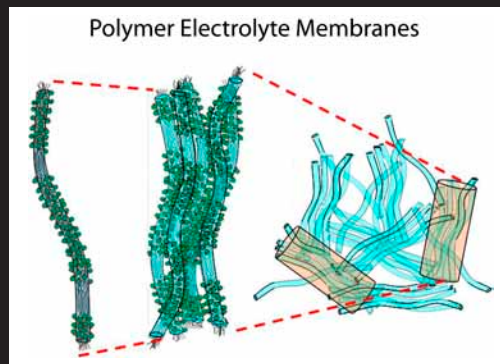


Energy Storage & Delivery Materials

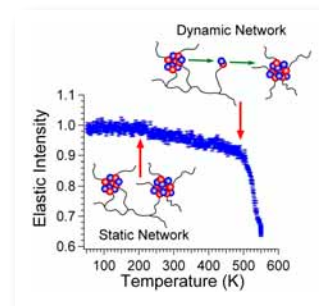
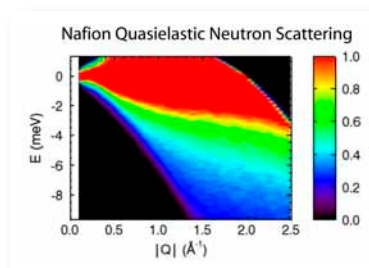
Objective

The goal of this project is to deliver measurement methods specific to polymeric and organic materials needed in next generation energy storage and delivery technologies, particularly the ion or charge transport media that are integral components of fuel cell and battery technologies. Our methods are focused on elucidating the role of the structure and dynamics in the transport media on the charge transport and electrical performance of the device.



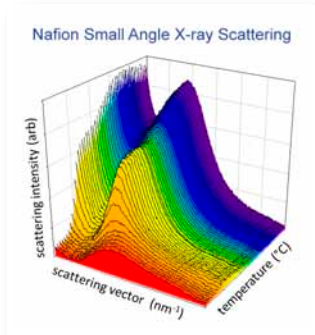
Impact and Customers

- Fuel cells and batteries are central to an array of alternative energy technologies, ranging from portable electronics to green vehicles, and are both underpinned by need to develop ion or charge transport media with enhanced mobility and improved stability.
- The materials limitations to achieving high charge mobility in transport media are poorly understood. Current measurements of the relevant structure and dynamic processes in Nafion™ type fuel cell membranes or, polyethylene oxide type Li ion battery electrolytes, are not sufficient to guide significantly improvements in the performance of the materials needed by industry.
- Acquisition of a new broad bandwidth, ultra-fast, optical spectrometer to enable advanced nonlinear, time-resolved studies of interfaces in batteries, fuel cells, and organic photovoltaics.
- The NIST team works closely with leaders in the energy storage and delivery field, including General Motors, University of Massachusetts, Amherst, Pennsylvania State University, Seoul National University, Johannes Gutenberg Universität Mainz, and the NIST Center for Neutron Research.



Approach

The team's efforts are focused on two areas where measurements are needed to advance the polymeric materials critical to next generation energy storage and delivery devices. The first area is to apply and develop measurements of the structure and properties of polymeric materials at interfaces. These interfaces form the junctions between the ion or charge transport media (electrolyte) and the electrode, and are often identified to be the source of the degraded performance of fuel cell membranes and batteries over time. We focus on measurement methods that can profile interfacial structure with nanometer resolution such as X-ray and neutron reflectivity, spectroscopic ellipsometry, phase modulated infrared absorption spectroscopy, and sum frequency generation spectroscopy. We couple these measurements with methods to quantify time resolved transport properties with techniques such as quartz crystal microbalance measurements.



The second area focuses on measurements of the dynamics of polymer material to elucidate the mechanisms responsible for the transport of charged particles (ions, counter-ions). It is generally accepted that there is an important dynamic coupling of the charge or ion transport with the local dynamics of the media or electrolyte, but the nature and extent of this cooperativity are still unclear. We are leveraging our expertise in inelastic neutron scattering, dielectric spectroscopy, and solid state nuclear magnetic resonance spectroscopy to measure the segmental dynamics of different polymer systems and enable device developers to optimize and design high performance materials.

Accomplishments

Interfacial Structure in Fuel Cell Membranes

In typical fuel cell membrane electrode assemblies (MEAs), interfaces play a vital role in the transport of water and ions. In the past there have been numerous attempts to tie the bulk structure of the polyelectrolyte membrane (PEM), such as Nafion™, to the performance of the fuel cell. However, considerable debate still exists and the structure-property relations to enable superior, low-cost alternatives to Nafion™ are lacking. Scientists are now beginning to realize that the interfacial, in addition to the bulk, structure in MEAs can significantly impact device performance in fuel cells. The interfaces are the critical regions where the ions make contact with the electrodes and catalysts.

In collaboration with the NIST Center for Neutron Research, we are developing X-ray and neutron reflectivity (NR) methods to measure the interfacial structure of Nafion-like PEM materials. We then correlate the water transport behavior (which mimics fuel cell ion transport) at the interface to the structure. The objective is to elucidate the role that these buried interfaces in the MEA play in the overall performance of the fuel cell.

We have developed model organosilicate (OSG) substrates with surface energies that can be systematically tuned from hydrophilic to hydrophobic to vary the interaction between Nafion™ thin films (~30 nm) and the supporting substrate. Measurements of the interfacial structure are obtained with NR while the film is exposed to 80 % relative humidity conditions that are relevant to fuel cells under operation. The results show that the hydrated Nafion™ films swell uniformly when in contact with a hydrophobic surface, without any apparent preferential surface structure. However, when the hydrated

Nafion™ is in contact with the hydrophilic substrate, an interfacial lamellar structures forms, with water channels running parallel to the interface. Such structure would be undesirable at the electrode interface in a fuel cell membrane because the transport channels would not have access to the active electrodes. Ideally the interface should provide easy access of the ions to the electrodes.

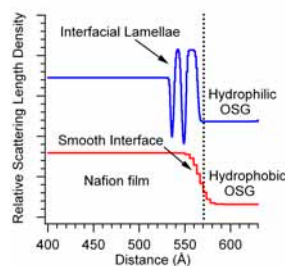


Figure 1: The plot shows the relative scattering length density profiles in a fully hydrated Nafion film as a function of distance from the OSG substrates, obtain by in-situ neutron reflectivity. The neutron contrast between the water and the Nafion allows us to visualize a lamellar like stacking of the water channels near the hydrophilic substrate. This order is disrupted on the hydrophobic substrate.

Li Ion Mobility in Hyper-Branched PEO

Polyethylene oxide (PEO) is widely used as a model polymer electrolyte for lithium-ion batteries. The Li ions are known to coordinate with the ethylene oxide units as they move through the transport media to the electrodes during the charge/discharge cycles. It is generally believed that the cooperative, segmental dynamics of the polymer gate the motion of the ions, thereby influencing the conductivity. However, the nature of this dynamic coupling is poorly understood. With long-chain PEO molecules—which are needed to move away from flammable, difficult to contain, liquid electrolytes—there

is the propensity for polymer crystallization, which ultimately hinders the segmental motions and decreases the level of conductivity. There are many groups actively developing methods to inhibit crystallization in these materials and increase conductivity over a larger temperature range.

One approach to inhibit crystallization is to introduce branching points along the PEO backbone. To understand how this approach impacts the charge mobility, we perform both dielectric relaxation spectroscopy (DRS) and quasi-elastic neutron scattering (QENS) measurements on a series of hyper-branched PEO molecules provided by Professor Holger Frey (Johannes Gutenberg Universität Mainz) with various degrees of branching. We find that Li ion mobility increases with degree of branching up to a maximum of approximately 12 molar % branching content, followed by a decrease at higher branching. More importantly, we find that the local, mean square atomic displacements (MSD) of the PEO segments on a nanosecond time scale, as determined by QENS, track the charge mobility. Future work on these materials is focused on identifying the geometry and length scale of the motions in the PEO responsible for the Li ion mobility.

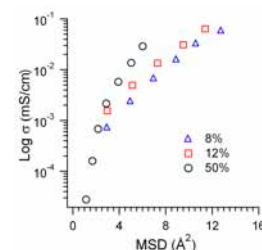


Figure 2: This graph shows a strong correlation between the Li ion conductivity (σ) and the mean square atomic displacement (MSD) of the PEO segment between 273 K and 333 K for chain architectures with different degrees of branching. Extensive atomic fluctuations on the nanosecond time scale facilitate ion conductivity.

Learn More

Kirt A Page
Huagen Peng
Scott Eastman
Sangcheol Kim
Shuhui Kang
Jae-Hwan Sim
Wen-li Wu
Joe Dura (NCNR)
Lee Richter (CSTL)

Christopher L Soles (Polymers Division)
(301) 975-8087
csoles@nist.gov
<http://www.nist.gov/polymers>

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