

Modeling of Fundamental Charge Transfer Processes in Stable Free-Radical Organic Polymers

Ross E. Larsen¹, Travis Kemper¹, Wade Braunecker² and Thomas Gennett³¹Computational Science Center²National Center for Photovoltaics³Chemical and Materials Sciences Center

National Renewable Energy Laboratory

15013 Denver West Parkway

Golden, CO 80401

Organic radical batteries (ORBs) comprise a relatively new technology that uses cathodes based on stable organic radical-based polymers. These materials show great promise as cathode materials because the neutral, radical species (at left, Figure 1) is remarkably stable and the one-electron oxidation depicted in Fig. 1 is fully reversible. The rate at which charge can be pushed into or extracted from an electrode is determined by the timescales on which charges are able to move within an electrode and across an electrode-electrolyte interface, but the molecular-level details of such events within radical-based polymer films are not yet fully understood. Hence, to guide the development of new ORB electrode materials and to aid in the design of improved electrode structures, a detailed understanding of the fundamental mechanisms involved in charge transfer in ORB systems is needed. In this paper we describe recent large-scale molecular dynamics simulations of polymeric organic nitroxide radical materials, and related *ab initio* electronic structure calculations of their projected spectroscopic properties.

Simulations and calculations were used to elucidate trends found with impedance spectroscopy measurements. General trends can be rationalized with anion charge density, anion-cation binding energies, the sizes of the molecular anions, and the role of solvation effects. Fully atomistic simulations of radical-based polymers relate experimental results to morphological features dictated by polymer structural properties, including tacticity and cross link density, as well as electrolyte properties such as the anion size and charge. The morphology of isotactic PTMA is depicted in Figure 2, where the most probable first and second nearest neighbor separations are indicated. We will discuss in detail the implications of our fully atomistic simulations for how ion transport is altered by experimental changes to polymer structure produced by synthetic modifications, including tacticity of the polymer, variations of the density of cross links in the polymer film, etc.

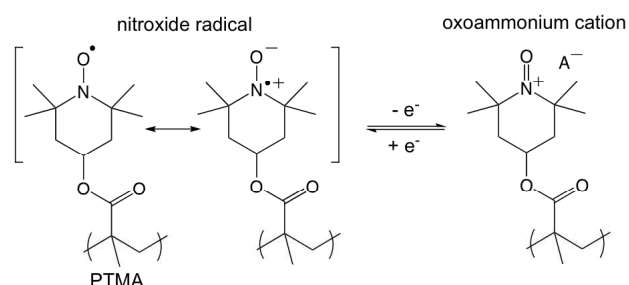


Figure 1: Reversible oxidation/reduction process for a stabilized nitroxide radical, poly-4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (PTMA).

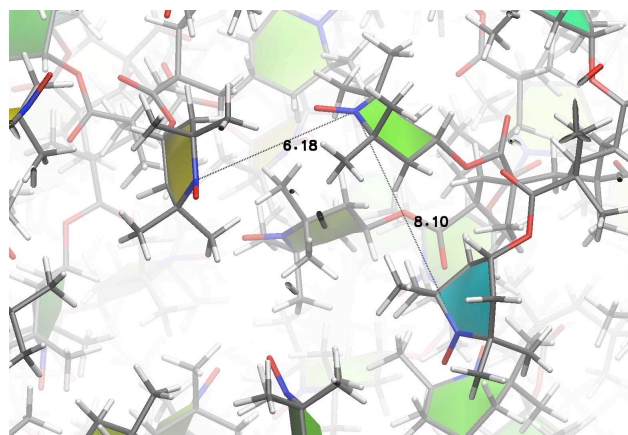


Figure 2: Close-up view of simulated PTMA film (white represents hydrogen, grey represents carbon, blue represents nitrogen, and red represents oxygen). For visualization purposes, the six-membered rings associated with the nitroxide radicals have been highlighted. The text indicates the separation, in Ångstrom, between nitrogen atoms on the same chain (8 Å) and different chains (6 Å) in the film.

Acknowledgements: This work is supported by a grant from the US Department of Energy Basic Energy Sciences Materials Division. Alliance for Sustainable Energy, LLC, managing and operating contractor for the National Renewable Energy Laboratory under U.S. Department of Energy M&O Contract No., DE-AC36-08GO28308