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The nature of water in hydrated acid-form Nafion membranes G. POLIZOS, Z. LU, D.D. MACDONALD, E. MANIAS, Materials Science & Eng, Penn State University — The nature of water in perfluorinated membranes in the acid form (Nafion) was quantified at several hydration levels by dielectric relaxation spectroscopy. Two different experimental setups were used to probe both the low frequencies $(10^{-2}-10^7 \text{ Hz}, -50 \text{ to } 25^{\circ}\text{C})$ and the microwave region $(0.045-26 \ 10^9 \text{ Hz}, 25 \ to \ 45^{\circ}\text{C})$. The competition between sulfonic-group/water attraction and water/water hydrogen-bonding, in addition to confinement effects, give rise to three states of water, manifested through distinct dynamical behaviors: The cooperative relaxation time distribution of free (isotropic) water networks is identified as the fastest process, whereas water molecules strongly bound to the charged sulfonic groups correspond to the lowest frequencies. A third relaxation mode is also observed with relaxation times at high frequencies close to the bulk water, which is attributed to "loosely" bound water. These water states can be correlated with the respective Nafion phase separated morphologies and the corresponding proton conductivities.

G. Polizos Materials Science & Eng, Penn State University

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