Physical Model of Transport in Polymer-Electrolyte Membranes

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In this paper, a physical model is developed that is semi-phenomenological and takes into account Schroeder's paradox. The model is based on the wealth of knowledge contained in the literature regarding polymer-electrolyte membranes. Along with the structural changes of the membrane due to water content, two different transport mechanisms are presented and discussed. These mechanisms and the structural changes represent the complete physical model of the membrane. The model is shown to agree qualitatively with different membranes and different membrane forms, and is applicable to modeling perfluorinated sulfonic acid (PFSA) and similar membranes. It is also the first physically based comprehensive model of membrane transport that includes the description of Schroeder's paradox.

INTRODUCTION

Polymer-electrolyte membrane (PEM) fuel cells have emerged as one of the eminent technologies of the 21st century. What makes PEM fuel cells unique among other fuel cells is that their electrolyte is an ionomer that conducts protons. Over the last couple of decades, PEM fuel cell research and improvements have reached an all time fervor (1)(2). Along with their attractiveness as efficient and clean energy producers, they may provide the energy structure of not only cars but also residential applications.

A critical problem and design issue of PEM fuel cells is water management (3). Due to the low operating temperatures, liquid water is produced. This can lead to the problem that too much water will cause flooding of the cathode region and not allow the reactant gases to reach the electrocatalyst. On the other hand, the membrane's transport properties are highly water dependent, and thus too little water will cause the anode side of the membrane to dry out and lose its conductivity. A correct water balance must be maintained in order to guarantee an optimal and sometimes even a functional performance, as well as control heat generation. Since the membrane is a key component in the water balance, it is desirable to understand and model the processes that occur in it, where there is room for new understanding and improvement. It should be noted that these processes include not only transport phenomena, but also observations like Schroeder's paradox: the uptake of water by the membrane from a liquid reservoir and a saturated vapor reservoir differ under the same conditions (4).

Although there have been various membranes used, none is more researched or seen as the standard than the Nafion family by E. I. du Pont de Nemours and Company. Like the other membranes used, the general structure of Nafion is a copolymer between...
polytetrafluoroethylene and polysulfonyl fluoride vinyl ether. These perfluorinated
ionomer membranes exhibit many interesting properties such as a high conductivity,
prodigious water uptake, and high anion exclusion, to name a few. Nafion will be the
base membrane studied in this paper. The model developed and presented in this paper
describes the transport in the membrane from a physical standpoint. This model goes
beyond those presently in the literature by striking a balance between its robustness and
scope; it is still essentially a macroscopic model. Throughout the paper and at the end,
the model is compared to qualitative experimental observations from the literature for
both Nafion and other membranes.

Background

In terms of modeling, polymer-electrolyte membranes have been modeled within two
extremes, the macroscopic and the microscopic. In terms of microscopic models, there
have been many models based on statistical mechanics (5), molecular dynamics (6), and
macroscopic phenomena applied to the microscopic structure of the membrane (7)(8).
These models provide the fundamental understanding of processes like diffusion and
conduction in the membranes on a microscopic scale. They allow for the evaluation of
how small perturbations like nonhomogeneity of pores and electric fields affect transport,
as well as incorporation of small-scale effects. While these models yield valuable
information about what goes on inside the membrane, some of which we will use, in
general they are usually too complex to use in an overall fuel-cell model.

On the other side of the scale are the macroscopic models. These often are more
empirical and focus only on describing the transport and relevant parameters of the
membrane. There have been many of them proposed over the last decade, and they can
be sorted into two main categories, those that assume the membrane is a single phase, and
those that assume it is two phases. The former usually leads to a diffusion type model
(9)(10)(11), and the later to a hydraulic type one (12)(13). Both types of models can be
made to agree with experimental data, but neither describes the full range of data nor all
of the observed effects, like Schroeder's paradox. It should also be noted that almost all
of the microscopic models treat the membrane as a pseudo two-phase system.

One of the earliest and most recognized models is that by Bernardi and Vebrugge
(12). That model treated the membrane as a two-phase system similar to a porous
medium, where there were separate gas and liquid channels, and the porosity remained
constant. Eikerling and coworkers (13) advanced this bundle-of-pores model to include
effects of saturation, pore-size distribution, and hydrophobicity. The problems with these
models are that they assume that the membrane is composed of two different pore
pathways, one for gas and one for liquid. This does not necessarily make physical sense.
For example, in the case of a porous medium that has pores filled with vapor, oxygen
should have a pathway to diffuse through with a larger flux than that observed (14). The
models just increase the tortuosity of the pore pathway, but this does not necessarily
agree with the complete physical picture of the membrane. Furthermore, in the case of a
low-saturated membrane, there is no continuous liquid pathway across the medium, and
the membrane matrix interacts significantly with the water. Thus, concentration and not
hydraulic pressure seems to be the more appropriate driving force; a one-phase model should be used.

On the other side of the modeling debate, Fuller (10) and Springer et al. (9) were the first to popularize the idea of the membrane as a single homogenous phase. They treat it like a solvent, and use experimental data to describe the diffusion-like transport mechanism through the polymer. This type of membrane modeling has also found a strong support base, and has been modified by Meyers (15) and Okada et al. (16) in order to account for additional effects. A very interesting adaptation of the single-phase model is that done recently by Janssen (11) and earlier by Thampan and coworkers (17), in which transport through the membrane is described using only gradients in chemical potential, avoiding the complication of trying to separate out diffusive and pressure-driven flow components. The single-phase models do have some limitations including the inability to predict completely the correct water profiles and transport. For example, they fail to predict the observed sharp drying boundary on the anodic side of the membrane (18). Furthermore, when the membrane is saturated, it does not make sense to have only a diffusion-type flow since the concentration of water in the membrane is uniform; there is no concentration gradient. Thus, a two-phase or hydraulic model should be used in this case.

Both types of macroscopic models mentioned above have both advantages and limitations. They describe part of the transport that is occurring, and this is why they are both still popular, but the correct model is some kind of superposition between them, as has been briefly mentioned before (19). The physical model that we develop in this paper combines the two types of models and is the first to pursue this combination in a consistent manner. The need for a combination model is also apparent in that the above models do not describe or present a physical picture of Schroeder’s paradox, whereas the combination model naturally describes it. As a side note, most of the models use a discontinuity in uptake when going from a vapor contact to a liquid contact or neglect the paradox altogether.

In this paper, we describe a membrane model that can be used easily in a complete fuel-cell model. Thus, it is robust enough to describe the membrane properties and transport under various operating conditions (liquid and vapor boundaries, constrained, swollen, temperature, etc.), but it is not too complex and unwieldy. In a specific sense, it is phenomenological, but we make a serious attempt at using all relevant data and observations, and imparting a physical significance to everything. Also, our model, like the ones above, is one-dimensional (1-D). It should be noted that there have been 2-D and 3-D models for the membrane proposed, and that these higher-dimension models are more often of the two-phase type (20)(21). Even with these higher dimension models, the membrane itself can usually be taken as a 1-D structure, and the higher dimensions are needed only to describe the complete transport in a fuel cell (e.g., depletion of reactants down the flow channel). In this paper, we describe the physical model of what is occurring in the membrane including the introduction of membrane structure and relevant phenomena, and qualitatively correlate it with observed phenomena.
The physical model of the polymer-electrolyte membrane that we use is relatively simple. It is based on experimental evidence and is in-line with modern thoughts of transport within the membrane. As alluded to above, transport in the membrane occurs by two separate mechanisms. The first is a diffusion type mechanism in which the membrane is treated as a single phase, and the second is a hydraulic mechanism in which the membrane is treated as a two-phase system. The first mode corresponds to a membrane in contact with water vapor, and the second to a membrane in contact with liquid water. By modeling the membrane in this fashion, Schroeder’s paradox and other phenomena can be described.

The key to the model is how the structure of the membrane changes with water content. The structure of the hydrated membrane is affected by many factors including pretreatment procedures, operating temperature, water content, length of side-chains, and equivalent weight to name a few. However, there are still some global changes and structural elements common to all of the perfluorosulfonated ionomers as a function of water content.

The general structure of the membrane as a function of water content has been the source of many studies including rheological (22), swelling (23)(24), infrared (25), porosimetry (26), and especially X-ray (27)(28)(29) and microscopy studies (30)(31)(32). For the most part, all of these have shown that a hydrated membrane contains two phases, an ionic phase which water is associated with, and a matrix or nonionic phase. The ionic phase is associated with the hydrated sulfonic acid groups, and the matrix phase with the polymer backbone. Thus, in our model, there are two separate regions, one is hydrophilic (ionic phase) and the other is hydrophobic (matrix phase). The actual form of the phases depends on the water content, as discussed below.

There are many different forms into which the two phases can separate. The consensus is that at lower hydration levels, those that correspond to a membrane equilibrated with vapor, the actual structure is that of an inverted micelle. This is known as the cluster-network model first proposed by Hsu and Gierke (33). In this model, the water is contained in a spherical domain of about a 4 nm diameter into which the polymer side-chains infiltrate. The reason for this structure is that it is an energetically favored state of the membrane (34). As the membrane initially takes on water, the sulfonic acid groups are hydrated and dissociate, creating charged groups that participate in coulombic repulsions. These interactions are opposed by the work required to deform the polymer matrix. Hence, there is a balance between the surface or electrostatic energy and the elastic or deformation energy (33)(35). The clusters are connected by short pathways of around 1 nm in diameter, as calculated experimentally (36), and were determined by Hsu and Gierke to be transient connections with a stability on the order of ambient thermal fluctuations. The cluster-network model has also been verified by microscopy studies.

The other popular model for vapor-equilibrated membrane structure is that of Yeager and Steck (37). They proposed the existence of three regions in the membrane: the matrix, the ionic cluster, and an interfacial zone. They further supposed that the ionic clusters are nonspherical. While the structure of the ionic clusters has been seen and...
calculated to be roughly spherical, there has been evidence of the interfacial zone. For example, transition electron microscopy of stained membranes shows that there is a region surrounding the ionic clusters containing a lower concentration of sulfonic acid sites along with some of the polymer backbone (31).

We treat the Hsu and Gierke model as an idealization of the Yeager and Steck model, where the channels are the interfacial regions. However, the concentration of the sulfonic acid sites is not high enough to make the channel entirely hydrophilic, and thus it is slightly hydrophobic. The reasoning is that the deformation caused by forming the clusters makes the channels hydrophobic in the middle, and with increasing sulfonic acid sites as the cluster is approached. For the whole channel though, the average surface is hydrophobic. As a final piece of evidence, the channels are attributed with causing co-ion exclusion, and thus must have some sulfonic acid groups in them, perhaps at their periphery (38). In all, for a vapor-equilibrated membrane, the structure is that of ionic clusters in the shape of inverted micelles that are hydrophilic and filled with water. These clusters are connected by channels that are continuously forming and deforming at ambient conditions and contain sulfonic acid sites at their periphery, making them more hydrophilic than the matrix, but still hydrophobic overall.

As the water content increases, the membrane clusters swell and reorganize themselves, trying to minimize the total energy of the system, aided by the fact that water plasticizes the membrane (22)(33). This reorganization is started by the presence of liquid water at the boundary of the membrane. The way in which water stabilizes the channels is unknown, but is undoubtedly due to the polar nature of water and the presence of a fluorocarbon-rich skin on the surface of Nafion (23)(32). This skin is repelled from the surface, causing the surface and the nearby channels to become more hydrophilic (39). Water then enters the channels and somehow helps to stabilize them and continue the process across the membrane. The reorganization results in an agglomeration of clusters such that they appear by X-ray analysis to be larger but the distance between sulfonic sites is about the same (27). Hence, the liquid water helps to stabilize and lower the hydrophobicity of the channels (although they are still hydrophobic overall) and the clusters are coming together and making the channels larger. In essence, this reorganization forms a porous structure. In fact, this is what has been seen in swollen membranes by the microscopy studies. The pore-size distribution shows an average pore size of about 2 nm, which agrees with the average size between a swollen channel and shrunken cluster.

In summary, Figure 1 shows the way our model describes the structural changes of the membrane with water content, where \( \lambda \) is the number of waters per sulfonic acid site. In the first step, the dry membrane absorbs water in order to solvate the acid groups, which form inverse micelles in the polymer matrix. With more water uptake, these clusters grow and form interconnections with each other. These connections are transitory and have hydrophobicities comparable to the matrix. This structure corresponds to a membrane that is in contact with saturated water vapor. If there is liquid water at the boundary of the membrane, structural reorganization occurs due to the fluorocarbon-rich skin of the ionomer and the liquid water infiltrating the channels, causing the channels to stabilize, and the various clusters to agglomerate along the channels; thus forming a pore-like structure. In this structure, the channels are still hydrophobic on average, but only slightly since the agglomeration causes a higher...
concentration and farther penetration of sulfonic acid sites into the channel. Since now the channels are filled with liquid, the uptake of the membrane has increased. Obviously, our model is somewhat of an idealization, but it is strongly based on and agrees with the physical evidence.

The values of $\lambda$ for the saturated vapor and liquid-equilibrated membranes are taken from studies of Schroeder’s paradox (15)(40). The behavior described above does not depend on whether the membrane is going from vapor to liquid or liquid to vapor. In the former, liquid water is present and infiltrates the channels, and in the latter, the liquid water is pushed out because the channels are hydrophobic and there is not any liquid water in contact with the membrane. Of course, the liquid water in the membrane will have some pressure at the very edge of the membrane due to capillary forces and the gas pressure at the boundary, but the capillary pressure will be zero and thus the water will move out due to the hydrophobicity of the channels. Furthermore, the reemergence of the fluorocarbon-rich skin may aid in this process. It is noted that the structural rearrangements, like the fluorocarbon skin and the fact that the water has to go through clusters and other channels, make the overall process relative slow, which is verified in the observed length of time it takes to reach equilibrium (41).

The above idea is not entirely novel and has been mentioned off-hand as one of a few possible explanations for Schroeder’s paradox (42), but it has never been incorporated into a model. There is also experimental evidence to back this explanation. First, as $\lambda$ goes from 14 to 22, the water is seen as becoming more bulk-like by various analysis and experimental data including freezing-point studies (5)(25)(43). These results indicate that a separate liquid phase if forming that is not like the bound water or cluster water

**Figure 1 – Evolution of membrane structure as a function of water content, $\lambda$ (the number of waters per sulfonic acid site). The gray area is the fluorocarbon matrix, the white the fluctuating channels, the black the polymer side-chains, and the light gray the liquid water.**
formed in the case of the vapor-equilibrated membrane. Also, the electroosmotic coefficient sharply increases with a membrane in contact with liquid (44) and approaches the value for a hydrated proton in pure water (45); the permeation coefficient of oxygen in the membrane increases greatly and approaches the value of oxygen in pure water (46); and the conductivity increases (16). All of these results suggest that there is now a continuous channel of liquid water where before there was not. One last piece of evidence for the channel structure is that while the vapor-phase uptake is temperature dependent due to the change in interaction energies, the liquid-phase uptake is not since it is the same as filling an inert porous medium (41). These observations are in exact agreement with our concept of what is occurring between a vapor-equilibrated and liquid-equilibrated membrane. With the defined physical structure of the membrane, we have been able to explain Schroeder’s paradox, and now can develop a transport mechanism that follows from these ideas.

TRANSPORT MECHANISMS

By the above physical model, there are two different types of transport occurring, depending on whether the membrane is in contact with liquid or vapor water. Thus, we should divide the model into two separate transport modes, the vapor and the liquid. The two different modes of transport are considered independent of each other except for properties that affect the entire membrane/water system as a whole, like density and pressure. A continuous transition is assumed between the two modes based on the water content of the membrane. Finally, based on various experimental data, all species transported through the membrane, including water, protons, and gases move by way of the clusters and channels and not through the fluorocarbon matrix (33)(37). Thus, we treat the fluorocarbon matrix as inert. All that it does is to add mechanical strength, raise the weight of the polymer, and make the channels hydrophobic.

Transport in a vapor-equilibrated membrane

For a membrane that is in contact with water vapor only, there is a percolation threshold value for the water content before it is conductive. There is liquid water in the clusters (the water condenses due to the hydrophilicity of the clusters), but none in the channels, except for the bound water hydrating the few sulfonic acid sites present. The channels are always fluctuating, but the clusters are close enough together to form conductive channels. Due to the nature of the fluctuating channels and the interfacial region, it is best to treat the membrane as a homogenous single-phase system. In this sense, the water vapor does not penetrate into the channels, but dissolves by an equilibrium mechanism into the membrane. Thus, the vapor-equilibrated membrane transport mechanism is similar to the single-phase transport models mentioned previously.

The conductivity and other properties in the single-phase model can be explained based on the percolation concept. Thus, they increase as more channels are formed and the pathways become less tortuous due to the addition of water into the system. The
electroosmotic coefficient, or the number of water molecules carried by a proton, is dependent on the type of complexes that water forms with a proton, and in the absence of a contiguous liquid pore network, the only complex that can form and be transported is a hydronium ion. Thus, the conductivity and the electroosmotic flow are due to a hydronium ion that hops from acid site to acid site through the clusters and across the channels. Finally, the nonelectroosmotic water movement is caused by a gradient in the water chemical potential. The above lays the foundation for the transport mode of the single-phase system when the membrane is in contact with a vapor boundary, and is shown pictorially in Figure 2.

![Figure 2 - Vapor-equilibrated membrane transport and structure.](image)

**Transport in a liquid-equilibrated membrane**

In this mechanism, the structure of the membrane can be interpreted to be more akin with a noninteracting porous medium rather than the interacting description given above. This is because only the channels connecting the clusters are being filled with liquid water, if the liquid pressure is enough to overcome the hydrophobicity of the pore. If it is not, then the liquid phase cannot penetrate further into the porous medium. The transport in this two-phase system is very similar to that modeled by Bernardi and Verbrugge (12) and Eikerling and coworkers (13) and is summarized in Figure 3.

![Figure 3 - Liquid-equilibrated membrane structure and transport.](image)

When filled with liquid water, the channels are able to make a continuous water pathway from cluster to cluster and membrane side to side. Thus, the nonelectroosmotic movement of water is caused by a liquid pressure gradient. The conductivity is explained by the Grotthuss mechanism and proton hopping or diffusion through the membrane,
where once again the conductivity will increase with water content since more water means more filled channels and better and shorter conduction pathways, up to a point. The electroosmotic flow is described by the vehicle mechanism and proton hydration effects, including the formation of the Zundel, H$_2$O$_2^+$, and Eigen, H$_3$O$,^+$, ions (47). Thus, unlike in the previous transport mechanism, the electroosmotic coefficient will be larger than one, and something more like 2.5 since it is slightly less than that in pure water because of the small pore sizes (48).

QUALITATIVE COMPARISONS OF THE MODEL WITH OBSERVATIONS

As mentioned previously, most of these membranes are based on the Nafion copolymer idea and as such are polyfluorosulfonic acid membranes. In this section, we briefly examine some of the observed behavior and effects, and see whether the physical model can qualitatively predict them. We first examine the family of Nafion membranes and then look at some other membranes.

The pretreatment conditions can have a large impact on the structure of the membrane. In order to make the ionomer active, it must be heated in the appropriate cationic solution. Next, the ionomer is usually dried, and the drying temperature can lead to drying out of the sulfonic groups, which leads to the destruction of the clusters. After this destruction, heating in an aqueous environment above the glass-transition temperature must be applied to allow sufficient reorientation of the polymer chains. This is why water uptake decreases with drying temperature, since there are not as many clusters that can accept water (49). The physical model predicts this behavior since there are not as many clusters and pores.

The equivalent weight of an ionomer is very similar to a molecular weight. The higher the equivalent weight, the more ionomer is needed for the same acid behavior, and the higher the content of the perfluorinated polymer matrix. For high equivalent weight Nafions, the clusters should be farther apart and smaller since it is harder to deform the polymer. Thus, the transport properties will not be as good, and the percolation threshold for conductivity is expected to be higher. These effects have been seen in comparing Nafion 1200 with Nafion 1100 (33). Furthermore, it has been shown that as the equivalent weight increases, the electroosmotic coefficient is higher, the diffusion coefficient is poorer, and the conductivity is lower, because water is now complexing with the fluorocarbon chains and ether oxygens in the clusters as well as the pores for a water-saturated membrane (25). The physical model explains this since the channels are longer and will have more interaction with the matrix, thus making them more hydrophobic and yielding lower water uptakes and worse properties. It should be noted that as the equivalent weight decreases past 1000 g/equiv, Nafion becomes soluble in water because there is not enough hydrophobic matrix to keep it in a gel-like state (50).

In addition to equivalent weight and structure, the ionic form of Nafion also leads to different behavior. The conductivity of the acid or H-form of Nafion is highest, and that is due to the enhancement by the Grothuss mechanism for proton transport, as explained by our physical model (48). With the other cations, the smaller the cation, the higher its hydration level and thus the higher the water content of the membrane. The physical
model explains this observation because the smaller cations can form larger clusters since their ionic radius is smaller and their preferential hydration level is higher (51). This is especially the case with cesium ions, since the uptake is almost nothing since the ions are too big and block the channels. The effect of cation functionality is also seen with hydrophilic versus hydrophobic cations. In that case, the hydrophilic cations give a higher water content, which agrees with the model since the clusters are filled with water and will be larger. Finally, the smaller cations have larger electroosmotic drag coefficients because the water is more bulk-like, meaning that larger water complexes can form. The reason for the bulk-like water is that the clusters and channels are larger and the water in the middle of the clusters is shielded by the water solvating the sulfonic acid sites (7).

Besides Nafion, other membranes have been considered. These membranes include the sulfonated polyetherketones (PEEK) membranes, the Aciplex and Flemion membranes, and the Dow company series of membranes. The PEEK membranes have a structure that has narrower channels and a less-connected network of clusters (42). This structure results in a higher dependence of the various transport properties on water content due to percolation ideas. In addition, it results in lower drag coefficients since larger water-proton complexes are inhibited from forming. These analyses are in accordance with the referenced data and our physical model. The Aciplex and Flemion membranes have a bilayer structure comprised of carboxylic type on the cathode side and sulfonic type on the anode side (52). This type of arrangement gives them lower gas permeation and lower resistance because they are thinner and have a higher ion-exchange capacity, meaning that physically the clusters are closer together and form a more hydrophilic and interlinking continuous network. This analysis is also verified by their higher water uptake (49). Finally, the Dow membranes are perhaps the most researched after those of Nafion. Their structure is very similar to Nafion, except that they have a much shorter side-chain (40)(53)(54). Due to the short side-chain, it is expected that the elastic deformation energy is higher and thus the formed clusters will be smaller. These smaller clusters allow for a slightly higher water content than for Nafion since there is a larger volume of interconnecting channels, but the water uptake when in contact with the vapor-phase should be slightly lower than that of Nafion for membranes with the same number and type of sulfonic acid sites. This water uptake description also means that diffusion coefficients and conductivities will be roughly the same for the vapor-equilibrated membrane, but will be higher than those in Nafion for the liquid-equilibrated membrane. In addition, gas diffusion can be described by the higher levels of interconnectivity between the clusters and thus a shorter overall diffusional path. All of the above is verified experimentally.

CONCLUSIONS

We have presented a physical picture of the membrane, which agrees with the observed data. In this model, the dry membrane forms a cluster-network model composed of ionic clusters and connected by fluctuating hydrophobic channels. This is true up to water contents equal to the equilibrium water content of the membrane when exposed to saturated water vapor. Due to the structure of the membrane, it is best to treat the membrane as a single-phase system even though there is a liquid water phase.
contained inside of the clusters. The transport is thus described by a gradient in water chemical potential and a hopping mechanism of hydronium ions. When the membrane is exposed to liquid water at a high enough pressure, water can infiltrate the channels between the clusters, thus forming a second phase. The liquid water also causes the clusters to rearrange into a more pore-like network. Hence, the transport is treated as a two-phase system or that in a porous medium. The flow of liquid water is described now by a pressure gradient, conductivity by the Grotthuss and diffusion mechanisms, and electroosmotic flow by the vehicle mechanism and proton hydration in the pores. When the membrane is neither completely in the liquid- or vapor-transport mode, the mode is assumed to be a superposition of the two with water being able to evaporate and condense between the two modes. Work is now on-going to make a mathematical transport model based on the above physical model.

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