



Optimization of a surfactant free polyol method for the synthesis of platinum–cobalt electrocatalysts using Taguchi design of experiments

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ABSTRACT

A design of experiments (derived from the Taguchi method) was implemented to optimize experimental conditions of a surfactant free polyol method for the synthesis of PtCo electrocatalysts. Considered responses were the active surface area and the catalytic activity toward oxygen reduction reaction. Metallic salt concentration, pH, temperature ramp, addition order of reactants and particle cleaning step were chosen as main parameters according to considerations coming from literature and previous experiments. Matrix models describing the behaviour of the synthesis system was elaborated taking into account the effects of each considered parameter and their interactions. From this model, an optimized PtCo/C catalyst, in terms of active surface area and activity towards the oxygen reduction reaction, was synthesized. Both the measured values of the active surface area and the electrocatalytic activity are in very good agreement with the calculated ones from the matrix model. Furthermore, actions of parameters and interactions between parameters can be better understood using this method.

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1. Introduction

Electrocatalysts for proton exchange membrane fuel cells (PEMFCs) are based on nanosized Pt particles dispersed on carbon black [1]. Due to its cost and availability, alloying platinum with foreign non-noble transition metals is field extensively studied for the preparation of Pt based catalysts; this allows not only decreasing the amount of platinum, but also increasing the catalytic activity [2–5] and making catalysts more tolerant to the presence of poisons [6–8]. Platinum cobalt materials are promising catalysts for the oxygen reduction reaction (orr) [9,10]. Nevertheless, most of researches on these materials are concerning synthesis procedures involving high temperature treatment step (more than 400 °C) [11–13] in order to obtain perfect alloys. Such a treatment may provoke a migration of cobalt inside the particles [12] and the sintering of metal particles; creation of agglomerates may cause the decrease of the active surface area. Moreover, a perfect control of size and dispersion of the catalyst on the carbon conductive support (generally used in PEMFC electrodes) is necessary for the study of the electrochemical activity of such nanoparticles.

The polyol method is very promising for the preparation of PtCo nanoparticles. This method, well described by Fievet et al. [14], allows obtaining metal nanoparticles by reduction of metallic salts

in ethylene glycol and can be performed without any surfactant. Nevertheless, polyol method needs to be optimized according to the considered application. Actually, polyol method is generally used for synthesis of anodic catalysts [15–17] but a few studies are found for the synthesis of cathodic catalysts active toward the orr.

The aim of this work is to optimize a polyol synthesis of catalysts active for the orr. For this purpose, a Taguchi design of experiments (DOE) has been used. Taguchi method is a combination of mathematical and statistical techniques often used in empirical studies [18]. This DOE allows reducing experimental time and cost, while giving reliable results. It also allows proposing, verifying and interpreting a simple model of the system, notably concerning the influence of synthesis parameters and of their possible interactions. The considered responses are the active surface area (as measured by integration of the charge in the hydrogen adsorption–desorption region) and the activity of catalysts toward the orr (as determined by the kinetic current density at 0.95 V vs RHE). The variation of the morphology of the catalyst with each parameter will also be observed by TEM. An attempt to correlate the data from electrochemical, microscopy measurements and synthesis parameters will be proposed.

2. Experimental

2.1. Synthesis of the PtCo/XC72 catalysts

H₂PtCl₆, 6H₂O and CoCl₂ (99.9% purity, Alfa Aesar) were dissolved in ethylene glycol (puriss. p.a., ≥99.5% Fluka) with nominal

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concentrations corresponding to a Pt/Co atomic ratio of 5:1. Then, pH (4, 7 or 11) was adjusted with NaOH 1 M solution in ethylene glycol. Vulcan XC72 thermally treated 4 h at 400 °C under Nitrogen (U Quality from l'air liquide) was added to the solution and the mixture was ultrasonically homogenized for 5 min. The mixture was then deoxygenated by bubbling N₂ (Nitrogen U quality from "Air Liquide") for 15 min and heated at reflux (197.3 °C) for 2 h maintaining nitrogen bubbling; the rate of temperature ramp was either 40 °C min⁻¹ or 6.7 °C min⁻¹. After cooling, the particle cleaning step consisted either in decreasing the pH of the mixture down to pH = 1 by addition of a HClO₄ 0.5 M solution and rinsing with ultra-pure water (MilliQ, Millipore, 18 MΩ cm) or consisted in directly washing the mixture with ultra-pure water, followed by filtration. At last, thermal treatment of the PtCo/C powder was performed at 200 °C under air for 1 h to remove remaining ethylene glycol.

Syntheses were carried out following two different procedures. The first one consisted in mixing both metal salts in EG + NaOH solution, adding the carbon powder and heating the mixture up to reflux. The second one consisted in dissolving cobalt salt alone, adding the carbon powder and heating the mixture up to reflux (197.3 °C). After 30 min at reflux, a solution of dissolved platinum salt in ethylene glycol at same pH as the Co salt solution was added.

2.2. Electrochemical measurements

The working electrode was prepared by deposition of a catalytic ink on a glassy carbon disc (0.126 cm² geometric surface area) according to a method proposed by Gloaguen et al. [19]. The catalytic powder was added to a mixture of 25 wt.% (based on the powder content) Nafion[®] solution (5 wt.% from Aldrich) and ultra-pure water (MilliQ, Millipore, 18 MΩ cm). After ultrasonic homogenization of the PtCo/XC72-Nafion[®] ink, a given volume was deposited from a syringe onto the fresh polished glassy carbon substrate yielding in a case of a Pt(40 wt.%)/C a 60 μg cm⁻² catalytic powder loading (i.e. 24 μg_{Pt} cm⁻²). The solvent was then evaporated in a stream of ultra-pure nitrogen at room temperature. By this way, a catalytic layer was obtained with a thickness lower than 1 μm.

Electrochemical measurements were performed using a RRDE (rotating ring disc electrode) set-up: a Pine Instrument Company AFMSRX modulator speed rotator mounted with an AFDT22 electrode including a 0.152 cm² Pt ring and a 0.126 cm² GC disc leading to a collection efficiency $N = 18\%$ at $\Omega = 2500$ rpm (as determined using ferri-ferrocyanide redox couple). A bi-potentiostat AFRDE-4 was used to control the ring and the disc potentials and to collect the respective currents. The electrochemical experiments were carried out at 20 °C in N₂-purged or O₂-saturated (U Quality from l'air liquide) support electrolytes, using a conventional thermostated three-electrode electrochemical cell. The counter electrode was a glassy carbon plate (8 cm² geometric surface area) and the reference electrode was a reversible hydrogen electrode (RHE). The support electrolyte was a HClO₄ 0.1 M (Suprapur, Merck) solution in ultra-pure water.

The active surface area was determined by integrating the charge in the hydrogen adsorption-desorption region of cyclic voltammograms recorded at a scan rate of 20 mVs⁻¹ in N₂-saturated electrolyte (corrected from the double layer capacity). The oxygen reduction reaction was studied by RRDE, with different electrode rotation rates (400, 900, 1600 and 2500 rpm) in order to access the kinetic data (Tafel slopes, limiting current densities and kinetic current densities) from Koutecky-Levich's equation and to verify that no hydrogen peroxide was formed at PtCo/XC72 catalysts (not shown). The disc potential was swept under quasi-steady state conditions at 3 mVs⁻¹.

2.3. TEM measurements

Catalysts were characterized by transmission electron microscopy (TEM) using a Philips CM 120 microscope analyzer equipped with a LaB₆ filament. To prepare the sample, a small drop of the solution was put on an Au grid and the solvent was evaporated. TEM observations allowed determining the mean particle size of platinum and evaluating the dispersion of the particles at the surface of the carbon support. However, great care had to be taken with the counting of the particles. In our case, only isolated-like particles were taken into account; in each case, 600 particles were measured for statistics. The mean particle size was determined using Feret's diameter due to the non-sphere like shapes of some particles.

3. Results and discussion

3.1. Definition of the design of experiments

Before establishing the DOE as a powerful tool for analyzing the influence of several experimental parameters on the catalytic performance, the most important step lies in the identification and choice of the control parameters.

The metal oxidation degree is one of the most important parameter controlling the reduction in polyol method [20]. Furthermore, pH is known to enhance the formation of acetaldehyde from ethylene glycol (one of the steps of the reduction mechanism) [20] and to govern the presence of oxide or hydroxide forms of the metals; moreover, pH not only changes chemical mechanisms, it is also believed that glycolate anions act as surfactant leading to stabilize the particle size [21]: the particle size is directly linked with glycolate concentration. At last, the pH value can modify the zeta potential of the particles, leading to change interactions between PtCo particles and the carbon support, which can have an effect on the metal loading [22]. All these previous observations show that pH is one of the most important parameters to be controlled for a polyol process.

Because pH of the medium may affect the zeta potential (and further the deposition on carbon support), decreasing the pH value (or not) before particle cleaning may also be an influent factor.

Polyol synthesis is based on the homogeneous nucleation of metal from a metallic salt. The density of nuclei will be directly linked with the metallic salt concentration [23]. A weaker number of nuclei will allow well separating germination and growth steps by limiting collision and coalescence of nuclei. Therefore, metallic salt concentration is another important parameter to be controlled.

The kinetics of a reduction reaction is a key parameter to control the form and the size of particles [24]; the reactor temperature and the rate of temperature ramp are parameters which can also be important. In this study, all syntheses are carried out at the temperature of ethylene glycol reflux; however, according to some authors [25,26], this temperature could be the optimal one. Therefore, only the influence of the rate of temperature ramp will be studied.

The reduction potential of Co²⁺ is far lower than that of Pt⁴⁺ as indicated by potential-pH diagrams [27]; therefore, the reduction kinetics of platinum salt is higher than that of cobalt salt. So the order in which metal salts are added will also be studied.

Other parameters could have an effect on the synthesis; for example, the nature of the metallic salt (notably the counter anion of the salt) may have an influence [28]; we restrict our study to the most used metal salts for the preparation of PtCo catalyst by a polyol method.

The five influent parameters considered in the present DOE will be called pH, cleaning method (N), order of addition of metallic salts (OS), salt concentration (c), and ramp temperature rate (T). The linear graph corresponding to the model is given in Fig. 1; straight line

Table 1
Considered synthesis parameter levels in the design of experiments.

Synthesis parameter	Level		
	1	1.5	2
pH	11	7	4
c	1 g L ⁻¹		3 g L ⁻¹
OS	Simultaneous		Pt after
T	Slow		Fast
N	pH decrease		Direct

represents the possible interactions between parameters. Table 1 gives the different levels used for the parameters in the present DOE. The model of the synthesis process can then be written as follows:

$$Y \sim = M + E_N + E_{pH} + E_c + E_T + E_{OS} + I_{pH-N} + I_{pH-T} + I_{pH-c} + I_{pH-OS} + I_{OS-T} + I_{OS-c} + I_{c-T} \quad (1)$$

levels 2 3 2 2 2 6 6 6 6 4 4 4
dof 1 1 2 1 1 1 2 2 2 2 1 1 1

where E_x is the effect of the parameter x , I_{x-y} is the interaction between two parameters x and y , M is the general average of experimental responses and $Y \sim$ is the calculated value of the response from the model for a given configuration of effects and interactions; dof is the degree of freedom for each effect and each interaction. The actions of a parameter at a given level (i) are calculated as follows:

$$E_{x_i} = (\text{average value of responses when } E_x \text{ is at level } i) - M \quad (2)$$

$$I_{x_i y_j} = (\text{average value of responses when } E_x \text{ is at level } i; E_y \text{ at level } j) - M - E_{x_i} - E_{y_j} \quad (3)$$

From this model, the minimum number of experiments needed in the DOE can be calculated respecting two conditions: (i) the num-

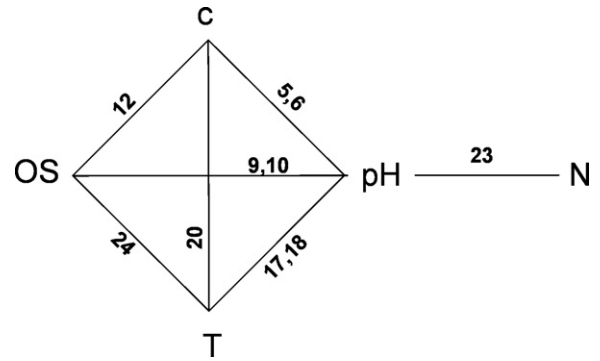


Fig. 1. Linear graph representing the synthesis parameters and the considered interactions (straight lines) for the DOE.

ber of experiments has to be superior or equal to the total number of dof ($\Sigma \text{dof} = 18$) (ii) the criteria for an orthogonal DOE impose that all discrete actions (effects and interactions) are orthogonal; the minimum number of experiments in this case is 24. A DOE with 4 parameters having 2 levels and 1 parameter having 3 levels ($2^4 \times 3^1$) cannot be drawn from a Tagushi table; it should then involve 48 experiments considering the full factorial DOE. However, it is possible to decrease the number of experiments by constructing a non-standard DOE using a modified $L_{32}(2^{31})$ table. It is possible to consume two columns with two levels of the table to build one column with 4 levels. Then, the number of levels can be reduced from 4 to 3 by considering for example that level 4 and 2 are equivalent. Table 2 shows the table of experiments obtained. Numbers in Fig. 1 indicate the columns considered in the Tagushi table which are assigned to each parameter and each interaction (and then the level of each of them in each experiment). This approach leads to reduce the number of experiments from 48 to 24, which is the minimal number required considering the dof and the criteria for orthogonal DOE. After realizing the experiments with the parameters in corresponding levels, the choice for the level of each parameter can

Table 2
Configurations of parameter levels for the realization of the experiments within the DOE, experimental active surface area (ASA) and kinetic current density j_k , and theoretical values as calculated with the model.

Exp.	pH	c	OS	T	N	ASA (exp.) (m ² g ⁻¹)	ASA (model) (m ² g ⁻¹)	j_k at 0.95 V (exp.) (mA cm ⁻²)	j_k at 0.95 V (model) (mA cm ⁻²)
1	1	1	1	1	1	24.5	24.5	0.44	0.34
2	1	1	1	2	2	40.3	40.0	1.34	1.18
3	1	1	2	1	1	29.7	22.5	0.33	0.13
4	1	1	2	2	2	38.4	36.5	0.44	0.90
5	1	2	1	1	2	34.8	36.5	0.83	1.06
6	1	2	1	2	1	17.4	16.0	0.05	0.08
7	1	2	2	1	2	28.7	34.0	1.13	1.22
8	1	2	2	2	1	26.9	21.0	0.52	0.16
9	1.5	1	1	1	2	12.1	4.5	0.14	-0.02
10	1.5	1	1	2	1	4.9	14.5	0.00	0.26
11	1.5	1	2	1	2	6.6	7.0	0.10	-0.04
12	1.5	1	2	2	1	28.1	25.5	0.11	0.16
13	1.5	2	1	1	1	23.9	26.5	0.51	0.64
14	1.5	2	1	2	2	3.1	-2.0	0.04	-0.20
15	1.5	2	2	1	1	24.3	28.5	0.79	0.98
16	1.5	2	2	2	2	10	8.0	0.12	0.06
17	2	1	1	1	1	25.5	23.0	0.51	0.24
18	2	1	1	2	2	18.7	19.5	0.31	0.66
19	2	1	2	1	1	26.9	21.5	0.23	0.16
20	2	1	2	2	2	19.4	26.5	0.54	0.50
21	2	2	1	1	2	14.2	19.5	0.10	0.28
22	2	2	1	2	1	7.8	4.0	0.09	-0.18
23	2	2	2	1	2	15.8	17.5	0.41	0.56
24	2	2	2	2	1	13.7	10.5	0.05	0.02
Mean value						20.6	20.2	0.38	0.38
Residues = $ \sum (Y_{i\text{model}} - Y_{i\text{exp}}) $						0.4		0.02	

Table 3

Mean particle size, related standard deviation and atomic composition of PtCo catalysts prepared from experiments within the DOE, determined by TEM and ICP-OES, respectively.

Experiment	TEM size (nm)	Co/Pt (at.%)
1	3.5 ± 1.2	0.3
2	4.0 ± 1.0	1.2
3	5.5 ± 1.9	0.4
4	4.0 ± 0.9	0.8
5	4.5 ± 2.4	2.1
6	6.5 ± 2.4	0.9
7	4.0 ± 1.2	1.5
8	4.5 ± 1.4	0.6
9	5.5 ± 2.4	1.8
10	5.5 ± 1.5	0.5
11	5.5 ± 1.8	1.2
12	5.0 ± 1.6	0.3
13	6.5 ± 2.8	1.5
14	8.0 ± 4.1	0.4
15	7.0 ± 2.6	1.0
16	7.0 ± 2.6	1.7
17	5.0 ± 2.0	0.7
18	5.0 ± 1.6	0.9
19	5.0 ± 2.0	0.4
20	5.5 ± 2.0	0.7
21	8.5 ± 3.5	1.3
22	7.5 ± 2.5	2.6
23	9.0 ± 3.0	1.6
24	8.0 ± 3.1	2.1

be determined to optimize the responses; a confirmation experiment can then be carried out to compare the obtained results with the calculated ones from the model and to check the reliability of the DOE.

3.2. TEM and ICP-OES characterization of the PtCo catalysts

First, the bulk composition of the different PtCo catalysts was determined using ICP-OES (Table 3). For all catalysts, the Co/Pt ratios are extremely low in the range 0.3–2.6 at.%, far from the nominal Co/Pt atomic ratio (1:5) in the reaction mixture. Actually, it appeared that a lot of cobalt was dissolved in course of the cleaning step for all catalysts. This seems to indicate that cobalt was more present on the particles surface, which is likely due to the lower reduction kinetics of cobalt salt. This dealloying effect and the resulting weak amount of cobalt in the particles are however enough to enhance activity compared to pure platinum catalyst [28]. This last aspect occurs for all prepared catalysts, but in a more or less drastic manner, and can then be considered as a part of the synthesis optimization. Moreover, although ca. 17 at.% less platinum is used in the synthesis route than for a Pt/C catalyst, meaning ca. 17 at.% less platinum in the catalytic powder, higher catalytic activity are obtained.

The mean particle size (Table 3) and the size distribution are very dependent on different factors. Fig. 2 displays size distributions depending on the pH of the synthesis medium (Fig. 2a) and on the metallic salt concentration (Fig. 2b). Actually, both these synthesis parameters displayed the most important influence on particle size and size distribution. The cleaning step does not influence the mean particle size and size distribution. The morphology of the particles is also observed as a function of experimental synthesis parameters. It appeared that, a great number of faceted particles could be obtained with polyol method, independently on the parameter levels; some distinct forms appeared at pH 4 (Fig. 3). However, only the pH value of the medium and the metallic salt concentrations seem to have an influence on the morphology of the particles; the other parameters are not determining parameters in that case.

3.3. Actions of parameters on the active surface area and on the electrocatalytic activity

The electrochemical active surface area (ASA) of the catalysts is evaluated from the cyclic voltammograms recorded at 20 mV s^{-1} in support electrolyte, by integration of the charge involved in the adsorption–desorption region of hydrogen after correction of the capacitive contribution of the carbon support and assuming $210 \mu\text{C cm}^{-2}$ for the adsorption of a monolayer of atomic hydrogen on a polycrystalline platinum surface [29], according to Eq. (4):

$$\text{ASA} = \frac{1/\nu \int idV}{210 \times 10^4 \times m_{\text{Pt}}} \quad (4)$$

where ASA is the active surface area ($\text{m}^2 \text{g}^{-1}$), ν the linear potential scan rate (V s^{-1}), i the current ($\mu\text{C s}^{-1}$), V the electrode potential (V) and m_{Pt} the mass of platinum deposited on the electrode (g).

This determination is realized after 20 voltammetric cycles between 0 and 1.2 V vs RHE until quasi-constant voltammograms [30] are obtained. This activation procedure is carried out in order to clean the platinum surface from organics coming from synthesis and Nafion® solution. A typical voltammogram of a PtCo/XC72 catalyst (experiment no 12 of the DOE) is presented in Fig. 4. Table 2, gives the results obtained for each prepared catalyst within the DOE. From these results, it is possible to quantify the influence of

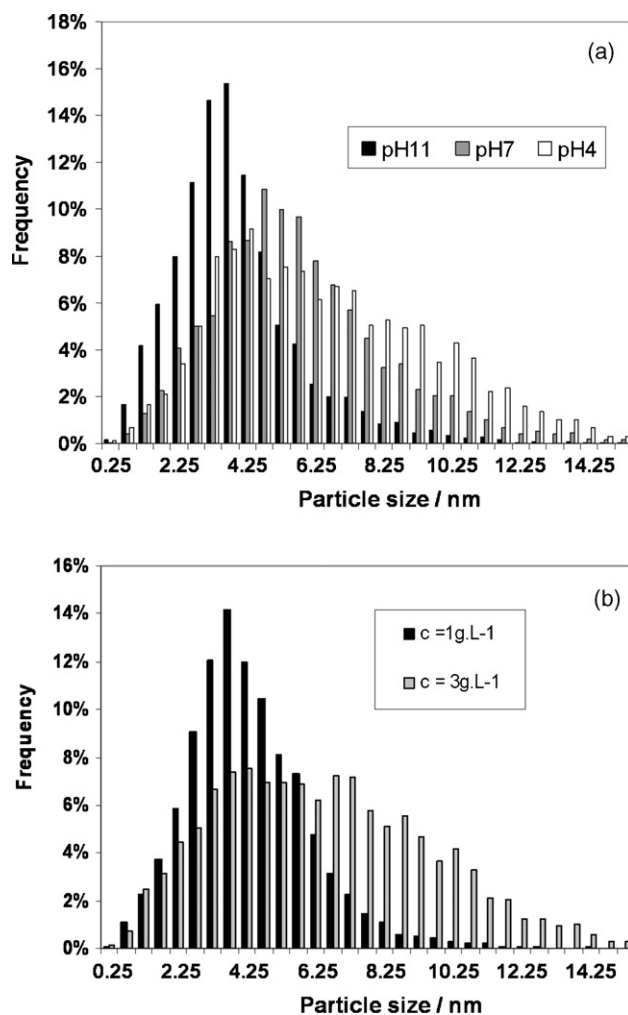


Fig. 2. Histograms of the size distributions for PtCo (40 wt.)/Vulcan XC72 catalysts synthesized by a polyol process under different conditions, (a) with different pH of the synthesis medium and (b) with different metallic salt concentrations c .

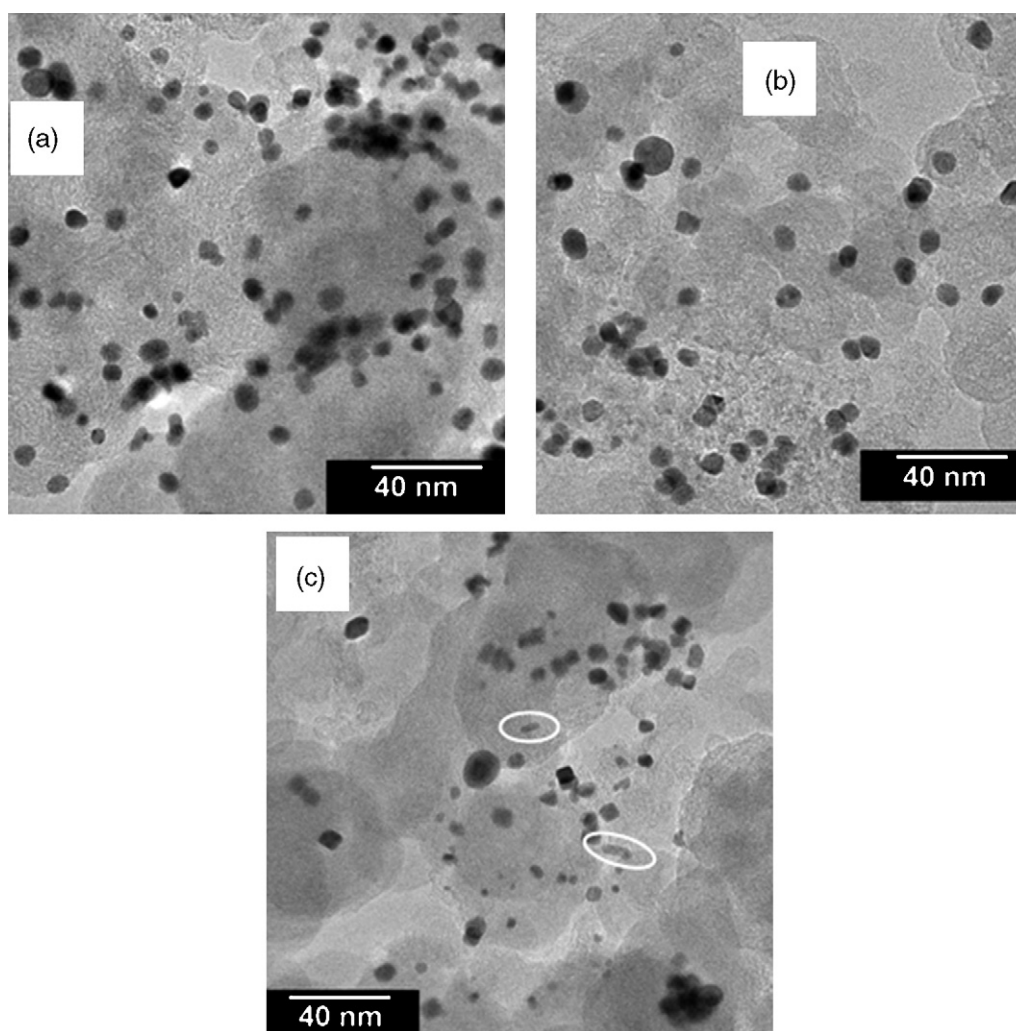


Fig. 3. Typical photographs of PtCo (40 wt.%) / Vulcan XC72 catalysts synthesized by a polyol process with different pH values of the synthesis medium, (a) pH = 11, (b) pH = 7 and (c) pH = 4. Rods are highlighted within white ellipses.

each effect and of their interactions, which leads to the following matrix equation for the model:

$$\begin{aligned}
 SA = & 20.7 + [9.4 \quad -6.5 \quad -2.9] [pH] + [2.3 \quad -2.3] [c] + [-1.7 \quad 1.7] [OS] + [1.6 \quad -1.6] [T] + [0.5 \quad -0.5] [N] \\
 + {}^t[pH] & \begin{bmatrix} 0.9 & -0.9 \\ -3.5 & 3.5 \\ 2.6 & -2.6 \end{bmatrix} [c] + {}^t[pH] \begin{bmatrix} 0.9 & -0.9 \\ -1.4 & 1.4 \\ 0.5 & -0.5 \end{bmatrix} [OS] + {}^t[pH] \begin{bmatrix} -2.3 & 2.3 \\ 1 & -1 \\ 1.3 & -1.3 \end{bmatrix} [T] + {}^t[pH] \begin{bmatrix} -5.9 & 5.9 \\ 5.7 & -5.7 \\ 0.2 & -0.2 \end{bmatrix} [N] \\
 + {}^t[c] & \begin{bmatrix} -0.2 & 0.2 \\ 0.2 & -0.2 \end{bmatrix} [OS] + {}^t[c] \begin{bmatrix} -3.6 & 3.6 \\ 3.6 & -3.6 \end{bmatrix} [T] + {}^t[c] \begin{bmatrix} 2 & -2 \\ -2 & 2 \end{bmatrix} [OS]
 \end{aligned} \tag{5}$$

Considering only the effects of parameters in model (5), the most influent parameters are, as expected from TEM observations, pH and metallic salt concentration (Fig. 5a); the following levels could be chosen for improving synthesis: pH(1), c(1), OS(2), T(1) and N(1). The calculated value of ASA from the model under this parameter configuration is $22.5 \text{ m}^2 \text{ g}^{-1}$. However, this value is far from the highest one obtained in the model. This fact indicates that interactions between parameters play an important role for the optimization of catalyst synthesis in terms of ASA. Notably, it can be seen in Fig. 5b that pH–N, c–T and OS–T interactions are the strongest ones. Because pH displays the higher effect at level 1, it can be kept at this level; the same is true for parameter c, moreover interaction pH–c has a posi-

tive effect with this configuration; conversely, N has to be put

in level 2 in order to obtain a positive effect of the interaction on the ASA, then, if c is kept at level 1, T has to be put at level 2; furthermore OS could be put in level 1 or 2. Consequently, the best result given by the model corresponds to the following parameter configuration: pH(1), c(1), OS(1), T(2) and N(2). A value twice higher ($40 \text{ m}^2 \text{ g}^{-1}$) is obtained, whereas the experimentally measured ASA increases from ca. 30 to ca. $40 \text{ m}^2 \text{ g}_{Pt}^{-1}$. This parameter configuration corresponding to the optimal one is fortuitously within the DOE.

The oxygen reduction reaction in acid medium is used as model reaction to evaluate the electroactivity of the PtCo/C catalysts. For each catalyst the polarisation curves of oxygen electroreduction in a 0.1 M HClO_4 O_2 -saturated electrolyte are recorded with differ-

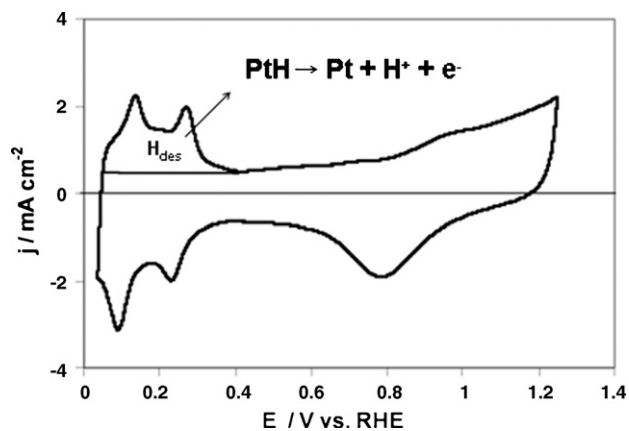


Fig. 4. Typical cyclic voltammogram recorded at a PtCo (40 wt.%) / Vulcan XC72 catalyst ($\nu = 50 \text{ mv s}^{-1}$, $T = 20^\circ \text{C}$, N_2 -saturated 0.1 M HClO_4 electrolyte).

ent rotating rates of the ring-disk electrode from 400 to 2500 rpm. Fig. 6 displays the typical polarisation curves obtained with a PtCo/Vulcan XC72 catalyst prepared according to the experiment no 4 of the DOE, as an example. First, it can be seen that the current plateau at 2500 rpm, as an example, is close to 7 mA cm^{-2} , which value corresponds to an oxygen reduction reaction pathway involving mainly four electrons to produce water. The calculated diffusion limiting current density j_l from the Levich law [31] according to Eq. (6) gives a value of 7.14 mA cm^{-2} for $n = 4$.

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

where n is the number of exchanged electrons per reduced oxygen molecule, F the Faraday ($96,500 \text{ C mol}^{-1}$), D_{O_2} the coefficient diffusion of oxygen in 0.1 M HClO_4 ($1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν the kinematic viscosity of the electrolyte ($1.0 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), c_{O_2} the oxygen concentration in the considered electrolyte ($1.3 \times 10^{-3} \text{ mol dm}^3$) [32], Ω the rotation rate of the electrode and 0.2 the coefficient used when Ω is expressed in revolution per minute [33].

Although the measured j_l value is lower than the calculated one, which can be interpreted as a production of a few percentage of hydrogen peroxide at high overpotentials, RRDE experiments did not allow detecting any hydrogen peroxide oxidation current at the ring electrode (not shown). Second, the presence of cobalt, even at a very low atomic ratio (0.8 at.% in the present case) leads to greatly increase the onset potential of oxygen reduction, which is a little higher than 1.0 V vs RHE, whereas at Pt/C alone, the onset potential is rather a little inferior to 1.0 V [7,34].

Kinetic current density j_k at 0.95 V vs RHE, which is an appropriate estimation of the activity of the catalyst [33], can be evaluated from the Koutecky-Levich plots drawn from such polarisation curves [34].

Results are given in Table 2. According to the matrix model in Eq. (6), pH, temperature ramp and cleaning step are the three key parameters influencing the activity towards oxygen reduction reaction. Initial concentration of metal salts seems astonishingly to have only a little influence on the catalyst activity. However, this parameter has very strong interactions with other parameters (T , OS and pH).

$$j_k = 0.38 + [0.25 \quad -0.15 \quad -0.1] [\text{pH}] + [-0.01 \quad 0.01] [c] + [-0.02 \quad 0.02] [\text{OS}] + [0.08 \quad -0.08] [T]$$

$$+ [-0.08 \quad 0.08] [N] + {}^t[\text{pH}] \begin{bmatrix} 0.01 & -0.01 \\ -0.13 & 0.13 \\ 0.12 & -0.12 \end{bmatrix} [c] + {}^t[\text{pH}] \begin{bmatrix} 0.05 & -0.05 \\ -0.04 & 0.04 \\ -0.01 & 0.01 \end{bmatrix} [\text{OS}] + {}^t[\text{pH}] \begin{bmatrix} -0.03 & 0.03 \\ 0.08 & -0.08 \\ -0.05 & 0.05 \end{bmatrix} [T] \quad (7)$$

$$+ {}^t[\text{pH}] \begin{bmatrix} -0.22 & 0.22 \\ 0.2 & -0.2 \\ 0.02 & -0.02 \end{bmatrix} [N] + {}^t[c] \begin{bmatrix} 0.09 & -0.09 \\ -0.09 & 0.09 \end{bmatrix} [\text{OS}] + {}^t[c] \begin{bmatrix} -0.16 & 0.16 \\ 0.16 & -0.16 \end{bmatrix} [T] + {}^t[T] \begin{bmatrix} -0.02 & 0.02 \\ 0.02 & -0.02 \end{bmatrix} [\text{OS}]$$

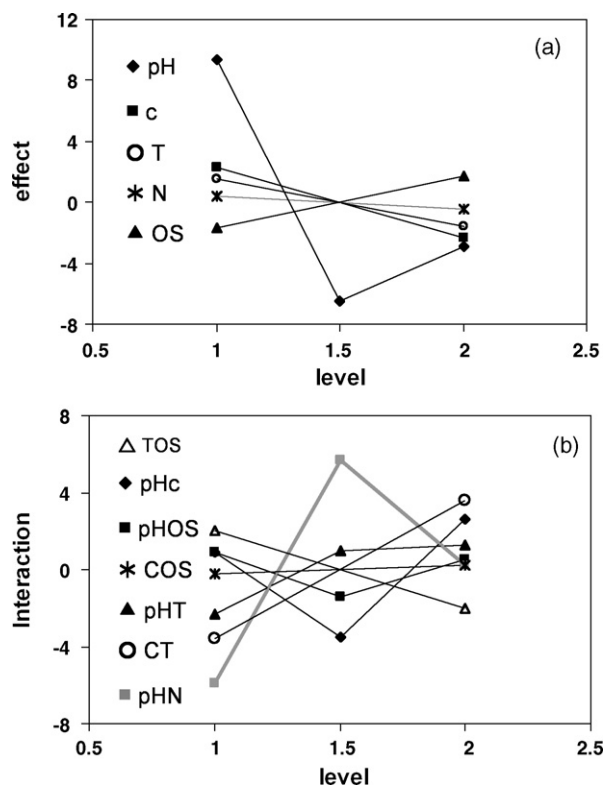
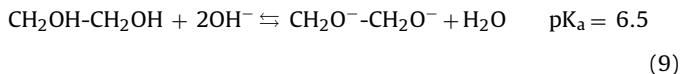
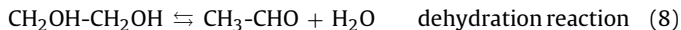


Fig. 5. Graphs representing the influence on the ASA of the level: (a) of each parameter pH, c , OS, T and N , (b) of each interaction between parameters pH- c , pH-OS, pH- T , pH- N , c - T , c -OS, and OS- T (interaction level = 1 is for both parameter at level 1, interaction level = 1.5 is for one parameter at level 1.5 and the other one at level 1, interaction level = 2 one parameter at level 2 and the other one at level 1).

In this case, the best configuration of parameters is not affected by the interactions between parameters. By considering only the parameters in model (6), the best configuration to obtain higher j_k is pH(1), c (2), OS(2), T (1), N (2). This configuration leads also to the higher calculated value of j_k within the DOE (1.22 mA cm^{-2}). The measured value of j_k with this configuration of parameters is of the same order than the calculated one: 1.13 mA cm^{-2} .

4. Discussion

In alkaline medium, ethylene glycol undergoes the following reactions:



Reaction (8) is catalyzed by hydroxyl ions and activated by temperature [19]. The increase of pH leads to favour acetaldehyde formation. The increase of the acetaldehyde concentration, which

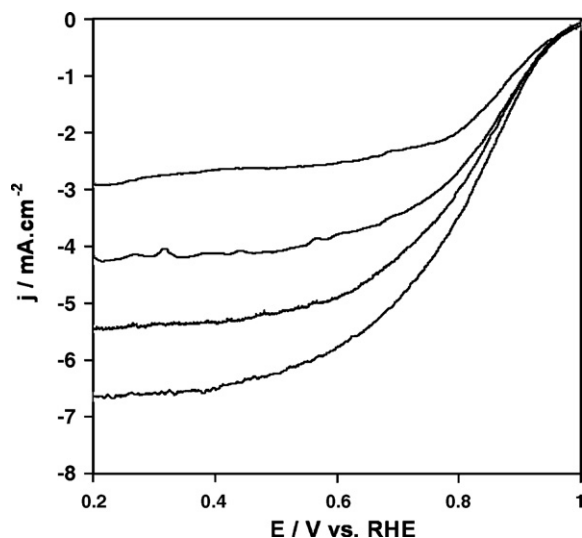
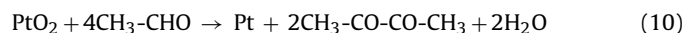


Fig. 6. Typical $j(E)$ polarisation curves at different rotation rates recorded at a PtCo (40 wt.%) / Vulcan XC72 catalyst in an O_2 -saturated 0.1 M $HClO_4$ electrolyte ($T = 20^\circ C$, $\nu = 3 \text{ mV s}^{-1}$, $\Omega = 400, 900, 1600$ and 2500 rpm).

is the reducing agent of the metallic salts (Eq. (10) in the case of Pt salt), leads to the increase of the number of platinum nuclei, and furthermore to the decrease the mean particle size [19].



TEM characterization of catalysts indicated that smallest particle sizes were obtained at pH 11; however, complementary syntheses performed at higher pH (not shown) led to catalytic powder with lower metal/carbon weight ratio (as determined by TGA) than that expected. Lowering the pH led to the formation of anisotropic forms of metal nanoparticles (particularly rods), as observed by TEM (Fig. 3). Under these conditions, the concentration of glycolate is decreased (according to Eq. (9)); now, glycolate species are supposed to act as surfactant in course of the metallic particle formation [20]. The lack of glycolate in the reaction medium may then be responsible of the anisotropic growth of the particles. Mean particle size, higher than that obtained at pH 11, is the same for both pH 7 and pH 4. But, ASA and activity are quite different for both pHs. Actually, the active surface areas are, in average, higher for pH 4. This fact can be due to several reasons: it is possible that at pH 7 the reduction of the metal salts, which are under oxide forms, leads to different particle surface structures than at pH 4 where metal oxides are not formed; however, one has to take into account the method for the counting of particles from TEM photographs. The lower is the pH, the higher is the proportion of anisotropic forms and faceted particles (then the lower the proportion of round shaped particles); it is likely that the estimation of the particle diameters leads to over evaluate the volume with respect to the surface of the faceted or non-isotropic shaped particles; it is also possible that the ASA, calculated assuming $210 \mu\text{C cm}^{-2}$ for the desorption of a monolayer of adsorbed hydrogen at polycrystalline platinum, value determined from an average value of the distribution of low Miller index crystallographic planes $\{1, 0, 0\}$, $\{1, 1, 0\}$ and $\{1, 1, 1\}$ on a polycrystalline platinum surface [35], is badly estimated in the case of anisotropic particles.

TEM observations indicated that the concentration of metallic salts in the synthesis medium had also an influence on the mean particle size of synthesized catalysts. A smaller mean particle size and a narrower size distribution were obtained with lowest salt concentration. As the concentration decreases, nucleus density decreases, and the probability of collision and coalescence of nuclei is lowered, which allows better separating the growth pro-

cess from the nucleation step, as shown by Nomura et al. [23]. But the salt concentration has another influence. Actually, at pH 11 the activity toward orr is only few altered by this synthesis parameter, although the active surface area decreases when higher platinum salt concentration is used. Therefore, the specific catalytic activity of the catalyst synthesized with the highest platinum salt concentration is higher. This can be due to the structure of particles, which are bigger, with fewer defects and less strains.

The very weak influence of the OS parameter on the cobalt composition of the particles was not expected. Actually, the cobalt atomic fraction is a little higher when metallic salts are simultaneously added. This can be explained by considering that cobalt needs the presence of seeds to grow. In this case, higher activity toward orr was achieved although lower active surface area (and lower mean particle size) was obtained than with catalysts prepared by addition of platinum salt after 30 min at reflux. This can be due to the higher content of cobalt in the catalyst.

On one hand, adding platinum after 30 min in the EG + $CoCl_2$ + NaOH mixture maintained at reflux, leads to the increase of the active surface area and to the decrease of the mean particle size. On the other hand, a slow rate of temperature increase leads to lower particle sizes and higher ASAs. In both cases, a part of water (coming from hydrated salts and ethylene glycol dehydration to form acetaldehyde) is evaporated from the reaction medium. Now, it is known that presence of water in course of the synthesis is an important factor for altering the catalyst morphology [26]. Moreover, in the first case, reduction reaction of added platinum salt occurs with a high kinetics due to the high temperature of the reaction medium ($197.3^\circ C$). High reduction kinetics and dehydrated ethylene glycol seems to be the best configuration for obtaining higher active surface area.

At last, the neutralization of the reaction medium before filtration of the catalytic powder appears to have a negative effect on the active surface area and on the activity. It is possible that under these experimental conditions, the surface of the catalysts becomes oxidized, which leads to lower its activity towards orr [36].

From these remarks, to obtain a good compromise between the ASA, the catalytic activity toward orr and a higher cobalt content in the catalyst, a synthesis has been carried out under the following experimental conditions: pH = 11 (level 1), $c = 1 \text{ g L}^{-1}$ (level 1), OS = simultaneous (level 1), $T = \text{slow}$ (level 1) and $N = \text{direct}$ (level 2). This parameters configuration is not within the DOE, and can then serve as a confirmation experiment. The mean particle size was estimated by TEM close to $3.5 \pm 0.9 \text{ nm}$ and the Co/Pt atomic ratio of ca. 2.4%. Expected electrochemical performances, calculated from the models with these parameters, give as results: $ASA = 36 \text{ m}^2 \text{ g}^{-1}$ and $j_k = 0.93 \text{ mA cm}^{-2}$, whereas measured ones under the considered experimental conditions gives $40 \text{ m}^2 \text{ g}^{-1}$ and 1.1 mA cm^{-2} , respectively. Experimental results are in very good agreement with calculated ones from the models and are consistent with those reported in Table 2, which shows the reliability of this DOE and the good repeatability of such a synthesis.

5. Conclusion

In this work, we used a DOE based on Taguchi method to optimize a polyol synthesis of a PtCo/C catalyst for PEMFC cathode. The influence of different synthesis parameters has been already discussed in the literature; however such a design of experiments allowed exploring interactions between each synthesis parameters. The knowledge and control of these interactions between parameters are very important, notably when some synthesis modifications are wanted or necessary, because they are not insignificant. Furthermore, the establishment of a model from Taguchi DOE allows predicting different characteristics of the cata-

lysts: particle size, active surface area and catalytic activity (in the considered definition domain for the considered synthesis parameters). In the present case, the best parameter configuration in terms of ASA, j_k , particle size and atomic ratio is: pH = 11 (level 1), $c = 1 \text{ g L}^{-1}$ (level 1), OS = simultaneous (level 1), $T = \text{slow}$ (level 1) and $N = \text{direct}$ (level 2).

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