Abs. 245, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Silsesquioxanes as Nanomaterials for Lithium Battery Applications

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Polyhedral silsesquioxanes (POSS) are nanometer size silica cubes ($SiO_{1.5}$) with eight functionizable SiH groups. For lithium battery applications, we have attached oligomeric polyethylene oxide (PEO) as well as lithium anion salts. Depending on the chain length, POSS-PEO$(n)_8$, where n is the length of the ethylene oxide (EO) chain, can be amorphous (n = 2, 3, and 4) or semicrystalline (n = 6, <8> and <12.5>)[1]. A schematic of POSS-PEO$(n)_8$ is shown in Figure 1. Addition of lithium salt forms viscous electrolyte solutions[2], which are solids when blended with high molecular weight PEO(600K) or methyl cellulose. For O/Li ratios < 12/1 the crystallization of semicrystalline POSS-PEO$(n)_8$ is suppressed. Amorphous POSS-PEO$(n)_8$ can be used to investigate the effects of anion size and lithium salt dissociation in PEO based electrolyte systems.

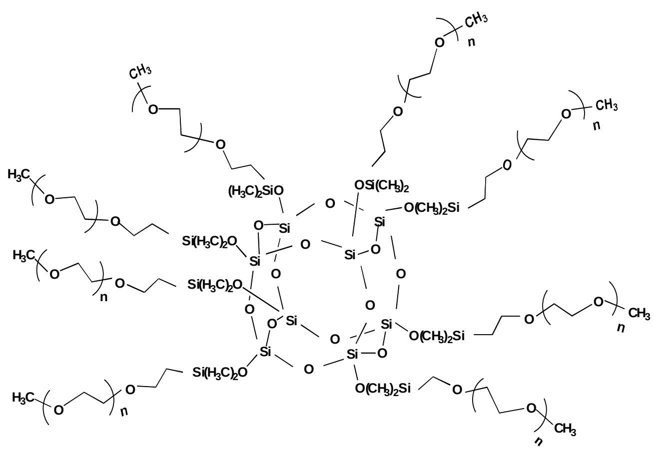

Figure 1. Structure of POSS-PEO$(n)_8$

The temperature dependent conductivity of POSS-PEO$(n=3)_8$ using $LiClO_4$ is shown in Figure 2. At high temperatures, the conductivity increased with increased salt concentration, due to increased ions or ion pairs. At low temperatures, this order was reversed. The conductivity decreased with increased salt concentration, since the glass transition temperature, T_g, increased with increased salt: T_g = -49.5 for O/Li = 8/1, T_g = -66.0 for O/Li = 16/1, and T_g = -78.4 for O/Li = 32/1. These trends were observed for all the amorphous POSS-PEO$(n=2,3,4)_8$. For the semicrystalline POSS-PEO$(n=6,<8> \text{ and } <12.5>)_8$, the onset of crystallization further decreased the low temperature conductivities. For the same studies using LiBETI, the T_gs were always lower and the conductivities therefore higher at low temperatures, compared with $LiClO_4$.

A comparison of conductivity data for O/Li = 16/ 1 is shown in Figure 3. At low temperatures, the crystallization of POSS-PEO$(n = 6 \text{ and } <8>)_8$ results in drastically reduced conductivities. At high temperatures, the conductivities increasewd with increasing percentage of PEO in the POSS-PEO$(n)_8$. This is the result of the dilution effect of inert $SiO_{1.5}$. The conductivity of neat PEO(600K) is slightly higher than for POSS-PEO(n=<8>) for that reason.

References
1. Maitra, P.; Wunder, S. L.; *Chem. Mater.* **2002**, *14*, 4494-4497.
2. Maitra, P.; Wunder, S. L.; *Electrochemical and Solid-State Letters* **2003**, *7*, A88-A92.

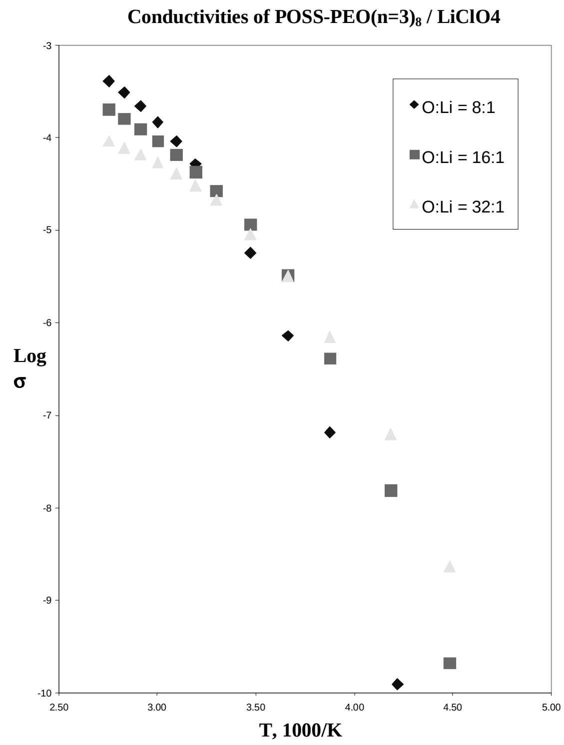

Figure 2. □ of POSS-PEO$(n=3)_8$

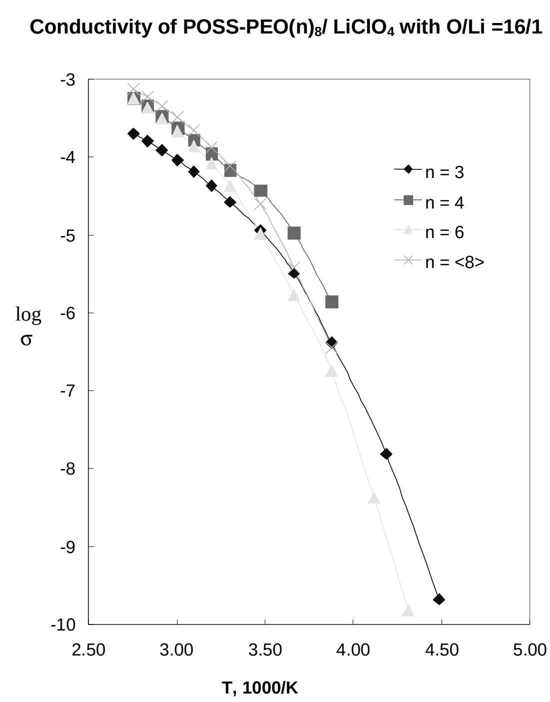

Figure 3. □ of POSS-PEO$(n)_8$ at O/Li = 16/1