Journal of Power Sources 196 (2011) 4226–4235

Contents lists available at ScienceDirect

Journal of Power Sources

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

Pt and PtRu electrocatalysts supported on carbon xerogels for direct methanol fuel cells

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ARTICLE INFO

Article history:
Received 20 July 2010
Received in revised form
23 September 2010
Accepted 18 October 2010
Available online 26 October 2010

Keywords:
Pt
PtRu
DMFC
Carbon xerogel
Functionalization
CO and methanol oxidation

ABSTRACT

Carbon xerogels (CXs) have been prepared by polycondensation of resorcinol and formaldehyde in water by the sol–gel method. Functionalization with diluted and concentrated nitric acid as oxidizing agents was carried out to create surface oxygen groups, acting as anchoring sites for metallic particles. Characterization techniques included nitrogen physisorption, scanning electron microscopy, temperature programmed desorption and temperature programmed oxidation. Functionalized xerogels were used as supports to synthesize Pt and PtRu electrocatalysts by a conventional impregnation method. Catalysts electrochemical activity towards the oxidation of methanol was studied by cyclic voltammetry and chronoamperometry to establish the effect of the surface chemistry on the catalysts synthesis. Carbon monoxide oxidation was also studied to determine the electrochemical active area and the CO tolerance of the as prepared catalysts. Results were compared to those obtained with commercial Pt/C and PtRu/C catalysts supported on Vulcan XC-72R (E-TEK). All electrocatalysts supported on carbon xerogel showed better performances than commercial ones, providing higher current density values for the oxidation of methanol.

1. Introduction

Direct methanol fuel cells (DMFCs) are regarded as promising power sources for portable electronic devices and domestic and automotive applications, having the advantages of ease of handling of the fuel and flexibility of cell operation [1]. However the commercialization of DMFCs is still hindered by some technical challenges, mainly: (1) slow kinetics of methanol oxidation reactions at the anode at low temperatures and (2) methanol crossover [2]. Pt-based catalysts have been widely recognized as the best electrocatalysts for DMFCs. However, the limited availability and high price of Pt are significant barriers to the widespread use of this type of fuel cells. To reduce the cost of fuel cells, one of the important challenges is the development of Pt free catalysts or catalysts with a lower content of this metal. For this reason, binary and ternary Pt-based catalysts and non-Pt-based ones have been tested as electrode materials for DMFCs [3]. Among bimetallic Pt catalysts, the Pt–Ru system is the best known for its activity in the electrochemical methanol oxidation reaction [4–8]. At room temperature methanol does not oxidize on Ru but this metal can promote the oxidation of CO adsorbed as intermediate of this reaction on Pt at more negative potentials [9]. The formation of an oxygenated species on Pt is reputedly difficult, as Pt–OH groups are only formed, in substantial quantities, above ca. +0.7 V vs. RHE. Ru is more easily oxidized than Pt and thus is able to oxidize the methanol adsorbate at a lower potential. The promotor acts via a so-called bi-functional mechanism, as was suggested for Ru [10]. Nevertheless the efficiency of the DMFC operating with this catalyst is still insufficient for practical applications. Therefore, further optimization of the anode material for DMFC is necessary for its development and commercialisation.

In this context, an attractive approach that appears as a possible solution to reduce Pt loading and increase the catalytic efficiency is to use novel carbonaceous materials as support. The nature of the support as well as the interaction between the former and the metal have been demonstrated to be extremely important, given that determines the physicochemical properties of catalysts, such as dispersion, stability and morphology of metallic crystallites [11–13]. In addition, characteristics of the support can also determine the electrochemical properties of catalysts by altering mass transport, active electrochemical area and metal nanoparticle stability during the cell operation [14,15]. Hence, the optimization of carbon supports is very important in DMFC technology development.

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doi:10.1016/j.jpowsour.2010.10.049

Among all kinds of carbon supports, carbon blacks are the most commonly materials used as support in the preparation of commercial electrocatalysts for DMFCs, being Vulcan XC-72R the most widely used support. This material shows high mesoporous distribution and high electrical conductivity [16]. However, although Vulcan XC-72R has a suitable specific surface area, it still exhibits insufficient properties for this purpose. This is due to other factors, such as pore size distribution or surface chemistry, that also affect the preparation and performance of the electrocatalysts. For this reason, novel non-conventional carbon materials are being studied as electrocatalyst support in order to replace Vulcan XC-72R. Among these novel carbon material, carbon nanotubes [2,11], carbon nanofibers [17–20] ordered mesoporous carbons [21] and carbon xerogels and aerogels [1,11,19,22–30] are being studied.

Carbon xerogels are attracting much attention for their unique and controllable properties, such as high surface area, mesopore structure with narrow pore size distribution, and high purity, which in turn, are attributed to the synthesis reaction mechanism, being similar to the sol–gel process. Their preparation, consisting on the polycondensation of resorcinol with formaldehyde followed by drying and pyrolysis, avoids supercritical drying required for the synthesis of carbon aerogels, offering great advantages in terms of cost and safety [1]. Besides, their three-dimensionally interconnected uniform pore structure allows a high degree of dispersion of the active phase and an efficient diffusion of reagents.

Some papers have appeared in the literature during the last decade concerning the use of carbon aerogels and xerogels as catalysts supports. Rolison and co-workers synthesized highly active electrocatalytic nanostructured architectures constructed from colloidal-Pt-modified carbon–silica composite aerogels. These materials increased by 4 orders of magnitude per gram of Pt the electrocatalytic activity for methanol oxidation than Pt-modified carbon powder [31]. More recently, the same group prepared thiophene-modified aerogels. The sulphur-functionalized carbon aerogel was tested in CO-stripping voltammetry and examined for oxygen reduction activity, in order to study the ability of the material to mimic the thiophene-mediated precious metal binding occurring with Vulcan carbon. The results obtained suggested that these functionalized nanoarchitectures may improve the applicability of carbon aerogel electrode structures for fuel cell and other electrocatalytic applications [32].

Job and co-workers [22] prepared Pt/C catalysts by impregnation using three xerogels with various pore textures as supports. The specific catalytic activity obtained for benzene hydrogenation was 4–10 times higher than that obtained with active charcoal-supported catalysts prepared by a similar method. The high dispersion of Pt was attributed to the presence in the xerogel of large mesopore or macropore volumes, which facilitates impregnation.

In a more recent paper [33], the same group synthesized carbon xerogels with various pore textures by evaporative drying and pyrolysis of resorcinol–formaldehyde gels, and used them as supports for Pt catalysts in PEM fuel cell cathodes. Results were compared with those for catalysts supported on carbon aerogels, yielding similar performances.

On the other hand, Mastragostino and co-workers [3] studied the specific catalytic activity of DMFC anodes based on PtRu catalysts deposited by chemical and electrochemical route on mesoporous cryo- and xerogel carbons. Their results were compared with those obtained with PtRu supported on Vulcan, being the specific catalytic activity more than double when Vulcan is substituted by former carbons.

Finally, Samant and co-workers [23] also synthesized highly mesoporous carbon via sol–gel condensation of resorcinol and formaldehyde. Electrooxidation of methanol in alkaline electrolyte was carried out using Pt and PtNi catalysts supported on highly mesoporous carbon xerogels. The electrocatalytic tests showed better performance of the catalysts when impregnated on this kind of carbon support.

In a more recent work [13], the same group prepared multiwalled carbon nanotubes and high surface area mesoporous carbon xerogel and used them as supports for monometallic Pt and bimetallic PtRu catalysts. In order to assess the influence of the oxygen surface groups of the support, the mesoporous carbon xerogel was also oxidized with diluted oxygen before impregnation. A remarkable increase in the activity was observed when the PtRu catalysts were supported on the oxidized xerogel. This effect was explained in terms of the metal oxidation state. It was shown that the oxidized support helps to maintain the metals in the metallic state, as required for the electro-oxidation of methanol.

In this paper, mesoporous carbon xerogels have been synthesized and functionalized by different oxidation treatments. Then, Pt and PtRu nanoparticles have been deposited by an impregnation method on the as-prepared xerogels. Physicochemical properties of catalysts have been studied by X-ray (EDX, XRD) and microscopic (TEM) methods in order to determine the influence of the support. On the other hand, cyclic voltammetry and chronoamperometry have been used to analyze the influence of the support on the activity towards carbon monoxide and methanol oxidation. Commercial Pt and PtRu supported catalysts (E-TEK) have also been studied for comparison.

2. Experimental

2.1. Synthesis of carbon xerogels

Resorcinol(1,3-dihydroxybenzoic acid)–formaldehyde organic gels were synthesized by the sol–gel method first proposed by Pekala [25]. The necessary amounts of resorcinol (*R*) (98% Sigma–Aldrich) and sodium carbonate deca-hydrated (*C*) (Panreac) (molar ratio $R/C = 50$) were dissolved in 120 mL of deionized water under stirring. Subsequently, the required volume of formaldehyde (*F*) (37 wt.% aqueous solution, Sigma–Aldrich) (molar ratio $R/F = 0.5$) was added to the former mixture and pH was adjusted to 6 with an aqueous solution of 2 M HNO_3. The mixture was stirred for 30 minutes and then poured into sealed flasks, followed by curing for 24 h at room temperature, 24 h at 50 °C and 5 days at 85 °C until curing was complete as described elsewhere [26]. Afterwards gels were washed with acetone for three days to exchange the initial solvent, water. Acetone was daily replaced after vacuum filtration. This procedure allows keeping the original gel structure, as surface tension caused by evaporation of the solvent is lower for acetone than for water [30]. Finally, wet gels were dried in an oven at 65 °C and held for 5 h, and then, temperature was risen up to 110 °C and held for another 5 h, as described elsewhere [27]. Pyrolysis of all organic gels was carried out in a tubular furnace at 800 °C for 3 h under a flow of 100 mL min^{-1} N_2.

2.2. Carbon xerogel functionalization

Carbon xerogels were oxidized under different conditions in order to create surface oxygen groups that act as anchoring sites for metallic particles, besides improving its dispersion onto the support [34–38]. The oxidation treatments were performed at room temperature with 2 M and concentrated HNO_3 (65%) for 30 and 120 min. Oxidized materials were subsequently washed with deionized water until complete removal of the acid, and dried in an oven at 108 °C for 24 h. Carbon xerogels so obtained were named as follows: for example, CX_Nc_30 corresponds to a carbon xerogel (CX) where Nc (or Nd) stands for concentrated (or diluted) nitric acid, and numbers (30 or 120) correspond to the duration (min) of the oxidation process.