

Optimization of Direct Methanol Fuel Cell Power System

Abstract. This paper presents a non-linear dynamic modeling of direct methanol fuel cell (DMFC) based on a simplified mechanism for methanol electro-oxidation reaction and the evolution intermediate species coverage with time. The model is developed to describe the I-V relationships based on designed experiments; it is then integrated into multiple optimizations to achieve the adaptation. Finally, numerical simulations are performed with Matlab software to optimize the underlying mechanisms of the proposed operation process in order to improve the energy efficiency of the cell.

Streszczenie. W pracy przedstawiono nieliniowe modelowanie dynamiczne bezpośredniego ogniwa paliwowego na metanol (DMFC) oparte na uproszczonym mechanizmie reakcji elektrotleniania metanolu i pokryciu w czasie form pośrednich ewolucji. Model został opracowany w celu opisanie relacji IV-V w oparciu o zaprojektowane eksperymenty; jest następnie integrowany z wieloma optymalizacjami, aby osiągnąć adaptację. Na koniec za pomocą oprogramowania Matlab przeprowadza się symulacje numeryczne, aby zoptymalizować mechanizmy leżące u podstaw proponowanego procesu działania w celu poprawy efektywności energetycznej ogniwa. (**Optymalizacja bezpośredniego systemu zasilania ogniw paliwowych z metanolem**)

Keywords: DMFC, Electrical Characterization ,Power Energy, Optimization.

Słowa kluczowe: ogniwo paliwowe, metanol

1.Introduction

In recent years, many research efforts have been devoted to improving the yield and the stability of the fuel cell system by improving the design and her internal and external components [1]. Direct methanol fuel cell (DMFC) has emerged as a promising power source for various kinds of electronic devices, considered as a future potential power source requirements ranging from micro Watts to several hundred Watts [2,3], it can provide high energy density and almost instant recharging with simple system configurations include low temperature operation and modularity of design. However, it is very important to involve accurate modeling of DMFC systems to study the underlying mechanisms of operating parameters [4]. Critical to the operation of the fuel cell is the proton exchange membrane (PEM) responsible for internal proton transport from the anode to the cathode [3].

The high energy density of methanol diluted in water an ideal feed for DMFC, whose operating principle is to convert chemical energy into electrical energy. To deepen the equilibrium analysis and the dynamic behavior of the fuel cell, it is very important to study each element in detail. The two catalytic electrodes where the oxidation of methanol (anode) and the reduction of oxygen (cathode) occur are separated by a membrane which conducts the protons from the anode to the cathode, while the other reverse diffusion is blocked. The set of electrodes and membranes is called a membrane electrode assembly (MEA); is made up of five layers [5,6,7] (Fig.1).

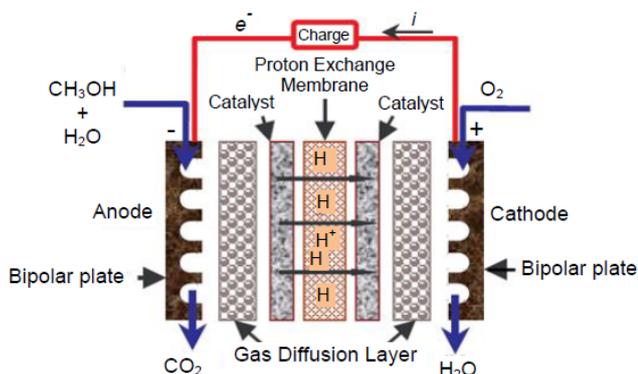


Fig.1. Principle of a direct methanol fuel cell.

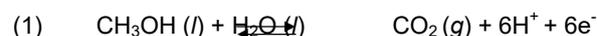
- One proton exchange membrane who ensure the transport of protons between the two compartments of anode and cathode, is Nafion based on fluorinated Teflon, more precisely Nafion which is characterized by high protonic conductivity, low electronic conductivity, impermeability to fuel gas or liquid, good mechanical toughness in both the dry and hydrated states, and high oxidative and hydrolytic stability in the actual fuel cell environment [3,8].

- Two catalyst layers containing the catalyst particles (Pt/Ru or Pt) and Nafion particles. Nafion is added to the catalyst to aid the movement of protons from the catalyst to the membrane; this reduces the electrical resistance of the catalytic layer [9]. The platinum metal is generally used as a cathode catalyst and platinum/ruthenium is used as an anode catalyst. Among its advantages, it is not oxidizing, inert in the presence of nitric and hydrochloric acid, moreover it absorbs hydrogen.

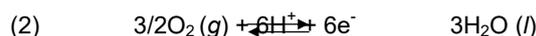
- Two gas diffusion layer located next to the three-phase region of the MEA. It facilitates the flow of reaction products and water; it is also used as electrical and thermal contact between the electrodes and the end plates, usually made of the porous conductor of raw paper or carbon cloth [10,11]. The bipolar plates are used as a current collector and fuel supply. On their surfaces, a network of channels is machined to drain the methanol by feeding the anode part. The best one used is parallel flow field [12,13,11].

According to the following chemical reactions:

Anode side reaction: Pt/Ru



Cathode side reaction: Pt



Total reaction:



An aqueous methanol solution is fed into the anode, where methanol reacts electrochemically with water to produce electrons, protons and carbon dioxide. The electrons produced at the anode carrying the free energy charge of the chemical reaction are forced to flow through an external circuit to deliver electrical work [14, 15], where as the protons can migrate through a proton exchange membrane to the cathode, where they combine with oxygen

from air and electrons coming back from the external circuit to form water [16,17,18].

2. Model description

To describe and analyze the behavior of a fuel cell based on direct methanol, it is necessary to respect all the physico-chemical phenomena prescribed above in order to develop a reliable mathematical model. A multi stage chemical reaction mechanism has been developed to describe the electrochemical oxidation of methanol in anode side platinum-ruthenium catalysts and the reduction of oxygen in the cathode side platinum catalyst. The proposed mechanism consists of five essential following steps [15, 19]:

1-The dissociative chemisorption of methanol on the active sites of platinum catalyst:



2-The formation of hydroxyl groups on the active sites of the ruthenium:



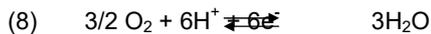
3-The surface absorption of molecules produced by reactions (4) and (5):



4-Desorption of carbon dioxide produced by the surface reaction:



5-The cathodic reduction of oxygen is given by :



The Butler Volmer's expression is often used to describe the rates of electro-oxidation of methanol at the anode [6,20]. However, the reaction rates of the oxidation (in the anodic direction) and reduction (in the cathodic direction) [15] are given by:

$$(9) \quad X_1 = k_1 \cdot \exp\left(\frac{\alpha_A \cdot F \cdot \eta_A}{R \cdot T}\right) \cdot \left(\beta_{\text{Pt}}^3 \cdot C_{\text{CH}_3\text{OH}}^M - \frac{\beta_{\text{Pt}_3\text{-COH}}}{k_1} \cdot \exp\left(-\frac{F \cdot \eta_A}{R \cdot T}\right) \right)$$

$$(10) \quad X_2 = k_2 \cdot \exp\left(\frac{\alpha_A \cdot F \cdot \eta_A}{R \cdot T}\right) \cdot \left(\beta_{\text{Ru}} - \frac{\beta_{\text{Ru-OH}}}{k_2} \cdot \exp\left(-\frac{F \cdot \eta_A}{R \cdot T}\right) \right)$$

$$(11) \quad X_3 = k_3 \cdot \left(\beta_{\text{Pt}_3\text{-COH}} \cdot \beta_{\text{Ru-OH}}^2 - \frac{\beta_{\text{Pt-COOH}} \cdot \beta_{\text{Pt}}^2 \cdot \beta_{\text{Ru}}^2}{k_3} \right)$$

$$(12) \quad X_4 = k_4 \cdot \left(\beta_{\text{Pt-COOH}} \cdot \beta_{\text{Ru-OH}} - \frac{C_{\text{CO}_2} \cdot \beta_{\text{Pt}} \cdot \beta_{\text{Ru}}}{k_4} \right)$$

$$(13) \quad X_5 = k_C \cdot \exp\left(\frac{\alpha_C \cdot F \cdot \eta_C}{R \cdot T}\right) \cdot \left(1 - \left(\frac{P_{\text{H}_2}^6 \cdot P_{\text{O}_2}^{3/2}}{P_{\text{H}_2\text{O}}^3} \right) \cdot \exp\left(-\frac{F \cdot \eta_C}{R \cdot T}\right) \right)$$

where β_i - surface coverage of the element i , η_A - the electrode potential; η_C - the electrode potential; C_{CO_2} - CO_2

concentration in the anode catalyst, k_1, k_2, k_3, k_4 and k_5 are the kinetic parameters of oxidation and reduction; P_{O_2} is pressure of oxygen; α_A and α_C are the charge transfer coefficients which indicate the direction of the favored reaction (whith: $\alpha_A + \alpha_C = 1$). If $\alpha_A > 0.5$, the reaction in anodic direction, if $\alpha_C > 0.5$, the cathodic direction is favored.

3. Modeling approach

In order to simplify the calculation of the differential equations in MATLAB, we have to change the variables as follows:

$$Y(1) = C_{\text{CH}_3\text{OH}}, Y(2) = \beta_{\text{Pt}_3\text{-COH}}, Y(3) = \beta_{\text{Ru-OH}}, Y(4) = \beta_{\text{Pt-COOH}}, Y(5) = \eta_A, Y(6) = \eta_C.$$

At the equilibrium of the chemical species on the surface of the two catalyst components of platinum and ruthenium, we will have: $\beta_{\text{Pt}} = 1 - Y(2) - Y(4)$ and $\beta_{\text{Ru}} = 1 - Y(3)$.

We need six differential equations to describe the system [21]. The first Eq.(14) represents the variation of the methanol concentration in the anode compartment, three other Eqs.(15),(16) and (17) to describe the coverage of the sites of matter by $\text{Pt}_3\text{-OH}$, Pt-COOH and Ru-OH . Eqs. (18) and (19) present the anodic and cathodic over potentials.

$$(14) \quad \frac{\partial Y(1)}{\partial t} = \frac{1}{\tau} (C_{\text{CH}_3\text{OH}}^F - C_{\text{CH}_3\text{OH}}^M) - \frac{A_S}{V_a} \cdot N_{\text{CH}_3\text{OH}}^M - \frac{A_S}{V_a} \cdot X_1 \quad (15)$$

$$(15) \quad \frac{\partial Y(2)}{\partial t} = \frac{1}{\gamma \cdot C_A} (X_1 - X_3)$$

$$(16) \quad \frac{\partial Y(3)}{\partial t} = \frac{1}{\gamma \cdot C_A} (3X_2 - 2X_3 - X_4)$$

$$(17) \quad \frac{\partial Y(4)}{\partial t} = \frac{1}{\gamma \cdot C_A} (X_3 - X_4)$$

$$(18) \quad \frac{\partial Y(5)}{\partial t} = \frac{1}{C_A} (i_{\text{cell}} - F \cdot (3X_3 + 3X_2))$$

$$(19) \quad \frac{\partial Y(6)}{\partial t} = \frac{1}{C_C} (-i_{\text{cell}} - 6F \cdot (X_5 + N_{\text{CH}_3\text{OH}}^M))$$

where: i_{cell} - current density of the cell, $C_{\text{CH}_3\text{OH}}^F$ - methanol concentration in the feed solution, $C_{\text{CH}_3\text{OH}}^M$ - methanol concentration through the membrane, τ - average residence time in the anode compartment, $N_{\text{CH}_3\text{OH}}^F$ - methanol flux through the membrane, γ - Roughness factor = V_a/Q were Q - feed flow rate, V_a - volume of the anode compartment, C_A - the anode double layer capacitance, C_C - the cathode double layer capacitance. To solve our system, we need to know the expression of the methanol crossover flux, however, the methanol will be transported through the membrane by diffusion and convection by [14,10]:

$$(20) \quad N_{\text{CH}_3\text{OH}}^M = \left(\frac{D_{\text{CH}_3\text{OH}}^M}{d^M} \cdot C_{\text{CH}_3\text{OH}}^M \cdot \frac{P_e \cdot \exp(P_e)}{\exp(P_e) - 1} \right)$$

The Peclet number is given by:

$$(21) \quad P_e = \left(\frac{v \cdot d^M}{D_{\text{CH}_3\text{OH}}^M} \right)$$

Where: v - the convective flow velocity; $D_{CH_3OH}^M$ - diffusion coefficient of methanol in the membrane. The convective flow velocity according to Schlögl [14,22] is given by:

$$(22) \quad v = -\frac{k\phi}{\mu} \cdot C_{H^+}^M \cdot F \cdot \frac{\partial\phi}{\partial z} - \frac{k_p}{\mu} \cdot \frac{(P_C - P_A)}{d^M}$$

Where: $d\phi/dz$ - the electrostatic potential gradient, dp/dz - the pressure gradient; d^M - thickness of the membrane; P_A - pressure on the anode side; P_C - pressure on the cathode side. The density of the proton flow through the membrane is given by Nernst-Plank [14,10]:

$$(23) \quad N_{H^+}^M = -\left(D_{H^+}^M \cdot \frac{F}{R \cdot T} + C_{H^+}^M \cdot \frac{k\phi}{\mu} \cdot F \right) \cdot C_{H^+}^M \cdot \frac{\partial\phi}{\partial z} - C_{H^+}^M \cdot \frac{k_p}{\mu} \cdot \frac{(P_C - P_A)}{d^M}$$

The proton flux density is related to the cell current density by Faraday's law:

$$(24) \quad i_{cell} = N_{H^+}^M \cdot F$$

The combination of the two Eq.s (23) and (24) gives:

$$(25) \quad \frac{\partial\phi}{\partial z} = -\frac{\frac{i_{cell}}{F} + C_{H^+}^M \cdot \frac{k_p}{\mu} \cdot \frac{(P_C - P_A)}{d^M}}{F \cdot C_{H^+}^M \cdot \left(\frac{D_{H^+}^M}{R \cdot T} + C_{H^+}^M + \frac{k\phi}{\mu} \right)}$$

The combination of Eq. (25) and Eq. (22) gives the following expression of the convective flow velocity:

$$(26) \quad v = -\frac{k\phi}{\mu} \cdot \frac{\frac{i_{cell}}{F} + C_{H^+}^M \cdot \frac{k_p}{\mu} \cdot \frac{(P_C - P_A)}{d^M}}{\left(\frac{D_{H^+}^M}{R \cdot T} + C_{H^+}^M + \frac{k\phi}{\mu} \right)} - \frac{k_p}{\mu} \cdot \frac{(P_C - P_A)}{d^M}$$

With the final expression of v , we can easily solve the previous equations of the model, the parameters k_ϕ , k_p , μ , $D_{H^+}^M$ and $C_{H^+}^M$ are given by Bernardi and Verbrugge [23].

The overall cell voltage is made up of the voltage of the open circuit cell, the anode and cathode overpotential and finally the ohmic losses in the PEM:

$$(27) \quad U_{cell} = U_{cell}^0 - \eta_A - \eta_C - \left(\frac{d^M}{k^M} \right) \cdot i_{cell}$$

In order to characterize the electrical performance of a DMFC, the power density P , which is the current density multiplied by cell potential, is given by:

$$(28) \quad P_{cell} = U_{cell} \cdot i_{cell}$$

4. Results and discussion

The differential equations of the modelization were solved numerically in MATLAB using the method provided (ode15). In this case, a program under MATLAB has been

developed to execute the numerical simulation of the dynamic model. The model operating parameters are shown in Table 1.

Table 1. Value of main operating parameters

Parameters	Symbol	Value
Volume of the anode compartment .	V_a	2.10^{-7} m^3
Temperature of the cell .	T	333 K
Roughness factor.	γ	100
Charge transfer coefficients in anode.	α_A	0,5
Charge transfer coefficients in cathode.	α_C	0,5
Perfect gases constant.	R	8,314 J/mol.K
Faraday's constant.	F	96485 C.mol ⁻¹
Electrode surface.	A_s	5.10^{-4} m^2
Active catalytic sites concentration.	C_t^*	$2.2.10^{-5} \text{ mol/m}^2$
Proton concentration in the membrane.	$C_{H^+}^M$	1200 mol/m ³
Diffusion coefficient of protons in the membrane.	$D_{H^+}^M$	$5.4.10^{-9} \text{ m}^2/\text{s}$
Hydraulic permeability of the membrane.	μ	$1,57.10^{-18} \text{ m}^2$
Pore fluid viscosity in the membrane.	k_p	$3,353.10^{-4} \text{ kg/m.s}$
Conductivity of the membrane.	μ	$17 \text{ } \Omega^{-1}.\text{m}^{-1}$
Electro kinetic permeability of the membrane.	k^M	$1,13.10^{-19} \text{ m}^2$
Standard cell voltage.	$k\phi$ U^0	1,21 V

At first, the rate constants are unknown; they were performed with the values provided by Sundmacher and al; although new parameters must be found to have good approximation. The following initial conditions must be considered: $\eta_A = 0V$; $\eta_C = 0V$; $P_A = 1 \text{ atm}$; $P_C = 1 \text{ atm}$; $Q = 1.67.10^{-8} \text{ m}^3/\text{s}$; $C_{CH_3OH}^M = 1000 \text{ mol/m}^3$; $y(2) = 0$; $y(4) = 0$; $y(3) = 0$.

4.1. Simulation of the polarization curve V-I

Fig.1 shows the difference between the two curves before and after the optimization. At the beginning, the current density calculated for a potential between 0.1 V and 0.7 V did not corresponding to the experimental data. However, a modification of the program under Matlab was performed in order to find new values of the adequate rate constants.

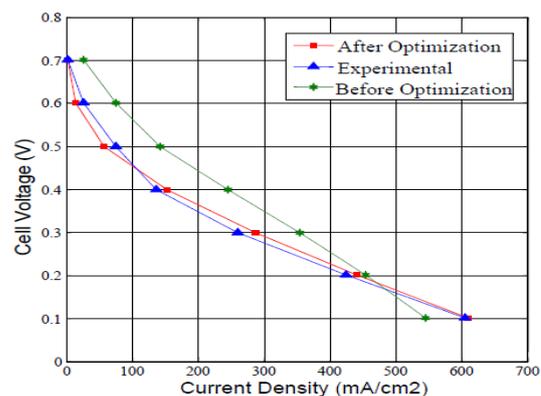


Fig.1. Comparison between experimental and model I-V curve (before and after) optimization for a membrane of Nafion 117 at 60 °C, $C_{CH_3OH}^M = 1 \text{ M}$ and at $P_C = 1 \text{ atm}$; $Q = 1.67.10^{-8} \text{ m}^3/\text{s}$.

The following new values of rate constants ($k_1 = 6.10^{-12} \text{ mol/m}^2.\text{s}$, $k_2 = 1.10^{-2} \text{ mol/m}^2.\text{s}$, $k_3 = 1.8.10^{-2} \text{ mol/m}^2.\text{s}$, $k_4 = 4.10^{-2} \text{ mol/m}^2.\text{s}$, $k_c = 1.10^{-2} \text{ mol/m}^2.\text{s}$) give a new curve perfectly adapted with the experiment curve.

Taking account the model curve, we define two different areas:

- The first area (cell voltage from 0.46 V to 0.7 V corresponding to current density of 26 mA/cm² to 100

mA/cm²) represents the activation loss due to the velocity of the electrochemical reaction,
 - The second area (cell voltage from 0.1 V to 0.46 V corresponding to current density of 100 mA/cm² to 610 mA/cm²) is related to the ohmic losses caused by the electrical resistances of the cell components.

4.2. Power density and cell voltage vs current density

The power density which is the current density multiplied by the cell potential, is usually plotted as a function of current density in conjunction with the I-V curve. Fig.2 shows the model I-V and I-P curves.

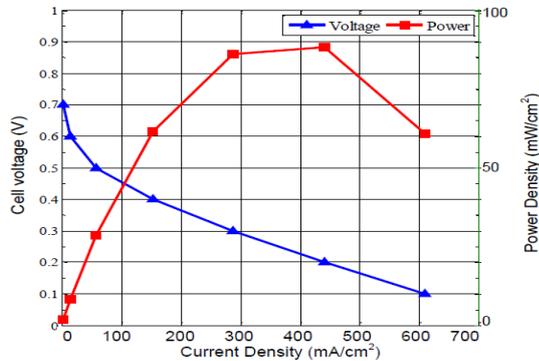


Fig.2. Polarization curve and power density under operating conditions (Membrane of Nafion 117, Anode side pressure = 1 atm, Operating temperature = 60 °C, Methanol concentration = 1000 mol / m³ and Feed flow rate = 1.67.10-8 m³/s).

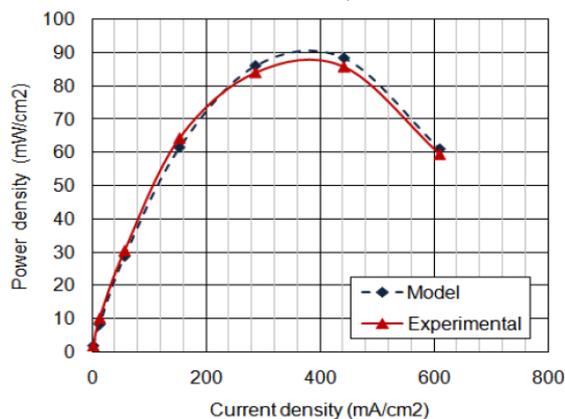


Fig.3. Comparison between experimental and model I-P curve after optimization for a membrane of Nafion 117 at 60 °C, C_{CH₃OH} = 1 M and at P_C = 1 atm; Q = 1.67.10-8 m³/s .

The power density is observed to have a maximum that occurs just before the dominant concentration polarization region. Under the previous conditions, the I-P curve shows that the maximum power density achieved is 89 mW/cm² corresponding to a current density of 442 mA/cm².

4.3. Comparison between experimental and model I-P curve

The comparison between the experimental data and the simulation curve I-P showed that the proposed model is close to the real behaviour of the cell, this was previously confirmed by the I-V curve.

4.4. Effect of pressure on the cathode side

Fig.4 shows the effect of the pressure variation at the cathode side on the cell potentials as a function of the current density under condition (the pressure of the anode = 1 atm, the operating temperature = 60 °C, the concentration

of methanol = 1000 mol / m³ and the feed flow rate = 1.67.10-8 m³/s).

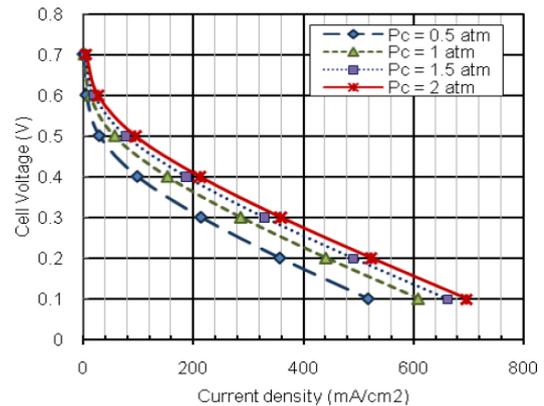


Fig.4. Cell voltage corresponding to variation in the pressures on the cathode side for a membrane of Nafion 117 at 60 °C, C_{CH₃OH} = 1 M and at P_A = 1 atm; Q = 1.67.10-8 m³/s.

It can be deduced that the pressure on the cathode side has a direct influence on the I-V characteristic. A current density gain of 121 mA / cm² is obtained at a potential of 0.1 V for a pressure variation from 1 atm to 2 atm. This is probably due to the oxygen reinforcement on the cathode side.

5. Conclusion:

In this paper, a nonlinear model of a DMFC with planar geometry has been developed to meet the needs of miniature and portable applications. It is specifically dedicated to the DMFC operating at a temperature of 60 °C and having a Nafion 117 membrane. However, the objective was to electrically characterize the DMFC fuel cell using a model able to take into account with the same degree of approximation most of the physical and chemical phenomena interacting within the cell such as the anode and cathode overvoltages, the surface coverage of Pt₃-COH, Pt-COOH and Ru-OH and the methanol concentration. A comparison between experimental data and simulation results has shown that the proposed model is close to the real behavior of the cell. However, the comparisons carried out highlight a small difference between measurement and simulation. This difference is due on the one hand to the closed operating mode with the presence of air in the tested cell, and on the other hand to the fact that thermal losses are not taken into account. Theoretically, it seems possible to rely on the model to predict cell performance under prior limited conditions such as temperature, pressure and especially engineering parameters. In the opposite case, it is therefore necessary to find new values of the rate constants *k_i* which agree with the experimental values.

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