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

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2012 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:** TBD, depends on progression of new milestones.	**Cell/battery Life** **Abuse Tolerance, Reliability and Ruggedness** **Performance (energy density)** **Cost**
Budget	**Partners**
Funding Received: **FY 11: $ 400K** **FY 12: $ 500K**	**Argonne National Lab (ANL)** **Dow Chemical** **Princess Energy Systems** **Sandia National Lab (SNL)** **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 solvents.
- ♦ Determine what phosphazene structures are more tolerant to high and low voltage, and to high temperatures.
- ♦ Gain understanding of molecular-scale interactions between phosphazenes and other electrolyte 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
Cell testing using LNMO/LTO and NMC/Carbon* couples: aging studies	Completed	October 2011
Phase 1 concept validation for alternative anode materials	Completed	October 2011
Cell testing using HE5050/Carbon couple: characterization of capacity and impedance attributes	Completed	December 2011
Cell testing using HE5050/Carbon couple: aging studies	Completed	March 2012
DFT study on complete FM Series (fluorinated cyclics)	Completed	February 2012
Synthesis of newer FM series	Completed	August 2011
Phase 2 concept validation for alternative anode materials	Completed	March 2012
Initial PALS measurements of alternative anode materials	Completed	March 2012
Synthesis of newer Ionic Liquid Phosphazenes	In Progress	
Abuse testing of INL Phosphazene electrolyte additives (SNL)	In Progress	
Collaboration with ANL regarding scale-up of INL electrolyte compounds	In Progress	
Various supporting characterization and cell testing will be ongoing throughout FY 2012.		

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) characterization, (3) DFT 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 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 have been sent to SNL for abuse-tolerance testing.*

Approach

Alternative 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

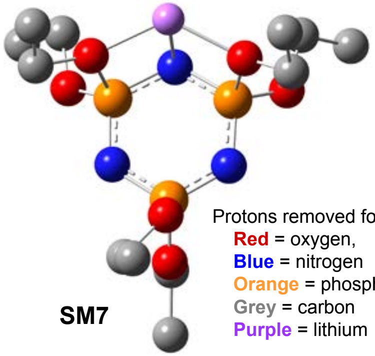
SM: employs ether groups attached to the phosphorus centers

AL: employs unsaturated analogues of the SM series

FM: employs fluorinated analogues of the SM series

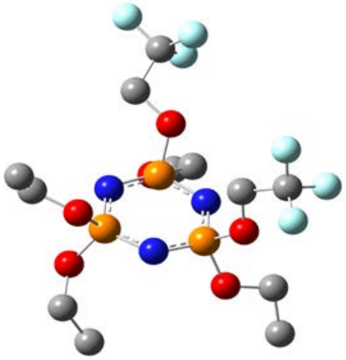
PhIL: ionic liquid variation

All materials covered by patents issued or pending.

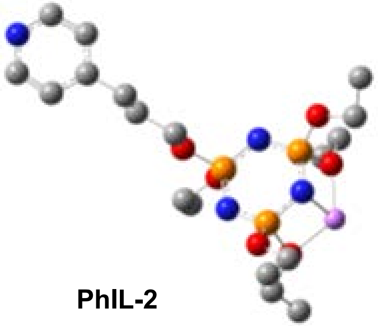


SM7

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



FM3

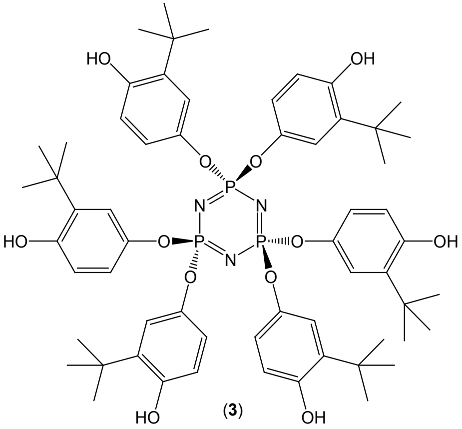


PhIL-2

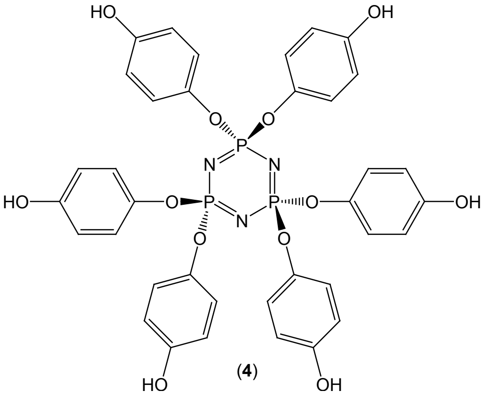
Novel Approach to Anode Engineering

- 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., competitive energy storage capacity could be achieved).
  - ☐ Inherently low flammability due to presence of phosphorous.
  - ☐ Economical method to apply phosphazene electrode material to metal current collectors.

Successful cell testing to 5V!



(3)



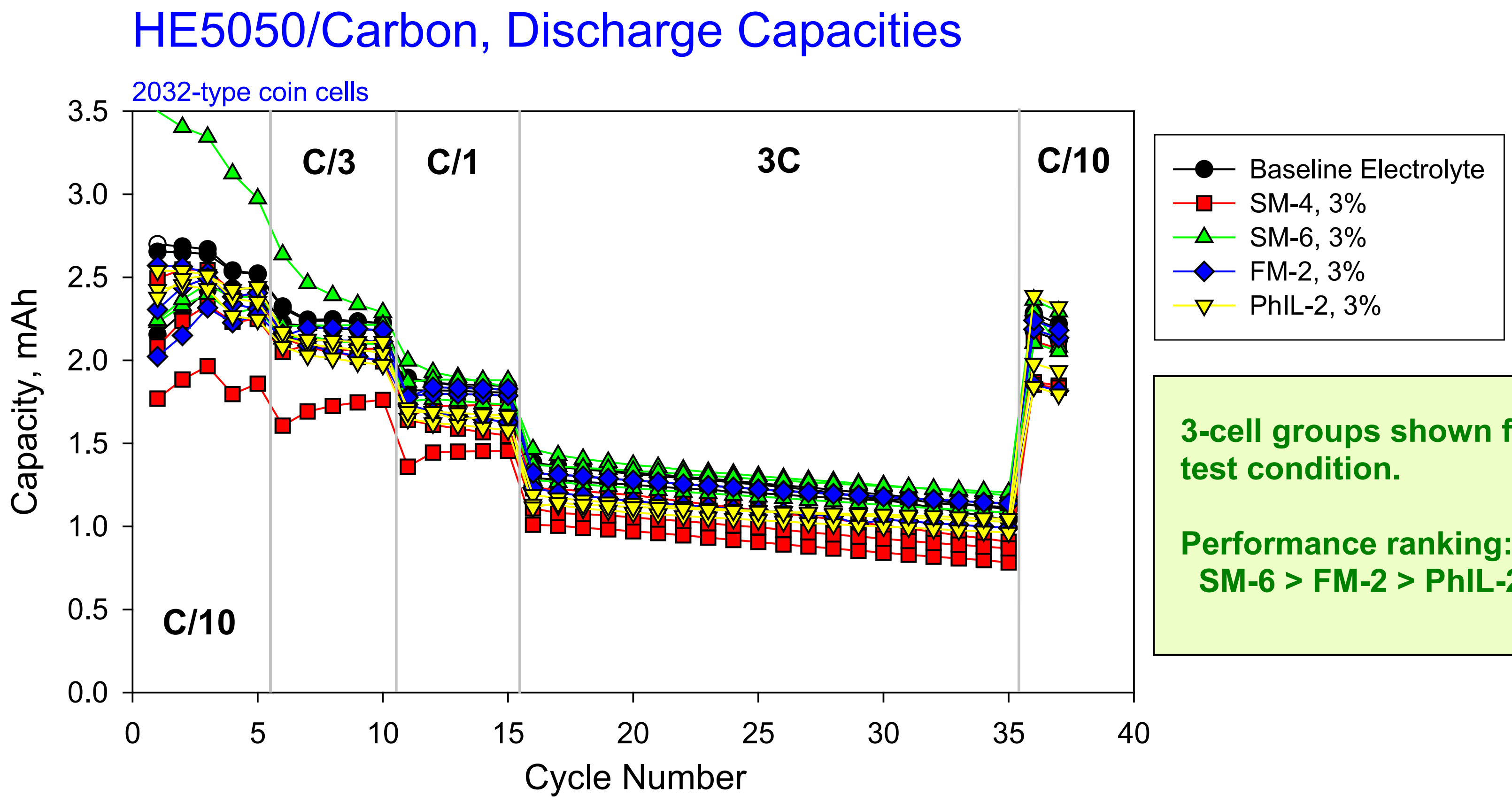
(4)

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

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).
- Cell testing has continued with ABR-relevant electrode couples (recently HE5050/Carbon). Test results are encouraging regarding capacity retention and aging trends, with INL additives exceeding performance of the baseline in some cases.
- Recent voltammetry measurements confirm INL additives provide expanded voltage stability. Our improved voltammetry technique yields more precise determination of SEI parameters.
- Initial abuse testing at SNL shows that INL electrolyte additives enhance thermal stability.
- Density Functional Theory (DFT) simulations have been performed to determine the solvent-to-lithium binding energies for key phosphazene additives (full FM series). Reducing this interaction will promote greater cell efficiency in terms of interfacial processes.
- Alternative anode materials based on phosphazene chemistry have been synthesized and tested to 5V, indicating these are viable hosts for lithium-ion cells. Three classes of materials have been tested, showing an evolution of improved performance.
- Initial Positron Annihilation Spectroscopy (PAS) measurements have been completed for first-generation INL alternative anodes.

Testing Additives with ABR-relevant Electrodes



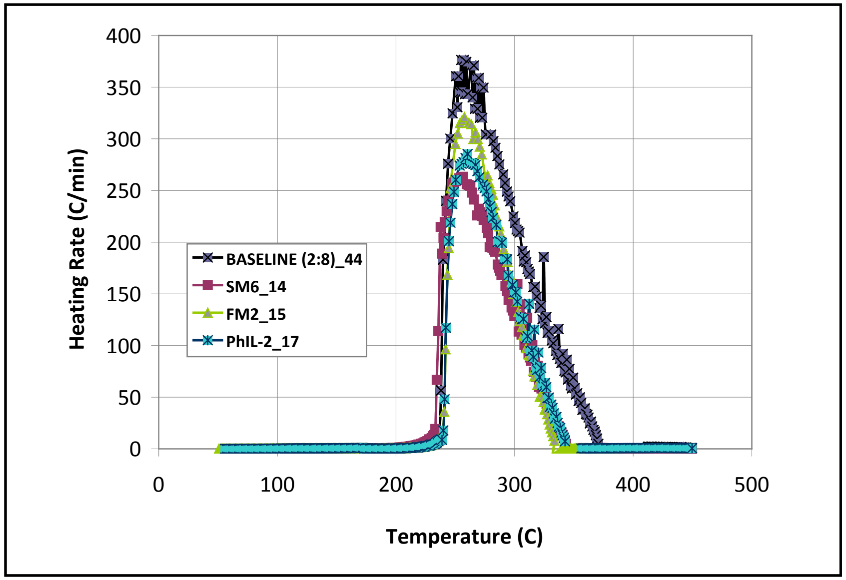
3-cell groups shown for each test condition.

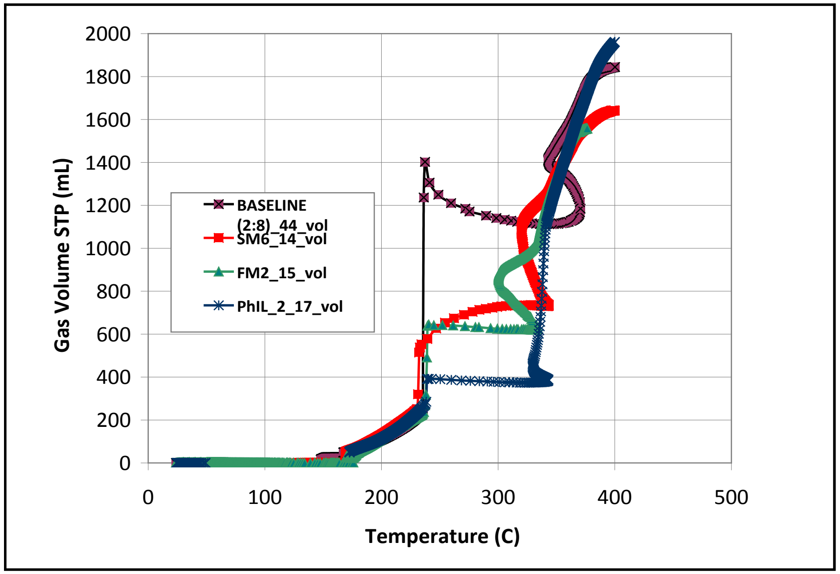
Performance ranking:
SM-6 > FM-2 > PhIL-2 > SM-4

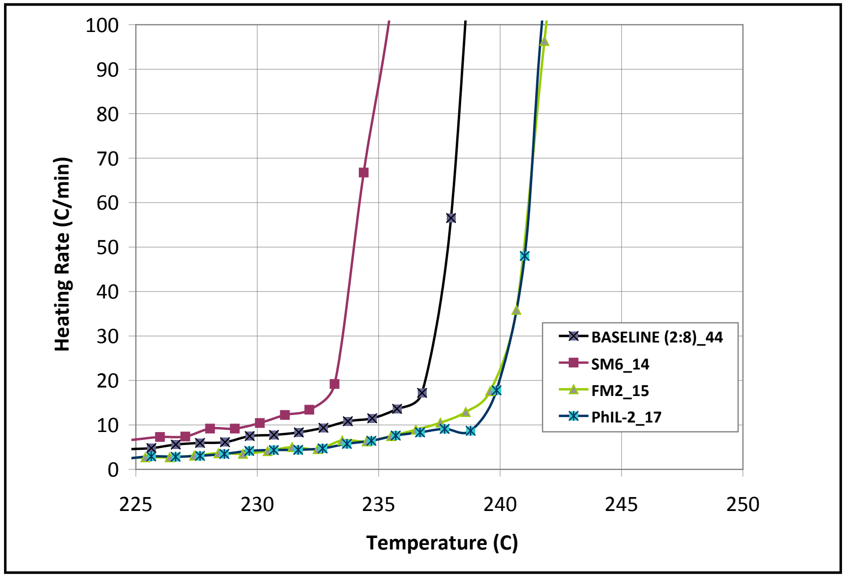
Improvement over baseline performance is seen in SM-6 and FM-2 in some cases.

SNL Abuse Testing of INL Additives (3%)

Shown Results are for initial testing, with more in progress.



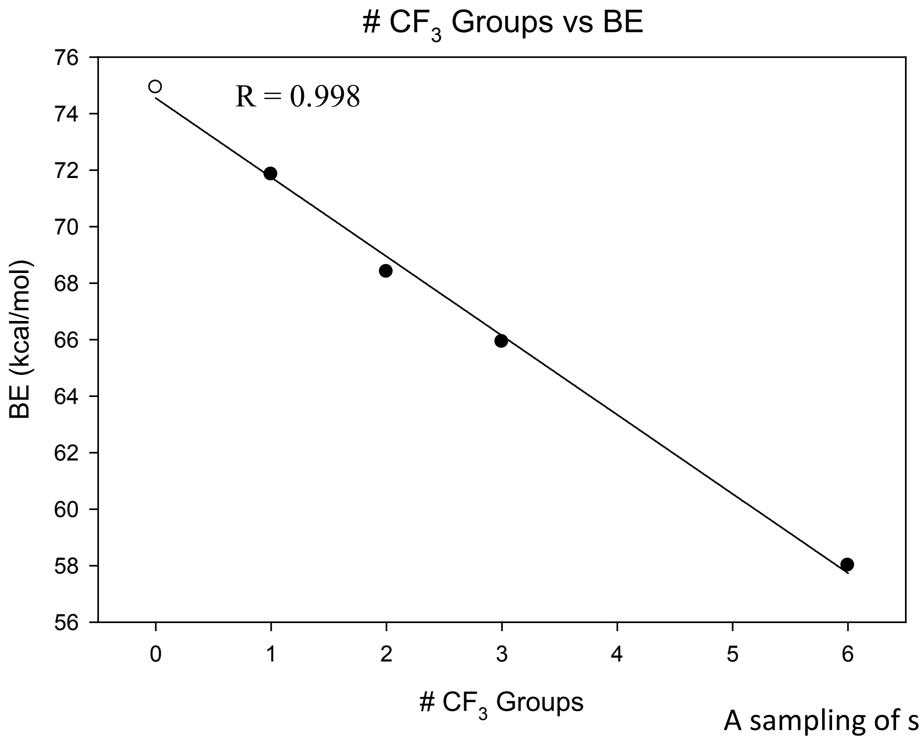




INL additives were tested within 18650 cells having NCA/Carbon. Additive levels were 3% in a baseline of 1.2M $LiPF_6$ in EC-EMC (2:8).

- All additives reduced the peak heating rate by as much as 100 °C/min, compared to BL.
- Some additives delayed the onset temperature a small amount.
- All additives dramatically changed the progression of gas evolution, compared to BL.

DFT Modeling of Li-Solvent Binding Energy

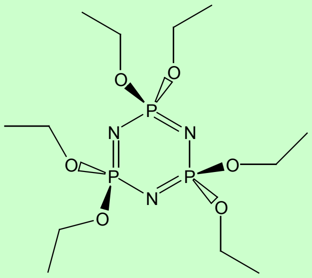


Modeling was done using Gaussian03, B3LYP/6-311++G(d,p). Structures are true minima (no imaginary frequencies).

BE is seen to decrease linearly, likely due to increasing electron withdrawing effect as more CF_3 groups are added. This also leads to molecular distortion and slightly weakened coordination to Li^+.

Lower BE translates to lesser solvation of Li^+ and more efficient charge transfer.

A sampling of structures that were modeled….



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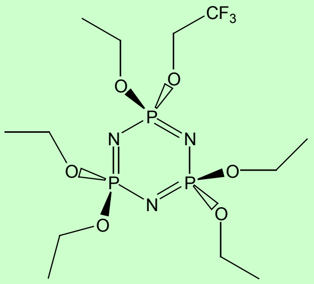
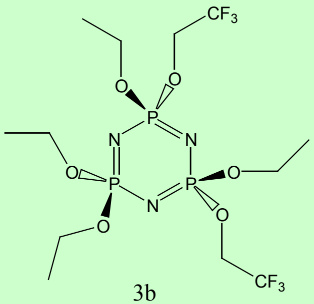
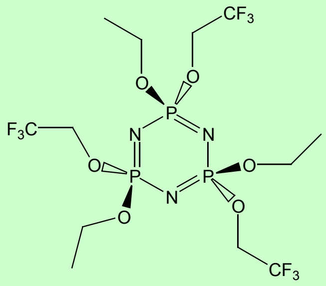


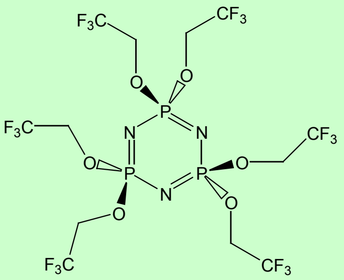
2



3b

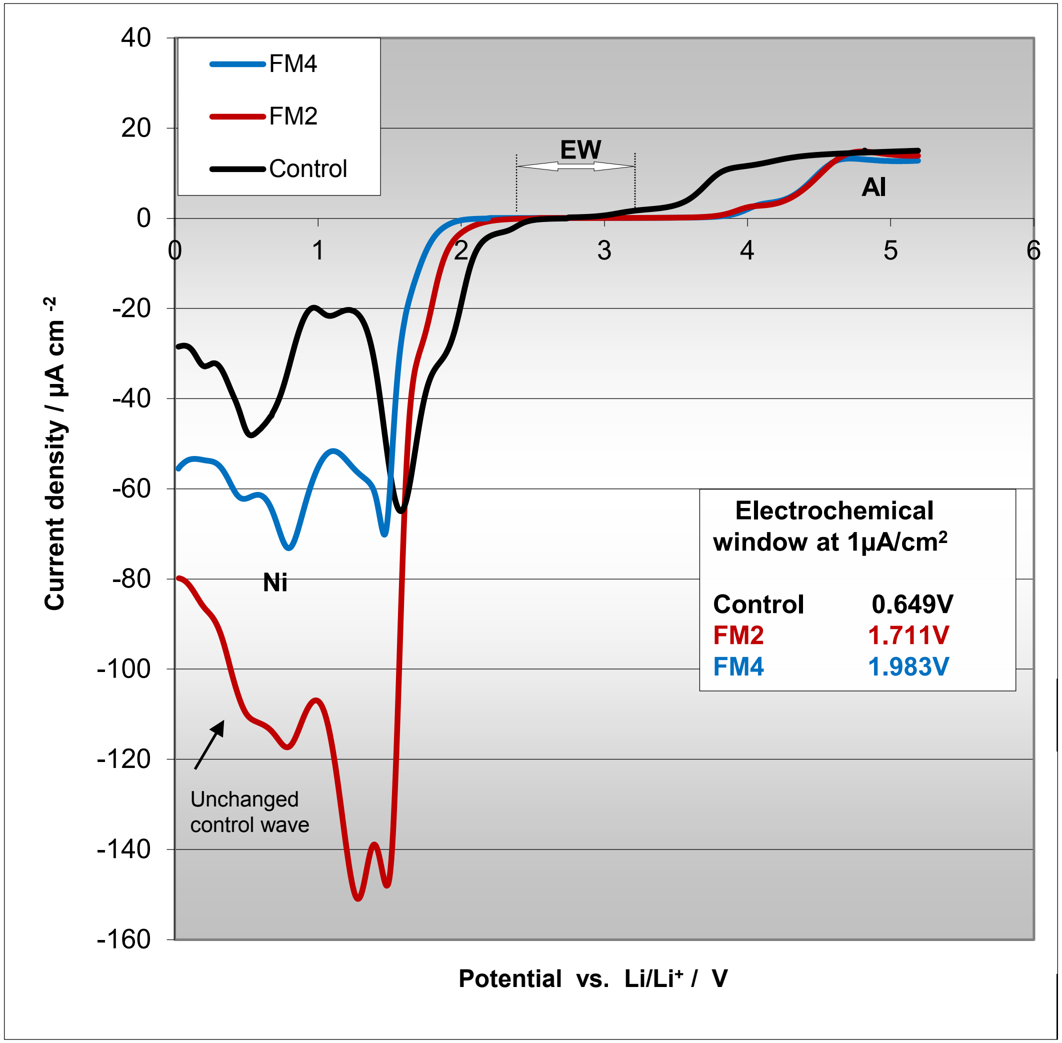


4b



5

Voltammetry of Phosphazene-based Electrolytes



Electrochemical window at 1μA/cm²

Control	0.649V
FM2	1.711V
FM4	1.983V

Example measurements (FM series)

- ***Phosphazenes do increase electrochemical window at negative and positive ends.***
- ***All the windows are less than operating voltage of Li-ion cells.***
- ***At potentials beyond the electrochemical window, passivation does occur forming SEIs.***
- ***Properties of passivating layers need to be measured quantitatively.***

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

Cell Testing, Alternative Anodes

Cell Testing was performed to determine cycling performance over voltage.

Stage 1: C/10 cycling to progressively higher voltage (max. 5V) with no taper charging.

Stage 2: C/10 cycling to progressively higher voltage (max. 5V) with 2.5 hr taper charging.

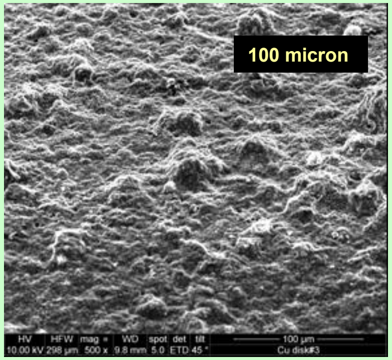
Cell Particulars:

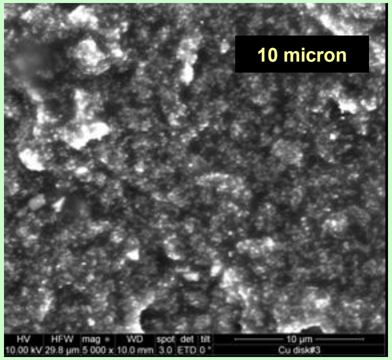
Case: coin cell (2032-type)

Anode: INL Phosphazene Matrix on Cu

Cathode: Li-NiMnCo Oxide (3M) on Al

Electrolyte: 1.2M $LiPF_6$ in EC-EMC (2:8)





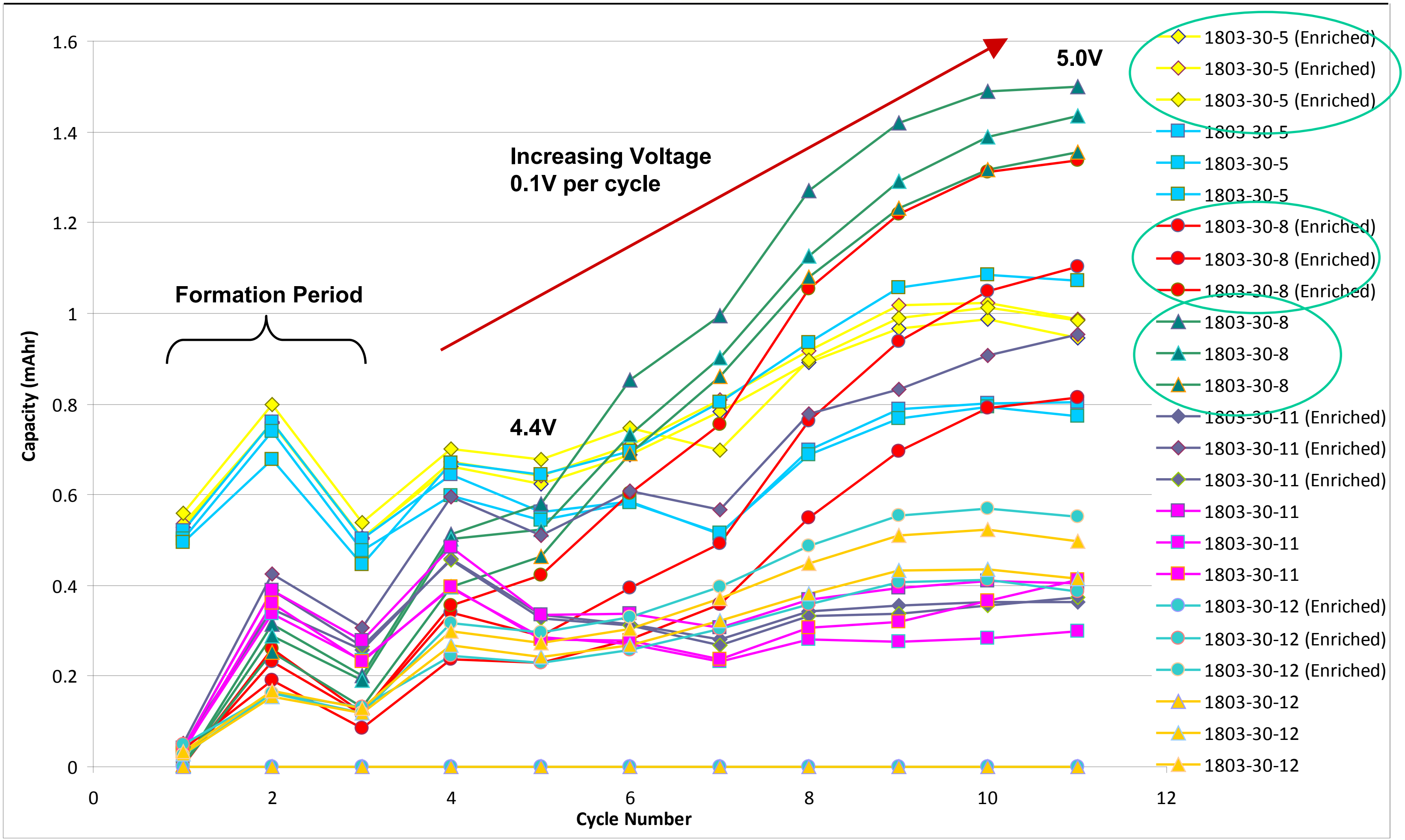
Anode laminate thickness: 70-90 μm in most cases, and are non-calandared.

- **Phase 1** and **2** studies are complete, covering a matrix involving three classes of polymeric materials.

- Initial test results confirm that INL anode materials are feasible in lithium-ion batteries, and that they perform better at higher voltages to support higher-power capability. Optimization of cyclomatrix, electrode formulation, charging protocol, and electrolyte will improve capacity, cycling rate, and longevity.

Phase 1 Study:

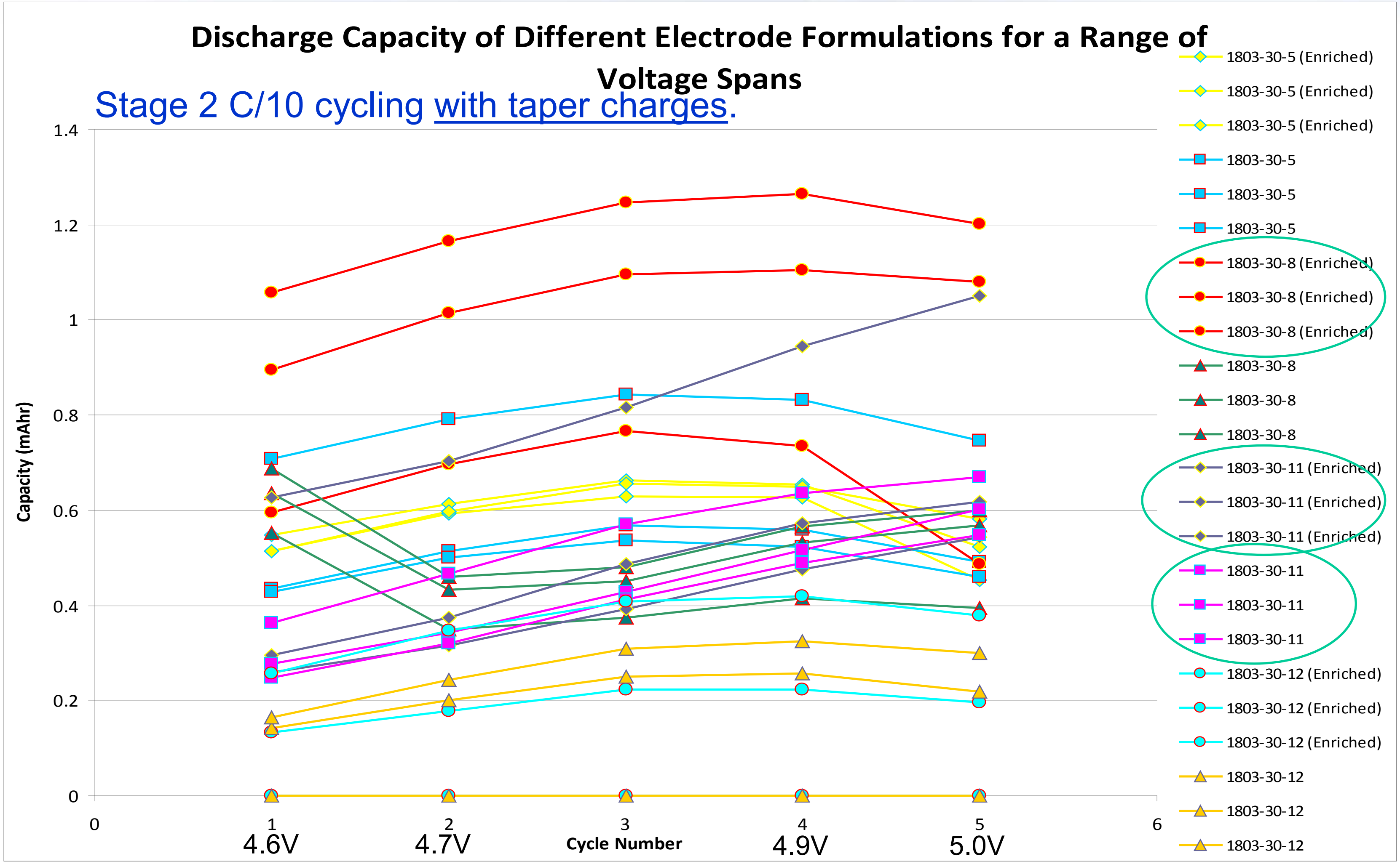
C/10 discharge cycling with no taper charges.



These tests are the first of their type for these new materials. **Cycling up to 5V is confirmed.** Performance could improve by optimizing polymerization, formulation, and charge protocol.

Tech. Accomplishments

Phase 1 Study



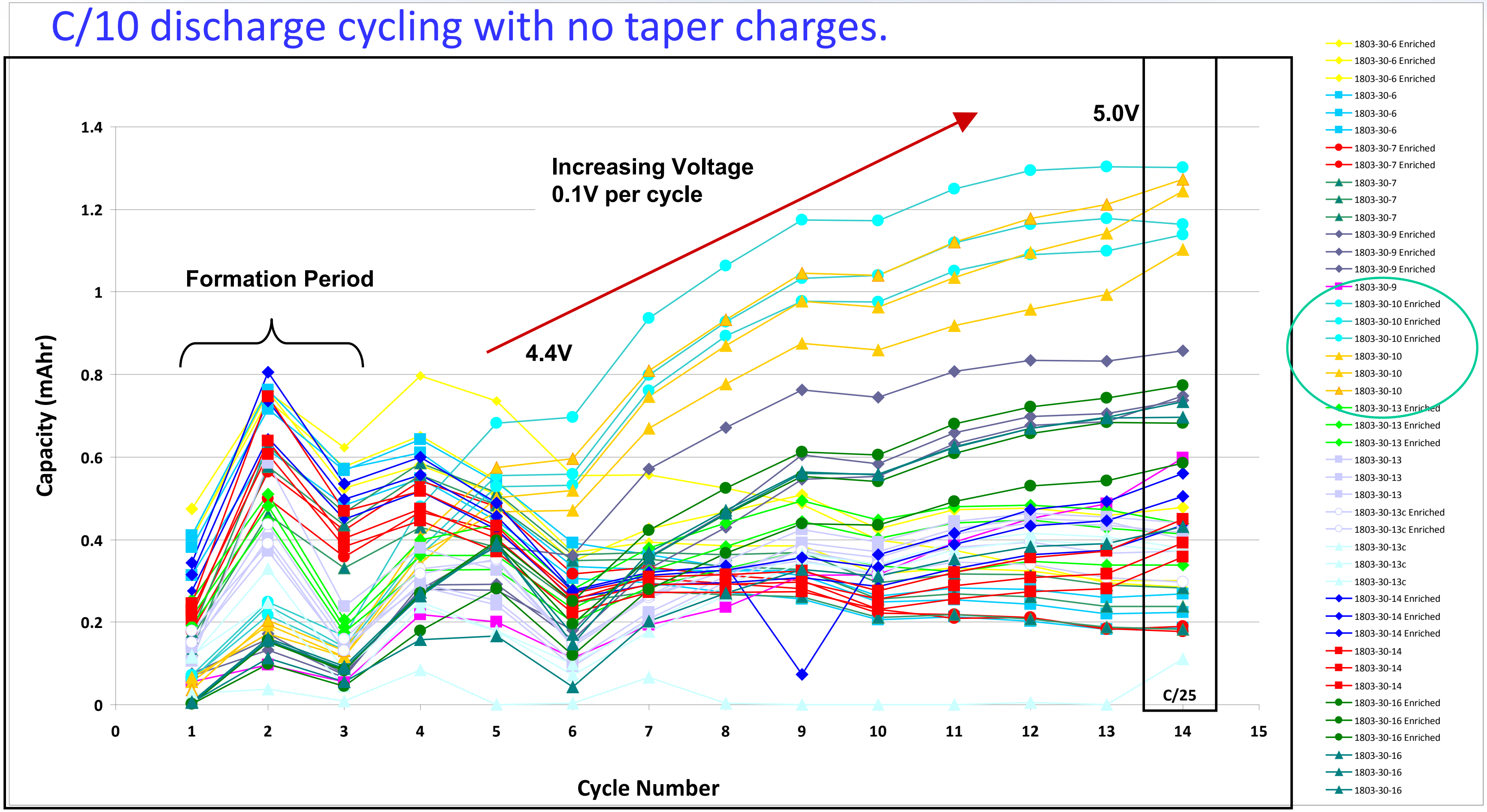
Discharge Capacity of Different Electrode Formulations for a Range of Voltage Spans

Stage 2 C/10 cycling with taper charges.

30-11 improves over entire voltage range! Optimal V_{max} is 4.8-4.9V for most systems; INL Electrolyte additives would increase this.

Phase 2 Study:

C/10 discharge cycling with no taper charges.



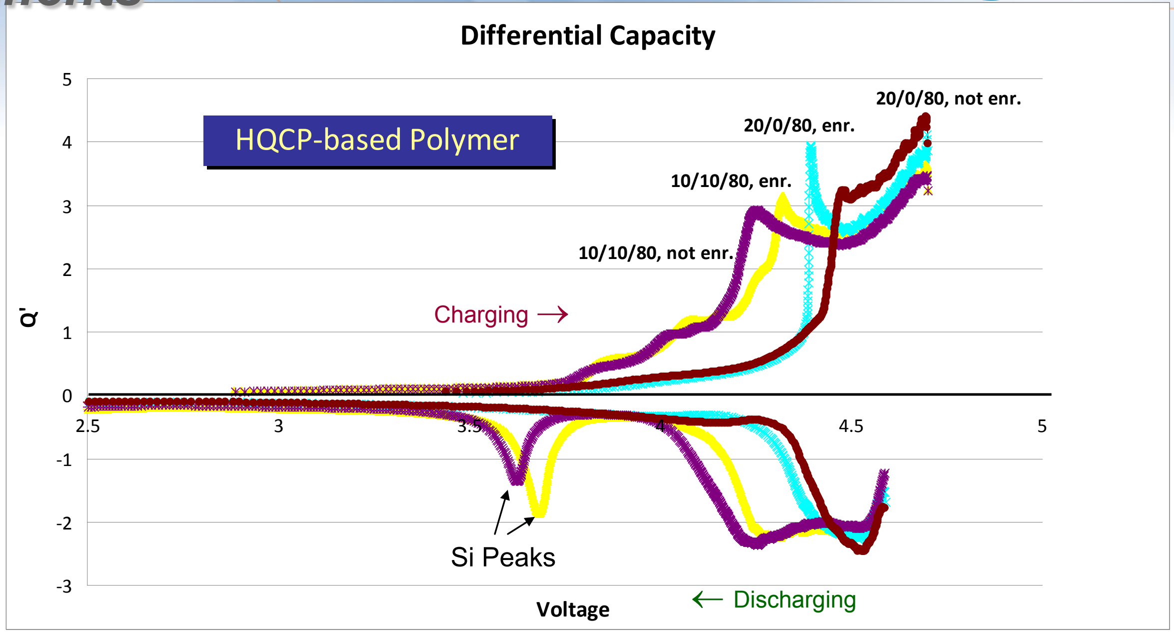
Higher capacity is attained at lower voltages, compared to Phase 1 materials. Distinct differences in polymeric chemistry result in differences in energy storage. We can utilize such correlations to engineer finely tuned materials.

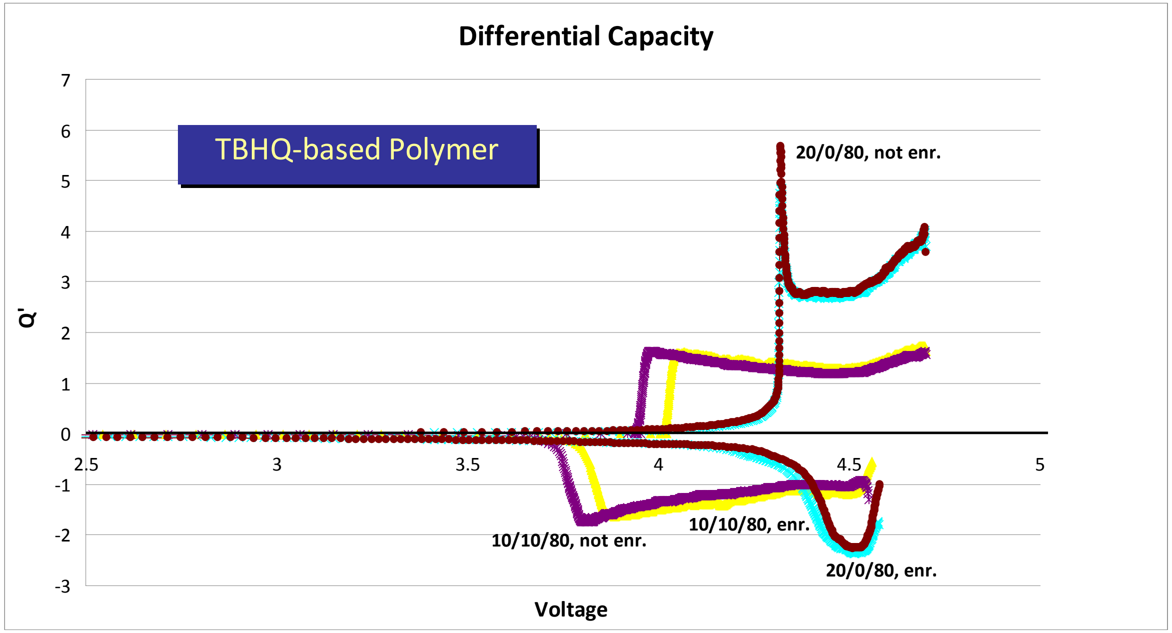
Tech. Accomplishments

Idaho National Laboratory

Selected

dQ/dV to 4.7V



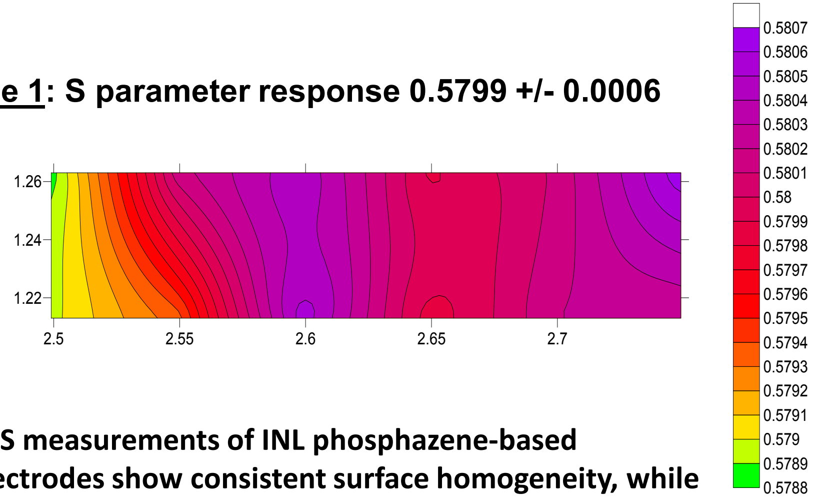


PAS & PALS for Electrode Material Characterization

Positron Annihilation Spectroscopy
Positron Annihilation Lifetime Spectroscopy

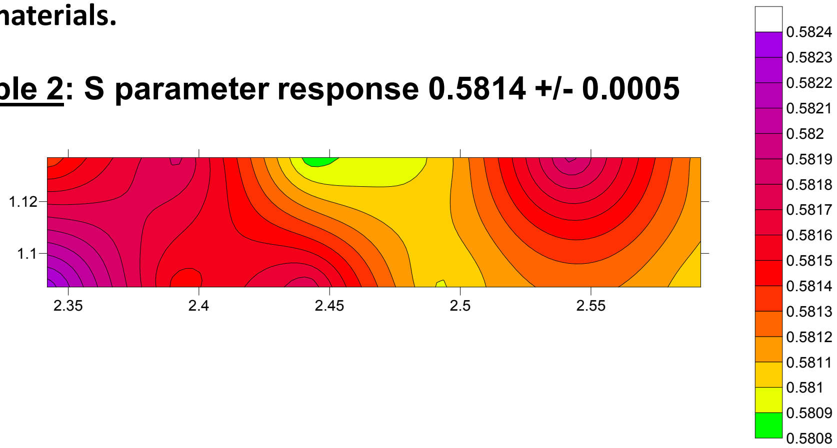
PAS and PALS are critically important tools for characterizing structural details of solids down to the nano-level. Through these tools we can look at defect attributes (dislocations), micro-porosity, and particle fracturing over aging.

Sample 1: S parameter response 0.5799 +/- 0.0006



PAS measurements of INL phosphazene-based electrodes show consistent surface homogeneity, while detecting differences in electronic structure of the materials.

Sample 2: S parameter response 0.5814 +/- 0.0005



Collaborations

- **Princess Energy Systems.** Involved in formative discussions of incorporating phosphazenes into Li-ion cells and corresponding intellectual property and market issues. Contact: Thomas Cripe
- **SNL.** Provided NMC/Carbon electrode material for INL coin cell studies. SNL is performing abuse tolerance testing on electrolytes having the best candidate INL additives to date. Contact: Chris Orendorff
- **ANL.** Provides ABR electrode materials for INL coin cell studies. Supports review of historical data from ANL testing of other electrolyte additives. This is ongoing. Contacts: Khalil Amine, Daniel Abraham
- **Dow Chemical.** Considering involvement in commercial production of INL electrolyte additives for Li-ion systems. Periodic discussions have been held, and a Non-disclosure Agreement (NDA) has been signed between INL and Dow. Contact: Dee Strand
- **US SOCOM**. Collaboration between USSOCOM, INL, and ANL will focus on producing a safer and more reliable lithium-ion battery chemistry for selected Navy platforms.

Future Work

- Continued synthesis work guided by DFT to fine tune solvent properties toward cell stability and lowered association with lithium.
- Parallel research at INL is targeting other phosphazene families and alternate salts to enable electrolyte systems having mostly phosphazene solvents that exploit the inherent low flammability of these additives.
- ^{7}Li NMR: look at mechanism for thermal stability induced by phosphazenes.
- Continued testing of INL electrolyte additives with ABR-relevant electrode couples. Half-cell studies on SEI films will be considered.
- Continued testing at SNL for abuse tolerance, with an eye on how INL additives mitigate the onset of thermal runaway.
- Alternative electrode materials: improvement and extension of performance (Phase 3): optimizing the cyclomatrix constituents (blends, and new scaffolds), enhancing conductivity, matching polymeric properties to other host materials (Si, carbon, etc.), usage of INL phosphazene electrolyte additives, and through understanding rate limitations. Economical synthesis and simple electrode manufacturing are advantages toward full-scale production.
- High-voltage testing of INL electrolyte systems with INL alternative electrodes, using aluminum-clad coin cell hardware. Progress toward an “inorganic battery”.
- Expanded characterization of electrode materials to include ellipsometry, PAS, PALS, solid-state NMR, and post-mortem analysis of coin cell internals.

Summary

- INL phosphazene materials aimed at battery electrolytes has grown to include more fluorinated and ionic liquid compounds to accomplish customized properties regarding lithium association.
- 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 greater operation at elevated temperatures.
- Cell testing with HE5050/Carbon: In some cases INL additives perform better than BL electrolyte.
- Per voltammetry, INL phosphazenes improve properties of the SEI on cathode (+) side and increase operating voltage. 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.
- Density Functional Theory (DFT) simulations confirmed lowered Binding Energy trends for successively higher fluorination of cyclic compounds.
- 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.
- INL Phosphazene-based intercalative host materials have undergone successful initial 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 materials function reversibly as lithium hosts, and allow operation at higher voltages (≥ **5V**). They accommodate other host materials (Si, graphite) by acting as an elastic polymeric binder. Electrochemical cycling efficiency increases with voltage. PALS will give insights on microstructure.

Acknowledgements

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

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This work would not be possible without the outstanding support from

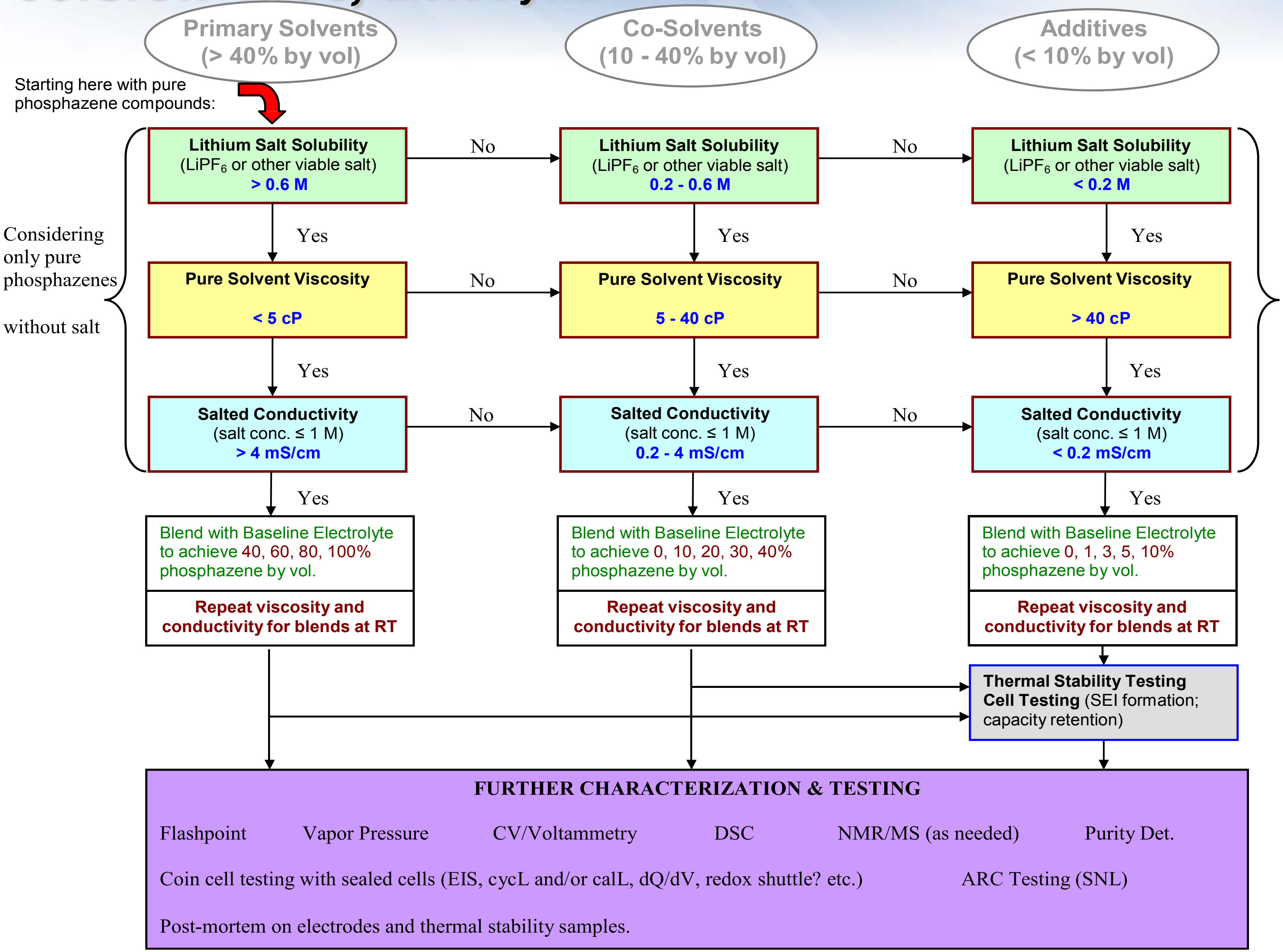
- **David Jamison, INL**
- **Christopher Michelbacher, INL**

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

Technical Back-Up Slides

Approach

Decision Tree, Electrolytes



Primary Solvents
(> 40% by vol)

Co-Solvents
(10 - 40% by vol)

Additives
(< 10% by vol)

Starting here with pure phosphazene compounds:

Considering only pure phosphazenes without salt

Lithium Salt Solubility
($LiPF_6$ or other viable salt)
> 0.6 M

No →

Lithium Salt Solubility
($LiPF_6$ or other viable salt)
0.2 - 0.6 M

No →

Lithium Salt Solubility
($LiPF_6$ or other viable salt)
< 0.2 M

Yes

Pure Solvent Viscosity
< 5 cP

No →

Pure Solvent Viscosity
5 - 40 cP

No →

Pure Solvent Viscosity
> 40 cP

Yes

Salted Conductivity
(salt conc. ≤ 1 M)
> 4 mS/cm

No →

Salted Conductivity
(salt conc. ≤ 1 M)
0.2 - 4 mS/cm

No →

Salted Conductivity
(salt conc. ≤ 1 M)
< 0.2 mS/cm

Yes

Blend with Baseline Electrolyte to achieve 40, 60, 80, 100% phosphazene by vol.

Repeat viscosity and conductivity for blends at RT

Blend with Baseline Electrolyte to achieve 0, 10, 20, 30, 40% phosphazene by vol.

Repeat viscosity and conductivity for blends at RT

Blend with Baseline Electrolyte to achieve 0, 1, 3, 5, 10% phosphazene by vol.

Repeat viscosity and conductivity for blends at RT

Thermal Stability Testing
Cell Testing (SEI formation; capacity retention)

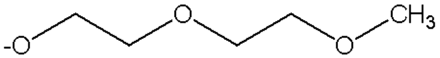
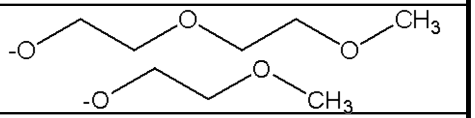
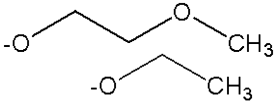
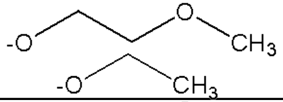
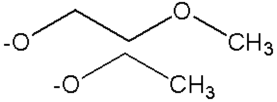
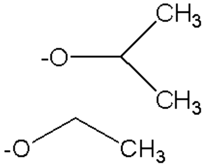
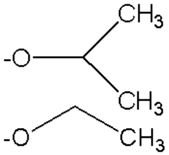
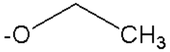
FURTHER CHARACTERIZATION & TESTING

Flashpoint   Vapor Pressure   CV/Voltammetry   DSC   NMR/MS (as needed)   Purity Det.

Coin cell testing with sealed cells (EIS, cycL and/or calL, dQ/dV, redox shuttle? etc.)   ARC Testing (SNL)

Post-mortem on electrodes and thermal stability samples.

INL SM Series of Phosphazenes

Formulation	%	OR
SM-0	100	
SM-1	38 62	
SM-2	69 31	
SM-3	37 63	
SM-4	14 86	
SM-5	21 79	
SM-6	69 31	
SM-7	100	

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 electrolyte. However, there is still no commercially available low-flammability electrolyte that has competitive transport properties and has been successfully applied in a 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 less detrimental to required SEI properties and we hope to eliminate this negative effect by synthetic pathways with great 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 closely 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 2012