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Dynamic model of solid polymer fuel cell water management

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Abstract

For system simplicity, it is advantageous to operate the solid polymer fuel cell on dry gases at low overpressures. Under these conditions, water management inside the cell is a critical issue. To determine the effect of operating conditions on performance, a two-dimensional dynamic model is developed. Water balance equations are written for each membrane element taking into account: production, drag and diffusion of water in the membrane, and diffusion of water vapour in the gas diffusion layers. The model can reasonably reproduce the polarisation curves of a cell operated on various oxygen fractions and can qualitatively describe the effect of various operating conditions (dry gases, current density level, co- and counter-flow, anode recirculation). © 1998 Elsevier Science S.A.

Keywords: Solid polymer fuel cell; Polymer electrolyte membrane; Fuel cell; Dynamic; Two-dimensional; Water management

1. Introduction

Operating an solid polymer fuel cell (SPFC) system at low overpressures (<1.5 bar) would strongly decrease the parasitic power required for air compression. In addition, operation on non-humidified (‘dry’) gases would eliminate the need of a humidification device, further reducing the size and complexity of the system. Under these conditions, water management inside the cell is a critical issue and cell performance strongly varies with operating conditions.

The current model allows determination of the effect of the operating conditions (cell temperature, degree of humidification of feed gases, etc.) on cell performance, more specifically on the water management inside the cell.

2. Model set-up

The model is two-dimensional (Fig. 1). In the y-direction, parallel to the gas channel, the membrane electrode assembly (MEA) is divided into a number of elements (typically 80). In the z-direction, perpendicular to the membrane, the membrane is further divided into a number of elements between anode and cathode (typically 5). Water balance equations are written for each membrane element, taking into account: water production (at the cathode), water drag by protons (electro-osmotic effect) and diffusion of water as a result of a concentration gradient. The water transport in the membrane is assumed to be zero in the y-direction. The equations for the flux due to water diffusion and drag are:

$$\phi_{\mathrm{H_2O,\ diff}} = n_0 \cdot D_{\mathrm{H_2O}} \frac{\partial \lambda}{\partial z} \tag{1}$$

$$\phi_{\mathrm{H_2O,\ drag}} = r_{\mathrm{drag}} \frac{j}{F} \tag{2}$$

At the interface of membrane and gas diffusion layers (GDL), water exchange between membrane and gas channels is determined by diffusion of water vapour in the GDL. The relative humidity of the gas adjacent to the membrane is assumed to be in equilibrium with the water content λ of the membrane. The transport of water vapour can then be calculated using the relative humidity in the gas channel and the Stefan–Maxwell equations. For the cathode, the Stefan–Maxwell equations are somewhat simplified, so the equations for a binary gas mixture can be used. Transport of reactants (H_2/air or O_2) through the GDL is also calculated using binary Stefan–Maxwell equations. Processes in the electrodes are modelled using simplified equations derived from an ‘agglomerate’ electrode model.

A simplified flow diagram of the numerical procedure is shown in Fig. 2. In a cell, the gas composition affects the current distribution and the current distribution, in turn, affects the gas composition. In the model the assumption is made that, given the membrane resistance, these two are

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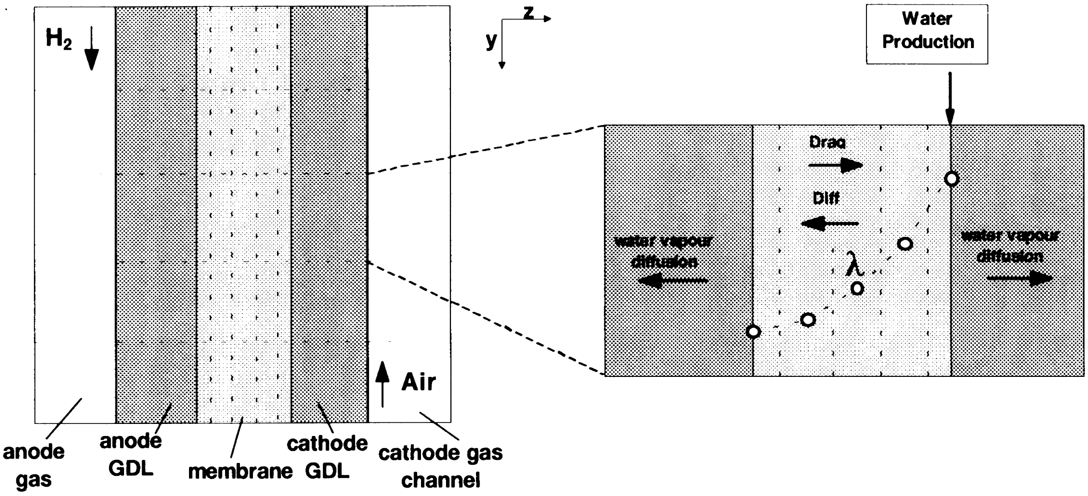

Fig. 1. Schematic of model set-up.

always in their stationary state. The time-dependent behaviour of the cell is determined by the membrane resistance. The water content, calculated after a small time interval dt using the water balance equations, yields a new value for the membrane resistance as a function of y.

3. Main assumptions

An important parameter in the model is the membrane water content λ, which is defined as the number of water molecules per sulfonic acid group. The water content determines the water diffusion coefficient D_{H_2O}, the proton conductivity σ and the water drag coefficient r_{drag} (the number of water molecules 'dragged along' with each proton). The drag coefficient as function of λ is found in the literature [1,2]. The dependency of both D_{H_2O} and σ on λ are derived from experiments carried out at ECN [3]. These dependencies are shown in Fig. 3. The concentration of sulfonic acid groups n_0 is 200 (mol/m^3).

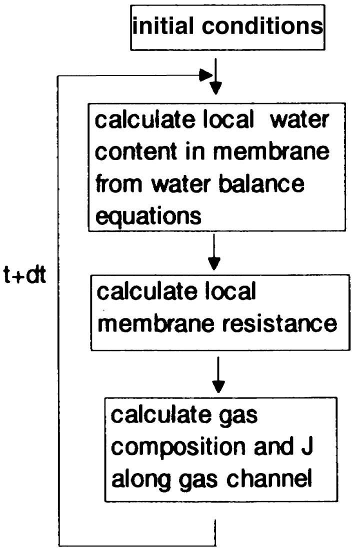

Fig. 2. Simplified flow diagram.

The equilibrium relation between λ and the relative humidity RH is given by [4] (measured at 80°C):

$$\lambda = 0.300 + 10.8\ \mathrm{RH} - 16.0\ \mathrm{RH}^2 + 14.1\ \mathrm{RH}^3$$

The parameters needed for the gas diffusion equations are listed in Table 1.

4. Results

4.1. Polarisation curve of Nafion 117 cell on humidified H_2/O_2 in co-flow

To compare model and experiment, the model is used to reproduce the polarisation curves of a Nafion 117 cell, operated on different O_2/N_2-mixtures. Fuel and oxidant pressures are 3 bar, gases are fed in co-flow and both are humidified (at 90 and 85°C, respectively). The model calculations and the experimental data are shown in Fig. 4a. It appears that the polarisation curves are reasonably well reproduced by the model.

As an illustration of the model output, the water content of anode side, middle and cathode side of the membrane along the gas channel is shown in Fig. 4(b). Also shown is the local current density J along the gas channel. The

Table 1

Parameters used in the gas diffusion equations in the model (values at 80°C)

Parameter	Value
Thickness of gas diffusion layer (mm)	0.25
Porosity of gas diffusion layer (%)	16.5
Pressure * diffusion coefficient of O_2 in N_2 (N/s)	2.8
Pressure * diffusion coefficient of water vapour in N_2 (N/s)	3.9
Pressure * diffusion coefficient of water vapour in H_2 (N/s)	22.3

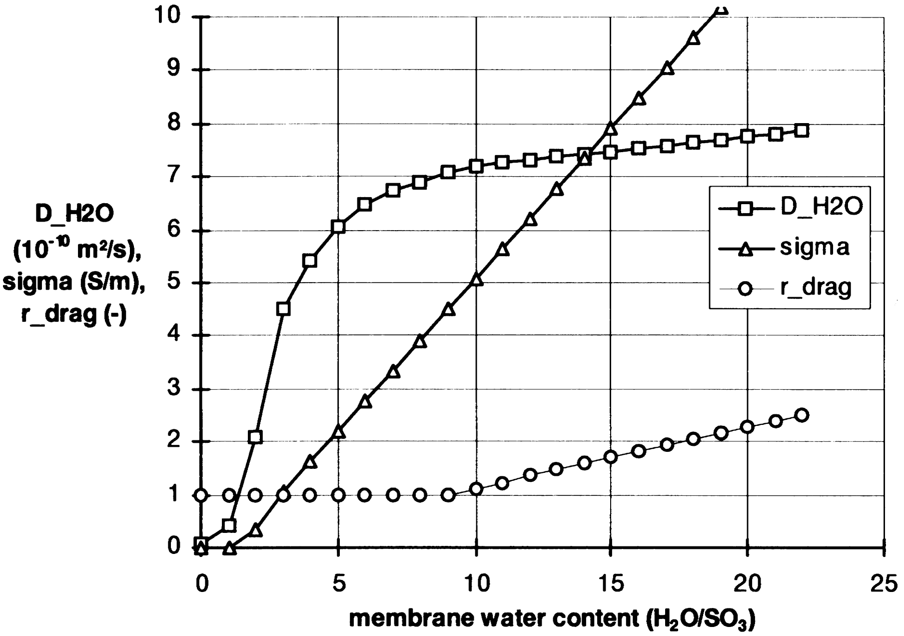

Fig. 3. Water diffusion coefficient D_{H_2O}, proton conductivity σ and drag coefficient r_{drag} (H_2O/H^+) as a function of membrane water content λ (at 80°C).

model data represent an experiment on pure oxygen, at 1.1 A/cm^2.

The calculations show that the downward slope of the curve for 100% O_2 at high current densities (>0.8 A/cm^2, Fig. 4a) is due to drying out of the membrane at the anode side (Fig. 4b). The deviation from linear behaviour cannot be ascribed to diffusion losses, because pure oxygen is used. Apparently, the loss of water at the anode side of the membrane through proton drag cannot be sufficiently compensated for by back-diffusion of product water or supply of water vapour through the anode GDL.

4.2. Nafion 112 cell operated on dry gases

In this model simulation, a Nafion 112 membrane was assumed to be fully humidified at $t = 0$ and the cell voltage was set to a constant value of 0.5 V. When feeding dry gases in co-flow configuration, modelled current density dropped to practically zero within minutes, while stable operation was obtained in counter-flow configuration.

Experiments confirmed the model calculations: stable operation could not be obtained with the gases in co-flow. On the other hand, stable operation appeared possible at 0.5

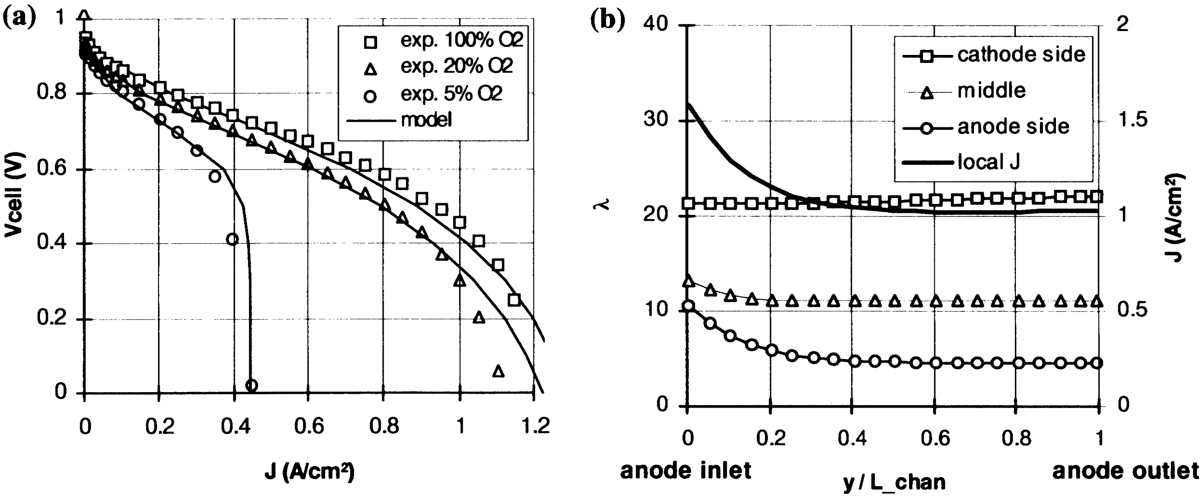

Fig. 4. (a) Polarisation curves of a Nafion 117 cell, operated on different O_2/N_2-mixtures. Model calculations (solid line) and experiment (symbols). (b) Model calculations of a cell operated on 100% O_2 at 1.1 A/cm^2: water content λ of anode side, middle and cathode side of the membrane along the gas channel. Also shown is the local current density J. Operating conditions: cell temperature 80°C, H_2/oxidant at 3.1/3.3 bar, humidified at 90/85°C, co-flow, constant gas flow (stoichiometry at 1 A/cm^2: 2/5).

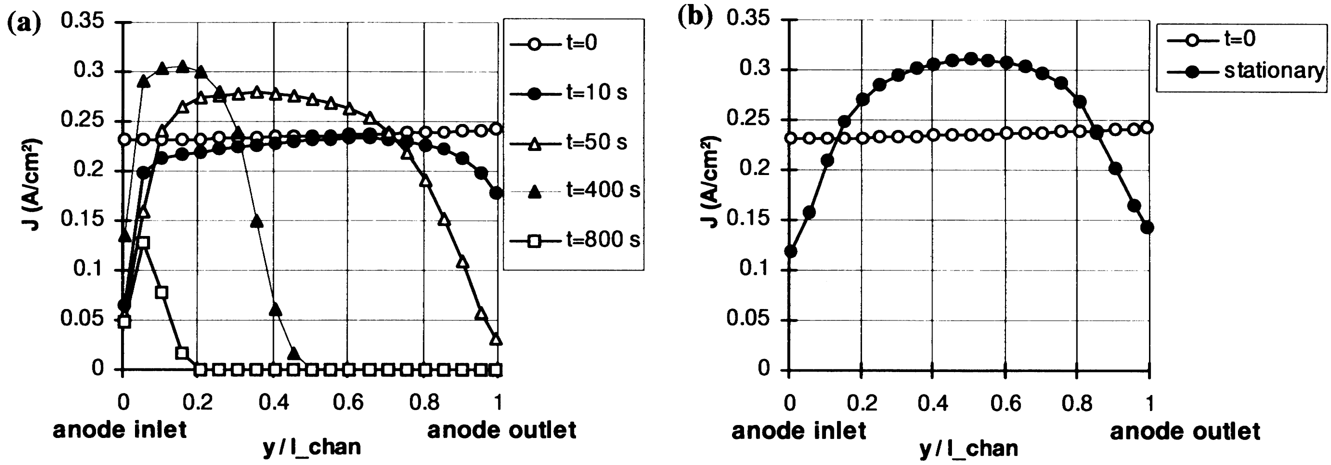

Fig. 5. Model calculations of local current density at different times in a Nafion 112 cell. At $t = 0$ the membrane is fully humidified. (a) No recirculation; (b) anode recirculation. Operating conditions: cell voltage 0.7 V, cell temperature 60°C, H_2/air at 1.5/1.5 bar, counter-flow, no humidification, stoichiometry 1.5/2. With anode recirculation the total anode stoichiometry is 4 relative to the total H_2-flow at the anode inlet (37.5% dry H_2 from the reservoir and 62.5% from the anode outlet).

V in a counter-flow configuration at low stoichiometric values.

Again in counter-flow configuration, the model was set to a constant cell voltage of 0.7 V, while all other operating conditions were held constant. Beginning with a fully humidified membrane, the calculations showed a steadily decreasing cell performance. As an illustration, the local current density along the gas channel at different times is shown in Fig. 5a.

It appears that in spite of the counter-flow configuration, water production is too low to keep the membrane humidified. This results in progressive drying of the membrane beginning at the anode outlet. Experiments with a Nafion 105 cell confirmed that stable operation on dry gases is not possible when the current density is too low.

The model was used to investigate anode recirculation as a possible remedy for the dehydration phenomena. Part of the anode outlet gas (83%) was led back to the anode inlet, to obtain a total stoichiometry of 4 (the stoichiometry relative to the dry gas from the hydrogen reservoir is still 1.5). It was assumed that the gas is recirculated isothermally, so that no water vapour is lost due to condensation. As a result, a stationary situation was obtained in which the cell delivered an average current density of 0.26 A/cm^2. The local current density along the gas channel is shown in Fig. 5b.

The beneficial effect of anode recirculation appears mainly due to the higher water content in the anode gas, especially at the anode outlet. As a result water is transported, through the anode GDL and the membrane, in quantities sufficiently high to humidify the incoming dry cathode gas. A secondary effect is the higher level of humidification of the anode gases at the anode inlet.

5. Conclusions

At this stage, the model is able to quantitatively reproduce the behaviour of an SPFC over a range of operating conditions in which the oxygen fraction in the oxidant was varied. In addition, the model can qualitatively describe the effect of operating conditions such as current density level, co-/counter-flow and anode recirculation.

The model shows that local current density can vary strongly along the gas channel, especially when the cell is operated on dry gases.

Further verification is needed for the model parameters, and data are needed for other types of membranes. The precise values of σ and D_{H_2O} for low values of λ seem to be critical. Besides that, the rate of water transport (vapour or liquid) through the GDL seems to have a significant effect when dry gases are used.

6. List of symbols

D_{H_2O}	diffusion coefficient of water in the membrane (m^2/s)
F	Faraday constant (C/mol)
j	current density (A/m^2)
n_0	concentration of sulfonic acid groups in a dry membrane (mole/m^3)
r_{drag}	drag coefficient (–)
RH	relative humidity (–)
y	coordinate along the gas channel (m)
z	coordinate perpendicular to the membrane (m)
ϕ	flux (mol/m^{2}s)
λ	water content (H_2O/SO^{3-})
σ	membrane conductivity (S/m)

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