Multi-ionic Lithium Salts for Solid Polymer Electrolytes
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In order to form solid polymer electrolytes (SPEs) with the desired high ionic conductivities and Li⁺ ion transference numbers (τ⁺), one approach is to use multi-ionic salts that contain organic groups. When dissolved in a polar matrix such as polyethylene oxide (PEO), phase separation can take place, so that the organic groups cluster and form a structural phase. The anionic groups on the salt then point outwards towards the polar matrix and the dissociated Li⁺ ions are solvated by ethylene oxide (EO) units. Two examples of multi-ionic salts investigated here are based on polyoctahedral silsesquioxane (POSS) [7]: POSS-phenyl\(\text{BF}_3\) and a half cube POSS, [PhSiO(BF\(\text{3}\)\(_7\)]\(_n\), (Figure 1). Both are prepared by addition of BF\(\text{3}\) etherates to the respective POSS-phenyl\(\text{Li}\) or [PhSiO(O\(\text{Li}\)])\(_n\). [7]

[PhSiO(BF\(\text{3}\)\(_7\)]\(_n\) has a higher ratio of Li⁺ ions/phenyl group than POSS-phenyl\(\text{BF}_3\)), but both have higher ionic densities compared with single ion conductors. POSS-phenyl\(\text{BF}_3\)) and [PhSiO(BF\(\text{3}\)\(_7\)]\(_n\) have Janus-like properties, with portions of the molecule either hydrophobic or ionic.

### Figure 1 (left) structure of [PhSiO(BF\(_3\)]\(_n\); (right) POSS-phenyl\(\text{BF}_3\)) showing Janus-like properties and pocket formed by three –Si-O-BF\(_3\) groups. (●) grey: phenyl rings and Si; (●) red: oxygen; (●) white: fluorine; (●) yellow: boron; (●) orange: Li ions (randomly placed).

Blends of PEO(600K) or POSS-PEG\(_8\) (eight polyethylene glycols at the apexes of the POSS cage) with POSS-phenyl\(\text{BF}_3\)) form SPE\(_s\), 4, and exhibit phase separation as observed by TEM or SEM (Figure 2 left). These SPEs remain true hard solids until ~100 °C, and then become elastomeric, despite an absence of PEO crystallization. The solid/elastomeric morphology is the result of cross-link sites provided by the phenyl aggregates and bridging of the POSS clusters by PEO chains: cluster-Si-O-BF\(_3\) “Li⁺” (EO\(_n\) “Li⁺” “F”-B-O-Si-cluster.

### Figure 2 (left). SEM image of POSS-phenyl\(\text{BF}_3\))/POSS-PEG\(_8\) with stainless steel working electrode and Li\(\text{SO}_2\) electrolyte; potential scanned from 2.6 V to 4.5V at 30mV/ sec.

Electrochemical evaluation of POSS-phenyl\(\text{BF}_3\))/POSS-PEG\(_8\) or POSS-phenyl\(\text{BF}_3\))/POSS-PeG\(_8\) was obtained for O/Li ratios between 6/1 and 20/1. The SPEs had electrochemical stability windows of 4.6 V and excellent interfacial stability with lithium metal. The salts are reversible towards Li²⁺ between 2.6 and 4.5 V, as shown by cyclic voltammetry (CV) scans (Figure 2 right). The highest room temperature conductivity (σ = 4 x 10\(^{-3}\) S/cm) was obtained for POSS-phenyl\(\text{BF}_3\))/PEO(600K) at O/Li = 14/1, and at T > 60 °C, when the materials were still solids, σ > 10\(^{-2}\) S/cm. The lithium ion transference number was τ⁺ = 0.6. We suggest that the rigid structure of the ionic pocket for POSS-phenyl\(\text{BF}_3\)) inhibits ion pair and conductive triplet formation.

However, for these multi-ionic salts decreasing O/Li in order to increase the number of Li⁺ ions also adds more phenyl groups. For POSS-phenyl\(\text{BF}_3\)), this results in a majority hydrophobic structural phase with non-connected inclusions of the conductive PEO/Li⁺ phase. In order to increase the amount of Li⁺ and still preserve a continuous conductive phase, the [PhSiO(BF\(_3\))\(_7\)]\(_n\) salt was synthesized, since it had a higher density of Li⁺ ions. (Figure 3). DSC of [PhSiO(OLi)]\(_n\)/POSS-PeG\(_8\) and [PhSiO(OBF\(_3\)\(_7\)]\(_n\)/POSS-PeG\(_8\) both with O/Li = 16/1

### Figure 3. DSC of [PhSiO(O\(\text{Li}\)])\(_n\)/POSS-PeG\(_8\) and [PhSiO(OBF\(_3\))]\(_n\)/POSS-PeG\(_8\) both with O/Li = 16/1

Preliminary data on [PhSiO(BF\(_3\))]\(_n\)/POSS-PeG\(_8\) indicates that it has much better solubility in POSS-PeG\(_8\) than does POSS-phenyl\(\text{BF}_3\)). As in the case of POSS-phenyl\(\text{BF}_3\)), the [PhSiO(BF\(_3\))]\(_n\) version has much greater Li⁺ ion dissociation than does the [PhSiO(O\(\text{Li}\)]\(_n\)). This is demonstrated by differential scanning calorimetry (DSC) data (Figure 3). The T\(_g\) increases and crystallinity suppression is the result of Li⁺ ion complexation with the ether oxygens of PEG.

### Figure 4. CV scan for 14/1 PEO(600K)/POSS-phenyl\(\text{BF}_3\)) with stainless steel working electrode and Li\(\text{SO}_2\) electrolyte; potential scanned from 2.6 V to 4.5V at 30mV/sec.

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