# Electrochemical characterisation of Pt/C suspensions for the reduction of oxygen

R. Benítez [a], A.M. Chaparro [a,*], L. Daza [a,b]

[a] *Dep. Combustibles Fósiles, CIEMAT, Av. Complutense, 22, 28040 Madrid, Spain*
[b] *Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie 2, Campus Cantoblanco, 28049 Madrid, Spain*

## Abstract

Electrodes based on carbon-supported platinum electrocatalysts (Pt/C) have been studied in aqueous electrolyte electrochemical cells. The electrodes are prepared from suspensions of commercial Pt/C catalyst, deposited onto a carbon-covered Pt disk. Three deposition methods have been used, impregnation, spray and electrospray. The utilisation of Pt, i.e. the amount of Pt that really participates in the electrochemical reaction, was determined for each preparation method from measurements of the mass of Pt deposited on the electrode, and of the electroactive area of Pt. Higher utilisation rates are found on electrodes prepared by the impregnation method. The activity towards oxygen reduction in aqueous electrolyte was studied with the rotating electrode at different temperatures.
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## 1. Introduction

So far, electrodes based on platinum nanoparticles are used for proton exchange membrane fuel cell (PEMFC), but their cost may hinder the future generalisation of the technology. The cost problem, and even the supply of Pt, will be increasingly acute in the next years considering that even the installation of state-of-the-art PEMFC of the highest efficiency, with the lowest platinum content $(0.4 \text{ mg Pt cm}^{-2})$ [1], in 10% of annually matriculated cars worldwide $(75 \times 10^6 \text{ U in } 2001)$, would require more than the annual production of Pt (170 tonnes) [2]. To deal with this problem research effort must concentrate on the reduction of the amount of Pt in the electrodes, as well as the search for alternative electrocatalysts, notwithstanding other solutions like increasing Pt production, the search for new reserves and recycling technologies.

In principle, the platinum load in the electrodes can be reduced to a limit when attaining maximum utilisation, i.e. the maximum amount of Pt atoms participates in the electrochemical reactions with the highest turnover frequency. High turnover rates, as well as low overvoltages, are electrocatalyst-dependent properties necessary for high power fuel cells. If assuming that Pt atoms are able to support turnovers rates until $10,000 \text{ atom}^{-1} \text{ s}^{-1}$, which is a maximum number typical for enzymatic sites, then a monolayer of Pt should be able to support the electrocatalysis for a current density of almost $700 \text{ mA cm}^{-2}$. This value is in the range of currents demanded to present electrodes at 0.7 V. Such estimation may conclude that an ultimate limit for the amount of Pt in the electrode is the amount of a monolayer, $0.54 \text{ μg cm}^{-2}$. However, this number must be increased if considering that Pt is in the form of spherical particles of 5 nm diameter, where about 10% of atoms are in disposition to be catalytic sites (i.e. disregarding bulk and 'buried' atoms), to give a more realistic limit of $50–5 \text{ μg cm}^{-2}$. This load is still one to two orders of magnitude below actual loads and may be considered an objective for future Pt based

* Corresponding author. Tel.: +34 913466622; fax: +34 913466269.
 *E-mail address:* antonio.mchaparro@ciemat.es (A.M. Chaparro).

electrodes. To attain such a reduction, the research efforts must concentrate on electrode structures with maximum utilisation and turnover rates, which is principally a matter of location of Pt atoms and of their chemical environment.

For the electrode of a PEMFC, Pt is disposed in the form of a dispersion of nanoparticles on a highly porous substrate where it is accessible to gas and liquid species. Different methods for preparing nanoparticles and dispersions are used, including chemical, electrochemical, electroless, spray, dry methods, vacuum methods, ... [3–5]. Methods departing from a suspension of platinum supported on carbon (Pt/C) ('ink') are mostly used because carbon is highly conductive and inert, and gives to the Pt nanoparticles a high resistance to sintering [1]. The application of the suspension on the substrate is a key process that may have a strong influence on the electrocatalyst performance. For instances, the disposition of Pt/C particles inside the electrode may differ and give different electroactive area, turnover rates, and electrochemical activity.

In this work, electrodes based on Pt/C suspensions deposited on carbon covered Pt substrate are studied as a function of the deposition method. Three methods are studied, impregnation, spray and electrospray. Pt/C suspension are prepared with two different solvents, one of them most simple and easy to eliminate (isopropanol) and the other an optimised mixture of butylacetate, ethanol, and glycerol (BEG). The second one is of interest because it is able to give long lasting stability to the suspension necessary for large area deposition processes. The influences of the deposition method and suspension solvent on the amount of electroactive Pt area ($A_{Pt}$) are studied with cyclic voltammetry [6]. The activity of the electrodes towards the reduction of oxygen in aqueous electrolyte is tested with the rotating disk electrode (rde) by applying a thin film of the Pt/C suspension on the carbon-covered platinum disk [7].

## 2. Experimental

The suspensions of Pt/C powder (E-TEK, 20 wt%, $130\,\mathrm{m^2\,g_{Pt}^{-1}}$, $250\,\mathrm{m^2\,g_T^{-1}}$) were prepared using two different solvents, (a) isopropanol and (b) a mixture of butylacetate, ethanol and glycerol. Isopropanol was chosen because it is most simple and easily eliminated after deposition of the catalyst. On the other hand, BEG is an optimised mixture of solvents that allows for more stable and long lasting suspension without formation of agglomerates of particles. This second solvent is intended to be used for large area deposition. Different properties of the solvents are
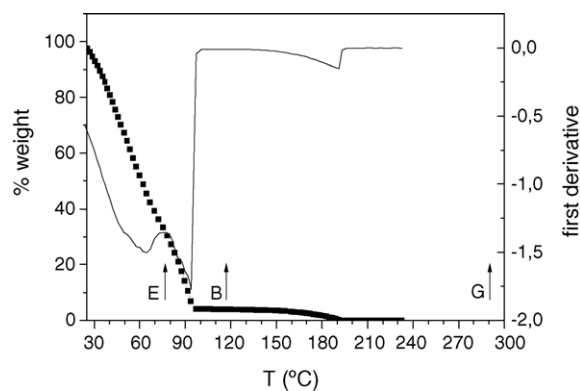


Fig. 1. Thermogravimetric analysis of a mixture of butylacetate, ethanol and glycerol (45/50/5) (BEG). The evaporation temperature of pure individual constituents is indicated with arrows.

summarised in Table 1. The thermogravimetric analysis of the mixture BEG is given in Fig. 1, showing that complete evaporation and elimination is attained at 180 °C, which is lower temperature than for glycerol. Except where indicated, Nafion® solution (5 wt%, Aldrich) was added to the suspensions as ionic conductor at the optimised proportion of 33 wt% referred to catalyst weight [8]. The suspensions were applied by three different methods (see below) onto the surface of a rotating Pt disk electrode (Tacussel, $r = 2\,\mathrm{mm}$) previously covered with a thin carbon black layer (Vulcan XC-72). The study was carried out inside a three electrodes cell with a Pt wire as counter electrode, and an Ag/AgCl reference electrode (0.205 V vs NHE) in contact with the electrolyte via a salt bridge. The electrode potential was controlled with a potentiostat (Autolab, Eco Chemie).

The methods studied for deposition of Pt/C suspensions on the electrode are (a) impregnation, by simply putting some drops on the disk with a micropipette; (b) spray, by painting the substrate with an airbrush (Vega System) using $N_2$ as carrier; and (c) electrospray [9] with a set up including a silica capillary (100 μm diameter), a needle and a voltage source (Bertran, Model 205B-10R) to impose a dc voltage of 3300–4000 V between the needle and the substrate. For electrospray deposition the substrate is placed on an $X$–$Y$ stage (Physik Instrumente), and the suspension is deposited in successive sweeps during about 15–30 min over a $9\,\mathrm{cm^{-2}}$ surface area and under the heat of an infrared lamp. More details of the technique are given in another communication of this volume [10]. For quantitative measurements the amount of Pt deposited on the electrode was determined by measuring the weight of a single drop of the suspension,

Table 1

Density ($\delta$), viscosity ($\eta$), dielectric constant ($\varepsilon$), conductivity ($\kappa$), and evaporation temperature ($T_{evap}$) of the two solvents, isopropanol and butylacetate/ethanol/glycerol (BEG), used in this work for the preparation of Pt/C suspensions

| Composition | $\delta$ (20 °C) (g cm$^{-3}$) | $\eta$ (20 °C) (mPa s) | $\varepsilon$ (25 °C) | $\kappa$ (25 °C) (μS cm$^{-1}$) | $T_{evap}$ (°C) |
|---|---|---|---|---|---|
| Isopropanol | 0.803 | 1.91 | 18.3 | 1.59 | 82.4 |
| Butylacetate/ethanol/glycerol, 45/50/5 (BEG) | 0.869 | 1.67 | 14.5 | 0.92 | 117/79/290[a] |

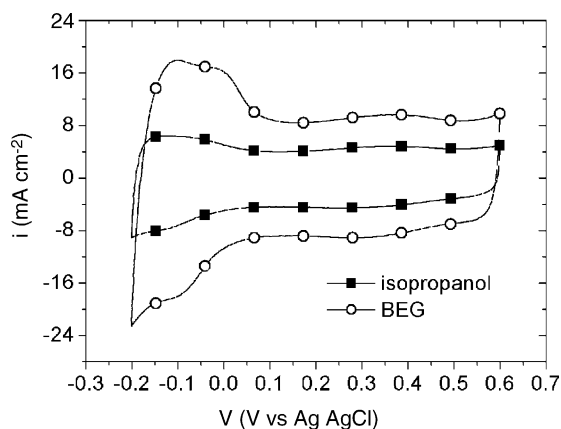[a] See the thermogravimetric analysis in Fig. 1.

Fig. 2. Voltammograms of Pt/C electrodes prepared by the impregnation method from two different suspensions, one using isopropanol and the other using BEG. $v = 800\,\mathrm{mV\,s^{-1}}$, 25 °C, electrolyte HClO$_4$ 0.5 M. The Pt load measured by weight determination for each electrode was 0.007 and 0.068 mg cm$^{-2}$ for the isopropanol and the BEG suspensions, respectively.

and/or by measuring the change of mass of an Al foil used as test substrate. Once deposited, the electrodes were heated at 60 °C overnight to eliminate the rest of the solvent.

## 3. Results

### 3.1. Determination of the electroactive area ($A_{Pt}$)

It is accepted that the electroactive area of a Pt electrode can be determined from the adsorption/desorption charge of hydrogen atoms measured by cyclic voltammetry in aqueous solution (Fig. 2). This charge is attributed to the adsorption/desorption of one hydrogen atom per Pt site ($\mathrm{Pt_s + H^+ + e^- \rightleftarrows Pt_s{-}H}$), which for a polycrystalline surface, amounts approximately to 210 $\mu$C cm$^{-2}$ after double layer charge subtraction [13]. The voltammetries were carried out in HClO$_4$ 0.5 M, previously degassed with N$_2$ bubbling during 30 min, and the hydrogen desorption charge was measured for area determination, instead of the adsorption charge or the average of the two charges, because it was found better defined and less affected by parallel processes (Pt oxide reduction may overlap with the adsorption charge). Optimal experimental conditions were determined previously. An effect of the sweep velocity ($v$) on the desorption charge was
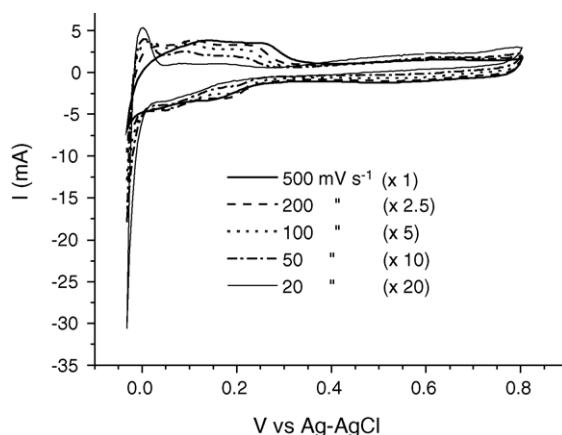


Fig. 3. Voltammograms of a Pt/C electrode under variable sweep rate. 25 °C, 0.5 M HClO$_4$, N$_2$ saturated electrolyte. Scale factors are indicated.
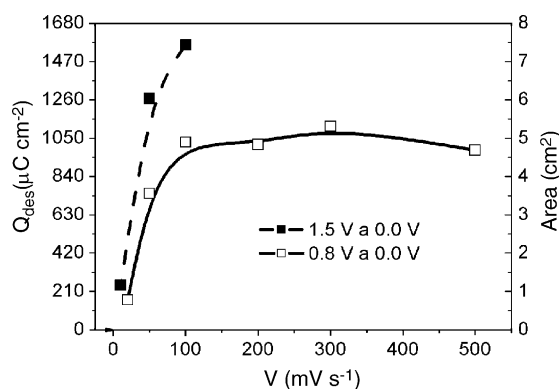


Fig. 4. Electroactive area measured for a Pt/C electrode using different potential range limits. Other conditions are as in Fig. 3.

found, as shown in Figs. 3 and 4. At low $v$, a decrease in the desorption charge, which is considered an artifact due to the massive evolution of H$_2$ (Fig. 3). Such effect may be avoided either by choosing more positive cathodic limit, but this could give rise to underestimation of the charge, or using higher sweep rates. Fig. 4 also shows that the anodic limit of the voltammetry influences the measurement of $A_{Pt}$. The area becomes a function of $v$ when using high positive limit (1.5 V versus Ag/AgCl) due the formation of the Pt–O alloy [11]. Based on these results the conditions chosen for measuring the electroactive area were 0.8–0.0 V versus Ag/AgCl interval at a sweep rate $v = 800\,\mathrm{mV\,s^{-1}}$.

Table 2
Results of Pt load, total estimated Pt area ($A_e$), measured electroactive area ($A_{Pt}$), and Pt utilisation ($\eta_{Pt}$) for electrodes deposited from Pt/C suspensions using different solvent compositions and methods

| Solvent | Deposition method | Pt load (mg cm$^{-2}$) | $A_e$ (cm$^2$) | $A_{Pt}$ (cm$^2$) | $\eta_{Pt}$ (%) |
|---|---|---|---|---|---|
| BEG | Impregnation | 0.11 | 4.5 | 3.6 | 80 |
| BEG[a] | Impregnation | 0.31 | 12.6 | 7.4 | 59 |
| Isopropanol[a] | Impregnation | 0.30 | 12.1 | 3.3 | 27 |
| Isopropanol | Impregnation | 0.19 | 7.4 | 3.5 | 50 |
| Isopropanol | Electrospray | 0.05 | 1.9 | 0.8 | 40 |
| Isopropanol | Electrospray | 0.006 | 0.25 | 0.1 | 40 |
| Isopropanol | Spray | 0.03 | 1.2 | 0.3 | 25 |

[a] Without Nafion solution.

Table 3
Results of the kinetic analysis for oxygen reduction corresponding to Pt/C electrodes prepared by different methods, at 25 °C

| Solvent | Deposition method | Pt load (mg cm$^{-2}$) | $n$ at 0.0 V | $b$ (mV dec$^{-1}$) at $V < 0.7$ V | $k_{TOF}$ ($n = 4$) (at$^{-1}$ s$^{-1}$) at 0.55 V | $E_{act}$ (kJ mol$^{-1}$) at 0.55 V |
|---------|-------------------|------------------------|--------------|-----------------------------------|---------------------------------------------------|-------------------------------------|
| Isopropanol | Impregnation | 0.007 | 3.2 | 154 | 0.7 | 9 |
| BEG | Impregnation | 0.068 | 2.9 | 122 | 0.8 | 33 |
| BEG | Spray | 0.025 | 2.8 | 128 | 0.05 | 43 |
| BEG | Electrospray | 0.035 | 2.0 | 137 | 0.006 | 27 |

Number of electrons ($n$), Tafel slope ($b$), turnover frequency if assuming $n = 4$ ($k_{TOF}$), and apparent activation energy ($E_{act}$). Potentials referred to the Ag/AgCl electrode (0.205 vs NHE).

Table 2 shows $A_{Pt}$ values for electrodes prepared from Pt/C suspensions using two different solvents (BEG and isopropanol), and three deposition methods (impregnation, spray and electrospray). The Pt load put in the electrodes is also included in the table, as well as the resulting total area of Pt ($A_e$), calculated for a distribution of spherical particles of 5 nm diameter. From both areas, electroactive and total, it is possible to estimate the Pt utilisation ($\eta_{Pt}$):

$$\eta_{Pt} = 100 \times \frac{A_{Pt}}{A_e} \qquad (1)$$

Values of $\eta_{Pt}$ are also included in Table 2. The results are affected by a certain experimental error (that we estimate around 10%) due to the manual manipulations and the
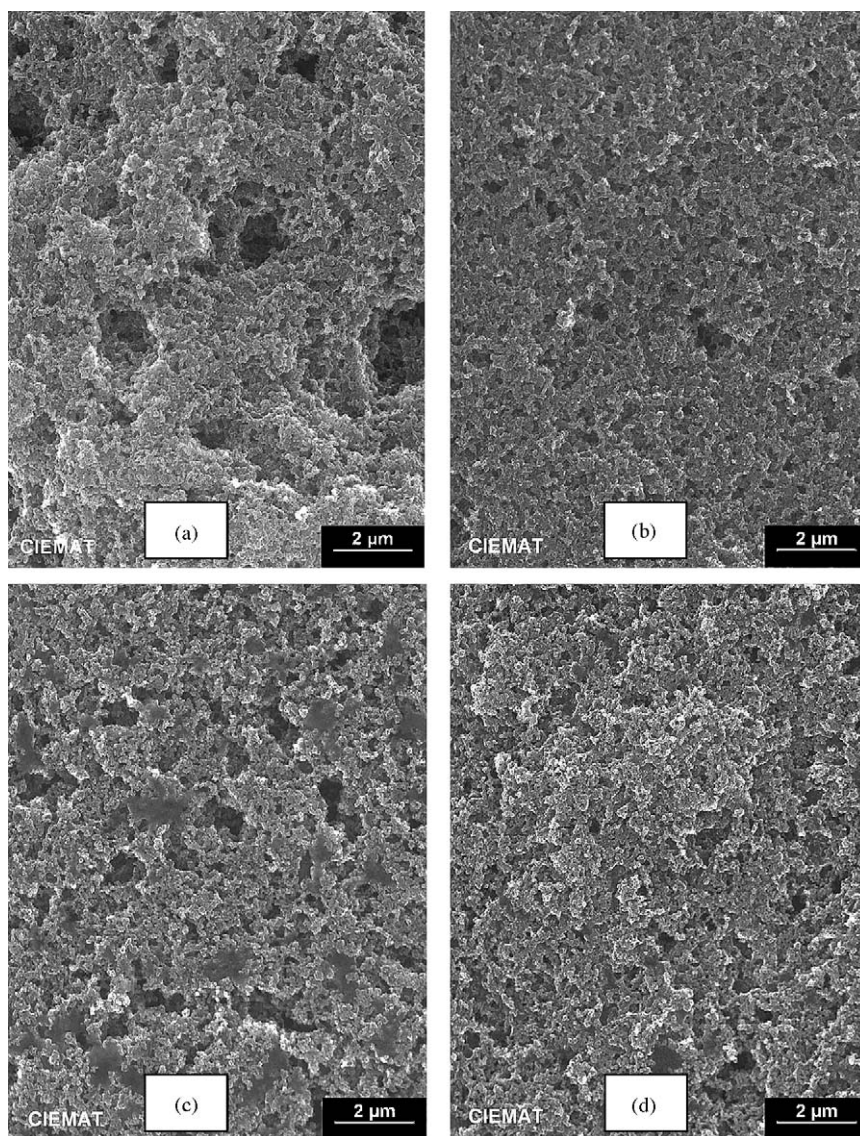


Fig. 5. SEM images of Pt/C electrodes, deposited by impregnation of isopropanol suspension (a), BEG suspension (b), by spray of BEG suspension (c) and electrospray of BEG suspension (d).

extremely small amounts of Pt to be measured. The values given are the most representative from all the electrodes prepared.

The morphology of the electrocatalyst films from Pt/C suspensions using isopropanol and BEG is shown in the SEM images of Fig. 5. Most important differences seem to be due to the solvent used, obtaining more porous structure with isopropanol suspension. The deposition methods, on the other hand, give apparently similar morphologies.

### 3.2. Study of the oxygen reduction reaction with rde

The rde technique is useful to test the behaviour of the electrocatalyst under normalised hydrodynamic conditions in a liquid electrolyte [12]. The current is a linear function of the square root of the rotating speed ($\omega$) [12]:

$$i = B^* \omega^{1/2} = 0.62\, n\, FAC^* D_{O_2}^{2/3} \nu^{-1/6} \omega^{1/2} \tag{2}$$

where $B^*$ is a constant under mass transfer limiting conditions [12], depending on the diffusion coefficient of oxygen ($D_{O_2}$), the number of exchanged electrons in the reaction ($n$), the Faraday constant ($F$), the geometric area ($A$), the viscosity of the solution ($\nu$), and the bulk concentration of $O_2$ molecules ($C_{O_2}^*$). With precise values of the other parameters it is possible to obtain $n$ from the slope of $i$ versus $\omega^{1/2}$. The
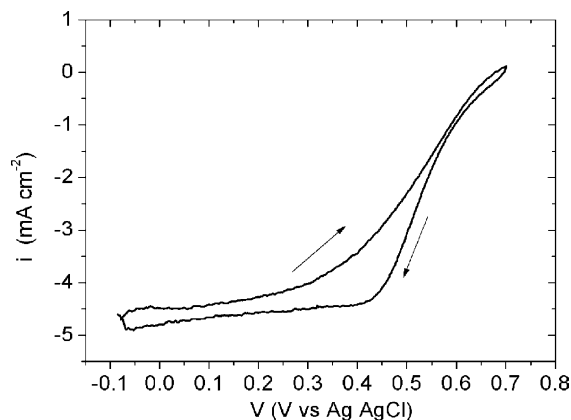


Fig. 6. Voltammogram of a Pt/C rde electrode in HClO$_4$ 0.5 M solution saturated with oxygen at 25 °C, 50 mV s$^{-1}$ sweep rate and 1000 rpm.

values given in Table 3 are calculated using approximated values for $C_{O_2}^*$ ($0.3 \times 10^{-3}$ M), $\nu$ (0.01 cm$^2$ s$^{-1}$), and $D_{O_2}$ ($10^{-5}$ cm$^2$ s$^{-1}$).

The variable rotation speed allows to decompose the resistance of the electrode into two series terms, the kinetic resistance and the diffusion resistance [13,14]:

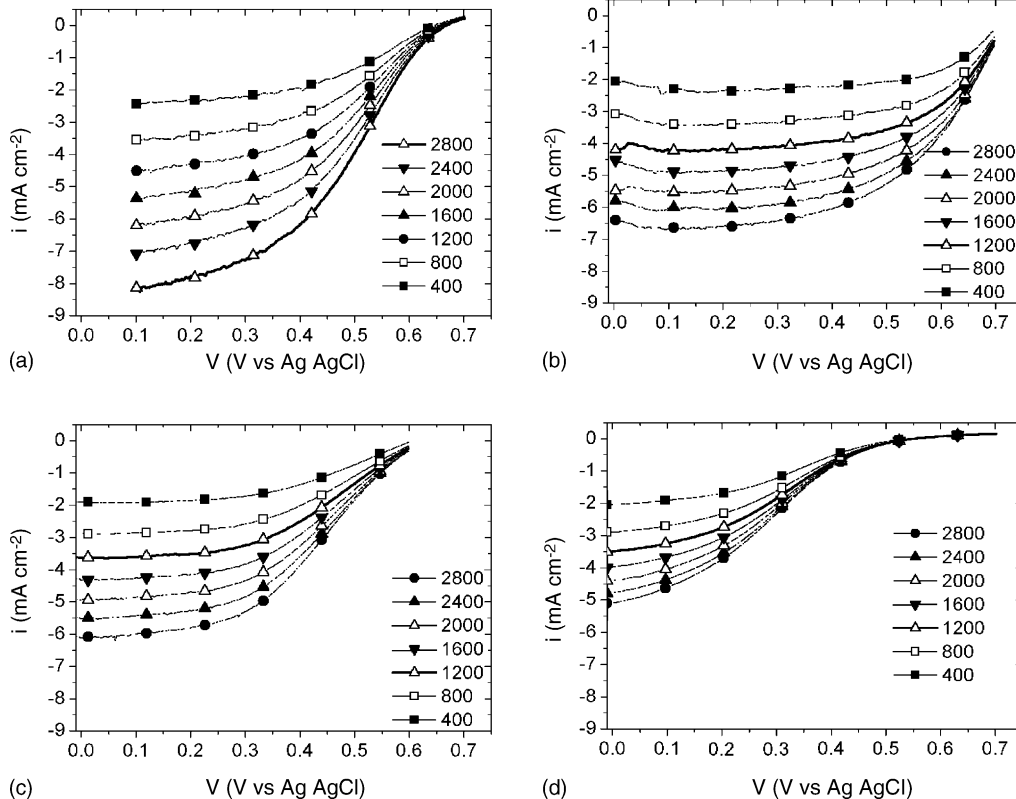$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B\omega^{1/2}} \tag{3}$$



Fig. 7. Rotating disk electrode (rde) voltammograms of four different Pt/C electrodes deposited by impregnation (a and b), spray (c) and electrospray (d), using isopropanol (a) and BEG solvent suspension (b–d). Other conditions: 25 °C, 50 mV s$^{-1}$, 0.5 M HClO$_4$, O$_2$ saturated electrolyte. The current densities are related to the geometric area of the disk. Rotation speeds (rpm) indicated in each figure.
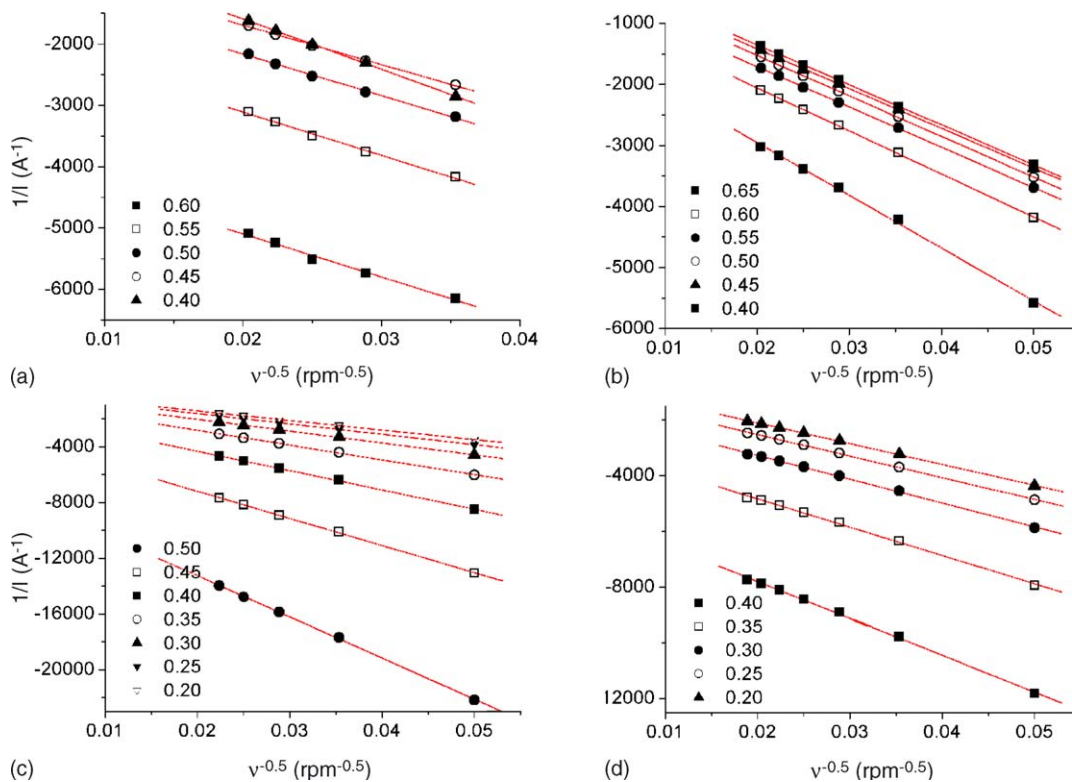
Fig. 8. Plots of $i^{-1}$ vs. $\nu^{-1/2}$ (Koutecky–Levich) corresponding to the voltammograms in Fig. 7. Applied voltages ($V$ vs. Ag/AgCl) indicated in each figure.
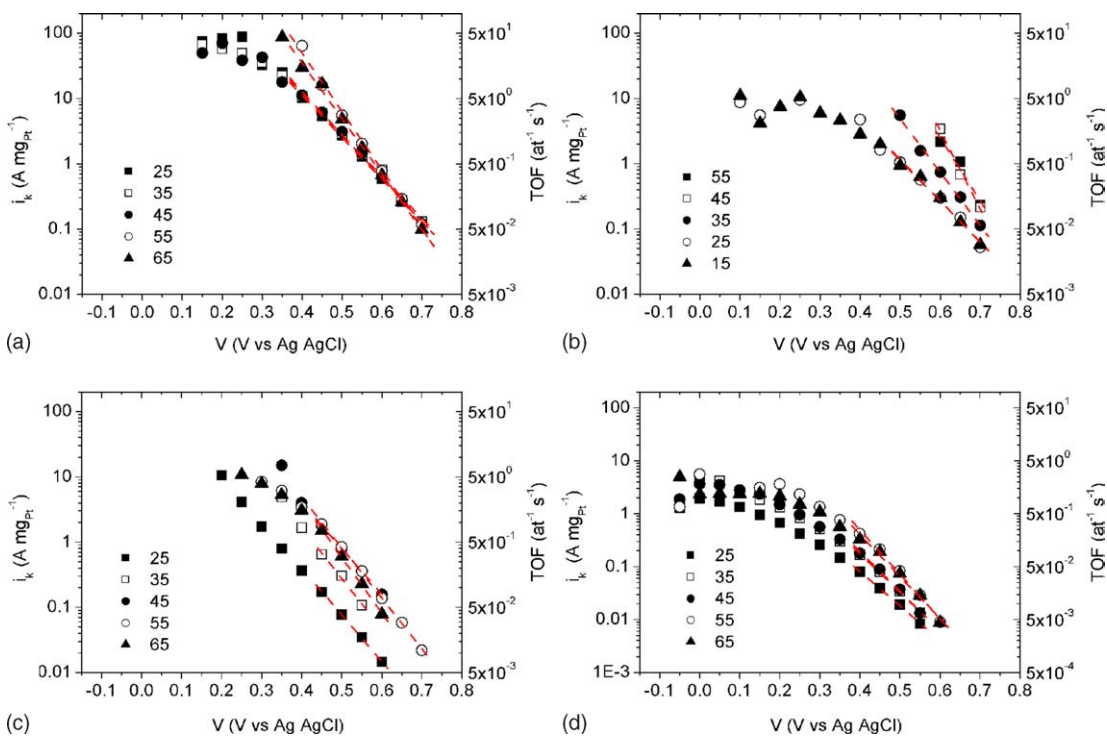


Fig. 9. Plots of the kinetic current ($i_k$) for oxygen reduction obtained from the analysis in Fig. 8 (see also Eq. (2)), in the temperature range 25–65 °C. Temperature (°C) indicated in each figure.

where $i$ is the total current, $i_k$ the kinetic current (both measured over the geometric area of the electrode), $\omega$ the angular rotation speed and $B$ $(= 0.62nFA(C^*_{O_2} - C^S_{O_2})D^{2/3}_{O_2}\nu^{-1/6})$ is now potential dependent through the factor $(C^*_{O_2} - C^S_{O_2})$ for overpotentials in the non-limiting diffusion range [12,15]. A third term could also be introduced in Eq. (2) to account for the resistance of the Nafion film to the transport of species $(1/i_f)$ [6], but the thickness of the film formed is well below the 0.5 μm limit to have an influence.

The rde voltammogram changes significantly from the anodic to the cathodic sweep (Fig. 6). The difference is mainly due to two effects, the double layer charging current, which is constant in this voltage range $(I = C_d v$, where $C_d$ is the capacitance of the double layer [12]), and the formation of Pt–O in anodic scan followed by reduction in the cathodic scan. Both effects superimposed to the oxygen reduction current. In order to study the reduction of oxygen without interference, the anodic sweep is measured until a potential just before the formation of the oxide $(V < 0.7$ V Ag/AgCl), and the double layer charging current is subtracted. Fig. 7 shows results for the reduction of oxygen in acidic medium at 25 °C at different rotation rates, on four Pt/C electrodes deposited by impregnation using isopropanol (Fig. 7a) and BEG suspensions (Fig. 7b), and by spray (Fig. 7c) and electrospray (Fig. 7d) using BEG suspension. In each case, the electrode was submitted to a cyclic voltage between −0.2 and 0.7 V, from which the anodic sweep is taken. The amount of Pt deposited in each electrode is given in Table 3. Plots of $1/i$ versus $\omega^{-1/2}$ are shown in Fig. 8 for the different electrodes. A linear dependence is obtained as predicted by Eq. (2), with decreasing slope at more cathodic potentials until a limiting value corresponding to the diffusion limited regime (see above). From this analysis, the value of the kinetic current $(i_k)$ is obtained from the intercept with the ordinate axis (Eq. (2)). Similar analysis was carried out at different temperatures, from 25 to 65 °C (not shown). The resulting values of $\log(i_k)$ as a function of the applied voltage and for different temperatures are plotted in Fig. 9. The curves show a linear dependence at low overpotential from which Tafel slopes
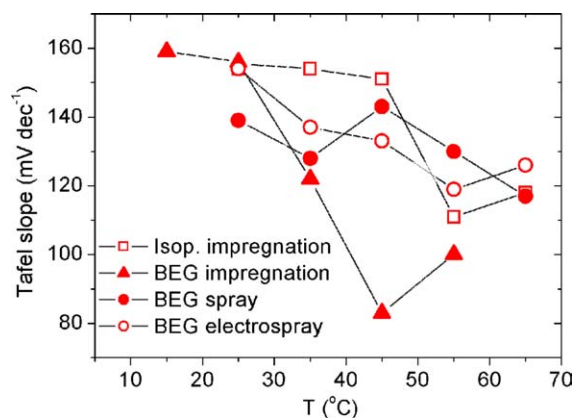


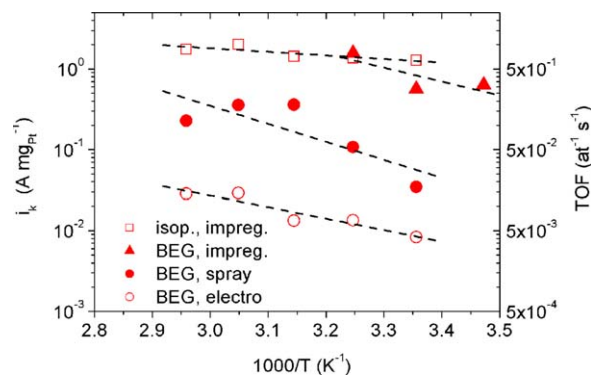Fig. 11. Values of the kinetic current $(i_k)$ as a function of $1000/T$, at $V = 0.55$ V vs. Ag/AgCl applied voltage, for oxygen reduction in HClO$_4$ 0.5 M, for four different Pt/C electrodes.

values can be obtained as a function of temperature (Fig. 10). It is also possible to perform the analysis on $i_k$ as a function of the inverse absolute temperature (Fig. 11). In this case, the apparent activation energies $(E_{act} = (d\log(i_k)/dT^{-1})/2.3R)$ can be obtained from a linear fit. A resume of the re-
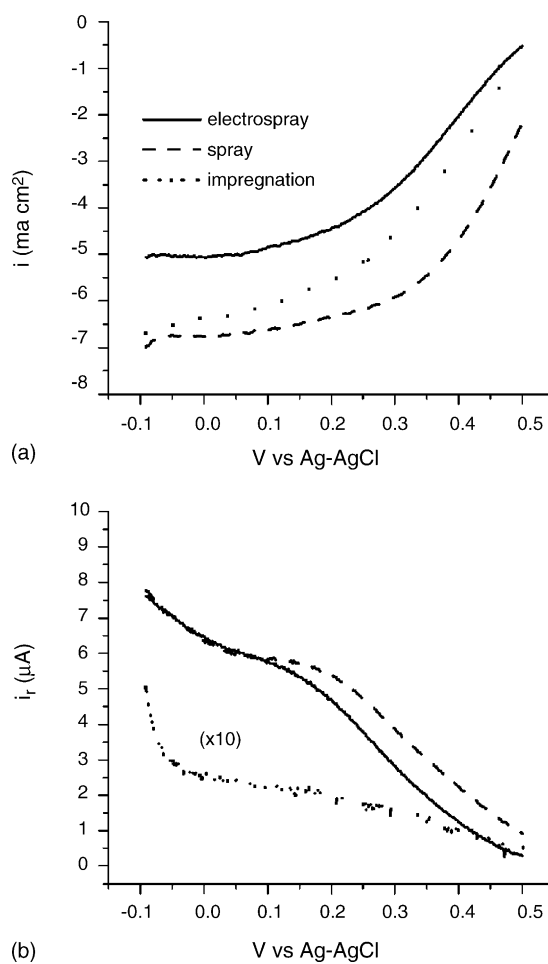




Fig. 12. Disk current (a) and ring current (b) of three Pt/C electrodes deposited by three different methods. Ring voltage $V = 0.8$ V Ag/AgCl. Rotation rate 2400 rpm. Other conditions: 60 °C, 50 mV s$^{-1}$, HClO$_4$ 0.5 M.



Fig. 10. Values of the Tafel slope as a function of temperature for oxygen reduction in HClO$_4$ 0.5 M for four different Pt/C electrodes.

sults obtained from the analysis of $i_k$ values is given in Table 3.

Further information is obtained from experiments where the ring current is also monitored. This current is related with the production of a species on the disk that are able to react electrochemically on the ring [12]. Particularly in oxygen reduction studies, the detection of hydrogen peroxide ($H_2O_2$) is of interest because it is an intermediate which presence denotes that the reaction is not proceeding completely (see reaction (4) below). The presence of hydrogen peroxide is monitored by polarising the ring whose polarised at oxidative voltage (0.8 V versus Ag/AgCl). Fig. 12 shows the disk current and ring current corresponding to three electrodes prepared by different methods.

## 4. Discussion

### 4.1. Pt utilisation

The value of $A_{Pt}$ obtained from hydrogen desorption voltammetry is attributed to the area of Pt in contact with the electrolyte which effectively catalyses the electrochemical reaction. A recent work has shown that this method also measures the Pt surface that is not in contact with the electrolyte but that can be reached by soluble H atoms (or $H^+$) via an uninterrupted Pt path [16]. Although it is not clear if this second contribution is also electrocatalytic, however, it is surely less important for nanoparticulated Pt electrodes where such a path is difficult to be established. Hence, it can be assumed that the area measured by hydrogen desorption corresponds to the Pt surface in direct contact with the electrolyte.

The results in Table 2 show the influence of the composition of the suspension and the deposition method on Pt utilisation. The addition of Nafion® solution in the suspension increases the utilisation of Pt, which is a well-known effect attributed to improved Pt-membrane contact [17]. Also Nafion® is a binder to the Pt disk substrate that avoids the detachment of particles and loss of catalyst. Among the deposition methods, the impregnation gives highest percentage of Pt utilisation. The electrospray and spray techniques give more reproducible results but medium or low Pt utilisation. Results in Table 2 also show that the suspension made with BEG solvent gives higher utilisation, which must be due to some loss of Pt to the electrolyte when using isopropanol.

### 4.2. Oxygen reduction on the Pt/C electrodes

Oxygen reduction on Pt is a reaction very dependent on the state of the electrode surface, in particular on the presence of oxides [21]. From the experimental procedure followed in this work, where anodic sweeps are taken after cycling in potential ranges before oxide formation, it may be assumed that Pt nanoparticles are in the reduced state, without oxide on their surfaces. A first insight into the electrocatalyst efficiency can be obtained from the value of $n$, number of electrons exchanged. The values in Table 3, calculated from $i$ versus

$\omega^{1/2}$ slopes, reflect differences in the oxygen reduction among the different electrodes. This reaction may proceed partially to $H_2O_2$, or completely to $H_2O$:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{4}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{5}$$

The partial reduction (reaction (4)) is a result of unefficient electrocatalysis that gives rise to voltage and current losses in PEMFC. The closer the value of $n$ to 4, the more predominant is the complete reduction (reaction (5)). Results in Table 3 show that this is more the case for the electrodes deposited by impregnation, whereas electrodes deposited by spray and electrospray show lower electrocatalyst activity with increasing predominance of two electrons reduction.

The same conclusion is attained when looking at disk-ring results (Fig. 12). The molar fraction of $H_2O_2$, $X(H_2O_2)$, can be calculated from disk and ring current, $I_d$ and $I_r$, respectively, based on the reaction scheme of Eqs. (4) and (5) [7]:

$$X(H_2O_2)(\%) = 100 \times 2 \frac{I_r/N}{I_d + (I_r/N)} \tag{6}$$

where $N$ (=0.236) is the experimental collection efficiency of the ring. Fig. 13 shows more important production of hydrogen peroxide on the electrodes deposited by spray and electrospray, which is indicative of the two electrons reduction of oxygen. These results are in accordance with the values of $n$ obtained for the different electrodes.

More information about electrocatalysts activity is provided by $i_k$ parameter obtained from an extrapolation of $1/i$ versus $1/\omega^{1/2}$ plot (Fig. 8). This parameter depends only on the charge transfer kinetics, and is directly related with the turnover frequency ($k_{TOF}$), i.e. the number of oxygen molecules reduced per second and Pt atom [18]:

$$i_k = neN_s k_{TOF} \tag{7}$$

where $n$ is the number of electrons involved (we take $n = 4$ which is most probable for small overpotentials [19]), $e$ the electronic charge, and $N_s$ is the number of surface Pt atoms.
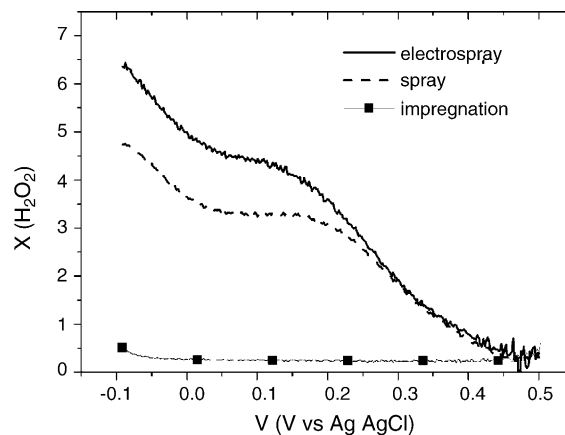


Fig. 13. Molar fraction of $H_2O_2$ produced by three Pt/C electrodes, calculated from Fig. 12.

Fig. 9 shows $k_{TOF}$ values as high as 50 at$^{-1}$ s$^{-1}$ for the impregnation method with isopropanol as suspension solvent, which are values similar to that observed before on Pt/C electrodes [14]. Electrospray gives sensitively lower turnover frequency indicative for less efficient electrocatalysis.

Fig. 10 shows the dependency of Tafel slopes, obtained from the from $i_k$ values, with temperature, for the different solvents and deposition methods. The values are in the range of 140–120 mV dec$^{-1}$, typical for oxide free Pt electrodes at these potentials [20], with some decrease with temperature. Temperature dependent Tafel slopes are not always found for oxygen reduction on Pt, and when observed, have been attributed either to a change in the mechanism affecting the structure of the activated complex [20], or to the effect of organic impurities on the catalyst [3]. For the electrodes deposited by the impregnation method, where the elimination of the solvent takes place after deposition of the suspension, rests of the solvent may be responsible for a higher temperature effect. On the other hand, there are no significant differences in the Tafel slopes for the different electrodes.

The analysis of the rde results shows that the electrode deposited by impregnation has higher electrocatalytic activity for oxygen reduction. This conclusion is based principally on $n$ values and turnover rates (Table 3). The explanation must be found in the different deposition mechanism for the suspension on the carbon covered Pt disk. With the impregnation, putting a drop and leaving to dry overnight, the elimination of the solvent takes place after the deposition and will provide a tortuous porous structure (Fig. 5). On the other hand, with spray and electrospray processes the suspension is divided into micrometric drops that deposit on the substrate. In these cases, the elimination of an important part of the solvent takes place before the deposition, giving rise to a catalytic layer with low porosity. Here, the dispersion of the electrocatlyst is however better controlled and uniform. The electrospray method has added factors that may influence the behaviour of the electrocatalyst, which is transformed in a jet of highly charged micrometric droplets [21], before deposition by electrostatic interaction with the substrate. It is not clear to us how these effects may influence the disposition of Pt particles for electrocatalysis. It is also not discarded that a modification of the experimental parameters that govern spray and electrospray may give rise to changes in the results.

## 5. Conclusions

Pt/C suspensions have been deposited over a carbon-covered Pt disk in order to study the influence of the deposition method on the electrochemical utilisation of Pt and on the electrocatalytic activity for oxygen reduction. Among the different methods, namely impregnation, spray and electrospray, highest Pt utilisation is observed for the electrodes prepared by impregnation. On the other hand, the kinetics analysis made from the rde technique shows that the electrodes prepared by impregnation have also higher electrocatalytic activity for oxygen reduction, as reflected by higher turnover rates and electronic exchange number, and lower hydrogen peroxide production.

As a final conclusion, the estimation made in Section 1 about the still possible reduction of Pt load to 50–5 μg cm$^{-2}$ was done on the basis of turnover rates of 10,000 at$^{-1}$ s$^{-1}$. However, turnovers above 100 at$^{-1}$ s$^{-1}$ are not attained with Pt/C electrodes, as shown by the results given here and by others [14]. On the other hand, the utilisation of Pt seems to be close to the maximum. Therefore, it may be concluded that the reduction of the Pt content resides more in increasing the turnover frequency of Pt sites than improving the disposition of particles.

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