Application of porous copper for GDL in PEM fuel cells

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The performance of a Proton Exchange Membrane Fuel Cell (PEMFC) is strongly influenced by the material of the gas diffusion layer (GDL). In general, a GDL is made of a carbon black mixed with Teflon micro-porous layer applied onto macro-porous carbon fiber substrate. This paper comes with the novelty that instead of the carbon based GDL we introduced a porous copper GDL. The copper plates were sintered in Ar-H2 gas mixture. Different amounts of naphthalene were mixed with copper filings in order to obtain the porous plates. The results showed that after sintering, there were no more amounts of naphthalene, fact proved by the pore appearance in their place, in the sintered copper filings. Tests have highlighted that the porous copper plates provide gas access from the flow-field channels to the catalyst layer, which is one of the main goals of the GDL.

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1. Introduction

In the present time, one of the pressing problems that humanity has to deal with is finding an alternative and viable replacement of fossil fuels, especially in the automotive sector. The main reasons are that the existing resources will rapidly decrease and will most likely not be able to keep up with the worldwide energy needs [1-4], and that the combustion of fossil fuels has a great impact of the environment, leading to global warming and large scale environmental damage [5]. In response to those problems, much attention has been given recently to the fuel cell technologies, mainly because of their efficiency (up to 60% for electrical energy conversion) and vastly reduced pollutants quantities [6].

Fuel cells have the ability to produce electrical energy by direct conversion of chemical energy that is stored in fuels such as hydrogen. In particular, due to its advantages, such as low operating temperature, good dynamic characteristics, extended runtime, scalability, reliability and high power density, Polymer Electrolyte Membrane Fuel Cells (PEMFC) have the greatest potential of being used to power all kinds of road vehicles. By the present time, many fuel cell vehicles have been demonstrated by major motor companies such as Ford, DaimlerChrysler, Honda, Toyota, Nissan etc., and even more, plans have been announced for commercialization of some of these vehicles by 2015 [7].

However, there are many problems to solve, among them, being the one of durability, which can lead to a better commercialization of PEMFCs [8].

One solution that can be achieved for this purpose is the improvement of GDLs material (gas diffusion layer), due to its impact regarding the fuel cell performance.

A PEMFC is an electrochemical device in which, on one side, the fuelled hydrogen is oxidized at the anode and splits into protons and electrons, and on the other side the fed oxygen is reduced at the cathode.

Because the proton exchange membrane is not electronic conductive (being only proton conductive as it has called "proton exchange membrane") the electrons are forced to circulate in an external circuit, generating an electrical current. The protons unleashed during the hydrogen oxidation are able to pass through the proton exchange membrane, reaching the cathode side, in which are reacting with the electrons and the oxygen and, forms water as a secondary product.

The equations that are taking place during the redox processes are the following:

at the anode: $2H_2 \rightarrow 4H^+ + 4e^-$ (1)

at the cathode: $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$ (2)

the overall reaction: $2H_2 + O_2 \rightarrow 2H_2O$ (3)

The "engine" of a PEMFC consists into a proton exchange membrane sandwiched among the porous catalyst layers and the gas diffusion layers (GDLs), forming the membrane-electrode assembly (MEA).

The MEA assembly can be made in two ways. One way consists in adding the catalyst layer directly to the proton exchange membrane, forming the so-called three layer MEA or catalyzed membrane. The second way are achieves by applying the catalyst layer onto the porous layer, forming the gas diffusion layer, and then pressed with the membrane at certain temperatures and pressure conditions [9].

In general, a GDL is made of a carbon black mixed with Teflon micro-porous layer applied onto macro-porous carbon fiber substrate.

A GDL provide mass transfer of the reactants and product water, electronic conductivity, heat removal, and

mechanical support [10]. Taking into account that in a PEMFC multiple processes are occurring simultaneously, the GDL must be optimized in such a way that the reactant gas may easily diffuse and at the same time, on the other part, the water has to be removed from the pores [9].

The main parameters that need to be focused on are the porosity and the thickness of the gas diffusion layer. Literature reviews showed many methods, which can give us information about these parameters, one of them is represented by the study of the liquid water flux through different structured GDLs [11]. Results showed that the water flux that passed through the GDL was directly proportional with the GDL porosity and inversely proportional to its thickness [11].

GDL optimization will lead also to achieve better efficiencies and greater performances of the PEMFCs.

In this paper, a porous copper GDL was studied. The porous copper was sintered at 800℃ in Ar-H2 gas mixture. The porosity of the copper plates was studied in two different ways, which are further presented.

2. Materials used for obtaining the porous copper plates

To make the copper plates we used copper filings mixed with a small amount of naphthalene (6%, 11%). We introduced naphthalene to achieve porosities into plates.

In order to obtain a square copper plate a stainless steel die, was manufactured. For its manufacture we used stainless steel no. 304, which cannot be treated with heat (including threaded rods, bolts and nuts). The alloy is resistant to corrosion and temperatures up to 820 °C, and it has approximately 140-225 Brinell hardness and tensile strength of about 30,000 psi. The die allows for a precise initial measurement of the thickness of the copper plate and, due to the side-loading procedure, it guarantees that this thickness will be constant along the length and the width of the plate.

After pressing, the copper plate can be easily and safely taken out of the die together with the bottom side, which is attached to the rest of the die with rare-earth permanent magnets.

The die allows us to obtain plates with a 30x30 mm footprint and a 20 mm maximum thickness, supports compression forces over to 500kN and does not requires any tools for assembly and disassembly.

2.1. Porous copper plates manufacturing

The manufacturing of the plates was made using the pressing and sintering processes.

Within the pressing process, we have obtained 4 copper plates, having 2.6 mm thickness each, with the following specifications: 2 plates with 6% naphthalene pressed at 19 tons- force; 2 plates with 11% naphthalene pressed at 19 tons-force.

For the thermal treatment of the copper plates, we used a tube furnace. Usually the temperature increases in the oven with a maximum speed of 300℃/hour, but in this case we worked at a 200-250℃/hour speed. The temperature control is oscillating with ±5ºC when is entering in thermal arrest. The furnace has a quartz tube of 150 cm length, used for leak having a diameter of 44 mm and a thickness of 2mm. The flow rate of the working gas, Ar-H_2 (5%), was 20 liters / hour.

To prevent the plates curvature we used a 20cm porous alumina support with which we obtained a sandwich sample. In the furnace were introduced 2 pressed plates, by-turn.

The copper plates with 11% naphthalene were thermally treated in a controlled atmosphere, first at 350 ºC for 5 hours, which was used to eliminate the naphthalene amount, and secondly, through a temperature increasing in the furnace at 800 ºC, for 45 minutes.

The copper plates with 6% naphthalene were thermally treated in several successive stages (in order to control more effectively the naphthalene removal from the mixture): 350ºC for 5hours, 350ºC-400ºC for 30 minutes, 400ºC-500ºC for 45 minutes, 500ºC-600ºC for 15 minutes, 600ºC-700ºC for 15 minutes, 800ºC for 40 minutes.

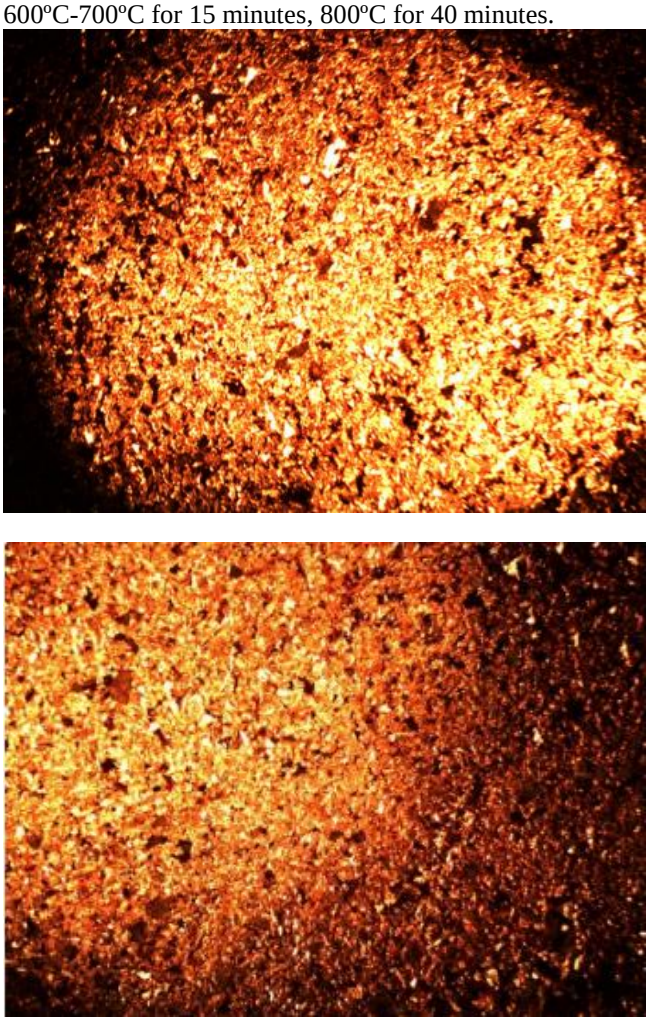


Fig.1. Sintered copper plates with 11% naphthalene (first image) and 6% naphthalene (second image), seen at optical microscope.

Fig.1 reveals the resulting images of each thermal treatment that was applied to the pressed copper plate, tak-

en by the optical microscope. We can observe areas with high porosity, pore congestion to the edges, and areas with little or no porosity, in the case with 11% naphthalene, and areas of high porosity in particular in the middle, small clusters of pores distributed largely uniformly to the edges and areas of low or no porosity at the center of the plate with 6% naphthalene.

3. Results and discussions

During the thermal treatment applied to the copper plates, we could observe, in both cases, naphthalene particles depositions on the ends of the quartz tube, the largest amount of naphthalene being deposed on the right, where the gas is removed. After the copper plates sintering we have seen no color changes in the copper aspect, patchy distributions of the pores (being more pronounced in the case of plates with 11% naphthalene) after, and that the copper plates surfaces showed no trace of oxide film, which was also confirmed by X-Ray analysis (Fig.2).

SEM and TEM characterization was performed to evaluate morphological and structural properties of Cu based GDL. TEM images and SAED pattern was used to analyze the morphological future and to confirm crystalline structure of GDL materials.

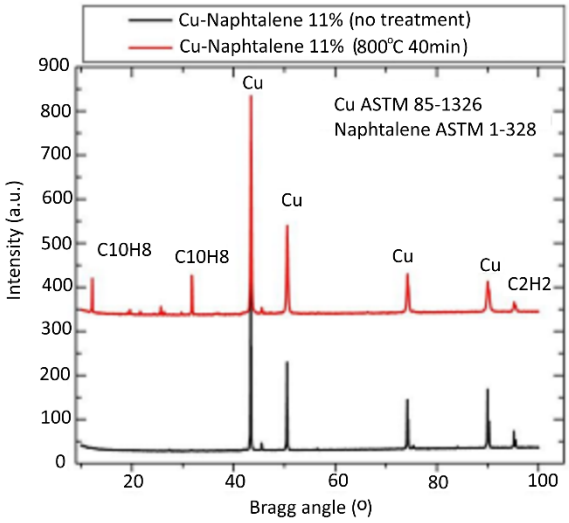


Fig.2. Copper plates (11% naphthalene) X-ray analysis

The structure of porous copper membrane is show in Fig. 3(SEM image), where presence of pore is highlight using arrow and pore diameter values. We see a typical micrometers pore and small pores with diameters around a few hundred nanometers. EDS spectra (Fig. 3) reveal Cu content of sample, but a small quantities of oxygen than will be confirmed by electron diffraction analysis as amorphous cooper oxide

Electron diffraction (inset Fig. 4) was used to evaluate crystallinity of sample. The SAED pattern shown in figure, reveal a cubic structure for Cu, but also a small amount of crystalline/amorphous Cu oxide. The profile extracted from SAED pattern with indexed lines is shown in Fig. 5. TEM image (Fig. 4) reveals morphological future of sample, with nanocrystalline particles (~24 nm as shown in histogram inset Fig. 4) embedded in amorphous matrix.

We use comparative method to indexing electron diffraction profile and modified Cohen method to evaluate lattice parameter. The lines identified shown a mixed phase Cu [WWW-Mincryst, Copper-994]-Cu_2O[WWW-Mincryst, Cupprite-1104]. We select Cu cubic cell as predominant phase, because the (220) line from cuprite phase are very weak, compared with calculated or experimentally determined intensity from X-Ray diffraction [~ 41.5% in WWW-Mincryst, Cupprite-1104].

Direct evaluation of lattice parameter for Cu gives 3.65762Å, with absolute error 0.04262 Å. Relative error in this case will be 1.1%. The result of Cohen method is 3.63549Å, evaluate using only 5 lines associated with Cu phase. The second result has smaller relative error, about 0.57%.

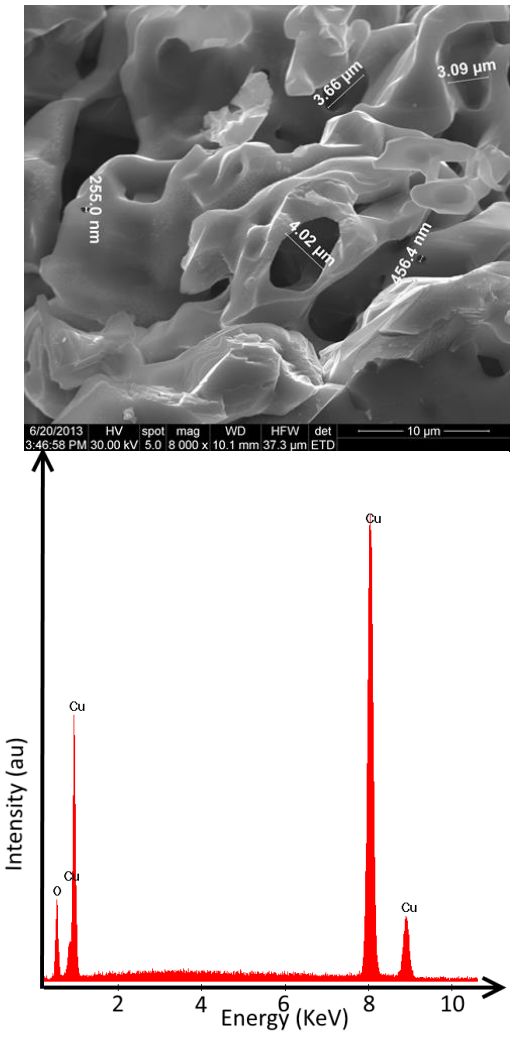


Fig. 3. SEM and EDS analysis of copper based GDL

4. Testing of the gas diffusion plates

In order to study the plates gas permeation we have made 2 pressure tests. In the first test, we have made a sandwich type assembly composed by aluminum plate- 2x

rubber gaskets-copper plate- polypropylene membrane-copper plate- 2x rubber gaskets- aluminum plate. The assembly had 26 mm thickness. We connected the assembly to the compressor by attaching a gas hose to the gas admission of the aluminum plate and we immersed it in a bowl filled with water and we made a 5 bar pressure test with compressed air.

Test has showed that the gas can pass through the copper plates porosities, obtained from the sintering process. After disassembly, we observed that the plates have remained undamaged (Fig. 6). The day after the pressure test has been noticed that the copper plates obtained in controlled atmosphere have oxidized in patches (Fig. 7).

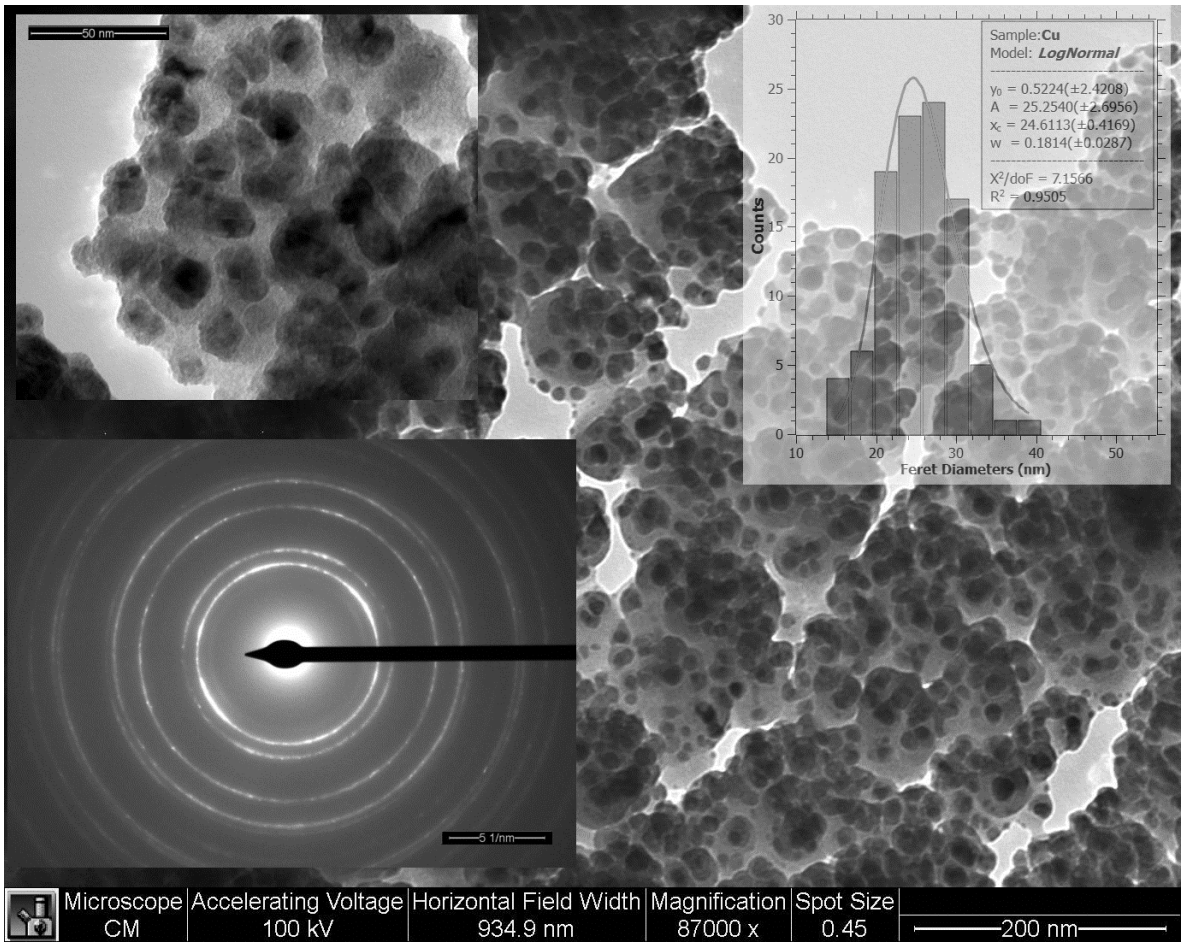


Fig.4. Cu based GDL morphological and structural investigation by TEM

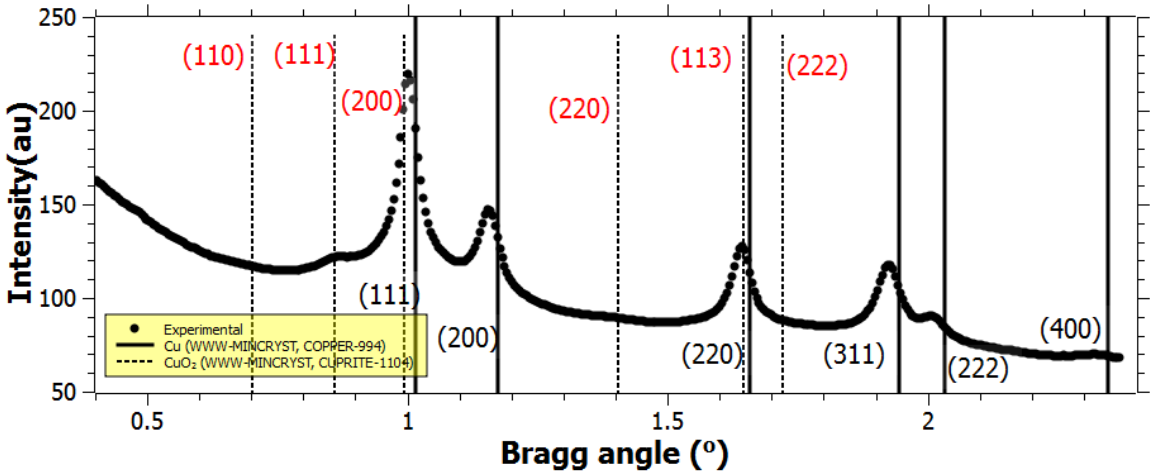


Fig.5. Indexed profile of electron diffraction pattern

Fig. 6. Copper plate after the pressure test

Fig.7. Copper plates a day after testing

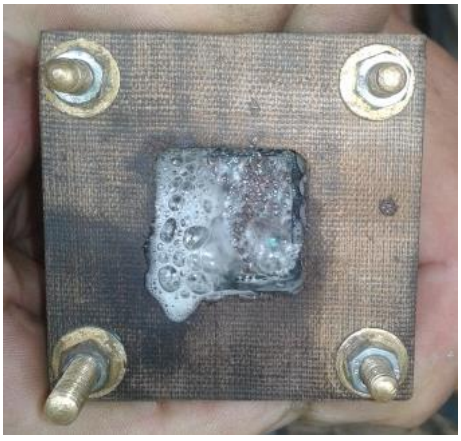
In the second test, we made a different assembly composed by aluminum plate- 2x rubber gaskets- copper plate- textolit plate fitted with window. We used the textolit plate fitted with window (23x 23 mm) because this time we wanted see exactly how the gas is passing through the copper plate pores. To make this possible we spread a small amount of liquid soap on the surface of the copper plate, which was in contact with the aluminum plate, and after that, we assembled the components. We connected the assembly to a compressor and we started the test at 2 bar pressure, and we continued to gradually increase it until 4 bar pressure.

In both cases, we could see that we achieve a large amount of bubble soap at the edges of the plate, because the pressurized air tends to push the liquid soap towards the edges (Fig. 8 a and b).

5. Conclusions

In this paper, porous copper plates for GDL in fuel cell were experimentally obtained and investigated. SEM and TEM characterization have revealed the presence of micrometers pore and smaller in the structure of porous copper membrane, meanwhile TEM images and SAED pattern showed the cubic structure of Cu having nanocrystalline particles around 24nm. The X-Ray analysis confirmed the naphthalene complete removal. Due to the fact that the quantity of the copper oxide found in the morphological and structural (SEM, TEM, SAED) investigation was very small it could not be observed on the X-Ray evaluation. Pressure tests have showed that the porous copper plates are gas permissive and high pressure resistant. Based on the experimental results and analysis we can say that the porous copper membrane might be considered as a good alternative for PEM fuel cells GDLs.

a



b

Fig.8. Copper plate assembly air pressure test: 2 bar (a) and 5 bar (b)

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