

Quantum Chemical Studies of Li Ion Hopping
Mechanisms in Polymer Electrolytes

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In this paper we report new results of quantum mechanical studies of potential energy surfaces for lithium ion movement between polymer chains in lithium polymer electrolytes. The polymers are modeled using small molecular models such as, for example, polyethylene oxide including as many as five carbon atoms and the associated oxygens and hydrogens. The calculations are done at various levels of theory including Hartree-Fock theory, density functional theory, and second-order perturbation theory. The potential energy surfaces for lithium movement are calculated as a function of the distance between the chains and for different coordination numbers. In previous work on models for polyethylene oxide we have found that the minimum in the barrier does not occur at the same geometry for which the coordination shell is optimal. In this paper we present new results for modification of the polymer backbone to show how modification can affect the barriers. Also we consider models for comb branch polymers in which ion hopping plays a role. Implications for ionic conductivity in polymer electrolytes are discussed based on these calculations and other studies.

*Work supported by the U.S. Department of Energy, BES-Chemical Sciences, under Contract W-31-109-ENG-38.