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Carbon-supported Pt-free catalysts with high specificity and activity toward the oxygen reduction reaction in acidic medium

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ABSTRACT

Specific carbon-supported Pt-free catalysts (Pd, PdFe, PdIr and PdFeIr) toward the oxygen reduction reaction (ORR) were developed. With this end, materials with high and low activity toward the ORR and the methanol oxidation reaction (MOR) were synthesized by the borohydride method (BM). Physicochemical characterization was carried out by several x-ray techniques, such as x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and x-ray dispersive energy (EDX). The ORR was studied at these materials in absence and presence of methanol in acidic medium in a half-cell configuration by the rotating disk electrode (RDE) technique. Additionally, the performance of the catalysts was evaluated as cathode material in a direct methanol fuel cell (DMFC) station. Main results indicate enhanced catalysis toward the ORR and improved tolerance toward the methanol by Fe and Ir insertion into the material, respectively. Membrane electrode assembly (MEA) with a cathode containing PdFeIr/C catalyst yields elevated performance in DMFC, while the electrode cost is dramatically reduced.

1. Introduction

Direct methanol fuel cells (DMFCs) are devices that convert efficiently chemical energy into electrical energy through electrochemical reactions while the fuel is supplied [1]. In this sense, DMFC emerges as an alternative technology to efficiently generate clean energy for portable applications [2,3]. Main advantages include high-energy density (6.1 kWh kg^{-1}), high solubility in liquid electrolytes, easy handling, transport, storage and availability at low cost [4,5]. Furthermore, the liquid-feed system does not require any reforming process that is time and cost consuming, as well as, the humidification and the heat management modules are much simplified compared with the proton exchange membrane fuel cell (PEMFC) due to methanol aqueous solution can provide the necessary heat control and humidification [4,6].

Despite the important advantages of DMFCs as power sources, a real DMFC has several drawbacks, being the crossover of methanol through the electrolyte from the anode to the cathode one of the major practical problems limiting the overall performance [7,8]. The simultaneous methanol oxidation and oxygen reduction reactions at the cathode produce the well known mixed potential that reduces the cell voltage, rises the required oxygen stoichiometry ratio, produces additional water and contaminates the Pt-based catalyst by reaction intermediates of the methanol oxidation reaction (e.g., CO_{ad}) [7–9].

A common strategy to overcome the problems associated to the cathode described above is the use of alternative materials to Pt. This ideal material should decrease the catalysts cost and increase the methanol tolerance without loss of catalytic activity toward the oxygen reduction reaction (ORR) [9]. In this context, Pd and Pd-based alloys appear as an interesting candidate to replace Pt due to its lower price and higher abundance [10–16]. In this sense, numerous studies demonstrated the high and low activity of Pd toward the ORR and methanol oxidation reaction (MOR), respectively [11–21]. However, the catalytic activity toward the ORR in acidic solution is much lower for Pd than Pt [22,23]. Thus, specific catalysts with enhanced activity toward the ORR in conjunction with a high methanol tolerance become necessary.

It is well known that many surface chemical reactions, such as the MOR and the ORR, are structure sensitive [15,23]. So, the surface reaction may be tuned by different factors such as changes in the interatomic distance of the active element (e.g., Pt or Pd), the

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composition of the alloy, the surface area, and the electronic configuration of the material [22–26]. In this way, the rate of a specific reaction could be controlled by the strength of the binding energy of the reactant molecule with the catalytic surface.

Some examples comprise Pd-based alloys (Fe, Ir, Ni, Ag and Co), in which higher activity and stability than pure Pd electrode during the ORR in presence of alcohol in the electrolytic medium were observed [16,19,24–32]. Likewise, well-dispersed PdIr nanoparticles on carbon support developed acceptable performances during the ORR [21]. Also, the effect of temperature treatment at carbon-supported catalysts was investigated. PdCo [13,33] and PdFe alloys [32,34] supported on carbon developed similar ORR performances than carbon supported Pt catalyst after a thermal treatment at 350 °C. On the other hand, fundamental studies using Pd(111) single crystal modified with a Pt monolayer obtained by galvanic replacement of Cu, showed an enhancement for the ORR in comparison with Pt(111) [35]. In the last work the mass specific activity (Pt + Pd) was twice higher than that of Pt/C. Additionally, Pd and Pd-based catalysts have been used as cathode in real fuel cell systems. In these experiments, the DMFC response was observed to depend on several factors, such as Pd loading and its interaction with the carbon support [23].

In the present work, carbon-supported Pd and Pd-based alloys (PdFe, PdIr, PdFeIr) were synthesized by the borohydride method (BM). Physicochemical characterization was carried out by several X-ray techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray dispersive energy (EDX). Their electro-catalytic activity toward the ORR in absence and presence of methanol was carried out in a half-cell configuration; meanwhile their performance as cathode material was evaluated in a DMFC station.

2. Experimental

2.1. Catalyst synthesis

Carbon-supported Pd/C, PdFe(3:1)/C, PdIr(3:1)/C and PdFeIr(2:1:1)/C were prepared by the BM [36]. Appropriate amounts of metal precursors ($IrCl_3$, $FeCl_3.4H_2O$ and $PdCl_2$, Sigma–Aldrich) were employed to obtain nominal metal loading of 20 wt.% on carbon Vulcan XC-72-R. The materials were labeled as Pd/C, PdFe/C, PdIr/C and PdFeIr/C.

Catalysts were synthesized by the impregnation method, in which a suspension of carbon Vulcan XC-72R in milli-Q water (Millipore system) is prepared under ultrasonic bath and posteriorly stirred during ca. 24 h. Then, a water solution containing the metal precursors was slowly added to the carbon solution, and later the pH was adjusted to 5 with a saturated sodium hydroxide solution. Subsequently, metal ions were reduced with a 26.5 mM sodium borohydride (99%, Sigma–Aldrich) solution, which was slowly added under sonication and controlled temperature of 20 °C. Finally, catalysts were filtered and washed copiously with ultra pure water and dried at ca. 80 °C overnight.

2.2. Physicochemical characterization

X-ray diffractograms (XRD) of the electrocatalysts were obtained with a PANalytical X'Pert Pro X-ray diffractometer operating with Cu Kα radiation (λ = 0.15406 nm) generated at 40 kV and 20 mA. Scans were done at 0.04° s^{-1} for 2θ values between 20° and 100°. In order to estimate the particle size from XRD, the Scherrer equation was used [37]. With the purpose to improve the fitting of the peak, diffractograms for specific 2θ values ranges were recorded at 0.028 min^{-1}. The lattice parameters were obtained by refining the unit cell dimensions by the least squares method [38].

The atomic composition of the electrocatalysts was determined by energy dispersive X-ray analysis (EDX) coupled to the scanning electron microscopy Jeol JSM 6300 with a silicon doped with lithium 6699 ATW detector applying 20 keV.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo-Scientific apparatus operating with Al Kα line radiation (1486.6 eV), containing a twin crystal monochromator and yielding a focused X-ray spot with a diameter of 400 μ at 3 mA × 12 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band, and 50 eV in a narrow scan to selectively measure the particular element range. Charge compensation was achieved with the flood gun system that provides low energy electrons and argon ions from a single source. The samples were placed into a pre-chamber during 4–5 h. The analysis chamber pressure during the measurement was maintained below 5×10^{-8} mbars. The binding energies (BE) were calibrated relative to the C 1s peak at 284.6 eV to take into account charge effects. The areas of the peaks were calculated by fitting the experimental spectra using gaussian/lorentzian combined shapes, after the elimination of background noise upon use of Shirley-type curves. The surface atomic contents for each component were calculated from such fittings, employing the corresponding atomic sensitivity factors.

2.3. Electrochemical measurements

All measurements were carried out in a three-electrode cell at room temperature (25 °C) controlled by an Autolab PGSTAT302N potentiostat–galvanostat. A carbon row was used as a counter electrode, while the reference electrode was a reversible hydrogen electrode (RHE) in the supporting electrolyte (0.5 M H_2SO_4, Merck p.a.). All potentials are referred to this electrode. A rotating electrode (RDE) with a glassy carbon disk (geometrical area = 0.071 cm^2) was used. An aliquot of catalyst ink (20 μL) was dried onto the glassy carbon disk under Ar atmosphere to be used as working electrode. The suspension was prepared by stirring 2 mg of catalyst with 15 μL of Nafion® (5%, Sigma–Aldrich) and 500 μL of water (Milli-Q, Millipore). Ar (Air Liquide 99.999%) was used to deoxygenate all solutions and O_2 (Air Liquide 99.995%) to perform the measurements related to the ORR.

Previous to the measurements an activation step of the working electrode was performed. The last consists of potentiodynamic cycles between 0.10 and 0.70 V at 0.20 V s^{-1} in the supporting electrolyte until a reproducible voltammogram was achieved. Then, a blank cyclic voltammogram (BCV) was recorded at 0.02 V s^{-1}. For the ORR experiments, O_2 was bubbled 20 min before each experiment and an oxygen atmosphere was maintained during all measurements. Steady state polarization curves were recorded between 1.00 and 0.20 V at rotating speeds of 400, 600, 900, 1600 and 2500 rpm to evaluate the ORR kinetic parameters. In this study, the working electrode was introduced into the electrolyte at a controlled potential of 1 V and subsequently a linear sweep scan (LSS) was initiated in the negative going direction at scan rate of 0.002 V s^{-1}. The voltammetric profiles of the catalyst and the ORR experiments were studied in absence and presence of methanol in solution. With this end, 0.5, 1, 2 and 3 M methanol solution in 0.5 M sulphuric acid medium were employed.

2.4. Membrane electrode assembly preparation and electrochemical characterization

20 wt.% PdX/C (X = Pt and FeIr) and commercial 20 wt.% PtRu (Premetek Co, USA) on Vulcan® XC72R (Cabot Corp.) catalysts were used for the cathode and the anode, respectively.