

ANALYSIS OF MASS AND CHARGE TRANSFER IN A PEM FUEL CELL

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Abstract. . The performance of a PEM fuel cell is largely controlled by the heat, mass and charge transfer across the polymer membrane. The heat and mass transfer are determined by the convection and diffusion fluxes along the distributing channels and by diffusion across the membrane. At the gas-membrane interface in the anode side, there is physical and chemical adsorption of chemical species, generating the ions that will flow across the membrane. The heat generated at the membrane is transmitted to the external environment through the channel walls. The liquid water formed at the cathode side must be properly distributed and removed in order to keep the flow channels open for gas flow. The simulation of the thermo-fluids and charge transport problem allows for predicting the polarization curve of the fuel cell and allows the optimization of flow and heat transfer redistribution. Here, we apply a mass and charge transfer model for a PEM fuel cell operating with hydrogen and air. The model is one-dimensional across the membrane width. Results show the expected behavior of the polarization curve as a function of the cell operating parameters. Comparison to measurements available in the literature show a good agreement.

Keywords: Fuel cell, PEMFC, hydrogen, environment.

1. INTRODUCTION

Research in fuel cells aims at developing more efficient and reliable systems at a lower cost. Because of the highly reactive environment and compact nature of fuel cells it is hard to perform detailed in situ measurements during operation. Therefore, a considerable amount of research has been spent in theoretical modeling since this allows for an easier path to system optimization (Biyikoglu, 2005; Hwang and Chen, 2006). The modeling needs to address the different reaction and mass transfer phenomena that take place within a fuel cell. Among these, here, we will focus on gas mass transfer across gas channel, diffusion barrier and polymer membrane, liquid water transfer across the membrane, electrochemical reactions, charge transfer, electrical current and voltage drop across electrodes.

A major requirement for the fuel cell operation is to keep the polymer humid during operation. Water is locally generated in the cathode side and this water migrates to the cathode gas and also across the polymer. Alternatively, the anode gas can also be humidified, providing extra partial pressure of water vapor in the anode side. The mass and charge transfer in a fuel cell is basically three-dimensional in the gas channel and membrane. However, in order to reduce computational effort a suitable simplification is to assume a two-dimensional model for the gas flow and a local one-dimensional model for the membrane transport. The one-dimensional model is then locally coupled to the two-dimensional flow solution for the channel gas flow to account for the full behavior of the fuel cell. Here, only the one-dimensional model for the membrane is developed as a local model for the fuel cell surface. Based on the reactants partial pressures in the anode and cathode sides, and the fuel cell temperature, the polarization curve is predicted. The results of the model are compared to measurements available in the literature (Dutta et al, 2000; Um et al, 2000a; Um et al, 2000b; Ren et al., 2006).

2. FUEL CELL COMPONENTS DESCRIPTION

The basic components forming a fuel cell are: The anode collector plate that acts as an electron conductor; anode gas channel that supplies the fuel cell with reactants; anode porous electrode/gas diffusers that transport reactants/products to and from the catalyst layers and conduct electrons from the catalyst layer to the collector plates; anode catalyst layers where the electrochemical reactions take place; polymer membrane that allows the transport of water and protons and separates the reactants H_2 and O_2 ; cathode catalyst layers where the electrochemical reactions take place; cathode porous electrode/gas diffusers that transport reactants/products to and from the catalyst layers and conduct electrons from the catalyst layer to the collector plates; cathode gas channel that supplies the fuel cell with reactants; cathode collector plate that acts as an electron conductor. In the following, each component is analyzed separately.

2.1. Collector plate

This plate is also known as the bipolar plate and is present in the anode and cathode sides. It is a hardware plate that serves both as a flow field conditioner and current collector. In a single fuel cell, these two plates are the last of the components making up the cell. Besides collecting the electrons coming from the anode diffuser, the anode collector plate is responsible to provide structural resistance to the device. It is generally made of a lightweight, strong, gas-impermeable, electron-conducting material; graphite or metals are commonly used, although composite plates are now being developed. Channels are etched into the side of the plate next to the backing layer. The pattern of the flow field in the plate (as well as the width and depth of the channels) has a large impact on how evenly the reactant gases are spread across the active area of the membrane/electrode assembly. Flow field design also affects water supply to the membrane and water removal from the cathode (U.S. Department of Energy, 2006). One of the most used channel designs is the interdigitated flow field, as discussed by Wood (1998), Kazim (1999) and Ren et al (2006). Here, the collector plate is not addressed.

2.2. Channel

The channel is the conduct, etched in the collector plate, in which the reactants are distributed along the surface of the gas diffusion layer (GDL). Gas transfer from the channel to the surface of the GDL occurs by surface diffusion enhanced by the flow conditions inside the channel. The flow is usually laminar. The reactants considered here are mixtures of hydrogen and water in the anode side and oxygen, nitrogen and water in the cathode side.

2.3. Porous Electrode Gas Diffusers (GDL).

It is also known as porous backing layer. Its functions involve acting as a gas diffuser, provide mechanical support, and help in managing water in the fuel cell. Besides these functions, the GDL provides an enhanced reaction area accessible to the reactant. The effect of using these diffusion layers is to provide an electrical pathway for electrons allowing a spatial distribution in the current density on the membrane in both the direction of the bulk flow and the direction orthogonal to the flow but parallel to the membrane (Dutta et al, 2000). Its thickness is about 4 to 12 sheets of paper. It is typically carbon-based (graphite matrix porous media) and may be in cloth form, a non-woven pressed carbon fiber configuration, or simply a felt-like material. The layer incorporates a hydrophobic material that has the function of avoiding the water flooding of the voids of the layer and facilitates the product water removal. Here, diffusion will be considered to occur along the effective porous medium that forms the GDL. A correlation for the effective diffusion coefficient will be used along with Fick's law.

2.4. Catalyst layers.

The catalyst is responsible for the electrochemical reactions happening at low temperature. These are the oxidation half-reaction at the anode side and the reduction half-reaction at the cathode side. In the anode, the hydrogen splits into two electrons and two protons. The electrons flow to an external circuit while the protons dissolve in the liquid water that impregnates the proton exchange membrane and travel through the membrane to the cathode catalyst. There, they oxidize with the electrons to form water. The protons flux through the membrane account for the electro-osmotic water flux that is balanced by the diffusion flux in equilibrium and steady state. The catalyst layer is usually formed by platinum as a metallic powder very thinly coated onto carbon paper or cloth that consists of micro-scale carbon particles. This catalyst layer, supported by a binder material, forms the electrode. Both are either applied to the membrane or else applied to the backing layer. Here, the kinetics of the catalytic reactions are assumed to be extremely fast when compared to the polymer and GDL mass transfer.

2.5. Polymer membrane.

The MEA consists of a perfluorosulfonic membrane electrolyte coupled with the electrode. The proton transfer can occur only when the membrane is strongly hydrated. The proton can be considered as a mobile charge that encounters a low resistance when moving across a potential gradient. Dupont's Nafion™ ion exchange membrane forms the basis of the proton exchange membrane fuel cell. Nafion is essentially PTFE (polytetrafluoroethylene) containing a fraction of pendant sulphonic acid groups, a un-dissociated SO_3H group. The ion containing fraction is normally given in terms of equivalent weight, i.e. number of grams of dry polymer per mole of acidic groups.

Figure 1 presents a rendering of the different layers forming the PEM fuel cell and of the anode and cathode heterogeneous chemical reaction. These layers are modeled here assuming one-dimensional mass and charge transfer.

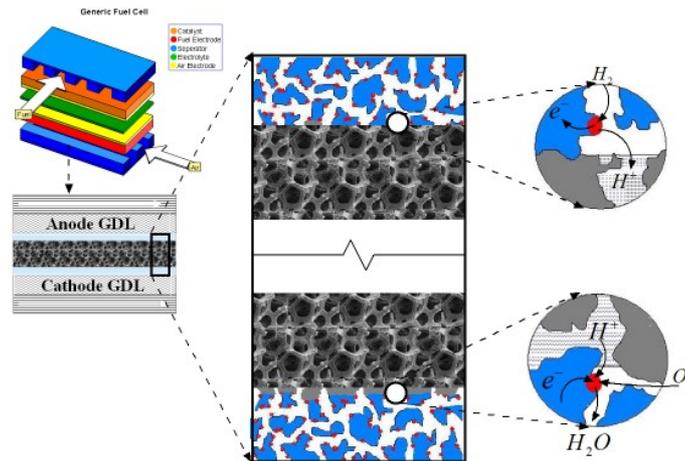


Figure 1. Rendering of the different layers forming the PEM fuel cell and of the anode and cathode heterogeneous chemical reaction.

In the following, the model developed is presented.

3. MODEL

The main assumptions are: 1. Steady-state; 2. Ideal-gas behavior; 3. Isothermal; 4. Thermodynamic equilibrium exists in the catalyst layer in the anode and cathode sides, 5. One-dimensional diffusion mass transfer occurs in the diffusion layer and polymer membrane, 6. The polymer membrane is impermeable to molecular hydrogen and oxygen diffusion; 7. The collector plates are ideally conductors; 8. Convective effects associated to diffusion are neglected; and 9. Fick's Law applies. .

Since the rate of dissociation is assumed fast, diffusion mass transport becomes the controlling process.

3.1. Cathode and anode reactions.

Expressing the rate of reaction of the half-cell reactions by $w_{r,cat}$, the rate of consumption of hydrogen and formation of protons and electrons in the anode side are

$$\begin{aligned} \dot{W}_{H_2} &= -\dot{w}_{r,an} \\ \dot{W}_{H^+} &= -2\dot{w}_{r,an} \\ \dot{W}_{e^-} &= -2\dot{w}_{r,an} \end{aligned} \tag{1}$$

Analogously, for the cathode side we have

$$\begin{aligned} \dot{W}_{O_2} &= \frac{-\dot{w}_{r,cat}}{2} \\ \dot{W}_{H_2O} &= \dot{w}_{r,cat} \\ \dot{W}_H &= -2\dot{w}_{r,cat} \\ \dot{W}_{e^-} &= -2\dot{w}_{r,cat} \end{aligned} \tag{2}$$

3.2. Mass balances.

In the one-dimensional model developed here, a node in a mass transfer circuit represents each interface. The mass balances are performed around each node. Figure 2 presents a diagram showing the reaction and diffusion paths for each chemical species considered.

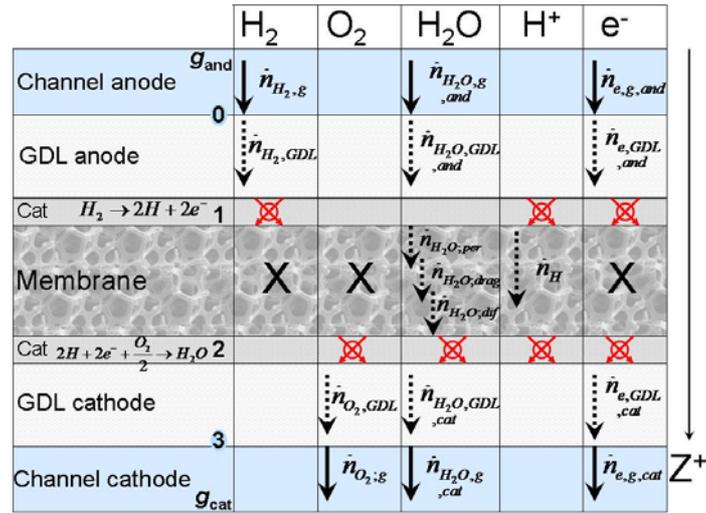


Figure 2. Diagram showing the reaction and diffusion paths for each chemical species considered.

Each interface is numbered from 0 to 3 and the anode and cathode channels are identified as anode and cathode gas. Figure 3 presents a rendering of the mass flux in a typical node and the steady-state mass balance.

$$\dot{n}_{i,in} - \dot{n}_{i,out} + \dot{W}_i = 0 \quad (3)$$

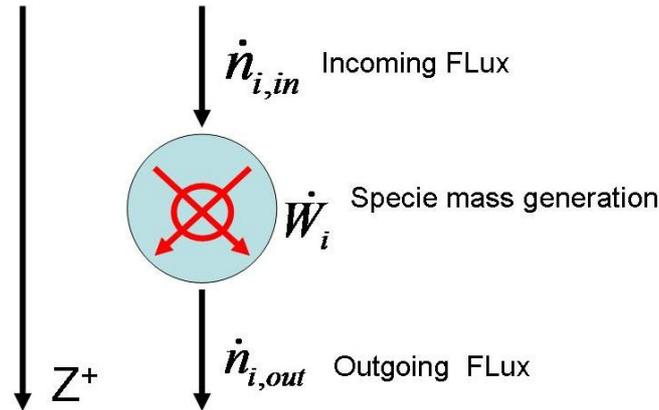


Figure 3. Rendering of the mass flux in a typical node and the steady-state mass balance.

Using this reference, the following mass balances are written for each node:

node 0

$$\dot{n}_{H_2O,g, and} - \dot{n}_{H_2O,GDL, and} = 0 \quad (4)$$

$$\dot{n}_{e_wire_and} - \dot{n}_{e_cell_and} = 0$$

$$\dot{n}_{H_2,g} - \dot{n}_{H_2,GDL} = 0$$

node1

$$\dot{n}_{H_2O,GDL, and} - \dot{n}_{H_2O, drag} - \dot{n}_{H_2O, dif} = 0$$

$$\dot{n}_{e_cell_and} + \dot{W}_{e^-} = 0 \quad (5)$$

$$\dot{n}_{H_2,GDL} + \dot{W}_{H_2} = 0$$

$$\dot{W}_{H^+, and} - \dot{n}_H = 0$$

node 2

$$\dot{n}_{H_2O,drag} + \dot{n}_{H_2O,dif} + \dot{W}_{H_2O} - \dot{n}_{H_2O,GDL,cat} = 0$$

$$\dot{W}_{e-} - \dot{n}_{e_cell_cat} = 0 \quad (6)$$

$$\dot{n}_H + \dot{W}_{H+,cat} = 0$$

$$\dot{W}_{O_2} - \dot{n}_{O_2,GDL} = 0$$

node 2

$$\dot{n}_{H_2O,GDL,cat} - \dot{n}_{H_2O,g,cat} = 0 \quad (7)$$

$$\dot{n}_{e_cell_cat} - \dot{n}_{e_wire_cat} = 0$$

$$\dot{n}_{O_2,GDL} - \dot{n}_{O_2,g} = 0$$

3.3. Water flux.

Only two water flux mechanisms are modeled here. The first, is the water diffusion, modeled using Fick's law and a water diffusion coefficient $D_{H_2O,Diff}$ according to Dutta et al (2000) as:

$$D_{H_2O,Deff} = n_{d,1} 5.5 \times 10^{-11} \exp \left[2416 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \quad (8)$$

where $n_{d,1}$ is the local electro-osmotic drag coefficient.

The second, is the electro osmotic drag flux induced by protons migration through the membrane from the anode to the cathode side. It is expressed as a function of the anode/cathode water activity and the electro osmotic drag flux coefficient as:

$$\dot{n}_{H_2O,drag} = n_{d,1} \frac{\dot{n}_H}{F} \quad (9)$$

where \dot{n}_H is the proton flux through the membrane, F is the Faraday constant (F=96487e3 C/kmol) and $n_{d,1}$ is the electro osmotic drag coefficient, given by

$$\dot{n}_{d,1} = \begin{cases} 0.0049 + 2.02a_a - 4.53a_a^2 + 4.09a_a^3; a_a \leq 1 \\ 1.59 + 0.159(a_a - 1); a_a > 1 \end{cases} \quad (10)$$

where a_a is the anode/cathode water activity defined as:

$$a_a = \frac{n_{w,a} p_{g, and}}{p_{w,T}^{sat}} \quad (11)$$

where $n_{w,a}$ is the is the anode/cathode water mol fraction rate of water, $p_{g, and}$ is the total inlet pressure in the anode, and $p_{w,T}^{sat}$ is the saturation pressure at the operation temperature.

3.4. Voltage drop.

The fuel cell voltage is established as a function of an equilibrium voltage and the potential loss (overpotential) as (Lee et al 2005)

$$V_{cell} = V_0 - \eta - \eta_{\Omega} \quad (12)$$

where V_0 is the equilibrium voltage, η is the total overpotential including activation and concentration overpotential (Dutta et al, 2000), and η_{Ω} is the ohmic loss in the membrane (Dutta et al, 2000).

The equilibrium voltage is defined as a function of the Nerst potential at the operation temperature. The Nerst equation gives the electrode potential $E(T)$, relative to the standard electrode potential E^0 of the electrode half—cells. These are given by

$$\begin{aligned} V_0 &= E(T) + \frac{R_u T}{4F} \ln(P_{H_2}^2 P_{O_2}) \\ E(T) &= E^0 - 0.9 \times 10^{-3} (T - 298) \\ E^0 &= -\frac{\Delta G^0}{2F} \end{aligned} \quad (13)$$

where R_u is the gas constant ($R_u = 8314,472$ J/kmol-K), T is the temperature P_{H_2} is the hydrogen pressure in the anode catalyst, P_{O_2} is the oxygen pressure in the cathode catalyst, ΔG is the Gibbs energy change and F is the faraday constant ($F = 96487E3$ C/kmol).

The total overpotential η is defined as a function of the current density as (Dutta et al., 2000)

$$\eta = \frac{R_u T}{0.5F} \ln\left(\frac{I_{cell}}{I_0 P_{O_2}}\right) \quad (14)$$

where I_{cell} is the total fuel cell current density, and I_0 is the reference current density defined as

$$\begin{aligned} I_0 &= I_{0,353} \exp[0.014189(T - 353)] \\ I_{0,353} &= 2.8 \times 10^{-5} \text{ A/m}^2 \end{aligned} \quad (15)$$

The ohmic loss in the membrane η_{Ω} is calculated as (Dutta et al, 2000):

$$\eta_c = I_{cell} \frac{t_m}{\sigma_m} \quad (16)$$

where t_m is the membrane width and σ_m is the local membrane protonic conductivity and is defined as (Um et al, 2000a)

$$\sigma_m = (0.5139\lambda - 0.326) \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (17)$$

where λ is the water content in the membrane and is define as (Ren et al, 2007):

$$\lambda = \begin{cases} 0.043 + 17.81a_a - 39.85a_a + 36.0a_a; & 0 < a_a < 1 \\ 14.0 + 1.4(a_a - 1); & 1 < a_a < 3 \\ 16.8 & \end{cases} \quad (18)$$

and a_a is the anode/cathode water activity defined before.

3. RESULTS AND DISCUSSION

Table 1 presents the parameters used in the simulation. These are the same parameters for the fuel cell reported in Um and Wang (2004). Results are obtained assuming completely saturated conditions in the anode and cathode catalyst sides.

Table 1. Cell parameters and properties at 353 K used in the simulations.

Description, Unit	Symbol	Value	Reference
Half gas channel height, m	L_{ch}	3.81×10^{-4}	Um and Wang, 2004
GDL width, m	L_{GDL}	2.54×10^{-4}	Um et al; 2000a
Membrane width, m	t_m	1.78×10^{-4}	Um and Wang, 2004
GDL porosity	ϵ_{GDL}	0,4	Um et al; 2000a
Oxygen diffusivity in gas, m^2/s	D_{O_2}	5.2197×10^{-6}	Um et al; 2000a
Hydrogen diffusivity in gas, m^2/s	D_{H_2}	2.63×10^{-6}	Um et al; 2000a
Water diffusivity, m^2/s	D_{H_2O}	$3,71 \times 10^{-5}$	Perry et al; 1984
Faraday constant, C/kmol	F	$96487 \times 10^{+3}$	
Gas constant, J/(kmol K)	R_u	8314.472	
Relative humidity of inlet air/fuel (anode/cathode)	--	100%	Um and Wang, 2004
Reference exchange current density per area, A/m^2	$I_{0,353}$	$1,0 \times 10^{-4}$	Um and Wang, 2004

Figure 4 presented the comparison between the predictions using the one-dimensional model and the measurements made by Um and Wang (2004) for a PEM fuel cell. Considering that the fuel cell has a three-dimensional mass, heat and charge transfer, the comparison is considered acceptable.

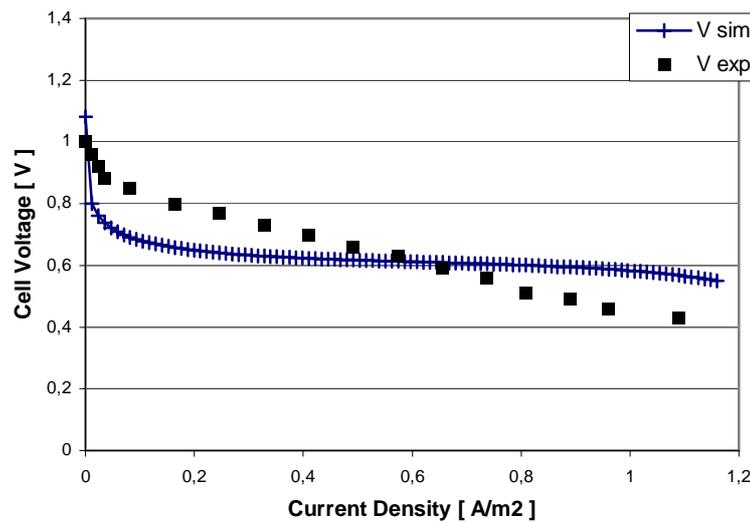


Figure 4. Comparison of simulation with an experimental polarization curve from Um and Wang (2004).

Figure 5 presents the full polarization curve calculated for 343 K and 2 atm of total pressure for both the anode and the cathode. The usual pattern is observed including: An initial strong drop of the voltage for low current density due to the activation loss, an intermediate almost linear small decrease due to ohmic losses and a final drop in voltage due to membrane mass transport limitation.

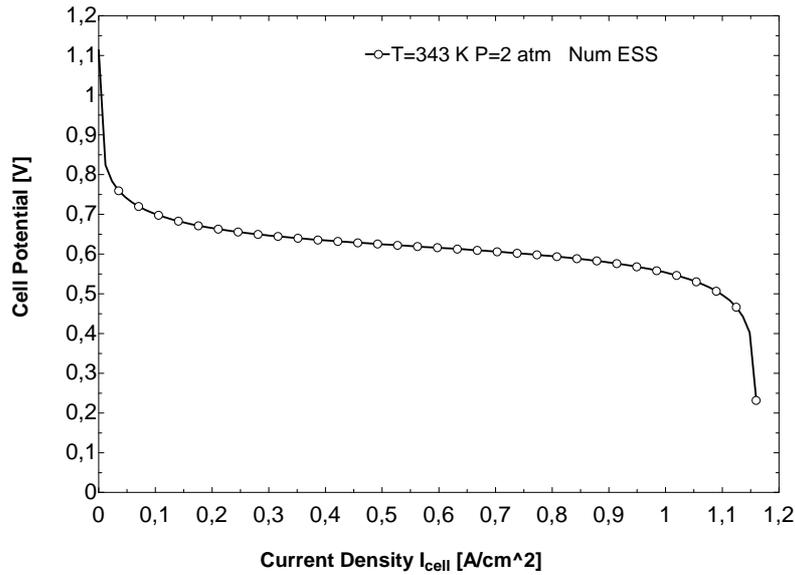


Figure 5. Polarization curve from model for 343 K and 2 atm.

Figure 6 presents the full polarization curve and the power density generated by the fuel cell. The power reaches a maximum for a current density of 1.05 A/cm² and then decays quickly to zero. It is important to observe that the current model neglects heat transfer, assuming an isothermal fuel cell.

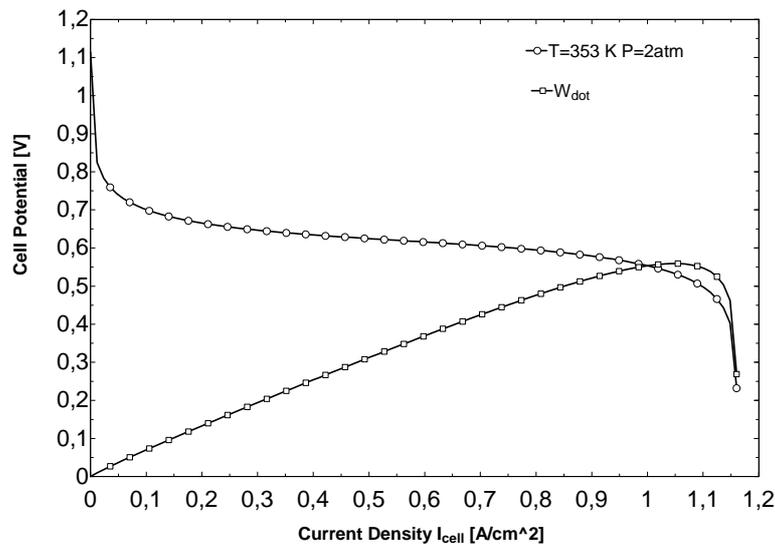


Figure 6. Polarization curve and generated power density curve from model for 343 K and 2 atm.

3. CONCLUSIONS

Here, a one-dimensional model for the membrane is developed as a local model for the fuel cell surface. The model includes gas mass transfer from the gas channel, diffusion barrier and polymer membrane, liquid water transfer across the membrane; charge transfer, electrical current and voltage drop across electrodes. Based on the reactants partial pressures in the anode and cathode sides, and the fuel cell temperature, the polarization curve is predicted.

The results of the model are compared to measurements available in the literature (Dutta et al, 2000; Um et al, 2000a; Um et al, 2000b; Ren et al., 2006) and they are in reasonable agreement. This one-dimensional model will be locally coupled to a two-dimensional flow model for the channel gas flow to account for the full behavior of the fuel cell. This will then be extended to include heat transfer effects, which is a serious limitation of the present model. Measurements are currently being performed in a 500 W PEM fuel cell and will be compared to the full model predictions.

3. ACKNOWLEDGEMENTS

The authors are grateful to CNPq (National Council for Scientific and Technological Development), a foundation linked to the Ministry of Science and Technology for the financial support.

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