

Towards Room Temperature Performance for Lithium-Polymer Batteries.

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The usefulness of lithium batteries based on lithium metal has been severely restricted due to the instability of the lithium-electrolyte interface. This leads to dendrite formation, unpredictable cycle life and safety problems. The use of polymer electrolytes mitigates many of these problems provided the electrolyte contains no free solvent. However, the commonly used polymers based on ethylene oxide ether units (e.g. PEO) possess lithium ion transport properties that provide unsatisfactory performance (power and energy density) at temperatures below 80°C[1-3]. Although operation at > 80°C is acceptable for EV batteries the use of such batteries for consumer purposes is limited by the high temperature requirement. It is therefore of interest to examine the factors that limit the mobility of lithium ions through polymers and to design new polymer structures that provide for acceptable performance at ambient and sub-ambient temperatures.

The theoretical aspects that describe the mechanism of ion conduction in polymer electrolytes have been developing rapidly in recent years[4, 5]. The need to avoid crystalline phases has been well demonstrated while the advantages of segmental motion in the polymer chain and the need for free volume have been recognized. As a rule of thumb, low  $T_g$  values have been sought but these lead to polymers with impractical mechanical properties. The effect of ion-pairing of the salt leads to significant differences in performance of different salts and has led to the use of the expensive bis(trifluorosulfonyl)imide salt, which further complicates the practicality of lithium/polymer batteries. Use of less expensive but more strongly ion-pairing salts is desirable.

Recent work on molecular simulations of the mechanisms of lithium ion conductance has pointed towards two types of limiting process[4, 5]. One has involved the commonly cited segmental motion while the other is related to energy barriers in the solvation shell of polymeric ether oxygens around the lithium ions. Calculations of the barriers to lithium ion migration[6, 7] have provided important indicators as to best design of the polymer. Overall, the mechanism that emerges is analogous to Marcus theory of electron transfer where the solvated ion moves through the polymer due to the segmental motion of the polymer chain and the ionic movement from one chain to another is controlled by the solvation sphere around the ion. This model has received support from recent neutron scattering experiments that has identified two types of polymer motion[8, 9].

The theoretical work has coincided with and guided some recent developments on polymer synthesis for lithium batteries[1]. Efforts to change the structure of the polymer solvation shell have been pursued by introduction of polypropylene oxide(PPO) and 1,3-

propanediol(PDO) units into the polymer. The PPO unit leads to poorer ion transport properties while initial conductivity measurements on polymers containing the PDO unit are encouraging (see Figure). The architecture of the polymer networks has been varied upon which the solvating groups are attached and significant improvements in sub-ambient performance are observed as a result. However, the above-ambient temperature performance appears controlled by an Arrhenius process consistent with the theoretical calculations described here.

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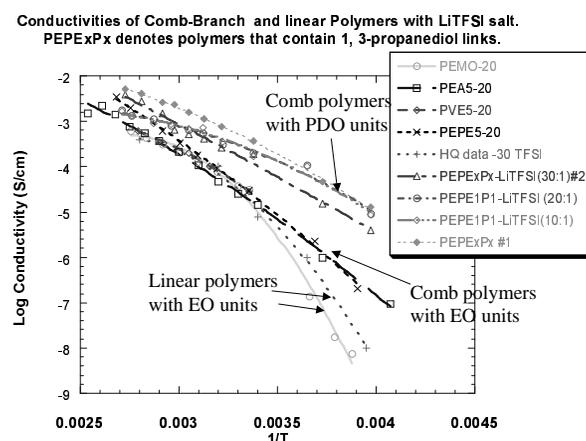


Figure. Conductivities of Linear and Comb Branch polymers with EO and PDO units