



Polyol synthesis of nanosized Pt/C electrocatalysts assisted by pulse microwave activation

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ABSTRACT

A polyol process assisted by pulse microwave activation was used to prepare efficient Pt/C electrocatalysts for PEMFC applications with reducing cost. Catalysts from pulsed microwave method were compared with a catalyst issued from a classical method, in terms of active surface area, platinum loading and activity towards the oxygen reduction reaction. A design of experiments (DOE derived from the Taguchi method) has been implemented to optimize experimental parameters only related to pulse microwave activation, the intrinsic synthesis parameters (concentration of platinum salt, platinum/carbon weight ratio and pH) being kept constant. Controlled parameters were duration of microwave pulse, maximum temperature and total duration of the synthesis. Considered responses were catalyst active surface area and the Pt/C loading. An optimized configuration of synthesis parameter was proposed. The confirmation experiment revealed a trend in agreement with that expected. Three catalysts (two from pulsed microwave synthesis method and one prepared by the classical method) were characterized by transmission electron microscopy, cyclic voltammetry and CO stripping. Catalysts from pulsed microwave method display higher characteristics than the one prepared by the classical method. The Pt/C catalyst from the confirmation experiment displays the highest catalytic activity toward oxygen reduction reaction.

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1. Introduction

Platinum particles supported on carbon are still the most used electrocatalysts in Proton Exchange Membrane Fuel Cell (PEMFC) electrodes [1,2]. Beyond the platinum availability and price, the preparation method of FC components is also an important issue for large-scale development of such technology, so what numerous preparation methods of Pt/C based catalysts are developed [3,4], notably for lowering cost and preparation time. Polyol synthesis method is very interesting for this purpose because it uses inexpensive solvent (ethylene glycol) and it does not need the presence of surfactant to achieve well dispersed platinum particles of small mean sizes, between 2 and 4 nanometers [5–15]. However, this synthesis method requires activation in order to allow metallic ion reduction by ethylene glycol. Generally, the reduction reaction is activated by temperature: the synthesis is carried out by heating the reaction mixture at reflux (ca. 200 °C with ethylene glycol as solvent) for approximately 2 h [5–9] or by continuous irradiation of microwaves [10–15].

Due to high radiation absorption of microwave by ethylene glycol, this second preparation method leads to the increase of the reaction mixture temperature up to that of reflux. Therefore, these activation methods do not allow controlling and separating the nucleation and growth steps. It is, however, well known that these steps influence the structure and the morphology of platinum nanoparticles [10,11]. Besides, some works [16–18] have been carried out by activating the polyol synthesis with pulsed microwaves.

The aim of the present work consists in the synthesis of Pt/C catalysts by a polyol method activated by microwave pulses. The microwave power, the pulse frequency, the activation time and the temperature reached by the reaction medium are controlled. The control of such experimental parameters is expected to further allow really controlling the different steps of platinum nanoparticles formation on a carbon support (Vulcan XC72-R). In previous works, the intrinsic synthesis parameters of Pt based catalysts (solvent, pH, concentration of metal salt and platinum loading on carbon) were optimized in terms of measured active surface area and electrocatalytic activity towards the oxygen reduction reaction (ORR) [6,19]. Here, these synthesis parameters remain unchanged and only the effects of parameters related to the microwave activation are studied. For this purpose, a Taguchi method is used to

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establish a design of experiments (DOE) with a minimum number of experiments [20]. The considered responses are the metal loading in Pt/C as determined by thermo gravimetric analysis (TGA) and the active surface area as determined by cyclic voltammetry (CV) [21,22]. Changes in the structure and morphology of the catalyst are observed by TEM. Comparisons with a catalyst prepared by the classical polyol synthesis method (heating at reflux) are made. At last, the catalytic activities of the catalysts toward the ORR and the electro-oxidation of a preadsorbed CO saturating layer (CO stripping measurement) are evaluated and compared.

2. Experimental

2.1. Synthesis of the Pt/C catalysts

For the classical preparation method, 100 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.9% purity, Alfa Aesar) are dissolved in 100 mL of ethylene glycol (puriss. p.a., $\geq 99.5\%$ Fluka). Then, pH of the solution is adjusted to 11 by adding dropwise a solution of 1 M NaOH in ethylene glycol. Carbon Vulcan XC72-R thermally treated for 4 h at 400 °C under Nitrogen (U Quality from “Air Liquide”) is then added to the solution (56.5 mg in order to obtain a nominal Pt loading of 40 wt% on carbon) and the mixture was ultrasonically homogenized for 5 min. The mixture was then deaerated by bubbling N_2 (Nitrogen U Quality from “Air Liquide”) for 15 min and heated at reflux (197.3 °C) for 2 h maintaining nitrogen bubbling.

For the microwave-assisted synthesis, the reaction mixture is prepared in the same way as above. The reactor equipped with a cooler is put inside a MARS oven from CEM Corporation. Such set up activates the synthesis reaction by microwave at atmospheric pressure, without evaporation of ethylene glycol and/or water due to temperature increase during microwave irradiation.

After preparation, catalytic powders are washed with acetone, abundantly rinsed with ultra pure water (MilliQ Millipore, 18 M Ω cm), and filtrated. Finally, thermal treatment of Pt/C catalysts is performed at 200 °C for 1 h under air to remove traces of ethylene glycol.

2.2. Thermogravimetric analyses (TGA)

Thermogravimetric measurements were carried out with a TA Instrument SDT Q600 apparatus. A few milligrams of catalytic powder is put in an alumina crucible and heated under air from 25 °C to 800 °C. Different temperature slopes were used according to the temperature range: 10 °C min⁻¹ from 25 °C to 400 °C, then 2 °C min⁻¹ from 400 °C to 600 °C and 10 °C min⁻¹ from 600 °C to 800 °C.

2.3. Transmission electron microscopy (TEM) measurements

Transmission electron microscopy (TEM) measurements were carried out with a JEOL JEM 2010 (HR) with a resolution of 0.35 nm, in order to verify the morphology and the structure of the catalytic powders. Moreover, TEM observations allow the direct observation of the particle dissemination on the carbon support. The determination of the nanoparticle size distribution was performed with the ImageJ free software and estimated from the measurement of 500 isolated nanoparticles.

2.4. Electrochemical measurements

All electrochemical measurements are carried out in a standard three-electrode electrochemical cell at room temperature with a reversible hydrogen electrode (RHE) as the reference electrode and

a glassy carbon plate as the counter electrode. The support electrolyte is a 0.5 M H_2SO_4 (Suprapur, Merck) solution in ultra pure water.

The working electrode is prepared by deposition of a catalytic ink on a 0.071 cm² Glassy carbon disk according to a method proposed by Gloagen et al. [23]. Catalytic ink is composed of 25 mg of catalytic powder dissolved into 2.5 mL of ultra pure water and 0.5 mL of Nafion[®] solution (5 wt% from Aldrich). After 30 min homogenization in an ultrasonic bath, a volume of 3 μL of catalytic ink is deposited from a syringe onto a fresh polished glassy carbon substrate, yielding 25 μg of catalytic powder. The solvent is then evaporated in a stream of ultra pure nitrogen at room temperature.

The active surface area (ASA) of Pt/C catalysts is determined from cyclic voltammograms (CV) by integrating the charge in the hydrogen desorption region corrected from the double layer capacity contribution [21,22]. For each catalyst, the average active surface area is determined by recording the CV on four different ink depositions. Measurements are carried out in a N_2 -saturated electrolyte at a scan rate of 50 mV s⁻¹ after 10 voltammetric cycles are performed between 0.05 V and 1.25 V vs. RHE in order to clean the platinum surface from organics coming from synthesis and to obtain quasi-constant voltammograms [22,24]. In order to obtain information on structure, morphology and activity of nanoparticles [25–30], CO surface saturation of platinum catalysts is performed at 0.1 V vs. RHE for 5 min. Before CO stripping measurements recorded at 20 mV s⁻¹ from 0 to 1.25 V, CO is removed from the electrolyte bulk by N_2 bubbling for 15 min, under potential control at 0.1 V. Cyclic voltammograms and CO stripping measurements are carried out using a Model 362 Scanning Potentiostat from Princeton Applied Research.

The oxygen reduction reaction is carried out to access kinetic parameters (Tafel slope, limiting current densities and kinetic current density) from Koutecky–Levich equation [21,22,31]. This reaction is studied using a rotating disc electrode (RDE) with different electrode rotation rates: 400, 900, 1600, 2500 revolution per minute (rpm). In this case, experiments are performed at a scan rate of 1 mV s⁻¹ in oxygen saturated electrolyte with a Voltalab VM4 PGZ100 from Radiometer analytical as potentiostat.

3. Results and discussion

3.1. Design of experiments according to Taguchi method

A full factorial design of experiments (DOE) allows the determination of the influence of several parameters on the studied process from a given number of experiments. The number of experiments necessary is dependent on the number of considered parameters and on the number of levels considered for each parameter (different values given to a parameter). Taguchi method allows minimizing the number of experiments while keeping a good accuracy in the results and in their interpretation [20].

The intrinsic parameters (pH, metal salt concentration, nature of solvent and metal loading on carbon) for the preparation of platinum nanoparticles dispersed on carbon substrate by a polyol method, having already been studied and optimized in previous works [6,19], only parameters concerning microwave activation are considered in this work. A solution of H_2PtCl_6 1.0 g L⁻¹ in ethylene glycol adjusted to pH 11 by dropwise addition of 1 M NaOH solution in ethylene glycol is the basic mixture used in the present work. Carbon Vulcan XC72-R powder is added in order to reach a nominal platinum loading of 40 wt% on carbon.

Taguchi method is a convenient mathematical and statistical method for empirical studies [20]. It has already evidenced as a powerful tool for optimizing synthesis parameter for platinum

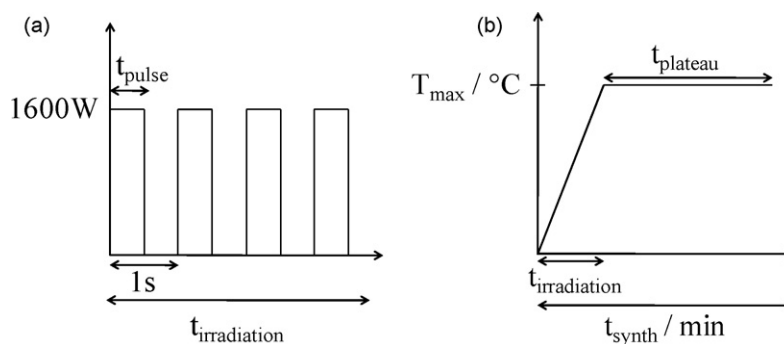


Fig. 1. Schemas representing (a) the microwave pulse sequence (t_{pulse} and $t_{\text{irradiation}}$) and (b) the temperature change as a function of time in course of the synthesis procedure by pulsed microwaves.

Table 1
Controlled microwave parameter levels in the design of experiments.

Factors	Level 1	Level 2	Level 3
T_{max} (°C)	80	100	120
t_{pulse}/s	0.1	0.3	0.5
$t_{\text{synth}}/\text{min}$	20	40	60

based catalysts synthesis [6,19]. In the present case, a simple model based on 3 parameters with 3 levels each is considered. The considered parameters, presented in Fig. 1, are the following: parameter 1 (t_{pulse}) is the duration of microwave pulse at 1600 W (% of the oven internal period), parameter 2 is the maximum temperature reached during the synthesis (T_{max}) and parameter 3 is the total duration of the synthesis (t_{synth}). Table 1 indicates the values assigned for each parameter at each level. In such configuration, the number of experiments for a full factorial DOE is $3^3 = 27$ experiments. However, if we are only looking for the optimization of the system, i.e. the best configuration of parameter levels, and not for its modelization, then interactions between parameters can be neglected, and the number of experiments in the DOE can be decreased down to 9. The L_9 (3^3) table of Taguchi composed of 9 lines (corresponding to the 9 experiments) and 3 columns (giving the level of each parameter for each experiment) can be used. The hypothesis which consisted in neglecting interactions between the three studied parameters will be checked with complementary experiments to confirm the model.

This DOE requires then the preparation of 9 Pt/C catalysts and the determination of the values of the responses (results). The plat-

inum loading (in Pt wt%) and the active surface area (in $\text{m}^2 \text{g}_{\text{catalyst}}^{-1}$) were chosen as relevant parameters to evaluate the catalyst synthesis procedure. The Pt loading gives information on the percentage of platinum salt reduced during the synthesis process and the active surface area is an important parameter for evaluating the catalytic performance of nanoscaled catalysts dispersed on a substrate. Active surface area is determined from cyclic voltammograms using Eq. (1):

$$ASA = \frac{(1/\nu) \int i(E)dE}{Q_{\text{HML}} \times m_{\text{catalyst}}} \quad (1)$$

where ν is the linear potential scan rate (Vs^{-1}), i is the current (A), E is the electrode potential (V), m_{catalyst} is the mass of catalyst (platinum and carbon support) deposited on the electrode (g) and Q_{HML} is the charge involved during the adsorption of a monolayer of atomic hydrogen on a polyoriented platinum surface (2.10 C m^{-2}) [21,22,32].

Table 2 gives the configuration of parameters for each synthesis and the response values measured on each prepared catalyst. The results recorded from a confirmation experiment (synthesis realized with a parameter configuration out of DOE) and from a catalyst prepared by the classical method are also reported. From the measurements of ASA and platinum loading, the effect of each parameter can be determined according to the following equation:

$$E_{A_i} = \frac{\sum_{i=1}^3 R_{A_i}}{3} - \bar{R} \quad (2)$$

where E_{A_i} is the effect of parameter A at the level i , R_{A_i} is the measured response for parameter A at the level i and \bar{R} is the average

Table 2
Configurations of parameter levels for the realization of the experiments within the DOE, values of the experimental active surface area (ASA) and platinum loading for experiments within the DOE, for the confirmation experiment and for the classical method.

Experiment	T_{max} (°C)	t_{pulse} (s)	t_{synth} (min)	ASA ($\text{m}^2 \text{g}_{\text{catalyst}}^{-1}$)	ASA standard deviation ($\text{m}^2 \text{g}_{\text{catalyst}}^{-1}$)	Pt loading (wt%)
1	3	1	1	24	1	33
2	3	2	2	24	1	38
3	3	3	3	23	2	39
4	1	1	2	28	1	38
5	1	2	3	23	2	36
6	1	3	1	22	1	28
7	2	1	3	26	1	36
8	2	2	1	25	2	33
9	2	3	2	25	1	37
Average:				24.444		35.333
Confirmation result						
C1	2	1	2	26	1	38
Catalyst prepared by classical heating method						
Classical	Heating at reflux 2 h at 200 °C			23	2	36

Table 3

Values of the effects calculated from the results obtained in the design of experiments and Eq. (2).

	$T_{\max} = 80\text{ }^{\circ}\text{C}$	$T_{\max} = 100\text{ }^{\circ}\text{C}$	$T_{\max} = 120\text{ }^{\circ}\text{C}$
ASA	-0.11	0.89	-0.78
Pt loading	-133	0.00	1.33
	$t_{\text{pulse}} = 0.1\text{ s}$	$t_{\text{pulse}} = 0.3\text{ s}$	$t_{\text{pulse}} = 0.5\text{ s}$
ASA	1.55	-0.44	-1.11
Pt loading	0.33	0.33	-0.66
	$t_{\text{synth}} = 20\text{ min}$	$t_{\text{synth}} = 40\text{ min}$	$t_{\text{synth}} = 60\text{ min}$
ASA	-0.78	1.22	-0.44
Pt loading	-4.00	2.33	1.66

value of the responses. Table 3 reports the values of the effects calculated from Table 2 and Eq. (2).

Considering the measured ASA, the best configuration of parameters is synthesis temperature (T_{\max}) at the level 2 ($100\text{ }^{\circ}\text{C}$), pulse duration (t_{pulse}) at level 1 (0.1 s) and total synthesis duration (t_{synth}) at level 2 (40 min). Considering the platinum loading, the best configuration of parameters is T_{\max} at level 3 ($120\text{ }^{\circ}\text{C}$), t_{pulse} at level 1 (0.1 s) and t_{synth} at level 2 (40 min). The double optimization leads to the following configuration of parameter: T_{\max} at the level 2 ($100\text{ }^{\circ}\text{C}$), t_{pulse} at level 1 (0.1 s) and t_{synth} at level 2 (40 min). Such configuration of parameters is out of the DOE. The calculation of the responses with such configuration of parameters leads to a value of $28\text{ m}^2\text{ g}_{\text{catalyst}}^{-1}$ for ASA and 38 wt% for the platinum loading, whereas the experimental values corresponding to the confirmation experiment C1 led to $26\text{ m}^2\text{ g}_{\text{catalyst}}^{-1}$ for ASA and 38 wt% for the platinum loading. The experimental values are in agreement with the theoretical ones, notably that concerning the platinum loading. The measured ASA is lower than the calculated one. This seems to indicate that interactions exist between parameters for this response, which have not been taken into account. However, the value is higher than the average value of ASA, which indicates that the trend is confirmed. But, the catalyst from synthesis 4 ($T_{\max} = 80\text{ }^{\circ}\text{C}$, $t_{\text{pulse}} = 0.1\text{ s}$ and $t_{\text{synth}} = 40\text{ min}$) presents the highest active surface area and the highest loading. These results highlight the effect of microwaves [33,34] on the proposed test parameters. Indeed, a temperature of $80\text{ }^{\circ}\text{C}$ is normally not high enough to activate metallic salt reduction by ethylene glycol [33,34] and it seems that this reduction reaction is then activated by microwave irradiation.

Results from the design of experiments clearly show that a too short duration of the synthesis (shorter than 40 min for our set of parameters) leads to lower platinum loadings than the nominal one (40 wt%). The reduction of all metallic ions is not achieved or the anchorage of platinum particles on carbon substrate is not totally realized. Moreover, it could be observed that a low duration of microwave pulses is favorable to obtain a high active surface area. Both these effects can be due to the following reasons. The shorter pulse duration (0.1 s) involves a longer time under controlled microwave irradiation before reaching the maximum temperature setpoint; the microwave activation may be more efficient in the whole reduction process than the thermal activation. This could limit the nanoparticle agglomeration and/or grain growth process forming larger particles, and further may lead to higher active surface area of Pt/C catalysts [33,34]. A higher maximum temperature setpoint for the synthesis leads indeed to catalysts with low active surface area. A high synthesis temperature may promote the agglomeration of nanoparticles or the growth of larger particles.

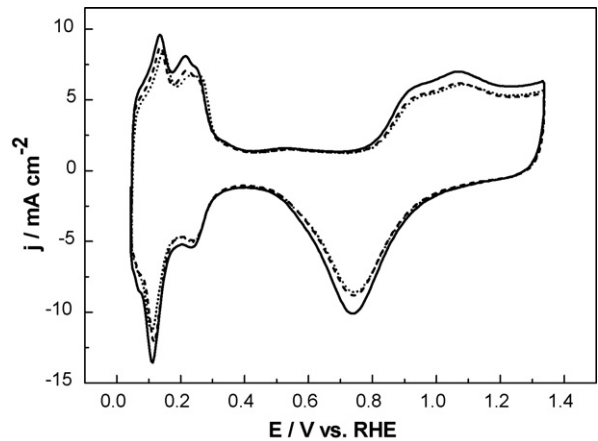


Fig. 2. Cyclic voltammograms of Pt/C issued from experiment 4 (solid line), Pt/C issued from experiment C1 (dashed lines) and Pt/C issued from classical method (dotted lines) recorded at 50 mV s^{-1} , $20\text{ }^{\circ}\text{C}$, in a N_2 -saturated $0.5\text{ M H}_2\text{SO}_4$ electrolyte.

3.2. TEM and electrochemical characterizations of Pt/C catalysts

Due to their high performance, catalysts from confirmation synthesis C1 and from synthesis 4 of the DOE were compared with that prepared by the classical polyol synthesis at reflux.

Catalysts from experiment 4, experiment C1 and classical method are characterized by transmission electron microscopy. Fig. 2 shows the TEM images and the related size distributions for each catalyst. The mean particle size is calculated using Eq. (3) considering only isolated particles:

$$\bar{d} = \frac{\sum_i n_i d_i}{n} \quad (3)$$

The mean particle size is found to be ca. 2.5 nm for both catalysts prepared by pulse of microwaves and ca. 3.0 nm for catalyst prepared by the classical method.

Both catalysts prepared using microwave activation display higher values of ASA ($\text{m}^2\text{ g}_{\text{catalyst}}^{-1}$) and platinum loading than those determined for the catalyst prepared by the classical method. The voltammograms of the catalysts, presented in Fig. 2, are used to determine the real surface areas RSA ($\text{m}^2\text{ g}_{\text{Pt}}^{-1}$) from the charge involved during the hydrogen desorption. From the value of the real surface area, the platinum particle size can be evaluated, assuming that particles are spherical, by using Eq. (4):

$$\text{RSA} = \frac{4\pi(d/2)^2}{4/3\pi(d/2)^3 \cdot \rho_{\text{Pt}}} \quad (4)$$

where d is the mean diameter of spherical particles and ρ_{Pt} is the density of platinum (21.45 g cm^{-3}). RSAs are found to be ca. $74\text{ m}^2\text{ g}_{\text{Pt}}^{-1}$, ca. $68\text{ m}^2\text{ g}_{\text{Pt}}^{-1}$ and ca. $64\text{ m}^2\text{ g}_{\text{Pt}}^{-1}$, for catalysts from experiment 4 of the DOE, from confirmation experiment C1, and from classical method, respectively.

From this equation, the mean particle diameter is found to be close to 3.7 nm for catalyst prepared at the experiment 4, 4.2 nm for catalyst prepared at the experiment C1 and 4.4 nm for catalyst prepared by the classical method.

The mean sizes determined from TEM are much lower than those obtained from the determination of real surface areas for the three catalysts. This discrepancy can be explained by a more important presence of agglomerates as observed on TEM photographs (Fig. 3), which could lead to decrease the real surface area and further to increase the value of calculated mean particle diameters. The ratio between the particle size determined from electrochemical measurement and that determined from TEM pictures (Fig. 3) is constant for the catalyst from experiment 4 of the DOE and from the

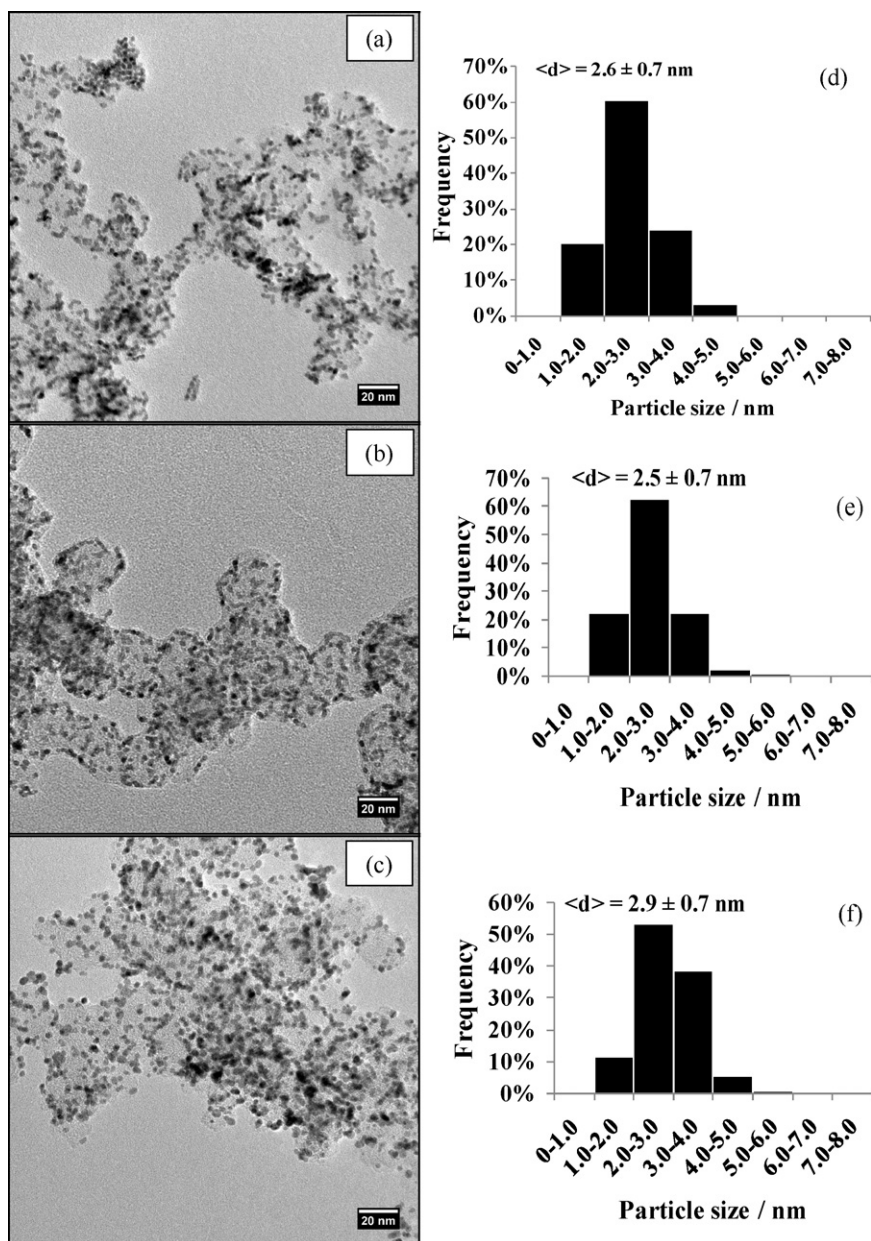


Fig. 3. TEM Photographs of Pt/C catalysts synthesized by polyol process and related histograms of the size distribution: (a and d) from experiment 4, (b and e) from experiment C1 and (c and f) from classical method.

classical one. It is higher for catalyst from the confirmation experiment C1, which can be due to higher agglomeration level. This could also explain the lower experimental ASA obtained with this catalyst than that expected in Section 3.1.

CO stripping measurements were also carried out (Fig. 4) according to the method described in experimental Section 2.4. After CO adsorption on the catalyst surface from a CO-saturated electrolyte at 0.1 V for 5 min, CO was removed from the solution by nitrogen bubbling and voltammetric cycles were recorded. For all catalysts, the complete disappearance of the current peaks in the hydrogen desorption region (from 0.05 V to 0.4 V) of the first voltammetric cycle shows that the platinum surface is completely blocked by the presence of adsorbed CO. Then, the oxidation of adsorbed CO in CO_2 is responsible for the positive current peaks in the potential range from 0.65 V to 1.0 V. In the negative going potential scan, current peaks in the hydrogen adsorption region

appeared and the second cyclic voltammogram is typical of a clean Pt/C catalyst, which indicates that adsorbed CO was totally removed from the platinum surface during the first voltammetric cycle. Since the work of Gilman [35], the CO electro-oxidation is described by a Langmuir–Hinschelwood mechanism (LH), according to Eqs. (5) and (6):



No significant differences in current peak intensity and shape are observable; all catalysts lead to an oxidation peak centered at ca. 0.84 V and a shoulder at ca. 0.75 V. The integration of the CO oxidation current (assuming that the desorption of a monolayer of adsorbed CO on a polyoriented platinum surface involves 4.20 C m^{-2} [21,36]) leads to very close value of real surface area,

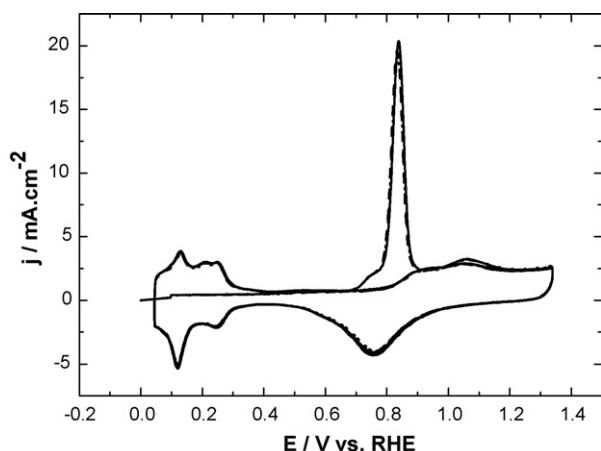


Fig. 4. CO stripping voltammograms of Pt/C from experiment C1 (solid line), Pt/C from experiment 4 (dashed lines) and Pt/C from classical method (dotted lines) recorded at 20 mV s^{-1} , 20°C , in a N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ electrolyte.

which is due to the difficulty to perform the baseline correction of the capacitive current and of the platinum surface oxidation for supported Pt/C catalyst. The simple subtraction of the current recorded in the second cycle from the current recorded in course of CO saturating layer oxidation does not likely lead to an accurate faradic charge extraction of the CO oxidation process due to the system complexity: carbon support generating an important double layer capacitive contribution, presence of Nafion in the active layer, etc. Beyond the peak intensity, the invariance of the shape is more interesting. According to Maillard et al. [26] and López-Cudero et al. [29], the increase of agglomerate density in a Pt/C catalyst should lead to the appearance and increase of a CO oxida-

tion peak at lower potentials than that observed in Fig. 4. However, in our case, no increase of the peak located at 0.75 V is observed on the CO stripping curves, although TEM and cyclic voltammetry measurements seems to indicate higher levels of platinum particle aggregation for catalyst from the C1 confirmation experiment.

3.3. Oxygen reduction reaction in acid medium

The Koutecky–Levich model is used to access kinetic parameters of the ORR on the different Pt/C catalysts in acid medium [21,22,31]. Fig. 5a displays the polarization curves at different rotating rates of the disk electrode obtained with the catalyst from experiment C1, as an example. Considering the reaction mechanism of oxygen reduction via the formation of $[\text{H}_2\text{O}_2]_{\text{ads}}$ as proposed by Tarasevich et al. [37], Koutecky–Levich plots can be drawn from these polarization curves, as it is shown in Fig. 5b, using Eq. (7) [21]:

$$\frac{1}{j} = \frac{1}{j_0(\theta/\theta_e)e^{\eta/b}} + \frac{1}{j_1^{\text{ads}}} + \frac{1}{j_1^{\text{film}}} + \frac{1}{j_1^{\text{diff}}} \quad (7)$$

where j_1^{film} and j_1^{ads} correspond to the diffusion limiting current density in the catalytic film and to the adsorption limiting current density of dioxygen, respectively; $\eta = E - E_{\text{eq}}$ is the overpotential; b is the Tafel slope; j_0 is the exchange current density; θ and θ_e are the coverage of platinum surface by species coming from oxygen adsorption at potential E and at the equilibrium potential E_{eq} (1.185 V vs. RHE), respectively, and j_1^{diff} is the diffusion limiting current density which can be calculated from the Levich law:

$$j_1^{\text{diff}} = 0.2nF(D_{\text{O}_2})^{2/3}\nu^{-1/6}c_{\text{O}_2}\sqrt{\Omega} \quad (8)$$

with n the number of electron exchanged per oxygen molecule, F the Faraday constant ($96,500 \text{ C mol}^{-1}$), D_{O_2} the coefficient diffusion of oxygen molecular in $0.5 \text{ M H}_2\text{SO}_4$ ($2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν the kinematic viscosity of the electrolyte ($1.07 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), c_{O_2} the

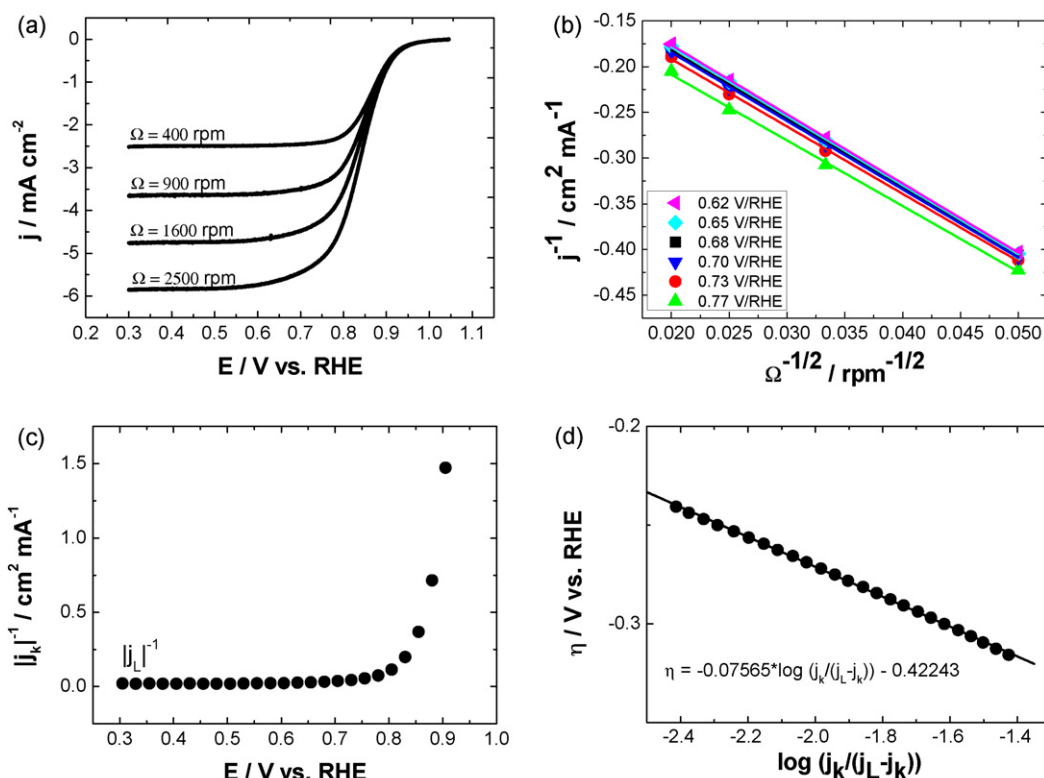


Fig. 5. (a) $j(E)$ polarization curves at different electrode rotation rates (Ω) recorded on Pt/C catalyst prepared at the experiment C1 in a O_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ electrolyte ($T=20^\circ\text{C}$, scan rate = 1 mV s^{-1}); (b) Koutecky–Levich plots determined from (a) at different potentials; (c) plot of $1/j_k$ as a function of the electrode potential; (d) related Tafel plot.

Table 4
Kinetic parameters of oxygen reduction reaction calculated from mathematical treatment of the Koutecky–Levich straight lines for Pt/C catalysts in H₂SO₄ 0.5 M medium at 1 mV s⁻¹.

	Experiment C1	Experiment 4	Experiment classical method
j_L (A cm ⁻²)	-51×10^{-3}	-62×10^{-3}	-62×10^{-3}
j_0 (A cm ⁻²)	1.3×10^{-7}	4.6×10^{-8}	1.4×10^{-8}
b (V decade ⁻¹)	0.076	0.070	0.070

bulk concentration of oxygen in a saturated electrolytic solution (1.03×10^{-3} mol L⁻¹) [31,38]. The coefficient 0.2 is used when the working electrode rotation rate Ω is expressed in revolutions per minute (rpm) [39–41].

The film diffusion limiting current density and the adsorption limiting current density are both independent on disk electrode rotation rates and applied potential (E), thus it is impossible to dissociate them. Eq. (7) can be written:

$$\frac{1}{j} = \frac{1}{j_0(\theta/\theta_e)e^{\eta/b}} + \frac{1}{j_i} + \frac{1}{j_i^{\text{diff}}} \quad \text{with} \quad \frac{1}{j_i} = \frac{1}{j_i^{\text{ads}}} + \frac{1}{j_i^{\text{film}}} \quad (9)$$

The potential scan rate is set at 1 mV s⁻¹ in order to consider the system under stationary state. Assuming that in the considered potential range the adsorption process of oxygen is more rapid than the charge transfer step, then $\theta \approx \theta_e$ for the whole electrode potential range [21]. The kinetic current density j_k can be written:

$$\frac{1}{j_k} = \frac{1}{j_0 e^{\eta/b}} + \frac{1}{j_i} \quad (10)$$

From Eq. (9) and Eq. (10), it is possible to draw $1/j_k$ as a function of the potential E to obtain $1/j_i$ because at high overpotentials $1/j_k$ tends toward $1/j_i$, as observed on Fig. 5c. Then, Eq. (10) can be transformed as follows:

$$\eta = b \left(\ln \frac{j_k}{j_i - j_k} + \ln \frac{j_i}{j_0} \right) \quad (11)$$

to access the Tafel slope b and the exchange current density j_0 represented in Fig. 5d. The set of curves presented on Fig. 5 corresponds to results obtained while carrying out the ORR on catalyst prepared at the experiment C1. The same Koutecky–Levich model was applied to catalysts prepared at experiment 4 and by the classical method to access their ORR kinetic parameters. Results are presented in Table 4.

Catalyst C1 is the more active one for the ORR with an exchange current density of 1.3×10^{-7} A cm⁻² and a Tafel slope of 75.7 mV decade⁻¹. Such a value of j_0 is consistent with that obtained by different authors with Pt/C catalysts prepared by classical polyol method (2.1×10^{-7} A cm⁻² at 70 °C [42] or by a microwave-assisted polyol process (1.25×10^{-7} A cm⁻² at 50 °C for a Pt/Vulcan catalyst [43]). Moreover, both Pt/C catalysts prepared by pulse microwaves are more efficient toward oxygen reduction reaction than Pt/C catalyst prepared by the classical method. This is certainly due to the higher values of ASA, platinum loading and also higher RSA of catalysts synthesized using pulsed microwave method compared to those calculated for the catalyst from classical synthesis procedure.

4. Conclusion

Pt/C catalysts prepared by polyol synthesis with pulsed microwave activation display higher active surface areas and better kinetic parameters toward oxygen reduction reaction than a Pt/C catalyst prepared by classical polyol synthesis based on heating at reflux. Catalysts synthesized using pulsed microwaves have mean particle size of ca. 2.5 nm against ca. 3.0 nm for that prepared by the classical method. TEM images indicate that such catalysts have non-negligible level of particle agglomeration. However, agglomeration process seems to be decreased by favoring the microwave activation instead of the thermal one for the metal salt reduction reaction. This work shows actually the importance of microwave activation on optimizing the active surface area of catalysts. Moreover, this method for the preparation of Pt/C allows for the decrease of the synthesis cost and time: it is possible to prepare efficient Pt/C catalyst with high loadings at a temperature as low as of 80 °C for 40 min instead of working at 200 °C for 2 h in the classical polyol method. Such synthesis method could be used for the preparation of bimetallic catalysts with the aim of decreasing the platinum amount and further the preparation cost of PEMFC catalysts.

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