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# A pulsed laser synthesis of nanostructured bi-layer platinum-silver catalyst for methanol-tolerant oxygen reduction reaction

J.C. Abrego-Martínez <sup>a,b</sup>, Youling Wang <sup>b</sup>, J. Ledesma-García <sup>c</sup>,  
F.M. Cuevas-Muñiz <sup>a,\*</sup>, L.G. Arriaga <sup>a</sup>, Mohamed Mohamedi <sup>b,\*\*</sup>

<sup>a</sup> Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Parque Tecnológico Querétaro S/N, Pedro Escobedo, Querétaro, 76703, Mexico

<sup>b</sup> Énergie, Matériaux et Télécommunications (EMT), Institut National de la Recherche Scientifique (INRS), 1650 Boulevard Lionel Boulet, Varennes, Québec, J3X 1S2, Canada

<sup>c</sup> División de Investigación y Posgrado, Facultad de Ingeniería, Universidad Autónoma de Querétaro, Cerro de las campanas S/N, Santiago de Querétaro, Querétaro, 76010, Mexico

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## ABSTRACT

In the present work, we report the synthesis by pulsed laser deposition technique of binder-free platinum layer coated with silver layer, with each layer having a thickness of about 25 nm. The resulting Pt/Ag material exhibits clear electrocatalytic activity for oxygen reduction reaction (ORR) in alkaline solution. More interestingly, it shows no activity for methanol oxidation reaction (MOR), in contrast to Pt. Furthermore, the Pt/Ag catalyst demonstrates selective activity for ORR even in the presence of concentration of methanol as high as 5 M. Such high methanol tolerance indicates good perspectives for the application of Pt/Ag catalysts in alcohol fuel cell cathodes. For portable electronic applications, the binder-free structure of the Pt/Ag catalyst with its planar deposition make it very attractive as a cathode for membrane-type DMFCs or for membraneless fuel cells such as mixed reactant microfluidic fuel cell that depends on the characteristics of the electrodes to separate the oxidation and reduction reactions.

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## Introduction

Direct methanol fuel cell (DMFC) a subcategory of polymer electrolyte fuel cells (PEFCs) is an electrochemical cell that produces electricity based on the oxidation of methanol and reduction of oxygen. Platinum is used as a catalyst for both

half-reactions. DMFC exhibits lower power densities than that of an H<sub>2</sub>/air PEFC. Nevertheless, the DMFC has the advantages of easier fuel storage (passive mode), no need for humidification, and simpler design. Thus, DMFC is presently considered as ideal power sources for portable power applications [1]. Current DMFCs are limited in the efficiency and power density they can produce because of: (i) low rate of methanol

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [fcuevas@cideteq.mx](mailto:fcuevas@cideteq.mx) (F.M. Cuevas-Muñiz), [mohamedi@emt.irms.ca](mailto:mohamedi@emt.irms.ca) (M. Mohamedi).

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oxidation kinetics on the anode, (ii) methanol crossover, (iii) water management, and (iv) heat management [2].

Crossover remains a key factor in inefficiencies, and often half of the methanol is lost to this phenomenon. The methanol crossover is a phenomenon by which methanol goes easily through the Nafion membrane and be oxidized at the cathode where the oxygen reduction reaction (ORR) occurs, instantaneously poisoning the electrocatalyst and degrading the fuel cell voltage and power density. The crossover is aggravated when a high concentration of methanol is fed to the anode side [3]. Obviously to prevent the crossover, the solution is to develop alternative membranes that would be impermeable to methanol. Still, to date no real breakthrough has been reached in this aspect. Thus in the actual DMFC to minimize the effects of methanol crossover low concentrations need to be used to levels such as 5 wt% which limits the maximum attainable power density of the cell [4].

A second approach to alleviate methanol crossover and/or its effects is to design new electrocatalyst with a methanol tolerance on the cathode side of the DMFCs, i.e., the electrocatalyst must be electro-inactive towards the oxidation of methanol but highly electroactive to the reduction of oxygen. Pt-free electrocatalysts such as Pd/Ag [5,6], Ru/Se [7,8], PdSe [9], Pd/Co [10] exhibited a high methanol tolerance, they however, are limited to practical DMFC applications because these transition metals show very low kinetics towards ORR compared to that of platinum (Pt). Recent progress in electrocatalysts for ORR appropriate for alkaline membrane fuel cells can be found in the recent review of Q. He, and Elton J. Cairns [11]. A third trial consists into combining Pt with another element, which allows ORR to evolve at Pt and at the same time suppresses the occurring of methanol oxidation reaction (MOR). Pt was then used with transition metals, such as Pt/Au [12], Pt-Pd-Co [13], Pt/Bi [14], Pt/Ni [15], and Cu/PtFe [16] or Pt/Ti or PtSe [17].

The primary objective of this work is to develop a catalyst that is tolerant to high concentrations of methanol during ORR while retaining catalytic activity for the ORR. We report here the synthesis of layer onto layer Pt/Ag nanostructures that exhibit excellent methanol tolerance up to 5 M without significantly sacrificing the electrocatalytic activity of Pt towards ORR. Such catalysts were grown by the pulsed laser deposition (PLD) technique and are characterized with scanning electron microscopy (SEM), Atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV) was employed to study the electrocatalytic properties towards ORR, MOR and tolerance properties in the presence of both oxygen and methanol. We have to emphasize that catalyst films particularly Ag was synthesized in various morphologies and thicknesses but only the optimum Pt/Ag structure is reported here.

## Experimental

### Synthesis

Platinum and silver deposits were carried out by single beam PLD. Pt (99.99%) and Ag (99.99%) targets used were purchased from Kurt J. Lesker Co. Pt was deposited onto untreated

carbon paper (CP, Toray) while Ag was deposited onto previously deposited Pt. All the deposits were made at room temperature using a pulsed KrF excimer laser ( $\lambda = 258$  nm), pulse width = 17 ns, and repetition rate = 40 Hz. The laser fluence was fixed to  $4 \text{ J cm}^{-2}$ . Optimum structures shown in this work were obtained by depositing Ag with 20,000 laser pulses under 0.5 Torr of He gas, and Pt with 20,000 laser pulses under 2 Torr of He gas. Pt and Ag loadings were of  $48 \mu\text{g cm}^{-2}$  each as measured by neutron activation analysis, NAA. Prior to each deposition, the chamber was evacuated with a turbo pump ( $4 \times 10^{-5}$  Torr). In all cases, the substrate-to-target distance was fixed at 5 cm. In order to obtain a uniform ablation over the target surface, the Pt and Ag targets were continuously rotated and translated during the deposition. More details regarding the PLD technique and the influence of the atmosphere chamber on the physical processes of laser-material interaction can be found elsewhere [18,19].

### Physicochemical characterization

The surface morphology of the deposits was studied by SEM (JEOL, JSM 7401F apparatus) operated at 10 kV and by AFM using a Nanoscope III microscope from Digital Instrument.

The crystalline structure of all samples was determined by XRD using a Bruker D8 Advance diffractometer equipped with a Cu K $\alpha$  source operated at 40 kV and 40 mA. All diffractograms were acquired in the Grazing Incidence Diffraction (GID) scan mode with an incident angle of  $2^\circ$ ,  $2\theta$  angular step size of  $0.05^\circ$  and acquisition time of 5 s/step.

XPS measurements were performed using a VG Escalab 220i-XL equipped with an Al K $\alpha$  (1486.6 eV). The anode was operated at 10 kV and 20 mA and the pass energy of the analyzer was fixed at 20 eV. The samples were analyzed with a spot size of  $150 \times 800 \mu\text{m}$  located approximately in the center of the sample. A survey spectrum ranging from 0 to 1350 eV was first acquired, and then higher resolution multiplex scan spectra (Ag 3d, Pt 4f, O 1s and C 1s core levels) were obtained. Quantification of the elements was carried out with CasaXPS software (Casa Software Ltd.) by fitting the core level spectra after a Shirley background removal. The C 1s core level peak 284.6 eV, resulting from hydrocarbon contaminants at the surface was used as an internal reference. All spectra have been recalibrated with respect to the C 1s core level peak of adventitious carbon contamination.

### Electrochemical characterization

The electrochemical properties of the samples were studied in alkaline medium (0.3 M KOH, Fisher chemical, 85.8%) using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in a three-compartment electrochemical cell at room temperature. The working electrodes have a geometric area of  $0.370 \text{ cm}^2$ . A Pt coil was used as counter electrode and an Ag/AgCl, 3 M KCl, as reference electrode (the potential is 0.210 V vs. normal hydrogen electrode (NHE)). All reported potentials in the present work are referred to the NHE. The reference electrode was separated from the analyte solution by a Luggin capillary that is very close to the working electrode to minimize the ohmic drop.

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