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

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Overview

| Timeline | Barriers |
|---|---|
| <p>Project Start: Jan. 2009</p> <p>Project End: Ongoing</p> <p>Percent Complete: Extent of project completion depends on meeting key decision points built into schedule</p> | <p>Cell/battery Life</p> <p>Abuse Tolerance</p> |
| Budget | Partners |
| <p>Funding Received:</p> <p>FY 10: \$ 400K</p> <p>FY 11: \$ 400K</p> | <p>Argonne National Lab (ANL)</p> <p>Dow Chemical</p> <p>Princess Energy Systems</p> <p>Sandia National Lab (SNL)</p> |

Relevance

Safety and longevity of Li-ion batteries continues to be an issue for future vehicular applications. This is complicated by the drive toward higher voltage cells (5V+).

Our objectives include:

- ◆ Synthesize novel solvents for Li-ion cells that are safer alternatives to volatile organics.
- ◆ Gain understanding of molecular-scale interactions between phosphazenes and other electrolyte components.
- ◆ Determine what phosphazene structures are more tolerant to high and low voltage, and to high temperatures.
- ◆ Determine the effect of phosphazenes on SEI films and cell aging in general, using ABR-relevant electrode couples.

This collective effort will enable us to engineer advanced electrolyte materials for more robust Li-ion cells.

Milestones

| Milestone | Status | Date |
|---|-------------|-----------------|
| Synthesis of Fluorinated Phosphazene series (FM1,2,3) | completed | March 2011 |
| Synthesis of Gen1 Ionic Liquid Phosphazene (PhIL-1) | completed | Feb. 2011 |
| Synthesis of newer SM series (SM 5,6,7) | completed | October 2010 |
| DFT simulations of selected phosphazenes regarding interaction with lithium ions | completed | Feb./March 2011 |
| Cell testing using LNMO/LTO and NMC/Carbon couples: characterization of capacity and impedance attributes | completed | March 2011 |
| Cell testing using LNMO/LTO and NMC/Carbon couples: aging studies | In progress | |
| Thermal stability testing, initial SM and FM series | completed | March 2011 |
| Synthesis of newer FM series and Gen2 Ionic Liquid Phosphazenes | In Progress | |
| <i>Various supporting characterization and cell testing will be ongoing throughout FY 2011.</i> | | |

Approach

□ The INL has foremost experts in phosphazene chemistry (e.g., Drs. 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 four primary tasks: *solvent synthesis, characterization, DFT modeling, and lithium-ion cell testing.*

Upfront issues are

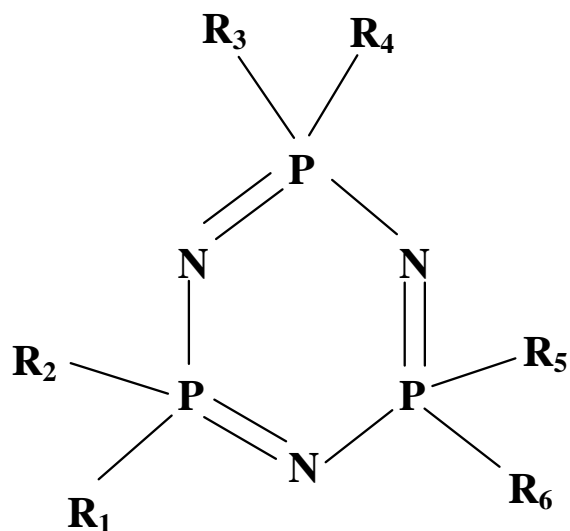
- ◆ voltage stability (CV)
- ◆ temperature stability
- ◆ flammability (flash point)
- ◆ lithium salt solubility
- ◆ transport properties (viscosity, conductivity)
- ◆ chemical compatibility with the cell environment
- ◆ molecular interactions (solvent-ion)

Coin cell testing covers issues of formation, interfacial impedance, polarization testing, and aging. We investigate the performance of our electrolytes with two electrode couples: LNMO/LTO and NMC/Carbon.

Note: Best Candidate electrolytes will be sent to SNL for abuse-tolerance testing.

General Aspects of INL Phosphazene Compounds

One example:



Heterocyclic Phosphazene
Ring Structure

MWT: 400-600

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

A change of chemical structure in the ring pendant arms has a strong influence on electrolyte properties, performance, and longevity in a higher-voltage system (5V+). We seek to improve transport properties while increasing flash point and having acceptable SEI characteristics and cell aging. This is a fundamental challenge.

Cell Testing

INL electrolyte blends were tested in 2032-type coin cells (sealed) using the following materials and conditions:

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ / $\text{Li}_4\text{Ti}_5\text{O}_{12}$, also referred to as LNMO/LTO

Voltage Range: 2.0 to 3.35 V

Rated Capacity: estimated at 1.536 mAh/cm² (C/1), anode-limited.

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ / Graphite, also referred to as NMC/Carbon

Voltage Range: 3.0 to 4.2V

Rated Capacity: 2.4 mAh/cm² (C/25), per SNL.

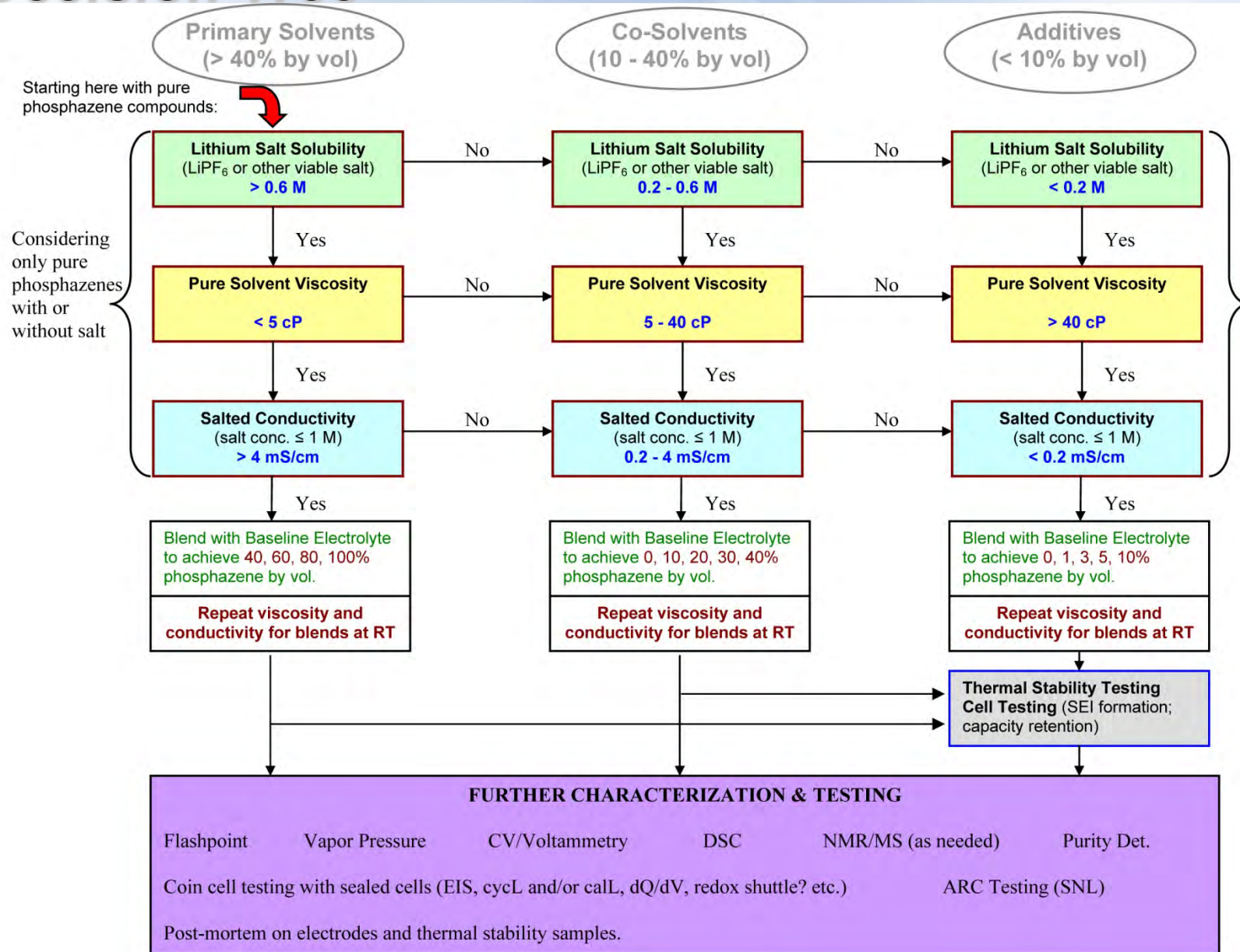
Baseline electrolyte: EC-EMC (2:8) + 1.2M LiPF₆

INL Additives: SM4, SM6, FM2, and PhIL-1*, at 10 and/or 3 wt% in the baseline.

Test Protocol: Formation cycling (C/10 @ 3), EIS, followed by a matrix of C/10, C/3, C/1, and 3C, all at 30 °C. Testing concludes with 3C cycling at 55 °C to determine how electrolyte additives affect high temperature tolerance.

* In this study the ionic liquid is comprised of 67% PhIL-1 and 33% SM7

Approach Decision Tree



Technical Accomplishments & Progress

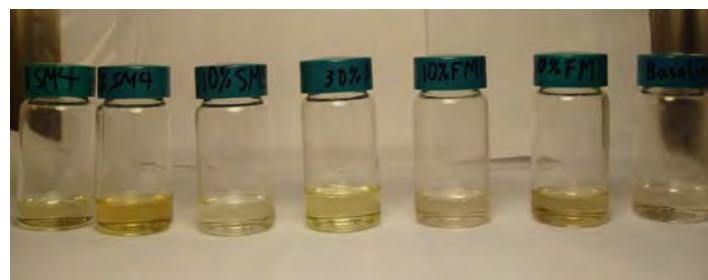
- New phosphazene compounds have been synthesized as part of our suite of materials aimed at voltage and temperature tolerant electrolyte additives.
- Thermal Stability testing has been completed on initial electrolyte blends containing small amounts of INL phosphazene additives. Results conclusively demonstrate that INL additives provide significant stabilization of the baseline electrolyte.
- Cell testing has been performed using INL electrolytes in cells made with LNMO/LTO or NMC/Carbon. Initial results are encouraging regarding capacity retention and aging trends.
- An improved electrochemical voltammetry technique allows more precise determination of key SEI parameters that enable quantification of the SEI formation process. This is used as a screening tool for electrolyte additives.
- Density Functional Theory (DFT) simulations have been performed to determine the solvent-to-lithium binding energies for key phosphazene additives. Reducing this interaction will promote greater cell efficiency in terms of interfacial processes.

Thermal Stability Testing, Study 1

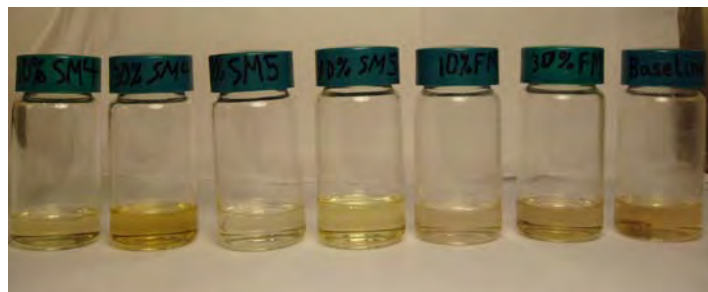
Day 1



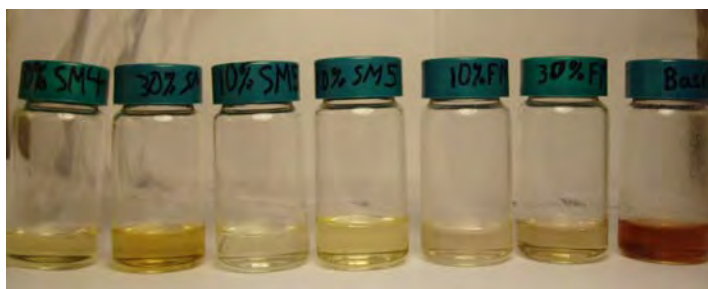
Day 8



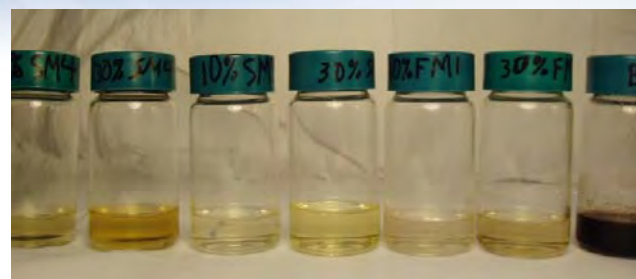
Day 18



Day 27



Day 41



Day 60
(end)



| | |
|------------|-------------|
| A: 10% SM4 | E: 10% FM1 |
| B: 30% SM4 | F: 30% FM1 |
| C: 10% SM5 | G: Baseline |
| D: 30% SM5 | |

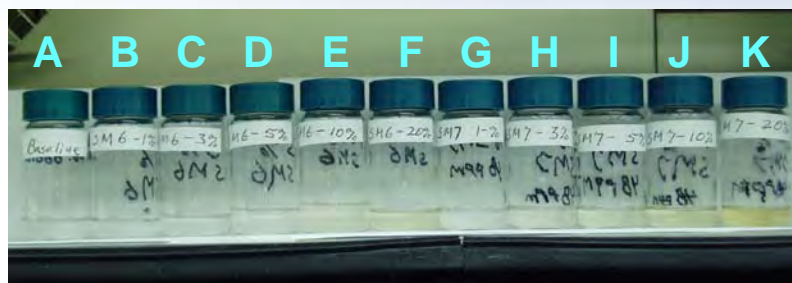
CONCLUSION:

The presence of INL phosphazene additives promotes chemical stability of the baseline electrolyte, making it more tolerant to higher temperatures. Here, SM5 and FM1 appear superior in this regard.

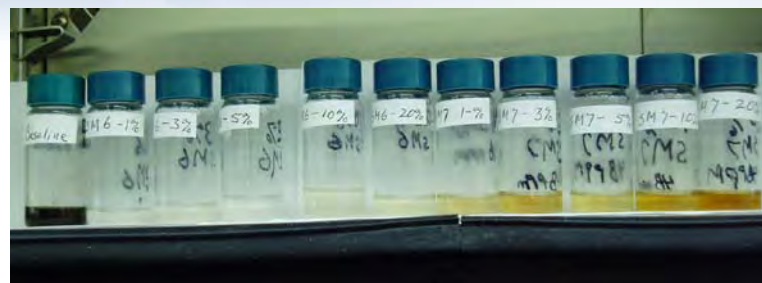
All tests at 60 °C. Baseline is 1.2M LiPF₆ in EC/EMC (2:8)

Thermal Stability Testing, Study 2

Day 1



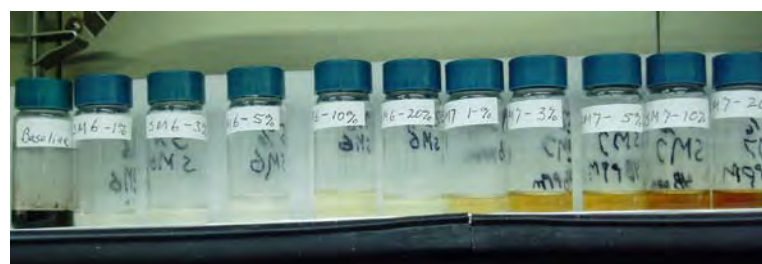
Day 40



Day 8

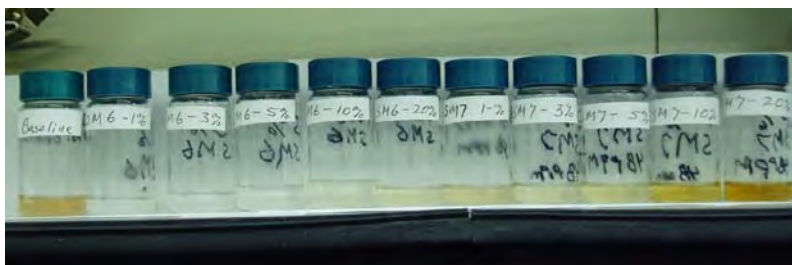


Day 62



(end)

Day 19



| | | |
|-------------|------------|------------|
| A: Baseline | E: 10% SM6 | I: 5% SM7 |
| B: 1% SM6 | F: 20% SM6 | J: 10% SM7 |
| C: 3% SM6 | G: 1% SM7 | K: 20% SM7 |
| D: 5% SM6 | H: 3% SM7 | |

Day 26



CONCLUSION:

The presence of INL phosphazene SM6 has a profound effect in stabilizing the baseline electrolyte at levels as low as 1%. SM7-doped samples discolor due to suspected 40 ppm water contamination; SM7 study will be repeated.

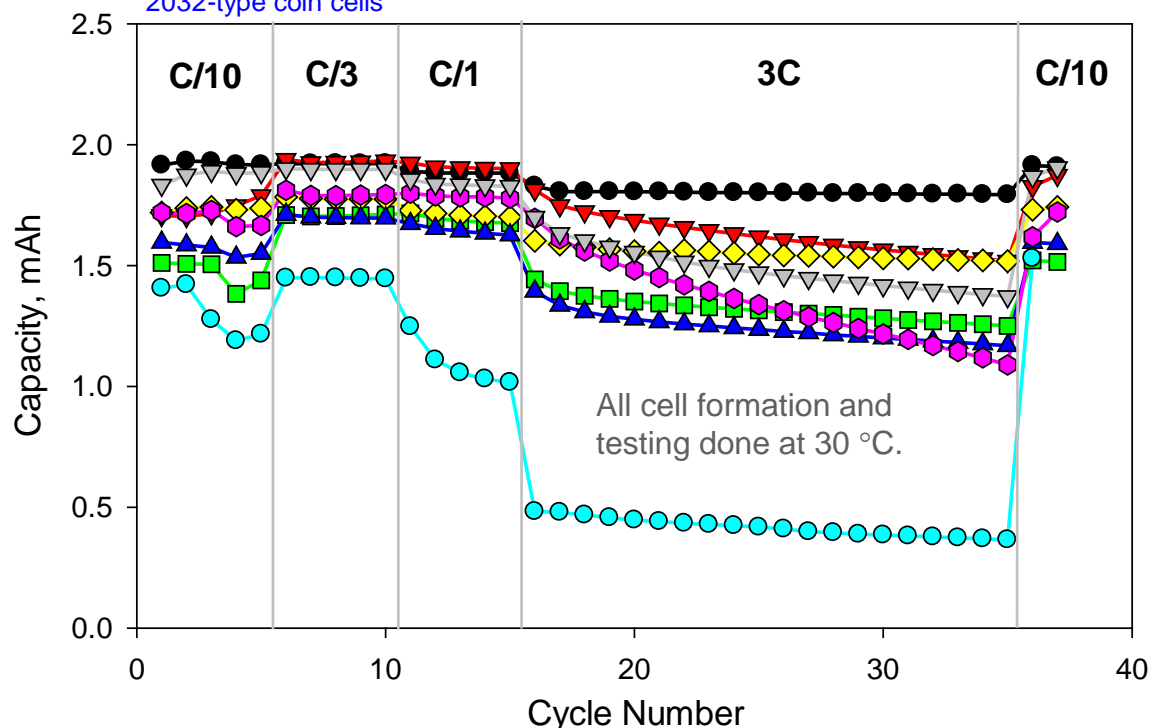
All tests at 60 °C. Baseline is 1.2M LiPF₆ in EC/EMC (2:8)

Cell Testing, Capacity Attributes

This slide might be updated at the time of the Merit Review to reflect ongoing cell aging at 3C cycling and 55 °C, done following the protocol below.

LNMO/LTO

2032-type coin cells



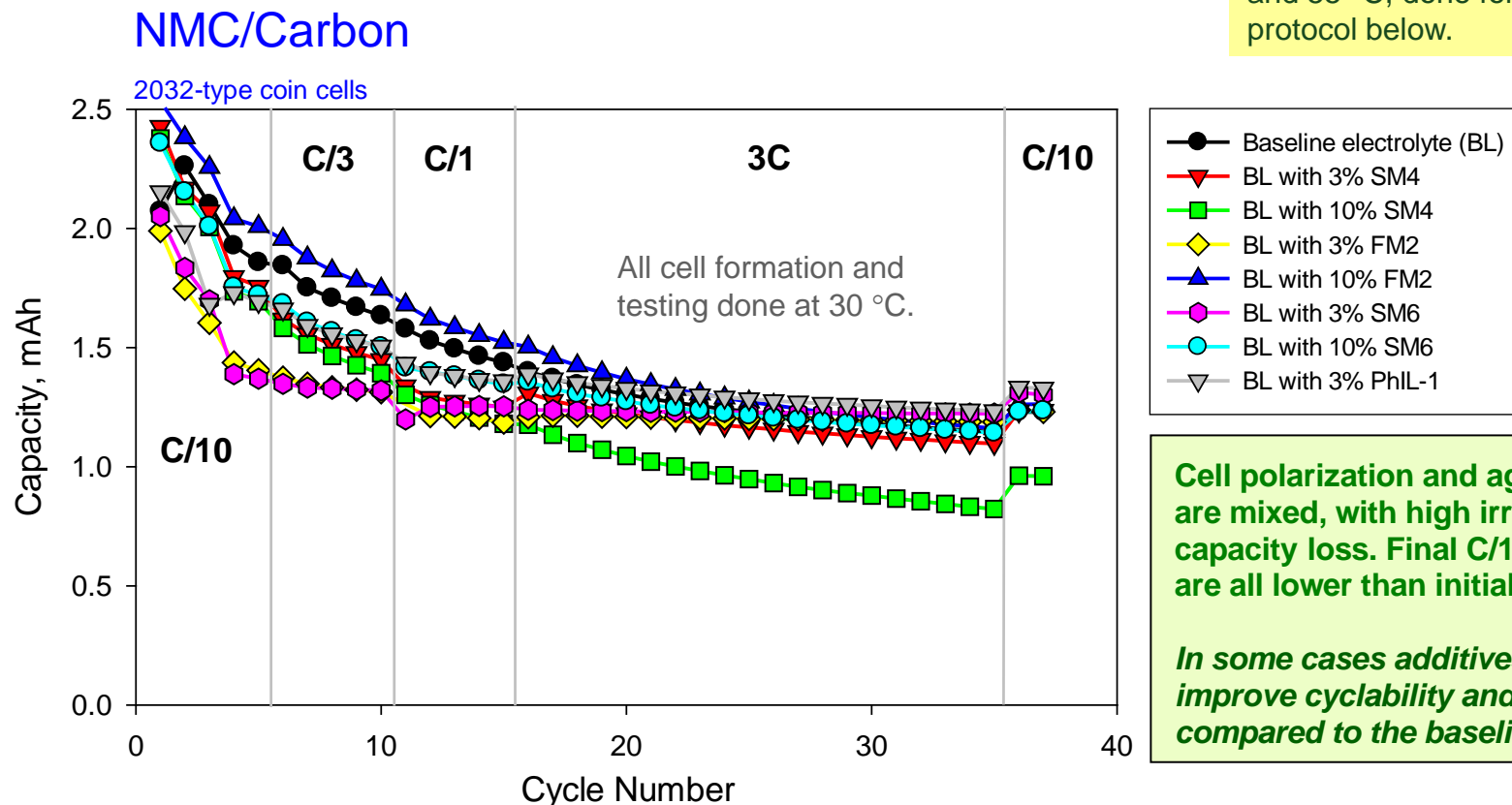
Cell polarization most evident at highest cycling rate and highest additive content (10%).

Final C/10 capacities are all higher than initial set, with no apparent cell aging.

Electrode materials provided by ANL

Cell Testing, Capacity Attributes

This slide might be updated at the time of the Merit Review to reflect ongoing cell aging at 3C cycling and 55 °C, done following the protocol below.



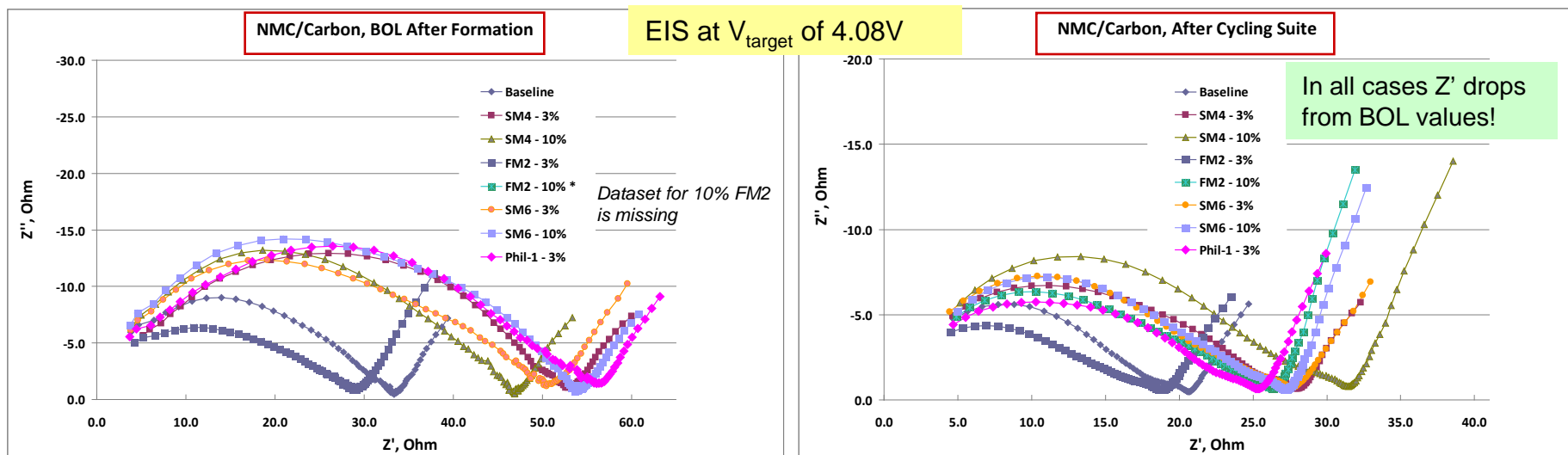
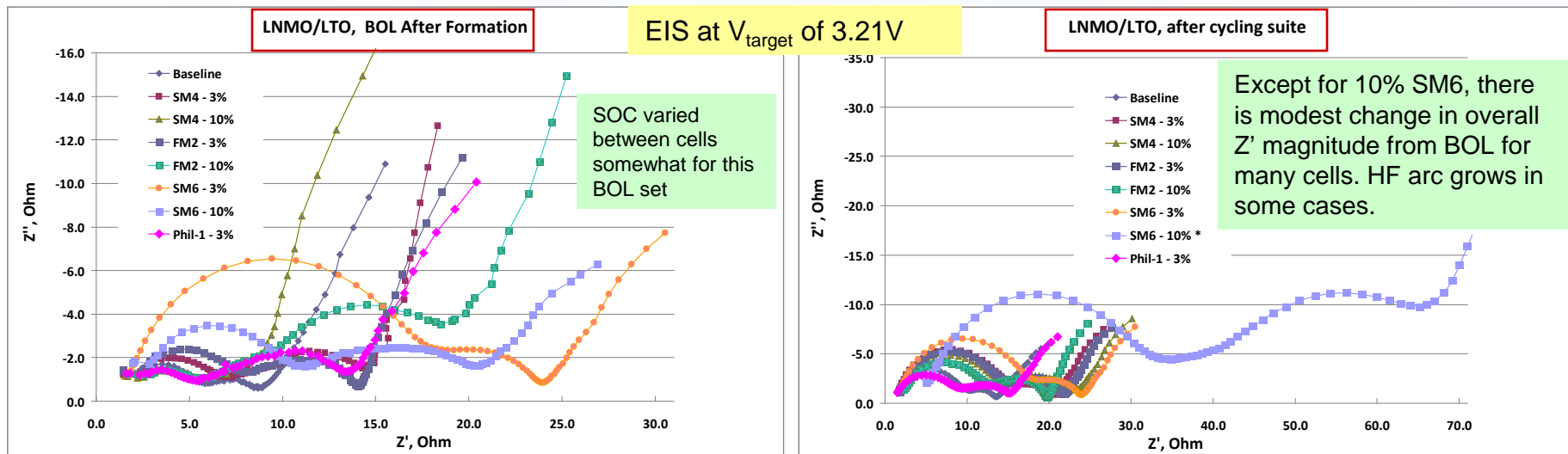
Cell polarization and aging effects are mixed, with high irreversible capacity loss. Final C/10 capacities are all lower than initial set.

In some cases additives appear to improve cyclability and reduce aging, compared to the baseline.

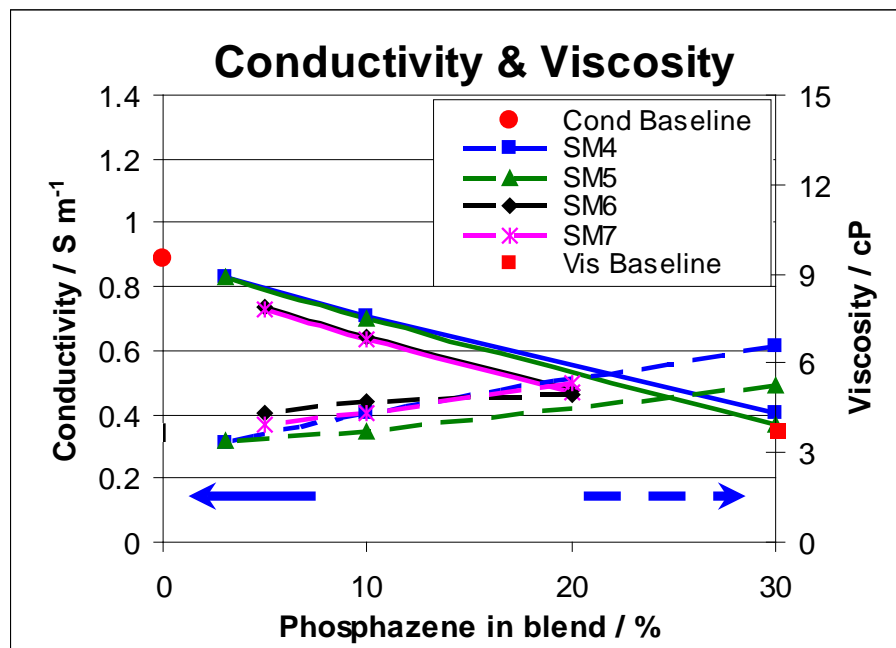
Electrode materials provided by SNL

Cell Testing, Impedance Attributes (EIS)

Data for 2032-type coin cells
100 KHz to 10 mHz sweeps

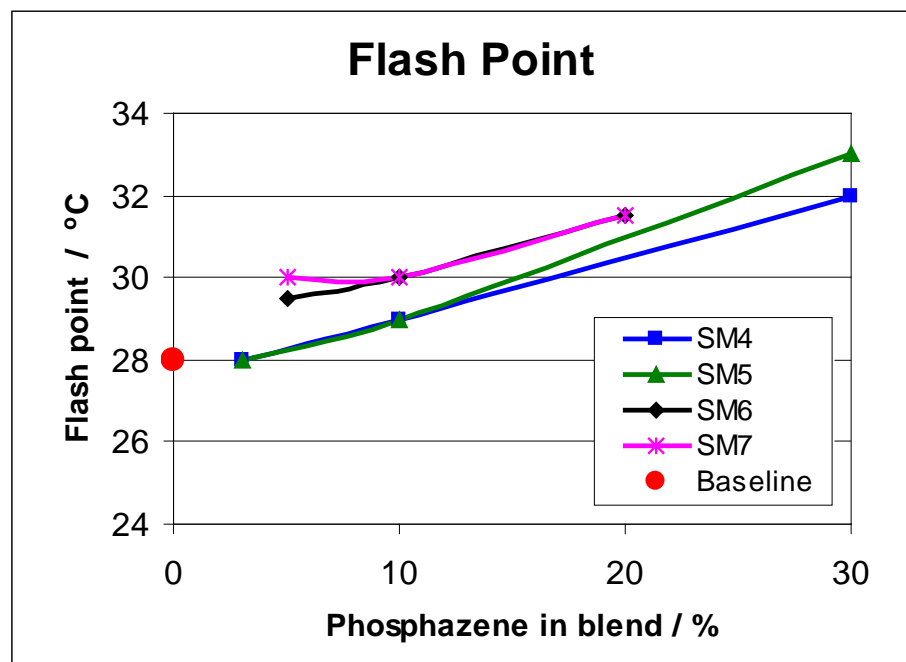


Recent Work on Blends with SM Series

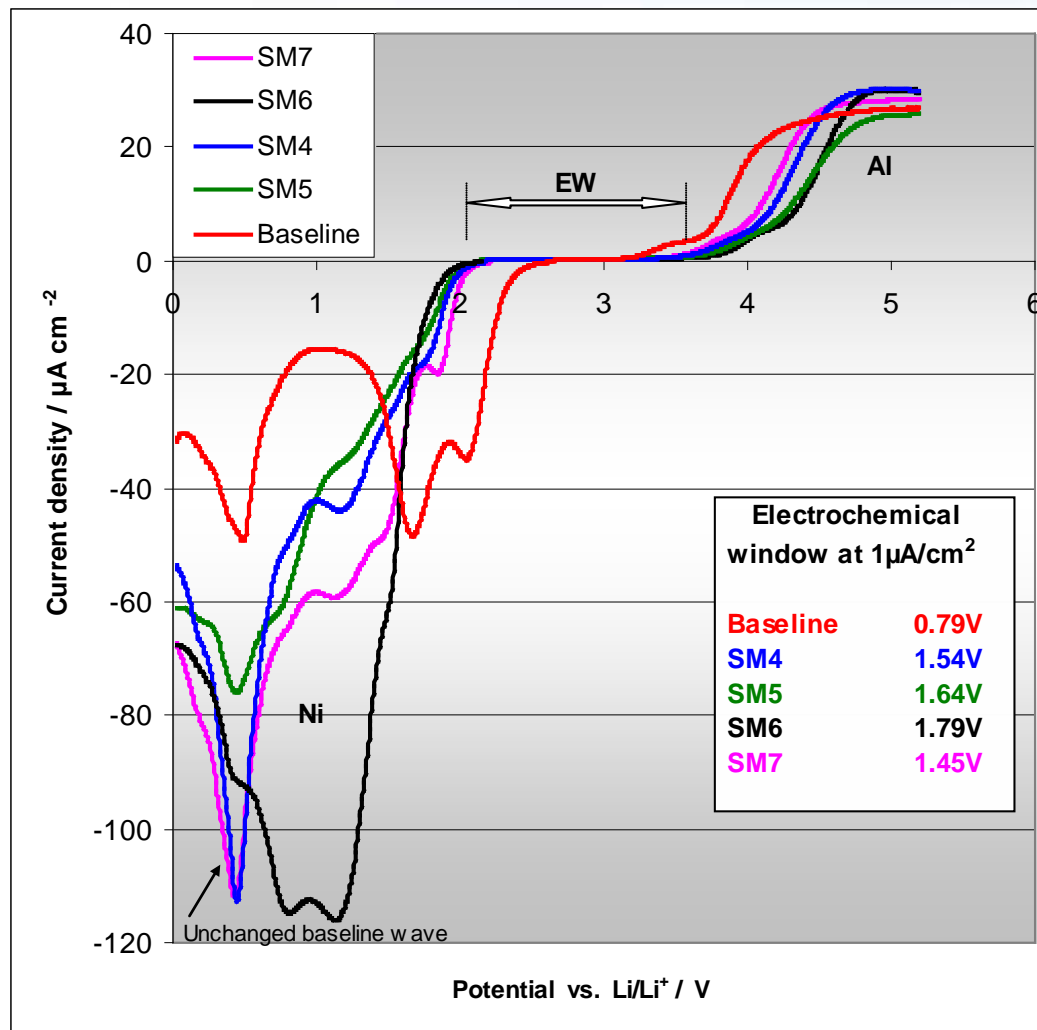


- Moderate changes in transport properties are seen for SM compounds kept at additive levels ($\leq 10\%$).

- Flash point of electrolyte increases with the addition of the SM additives.



Voltammetry of Phosphazene-based Electrolytes



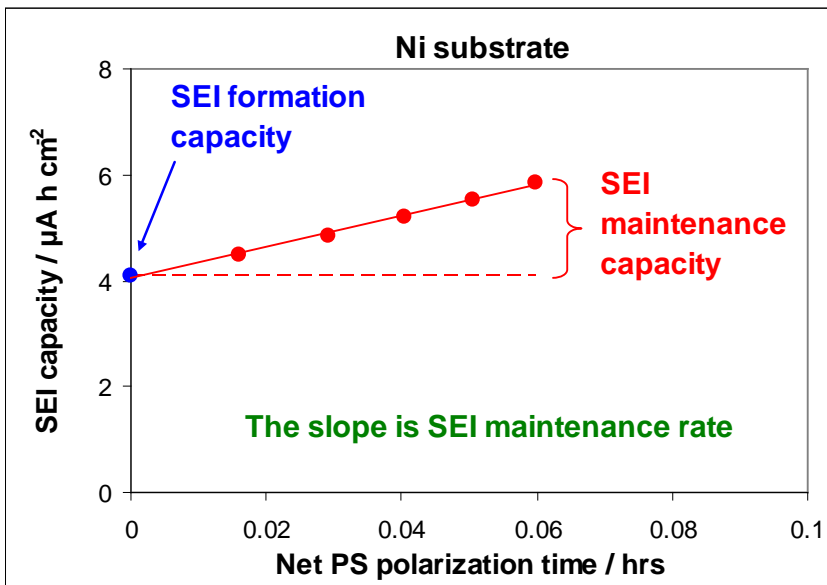
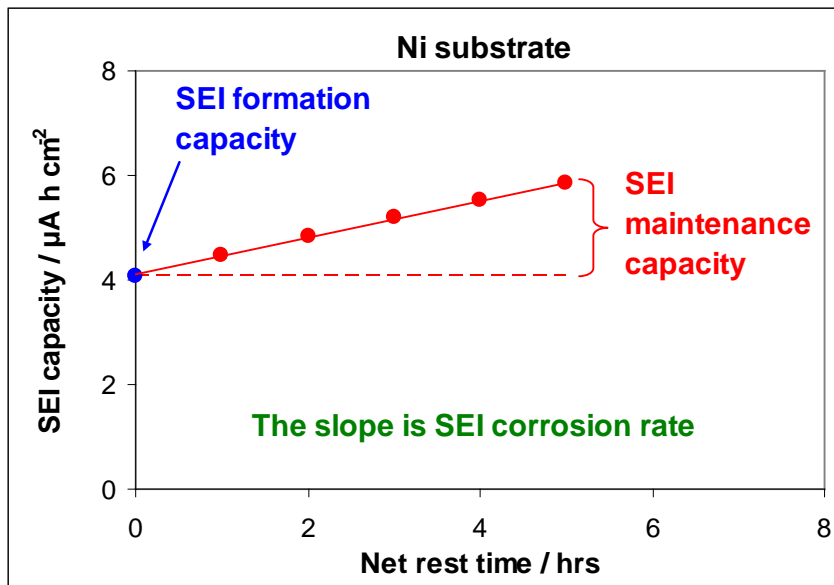
- Phosphazenes do increase electrochemical window at negative and positive ends.
- All the windows are less than operating voltage of Li-ion cells.
- At potentials beyond the electrochemical window, passivation does occur forming SEI films.
- Properties of passivating films need to be measured quantitatively.
- Last year a new method and new criteria were developed for this topic. This year we presented an improved version of the method which is more logical and informative.

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

Electrochemical Characterization of Electrolytes and SEI

Method: Potentiodynamic (PD) and potentiostatic (PS) coulometry (“bulk electrolysis” of passivation processes).

Electrodes: *Ni* (from OCV to 20 mV vs. Li/Li⁺)
Al (from OCV to 5.2 V vs. Li/Li⁺)



Red points in the graphs represent capacities at subsequent PS polarization series received with rest time between the series

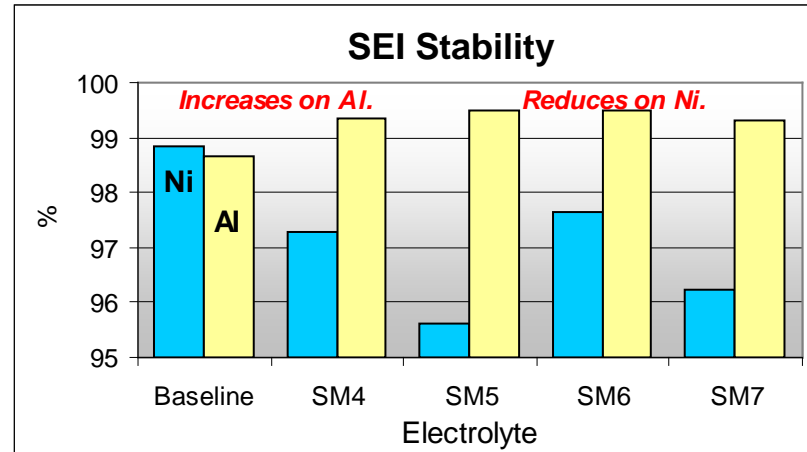
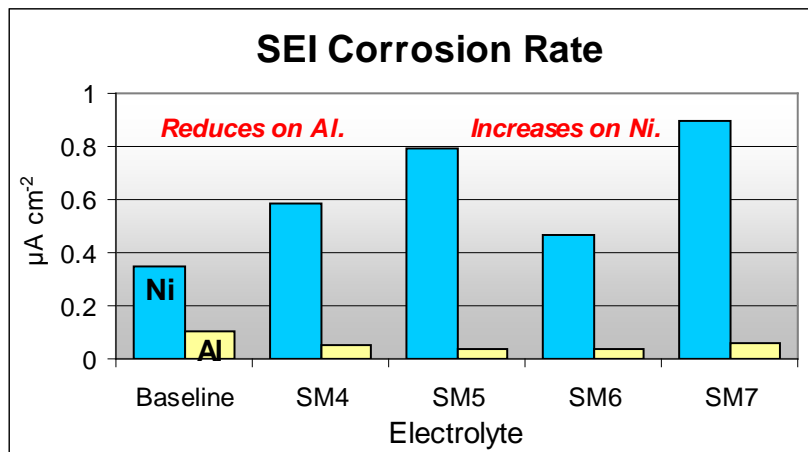
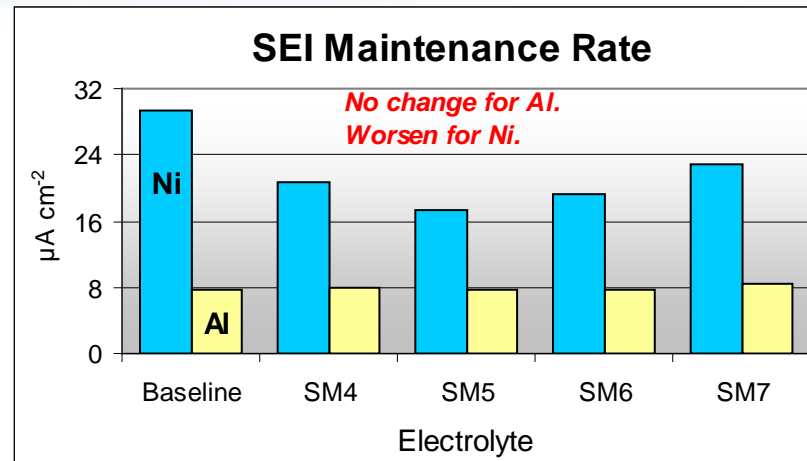
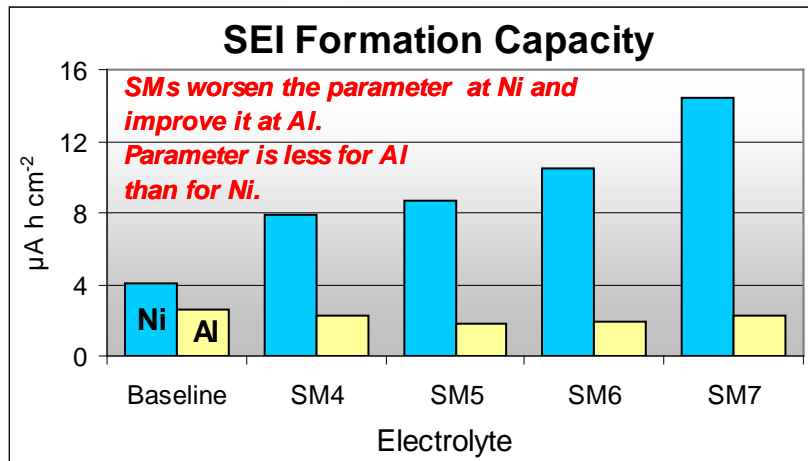
Capacity of SEI formation: relates to irreversible capacity at cell formation. Lower values are better.

Rate of SEI corrosion (degradation) = f (electron transport + physical defects + solubility of SEI). Relates to cell self-discharge. Lower values are better.

Rate of SEI maintenance = f (mostly Li⁺ mobility in SEI). Relates to cell power capability (higher is better).

SEI kinetical stability = $[(\text{maintenance rate} / (\text{maintenance} + \text{corrosion rates})) \times 100\%]$. Higher values are better.

SEI Voltammetry Parameters – SM Series



- Defectiveness of SEI and capacity required for SEI formation on Al is significantly less than on Ni.
- Phosphazenes reduce defects of SEI on Al and increase on Ni. Al SEI is less defective than Ni SEI.
- Phosphazenes do not change Li⁺-ion transport in Al SEI and worsen it in Ni SEI. Ni SEI is more conductive.
- Phosphazenes improve stability of SEI on Al and worsen on Ni. Al SEI is more stable than Ni SEI.

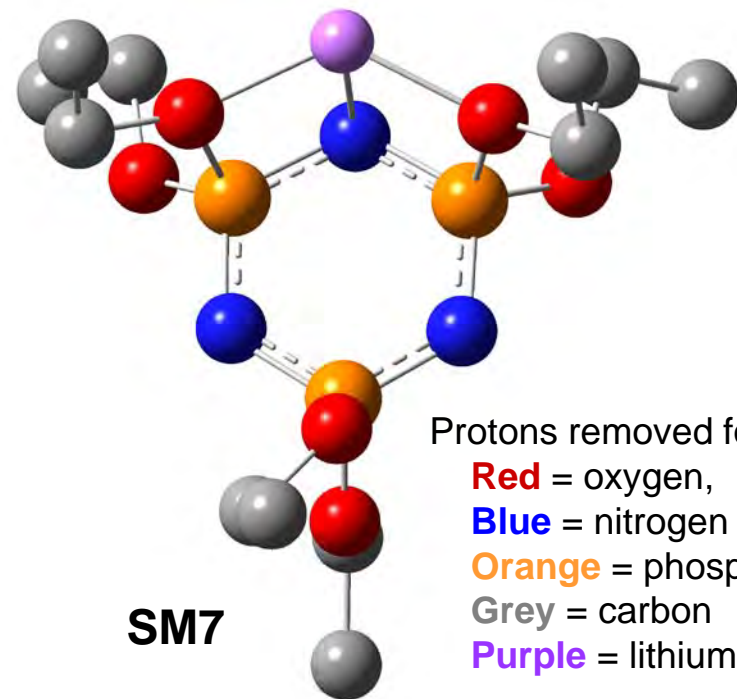
Electrolytes: baseline (1.2M LiPF₆ EC:MEC (2:8)) and the blends of 20% of each phosphazene with 80% baseline.

DFT Modeling of Phosphazene Trimers

Looking at solvent-to-Li⁺ Binding

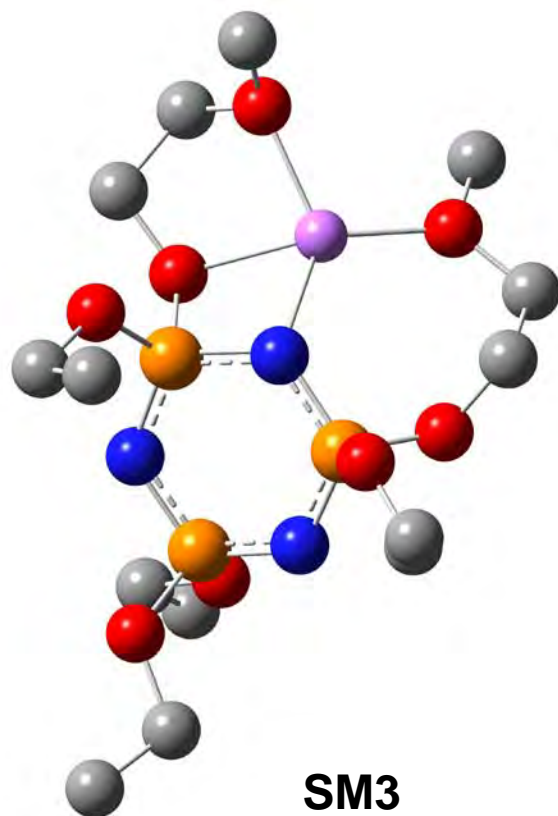
Previous modeling (some INL) has been performed for lithium binding in phosphazene polymers (*J. Phys. Chem B* **2004**, 108, 15694 and *J. Phys. Chem. B* **2003**, 107, 3168), but not for phosphazene trimers.

Density functional theory performed with Gaussian03, B3LYP, 6311-G(d,p) basis set. All structures are minima (no imaginary frequencies).



- Coordination of lithium with simple pendent groups occurs with 2 pendent oxygens and 1 ring nitrogen.
- With varying pendent groups (ethoxy, isopropoxy), the binding energy varies between **72.6 and 76.7 Kcal/mol**.

DFT Modeling of Phosphazene Trimers

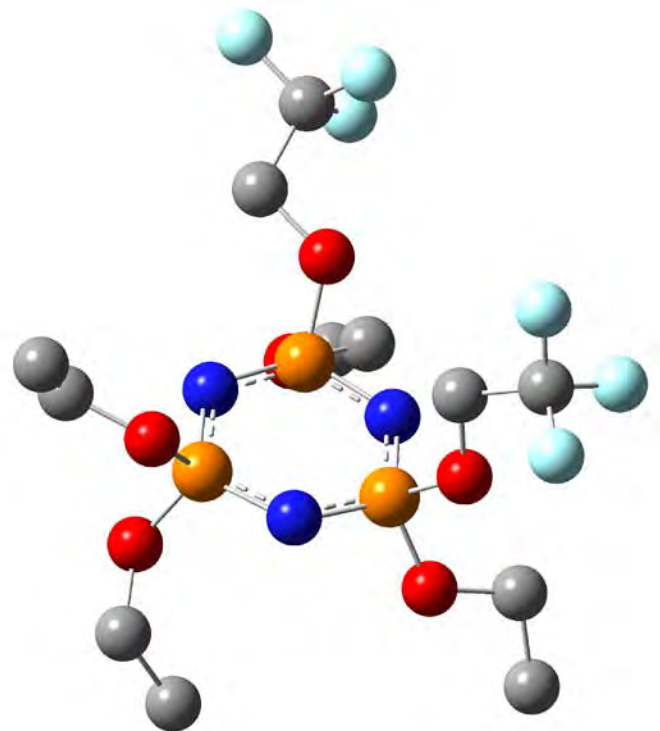


- The flexibility of phosphazene pendant groups allows 4 to 5 coordinating atoms, with higher (~102 Kcal/mol) binding energies.
- Phosphazene trimers with ether pendent groups can coordinate lithium similar to the polymer, i.e. more than 3 coordinating atoms.
- **Binding energy = 98.4 Kcal/mol**
- More ether linkages and longer ether linkages will increase the binding energy.

DFT Modeling of Phosphazene Trimers

Fluorinated Phosphazenes

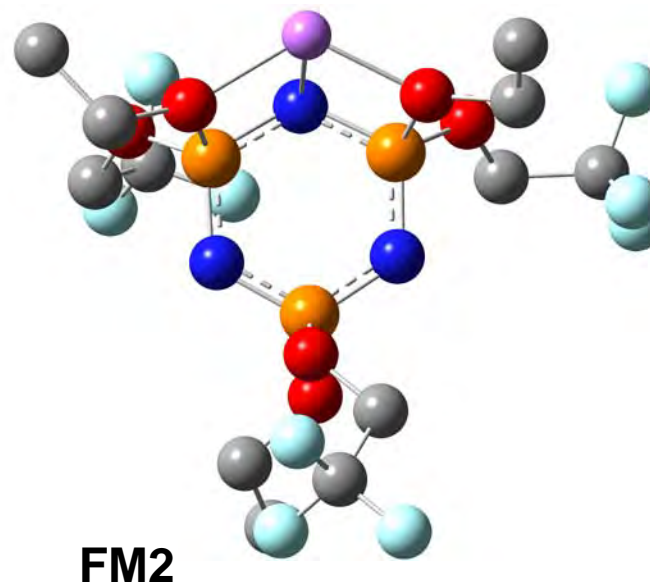
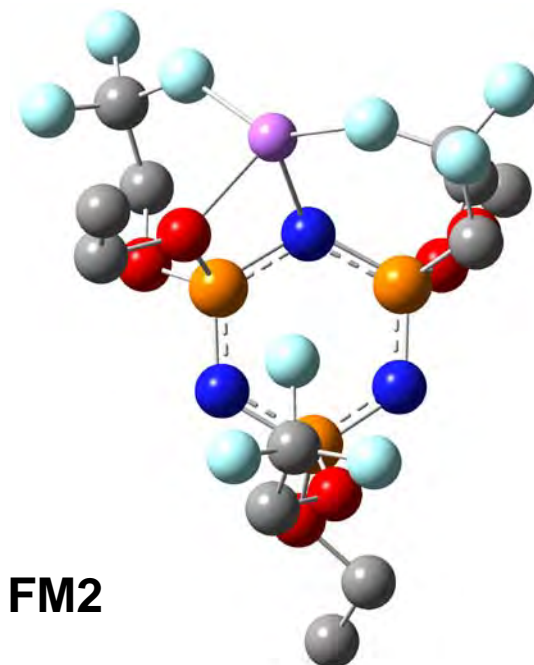
- Fluorines added to pull electron density away from the ring and oxygens, thus weakening lithium binding
- Experimental studies include 6, 3, 2, and 1 added CF_3 groups
- Experimental results are an average of possible isomers, the modeling has to explicitly do the same
- 23 unique isomers with lithium coordination included



FM3

DFT Modeling of Phosphazene Trimers

Lithium Binding in Fluorinated Trimers



Binding can be with (L) or without (R) fluorine coordination

DFT Modeling of Phosphazene Trimers

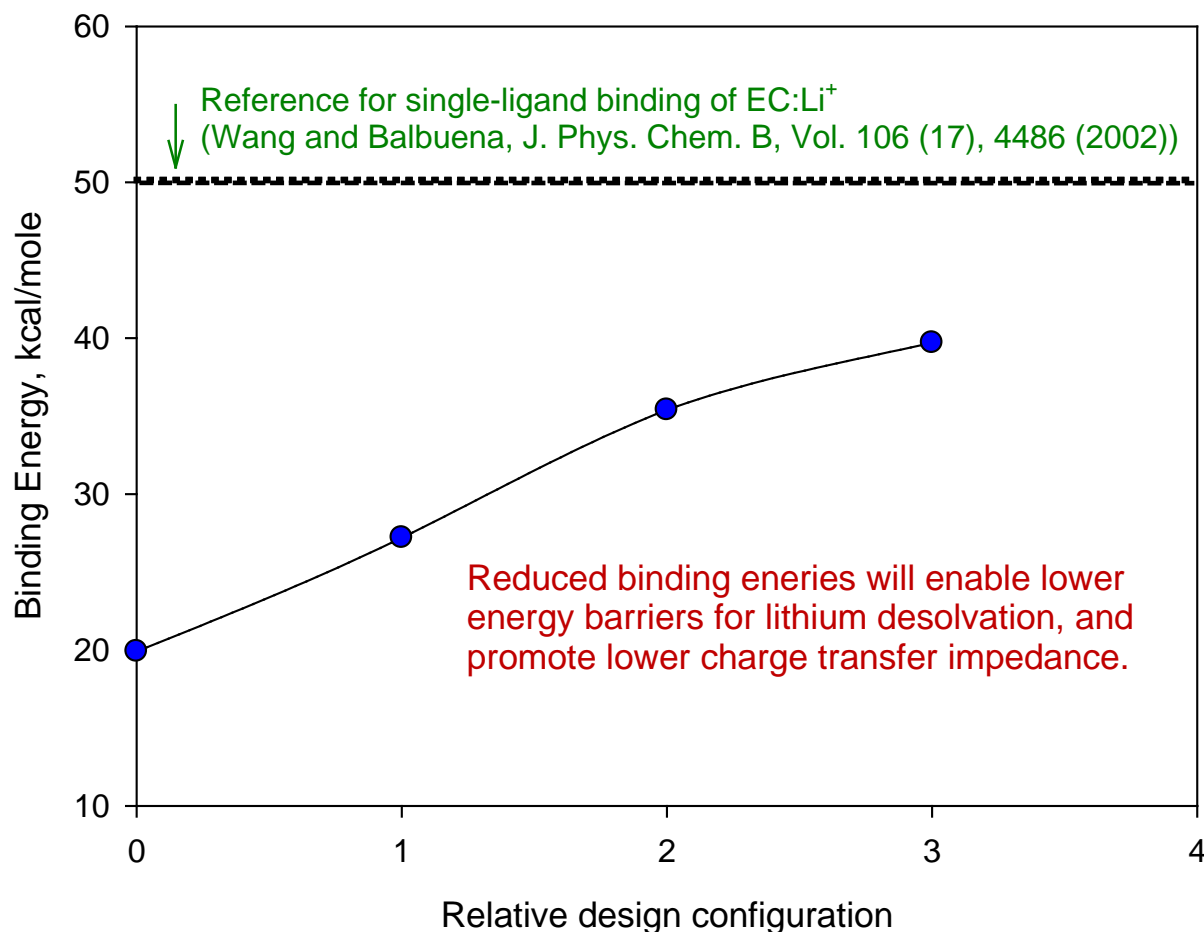
Fluorinated Trimer Binding Energy

| Name (# of CF ₃ groups) | # of possible isomers | Average binding energy (Kcal/mol) |
|------------------------------------|-----------------------|-----------------------------------|
| FM1 (6) | 1 | 65.0 |
| FM2 (3) | 10 | 70.2 |
| FM3 (2) | 8 | 70.7 |
| FM4 (1) | 4 | 72.7 |

- There is an electron withdrawing effect by adding fluorines. The lowest binding energy calculated is 62.9 Kcal/mol (3 CF₃ groups, no F-Li interaction), a decrease of ~10-15 Kcal/mol from the non-fluorinated trimers.
- Electron withdrawing effect is almost completely offset by fluorine coordination to lithium.

DFT Modeling of Phosphazene Ionic Liquids

DFT Results for Nitrogen-to-Li⁺ Binding Energy for Various Design Configurations of Gen1 Ionic Liquid Phosphazene (strongest binding site shown)



A major consideration of our Gen1 Ionic Liquid additive is to diminish the inherent association between phosphazene nitrogens and free cations (Li⁺).

INL Gen1 Ionic Liquids have lower binding energies with lithium, compared to conventional organic solvents (EC).

Collaborations

- **Princess Energy Systems.** Involved in formative discussions of incorporating phosphazenes into Li-ion cells and corresponding intellectual property and market issues.
- **SNL.** Provided NMC/Carbon electrode material for INL coin cell studies. SNL will perform abuse tolerance testing on electrolytes having the best candidate INL additives.
- **ANL.** Provided LNMO/LTO electrode material for INL coin cell studies. Supports review of historical data from ANL testing of other electrolyte additives. This is ongoing.
- **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.

Future Work

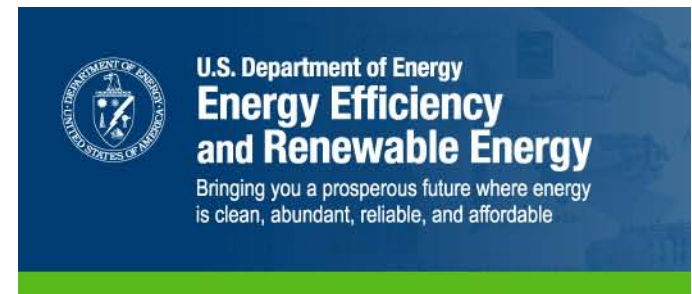
- Non-cyclic phosphazene compounds will also be targeted to reduce viscosity, enabling electrolyte systems having mostly phosphazene solvents to exploit the inherent low flammability of these additives.
- Continued testing with coin cells (and possibly pouch cells) will be done to characterize electrolyte behavior in terms of cycling efficiency, materials compatibility, aging trends, SEI attributes, etc. Half-cell studies on SEI films will be considered. Other combinations of electrode couples will be investigated (5V).
- More voltammetry work is planned to look at newer compounds (PhIL-1, FM series, AL series) and specific interactions between phosphazene-based electrolytes and cell components such as electrode active materials. The effect of these compounds on SEI properties is of keen interest.
- Salts other than LiPF_6 will be considered (e.g., LiTFSI, mixed salts), to avoid potential detrimental interactions between anion and phosphazenes over voltage.
- The best candidate additives will be tested for abuse tolerance at SNL to determine how our additives alter the onset of thermal runaway. At this point, this would include SM4 or SM5, FM1 or FM2, and PhIL-1 in amounts not to exceed 5% in the baseline electrolyte.

Summary

- The INL suite of phosphazene materials aimed at battery electrolytes has grown to include fluorinated and ionic liquid compounds.
- Thermal Stability testing on electrolyte blends demonstrated a strong stabilizing effect from small amounts of INL phosphazene additives. This behavior could prolong battery life and enable greater operation at elevated temperatures.
- Cell testing with LNMO/LTO and NMC/Carbon: The LNMO/LTO system with our additives showed excellent capacity retention while undergoing moderate polarization at higher cycling rates, and had generally lower interfacial impedances per EIS. The NMC/Carbon system underwent more aggressive aging overall (including the baseline), yet the additives appear to slow the rate of aging compared to the baseline.
- Using an improved voltammetry technique, we see that phosphazenes do improve properties of the SEI on cathode (+) side and increase operating voltage. This 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 that charge-neutral compounds (e.g., FM and SM series) have relatively high solvent-to-lithium binding energies compared to conventional organic solvents such as EC. However, we are able to reduce this interaction significantly (less than EC levels) with our new ionic liquid phosphazenes, which should improve the lithium desolvation process.

Acknowledgements

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



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 CO₂
 - 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

Chemical Synthesis Capabilities

- Over 3,000 ft² 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 ft² research laboratory facility (REL) scheduled for occupancy in 2012

