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DEVELOPMENT OF A PASSIVE MINI-DIRECT ETHANOL FUEL CELL: EFFECT OF MEA ASSEMBLY PARAMETERS BY HOT PRESSURE

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Abstract

This paper presents preliminary results on the design, construction and evaluation of a passive mini direct ethanol fuel cell (DEFC), capillary fed with 2 mol l^{-1} aqueous ethanol, at a rate of 2.03 µL min^{-1}, and air oxygen in the cathode through an air vent. Parameters such as pressure, temperature and time of manufacturing a membrane-electrode assembly (MEA) by hot-pressure were evaluated. As the electrode holder used a 0.25 cm^2 carbon tissue which was deposited on the catalytic layer (C. L.) for both the anode (0.8 mg cm^{-2} of PtRu/C) and the cathode (0.8 mg cm^{-2} of Pt/C), Nafion® 115 membranes were used as the electrolyte. The results show, an average power density of 302 µWcm^2 under the best conditions used, a catalytic layer with a Nafion percentage of 50% at 25 °C. A temperature of 125 °C, a pressure of 49.2 Kg/cm^2, and 90 seconds duration were used to obtain the MEA.

Keywords: mini passive direct ethanol fuel cells, alcohol fuel cells, ethanol electro-oxidation.

1 Introduction

Fuel cells allows obtaining an electrical current by direct conversion of chemical energy from oxidation of the fuel at the anode and reducing oxygen at the cathode in a quiet, efficient system (40-50%) and with low emission of pollutants when is compared with other devices for energy production [1]. The proposal for years is that these devices when are fed with methanol or ethanol which have energy densities of 6.1 KWh Kg^{-1}[2] and 8 KWh kg^{-1} respectively, may eventually replace conventional batteries, such as lithium-ion of 150 Wh Kg^{-1} approximate energy density [3].

Of the two alcohols used as fuel, with methanol, higher levels of current are obtained due to the lower complexity of its mechanism on platinum when compared to ethanol. However, the use of ethanol has advantages such as lower toxicity and industrial production from different raw materials at lower production costs.

Alcohol fuel cells operating with polymer membrane as the electrolyte can be classified as passive or active according to their mode of fuel supply. Where active cells use auxiliary devices for the supply of oxygen and/or fuel [4] and operate at temperatures between 60 and 100 °C and passive cells operate at room temperature and pressure, with transport of the fuel and oxygen made by natural convection and by diffusion [5]. The latter do not require recharging of the electrical network, as conventional batteries, only a simple change of the fuel cartridge [6].

Reports by Ye et al. [5], show that the fuel supplied in a Passive Direct Methanol Fuel Cell (DMFC), self-pumping liquid fuel by CO_2 bubbles (generated from the electrochemical reactions) into a single streamer flow field. The results show that with this feeding system it was able to achieve performance comparable to that of an active pumping system with methanol 0.5 - 4.0 M. Recently Sun et al. [7], investigated a passive fuel supplied in a micro-cell direct methanol using metalized polymer bipolar plates (UV-LIGA and nano-auto assembly). A peak power density of 7.4 $mWcm^{-2}$ was found using mathematical modeling and evaluating the response of the system at different concentrations of methanol, when the cell is fed with 3 M solution of methanol and oxygen in the atmosphere, making possible to omit the auxiliary devices for circulating the fuel cell.

Although the passive operation in a DEFC is convenient because of its reduced costs, to improve the performance of the cell should also take into account parameters such as the catalysts, electrodes and membrane/electrode interfase structure, type of electrolyte and supply system of the reagents. The following studies support this idea: Peng et al. [8], using various mechanisms such as the integration of micro and nano structures with Microelectromechanical Systems (MEMS) technology were able to improve the performance of a PEM micro fuel cell increasing the surface area of reaction reaching a power density of 26 mW cm^{-2}. Yuan, W. et al. [9], investigated the effect of varying the structure of the anode and cathode in a direct methanol passive fuel cell. Some of the results confirm that the passive cell performance can be improved when at the anode and cathode, carbon fibers and carbon paper are respectively used.

No less important are the conditions of the method of manufacturing the membrane-electrode assembly (MEA). A widely used method is to use hot-pressing, which is thermo-welding two electrodes on a membrane of Nafion® under certain experimental conditions [10]. Improving MEA manufacturing process by hot-pressing can not only reduce the electric potential drop or resistance within the cell and collaborate with less dehydration of the membrane and a preservation of the same, but also because it promotes good contact in the membrane-electrode interface and increased system efficiency. The structure of the MEA can vary dramatically during the hot pressing process when the temperatures are above 100 - 160 °C and the pressures lie between 20 and 100 kg cm^{-2} causing irreversible loss of cell performance by dehydration or mechanical destruction of the membrane or system [11]. Several papers are focused on optimizing the hot-pressing procedure [12, 14].

In order to improve the membrane-electrode contact, Gan et al. [15] found that this is favored by using glycol in the preparation of cathode catalyst with cobalt tri-ethylene-tetra-amine supported on carbon (CoTETA/C) when the MEA is manufactured by hot pressing.

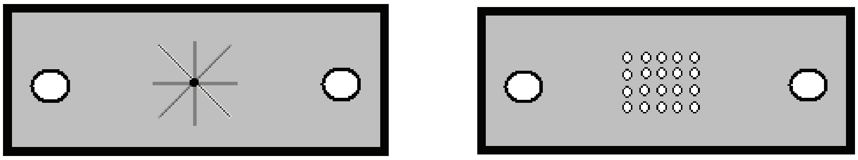
In this work we studied the effect of assembly conditions (time, temperature and pressure) of a membrane-electrode assembly for the electrochemical response of a passive miniDEFC which was necessary to build.

2 Experimental

2.1 Construction of the cell

2.1.1 Design and construction of the mini fuel cell

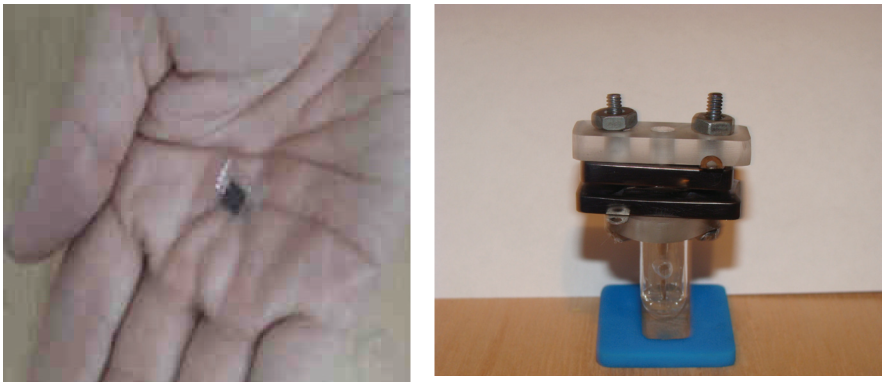
Current collector plates were manufactured in pyrolytic graphite and on them were carved some channels radially in the anode plate (Figure 1A). The fuel is fed through capillarity from a tank at the bottom and the cathode layer which functions as a vent was perforated with a series of holes for the collection of O_2 as shown in Figure 1B.



A B

Figure 1. *Images of anodic and cathodic plates (A and B).*

Figure 2A shows the dimension of the MEA and Figure 2B shows the final system of the passive DEFC, with a compartment where the fuel is stored (aqueous ethanol), the graphite anode plate and cathode plate. A third piece of nonconductive material prevents electrical contact between the screws and monopolar graphite plates. The constant flow of 2 M ethanol solution was 2.03 μL min^{-1}.



a b

Figure 2. *a) Left: MEA, b) Passive miniDEFC system*

2.1.2 Fabrication of Membrane Electrode Assembly (MEA)

The MEAs were constructed using polymer electrolyte membranes of Nafion® 115 from DuPont, which were treated and cleaned in a solution of 3% H_2O_2 at temperatures ranging from 80°- 100 °C for enough time to remove organic impurities as reported by Paganin et al. [16].

Consecutively the membranes were washed several times with hot MilliQ water, then were treated in a solution of H_2SO_4 0.5 mol L^{-1} at a temperatures ranging from 80° to 100 °C to remove metallic impurities and finally washed several times with hot MilliQ water to remove excess acid. As the electrode holder used Stackpole carbon fabric, which was treated at a temperature of 450 °C for one hour. Subsequently, it was dipped into a solution of 0.5 mol L^{-1} of HNO_3 at a temperature of 80 °C for the required time. Finally, several washes were performed with purified water from a MilliQ system.

The catalyst powder used in the ElectroChem., Inc. was Pt/C 20 wt.% (0.8 mg cm^{-2} Pt/C) for the cathode and PtRu/C 20 wt.% (0.8 mg cm^{-2} PtRu/C) for the anode. It was mixed with Nafion® solution (Aldrich, 5% alcohol), to be deposited directly onto the carbon tissue treated by a spraying process as described by Paganin et al. [16]. The geometrical electrode area was 0.25 cm^2.

In all cases we used carbon tissue treated as support for the catalytic layer. Finally, after the preparation of the electrodes with their respective catalytic loads membrane assemblies were manufactured using hot-pressed electrodes, varying the parameters of time, temperature and pressure: being time (60, 90 and 120 s), Temperature (120, 125 and 130 °C) and pressure (38.7, 49.2 and 59.8 kg cm^{-2}).

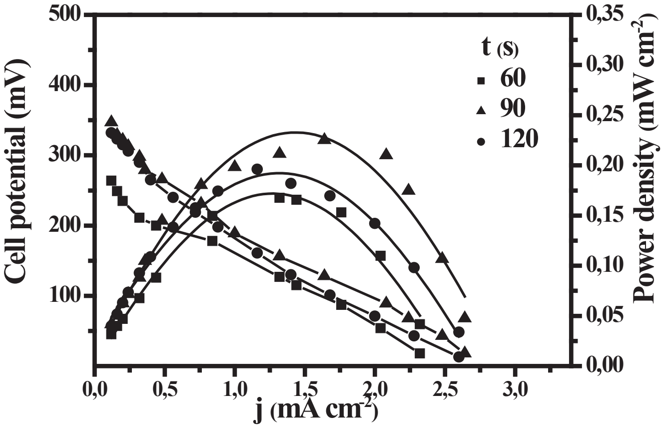
2.1.3 Electrochemical evaluation of the passive mini DEFC

After 4 hours of stabilization for each assembly prepared by hot pressing, the electrochemical response was measured by obtaining polarization curves of cell potential vs. current density using a variable resistor and conventional multimeters. The passive mini DEFC was operated at room temperature (25 °C) fed by capillary at 2.03 μL min^{-1} flow of 2 mol L^{-1} ethanol solution and oxygen fed at atmospheric pressure in the cathode.

3 Results and discussions

3.1 Effect of time of assembly

Figure 3 shows the curves of cell potential (mV) vs. current density (mA cm^{-2}) and power density (mW cm^{-2}) vs. assembly time varying the time in which the system is under a pressure of 59.8 kg cm^{-2} at 125 °C. The higher power density 0.23 mW cm^{-2} was obtained at a press time of 90 s. The power density found here is highest may be because lower assembly times are not conductive to good contact electrodes/membrane causing the catalytic layer separation of the membrane and thus a decrease in proton conductivity [11, 17] and at pressing times greater, the membrane is dehydrated decreasing proton conductivity.



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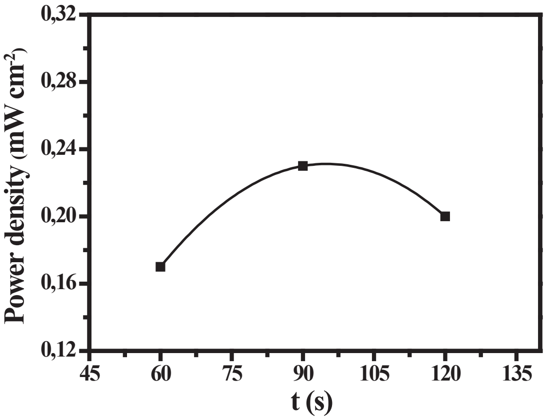
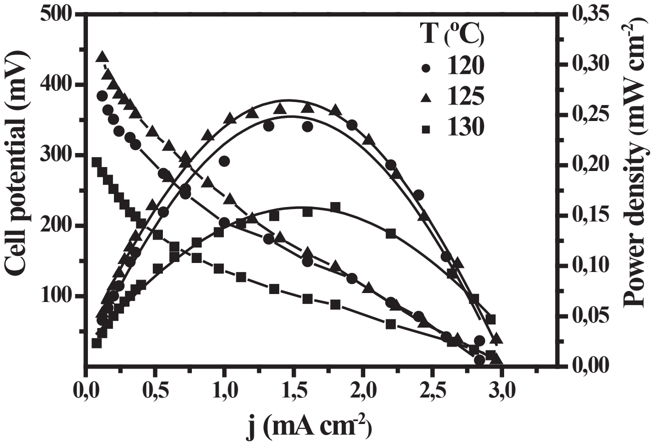


B

Figure 3. *(A) Cell potential curves (mV) vs. current density (mA cm^{-2}) (B) Power density (mWcm^{-2}) vs. Assembly time (s). Pressure = 59.8 kg cm^{-2} and T = 125 ° C. Electrode area = 0.25 cm^{2}.*

3.2 Assembly temperature effect

The influence of mini MEA assembly temperature (120, 125 and 130 °C) at 59.8 Kg cm^{-2} and 90 s, in the mini-cell electrochemical response shown in figure 4, which showed an increase in power levels of the system when the pressing temperature is about 125 °C. This can be explained considering that lower values do not contribute to a good membrane-electrode contact and values above 125 °C favors the dehydration of the membrane. A simple difference of 5 °C at the MEA hot press causes a decrease in the power from 0.27 to 0.16 mW cm^{-2} when the temperature increases from 125 to 130 °C.



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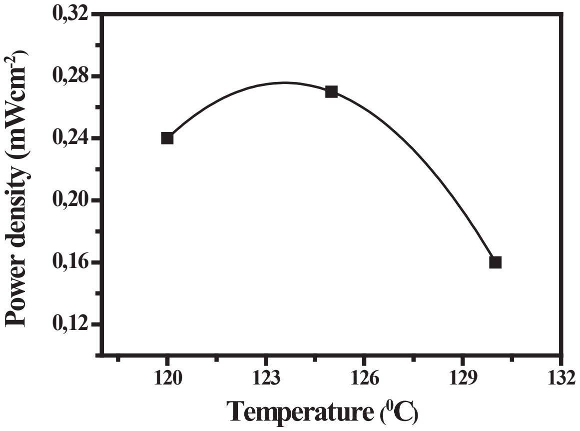

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Figure 4. *(A) Cell potential curves (mV) vs. Current density (mA cm^{-2}) and (B) Power density (mW cm^{-2}) vs. assembly temperature (°C). Pressure = 59.8 kg cm^{-2} and t = 90 s. Electrode area = 0.25 cm^2.*

3.3 Assembly pressure effect

The assembly pressure effect on the power density obtained from the system shown in Figure 5.

It is observed that from the values of pressure tested at 49.2 kg cm^{-2} is obtained a better contact between the membrane and the electrode, obtaining a power value of 0.30 mW cm^{-2}. Higher values of pressure can generate fractures in the membrane and reduce the porosity of the catalytic layer and therefore the space for movement of species.

Smaller values of pressure can generate an inadequate membrane-electrode contact, in both cases systems efficiency will decrease. These results are similar to those obtained by Therdthianwong et al., [11] who found that MEA suitable manufacturing conditions by hot-pressed for a PEMFC were at 70 kg cm^{-2}, 100 °C and 2 min. Although it is apparent that the power density (0.30 mW cm^{-2}) and the open circuit voltage generated in this passive DEFC was significantly lower (0.45 V) compared with the Gibbs free energy value (1.1 V), we believe that the reduced area of 0.25 cm^2 electrodes, the low catalyst loading of Pt/C and PtRu/C (0.8 mg cm^{-2}) and the concentration of ethanol (2 M) have a significant influence on the efficiency electrochemical system.

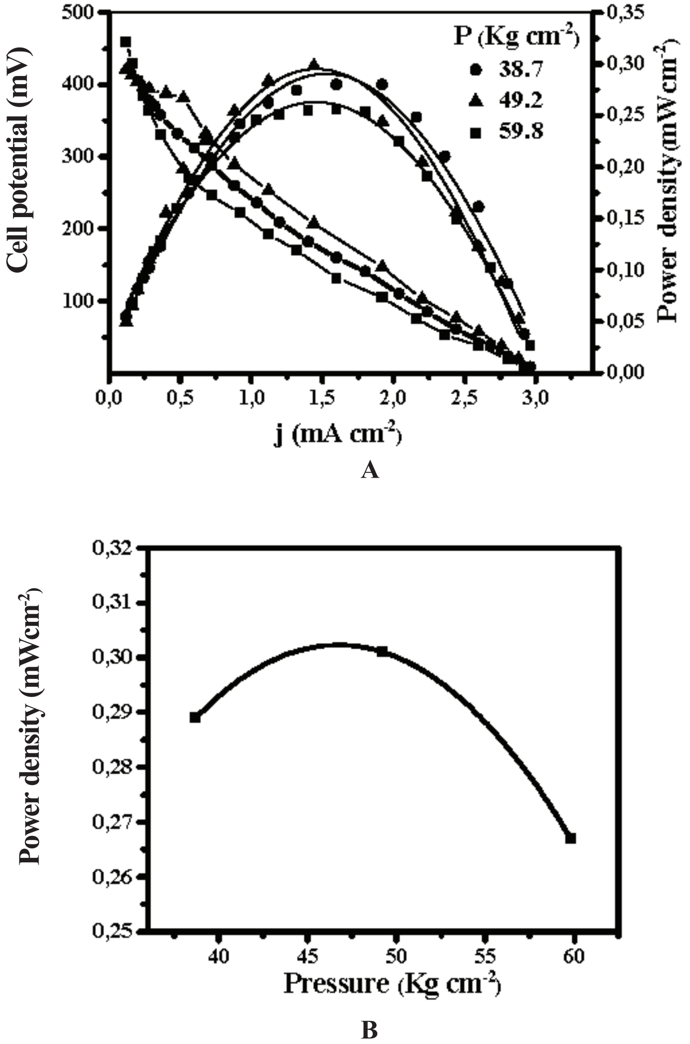

Figure 5. *(A) Cell potential curves (mV) vs. Current density (mA cm^{-2}) and (B) Power density (mW cm^{-2}) vs. assembly pressure (kg cm^{-2}). T = 125 ° C and t = 90 s. Electrode area = 0.25 cm^2.*

4 Conclusions

A passive mini DEFC was designed, built and tested. The fuel supply was made by capillarity and the oxygen supply by diffusion into the cathode through a vent. The average power density found, under the best conditions (MEA) of temperature, pressure and time equal to 125 °C, 49.2 kg cm^{-2} and 90 s respectively was 302 µW cm^{-2}, using electrodes with geometric area of 0.25 cm^{2} with real anodic and cathodic metal loads of 0.8 mg cm^{-2} respectively. Carbon tissue was used as support without a diffusing layer and an ethanol concentration of 2 M.

The power of the passive mini DEFC increases about 25% adjusting MEA variables (pressure, temperature, time), which shows not only that the effect of themselves is reasonable in efficiency system as the need for strict control of them during the assembly process.

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