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Novel Phosphazene Compounds for Enhancing Stability and Safety of Lithium-ion Batteries

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May 14, 2013

Project ID ES027

2013 DOE Vehicle Technologies Program Annual Merit Review

www.inl.gov

Idaho National
Laboratory

Overview

Timeline	Barriers
Project Start: Jan. 2009 **Project End:** Ongoing **Percent Complete:** 90%, based on remaining funds.	• **Cell/battery Life** • **Abuse Tolerance, Reliability and Ruggedness** • **Performance (energy density)** • **Cost**
Budget	**Partners**
Funding Received: **FY 12: $ 500K** **FY 13: $ 450K**	**Argonne National Lab (ANL)** **Princess Energy Systems** **Sandia National Lab (SNL)** **Washington State Univ.** **Lead: INL**

Relevance

Safety, life and cost of Li-ion batteries continues to be an issue for future vehicular and other high-demand applications. This is complicated by the drive toward higher energy systems (5V+ Cells).

Our objectives include:

- Synthesize novel solvents for Li-ion cells that are safer alternatives to volatile organics. **Targets:** prolonged operation at 5V+ and 60 C, 3C rate, 300 mAh/g.
- Target alternative electrode materials that would further integrate stable performance and be chemically compatible with novel INL inflammable solvents.
- Enhance abuse tolerance: determine what phosphazene structures are more tolerant to high and low voltage and elevated temperatures.
- Gain understanding of molecular-scale interactions between phosphazenes and other cell components.
- Determine the effect of phosphazenes on SEI films and cell aging in general, using ABR-relevant electrode couples.

Our vision is to leapfrog lithium-ion technology to achieve a *highly tunable inorganic battery chemistry* with extremely high safety, stability, and longevity.

Milestones

Milestone	Status	Date
Abuse testing of INL electrolyte additives at SNL, Phase 1	Completed	Nov. 2012
Synthesis of newer FM series and second-generation Ionic Liquid Phosphazenes	Partially complete; In Progress	Newer FMs Dec. 2012
Cell testing using NCA (Toda)/Carbon couple: characterization of capacity and impedance attributes	Completed	December 2012
Phase 3 concept validation for alternative anode materials	Completed	March 2013
Prolonged thermolysis experiments at 60°C using FM and SM series additives with two baseline electrolytes	75% complete	Initiated Nov. 2012
Phase 3 Alternative Anode materials with improved electronic conductivity, porosity, and capacity	In Progress	
Abuse testing of INL Phosphazene electrolyte additives at higher amounts (SNL), Phase 2	In Progress	
NMR evaluation of electrolyte fate at elevated temperatures (Washington State Univ.)	In Progress	Initiated May 2012
Collaboration with ANL regarding scale-up of INL electrolyte compounds	In Progress	

Approach

❒ The INL has foremost experts in phosphazene chemistry (Stewart, Harrup, and Klaehn) that are producing new classes of novel compounds for use in Li-ion batteries. They maintain historical knowledge of phosphazene chemistry and related applications.

❒ This work is split under (1) synthesis (solvents, electrodes), (2) materials characterization, (3) modeling, and (4) lithium-ion cell testing.

Upfront issues are

- ♦ Voltage and thermal stability
- ♦ Lithium salt solubility
- ♦ Transport properties
- ♦ Effective energy density
- ♦ Overall chemical compatibility in cell and related aging
- ♦ Molecular interactions (solvent-ion) and SEI

Coin cell testing covers issues of SEI formation, interfacial impedance, polarization testing, and aging. We investigate the performance of our electrolytes against relevant ABR electrode couples as they become available.

***Note:* Best Candidate electrolytes are sent to SNL for abuse-tolerance testing.**

INL Highly Targeted Battery Materials

Rationale in Support of "Inorganic" Lithium-ion Batteries

***Our vision is to leapfrog lithium-ion technology to achieve a highly tunable inorganic battery chemistry with extremely high safety, stability, and longevity*.**

We leverage this vision with a deep and established capability in phosphazene-based chemical synthesis. Toward this goal we have taken fundamental strides in using ABR tools to engineer materials into an integrated system to achieve:

❶ Chemical compatibility across the entire cell; potential for Na and Mg scenarios.

❷ Reduced carbon in electrolyte and in anode

❸ Superior resilience over temperature and voltage

❹ Very low flammability due to phosphorus in electrolyte, anode, and surface pre-treatments

❺ Long product life in diverse application platforms

To date our INL phosphazene electrolyte compounds and alternative electrode materials are showing strong potential for a breakthrough chemistry of unparalleled stability with highly customizable properties. Our physics-based modeling tools can support materials selection and aging diagnostics (AEM and CellSage). We will seek continued DOE support while we extend the maturity and validation of our battery materials.

Advanced Electrolyte Materials

Phosphazenes

Benefits:

- ❑ Inherently stable and non-flammable
- ❑ Very low vapor pressure
- ❑ Choice of R groups (pendant arms) has a profound influence on properties
- ❑ Good lithium salt dissolution

Challenges:

- ➢ High viscosity
- ➢ Need to attenuate N-Li^+ attraction that occurs due to electron doublet transfer

Selected Series of INL Phosphazene Compounds

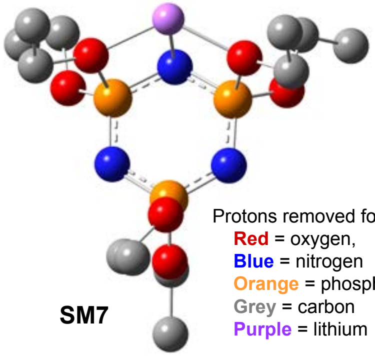
SM: employs ether groups attached to the phosphorus centers

AL: employs unsaturated analogues of the SM series

FM: employs fluorinated analogues of the SM series

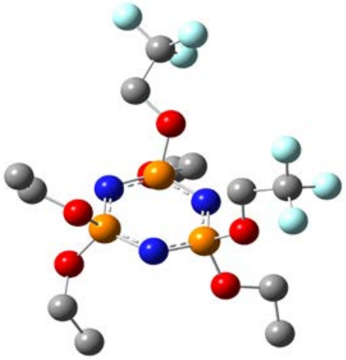
PhIL: ionic liquid variation

All materials covered by patents issued or pending.

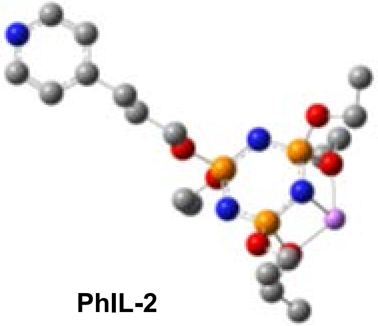


SM7

Protons removed for clarity.
Red = oxygen,
Blue = nitrogen
Orange = phosphorus,
Grey = carbon
Purple = lithium



FM3



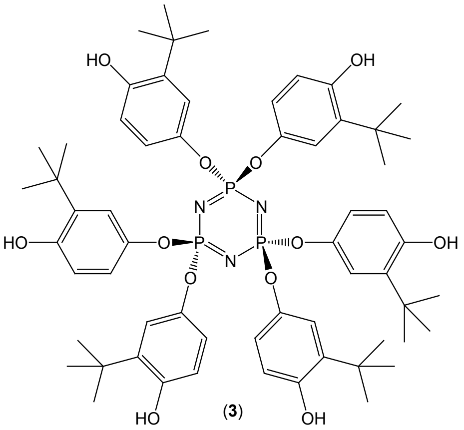
PhIL-2

Novel Approach to Anode Engineering

- Classes of phosphazene compounds are being tested as new intercalative host materials for lithium-ion battery anodes. These compounds and their formulations provide the following benefits:
  - ❑ Synthesis of novel 3D polyphosphazene scaffolds, which can support addition of custom functional groups and dynamic materials (nano-Si).
  - ❑ Addition and formulation of materials to enhance electronic conductivity, energy storage capacity, and other physical properties,
  - ❑ Highly engineerable to achieve particular properties, e.g., through various cross-linking routes. Rate capability and net energy storage are primary targets.
  - ❑ Inherently low flammability due to presence of phosphorus.
  - ❑ Economical method to apply phosphazene electrode material to metal current collectors.

Successful cell testing to 5V!

Examples of base phosphazene structures: tbuHQCP or TBHQ (left) and HQCP (right).



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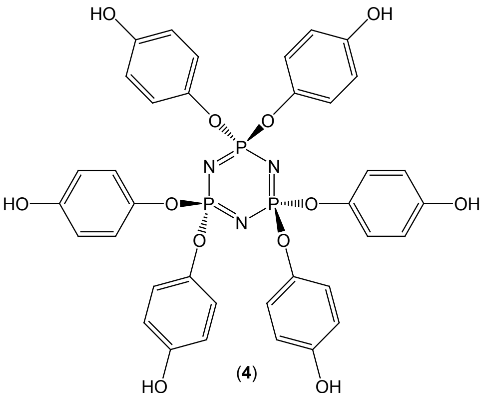

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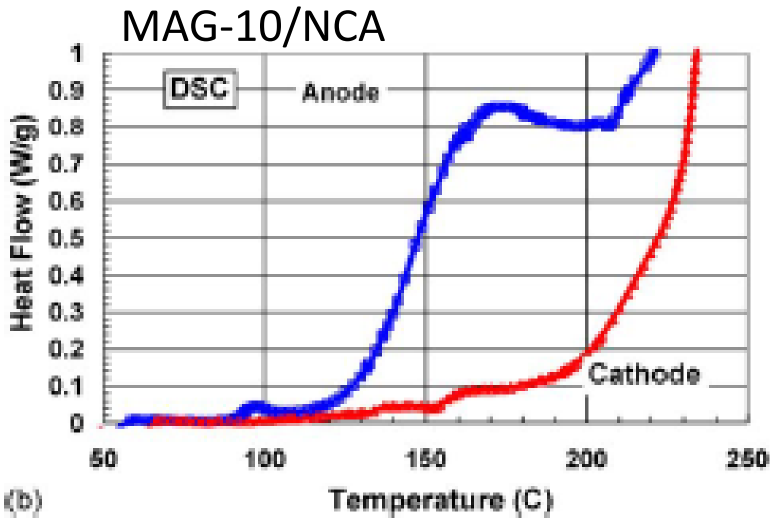
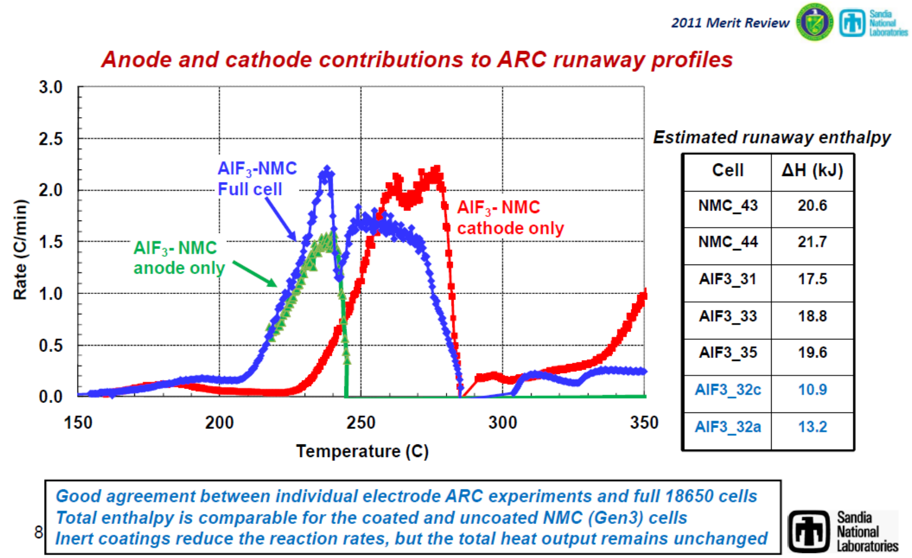
Why Alternative Polymer-based Anodes?

Carbon Anodes Cause Safety Issues during Thermal Runaway



Per SNL data, reactions at the carbon anode at moderate T provides a threshold heating rate that initiates cathode SEI breakdown.

[D.P. Abraham et al., J. Power Sources 161 (2006) 648–657]



2011 Merit Review

Anode and cathode contributions to ARC runaway profiles

Estimated runaway enthalpy

Cell	ΔH (kJ)
NMC_43	20.6
NMC_44	21.7
AIF3_31	17.5
AIF3_33	18.8
AIF3_35	19.6
AIF3_32c	10.9
AIF3_32a	13.2

Good agreement between individual electrode ARC experiments and full 18650 cells
Total enthalpy is comparable for the coated and uncoated NMC (Gen3) cells
Inert coatings reduce the reaction rates, but the total heat output remains unchanged

8

Changing to a non-carbon anode that is also highly non-flammable will push the onset of thermal runaway to higher (safer) levels.

Technical Accomplishments & Progress

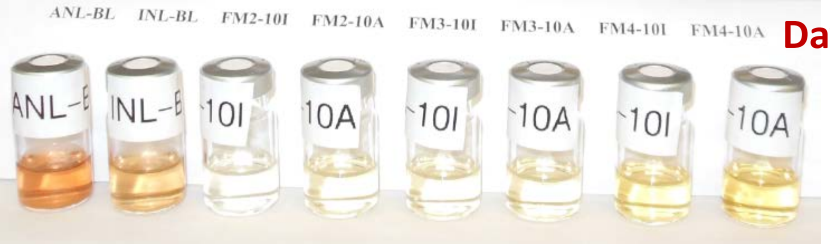
- New phosphazene compounds have been synthesized as part of our suite of materials aimed at voltage and temperature tolerant electrolyte additives (FM, PhIL), based on performance characteristics of previous generations.
- INL additives stabilize electrolytes under prolonged exposure at elevated temperature, 60 °C.
- Abuse testing at SNL shows that INL electrolyte additives enhance thermal stability and reduce flammability of Li-ion electrolytes, even at low amounts (3%).
- Voltammetry measurements confirm INL additives provide expanded voltage stability. Our voltammetry technique yields precise determination of SEI parameters. A patented purification technique removes impurities and enables further expansion of the electrochemical window.
- Cell testing has continued with ABR-relevant electrode couples (recently NCA (Toda) + Carbon). Test results are encouraging regarding capacity retention and aging trends, with INL additives exceeding performance of the baseline electrolyte in some cases.
- NMR-based analysis of electrolyte fate at elevated temperature has begun under collaboration with Washington State University NMR Center.
- Alternative anode materials based on phosphazene polymer chemistry have been synthesized and tested to near 5V, indicating these are viable hosts for lithium-ion cells. Several classes of materials have been tested and characterized toward investigating lithium insertion mechanisms and toward improving fundamental performance in terms of energy storage and rate capability.

Prolonged Thermolysis Testing at 60℃ (10% Additives)

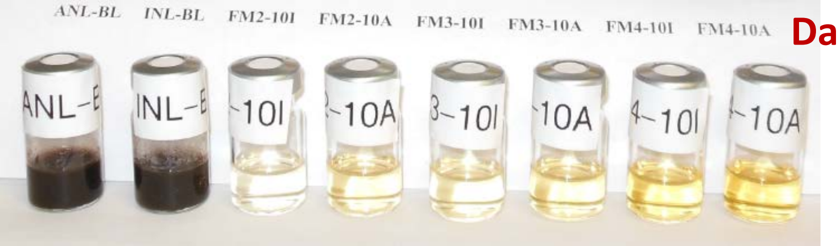
FM Series

SM Series

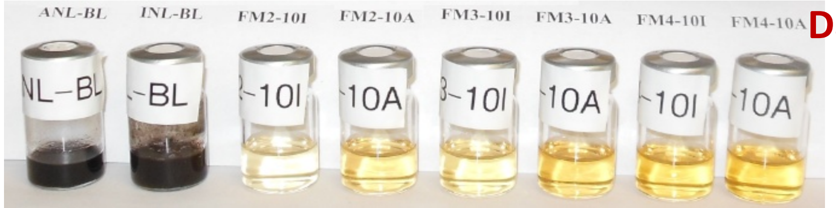
Day 0



Day 30



Day 60



Day 90

Baselines (BL) Used:

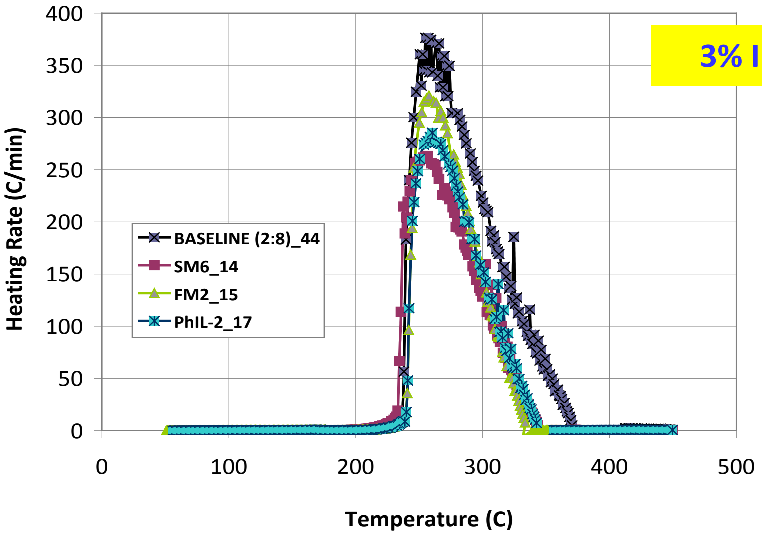
“I” : 1.2M LiPF6 in EC-EMC (1:2, mass)

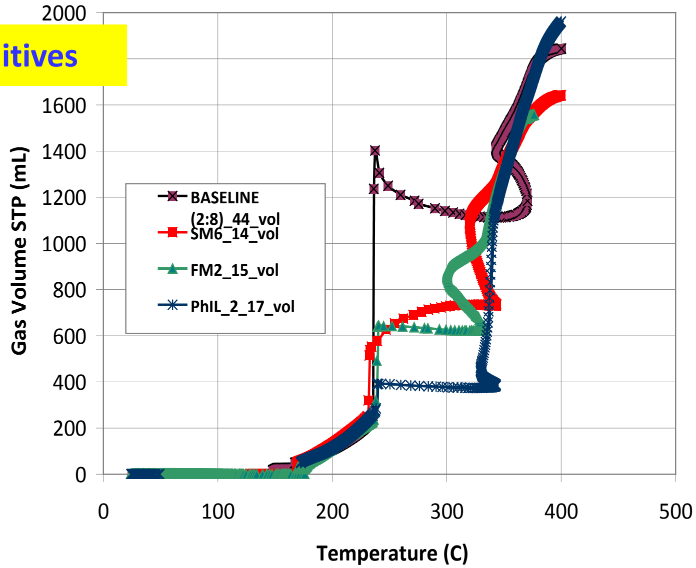
“A” : 1.0M LiPF6 in EC-DEC (1:1, mass)

Tech. Accomplishments

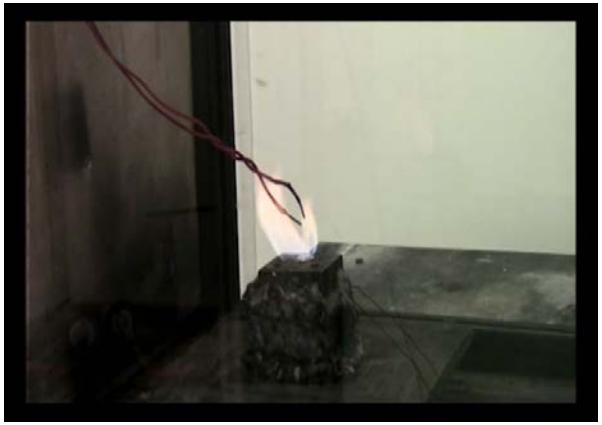
INL additives lower both the heating rate and gas production during thermal runaway…..

3% INL Additives

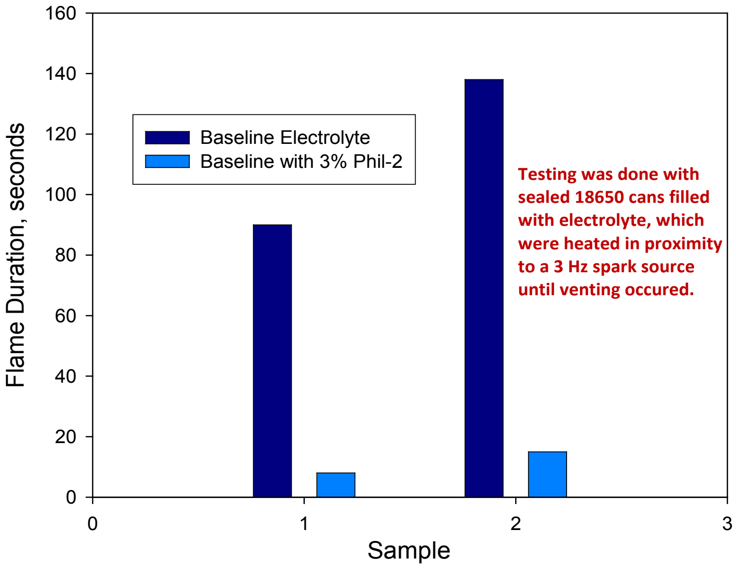




…and can significantly reduce flame duration.



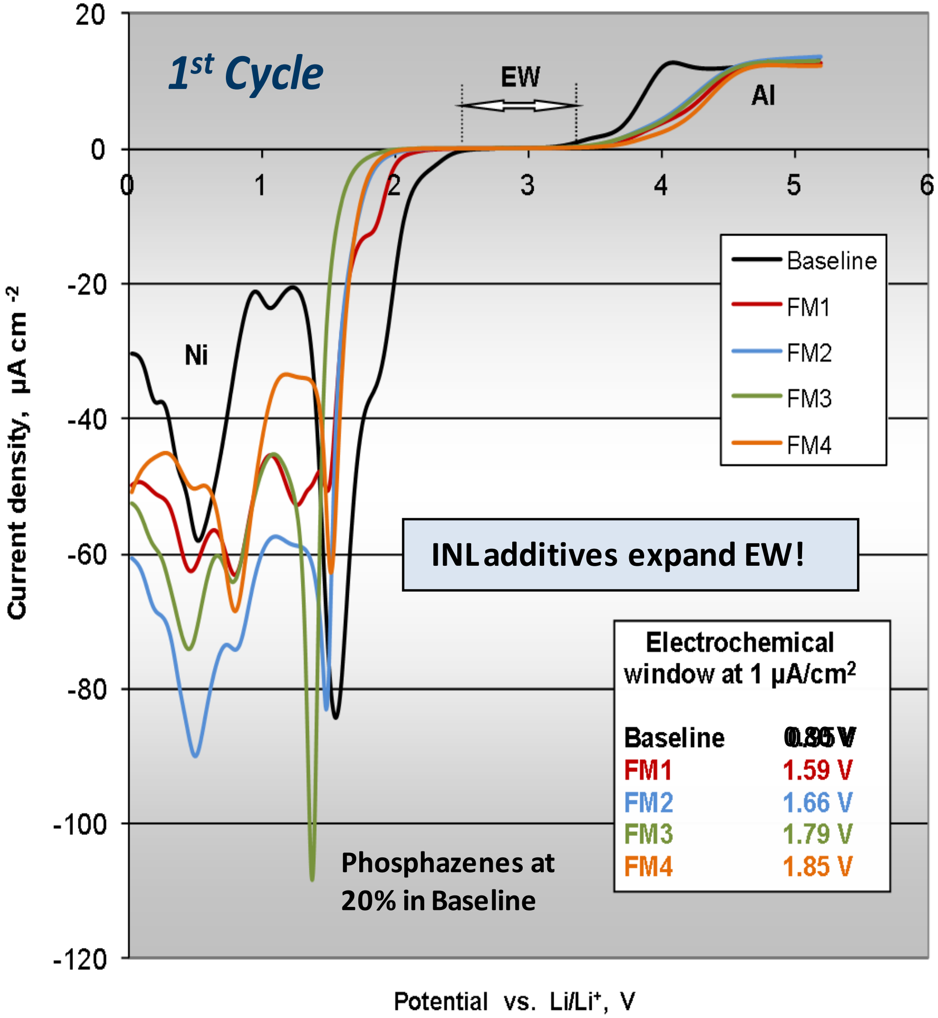
Short-lived ignition of electrolyte with PhIL-2 (the vent was very subtle and difficult to observe).



Testing was done with sealed 18650 cans filled with electrolyte, which were heated in proximity to a 3 Hz spark source until venting occured.

- Testing performed by SNL (Orendorff).
- All Cell Results: NMC/carbon, with **3% additives** in EC-EMC (1:4) + 1.2M $LiPF_6$.

Voltammetry of Phosphazene-based Electrolytes (FM series)



INL additives expand EW!

Electrochemical window at 1 µA/cm²

Baseline	0.85 V
FM1	1.59 V
FM2	1.66 V
FM3	1.79 V
FM4	1.85 V

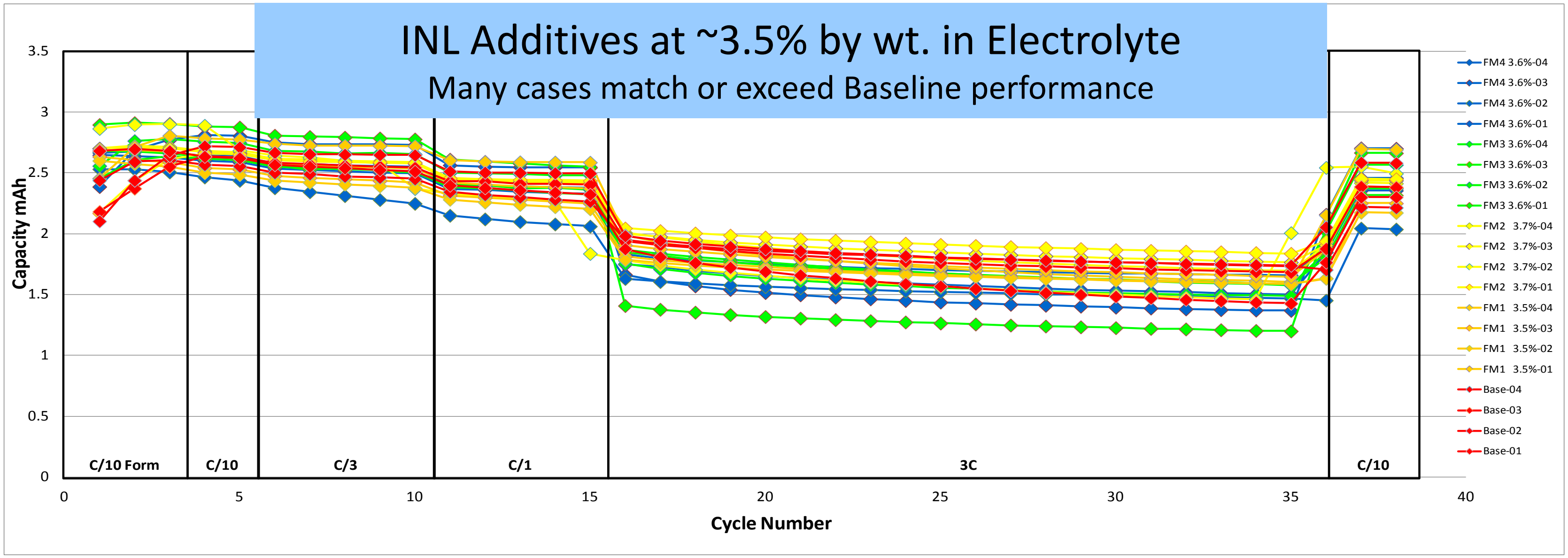
Phosphazenes at 20% in Baseline

The electrochemical window (EW) is the region over which no redox reactions occur involving the electrolyte. The larger the window, the more stable the electrolyte and the greater voltages that the battery can achieve in normal operation.

- Phosphazenes increase the EW at both negative and positive ends, in this case more than doubling the EW past the baseline!
- At potentials beyond the electrochemical window, passivation does occur forming SEIs.
- Properties of passivating layers are measured quantitatively via new INL voltammetry techniques.
- EW expands further with electrolytes pretreated with patented purification technique (US Patent 5849429. Purification process for lithium battery electrolytes. S. Sazhin, M. Khimchenko, Y. Tritenichenko.).

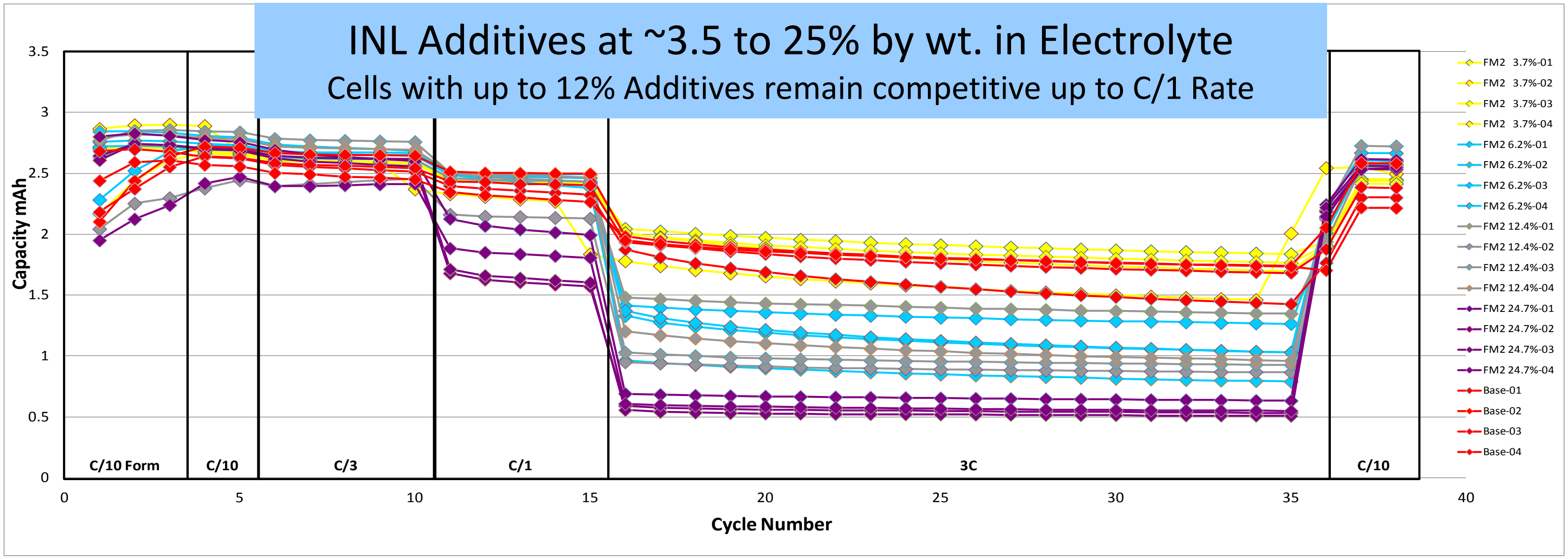
Electrolytes: baseline (1.2M $LiPF_6$ EC:MEC (2:8)) and the blends of 20% of each phosphazene with 80% baseline.

Cell Testing (NCA-Toda/Carbon) with FM Electrolyte Additives



INL Additives at ~3.5% by wt. in Electrolyte

Many cases match or exceed Baseline performance



INL Additives at ~3.5 to 25% by wt. in Electrolyte

Cells with up to 12% Additives remain competitive up to C/1 Rate

NMR Characterization of Electrolyte Fate at Elevated T

In a collaboration between INL and Washington State University NMR Center, we are determining the fate of electrolytes at higher temperature and protection modes afforded by INL phosphazene additives. This work is in early stages, as summarized below:

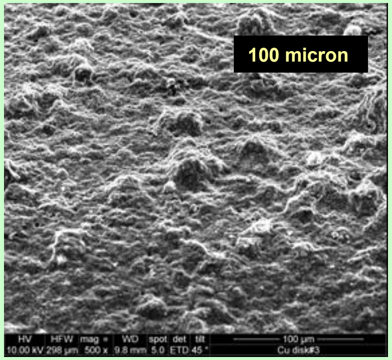
- High resolution multi-dimensional solution NMR is used to identify early degradation fragments from conventional electrolytes and determine the primary mechanisms of thermal degradation.
- Electrolyte formulations containing INL phosphazene additives are being studied using the same techniques in an attempt to elucidate the mechanisms by which the phosphazene additives prevent the organic carbonate degradation.
- From initial WSU findings, the baseline sample ($LiPF_6$ in a mixture of organic carbonates that contain no phosphazene), formed a gel at the bottom of the sealed tube over time at 60˚C. The sample has become much more viscous overall than Sample 1 (having the protective cyclic phosphazene additive),
- The evidence of phosphorus-proton coupling in the reaction products of the baseline sample suggest that phosphorus is interacting with the solvent mixture. These NMR-observable product species may be intermediates in polymerization of the carbonates, leading to a polycarbonate formation (this might explain the apparent increase in viscosity).
- However, formation of dimers, trimers, etc. of solvent molecules containing PF2 linking units, may explain why the new PF2 signals have continued to increase in intensity with respect to PF_6^- signals, and why they appear to be stable products in the mixture.
- The complexity of this system (5+ observable nuclei with spin-spin coupling interactions among at least 4 of them) will require a number of approaches to fully elucidate the mechanisms of degradation, as well as the protection afforded by the phosphazenes.

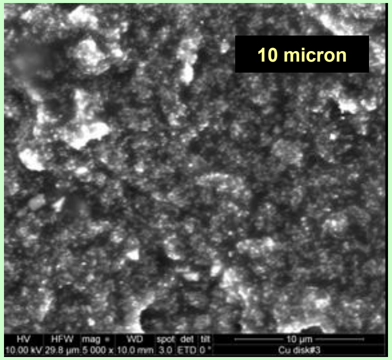
Alternative Polymer Anodes for Li-ion Batteries

To Replace Conventional Carbon Anodes

Cell Testing and Electrochemical Characterization was performed to determine cycling performance over voltage, as well as aging trends.

Typical Conditions: C/10 cycling to progressively higher voltage (max. 5V) with no taper charging. Prolonged cycling: 3.5 to 4.7 - 4.9V.





Cell Particulars:

- Case: coin cell (2032-type)
- Anode: INL Polymer Matrix on Cu
- Cathode: Li-NiMnCo Oxide (3M) on Al
- Electrolyte: 1.2M $LiPF_6$ in EC-EMC (2:8)

Anode laminate thickness: 70-90 µm in most cases; some are non-calandared.

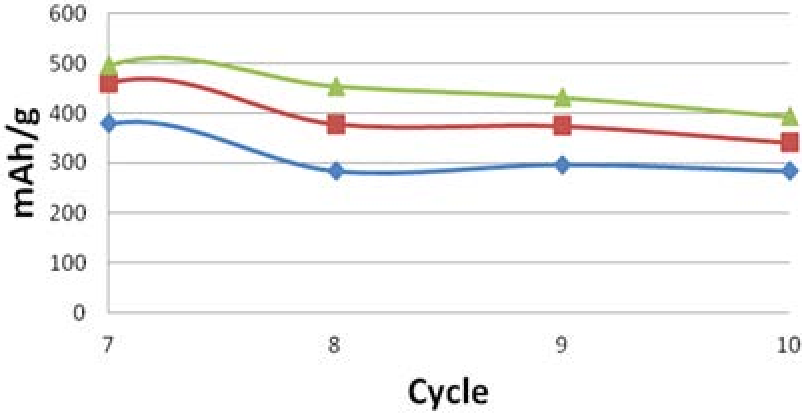
- ➢ **Phase 1, 2,** and **3** studies are complete, covering a matrix involving four classes of polymeric materials.
- ➢ Initial test results confirm that INL anode materials are feasible in lithium-ion batteries, and that they function at higher voltages to support higher-power capability. Optimization of poly-matrix, electrode formulation, charging protocol, and electrolyte will improve capacity, cycling rate, and longevity.

Alternative Anode Testing & Characterization

Advantages to adopting a phosphazene polymer basis for anodes:

- Ability to form 3-D scaffolds populated with desirable chemical moieties,
- Li host capability,
- Supports overall move to a more inorganic battery chemistry,
- Phosphorus mitigates cell flammability,
- Reduces energy released during thermal runaway, amenable to higher cell voltages,
- Physical and electronic properties that are highly engineerable,
- Host polymer also serves as a binder (no need for PVDF).

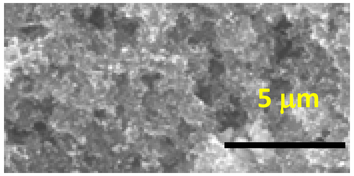
- The electronic/electrostatic environment of these polymeric hosts encourages and sustains lithium insertion at relatively high voltages to enable usage of high voltage cathodes.
- This new class of anodes has shown noteworthy voltage stability and gravimetric capacity (competitive with graphite).



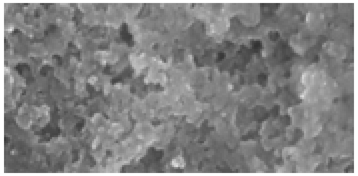
Gravimetric Discharge Capacities for a cell with Phase 3 anode vs HE5050 (post formation).

Alternative Anode Testing & Characterization

INL phosphazene polymer anodes can be processed by conventional methods, or spray cast onto copper foil. We are optimizing deposition techniques to maximize adhesion and conductivity.

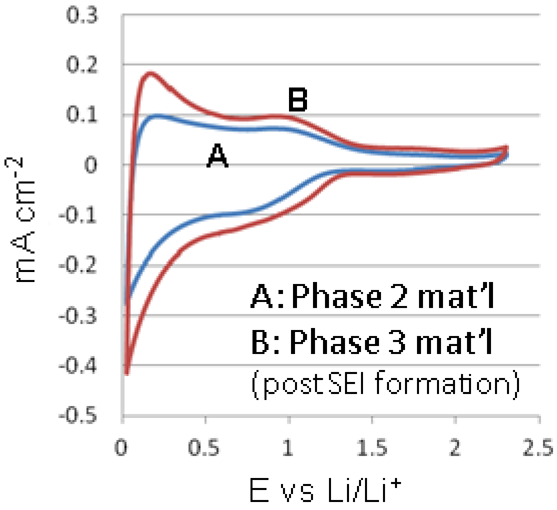


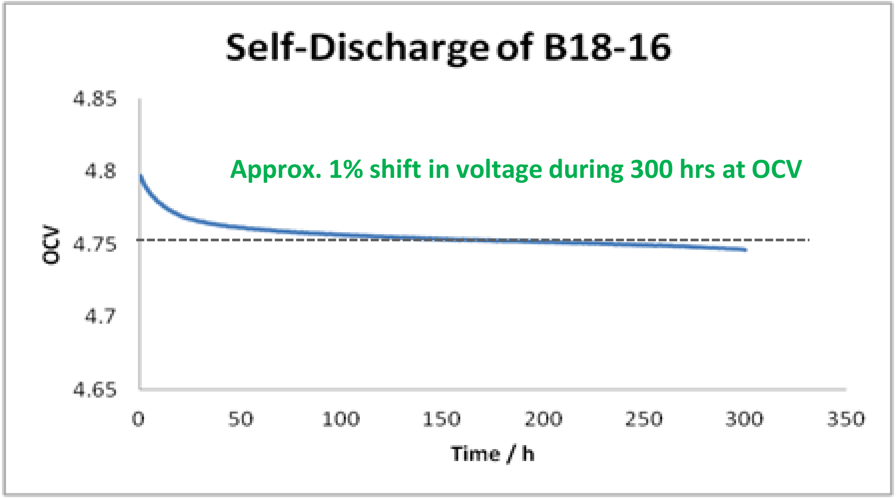
As Prepared



After Cycling
(more than 60 full cycles)

Structural stability confirmed during post-mortem analysis with SEM.



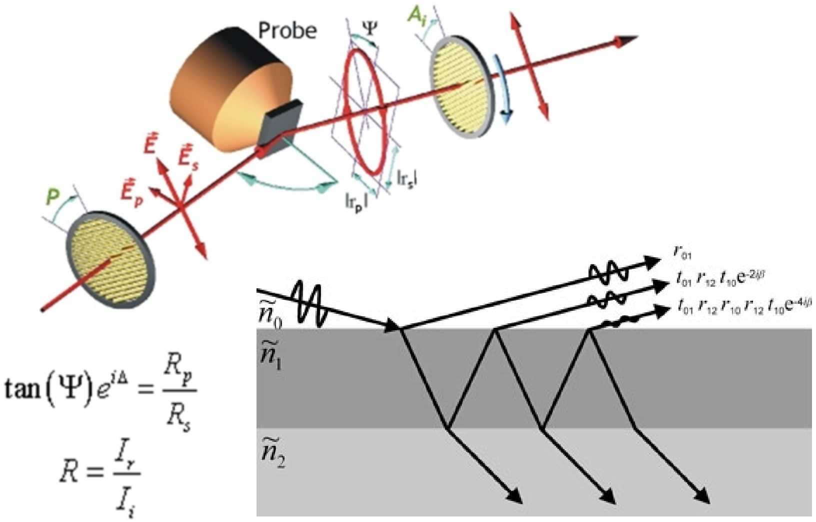


Approx. 1% shift in voltage during 300 hrs at OCV

While these are early scoping results, they are indicative of a viable class of materials.

Ellipsometry for Electrode Material Characterization

- ☐ **INL has recently obtained Spectroscopic Ellipsometry capability, a powerful tool for characterizing surface morphology features and interfacial processes to near nano-resolution.**
- ☐ **Critical surface attributes (SEI films) can be monitored over aging through *in-situ* analysis.**
- ☐ **Effects of extreme conditions can be evaluated (low temperature, high/low SOC, etc.)**



$$\tan(\Psi) e^{i\Delta} = \frac{R_p}{R_s}$$

$$R = \frac{I_r}{I_i}$$

Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. The measured parameter values are related to the ratio of Fresnel reflection coefficients R_p and R_s for *p* and *s* polarized light, respectively.

Collaborations

- **SNL.** SNL is performing abuse tolerance cell testing with electrolytes having the best candidate INL additives. Contact: Chris Orendorff
- **ANL.** Provides ABR electrode materials for INL cell-level studies. Supports review of historical data from ANL testing of other electrolyte additives. Oversees scale-up activities for production of ABR materials. This is an ongoing collaboration. Contacts: Khalil Amine, Daniel Abraham, Gregory Krumdick
- **Dow Chemical.** Supported INL electrolyte modeling of Dow proprietary systems. Considering involvement in INL electrolyte additives for Li-ion systems. Periodic discussions have been held under Non-disclosure Agreements (NDA). Contact: Gretchen Baier
- **Princess Energy Systems (PES).** Involved in formative discussions of incorporating phosphazenes into Li-ion cells and corresponding intellectual property and market issues. Contacts: Thomas Cripe, John Burba
- **Bren-tronics Energy Systems (BES).** INL and BES are collaborating on scale-up and deployment issues for nonflammable electrolyte additives. Contact: Joseph Barrella
- **US SOCOM**. Collaboration between US SOCOM, INL, and ANL focuses on producing a safer and more reliable lithium-ion battery chemistry for selected Navy platforms.
- **Washington State University (NMR Center).** Performing NMR studies to determine fate analysis of electrolytes at higher temperature and protection modes afforded by INL phosphazene additives. Contact: Prof. Bill Hiscox

Future Work *(pending further funding)*

- ❑ Continued synthesis work for newer generation ionic liquid phosphazenes and linear variants.
- ❑ Cell testing of INL electrolyte systems with ABR-relevant high-voltage couples, complemented by half-cell studies.
- ❑ Continued testing at SNL for abuse tolerance, looking at 10-20% phosphazene levels in electrolytes.
- ❑ Alternative anode materials: improvement and extension of performance (Phase 4): optimizing cross-linking constituents, enhancing electronic conductivity, matching polymeric properties to other host materials (Si, carbon, etc.), and achieving balance of micro/macro porosity. INL phosphazene electrolyte additives will be standard for all future cell chemistries. Economical synthesis and simple electrode manufacturing are advantages toward full-scale production.
- ❑ Expanded characterization of electrode materials to include ellipsometry, PAS, PALS, solid-state NMR, and post-mortem analysis of cell internals. Publish NMR study jointly done with Washington State University.
- ❑ Continue to work with ANL Materials Scale-Up Facility to determine metrics for production of best candidate INL additives.

Summary

- INL phosphazene additives protect the battery electrolyte under conditions of elevated temperature and high voltage.
- New phosphazene materials for battery electrolytes have been added to include more fluorinated and ionic liquid compounds, based on our knowledge of previous compounds' efficacy.
- At additive levels (3%) INL phosphazene additives provide Thermal Stability within both the electrolyte and cell environment (e.g., SNL abuse test data). This behavior is advantageous toward prolonged battery life and to enable safer and reliable operation at elevated temperatures.
- Cell testing with NCA-Toda/Carbon: Excellent compatibility and performance is seen. In some cases electrolytes with INL additives perform better than BL electrolyte.
- Per voltammetry, INL phosphazenes generally improve properties of the SEI and extend the operating voltage range. Our method provides clear metrics by which to quantify SEI properties that are relevant toward issues of irreversible capacity loss, power, self-discharging, and shelf-life.
- An underlying driver for this work is that replacement of carbon anodes would further improve safety of lithium-ion cells, particularly in cases of thermal runaway. We continue to build in the theme of a carbon-reduced "inorganic" battery chemistry to achieve longevity and safety under broader use conditions.
- Phase 3 INL Phosphazene-based intercalative host materials have undergone successful characterization and testing as anodes in lithium-ion cells. These materials offer a safer alternative to graphitic-based anodes, and are relatively inexpensive to produce.
- These polymer anode materials function reversibly as lithium hosts, and allow operation at higher voltages (approach **5V**). They accommodate other host materials (Si, graphite) by acting as an elastic polymeric binder (no PVDF needed).

Acknowledgements

- **DOE Vehicle Technologies Program (VTP)**
- **Peter Faguy, DOE-EERE, VTP**
- **David Howell, DOE-EERE, VTP**
- **Tim Murphy, INL**
- **Daniel Abraham, ANL**
- **Chris Orendorff, SNL**

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This work would not be possible without the outstanding support from

- **David Jamison, INL**
- **Christopher Michelbacher, INL**

This work was performed for the United States Department of Energy under contract DE-AC07-05ID14517.

Technical Back-Up Slides

Rationale for Working with Phosphazenes

- Classes of non-flammable materials:
  - Phosphorus-based: phosphates, phospholanes, phosphines, phosphazenes etc.
  - Borates
  - Pyrocarbonates, which release CO_2
  - Halogenated: fluorinated carbonates, fluorinated ethers
  - Silicon-based: siloxanes, silanes.
- For over a decade there have been many reports of studies directed at decreasing the flammability of Li-ion electrolytes. However, there is still no commercially available low-flammability electrolyte that has competitive transport properties over broad temperature ranges, and has been successfully applied in a commercial battery.
- Most of studied compounds provide some safety benefit, however, seriously undermine the SEI-forming properties of Li-ion electrolytes which is an unacceptable cost to cell performance.
- We chose to work with phosphazenes because they appear to be more beneficial to critical SEI properties and we aim to expand phosphazene options by synthesis pathways that offer greater variability of final molecular design.

Electrolyte Production Highlights

- Amenable to production via continuous synthesis
  - Not interrupted production (like batch, semi-batch processes)
  - Very high volume, low worker numbers
  - Most efficient chemical production method known
- Purification is extremely simple
  - Continuous counter-current aqueous extraction
  - Waste products low toxicity/very low disposal cost
  - Excess reagents easily recovered for reuse
- Required ultra-drying is unusually easy as the electrolyte is non-volatile and thermally very robust

We are working with ANL to initiate scale-up of INL phosphazene additives at their materials scale-up facility.

Chemical Synthesis Capabilities

- Over 3,000 ft^2 of wet chemistry labs
- Multiple fume hoods (11) and air-free synthetic manifolds
- Focused on a variety of synthetic projects
  - Electrolytes
  - Polymers
  - Membranes
  - Selective extractants

- The new 140,000 ft^2 research laboratory facility (REL) scheduled for occupancy in 2013.