



# Synthesis of Pt nanoparticles with preferential (100) orientation directly on the carbon support for Direct Ethanol Fuel Cell



R.M. Antoniasse, L. Otubo, J.M. Vaz, A. Oliveira Neto, E.V. Spinacé\*

Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-900 São Paulo, SP, Brazil

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## ABSTRACT

The synthesis of Pt nanoparticles with preferential (100) orientation directly supported on carbon was done by an alcohol-reduction process using KBr as a shape directing agent. The synthesis conditions were varied and the obtained materials were characterized by transmission electron microscopy and cyclic voltammetry. The order of addition of the Pt precursor and KBr was crucial to obtain cubic Pt nanoparticles with small particle size highly dispersed on the carbon support. DEFC experiments showed that Pt nanoparticles with preferential (100) orientation supported on carbon provided superior power densities and CO<sub>2</sub> selectivity compared to supported polycrystalline Pt nanoparticles.

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## 1. Introduction

Coal, oil and natural gas are non-renewable sources that supply the majority of the energy used worldwide. The intensive use of these matrices became a matter of concern especially from an environmental point of view due to emission of greenhouse gases. Thus, much is expected of those technologies that could decentralize the current energy matrix to a clean generation from renewable sources and the use of more efficient energy conversion devices like fuel cells. Among various types of fuel cells, Proton Exchange Membrane Fuel Cell (PEMFC) has received particular attention for potential implementation in portable, mobile and stationary applications. Hydrogen is the fuel used in PEMFC and it is mainly obtained by water electrolysis and steam reforming of hydrocarbons. Electrolysis is a high cost process, consumes a lot of energy and produces hydrogen of high purity, while steam reforming is a cheaper approach, however, the produced hydrogen must be further purified to fuel the PEMFCs. Furthermore, the hydrogen storage still presents a number of difficulties [1]. Instead, the adoption of directly alcohols such ethanol as combustible in fuel cells has attracted great interest, since it is a renewable combustible easily originated from biomass. Direct Ethanol Fuel Cell (DEFC) presents some technological challenges, particularly regarding the anodic catalysis. Due to the difficulty of C–C bond breaking of ethanol molecule, Pt/C electrocatalyst produces princi-

pally acetaldehyde and acetic acid and only minor amounts of CO<sub>2</sub>, leading to a lower system efficiency. Also, the formation of CO and CH<sub>x</sub> intermediates strongly poisons the Pt sites reducing its catalytic activity with time [2–5]. Considering such DEFC challenges, a development of new more efficient electrocatalysts for complete oxidation of ethanol to CO<sub>2</sub> is a promising field to be explored.

Studies have been shown that ethanol electro-oxidation on (100) preferentially oriented Pt nanoparticles is more selective for CO<sub>2</sub> formation when compared to (110) and (111) surfaces [6]. Thus, exposing certain crystallographic facets on the catalyst surface (consequently modifying its morphology) may improve the catalytic activity so as reactional products selectivity. Growth and morphology of the nanoparticles are governed by energy aspects, always following the concept of minimizing the surface energy. All noble metals crystallize in face-centered cubic structure (FCC) and by following the Wulff's construction to predict the shape of nanoparticles [7], surface energy increases according to the direction  $\gamma\{111\} < \gamma\{110\} < \gamma\{100\}$ , resulting in crystallization in the form of truncated octahedra [8,9]. Eventually, the crystallization process can be modified by the addition of species that interact selectively with the metal surface. Various methods to produce Pt nanoparticles with desired morphological characteristics have been reported in the literature [10–12]. Among them, chemical methods are most suitable, by virtue of providing greater control over the size and shape of the nanoparticles. El-Sayed et al. [13] were the first group to synthesize Pt colloids with different morphologies employing a polymer (sodium polyacrylate) as stabilizing agents. Pt nanoparticles in the form of cubes and tetrahe-

\* Corresponding author. Fax: +55 11 3133 9193.

E-mail addresses: [espinace@ipen.br](mailto:espinace@ipen.br), [espinace@yahoo.com.br](mailto:espinace@yahoo.com.br) (E.V. Spinacé).

drons were produced by modifying the metal/stabilizing agent ratio. Since then, the use of stabilizing agents like polyvinylpyrrolidone (PVP), sodium polyacrylate, oleylamine, has become quite common in colloid synthesis with different morphologies [14,15]. On the other hand, these organic agents might be completely removed from the surface of the nanoparticles before they are used as electrocatalysts in fuel cells, since the surface of Pt nanoparticles is largely blocked by such compounds. Currently methods to remove these impurities normally require great quantities of organic solvents [16], strong oxidizing compounds, like  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$  solution [17], or the use of electrochemical oxidation or ultraviolet irradiation techniques [18,19]. Besides, aggregation and destruction of nanoparticles are still reported [20] making this approach impractical for large applications. It also could be considered that Pt nanoparticles must be further anchored on carbon to be used as electrocatalyst in PEMFC. Thus, the preparation of Pt nanoparticles with desired morphology and free of organic surface impurities is a major challenge. Solla-Gullón and collaborators [21,22] prepared cubic Pt nanoparticles with a preferential (100) surface structure by a water-in-oil microemulsion method using HCl or  $\text{H}_2\text{SO}_4$  as surface modifiers in the water phase. The obtained Pt nanoparticles showed good performance for ammonia and CO electro-oxidations, which are (100) structure-sensitive reactions. Recently, these Pt nanoparticles were supported on a carbon with different metal loadings and tested for ammonia and acid formic electro-oxidation [23]. Kim et al. [24] prepared Pt cubes directly nucleated and overgrown on support by reducing Pt precursors in the presence of carbon supports and anchoring agents, like cysteamine. The obtained materials showed superior activity and long-term stability for oxygen reduction reaction. Cheng et al. [25] prepared Pt nanocubes on various supports by reducing Pt precursor under a CO atmosphere in benzyl alcohol and their materials exhibited high activity for methanol electro-oxidation.

The synthesis of Pt nanoparticles with (100) preferential orientation directly supported on carbon and their application as anodic catalysts in DEFC is extremely rare in the literature. Recently, Figueiredo et al. [26] supported (100) preferentially oriented Pt nanoparticles, prepared by a water in oil microemulsion method as described in reference [21] and used as anodes for DEFC. They have showed the benefit of these faceted materials in fuel cell performance when compared with cuboctahedral Pt nanoparticles and polycrystalline commercial Pt catalyst.

Halide ions and other small anions [27] has a strong tendency to adsorb on the metal surface and results in a surface energy modification, leading to an anisotropic growth; however, such ions could be removed by a feasible water washing process. In this work, we describe a simple synthesis strategy to prepare Pt nanoparticles with preferential (100) orientation directly supported on carbon using only bromide ions as shape directing agent.

## 2. Experimental

### 2.1. Preparation of Pt nanoparticles with preferential (100) orientation directly on the carbon support (Pt/C electrocatalysts)

The following materials were used: hydrated hexachloroplatinum(IV) acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , 99.95% purity) as metal source, potassium bromide (KBr, 99.7%), Vulcan Carbon (X72R – Cabot Corporation), deionized water and ethylene glycol (EG). Pt/C (20 wt% of metal load) electrocatalysts were prepared by an alcohol-reduction process [28] by adding  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and KBr into a EG: $\text{H}_2\text{O}$  3:1 (v:v) solution. The carbon support was added into this solution, which was submitted for 5 min in an ultrasonic bath. The resulting mixture was kept under reflux at 150 °C for 3 h before being filtered, washed with abundant water and dried for 2 h at

80 °C. Others parameters evaluated were the order of addition of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and KBr and the amounts (wt%) of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  added at different steps.

### 2.2. Physico-chemical characterizations

Size, dispersion and morphology of Pt nanoparticles were evaluated by transmission electron microscopy (TEM –JEOL model JEM 2100, operating at 200 kV). For TEM analysis, an amount of the electrocatalyst was suspended in isopropyl alcohol and dropped in TEM copper-grid coated with collodion film. The size was measured by end-to-end particle's extension. X-ray diffraction analyses were performed using a Rigaku diffractometer model Miniflex II, using Cu K $\alpha$  radiation source ( $\lambda = 0.15406$  nm). The diffractograms were recorded in the range of  $2\theta$  between 20° and 90° with a step size of 0.05° and a scan time of 2 s per step.

Cyclic voltammetry technique (CV) was employed for electrochemical and surface studies, using a 910 PSTAT (Metrohm) potentiostat. A three-electrodes cell system with an ultrathin vitreous carbon layer previously polished was used as work electrode, a platinum plate as counter electrode and hydrogen electrode (HRE) as reference. An aliquot of 10  $\mu\text{L}$  of ultrasonicated catalytic ink containing water (0.9 mL), isopropyl alcohol (0.1 mL), Nafion solution 5% (0.02 mL) and the catalytic powder (1 mg) was dropped on the tip of vitreous carbon and let air dried. Sulfuric acid medium (0.5 mol L $^{-1}$ ) was used as electrolyte. After nitrogen gas was bubbled into  $\text{H}_2\text{SO}_4$  solution for 30 min, CVs were recorded at 50 mV s $^{-1}$  at ambient temperature.

### 2.3. Single DEFC electrical performance

For MEAs (Membrane Electrode Assembly) preparation, synthesized Pt/C electrocatalysts were tested as anodes (1 mg Pt cm $^{-2}$ ) while commercial Pt/C (purchased from BASF, lot# F0381022) was chosen as cathode (1 mg Pt cm $^{-2}$ ). Both 5 cm $^2$  electrodes were hot pressed to a pretreated Nafion 115 membrane (Dupont) electrolyte at 125 °C for 10 min. All prepared MEAs were inserted in a single cell, operating at 100 °C, fueled with 2 mL min $^{-1}$  of ethanol (2 mol L $^{-1}$ ) and 500 mL min $^{-1}$  of oxygen at 2 bar. Polarization and power density curves were employed to determine the real DEFC electrical performance of the synthesized catalysts.

### 2.4. Products distribution by gas chromatography

The products of ethanol electro-oxidation were determined and quantified by gas chromatography using a gas chromatograph (GC), model Agilent 7890 A. For these experiments a capillary column Plot-U (30 m) and a thermal conductivity detector (TCD) were employed. The elution gas was carried out using hydrogen gas with a flow rate of 45 mL min $^{-1}$  and the oven temperature was maintained at 80 °C for 5 min and, afterward, it was increased at 10 °C min $^{-1}$  until reach 160 °C. Inlet and detector temperatures were set to 180 °C and 220 °C, respectively. An aliquot (collected at maximum power density condition) of anodic effluent of the single cell was cooled in an ice bath before to be manually injected into GC.

The selectivity (S) was based on total amount of the reaction products from the anodic effluent and it was calculated by Eq. (1):

$$\%S_i = \left( \frac{C_i}{C_{AAL} + C_{AA} + C_{CO_2}} \right) 100\% \quad (1)$$

where C is the concentration of the product i; acetaldehyde (AAL), acetic acid (AA) and CO $_2$ . The products were quantified using calibration curves.

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