Journal of Power Sources 278 (2015) 458–463

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Platinum supported on mesoporous carbon as cathode catalyst for direct methanol fuel cells

Mariano M. Bruno [a, b], Federico A. Viva [a, *], M. Agustina Petruccelli [a], Horacio R. Corti [a, c]

[a] *Grupo Celdas de Combustible, Departamento de Física de la Materia Condensada, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica (CNEA), Av. General Paz 1499 (1650), San Martín, Buenos Aires, Argentina*
[b] *Escuela de Ciencia y Tecnología, Universidad Nacional de Gral. San Martín, Martin de Irigoyen 3100 (1650), San Martín, Buenos Aires, Argentina*
[c] *Instituto de Química Física de los Materiales, Medio Ambiente y Energía (INQUIMAE), Facultad de Ciencia Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2160 (1428), Ciudad Universitaria, Buenos Aires, Argentina*

HIGHLIGHTS

- Pt nanoparticles supported on mesoporous carbon as cathode catalyst for DMFC.
- Improved nanoparticles distribution over the mesoporous carbon.
- Polarization measurements of active feed fuel cell.
- Higher peak power density for Pt/MC than Pt/C.
- Lower O_2 flow needed for Pt/MC to exceed Pt/C performance.

ARTICLE INFO

Article history:
Received 17 September 2014
Received in revised form
19 December 2014
Accepted 20 December 2014
Available online 23 December 2014

Keywords:
Mesoporous carbon
Pt catalyst
Oxygen reduction reaction
Direct methanol fuel cells

ABSTRACT

Platinum nanoparticles supported on mesoporous carbon were obtained by an impregnation and reduction method with $NaBH_4$ as the reducing agent. The high specific surface area mesoporous carbon was obtained by carbonization of a resorcinol-formaldehyde polymer with a cationic polyelectrolyte as a soft template. Surface characterization performed by transmission electron microscopy and powder X-ray diffraction showed a homogeneous distribution and high dispersion of the metal particles on the mesoporous support. The carbon-supported Pt catalyst was employed as cathode catalyst in a direct methanol fuel cell where a 30% increase in power density was obtained when compared to Pt supported on Vulcan carbon, under the same conditions.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical devices proposed as a convenient power source for stationary and portable applications. Particularly, direct methanol fuel cells (DMFC) have showed the advantages of using a fuel with high volumetric energy density, easy handling, transport and operation [1–3]. However, the commercial viability of the DMFCs technology has been hindered by several challenges like the sluggish methanol oxidation and the methanol crossover through the membrane. Pt catalyst has been recognized as the best catalysts for oxygen reduction reaction (ORR) for the cathode of DMFCs [4,5]. However, the low Pt natural abundance, and therefore high cost, together with a complex reaction kinetic are drawbacks that must be overcome.

The use of a catalyst support has been proved to be an effective approach to lower the loading of noble metal in the catalysts and improve the catalytic mass activity [6–8]. In this regard, the preparation of particles with homogeneous size and dispersion, while reducing the Pt loading emerged as a solution to increase the catalytic mass efficiency [9]. Hence, synthesis conditions of Pt or Pt alloys nanoparticles as electrocatalytic materials possessing the aforementioned properties, have become of paramount importance [10,11]. The physical and chemical properties of the carbon support affect the structure and properties of the catalyst [12]. Carbon black, like Vulcan XC-72R, has been for long the material most commonly

---

* Corresponding author.
E-mail address: viva@tandar.cnea.gov.ar (F.A. Viva).

http://dx.doi.org/10.1016/j.jpowsour.2014.12.097

used as support in the preparation of commercial electrocatalysts for fuel cells [13]. Nonetheless, other types of carbon morphologies have been studied to improve the characteristics offered by carbon Vulcan XC-72R as support [14]. These include: carbon nanotubes, carbon nanofibers, carbon nanocoils, ordered carbons and macroporous carbons just to mention the most used [14–16]. High specific surface area in combination with a large number of anchoring sites of the carbon support provides highly dispersed particles of small size. However, a high specific surface area is associated with small pore sizes, which may not be advantageous. It is known that perfluorosulfonate-ionomer (Nafion) cannot penetrate into pores smaller than 20 nm [17–19]. Consequently, Pt nanoparticles deposited into these pores can become unavailable to participate in establishing a triple phase boundary [17,20]. Furthermore, small size pores provide inefficient mass transport for the reactants and products [18,19], suggesting that tailoring the carbon structure is necessary to achieve the best catalyst performance.

Structured carbons have emerged as promising materials to meet the aforementioned challenge [21–23] by adjusting the pore structure according to the one needed by the application [24,25]. In this sense, the porous material structure must provide an adequate substrate for nanoparticle anchoring, facilitate reactants mass transport and posses water handling capability for removing water generated at the cathode [26,27]. Although promising results were found for several structured carbon materials as supports, there is still information lacking about the best morphological structure of carbon supports on the cathode side of DMFCs, as well as the optimized methods to prepare MEAs with the structured carbon supported catalyst.

In this work, carbon with a pore size distribution centered at 20 nm was used as the catalyst support. The mesoporous carbon (MC) was obtained by carbonization of a structured resorcinol formaldehyde polymer, using a cationic polyelectrolyte as a structuring agent [28]. Specific surface area and pore size distribution of the carbon support were determined by nitrogen adsorption isotherm. Platinum nanoparticles supported on mesoporous carbon were obtained by the impregnation and reduction method with $NaBH_4$ as a reducing agent in basic aqueous media. Transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD), as well as electrochemical surface area measurement, were employed for the catalyst nanoparticles characterization. Finally, the performance of membrane electrode assembly (MEA) prepared with Pt nanoparticles supported on the MC as cathode catalyst of a DMFC was measured and compared against Pt deposited on Vulcan carbon by the same procedure.

2. Experimental

2.1. Mesoporous carbon preparation

Mesoporous carbon support was obtained using the method described elsewhere [29]. In brief, a precursor was prepared by polymerization of resorcinol (Fluka) and formaldehyde (Cicarelli, 37 wt %). Sodium acetate (Cicarelli) was used as catalyst, and a cationic polyelectrolyte (polydiallyl-dimethylammonium chloride, PDADMAC, Sigma–Aldrich) was used as a structuring agent. The reactive mixture of resorcinol (R), formaldehyde (F), and sodium acetate (C) was stirred at 40 °C for 10 min before the addition of PDADMAC (P) in a molar ratio of 1:3:0.04:0.03 (R:F:C:P), respectively. Once the mixture became homogeneous, the solution was heated to 70 °C for 48 h at atmospheric pressure. The resulting brown R–F piece was dried in air for 3 days. The polymer was then carbonized under nitrogen stream in a tubular furnace from ambient temperature to 1000 °C at a heating rate of 40 °C/h. Finally, the material was grinded and passed through a 40 μm pore sieve. An ASAP 2020 (Micrometrics) instrument was used to measure the nitrogen adsorption–desorption isotherms at −196 °C. The t-plot and Brunauer–Emmett–Teller (BET) methods were used to determine the micropores volume and the specific surface area, respectively. The pore size distribution was obtained from the desorption branch of the nitrogen isotherm by the Barrett–Joyner–Halenda (BJH) method.

2.2. Catalyst preparation

A solution of Pt metal precursor ($H_2PtCl_6 \cdot 6H_2O$, Tetrahedron) was added in a calculated amount to the slurry of the MC in order to achieve a metal loading of 40% w/w. The pH was adjusted to 8 with 1 M NaOH solution (Pro Analysis, Merck). The dispersion was heated at 80 °C. Then, $NaBH_4$ (granular 98%, Sigma–Aldrich) was added in a molar ratio $NaBH_4$ to metal salt of 5:1, and the temperature was maintained for an additional 2 h, followed by stirring for 12 h. The solid was separated by centrifugation, and it then was successively washed until the supernatant solution showed a neutral pH and absence of Cl^- by reaction with $AgNO_3$ (saturated solution). Pt supported on Vulcan carbon (Vulcan XC-72, Cabot) was prepared following the same procedure described above. The Vulcan was previously washed by boiling it in 30 wt % HCl aqueous solution.

2.3. Catalyst characterization

Powder X-ray diffraction pattern of the catalyst was obtained using a Siemens D5000 diffractometer with a Cu Kα source operating at 40 kV and 30 mA. The angle extended from 20° to 100° with a step size of 0.02° and a counting time of 2 s. Transmission electron microscope images were acquired with a Philips CM200, while energy dispersive X-ray spectrometry (EDS) was performed using an EDAX DC X4 to confirm the presence of Pt and the absence of other metals.

Thermogravimetric analyses (TGA) were performed with a Shimadzu TGA-51 instrument. Supported catalyst samples (5–10 mg) were heated up to 1000 °C at 5 °C per minute on a titanium crucible in air atmosphere (flow: 100 cm^3 min^{-1}). The metal content of the supported catalysts were calculated from the difference between the initial and final weights.

2.4. Electrochemical surface area (ECSA) determination

In order to determine the electroactive Pt surface area, CO stripping voltammetry was performed. A suspension of the supported catalyst was prepared and spread over the working electrode (WE), which contained a glassy carbon (SPI) disk 5 mm in diameter mounted in a Teflon rod connected through a gold wire. The Pt nanoparticles supported on the MC (Pt/MC) and on Vulcan carbon (Pt/C) were analyzed. The exposed face of the WE was sanded with 400 grit paper to get a rough surface before it was covered with the suspension. The CO stripping was performed in a double walled electrochemical cell with three electrodes and the temperature was maintained at 25.0 °C with a Tempunit TU-16D (Techne) temperature controller. The counter electrode (CE) consisted of a coiled Pt wire 0.5 mm in diameter and 30 cm length, whereas a Ag/AgCl (sat. KCl) electrode was used as a reference electrode (RE). All potentials were converted against the standard hydrogen electrode (SHE). A 0.5 M H_2SO_4 (95–97 %, Merck) solution was saturated with carbon monoxide (RG 4.8, Indura) for 60 min to allow the complete coverage of CO onto the catalyst surface, while maintaining the working electrode potential at 0.25 V vs. SHE. The excess CO in the solution was purged with N_2 (RG 4.8, Indura) gas for 15 min at a constant potential of 0.25 V vs. SHE. Finally, the