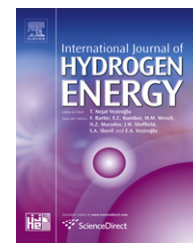


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# Carbon-supported Pt encapsulated Pd nanostructure as methanol-tolerant oxygen reduction electro-catalyst

Karimbintherikkal Gopalan Nishanth, Parthasarathi Sridhar\*, Sethuraman Pitchumani

CSIR-Central Electrochemical Research Institute, Madras Unit, CSIR Madras Complex, Tamil Nadu, Chennai 600113, India

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## ABSTRACT

Pt@Pd/C nanoparticle was prepared by the galvanic displacement reaction between  $Pt^{4+}$  and Pd. A simple synthesis strategy was followed to prepare carbon-supported Pd nanostructure. Pt modified Pd nanostructure on carbon was characterized by transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Cyclic Voltammetry and Linear Sweep Voltammetry. Pt@Pd/C electro-catalyst exhibited higher catalytic activity toward oxygen reduction reaction with excellent methanol tolerance than Pt/C. Pt@Pd/C catalyst showed consistent catalytic activity before and after the durability study. Higher methanol tolerance of Pt@Pd/C with less Pt content than Pt/C suggests that it could be a potential alternative cathode electro-catalyst for DMFCs.

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## 1. Introduction

Direct Methanol Fuel Cells (DMFCs) have significant advantages such as high energy density, rapid start-up and compactness over rechargeable batteries and other types of fuel cells. Despite these, there are still scientific and technological difficulties hampering the widespread commercialization of DMFCs. For instance, methanol crossover from the anode to the cathode through proton exchange membrane has been a major bottleneck in the performance of DMFCs and results in parasitic methanol oxidation on the cathode, which leads to the formation of a mixed potential that not only lowers fuel utilization efficiency but also adversely affects the cathode performance, and thus a loss in the overall fuel cell efficiency [1,2]. Although Pt is one of the best oxygen reduction catalysts, its activity is not selective to the oxygen reduction reaction (ORR) in presence of methanol and hence the fuel

crossover can cause significant reduction in fuel cell performance [3]. A much higher loading of Pt is therefore used at the DMFC cathode than that at the cathode of a hydrogen PEM fuel cell. Besides methanol crossover, there are also conscious efforts to reduce the amount of Pt used in the cathode catalyst [1–3]. Hence, one of the main objectives in the ongoing work on DMFC cathode catalysts is to develop alternative catalysts with ORR activity equivalent to that of Pt and yet demonstrating good methanol tolerance.

The high cost and scarcity of Pt pose serious problems for the widespread commercialization of fuel cell technologies. Pd is another noble metal with significant ORR activity besides Pt. It is stable in acidic solution and has good methanol tolerance compared with Pt. Pd is at least 50 times more abundant than Pt and its cost is currently about one-third of Pt [4]. Recently, Pd and Pd alloy catalysts have been found to exhibit good ORR activities with methanol tolerance even

\* Corresponding author. Tel.: +91 44 2254 2068; fax: +91 44 2254 2456.

E-mail addresses: [psridhar@csircmc.res.in](mailto:psridhar@csircmc.res.in), [psridhar55@gmail.com](mailto:psridhar55@gmail.com) (P. Sridhar).

though the intrinsic ORR activity of Pd is lower than that of Pt [5–9].

Development of Pt-based core-shell nanoparticles as electro-catalysts for polymer electrolyte membrane fuel cells has been an emerging research area as this class of material can offer great scope for cost reduction as well as electrochemical stability [10–15]. The core-shell construction can lead to the use of a low-cost metal core and a noble metal overlayer to reduce the cost of the catalyst. It has been reported that the strain caused by the lattice mismatch between the surface and core components may be used to modify the electronic properties of the surface metal atoms resulting in an improvement in the catalytic activity toward ORR. The enhancement in the activity was accounted for electron transfer from Pd to the Pd-modified Pt surface and the contraction of the Pt lattice in a related computational study [13,14].

Recent studies show that it is necessary to improve the Pd core catalytic activity for which several approaches have been developed such as incorporation of a second element namely, Fe, Co etc. [10,13–15]. However, incorporation of such elements into Pd may lead to dissolution within the Pd nanostructure under fuel cell operating conditions akin to that observed in the case of Pt-based alloy catalysts, such as Pt–Fe, Pt–Co, Pt–Ni etc. As a consequence, the dissolution of the non-noble metal components limits the life of DMFCs [16]. In the present study, instead of incorporating a second element, we have adopted a different synthetic method of encapsulating the Pd nanostructure on carbon with Pt. In order to prepare Pd/C we have used different reducing agents like, formic acid, sodium borohydride ( $\text{NaBH}_4$ ) and ascorbic acid. Carbon-supported Pt@Pd nanoparticles are synthesized by a galvanic displacement reaction between  $\text{Pt}^{4+}$  and Pd. As no external reducing agent was involved, the deposition of Pt occurred exclusively on the Pd surface and isolated monometallic Pt nanoparticles were not formed. The deposition reaction of Pt on the Pd surface was spontaneous because the equilibrium electrode potential of the  $\text{PtCl}_4^{2-}/\text{Pt}$  couple [0.775 V vs. standard hydrogen electrode (SHE)] is more positive than that of  $\text{PdCl}_4^{2-}/\text{Pd}$  (0.591 V vs. SHE) [15]. Weight percentages of Pt and Pd in the catalyst are 10 and 30, respectively.

The crystalline nature of the Pd/C and Pt@Pd/C catalysts were characterized by powder X-ray Diffraction (XRD). The morphology of the catalysts was studied by Transmission Electron Microscopy (TEM). The composition analysis of the catalysts was performed with inductively coupled plasma atomic emission spectroscopy ICP-AES. Pt (4f) core level regions in Pt/C and Pt@Pd/C catalysts were studied by X-ray photoelectron spectroscopy (XPS). In addition, the electro-catalytic characteristics of Pt@Pd/C for ORR and methanol-tolerant activity were investigated. The electrochemical stability of the catalyst was studied by using Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV).

## 2. Experimental

### 2.1. Preparation of Pd/C nanoparticles

40 wt.% Pd supported on VulcanXC-72R carbon black (Pd/C) was prepared as follows. In brief, the support was suspended

in DI water and subjected to ultrasonication for 20 min. To the resulting ink, the solution of Pd precursor was added followed by mixing for 15 min. Subsequently, the temperature was raised to 80 °C followed by the addition of one of the reducing agents, such as formic acid, sodium borohydride and ascorbic acid. After 45 min, the prepared Pd/C was filtered, washed with hot DI water and dried.

### 2.2. Preparation of Pt@Pd/C nanoparticles

Pt modified Pd/C nanoparticles were prepared by a spontaneous displacement reaction following a procedure reported in the literature [15]. 100 mg of the as-prepared carbon-supported Pd nanoparticles were suspended in  $\text{K}_2\text{PtCl}_4$  solution. The nominal weight percentages of Pt and Pd are 10 and 30, respectively. After ultrasonic blending for 30 min, the suspension was then heated to 60 °C under magnetic stirring and left to react for 5 h. The solid product that remained at the end of the reaction was filtered and washed with hot DI water and dried. Fig. 1 gives a schematic illustration of the synthetic procedure of Pt@Pd/C.

### 2.3. Physical and electrochemical characterizations

The crystalline structure of the supported catalysts were studied by recording their X-ray powder diffraction patterns between 20° and 80° in reflection geometry in steps of 5°  $\text{min}^{-1}$  using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). For recording X-ray powder diffraction patterns, about 30 mg of catalyst powder was pressed onto a quartz block using a glass slide to obtain uniform distribution. X-ray photoelectron spectra for the various catalysts were recorded on a VG Micro-Tech ESCA 300° instrument at a pressure  $>1 \times 10^{-9}$  Torr and pass energy of 50 eV with electron take-off angle of 60° and overall resolution of  $>0.1$  eV. The structure and morphology of electro-catalysts were characterized using a Transmission Electron Microscope (JEOL model 1200 EX) operating at an accelerating voltage of 120 kV. For transmission electron microscopy, samples were prepared by placing a drop of the catalyst sample well dispersed in 2-propanol onto a standard carbon-coated Cu grid that was dried in air before loading into the electron microscope chamber. For comparative purpose, 40 wt.% Pt on carbon purchased from Alfa Aesar was used.

### 2.4. Electrochemical measurements

Electrochemical measurements were performed with an electrochemical analyzer (Autolab PGSTAT-30), using a conventional 3-electrode test cell with a saturated calomel electrode (SCE) and a platinum foil as the reference and counter electrodes, respectively. A glassy carbon (GC) disk with a geometrical area of 0.071  $\text{cm}^2$  was polished using alumina slurry to a mirror finish, followed by washing with water and acetone. High-pure nitrogen was used for de-aerating the solutions. All experiments were carried out at 25( $\pm$ 3) °C. The working electrode was prepared as follows: 10 mg of supported catalyst, 10 wt.% of Nafion solution (DuPont, USA) and 3 ml of ultra pure water were mixed ultrasonically, and 20  $\mu\text{L}$  of the suspension containing 0.37  $\text{mg}/\text{cm}^2$  metal was quantitatively transferred to the

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