Anode flow field design effect on direct methanol fuel cells

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Abstract:

Within the last years, there has been an increasing interest in the use of alternative fuels, among others, methanol. This fuel is liquid at ambient temperature and pressure and can be obtained through a synthesis process from hydrogen and captured CO_2, becoming e-methanol. Direct methanol fuel cells (DMFC) are devices that use this fuel in liquid form, without a reforming step, to produce electricity. These fuel cells have few moving parts and are used in portable electronic devices and electric vehicles. However, DMFC have efficiencies around 32 % and its commercial application is limited at present. Besides, advances need to be made to solve problems such as methanol crossover, sluggish methanol oxidation reaction and demand of noble metal for fabrication of these fuel cells. In this work, the effect of the depth of an anode serpentine flow field design on the performance of a direct methanol fuel cell is investigated experimentally. Stainless steel plates (SS316L) with single serpentine flow fields of different depths are designed, fabricated and tested. The study is conducted with these plates forming a single cell of 16 cm^2 of active membrane area. The aim of this work is to study the effect of the anode channel depth on the performance of a DMFC, analysing the influence of this parameter on the power density of this device and the methanol crossover that takes place during its operation. When the channel depth decrease from 1.5 mm to 0.5 mm, can be observed a power density increment of 18.86 %. However, the decrease of the channel depth resulted in an increase of the limiting methanol crossover current density by 28.75 %.

Keywords:

Methanol; fuel cell; anode flow field design; single serpentine flow field.

1. Introduction

Fuel cells are electrochemical devices that convert the chemical energy from a fuel and oxidant directly into electrical energy and heat. Theoretically, this way of obtaining electrical energy has higher efficiency as compared to internal combustion engines [1]. Fuel cells have the capability of supplying energy meanwhile the corresponding reactants are fed, and they are very versatile and scalable. Therefore they are a good alternative to traditional energy devices such as Li-ion batteries, having an enormous growth potential [1]–[3]. Considering the type of electrolyte used, there is a wide variety of fuel cell types. One of the most popular choices for renewable and sustainable energy conversion devices is the Proton Exchange Membrane Fuel Cell (PEMFC) [2]. This type of fuel cell is popular due to its high-power output, high efficiency, high specific energy, cleanliness, low operating temperature (below 100ºC), quick start-up times, longer life span and quiet operation [4],[5]. The main feature of the PEMFC is the electrolyte used, a proton conductive polymer membrane whose main function is the transport of protons from the anode to the cathode. Meanwhile, this membrane avoids the transport of electrons or reactants [5],[6]. PEMFC can use different fuels, being hydrogen the most studied, but its properties imply some drawbacks that make difficult their commercialization at this moment [3],[7]. Hydrogen has high flammability and a low volumetric energy density (hydrogen volumetric energy density in liquid state is 10.1 MJ/L, and compressed at 70 MPa is 5.6 MJ/L, while the volumetric energy density of natural gas is 22.2 MJ/L) [8]–[10]. This leads to the use of high-pressure technologies (like bulky pressure tanks or compressors) or/and very low temperature technologies for its handling, storage and

distribution [8]. These particularities represent a technological challenge at this moment. Nevertheless, the use of liquid fuels at room temperature, like methanol or ethanol, requires a notably easier storage and refuelling systems, because liquid fuels can be operated at standard temperatures and pressure [3],[9].

Direct methanol fuel cells (DMFC) use methanol as fuel, which offers advantages compared to hydrogen fuel cells, as a cheaper refuelling system, as methanol is easy to handle at standard temperatures and pressures derived from its liquid state [3],[11]–[13]. DMFCs are especially effective at delivering electricity for portable electronic devices and other mobile applications. [9],[13],[14].

DMFCs are fuel cells of PEMFC type and essentially consist of a membrane-electrode assembly (MEA), composed by two electrodes (anode and cathode) separated by an electrolyte (usually a polymeric membrane) [13]. The MEA is sandwiched between two bipolar plates (BPs) which have channels to distribute the fuel and oxidant through the gas diffusion layer [12],[13].

In DMFCs, methanol is oxidized at the anode yielding protons, electrons and CO_2. The protons are transported to the cathode, through the membrane, while the electrons are transported via an external circuit to the cathode. On the cathode the electrons and protons react with oxygen to produce water. By-products from both reactions, methanol oxidation and oxygen reduction, CO_2 and water are formed on anode and cathode respectively, and they are evacuated by BPs [3],[12],[13],[15]. The reactions are:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (R1)

Cathode: $\frac{3}{2}O_2 + 6e^- + 6H^+ \rightarrow 3H_2O$ (R2)

Overall: $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 3H_2O$ (R3)

The efficiency of fuel cells is determined by many variables, including operational parameters, such as cell operating temperature, mass transport, flow rates and other physical components of the cell like the membrane electrode assembly (MEA) as well as the BPs [4], [16].

BPs have fundamental roles that affect the performance of the fuel cell. Their design determines water management for the DMFC, preventing the flooding of the cathode. Also, BPs provides structural support for the thin and mechanical weak MEAs, facilitating heat and electrical conductivity, and mass transport (reactants and by-products). In fact, the geometry of BP channels helps the entry and distribution of the reactants onto the active surface of the cell, the gas diffusion layer, and the evacuation of the by-products. In addition, the geometry of BP channels influences the crossover process. Experimental results show that single serpentine flow fields present low pressure drops between the inlet and the outlet of the channel, which effectively removes products and prevents blockages of the flow field [11],[17].

The objective of this work is to determine the influence of channel depth on the electrochemical performance of a DMFC and crossover produced during the operation of this device. For that purpose, three different anode channel depths (0.5, 1.0 and 1.5 mm) have been studied. Channels depth affects the mass transport, fluid velocity and the fraction of the two phases (gas and liquid phase) thus affecting the cell performance [14]. In this work, a series of experiments was designed to obtain the polarization curves and measure the limiting methanol crossover current density for each depth.

2. Methodology

This section outlines the methodology used to determine the impact of the anode channel depth on the performance of a DMFC. The parameters of the anode channel configuration, as well as the material of the single cell plates, are set except for the depth.

As previously stated, BPs have fundamental roles on cell performance, as supply reactants, remove reaction products, act as current collectors and facilitate thermal management and structural support [4]. Having those fundamental roles in mind, the material used in this work for bipolar plates is stainless steel 316L (SS316L). As metallic material, SS316L has good mechanical resistance, high electrical conductivity, it is easily machinable [19] and it has good characteristics over a prolonged period of time [20]. Stainless steel is also capable of self-passivating, which allows a significant reduction of corrosive rate, however, it results in a notable increase in interfacial contact resistance with other elements such as gas diffusion layer in the case of fuel cells [21].

The DMFC single cell used this work (Figure 1A) is composed by two plates of stainless steel 316L (anode and cathode plates), two gaskets which prevent the electrical contact between the plates and avoid fluid leaks, and a MEA. The MEA is composed by a Nafion membrane, sandwiched between two layers of commercial electrodes.

Figure 1B shows the front view of the flow field plate used in this work, depicting stainless steel plates for the anode flow field. These plates feature single-channel serpentines measuring 1 mm of channel width. The channel depths studied include 0.5, 1.0 and 1.5 mm. As introduced before, according to literature the single-channel serpentine configuration prevents the blockage of the channel, allows the effective removal of products, suitable two-phase mass transport and appropriate flow behind the ribs [22], and facilitates a uniform reactant distribution [23]. For all these reasons single-serpentine flow field is the flow pattern more commonly used at present. However, this flow pattern presents significant concentration gradient between the inlet and the outlet [23].
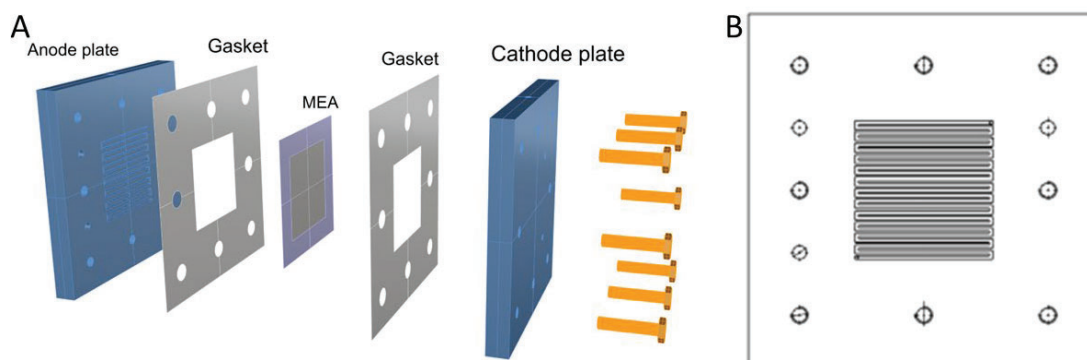

Figure 1. A- Exploded view of the designed and fabricated in-house DMFC single cell used in this work. B- Front-view projection of the flow field design of the anode plate studied.

The performance of the DMFC is also affected by the direction of the supply of the reactant, as this direction is related to the uniformity of the reactant distribution and temperature over the cell [24]. The methanol solution inside the anode is supplied bottom-up, against gravity. In this way, the formed gaseous CO_2 would be swept by the methanol solution, following the natural pressure gradient for easier evacuation [25]. Analogously, the oxidant, oxygen, is supplied from the top inlet of the cell to ease the evacuation of the liquid water produced in the cathode, to prevent the cathode channels from flooding [24].

The design parameters of the anode and cathode plates, used with the aim of determining the effect of the depth channel on the cell performance, are summarized in Table 1.

Table 1. Parameters of the anode channels studied in this work.

Parameter	BP1	BP2	BP3
Depth of anode channels, mm	0.5	1.0	1.5
Depth of cathode channels, mm	0.5	0.5	0.5
Material of the bipolar plates	SS316L	SS316L	SS316L
Number of channels	25	25	25
Width of the channel, mm	1.0	1.0	1.0
Open Ratio	0.624	0.624	0.624
Contact surface treatment	N3	N3	N3

The fuel and oxidant flow rates are set to obtain excess supply of the reactants avoiding possible mass transfer losses. The parameters used in this work are summarized in Table 2.

Table 2. Parameters used during the experimental tests developed in this work.

Parameter	Value
Temperature, °C	60
Methanol concentration, mol/l	1
Methanol flow rate, ml/min	3
Methanol supplier	Panreac AppliedChem (99.9%)
Oxygen flow rate, ml/min	110
Oxygen pressure, MPa	0.1
Anode catalyst	Pt/Ru
Anode catalyst charge, mg/cm^2	3
Anode commercial reference	BC-H225-10F
Anode supplier	Quintech
Cathode catalyst	Pt
Cathode catalyst charge, mg/cm^2	1
Cathode commercial reference	BC-M100-30F
Cathode supplier	Quintech

3. Results and discussion

Figure 2 shows the polarisation and power density curves obtained for each of the anode channel depths studied.
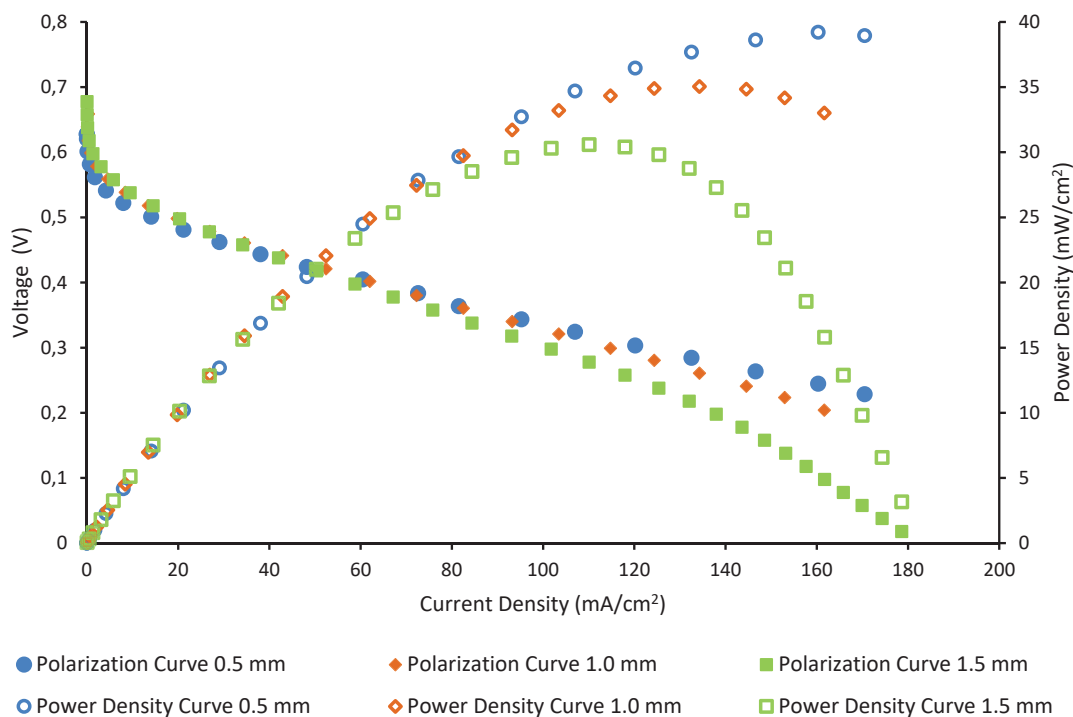

Figure 2. Polarization and power density curves of the DMFC single cell with anode channel depths of 0.5 mm, 1.0 mm and 1.5 mm, results obtained at a temperature of 60 ºC, cathode pressure 1 bar, oxygen flow rate of 110 ml/min, a methanol concentration of 1 M and methanol flow rate of 3 ml/min.

The results suggest that, for a given operating condition, a decrease in the anode channel depth leads to an improvement in the DMFC performance, contrary to the conclusions of the work of Chen et al. for a DMFC stack [14], as a reduction in the depth of the anode channels of the stack does not cause significant changes in the analysed stack performance. This may mean that the performance of the channel configuration in a single cell and a stack could not have a directly proportional relationship, so smaller improvements can be observed when working with a stack.

Furthermore, during the tests for obtaining polarization curves using the anode channel depth of 1.5 mm it was observed an accumulation of CO_2 in the anode channel. Results suggest that difficulties on CO_2 removal can affect the DMFC performance producing a decrease in peak power density.

In Figure 2 it can be observed that the peak power density increases from 32.76 mW/cm^2 with 1.5 mm of depth to 38.94 mW/cm^2 with 0.5 mm of depth. However, it should be noted that reducing the depth of the flow channel results in increased pressure drops along the channel [27]. This, in turn, increases the power required for pumping the methanol solution. Consequently, the overall efficiency of a DMFC system may decline. Furthermore, a higher pressure drop could cause a portion of the methanol solution to bypass the flow channel and instead flow directly through the diffusion layer. Also, a lower channel depth than the 0.5 mm tested could produce a worst performance due to factors including methanol crossover and the void fraction of CO_2 [27]. For these reasons, future research should examine the trade-off between the advantages and disadvantages arising from the alteration in channel depth for a DMFC stack and its auxiliary systems.

Figure 3 shows the impact of channel depth on limiting crossover current density. Methanol crossover causes electrode depolarization, mixed potential, resulting in an open-circuit voltage below 0.8V. Besides it consumes some reactant at the cathode, so it produces intermediates of the reaction, like carbon monoxide, that poisons the cathode catalyst and generates water accumulation on the cathode. Consequently, the crossover current density cause the reduction of fuel cell performance [26],[15].
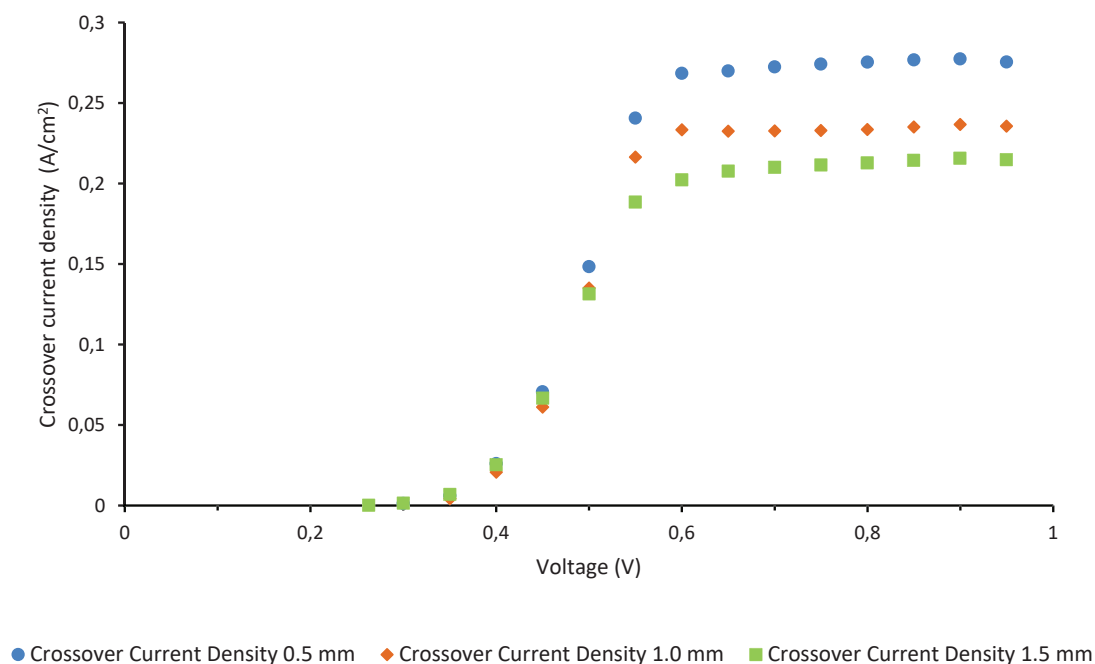

● Crossover Current Density 0.5 mm   ◆ Crossover Current Density 1.0 mm   ■ Crossover Current Density 1.5 mm

Figure 3. Crossover current density of the DMFC with bipolar plate with 0.5 mm, 1.0 mm and 1.5 mm of channel depth, results obtained at a temperature of 60 ºC, cathode pressure 1 bar, nitrogen flow rate of 110 ml/min, a methanol concentration of 1 M and methanol flow rate of 3 ml/min.

The graph presented in Figure 3 illustrates the relationship between the applied potential and the current density generated by the oxidation of methanol as it passes through the assembly. The maximum current density observed for each MEA represents its respective limiting crossover current density. Minimizing methanol crossover through the membrane is crucial for enhancing both fuel utilization and the potential at the cathode in DMFC operations [28]. Regarding this matter, Figure 3 demonstrates that deeper channels feature superior properties in preventing methanol crossover compared to shallower channels. This is evident from its slightly lower limiting methanol current density. As a result, the DMFC with the 1.5 mm channel displays the lowest limiting crossover current density value (215 mA/cm^2), which is significantly lower than that of 1 mm (236 mA/cm^2) and 0.5 mm (277 mA/cm^2).

Comparing the results shown in Figures 2 and 3, it can be concluded that despite producing a higher crossover, a shallower channel depth seems to give better results when analysing the power density of the studied single cell.

4. Conclusions

The effect of the anode channel depth on the DMFC performance has been investigated experimentally. The results show that an anode channel depth of 0.5 mm provides a higher peak power density than 1.0 mm and 1.5 mm channels depths, obtaining an increase of 18.86 % in peak power density with respect to the deepest channel. It has also been found that gas bubbles, formed during the reaction on the anode, can generate a decrease in the cell performance when the channel depth increases. These results suggest that shallower channels improve CO_2 removal and consequently cell performance. However, changes in the anode channel depth also have an influence on the limiting crossover current density obtained, as measurements of this parameter with 0.5 mm channel depth show an increase of 28.75% over those obtained with 1.5 mm channel depth.

Future studies should be carried out to analyse the effect of anode channel depth in combination with other parameters, like temperature, methanol concentration and oxygen flow rate, to improve the performance of DMFC.

Acknowledgments

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