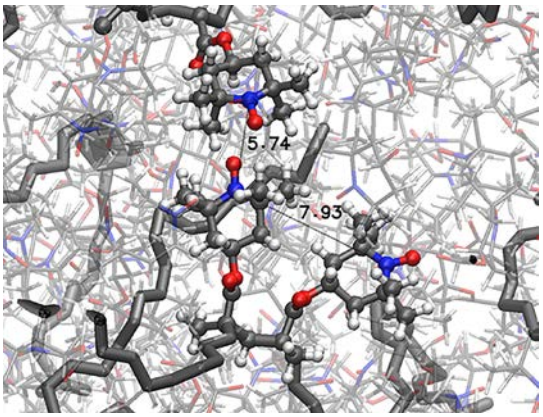
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

NREL Simulations Provide New Insight on Polymer-Based Energy Storage Materials

Highlights in Science

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.



A snapshot of the molecular packing of PTMA, where atomic colors are N (blue), O (red), C (gray), and H (white), and inter-atomic distances are shown in ångstroms.

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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Reference: Kemper, T.W.; Larsen, R.E.; Gennett, T. (2014). "Relationship between Molecular Structure and Electron Transfer in a Polymeric Nitroxyl-Radical Energy Storage Material." *J. Phys. Chem. C* 118 (31); pp. 17213–17220. DOI: 10.1021/jp501628z.

Key Research Results

Achievement

Nitroxide radical based energy storage material was modeled using atomic-scale molecular dynamics simulations, and the electronic coupling between radical sites was calculated to determine the effect of molecular packing on electron transfer.

Key Result

By simulating stable organic radical polymer films and introducing a general electronic-coupling-weighted measure for charge transport, it was demonstrated that multiple length scales contribute to the rapid electron transport kinetics within PTMA.

Potential Impact

These simulations provide insight into molecular packing in PTMA and into how this packing relates to experimentally measurable properties such as conductivity and electron transfer rates. The results are being correlated to extensive electrochemical analysis. The methodology developed can be applied to any organic electronic material.

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