272a Functionalized Mesostructured Silica for Proton-Exchange Membranes

George L. Athens and Bradley F. Chmelka

To improve the performance of stationary and automotive fuel cells, it is desirable to operate them at higher temperatures than currently possible for existing proton-exchange membranes (PEMs). Especially for fuel cells that use steam-reformed hydrocarbons as a source of hydrogen, CO poisoning of electrode catalysts is problematic at temperatures below approximately 120°C. Most current membrane materials based on perfluorinated or aromatic acid polymers, however, display proton conductivities that dramatically decrease above 80°C, due to dehydration of the membrane. One approach to overcoming this is to increase the hydrophilicity of the membrane. To this end, we report the synthesis, processing, and characterization of new acid-functionalized mesostructured inorganic proton-exchange-membranes that have significantly improved water retention capacities and proton conductivities at temperature approaching 100°C and higher. The membranes are prepared by using block-copolymer species to direct the structures of network-forming silica, which is cast, calcined, and grafted with active species to yield inorganic membranes with interconnected mesostructured channels. These materials are processable into a variety of morphologies, including films with thicknesses ranging from hundreds of nanometers to several microns and monoliths with dimensions exceeding several millimeters.

Results will be presented on the post-synthetic grafting of different functional groups onto the interior channel surfaces of mesostructured silica membranes. Elemental analysis and solid-state NMR spectroscopy are used to quantify the density and local structures of the grafted functional groups. In addition, small-angle X-ray diffraction, electron microscopy, and nitrogen adsorption porosimitry show that mesostructural ordering and macroscopic integrity of the functionalized inorganic membranes are preserved during the post-synthetic grafting treatments. TGA-MS analyses establish that hydration capacity and water retention of the functionalized membranes are significantly improved, compared to commercially available Nafion® 117 membranes. AC impedance measurements of the functionalized inorganic membranes show proton conductivities comparable to those for Nafion® at temperatures under 100°C, and promising conductivities at temperatures approaching 120°C and higher. Synthesis and processing protocols for the preparation of these functionalized mesostructured inorganic membranes will be described, along with characterization of their molecular, mesoscopic and macroscopic compositions, structures, and properties.