

Section IV.D.3 for DOE 2013 Annual Report: Novel Phosphazene-Based Compounds to Enhance Safety and Stability of Cell Chemistries for High Voltage Applications (INL)

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Kevin L. Gering
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Sergiy V. Sazhin
Fred F. Stewart
John Burba¹

¹Princess Energy Systems

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**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

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IV.D.3 Novel Phosphazene-based Compounds to Enhance Safety and Stability of Cell Chemistries for High Voltage Applications (INL)

Kevin L. Gering, PhD

Idaho National Laboratory

2525 N. Fremont Ave.

Idaho Falls, ID 83415-2209

Phone: (208) 526-4173; Fax: (208) 526-0690

E-mail: kevin.gering@inl.gov

Collaborators (INL): Eric J. Dufek, Mason K. Harrup, David K. Jamison, Harry W. Rollins, Sergiy V. Sazhin, Fred F. Stewart

(non-INL): John Burba, Princess Energy Systems

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Projected End Date: Sept. 2013

Objectives

Our focus is producing electrolyte and electrode compounds resilient in both temperature and voltage regimes, while meeting a competitive baseline performance in transport properties and SEI characteristics. In meeting these goals we aim to reduce the presence of carbon in Li-ion cells to produce a more robust inorganic-based cell chemistry. We seek compounds that will:

- enable prolonged usage of advanced higher-voltage electrode couples,
- promote better safety performance under abusive thermal conditions,
- enhance cell life.

Another objective is to gain fundamental understanding of molecular-scale interactions between phosphazenes and other electrolyte species and cell components.

Technical Barriers

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+) and some usage patterns and conditions that would cause batteries to operate at higher temperatures. A viable alternative electrolyte for Li-ion batteries must simultaneously meet multiple criteria regarding

transport properties, SEI film formation, voltage stability, flammability, aging mechanisms, chemical compatibility, performance at high and low temperatures, etc. A fundamental challenge remains to produce electrolyte components that will provide noteworthy levels of flame retardance while reducing viscosity to competitive levels to maintain attractive transport properties, and some success has been had at the INL toward that goal in 2013 within our overall ES materials program.

Technical Targets

Our targets are defined by primary categories:

- *Phosphazenes as primary solvents (>40%)* to greatly reduce electrolyte flammability. Our requirements for the pure phosphazene (with lithium salt) to be viable as a primary solvent: room temperature viscosity less than 5 cP, conductivity greater than 4 mS/cm, and lithium salt (LiPF₆) solubility at least 0.6 M.
- *Phosphazenes as cosolvents (10-40%)* to provide mixed benefits of reduced electrolyte flammability and prolonged cell life. Properties for the pure salted phosphazene to be defined as a cosolvent: room temperature viscosity within 5-40 cP, conductivity 0.2-4 mS/cm, and lithium salt solubility within 0.2-0.6 M.
- *Phosphazenes as additive solvents (≤10%)* to enhance chemical/thermal stability of the bulk electrolyte and improve SEI properties in terms of thermal runaway and stability over life. Viable additive candidates are defined as follows: room temperature viscosity exceeds 40 cP, conductivity ≤ 0.2 mS/cm, and lithium salt solubility < 0.2 M.
- Abuse testing at SNL of INL electrolytes looks squarely at how these compounds provide benefit to cell operation and safety at extreme conditions of temperature and voltage. Improvement over a baseline is sought.
- We have worked with ANL and DOE toward scale-up of the best INL phosphazene candidates. One of our compounds is now in the scale-up queue.
- Replace the typical carbon anode with a highly nonflammable polymer-based host that also adds benefit toward chemical compatibility across the cell.

Accomplishments

- Various forms of heterocyclic phosphazene solvent compounds have been synthesized, characterized, and tested in coin cells. More efficient and economical synthesis routes have been found for some classes of compounds to decrease manufacturing costs. Of note for 2013 are newer FM and PhIL (ionic liquid) series compounds.
- Cell testing completed for using INL electrolytes with the NCA (Toda)/Carbon couple, covering characterization of capacity and impedance attributes. Overall results show good compatibility of phosphazenes with the various cell environments, promoting stability at elevated temperatures.
- Completed prolonged thermolysis experiments at 60°C using FM and SM series additives with two markedly different baseline electrolytes.
- Investigation of Phase 3 polymeric alternative anode materials with improved electronic conductivity, porosity, crosslinking, and capacity.
- NMR evaluation of electrolyte fate at elevated temperatures (with Washington State Univ.)
- We further refined and expanded our methods for voltammetric electrolyte and interface characterization, which has the potential of being an important new tool for materials selection.
- Success of INL phosphazene-based electrolyte additives resulted in priority of scale-up of INL electrolyte compounds at ANL; one INL compound is in the scale-up queue.
- DFT Modeling results published for trends between molecular configuration and phosphazene solvent-to-lithium binding energy.

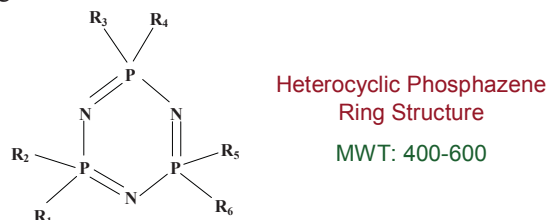


Introduction

Electrolytes play a central role in performance and aging in most electrochemical systems. As automotive and grid applications place a higher reliance on electrochemical stored energy, it becomes more urgent to have electrolyte components that enable optimal battery performance while promoting battery safety and longevity. Safety remains a foremost concern for widespread utilization of Li-ion technology in electric-drive vehicles, especially as the focus turns to higher voltage systems (5V). This work capitalizes on the long established INL expertise regarding phosphazene chemistry, aimed at battery-viable compounds that are highly tolerant to abuse. Various references document or relate to this work for 2013 [1-5].

Approach

The general heterocyclic phosphazene structure is given as follows:



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+) and at higher temperatures. By customizing the pendant structures we seek to improve transport properties while increasing flash point and having acceptable SEI characteristics and cell aging. Benefits include inherent stability and non-flammability, very low vapor pressure, good lithium salt dissolution, and choice of R groups (pendant arms) can be customized to precisely engineer properties. Challenges would include high viscosity and the need to attenuate N:Li⁺ attraction that occurs due to electron doublet transfer. To date our numerous compounds derive from the following four groups:

SM: ether groups attached to the phosphorus centers

AL: unsaturated analogues of the SM series

FM: fluorinated analogues of the SM series

PhIL: based on an ionic liquid structure.

The ionic liquid series helps to mitigate some of the limitations seen with traditional cyclic phosphazenic solvents, such as N:Li⁺ association that can adversely affect conductivity. Non-cyclic phosphazene compounds are also being targeted through the INL internal R&D program (with success), and salts other than LiPF₆ are being considered.

We employ a number of diverse testing and characterization methods to determine viability of candidate compounds, including advanced voltammetry techniques, coupled viscosity and conductivity analysis, flash point, EIS, cell testing, as well as chemical physics and DFT modeling. Coin cells (type 2032) are used to test candidate electrolytes in an actual cell environment, covering crucial issues of formation, interfacial impedance, polarization testing, and aging.

Results

Summarized below are salient results from 2013 research. For brevity, only representative summaries are given. The baseline (BL) electrolyte is 1.2M LiPF₆ in EC-EMC (1:4, wt.), unless otherwise defined.

Figure 1 shows the result of prolonged thermolysis conditions at 60 °C for electrolyte systems with and

without (baseline) FM and SM phosphazene additives at 10% levels within each baseline. The baseline samples are the two left-most vials in each row. It is readily seen that the presence of the phosphazenes mitigates degradation of the baseline and have a preservation role at elevated temperatures. Benefits are longer cell life under higher-temperature conditions, and the opportunity to scale-back battery thermal management to balance with the resilient electrolyte.

Figure 2 attests that INL FM-series phosphazene additives extend the electrochemical window (EW) past what is achievable with the BL electrolyte. Presence of the phosphazene more than doubles the EW past the BL value. These additives act to moderate the oxidative processes at the positive electrode, and hence enhance stability at higher voltages. This attribute is also observed for other INL phosphazene compounds (SM, AL, etc.). **Figure 3** shows the clear benefit of having 3% PhIL-2 in the baseline electrolyte, where the flame duration was dropped by an order of magnitude below the baseline. This adds greatly to a safe cell chemistry.

Cell testing was performed using 2032-type coin cells to judge performance of the electrolytes with ABR electrode couples. **Figures 4 (a,b)** summarize the early life capacity performance of coin cells using NCA/graphite, having FM series compounds at various amounts in the baseline. In Fig. 4a improvement over baseline performance is seen in particular for FM-2 cases. In Fig. 4b, systems with FM2 levels of at least 12.4 percent show good viability for rates up to C/1.

From initial WSU findings, the BL sample (LiPF₆ 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. This sample became 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 BL sample suggests 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).

Figure 5 contains post-formation capacities for representative cells containing phosphazene-based polymer anodes and thicker HE5050-type cathodes. The capacity range observed is competitive with that of graphitic anodes. **Figure 6** demonstrates that cells with early-generation phosphazene anodes have reasonably low self-discharging behavior at elevated voltage; this behavior can be improved by modification of polymer attributes optimized over voltage. Better capacities were observed as we increased effective surface area within the polymer matrix (**Fig. 7**). The mode of lithium insertion into the polymer host is facilitated in part by the by the electrostatic attributes of the phosphazene moiety, overall exhibiting a dual or hybrid

mode of lithium residency surmised in **Fig. 8** (atomistic + micro-clustering) that is a function of voltage, and is highly reversible. The anode in Fig. 8 was comprised mostly of INL polymer and A12-type graphitic carbon. ***These anode materials are a breakthrough*** that represents a highly “engineerable” option to anodes for Li-ion systems.

Conclusions and Future Directions

INL phosphazene materials improve electrolyte stability at higher voltage and elevated temperatures. The choice of the pendant R groups allows customization of the molecules to fine tune electrolyte properties tied to fate and performance in Li-ion cells. Ionic liquid phosphazenes drastically reduce the inherent association between nitrogen and Li⁺, and have shown superior performance in abuse testing at SNL. In FY 13 we explored electrolytes having higher amounts of phosphazene solvents to exploit their low flammability, wherein amounts of at least 12.4% additives appear feasible for cells requiring modest rates. Newer compounds within the FM and PhIL series support optimization of these compound classes. NMR studies revealed mechanistic information regarding molecular fate and why/how our additives provide resilience to the baseline system.

Good progress was had on developing alternative anodes for Li-ion systems, wherein a phosphazene polymer basis was employed as the core host material, with modifications undertaken to modify crosslinking, porosity, and electronic conductivity. Cell capacities (vs HE5050-type thicker cathode) were often on the order of 300-500 mAh/g for these new materials.

FY 2013 Publications/Presentations (selected)

1. M. T. Benson*, M. K. Harrup, K. L. Gering, “Lithium binding in fluorinated cyclic triphosphazenes”, *Computational and Theoretical Chemistry* 1005 (2013) 25–34.
2. S. V. Sazhin*, K. L. Gering, M. K. Harrup, H. W. Rollins, “Highly Quantitative Electrochemical Characterization of Non-Aqueous Electrolytes & Solid Electrolyte Interphases”, submitted to the *Journal of the Electrochemical Society*, manuscript tracking number JES-13-2932.
3. K. L. Gering* et al., “Advances Toward Inorganic Li-ion Cell Chemistries”, *Next Generation Batteries* (April 30, 2013, Boston, MA).
4. K. L. Gering*, “The Influence of Molecular Interactions on Battery Electrolyte Properties and Processes”, 222nd Meeting of the Electrochemical Society (October 11, 2012, Honolulu, HI).

* Lead author or presenter.

Prolonged Thermolysis Testing at 60 °C (10% Additives)

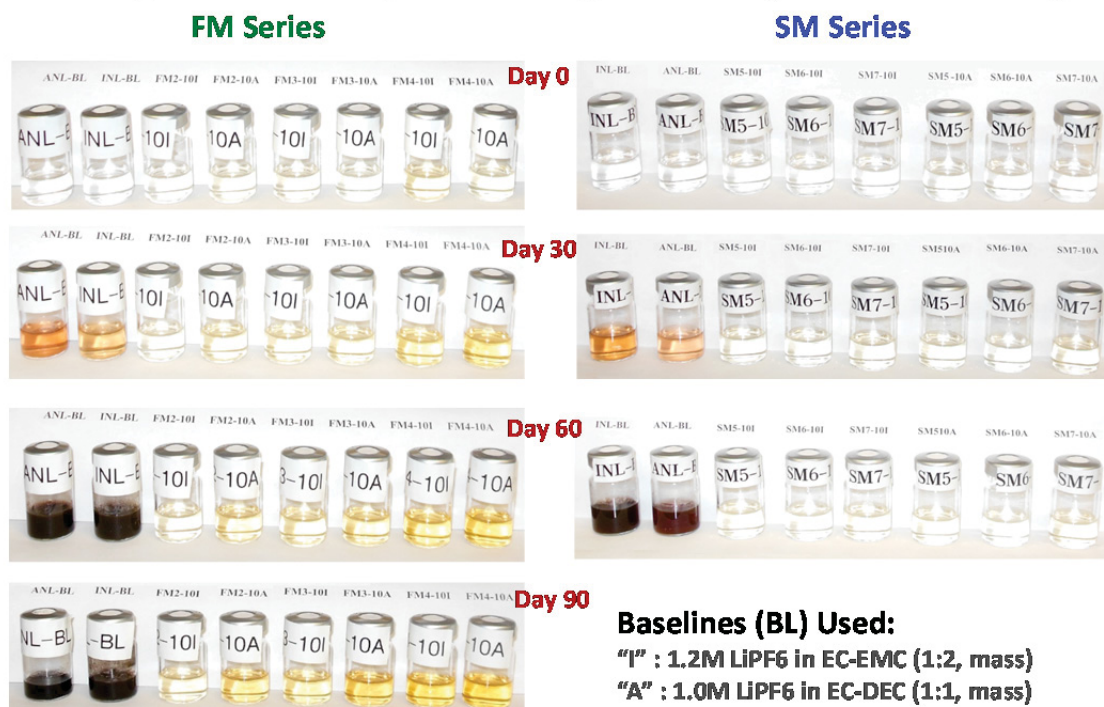
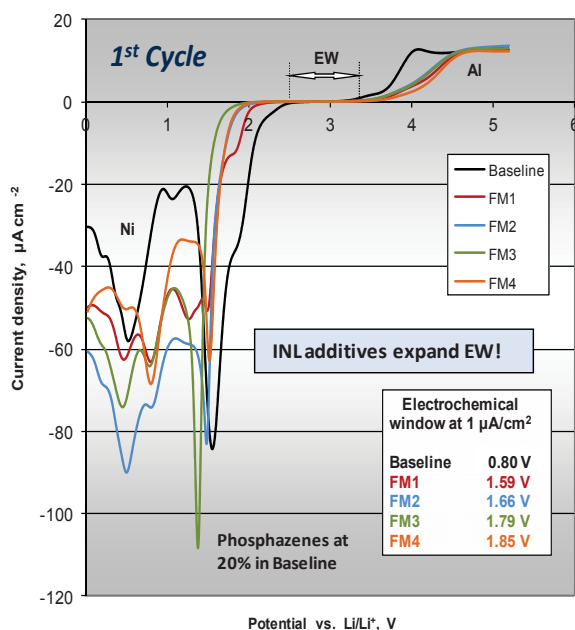


Fig. 1

INL additives greatly enhance thermal stability



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

Fig. 2

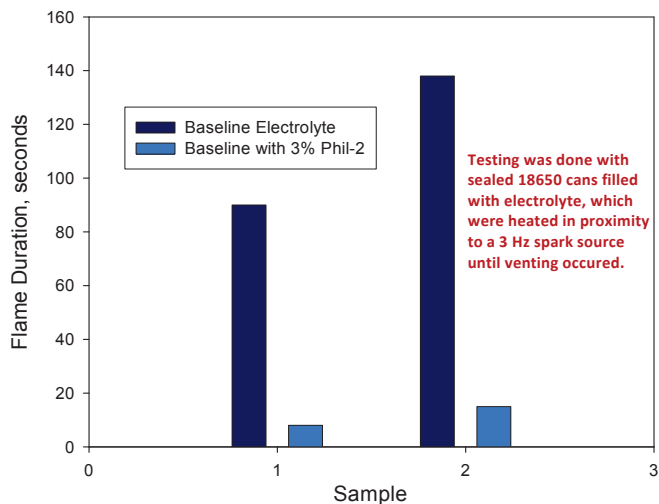


Fig. 3

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

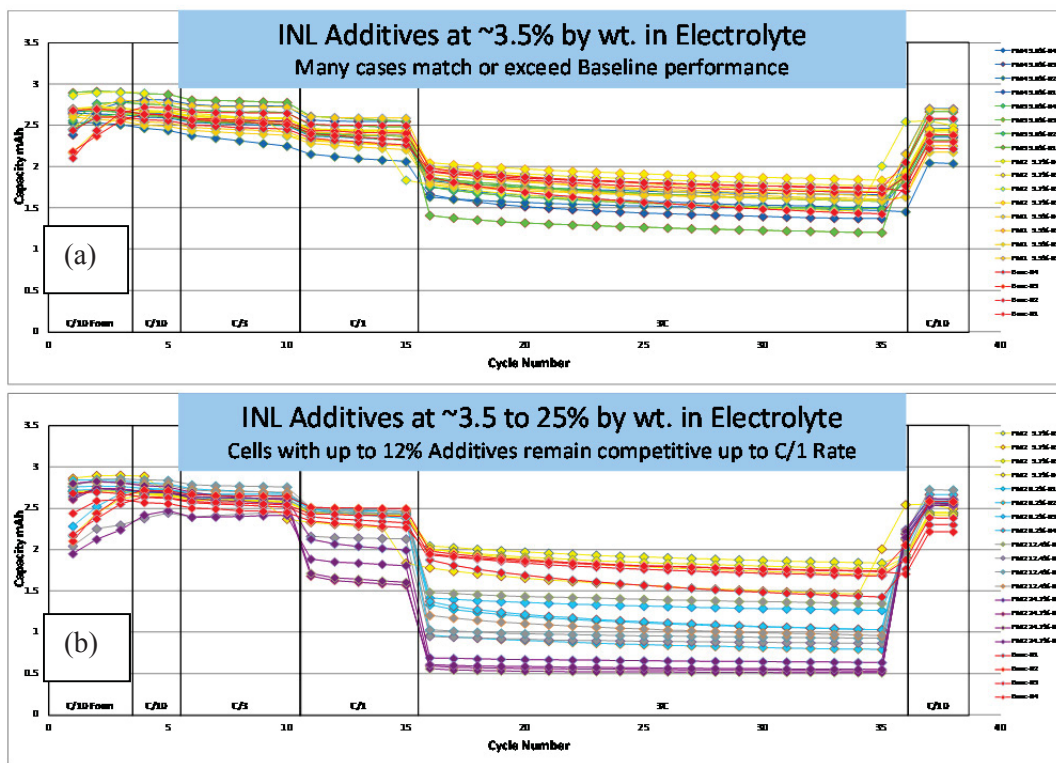


Fig. 4

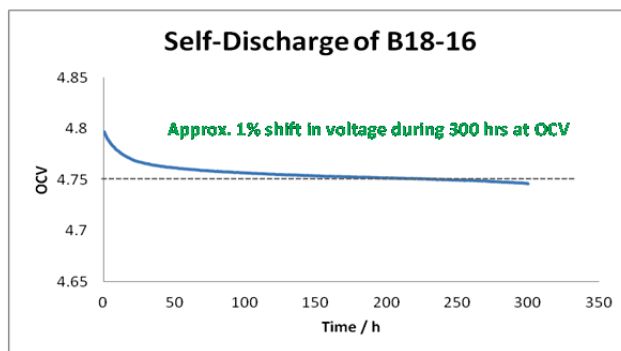
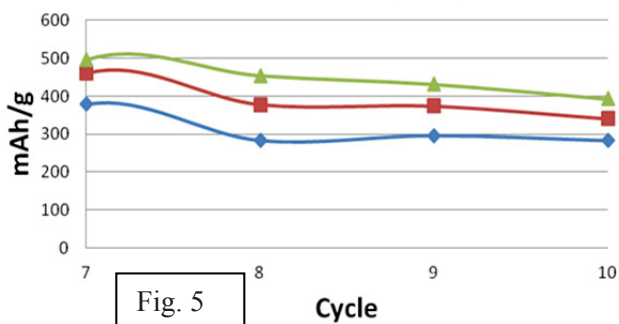


Fig. 6

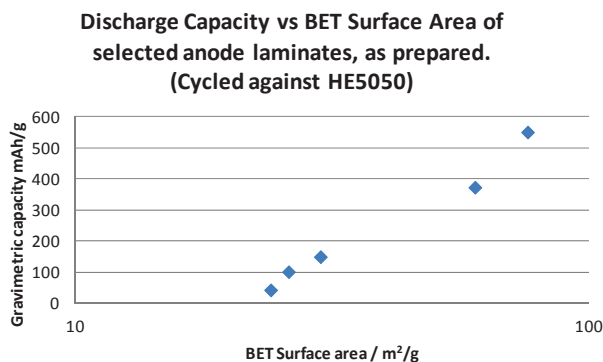


Fig. 7

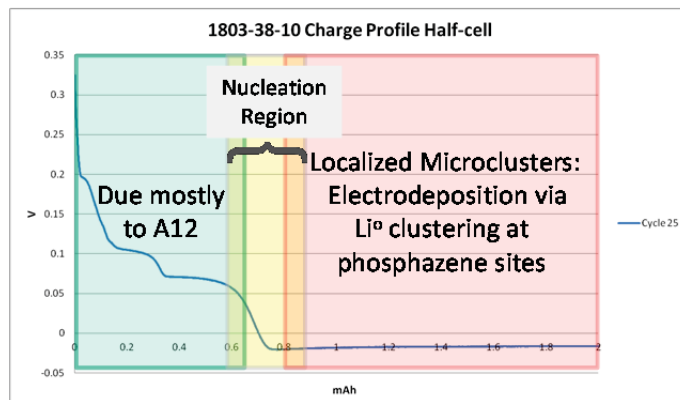


Fig. 8