

Mathematical Modeling of Water Management in PEM Fuel Cells

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ABSTRACT

The efficient operation of polymer electrolyte fuel cells requires effective management of gas, ion, and liquid transport. The catalyst layer forms an interface between the polymer electrolyte and the gas diffusion backing which is a crucial nexus for reaction and transport. The dynamics in this region are controlled by nano-scale factors of wettability, pore size, and water uptake. We outline a model of heat and mass transport which displays the crucial role of these interface kinetics in the overall fuel cell performance.

Keywords: PEM fuel cell, two-phase flow, interface kinetics

1 Introduction

Water management is central to the effective operation of polymer electrolyte (PEM) fuel cells. The accurate modeling of liquid water transport requires understanding of all aspects of the complicated fuel cell environment, in particular the heat and mass exchange which occurs at the catalyst interfaces between the gas diffusion electrodes and the PEM. The treatment of these interface regions with a hydrophobic catalyst ink is essential to efficient fuel cell operation, but renders them very complicated to model mathematically. We will argue that the *non-equilibrium* kinetic interface conditions (Butler-Volmer equation, water uptake by membrane, dissolution of O_2 into membrane) are dominant factors in fuel cell operation. These non-equilibrium kinetics are very sensitive to the nano-scale composition of the catalyst ink and of the membrane and its pores, in particular on surface wettability and pore size, which in turn are sensitive to the presence of liquid water. Water transport within the polymer electrolyte membrane (PEM) is governed by nano-pores and ion concentrations, and is subjected to concentration gradients, capillary pressure, and electro-osmotic drag which determine water transport in the bulk of the PEM. While the proper modeling of these bulk forces is hotly debated, there is even less known about the kinetic interface conditions which govern the water up-take into the PEM, and of water release from the PEM to the surrounding catalyst and gas-diffusion layers.

For brevity we present a model of the cathode gas diffusion layer (GDL) and the PEM only, focusing on two-phase flow and interface kinetics.

2 Cathode GDL Model

The unknowns are C_1, C_2, C_3 , the molar concentrations of oxygen, water vapor, and nitrogen, T the temperature, and β the liquid water volume fraction. The molar concentrations are related to densities $\rho_k = M_k C_k$ where M_k is a constant molar mass of the k 'th species. The mixture density, ρ is then given by

$$\rho = \sum_{k=1}^3 \rho_k = \sum_{k=1}^3 M_k C_k. \quad (1)$$

We will eliminate the molar concentration of nitrogen, C_3 , in favor of the mixture density ρ . Conservation of mass and energy takes the following form

$$\frac{\partial}{\partial t}((1 - \beta)\rho) + \nabla \cdot (\rho U_g) = -M_2 \Gamma, \quad (2)$$

$$\frac{\partial}{\partial t}(\alpha C_1) + \nabla \cdot (C_1 U_g + J_1) = 0, \quad (3)$$

$$\frac{\partial}{\partial t}(\alpha C_2) + \nabla \cdot (C_2 U_g + J_2) = -\Gamma \quad (4)$$

$$\frac{\partial}{\partial t}(\beta) + \nabla \cdot (\beta U_l) = \Gamma / C_l \quad (5)$$

$$\frac{\partial}{\partial t}(\tilde{\rho} c T) + \nabla \cdot (\tilde{\rho} c \tilde{U} T - \tilde{\kappa} \nabla T) = h_{lg} \Gamma, \quad (6)$$

where C_l is the molar density of liquid water, U_g and U_l are the gas and liquid velocities respectively, Γ is the condensation rate, h_{lg} is the heat of vaporization, and the averaged quantities are computed as

$$\tilde{f} = (1 - \epsilon) f|_{\text{solid}} + \epsilon(1 - \beta) f|_{\text{gas}} + \epsilon \beta f|_{\text{liquid}}$$

The quantities J_k denote the diffusive fluxes associated to gradients in densities, while the total flux $N_k = C_k U_g + J_k$ contains the contribution to the flux arising from the gas velocity U_g . The diffusive fluxes are computed from the Maxwell-Stefan equations, see equations (4-5) of [4]. We have as well the constitutive relations. Namely the ideal gas law

$$P_g = C R T, \quad (7)$$

and Darcy's law for the gas

$$U_g = - \frac{K k_{rg}(\beta)}{\mu_g} \nabla P_g, \quad (8)$$

and the liquid

$$U_g = -\frac{K k_{rl}(\beta)}{\mu_l} \nabla P_l, \quad (9)$$

phase, where the gas and liquid relative permeabilities are given by $k_{rg}(\beta) = (1 - \beta)^3$ and $k_{rl} = \beta^3$ where the reduced water saturation is given in terms of the immobile water fraction β_* as $\beta = \frac{\beta - \beta_*}{1 - \beta_*}$. The liquid pressure P_l is related to the gas pressure P_g by the capillary pressure, $P_c = P_l - P_g$ which models the wettability of the pores of the gas diffusion electrode

$$P_c = \gamma |\cos \theta| (\epsilon/K)^{\frac{1}{2}} \mathcal{J}(\beta). \quad (10)$$

Here γ is the surface tension, θ is the contact angle, and for the capillary function J we take the van Genuchten function [6]

$$J(\beta) = \begin{cases} b \left(\tilde{\beta}^{-1/a_2} - 1 \right)^{1/a_1}, & \beta_* < \beta \\ 0, & 0 \leq \beta < \beta_* \end{cases}, \quad (11)$$

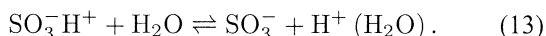
where $a_2 = 1 - 1/a_1$ and typical values are $b = 5$ and $a_1 = 10$. We complete these equations by specifying the condensation rate Γ as a function of the oversaturation

$$\Gamma = \begin{cases} H_0^+ (1 - \beta) (C_2 - C_{\text{sat}}(T)), & C_2 \geq C_{\text{sat}}(T), \\ H_0^- (\beta (C_2 - C_{\text{sat}}(T))), & C_2 \leq C_{\text{sat}}(T), \end{cases} \quad (12)$$

where the saturation concentration of water is given in terms of the saturation pressure P_{sat} by $C_{\text{sat}} = P_{\text{sat}} \mathcal{R}T$.

3 The Polymer Electrolyte Membrane

The main feature of a proton exchange membrane is the equilibrium between the local water content, the protons bound to the fixed charge (acid) groups, and the mobile protons dissolved in the water, which form complexes with surrounding water molecules. The ion exchange equilibrium arises from the reaction



We suppose that the reaction (13) reaches equilibrium on the time scales of interest in a fuel cell [3]. In this case the concentration of bound protons $c_b = [\text{SO}_3\text{H}]/a$ as normalized by the acid weight, $a = [\text{SO}_3] + [\text{SO}_3\text{H}]$, is determined by the hydronium concentration $c_+ = [\text{H}_3\text{O}^+]/a$ and the local free water content, $c_w = [\text{H}_2\text{O}]/a$

$$c_b c_w K_e(T) = c_+ (1 - c_b), \quad (14)$$

where the equilibrium constant depends sensitively on temperature

$$K_e(T) = K_0 \exp \left[-\frac{H_0}{\mathcal{R}} \left(\frac{1}{T} - \frac{1}{298} \right) \right]. \quad (15)$$

Under the assumption of local electro-neutrality (LEN) we have the relation

$$1 - c_b - c_+ = 0, \quad (16)$$

which together with (14) relates the ion concentration to the water concentration and temperature

$$c_+(c_w, T) = -\frac{K_e c_w}{2} + \sqrt{\left(\frac{K_e c_w}{2} \right)^2 + K_e c_w}, \quad (17)$$

The membrane total water content determines the free water, the bound water and the hydronium concentration at given temperature.

The transport equations in the membrane are determined by a dusty-gas model based upon the Maxwell-Stefan equations for the flux. Due to the low permeability of the membrane we will neglect pressure gradients, and in particular capillary pressure. The fluxes of free water and hydronium are governed by the Poisson-Nernst-Planck equations. The electro-osmotic drag term is incorporated in the assumption that only hydronium and free water are present in the membrane and that any frictional effects between the two are negligible. Effectively, this yields a drag coefficient of $N = 1$ and the following equations for the hydronium and free water flux

$$\div \cdot \left(-D_+ \nabla c_+ - \frac{F}{\mathcal{R}T} D_+ c_+ \nabla \phi \right) = 0, \quad (18)$$

$$\div \cdot (-D_w \nabla c_w) = 0. \quad (19)$$

The diffusion coefficients

$$D_+(c_w, T) = 1.6 \cdot 10^{-8} \exp(-1683/T) \left(\frac{c_w}{a} \right) \quad (20)$$

$$D_w(c_w, T) = 2.1 \cdot 10^{-7} \exp(-2436/T) \left(\frac{c_w}{a} \right) \quad (21)$$

are assumed to increase linearly in the water content, reflecting in a very simplified manner the water-ion interaction within the membrane nano-pores as well as the change of membrane morphology and pore structure under water uptake. Since c_w and c_+ are correlated as shown above, (18) and (19) constitute two equations for the membrane potential ϕ and the free water concentration c_w .

4 Interface Conditions

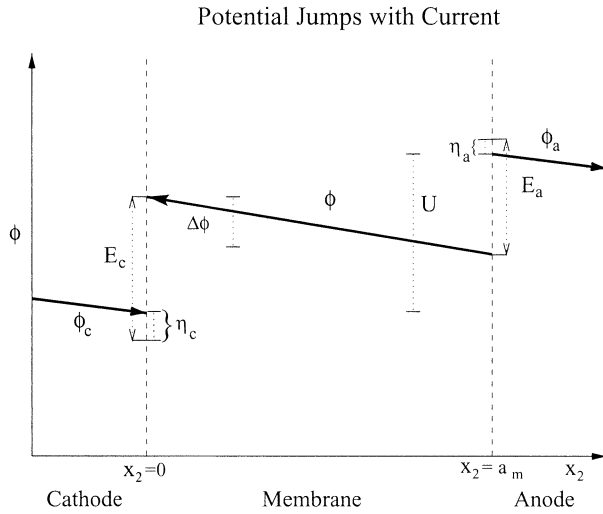
A fundamental role is played by the interface conditions which describe the non-equilibrium exchange of mass and energy between the gas-diffusion electrode and the polymer electrolyte membrane. The exchange occurs over the catalyst layer, which we take to be vanishingly thin.

4.1 Electro-chemistry

We treat the catalyst layer as an interface where the current generating reaction takes place, as modeled by the Butler-Volmer equations

$$I = \frac{i_{o,c}}{F} \left(\frac{c_O}{c_{O,\text{ref}}} \right)^{e_c} \left[\exp \left(\frac{\alpha_c F}{\mathcal{R}T} \eta_c \right) - \exp \left(-\frac{\alpha_a F}{\mathcal{R}T} \eta_c \right) \right] \quad (22)$$

Assuming first order reactions, we take $e_c = 1$. These equations permit one to define the cathode over-potentials η_c as a function of the current, I , which is related to the proton flux $I = J_+/F$.



Graph of the potential ϕ as a function of position x_2 through the MEA. The equilibrium jump in potential at the boundary layers are given by the half-electrode potentials, E_a and E_c respectively. When current is drawn, the jumps are reduced by the over-potentials η_a and η_c . The useful potential is given by $U = E_o - \eta_c - \eta_a - \Delta\phi$, where the last term describes the resistive losses in the membrane.

The boundary layers in the potential at the catalyst layer are modeled as jump discontinuities. In the remainder of the domain we have continuous potentials ϕ_c in the electrically conductive region of the cathode and ϕ in the membrane. The open-circuit half-reaction potentials E_c and E_a are related to the double layer of charge formed at the catalyst surface when the electrode is supplied a reference amount of reactant and no current is drawn. The overpotentials are kinematic conditions describing the response of the potential when electric current is drawn (reducing the double layer) and the reactant is consumed. Boundary conditions for the membrane potential ϕ , take the form

$$\phi(x_1, x_2 = 0^+, x_3) = E_c - \eta_c, \quad (23)$$

$$\phi(x_1, x_2 = a_m^-, x_3) = U - E_a + \eta_a. \quad (24)$$

The value of U is the “driving force” for the fuel cell model, which stimulates consumption of reactants and generates current. Prescribing $U = 0$ yields homogeneous solutions. Prescribing the voltage is a simplifying step, since our reduced model does not include an electrical connection between the cathode and anode.

4.2 Mass flux

In the cathode, the reaction stoichiometry prescribes an oxygen flux out of the cathode GDL equal to one-fourth the electric current,

$$N_1 \cdot \vec{n} = -\frac{I \cdot \vec{n}}{4F}. \quad (25)$$

Since there is no consumption of nitrogen in the catalyst layer we have the no-flux boundary condition

$$N_3 \cdot \vec{n} = 0. \quad (26)$$

The flux of water from the cathode GDL into the membrane at the cathode catalyst is dependent upon water production and the hydration level of the membrane. The equilibrium total water content of Nafion 117 membrane in contact with water vapor was found to fit the form, [7],

$$c_w^*(r) = 0.043 + 17.81r - 39.85r^2 + 36.0r^3, \quad (27)$$

where the relative humidity r , in the GDL is given by

$$r = \frac{P_v}{P_{\text{sat}}(T)}, \quad (28)$$

and $P_v = C_2 \mathcal{R}T$ is the partial pressure of the vapor at the catalyst interface and $P_{\text{sat}}(T)$ the saturation pressure of water in the GDL as a function of temperature. However, if the membrane is exposed to liquid water, then the equilibrium value jumps to $c_m = 22.8$, an effect sometimes referred to as the Schroeder paradox [3].

The appropriate boundary condition for water at the interface is a kinetic condition which describes the dynamic restoration of equilibrium in the face of water production and flux. Experiments show that the time scale on which the membrane assumes this equilibrium value c_w^* is compatible with the time scale on which water is produced in the catalyst layer and carried away from the catalyst layer by electro-osmotic drag and diffusion within the membrane [1]. We assume a first order relaxation and take a Robin condition for the water flux between the cathode GDL and the membrane,

$$N_2 \cdot \vec{n} = \gamma(c_w - c_w^*(r)), \quad (29)$$

where c_w is the total membrane water content. Comparison with water-uptake data for membranes leads us to a value of $\gamma = 10^{-4} \text{ m/s}$. If the dimensionless membrane water content approaches the maximum value c_m , then the incompressibility of the membrane implies that water pressure can no-longer be neglected and any further water produced will be forced out into the channel. This could be modeled by a $\gamma = \gamma(c_w)$ which changes dramatically at $c_w \approx c_m$. Moreover, if the membrane is exposed to liquid water then the equilibrium value will also behave non-smoothly.

On the cathode side of the membrane, the flux of water N_w is then given by

$$N_w \cdot \vec{n} = -\gamma(c_w - c_w^*(r)) - \frac{3I \cdot \vec{n}}{2F}, \quad (30)$$

where we balance water production against the water exchange with the GDL. The normal \vec{n} points from anode to cathode.

Note that our boundary conditions implicitly assume all the water which enters or leaves the gas diffusion electrode does so in a vapor state. Indeed it is difficult to predict the state in which water which leaves the membrane, however phase change is permitted in the gas diffusion electrode, and the water is free to assume its thermodynamically appropriate state.

A boundary layer also exists in the mole fractions between the air phase in the gas diffusion layer and the liquid phase in the membrane. This is most important for the oxygen concentration, which enters into the Butler-Volmer equations for the over-potential. The thermo-dynamic relation, called Henry's law [5] is given by

$$c_o^* = \frac{\mathcal{R}T}{H} C_1$$

where c_o^* is the equilibrium concentration of oxygen in water given a gas oxygen concentration of C_1 . Henry's constant, H is approximately $2 \times 10^5 \text{ atm cm}^3/\text{mol}$. However the proper boundary condition for the oxygen concentration in the membrane is a kinetic one, relating the interface concentration to the rate of oxygen consumption,

$$\gamma_H(c_O - c_o^*) = \frac{I \cdot \vec{n}}{4F}, \quad (31)$$

where the relaxation function γ_H must be determined experimentally.

4.3 Heat Flux conditions

Finally, we must prescribe the temperature BCs. We demand that the temperature be continuous across the interface

$$[T] = 0, \quad (32)$$

while the jump in heat fluxes must equal the heat produced

$$[-\kappa \nabla T \cdot \vec{n}] = \dot{q}, \quad (33)$$

where the thermal conductivity κ is different in the membrane and the GDL. At the catalyst GDL the heat production is given by

$$\dot{q} = \left(\frac{Th_{rc}}{4F} + \eta_c \right) I_c - h_{lg} \gamma(c_T - c_T^*(r)). \quad (34)$$

We take the heat of reaction above as $h_{rc} = 326 \text{ J}/(\text{mole } K)$, see [2]. For comparison, with a temperature of $T = 300 \text{ K}$, then $Th_{rc}/(4F) = 0.25 \text{ Volts}$, while the over potential η_c is often measured in tens of mille-Volts. The process of water transfer between the GDL and the membrane is taken to include phase change. This is reflected by the last term on the right-hand side of the heat production equation, where h_{lg} is the heat of vaporization of liquid water.

5 Results

This talk addresses the mathematical features of the model presented. In particular we will show that the interface kinetics parameters, γ , γ_H , and the exchange current $i_{o,c}$ of the Butler Volmer equations dominate the dynamics of the fuel cell. An accurate estimation of these parameters is central to fuel cell device modeling.

We also consider the limit $H_0^\pm \rightarrow \infty$ in the mass transport equations (2-6) for the gas diffusion layer. In this scaling of the equations the water concentration C_2 becomes slaved to the saturation concentration

$$C_2 = C_{\text{sat}}(t) + O(1/H_0), \quad (35)$$

while equation (4) becomes an equation for Γ . Moreover the phase change term $h_{lg}\Gamma$ scales out of the temperature equation (6) but plays a leading order role in (2). Most importantly, liquid water equation (5) rescales to a much slower time evolution $\tau \approx t/1000$, so that the remainder of the equations (2-4), (6), and the equations of the membrane, can be taken to be driven adiabatically at their $\beta(\tau)$ dependent quasi-steady states. This affords a significant reduction in computational effort required to reach the liquid phase equilibrium dynamics, which occur on the order of hours.

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