A Fully Coupled Three-dimensional Dynamic Model of Polymeric Membranes for Fuel

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Abstract: The proton exchange membrane is a key component in the currently widely studied Proton Exchange Membrane Fuel Cells. In this paper a fully coupled three-dimensional dynamic numerical model of the membrane including all the physically relevant phenomena, i.e. ion transport, hydration-dependent conductivity and thermal effects is presented. The highly non-linear model is discretized by means of the Finite Element Method provided by the COMSOL Multiphysics simulation environment.

Keywords: Fuel Cells, Proton Exchange Membrane, Electrochemistry, Multiphysics.

1. Introduction

Fuel Cells (FCs) are considered a very promising energy source for a number of different applications, ranging from small units for portable electronic devices to mid-size generators for the automotive industry and to large stationary power supply systems. The proton exchange membrane (PEM) is a key component in all so-called Proton Exchange Membrane Fuel Cells (PEMFCs), shown in figure 1. It is the component where most Ohmic losses occur, since ionic conduction is orders of magnitude lower than electron conduction in the anode and cathode current collectors. The presence of the PEM also limits the maximum operational temperature of the FC and presents fuel cross-over effects, which reduce fuel efficiency, increase electrochemical kinetics losses and causes cathode catalyst poisoning. For all these reasons, an accurate modeling of the membrane is needed for studying the overall electrical and physical behavior of real FCs. In this paper a three-dimensional model which includes all the most relevant physical phenomena (ion transport, hydration-dependent conductivity and thermal dependency) is developed and discretized with the help of the Finite Element Method provided by the COMSOL Multiphysics simulation environment.
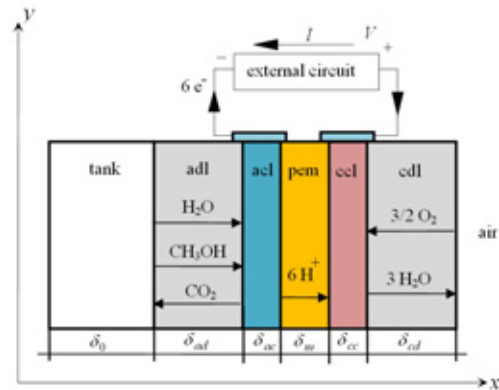

Figure 1. Schematic of a passive μ-DMFC (a=anode, c=cathode, pem=proton exchange membrane, dl=diffusion layer, cl=catalyst layer).

2. Coupled model

A thorough description of the derivation of all equations is beyond the scope if this paper, further details can be found in [1]. All units are S.I. unless otherwise stated.

2.1 Polymeric conductivity model

The polymeric conductivity σ can reach values as high as 20 S/m at 100 °C, but strongly depends on the temperature T and on the membrane hydration λ, which varies from point to point being the ratio between the water concentration c_w and the sulfonic acid concentration c_{sa}=1970 mol/m³, according to the following semi-empirical expression:

$$\sigma(\lambda, T) = (51.93\lambda)e^{\frac{W_a}{k}\left(\frac{1}{303}-\frac{1}{T}\right)} \qquad (1)$$

with W_a the activation energy and k the Boltzmann's constant. In our case $W_a/k = 1268$ K. Measurements show that λ is in the range [0,0.22]. Unfortunately, λ cannot be measured directly at the membrane's surface and therefore must be expressed as a function of more readily measurable quantities. This can be achieved by following empirical relationship:

$$\lambda =
\begin{cases}
4 \cdot 10^{-5} + 0.18a_w - 0.4a_w^2 + 0.4a_w^3 & a_w \in [0,1] \\
0.14 + 1.4(a_w - 1) & a_w \in [1,3]
\end{cases}$$
(2)

where a_w is the relative humidity, i.e. is the ratio between the partial water steam pressure p_w and the saturation value p_{ws} [bar] which depends on the temperature T according to:

$$a_w = \frac{p_w}{10^{(-20+0.11T-2.1\cdot10^{-4}T^2+1.4\cdot10^{-7}T^3)}}$$ (3)

The partial water steam pressure p_w, which can be measured at the membrane interface, is determined at the catalyst layers according to the electrochemical semi-reactions (fuel oxidation at the anode and oxygen reduction at the cathode) and the mass transport in the diffusion layers. The distribution of λ inside the membrane thickness depends on two effects, namely electro-osmotic drag and back-diffusion. The water molar flow due to the former effect can be expressed as:

$$N_{we} = v_w J_{prot} = \frac{v_w J}{F}$$ (4)

where $v_w = r_w = 2.5$ is the electro-osmotic drag coefficient and F is Farady's constant. Based on Fick's first law, water molar flow due to the back-diffusion effect is:

$$N_{wd} = -D_w c_{sa} \nabla \lambda$$ (5)

where D_w is the water diffusivity in the membrane which can be expressed by following semi-empirical expression:

$$D_w(\lambda,T) =$$
$$(2.6 - 33\lambda + 264\lambda^2 - 671\lambda^3)e^{2416\left(\frac{1}{303}-\frac{1}{T}\right)-23}$$
(6)

The total water molar flow N_w across the membrane is therefore:

$$N_w = N_{we} + N_{wd} = \frac{v_w J}{F} - D_w c_{sa} \nabla \lambda$$ (7)

Its dynamic behavior conforms Fick's second law, expressed in terms of λ:

$$\nabla \cdot N_w + c_{sa} \, \partial_t \lambda = 0$$ (8)

that, together with (7), gives the following diffusion equation:

$$\nabla \cdot D_w \nabla \lambda - \partial_t \lambda - \nabla \cdot \frac{v_w}{Fc_{sa}} J = 0$$ (9)

The current density J of (9) is the same one appearing in Maxwell's equations so that, introducing the electric scalar potential V, (9) can be rewritten as:

$$\nabla \cdot D_w(\lambda, T)\nabla \lambda - \partial_t \lambda + \nabla \cdot \frac{v_w}{Fc_{sa}} \sigma(\lambda, T)\nabla V = 0$$
(10)

2.2 Current flow model

The electric scalar potential of (10) must obey the charge conservation equation:

$$\nabla \cdot \sigma(\lambda, T)\nabla V = 0$$ (11)

where the conductivity σ depends upon the temperature and the hydration according to (1). This equation allows to eliminate the last term in (10).

2.3 Thermal model

Since most quantities appearing in the polymeric conductivity model and the current flow model depend on the temperature it is also necessary to solve the transient heat equation

$$\rho c_p \partial_t T - \nabla \cdot k(\lambda)\nabla T - \sigma(\lambda, T)(\nabla V)^2 = 0$$
(12)

where the last term on the left hand side represents the Joule losses. It has been shown in [3] that the thermal conductivity in (12) can be represented by $k = 0.12 + 0.81\lambda$.

3. Use of COMSOL Multiphysics

The complete model to be solved is assembled from (10), (11) and (12) together with nonlinearities (1) and (6) and with appropriate boundary (time-dependent Dirichlet and homogeneous Neumann) and initial conditions. The peculiarities of the set of equations and the

very small thickness of the membrane with respect to its planar extension result in a very badly conditioned system of equations which is one side too large to be handled with a direct solver and on the other hand very difficult to precondition. Furthermore, the kind of nonlinearities in the model are such that the Newton-Raphson algorithm does not converge without strong underrelaxation. All these difficulties make it unadvisable to try and solve the full problem with naïve tools and call for the use of extremely robust nonlinear and linear solvers. Therefore the coupled model has been implemented with the help of the COMSOL Multiphysics environment [4].

4. Results

The coupled model has been used to study a typical laboratory 2cm x 2cm x 200μm membrane. Figure 2 shows the relative magnitude of the electro-osmotic and back-diffusion flows, while figure 3 shows the behavior of the electrical conductivity across the membrane during a 10 minute transient (one line per minute).
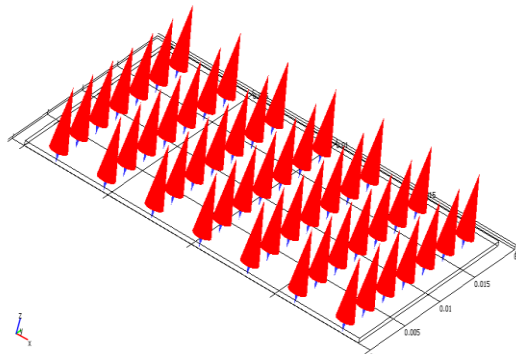

Figure 2: Electro-osmotic drag (red cones) and back-diffusion (blue cones)

6. Complete system modeling

Some of the results obtained with the above described model have also been used inside the building blocks of a hybrid power source based on fuel cells and batteries. The working principle of the hybrid system is the following: during periods of low power demand, the DMFC is controlled to both supply the load and charge the Li-ion battery, while during periods of high
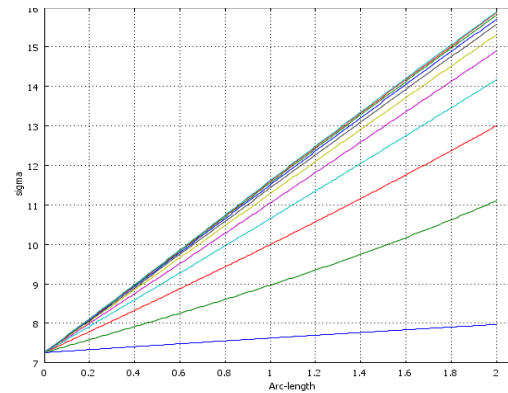

Figure 3: σ across the membrane during transient

power demand, the fuel cell generates only the average power and the battery provides the peak power. Therefore, the Li-ion battery behaves like a storage device, while the DMFC is operated at constant current density with benefit for the cell efficiency and lifetime.

Figure 4 shows the schematic of the proposed hybrid system: the electronic device is connected directly to the DC-bus, while the fuel cell and the battery are interfaced by power converters. A synchronous boost converter steps the fuel cell voltage up to the DC-bus voltage (usually 3.3 V). The fuel cell consists of 4-6 series connected stacks, in order to obtain adequate voltage levels at full load (2-2.4 V). On the battery side, a H-bridge topology buck-boost converter controls theb charge and discharge cycles. H-bridge converters can operate either as a buck converter (when the Li-ion battery is fully charged and its voltage is greater than the DC-link voltage), or as a boost converter (when the cell is almost discharged and its voltage drops down below the DC-link voltage). The controller manages power flows between fuel cell, battery and load by varying the duty cycle of the MOSFETs in the power converters.
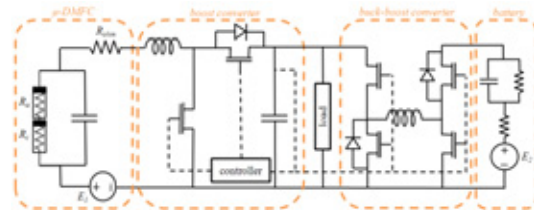

Figure 4: Schematic of the hybrid power system (DMFC + Li-ion battery).
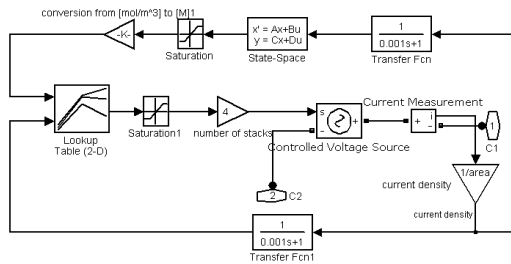
Figure 5: Simulink® model of the DMFC for long time-scale dynamics.

A model of the hybrid power system for simulating the cell dynamics over long time scales has been implemented in Matlab/Simulink® (Figure 5). The electric behaviour of the DMFC is modelled by a look-up table, which provides the output signal voltage for methanol concentrations and current densities. Polarization curves, i.e., the input data of the look-up table, are computed for inlet methanol concentration values ranging from 0.1 to 4 M. By using a saturation block, the output voltage signal for small current loads is approximated to the open circuit voltage of the DMFC, which is evaluated experimentally (about 0.6 V for a single stack). The signal from the look-up table block is converted into a power signal by using a controlled voltage source generator. The discharge process is modelled by using a state space system. The slow dynamics model is non-linear as the discharge rate of the fuel cell is determined by the reactant flow, which depends on the load current. This non-linear behaviour can be modelled in Simulink® by using algebraic loops, which provide a feedback from the power circuit. Current through DMFC is sensed at the controlled voltage generator. This signal is transformed into a current density signal, which is used either to evaluate the voltage signal from look-up table, or the concentration signal from state space block. The dynamics of the rechargeable battery is simulated by using the model implemented in the SymPower® library of Simulink®. The considered load corresponds to an electronic device supplied by a 6-stack fuel cell with 10 cm2 cross section and 0.2 A output current. Typical parameters of mobile phone batteries are considered for simulating the Li ion battery (3.6 V, 750mAh). Figure 6 shows the voltage discharge profile of the hybrid system and a comparison with the Li-ion battery only. It

can be observed that the battery is recharged when the electronic load is in standby so that the total runtime of the power source is almost doubled.
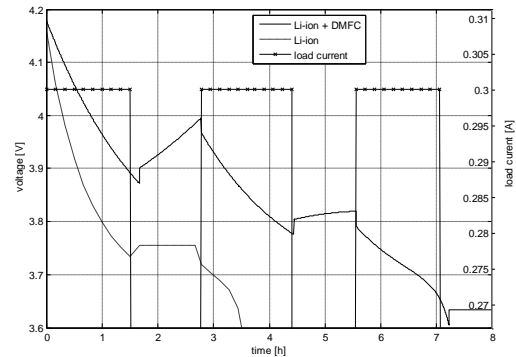

Figure 6:. Li-ion battery voltage profile during the discharge.

7. Conclusions

The presented fully coupled three-dimensional dynamic model of polymeric membranes for fuel cells has been used to simulate the transient behavior of a PEMFC membrane under realistic operating conditions. Complete system modeling efforts have also been presented. A tighter couplic between the membrane model and the full system is currently under way.

8. References

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9. Acknowledgements