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Temporal and Spatial Distributions of Water in Ion-Containing Perfluorosulfonic Polymers¹

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The spatial distribution and the molecular dynamics of water in perfluorinated ionomer polymeric membranes (Nafion 11x in the acid form) were quantified at several hydration levels by Atomic Force Microscopy and Dielectric Relaxation Spectroscopy, respectively. A variety of concurrent AFM modes, including interleave and intermittent contact methods, is necessary to map the water-containing domains on the polymer surfaces, whereas at least two different dielectric relaxation setups are needed to record the range of water dynamics that develop in these systems as the hydration level changes. The competition between sulfonic-group/water attraction and water/water hydrogen-bonding, in addition to confinement effects, give rise to at least three “states” of water, manifested through distinct dynamical behaviors: The fastest process observed was identified as the cooperative picosecond relaxation of free/isotropic, bulk-like water, whereas the slowest process –with microsecond relaxation times– corresponds to water molecules strongly bound to the charged sulfonic groups. An intermediate relaxation, in the picosecond range and about three times slower than those of bulk water, is shown to contain substantial dynamical heterogeneities and most probably corresponds to a variety of local environments that are cumulatively defined as “loosely bound” water. AFM studies, probing the same surfaces at various hydration levels, provides insights on the location and geometry of the water domains that contribute to the various dynamical “states”. Both the spatial and temporal distributions of water are sensitive to the sample preparation conditions, especially with respect to the geometry and dynamics of the “loosely bound” water domains.

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