



Morphological impact onto organic fuel oxidation of nanostructured palladium synthesized via carbonyl chemical route



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ABSTRACT

Nanostructured palladium (Pd) supported on carbon (Vulcan XC-72) substrate, prepared via carbonyl chemical route, showed Pd-mass depending morphology, reflected on the surface electrochemistry via cyclic, CO-stripping voltammograms, and performance in direct formic acid and direct methanol micro laminar flow fuel cell arrangement. Comparison was done with commercial Pd/C (30 wt.%, ETEK) catalyst. The formic acid oxidation reaction (FAOR) studied in different acid media (0.1 M HClO₄, 0.5 M H₂SO₄ and 0.5 M H₃PO₄), indicated an enhanced FAOR activity on nanowire-like as compared to nanoparticles and nanorods as well as the commercial one in each electrolyte. Besides, the nanowire-like Pd/C catalyst also favored methanol (MOR) in 0.1 M KOH. These facts confirm favorable morphological effect of nanowires for organic fuel oxidation in both acid and alkaline media.

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1. Introduction

Platinum-based electrocatalyst materials are essentially used for oxidation of small organics, such as formic acid, methanol, and ethanol, in low-temperature polymer membrane fuel cell (PEMFC) [1–6]. However, Pt is a very expensive and rare on the earth crust. In addition, pure Pt active sites can be easily poisoned by intermediates, e.g. CO, generated as an intermediate in the formic acid oxidation (FAOR) or methanol oxidation reaction MOR [7]. These facts limit the commercialization and efficiency of PEMFC.

Palladium, a member in Pt group metals (PGM), showed better catalytic activity toward organic oxidation. This metal is cheaper than Pt [8–10]. Hence, Pd is a promising candidate to replace Pt in this area. The synthesis of Pd-based nanomaterials aiming at controlling the particle size and morphology is still a great challenge. Nanostructured Pd materials were generally prepared by using strong surfactants [11–14]. On one hand, the particle shape and size can be well controlled with the help of surfactants. On the other hand, the strong surfactant capping the Pd surface is hard to remove, leading to a “dirty” Pd surface with the consequence of reducing the number of active site, and a low efficiency in the catalytic activity. Recently, many works focused on developing a synthetic route using weak surfactant or no surfactant

[15–17]. Among these methods, the carbonyl chemical route, employing CO molecules to form Pd-carbonyl complexes [18] and releasing Pd nanostructure by decomposing the carbonyl complex, forms a mass-depending Pd morphology without using any surfactant [19]. Since different Pd morphologies can be generated from the same synthetic method depending of the active metal loading [19], it thus permits us to study the morphological effect on the catalytic activity. Indeed the oxygen reduction reaction (ORR) activity on Pd nanowires (NWs) and nanorods (NRs) revealed an improvement with respect to the commercial nanoparticles (NPs) [19]. In fact, only few works devoted to study the morphological effect of Pd on electrocatalysis, e.g. the ORR has been described [20,21]. It was reported that Pd NWs showed high performance for organic fuel oxidation [21–23], however, no systematic study on the morphological effect of Pd toward organic fuel oxidation has been described so far. Therefore, it is of paramount importance the study of such an effect vis-à-vis the anodic reactions, such as formic acid oxidation reaction (FAOR) and methanol oxidation reaction (MOR).

Herein, we report nanostructured Pd materials supported on carbon black (Vulcan XC-72), prepared via the carbonyl chemical route, showing a mass-depending morphology. The FAOR activity was studied respectively in 0.1 M HClO₄, 0.5 M H₂SO₄ and 0.5 M H₃PO₄ in half-cells, confirming the morphologically depending catalytic activity. The MOR in alkaline solution, in half-cell, demonstrated a relationship between morphology and catalytic activity. Then the best home-made catalyst for organic fuel oxidation in half-cell was selected as anode, and applied in micro laminar flow fuel cell (μLFFC) studies.

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2. Experimental section

2.1. Synthesis of Pd/C catalysts

The synthesis of Pd/C catalysts was described in a previous work [19]. In short, 153.6 mg potassium hexachloropalladate (IV) (K_2PdCl_6 , 99.9%, Alfa-Aesar) and 231.6 mg sodium acetate (NaAc, 99.9%, Alfa-Aesar) were dissolved in 25 mL methanol (CH_3OH , anhydrous, 99.9%, Alfa-Aesar) in a two-neck flask. The flask was sealed under nitrogen (N_2 , 99.99%, Air Liquide) flux for 20 min, then under carbon monoxide (CO, 99.99%, Air Liquide) for 10 min. Afterwards, it was sealed under CO atmosphere and placed into an ice-water bath (ca. 2 °C) with continuous stirring for 2 h. In this process, the solution color turned from orange to brown color. The cooling bath was removed and the flask was purged by N_2 gas. After 30 min, 450, 200, 117 or 75 mg carbon black (Vulcan XC-72, prior pretreated at 400 °C for 4 h under N_2) was added into the flask, and then the system was sealed under N_2 for 12 h. The black powder was filtrated and rinsed by ultra-pure water (MilliQ, Millipore), dried at 60 °C under air overnight.

2.2. Electrochemical measurements in half-cell

The ink was prepared by ultrasonically a suspension containing 5 mg catalyst, 710 μ L ultra-pure water and 40 μ L Nafion (5 wt.%) for 2 h. 3 μ L of homogeneously dispersed ink was deposited onto a glassy carbon electrode (0.071 cm^2), as working electrode, dried by N_2 flux at room temperature. The electrochemical behavior of the samples was studied in 0.1 M perchloric acid (diluted by ultra-pure water from 70% $HClO_4$, Suprapur, Merck), 0.5 M sulfuric acid (diluted by ultra-pure water from 96% H_2SO_4 , Suprapur, Merck), 0.5 M H_3PO_4 (diluted by ultra-pure water from 85% H_3PO_4 , Suprapur, Merck) and 0.1 M KOH (prepared with ultra-pure water, 99.9%, Alfa-Aesar) at 25 °C using an Autolab potentiostat/galvanostat. The counter electrode was a piece of glassy carbon, and reversible hydrogen electrode (RHE) served as reference electrode. The cyclic voltammograms (CVs) were recorded at scan rate of 50 $mV s^{-1}$ in the potential interval of 0.05 to 1.2 V vs. RHE in N_2 -saturated electrolyte. The CO was electrochemically adsorbed at 0.1 V vs. RHE for 10 min. Then the CO-stripping voltammograms were recorded (2 cycles) at a scan rate of 5 $mV s^{-1}$ from 0.05 to 1.2 V vs. RHE in N_2 -saturated electrolyte. The CVs for FAOR was recorded at a scan rate of 50 $mV s^{-1}$, in acid solution with 0.5 M formic acid ($HCOOH$, $\geq 95\%$, Sigma-Aldrich). CVs for MOR were measured at a scan rate of 50 $mV s^{-1}$, in alkaline electrolyte with 0.5 M CH_3OH ($\geq 99.9\%$, Sigma-Aldrich). The chronoamperometry was firstly performed at 0.05 V vs. RHE for 30 s, then switched to 0.4 V vs. RHE and 0.8 V vs. RHE for 1500 s, respectively for oxidation of 0.5 M formic acid in 0.1 M $HClO_4$ and of 0.5 M methanol in 0.1 M KOH.

2.3. Fuel oxidation in air-breathing micro laminar flow fuel cell (μ LFFC)

μ LFFC electrodes' preparation was done from suspensions, ultrasonicated for 2 h, containing 10 mg catalyst, 1250 μ L ultra-pure water and 250 μ L Nafion (5 wt.%). The ink was N_2 -sprayed on a carbon paper (AvCarb T P75T) and pre-heated at 80 °C under air atmosphere. The assembly of air-breathing μ LFFC was previously reported [24]. In brief, fuel cell was made of two TK (PEEK)® plates 25 mm high and 6 mm wide. Each plate had two channels used as inlet and outlet for catholyte/anolyte streams. Both cathode and anode are "sandwiched" between the two plates where a copper sheet served as electrical contacts on each electrode to collect the generated current. A small-opened window (1 cm \times 1 cm) allowed for air-breathing at the cathodic side. In addition, between the electrodes there are two pieces of SU-8 structures with an array of 10 micro-channels arranged in parallel, each channel presents 250 μ m high, 500 μ m wide and 20 mm long. A nanoporous polycarbonate filter Cyclopore (0.1 μ m pore size) was put between the two SU-8 structures to prevent the crossover phenomenon

of the electrolyte streams. The fabrication of the structures with micro-channels was achieved on Si wafers covered by a 400 nm thermally grown SiO_2 layer as substrates. For direct-formic micro laminar flow fuel cell (DF μ LFFC), the anode stream was 5 M $HCOOH$ in 0.5 M H_2SO_4 solution. The cathode stream was 0.5 M H_2SO_4 solution. For direct-methanol micro laminar flow fuel cell (DM μ LFFC), the anode stream was 5 M CH_3OH in 1 M KOH, and the cathode stream was 1 M KOH. Current-potential measurements were carried out with a 2611A Keithley Sourcemeeter, which served as an electronic power source, whereas the current and the voltage produced by the micro-fuel cell were measured with the same device. To measure the potential of each electrode separately it was necessary to use of a 2100 Keithley digital multimeter and an RHE with a Luggin microcapillar plunged into the cathode reservoir.

3. Results and discussions

3.1. Mass-depending Pd morphology

Fig. 1A–C summarizes the crystallite size (L_v), stacking fault (α) and strain (ϵ) parameters estimated by the Williamson–Hall method of home-made Pd/C catalysts: 11.5, 14.7, 27.1 and 38.5 wt.%, noted as Pd/C-1, Pd/C-2, Pd/C-3 and Pd/C-4 [19]. The lattice parameter, a (0.3889 to 0.3891 nm), estimated by Scherrer's equation, was basically the same for the home-made and commercial samples [19]. The following trend for L_v , Pd/C-1 > Pd/C-4 > Pd/C-2 > Pd/C-3 can be observed; whereas α mirrors this order. Alike L_v , and α , ϵ shows a different sequence, i.e., Pd/C-2 > Pd/C-4 > Pd/C-1 > Pd/C-3. The TEM pictures in Fig. 1D–F display their corresponding morphologies [19]. The TEM analysis revealed agglomerated Pd NPs with diameter (d) of ca. 18 \pm 6 nm in Pd/C-1 sample. Pd/C-2 are NWs with a length (L) from ca. 18 to 50 nm and d of ca. 13 \pm 4 nm, homogeneously dispersed onto carbon substrate. Large amount of NRs ($L = ca. 6–8$ nm, $d = ca. 2.8 \pm 0.7$ nm) mixed with a few NPs ($d = ca. 2.6 \pm 0.5$ nm) dispersed on substrate was identified in Pd/C-3. Agglomerated NPs and NRs were observed on carbon in Pd/C-4, forming a network-like structure. All these data indicate that a mass-depending Pd morphology was generated via the carbonyl chemical route, by using a different ratio of Pd precursor to carbon substrate.

3.2. Surface electrochemistry in acid medium

The surface electrochemical behavior for Pd/C-1, Pd/C-2, Pd/C-3, Pd/C-4 and Pd/C (ETEK) is contrasted in Fig. 2A–C, in N_2 -saturated $HClO_4$ (0.1 M), H_2SO_4 (0.5 M), and H_3PO_4 (0.5 M). It can be seen that the double-layer behavior for home-made and commercial catalyst is very similar in all three acid media, suggesting a similar substrate electrochemical behavior. However, the shape of the hydrogen underpotential deposition, H_{upd} , region of home-made catalysts, and that of the reference, is different. Such differences in the H_{upd} region, testify the different hydrogen adsorption–desorption energy on each sample. This phenomenon can be associated to the morphology of the nano-objects cf. Fig. 1D–G. In order to probe the morphological impact on the number of Pd active sites in acid medium, the Pd active surface area was calculated from the coulometry of H_{upd} region, see Fig. 2D. Combined with the analysis on Pd morphology, Fig. 1D–G, one can notice that the active surface trend can be associated with that of L_v and α (Fig. 1A–B) in $HClO_4$ and H_3PO_4 . In H_2SO_4 , the ECSA trend for Pd/C-1, Pd/C-2 and Pd/C-3 corresponds to that of L_v and α , whereas hydrogen adsorption–desorption in Pd/C-4 differs from other catalysts. The differences in active surface of Pd/C-1 to Pd/C-4 samples in the various acids might be due to the different adsorption strengths of anions. It is worth to assess that active surface of the commercial catalyst spans in the various acids [25], and that such an effect is even more important on home-made catalysts.

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