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INTERFACIAL IONIC AND ELECTRONIC CONDUCTIVITY IN POLYMERS

Progress Report

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Abstract

New phosphazene-based single ion conductors were synthesized based on a polyphosphazene backbone and short-chain polyether sidechains, some of which are terminated with tetraalkylammonium groups. These materials are good anion conductors at room temperature. Related cation conductors were also prepared and characterized. Effects of interionic attractive interactions on the diffusion of a tracer were investigated theoretically. The results are relevant to ion pairing and trapping in polymer electrolytes.

Progress

Polyphosphazenes of the type $[NP(OR)_x(OC_2H_4SO_3Na)_{2-x}]_n$ were prepared and chemically characterized. Conductivities are on the order of 4×10^{-7} ohm^{-1} cm^{-1} at 30°C and 10^{-6} ohm^{-1} cm^{-1} at 80°C. These low conductivities are attributed to tight ion pairing between Na^+ and the sulfonate groups. Similar anion conductors were prepared eg. $[NP(OMee)_{1.81}(OC_2H_4NMe_2Et^+I^-)_{0.19}]_n$. These materials have much higher conductivity (ca. 10^{-4} ohm^{-1} cm^{-1} at 80°C). These polyelectrolytes form an excellent testing ground for theories of ion transport in polymers because single ion diffusion coefficients are readily calculated from conductivity data.

The effects of interionic attractive interactions on the diffusion of a tracer ion in polyelectrolytes were studied using a one-dimensional hopping model. In this model the tracer cation is assumed to interact with anions placed at regular distances apart, but all inter-cation repulsions are ignored. The effects of both anion density and temperature on the diffusion of the tracer were evaluated through simulation. The tracer is found no longer to undergo simple diffusion, but to display two different diffusion rates, one for local diffusion near an anion, and another slower rate for long-range diffusion. The local diffusion rate varies little with either stoichiometry or temperature,whereas the long-range diffusion is highly correlated to these variables. These behaviors are relevant to ion-pair trapping in polymer electrolytes.

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