

Carbon Aerogels -Supported Pt with Applications in Fuel-Cells

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ABSTRACT

Highly dispersed platinum (Pt)-based nanoparticles still remain the most practical catalysts in fuel cells technology [1]. These Pt nanoparticles are normally supported on carbon particles in order to increase the active Pt surface and improve the catalyst utilization [2]. The researches in field are oriented to improve the support materials with nanometer Pt aiming at low densities, high surface area, continuous porosity and high catalytic activity, lower poisoning [3-5].

The main focus of this paper is the development of carbon aerogel-supported Pt as better alternative catalyst to Pt/C. The carbon aerogel-supported Pt catalysts were prepared by a conventional borohydride reduction method.

The electrochemical characteristics and the catalytic activity for oxygen reduction of the carbon aerogel-supported Pt based catalysts were evaluated and compared with Pt/C. In addition EDAX measurements were done to evaluate the final content of metal catalyst related to the carbon content.

The results conclude that carbon aerogels are promising low Pt loading support keeping the catalyst activity at high level.

Keywords: Carbon aerogel, Pt catalysts, fuel cell

1 INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) have drawn a great deal of attention in both fundamental and application in recent years [6]. Carbon-supported Pt or Pt-based alloys still remain as reference electrocatalysts for the anodic and cathodic reactions in fuel cells [1]. Pt loading and particle size, as well as the nature of the catalyst support, are key issues for efficiently electrodes for electrocatalysis reactions.

Some promising approaches and results are reported for Pt loading reduction through alloying or nanoparticle supporting procedure. For MEA Pt loading reduction, the researches are focused on improving the reactive surface area for Pt. In this respect Pt was supported on some high-surface area electronically conductive substrates such as carbon particles.

Carbon aerogels [3], first developed at the end of the 1980s, have received considerable attention in the literature because of their chemical and textural properties and simple preparation [7, 8]. Carbon aerogel-supported Pt (Pt/CA) joins the catalytic properties of the Pt with controllable and attractive structural properties of the aerogels. The research is focused on mesoporous carbon aerogels synthesized by sol-gel method- CO₂ supercritical drying with subsequent nitrogen atmosphere pyrolysis.

The main purposes for using carbon aerogel (CA)-supported Pt catalysts are to reduce Pt loading through increasing the catalyst utilization, and improving the catalyst activity/performance. This contribution focused on the development of Pt based catalysts prepared by impregnation-reduction method using NaBH₄ and Pt metal precursor. The carbon aerogel (CA) was used as Pt support. The catalytic activity for oxygen reaction reduction (ORR) is an important issue that is addressed in the fabrication of fuel cell systems because it limits their performance. Pt/CA and Pt/C electrocatalysts will be tested in acidic media to assess the electrocatalytic activity toward the ORR. In addition, EDAX measurements were done to evaluate the final content of Pt:CA.

2 EXPERIMENTAL

Carbon aerogels with meso- and macroporosity were obtained by sol-gel method using a proprietary method [9]: wet resorcinol-formaldehyde (RF) gels were prepared by polycondensation of resorcinol (R) and formaldehyde (F), in the presence of a basic catalyst (C). RF gels were

transformed into organic aerogels by CO₂ supercritical drying. RF converted in CA by pyrolysis under nitrogen atmosphere.

Surface area and pore size distribution were performed by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods using an ASAP 2000 surface area analyzer (Micrometrics Instruments Corp.). About 0.03g of sample was heated under vacuum (10⁻⁵ torr) to 110°C (for organic aerogels) and 130°C (for carbon aerogels) for at least 20 hours to remove all adsorbed species.

The Pt/CA and Pt/C catalysts were prepared by a conventional borohydride reduction method using NaBH₄ (15 mM) and H₂PtCl₆ (10%) – (Sigma-Aldrich products) as metal precursor. The composition was determined by energy-dispersive X-ray analysis (EDAX). The electrochemical measurements were carried out with a VoltaLab 40 potentiostat using a conventional three-electrode electrochemical cell (Pt mesh, counter and CR5/Hg₂SO₄ - MMS reference electrode). The working electrode: PTFE 20% toray carbon paper loaded by spraying with Pt/C and Pt/CA catalysts ink. The catalyst ink was prepared by sonicating the catalyst powder in isopropyl alcohol for 60 min. The cyclic voltammetry (CV) were carried out at room temperature in a solution containing 0.5M H₂SO₄ degassed with nitrogen (30 min) and saturated in oxygen. All CVs were reported to current background in degassed nitrogen solution. To characterize the activity of the Pt-catalyzed electrodes toward the ORR, linear sweep cyclic voltammograms were recorded at a scan rate of 10 mV s⁻¹ in 0.5 M H₂SO₄ saturated with oxygen.

The composition of the prepared catalysts was determined by energy-dispersive X-ray analysis (EDAX) in a FEI-Quanta 400 scanning electron microscope provided with microanalyser.

3 RESULT AND DISSCUTIONS

Using the reactants ratios R/C = 50 [mol/mol], R/F = 0,5 [mol/mol] and R/H₂O = 0,2 [g/cm³] a mesoporous carbon aerogel with BET surface of 860 m²/g (fig 1) was obtained.

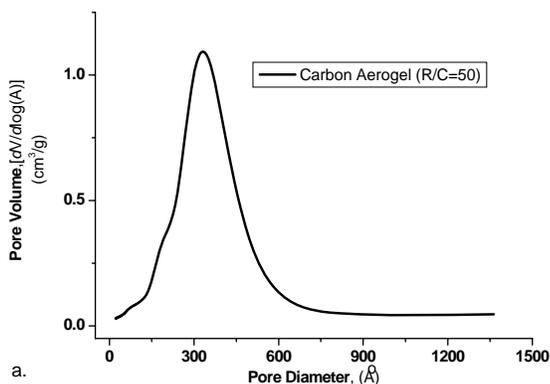


Figure 1. Pore size distribution of the carbon aerogels

The surface area of carbon aerogel is much higher than that of common support material, Cabot Vulcan XC-72, 235 m²/g [10].

By EDAX analysis the following composition was obtained C: 65,18 (wt%), Pt: 32,47 (wt%), and O: 2,35 (wt%) for Pt/CA and C: 60,33 (wt%), Pt: 38,82 (wt%), and O: 0,85 (wt%) for Pt/C. Results by EDAX analyses have indicated that the final compositions of Pt/CA and Pt/C were close to the proposed one of Pt (40 wt%):CA(60 wt%).

Figure 2 shows cyclic voltammetry measurements (CVs) of carbon supported platinum and carbon aerogels supported platinum. Taking in account the EDAX results the current density scale was normalized for the Pt loading. Well-defined hydrogen adsorption-desorption features are seen in the cyclic voltammogram curve of the Pt/CA electrode in 0.5M H₂SO₄ solution at 25 °C compared with Pt/C (Fig. 2) therefore indicating that the prepared Pt/CA materials have active sites that might be suitable for use in electrocatalysis.

Figure 2 show that the area of the hydrogen adsorption and desorption peaks for Pt/CA catalyst are larger in respect with the Pt/C indicating that the electrochemically active surface area of the Pt/CA catalyst is much larger. That is a consequence of the high CA- surface area which rises to larger activity surface displayed by Pt-catalyst centers.

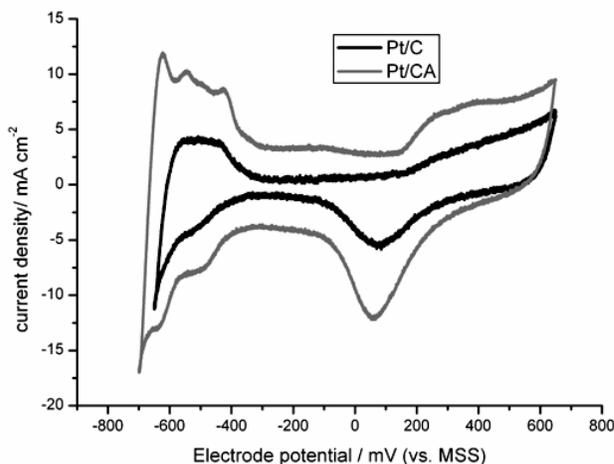


Figure 2. CVs: Pt/C and Pt/CA(c) in 0.5M H₂SO₄ solution at 25 °C (10mV/s scan rate).

To have a comparison of electrocatalysts activity towards ORR, Fig. 3 displays the linear sweep voltammograms (LSV) in saturated oxygen - 0.5 M H₂SO₄ solution of Pt/C and Pt/CA catalyst electrodes. The current density scale was normalized for the Pt loading in concordance with EDAX analysis. Pt/C and Pt/CA have a good electroactivity towards ORR, the oxygen reduction occurs at ca. 0, 52 for Pt/CA and 0,54 V for Pt/C. Moreover, the LSV show that

the limiting current density towards ORR for Pt/CA catalyst electrode is higher than for Pt/C.

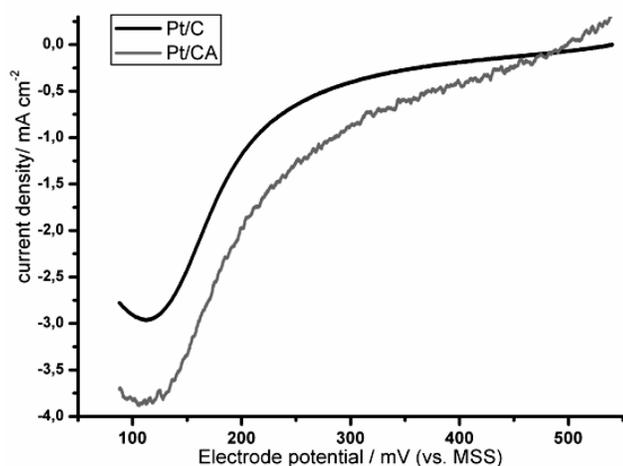


Figure 3. LSV with 5 mV/s scan rate of Pt/C and Pt/CA in 0.5 M H₂SO₄ saturated O₂

How it can be observed from Figure 3, the catalytic activity towards ORR of the Pt/CA nanoparticles is better but comparable with that of the Pt/Vulcan XC72.

4. CONCLUSIONS

A simple and effective chemical method has been successfully used for synthesis of carbon aerogel-supported platinum. Pt/CA catalysts prepared by the borohydride reduction method shown an improved electrocatalytic activity with better electrochemically active surface area compared with the Pt/C. The linear sweep voltammetry show the limiting current density in ORR oxygen reduction larger for the Pt/CA catalyst electrode than Pt/C. Based on these results we can conclude that carbon aerogel is a better alternative to support Pt instead of black carbon: increase catalyst loading, surface area and current density keeping high catalytic activity. According to the results obtained, carbon aerogels -supported Pt catalysts could be very promising materials to fuel cell technology.

ACKNOWLEDGMENT

This work was supported by the Grants CEEEX No. 760/2006.

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