Applied Catalysis A: General 355 (2009) 132–138

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Characterization of nitric acid functionalized carbon black and its evaluation as electrocatalyst support for direct methanol fuel cell applications

Marcelo Carmo [a,b,*], Marcelo Linardi [b], João Guilherme Rocha Poco [a]

[a] Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Av. Prof. Almeida Prado 532, Cid. Universitária, 05508-901 São Paulo, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN, Av. Prof. Lineu Prestes 2242, Cid. Universitária, 05508-000 São Paulo, Brazil

ARTICLE INFO

Article history:
Received 17 March 2008
Received in revised form 4 December 2008
Accepted 5 December 2008
Available online 11 December 2008

Keywords:
Carbon functionalization
HNO_3
Electrocatalysis
Fuel cell
PEMFC
DMFC

ABSTRACT

This study presents results on PtRu electrocatalysts supported on both as received and functionalized carbon black. The electrochemical properties of both home-made and commercial PtRu electrocatalysts were compared to PtRu supported on functionalized carbon black. The PtRu nanoparticles were synthesized by the impregnation method and subsequent alcohol reduction. Transmission electron microscopy experiments revealed that the PtRu electrocatalysts supported on functionalized carbon black are more homogeneously distributed than all other studied materials. Cyclic voltammetric electrocatalyst curves experiments showed higher activity for the PtRu supported on functionalized carbon black. This enhanced performance is related to the better nanoparticle distribution on functionalized carbon black. The better performance can also be inferred by the better nanoparticles utilization. The nanoparticles are now located outside from the pore structure of the carbon black. Hence, the nanoparticles are more exposed and available to the reactants, enhancing the catalyst performance and avoiding the waste of noble catalysts.

1. Introduction

Hydrogen is currently the most efficient and commonly used fuel for polymer electrolyte membrane fuel cell (PEMFC). However the cost of its production and the problems associated with its storage and distribution make the application of this fuel a challenge [1,2]. Several studies investigate the utilization of methanol as a fuel to operate the PEMFC [3–6]. In this case the cell is called as direct methanol fuel cell (DMFC). However, there are still drawbacks regarding the use of such a fuel. The electrochemical oxidation reaction of methanol is a less efficient process compared to the hydrogen oxidation. Poisoning intermediates are formed due to incomplete methanol oxidation, mainly carbon monoxide (CO). In order to overcome the CO poisoning, an alternative to favor the CO oxidation is the use of a second metal, e.g. ruthenium (Ru) [7]. The added Ru is able to form oxygenated species, facilitating the oxidation of the CO_{ads} to carbon dioxide (CO_2) at lower potentials than platinum. This phenomenon is called bifunctional mechanism and was first considered by Watanabe and Motoo [8]. Moreover, an electronic effect, which weakens the CO_{ads} bond on the surface and results in a higher power density for DMFC application was proposed [9]. Carbon black is frequently used as the catalyst support because of its relative high stability in both acid and basic media, good electronic conductivity and high specific surface area. The support material has a strong influence on the properties of the catalysts, such as metal particle size, electrochemical active area and size distribution. Furthermore, degree of alloying, stability, mass transport and electronic conductivity of the catalytic layer are also affected by the chosen support material. Hence, the optimization of carbon supports plays an important role for the future PEMFC technology. The support should be well selected, with a suitable specific surface area, porosity, morphology, surface functional groups and electronic conductivity. Corrosion resistance is also a crucial parameter to be considered, while developing an active commercial catalyst. Most of these parameters are affected by the process used to prepare the carbon black. Carbon black still reveals inadequacies for this purpose [10,11]. Consequently, the carbon support can be modified at the micro(nano)scopic level. One would be the chemical modification of the carbon black surface used to anchor the nanoparticles of the electrocatalysts. Chemical reactions could be applied to encapsulate, protect and change the hydrophobic/hydrophilic character of the materials. By this means, the reactivity can be changed, catalytic properties modified as well as, composites created and polarities changed (zeta potential) [12–17].

---

[*] Corresponding author at: Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Av. Prof. Almeida Prado 532, Cid. Universitária, 05508-901 São Paulo, Brazil.
E-mail address: marcelocarmo1@gmail.com (M. Carmo).

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.12.010

In this study, functionalization of the carbon black surface by nitric acid treatment was carried out; introducing oxygenated functional groups, modifying its properties and hindering both agglomeration and/or loss of active surface.

2. Experimental

A commercial carbon black Vulcan XC72R (Cabot) was used as a support. This carbon was functionalized with concentrated nitric acid at 80 °C, refluxed for 24 h (sample labeled XC72R-HNO_3). The functionalized carbon was filtered, washed until water reached pH neutral and dried at 110 °C overnight. The functionalized carbon was labeled C-HNO_3.

Carbon-supported electrocatalysts were prepared through impregnation method and subsequent alcohol reduction [18–20]. A mixture of the desirable metallic ions solution was used as precursor, where the ions were reduced to their metal forms, using ethylene glycol (Merck) as solvent and reducing agent in the presence of the carbon support. PtRu/C (20 wt.%, Pt:Ru atomic ratio of 1:1) was prepared using this procedure. $H_2PtCl_6{\cdot}6H_2O$ (Aldrich) and $RuCl_3{\cdot}2H_2O$ (Aldrich) were used as metal sources. High surface area carbon black Vulcan XC-72R as delivered and functionalized carbon black C-HNO_3 were used as supports. In this procedure the salts were first added to the carbon support, followed by an ethylene glycol solution (75:25—ethylene glycol:water). The system was ultrasonically treated for 15 min. It was then refluxed and heated at 160 °C for 1 h. The resulting powder was filtered, washed with distillated water and dried in air at 110 °C overnight. PtRu/C (20 wt.%, Pt:Ru atomic ratio of 1:1) commercial electrocatalysts from Etek® Basf Fuel Cell Inc. was used for comparative purposes.

The chemical analysis of the surface functionalities was carried out following the Boehm method [21], which uses aqueous solutions of bases of different strengths to determine the acidic groups: carboxyls, lactones and phenols. For this purpose, different batches of 0.25 g of sample was in contact, at 298 K for 60 h, with 25 cm^3 of solutions of $NaHCO_3$ (0.1 M), Na_2CO_3 (0.05 M) and NaOH (0.1 M), respectively. Then the aqueous solutions were titrated with standard HCl. According to the method, $NaHCO_3$ neutralizes the carboxyl groups, lactones are determined by the difference between the groups neutralized by Na_2CO_3 and $NaHCO_3$ and the difference between the groups neutralized by NaOH and Na_2CO_3 is phenols. Moreover, the basic groups are analyzed in a similar way by neutralization with HCl solutions and further titration with NaOH.

A NOVA 300 Brunauer–Emmet–Teller (BET) analyzer was used to determine the specific surface area of the carbons. Prior to measurement, the carbon samples were purged with pure nitrogen gas overnight at a temperature of 150 °C to remove any contaminants and moisture that may have been present in the carbon support.

A laser scattering (LS) LS230 small volume module plus–coulter was used to estimate the average particle size of the carbons in an aqueous colloidal system. Before measuring, 5 mg of the sample was dispersed in water and sonicated for at least 48 h.

A thermal analysis system Star SDTA851^e module from Mettler/Toledo with Stare version SW 8.01 software was used for thermal gravimetric analysis at a heating rate of 10 °C min^{-1} from 25 to 1000 °C, in nitrogen flow at 50 mL min^{-1}.

Electrokinetic potentials (zeta potentials) for the carbon particles were determined by using a zeta probe zeta potential analyser–colloidal dynamics, 250 mg of sample was dispersed in 250 mL of 0.01 mol L^{-1} KCl solution, sonicated and magnetically stirred for at least 48 h before the measurements were carried out. To generate the zeta potential vs. pH curves and from them the isoelectric point or zero charge potential (E_{zc}), the pH of the slurry was adjusted using HCl and NaOH solutions, followed by mechanical stirring (usually 24 h).

The Pt:Ru atomic ratios of the electrocatalysts were obtained by using a Philips XL30 scanning electron microscope coupled to an EDAX DX-4 microanalyzer with a 20 keV electron beam.

The X-ray diffraction (XRD) analyses were performed using a STOE STADI-P diffractometer with germanium monochromized Cu Kα radiation and position-sensitive detector with 40 apertures in transmission mode. The X-ray diffractograms were obtained with a scan rate of 1° min^{-1} and an incident wavelength of 1.5406 Å (Cu Kα). The average crystallite size was estimated with the XRD data and the Scherer equation [22].

The transmission electron microscopy (TEM) characterization was done using a JEOL JEM-1200EX microscope and the average particle size was calculated using the Image Tool Software Lince with one TEM micrograph for each catalyst and counting 300 particles/picture.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [23,24]. An amount of 10 mg of the electrocatalysts was added to 10 g of water. The mixture was submitted to an ultrasound bath for 5 min, where two drops of a 6% PTFE (polytetrafluorethylene) water suspension were added. Again, the mixture was submitted to an ultrasound bath for 5 min, filtered and transferred to the working electrode support cavity (0.30 mm deep and area of 0.36 cm^2). The quantity of the electrocatalysts in the working electrode was determined with a precision of 0.0001 g. In the cyclic voltammetry (CV) experiments, the current values (I) were expressed in Ampere and were normalized per gram of platinum ($Ag_{metal}{}^{1-}$). The reference electrode was an RHE (reversible hydrogen electrode) and the counter electrode was a platinized Pt net with 4 cm^2. Electrochemical measurements were taken using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a computer and using the Microquimica Software. Cyclic voltammetry was performed in a 0.5 mol L^{-1} H_2SO_4 solution saturated with N_2.

The evaluation of the 1.0 mol L^{-1} methanol solution oxidation was performed at 25 °C in H_2SO_4 0.5 mol L^{-1}. For comparative purposes, a commercial carbon supported Pt and PtRu catalysts from Etek® (20 wt.%; Pt:Ru molar ratio 1:1) was used.

3. Results and discussion

The results of the chemical titrations (Boehm method), collected in Table 1, show that the treatments with nitric acid produce changes in the chemical surface group content. This is probably because the very strong oxidizing character so that the activation energy to react with carbon is almost negligible [24]. The reaction with nitric acid introduces a very large amount of acidic groups. This is particularly relevant for carboxyls and phenols, although the amount of lactones is threefold larger than in the original sample.

The results of the BET surface area are summarized in Table 2. The BET surface area of the support decreased 44% after nitric acid treatment. It indicates that the treatment changed the carbon structure. A small reduction in the surface area of carbons after oxidants treatment was already observed [25]. The authors showed that the oxygenated groups are introduced in the carbon pore structure, resulting in a carbon pore blockage.

Table 1
Chemical surface groups (mequiv. g^{-1}).

Sample	Carboxyls	Lactones	Phenols	Basic
Vulcan XC72R	0.180	0.126	0.098	0.207
Vulcan XC72R-HNO_3	1.467	0.384	0.875	0.231