Dynamic Operation of a 1.2 kW PEM Fuel Cell

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Abstract:

In this work, we derive a simple dynamic model for a 1.2 kW polymer electrolyte membrane (PEM) fuel cell stack and compare the model results to the operation of a real 1.2 kW cell stack. This dynamic model expands upon previous work done by our group [1] by including component balances, and considerations for water, oxygen, and nitrogen. We first develop a mathematical model that captures the characteristics of a single PEM fuel cell, and then generalize this model to capture the behavior of the entire stack. We choose to model this single cell by two linked continuously stirred tank reactor (CSTR) chambers separated by a proton exchange membrane which allows for charge and mass transfer. The model is coupled to dynamic mass and energy balances that quantify the transport of hydrogen, nitrogen, and water components.

Introduction:

PEM fuel cells are receiving national interest due to their promising applications in both mobile (automotive) and stationary distributed power generation. This environmentally friendly new technology converts the chemical energy of hydrogen and oxygen into electrical energy, water, and heat at high thermodynamic efficiencies. The processes that take place in these cells are complicated and include chemical kinetic, thermodynamic, and transport processes in up to three different phases. By modeling PEM fuel cells mathematically we can get useful insight into possible methods for increased performance.

Many cells can use pure oxygen as their oxidant feed, but for most uses (including automotive and distributed power generation) it is often impractical to use pure oxygen as the oxidant and instead air is used. The use of air introduces inerts (mostly nitrogen) into the system, which creates a concentration difference across the cell. It now becomes possible for these impurities to diffuse through the PEM from the cathode to the anode side. Since there is no outlet on the anode side of the stack there is an accumulation of impurities over time. This accumulation causes a drop in the partial pressure of hydrogen on the anode side and thus reduces the voltage output from a cell. In a typical commercial fuel cell stack these impurities are concentrated in the last cell, usually called a "purge cell."

Our goal is to create a dynamic model for a PEM fuel cell stack that takes into account this counter-diffusion of impurities and the resulting voltage drop. The model results will then be compared to experiments on a Ballard® Nexa Power Module fuel cell to determine the accuracy of the model.

Experimental:

The PEM fuel cell stack used to test our model is a Ballard® Nexa Power Module (310-0027 firmware revision 00.03.01) with NexaMon® OEM 2.0 software for monitoring and control. This fuel cell stack is rated to supply up to 1200 W of unregulated net DC power with an output voltage of 26 V (the stack is capable of higher power output but power is consumed in the parasitic loads associated with the fuel cell (fans, control, etc.)) The fuel supply to the cell is dry, ultra high purity hydrogen (99.999%) and the cathode feed is ambient air supplied by a fan. In order to simulate different load resistances, 5,10,25,50,100 Ω power resistors from Ohmite® wired in parallel were used. All cells in the stack are connected electrically in series. The NexaMon® software outputs real-time data for the cell (cell voltage, current, purge cell voltage, air flow rate, etc.) at less than one second intervals. We used an Omega FMA 1824 flow meter to measure the exact amount of Hydrogen fed to the cell stack and to test the current efficiency of the cell (current produced per mole of Hydrogen fed.)

The membrane in the Nexa Power Module was assumed to be similar to Nafion 117 and thus parameters for this material from the literature were used. Several other properties of the fuel cell could not be obtained due to proprietary reasons, and were estimated using data from the literature.

When the voltage output from the last two cells in the stack drops to 90% of the average cell voltage the last two cells are quickly vented with excess Hydrogen to purge the impurities from the system; this is the behavior we are trying to capture in our model.

Cell Model:

The following assumptions were used in the formulation of our model: first, that the membrane is completely hydrated (due to the self-hydrating operation of the cell). Activation overpotentials were taken into account on both the anode and cathode side, as well as a resistive overpotential. The concentration overpotentials were ignored for several reasons; the partial pressures of both oxygen and hydrogen are relatively high in the cathode and anode respectively. Also the diffusion of hydrogen is very fast so no concentration difference occurs on the anode side.

The total mole balance on the anode side of the fuel cell is:

$$(1) \qquad F_i^{in} = F_i^{out} + N_{H_2,i}A_i - N_{N_2,i}A_i - N_{H_2O,i}A_i$$

where F_i^{in} is the total molar flow fed to the ith cell, F_i^{out} is the total molar flow out of the ith cell, and $N_{H_2,i}$, $N_{N_2,i}$, $N_{H_2O,i}$ are the molar fluxes of hydrogen, nitrogen, and water out, in, and in the ith cell's anode side, respectively. A_i is the cross-sectional area of the ith cell. This balance must hold for every cell at every moment in time.

The component mole balances on the anode side of the fuel cell are:

$$(2) \qquad \frac{P^a V_i}{RT}\frac{dy_{H_2,i}^{out}}{dt} = y_{H_2,i}^{in}F_i^{in} - y_{H_2,i}^{out}F_i^{out} - N_{H_2,i}A_i - 2N_{O_2}A_i$$

$$(3) \qquad \frac{P^a V_i}{RT}\frac{dy^{out}_{N_2,i}}{dt} = y^{in}_{N_2,i}F^{in}_i - y^{out}_{N_2,i}F^{out}_i + N_{N_2,i}A_i$$

$$(4) \qquad \frac{P^a V_i}{RT}\frac{dy^{out}_{H_2O,i}}{dt} = y^{in}_{H_2O,i}F^{in}_i - y^{out}_{H_2O,i}F^{out}_i + N_{H_2O,i}A_i + 2N_{O_2}A_i$$

for hydrogen, nitrogen, and water respectively; y^{out}_X is the mole fraction of component X in the cell (and therefore also at the cell's outlet), y^{in}_X is the mole fraction of component X in the cell inlet, P^a is the total pressure in the anode, V_i is the total volume of the anode for the ith cell, R is the universal gas constant, and T is the temperature. No component balance is performed on oxygen because the feed is assumed to be oxygen-free and any oxygen that diffuses through the membrane to the anode side catalyst layer is assumed to react instantaneously and completely with hydrogen to form water. Each of these balances must be solved simultaneously to give the concentration of impurities at a given moment in time. Once these impurity levels reach a certain threshold, the purge cell must be flooded with Hydrogen to get rid of the impurities and return the cell voltage to the desired level, which is determined through the Nernst relation:

$$(5) \qquad E_i = E^0 - \frac{RT}{zF}\ln\left(\frac{\left(P_{H_2O}\right)^2}{\left(P^*_{H_2,i}\right)^2 P_{O_2}}\right) + \eta_c - \eta_a - iR_{cell}$$

where E^0 is the reference potential adjusted for the temperature using equation (6) as follows:

$$(6) \qquad E^0 = E^0_{298} + \frac{\Delta S}{2F}(T - 298.15)$$

The anode and cathode overpotentials (η_a, η_c) can be calculated using equations (7) and (8) respectively at a given current density.

$$(7) \qquad i = i^0_c\left(e^{\frac{\overleftarrow{\alpha}_c F\eta_c}{RT}} - e^{\frac{-\vec{\alpha}_c F\eta_c}{RT}}\right)$$

$$(8) \qquad i = i^0_a\left(e^{\frac{\overleftarrow{\alpha}_a F\eta_a}{RT}} - e^{\frac{-\vec{\alpha}_a F\eta_a}{RT}}\right)$$

where F is Faraday's constant and $\overleftarrow{a}_a$, $\vec{a}_a$, $\overleftarrow{a}_c$, and $\vec{a}_c$ are transfer coefficients for the cathode and anode respectively. The internal cell resistance is assumed to be a function of the membrane resistivity, ρ_m and its thickness, δ_m:

$$(10) \qquad R_{cell} = \rho_m \delta_m$$

We use the following equations to define the fluxes of each species:

(11) $$N_{H_2,i} = \frac{k_g^H}{RT}\left(y_{H_2,i}^{out}P^a - P_{H_2,i}^*\right)$$

(12) $$N_{O_2} = \frac{k_g^O}{RT}\left(P_{O_2}\right)$$

(13) $$N_{N_2,i} = \frac{k_g^N}{RT}\left(P_{N_2} - y_{N_2,i}^{out}P^a\right)$$

(14) $$N_{H_2O,i} = \frac{k_g^W}{RT}\left(P_{H_2O}^{sat} - y_{H_2O,i}^{out}P^a\right) - \frac{\eta_d I_{tot}}{F}$$

where the mass transfer coefficients k_g^X are calculated from the Sherwood number as follows:

(15) $$Re = \frac{W v^0 \rho}{\mu}$$

(16) $$Sh = 0.128 Re^{0.62}$$

(17) $$k_g^X = \frac{Sh D_X}{W}$$

Solution Method:

The mathematical model is coded in Matlab®; the program first sets the parameters for the fuel cell stack. Next the initial conditions of the stack are set; an explicit Euler discretization allows us to step forward in time solving all variables at each time step. We assume that the anode side operates as a CSTR to simplify the model so that the variables only change with respect to time. The model does not consider concentration changes on the cathode side due to constant fresh feed of excess oxidant (air). A shooting method is employed at each time step to solve for the current density. Comparison of the model prediction with experiment results is carried out.

References:

[1] Chen et al., *AIChE Spring Meeting - Session 14: Fuel Cell System Modeling and Optimization I*; April 2004