Nafion® - Perfluorosulfonate Ionomer

NAFION® PERFLUOROSULFONATE IONOMER MEMBRANES

Although ion-containing polymers have been around for some time, the past fifteen years have been witness to an explosion of information in the literature. Most of the research effort on these ionomers have been devoted to only a small number of materials, notably the ethylenes, styrenes, rubbers, and those based on poly(tetrafluoroethylene). Nafion® is one such example of a poly(tetrafluoroethylene) based ionomer. From its development by DuPont in the 1960s, it has etched applications in liquid and gas separations, fuel cells, and the chlor-alkali industries. Because of its thermal and chemical resistance, ion-exchange properties, selectivity, mechanical strength, and insolubility in water, its application is only limited by imagination and foresight.

A. Nafion®

Nafion® is a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups. Its general chemical structure can be seen below in Figure 1, where X is either a sulfonic or carboxylic functional group and M is either a metal cation in the neutralized form or an H+ in the acid form.

Figure 1. Nafion® Perfluorinated Ionomer

Structurally, Nafion® is complex. Although the exact structure is not known, several models have been proposed since the early 1970s, to describe the way in which ionic groups aggregate within the Nafion® polymer. Recently, Robertson, has summarized many of these such models, to include, The Mauritz-Hopfinger Model, The Yeager Three Phase Model, The Eisenberg Model of Hydrocarbon Ionomers, and The Gierke Cluster Network Model. A common objective of these models is to predict the fundamental feature of unique equilibrium ionic selectivities, as well as, the ionic transport properties of perfluorinated ionomer membranes.
As a result of electrostatic interactions, these ionic groups tend to aggregate to form tightly packed regions referred to as clusters.\textsuperscript{7} The presence of these electrostatic interactions between the ions and the ion pairs enhance the intermolecular forces and thereby exert a significant effect on the properties of the parent polymer.

\textbf{B. Structural Model}

Previous small angle x-ray scattering (SAXS)\textsuperscript{4} and neutron scattering experiments clearly indicate that ionic clustering is present in Nafion\textsuperscript{®}. However, details on the arrangement of matter within these clusters have not fully been realized. Although no one model has been found to provide a complete explanation of the properties and selectivities found, several, base these properties and selectivities on an extensive micro-phase separated morphology.\textsuperscript{1,3-10} A stylized, semi-empirical view of a polar/nonpolar microphase separation in a hydrated ionomer can be seen below in Figure 2.

![Stylized view of polar/nonpolar microphase separation in a hydrated ionomer.](image)

This over-simplification shows a phase separated morphology of discrete hydrophobic and hydrophilic regions. The hydrophobic region is composed of the polymer fluorocarbon backbone. Conversely, the hydrophilic region contains the ionic groups and their counter ions.

As seen in Figure 3, the Yeager Three Phase Model is a phenomenological based model. This model is based on a three-phase clustered system with interconnecting channels within the polymer. The three regions consist of (A) a fluorocarbon backbone, some of which is microcrystalline, (B) an interfacial region of relatively large fractional void volume containing some pendant side chains, some water, and those sulfate or carboxylic groups and counter ions which are not in clusters, and (C) the clustered regions where the majority of the ionic exchange sites, counter ions, and sorbed water exists.\textsuperscript{2,10}
From experimental means, such as, small-angle x-ray scattering (SAXS) it has been determined that the phase-separated morphology is on the order of 30-50Å Bragg spacing.\textsuperscript{10} However, upon hydration, Nafion\textsuperscript{®} with its unique ability to sorb relatively large amounts of water, can increase its dry weight by as much as 50 percent or more depending upon equivalent weight, counter ion, and temperature. Upon hydration, however, cluster diameter and the number of exchange sites are thought to increase, leading to fewer, larger clusters.\textsuperscript{10}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{nafion_clusters.png}
\caption{The Yeager 3 Phase Model of Nafion\textsuperscript{®} Clusters}
\end{figure}

Nafion\textsuperscript{®}, with its existing ionic clusters and postulated inter-cluster channels, serves not only as a stable platform or template, but also as a catalyst. The sulfonate exchange sites in the ionomer are extremely acidic. Therefore, the clusters in Nafion\textsuperscript{®} serve as reaction vessels in which future polymerizations can occur without addition of an external catalyst. The pre-existing morphology of Nafion\textsuperscript{®}, as discussed above, has a direct influence on the in situ grown morphology of any inorganic phase in view of the fact that the clusters are only 30-50Å in size. Therefore, one can generate distinct ordered structures in the clusters and form a network between clusters using the short channels that connect the aggregates. Upon doing so, the original ionomer properties can be altered and tailored to specific uses and needs, such as, specific gas and liquid separations and fuel cell operations.
C. Summary

Clearly, the basis for the unusual properties exhibited in Nafion\textsuperscript{®} arises from the extensive microphase separation morphology as seen from numerous researchers.\textsuperscript{1,3,9} Moreover, the way in which the phase separated regions interact and act upon other substances is of great interest, not only in the scientific world, but in industry, as well. Because of this ionic morphology and the inherent ionomer properties of Nafion\textsuperscript{®}, its interest scientifically and usefulness technologically should continue well into the future.

References

2. Nafion\textsuperscript{®} is a registered trademark of E.I. DuPont de Nemours & Co.

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