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# Study of the effect of ADL anodic diffusion layer on the performance of a direct methanol fuel cell (DMFC)

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### Abstract

In this study we investigated the properties of the species diffusion layer (ADL) affect the optimal performance of the electrode [1]. Diffusion layers (DL) are porous media allowing reactive gases and liquids to move from distribution channels to catalyst layers (CC). Diffusion layers are an essential part of the PEM fuel cell and the porosity of these layers has a significant effect on the performance of the PEM fuel cell. The effects of diffusion layer porosity (ADL) on fuel cell performance are illustrated by the distribution curves of methanol and carbon dioxide at the anode, water and oxygen distribution at the cathode. and polarization curves.

**Keywords:** COMSOL multiphysique; direct methanol fuel cell; modeling; methanol crossover; water crossover; Mass transport.

### 1. Introduction

The biggest challenge of the 21st century is to provide clean energy without affecting the environment. The technology of fuel cells is known to be one of the key technologies in the energy supply for stationary applications and mobile applications [2]. Recently, the direct methanol fuel cell (DMFC) is identified as an alternative power generator for transportation and portable applications because it is such a compact design and simplified system it has no fuel processing unit (reforming) and storage [3]. Although the practical application of DMFCs remains modest due to technological problems, such as the low catalytic activity of the anodic catalyst, slow anode kinetics, the crossover of methanol through the electrolyte membrane. In order to maintain a high efficiency of the system, the cross-over rate of methanol must be minimized for the existing operating conditions. The effect of the design parameters (porosity of the different diffusion layers) on the performance of the fuel cell is evaluated. Custom

membrane electrode assemblies with different structures and combinations of membrane thicknesses, diffusion layers are designed and tested in order to select optimal working conditions with high concentrations of Methanol and cross levels of water and Relatively low methanol for portable applications. This article focuses on the modeling of this DMFC cell by the multiphysics COMSOL software for a biphasic and twodimensional mixture by adopting universal governmental equations applicable to the entire computational domain. The results for the methanol diffusion and the corresponding current density are presented below [4].

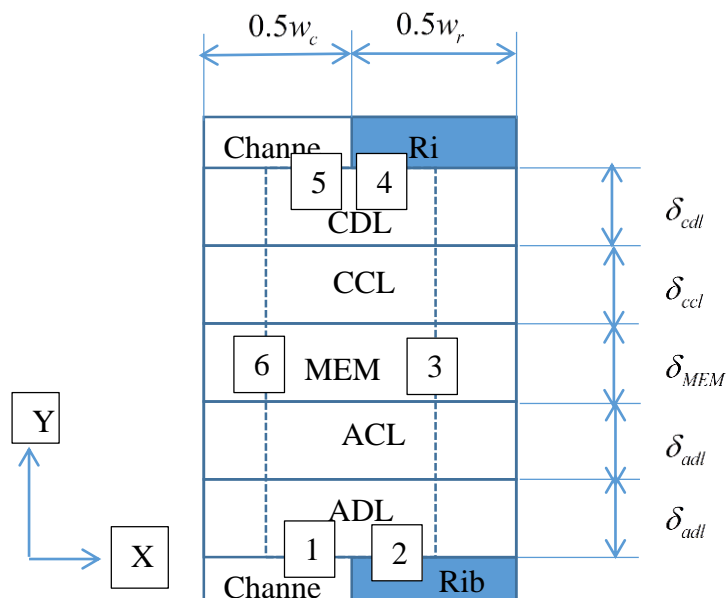
## 2. Battery principle and model

Taking DMFC as the research object, its schematic diagram is shown in Figure 1. The methanol aqueous solution flows in from the anode flow channel, passes through the anode diffusion layer through diffusion and convection, and reaches the anode catalytic layer. On the anode catalytic layer, methanol is oxidized to generate carbon dioxide gas, electrons and hydrogen ions. The hydrogen ions are carried by water molecules through the proton exchange membrane to reach the cathode, and electrochemically react with oxygen on the catalytic layer on the cathode side to produce water. The exhaust gas is discharged from the channel. The generated carbon dioxide returns to the microchannel through the hydrophobic pores in the electrode, and is discharged along with the aqueous solution, while the electrons pass through the outer channel and reach the cathode through the load. At the same time, part of the methanol reaches the cathode through the proton exchange membrane due to permeation, and directly reacts with oxygen to generate carbon dioxide.

Anodic oxidation reaction:  $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathodic reduction reaction:  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

The two-dimensional domain, as illustrated in Fig.1, represents the geometry of a membrane electrode assembly (MEA) which consists of a fuel tank, anode diffusion layer (ADL), an anode catalyst layer (ACL), a membrane (MEM), a cathode catalyst layer (CCL), cathode diffusion layer (CDL) and cathode flow channel. The MEA is sandwiched between two parallel flow-field plates [5]. In the following, we present a two-dimensional two-phase mass transport model to analyze the characteristics of methanol transport in the DMFC. The computational domain is the region that is enclosed by the dashed lines Fig.1.



**Figure 1** - Diagram of the computational model of a DMFC fuel cell in the x-y

### 3. Mathematical model of direct methanol fuel cell

The  $\mu$ DMFC model includes the anode (cathode) channel, the anode (cathode) diffusion layer, the anode (cathode) catalytic layer and the proton exchange membrane. The model calculation unit is shown in Figure 1. Inside the direct methanol fuel cell, the main consideration is the mass conservation equation, momentum conservation equation in the flow channel and porous media, and the energy exchange and conservation between substances.

Aiming at the steady-state characteristics of this model, the momentum conservation equation is:

$$C_{M,l} : \nabla \cdot \left[ \left( -\frac{Kk_{rl}}{\mu_l} \nabla p_l \right) C_{M,l,a} - D_M^{eff} \nabla C_{M,l,a} \right] = \dot{R}_{M,l,a} \quad (1)$$

$$C_{O_2,g} : \nabla \cdot \left[ \left( -\frac{Kk_{rg}}{\mu_g} \nabla p_{g,c} \right) C_{O_2,g,c} - D_{O_2,g}^{eff} \nabla C_{O_2,g,c} \right] = \dot{R}_{O_2,g,c} \quad (2)$$

In the anode catalytic layer and proton exchange membrane of  $\mu$ DMFC, the fluid substances are liquid water, hydronium ions, and methanol molecules that penetrate from the anode to the cathode. The source term  $S_{l,a}$ ,  $S_{l,c}$  should be:

$$S_{l,a} : \nabla \cdot \left[ \left( -\frac{Kk_{rg}}{\mu_g / \rho_g} \right) \underbrace{\left( \frac{dp_c}{dS} \nabla S_{l,a} + \nabla p_{l,a} \right)}_{\nabla p_{g,a}} \right] = \dot{m}_{g,a} \quad (3)$$

$$S_{l,c} : \nabla \cdot \left[ \left( -\frac{Kk_{rl}}{\mu_l/\rho_l} \right) \underbrace{\left( -\frac{dp_c}{dS} \nabla S_{l,c} + \nabla p_{g,c} \right)}_{\nabla p_{l,c}} \right] = \dot{m}_{l,c} \quad (4)$$

### 3.1 Electrochemical reaction rate

Inside the  $\mu$ DMFC, the reaction mechanism of the oxidation reaction of methanol on the anode side and the reduction reaction of oxygen on the cathode side is more complicated, and many stable and unstable intermediate substances are generated during the reaction. At the same time, it can be seen from the law of conservation of mass and the mass transfer equation that these equations are a series of partial differential equations coupled with the electrochemical reaction kinetics, so it is very important to solve the local electrochemical reaction rate relationship. Electrochemical reaction rate of anode catalyst layer.

$$j_a = A_{v,a} j_{0,M}^{ref} \left( \frac{C_M}{C_M^{ref}} \right)^\gamma \exp \left( \frac{\alpha_a F}{RT} \eta_a \right) \quad (5)$$

On the chemical layer side, the oxygen reduction reaction current includes not only the external current of the battery, but also the parasitic current generated by the direct oxidation of methanol and oxygen permeating the proton exchange membrane. Therefore, the electrochemical reaction rate on the cathode side of the  $\mu$ DMFC is.

$$j_c = A_{v,c} j_{0,O_2}^{ref} \left( \frac{C_{O_2}/k_{H,O_2}}{C_{O_2}^{ref}} \right) \exp \left( \frac{\alpha_c F}{RT} \eta_c \right) \xi_1 \xi_2 \quad (6)$$

### 3.2 Model parameters

The geometric parameters and working parameters in the relevant model are shown in Table 1. The mathematical modeling of  $\mu$ DMFC requires the following assumptions: The gravity effect is negligible. The oxidation gas in the cathode flow channel is a gas mixture and an ideal gas mixture. The gas flow in the cathode flow channel is laminar. The pressure of the methanol aqueous solution in the anode flow channel is constant. The flow of methanol aqueous solution in the anode flow channel is incompressible laminar flow. The diffusion layer, catalyst layer, and proton exchange membrane are isotropic, and gas cannot pass through the membrane.

#### Model verification

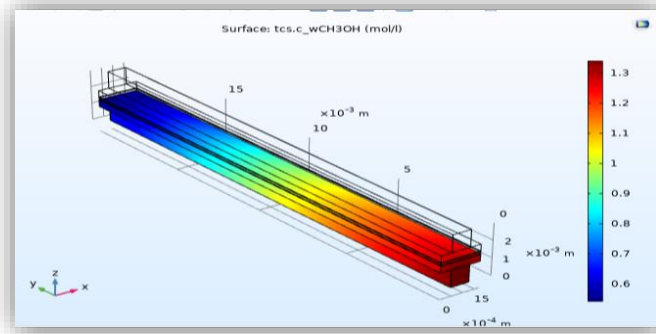
In research, the power density test curve is the same as the actual  $\mu$ DMFC test curve [6].

Table 1. Geometric parameters and working parameters of the  $\mu$ DMFC model.

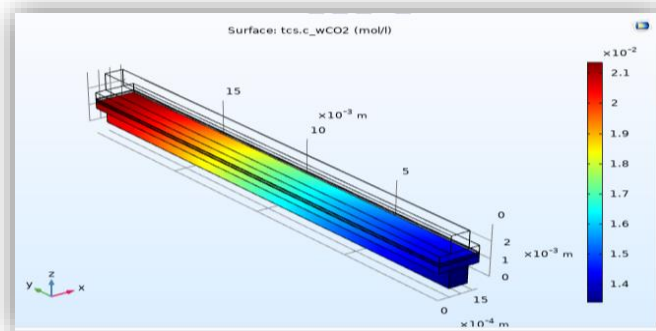
Parameter	value
Working temperature	353 (K)
Runner depth	300 ( $\mu\text{m}$ )
Thickness of diffusion layer	200 ( $\mu\text{m}$ )
Proton exchange membrane thickness	100 ( $\mu\text{m}$ )
Catalytic layer thickness	30 ( $\mu\text{m}$ )
Diffusion layer porosity	0.5
Catalytic layer porosity	0.4
Diffusion coefficient of methanol in water	$2.8 \times 10^{-9}$ ( $\text{m}^2/\text{s}$ )
Two-phase diffusion coefficient of oxygen and water	$3.58 \times 10^{-5}$ ( $\text{m}^2/\text{s}$ )
Permeability coefficient of diffusion layer	17.6 ( $\mu\text{m}^2$ )
Permeability coefficient of catalytic layer	18 ( $\mu\text{m}^2$ )
Viscosity coefficient of methanol aqueous solution	$3.15 \times 10^{-4}$ ( $\text{Pa}\cdot\text{s}$ )
Air viscosity coefficient	$2.05 \times 10^{-5}$ ( $\text{Pa}\cdot\text{s}$ )
Proton exchange membrane conductivity	9.8 (S/m)

#### 4. Results and conclusion

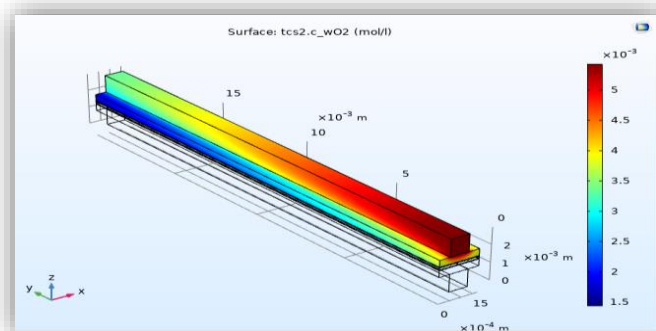
In this study we investigated the properties of the species diffusion layer (ADL) affect the optimal performance of the electrode [7]. Diffusion layers (DL) are porous media allowing reactive gases and liquids to move from distribution channels to catalyst layers (CC). Diffusion layers are an essential part of the PEM fuel cell and the porosity of these layers has a significant effect on the performance of the PEM fuel cell. The effects of diffusion layer porosity (CD) on fuel cell performance are illustrated by the distribution curves of methanol and carbon dioxide at the anode, water and oxygen distribution at the cathode. And polarization curves in Figure 2-3-4-5. for three different porosities of the CD of 0.1,0.3,0.5. It is shown that the variation of the porosity in the diffusion layers of the reactants has a significant influence on the diffusion of the methanol and oxygen reactants and the current density; it is evident that the fuel cell with a larger CDS porosity expands the limitation of the diffusion of the reagents towards the CCA anodic reagent zones. Note that the increase in methanol must be eliminated or limited for that of the porosity of the membrane layer which must be in a very limited interval between 0.1 and 0.15 [7].



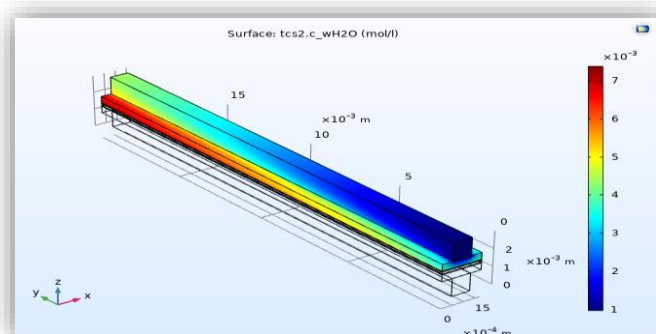
(a)



(b)



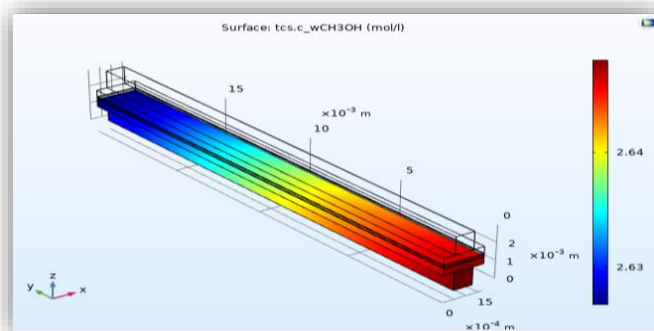
(c)



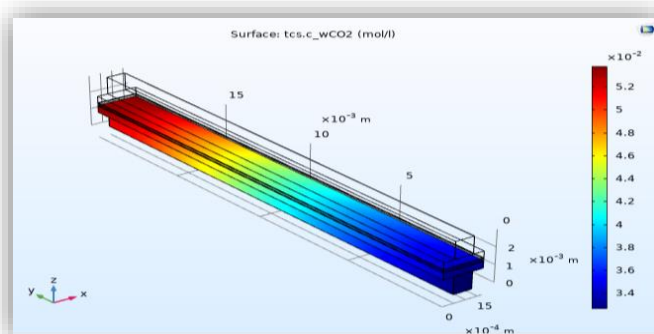
(d)

Figure 2 - Distribution of concentrations (a) of methanol at the anode, c) of oxygen at the cathode b) of carbon dioxide at the anode, d) Distribution of water at the cathode with CD

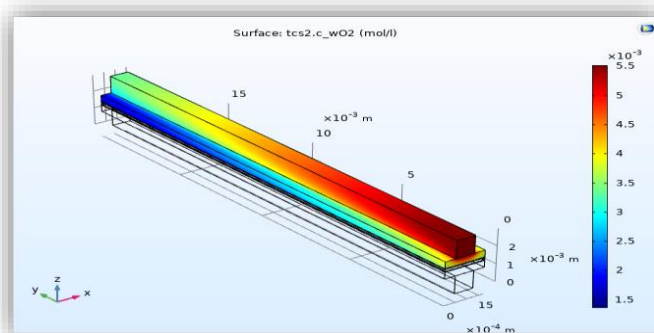
porosities  $\varepsilon_{agdl} = 0.1$  and  $\varepsilon_{mem} = 0.1$



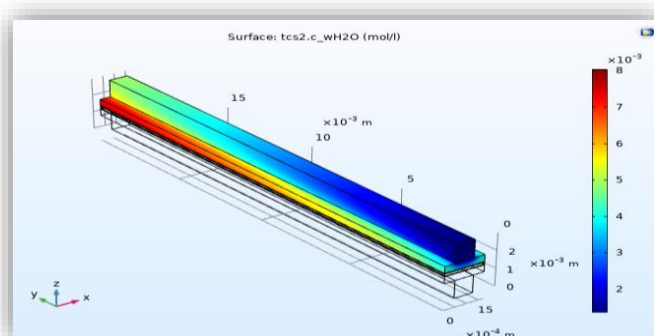
(a)



(b)



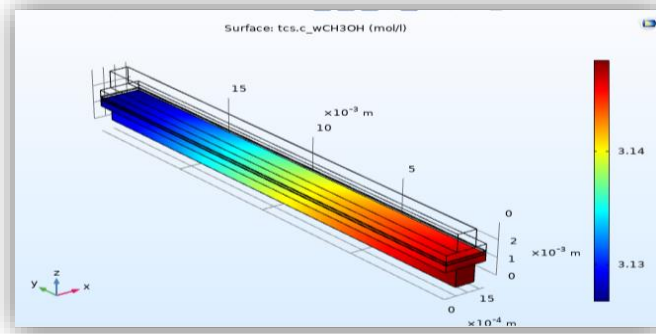
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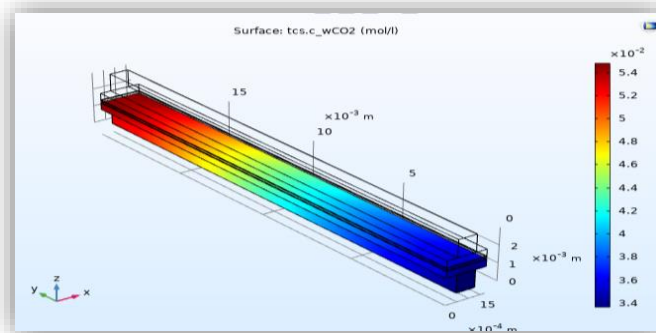
(d)

Figure 3 - Distribution of concentrations a) of methanol at the anode, c) of oxygen at the cathode b) of carbon dioxide at the anode, d) Distribution of water at the cathode with CD

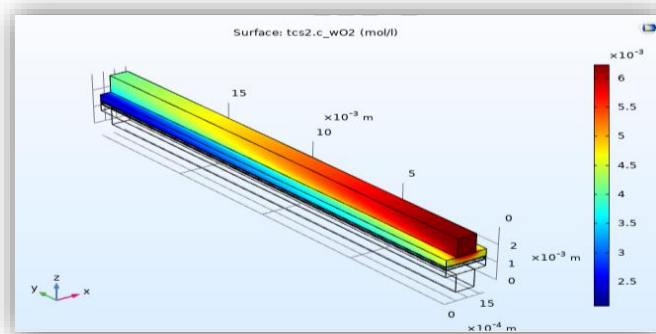
porosities  $\varepsilon_{agdl} = 0.3$  and  $\varepsilon_{mem} = 0.1$



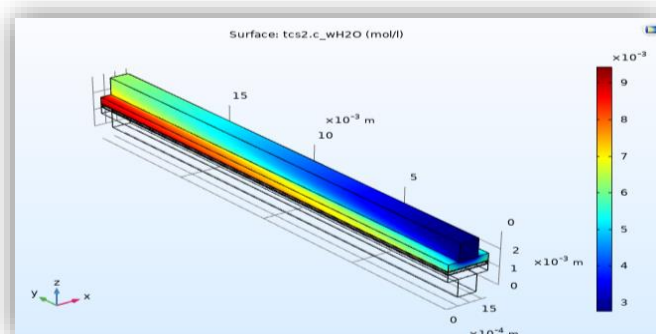
(a)



(b)



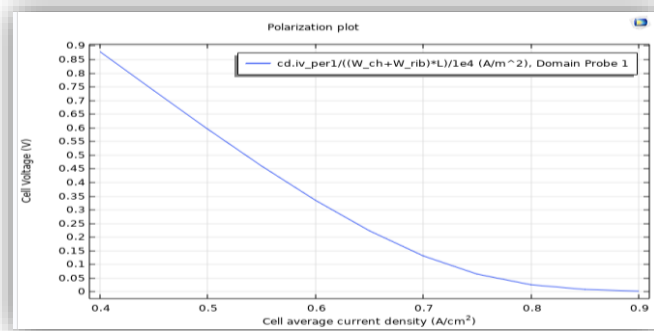
(c)



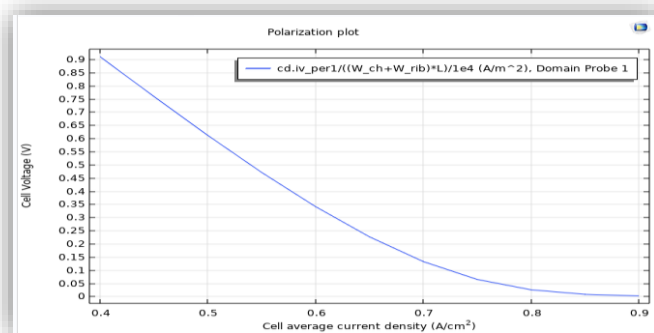
(d)

Figure 4 - Distribution of concentrations (a) of Methanol at the anode, c) of oxygen at the cathode b) of carbon dioxide at the anode, d) Distribution of water at the cathode with CD porosities  $\varepsilon_{agdl} = 0.5$  and  $\varepsilon_{mem} = 0.1$

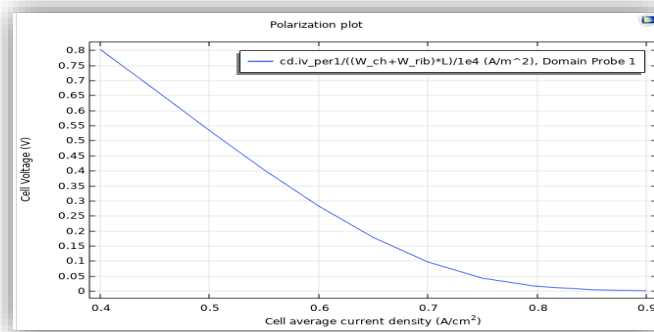




(a)



(b)



(c)

Figure 5 - Effects of CD porosity on the performance of the DMFC fuel cell

$$(a) \varepsilon_{CDA} = 0.5 (b) \varepsilon_{CDA} = 0.3 (c) \varepsilon_{CDA} = 0.1$$

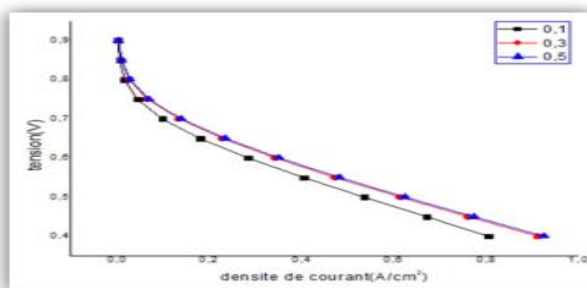


Figure 6 - Effects of CD porosity on the performance of the DMFC fuel cell

$$(a) \varepsilon_{CDA} = 0.5 (b) \varepsilon_{CDA} = 0.3 (c) \varepsilon_{CDA} = 0.1$$

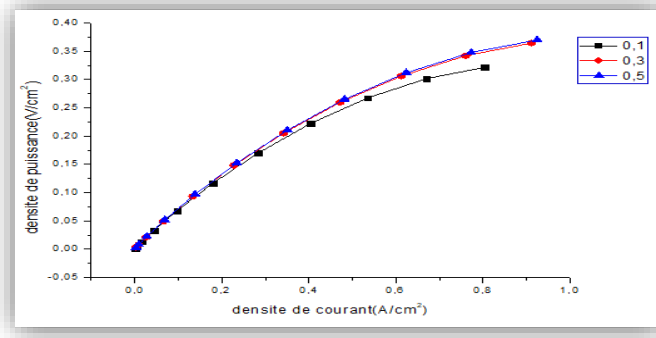


Figure 7 - Fuel cell performance, power density ( $V / cm^2$ ) as a function of current density ( $A/cm^2$ ). Modeling conditions,  $\epsilon_{CDA} = 0.1, \epsilon_{CDA} = 0.3, \epsilon_{CDA} = 0.5$  plotted with OriginPro8.

Figure 6 where the curves were drawn by OriginPro 8 and in which we put together the three curves for the three with CD porosities  $\epsilon_{agdl} = 0.1$  and  $\epsilon_{mem} = 0.1$  using the values that were taken from COMSOL 5.4. With these curves we can clearly see the difference between the graphs.

Figure 2, Figure 3, Figure 4, shows the distribution of the mole fraction of oxygen, and water at the side of the cathode and of methanol and carbon dioxide CO2 at the side of the anode in different porosities of the CDA anodic diffusion layer. The methanol mole fraction increases with a higher porosity of the anode CD  $\epsilon_{CDA} = 0.5$  than in the case of a porosity of  $\epsilon_{CDA} = 0.3$ , and  $\epsilon_{CDA} = 0.1$  since increased volume porosity reduces the resistance to mass transport, thus allowing a more complete electrochemical reaction, and the same for oxygen and other products resulting from electrochemical reactions in the anode and cathode catalyst layer is which are carbon dioxide CO2 and water.

Figure 5 shows again that for a larger CDA porosity we will have an upper limiting current density  $a, (9(A/cm^2))$  because a lower current density is produced with a lower porosity due to the reduction in the diffusion of methanol to the catalyst layer. CCA anodic. Higher volume porosity has positive effects on the mass transport of oxygen on the cathode side as well as methanol on the anode side. This permutation of methanol through the membrane allows to have the phenomenon of methanol growth and which allows us to have the parasitic current which decreases the performance of the DMFC battery.

For carbon dioxide CO2, note that the latter plays a large role in the displacement of methanol towards the cathodic side of which the growth of methanol results, because it plays the role of a barrier to the diffusion of methanol. So the increase in CO2 is significant in some way.

Figure 6 illustrates the power density curves of the cell with different porosity  $\varepsilon_{CDA} = 0.1, \varepsilon_{CDA} = 0.3, \varepsilon_{CDA} = 0.5$  which indicates as the porosity increases, the power density curves of the models also increase and higher peak power densities are obtained.

However, the voltage corresponding to the peak power density decreases resulting in a decrease in the efficiency of the cell. In order to maintain high efficiency, the fuel cell operates at  $\varepsilon_{CDA} = 0.3$  , and  $\varepsilon_{CDA} = 0.5$  . Interestingly, the experimental data imply a continuous increase in power as the current density increases [7].

Our conclusion in this case is to use the average porosity to avoid having the phenomenon of increased methanol on the one hand and to have the highest yield for this battery on the other hand. So we will take the porosity  $\varepsilon_{CDA} = 0.3$  .

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