



Short communication

Evaluation of bimetallic catalyst PtAg/C as a glucose-tolerant oxygen reduction cathode

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ABSTRACT

PtAg/C nanoparticles were synthesized by chemical reduction and evaluated for the oxygen reduction reaction (ORR) in the absence and presence of glucose. PtAg/C catalyst formed onion-like layered structures, which are uniformly distributed on the support. PtAg/C showed activity comparable to that of Pt/C ETEK for ORR. Further, the catalyst exhibited high selectivity for ORR in the presence of glucose. PtAg/C was evaluated as cathode in a microfluidic fuel cell operated with high concentration of glucose (100 mM) as fuel. The results demonstrated that the use of PtAg/C as cathode electrode achieved higher selectivity and better performance compared with Pt/C catalyst.

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1. Introduction

Recently, the development of glucose fuel cells has attracted the attention of many groups [1–3]. One type, the non-biological glucose fuel cell, utilizes noble metal catalysts such as platinum and gold [4]. However, the use of these materials results in self-poisoning due to fuel crossover. Because of this, it is necessary to develop a glucose-resistant catalyst for the oxygen reduction reaction's cathode catalyst. Silver is a viable option in that it should reduce this self-poisoning effect, and has the additional advantage of reducing the amount of inordinately expensive precious metals in the fuel cell [5]. In this work, PtAg/C bimetallic catalyst was synthesized and evaluated for the oxygen reduction reaction ORR and demonstrated an increased current density in comparison with commercial Pt/C (from ETEK), and of even greater interest, this bimetallic electrocatalyst material was found to possess high selectivity for the ORR in the presence of glucose as is shown in microfluidic fuel cell performance.

2. Experimental

2.1. Synthesis of bimetallic catalyst PtAg/C

The bimetallic catalyst PtAg was prepared following a previously reported procedure [6]. Briefly, aqueous solutions 10.3 grams of AgNO₃ (J.T. Baker) and 1.5 mL of H₂Pt(NO₂)₂SO₄ (Alfa Aesar) 6% were added to 10 mL of toluene (Aldrich) containing 0.34 mM tetraoctyl-ammonium bromide TOAB (98%, Fluka). Dodecanethiol (Aldrich) was added to this solution, followed by the addition of NaBH₄ (99.9% Aldrich) in excess as the reducing agent. The reaction proceeded under stirring at 2 °C for 3 h. Finally, a yellow brown dispersion was obtained, which was purified several times with ethanol (J.T. Baker). The resulting nanoparticles were supported by the impregnation method on XC-72 Vulcan 30:70 (w/w) ratio. Successively, the material was thermally treated at 300 °C for 3 h. For comparison purposes, we used Ag/C, which was synthesized following the same method described previously by our group, and Pt/C.

2.2. Physicochemical characterization

The physicochemical characterization was performed by TEM and XRD. TEM was accomplished using a JEOL JEM2200Fs + Cs STEM, and the X-ray diffraction was obtained using a Bruker D8 Advance diffractometer operated at 40 mV and 40 mA.

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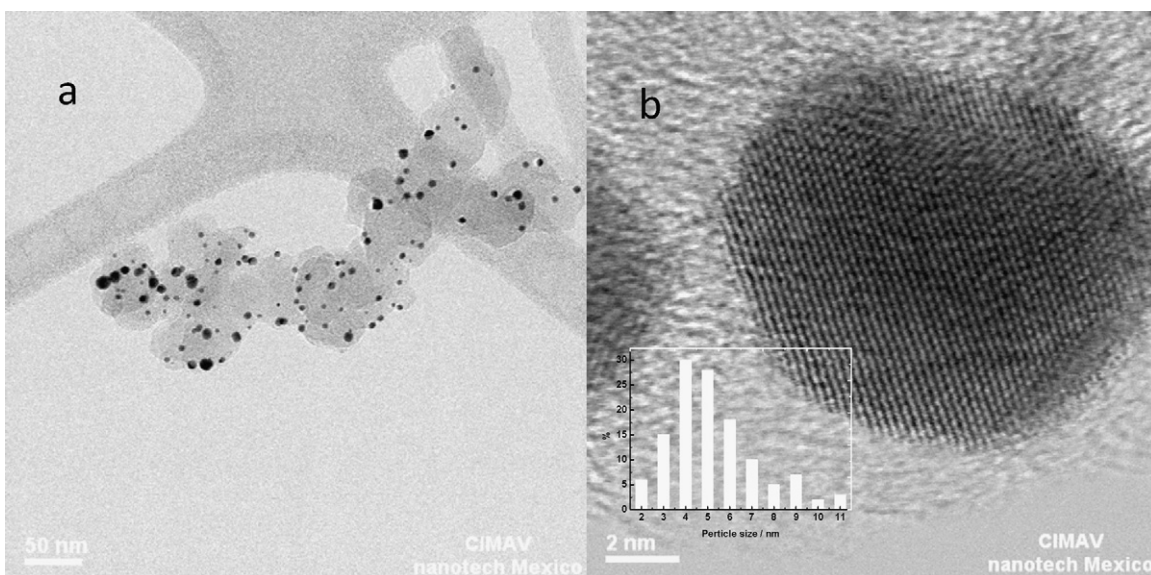


Fig. 1. TEM micrographs and particle size histogram of PtAg/C.

2.3. Electrochemical characterization

Electrochemical experiments were performed with linear scanning voltammetry (LSV), cyclic voltammetry (CV) and a rotating disk electrode (RDE) with a VSP Biologic Potentiostat/Galvanostat. Glassy carbon electrode (GCEs) was used as the catalyst substrate (3 mm in diameter). A standard three-electrode glass cell was used with a Hg/HgO (1 M KOH) reference electrode (0.115 V vs. NHE; 0.910 V vs. RHE at pH 13.5) and a graphite rod as counter electrode. Potentials in the manuscript are referenced to Reversible Hydrogen Electrode (RHE).

The GCEs were polished with alumina (0.05 μm) and rinsed with an excess of DI water. Following the rinse, the electrodes were sonicated for 10 min. Finally, they were cleaned with both ethanol (analytical grade from J.T. Baker) and DI water. In this paper, PtAg/C, Ag/C and Pt/C were all used as working electrodes.

2.4. Microfluidic fuel cell evaluation

Microfluidic fuel cell setup has been already reported [1,6]. Briefly, a microfluidic fuel cell was constructed with PtAg/C as cathode (1 mg cm^{-2} loading) using the spray technique. Au/C was used as catalyst in the anodic compartment with 1 mg cm^{-2} of Au loading. In addition 100 mM D(+) glucose (Aldrich) in 0.3 M KOH (J.T. Baker) was used as fuel with a flow rate of 0.1 mL min^{-1} . Cathodic compartment is fed with 0.3 M KOH previously saturated with oxygen (4.3 U.A.P. Praxair) using a saturation tower at 0.5 mL min^{-1} of flow rate. Fluid flow in all fuel cell tests is pressure driven and regulated using a pump (Masterflex from Cole-Palmer 7553-70). Polarization curves were recorded at 20 mV s^{-1} . For comparison a microfluidic fuel cell was constructed using commercial Pt/C as catalyst in the cathodic compartment.

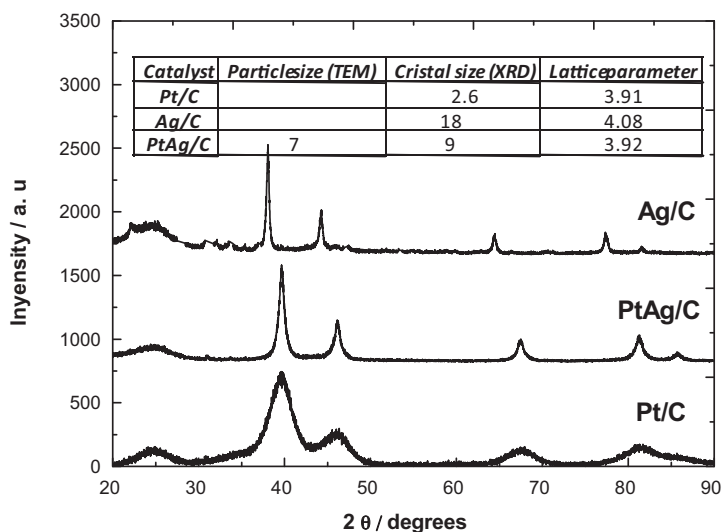


Fig. 2. Diffraction patterns of Pt/C, Ag/C and PtAg/C catalysts.

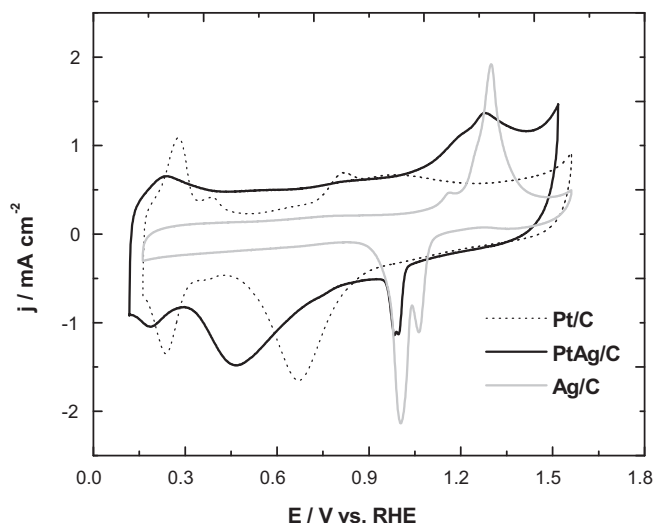


Fig. 3. Cyclic voltammetry of Pt/C, Ag/C and PtAg/C catalysts in 0.3 M KOH, N₂ atmosphere, 20 mV s⁻¹.

3. Results and discussion

3.1. Characterization of PtAg/C

The TEM analysis showed that the metal particles formed onion-like layered structures, which are uniformly distributed on the support. The metallic particles were characterized to determine the interaction between the Pt and Ag particles. The particle structure had a core-shell type with a platinum centre coated with silver, as is clearly shown in Fig. 1b.

The EDS analysis of the catalyst revealed the mean composition of PtAg/C to be 81% Pt and 19% Ag. This composition is in close agreement with that of the metallic precursors that were used. In the TEM images, the mean particle size of the PtAg nanoparticles is approximately 7 nm.

Fig. 2 shows the X-ray diffraction patterns of Pt/C, PtAg/C and Ag/C, along with the characteristic peaks of a single fcc structure. The peak located at approximately 25° may be attributed to the graphite (002) crystalline plane of carbon. The peaks located at 38°, 45°, 65°, 78° and 82° correspond to the planes (111), (200), (220), (311) and (222), respectively. The lattice parameters calculated from this experimental data concur with the reported values given in the literature [7–9] and are shown in the inset table in Fig. 2. The observed diffraction angles for the PtAg/C catalyst are located between those of the two pure metal elements Pt and Ag, suggesting the formation of alloy nanoparticles.

3.2. Electrochemical characterization

Fig. 3 shows the cyclic voltammetry of PtAg/C, Pt/C and Ag/C electrodes in 0.3 M KOH under nitrogen atmosphere. The Pt/C electrode shows the hydrogen adsorption and desorption to be located at 0.31 V vs. RHE. In the case of the Ag/C electrode, it is possible to observe an oxide peak around 1.1 V vs. RHE that corresponds to the formation of silver oxides. In the case of the PtAg/C catalyst, we see a voltammetry similar to Pt/C, although both oxide and reduction peaks appear at 0.7 and 0.9 V vs. RHE, which is similar to the Ag/C catalyst [10].

To evaluate the oxygen reduction reaction's (ORR's) catalytic activity, polarization curves were obtained for the Ag/C, Pt/C and PtAg/C catalysts in 0.3 M KOH in an oxygen-saturated atmosphere at rotation rates that varied from 100 to 2500 rpm. The disk-limiting current density was used to construct the Levich plot [11],

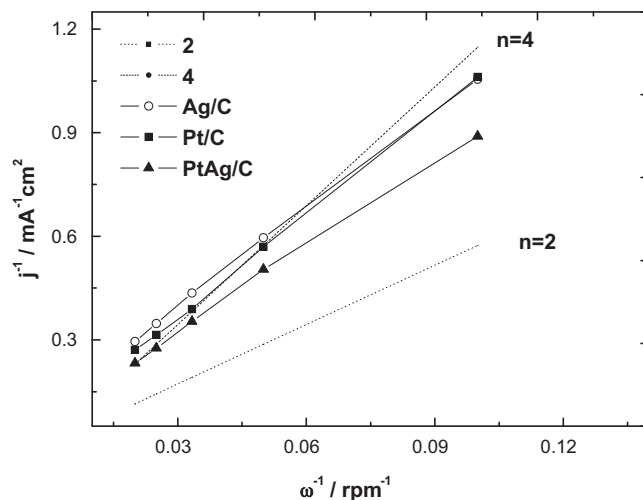


Fig. 4. Levich plots of O₂ reduction on PtAg/C, Ag/C and Pt/C and theoretical curves for two and four electron transfers.

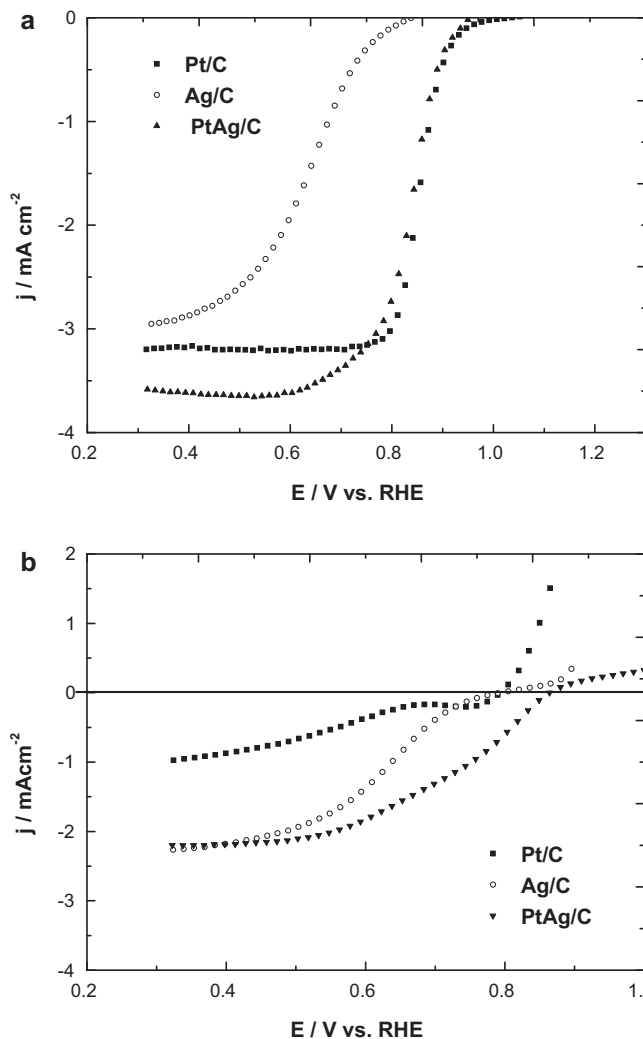


Fig. 5. ORR polarization curves obtained in (a) 0.3 M KOH under oxygen atmosphere and (b) 30 mM glucose + 0.3 M KOH under oxygen atmosphere.

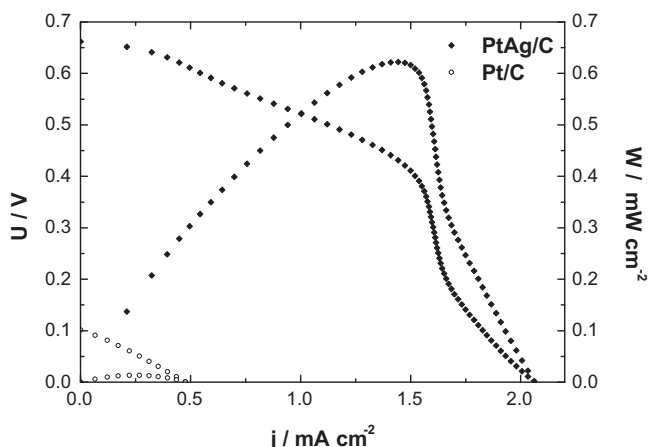


Fig. 6. Polarization and power density curves in 100 mM glucose + 0.3 M KOH for a microfluidic fuel cell equipped with PtAg/C and Pt/C cathode electrodes at 20 mV s⁻¹.

as shown in Fig. 4. The theoretical plots for the transfer of two and four electrons were calculated for the ORR using the Levich equation. It is worth noting that all of the catalysts show mechanism behaviour consistent with the transfer of 4 electrons. This is demonstrated in the Levich plot by the straight lines corresponding to the various catalysts, which exhibit slopes that are in close agreement with that of four-electron transfer mechanism. Conversely, we see that the mechanism of the oxygen reduction reaction is not dependent on the metallic content of the catalyst material.

The ORR curves for the PtAg/C, Pt/C and Ag/C catalysts are shown in Fig. 5a (which only shows the 1600 rpm results). The onset potential of the ORR is very similar for both Pt/C and PtAg/C (0.96 V vs. RHE), while the onset potential for Ag/C shows a negative shift of approximately 100 mV when compared with both Pt/C and PtAg/C. A higher current density is reached in the case of PtAg/C while using nearly 20% less loading than the Pt catalyst. These results show a better activity toward oxygen reduction reaction in an alkaline medium in the case of PtAg/C compared with Pt/C, which could be related to the synergistic relation between both metals as a bimetallic electrocatalyst.

The electrochemical behaviour for the ORR in the presence of glucose was also evaluated (Fig. 5b). The glucose concentrations used were 1, 3, 10, 30 and 100 mM (only curves using 30 mM are shown). The oxygen reduction reaction in the presence of glucose was maintained in the case of Ag/C and PtAg/C, but for the case of the Pt/C catalyst it was clearly decreased, exhibiting a higher positive current density, which is associated mainly with glucose oxidation and, thus, a severe decrease in performance. The higher ORR performance and selectivity demonstrated by PtAg/C in the presence of varying glucose concentrations can be related to the change in the electronic properties of platinum and silver due to the core-shell structure, which appears to protect the Pt nanoparticles' catalyst functionality toward glucose organic fuel via a covering of Ag.

It has been reported in the literature [12] that some metals bind oxygen strongly. Due to the high adsorption strength of O₂, the O–O bonds can be broken, but they generate a high degree of oxygenated species coverage. In contrast, some metals bind oxygen more weakly and leave a lower degree of coverage; however, in these metals, O–O bond cleavage is not efficient. It has been

demonstrated in several works that platinum exhibits the highest activity for the ORR because the oxygen adsorption on Pt is neither too weak nor too strong. The highest activity is reached when a catalyst displays adsorption that is strong enough to split the O–O bond while also demonstrating the rapid reduction of oxygen intermediates. In this work, the efficient combination of two metals with both properties produced a more efficient electrocatalyst for the ORR.

3.3. Microfluidic fuel cell performance

The microfluidic fuel cell was evaluated at high concentration of glucose (100 mM) in order to promote the glucose crossover to the cathodic compartment. Fig. 6 presents the polarization and power density curves for the microfluidic fuel cell equipped with PtAg/C and Pt/C cathode electrodes. The maximum power density achieved with PtAg/C was 0.63 mW cm⁻². In the case of the microfluidic fuel cell equipped with Pt/C as cathode, the maximum power and open circuit potential dropped dramatically below 0.01 mW cm⁻² and 100 mV, respectively. This behaviour is attributed to poisoning effect of the cathode caused by the glucose crossover. This experiment confirms the higher selectivity of PtAg/C compared with Pt/C for the ORR in the presence of glucose.

4. Conclusions

The bimetallic catalyst PtAg/C was synthesized and physico-chemically characterized. This catalyst shows two main characteristics: the enhanced activity for the ORR compared to Pt/C in an alkaline medium and the high selectivity for the ORR in the presence of glucose. In this context, PtAg-based material could be an excellent candidate for use in alkaline fuel cells, bio-fuel cells and microfluidic fuel cells that use glucose as fuel, with an additional advantage arising from the use of less expensive catalytic materials, such as silver. A stability study of PtAg/C electrode is carried out at different glucose concentrations and applied current/voltages in order to know the life time of the catalyst.

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