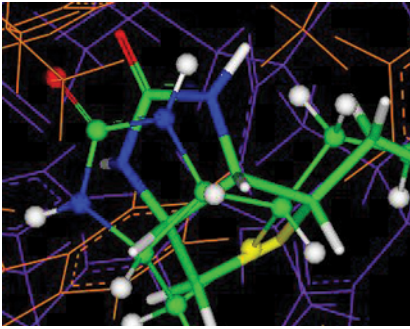


MORPHOLOGY OF HYDRATED PERFLUORONATED IONOMER MEMBRANES



Simulations to model the drying out of prehydrated membranes showed that path dependent phases can also be explored with dynamic density functional theoretic calculations.

Module used

- Materials Studio® MesoDyn®

Organization

- General Motors

Contributors

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PFSA membranes, particularly Nafion®, are primarily used as proton exchange membranes (PEMs) in fuel cell applications. Improving the performance of PEMs focuses on both increasing the proton conductivity at low relative humidity and high temperature, and improving the mechanical, thermal and chemical stabilities of the membrane.

Nafion consists of a highly hydrophobic polytetrafluoroethylene (PTFE) backbone with a fully perfluorinated ether side chain terminated by a strongly hydrophilic –SO₃H group (Fig. 1). This structure leads to spontaneous phase segregation at the nano-structural level, especially in solvent.

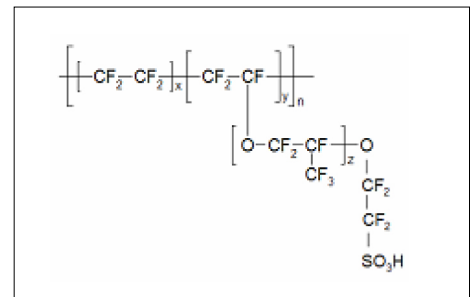


Fig. 1. Chemical formula of Nafion® 1100 ($x=7, y=z=1$).

The water content of hydrated membranes is usually stated in terms of the parameter, λ , defined as the number of water molecules per sulfonic group. It is well accepted that in hydrated PFSA membranes, the sulfonic groups and associated water molecules develop an interconnected proton conducting network above a threshold of water content ($\lambda \approx 2$), while the fluorocarbon backbone forms a semi-crystalline hydrophobic phase.

Clearly the polymer morphology has a strong influence on the proton conductivity and the mechanical performance; thus, a detailed understanding of the nanoscale structure is of great interest.

As reported in the Journal of Chemical Physics¹, a suitable coarse-grained model for hydrated Nafion® membranes was developed (see Fig 2) and Materials Studio® MesoDyn® code was used to predict the morphology at hydration levels of $\lambda=2, 4, 8$ and 16.

Suitable MesoDyn parameters for the interaction energies between the coarse-grained beads were generated by extracting the cohesive energies of the chemical groups from classical molecular dynamics simulation based on COMPASS® forcefield parameters.

The results showed that spherical water clusters form as the water content is increased to a level of $\lambda=4$ (Fig. 3). Above $\lambda=4$, some of the water clusters also exhibit irregular shapes (elliptical or barbell shape) due to the coalescence of smaller clusters (Fig. 4).

By simulating the small angle scattering signal from the density distributions and extracting the Bragg spacing, a linear increase in the characteristic length of the hydrophilic domains was observed (Fig. 5). Similar experimental SAXS and SANS data has previously been used to assert that PFSA has a lamellar structure². These simulations, with an arrangement of nearly spherical domains that swell and coalesce, provide a counter-example to this assertion.

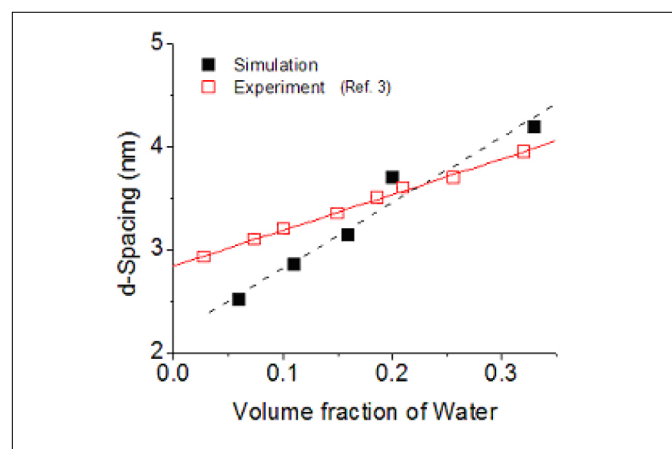


Fig. 5. Comparison of the d-spacings of hydrophilic domains extracted from small angle scattering calculations with increasing water content.

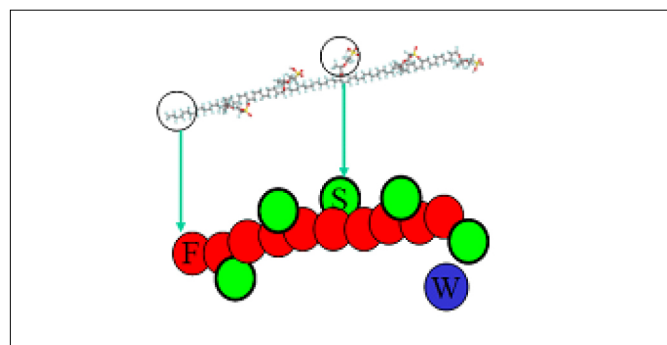


Fig. 2. The mesoscale model represented the ether-sulfonic acid side chain group as bead (S), the fluorocarbon backbone units with beads (F) and defined a water bead (W) representing 10 water molecules.

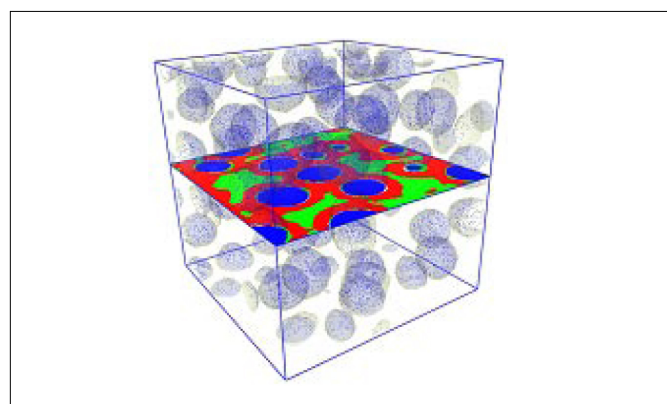


Fig. 3. Inverse micelles of water density at a water level of $\lambda=4$ are shown as transparent blue isosurfaces. A density slice shows the water micelles (blue) contained within the PTFE matrix (red), within the water-PTFE interface, mediated by the ether-sulfonic side chain.

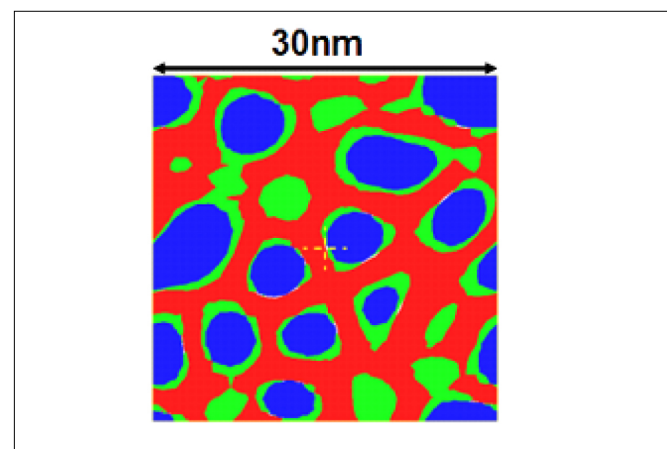


Fig. 4. A density slice at a water level of $\lambda=8$.

Further analysis of the density distributions showed that full percolation of the water domains (Fig. 6) only occurs at much higher water content than is seen experimentally. Therefore, the presence of either a second undetected hydrophilic phase at a scale finer than this mesoscale model can resolve, or some other mechanism that provides early percolation, must be inferred.

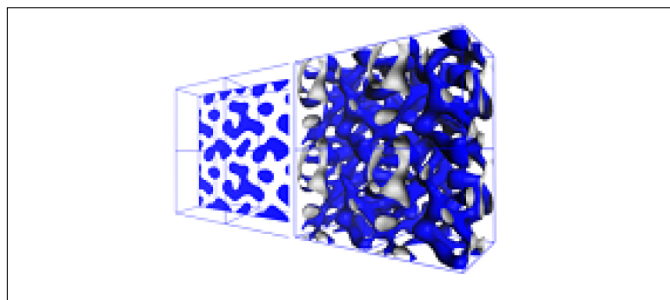


Fig. 6. Water density isosurface (large image) and density slice (small image) at water level of $\lambda=16$ showing interconnection of domains/

An additional simulation was performed, which was designed to closely model the processing of a cast membrane that is initially immersed in excess solvent and then dehydrated to the given water content. For this simulation, a water swollen membrane ($\lambda=6$) was simulated to produce the inverted micellar phase. The water volume concentration was then reduced in steps of 1% to a level of 6% ($\lambda=2$) by stopping the MesoDyn run and then restarting it, while using the reduced water content level. Internally, the existing density fields were rescaled to the level appropriate for the new composition, and the change was accommodated by a few iterations of the field solver.

Unlike the previous simulation at water content of $\lambda=2$, the dehydrated membrane morphology remained phase separated, albeit with fewer and smaller water domains. Comparison of the free energies reported for the two phases suggest that the dehydrated case is the thermodynamically more stable of the two.

CONCLUSION

A multiscale modeling approach was used to investigate the details of morphology development in hydrated Nafion membranes, which captured the phase segregation at scales consistent with those experimentally observed at increasing levels of hydration. The simulations support the Yeager-Steck three-phase model³ of sulfonic side groups surrounding the PTFE cavities, and are consistent with surface morphology determined by TEM and AFM⁴. A smaller scale hydrophilic phase, like that proposed in the Gierke cluster channel model⁵, or another mechanism yet to be determined, needs to be inferred in order to obtain the early percolation threshold observed experimentally. Simulations to model the drying out of prehydrated membranes showed that path dependent phases can also be explored with dynamic density functional theoretic calculations.

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