Atomistic simulations correlate molecular packing and electron transport in polymer-based energy storage materials.

In recent years, stable organic radical functional groups have been incorporated into a variety of polymeric materials for use within energy storage devices, for example, batteries and capacitors. With the complex nature of the charge-transfer processes in a polymer matrix, the morphologies of the polymer films can have a significant impact on the physiochemical properties of the organic-based radical.

In order to elucidate the possible effects of packing on electron-transport mechanisms, researchers at the National Renewable Energy Laboratory (NREL) conducted theoretical modeling of the well-characterized cathode material poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA). Polymer morphologies were modeled using classical molecular dynamics simulations, and subsequently, the electronic-coupling matrix element between each radical site was calculated.

Building on a previously derived treatment of diffusion in inhomogeneous materials, expressions for an effective electron diffusion length and an effective electron diffusion rate were derived in terms of an electronic-coupling-weighted radial distribution function. Two primary distances were found to contribute to the effective electron transfer length of 5.5 ångstroms (Å), with a majority of the electron transfer (nearly 85%) occurring between radical sites on different polymer chains in the solid state.

This analysis of charge transfer using an electronic-coupling-weighted radial distribution function has applications beyond the specific system addressed here; it may prove useful more generally for simulating electron-transfer processes in disordered molecular materials.

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Technical Contact: Ross Larsen, ross.larsen@nrel.gov