

Electrochemical study of platinum deposited by electron beam evaporation for application as fuel cell electrodes

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ABSTRACT

Platinum is the most used catalyst in electrodes for fuel cells due to its high catalytic activity. Polymer electrolyte and direct methanol fuel cells usually include Pt as catalyst in their electrodes. In order to diminish the cost of such electrodes, different Pt deposition methods that permit lowering the metal load whilst maintaining their electroactivity, are being investigated. In this work, the behaviour of electron beam Pt (e-beam Pt) deposited electrodes for fuel cells is studied. Three different Pt loadings have been investigated. The electrochemical behaviour by cyclic voltammetry in H_2SO_4 , HClO_4 and in $\text{HClO}_4 + \text{MeOH}$ before and after the Pt deposition on carbon cloth has been analysed. The Pt improves the electrochemical properties of the carbon support used. The electrochemical performance of e-beam Pt deposited electrodes was finally studied in a single direct methanol fuel cell (DMFC) and the obtained results indicate that this is a promising and adequate method to prepare fuel cell electrodes.

1. Introduction

Two of the major challenges that low temperature fuel cells (PEM H_2/O_2 and DMFC) must address to attain viable commercial use and the subsequent mass production stage are cost and durability. In addition to the transportation industry, other important energy dependent fields such as residential,

back-up and portable power supply face the high cost of these fuel cells as the main barrier to their widespread applications in these areas.

One of the primary drivers of cost in a fuel cell is due to the MEA [1] which consists of the membrane, plus the anode and cathode electrodes which are integrated by the diffusion media and catalyst layers, typically wearing platinum-based (Pt-based) catalysts. Regarding PEM and DMFC costs, the

electrodes represent about 40% of the total cost of PEMFC [2], with the Pt cost share being 1.7%. For mass production, the catalyst ink cost is approximately 34% of the total stack cost [3]. For DMFC, Pt is until now the most effective metal for methanol oxidation, though pure Pt is not efficient and Pt-based bimetallic catalysts are used instead [4–6]. In any case, Pt is the most common catalyst for oxygen reduction in PEMFC and DMFC.

There are several approaches to reduce the cost of PEMFC stacks, where a number of MEAs must be created to obtain significant power values. This feature becomes especially important in DMFC for two main reasons: these fuel cells are mainly used for portable power devices, and methanol electrooxidation requires higher Pt quantities than hydrogen, so its electrodes require greater amounts of catalyst than PEM fuel cells do [7]. The Pt loading has been reduced by two orders of magnitude in the past decade and there is still room for further reductions [1]. One possible approach to lower PEMFC and DMFC cost is to investigate alternative electrocatalysts to Pt including non-noble metals [1,8]. Another important option consists in lowering the Pt content in the catalyst layer, either by using alloys or by improving electrode or catalyst preparation methods with higher control for Pt particle deposition [2,8–14]. In summary, Pt and its alloys are commonly used as electrocatalysts and a variety of deposition methods have been used with this purpose. With regards to the fabrication of electrodes for fuel cells, low Pt loading is being achieved fusing of a variety of procedures such as thin-film, vacuum deposition or electrodeposition methods [10].

Vapour deposition methods include, among others, sputtering and electron beam physical vapour deposition, also called electron beam evaporation or e-beam evaporation [15]. Physical preparation methods offer the advantage over chemical ones of being one-step processes [13] leading to the formation of thin films of metal nanoparticles, thus giving rise to lower Pt loading electrodes. Both methods allow the obtention of thin catalyst layers ejecting atoms from a given material (target) which are deposited on the surface of a near-placed substrate. The sputtering technique does not cause the target to evaporate so it remains in a solid state, but atoms are dragged away from the target. With the e-beam evaporation method, the target melts and releases gas phase atoms that then precipitate on the substrate. Whereas sputtering allows metal and insulating materials deposition, e-beam evaporation can only be used with metals. Also, high melting point metals can be deposited more easily by sputtering than by e-beam evaporation. Moreover, in general, sputtering targets are bigger and more costly than e-beam ones. Besides, if an alloy is to be deposited, a target with a specified composition must be prepared and such target must be discarded if another composition is to be investigated. By using an e-beam evaporator equipped with various heads and controlling the evaporation rates of the diverse metals, deposition and further study of different alloys can be easily implemented. Then, bearing in mind the possibility of investigating bi- or tri-metallic catalyst layers with different atomic ratios for fuel cell electrode preparation, the e-beam evaporation technique is seen as a highly controllable and cost-effective deposition method.

Although a number of works have been devoted to study Pt sputtering to be used as electrodes in H_2/O_2 PEMFC or even in

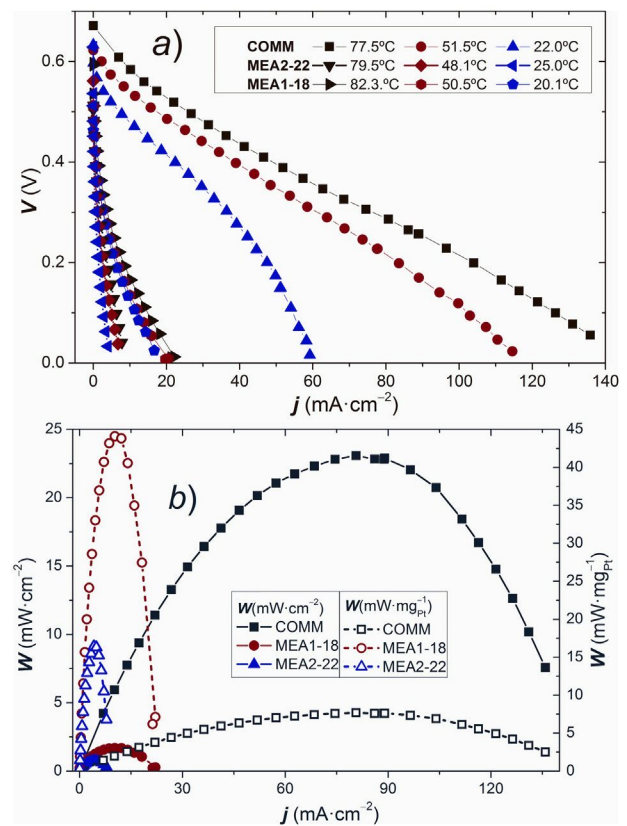


Fig. 1 – a) DMFC polarisation curves of three MEAs: one of them prepared with commercial electrodes (COMM) and the other two, MEA1-18 and MEA2-22 are custom MEAs with low Pt loading cathodes deposited by e-beam on GDL2 and GDL1 carbon cloths at 80 °C, 50 °C and 20 °C; b) power output per surface unit and per unit Pt mass curves at 80 °C. (See Subsection 2.5 for nomenclature).

DMFC [16–23], studies on e-beam evaporation as a Pt deposition technique for such purpose are very scarce [24,25] and no use for DMFC has been found. In one study [25] e-beam Pt deposited electrodes are used in a microbial fuel to investigate

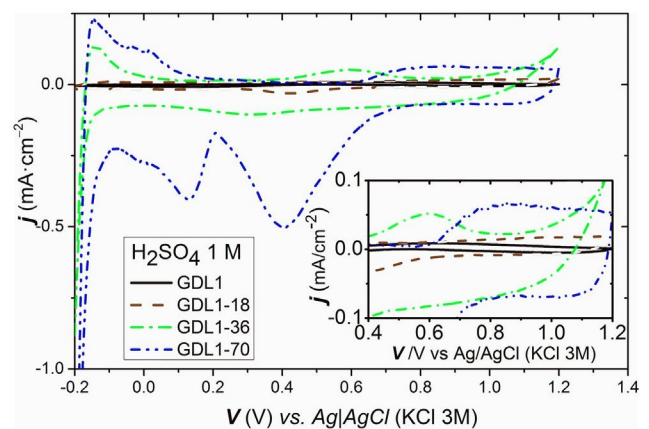


Fig. 2 – Cyclic voltammograms of samples GDL1 (—), GDL1-18 (---), GDL1-36 (····) and GDL1-70 (— · —) in 1 M H_2SO_4 . (See Subsection 2.1 for nomenclature).

Table 1 – Total oxidation and reduction charge of samples without and with e-beam deposited Pt in H₂SO₄ 1 M.

Medium	Sample	Q _{ox} (mC cm ⁻²)	Q _{red} (mC cm ⁻²)	Q _{red} /Q _{ox}	Q _{EAS} (mC cm ⁻²)	S _{EAS} (cm ² Pt mg ⁻¹)
H ₂ SO ₄ 1 M	GDL1	0.2681	0.2777	1.036	0.0966	
	GDL1-18	1.0628	1.1787	1.109	0.2875	35.49
	GDL1-36	4.8885	4.4578	0.912	1.9177	118.37
	GDL1-70	3.6725	18.0594	4.917	7.3191	232.35

electricity generation. Comparison with other tested electrodes, including commercial ones, showed that e-beam electrodes were the most effective in terms of mass-specific current density. The results obtained suggest the potential of using e-beam deposited Pt electrodes for fuel cells improvement with low Pt loading.

The aim of this work has been to investigate the electron beam evaporation technique for preparing thin Pt layers deposited on the un-catalysed gas diffusion layers for PEMFC and especially for DMFC electrodes. The electrochemical behaviour of the catalyst support and the electrodes has been studied by cyclic voltammetry. Their electrochemical active surface area has been determined and their morphological characteristics have been examined by SEM. The performance of a single Direct Methanol Fuel Cell with the e-beam deposited electrodes on the cathode side has been also investigated.

2. Experimental

2.1. Electrode material and preparation

Two base materials have been used as Gas Diffusion Layer (GDL). Both were commercial non-woven carbon cloth with hydrophobic treatment: Freudenberg H2315 I3C1, with microporous layer and named henceforth GDL1, and Freudenberg H2315 T10A, without microporous layer, denominated GDL2. On these two materials, pure Platinum (Pt) has been deposited by electron beam evaporation.

Pt films were evaporated from a Pt rod (99.95% purity, supplied by Testbourne Ltd) with a carbon sleeve in a vacuum chamber using an e-beam evaporator QUAD-EV-C, Mantis. The pressure during deposition was 10⁻⁶ torr and the evaporation rate was 0.5 nm min⁻¹. The distance between the Pt rod and the substrate was over 10 cm to ensure a homogeneous thickness of the film over the whole substrate (2.5 × 3.5 cm). In each evaporation process a silica substrate with a mask was placed by the electrode. Such device has been used to

determine the actual thickness of the Pt film using a profilometer. A 18 nm, a 36 nm and a 70 nm thick layers of Pt were deposited on GDL1 and a 22 nm thick Pt layer on GDL2. The resulting electrodes had a Pt loading of 0.04 mg cm⁻² (18 nm), 0.08 mg cm⁻² (36 nm), 0.15 mg cm⁻² (70 nm) and 0.05 mg cm⁻² (22 nm). They were denoted with the name of the base material followed by the thickness of the Pt layer, GDL1-18, GDL1-36 GDL1-70 and GDL2-22, respectively.

2.2. Chemicals

Methanol (MeOH) was supplied by Panreac (99.9% purity), sulphuric acid was supplied by Carlo Erba Reagenti (98% purity) and perchloric acid was supplied by VWR International (60% purity). Distilled water has been used to prepare the aqueous solutions of H₂SO₄ 1 M, HClO₄ 0.1 M and MeOH 1 M in HClO₄ 0.1 M, as well as aqueous solutions of MeOH 1 M used as fuel in DMFC.

2.3. Surface characterisation

A JEOL JSM-6330F Electron Microscope operating at 10 kV was employed to analyse surface morphologies by scanning electron microscopy (SEM) and to obtain the relative amount of Pt in the samples' surface.

2.4. Electrochemical measurements

Electrochemical measurements were carried out in a three electrode cell with a Pt wire used as auxiliary electrode. The working electrode was a circular carbon cloth of 0.78 cm². The reference electrode was Ag/AgCl (3 M). For this purpose a PAR Model 237A potentiostat/galvanostat was used. Experiments were carried out under a nitrogen atmosphere at room temperature.

Before each measurement the electrolyte cell was purged with N₂ for 20 min to remove the dissolved oxygen.

The samples were cleaned to remove any adsorbed species by scanning potential between -0.2 V and 1.2 V vs Ag/AgCl

Table 2 – Total oxidation and reduction charge of samples without and with e-beam deposited Pt in different electrolyte medium: HClO₄ 0.1 M, HClO₄ 0.1 M + MeOH 1 M (cycle 10).

Medium	Sample	Q _{ox} (mC cm ⁻²)	Q _{red} (mC cm ⁻²)	Q _{red} /Q _{ox}	Q _{EAS} (mC cm ⁻²)	S _{EAS} (cm ² Pt mg ⁻¹)
HClO ₄ 0.1 M	T	0.3319	0.2471	0.745	0.2116	
	GDL1-18	0.3741	0.4124	1.102	0.0901	10.73
	GDL1-36	0.5177	0.6281	1.213	0.2025	12.05
	GDL1-70	4.5753	9.4093	2.057	2.3599	74.92
HClO ₄ 0.1 M + MeOH 1 M	T	0.2710	0.2651	0.978	0.1800	
	GDL1-18	2.5871	1.1036	0.4266	0.1044	12.42
	GDL1-36	16.1234	0.5546	0.0344	0.2920	17.38
	GDL1-70	33.9734	2.6438	0.0778	2.6438	83.93

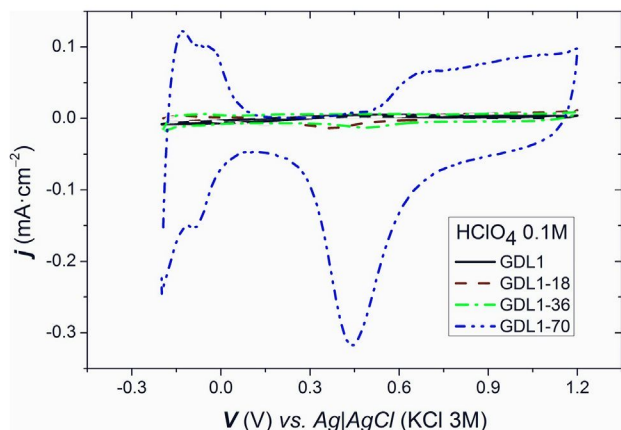


Fig. 3 – Cyclic voltammograms of samples GDL1 (—), GDL1-18 (---), GDL1-36 (····) and GDL1-70 (— · —) in 0.1 M HClO₄. (See Subsection 2.1 for nomenclature).

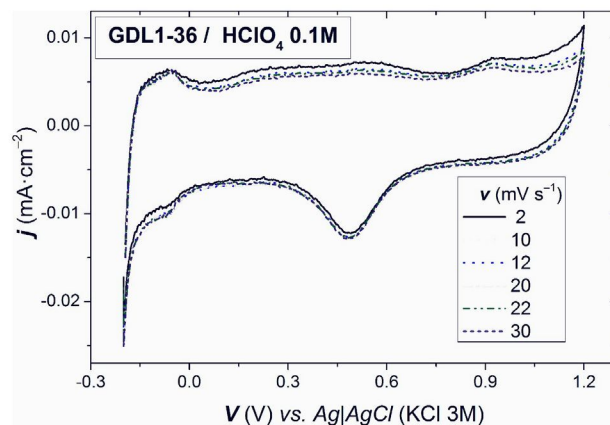


Fig. 4 – Cyclic voltammograms of sample GDL1-36 in 0.1 M HClO₄ at different scan rates. (See Subsection 2.1 for nomenclature).

(KCl 3 M) at a linear sweep rate of 0.5 V s⁻¹ at 200 cycles in H₂SO₄ 1 M. Once completed, several cyclic voltammograms were obtained between the same potential limits at 0.01 V s⁻¹.

All samples were characterised in H₂SO₄ 1 M, that is the usual standard, and their catalytic activity tested in HClO₄ 0.1 M, and MeOH 1 M in HClO₄ 0.1 M by scanning potential between -0.2 V and 1.2 V vs Ag/AgCl (KCl 3 M) at a linear sweep rate of 0.02 V s⁻¹.

2.5. Fabrication of MEAs and DMFC polarisation curves measurements

The prepared and characterised e-beam Pt evaporated electrodes have been measured using membrane electrode assemblies (MEAs) in a single DMFC of 5 cm² of active area. A commercial anode containing about a total PtRu loading of 3 mg cm⁻² (molar ratio 1:1) onto GDL1 has been used to fabricate all the MEAs. The e-beam deposited electrodes have been used as cathodes because they didn't contain Ruthenium at all. Henceforth the prepared MEAs will be named with a first digit identifying the base material and another two corresponding to the Pt loading thickness in nm (as an example, MEA1-18 is the MEA prepared using as cathode a 18 nm thick Pt layer e-beam deposited on GDL1). A commercial cathode, containing about 3 mg Pt cm⁻² on GDL2, has been used to prepare a MEA for purposes of comparison, named COMM in the future. The custom-made experimental setup, i.e., the single fuel cell and measurement and control equipment, has been described in a previous work [26]. Nafion® 117 has been pre-treated with 3 wt % hydrogen peroxide, 0.5 M sulphuric acid and distilled water at 80 °C, before being sandwiched between the cathode and the anode. After keeping the ensemble under hot pressing, homogeneity in terms of electrical conductivity has been checked. Electrochemical activation of the MEAs has been conducted before carrying out the experiments. The procedure, described in Refs. [26], aims at bringing the MEA to its highest and stabilised performance.

DMFC commercial electrodes have been prepared by QuinTech e.K. The anode contains a total PtRu loading of about 3 mg cm⁻² (molar ratio 1:1) onto GDL1. The commercial cathode contains a total Pt loading of 3 mg cm⁻² onto GDL2.

Three polarisation curves were registered at three different temperatures with each DMFC: about 20°, 50° and 80 °C.

For comparison purposes, a MEA with QuinTech e.K. commercial electrodes has been prepared and its polarisation curves at the same temperatures have been registered.

3. Results and discussion

3.1. Study of the carbon cloth performance

To initiate the study of the performance of the e-beam Pt deposited electrodes the two carbon cloths GDL1 and GDL2 have been checked.

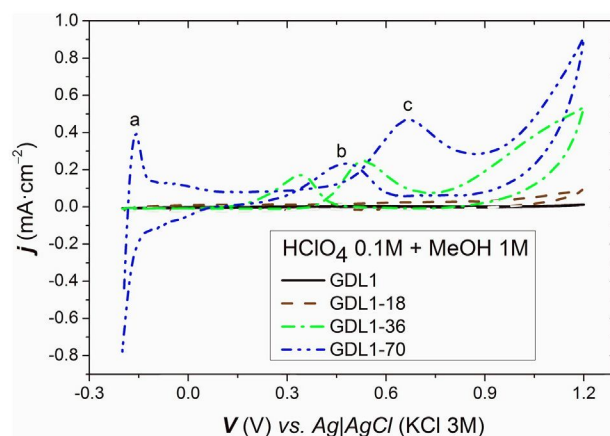


Fig. 5 – Cyclic voltammograms of samples GDL1 (—), GDL1-18 (---), GDL1-36 (····) and GDL1-70 (— · —) in 0.1 M HClO₄ + MeOH 1 M. (See Subsection 2.1 for nomenclature).

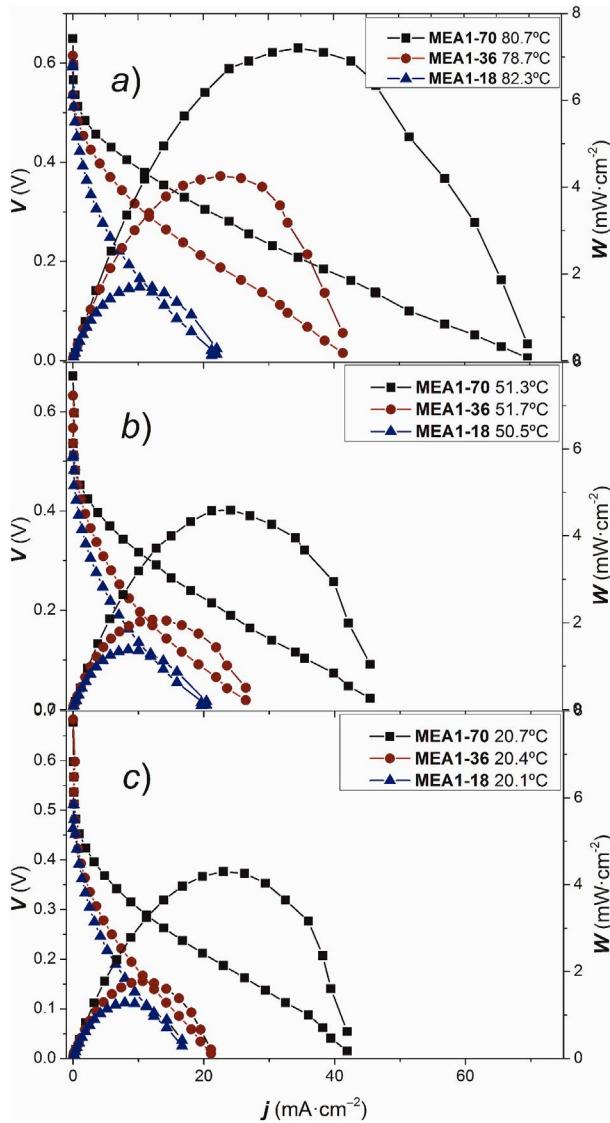


Fig. 6 – DMFC polarisation and power density curves working with three different custom-made MEAs using e-beam Pt deposited electrodes on the cathode side, with increasing Pt loading. Nafion 117 and a commercial $3 \text{ mg} \cdot \text{cm}^{-2}$ PtRu (1:1) anode are used in all cases. a) 80 °C; b) 50 °C; c) 20 °C. (See Subsection 2.5 for nomenclature).

The performance of MEA1-18, MEA2-22 and COMM have been compared in a DMFC at three different temperatures. The resulting polarisation curves can be seen in Fig. 1a. The polarisation curves corresponding to MEA1-18 show a clearly better performance than those of MEA2-22. This advantage is made clearer in Fig. 1b, which shows the power output per surface unit and per unit Pt mass at 80 °C. It can be seen that using the same commercial anode, the MEA prepared with e-beam Pt deposited on GDL1 behaves much better than that prepared using GDL2. Therefore, GDL2 has been discarded as carbon support for e-beam Pt evaporation. The lower performance of GDL2 may be attributed to the absence of microporous layer, as the primary role of a microporous layer seems to

be to lower the rate of water crossover by improving the wicking of liquid water from the catalyst layer into the diffusion media [27]. Nevertheless, it must be taken into account that although the microporous layer is known to improve fuel cell performance, its exact function is still being debated [28].

3.2. Voltammetric characterisation under inert gas

After the activation process described in Section 2.4, a continuous cycle between -0.2 and 1.2 V was applied to the samples at a scan rate of 0.02 V s^{-1} . Fig. 2 shows the electrochemical response of four samples: GDL1 (without Pt), and GDL1-18, GDL1-36 and GDL1-70 (with Pt) in H_2SO_4 1 M in cycle 10.

The cyclic voltammogram of carbon cloth, sample GDL1, shows low electroactivity. No oxidation and reduction peaks were observed. E-beam deposition of a thin Pt layer on the carbon cloth, samples GDL1-18, GDL1-36 and GDL1-70, gives rise to an increment in the film electroactivity as observed in Fig. 2. Samples with e-beam Pt deposited show the characteristic features of hydrogen adsorption and desorption, better defined as the Pt content is increased. However, in GDL1-18 the Pt content is not enough to appreciate all of them, being necessary to increase the Pt content to observe more defined peaks. In GDL1-70, well defined peaks corresponding to hydrogen adsorption-desorption at -0.2 to 0 V and a wave corresponding to platinum-oxide formation at 0.7 – 1.2 V (see the inset) and reduction at 0.4 V , are distinguished.

When a continuous cycling of oxidation and reduction is applied to the samples, waves are more defined, increasing its current density. A little shift of those peaks to positive or negative potentials is also observed.

The hydrogen desorption peaks were integrated using charge density associated to the monolayer of hydrogen (Q_{EAS}). According to the coulombic amount (Q_{EAS}) associated with the peak area, the electroactive surface (S_{EAS}) in $\text{cm}^2 \text{ Pt mg}^{-1}$ can be calculated using the following expression [29,30]:

$$S_{\text{EAS}} = \frac{Q_{\text{EAS}}}{m \cdot C}$$

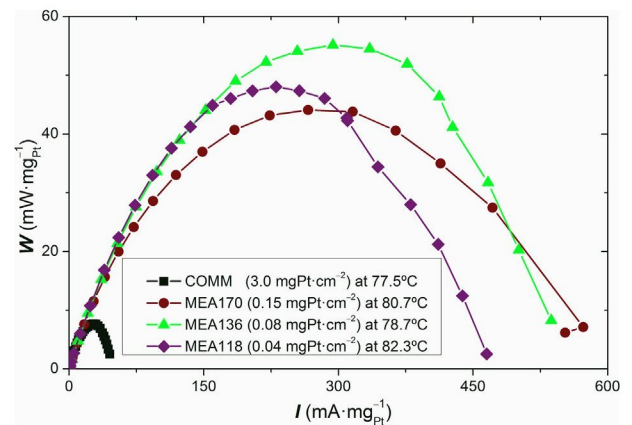


Fig. 7 – Power output per cathode unit Pt mass curves at 80 °C of three MEAs prepared with e-beam Pt deposited cathodes compared with a MEA fabricated with a commercial cathode (See Subsection 2.5 for nomenclature).

where C is the quantity of electricity when hydrogen molecules absorb on platinum with a homogeneous and single layer. Here, it is equal to 0.21 mC cm^{-2} which arises from considering a surface density of $1.3 \times 10^{15} \text{ atom cm}^{-2}$, a generally adopted value for polycrystalline Pt. The actual mass of platinum is represented as m . This calculation has been performed in the three studied media described in Section 2.4, considering that the hydrogen precedence (acidic protons or methanol) is not relevant to evaluate the electrochemical active surface area.

Table 1 shows the total oxidation (Q_{ox}) and reduction (Q_{red}) charges and the corresponding one to the electrochemical active surface (Q_{EAS}) for the tenth cycle. The electrochemically active surface area, S_{EAS} , was determined for the samples with Pt. It can be observed that both oxidation and reduction processes after Pt deposition increase significantly. After continuous cycling Q_{ox} diminishes a little while Q_{red} remains nearly unchanged, getting higher the irreversibility of the processes as Q_{red}/Q_{ox} increases. The specific area increases with the Pt content, however this factor slightly diminishes with the continuous cycling. The S_{EAS} obtained in H_2SO_4 are similar to those obtained by Watt Smith et al. [29] for Pt/C fuel cell electrodes chemically obtained and a little bit lower than that reported by Fedotov [12] for Pt nanoparticles deposited on carbon Vulcan XC72R by magnetron sputtering.

Afterwards, the samples were characterised in HClO_4 0.1 M and in a 1 M solution of MeOH in HClO_4 0.1 M. In Table 2 the total oxidation (Q_{ox}) and reduction (Q_{red}) charges and the corresponding one to the electrochemical active surface (Q_{EAS}) are shown for the tenth cycle. The electrochemically active surface area, S_{EAS} , was determined for the samples with Pt.

The characteristic voltammogram of Pt in HClO_4 medium can be seen in Fig. 3. The electroactivity substantially increases with the Pt content, but the total oxidation and

reduction charge densities were lower than that obtained in H_2SO_4 due to the lower proton concentration in this medium.

The influence of the scan rate was analysed in the range of $2\text{--}30 \text{ mV s}^{-1}$. The oxidation processes were slightly shifted to higher positive potentials. Fig. 4 shows an example of these analyses for sample TPt36.

The cyclic voltammograms of methanol oxidation in HClO_4 0.1 M + MeOH 1 M are depicted in Fig. 5. The GDL1-70 electrode cycle presents three pronounced oxidation peaks at -0.16 V (a), characteristic of Pt in the acidic medium, and at 0.48 V (b) and 0.67 V (c) due to the methanol oxidation. The onset oxidation potential of the positive scan is located at 0.67 V with the corresponding oxidation peak current density being 0.470 mA cm^{-2} . The onset oxidation potential of the negative scan occurs at 0.48 V with the corresponding oxidation peak current density being 0.234 mA cm^{-2} . A similar behaviour is observed in the case of sample GDL1-36. Nevertheless, only a little oxidation wave can be observed at 0.7 V in sample GDL1-18. The significant Q_{ox} increment from sample GDL1-18 to GDL1-36 (see Table 2) seems to indicate the existence of a lower limit in the Pt quantity to get a clear MeOH evolution. On the other hand, electrochemical active surface area values are very similar in both media, showing an important increment in the GDL1-70 sample compared with the other two.

3.3. DMFC polarisation measurements

In order to evaluate the adequacy of the electron beam evaporation technique for fuel cell electrodes preparation with low Pt loading, the performance of a custom single DMFC [26] with MEAs containing the prepared e-beam Pt deposited electrodes (MEA1-18, MEA1-36 and MEA1-70) has been studied.

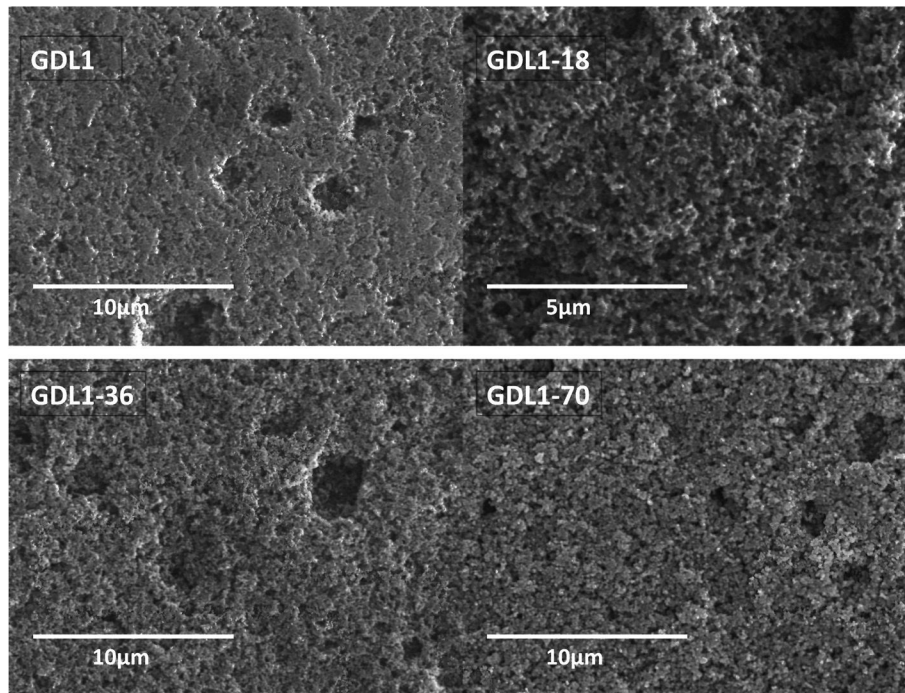


Fig. 8 – Top view SEM images: GDL1, GDL1-18, GDL1-36 and GDL1-70. (See Subsection 2.1 for nomenclature).

Polarisation and power density curves of three MEAs fabricated with the e-beam Pt deposited electrodes with different Pt loadings, used on the cathode side of the DMFC, are shown and compared in Fig. 6. Nafion[®] 117 and the commercial anode described in Section 2.5 have been used in all cases. Each MEA has been measured at three temperatures, about 80, 50 and 20 °C. The Pt loadings giving rise to the three custom MEAs have been, as previously said, 0.04, 0.08 and 0.15 mg·cm⁻². The results indicate that the current and power density values increase when Pt loading increases. The maximum power densities obtained at 80 °C present a 1:2.5:4.3 ratio (MEA1-18:MEA1-36:MEA1-70), while the Pt loading are in 1:2:3.75 ratio. So a linear-like relationship is found between Pt loading and maximum power density. Therefore, at low Pt loadings, the e-beam evaporation technique seems to be an easily scalable preparation method for fuel cell electrodes.

Since the Pt loading of the commercial cathode used in the MEA of reference COMM described in Section 2.5 is 3 mg·cm⁻² whereas that in the e-beam Pt deposited GDL1-70 electrode, used in MEA1-70, is 0.15 mg cm⁻², the performance of the single DMFC operating with this new cathode can be considered quite satisfactory. Then, the Pt loading has been diminished 20 times whereas the maximum power density only decreased 3.2 times. Similarly, regarding MEA1-36, the Pt loading of its cathode GDL1-36 has been divided by 37.5 and the corresponding maximum power density only decreased 5.4 times. Finally, the Pt loading in the cathode GDL1-18 of the MEA1-18 has been 75 times lower than that in the cathode of reference but the maximum power density only decreased by 13.6 times. This feature becomes quite clear in Fig 7, where power per Pt mass unit is represented.

Therefore, to investigate low Pt loading deposition by e-beam evaporation technique for fuel cell electrodes preparation appears to be an interesting topic.

3.4. Scanning electron microscopy

Fig. 8 shows the top view SEM images, i.e. the side in contact with the solution, of GDL1, GDL1-18, GDL1-36 and GDL1-70 samples. A homogeneous and smooth structure, corresponding to the conducting carbon deposit is observed in sample GDL1 although there are some regions where the coating is not homogeneous probably due to the carbon losses. While a similar structure is maintained in samples GDL1-18, GDL1-36 and GDL1-70, the e-beam Pt deposition provokes a certain breaking of the carbon cloth structure, so its homogeneity and the smooth appearance are a bit lost.

4. Conclusions

Low Pt loading electrodes have been prepared by e-beam evaporation technique. The electrochemical activity of carbon cloth without and with e-beam Pt deposited has been studied by cyclic voltammetry and fuel cell tests. Cyclic voltammetry measurements show how electroactivity increases with Pt loading increase. Electrochemical active surface areas determined in this study are in good agreement with those reported for electrodes prepared by other deposition methods. The performance of a custom single DMFC, with MEAs wearing the

prepared e-beam Pt deposited electrodes on the cathode side and a commercial anode, has been studied. At low Pt loadings, the e-beam evaporation technique seems to be an easily scalable preparation method for fuel cell electrodes. Compared with a MEA with commercial electrodes, the power density per Pt loading mass of MEAs prepared with e-beam evaporated cathodes results clearly higher. The present study suggests that electron beam evaporation deposition is an effective method to obtain low Pt loading and effective electrodes for fuel cells.

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