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# Ultrasonic-assisted galvanic displacement synthesis of Pt–Pd/MWCNT for enhanced oxygen reduction reaction: Effect of Pt concentration

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## ABSTRACT

The most important issue for proton exchange membrane fuel cells (PEMFC) is the catalyst which is predominantly Pt-based materials. The simple and fast galvanic displacement (GD) method is a novel alternative does not require any surfactants, additive reagent, or post-treatment in the synthesis of bimetallic materials. The parameters investigated were Pt concentration and sonication in GD bath, finding that both play a key role in the physicochemical features, and thereby, modifying the performance of the catalysts towards the oxygen reduction reaction (ORR) activity. The materials obtained by GD were studied using TGA, ICP-OES, TEM and evaluated as catalysts for ORR in acidic media. Among all synthesized catalysts, highly dispersed Pt<sub>10</sub>Pd<sub>90</sub>/MWCNT synthesized by GD in sonication, exhibited the highest electrocatalytic activity and H<sub>2</sub>O<sub>2</sub> was not detected, showing as a promising catalyst for the use in PEMFC applications.

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## Introduction

During the last few decades, proton exchange membrane fuel cells (PEMFC) had become an attractive power source due to their high energy conversion efficiency and low emission for vehicles and portable applications [1]. Research on PEMFC technology involves several scientific fields such as simulation, engineering and synthesis of new materials [2–4]. It is well known that the ORR taking place at the PEMFC cathode is

kinetically slower than hydrogen oxidation at the anode, thereby several catalysts have been studied to address this limitation [5–7]. The synthesis of new materials requires the control of structure and morphology, because these are the key factors that have a great influence on the kinetics of the electrochemical reactions involved. The current approaches are broadly classified into Pt-based metals in order to study the relationship between size and support of the platinum particles upon electrocatalytic activity, and non-Pt metals catalysts to analyze different alternatives to enhance the ORR

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kinetics through the metal–metal interactions [8–14]. Furthermore, Pt is a highly efficient catalytic element for low temperature reactions and Pt nanoparticles (NPs) supported on porous carbon such as carbon nanotubes, fullerenes, graphene, etc., have been most widely used as the catalyst in PEMFC. Limpattayanate and Hunsom studied the effect of different supports such as carbon Vulcan XC-72, multiwalled carbon nanotubes (MWCNTs) and  $\text{TiO}_2$  [15].

In addition, the Pt NPs with rough surface on Pd (Pt–Pd) exhibit significantly higher electrochemically active surface area when compared to the conventional Pt NPs, with remarkably enhanced ORR activity and durability. The main drawbacks in real applications for Pt-based catalyst are its high cost and catalyst degradation due to (i) platinum dissolution, which is caused by corrosion of carbon support or release of Pt NPs by effect of anodic/cathodic polarization and (ii) poisoning by intermediate products from the oxidation of fuels or corrosion of the support. Meier et al. proposed a degradation mechanism of Pt NPs onto carbonaceous support under start–stop conditions [16]. On the other hand, Tang et al. employed electrochemical impedance spectroscopy (EIS) in order to evaluate the CO tolerance of several Pt-based catalysts [17].

On the other hand, the use of Pt–M alloy (M: Au, Ru, Pd, Ir, Cu, Ni) [8–13] has attracted immense attention due to its enhanced catalytic properties and reduced Pt loading.

Among metals, Pd is a suitable candidate to alloy with Pt due to their same face-centered cubic structure and the nearly identical lattice constant [18]. Pt- or Pd-based catalysts are adopted as cathodes and anodes for fuel cell systems, because they are highly active catalysts for ORR and alcohol oxidation reactions [19–21]. In this context, significant effort has been dedicated in the control of the structure of Pt–Pd catalysts to improve the performance. Different morphologies, such as alloys, dendrites, core-shells, multi-shells, and monolayers have been widely studied [22]. An appropriate synthesis route determines either the success or failure of the catalytic activity because the features, physical properties, and applications of these materials are heavily dependent upon their structure. Consequently, several methods have been reported including layer-by-layer electrochemical deposition, sol–gel process, solvothermal methods, successive reduction, reduction-precipitation, microemulsion, microwave heating and mechanical alloying methods [23–27]. However, the high toxicity of the chemical reagents has encouraged the search for alternative synthesis methods. In this sense, an excellent option for the preparation of bimetallic catalysts by an easy, inexpensive and eco-friendly route is the galvanic displacement (GD). This redox reaction consists in the spontaneous partial displacement of a metal by another metal with higher reducing potential, upon immersion of the sacrificial metal template such as Co, Cu, Ni or Pd, under a solution containing ions of a more noble metal such as Pt. This synthesis produces more efficient catalysts for fuel cell reactions, due to metal–metal interactions with focus on experimental control and enhanced catalytic properties [28–31]. Tellez-Cruz et al. explained that Pt NPs deposited by GD increase the catalytic activity and at the same time maximize the Pt dispersion on the surface, decreasing the metal loading [32]. In addition, research groups have studied the electroless surface limited

redox replacement (ESLRR) for the growth of Pt on different substrates [33,34]. In the specific case of Pt–Pd catalyst, the driving force (the difference between reduction potentials of species) is low, limiting the kinetics of GD reaction. Si et al. have reported the synthesis of Pt–Pd catalysts by enhanced GD using additives such as  $\text{Br}^-$  and  $\text{Cl}^-$  ions [28]. We propose to avoid the use of additives, in order to improve the driving force of the GD by using an external energy source, like sonication [35]. Taking advantage of sonochemistry, catalysts with excellent features, such as dispersion, tunable particle size and good alloying properties, can be synthesized [26,36].

In this paper, the effects of sonication and Pt concentration were investigated in the synthesis of Pt–Pd/MWCNT catalysts by GD. The catalysts were evaluated for their performance for the ORR in acid media. It is noteworthy that the synthesis method leads to catalysts with small size NPs, well dispersed and low amounts of Pt.

## Experimental

### Chemicals

All chemical reagents were used as received without further purification. Cetyltrimethylammonium bromide (CTAB, 98%), potassium hexachloroplatinate (IV) ( $\text{K}_2\text{PtCl}_6$ , 98%), sodium tetrachloropalladate (II) ( $\text{Na}_2\text{PdCl}_4$ , 98%), 2-propanol ( $\text{C}_3\text{H}_8\text{O}$ , 99%), Nafion® 117 solution (~5% mixture of lower aliphatic alcohols and water), sodium borohydride ( $\text{NaBH}_4$ , 99%), sodium citrate tribasic dehydrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ , 99%), ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ , 98%), toluene ( $\text{C}_7\text{H}_8$ , 99%), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%) and nitric acid ( $\text{HNO}_3$ , 70%) were purchased from Sigma Aldrich. All aqueous solutions were prepared with Milli-Q water (18 M $\Omega$ , Millipore).

### Synthesis and oxidation of MWCNT

MWCNT was synthesized by spray pyrolysis method, accordingly to Aguilar-Elguézabal et al. [37] with minor modifications. A solution was prepared by dissolving 0.5 g of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  in 20 mL of  $\text{C}_7\text{H}_8$ , and the solution was sprayed out into a quartz tube placed in a tubular furnace at 850 °C using Ar as a carrier gas at 7 mL  $\text{min}^{-1}$ . The spray time of the procedure was 30 min, once the temperature was reached. Afterward, the product was removed from the quartz tube. Finally, an acid treatment was performed with a  $\text{HNO}_3/\text{H}_2\text{SO}_4$  3:1 solution for 2 h in order to oxidize the MWCNT surface.

### Synthesis of Pt/MWCNT and Pd/MWCNT by microemulsion

A main solution was prepared with 2 g of CTAB in 60 mL of 2-propanol/water (93/7 v/v %). 20 mg of oxidized MWCNT was dispersed by sonication in 40 mL of the main solution in a three-necked round bottom flask. The dispersion was stirred at reflux for 20 min. Afterward, 10 mL of the main solution was mixed with 2.5 mL of an aqueous solution of 80 mM  $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$  and 80 mM of  $\text{NaBH}_4$ . This solution was added to a three-necked round bottom flask and kept for 20 min under reflux. Other microemulsion solution was prepared by mixing 2.5 mL of aqueous solution of 26 mM of

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