

Multi-ionic Lithium Salts for Solid Polymer Electrolytes
 Parameswara Rao Chinnam and Stephanie L. Wunder
 Department of Chemistry, Temple University
 Philadelphia, PA 19122

In order to form solid polymer electrolytes (SPEs) with the desired high ionic conductivities and Li^+ ion transference numbers (t_0^+)¹, 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)²: POSS-phenyl₇(BF₃Li)₃, and a half cube POSS, [PhSiO(BF₃Li)]₄ (**Figure 1**). Both are prepared by addition of BF₃ etherates to the respective POSS-phenyl₇(Li)₃ or [PhSiO(OLi)]₄.^{3,4}

[PhSiO(BF₃Li)]₄ has a higher ratio of Li^+ ions/phenyl group than POSS-phenyl₇(BF₃Li)₃, but both have higher ionic densities compared with single ion conductors. POSS-phenyl₇(BF₃Li)₃ and [PhSiO(BF₃Li)]₄ have Janus-like properties, with portions of the molecule either hydrophobic or ionic.

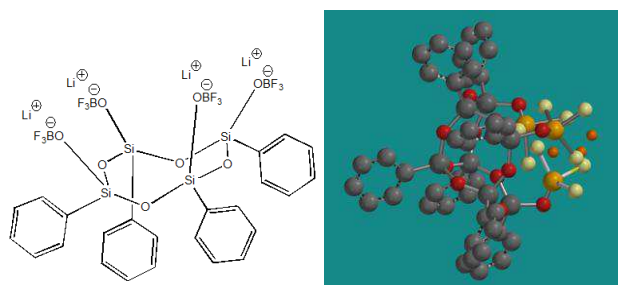


Figure 1 (left) structure of [PhSiO(BF₃Li)]₄; **(right)** POSS-phenyl₇(BF₃)₃ showing Janus-like properties and pocket formed by three $-\text{Si}-\text{O}-\text{BF}_3^-$ groups. (●) grey: phenyl rings and Si; (●) red: oxygen; (○) white: fluorine; (●) yellow: boron; (●) orange: Li ions (randomly placed).

Blends of PEO(600K) or POSS-PEG₈ (eight polyethylene glycols at the apexes of the POSS cage) with POSS-phenyl₇(BF₃Li)₃ form SPEs^{3,4}, 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-BF₃⁻ \cdots Li⁺ \cdots (EO)_n \cdots Li⁺ \cdots F₃B-O-Si-cluster.

Electrochemical evaluation of POSS-phenyl₇(BF₃Li)₃/PEO(600K) or POSS-phenyl₇(BF₃Li)₃/POSS-PEG₈ 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 Li⁰ between 2.6 and 4.5 V, as shown by cyclic voltammetry (CV) scans (**Figure 2 right**). The highest room temperature conductivity ($\sigma = 4 \times 10^{-4}$ S/cm) was obtained for POSS-phenyl₇(BF₃Li)₃/PEO(600K) at O/Li = 14/1, and at $T > 60$ °C, when the materials were still solids, $\sigma > 10^{-3}$ S/cm. The lithium ion transference

number was $t_0^+ = 0.6$. We suggest that the rigid structure of the ionic pocket for POSS-phenyl₇(BF₃)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-phenyl₇(BF₃Li)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(BF₃Li)]₄ salt was synthesized, since it had a higher density of Li⁺ ions.

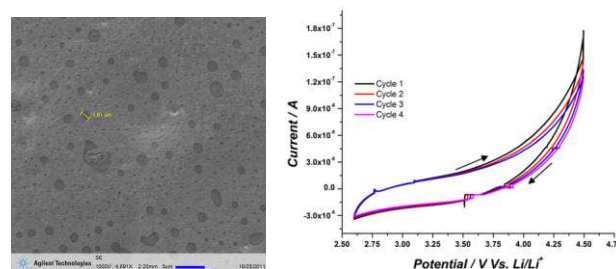


Figure 2 (left). SEM image of POSS-phenyl₇(BF₃Li)₃/PEO(600K) O/Li = 10/1; CV scan for 14/1 PEO(600K)/POSS-phenyl₇(BF₃Li)₃ with stainless steel working electrode and Li⁰ reference and counter electrode; potential scanned from 2.6 V to 4.5 V at 30mV/sec.

Preliminary data on [PhSiO(BF₃Li)]₄/POSS-PEG₈ indicates that it has much better solubility in POSS-PEG₈ than does POSS-phenyl₇(BF₃Li)₃. As in the case of POSS-phenyl₇(BF₃Li)₃, the [PhSiO(BF₃Li)]₄ version has much greater Li⁺ ion dissociation than does the [PhSiO(OLi)]₄. 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 PEG₈.

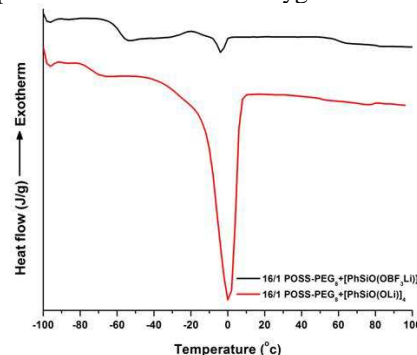


Figure 3. DSC of [PhSiO(OLi)]₄/POSS-PEG₈ and [PhSiO(OBF₃Li)]₄/POSS-PEG₈ both with O/Li = 16/1

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