



## Hybrid phosphazene anodes for energy storage applications



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### HIGHLIGHTS

- Hybrid cyclic phosphazene/graphite anodes are new materials for lithium batteries.
- Capacity resides with both the graphite and cyclic phosphazene.
- Within the cyclic phosphazene matrix isolated Li deposits are the main source of capacity.
- Tightly controlling the charging voltage provides enhanced cycling efficiency.

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### ABSTRACT

The use of hybrid cyclic phosphazene polymer/graphite anodes, where the phosphazene serves as distributed loci for Li deposition, has been investigated. Capacity within the hybrid system was found to occur reversibly in distinct regions. At the most positive voltages, above 0.06 V vs Li/Li<sup>+</sup>, the capacity was associated mostly with Li<sup>+</sup> intercalation into graphite. In the most negative region, deposition of Li within the polymer was the predominate mechanism. A transitional region is inferred by the data whereby bulk aggregation or clustering of Li atoms occurs in proximity to the phosphazene sites that then serve as a template for more widespread population of Li within the anode at higher voltages, akin to a nucleation process. In full cells with a mixed oxide cathode, controlling the extent of Li deposition by limiting the charging voltage to 4.45 V enabled repeated cycling with no loss in capacity. Capacities as high as 183 mAh g<sup>-1</sup> have been achieved for systems containing as little as 10% graphite while retaining coulombic efficiencies of 98% over 50 cycles. This level of cycling equates to the deposition of 7.4 Li per cyclic phosphazene.

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## 1. Introduction

Recent, safety related events have been a key concern for the continued market entry of Li-ion batteries (LIBs). While safe for the majority of operating conditions, improper use, exposure to harsh conditions and the puncturing of cells can lead to catastrophic failure. Despite concerns with safety, electrification of the transportation fleet in the United States remains an emphasis. To meet the need for enhanced safety, a host of new materials have been proposed. An important class of compounds are those that, when included in LIB electrolyte, reduce the risk of fire [1–8]. Electrolyte additives can significantly reduce safety concerns, but during heating events the majority of the electrolyte can be vented from cells while leaving the highly combustible anode materials

remaining within the LIB. Thus, a different route to increasing the safety of batteries is the use of non-flammable electrode components which remain present even after a venting event.

During LIB thermal events it has been found that the anode is one of the key players in the initiation of the catastrophic failure process [9]. In instances where heating occurs, the solid electrolyte interphase (SEI) on the anode becomes less stable leading to a cascade of reactions which expose lithiated and non-lithiated graphite surfaces. Both are active to the decomposition of electrolyte. Upon sufficient heating, cathodic oxygen generation causes oxidation of electrolyte and eventually the anode during a thermal runaway event [9–11]. In the events described above, materials, such as phosphazenes, that either decrease or inhibit the initiation events, or which minimize the amount of material which can be oxidized provide the opportunity to limit the extent of thermal events and thus enhance the safety of LIBs.

Phosphazenes are a class of inorganic compounds containing P=N bonds that have received some interest primarily as

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electrolyte additives, components in polymer electrolytes and to a lesser extent as binders [1,8,12–18]. One of the attractions of phosphazenes is their ability to act as flame retardants. Additional benefits of phosphazenes are their high adaptability which provides the opportunity to synthesize functionality into the overall molecular framework. This adaptability has led to the construction of both small cyclic phosphazenes which have been incorporated in electrolytes [1,18] and much larger linear polyphosphazene compounds which can act as effective ionic transporters [12–14,19,20]. Lastly, phosphazenes have shown electrochemical stability over a sufficiently large window to allow functionality in LIB systems [1,8,17,18].

One of the primary reasons for investigating the use of hybrid phosphazene anodes is the ability of phosphazenes to act as free-radical scavengers. Combustion can be viewed as a cascading radical pathway, thus the ability to stop the early stages of combustion are essential when trying to minimize the overall flammability of batteries. The use of solid-state cyclic phosphazenes as an anode component looks to build on the previous success of phosphazene electrolyte additives [1,8,18] to further enhance the safety of cells by providing the possibility of retaining the phosphazene in the vicinity of combustible carbon in the cell anode should electrolyte-based phosphazene be ejected during cell venting.

As electrode materials, only a few instances where phosphazenes have been used as cathodes have been reported [21,22]. These cathodes, while showing cyclability, suffer from the low reduction potential of the S–S bond which occurs below 3 V versus Li/Li<sup>+</sup>. In another application as polymer-based electrolytes, phosphazenes have shown Li-ion conductivity values as high as  $2.58 \times 10^{-4} \text{ S cm}^{-1}$  when employed as polymer based electrolytes [14]. Additionally, both experimental and modeling data for liquid electrolytes indicate an association of Li<sup>+</sup> with the O and N components of the phosphazene backbone [19,23]. In the case of N:Li<sup>+</sup> association, this electrostatic attraction is caused by the electron pair donation centered at N that responds to cationic fields. Such associative effects enable nitrogen-containing aprotic solvents to be very aggressive, competitive solvators of cations as indicated by their high donicity numbers [24]. Consequently, the association of Li with the polymer phosphazene moieties creates the situation where Li<sup>+</sup> are less

than fully solvated and as such when reduced to Li<sup>0</sup> the interaction with liquid electrolyte is minimized due to less electrolyte in the vicinity of the Li deposit. The N-based electron pair also serves to provide an electrostatic repulsion with the negative dipole of free solvents providing an additional short-range minimization of electrolyte near deposits of Li. Decreasing the electrolyte in contact with Li serves to increase the coulombic efficiency of hybrid electrodes by decreasing electrolyte decomposition. An additional side benefit is that hybrid phosphazene anodes may minimize the formation of dendrites by creating micro-clusters of Li in the electrode interior as has been recently reported for porous graphene electrodes [25]. When combined with traditional anode materials such as graphite, the use of solid-state phosphazenes provides a route to a hybrid Li-ion, Li-metal anode where the phosphazene serves as a template for selective, localized Li deposition which is isolated from the bulk electrolyte. Such a hybrid anode has the potential, if fully optimized, to be tunable with regard to capacity while retaining the safety enhancing aspects of phosphazene systems. A recent patent application covers this new class of materials [26].

## 2. Experimental

### 2.1. Anode film preparation

Cyclic phosphazenes were prepared using well established procedures with the primary compounds of interest being methyl hydroquinone cyclophosphazene (MeHQCP) and tert-butyl hydroquinone cyclophosphazene (tbu-HQCP) [27,28]. The structure for MeHQCP is shown in Fig. 1, as an example. Following synthesis, purity was confirmed by <sup>1</sup>H NMR.

Casting solutions were prepared, using a method developed in-house, by first dissolving the appropriate amount of phosphazene in tetrahydrofuran (THF, 10–15 mL) followed by the addition of varying quantities of C65 conductive carbon additive (Timcal), and A12 graphite (Conoco-Philips). An assortment of sample formulations is shown in Table 1. The solids and phosphazene solution was mixed by inversion and then sonicated to enhance homogeneity. Following sonication, 0.10–0.50 g of hexamethylene tetramine (HMTA) dissolved in 0.25–1.0 mL H<sub>2</sub>O was added to the suspension. The quantity of HMTA added varied with the cyclic phosphazene loading. Following addition of HMTA, the casting solution was again mixed by inversion. The solution was then loaded into a chromatography sprayer and sprayed onto high purity Cu foil or polyimide sheets. During the spray casting process these substrates were fixed onto a vertically mounted, rotating wheel to ensure uniform coating over multiple substrates.

Spraying occurred in multiple steps where a portion of the solution was sprayed evenly on the substrate followed by a brief pause during which THF evaporated. The evaporation step ensured that the sprayed film did not flow during the casting process. During evaporation steps the casting solution in the sprayer was continuously swirled to maintain uniform dispersion of the solid particles. Following the last spray step, the coated substrates were removed and placed onto a clean, stainless steel sheet. The sheet was loaded into an oven (130 °C). During the curing step the temperature in the oven was ramped from 130 °C to 210 °C. The entire curing protocol took approximately 30 min to complete. The curing protocol served two purposes. First it allowed HMTA to decompose to formaldehyde which allows cross-linking of multiple rings through a phenol-formaldehyde mechanism. Second the temperature ramp served to fully evaporate any trace THF and H<sub>2</sub>O which remained in the electrode. For each of the investigated formulations

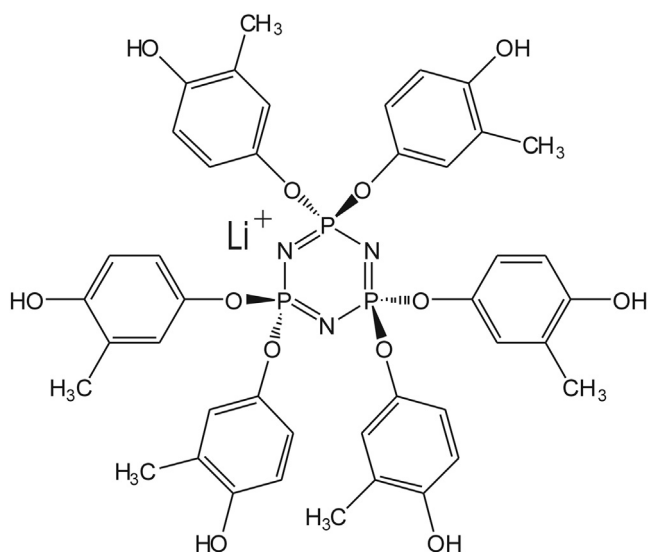


Fig. 1. Molecular structure of MeHQCP with the location of Li noted.

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