>
<tr>
<td>2C</td>
<td>1.5</td>
</tr>
<tr>
<td>3C</td>
<td>1.25</td>
</tr>
</tbody>
</table>

- Lines of \( \gamma = 0.3, 0.6 \) & \( 0.9 \)
- Open symbols transformed from: Battaglia \textit{et al.}, LFP/Gr & NMC333/Gr

Designs should target electrode thicknesses of \( 0.3 \times L_{\text{conc}} \) or less at required C-rate
Pulsed sonochemical setup and reaction pathway for alumina coating on LMR-NMC oxides

LMR-NMC + deionized H₂O \longrightarrow \text{dispersed LMR-NMC}
+ Al(NO₃)₃ \rightarrow \text{sonicated}
\text{dispersed LMR-NMC} + Al³⁺(aq) + 3NO₃⁻(aq)
+ 3NH₄¹⁺(aq) + 3OH⁻(aq) \rightarrow \text{sonicated}
LMR-NMC@Al(OH)₃(s) + 3NH₄NO₃ (aq byproduct)
\rightarrow 200–800°C/2h/air
LMR-NMC@Al₂O₃

Relationships between Al(NO₃)₃ precursor concentration and Al₂O₃ wt% on oxide

<table>
<thead>
<tr>
<th>Al(NO₃)₃ (wt %)</th>
<th>Temperature (°C)</th>
<th>Al wt% (ICP-MS)</th>
<th>Al₂O₃ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>200</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>0.28</td>
<td>0.53</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>0.43</td>
<td>0.75</td>
</tr>
<tr>
<td>8</td>
<td>800</td>
<td>0.55</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Pulsed cycles (4 seconds ON, 4 seconds OFF) for 15 minutes. Pulsing minimizes changes to morphology of oxide particles.

DOE-EERE-Vehicle Technologies Program

Pol et al., J. Power Sources 258 (2014) 46
Physicochemical Characterization of Coated LMR-NMC

Surface characterization by XPS

Reduction in surface Al content with increasing temperature.
Suggests Al migration into oxide at high temperatures.

NMR characterization (F. Dogan)
$^{27}$Al MAS NMR @ 11.7 Tesla, 30kHz spinning speed

Al-O co-ordination changes with processing temperature.
Decrease in 6-coord Al seen at higher temperatures.

DOE-EERE-Vehicle Technologies Program
Electrochemical Characterization of Coated LMR-NMC

Met milestone – Assess electrochemical performance of alumina coatings deposited under various conditions
### CAMP Facility Support of DOE-EERE Award Recipients

#### High Energy Cell Couple
- K. Amine (ANL)

- Baseline xx3450 pouch cells made (SiO$_x$-Sn-Co/NCM622) and under test at INL (FY14)
- Interim xx3450 pouch cells being made (SiO$_x$-Sn-Co//Gradient Cathode) and will deliver to INL (July 2015)

#### High Voltage Electrolyte
- J. Zhang (ANL)

- Baseline Cells (Gr/LiMn$_{1.5}$Ni$_{0.5}$O$_4$) made and delivered to EADL (April 2015)
  - 3.5 to 4.7V @ C/10
- Interim Cells (Gr/LiMn$_{1.5}$Ni$_{0.5}$O$_4$) made and delivered to EADL (June 2015)
  - 3.5 to 4.7V @ C/10
Reviewer Comments from 2014 Annual Merit Review

- The reviewer emphasized that the CAMP facility is critical to the battery research and development (R&D) community.”
- This was a common sentiment among the six reviewers.
- “…the reviewer suggested that the formulation and material of choice was limited and could be more inclusive so that cause and effect could be established for mode of failure in silicon (Si) anodes.”
- Now that the CAMP Facility has a mechanically viable silicon-graphite electrode, it is working more closely with diagnostic researchers and the Post Test Facility in elucidating the failure mechanisms in silicon systems. At this stage, it is generally assumed that the swelling and contraction of the silicon is at fault.
- “…review a summary of the coin cell work that occurred in this area …. would allow for a more informed review … as to the additional knowledge that the larger format work provided.”
- More emphasis was placed in this year’s review presentation on the steps taken to produce a silicon-graphite electrode with good flexibility and high capacity loading. Publications are now in the writing stage to document these observations.
- “…the scope of objectives was very broad and criticized that they could not see any clear decision-making plan or critical-path analysis.”
- This is a recognized concern in the CAMP Facility and tied to balancing the overall mission of advancing high energy systems being created in the R&D community, while not being too eager to terminate novel technologies in their infancy.
CAMP Electrode Library Serves Battery Community

- The Electrode Library serves as a supply of standard electrodes that are designed to be interchangeable with one another (capacity matched).
- Electrodes can be made with as little as 50g of experimental material, and can be made to match an existing counter electrode.

<table>
<thead>
<tr>
<th>Collaboration</th>
<th>Electrodes Delivered</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>FY 13</td>
</tr>
<tr>
<td>Argonne</td>
<td>79</td>
</tr>
<tr>
<td>Other Labs</td>
<td>102</td>
</tr>
<tr>
<td>Universities</td>
<td>56</td>
</tr>
<tr>
<td>Industry</td>
<td>98</td>
</tr>
<tr>
<td>Total</td>
<td>335</td>
</tr>
</tbody>
</table>

Currently Available:
- 10 anodes
- 18 cathodes
- Neg:Pos Balanced
- 2 mAh/cm²
- 220 mm x 110 mm of coating per sheet
CAMP Facility: Electrode & Cell Fabrication Collaborators

Universities

Industry

National Laboratories

- BYU
- Georgia Institute of Technology
- IIT
- UK
- University of Kentucky
- University of Maryland
- University of Wisconsin
- The Ohio State University
- RIT
- Uppsala Universitet
- Iowa State University
- UIC
- University of Rochester
- Toda America
- Superior Graphite
- Wildcat Discovery Technologies
- Silatronix
- BASF
- NEI Corporation
- Miltec
- XG Sciences
- Boulderionics
- Arkema
- Solvay
- BTR
- DuPont
- Inventek
- Paraclete Energy
- NOHMs Technologies
- SolRayo
- DSM
- Zeon
- JSR Micro
- Honeywell
- Blue Current
- TDA Research
- Xtallic
- Aerospace
- SiNode Systems
- FSI Physical Sciences Inc.
Work in Progress/Future Work

- Continue work with Post-Test Facility on determining failure mechanisms in silicon-based cells
- Fabricate final electrode and cell builds for DOR-EERE Award recipients
- Continue support of High-Energy High Voltage Project
- Conduct electrode and cell builds to improve the performance of silicon-based cells with LMR-NMC cathodes
  - Using silicon materials from 3M, XG Sciences, NanoAmor, American Elements, + others
  - Using LMR-NMC from MERF, Toda, and others
- Determine impact of electrode thickness on cycle life under EV driving profiles
  - Use reference electrodes to determine rate limiting electrode (anode or cathode)
- Continue development of binder systems and electrolyte additives for silicon-based cells
- Continue development of Gr-Si electrode electrochemical model
- Continue work with MERF on demonstrating scaled-up coated LMR-NMC cathodes (with JPL) and new approaches with conductive binders for silicon (with LBNL)
- Supply silicon-based pouch and 18650 cells to SNL for thermal abuse testing
Summary

- A silicon-graphite electrode was developed that is flexible, mechanically robust, and with a loading of \(~4\) mAh/cm\(^2\) and \(~700\) mAh/g (active material).
  - However, cycle life is still severely limited due to poor cycling coulombic efficiency
  - Silicon has negative impact on voltage profile and electrode kinetics
  - Electrode surface being analyzed by Argonne’s Post-Test Facility
  - Volume expansion of silicon-electrodes must be accounted for in electrode and battery design
  - The use of 10 wt.% FEC improves the capacity retention and coulombic efficiency, but cycling performance still not good enough for practical applications.
  - **More electrode design and SEI Formation work needed!**

- Electrode loading of <4 mAh/cm\(^2\) best for C/3 rate applications (EV driving)
- Alumina coating on cathode particles shows some improvement in capacity retention
- Fabricated electrodes and pouch cell builds for DOE-EERE Awards
- Provided High-Energy High-Voltage Project with baseline electrodes, baseline single-layer pouch cells, and assisted with protocol development
- Supplied numerous electrodes via Electrode Library and expanded its offerings
Contributors and Acknowledgments

Argonne CAMP Team
- Daniel Abraham
- Shabbir Ahmed
- Khalil Amine
- Dominick Baker
- Javier Barenco
- Martin Bettge
- Tony Burrell
- Ira Bloom
- Dennis Dees
- Nancy Dietz-Rago
- Kevin Gallagher
- Fulya Dogan
- James Gilbert
- Sanketh Gowda
- Seonbaek Ha
- Andrew Jansen
- Matilda Klett
- Wenquan Lu
- Paul Nelson
- Bryant Polzin
- Steve Trask
- Huiming Wu
- Qingliu Wu
- John Zhang

Outside Argonne
- Robert Kostecki (LBNL)
- Gao Liu (LBNL)
- Claus Daniel (ORNL)
- David Wood III (ORNL)
- Kyle Fenton (SNL)
- Chris Orendorff (SNL)

Research Facilities
- Materials Engineering Research Facility (MERF)
- Post-Test Facility (PTF)
- Electrochemical Analysis and Diagnostic Laboratory (EADL)
- Center for Nanoscale Materials (CNM)
- Advanced Photon Source (APS)

Industry
- XG Sciences
- PPG Industries
- 3M
- Toda America/Kogyo
- Superior Graphite
- Johnson Controls
- JSR Micro

Support from Peter Faguy and David Howell of the U.S. Department of Energy’s Office of Vehicle Technologies is gratefully acknowledged.
Technical Back-up Slides

The following slides are available for the presentation and included in the DVD and Web PDF files released to the public.
Comparing SiGr and Gr-only Negative vs. Li:
GITT protocol 30°C, 1.5-0V window

Significant voltage hysteresis for SiGr electrode
Electrode kinetics is slow because of Si component

Minimal voltage hysteresis for Gr electrode
Rapid electrode kinetics for Gr electrode
### Composition of CAMP Facility Electrodes Used in Much of This Work

<table>
<thead>
<tr>
<th>LN3012-36-2</th>
<th>LN3012-7, 92/2/6, MAGE/C45/LiPAA -&gt; ~1.75 mAh/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Positive Electrode:</strong></td>
<td><strong>Negative Electrode:</strong></td>
</tr>
<tr>
<td>LN3012-7-1(-): Trial electrode made by S Trask</td>
<td>92 wt% Hitachi MAGE Graphite</td>
</tr>
</tbody>
</table>

**A-C013(+)**: made by CAMP (NCM523)  
**A-A006(-)**: made by CAMP (NanoAmorSi_MagE Graph)

<table>
<thead>
<tr>
<th>Positive Electrode</th>
<th>Negative Electrode</th>
<th>Negative Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>90 wt% Li_{1.03}(Ni_{0.5}Co_{0.2}Mn_{0.3})<em>{0.97}O</em>{2}</strong></td>
<td><strong>73 wt% Hitachi MAGE Graphite</strong></td>
<td><strong>92 wt% Hitachi MAGE Graphite</strong></td>
</tr>
<tr>
<td><strong>5 wt% C45 (Timcal)</strong></td>
<td><strong>2 wt% C45 (Timcal)</strong></td>
<td><strong>2 wt% C45 (Timcal)</strong></td>
</tr>
<tr>
<td><strong>5 wt% PVdF binder (Solvay 5130)</strong></td>
<td><strong>10 wt% Li-PAA binder (LiOH titrate)</strong></td>
<td><strong>6 wt% Li-PAA binder (LiOH titrate)</strong></td>
</tr>
<tr>
<td><strong>11.33 mg/cm² loading density - coating</strong></td>
<td><strong>2.94 mg/cm² loading density - coating</strong></td>
<td><strong>6.09 mg/cm² loading density - coating</strong></td>
</tr>
<tr>
<td><strong>10.197 mg/cm² loading density - active/oxide</strong></td>
<td><strong>2.646 mg/cm² loading density - active MagE, Si, C45</strong></td>
<td><strong>5.72 mg/cm² loading density - active MagE, C45</strong></td>
</tr>
<tr>
<td><strong>2.7 g/cm³ total coating density</strong></td>
<td><strong>1.18 g/cm³ total coating density</strong></td>
<td><strong>1.15 g/cm³ total coating density</strong></td>
</tr>
<tr>
<td><strong>33.5% electrode porosity</strong></td>
<td><strong>42.4% electrode porosity</strong></td>
<td><strong>45% electrode porosity</strong></td>
</tr>
<tr>
<td><strong>42-µm-thick composite coating</strong></td>
<td><strong>25-µm-thick composite coating</strong></td>
<td><strong>53-µm-thick composite coating</strong></td>
</tr>
<tr>
<td><strong>20-µm-thick Al current collector</strong></td>
<td><strong>10-µm-thick Cu current collector</strong></td>
<td><strong>10-µm-thick Cu current collector</strong></td>
</tr>
</tbody>
</table>
The FEC and VC additives affect the first charge profile; the voltage location indicates that the additives affect electrolyte “reduction” behavior on the graphite electrode.

The FEC and VC additives affect the 1st charge differential capacity plots. The peak associated with EC reduction is around 3.02 V. VC addition changes peak location to 2.87 V; note additional intensity near ~2.67 V. FEC addition creates a strong peak around 2.49 V; the EC reduction peak may have shifted to ~ 2.74 V.
Modeling of Multi-layer Full Pouch Cell with NCM523

**Assumptions:**

- 13 TTL Layers
  - 6 Anodes DS
  - 5 Cathodes DS
  - 2 Cathodes SS
- Used electrode parameters from previous work for model calculations
- Max Cathode thickness: 90 µm (NCM523)
- Separator: 20 µm
- Cu Foil: 8 µm
- Al Foil: 12 µm

<table>
<thead>
<tr>
<th></th>
<th>Cell Thickness (After Formation) @ 0 % SOC, µm</th>
<th>Cell Thickness (After Formation) @ 100 % SOC, µm</th>
<th>% Rise in Cell Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>3186</td>
<td>3385</td>
<td>6.2</td>
</tr>
<tr>
<td>Si (130nm) + Graphite</td>
<td>2861</td>
<td>3099</td>
<td>8.3</td>
</tr>
<tr>
<td>Si Alloy + Graphite</td>
<td>2593</td>
<td>2664</td>
<td>2.7</td>
</tr>
<tr>
<td>Si-Graphene + Graphite</td>
<td>2626</td>
<td>2842</td>
<td>8.2</td>
</tr>
</tbody>
</table>
A-A006 (15 wt% Si+ Graphite) vs. Various Cathodes - Coin Cell Data

**Capacity, (mAh/g*)**

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>LN3032-8, LCO</th>
<th>LN3032-9, 622</th>
<th>LN3032-10, 4V</th>
<th>LN3032-11, 523</th>
<th>LN3032-12, NCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>140</td>
<td>120</td>
<td>100</td>
<td>120</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>110</td>
<td>90</td>
<td>110</td>
<td>130</td>
</tr>
<tr>
<td>20</td>
<td>120</td>
<td>100</td>
<td>80</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>30</td>
<td>110</td>
<td>90</td>
<td>70</td>
<td>90</td>
<td>110</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>80</td>
<td>60</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>90</td>
<td>70</td>
<td>50</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>60</td>
<td>40</td>
<td>60</td>
<td>80</td>
</tr>
</tbody>
</table>

*mAh/g in terms of cathode oxide weight
Data does not include formation cycles

**Procedure**

<table>
<thead>
<tr>
<th>Procedure Name</th>
<th>SET-Si-Full-CYC-4p1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procedure Description</td>
<td>Silicon-Graphite in Full Cell, Cycling, C/5 at 3.0 to 4.1 V</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Gen2 + 10 wt.% FEC</td>
</tr>
<tr>
<td>Testing Temp.</td>
<td>30°C</td>
</tr>
</tbody>
</table>