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Characterization and electrocatalytic properties of sonochemical synthesized PdAg nanoparticles

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ABSTRACT

High intensity ultrasound was used in the synthesis of PdAg nanoparticles. PdAg nanoparticles were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), energy dispersive spectroscopy (EDS), scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM). Catalytic properties for oxygen reduction reaction (ORR) were determined by electrochemical techniques of cyclic voltammetry (CV) and thin-film rotating disk electrode (TF-RDE). Finally the electrocatalyst was tested as a cathode in a single polymer electrolyte membrane fuel cell (PEMFC). Sonochemical synthesis (SS) decreased the overpotential required for the ORR and increased the double-layer capacitance (DLC) respect to the sodium borohydride reduction method due to a better distribution on vulcan carbon support. The electrocatalytic activity of the nanometric bimetallic electrocatalyst for the ORR in acid media showed a favorable multielectron charge transfer process ($n = 4e^-$) to water formation. The performance of the membrane electrode assembly (MEA) prepared with dispersed PdAg/C as a cathode catalyst in a single PEMFC is lower in comparison to platinum.

1. Introduction

PdAg nanoparticles are known by their catalytic properties for hydrogenation reactions [1] and hydrogen separation membranes [2–5]. Pure palladium is not attractive for these practical applications because hydrogen causes a phase transformation that produces embrittlement [6]. There are many methods for synthesizing PdAg nanostructures such as: chemical reduction of the metallic ions from their salts by sodium borohydride [7], polyol method [1] and sol-gel [8]. It is known that morphology, surface and catalytic properties changes due to the synthesis method. Novel synthetic methods can be useful for some applications, like catalysis, where the density of particles on the electrode surfaces is important. Synthesis by high intensity ultrasound method has resulted in nanoparticles with a variety of physical and chemical characteristics which result attractive for a study of the catalytic properties of the materials prepared in that way. [9,10]. Moreover, high intensity ultrasound has been reported as a simple and clean method to synthesize nanostructured particles. So it can be an optional method to synthesize PdAg nanoparticles.

In recent years, many research groups are working intensively in the development of novel electrocatalysts for polymer electrolyte membranes fuel cells (PEMFC) with the goal of attaining practical power density levels and at the same time to reduce the costs in the fabrication of mobile and portable devices [11–15]. The promise of conversion of chemical to electrical energy in a direct and efficient way makes fuel cells development an area of technological interest. One of the main line of research in PEMFC is in the synthesis and characterization of nanocatalysts to promote the dissociation of the O–O bond during the oxygen reduction reaction (ORR) for a better performance and stability of numerous portables and stationeries' devices. Bimetallic Pd-based alloy cathodes have demonstrated better stability and performance than metallic catalysts alone due to the improved electronic and geometric structure [16–18].

In this work PdAg bimetallic nanoparticles were synthesized by high intensity ultrasound. The nanoparticles were distributed on porous carbon Vulcan XC-72 for studying the electrocatalytic properties. Structural characterization was carried out by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM). The electrochemical characterization by cyclic voltammetry (CV), thin-film rotating disk electrode (TF-RDE) and

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membrane-electrode assembly test was accomplished as a part of this work.

2. Experimental

2.1. Electrocatalysts synthesis and characterization

PdAg-Vulcan carbon supported electrocatalyst was produced through the irradiation with high intensity ultrasound of 60 mL of a mixture of 50 vol% ethylene glycol – 50 vol% water containing 14.4 mM $Pd(NO_3)_2$, 9.8 mM $AgNO_3$ and 420 mg Vulcan carbon XC-72 (Cabot). The solution was kept at 0 °C by cooling it using a special device for that. The suspension was prepared for a final ratio catalysts/support of 17 wt% using a high power ultrasonic processor (Sonic and Materials, VC750, 0.5 in standard probe, Ti horn, working to 80% of the maximum amplitude) at 20 kHz under N_2 atmosphere. After some minutes of oscillation and formation of cavitation bubbles the color of the suspension changed to a dark color, indicating that there was a chemical reaction. A total time of 3 h of irradiation (20 s the equipment turned on and 20 s turned off), were enough to produce the supported bimetallic nanoparticles. Then, the catalyst was centrifuged and exhaustively rinsed with distilled water and ethanol and dried overnight at room temperature. Afterward, the catalyst was maintained in a closed recipient prior to structural and electrochemical characterization. PdAg/C electrocatalytic powder prepared by sodium borohydride ($NaBH_4$) reduction was used in order to compare the double-layer capacitance (DLC) respect to sonochemical synthesis (SS). Equal reactive concentrations than SS method were used, in aqueous media and the reduction was carried out by an aqueous solution of $NaBH_4$ added drop by drop [16].

X-ray diffraction (XRD) was employed to determine the phases and the crystallite size in the powder catalyst, using a Rigaku Diffractometer with Co Kα radiation ($\lambda = 1.78899$ Å) operated at 30 kV and 16 mA. The surface morphology was examined using atomic force microscope (AFM) from Digital Instrument Dimension 3100, with a silicon nitride cantilever. Energy dispersive spectroscopy (EDS) was carried out by a Phillips instrument. Electronic mapping was carried out with an STEM mode Hitachi S-5500 operated at 5 kV, the particle size was obtained using high-resolution transmission electron microscopy (HRTEM), ARM 200F (Atomic Resolution Microscope) operated at 180 kV.

2.2. Electrochemical set-up and electrode preparation

Electrochemical experiments were evaluated in a double compartment three-electrode test cell at 298 K. The electrolyte was a 0.5 F H_2SO_4 solution prepared from double- distilled water which was degassed with N_2, for the activation of the working electrode and saturated with O_2 for 20 min before each ORR electrochemical measurement. A platinum wire was used as the counter electrode and $Hg/Hg_2SO_4/0.5$ M H_2SO_4 (MSE = 0.680 V/NHE) as the reference electrode. The potentials in the electrochemical experiments are referred to NHE (normal hydrogen electrode). Electrochemical studies were performed in a Voltalab potentiostat (model PGZ402). Cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements were conducted on a thin-film catalysts deposited on a glassy carbon disk electrode (0.196 cm^2). The thin-film was deposited from a solution prepared by adding 6 μL of a suspension resulting by mixing 9 μL ethyl alcohol, 9 μL Nafion® monomer (5 wt %, Du Pont 1000EW) and 1 mg PdAg (17 wt%/C). Previously, the suspension was placed in an ultrasonic bath for 5 min until an homogeneous suspension was obtained. The estimated amount of PdAg catalyst in the thin-film supported on the glassy carbon electrode surface was about 1.7 mg cm^{-2}. For the Pt electrode used for comparison, 6 μL of a suspension was prepared resulting from sonicating a mixture of 2.2 mg of Pt 20 wt%/C (E-tek) and 60 μL of an alcoholic Nafion estimating 1.12 mg cm^{-2} catalyst on the electrode surface. The rotation velocity of the working electrode was varied between 100 and 1600 rpm at 5 mV s^{-1}.

2.3. Membrane electrode assembly (MEA) preparation and characterization

Membrane electrode assemblies were prepared using Nafion® 115 membranes. An anodic loading of 0.8 mg cm^{-2} of 10 wt% Pt/C (E-TEK) was used in all MEAs prepared. Cathode catalyst loading was 1.0 mg cm^{-2} at 17 wt% of the PdAg/Vulcan carbon XC-72. The catalytic suspension was prepared by mixing 14 μL of Nafion® 5 wt% (Du Pont, 1100 EW) and 240 mL of ethyl alcohol per each 5.0 mg of PdAg carbon supported. The gas diffusion medium at cathode and anode sides were Teflon treated carbon cloths (from ElectroChem). The catalytic suspension was sprayed onto a Nafion® 115 membrane using a lab-made electronic automatic device. In order to prevent ohmic resistance and to form good contact between the electrodes and the polymer membrane, the MEAs were hot pressed at 120 °C and 6.0 kg cm^{-2} for 1.0 min, resulting in an active area of the anode and cathode of 5 cm^2. PEMFC performance experiments were carried out in an Electrochem Fuel Cell Tester System (Mod. 890B). High purity H_2 and O_2 were fed to the single fuel cell at 400 cm^3 min^{-1}. The fuel cell performance was measured between 25 and 80 °C at 30 psi for both gases. The fuel cell station was equipped with a humidifying system for the reactant gases; humidifier temperatures were fixed at 5 °C higher than cell temperature.

3. Results and discussion

3.1. PdAg formation

Formation of PdAg bimetallic alloy can be explained by the chemical effects associated with the sonolysis of water attributed to the acoustic cavitation, which is the formation and violent collapse of microbubbles or gas cavities, in the liquid being irradiated. Suslick has shown how acoustic cavitation leads to the formation of highly reactive $^{\bullet}H$ and $OH^{\bullet}$ radical species in aqueous solutions [10]. This radical, $^{\bullet}H$, reacts directly with metal ions in bulk solution or are scavenged by the added organic solutes [19]. In the latter case, the organic radicals that are produced subsequently reduce the metal ions in solution [20]. The exact mechanism after the homolysis of water leading to the sonochemical reduction of metal ions in aqueous solution is discussed in previous reports. Pd^{2+} ions are much faster reduced than Ag^{1+} at the same conditions. So that palladium colloids may act as nanoelectrodes. In that way the electrons are transferred to the palladium surface from the reducing radicals produced by ethylene glycol during sonication, as Henglein showed [21]. Those electrons may initiate the reduction of other solutes like Ag^{1+} [22,23].

3.2. Catalyst characterization

The X-ray diffractogram for the synthesized PdAg/C catalyst is shown in Fig. 1a. Pd and Ag characteristic diffractogram signals are depicted for comparison. It can be observed that planes (111), (200), (220) and (311) corresponding to pure palladium and pure silver are in different positions regarding to the PdAg synthesized catalyst. This means that signals of the bimetallic material are between those of the Pd and Ag. Thus the sonochemical synthesized PdAg planes match almost perfectly with the XRD pattern of Pd_1Ag_1 alloy. This is a strong indication that the obtained material is a PdAg solid