Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbon 44 (2006) 133–140
CARBON
www.elsevier.com/locate/carbon

Effects of ozone treatment of carbon support on Pt–Ru/C catalysts performance for direct methanol fuel cell

Zhen-Bo Wang *, Ge-Ping Yin, Peng-Fei Shi

Department of Applied Chemistry, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China

Received 17 August 2004; accepted 28 June 2005
Available online 18 August 2005

Abstract

This research is aimed to increase the activity and utilization of Pt–Ru alloy catalysts and thus to lower the catalyst loading in anodes for methanol electrooxidation. The Pt–Ru/C catalysts were prepared by chemical reduction. The support of Vulcan XC-72 carbon black was pretreated by ozone at different temperatures for different times. The specific surface area of the samples was evaluated by the standard BET method. The surface concentrations of oxygen were determined by XPS. The results showed that the surface concentrations of oxygen on the carbon were first decreased and then increased with pretreating times, and the specific surface area of the carbon was decreased with pretreating times at the same temperature. The specific surface area was increased with increasing temperature, and the surface concentration of oxygen was first decreased and then increased with increasing temperature for the same pretreating time. Pt–Ru/C catalysts supported by untreated and O_3 treated carbon black were characterized and tested for methanol electrooxidation. X-ray diffraction (XRD) was used to characterize the influence of carbon treated with ozone on Pt–Ru/C catalysts. It was found that the catalysts were composed only of f.c.c. Pt–Ru alloy particles without metallic Ru or Ru oxide. Cyclic voltammetry (CV) and Tafel curves were used for methanol electrooxidation on Pt–Ru/C catalysts in a solution of 0.5 mol/L CH_3OH and 0.5 mol/L H_2SO_4, showing that the catalytic activity of Pt–Ru/C catalysts supported by ozone treated carbon was higher than that by the untreated one. The ozone treatment time and temperature, which affect the performance of Pt–Ru/C catalysts, were discussed. Electrochemical measurements showed that the catalysts supported by the carbon after ozone treatment for 6 min at 140 °C had the best performance.

Keywords: Carbon black; Ozone treatment; Electrochemical analysis; Electrochemical properties

1. Introduction

The direct methanol fuel cell (DMFC) uses aqueous methanol directly without prior reforming [1,2]. The structure of the DMFC is simple. DMFC has been receiving increasing attention due to its advantages of easy transportation and storage of the fuel, reduced system weight, size and complexity, high energy efficiency and low exhaustion [3]. The current main drawback of DMFC is its very sluggish anode reaction of methanol electrooxidation, which gives rise to a very low overall cell performance, especially at low temperatures. There is a need to improve the activity of catalysts for methanol electrooxidation [4]. Pt–Ru alloys are still considered to be the best catalysts because of their tolerance to CO, and are widely used in DMFC. The performance, structure, dispersivity and morphology of the catalysts are influenced by the preparation methods, their technology [5–7], and the pretreatment of the carbon support [8,9]. There are many methods for pretreating the carbon. For instance, carbon is heated in air to increase the surface concentration of the active functional groups containing oxygen [10]. But heat treatment at 950 °C or higher with

* Corresponding author. Tel./fax: +86 451 86402576.
E-mail address: wangzhenbo1008@yahoo.com.cn (Z.-B. Wang).

0008-6223/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbon.2005.06.043

argon atmosphere consumes energy and gives a poor result. Such groups are produced when activated carbon is treated in a solution with different oxidizing agents of NaOH [11], HNO_3 [12], $(NH_4)_2S_2O_8$ and H_2O_2 [13], or anodically oxidized in KOH solution [14]. However, these wet treatments, in most cases, are not easy to be controlled and to clean the residuals on the carbon, and may cause environmental pollution by the acid and alkaline left. Plasma of oxygen [13,15] and oxygen [16] treatments seem to be the promising techniques, as they are able to introduce different chemical groups on the surface and bring about small changes in pore volume, surface area, and pore size distribution. However, these methods of treatment use complex equipment for a long treating time. The oxygen-containing functional groups can be formed in the surface when carbon fibers [17] and activated carbon [18] are treated by ozone. The surface oxygen concentration on carbon treated with O_3 is high. O_3 treatment is rapid without pollution, and reproducible. Activated carbon after O_3 treatment is usually used for making electrochemical capacitors. The O_3 treated carbon black used as a support for catalysts has not been reported, and its effect on the performance of catalysts is unknown.

In this work, the surface oxygen concentration and specific surface area of Vulcan XC-72 carbon black were determined after different temperatures and times of O_3 treatment. The O_3 treated carbon black was used as a support for the catalyst. The Pt–Ru/C catalysts were prepared by chemical reduction of the precursors. The effect of O_3 treated carbon support on catalysts performance was studied.

2. Experimental

2.1. Carbon support pretreatment

10 g of carbon black (Vulcan XC-72, Cabot International) was weighed and put smoothly in each of the four culture dishes with a diameter of 20 cm. Then they were treated by O_3 of 45 mg/L at a temperature of 100 °C for 2, 4, 6 and 8 min, respectively. Then 10 g carbon black was treated by O_3 for 6 min at 60, 100, 140 and 180 °C, respectively. The treated carbon black was then transferred into a vacuum vessel for storage.

2.2. Preparation of catalysts

The O_3 treated carbon black powder was used as a support for the catalyst. All the samples contained 20% in weight of catalyst. 0.25 g Pt–Ru(with an atomic ratio of 1:1)/C catalyst was obtained by chemical reduction with formaldehyde of H_2PtCl_6 and $RuCl_3$ as precursors at 80 °C. The O_3 treated carbon black was ultrasonically dispersed in ultrapure water and isopropyl alcohol for 20 min. The precursors were added to the ink and then mixed thoroughly for 15 min. The pH value of the ink was adjusted by NaOH solution to 8 and then increased its temperature to 80 °C. A solution of formaldehyde (1 mol/L) was added into the ink drop by drop and the bath was stirred for 1 h. The reductive reactions can be expressed by the following equations:

$$H_2PtCl_6 + 6NaOH + HCHO \rightarrow Pt + CO_2 + 6NaCl + 5H_2O \quad (1)$$

$$4RuCl_3 + 12NaOH + 3HCHO \rightarrow 4Ru + 3CO_2 + 12NaCl + 9H_2O \quad (2)$$

The mixtures were cooled, dried and washed repeatedly with ultrapure water until no Cl^- ions exist. The catalyst powder was dried for 3 h at 80 °C and stored in a vacuum vessel.

2.3. Preparation of powder microelectrode and electrochemical measurements

Powder microelectrode was made of a glass tube of 5–6 mm inner diameter and a total length of 150 mm sealed with a platinum wire of 130 μm diameter and 2 cm length, and a copper wire of 300 μm diameter as a conducting one in the glass tube was end to end adhered to the Pt wire by electroconductive adhesive. The other end of the Pt wire with the lower end of the tube was dissolved by aqua regia, forming a cylindrical cavity with a depth of 130 μm. After cleaning and drying, the Pt–Ru/C catalyst powder was filled into the cylindrical cavity, becoming the powder microelectrode.

Electrochemical measurements were carried out with a two-electrode cell at 25 °C. The powder microelectrode was the working electrode, and a Pt foil of 1 cm^2 area was the counter one. All potential values are vs. RHE. A solution of 0.5 mol/L CH_3OH and 0.5 mol/L H_2SO_4 was stirred constantly and purged with ultrapure argon gas. All chemicals used were of analytical grade. Electrochemical experiments were performed with a CHI630A electrochemical analysis instrument. Cyclic voltammetry (CV) was performed within a potential range of 0.05–1.2 V. The scanning rate was 0.02 V/s. Tafel curves were plotted for determining the exchange current i^0.

2.4. Physical measurements

XRD analysis was carried out for Pt–Ru/C catalysts with a D/max-rB (Japan) diffractometer using a Cu Kα X-ray source operating at 45 kV and 100 mA. The XRD patterns were obtained at a scanning rate of 4°/min with an angular resolution of 0.05° of the 2θ scan. The particle size was computed by using Debye–Scherrer equation.