Quantum Chemical Studies of Li Cation Migration Mechanisms in Polymer Electrolytes

Larry A. Curtiss and Paul C. Redfern

Chemistry and Materials Science Divisions
Argonne National Laboratory
Argonne, IL 60439-4828

There has been much interest in lithium polymer electrolyte for their potential applications in secondary battery systems, fuel cells, and other electrochemical devices. We have previously reported on theoretical investigations of lithium ion migration mechanisms in polyethylene oxide (PEO).[1,2] In this paper we report on a comparative study of the lithium cation migration mechanisms in poly(trimethylene oxide) (PTMO) with polyethylene oxide (PEO) using *ab initio* molecular orbital theory and molecular models for the polymers. Some of the results on the PTMO binding energies have been previously reported.[3]

We have investigated the effect on binding energies and migration barriers of replacing the $(CH_2)_2$ group in PEO by a $(CH_2)_3$ group in PTMO. The local minima corresponding to different coordination sites of Li^+ and transition states between them have been located. The Li^+ -PTMO binding energies increase with increasing coordination of Li^+ by oxygen, although the binding per Li–O bond decreases, and structures with higher coordination of Li^+ by oxygen exhibit longer Li–O bond lengths than the ones with lower coordination number. The PTMO barrier heights for $n+1 \rightarrow n$ coordination of the cation by oxygen decrease with increasing coordination number n, with the smallest Li^+ migration barriers occurring for complexes with the highest coordination numbers.

The results for PTMO are similar to what has been found for the potential energy surfaces of Li^+-polyethylene oxide (PEO) complexes, but the barriers are somewhat smaller. The reason for the smaller barriers and possible implications for conductivity in these materials are discussed.

References

1. A. Sutjianto and L. A. Curtiss, *Journal of Physical Chemistry* **102**, 968-974 (1998).
2. A. G. Baboul, P. C. Redfern, A. Sutjianto, and L. A. Curtiss, *Journal of the American Chemical Society,* **121**, 7220-7227 (1999).
3. P. C. Redfern and L. A. Curtiss *Journal of Power Sources* **110**(2), 401-405 (2002).

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