# Nanostructured palladium tailored *via* carbonyl chemical route towards oxygen reduction reaction

Y. Luo [a], J.M. Mora-Hernández [a,b], L.A. Estudillo-Wong [a], E.M. Arce-Estrada [b], N. Alonso-Vante [a,*]

[a] IC2MP, UMR-CNRS 7285, Université de Poitiers, 4 rue Michel Brunet, 86022 Poitiers, France
[b] IPN-ESIQIE-DIMM, Unidad Profesional Adolfo López Mateos 07738, México D.F, Mexico

## ARTICLE INFO

## ABSTRACT

Carbon supported palladium nanostructures were synthesized via the carbonyl chemical route. Compared with nanostructured platinum, prepared via carbonyl chemical route, Pd nanomaterials showed mass-loading morphology, whereas particle size and morphology of Pt nanostructures was constant. The oxygen reduction reaction (ORR) on nanostructured Pd, with different morphology in both acid and alkaline medium was investigated. A relationship, based on X-ray diffraction structural analysis pattern, transmission electron microscope, with the Pd morphological effect on ORR activity was identified.

## 1. Introduction

Among platinum group metals, palladium-based cathode catalysts for low-temperature fuel cell received lots of attention because of their catalytic performance towards the oxygen reduction reaction (ORR) [1–4]. However, the development of Pd-based catalysts is a great challenge, since the control of morphology for such nano-materials is still under investigation. The Pd-based nanomaterials prepared *via* a direct reduction of Pd salts usually produces agglomerations [5]. Strong binding surfactants, e.g. the trialkyphosphines, 1-alkanethiols, have been used to prevent agglomeration of nanostructured Pd NPs [6–9]. On one hand, the nanostructured Pd morphology can be tailored by using organic surfactants; on the other hand, these surfactants, strongly bonded to Pd NPs surface, are difficult to be removed, thus preventing the contact between the active catalytic sites with the species, hence reducing the catalytic activity. Therefore, many works focused on the synthesis of "clean" surface of Pd nano-materials *via* various chemical routes [10–12]. In addition, it is well known that the morphology significantly impact the catalytic activity of Pd catalysts [13,14]. Abruña et al. reported, an enhanced ORR activity on Pd nanorods (NRs) with respect to NPs, prepared *via* the same procedure [14], indicating that ORR activity of Pd nanomaterials should be highly dependent on the morphology.

Herein, we report the synthesis of Pd nanomaterials via carbonyl chemical route. This latter was selected based on the following reasons. Previous works demonstrated that this method is powerful to control the size (ca. 2–5 nm) and morphology of Pt-based NPs without surface faceting (spherical NPs) [15,16]. The particle size and morphology are controlled via the formation of clusters di-anions $[Pt_3(CO)_6]_n^{2-}$ under CO atmosphere, which then decompose and release Pt NPs [15,16]. Likely, this carbonyl chemical route should also allow for the formation and decomposition of $[Pd_x(CO)_y]_n^{2-}$ clusters [17]. Methanol is used as solvent during the synthesis via the carbonyl chemical route. Pd NPs surface is free of surfactants and thus "clean". To best of our knowledge, no work done on the use of carbonyl route to tailor Pd-based nanomaterials supported on carbon substrate has been reported. Therefore, in order to develop a reliable synthetic method, a systematic study on the comparison of nanostructured Pt and Pd, tailored via carbonyl chemical route was necessary. As reported in this work, different Pd morphologies derived from the same synthetic procedure of carbonyl chemical route led us to study its effect on the ORR activity in acid (0.1 M $HClO_4$), and alkaline (0.1 M KOH) media, compared with the performance of a reference commercial Pd catalyst.

* Corresponding author. Tel.: +33 5 4945 3625; fax: +33 5 4945 3580.
*E-mail address:* Nicolas.Alonso.Vante@univ-poitiers.fr (N. Alonso-Vante).

## 2. Experimental

### 2.1. Synthesis of Pd nanomaterials via carbonyl chemical route

The nanosized Pd/C catalysts were prepared via a Pd-carbonyl chemical route. Briefly, $K_2PdCl_6$ (Alfa-Aesar, 99.9%) and the sodium acetate (Alfa-Aesar, 99.9%) were used as precursors. These precursors were dissolved in methanol (VMR, 99.9%), reacting with CO (99.99%, Air Liquide) in ice bath (ice-water mixture, ca. 2 °C) for 2 h. Thereafter, carbon substrate was added into the solution at room temperature under $N_2$ (99.99%, Air Liquide). 153.6 mg $K_2PdCl_6$ with 231.6 mg sodium acetate were dissolved in 25 mL $CH_3OH$ in 50 mL two-neck flask, and flushed with $N_2$ for 20 min. Then, the system, in ice bath, was exchanged to CO atmosphere for 2 h under continuous stirring. The colour of the solution turned instantaneously from orange to black-brown during the reaction. The ice bath was removed, and for each synthesis 450, 200, 117 or 75 mg carbon (Vulcan XC-72) was added under $N_2$ atmosphere. The system was under $N_2$ for 12 h under continuous stirring at room temperature. The solvent was evaporated at 80 °C. The black powder was filtrated and rinsed by ultra-pure water (Milli-Q, Milipore) at least three times. Finally, the powder was dried at 60 °C under air overnight. The generated carbon (Vulcan XC-72) supported Pd with metal mass-loadings of *ca.* 11.5, 14.7, 27.1 and 38.5 wt% (*cf.* Table 2), are noted respectively as Pd/C-1, Pd/C-2, Pd/C-3 and Pd/C-4.

### 2.2. Physical characterizations

The Pd mass-loading of catalysts were determined by thermogravimetric analysis (TGA). The sample was heat-treated under air flux (Air Liquide) at a heating rate of 5 °C per minute, from 25 to 850 °C and kept at 850 °C for 30 min. The morphology of the nanomaterials was investigated by transmission electron microscopy (TEM) on a JEOL (JEM-2001) microscope. The particle size was estimated on 100 isolated particles using the free software "ImageJ". The powder X-ray diffraction (*p*XRD) was performed on an Empyrean Panalytical X-ray diffractometer using Cu-Kα radiation (λ = 0.15406 nm). The *p*XRD patterns were obtained, using high resolution, with step-scanning mode, slit at 1/16°, and counting time of 240 s/0.05° in the range of 20–95°. Using the Joint Committee on Powder Diffraction Standard International Centre for Diffraction Data (JCPD-ICDD), the structural phase in *p*XRD pattern was identified. Prior to analysis of *p*XRD patterns of Pd/C catalysts, XRD patterns for XC-72 was used to calibrate the background contribution of the supporting materials. The instrumental broadening was corrected by the standard pattern of $LaB_6$. The lattice parameter, a, of catalysts was estimated using Eqs. (1), and (2).

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{1}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{2}$$

Where λ = 0.154056 nm, θ diffraction angle in radians, hkl Miller indices, and $d_{hkl}$ the interplanar distance.

In this work, a, was the average value of calculations of 5 typical diffraction peaks belonging to Pd and Pt face centred cubic (fcc). Strain effect (ε), stacking fault (α) and crystallite size ($L_v$) for Pd-based catalyst were estimated based on Williamson-Hall method, following the same calculation procedure via Eq. (3) in our previous works [18,19].

$$\frac{\beta\cos\theta}{\lambda} = \frac{k}{L_v} + \frac{K_{hkl}}{a}\alpha + \frac{4\sin\theta}{\lambda}\epsilon \tag{3}$$

Where β is the full width at half-maximum (FWHM) of diffraction peak, λ = 0.154056 nm, θ diffraction angle in radians, $k$ is the Scherrer Constant considering equal to 1, K(111) = 0.43, K(200) = 1, K(220) = 0.71, K(311) = 0.45 and K(222) = 0.43. Therefore, each diffraction peak was fitted with a Pearson VII function in order to obtain the diffraction peaks $\theta_p$ and β, equations (4)–(6).

$$I_C = \frac{I_p}{(1 + \kappa * \Delta2\theta^2)^m} \tag{4}$$

$$\Delta2\theta = 2\theta_i - 2\theta_p \tag{5}$$

$$\kappa = \frac{4(2^{\frac{1}{m}} - 1)}{\beta^2} \tag{6}$$

Where $I_C$ is the calculated profile intensity of a data point $i$ in equation (5), $I_p$ is the peak height, $2\theta_p$ is the peak position, and $m$ is the exponential parameter in the function. The $\kappa$, $\theta_p$, β and m were extracted by Leverberg-Marquardt algorithm implemented in Fityk (free software). The crystallite size ($D_v$) of all Pt-based catalysts was calculated via Scherrer's law (ignoring other effects, e.g., strains and stacking faults).

### 2.3. Electrochemical measurements

The catalysts were evaluated in 0.1 M $HClO_4$ and 0.1 M KOH solution at 25 °C. A standard three-electrode system was used for recording the electrochemical behaviour. The reference electrode was a reversible hydrogen electrode (RHE), and the counter electrode a piece of glassy carbon. The rotating disk electrode (RDE) with glassy carbon disk (3 mm dia.) was used as working electrode. The ink was prepared by mixing 5 mg catalysts, 40 μL Nafion (5 wt%) and 710 μL ultra-pure water (Milli-Q, Millipore), and ultrasonicated for 2 h. 3 μL ink was dropped at the surface of RDE. The cyclic voltammograms (CVs) were recorded at scan rate of 50 mV s$^{-1}$ in $N_2$-saturated electrolyte, from 0.05 to 1.2 V vs. RHE. A stable CV cycle was recorded (20th cycle). For CO-stripping, the CO was electrochemically adsorbed on the electrode surface at 0.1 V vs. RHE for 10 min in the CO-saturated electrolyte, followed by 2 cycles of CV at 5 mV s$^{-1}$ in $N_2$-saturated electrolyte. The polarization curve of oxygen reduction reaction was recorded via linear sweep voltammograms (LSVs) at a scan rate of 5 mV s$^{-1}$ in $O_2$-saturated electrolyte, from 1.0 to 0.2 V vs. RHE, on RDE with rotating speed of 400, 900, 1600 and 2500 rpm (cf. Fig. S1 in supplementary content). The kinetic current was calculated with the Koutecky-Levich (K-L) Eq. (7) [20]:

**Table 1**
Mean particle size (d/nm) and morphology (Morph.) estimated from TEM images; crystallite size ($D_v$ / nm) calculated via Scherrer's law based on pXRD patterns; dispersion for Pt/C catalysts prepared via carbonyl route with 10–40 wt % Pt mass loading. Data extracted from Ref. [21].

|       | Pt/C (10 wt.%) | Pt/C (20 wt.%) | Pt/C (30 wt.%) | Pt/C (40 wt.%) |
|-------|----------------|----------------|----------------|----------------|
| d     | 2.0 ± 0.9      | 2.0 ± 1.0      | 2.0 ± 0.6      | 1.9 ± 0.7      |
| $D_v$ | 3.9            | 2.5            | 3.3            | 3.3            |
| Morph.| Spherical NPs  | Spherical NPs  | Spherical NPs  | Spherical NPs  |