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Preparation and characterization of carbon-related materials supports for catalysts of direct methanol fuel cells

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ABSTRACT

In this work, two types of carbon materials such as CBs and GNFs were treated by a fluorination in order to study the effect of surface modification. The carbon-supported platinum (Pt) and ruthenium (Ru) catalysts were prepared using two types of carbon materials to check the influence of the fluorinated carbon supports on the activity of catalysts. The crystalline characteristics of the carbon-supported catalysts were determined by XRD method. Electrochemical properties of the electrocatalysts were analyzed by cyclic voltammetry (CV) experiments. When fluorinated GNFs were used as catalyst supports, the current density obtained in fuel cell was greater than that of CBs-supported catalyst; meaning GNFs-supported catalysts had a higher performance relative to CBs-supported catalysts. These results were supported with the CV results that showed the greater activity for PtRu at higher potentials.

1. Introduction

Fuel cells, the energy converting devices with a high efficiency and low or zero emission, are attracting increasing attention in recent decades due to high energy demands, fossil fuel depletion, and environmental pollution.

During the last decade there have been expensive efforts in the research of the electrochemical oxidation of methanol and the development of the direct methanol fuel cells (DMFCs). DMFCs have been considered to be promising alternative powers sources for electric vehicles, portable electronic devices and mobile applications [1–5]. Direct injection of the methanol fuel would avoid the problems related to the production, purification and storage of hydrogen. However, the performances of DMFCs are still limited by several problems, including the poor kinetics of both the anodic and cathodic reactions and the cross over of methanol through the proton exchange membrane from the anode to the cathode. Pt has been shown to be the only active and stable single metal catalyst for dissociative chemisorptions of methanol in acidic media, but it is very sensitive to CO poisoning which are formed by the initial de-hydrogenation of the methanol molecules. This problem becomes inactive for methanol oxidation in the potential region of fuel cell interest. Fortunately, it is found that addition of other metals such as Ru, Sn, Rh and Mo to Pt can mitigate poisoning and increase the catalytic activity of Pt. In particular, binary Pt–Ru alloys are still the state-of-the-art catalysts for methanol oxidation in DMFCs. The enhanced activity of Pt–Ru compared to Pt for methanol oxidation has been attributed to both electronic and bifunctional effects. The bifunctional effects involve the adsorption of oxygen containing species on Ru atoms at lower potentials, which promotes the conversion CO to CO_2 on Pt [6–10]. In DMFCs systems, interest has focused on the development of a supporting material, one of key factors in increasing the utilization of noble metal catalysts. The most common low Pt or Pt alloys supported by high surface carbon and used in both the cathode and anode. In other to achieve high catalytic performance with the low Pt loading, great effort must be put in Pt utilization and the enhancement of catalyst activity. Of the several factors which influence electrocatalytic activity of carbon-supported Pt or Pt-based alloys in the electrocatalysts, particle shape, size, and size-distribution, are of crucial importance [11,12].

In fact, the choice of a suitable supporting material is an important factor that may affect the performance of supported electrocatalysts owing to interactions and surface reactivity. Carbon materials are widely used as support materials. The ideal carbon-related material for catalyst support in fuel cells should have the following characteristics. It provide a good electrical conductivity, allow the reactant gas to get to the electrocatalysts easily, have adequate water-handling capability at the cathode where water is generated, and also show good corrosion resistance because cathodes in DMFCs are under strongly oxidizing conditions. Whereas carbon blacks are the common support materials for electrocatalysts, new forms of carbon materials such as carbon or

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graphite nanofibers (GNFs) and carbon nanotubes (CNTs) have been investigated as catalyst supports [13–19].

On the other hand, carbon materials are of great importance in a wide variety of fields. Surface modification is accomplished through different types of treatments such as thermal treatment, chemical or electrochemical oxidation, and plasma treatment. In recent years, fluorination treatment has been investigated as an interesting surface modification tool. In comparison with other surface modification techniques, fluorine atoms penetrate the material surfaces to relatively great depths that are controllable [20–25].

In the present article, surface modification effects of carbon supports were studied to analyze the size and the loading efficiency of platinum–ruthenium catalysts. Furthermore, binary carbon-supported platinum (Pt)–ruthenium (Ru) catalysts nanoparticles were prepared using two types of carbon materials such as carbon black (CBs) and graphite nanofibers (GNFs) to check the influence of carbon supports on the electroactivity of catalysts electrodes.

2. Experimental

2.1. Materials and surface modification of carbon materials

The CBs and GNFs were used as a support for the metal catalysts. Carbon blacks (CBs) of 24 nm size, 153 (cc/100 g) DBP adsorption 112 (m^2/g) specific surface areas, supplied by Korea Carbon black Co., were used in our experiments. Graphite nanofibers (GNFs) which were supplied by Showa Denko Co. (Japan). These carbon fiber materials have a diameter of 100–150 nm and a length of 5–50 μm, resulting a large aspect ratio. Chloroplatinic acid (H_2PtCl_4) and ruthenium chloride ($Ru(OH)_3$) catalysts were purchased from Aldrich. The reducing agent, HCHO (35%), was also obtained from Aldrich. Before catalyst deposition, CBs and GNFs were preformed to treatment at different temperatures (RT–400 °C) under fluorine gas flow in order to realize their different Pt and Ru loading contents, respectively. The fluorine pressure was fixed to 0.1 MPa, and the nominal reaction time was fixed to 15 min at the given treatment temperature. We had considered carbon samples such as pristine CBs, CBs-RT, CBs-100, CBs-300, CBs-400 and pristine GNFs, GNFs-RT, GNFs-100, GNFs-300, GNFs-400.

2.2. Catalyst preparation

The carbon materials-supported Pt and Ru catalysts were prepared by chemical reduction of Pt/Ru colloids in an aqueous solution using HCHO as a reducing agent.

Prior to using the as-synthesized CBs and GNFs, the metal catalysts used in the synthesis and the amorphous carbons were removed by two-step purification: exposure at 500 °C in an O_2 stream for 90 min and soaking in 5 M HNO_3 for 3 h. These purified CBs and GNFs were named pristine CBs and pristine GNFs.

Fluorinated carbon materials (125 mg) were suspended in 25 ml of deionized water and stirred. Separately, 58.3 mg of H_2PtCl_4 and 30 mg of $Ru(OH)_3$ in dissolved deionized water was slowly added dropwise to the above solution which was stirred mechanically for 1 h. A 5 M NaOH aqueous solution was added to adjust the pH of the mixture to 12–13 approximately. Then, HCHO (37%, 0.75 ml) was added to the solution to reduce the Pt and Ru, Reduction reaction was performed by heating the mixture solution at 80 °C for 1 h, during which high purity argon gas was passed through the reaction system to remove the organic by-products. After cooling to the room temperature, the resulted catalyst was washed with distilled water and ethanol. The obtained powder was dried in a vacuum oven at 70 °C for 24 h.

2.3. Physical and chemical characterization

The carbon and fluorine loading level was calculated by the energy dispersive X-ray spectroscopy (EDS) method, considering the atomic ratio of the carbon and fluorine intensity. X-ray diffraction (XRD) analysis with a Rigaku D/MAX-2200V diffractometer using a Cu Kα (λ = 0.15406 nm) source operating at 40 kV and 40 mA, was carried out on catalysts from different precursors. The XRD patterns were plotted at a scanning rate of 4°/min with an angular resolution of 0.05° for the 2θ scan. The X-ray diffractograms were obtained for 2θ values varying between 10° and 100°.

The loading masses of the Pt and Ru were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) using a Jobin Yvon Ultima C-spectrometer.

Transmission electron microscopy (TEM) photographs of the catalyst samples were taken by 1 nm-spatial-resolution TEM. Before taking the electron micrographs, the catalyst samples were ultrasonically dispersed in isopropyl alcohol, and a drop of the resultant dispersion was deposited and dried on a standard copper-grid coated with a polymer film. The applied voltage was 100 kV for the catalysts.

2.4. Electrochemical characterization

Electrochemical measurements were carried out on a conventional three electrode electrochemical cell at 25 °C. A conventional three-compartment electrochemical cell was employed for all electrochemical tests. A KCl-saturated Ag/AgCl electrode was used as the reference electrode and a platinum wire as the counter electrode. All electrochemical tests were carried out at room temperature. Glassy carbon (GC) electrode (Bioanalytic Systems, Inc., 3 mm diameter) was used as a substrate for the working electrode. We prepared a working electrode by coating the catalyst powder mixed with Nafion® polymer (5 wt.%, Aldrich) onto a glassy carbon electrode. The solution of 1 M CH_3OH and 0.5 M H_2SO_4 was stirred constantly and purged with ultra-pure argon gas. Electrochemical experiments were performed using Autolab with PGSTAT 30 (Eco Chemie, The Netherlands), an electrochemical analysis instrument. A Cyclic potential was swept between −0.2 V and 0.8 V vs. Ag/AgCl with a scan rate of 10 mV/s.

3. Results and discussion

3.1. Surface characteristics of modified carbon materials

Element contents of the fluorinated CBs and GNFs were investigated by EDS method. The results are shown in Tables 1 and 2. The fluorine contents were increased with the fluorination temperature, which can be attributed to the increase of fluorine-containing functional groups of carbon surfaces by the fluorination. By a fluorination treatment, fluorine diffuses only slightly and slowly inside the carbon materials and then the diffusing fluorine atom produces

Table 1
Elemental contents of fluorinated CBs as measured by EDS.

	C (wt.%)	F (wt.%)
Pristine CBs	97.59	0
CBs-RT	96.92	1.82
CBs-100	96.02	2.59
CBs-300	95.62	3.27
CBs-400	93.83	3.55