

Integrated Carbon-reduced Battery Chemistries for Safer Alternative Li-ion Cells

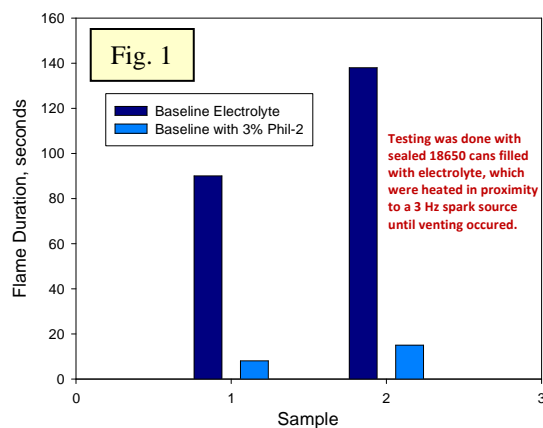
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Despite many advancements made in Li-ion technology, there remain fundamental challenges in designing cell chemistries that provide safe and reliable operation at high voltage and elevated temperatures. The quest for viable electrode couples viable to 5V and beyond carries with it a companion challenge of producing electrolytes that will survive at such conditions. Work at Idaho National Laboratory (INL) has made inroads into producing carbon-reduced cell chemistries wherein volatile electrolyte solvents are augmented or replaced with compounds based on P-N chemistry (e.g., phosphazenes), and graphitic anodes are replaced by a phosphazene-based polymer matrix that possesses multiple functionality in terms of being a lithium host, binder, and non-flammable component. By such targeted substitution of carbon-reduced P-N based components we approach our goal of creating a new and novel class of inorganic battery chemistries for lithium-ion cells, as well as for “beyond lithium” systems.

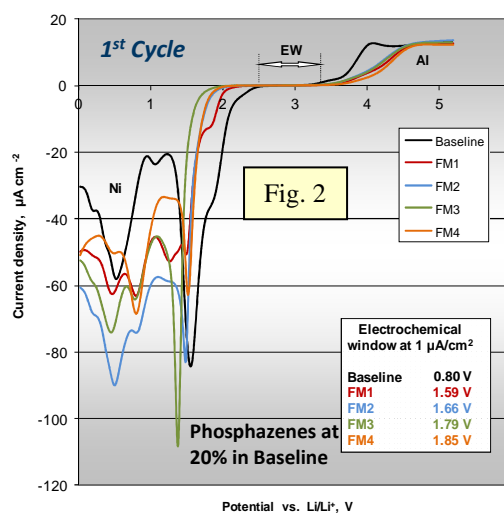
Studies that focus on the fate of cells at elevated temperature have conclusively found that carbon anodes play a pivotal role in promoting thermal runaway in Li-ion cells [e.g., Ref. 1]. Reactions at carbon anodes at moderate temperatures provide a threshold heating rate that initiates cathode SEI breakdown. Changing to a non-carbon anode that is highly non-flammable would push the onset of thermal runaway to higher, safer levels. The presence of phosphorus in phosphazene compounds provides inherent protection against flammability, while having a common chemical basis in the electrolyte and anode will enhance long-term chemical compatibility in the cell environment. Strategic placement of such inorganic-rich chemistries within a robust well-engineered battery architecture can produce transformative (disruptive) improvements in battery safety for EDV applications.

When used as additives or co-solvents, INL phosphazene compounds improve thermal and voltage stability of baseline organic electrolyte systems. For example, abuse testing at Sandia National Laboratory (SNL) showed cases wherein our compounds at three percent levels significantly reduce the volume of gas produced under thermal runaway and reduce the flame duration of the electrolyte by an order of magnitude (Fig. 1). Also, our compounds significantly increase the initial pre-SEI electrochemical window (EW) of electrolytes past baseline levels, to nearly 2 V in many cases (Fig. 2). After SEI formation, the EW widens further making possible the use of high-voltage cell couples with high efficiency. Our portfolio of phosphazene solvent compounds includes cyclic and linear varieties, which are assessed to maximize performance and longevity of the chosen electrode couple and related passivation consequences (i.e., SEI films). There are a number of advantages to adopting a phosphazene polymer basis for anodes that showcase this innovative approach: ability to form 3-D scaffolds that are populated with desirable chemical moieties, Li host capability, supports overall move to a more inorganic battery chemistry, mitigates cell

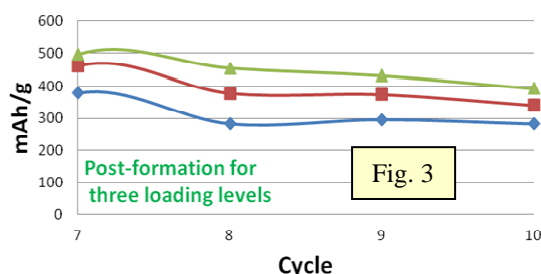
flammability, reduces energy released during thermal runaway, amenable to higher cell voltages, physical and electronic properties that are highly engineerable, and the host polymer also serves as a binder (no need for PVDF). The electronic environment of these polymeric hosts encourages and sustains lithium insertion at relatively high voltages. This family of anodes has shown noteworthy voltage stability and gravimetric capacity. Fig. 3 shows discharge capacity plots for one of our materials cycled to above 4.5V vs HE5050 (LMR NMC/spinel) cathodes, with gravimetric capacities exceeding 300 mAh/g in most cases (competitive with carbon anodes). Other work has looked at cycling these materials against NMC and LNMO cathodes, as well as vs. lithium metal within half cells. For full cells, many cases showed cycling viability past 4.5V while using conventional carbonate-based electrolytes with and without phosphazene additives. This work was supported by the DOE Applied Battery Research (ABR) program.



Baseline Electrolyte: 1.2M LiPF₆ in EC-EMC (1:4)



Gravimetric Discharge Capacities



References

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