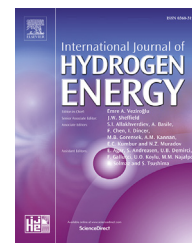




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Oxygen reduction reaction on Pt-Pd catalysts supported on carbon xerogels: Effect of the synthesis method

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ABSTRACT

In this work, Pt-Pd nanoparticles supported on carbon xerogels (Pt-Pd/CX) were synthesised employing unusual routes, in order to evaluate its activity toward the oxygen reduction reaction (ORR). The synthesis methods produced materials with the planned composition (metal content close to 40 wt % and Pt:Pd atomic ratios around 1:2), with Pt, Pd and alloyed Pt-Pd nanoparticles well dispersed on the carbon support. The content of Pt in the nanoparticles was optimised through these procedures, placing this metal at the surface. As a consequence, the Pt-Pd/CX catalysts displayed high activity toward the ORR and remarkable resistance to corrosion, overcoming the electrocatalytic properties of a commercial Pt/C catalyst. Moreover, these catalysts involve four electrons in the ORR. Therefore, the study here presented indicated that the as-synthesised Pt-Pd/CX catalysts are suitable candidates to be employed as cathodes in proton exchange membrane fuel cells.

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Introduction

The synthesis of catalysts for proton exchange membrane fuel cells (PEMFCs) at high scale requires the design and implementation of novel procedures allowing the preparation of electrodes with high catalytic performance. Generally, these materials are conformed by a carbon material supporting the catalytic nanoparticles [1], each one of these components having specific properties with important roles. On the one hand, the metal nanoparticles must possess a crystalline facets distribution that guarantees their activity [2], well

dispersion on the carbon support [3] and a particle size distribution limited to a small range of diameters [4]. On the other hand, the carbon support must have a high surface area to properly disperse the nanoparticles [3], a good pore size enabling the diffusion of the electroactive species [5] and high electrical conductivity [6].

In the cathode of the PEMFCs, Pt nanoparticles are the most employed catalytic phase because of its high activity that guarantees a remarkable performance during the oxygen reduction reaction (ORR) [7]. Nevertheless, this reaction on Pt is characterised by a sluggish kinetics due to the strong Pt-O binding, enabling the oxygen dissociation but also

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promoting the formation of oxide/hydroxide species occupying active sites on Pt [8,9]. Moreover, O₂ reduction involves several mechanistic pathways including electron/proton transfers and O–O bond cleavage. One of the products generated from these pathways is the hydrogen peroxide, a very corrosive substance that involves only two electrons during its production, meaning a decrease in the performance of the cathode catalysts during its operation [10].

In order to increase the kinetics of the ORR and diminish the production of hydrogen peroxide, the use of Pt alloys with metals such as palladium has been suggested, due to its high activity toward the ORR in acidic media has suggested it as a good alternative to partially replace platinum in cathode alloys [11]. The enhanced activity of Pt-Pd alloys has been attributed to the shift in the d-band center of Pt, the changes in its coordination number and the decrease in the Pt-Pt interatomic distance, thus increasing the number of active sites for the adsorption of oxygen [12–14]. Nowadays, many works have been focussed in the development of non platinum group-metals (PGM) catalysts such as non-precious metal catalysts [15], transition metal complex [16,17] and nitrogen- or boron-modified carbon nanotubes [18–20] to replace Pt and PGM in the PEM fuel cell cathodes. However, the synthesis and characterisation of PGM-based catalysts is a crucial challenge for our research, since South Africa possess more than 75 % of the known platinum group metal reserves in the world. Therefore, clean energy technologies must be developed using national resources [21].

To synthesise Pt-Pd nanoparticles supported on carbon materials, several routes have been reported in literature employing common reducing agents such as ethylene glycol [22,23], hydrogen gas [24], sodium borohydride [25,26], hydrazine [27] and sodium citrate [28]. In the case of sodium borohydride and hydrazine, the fast reducing kinetics promotes the formation of nanoparticles with large diameter, prejudicing the catalytic activity [29–33]. Hydrogen gas reduction also induces the agglomeration of nanoparticles due to the employment of high temperatures [24]. In this work, Pt-Pd nanoparticles supported on carbon xerogels have been synthesised using unusual reducing agents such as methanol, ethanol, *n*-propyl alcohol, formaldehyde and ascorbic acid, in order to propose new practical alternatives in the high scale-synthesis of cathode catalysts with high activity toward the ORR. Currently, the use of primary alcohols (methanol, ethanol and *n*-propanol) as reducing agents is rare; in fact, only few recent works reported their use [34,35], while in the early 2000's, these molecules were widely employed during the synthesis of PEMFCs catalysts [36–40]. We justify the use of primary alcohols as reducing agents considering its easy oxidation to aldehydes, carboxylic acids and CO₂, making them efficient reagents to synthesise Pt-Pd nanoparticles supported on any carbon material. Moreover these alcohols possess a low boiling point compared to that of ethylene glycol, decreasing the energy to perform the preparation procedures, since they require high temperature refluxes to guarantee the total metal precursors reduction. Another important aspect is the easy elimination of the synthesis residues, especially in the case of the formaldehyde and ascorbic acid reduction routes [35]. The use of carbon xerogels is justified by its morphological properties that increase the

activity of the catalysts, such as high surface area, high content of mesopores, low microporosity and corrosion resistance [3,41,42]. Particularly, carbon xerogels contains a rich-mesopore structure that enables the oxygen diffusion toward the catalytic nanoparticles, in comparison with other carbon structures [42]. Moreover, it is important to highlight that there are no recent reports about the use of carbon xerogels as support for Pt-Pd nanoparticles and the use of these catalysts as cathodes for the oxygen reduction reaction, while there are several studies about the activity of Pt-Pd catalysts supported on carbon blacks [19,43,44], carbon nanotubes [45,46] and carbon nanofibers [47]. The influence of the synthesis method on the physical properties, electrochemical behaviour and performance of the Pt-Pd catalysts toward the ORR has been studied and compared to those observed for a commercial carbon black-supported Pt catalyst with a metal content close to 34 wt % from Alfa Aesar®.

Experimental

Preparation of carbon xerogel-supported Pt-Pd catalysts

Pt-Pd catalysts supported on carbon xerogels (CX, NANOLIT®) were synthesised by five different methods described below. In all these procedures, an appropriate concentration-solution of the precursor salts (H₂PtCl₆, 8 %, w/w, solution and K₂PdCl₄, 98 %, Sigma–Aldrich) was used to obtain a metal content close to 40 wt % and a Pt:Pd atomic ratio near to 1:2. Nafion® and surfactants were employed in some of the procedures to increase the dispersion of the impregnated metal precursors on the carbon support.

Methanol reduction method (MeOH)

Carbon xerogels (30 mg) were ultrasonically dispersed in a methanol/water (1:3, v/v) mixture during 30 min. Then, 12.5 mg of the SB-12 surfactant (0.233 mM, Sigma–Aldrich) were added to prevent the agglomeration of metal colloids during its formation [36]. This suspension was stirred and refluxed at 90 °C before to add drop by drop the metal precursors solution (1.23 mM H₂PtCl₆; 2.46 mM K₂PdCl₄), which is prepared in the same 1:3 v/v-methanol/water mixture. The suspension was kept at 90 °C for 1 h and then filtered, washed with ultrapure milli-Q water (Millipore system) and dried at 60 °C. This catalyst was labelled as Pt-Pd/CX-MeOH.

Ethyl and *n*-propyl alcohol reduction method (EtOH and *n*PrOH)

The carbon support was mixed with 20 mL of ethanol (94–96 %, Sigma–Aldrich), 30 mL of water and 500 μL of Nafion® (5 %, dispersion in low weight alcohols, Sigma–Aldrich; final concentration: 0.0803 M). This mixture was sonicated for 30 min previously to the drop-by-drop-adding of the metal salts solution (1.23 mM H₂PtCl₆; 2.46 mM K₂PdCl₄). Then, the reaction mixture was refluxed at 110 °C during 3 h. Afterwards, the pH of the mixture was adjusted to 8.5 and kept during 12 h under magnetic stirring. Finally, the suspension was filtered, washed with ultrapure water and dried at 60 °C. This material was labelled as Pt-Pd/CX-EtOH. Other catalyst was synthesised following the same procedure but using 20 mL *n*-propanol (99.7 %, Sigma–Aldrich) as solvent instead

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