Quantum Chemical Studies of Li Ion Hopping Mechanisms in Polymer Electrolytes

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The lithium cation transport mechanism in lithium polymer electrolytes has been the subject of numerous studies, but is still not well understood. Among the possible lithium cation transport mechanisms are Li cation migration along a polymer chain, Li cation hopping from one chain to another, and cation diffusion with a chain. We have previously reported on quantum chemical investigations of lithium ion migration mechanisms involving motion along a chain in polyethylene oxide (PEO).1,2 In addition, we have reported on comparative studies of the lithium cation motion along chains having modified backbones to determine the effect on migration barriers.3

In this paper we will report results of a new quantum mechanical study of the hopping mechanism. Molecular models for polyethylene oxide are used to investigate the potential energy surface for hopping of the lithium ion from one chain to another. The calculations are done at the HF/6-31G* level of theory as well as some higher levels of theory (larger basis sets, correlation) to assess the lower level results. The effects of the coordination number and modification of the polymer backbone is considered in this study. The results indicate that the barrier for hopping is sensitive to the distance between the chains and the coordination number.
