

# Relevance of the nature of bimetallic PtAu nanoparticles as electrocatalysts for the oxygen reduction reaction in the presence of methanol

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## Abstract

A series of carbon supported PtAu electrocatalysts has been prepared. The performance of the samples in the methanol oxidation reaction and in the oxygen reduction reaction has been investigated by means of electrochemical techniques. The combined process, oxygen reduction reaction in the presence of methanol, has also been studied by electrochemical methods and in a single-cell. Irrespective of the performance of the samples in the oxygen reduction reaction, the ones displaying poor activity in the methanol oxidation reaction are the optimum cathode electrocatalysts for direct methanol fuel cell applications. The role of Au was found to be dependent on the actual nature of the catalyst. When alloyed, the role of Au on the methanol oxidation reaction is negligible. This is the first time that Au is being proposed as a component of methanol resistant cathode electrocatalysts.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are attracting considerable attention as alternative power sources, especially for portable devices and small vehicles. DMFCs offer a number of advantages over the best rechargeable batteries or even over hydrogen feed fuel cells (PEMFC), namely, the higher specific energy density of methanol, its easy handling and instantaneous refuelling [1–4].

Despite the many efforts applied to their development, especially over the past two decades, many hurdles have yet to be overcome if they are to be widely used in commercial applications [5,6]. For instance, the actual energy density and operating cell voltage of DMFCs are lower than theoretical values due to the poor activity of the anode catalyst and the methanol crossover

effect on the cathode electrode [7,8]. Several approaches are under study for anode catalyst activity. Basically these include avoiding CO poisoning by means of bimetallic catalysts (see, e.g., [9]) and modifying the nature of the carbonaceous support [10]. However, the methanol crossover effect is still a challenge, at least from the catalytic point of view [11]. The methanol crossover effect is due to the permeation of methanol through the ionomer membrane from the anode to the cathode. Accordingly, there is a large body of work dealing with the optimization of membrane permeability: for instance, see [12] and references therein. However, once methanol reaches the cathode, the Pt sites that should be performing the reduction of O<sub>2</sub> (ORR) begin to oxidize methanol instead (or in parallel), generating the so-called mixed potentials. This feature results in a shifting of the cathode potential towards less positive values, thereby decreasing cell voltage and severely compromising the performance of the fuel cell. Both catalytic reactions involved in the cathode (ORR and methanol oxidation) are of a complex nature [13]. The rate-determining step of the ORR is the breaking rate of the O<sub>2</sub> bond to form water. The kinetics of the reaction depends on the degree

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of interaction of O<sub>2</sub> with catalyst adsorption sites, and it appears highly unlikely that these reactions proceed fully independently without affecting each other. Hitherto, Pt/C is the archetypal cathode electrocatalyst in a DMFC. However, more active and more methanol tolerant electrocatalysts for the ORR have yet to be designed. In some cases, noble metals other than Pt have been proposed as alternatives [14]. Ideally, the ultimate goal would be the production of Pt-free electrocatalysts [15–21]. Other approaches involve the preparation of Ni- [22] or Se-containing catalysts [23,24]. When prepared as nanosized particles, Au-based catalysts display very high activity towards CO oxidation even under mild operating conditions. Furthermore, the electrocatalytic activity of gold nanoparticles for CO and methanol oxidation reactions has recently been reported [25–27]. However, the actual role of Au in the higher CO tolerance recorded by such materials was found to be dependent on various parameters, such as pH, the nature of the alloyed material or particle size, amongst others [18,28,29]. The high activity described for those systems triggered interest in the preparation of Au-based catalysts [30,31]. Within this scenario, PtAu nanoparticles supported on silica have been studied intensely over the past twenty years [32–34]. Recently, Au-based samples have also been studied as cathode electrocatalysts for fuel cell applications [35–37]. In fact, bimetallic PtAu electrodes record good properties for the ORR, probably due to a decrease in the oxophilicity of such electrodes [38]. Besides, the presence of Au-clusters seems to improve the durability of Pt-based electrocatalysts on the ORR [39]. However, to the best of our knowledge, this is the first time that Au-containing catalysts are proposed as methanol tolerant cathode electrocatalysts for DMFCs. In a previous contribution, we have described the preparation details and physicochemical properties of carbon-supported PtAu electrocatalysts, as well as their performance in the oxygen reduction reaction [38]. Here, we have extended the former study in an attempt to evaluate the performance of nanosized PtAu particles supported on carbon (PtAu/C 20 wt%) in the oxygen reduction reaction in the presence of methanol. To this end, the thin film rotating disk electrode technique was used. The influence of methanol (0.1 and 0.01 M) crossover in the oxygen reduction reaction was evaluated and the results were compared with those obtained with Pt/C 40 wt% commercial catalyst (Johnson Matthey). A comparison based upon results obtained with direct methanol fuel cell test for PtAu/C 20 wt% and Pt/C 40 wt% nanoparticle as cathode is also reported.

## 2. Experimental

### 2.1. Catalyst preparation

PtAu nanoparticles were synthesized using different approaches, such as microemulsion, impregnation and a colloidal method, following the procedures reported in Ref. [38]. Three electrocatalysts were obtained and labelled as M-PtAu/C, I-PtAu/C and C-PtAu/C (20 wt% metal basis: Pt/Au, 2/1 nominal atomic ratio). Relevant details about sample nature and physicochemical properties are summarized in Table 1. These samples were tested as electrocatalysts for the cathode in a DMFC. Their performance was compared to that of a commercial Pt/C 40 wt% sample (Johnson Matthey).

### 2.2. Electrochemical study

Electrochemical measurements were taken by a computer-controlled potentiostat/galvanostat EG&G 273A. The electrode rotation speed was regulated by a Metrohm 628-10 unit. In order to investigate the ORR rotating disk electrode (RDE), assays were performed at 25 °C in a conventional three-compartment electrochemical glass cell. Experiments were conducted in both methanol-free and methanol-containing solutions. A glassy carbon rotating disk electrode (0.071 cm<sup>2</sup>, GC-Typ zu628) was used as a substrate for the catalysts. Prior to each test, the electrode was polished with alumina 0.05 μm to obtain a mirror finish, and was rinsed with triply distilled water in an ultrasonic bath. A mercury/mercury sulphate electrode and an Au plate were used as reference and counter electrode, respectively. All potentials are referred to the reversible hydrogen electrode (RHE).

The samples under study were deposited onto the working electrode by means of an ink. Details for the ink preparations are reported elsewhere [38]. Briefly, 5 mg of the catalysts were ultrasonically dispersed in 0.7 ml of water + 30 μl Nafion. 30 μl of the prepared ink was dropped onto the glassy carbon electrode. The final Pt loading on each electrode was 82 μg for the commercial sample and 27 μg for the bimetallic PtAu/C catalysts.

A 0.5 M H<sub>2</sub>SO<sub>4</sub> (Merck) was used as the electrolyte, and henceforward it will be considered the blank solution. All solutions were prepared with Mili-Q water. The appropriate amount of methanol (Panreac) was added to the electrolyte to obtain a final concentration of 0.01 or 0.1 M.

In order to clean and activate the electrode surface, a series of cyclic voltammetry (CV) experiments were conducted in Ar

Table 1  
Particle size was calculated using Scherrer's equation

Sample	Synthesis	Particle size (nm)	Pt/Au (ICP)	$I_a$ (mA cm <sup>-2</sup> mg <sub>Pt</sub> <sup>-1</sup> )	$I_a/I_c$
M-PtAu/C	Microemulsion	4.4	2.7	552.3	1.69
I-PtAu/C	Impregnation	4.1	2.2	489.8	1.66
C-PtAu/C	Colloidal	6.6 <sup>a</sup> , 3.9 <sup>b</sup>	2.0	418.1	3.34
Pt/C	Commercial	–	–	573.3	1.43

The 220 reflection was selected in order to overcome the contribution of the graphite phase.

The Pt/Au atomic composition was determined from ICP analysis as reported in Ref. [21],  $I_a$  and  $I_c$  are the anodic and cathodic current density values, respectively.

<sup>a</sup> Parameters for the Pt phase.

<sup>b</sup> Parameters for the Au phase.

purged (during 30 min) blank electrolyte. PtAu/C and the commercial samples were cycled at  $100 \text{ mV s}^{-1}$  between  $-0.1$  and  $1.6 \text{ V}$  until reproducible voltammograms were obtained.

For the methanol oxidation study, a series of cyclic voltammetry experiments were recorded in deaerated  $\text{H}_2\text{SO}_4$  [ $0.5 \text{ M}$ ]/ $\text{CH}_3\text{OH}$  [ $0.1$  and  $0.01 \text{ M}$ ] solutions. The experiments were carried out at  $10 \text{ mV s}^{-1}$  between  $-0.1$  and  $1.6 \text{ V}$ .

Linear sweep voltammetry was conducted to study the impact of methanol in the oxygen reduction reaction (ORR). Methanol ( $0.01$ – $0.1 \text{ M}$ ) was added to the blank electrolyte and the solution was saturated with high purity oxygen (Air Liquid) for 20 min. The polarization curves were obtained keeping the rotation rate at  $2500 \text{ rpm}$  between  $-0.05$  and  $1.1 \text{ V}$  at room temperature.

### 2.3. Studies in the direct methanol fuel cell

The electrochemical activity of the PtAu/C samples as cathode catalysts in the DMFC was evaluated. PtRu/C (Johnson Matthey,  $20 \text{ wt}\%$  Pt,  $10 \text{ wt}\%$  Ru) was used as anode catalyst. Such catalyst is the archetypal one for DMFC's applications. The metal loading was  $1 \text{ mg cm}^{-2}$ ; therefore, the amount of Pt in the cathode was  $1$  and  $0.7 \text{ mg cm}^{-2}$  for the commercial and prepared samples, respectively.

A commercial Nafion 117 membrane (Dupont) was treated by following a protocol described in Ref. [40]. After treatment, the membrane was dried at  $60^\circ\text{C}$  for 10 min and pressed at  $50 \text{ kg cm}^{-2}$  and  $90^\circ\text{C}$  for 10 min.

A three-layered structure was used to prepare the MEA. Both anode and cathode consisted of a backing layer, a gas-diffusion layer and a catalyst layer. Teflon treated carbon cloth (Electrochem. Inc.) was used as the backing and gas diffusion layer.

The catalyst layer was sprayed onto the membrane by means of an ink. Typically, the ink was formed by isopropanol (Merck), Mili-Q water, Nafion solution ( $5 \text{ wt}\%$  Aldrich) and catalyst powders. Nafion content in the ink was  $45 \text{ wt}\%$ . The amount of Nafion in the ink has been optimized to avoid the flooding of the electrodes or the decrease in the performance of the fuel cell [41,42]. The suspension was dispersed in an ultrasonic bath for 45 min resulting in a homogenous ink. Once the ink was sprayed onto the electrolyte, the MEA was obtained by hot pressing the carbon cloth onto both sides of the anode–membrane–cathode assembly at  $123^\circ\text{C}$  and residual press for 3 min [43].

The DMFC was assembled by mounting the MEA into a  $5 \text{ cm}^2$  single-cell (Electrochem. Inc.). The single-cell was initially activated at open-circuit, keeping the following operating conditions for 30 min;  $\text{H}_2$ ,  $100 \text{ cm}^3 \text{ min}^{-1}$ , 3 bar;  $\text{O}_2$ ,  $100 \text{ cm}^3 \text{ min}^{-1}$ , 3 bar; temperature  $45^\circ\text{C}$  [44]. After the activation process, the DMFC was tested by feeding methanol  $2 \text{ M}$  at a flow rate of 3 and  $5 \text{ ml min}^{-1}$  using a high pressure pump (Gilson 307). The methanol solution was heated at  $80^\circ\text{C}$ . The oxygen was fed into the cathode inlet at a flow rate of  $200 \text{ cm}^3 \text{ min}^{-1}$  and a pressure of 3 bar. Polarization curves were recorded at two temperatures,  $90$ – $100^\circ\text{C}$  by fixing the load current, which was controlled with an electric load system (Electrochem. Inc. ECL150). To ensure measurement repeatability and reproducibility, the same MEA was tested three times and

the experiments were repeated at least two times with different MEAs.

### 3. Results and discussion

Prior to the study of the mutual influence of the ORR and the MOR, both individual processes were studied. Specifically, the performances of Pt/C and the series of PtAu/C electrocatalysts in (i)  $\text{N}_2$  saturated  $\text{CH}_3\text{OH}$  ( $0.01$  and  $0.1 \text{ M}$ )/ $\text{H}_2\text{SO}_4$  ( $0.5 \text{ M}$ ), (ii)  $\text{O}_2$  saturated  $\text{H}_2\text{SO}_4$  ( $0.5 \text{ M}$ ) and (iii)  $\text{O}_2$  saturated  $\text{CH}_3\text{OH}$  ( $0.01$  and  $0.1 \text{ M}$ )/ $\text{H}_2\text{SO}_4$  ( $0.5 \text{ M}$ ) were studied.

Fig. 1 depicts the voltammograms of the bimetallic PtAu/C catalysts recorded in deaerated  $\text{H}_2\text{SO}_4$  ( $0.5 \text{ M}$ ) and in  $\text{CH}_3\text{OH}$  ( $0.1 \text{ M}$ )/ $\text{H}_2\text{SO}_4$  ( $0.5 \text{ M}$ ) solutions. The shape of the voltammograms depends on the nature of the samples, which in turn depends on the preparation route. In the blank solution, the voltammograms of M-PtAu/C and I-PtAu/C record two peaks between  $0.3$  and  $0.0 \text{ V}$ , followed by a sharp hydrogen desorption peak centred at  $-0.09 \text{ V}$ . According to the literature [45–47], the presence of the latter peak could be ascribed to the predominance of Pt (1 1 0). The voltammogram of C-PtAu/C showed a broad peak in the potential region from  $0.3$  to  $-0.1 \text{ V}$ , attributed to the predominance of Pt (1 1 1). In comparison to the data obtained from the blank solution, there is a large anodic wave at ca.  $800 \text{ mV}$  corresponding to methanol oxidation. The current density associated to the methanol oxidation process increases both with the concentration of methanol and with the actual Pt atomic ratio in the bimetallic electrodes (see Table 1). A deeper inspection of the voltammograms reveals that the extension of the oxidation process can be related to the apparent predominance of the Pt (1 1 0) surface deduced from the voltammograms recorded in the blank solution. In fact, this phase is proposed as the most active one for the methanol oxidation reaction [48], and it may be the reason for the enhancement of this reaction on M-PtAu/C and I-PtAu/C. It should be noted that the performance of M-PtAu/C and I-PtAu/C in methanol oxidation is similar (when normalized to the actual amount of Pt) to that of sample Pt/C. Even if normalized to the total amount of Pt on the electrode, the performance of C-PtAu/C is the worst in the series, considering both the magnitude of the oxidation ( $I_a$ ) process and the onset of the oxidation wave. This feature is even more evident from the observation that the magnitude of the oxidation process is much smaller in the reverse ( $I_c$ ) than in the forward sweep ( $I_a$ ). Selected electrochemical parameters are collected in Table 1. The reactivation of the catalytic sites after the anodic sweep appears to be modified by the presence of Au. In fact, the onset of the net anodic current is shifted to negative potentials in the bimetallic electrocatalyst compared to that of the commercial sample, especially in C-PtAu/C. The relative current density of the forward/reverse wave ( $I_a/I_c$ ) is also found to be dependent on the actual amount of Au in the bimetallic electrodes as shown in Table 1.

Fig. 2 depicts the forward scan of the MOR [ $0.1 \text{ M}$ ] on the studied electrocatalysts normalized to the actual amount of Pt of each sample. It can be seen how the methanol electrooxidation process commences at slightly more positive potentials on the M-PtAu/C electrode.

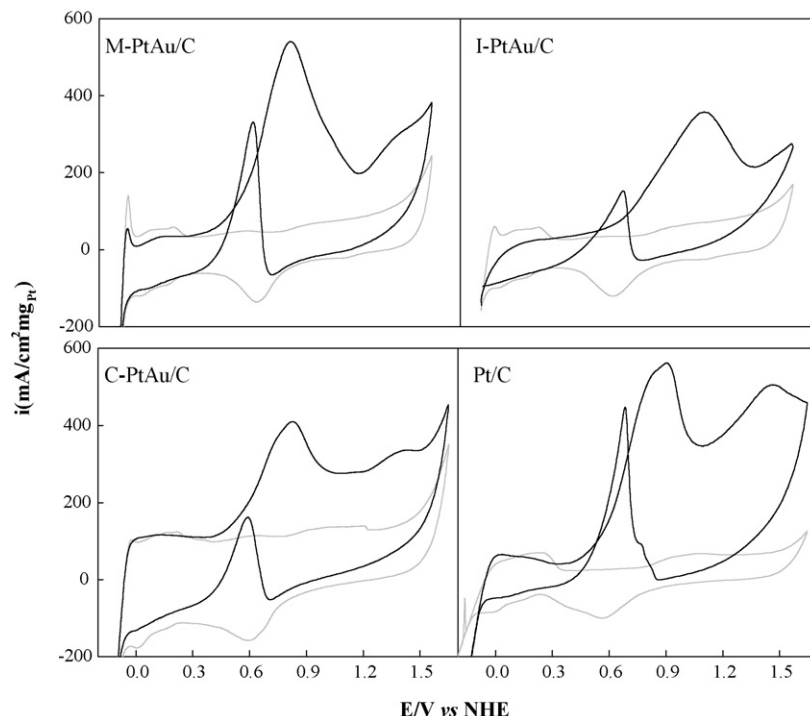


Fig. 1. Cyclic voltammograms for the bimetallic catalysts recorded at  $10 \text{ mV s}^{-1}$ : black line,  $\text{CH}_3\text{OH}$  (0.1 M)/ $\text{H}_2\text{SO}_4$  (0.5 M); grey line,  $\text{H}_2\text{SO}_4$  (0.5 M).

So far, the performance of the samples on the methanol oxidation reaction has been justified by the apparent predominance of Pt (1 1 0) on M-PtAu/C and I-PtAu/C samples deduced from the base voltammograms on blank solutions. A deeper characterization of the PtAu particles can be found in [38]. HRTEM analyses reveal that the {1 1 1} direction is slightly favoured on

such electrodes. However, those results do not exclude the presence of Pt (1 1 0) facets on M-PtAu/C and I-PtAu/C samples. As discussed above, the performance of C-PtAu/C on the methanol electrooxidation reaction is different to that of M-PtAu/C and I-PtAu/C, with the latter two displaying a similar pattern. In fact, M-PtAu/C and I-PtAu/C are actually formed by PtAu alloyed particles, whereas C-PtAu/C consists of Pt and Au segregated phases [38]. Although without alloyed particles, C-PtAu/C consists of both Pt and Au metals located in the vicinity of each other as demonstrated from the EDX analysis depicted in Fig. 3. This analysis was performed by focusing the electron beam onto single particles (the diameter of the beam is ca. 2–5 nm). As discussed above, the performance of this sample in the MOR is by far the worst in the series. It is therefore likely that the presence of Au modifies the performance of Pt particles in the adsorption of methanol through a dilution rather than an electronic effect. The electrocatalytic activity of gold nanoparticles for CO and methanol oxidation reactions has been explored recently [25,26]. The enhancement of MOR activity on PtAu/C catalysts has been reported [49]. Unfortunately, these studies were undertaken in an alkaline medium where Au is known to be active for methanol oxidation. Mihut et al. have reported that PtAu catalysts prepared by impregnation display a similar performance in the MOR to monometallic Pt catalysts, indicating that the role of Au in the overall process could be negligible [50]. Recently, some papers describing an enhancement of the MOR due to the presence of Au have been reported [51,52]. However, the Au used in those works was either a matrix to disperse the Pt sites or the other way round, rather than entailing alloyed particles. Here, we have observed a similar effect of the methanol oxidation reaction on Au-containing samples

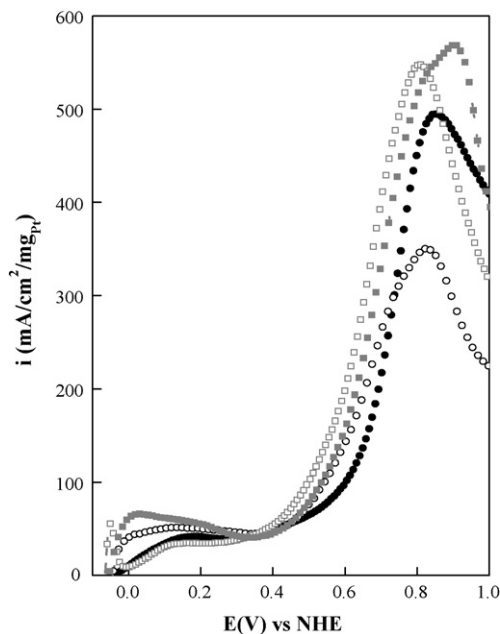


Fig. 2. Forward scan of the methanol oxidation reaction on selected electrodes recorded in  $\text{H}_2\text{SO}_4$  0.5 M/ $\text{CH}_3\text{OH}$  0.1 M. (□) M-PtAu/C, (●) I-PtAu/C, (○) C-PtAu/C and (■) Pt/C.

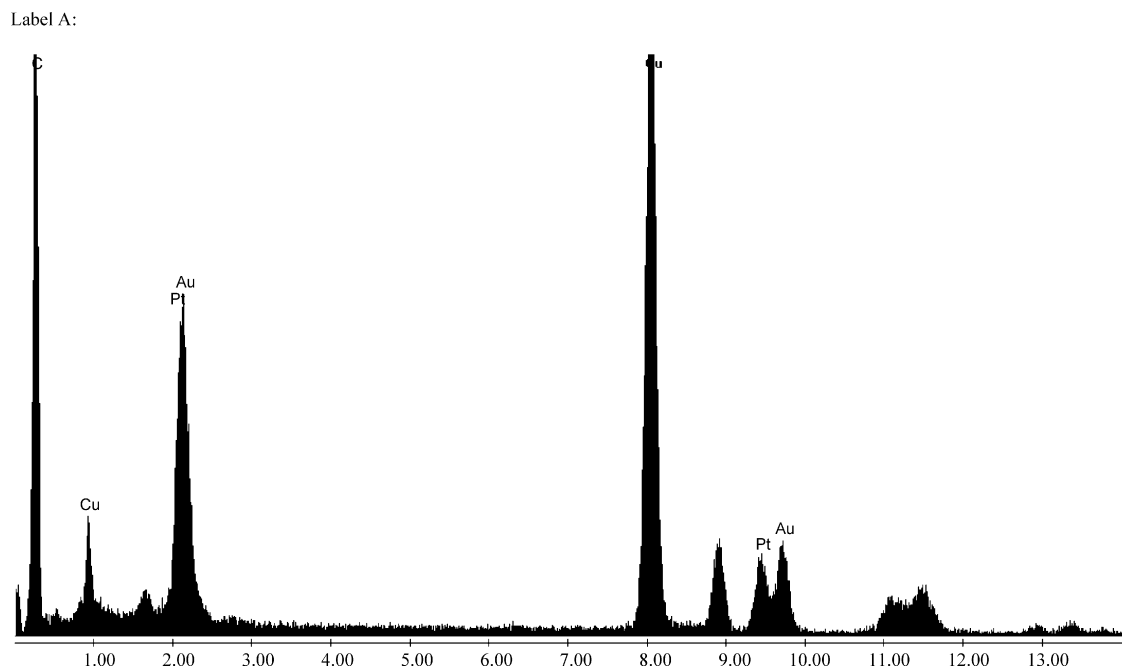


Fig. 3. EDAX analysis of sample C-PtAu/C.

when the catalysts consisted of actual alloyed PtAu particles. However, an inhibition of the methanol oxidation reaction is observed for the C-PtAu/C sample (non-alloyed bimetallic sample). The actual reason for this inhibition could be related to the lower possibility of finding enough Pt sites together for methanol dehydrogenation to proceed, due to Au dilution. It is known that methanol oxidation occurs on Pt sites through a dehydrogenation mechanism. The methanol adsorption–dehydrogenation process requires at least three neighbouring Pt atoms in the proper crystallographic arrangement [53,54]. In the C-PtAu/C sample, the Pt/Au ratio is 2.0 and the probability of finding three neighbouring Pt atoms on the surface is lower than for M-PtAu/C (Pt/Au = 2.7) and I-PtAu/C (Pt/Au = 2.2). Also, other features could be contributing to the performance of the electrocatalysts, as the Pt/Au ratio of the I-PtAu/C sample is somewhat similar to that of C-PtAu/C. For instance, and as discussed above, the predominance of Pt (1 1 0) is reported to promote methanol oxidation. Such crystalline phase is deduced from the voltammograms of M-PtAu/C or I-PtAu/C. Admittedly further studies are needed to elucidate the overall reaction mechanism. It is accepted that the actual size and shape of the particles play a certain role in the methanol oxidation process, with the optimum size range for the complete oxidation to CO<sub>2</sub> being between 3 and 10 nm [55]. Particle sizes as determined from XRD are collected in Table 1. It can be seen that samples display sizes between 4 and 6 nm and their shape is rather similar as well (see Ref. [38]); consequently, major differences in the MOR due to distinct particle size could be excluded.

The low ability of PtAu for adsorbing/oxidizing methanol is a handicap for these samples to be used as methanol oxidation electrocatalysts, particularly for the C-PtAu/C sample. However, this feature could turn out to be an advantage for the designing of methanol tolerant cathode catalysts. Hence, the performance of

PtAu/C electrocatalysts in the oxygen reduction reaction in the presence of methanol was also studied. The response of the ORR in the presence of methanol on the PtAu/C samples was obtained from linear voltammetry experiments. Fig. 4 depicts the results obtained for M-PtAu/C as representative of the other samples. Compared to the ORR in H<sub>2</sub>SO<sub>4</sub>, the electrocatalyst recorded an increase in the overpotential for the ORR at any current density, due to the presence of methanol. This significant increase in the overpotential of the ORR on Pt/C and PtAu/C bimetallic electrocatalysts reflects the competitive reaction between oxygen reduction and methanol oxidation reactions. Considering

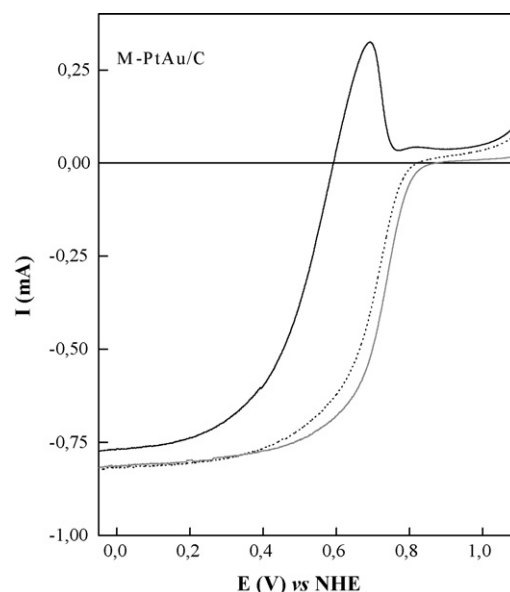


Fig. 4. RDE measurements of ORR on M-PtAu/C recorded in H<sub>2</sub>SO<sub>4</sub> (0.5 M) (—), methanol 0.01 M (···) and methanol 0.1 M (---) recorded at 1 mV s<sup>-1</sup>.

the complex nature of both reactions, it appears highly unlikely that these two reactions proceed fully independently, without affecting each other. Moreover, the presence of both  $O_2$  and methanol could affect either reaction pathways (ORR and MOR) [23]. Nonetheless, three regions can be observed in the ORR curves in the presence of methanol; however, the margins are modified with respect to methanol-free solutions. The diffusion-controlled region is observed at more negative potentials than 0.45 V, being smaller when methanol is present in the reaction medium. This effect could be ascribed to the fact that a fraction of the active sites for the ORR are blocked by adsorbed intermediates arising from the methanol oxidation reaction, or even by methanol itself. In fact, the limiting current ( $i_L$ ) actually depended on the concentration of methanol in the medium, as observed in Fig. 4. In the region of more positive potentials than 0.9 V, both PtO and AuO formation occurs. In fact, at such potentials both ORR and MOR are hindered, and the current response is similar to that recorded in the base linear voltammetry experiments. A strong competition between ORR and MOR was observed for experiments conducted in 0.1 M methanol, particularly for the Pt/C catalyst. In the potential region between 0.45 and 0.9 V, the net current changes between these two regimes and the behaviour for PtAu/C bimetallic electrodes and Pt/C electrode are different. When the methanol concentration was 0.1 M, with results depicted in Fig. 5, the potential at which the ORR predominates, actually yielding a net reducing current, is shifted by ca. 0.3 V for Pt/C, M-PtAu/C and I-PuAu/C compared with the ORR (methanol-free) in Pt/C. Noticeably, the overpotential for the C-PtAu/C is smaller, the onset of the net reduction current being shifted only ca. 0.1 V. The shifting is negligible for the experiments conducted under  $CH_3OH$  (0.01 M).

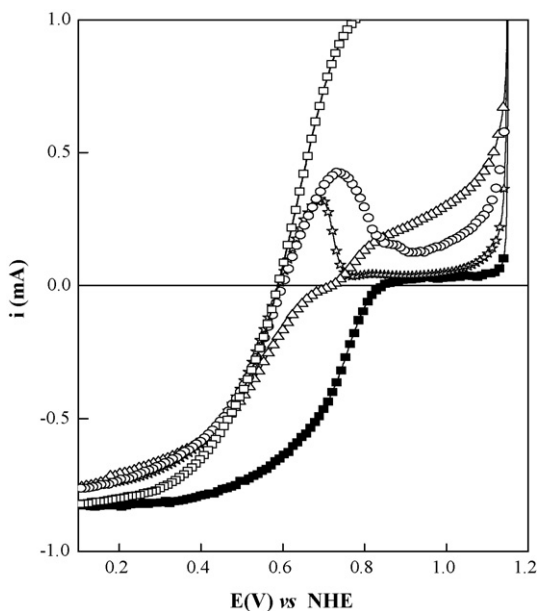


Fig. 5. Polarization curves for the methanol oxidation reaction. Curves were recorded in  $O_2$ -saturated  $H_2SO_4$  (0.5 M) and with a methanol concentration of 0.1 M, obtained using a rotating disk electrode at 2500 rpm at  $1 \text{ mV s}^{-1}$  sweep rate. ( $\square$ ) Pt/C, ( $\Delta$ ) C-PtAu/C, ( $\circ$ ) I-PtAu/C and ( $\star$ ) M-PtAu/C. For the sake of comparison, the ORR on Pt/C in methanol-free solutions is also depicted ( $\blacksquare$ ).

This result shows how the nature of the catalyst affects tolerance to the methanol crossover process. If the methanol reaching the cathode finds the proper sites for its adsorption, it can modify the performance of the catalyst in the ORR. In fact, the kinetic-diffusion control region is modified by the presence of methanol in the cathode in two ways: on the one hand, it blocks the adsorption sites for  $O_2$  impeding the ORR; on the other hand, once adsorbed, the methanol oxidation reaction can actually proceed resulting in the corresponding net oxidation current, overlapping with the desired net reducing current that should be obtained in the cathode electrode.

It thus seems that to attain good ORR activity in the presence of methanol (DMFC) the methanol tolerance of the catalyst is at least as important as the intrinsic activity in the oxygen reduction reaction. In fact, in methanol-free  $O_2$ -saturated solutions, C-PtAu/C is the less active electrocatalyst in the series. However, due to its poor activity towards methanol oxidation, the ORR is less impeded by the presence of methanol when compared with the other catalysts. The reason for this behaviour is related to the actual nature of the bimetallic samples. M-PtAu/C and I-PtAu/C consists of actually alloyed particles with an apparent predominance of Pt (1 1 0), as revealed by the electrochemical analysis (see Fig. 1). Such phase is proposed as the most active in the methanol oxidation reaction [48]. On the other hand, both electrochemical (Fig. 1) and HRTEM [38] analyses reveal the predominance of Pt (1 1 1) on C-PtAu/C. This latter crystalline phase is less active in the MOR than Pt (1 1 1). These data, along with the dilution of the Pt sites by Au in C-PtAu/C, could explain the lower tendency of the latter towards methanol adsorption/oxidation and therefore justify the performance of the samples under oxygen/methanol. A compromise between the performance on both ORR and MOR reactions is necessary to develop improved cathode catalysts for DMFC.

The catalytic performance of the bimetallic PtAu/C and Pt/C samples as cathode materials in DMFC was studied. In all experiments, PtRu/C ( $1 \text{ mg cm}^{-2}$ ) was used as the anode catalyst. Two sets of results were obtained by operating the fuel cell at  $90^\circ\text{C}$  and  $3 \text{ ml min}^{-1}$  (methanol flow) and  $100^\circ\text{C}$  and  $5 \text{ ml min}^{-1}$  (methanol flow). In the present paper, only the latter results are described, as both sets of experiments follow similar trends. From results depicted in Fig. 6, it can be observed that the polarization curve of the Pt/C is rather similar to that of C-PtAu/C. Power losses were evident even at the early stages of the polarization process, but the results depicted here are similar to already published results, at least when normalized to the actual amount of Pt on the electrode. An interesting feature observed from the polarization curves is that the performance of the Pt/C catalysts is better than that of the C-PtAu/C sample until ca. 180 mV. As from this voltage, oxygen mass transport phenomena actually take control of the performance of the fuel cell. Consequently, any competition between  $O_2$  and  $CH_3OH$  for the Pt sites would be magnified. Since, methanol adsorption on C-PtAu/C is impeded, at least to some extent, the oxygen reduction reaction is not severely affected, and from that voltage, the performance of C-PtAu/C surpasses that of the Pt/C catalyst.

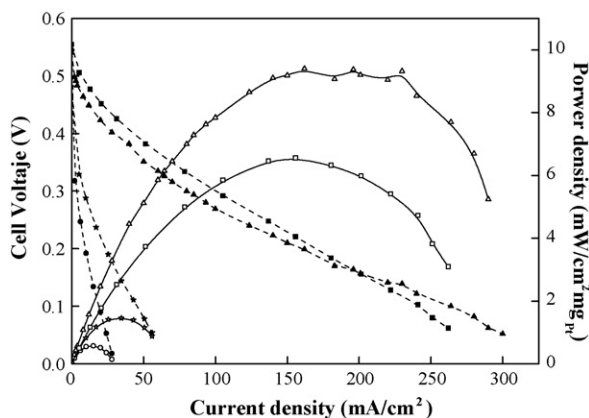


Fig. 6. Polarization (dashed lines) and power density (straight lines) curves of PtAu/C catalysts and Pt/C as cathode in DMFC at 100 °C and a flow rate of 5 ml min<sup>-1</sup> of methanol. The anode catalyst was a commercial PtRu/C sample (Johnson Matthey). Metal loading in the anode was 1.0 mg cm<sup>-1</sup><sub>MEA</sub>. Pt loading in the cathode was 0.7 and 1.0 mg cm<sup>-1</sup><sub>MEA</sub> for the bimetallic samples and Pt/C respectively. Note that the power density was normalized to the platinum loading. (Δ) C-PtAu/C, (○) I-PtAu/C, (☆) M-PtAu/C and (□) Pt/C.

The rest of the Au-containing samples (M-PtAu/C and I-PtAu/C) display rather poor performances throughout the entire polarization range. The performance of C-PtAu/C and I-PtAu/C as cathodes in hydrogen/oxygen PEMFC has been tested. For the sake of comparison, the performance obtained with a commercial Pt/C catalyst as cathode has been also depicted in Fig. 7. The experimental setup is similar to the one described above, only hydrogen (humidified at 80 °C) was fed at the anode site of the cell. The anode catalyst was a Pt/C commercial one from Johnson Matthey. The Pt loadings were 0.3 and 0.6 mg<sub>Pt</sub> cm<sup>-1</sup><sub>MEA</sub> for the anode and the cathode, respectively. Polarization and power density curves are depicted in Fig. 7. It can be seen how the performance of I-PtAu/C as cathode is far superior to that of C-PtAu/C. In fact, this result is in good agreement

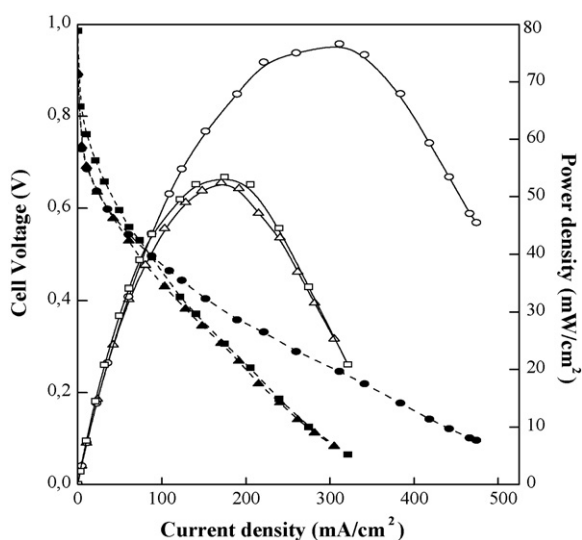


Fig. 7. Polarization (dashed lines) and power density (straight lines) curves of (○) I-PtAu/C, (Δ) C-PtAu/C and (□) Pt/C as cathode in H<sub>2</sub>/O<sub>2</sub> at 80 °C. The anode catalyst was a commercial Pt/C sample (Johnson Matthey). Pt loading was 0.3 and 0.6 mg<sub>Pt</sub> cm<sup>-1</sup><sub>MEA</sub> for the anode and the cathode, respectively.

with the ones obtained by means of the linear sweep voltammetry technique using a rotating disk electrode to study the oxygen reduction reaction in acid media reported in [38]. Both results coincide in that I-PtAu/C and M-PtAu/C are better catalysts for the ORR than C-PtAu/C, at least in the absence of methanol. Therefore, the results described in the present manuscript, together with those reported elsewhere [38], confirm that the MOR actually proceeds to a great extent in the cathode electrode for the M-PtAu/C and I-PtAu/C samples, especially when operating at high methanol flow (5 ml min<sup>-1</sup>) and high temperature (100 °C). This result suggests that the presence of alloyed PtAu lacks any advantage over Pt/C electrocatalysts. It must be recalled that the bimetallic catalysts record a lower amount of Pt than Pt/C. Thus, the power density has been normalized to the actual amount of Pt contained in each electrode. However, it can be seen how the performance of C-PtAu/C is superior in terms of power density (mW cm<sup>-2</sup>) per mg of Pt to the rest of the series, even to that of the commercial sample. As expected from the electrochemical experiments (their onset for the ORR was shifted some 0.3 V vs. Pt/C), the performance of M-PtAu/C and I-PtAu/C samples as cathodes in DMFCs is the worst in the series, as they are neither tolerant to methanol crossover nor good catalysts for the ORR. This feature was found at both reaction temperatures mentioned above, although it is more pronounced at 100 °C and with methanol flux of 5 ml min<sup>-1</sup>, which, in principle, would be the most favourable conditions for enhancing the methanol crossover effect.

#### 4. Conclusions

The oxygen reduction reaction in the absence and presence of methanol on bimetallic PtAu/C catalysts with 20 wt% metal loading and their application in a direct methanol fuel cell have been studied. Such catalysts exhibited significantly enhanced electrocatalytic activity for the ORR in methanol-containing electrolytes compared to a pure Pt/C 40 wt%. The high methanol tolerance of C-PtAu/C catalyst during the ORR could be explained by the lower reactivity of the methanol oxidation process due to a partial dilution of the Pt sites and to the predominance of Pt (1 1 0) on the actual alloyed samples I-PtAu/C and M-PtAu/C. Clearly, a compromise between the performance on both ORR and MOR reactions is necessary to develop improved cathode catalysts for DMFC. Fuel cell tests are in parallel with the results obtained by means of electrochemical techniques.

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