Hydration of proton exchange membranes (PEMs) is important for achieving optimum performance and durability of PEM fuel cells. PEMs need to be properly hydrated in order to prevent problems associated with either drying or flooding of the membrane. Such problems happen mainly because of various water transport mechanisms inside the PEM fuel cell stack, i) convective transfer caused by pressure gradients inside the fuel cell stack, ii) back diffusion of water from the cathode to the anode, and iii) electro-osmotic drag from the anode to the cathode. Under nominally identical operating conditions, water flooding can occur, which makes the performance of the cell unreliable, unpredictable, and unrepeatable. This article discusses such issues and presents a model that addresses water flooding.

An attempt was made to model the entire phenomena for better understanding the importance of water management (water flooding) vis-à-vis changes in operating conditions and fuel cell components. The article thus presents a two-phase, non-isothermal, transient and two-dimensional model of the fuel cell with the focus on water uptake by proton exchange membranes. The developed two-phase flow model is found to be useful in analysing both the importance of water management and the sensitivity of water flooding to changes in operating conditions and fuel cell components. Further, in order to obtain the equilibrium concentration of water in the membrane, two different approaches of water uptake by the membrane were considered; each takes into account Schroeder's paradox as well as the individual contributions of water vapour and liquid water in the membrane. The model results show good agreement with the experimental results. A comparative analysis of the two approaches is presented for various results such as cell voltage against current density, net drag coefficient, and the rate of water uptake by the membrane from both water vapour and liquid water phases.

Introduction

Environmental problems and fast depletion of fossil fuel reserves are of extreme concern for today's world. Hydrogen and bio-fuels are therefore being considered as feasible and sustainable as clean energy sources for the future. Fuel cells have attracted the attention of researchers as promising energy converters because of their high energy efficiency and low or zero emissions. By definition, a fuel cell (FC) is an electrochemical energy conversion device that produces energy (electricity), heat, and water. The unit operates much like a battery except it does not require electrical recharging. In a battery, all of its chemicals are stored inside and then it converts the chemical energy into electricity; however, once the stored chemicals are exhausted, the battery is dead. On the other hand, in a fuel cell, chemicals flow from the outside and hence an FC does not die. Thus, the FC enables us to generate power almost indefinitely as long as it has a fuel supply. Another advantage of fuel cells is that their components such as proton exchange membranes (PEMs) are environment friendly.

Fuel Cells

The common components of FCs are an anode, a cathode, and an electrolyte barrier. The electrodes are separated by the electrolyte barrier. The electrolyte allows charges to move between the two sides of the fuel cell. Fuel is supplied to the anode side, whereas oxygen (or just air) is supplied to the cathode side. The electro-chemical reactions occur at the electrodes. Both of the chemicals
hit the electrolyte barrier, causing electrons to split off. Electrons then travel from the anode to the cathode through an external circuit, creating an electric current. The electrons produced are drawn outside (externally) the electrolyte barrier. Adjacent to the PEM on both sides, the chemical catalyst layers increase the reaction rate.

Fuel Cells are characterized by the type of electrolyte used, and each type of FC differs in terms of its start-up time. Proton exchange membrane fuel cells (PEMFCs) have start-up times of 1–5s, whereas solid oxide fuel cells (SOFCs) have start-up times of 8–12 min. Figure 1 depicts the membrane electrode assembly (MEA) with other components of a fuel cell. Gas diffusion layers (anode and cathode sides) are attached to the in situ prepared membrane and catalyst layers.

A simple schematic of a PEM hydrogen–oxygen fuel cell with its related reactions are shown in Figure 2. Hydrogen molecules dissociate and are adsorbed at the anode to oxidize into protons and electrons. Electrons travel through an external load resistance. Protons diffuse through the PEM to the cathode under an electrochemical gradient. Oxygen molecules adsorbed at the cathode are reduced and react with the protons to produce water. The product water is either absorbed into the PEM, or it evaporates at the anode and cathode.

**Proton Exchange Membrane**

PEMFCs utilize a PEM that consists of acid side groups to conduct protons from the anode to the cathode. As is discussed later, water management is critical for PEM fuel cell operations. PEMs function efficiently if an adequate amount of water remains absorbed in the membrane to ionize the acid groups. On the other hand, the presence/generation of excess water may flood both the cathode and the PEM, reducing the fuel cell performance. The power output can thus be severely affected.

As mentioned earlier, proton conductivity in PEMs increases with increasing water activity \(a_w\). This conductivity can be maximized if the membrane is properly equilibrated with water. The PEM functions most efficiently once \(a_w\) approaches 1.0, which minimizes the membrane resistance for proton conduction. However, this also results in water condensation, which inhibits mass transfer to the electrodes.

**Limitations in Proton Exchange Membrane Fuel Cells**

PEMFCs are the most promising candidates among the various types of fuel cells for future automobile applications because of their quick start-up, high energy density at low operating temperatures, zero emissions, and system robustness.

Sincere attempts are being made world-wide for large-scale commercialisation of PEMFCs, and significant advances have indeed been made. In spite of these advances, however, large-scale commercialisation of PEMFCs is still restricted because the materials used (such as ionomer materials and platinum-based catalysts)
are expensive and the reliability of the devices is low. Currently, active research is underway to reduce the cost by (i) reducing the loading of the platinum catalyst, (ii) seeking inexpensive materials and construction methods, and (iii) improving cell performance and durability. Any improvement, such as reducing the cost by reducing the loading of the platinum catalyst or searching for low-cost materials/fabrication methods, will increase the acceptance of fuel cells. Therefore, attempts are being made world-wide towards improving the cell's performance and durability.

Cathode performance also plays vital role in the fuel cell's performance. There are two major reasons why cathode performance acts as a limiting factor in cell performance. First, the kinetics of the oxygen reduction reaction (ORR) at the cathode decreases relative to the hydrogen oxidation reaction (HOR) at the anode. Quantitatively, the rate of the ORR is 4–6 orders of magnitude lower than that of the HOR. This rate reduction occurs despite much improvement in the catalyst formulations. Accordingly, the cathode reaction rate acts as a limiting step. Second significant limiting mass transport is the removal of water from the cathode side. It is often observed that the removal of water becomes exceedingly difficult. Such difficulties occur especially at high current densities. Accordingly, the transfer of oxygen to the reaction sites at the cathode electrode becomes restricted and this too limits the cell performance.

**Water Flooding**

One of the significant technical challenges is the formation of excess water in the PEMFC. This water formation is due to water production from the ORR at the cathode. This leads to the filling of the pores in the gas diffusion layer (GDL). Once the pores are filled with water, the transport of oxygen to the catalyst layer (CL) gets blocked. The catalyst sites then get covered. The overall effect is a reduction in the fuel cell performance. This effect is referred to as 'GDL/CL flooding'. Furthermore, in a PEMFC, if the accumulation of water reaches a point where water columns or water bands form inside the flow channels, gas flow becomes blocked or clogged. This is known as 'flow channel flooding'. GDL/CL and/or flow channel flooding are therefore simply the accumulation of water in the fuel cell.

Because of the accumulation of water, oxygen mass transport becomes limited in a PEMFC, which is also a major reason for the non-acceptance of PEMFCs on a larger scale. The cathode receives water by electro-
osmotic drag and ORR (\(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\)), which generates water. Electro-osmotic drag occurs when water is transported with the protons as they travel across the electrolyte from the anode to the cathode. The only way by which the cathode loses water is by back diffusion. This process, however, occurs at a much slower rate than water generated by ORR and electro-osmotic drag. Therefore, it is important that water be removed either continuously or periodically. If the rate of removal is slower than the generation and drag rates (at the cathode in particular), excess water will accumulate. The overall effect causes water flooding, which hinders the transport of oxygen by blocking the pores of the cathode and anode catalyst, resulting in plugging of the gas transport channels in the flow field. Figures 3a & 3b depict the flow-paths of water.

Water flooding also occurs within the GDL and/or gas flow channels, as well as within the catalyst layer. A non-uniform distribution of reactants is observed over the active catalyst area and among the cells in the stack. Erroneous results are obtained because of the incomplete reactions or the non-uniformity of distribution, resulting in poor performance of the PEMFC and variable performance of the cell-to-cell transport within a stack. Accordingly, cell performance will become unpredictable, unreliable, and unrepeatable owing to flooding.

In contrast to water flooding, when the water removal rate is greater than the water generation and electro-osmotic drag rates, membrane dehydration occurs. This can also result in a poor performance of PEMFCs as it degrades the polymer and increases ohmic losses owing to a significant increase in the membrane’s electrical resistance. Thus, a proper balance should be made between water production and removal. This is essential for the optimal performance of PEMFCs.

The main characteristic of a proton-conducting membrane is high ionic conductivity, which mainly depends upon how the membrane is prepared; in particular, its degree of humidification or presence of adequate amount of water, providing high ionic conductivities at maximum humidification.

**Water Management**

As discussed above, electrochemical water production and electro-osmotic drag transport cause accumulation of water in the fuel cell, which leads to flooding at the cathode side. However, these mechanisms also cause a water concentration gradient across the anode and cathode. This leads to the back diffusion of water from the cathode to the anode, resulting in drying of the membrane from the anode side. The water concentration gradient...
between the cathode and the anode can be estimated by knowing the thickness of the membrane, its water content (at both its upstream and downstream surfaces), and the humidity of the reactant gases. It has been observed by several researchers that at low current densities, back diffusion is comparable to the electro-osmotic drag. However, at high current densities, electro-osmotic drag will prevail over back diffusion. Therefore, even if the cathode is well hydrated, the anode will tend to dry out.

Thus, there is an inherent contradiction in the preparation and casting of PEMs. On the one hand, in order to achieve good proton conductivity, water is needed in the ionomer phase of the PEM. Presence of water allows the movement of protons to occur within the hydrated parts of the ionomer via dissociation of sulfonic acid bonds. The sulfonic acid bonds cannot be dissociated and hence protons cannot migrate in a dry ionomer phase. This results in decreasing the ionic conductivity. Furthermore, the actual number of active sites in the catalyst layer decreases (increasing the activation polarization) when the access of protons to the catalyst surface is hindered because of the low ionic conductivity of PEMs. In addition to this, under severe drying conditions, irreversible membrane degradation in the form of delamination, pinholes, etc., takes place within approximately 100 s. In effect, the ohmic resistance of the entire cell system increases remarkably. In contrast to this, a fully hydrated membrane can achieve much higher conductivity than a dry PEM. It is therefore obvious from the above discussion that it is better to maintain high PEM water content in order to ensure a higher ionic conductivity.

On the other hand, the presence and accumulation of water in the flow-field channels must be removed from the catalyst layer. Water can be removed by water–vapour diffusion and evaporation. Removal of water can also be carried out by capillary transport of water through the gas diffusion layer (GDL) into the flow channels of the flow field. Otherwise, the excess water will block the flow channels and/or the pores of the GDL and catalyst layer (CL), thus reducing the number of catalyst active sites of the CL. To sum-up, the presence of water in a PEMFC is necessary as it acts as a lubricant and makes the cell run smoothly. However, too much water drowns the cell, reducing its functionality; in contrast, too little water dehydrates the cell. Therefore, finding a suitable equilibrium between membrane drying and flooding is critical for guaranteeing the high performance of PEMFCs. Understanding the water transport mechanism in PEMs is a key issue for avoiding cathode flooding and membrane dehydration; it can also serve as a guide for material optimization and development of new MEAs. Thus, different models have been developed over the last decade to describe water transport mechanisms through the membrane. In our group, attempts are being made to develop models that would be useful in understanding both the importance of water management and the sensitivity of water flooding to changes in operating conditions and fuel cell components. One such model development is described and discussed in brief.

**Modelling of Water Uptake in PEMFC**

The approach usually taken is to model the non-equilibrium rate of water uptake by the membrane. Thus, the rate of uptake is proportional to the difference between the equilibrium concentration of water in the membrane and the actual concentration of water in the membrane. The contributions of both water vapour and liquid water are thus taken into account. However, these models may be considered to neglect Schroeder's paradox as they consider the water content of the membrane to be a function of water vapour activity alone. Our group's first task was to understand and address such a discrepancy in modelling the water uptake by PEMs, and we adopted the following methodology: i) begin with two-phase, non-isothermal modelling, ii) consider two different approaches for water uptake by the membrane, accounting for Schroeder's paradox as well as the individual contributions of water vapour and liquid water, iii) consider an agglomerate approach in order to model the local rate of reaction in the catalyst layers, and iv) study the response of fuel cells under a transient state when a step change is applied to the cell voltage. The model development was based on the assumptions of an ideal gas mixture and negligible cross-over of the fuel.

Figure 4 shows the computational domain of the model used in the COMSOL Multiphysics® software, along with the governing equations in each domain and boundary labels.
Model Development with Governing Equations

i) Vapour and gaseous species transport: For the gaseous mixture, a continuity equation (Eq. 1) and Darcy’s Law (Eq. 2) were solved to obtain velocity and pressure profiles.

\[
\frac{\partial (\rho_g u_g)}{\partial t} + \nabla (\rho_g u_g) = S_m
\]

\[
u_g = -\frac{KK_{rg}}{\mu_g} \nabla p
\]

2) \( u_g = -\frac{KK_{rg}}{\mu_g} \nabla p \)  

3) \( \frac{\partial (\rho_g C_i)}{\partial t} + u_g \nabla C_i + \nabla (-D_{i,eff} \nabla C_i) = \frac{\partial (\varepsilon_{eff} \rho_g)}{\partial t} + \nabla (\varepsilon_{eff} \rho_g v_i) = S_i \)

4) \( \frac{\partial (\varepsilon_{eff} \rho_g)}{\partial t} + \nabla (\varepsilon_{eff} \rho_g v_i) = S_i \)

5) \( v_i = -D_{c} \nabla S + \frac{K_m}{K_{rg} \mu_g} \mu_g \)

the absolute permeability of the porous matrix and relative permeability for the gas phase, respectively; \( \mu_g \) the viscosity of the gas phase; and \( p \) the pressure. Empirical and other constitutive relations were used in the model, including the source terms used in the various governing equations. The details may be referred in Chaudhary et al., 2014. The species conservation equation for gaseous species is

\[
\frac{\partial (\rho_{g} C_{i})}{\partial t} + \nabla (\rho_{g} C_{i}) + \nabla (-D_{i,eff} \nabla C_{i}) = S_{i}
\]

Figure 4: Computational domain along with boundary labels with governing equations to be solved in each domain.
ii) **Liquid water transport:** Because of the low operating temperatures, water produced by electrochemical reactions is in the liquid phase. Liquid water transport in porous media occurs owing to the shear force exerted by gas movement and to the capillary pressure gradient that exists owing to a saturation gradient. The following equation was used to model liquid water transport:

\[ \frac{\partial (\varepsilon \rho_l \nu)}{\partial t} + \nabla (\varepsilon \rho_l \nu) = S_l \]  

(4)

where \( \rho_l \) is the density and \( \nu \) the velocity of liquid water. The equation for \( \nu \) was derived.

iii) **Membrane water transport:** The conservation equation for water in the membrane phase was solved in both the membrane and in the catalyst layers. These are written as

\[ \frac{d(\varepsilon_m C_w)}{dt} + \nabla N_w = S_d \]  

(5)

\[ N_w = \frac{n_l I}{F} M_{H_2O} - D_w \nabla C_w \]  

(6)

where \( \varepsilon_m \) is the porosity of the membrane, \( N_w \) is the mass flux of water from the anode to the cathode, \( n_l \) is the electro-osmotic drag coefficient (number of water molecules dragged by each proton across the membrane), \( I \) is the electrolyte current density vector, \( D_w \) is the diffusivity of water in the membrane, and \( C_w \) is the mass concentration of water in the membrane. Because of the low permeability of the membrane and similar pressure conditions on the anode and cathode sides, the hydraulic flux of water is neglected. The source term \( S_d \) describes the rate of water uptake by the membrane. It consists of two components, \( S_{vd} \) and \( S_{ld} \), which are described below.

iv) **Local rate of reaction in catalyst layers:** In catalyst layers, both hydrogen and oxygen first diffuse through the ionomer layers covering the catalyst particles to reach the catalyst surface and then react. In Eq. (7), the local rate of reaction of the oxygen was used.

\[ R_{O_2} = \frac{P_{O_2}}{H_{O_2}} \left( \frac{1}{E_r k_{c,O_2} (1 - \varepsilon_{cat})} + \frac{(r_{agg} + \delta) \delta}{d_{agg} r_{agg} D_{O_2,m}} \right) \]  

(7)

where \( P_{O_2} \) is the partial pressure of oxygen and \( H_{O_2} \) is Henry’s constant of oxygen between air and the membrane phase; \( \varepsilon_{cat}, r_{agg}, \delta, \) and \( a_{agg} \) are the catalyst layer porosity, agglomerate radius, thickness of ionomer layer covering the agglomerates, and specific surface area of the agglomerates, respectively; and \( D_{O_2,m} \) are the diffusivity of hydrogen and oxygen in the membrane phase, respectively. In the cathode CL, \( k_{c,O_2} \) was estimated using an empirical equation. Likewise, on the anode side, the effect of hydrogen diffusion through the thin ionomer film and the effect of Pt on its rate of reaction were neglected, and an empirical equation was used to estimate the rate of reaction of hydrogen.

v) **Charge balance:** Charge balance equations were solved to obtain the solid phase and electrolyte phase potentials.

\[ \nabla (-\sigma_{eff}^s \nabla \phi_s) = - S_q \]  

(8)

\[ \nabla (-\sigma_{eff}^m \nabla \phi_m) = S_q \]  

(9)

where \( \sigma_{eff}^s \) is the effective electronic conductivity of the solid phase, \( \sigma_{eff}^m \) is the effective protonic conductivity of the membrane, and \( \phi_s \) and \( \phi_m \) are the solid phase and electrolyte phase potentials, respectively.

vi) **Energy balance:** The energy balance equation was solved for the entire computational domain.

\[ (\rho c_p)_{eq} \frac{\partial T}{\partial t} + \nabla \cdot (\rho \nabla T) = \nabla \cdot (k_{eq} \nabla T) + S_r \]  

(10)

where \( \rho \) is the fluid mixture density, \( c_p \) is the specific heat capacity of the fluid mixture, and \( (\rho c_p)_{eq} \) is the equivalent heat capacity of a solid and fluid.

Source Terms

Source terms used in the governing equations are given in Chaudhary, et al., 2014. Some of them are described below:

i) **Phase change:** The phase change between water vapour and liquid water by condensation or evaporation was considered.

ii) **Water uptake by membrane:** Inside the pores in the catalyst layer, both water vapour and liquid water are in contact with the membrane phase, and hence both contribute to the water uptake by the membrane. Experimental studies have shown that water uptake by a
membrane from liquid water is significantly different and much higher than water uptake from saturated water vapour. This is more popularly known as Schroeder's paradox. Thus, two different approaches of water uptake by the membrane are proposed; however, both approaches take into account Schroeder's paradox and the individual contributions of water vapour and liquid water. The difference between the two approaches lies in defining the equilibrium concentration of water in the membrane, \( C_{w}^{eq} \). Figure 5 shows the difference between the two approaches.

In the first approach, two separate equilibrium concentrations of water are defined in the membrane, which depend upon whether the water uptake is from the vapour phase or the liquid phase. In the second approach, the equilibrium concentration is calculated by a weighted average of water uptake from both the vapour and liquid phases. These two different approaches in determining the water balance in a fuel cell were used in order to observe the difference and to obtain a better understanding of water uptake by the membrane.

**Boundary Conditions**

Appropriate boundary conditions were considered at specified locations (refer to the numbers depicted in Figure 4): Anode gas channel – Anode GDL (1), Bipolar plate – Anode GDL (2), Anode GDL – Anode CL (3), Anode CL – Membrane (4), Cathode CL – Membrane (5), Cathode GDL – Cathode CL (6), Bipolar plate – Cathode GDL (7), and Cathode gas channel – Cathode GDL (8).

**Solution Methodology**

The model was implemented in COMSOL Multiphysics® 4.2. A triangular mesh consisting of 3804 elements was developed using the in-built module to implement the governing equations.

**Results and Discussion**

Validation of the model was performed by comparing the polarization curves obtained by the simulation with the available experimental results. Figure 6 shows that there was a good match between the experimental results and simulation results. Figure 7 shows the net drag coefficient
of water across the membrane at different operating voltages. The net drag coefficient of water is defined as the number of water molecules dragged by each proton across membrane from anode to cathode side. The net drag coefficient is a combination of electro-osmotic drag and the backward diffusion of water from the cathode towards the anode owing to a concentration gradient. At higher voltages (lower current densities), both the electro-osmotic drag and the backward diffusion of water is small, resulting in small values of net drag coefficient. At moderate current densities, electro-osmotic drag predominates over the backward diffusion of water from the cathode, resulting in an increased net drag coefficient. As the current density further increases, electro-osmotic drag also increases. However, a large amount of liquid water is now produced in the cell, and the backward diffusion of water counteracts the electro-osmotic drag, decreasing the net drag coefficient. Still, electro-osmotic drag predominates over backward diffusion, and hence the net drag coefficient is positive.
Professor PK Bhattacharya of the chemical engineering department has been involved for more than thirty-seven years in research, teaching, administration and service to the profession. He is among the top researchers of the country in the industrially important and scientifically vibrant area of membranes and membrane separations. His research interests and important contributions cover the entire range of cutting-edge in membranes, including nano, microporous and charged. He has pioneered much of the fundamental research and development work in membrane separations in this country and has established unique experimental facilities at IIT Kanpur. His involvements in membrane separations include processes like ultrafiltration, pervaporation, membrane contactor, enzymatic membrane reactor with the focus on design modelling and simulation, industrial pollution, case studies and process development.

Acknowledgement

Author is thankful to Shivesh Chaudhary (dual degree graduate in chemical engineering from IIT-Kanpur in 2013) for his efforts in developing the model. Efforts of Juhi Chandra (a student under dual degree program in chemical engineering) in preparing the figures are also appreciated.

References

