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Final Degree Project

Study of platinum catalyst deposition on Nafion membranes and its development in fuel cells

(Estudio de la deposición de catalizador de platino sobre membranas de Nafion y su desarrollo en pilas de combustible)

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ABSTRACT:

Proton Exchange Fuel Cells (PEFCs) are a promising technology for reaching a sustainable energy development due to their low emissions and high efficiency. However, if they want to compete in the market, their costs must be improved; mainly those related to the platinum catalyst. For that reason more efficient metals and ways to reduce the amount of catalyst used are being developed.

This work is part of one of the research lines of the Advanced Separation Processes group (PAS) in the development of new electrolytes more efficient based on ionic liquids for fuel cells applications. Thus, this project is focused on the set-up of an experimental technique to deposit the catalyst on fuel cell membranes in order to improve the performance of a polymer electrolyte fuel cell fed by hydrogen. Two alternatives have been tested: gas diffusion electrode (GDE) incorporation and catalyst coated membrane (CCM) fabrication. Additionally, the influence of different operation variables (temperature, gas humidity and amount of catalyst deposited) was studied. As main result, this paper has proved the potential of the CCM fabrication as a possible electrolyte for fuel cells under anhydrous conditions.

RESUMEN:

Las pilas de combustible de intercambio protónico (PEFCs) son una prometedora tecnología para alcanzar un desarrollo energético sostenible gracias a sus bajas emisiones y su alta eficiencia. Sin embargo, si quieren competir en el mercado, los costes deben ser reducidos; principalmente los relacionados con el catalizador de platino. Por esa razón se están desarrollando nuevos metales más eficaces y formas de reducir la cantidad de catalizador usado.

Este trabajo forma parte de una de las líneas de investigación del grupo Procesos Avanzados de Separación (PAS) en el desarrollo de nuevos electrolitos más eficientes basados en líquidos iónicos para pilas de combustible. Este proyecto se centra en la puesta a punto de una técnica experimental para la deposición de catalizador en membranas con el objetivo de mejorar el rendimiento de una pila de intercambio protónico. Se analizaron dos alternativas: incorporación de electrodos de difusión gaseosa (GDE, "Gas Diffusion Electrode") y la fabricación de membranas cubiertas de catalizador (CCM, "Catalyst Coated Membrane"). También se estudió la influencia de diferentes variables de operación (temperatura, humedad de los gases y cantidad de catalizador depositado). Como principal resultado, este proyecto ha probado el potencial de la fabricación de CCMs como posibles electrolitos para su uso en pilas de combustible bajo condiciones anhidras.

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1. INTRODUCTION



As a consequence of the increase of the world's population and climate change, new renewable energy sources are being developed.

Figure 1: World energy consumption by fuel type, 1990-2040 [1]



Figure 2: Renewable energy as share of total primary energy consumption, 2011 [2]

Figure 1 and figure 2 show our dependence on non-renewable sources and the future trend of the energy. Although renewable energy still represents a low percentage in the world's consumption, in the near future they will play an important role in meeting our energy requirements and in developing a sustainable world.

These energy sources are more eco-friendly compared to those traditional ones and also, they will not be depleted in the future. However, in order to compete successfully in the market some problems must be solved: high costs, variable energy supply and storage issues [3].

1.1 Fuel cells as an alternative energy source

Fuel cells are electrochemical devices which provide energy via oxidation-reduction reactions. Contrary to other energy apparatus like combustion engines, fuel cells are not limited by thermodynamic so, their efficiency is higher as seen in figure 3; furthermore, they release very low carbon emissions and hazardous compounds.



Figure 3: A comparison of electrical system efficiencies between a commercial fuel cell [4]

1.1.1. <u>Fundamentals</u>

The basic fuel cell consists on an electrolyte in contact with an anode and a cathode. The fuel is fed to the anode and an oxidant (mostly oxygen) is fed to cathode, then an electrochemical reaction takes place at the electrodes producing electrons, which goes to an external circuit, and a product which can be formed in the anode or in the cathode depending on the fuel cell. Figure 4 represents a general diagram of how a fuel cell works.



Figure 4: Fuel cell scheme [5]

In order to have a proper performance, fuel cells should meet the following requirements [4]:

- Electrodes must be fuel/oxidant permeable
- Electrolyte has to have a low permeability to reactants

To measure the fuel cell performance, polarization and power curves are carried out. The polarization curve consists on a voltage versus current (or current density) plot which gives us information about losses and the influence of the operation conditions (pressure, flowrate, temperature, etc.). The power curve is a power (or power density) versus current (or current density) plot which provides us an idea of how much energy is being produced within the fuel cell.



Figure 5: Example of (a) polarization curve and (b) power curve [4]

As seen in Figure 5 (a), we can distinguish three zones in the polarization curve:

- At very low current densities (activation polarization region), the potential sharply drops due to oxygen reduction kinetics.
- II. At intermediate current densities (ohmic polarization region), a linear relationship is found because the ohmic resistance is the most important phenomenon.
- III. At high current densities (concentration polarization region), mass transfer is the main resistance; as a consequence the performance decreases.

Regarding the power curve (Figure 5(b)), it is clearly shown that the power increases until a maximum.

1.1.2. <u>Fuel cell types</u>

There are many ways to classify fuel cells, the most typical regards to the working temperature or the electrolyte used. Table 1 summarizes these fuel cells and their main characteristics.

| | AFC (Alkaline) | PEMFC (Polymer Electrolyte Membrane) | DMFC (Direct Methanol) | PAFC (Phosphoric Acid) | MCFC (Molten Carbonate) | SOFC (Solid Oxide) |
|---|---|--|-------------------------------------|---|--|--|
| Operating temperature (°C) | <100 | 60-120 | 60-120 | 160-220 | 600-800 | 800-100 but 500-600 is possible |
| Applications | Transpo | ortation, space, militar storage systems | y and energy | Combined heat and power for decentralize d stationary power systems | Combined heat and power for decentralized stationary power systems and for transportation (trains, boats) | |
| Power | Small plants, 5- 150 kW, modular | Small plants, 5-250 kW, modular | Small plants, 5 kW | Small- medium sized plants, 50 kW-11 MW | Small power plants, 100 kW- 2 MW | Small power plants, 100 - 250 kW |
| Charge Carrier in the Electrolyte | OH | H⁺ | H⁺ | H⁺ | CO ₃ ²⁻ | 0 ²⁻ |

Table 1: Fuel cell types and their main characteristics [4]



Figure 6: Different fuel cells performances

Figure 6 shows the mechanism of different fuel cells as well as the reactants used, charge carriers and the working temperature. As seen in that figure, while the fuel varies, oxygen is used to feed the cathode and water and carbon dioxide (depending on the fuel cell) are formed.

1.2 <u>PEMFC (Polymer Electrolyte Membrane Fuel Cell)</u>

PEMFCs (Polymer Electrolyte Membrane Fuel Cell) also known as PEFCs (Proton Exchange Fuel Cell) have as their main characteristic that the membrane is a solid material, generally a polymer, which operates at low temperatures (60-120 $^{\circ}$ C). These fuel cells have major advantages as their fast and easy start-up, and durability; nevertheless some inconveniences related to the use of expensive catalysts (mainly platinum), the sensitivity to impurities and working with humidified gases are found. Their most likely application will be those relative to portable and transportation, though they could be used for other issues like energy storage.

Figure 7 presents how this fuel cell works: in the anode, hydrogen is oxidated and dissociated into protons and electrons; protons pass through the membrane while electrons go to an external circuit generating electricity. Oxygen is reduced in the cathode and O^{2-} ions are formed. Subsequently, electrons, protons and O^{2-} react in the cathode forming water as the only byproduct. Finally, unreacted compounds and water leave the system on their corresponding place.



Figure 7: PEMFC [6]

1.2.1 <u>Components</u>

A PEMFC is mainly composed of a diffusion media, an electrolyte (membrane) sandwiched between the anode and the cathode and bipolar plates as seen in Figure 8.



Figure 8: PEMFC components [7]

The aim of the diffusion layer is to distribute efficiently the reactants. It is also known as gas diffusion layer (GDL) and is commonly made of carbon paper.

The combination of the electrodes together with the electrolyte represents the MEA (Membrane Electrode Assembly) which is the core of the fuel cell.

In the anode and cathode the reactions take place as follow:

- Anode: $H_2 \rightarrow 2H^+ + 2e^-$
- Cathode: $\frac{1}{2}$ O₂ + 2e⁻ + 2H⁺ \rightarrow H₂O
- General: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

The electrolyte must keep the reactants separated, allow protons pass from the anode to the cathode and support the catalyst. A catalyst is used in order to accelerate the reaction kinetics and improve the performance; this catalyst is platinum.

The bipolar plates are used to keep the whole structure together and allow electrons flow in the circuit; to reach that, a conductive material (graphite) is used.

1.2.2 <u>Catalyst</u>

Together with the membrane, catalyst must be optimized in fuel cell technology due to its high price; in fact, in a PEMFC the cost related to catalysts are 34% of the total [8]. For that reason, researchers are looking for more efficient metals and ways to reduce the amount of catalyst used.

There are two options in order to add the catalyst in the MEA: incorporation of the catalyst either on the GDL or the membrane. In the first option the catalyst is incorporated in the GDL, which receives the name of GDE (Gas Diffusion Electrode). The GDE is frequently treated with some quantity of PTFE which is used in order to increase the hydrophobicity and it acts as a binder between particles. This option is suitable for research issues because it is the simplest option.

In the second option, the catalyst is directly supported in the membrane, forming the catalyst coated membrane (CCM). There are several ways to form a CCM (for example: spraying, brushing, electrodeposition, inkjet printing, ultrasonic spraying...) but in the end the objective is the same, a more efficient Pt use without reducing the fuel cell performance [8-10].

In order to incorporate the catalyst to the membrane, an ink (or slurry) must be made. The most commonly composition of the catalyst ink is the following [11-15]:

- The catalyst itself: generally Pt supported on high-surface area carbon is used but alloys also can be used.
- Ionomer: a Nafion solution is used in order to increase the reaction zone, conductivity and catalyst performance. It is the binding and conductor agent.
- Mixing agent: a solvent (e.g.: isopropyl alcohol) is used to mix the compounds without any damage. This mixing agent is removed during the CCM fabrication.

 Others: depending on the technique used some compounds can be added, for example nitrogen can be used to avoid ignition problems.

1.2.3 <u>Membrane types</u>

In PEMFCs, membranes are one of the key components for an optimal work. The features those membranes should be: high proton conductivity, mechanical and chemical stability and adequate cost [6].

The most widely used membranes are based on perfluorosulfonic acid ionomer (PFSI, perfluorinated membranes) because of the fact that they almost fulfill the requirements aforementioned. However, they are expensive and at high temperatures (above 100 $^{\circ}$ C) the conductivity is decreased due to dehydration issues. The commercial name of this type of membrane is Nafion and it was developed by DuPont. The molecule backbone is based on polytetrafluoroethylene (PTFE, Teflon) with fluorocarbon side chains and sulfonic groups which give this molecule a high conductivity.



Figure 9: Nafion molecule [16]

In order to overcome those disadvantages, several researchers are trying to promote new membranes. One alternative is the usage of partially or non-fluorinated membranes which are less expensive but their durability and performance are lower compared to Nafion.

Another substitute to PFSI membranes would be the acid-base ones which have a high stability and acceptable proton conductivity

but its durability is poor. The structure of these membranes consists on the blending of an acid compound into an alkaline polymer.

Membranes based on ionic liquids are also being considered. Ionic liquids are organic salts whose melting point is below room temperature. They are being considered as potential electrolyte in PEMFC due to their high conductivity and stability but the difficulties to build up a membrane are their main drawback.

The research group Advanced Separation Process (ASP), where this work has been carried out, has demonstrated the potential of membranes based on polymerized ionic liquid for fuel cell applications [17-19]. One of the issues of these membranes that must be optimized is the contact between the membrane and electrode. For this reason, the motivation of this work is to set-up an experimental technique to deposit catalyst on fuel cell membranes in order to improve the performance in a proton exchange fuel cell.

1.3 Objectives of this project

The main objective of this project is to set-up an experimental technique to deposit catalyst on the surfaces of proton exchange membranes and studying the effects of the quantity of deposited catalyst in the fuel cell performance. For this purpose, the following tasks were delivered:

- Review of the state of the art of catalysts in proton exchange membrane for fuel cell applications
- Synthesis of catalyst ink
- Deposition of catalyst on the surfaces of proton exchange membranes
- Study of the influence of the operation conditions:
 - amount of catalyst in the membrane: 0.2; 0.3; 0.4;
 0.5 and 3 mg Pt/cm²

- fuel cell temperature: 25, 50, 80 °C
- humidity of the inlet gases
- Comparison between two alternatives: CCM and GDE.

2 **DEVELOPMENT**

2.1 <u>Materials</u>

The compounds used to prepare the catalyst ink are: platinum on graphitized carbon (Aldrich Chemistry, 20% wt. loading), Nafion solution (DUPONT, D2020 Nafion solution) and isopropanol (Panreac) as mixing agent, these compounds can be seen in figure 10.



Figure 10: Ink compounds; from left to right: catalyst, Nafion solution and isopropanol

Nafion NR-212 membranes (Ion Power) were used for the deposition of the catalyst ink. In order to pretreat Nafion membranes the following compounds were prepared: hydrogen peroxide (3%

w/w), hydrochloric acid (0.5 M). Deionized water was used in the solution preparation.

2.2 <u>Nafion pretreatment</u>

Nafion membranes could be deprotonated so it is fundamental their pretreatment before their use. First of all, the membrane is cut in the desired size and then is pretreated as follow [20]:

- I. The membrane is put in a vessel with hydrogen peroxide (3% w/w) at 80°C for an hour
- II. It is cleaned with deionized water and put in a recipient with hot deionized water for two hours
- III. The membrane is laid down with an acidic solution, in this case hydrochloric acid 0.5 M for an hour at $80^{\circ}C$
- IV. Finally, the membrane is washed with deionized water and stored with deionized water in a Petri dish for its further usage



Figure 11: pretreated Nafion

2.3 Gas diffusion electrode incorporation

Once the membrane has been pretreated, two 5 cm^2 GDE pieces (Baltic fuel cells) are cut and placed at both sides of the membrane. GDEs with loads of 0.5 and 3 mg Pt/cm2 were used and compared in this work.

2.4 <u>Catalyst coated membrane fabrication</u>

2.4.1. <u>Ink synthesis</u>

Previously to the CCM fabrication some catalytic ink must be prepared. The compounds are weighed in a balance with the coming order and quantities:

- Catalyst: 0.06 grams
- Nafion solution: 0.2 grams
- Isopropanol: 5 grams

The solids (Nafion and catalyst) content of the ink is 0.1 g which represents about 1.90% of the total ink. From these solids, 60% is catalyst and the remaining 40% is Nafion.

Once the components are weighed, they must be mixed for half an hour, so a sonicator is used for this purpose. Figure 12 presents the sonicator used.



Figure 12: Sonicator (Fisher Scientific FB 15050)

Figure 13 shows an example of the resulting ink.



Figure 13: Catalyst ink sample

2.4.2. Spraying

First of all, a pretreated membrane is weighed and placed in a support with a 6.25 cm^2 hole which will be the "pattern". This pattern has been oversized just to ensure the active area is correctly placed in the fuel cell.

Then the support is heated in a hot plate until the membrane reaches 70 °C; the temperature is measured by using an IR thermometer. Meanwhile, the necessary catalytic ink for each catalyst quantity is weighed and placed in the deposit of an airbrush, which is connected to an air intake. Once the membrane reaches this temperature, one side of the membrane is coated with the solids contained in the ink. It is important to maintain high temperature during all the process to evaporate the isopropanol. When one side of the membrane has been sprayed, the MEA is weighed again to check the amount of catalyst that has been deposited. The same procedure is carried out to deposit the catalyst in the other side of the membrane.

Figure 14 illustrates the tools used for the spraying step.



Figure 14: Tools used during the spraying step: airbrush (top) and support (bottom)

The aspect of a CCM with 0.2 mg Pt/cm^2 is shown in figure 15:



Figure 15: CCM with a load of 0.2 mg Pt/cm²

2.5 <u>Experimental setup</u>

The following apparatus were used during the MEA testing:

- Fuel cell (5 cm² active area, Baltic Fuel Cell, qcF 25/100)
- Electronic load (Höcherl & Hackl GmbH, ZS Electronic Load)
- Flow controller (Iberfluid, IB-32)
- Manometers and pressure valves
- Heating coils and hot plates
- Bubblers
- Temperature controller
- Beakers

An illustration of the setup is shown in figure 16:



Figure 16: Experimental setup

The main device of the setup is the fuel cell whereas the electronic load allows the realization of the polarization curve by measuring current and voltage data.

Figures 17 and 18 show those apparatus:



Figure 17: Fuel Cell



Figure 18: ZS Electronic Load

2.6 <u>Membrane electrode assembly testing</u>

The MEA must be fixed in the fuel cell; this can be seen in figure 19. If the MEA was made by CCM technique two 5 cm² GDL (one on each side) must be added and then the MEA is pressed under slightly conditions $(30^{\circ}C, 300 \text{ psi during 3 minutes})$ to assemble the components. In case of working with GDE and membrane no auxiliary components are necessary.



Figure 19: MEA placed in the fuel cell

Thereafter, the flowrates (320 ml/min for the hydrogen and 500 ml/min for the air), pressure (1.5 bars) and temperature ($25^{\circ}C$, $50^{\circ}C$ or $80^{\circ}C$ depending on the experiment) are set. If the testing is with humidified gases, some deionized water is poured into the bubblers and immersed into the water-filled beakers which are heated by the heating plates. Then, the system is left in open circuit for 15 min until stabilization.

Then, the system is left at 0.3 V to hydrate the MEA with the generated water and afterwards, the polarization curve is carried out by decreasing 0.05 V from the top voltage value (Open Circuit Value, OCV) to 0.15 V every two minutes.

With the collected data, apart from the polarization curve, we can obtain the power curve since power density is the voltage multiplied by current density.

3 RESULTS AND DISCUSSION

Table 2 summarizes the maximum power reached for every MEA under the analyzed operation conditions.

Table 2: Maximum power reached

| Douro | $r(m)\Lambda(m^2)$ | Non-humidified gases | | | Humidified gases | | |
|-------|---------------------------|----------------------|-------|-------|------------------|-------|-------|
| Powe | r (mvv/cm) | 25 °C | 50 °C | 80 °C | 25 °C | 50 °C | 80 °C |
| | 0.2 mg Pt/cm ² | 66.6 | 112.8 | 5.81 | 61.6 | 139.2 | 45.5 |
| Spray | 0.3 mg Pt/cm ² | 85.5 | 97.8 | 16.2 | 69.3 | 125.6 | 30.1 |
| Spray | 0.4 mg Pt/cm ² | 89.1 | 84 | 3.6 | 78.3 | 128.8 | 54.4 |
| | 0.5 mg Pt/cm ² | 56.7 | 123.3 | 16.8 | 57.2 | 135.9 | 70 |
| | 0.5 mg Pt/cm ² | 84 | 86.1 | 12 | 78.3 | 143.1 | 24.4 |
| GDE | 3 mg Pt/cm ² | 197.1 | 222.3 | 0.8 | 266.4 | 250.2 | 3.7 |

In the following sections the effects of the studied variables in the fuel cell performance have been analyzed.

3.1 Influence of the amount of catalyst

In order to study the amount of platinum catalyst in the MEA, polarization and power curves were carried out under the same conditions (50°C using humidified gases). Commercial MEA data was taken from [7].



Figure 20: Polarization curves at 50 °C and humidified gases



Figure 21: Power curves at 50 °C and humidified gases

As seen in figures 20 and 21, the best results are provided with the GDE with 3 mg Pt/cm², reaching 0.964 volts at open circuit and 250.2 mW/cm² of maximum power density value. However, if the results are compared with the GDE with a load of 0.5 mg Pt/cm² it is clearly shown that the increase in the performance is not proportional to the amount of catalyst, in other words, by increasing 6 times the load we increase only about 1.75 times the power. Therefore, from an efficient point of view, it is not worthy working with high amount of catalyst.

Regarding the spray technique, a clear trend was not found yet the results were in the same range of magnitude. Comparing the same platinum loading, 0.5 mg Pt/cm², the best performance was reached by the commercial MEA but those from GDE and spraying are very close between them, around 140 mW/cm² of maximum density power.

3.2 Influence of the temperature

A comparison between the performance of two MEAs (one using GDEs and other using spraying) with the same platinum load at different temperatures, is shown in the following figures:



Figure 22: Polarization curves at different temperatures using 0.5 mg Pt/cm² GDEs and humidified gases



Figure 23: Polarization curves at different temperatures using 0.5 mg Pt/cm² sprayed and humidified gases



Figure 24: Power curves at different temperatures using 0.5 mg Pt/cm² GDEs and humidified gases



Figure 25: Power curves at different temperatures using 0.5 mg Pt/cm² sprayed and humidified gases

A similar trend is found in both alternatives: the best temperature is found at 50° C because the reaction kinetics is accelerated by temperature. 143.1 mW/cm² and 135.9 mW/cm² were obtained with GDE and CCM respectively. Nevertheless, at 80° C the performance sharply drops due to the beginning of the membrane dehydration. This effect is more pronounced in the case of using GDEs as it is shown in figure 24.

3.3 Influence of the inlet gases humidity

Figures 26 and 27 presents the results obtained of same-loading MEAs by using the two alternatives at 50° C.



Figure 26: Polarization curves of different MEAs at 50°C



Figure 27: Power curves of different MEAs at 50°C

Regarding the GDE, it is shown that by humidifying the inlet gases the performance increases. The maximum power with humidity was almost doubled compared with the non-humidified gases, reaching 86.1 mW/cm² when using non-humidified gases compared to 143.1 mW/cm² obtained when using humidified inlet gases. On the other hand, CCMs have similar performance at both condition and close to the performance obtained with GDE membranes with humidity, so these membranes are promising candidates to be used at anhydrous conditions.

4 <u>CONCLUSIONS</u>

The main objective of this project was to set-up an experimental technique for the catalyst deposition on membranes for fuel cell technology.

For this reason, catalyst coated membranes were developed by spray coating technique and compared with gas diffusion electrodes membranes in terms of fuel cell performance at different operation conditions: catalyst load, temperature and humidity.

The main conclusions of this work are the following:

- Regarding CCM fabrication, in the range of 0.2-0.5 mg platinum/cm², a clear trend between the amount of catalyst and the performance could not be found. GDE showed high performance at higher catalyst load. However, this improvement was not proportional to the amount of catalyst. At the same catalyst loading, 0.5 mg Pt/cm², both alternatives provide similar fuel cell performance at 50 °C with humidified gases.
- Both alternatives reached their best performance at 50°C. At 80°C the performance decreased due to membrane dehydration.
- The effect of humidity is more pronounced with GDE membranes reaching higher performance using humidified gases. CCM have similar performance at both condition, and it is close to that reached with GDE with humidified gases, proving the potential of these membranes in anhydrous fuel cell applications.

Additionally, future works should reach a full-characterization of the MEAs used by including adsorption, conductivity and durability

testing. Furthermore, different ways to the catalyst deposition (e.g.: electrodeposition) may be studied as well as the catalyst implementation in different types of fuel cells, for example direct methanol fuel cell. Also, it would be very interesting to study the catalyst deposition on other electrolytes, for instance, those based on ionic liquids.

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