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Modeling the Dynamic Behavior of Proton-Exchange Membrane Fuel Cell

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A two-phase transient model that incorporates the permanent hysteresis observed in the experimentally measured capillary pressure of GDL has been developed. The model provides explanation for the difference in time constant between membrane hydration and dehydration observed in the HFR experiment conducted at LANL. When there is liquid water at the cathode catalyst layer, time constant of the water content in the membrane is closely tied to that of liquid water saturation in the CCL, as the vapor is already saturated. The water content in the membrane will not reach steady state as long as the liquid water flow in the CCL is not at steady state. Also, Increased resistance to proton transport in the membrane is observed when the cell voltage is stepped down to a very low value.

Introduction

The dynamic behavior is a major consideration in the design of proton-exchange membrane fuel cells for applications that are subject to rapid load changes, as in automotive or portable power. The combination of the various length scales of the fuel cell components and the different time scales of the processes taking place in the fuel cell make it extremely challenging to conduct *in situ* measurements [1]. This challenge is most obvious when interpreting through-plane experimental data because of the small length scale involved. Thus, there is a need for numerical modeling in order to understand the various electrochemical and transport processes taking place in fuel cells and interpreting water-content data. However, a model that will best explain these processes must represent as close as possible the underlying physics of the processes.

Experimental studies have shown that negative pressure capillary pressure, with capillary pressure defined as total gas pressure minus liquid pressure, is required to force water into the GDM, while positive capillary pressure is required to withdraw the water from the GDM [2, 3]. Also, Gostick et al.[2] and Harkness et al. [3] observed that primary intrusion of water into the GDM occurs at somewhat higher capillary pressure than the subsequent intrusion and that secondary intrusion is more likely to be relevant in fuel cell operation. A number of numerical studies have used experimentally measured capillary pressure in their work. Wang and Nguyen[4, 5] developed steady-state models in which their previously reported capillary pressure [6], which showed good agreement between the imbibition and drainage curve, was used. Wu et al. [1, 7] used modified Leverett function originally developed for GDM by

Kumbur et al. [8] in both GDM and catalyst layer of their models. Their results did not show saturation discontinuity at the interface between GDM and CL which is usually caused by two media with different capillary properties coming into contact. To the best of our knowledge, none of these works include hysteresis effect observed in the capillary pressure of the GDM. The focus of this work is therefore to develop a 1-D two-phase transient model of PEMFC that incorporates the permanent hysteresis observed in the capillary pressure of the gas diffusion media (GDM).

Mathematical Model

The modeled domain consists of the anode gas diffusion layer (aGDL), anode catalyst layer (aCL), membrane, cathode catalyst layer (CCL) and cathode gas diffusion layer (CGDL). The liquid water in the GDL and CL is assumed to move to capillary force only (convective force is neglected). Water in the membrane is assumed to be in the membrane phase. Desorption is assumed to go to vapor phase if the vapor pressure is less than the saturated vapor pressure at the operating conditions. However, once the vapor pressure exceeds the saturated vapor pressure, desorption goes to liquid phase. Absorption is assumed to come from the vapor phase if the vapor pressure is less than the saturated vapor pressure but comes from both vapor and liquid phases once the vapor pressure exceeds the saturated vapor pressure. As a simplified approach, we assume that the fraction of the absorption from liquid phase is proportional to saturation, s while that from vapor phase is proportional to $(1-s)$. Other assumptions made in this work are:

1. The total gas pressure is assumed to be constant.
2. Temperature is assumed to be uniform. The uniform temperature assumption is reasonable for a single cell where constant temperature conditions are easier to maintain.
3. Transport in the membrane is governed by dilute solution theory.
4. The double-layer charging time constant has been shown to be in the order of micro seconds and can therefore be safely neglected [9].
5. Reactant gases and vapor behave as ideal gases.
6. Gas transport is assumed to be dominated by diffusion (convection is neglected).

Governing Equations

The governing equations of each domain are summarized in Table I below. The catalyst layer is assumed to have finite thickness and it is modeled using porous electrode theory. At CCL, the effectiveness factor is determined from agglomerate model with the potential assumed uniform in each of the spherical agglomerates but varies across the thickness of the catalyst layer. The binary diffusion coefficients of gases are corrected for porosity and tortuosity, which are functions of saturation. The fraction of the pores in the CL and GDL filled by liquid water are account for by multiplying porosity and tortuosity by $(1-s)$, where s is the liquid water saturation. The development of most of our governing equations follows the work of Weber and Neuman [10].

Table I. Summary of the Governing Equations

Anode Gas Diffusion Layer	
Electronic current density, i_1	$\nabla \cdot \vec{J}_1 = 0$
Electronic potential, ϕ_1	$i_1 = -\sigma_s^{eff} \nabla \phi_1$
Flux of water vapor, N_0	$\frac{e_s}{RT} \frac{\partial p_0}{\partial t} = -\nabla \cdot \vec{N}_0 + R_w$ $R_w = \frac{k_e e_s p_0}{M_0} s (p_0^{sat} - p_0) \times switch + \frac{k_c e_s (1-s) p_0}{p_G} \frac{(p_0^{sat} - p_0)}{RT} \times (1 - switch)$ $switch = \left[\frac{1}{2} + \frac{ p_0^{sat} - p_0 }{2(p_0^{sat} - p_0)} \right]$
Liquid water saturation, s	$e_s \rho_L \frac{\partial s}{\partial t} = -\nabla \cdot \vec{N}_L - M_0 \times R_w$ $N_L = \frac{\rho_L k_r k_{abs}}{\mu_L} \frac{dp_c}{ds} \frac{ds}{dx}$ $k_{abs} = s^3$
Flux of hydrogen gas, N_{H_2}	$\frac{e_s}{RT} \frac{\partial p_{H_2}}{\partial t} = -\nabla \cdot \vec{N}_{H_2}$
Partial vapor pressure, p_0	$\nabla p_0 = \frac{RT}{p_G D_{0,H_2}^{eff}} (p_0 N_{H_2} - p_{H_2} N_0)$
Partial pressure of hydrogen, p_{H_2}	$p_0 + p_{H_2} = p_G$, where p_0 is the vapor partial pressure.
Anode Catalyst Layer	
Membrane Water Content, λ	$\frac{e_i}{V_m} \frac{\partial \lambda}{\partial t} = -\nabla \cdot \vec{N}_{wm} + k_{a/d} (\lambda_{eq} - \lambda)$ $N_{wm} = -\frac{e_i^{eff}}{V_m} D_{\lambda}^{eff} \frac{\partial \lambda}{\partial y} + \frac{\zeta i_2}{F}$
Ionic current density, i_2	$\nabla \cdot \vec{J}_2 = a_{12}^0 (1-s) i_{HOR}$ $i_{HOR} = i_{0_{HOR}} \exp \left[\frac{p_{H_2}}{p_{H_2}^{ref}} \exp \left(\frac{\alpha_a F}{RT} (\Phi_1 - \Phi_2) \right) - \exp \left(\frac{-\alpha_c F}{RT} (\Phi_1 - \Phi_2) \right) \right]$
Electronic current density, i_1	$\nabla \cdot \vec{J}_1 + \nabla \cdot \vec{J}_2 = 0$
Electronic potential, ϕ_1	$i_1 = -\sigma_s^{eff} \nabla \phi_1$
Ionic potential, ϕ_2	$i_2 = -\sigma_i^{eff} \nabla \phi_2$
Flux of water vapor, N_0	$\frac{e_s}{RT} \frac{\partial p_0}{\partial t} = -\nabla \cdot \vec{N}_0 - k_{a/d} (\lambda_{eq} - \lambda) + R_w$
Liquid water saturation, s	$e_s \rho_L \frac{\partial s}{\partial t} = -\nabla \cdot \vec{N}_L - M_0 \times R_w - M_0 \times k_{a/d} (\lambda_{eq} - \lambda)$

Flux of hydrogen, N_{H_2}	$\frac{e_s}{RT} \frac{\partial p_{H_2}}{\partial t} = -\nabla \cdot N_{H_2} - \frac{1}{2F} a_{12}^o i_{HOR} E$
Partial vapor pressure, p_0	$\nabla p_0 = \frac{RT}{p_G D_{0,H_2}^{eff}} (p_0 N_{H_2} - p_{H_2} N_0)$
Partial pressure of hydrogen, p_{H_2}	$p_0 + p_{H_2} = p_G$
Membrane	
Membrane Water Content, λ	$\frac{1}{V_m} \frac{\partial \lambda}{\partial t} = -\nabla \cdot N_{wm}$ $N_{wm} = -\frac{1}{V_m} D_{\lambda}^{eff} \frac{\partial \lambda}{\partial y} + \frac{\zeta i_2}{F}$
Ionic current density, i_2	$\nabla \cdot i_2 = 0$
Ionic potential, ϕ_2	$i_2 = -\sigma_i^{eff} \nabla \phi_2$
Cathode Catalyst Layer	
Membrane Water Content, λ	$\frac{e_i}{V_m} \frac{\partial \lambda}{\partial t} = -\nabla \cdot N_{wm} + \frac{1}{2F} a_{12}^o i_{ORR} E + k_{a/d} (\lambda_{eq} - \lambda)$ $N_{wm} = -\frac{e_i^{eff}}{V_m} D_{\lambda}^{eff} \frac{\partial \lambda}{\partial y} + \frac{\zeta i_2}{F}$
Ionic current density, i_2	$\nabla \cdot i_2 = a_{12}^o (1-s) i_{ORR} E$ $i_{ORR} = -i_{0_{ORR}} \left(\frac{p_{O_2}}{p_{O_2}^{ref}} \right) \exp \left[\frac{-\alpha_c F}{RT} (\Phi_1 - \Phi_2 - U^{\theta}) \right]$ $\text{Effectiveness, } E = \frac{1}{3\phi^2} (3\phi \coth(3\phi) - 1)$ $\text{Thiele Modulus, } \phi = \sqrt{\frac{R_{agg}^2 k'}{\psi_{agg}}} = \sqrt{\phi_{mt} k'}$ <p>where ϕ_{mt} and k' are the mass transfer portion and the kinetic [10] portion of the Thiele modulus respectively.</p>
Electronic current density, i_1	$\nabla \cdot i_1 + \nabla \cdot i_2 = 0$
Electronic potential, ϕ_1	$i_1 = -\sigma_s^{eff} \nabla \phi_1$
Ionic potential, ϕ_2	$i_2 = -\sigma_i^{eff} \nabla \phi_2$
Flux of water vapor, N_0	$\frac{e_s}{RT} \frac{\partial p_0}{\partial t} = -\nabla \cdot N_0 - k_{a/d} (\lambda_{eq} - \lambda) + R_w$
Liquid water saturation, s	$e_s \rho_L \frac{\partial s}{\partial t} = -\nabla \cdot N_L - M_0 \times R_w - M_0 \times k_{a/d} (\lambda_{eq} - \lambda)$
Flux of oxygen, N_{O_2}	$\frac{e_s}{RT} \frac{\partial p_{O_2}}{\partial t} = -\nabla \cdot N_{O_2} - \frac{1}{4F} a_{12}^o i_{ORR} E$

Partial vapor pressure, p_0	$\nabla p_0 = \frac{RT}{p_G D_{0,O_2}^{eff}} (p_0 N_{O_2} - p_{O_2} N_0)$
Partial pressure of oxygen, P_{O_2}	$p_0 + p_{O_2} = p_G$
Cathode Gas Diffusion Layer	
Electronic current density, i_l	$\nabla \phi_l = 0$
Electronic potential, ϕ_l	$i_l = -\sigma_s^{eff} \nabla \phi_l$
Flux of water vapor, N_0	$\frac{e_s}{RT} \frac{\partial p_0}{\partial t} = -\nabla N_0 + R_w$
Liquid water saturation, s	$e_s \rho_L \frac{\partial s}{\partial t} = -\nabla N_L - M_0 \times R_w$
Flux of oxygen, N_{O_2}	$\frac{e_s}{RT} \frac{\partial p_{O_2}}{\partial t} = -\nabla N_{O_2}$
Partial vapor pressure, p_0	$\nabla p_0 = \frac{RT}{p_G D_{0,O_2}^{eff}} (p_0 N_{O_2} - p_{O_2} N_0)$
Partial pressure of oxygen, N_{O_2}	$p_0 + p_{O_2} = p_G$

Table II gives the electrochemical and physical relationships used in this work. The physical parameters used in this study are listed in Table III.

Table II. Electrochemical and physical relationships

Description	Expression
Equilibrium Membrane water content, λ_{eq}	$\begin{cases} 0.3 + 6a[1 - \tanh(a - 0.5)] + 3.9\sqrt{a} \left[1 + \tanh\left(\frac{a - 0.89}{0.23}\right) \right] & a \leq 1 \\ 16.8s + \lambda _{(a=1)}(1 - s) & a > 1 \end{cases}$ <p>Equilibrium membrane water content used in Wu et al. [1] is slightly modified here.</p>
Membrane water diffusivity, D_λ (cm ² S ⁻¹)	$4.1e-6 \left(\frac{\lambda}{25}\right)^{0.15} \left[1 + \tanh\left(\frac{\lambda - 2.5}{1.4}\right) \right]$ [11]
Electro-osmotic drag coefficient, ζ	$\zeta = \begin{cases} 1 & \lambda < 9 \\ 0.117 - 0.0544 & \lambda \geq 9 \end{cases}$ [11]
Proton Conductivity, σ_i	$\sigma_i = (0.005139\lambda - 0.00326) \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right]$ [12]
Absorption Rate, k_a (S ⁻¹)	$k_a = \frac{4.59e-5 f_v}{d_{CL}} \exp\left[2416\left(\frac{1}{303} - \frac{1}{T}\right)\right], f_v = \frac{\lambda V_w}{V_m + \lambda V_w}$ [13]
Desorption Rate, k_d (S ⁻¹)	$k_d = \frac{4.59e-5 f_v}{d_{CL}} \exp\left[2416\left(\frac{1}{303} - \frac{1}{T}\right)\right]$ [13]

Table III. Parameters used in the model

Parameters	Value
Thickness of CL/GDL	20 μm /250 μm [14]
Thickness of membrane, Nafion [®] 117	177.8 μm [14]
Porosity of CL/CGL, e_s	0.3/0.6[1]
Nafion [®] content in CL, e_i	0.3wt%[1]
Liquid water density, ρ_L	0.9718 g/cm^3
Molar volume of dry membrane, V_m	550 cm^3/mol
Evaporation rate constant, k_e	100 $\text{atm}^{-1}\text{s}^{-1}$ [4]
Condensation rate constant, k_c	100 s^{-1} [4]
Cathode exchange current density, i_{ORR}	$1.5e-7 \text{ A}/\text{cm}^2$ [10]
Anode exchange current density, i_{HOR}	$1.4e-3 \text{ A}/\text{cm}^2$ [10]
Cathodic transfer coefficient, α_c	1
Anodic transfer coefficient, α_a	1
Reference partial pressure of O ₂ , p_{H_2ref}	1.01325bar
Reference partial pressure of H ₂ , p_{O_2ref}	1.01325bar
O ₂ permeation coefficient in agglomerate, p_{O_2agg}	$1.5e-11 \text{ mol}/(\text{barcm})$ [14]
Agglomerate radius in cathode, $r_{aggrcat}$	$110e-5 \text{ cm}$ [14]
Electrode specific surface area, a_{12}^o	$1e5 \text{ cm}^{-1}$ [10]
Water vapor /O ₂ diffusion coefficient, pD_{0,O_2}^{eff}	$0.282 \left(\frac{T(k)}{307.1} \right)^{1.5} \text{ barcm}^2/\text{s}$ [15]
Water vapor/ H ₂ diffusion coefficient, pD_{0,H_2}^{eff}	$0.915 \left(\frac{T(k)}{307.1} \right)^{1.5} \text{ barcm}^2/\text{s}$ [15]
Electronic conductivity, k_s	100 S/cm [10]
CL absolute permeability, k_{abs}^{CL}	$1e-12 \text{ cm}^2$
GDL absolute permeability, k_{abs}^{GDL}	$8.7e-10 \text{ cm}^2$
Liquid water dynamic viscosity, μ_L	3.5e-9bars[7]

For ease of use in modeling, we fitted polynomials to the experimentally measured capillary pressures of compressed Toray 120C in Gostick et al.[2]. Figure 1 shows the plots of the measured secondary injection and primary withdrawal capillary pressures of compressed Toray 120C and that of the polynomial fitted to them. The polynomials fitted to the measured capillary pressures are as shown in appendix A. The only work in the literature we were able to find that includes experimentally measured capillary pressure of CL is that of Wang and Nguyen [4, 5]. However, as mentioned in the introductory section, Wang and Nguyen [4, 5] did not see any hysteresis in their measured capillary pressures and therefore the use of their measured capillary pressure may not be appropriate for this work as Gostick et al [2] experimentally measured GDL capillary pressure where hysteresis is observed is being used. In absence of

suitable measured CL capillary pressures, we choose an approach similar to that of Leverett function where CL capillary pressure is a constant multiply by the GDL capillary pressure. In the case of Leverett function, the constant is given as

$$\text{constant for Leverett function} = \frac{\cos(\theta_{CL})}{\cos(\theta_{GDL})} \left(\frac{e_s^{CL}}{k_{abs}^{CL}} \right)^{0.5} \left(\frac{k_{abs}^{GDL}}{e_s^{GDL}} \right)^{0.5} \quad [1]$$

Figure 1. Capillary pressures of compressed Toray 120C

As an initial approximation, we choose $p_c^{CL} = 1.3 p_c^{GDL}$ as our base case for both secondary injection and withdrawal CL capillary pressures. The plots of the base case CL capillary pressures are also shown in figure 1. In this work, we assume that CL capillary pressure also exhibits hysteresis. However, more research work is needed to determine whether or not CL capillary pressure shows hysteresis.

Boundary Conditions

The boundary conditions used in this model are summarized in Table IV below. Fully saturated inlet condition is used as the base case for anode and cathode. As no liquid water is observed at the anode side in all the cases considered, we choose, as our base case, the saturation, s_0 at the anode side to be zero while that at the cathode side to be 0.05.

Table IV. Summary of the boundary conditions

Variables	aGC/aGDL	aGDL/aCL	aCL/Mem	Mem/CCL	CCL/CGDL	CGDL/CGC
λ		$\frac{\partial \lambda}{\partial y} = 0$			$\frac{\partial \lambda}{\partial y} = 0$	
p_0	p_0 given					p_0 given
p_{H_2}	p_{H_2} given					
p_{O_2}						p_{O_2} given
N_0			$N_0 = 0$	$N_0 = 0$		
N_{H_2}			$N_{H_2} = 0$	$N_{H_2} = 0$		

N_{O_2}		$N_{O_2} = 0$	$N_{O_2} = 0$	
i_1		$i_1 = 0$	$i_1 = 0$	
i_2		$i_2 = 0$		$i_2 = 0$
ϕ_1	$\phi_1 = 0$			$\phi_1 = V_{cell}$
ϕ_2		$\frac{\partial \phi_2}{\partial y} = 0$		
s_{GDL}	$s = s_0$	$N_L^{GDL} = N_L^{CL}$		$N_L^{GDL} = N_L^{CL} \quad s = s_0$
s_{CL}		$p_c^{GDL} = p_c^{CL} \quad N_L^{CL} = 0$	$N_L^{CL} = 0$	$p_c^{GDL} = p_c^{CL}$

Numerical Implementation

The governing equations are solved using control-volume approach. The same approach was used by Weber and Newman[16] in their modeling work. The domain of interest is discretized into finite elements or boxes and the governing equations are also cast into finite-difference form. The flux density leaving the left-side half box is set equal to that entering the right-side half box, so that the material is rigorously conserved. In this technique, all vectors are defined at half-mesh points, while the scalars are defined at full-mesh points. All reaction terms are evaluated at quarter-mesh points. The coupled differential equations are solved using a MATLAB[®] version of Newman BAND (J) sub-function.

Results and Discussion

As acknowledged by Gostick et al.[2], secondary injection capillary pressure is likely to be relevant to fuel cell operation because the pores in GDL are likely to be partially wet by vapor condensation before any liquid water is formed in the pores. We therefore use only secondary injection and primary withdrawal capillary pressures in this model. In all the cases considered, the initial condition is the steady state at the starting condition. When voltage is stepped down, the initial condition is computed using primary withdrawal capillary pressure. Also, when voltage is stepped up, the initial condition is computed using secondary injection capillary pressure.

High Frequency Resistance (HFR) measurement conducted at Los Alamos National Laboratory (LANL) shows that the time constant for the membrane hydration when current is increased is shorter than that of membrane dehydration when current is decreased, as shown in figure 2. For the case shown in figure 2, the relative humidity of the anode inlet gas is 100% while that of the cathode gas is 50%. Also, the gas flows were increased 4s prior to increasing the current to ensure that enough reactant gases get to the CL when current is stepped up.

The fuel cell hardware used for testing at LANL was Fuel Cell Technologies, Inc. standard single serpentine flow field 50 cm² hardware. The MEA used was a Gore[™] Primea[®] MEA Series 57 with 18 mm thick GORE-SELECT[®] membrane and carbon supported 0.2 mg Pt cm⁻² on the cathode and 0.1 mg Pt cm⁻² on the anode (GORE-SELECT, PRIMEA and GORE are trademarks of W. L. Gore & Associates, Inc). The GDLs used were SGL Carbon's carbon paper GDLs with specified polytetrafluoroethylene (PTFE) loadings in the substrate and microporous

layer (MPL). GDL 24 BC (5% PTFE in substrate, 23% PTFE in MPL) was used on the anode and GDL 24 DC (20% PTFE in substrate, 10% PTFE in MPL) was used on the cathode.

Figure 2. MEA High Frequency Resistance

Other researchers too have seen similar phenomenon. Wu et al. [17] found that membrane hydrates faster when the relative humidity is increased compared to how fast it dehydrates when the relative humidity is decreased. They suggested that this is due to non-diffusion in the membrane. Wang and Wang [9] increased cathode relative humidity from 0% to 100% for different cell voltage and found that the time constant for membrane hydration increases at voltage increases. However, when the cathode relative humidity is decreased from 100% to 0%, they found the dehydration time to be shorter for cell with higher voltage.

In this study we try to provide some explanation for the difference in time constant in membrane hydration and dehydration when voltage is stepped down and up respectively. It should be noted that both the operating conditions and the thickness of the MEA used in the LANL HFR experiment are different from those used in this model. In the HFR experiment, the thickness of aCL, membrane and CCL are $4.5\mu\text{m}$, $18\mu\text{m}$ and $9\mu\text{m}$ respectively while in this model, the thickness of the aCL, membrane and CCL are $20\mu\text{m}$, $177.8\mu\text{m}$ and $20\mu\text{m}$ respectively. Also MPL is included in the HFR measurement while no MPL is included in this current model. More work is underway to match as close as possible both the operating conditions and the through-plane dimension of the fuel cell hardware used in the HFR experiment.

Figure 3 shows the water content when the voltage is stepped up from 0.5V to 0.85V and vice versa for fully saturated inlet condition. On the x-axis, the first $20\mu\text{m}$ and the last $20\mu\text{m}$ represent the water content in the aCL and CCL respectively while the water content in between them is that of the bulk membrane. For ease of comparison, we only show the water content for the first 150s. It can be seen that the water content, λ increases more rapidly when the voltage is decreased compared to when it is increased. The water content profile reaches steady state at round 100s when the voltage is increased while it is decreasing at 150s when the voltage is increased. Also, the water content at the electrode side reaches steady state faster than the water content in the bulk membrane. For instance, when the voltage is decreased, the water content at the cathode side is almost at steady state at around 50s, while the water content in the bulk membrane does not reach steady state until around 100s. Similarly, when the voltage is

increased, the water content at the cathode side reaches steady state around 120s while the water content in the bulk membrane is still decreasing at 150s. The difference in the time to reach steady state between the cathode side and the bulk membrane can be accounted for by the time for the water to diffusion across the membrane. For Nafion[®] 117 and $\lambda=10$, the time constant, $\tau_{m,D}$ for water diffusion across the membrane can be estimated as $\tau_{m,D} = \delta_m^2 / D_\lambda^{eff} \approx 45s$ and the time constant increases as water content goes down.

Figure 3. The plot of water content for when voltage is stepped up from 0.5V to 0.85V and vice versa.

The water content at the anode interface of the membrane is shown in figure 4. It can be seen that the water content at the anode interface increases rapidly to the peak value and the decreases slightly until it reaches steady state when the voltage is stepped up. The reverse is seen when voltage is stepped down. The time it takes to reach the peak or minimum value when voltage is stepped up or down respectively is almost the same. When voltage is stepped down, current increases and more water is dragged from anode to cathode. Similarly, when the voltage

is stepped up, current decreases and less water is dragged from anode to cathode. Because less water is dragged when the voltage is stepped up, more of the water absorbed from humidified H_2 gas gets retained at the anode side. Also water already in the bulk membrane diffuses to the anode side. This accounts for why water at the anode side increases when the voltage is stepped up. It appears that electro-osmotic drag effect finally balances that of back-diffusion when the water content profile at the anode side reaches peak or minimum value when the voltage is decreased or increased respectively.

Figure 4. Water Content and Saturation Profile for when voltage is stepped up from 0.5V to 0.85V and vice versa.

Also shown in figure 4 is the water content profile at the cathode side of the membrane. When the voltage is stepped down, the increased water generated by the oxygen reduction reaction causes the water content at the cathode side to go up rather quickly. However, when the voltage is increased, less water is generated at the cathode. The water content at the cathode interface decreases slowly in comparison to how it increases when the voltage is stepped down. The injection and withdrawal saturation profiles shown in figure 4 are for when the voltage is stepped down and up respectively. In both injection and withdrawal saturation profiles, the first $20\mu m$, along the x-axis, represents the saturation in the CL while the rest is the liquid water saturation in the GDL. When the voltage is decreased, the saturation in the CL increases rapidly, in a similar fashion to how the water content at the cathode side of the membrane increases. Also, when the voltage is increased, the saturation in the CL moves away slowly by capillary

force. This is also similar to how water content at the cathode decreases slowly when the voltage is decreased.

Figure 5 shows the relationship between the various phases of water at both membrane anode and cathode interfaces. In all the cases considered, we only saw liquid water at the cathode side of the membrane. At the anode side, where there is no liquid water, the water content and the vapor pressure follows a similar trend. When the voltage is increased, they both increase rapidly to the peak values and then decrease slightly before reaching the steady state. Also, when the voltage is decreased, both the water content and the vapor pressure decrease rapidly until they reach minimum values, after which they both increase slightly before reaching the steady state. However, at the cathode side where there is liquid water, vapor pressure decreases instantaneously when the voltage is increased while the water content and the liquid water saturation decrease rapidly at first and then slowly until the steady state is reached. When the voltage is increased, the vapor pressure at the cathode side increases slowly after the initial overshoot. Unlike vapor pressure, the water content and the saturation at the cathode side do not show any overshoot. Also, because there is liquid at the CCL, the absorption and desorption of water in the membrane phase is determined by the fraction of the pores in the CCL that is filled with liquid water as vapor pressure is already saturated. It can therefore be said that how quickly liquid water in the CL pores is removed determined how fast the water content and hence the ionic resistance in the membrane reaches steady state.

Figure 5. Comparison of various water phases at membrane interface

The Effects of Different CL Capillary Pressure

We choose as our base case CL capillary pressure to be 1.3 of GDL capillary pressure for both secondary injection and primary withdrawal. In this section, we study the effects of different CL capillary pressure. We consider three cases: when CL capillary pressure is 1.3 of GDL capillary pressure (CL is more hydrophobic during injection but more hydrophilic during withdrawal), when CL capillary pressure is equal to the GDL capillary pressure (CL has the same hydrophobicity as GDL during both injection and withdrawal) and when CL capillary pressure is 0.8 of GDL capillary pressure (CL is more hydrophilic during injection but more hydrophobic during withdrawal).

Figure 6. Comparison of ionic resistance, water content and saturation for different CL capillary pressure

Figure 6 shows the ionic resistance in the membrane, the water content at both anode and cathode interfaces of the membrane and the saturation at the cathode interface of the membrane for the three cases of CL capillary pressure considered. The ionic resistance R is computed as:

$$R = \frac{\Delta\phi_2}{I_2} \quad [2]$$

where $\Delta\phi_2$ and I_2 are the potential drop and the ionic current density in the membrane respectively. It can be seen from figure 6 that the ionic resistance when CL capillary pressure is 1.3 of GDL capillary pressure is the highest, followed by when CL capillary pressure is equal to the GDL capillary pressure. The case when CL capillary pressure is 0.8 of GDL capillary pressure has the least ionic resistance. The effects of hydrophobicity of CL seem to be more pronounced during injection. The change in the water content and in the liquid water saturation is very small during withdrawal compared to that of injection. The case when CL is more hydrophilic during injection has more water content, more liquid water saturation and lowest ionic resistance. In all the three cases, the time scale for membrane hydration is smaller than that of membrane dehydration. As mentioned earlier, it is important that more research work be done to determine how CL behaves during liquid water imbibition and withdrawal and also to determine a precise relationship between CL capillary pressure and liquid water saturation.

From figure 6, as the hydrophobicity of CL increases during injection, the liquid water saturation in the CL pores goes down at the expense of increased ionic resistance in the membrane. It is therefore desirable that an optimum amount of hydrophobic material, such as, PTFE be added to CL, as suggested by [5], to reduce the liquid water saturation in the CL while the ionic resistance in the membrane is still moderately low.

The Effects of Different Load Changes

Figure 7. The effects of different load changes

To study how the proton exchange membrane responds to different load changes, we change the cell voltage from 0.8 to various lower values. Figure 7 shows the comparison of the ionic resistance in the membrane, water content and liquid water saturation at the membrane interface for the various cases considered. We first step the voltage up to 0.8V and then down to 0.6V, 0.5V, 0.4V, 0.3V and finally 0.2V. As we increase the voltage to 0.8V, the water content at the anode side of the membrane increases as a result of reduced electro-osmotic drag and increased back-diffusion from cathode side while the water content and the liquid water saturation at the cathode side of the membrane decreases because less water is drag from the anode and less water is generated by the ORR. The ionic resistance in the membrane increases when voltage is increased to 0.8V because the average water content in the membrane goes down. When voltage is stepped down from 0.8V to 0.6V, the ionic resistance in the membrane decreases because more water is generated at the cathode side and the increase in electro-osmotic

drag effect is not sufficient enough to cause the water content at the anode side to go down to a very low value. Likewise, when the voltage is stepped down from 0.8V to 0.5V, the ionic resistance decreases to a much lower value compared to when the voltage is decreased from 0.8V to 0.6V. This is because the average water content in the membrane goes up when the voltage is stepped down to 0.5V compared to when it is stepped down to 0.6V and at the same time, the water content at the anode side is still moderately high, 7.83.

When the voltage is stepped down from 0.8V to 0.4V, the ionic resistance still decreases but to a higher value compared to when the voltage is stepped down from 0.8V to 0.5V. Even though more water is generated at the cathode side when the voltage is stepped down to 0.4V compared to when it is stepped to 0.5V, the water content at the anode side has gone down considerably, to a value of 7.0, as a result of increased electro-osmotic drag. The lower water content at the anode side increases the average ionic resistance in the membrane. Similarly, when the voltage is stepped down to 0.3V, the ionic resistance only decreases slightly after initial overshoot. The overshoot is because it takes some time for the back-diffusion from cathode to balance the electro-osmotic drag effect while the slight decrease in ionic resistance after the overshoot is due to the fact that diffusion effect now dominates that of electro-osmotic drag. Finally, when the voltage is stepped down to 0.2V, the ionic resistance goes up with an initial shoot. This is because the water content at the anode has gone to a very low value, 4.8. The increased ionic resistance at the anode resulted from such low a value of water content causes the average ionic resistance in the bulk membrane to go up. The phenomenon is called 'anode dry-out'. Besides the anode dry-out effect at very high voltage, the liquid water saturation value at the cathode CL increases considerably, to 0.55 when the voltage is stepped down to 0.2V. The increased liquid water saturation reduces the path available for the transport of reactant gases and leads to a significant concentration overpotential loss.

The effects of different saturation at gas channel and cathode GDL interface

The boundary condition at the gas channel/GDL interface depends on GDL pore sizes and shape, GDL permeability and flow condition in the gas channel. For simplification purpose, we choose the liquid water saturation at the gas channel/GDL interface to be a constant value, s_0 . In this section, we examine how choosing different saturation value at the gas channel/GDL interface affects the saturation in the CCL, the water content and hence the ionic resistance in the membrane. The s_0 at the anode gas channel/GDL is kept at zero value while we vary the value of s_0 at cathode gas channel/GDL.

From figure 8, we see that increasing the value of s_0 at cathode gas channel/cathode GDL interface increases the lowest steady state value of saturation in the CCL when voltage is stepped up. However, when voltage is stepped down, the amount of liquid water in the CCL seems not to be affected by the value of s_0 . It therefore seems that increasing the value of s_0 only increases the amount of liquid water retained in the CL and GDL after most of the liquid water formed has been removed by capillary forces. It should be mentioned that we only consider cases where the value of s_0 is very small, i.e., $s_0 < 0.08$. Liu et al., in their steady state work, [18] saw that a higher value of s_0 has more profound effect on the level of saturation in the CL.

The effect of different value of s_0 on water content is similar to that of saturation,

especially at the cathode side of the membrane where liquid water is formed. As more liquid water is retained in the CL and GDL, amount of water absorbed by the membrane increases so that the lowest steady state value of water content in the membrane goes up. Because the average lowest steady state value of water content in the membrane increases, the highest value of ionic resistance in the membrane goes down.

Figure 8. The effect of different value of saturation at CGDL/CGC interface

The Effects of Cathode Side Relative Humidity

In this section, we look at cases where the cathode inlet gas is not fully saturated. For comparison, we also include the case when the cathode inlet gas is fully saturated. Zero saturation is chosen for both anode and cathode side of gas channel interface. The voltage is stepped up from 0.4V to 0.8V and then back to 0.4V. No liquid water is seen at the CCL when the relative humidity is 0.8, 0.7 and 0.6. Figure 9 shows the ionic resistance in the membrane and the water content at the cathode side of the membrane. Also shown in figure 9 are a combined plot of the water content and the vapor pressure for partially saturated cathode inlet conditions and a combined plot of the water content and the saturation for fully saturated cathode inlet condition at the cathode side of the membrane.

From figure 9, the time constant for membrane hydration and dehydration for fully saturated cathode inlet condition is longer than those of partially saturated cathode inlet conditions. As shown in figure 5, the liquid water saturation and the water content at the cathode interface of the membrane vary in a similar fashion while vapor pressure decreases instantaneously when the voltage is stepped up and shows an overshoot when the voltage is stepped down. However, for partially saturated cathode inlet condition, where there is no liquid water at the CCL, the vapor pressure at the cathode interface of the membrane varies in a similar fashion to the water content at the same interface.

Figure 9. The effects of different cathode side relative humidity

As mentioned earlier, when there is liquid at the CCL, the absorption and desorption of water in the membrane phase is determined by the fraction of the pores in the CCL that is filled with liquid water as vapor pressure is already saturated. However, when there is no liquid water in the CCL, the absorption and desorption of water in the membrane is determined by vapor pressure in contact with the membrane. Figure 9 shows that the vapor pressure at cathode side of the membrane partially saturated inlet condition has smaller time constant compared to that of the liquid water saturation at the cathode side of the membrane for fully saturated cathode inlet condition. Since the vapor pressure in contact with the membrane for partially saturated cathode inlet condition reaches steady state faster than the liquid water in the CCL for fully saturated cathode inlet condition, the time for membrane hydration and dehydration for fully saturated

cathode inlet condition is longer than those of membrane hydration and dehydration for partially saturated cathode inlet condition.

The comparison of the cases when the cathode reactant gas is not fully saturated shows that the time it takes the water content and hence the ionic resistance in the membrane to reach steady state increases as the relative humidity decreases when the voltage is stepped up. However, when the voltage is stepped down, the ionic resistance decreases rather rapidly in all the cases considered. As the water content in the membrane decreases, the time for water to diffuse across the membrane increases because the water in the membrane becomes more bound to the sulfonic acid group at the water content decreases [19]. The increase in diffusion time as water content in the membrane decreases accounts for the increase in time constant as the cathode relative humidity decreases.

The Effects of Total Gas Pressure

Figure 10. The effects of different total gas pressure

It is well known that the performance of fuel cell increases as the total gas pressure increases. Obviously, when the total gas pressure is increased, the partial pressure of reactant gases increases and according to Nernst Equation, the equilibrium potential increases [20]. The exchange current density also increases as partial pressure of the reactant gases increases. In this

section, we examine how increase in total gas pressure affects the saturation in the CCL, water content and hence ionic resistance in the membrane.

From figure 10, as the pressure increases from 1bar to 2bar, the water content at the anode side of the membrane decreases while the water content and the saturation at the cathode side goes up. The reaction rate increases as the pressure increase, thus more water is moved from anode to cathode by electro-osmotic drag and more is also generated at the cathode by ORR. On the average, the water content in the membrane goes up when the pressure is increased from 1bar to 2bar and thus the decrease in the ionic resistance in the membrane. As seen also in figure 10, the liquid water saturation in the CCL increases as the pressure increases. Even though the ionic resistance in the membrane decreases, increase in pressure can lead more pores in the CCL being blocked by the liquid water thereby preventing the reactant gas from reaching the reaction sites in the CCL.

Conclusion

A 1-D two-phase transient model that incorporates the permanent hysteresis observed in the experimentally measured capillary pressure of the gas diffusion media has been developed. The model shows that when there is liquid water at the CCL, because vapor is already saturated, the time constant of water content in the membrane is closely tied to that of liquid water saturation in the CCL. Both the profiles of water content and the liquid water saturation at cathode side interface of the membrane show similar trend when voltage is stepped up and down while vapor pressure drops instantaneously when the voltage is stepped up. As long as the liquid flows in the CCL is not at steady state, the water content in the CCL and hence in the membrane will continue to change. Thus, water content in the membrane will not reach steady state until the liquid water saturation reaches steady state. We also observe that the water content at the electrode sides reaches steady state faster than the water content in the membrane. The difference in the steady state time between the water content in the electrode sides and that in the bulk membrane is ascribed to the time constant for water to diffuse across the membrane.

When there is no liquid water in the CCL, the water content profile in the CCL follows that of vapor pressure in the CCL. Also, the vapor pressure in the CCL reaches steady state faster when there is no liquid water in the CCL than the liquid water saturation in the CCL when there is liquid water in the CCL. As the absorption and desorption of water content in the membrane is determined by vapor pressure in the electrode sides when there is no liquid water while the absorption and desorption of water content in the membrane is determined by liquid water saturation when there is liquid water in the CCL, the time constant for water content in the membrane is longer when there is liquid water compared to when there is no liquid water.

The model also shows that ionic resistance in the membrane increases when the cell voltage is stepped down to a very low value, like 0.2V. This phenomenon is known as “anode dry-out”. In addition, when the gas pressure is increased, more water is dragged from anode and more water is produced by ORR at the cathode because reaction rate increases. The increased liquid water saturation in the CCL caused by the increase in gas pressure can lead to significant concentration overpotential loss.

Appendix A

The polynomials fitted to the experimentally measured capillary pressure of compressed Toray 120C by Gostick *et al.*[2] are as follows:

Secondary injection: Compressed Toray 120C

$$p_c = -6.815853557x + 9476.607940x^4 + 114.8427251x^2 - 1245.668744x^3 - 53235.90920x^5 \\ + 2.278741162e5x^6 - 7.579214265e5x^7 + 1.981630094e6x^8 - 4.094976567e6x^9 + 6.688276451e6x^{10} \\ - 8.586342162e6x^{11} + 8.560416009e6x^{12} - 6.490861587e6x^{13} + 3.616006831e6x^{14} \\ - 1.395166990e6x^{15} + 3.329950426e5x^{16} - 37033.19125x^{17} + .1306720762$$

Primary withdrawal: Compressed Toray 120C

$$p_c = -11.21390501x + 15417.52950x^4 + 190.4837207x^2 - 2051.851672x^3 - 85246.91137x^5 \\ + 3.582225366e5x^6 - 1.167147588e6x^7 + 2.983554838e6x^8 - 6.017345300e6x^9 + 9.576060837e6x^{10} \\ - 1.195942393e7x^{11} + 1.158145141e7x^{12} - 8.517175868e6x^{13} + 4.595434584e6x^{14} \\ - 1.714842892e6x^{15} + 3.953203277e5x^{16} - 42407.35124x^{17} + .3824473506$$

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