



Hydrated paths and water dynamics in functionalized syndiotactic-polystyrene proton conductive membranes studied by extended Q-range SANS and multi-resolution QENS.

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Using the selectivity of the crystalline δ -form for hydrocarbon solvents, a controlled functionalization by sulfonation of the semi-crystalline syndiotactic polystyrene (sPS) films can be achieved when large sulfonation agents such as lauroyl sulfate in chloroform solution are used, which provides homogeneous sulfonation of only of the phenyl rings in the amorphous region without affecting the crystallinity of the material. Sulfonated sPS (s-sPS) is hydrophilic and shows a high proton conductivity comparable to Nafion, that is the benchmark in proton exchange membranes fuel cell technology. Thus, s-sPS membranes may be used in ion conducting applications since they are characterized by a nanoscale phase separation into hydrophilic domains and hydrophobic regions, which is a combination that enables a high ion conductivity and provides a good chemical and thermomechanical stability. The proton conduction in PEMs depends on water and is governed by the hydrated paths at nano- and mesoscale and the water micro-dynamics at different time scales. Therefore, in order to understand the transport properties in different conditions one should first of all understand the membrane morphology over a wide length scale, between a few Å (crystal structure) and the mesoscopic scale (hundreds of nm), as a function of hydration level (relative humidity RH and water uptake) and temperature (T), and learn about the micro-dynamics in hydrated membranes under such conditions.

We carried out a detailed microstructural characterization of uni-axially deformed s-sPS membranes by using the extended Q-range (10^{-3} to 2 Å^{-1}) SANS method with the variation of the SLD achieved in the crystalline regions by using the guest-exchange phenomenon between H/D guest molecules in the δ -form clathrates of sPS, and in the hydrated regions by using different H₂O/D₂O combinations. We also investigated the slow (100 ps) and fast (10 ps) water micro-dynamics in such membranes in a semi-free water hydration regime, at different temperatures (30°C, 50°C and 80°C) by multi-resolution QENS. Our experimental results concluded that the anomalous ionic conductivity behavior observed in the s-sPS membranes is an effect of structural features of the system: water accumulates in s-sPS in spherical clusters that grow in size and become interconnected in increasing the hydration level, ultimately giving rise to occurrence of water channels at very high humidity or in membranes equilibrated in liquid water; at limited RH, the water clusters lose interconnectivity with increasing temperature, what explains the observed drastic decrease in ionic conductivity for very little or no water desorption as delivered by SANS.

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