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

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Overview

Timeline	Barriers
Project Start: Jan. 2009 **Project End:** Ongoing **Percent Complete:** Extent of project completion depends on meeting key decision points built into schedule	**Abuse Tolerance** **Cell/battery Life**
Budget	**Partners**
Funding Received: **FY 09: $ 150K** **FY 10: $ 400K**	**Argonne National Lab (ANL)** **Dow Chemical** **Princess Energy Systems** **Sandia National Lab (SNL)**

Objectives / 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 heat.
- Determine the effect of phosphazenes on SEI films and cell aging in general.

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

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 currently in its early stages, split under three primary tasks: *solvent synthesis, characterization*, and *Li-ion cell testing*. Upfront issues are
  - voltage stability (CV),
  - flammability (flash point),
  - lithium salt solubility,
  - transport properties (viscosity, conductivity),
  - chemical compatibility with the cell environment.

Coin cell testing covers issues of formation, interfacial impedance, polarization testing, and aging.

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

Characterization Matrix for Phosphazene-Based Electrolyte Additives

Phosphazene Series under Study: AL-4, AL-5, SM-4, SM-5, SM-6, SM-7, AP-1, FM-1, FM-2

Baseline Electrolyte used for Blends: EC-EMC (2:8) + 1.2M $LiPF_6$

Proportions of Phosphazenes in Electrolytes: 0, 3, 10, 30, 50, 100%

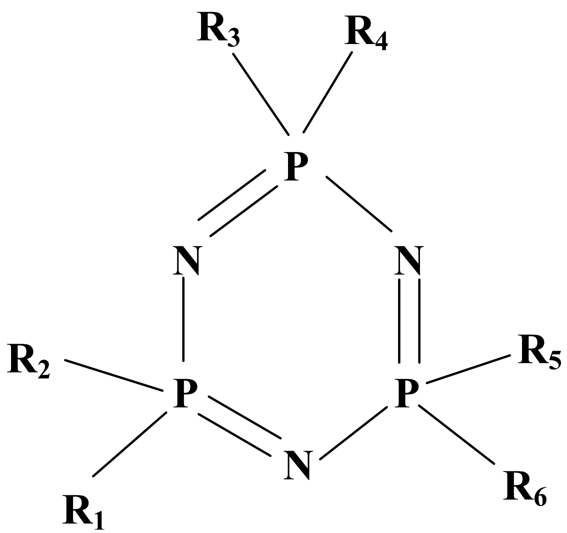
Characterization Measurements: Conductivity, Viscosity, Voltammetry, Flash Point, Lithium salt dissolution ($LiPF_6$), Chemical Compatibility

Cell Testing: Candidate electrolytes are tested in 2032-type button cells having $LiCoO_2$/graphite to determine how they perform in a working cell environment in terms of capacity loss, self discharge, impedance rise, etc.

Status: Work is currently progressing in testing and characterizing SM-4, SM-5, and FM-1 electrolytes, and further investigations are underway toward more efficient synthesis of AP-1, FM series, and similar compounds. We are seeing mixed results that will guide future synthesis: e.g., decreased flammability but higher viscosity and lower conductivity.

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

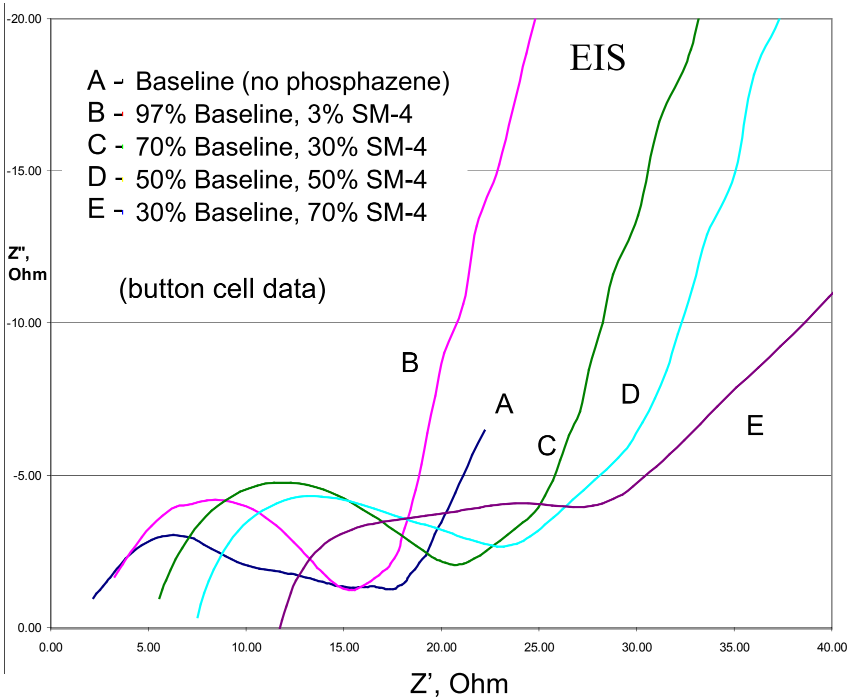
FM: employs fluorinated analogues of the SM series

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.

Technical Accomplishments & Progress

- Early generations of phosphazene solvents have been synthesized specifically for this work (AL4, AL5, SM4, SM5, SM6, SM7, FM1, FM2, AP1). More efficient and economical synthesis routes are being sought to decrease electrolyte cost.
- Electrolyte blends for key phosphazenes have been prepared and characterized by multiple methods, using a baseline system of EC:EMC (2:8) + 1.2M $LiPF_6$.
- Coin cell testing has been performed for the most promising candidates.

Sampling of Early Results



These early datasets are encouraging for using phosphazene additives in Li-ion cells.

Table 1. Viscosity of selected INL phosphazene additives at room temperature with and without salt.

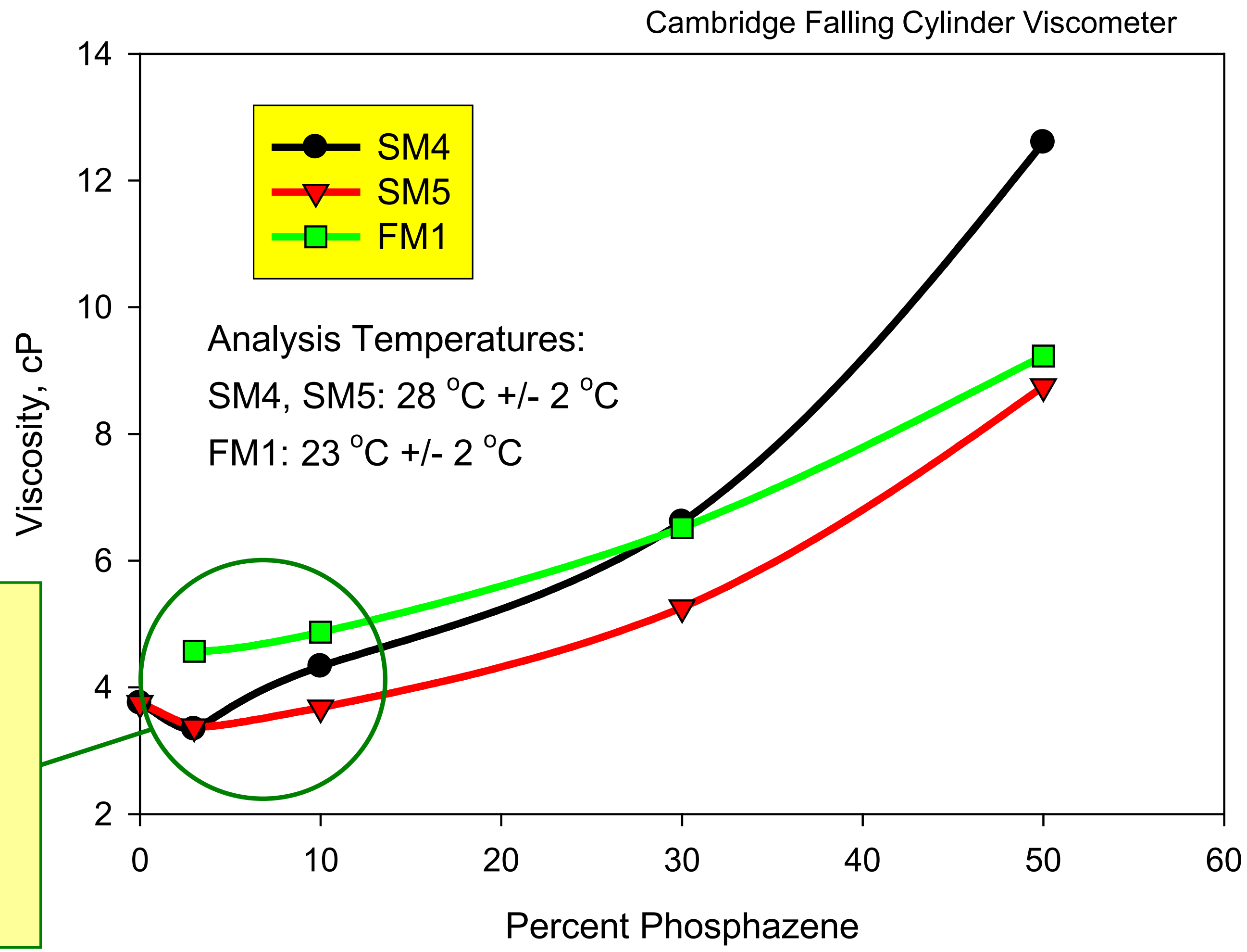
Recent SM compounds have reduced viscosity!

Formulation	Viscosity neat (cP)	Viscosity sat. w/$LiPF_6$ (cP)
AL-2	68	305
AL-3	46	440
SM-1	58	605
SM-2	39	1750
SM-3	27	640
SM-4	21	260
SM-5	18	45

Table 2. Salt saturation limits ($LiPF_6$) in INL phosphazenes at room temperature.

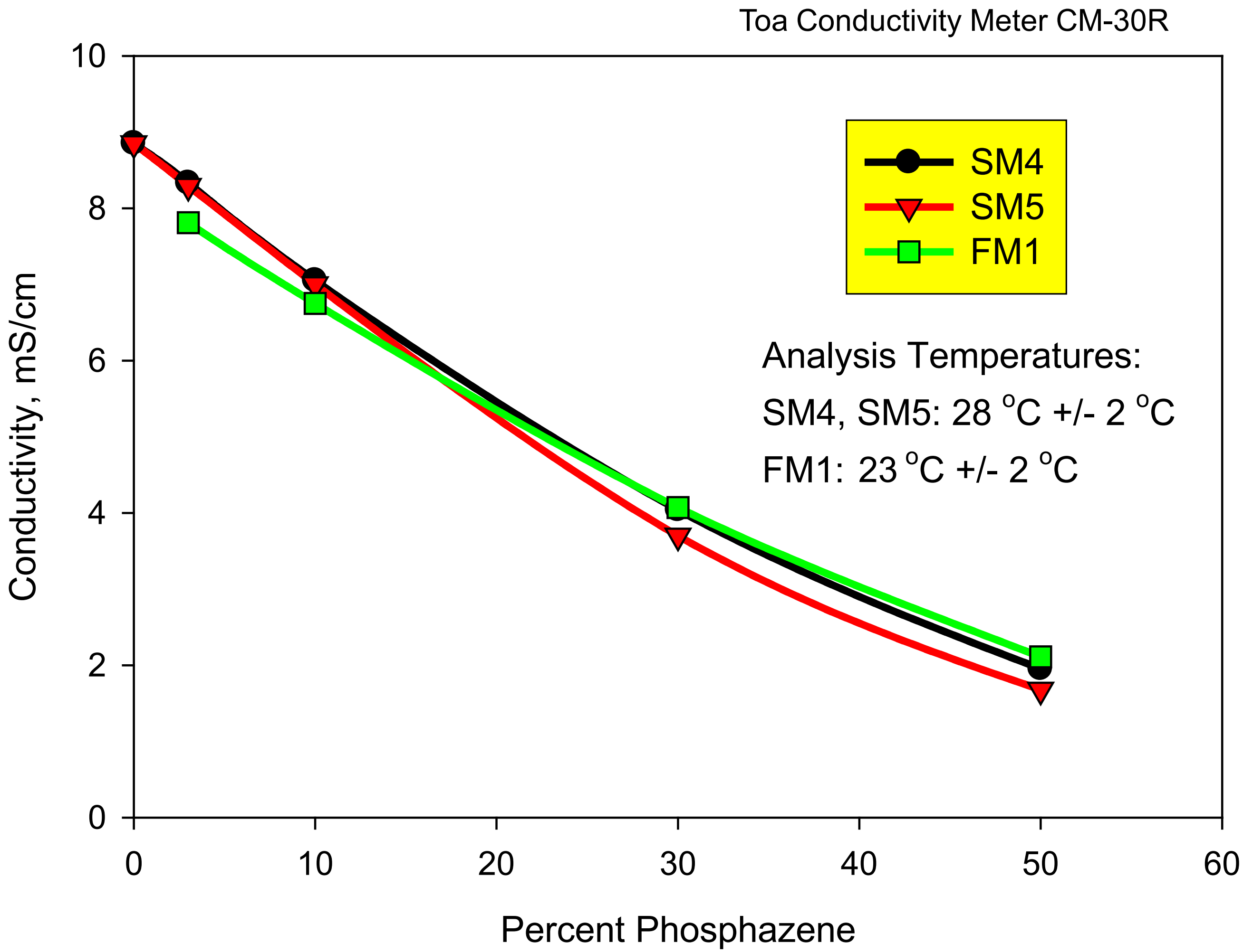
Formulation	Solubility limit (mM)
AL-2	n/a
AL-3	860
SM-1	950
SM-2	950
SM-3	880
SM-4	840
SM-5	660

Electrolyte Viscosity



Viscosity decrease or plateau at low concentrations is encouraging, but there is not a corresponding increase or plateau in conductivity.

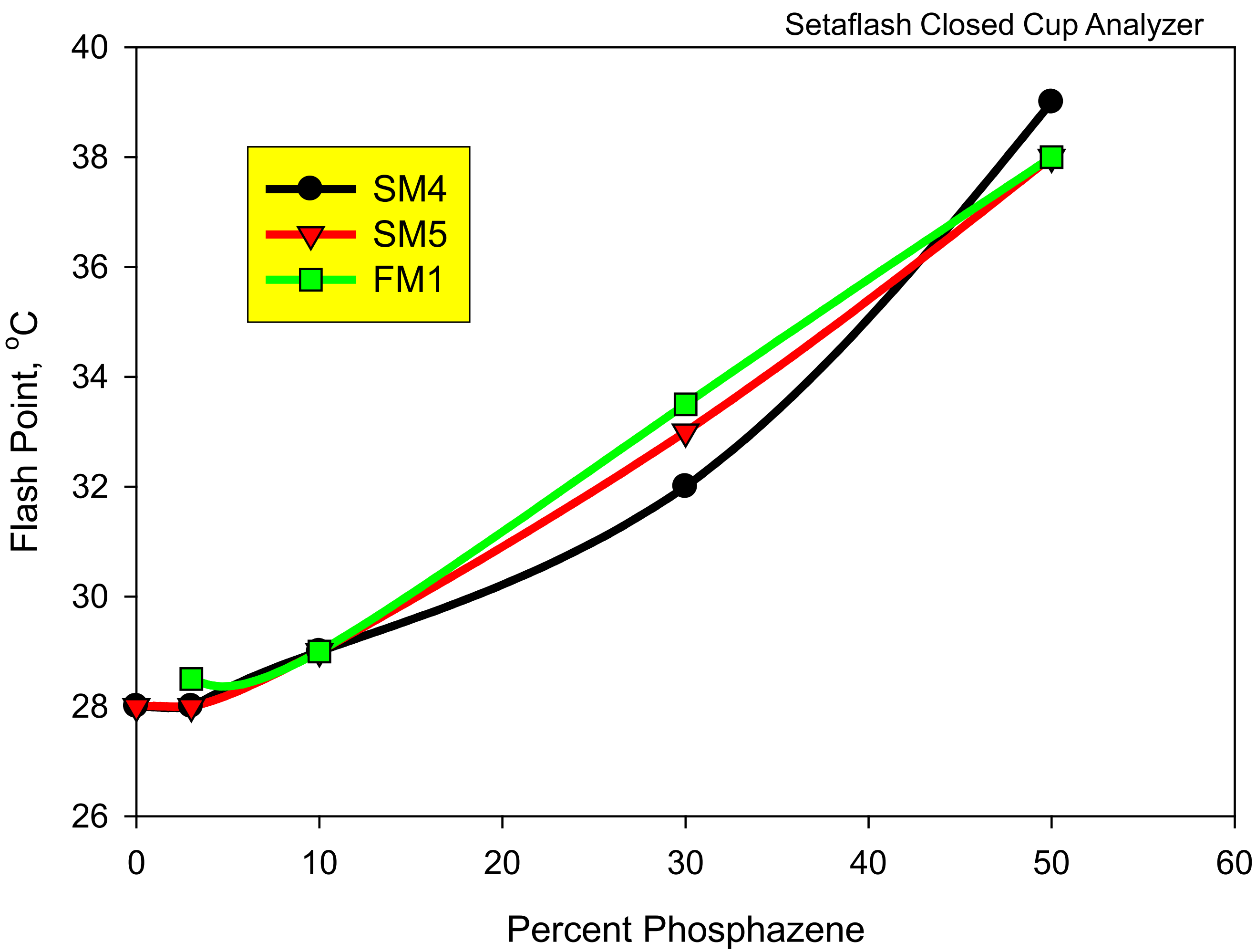
Electrolyte Conductivity



In some cases (SM5), the increase in viscosity over concentration does not account for the total observed decrease in conductivity.

This suggests there is another mechanism that impacts conductivity, such as strong association between the phosphazene and lithium ions through N:Li^+ interactions. This issue influences our synthesis goals.

Electrolyte Flash Point



We see only modest improvement in flash points, and minimal effect at the "additive" region (3-10%).

Higher flash points will be obtained by using a less flammable baseline or when higher amounts of phosphazenes are present that are competitive with conventional organic solvents in terms of transport properties.

Pure phosphazenes do not flash, but undergo thermal decomposition at approx. 280 °C.

Stability Over Voltage (CV) *Case Studies with SM4, SM5*

Experimental Conditions

Test Electrolytes: blends having 30% SM4, SM5

Baseline/control: 1.2M $LiPF_6$ in EC-EMC (2:8)

Working Electrodes:

Ni (potentials below OCV)

Al (potentials above OCV)

Counter Electrode: Li

Reference Electrode: Li

Electrode Area: 1cm^2 (WE), 1.44 cm^2 (CE)

Sweep Rate: 5 mV/s

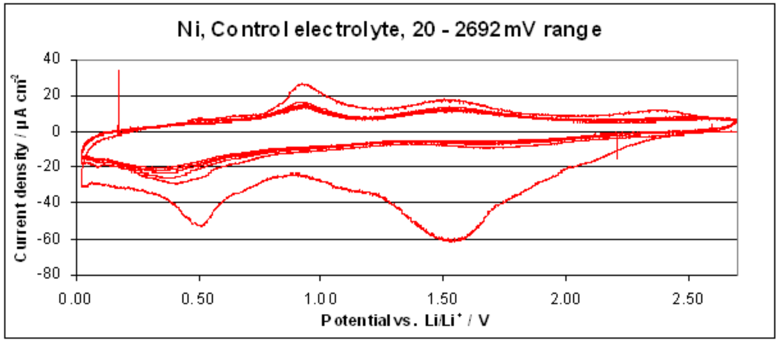
Total CV cycles per run: 20 (Ni), 10 (Al)

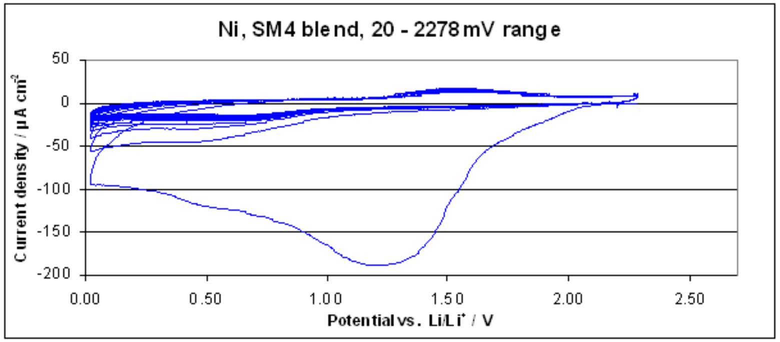
Temperature: 24 °C

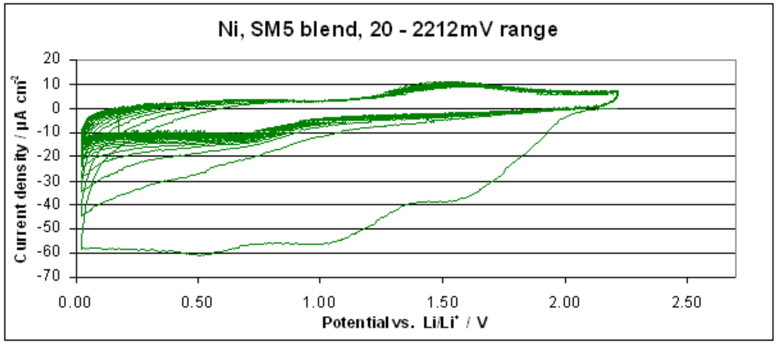
Stability Over Voltage (CV) Case Studies with SM4, SM5

Note the difference in vertical scales

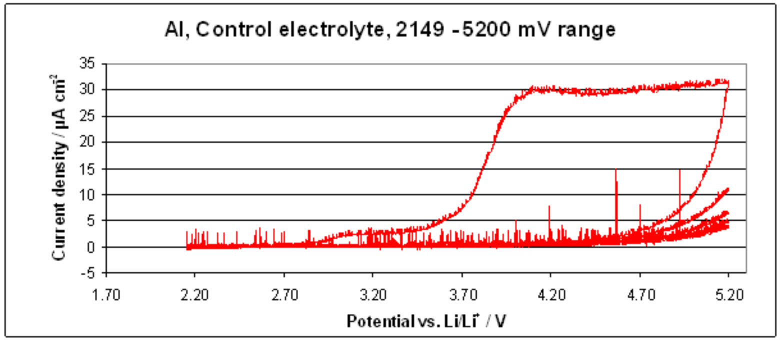
For Potentials Below OCV

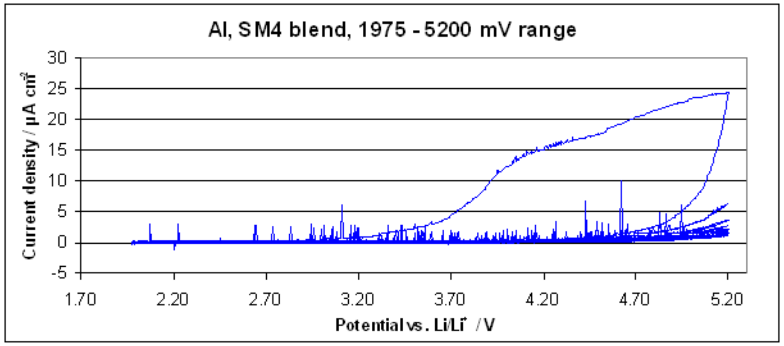


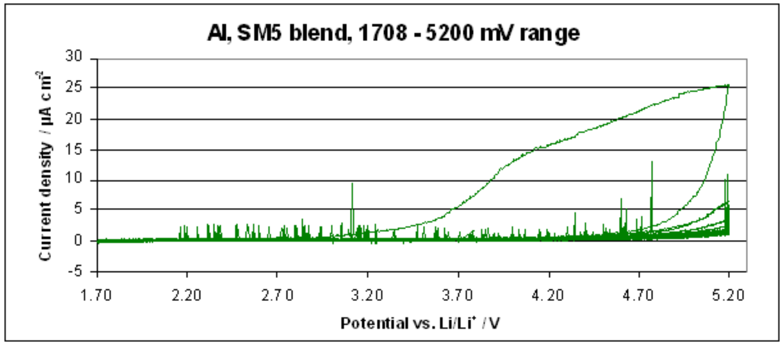




For Potentials Above OCV







Stability Over Voltage (CV) *Case Studies with SM4, SM5*

Conclusions from Initial Studies

Under most conditions shown, consecutive CV cycles converge well after 3-5 cycles.

SM4 and SM5 additives have a greater effect on the reductive stability at the negative electrode, compared to the baseline. This results in a more prolonged SEI formation process that will likely yield a higher interfacial impedance at the negative electrode.

These additives act to moderate the oxidative processes at the positive electrode, and hence slightly enhance stability at higher voltages.

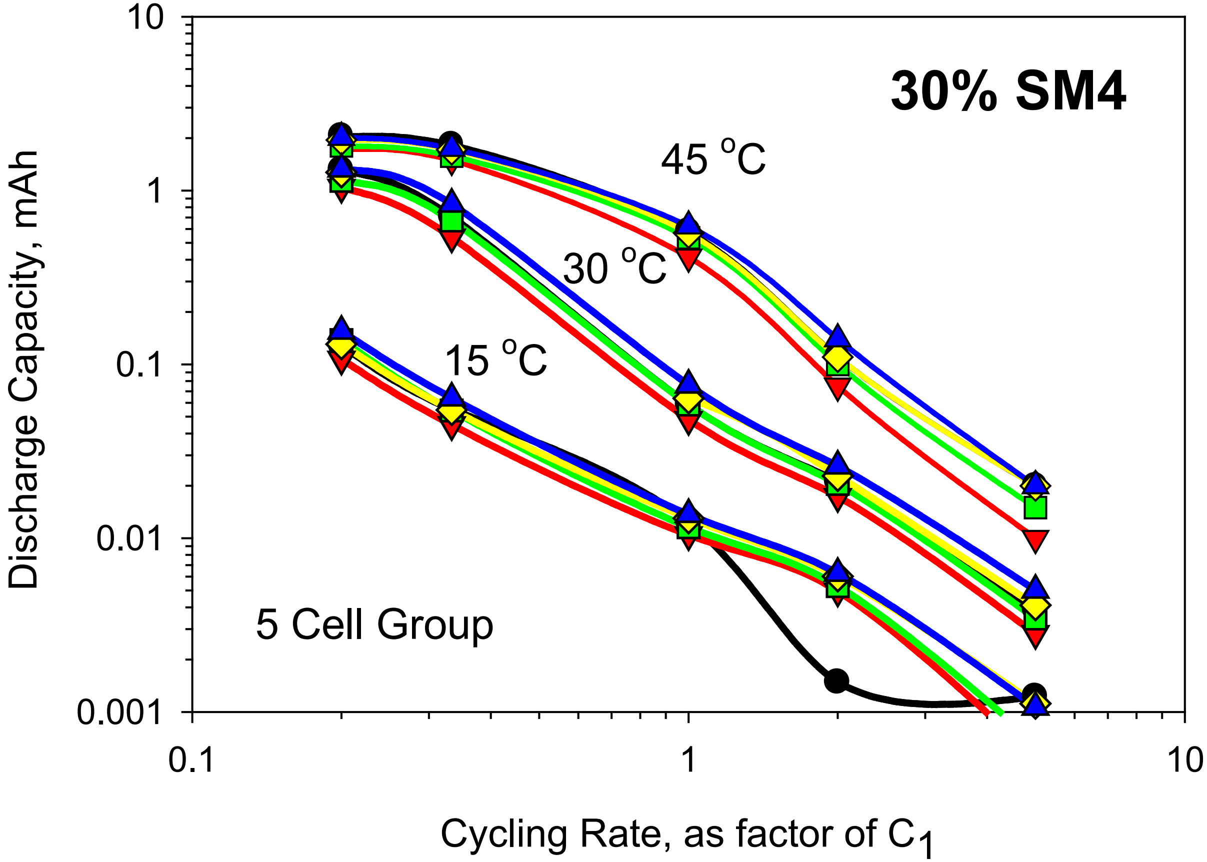
Thus, if cell voltages are kept above OCV, then some overall benefit is seen with regard to voltage tolerance. SM4 is the better choice under these conditions.

Polarization Testing

Using 2032-type coin cells

Coin cells: LiCoO$_2$ cathode, Graphitic anode } effective rating 2.2-2.3 mAh/cm^2

Celgard 2300 series separator



Appreciable capacity limitations are seen over both cycling rate and temperature. This is due in part to higher viscosity of the electrolyte and higher interfacial (SEI) impedance.

Lesser polarization will be achieved when phosphazenes are present that are competitive with conventional organic solvents in terms of transport properties and SEI characteristics. This is a major focus of our work.

Collaborations

- **Princess Energy Systems.** Involved in formative discussions of incorporating phosphazenes into Li-ion cells and corresponding intellectual property and market issues.
- **SNL.** Will perform abuse tolerance testing on electrolytes having the best candidate INL additives.
- **ANL.** Support review of historical data from ANL testing of other phosphazene additives. This is ongoing.
- **Dow Chemical.** Considering involvement in commercial production of INL electrolyte additives for Li-ion systems.

Summary / Conclusions

- Early data is revealing the nature of heterocyclic phosphazene compounds in Li-ion electrolytes. At additive levels (3-10%), only modest shifts are seen in flammability, conductivity, and viscosity. While we are targeting the additive region, we also want to explore systems having mostly phosphazene solvents, requiring that they possess lower viscosity.
- Early voltammetry data shows subtle differences between phosphazene compounds (e.g., SM4 and SM5), indicating that the electronic and molecular structure of some compounds provide better SEI characteristics. SM4 and SM5 additives have a greater effect on the reductive processes at the negative electrode, compared to the baseline, yet these additives act to moderate the oxidative processes at the positive electrode, and hence slightly enhance stability at higher voltages.
- Cycling performance data from coin cells indicates appreciable polarization effects for phosphazenes at moderate levels (30%). Other data (not shown) suggests that we check the compatibility between the choice of salt and phosphazenes on a case-by-case basis. Some additives might show optimal benefit with salts other than $LiPF_6$.

Future Work

- We will also explore electrolyte systems having mostly phosphazene solvents to exploit the inherent low flammability of these additives. To accomplish this, non-cyclic phosphazene compounds will be targeted to reduce viscosity.
- For systems containing volatile organics, we aim to reduce flammability further by selective association between phosphazenes and volatile solvents (e.g., DMC, EMC). We will add flame propagation rate as another flammability measure.
- Newer compounds (e.g., FM and AP series) will indicate whether these structures provide superior transport properties and SEI-forming qualities compared to other phosphazenes. Half-cell studies on SEI will be considered.
- More CV work is planned to look at specific interactions between phosphazene-based electrolytes and cell components such as electrode active materials.
- Salts other than $LiPF_6$ will be considered (e.g., LiBOB, LiFBOB, mixed salts), to avoid possible detrimental interactions between anion and phosphazenes over voltage.
- Best candidate additives will be tested for abuse tolerance at SNL.

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