

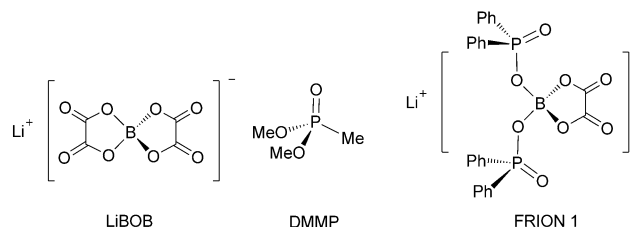
Phosphoryl-Rich Flame-Retardant Ions (FRIONs): Towards Safer Lithium-Ion Batteries**

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Abstract: The functionalized catecholate, tetraethyl (2,3-dihydroxy-1,4-phenylene)bis(phosphonate) (H_2 -DPC), has been used to prepare a series of lithium salts $Li[B(DPC)(oxalato)]$, $Li[B(DPC)_2]$, $Li[B(DPC)F_2]$, and $Li[P(DPC)_3]$. The phosphoryl-rich character of these anions was designed to impart flame-retardant properties for their use as potential flame-retardant ions (FRIONs), additives, or replacements for other lithium salts for safer lithium-ion batteries. The new materials were fully characterized, and the single-crystal structures of $Li[B(DPC)(oxalato)]$ and $Li[P(DPC)_3]$ have been determined. Thermogravimetric analysis of the four lithium salts show that they are thermally stable up to around 200°C. Pyrolysis combustion flow calorimetry reveals that these salts produce high char yields upon combustion.

Lithium-ion batteries (LIBs) have become the battery of choice for portable electronics and mobile communication devices because of their high energy density and their lack of a memory effect. As their size scales towards transportation applications there have been concerns surrounding their safety in light of an increasing number of well-publicized battery fires. High energy density LIBs present unique challenges, for a fully charged battery contains reactive and hazardous materials in the presence of flammable organic solvents. Catastrophic failures of a lithium-ion battery often include thermal runaway combined with fire and toxic fumes. It is thus unsurprising that a number of strategies are actively being pursued to manage the risks associated with LIBs.^[1]

One of the primary components of LIBs is the electrolyte, which in most commercial LIBs is a solution of $LiPF_6$ in mixtures of organic carbonates, including ethylene carbonate, dimethyl carbonate, and diethyl carbonate.^[2,3] Of note is the

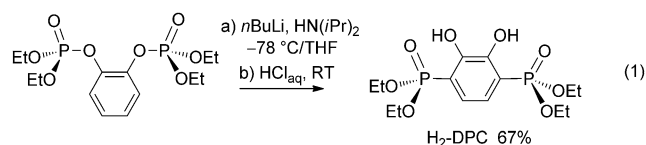


novel salt lithium bis(oxalato)borate (LiBOB),^[4] which has been shown to improve certain aspects of the solid electrolyte interface (SEI) formed at the LIB battery anode.^[5]

One means to reduce the flammability of the electrolyte solution is to add flame-retardant compounds to the mixture. A number of studies have shown that addition of organophosphorus(V) compounds, such as DMMP,^[6] result in desirable protection to systems.^[7] However, such additives may have deleterious effects on the operation of the battery, especially if they are susceptible to reduction at the low potentials of the anode, and could thus lead to capacity fading. Additives can also disrupt formation of a robust SEI. Finally, incorporation of additives to a closed system requires displacement of vital LIB components, and hence also lead to loss of capacity.

Our particular strategy involves the synthesis of flame-retardant ions (FRIONs) as bifunctional electrolytic salts. The ground-up design of FRIONs offers one the opportunity to replace some or all of a conventional lithium salt, such as $LiPF_6$, without jeopardizing loss of the LIB capacity as well as risk incompatible chemistries. Our first foray into FRIONs resulted in the identification of FRION 1.^[8] The particular FRION combines attributes of LiBOB^[9] and the flame-retardant qualities introduced by the presence of phosphinate groups. Unfortunately, FRION 1 suffered from low yields and limited solubility. Herein we communicate the successful design of a new class of lithium salts having attributes suitable for applications of anions where flame-retardant qualities are desired.

To enhance the thermal stability of FRIONs, we sought to utilize a chelating organophosphorus entity to replace the two phosphinato groups in FRION 1. We thus examined the use of tetraethyl (2,3-dihydroxy-1,4-phenylene)bis(phosphonate) [H_2 -DPC, Eq. (1)]. This particular material was previously



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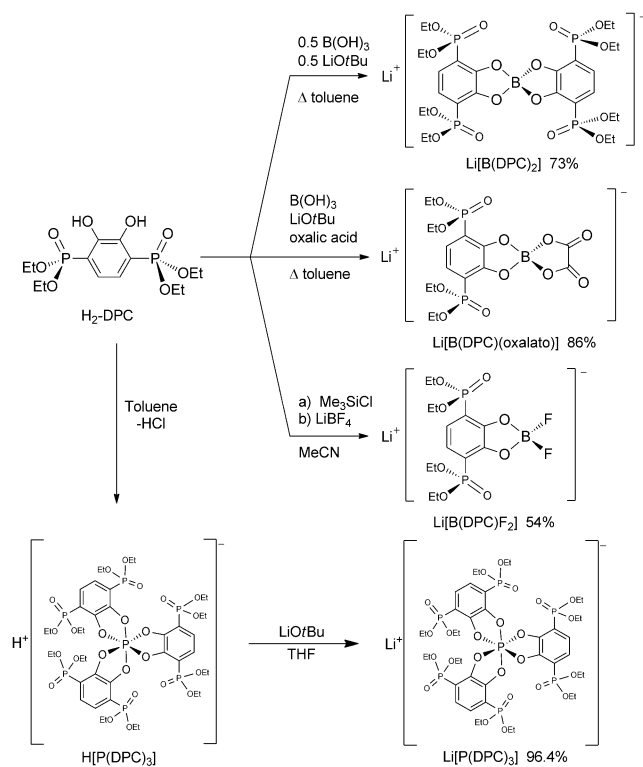
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prepared in an impure fashion by the anionic phospho-Fries rearrangement of 1,2-phenylene tetraethyl bis(phosphate).^[10] Changing the aqueous ammonium chloride quench to an aqueous hydrochloric acid (4 M) quench leads to a significantly purer product which is suitable for subsequent use.

Reaction of two equivalents of H₂-DPC with boric acid and LiOtBu in refluxing toluene leads to Li[B(DPC)₂], in 73% yield, as an analytically pure white solid after drying (Scheme 1). Likewise, reaction of H₂-DPC with oxalic acid,



Scheme 1. Conversion of a 1,2-diphosphinatocatechol into lithium salts.

boric acid, and LiOtBu in refluxing toluene leads to the asymmetric salt Li[B(DPC)(oxalato)] in 86% yield as a white solid after drying. Reaction of H₂-DPC with Me₃SiCl, and then with LiBF₄, allows isolation of Li[B(DPC)F₂] in 54% yield as an analytically pure white solid after filtration and drying under vacuum. These three new materials are readily identified by multinuclear NMR spectroscopy. The ³¹P{¹H} NMR spectra ([D₆]DMSO) for Li[B(DPC)₂], Li[B(DPC)(oxalato)], and Li[B(DPC)F₂] present resonances at δ = 16.4, 15.2, and 17.7 ppm, respectively. Notably, a mixture of Li[B(DPC)₂] and Li[B(DPC)(oxalato)] in [D₆]DMSO shows distinct ³¹P NMR signals indicating that any ligand exchange or disproportionation processes are slow on the NMR timescale. Sharp ¹¹B NMR resonances are also observed at δ = 11.8, 11.8, and 11.5 ppm for Li[B(DPC)₂], Li[B(DPC)(oxalato)], and Li[B(DPC)F₂], respectively. These values are shifted slightly upfield compared to that reported for LiBOB (δ = 12.2 ppm).^[4a]

X-ray-quality crystals of Li[B(DPC)(oxalato)] were grown by vapor diffusion of hexanes into a THF solution of

Li[B(DPC)(oxalato)], and the results of a crystallographic analysis are presented in Figure 1.^[11] The 1:1 ratio of DPC and oxalato ligands is rigorously established, and geometries about the boron and lithium centers are tetrahedral. The lithium ion is coordinated by a phosphoryl oxygen atom (O10) and a catecholate oxygen atom (O2) of one [B(DPC)(oxalato)] anion, as well as by a phosphoryl oxygen atom (O7) and an oxalato oxygen atom (O5) of two other [B(DPC)(oxalato)] anions, and gives rise to a coordination polymer in the solid state. The Li-O distances span the range from 1.867(1) to 1.989(2) Å, and are within the range of Li-O distances reported for other lithium oxalatoborate and lithium catecholoborate salts.^[12]

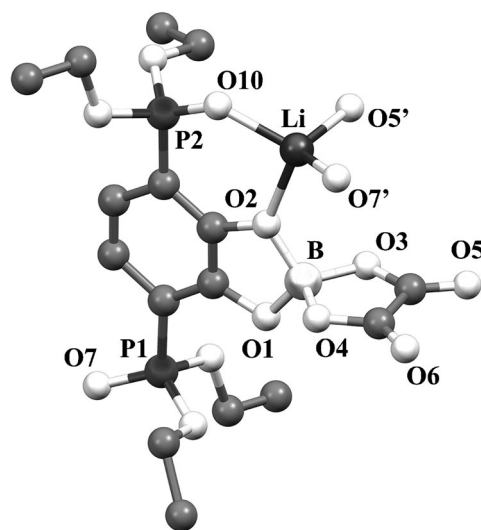


Figure 1. Molecular structure of Li[B(DPC)(oxalato)] in the solid state (hydrogen atoms omitted for clarity).

Having successfully prepared boron-centered anions we sought to extend the syntheses to a phosphorus-centered anion. Reaction of a slight excess (3.3 equiv) of H₂-DPC with PCl₅ in toluene led to the evolution of HCl gas. Upon the end of HCl evolution, the solvent was removed to yield an off-white solid. ³¹P{¹H} NMR spectroscopic analysis of the crude material suggested that H[P(DPC)₃] ([D₆]DMSO: δ = −81.3, 19.4 ppm) was produced, along with some amount of [P(H-DPC)(DPC)₂] (−35.6, 15.0). Analogous mixtures were generated during the synthesis of H[P(catecholate)₃].^[13] Washing the solid with diethyl ether and drying for 24 hours under vacuum yielded H[P(DPC)₃] as a white solid in 97.1%. Treatment of H[P(DPC)₃] with LiOtBu in THF (18 h) led to a white precipitate which upon filtration and drying gave Li[P(DPC)₃] in 96.4% yield. This compound displays resonances at δ = 10.7 and −85.7 ppm in [D₆]DMSO for the phosphoryl and the central phosphorus atoms, respectively. In [D₆]acetone Li[P(catecholate)₃] shows a single phosphorus resonance at δ = −82.0 ppm.^[13]

The results of an X-ray diffraction study upon a single crystal of Li[P(DPC)₃] (grown by vapor diffusion of EtOH into DMF solution of Li[P(DPC)₃]) are shown in Figure 2.^[11] As expected, the geometry about the central phosphorus

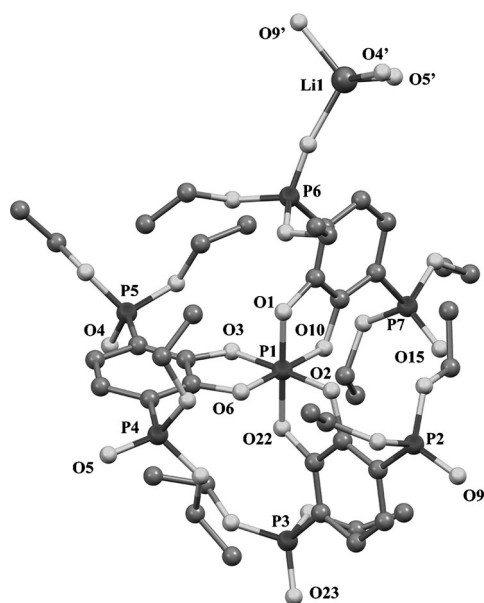


Figure 2. Molecular structure of $\text{Li}[\text{P}(\text{DPC})_3]$ in the solid state (hydrogen atoms omitted for clarity).

atom is octahedral. As found for $\text{Li}[\text{B}(\text{DPC})(\text{oxalato})]$, the lithium ion is tetrahedrally coordinated. Each lithium ion is surrounded by four phosphoryl oxygen atoms from four different $[\text{P}(\text{DPC})_3]$ anions, and gives rise to a network-type structure in the solid state. The Li-O distances span the range from 1.906(7) to 1.917(7) Å. The P-O distances for the octahedral phosphorus atom range from 1.700(2) to 1.719(2) Å. The structure of $\text{Li}[\text{P}(3,5\text{-di-}t\text{-butyl-catecholate})_3]$ serves as a useful comparison and has for the central phosphorus atom P-O distances of 1.690(3)–1.724(3) Å.^[14]

A desired feature of these anions is their thermal stability. Each of the new FRIONs were thus examined by thermal gravimetric analysis (TGA). The results are presented in Figure 3. Each material is stable to up to 200 °C, but the $\text{Li}[\text{B}(\text{DPC})\text{F}_2]$ shows additional stability up to 280 °C.

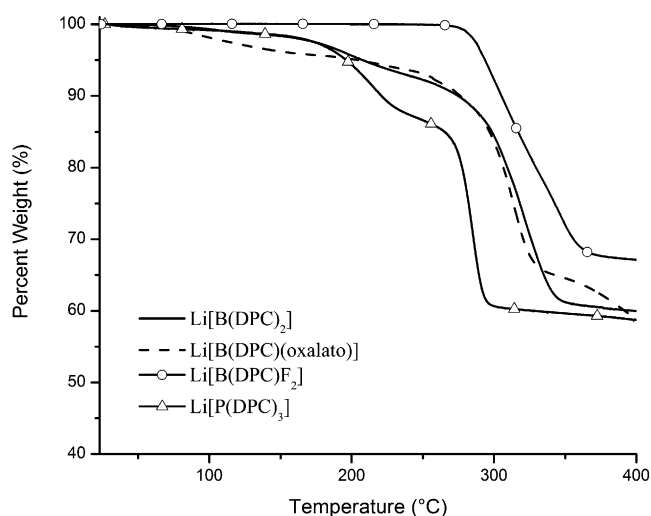


Figure 3. Thermal gravimetric analysis of lithium salts.

Organophosphorus-based flame-retardant compounds are well known.^[15] One proposed mechanism for their efficacy is based on the fact that when many of these materials undergo combustion, a layer of char (polyphosphoric acids) is produced that acts as a thermal and gas barrier.^[15,16] Further, boron compounds can form a variety of boron oxide enhanced chars, depending upon other neighboring species, during thermal decomposition/pyrolysis.^[17] The data for pyrolysis combustion flow calorimetry (PCFC)^[18] obtained for three of the new salts, as well as corresponding data for FRION 1 and LiBOB, are shown in Table 1. From the data in

Table 1: Microcombustion calorimetry results for FRIONs and LiBOB.^[a]

Compound	Avg. char yield ^[b] [%]	Avg. HRR Peak T [°C]	Avg. HRR peak value [W g ⁻¹]	Avg. total heat release [kJ g ⁻¹]
FRION 1	23.6(4)	158(1), 178(1), 300(0), 561(1)	49(1), 82(3), 4(2), 225(8)	20.5(5)
$\text{Li}[\text{B}(\text{DPC})_2]$	42.2(4)	312(2), 446(8)	200(17), 35(3)	12.2(3)
$\text{Li}[\text{B}(\text{DPC})(\text{Oxalato})]$	49.60(5)	304(1), 327(1), 534(1)	102(1), 111(1), 42(1)	8.7(1)
$\text{Li}[\text{P}(\text{DPC})_3]$	40.2(7)	239(2), 299(2)	20(1), 488(14)	10.4(1)
LiBOB	19(5)	360(1), 492(1)	69(2), 9(0)	3.0(1)

[a] Standard deviation shown within parentheses. Samples were tested at a 1 °C/sec heating rate under nitrogen from 75 to 800 °C using method A of ASTM D7309. [b] Average of three runs (full data in the Supporting Information).

Table 1, we can infer that the lithium boron complexes as well as the lithium boron phosphorus species are forming high levels of char and showing reduced heat release. As higher levels of char are formed, less of the electrolyte is available for burning in the event of a battery fire, and further, depending upon how the battery is penetrated/damaged in a fire, the chars may help form seals/caps between layers to slow fire growth in the battery. The LiBOB material shows the lowest total heat release and some of the lowest heat release rate (HRR) values, thus indicating it is the least flammable material tested, yet it has a low char yield. Given that LiBOB has very little carbon present in its structure, we hypothesize that most of the carbon which is present decomposes in the form of carbon dioxide, and would thus give off no additional heat. Evolved gas analysis would be needed to confirm this hypothesis, however. For the other compounds we can see higher char yields and a range of total heat release. The higher char yields are responsible for lower total heat release as more of the structure is bound up as char, which is preferable to being part of a substance that can be pyrolyzed and combusted. These PCFC results show that these new ions have reduced flammability and should have great potential as flame-retardant ions in LIBs.

The utility of anions in LIBs depends on their ability to be stable under a range of oxidation potentials. Studies have now shown linear correlations between the experimental E_{ox} and

computed E_{HOMO} of anions. Following the computational procedures of Xue and co-workers,^[19] we first minimized the structure (DFT B3LYP 6-311++G(2df,2p)) of a model anion [B(DPC')(oxalato)]⁻ where in the DPC' group the ethyl groups of DPC were replaced by methyl groups for computational simplicity. This structure was then subjected to a single point calculation (HF 6-311++G(3df,3dp)), thus yielding $E_{\text{HOMO}} = -5.69$. This orbital is comprised of the catechol core π orbitals (see the Supporting Information). The presence of the two O=P(OMe)₂ units drives the energy of the HOMO orbital down by 0.83 eV relative to that of [B(catechol)(oxalato)]⁻,^[19b] and thus allows one to predict greater oxidative stability (in the absence of kinetic effects) for catechol borate anions bearing O=P(OR)₂ residues. Electrochemical measurements are now underway to examine the behavior and performance of the new FRIONs in LIBs.

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