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Preparation and characterization of high metal content Pt–Ru alloy catalysts on various carbon blacks for DMFCs

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Abstract

High metal content Pt–Ru alloy catalysts (80 and 90 wt.%) with various carbons were prepared by the colloidal method without increasing particle size. As increasing the specific areas of supporting materials, catalysts exhibited homogeneous dispersions. The 90 wt.% Pt–Ru/Ketjen Black showed the best performance as the anode catalyst in unit cell and the 80 wt.% Pt–Ru/Ketjen Black in electrochemical experiments. This difference comes from types of electrolytes, i.e. liquid and solid.

Keywords: DMFC; Catalyst; Supporting material; High metal content; Agglomeration

1. Introduction

Direct methanol fuel cells (DMFCs) are very promising power sources for their high efficiency and portable applications. However, they need more catalyst loading in the electrodes compared with proton exchange membrane fuel cells (PEMFCs) because of sluggish electrochemical methanol oxidation. One strategy to overcome this problem is to prepare the high metal content catalysts, i.e. 80 wt.% metal on carbon or more. If low metal content catalysts are used on DMFCs, more catalysts have to be applied to the electrodes to increase the activity of the cell, which causes a thick catalyst layer. Reactant transport to the reaction sites is retarded by the long path of the catalyst layer. Moreover, cracks can occur at the electrodes and it can also cause the poor contact between the polymer electrolyte membrane and the electrode. Consequently, it increases the internal resistance and decreases the cell performance. In the past unsupported Pt and Pt-based alloy nanoparticles were studied as electrocatalysts for anode and cathode [1–3], but they have disadvantages such as the heterogeneous dispersion of the catalyst ink and agglomeration of the particles because of high density and high metal content, respectively. Therefore, unsupported electrocatalysts show poor performances compared to high metal content catalysts.

One of drawbacks in the DMFC technology is deterioration of the platinum surface during the oxidation of methanol molecules. Binary Pt–Ru/C is a promising anode electrocatalyst in order to prevent this problem. Alloying with Ru is a commonly adapted method to promote methanol oxidation reaction by the bifunctional mechanism [4], with Ru acting as an oxygen supplier to alleviate CO poisoning on Pt.

By preparing 80 wt.% Pt–Ru or more on commercially available carbon blacks, thin catalyst layer which facilitates the mass transportation and enhances the catalyst utilization could be fabricated on the anode side of the MEAs (membrane electrode assemblies) [5].

This work explores the effect of various carbon blacks as supporting material for the high metal content anode electrocatalysts and the performances of the DMFC system. It is expected that the increase in specific surface area of supporting material brings some reduction of particle agglomeration. Much interest has been devoted to search suitable supporting materials for catalysts in fuel cell recently [6–12]. Uchida et al. reported that the cells with Acetylene Black which has the smallest specific surface area had better performance on PEMFCs [12]. However, there have been little work on the high metal content electrocatalysts for DMFCs without increasing the metal particle size of less than 3 nm.

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2. Experimental

2.1. Preparation of anode electrocatalysts

Three types of carbon blacks were used as supporting materials: Acetylene Black (Denka, Japan), Vulcan XC-72 (Cabot, USA), and Ketjen Black EC-300J (Mitsubish Chemical, Japan). Carbon supported Pt–Ru alloy catalysts were prepared by the surfactant stabilized colloidal method proposed by Bönnemann and coworkers [13,14]. All experiments were carried out in dry solvents under inert atmosphere from anhydrous metallic salts in THF in the presence of a quaternary ammonium salt as a surfactant. Four different types (80 wt.% Pt–Ru/Acetylene Black, 80 wt.% Pt–Ru/Vulcan XC-72, 80 and 90 wt.% Pt–Ru/Ketjen Black) of electrocatalysts were prepared from the same precursors, $PtCl_2$ (Aldrich) and $RuCl_3$ (Aldrich). Additionally, the catalysts were heat-treated at 300 °C in an atmosphere of 10% O_2 in N_2, then 10% H_2 in N_2 to remove the surfactant shell and to reduce the oxidized catalyst, respectively.

2.2. Characterization of carbon supporting materials

Carbon powder was investigated in terms of specific surface area by Brunauer–Emmett–Teller (BET) analyses with nitrogen adsorption using an ASAP 2010 (Micromeritics, USA).

2.3. Preparation of TEM grid

High-resolution transmission electron microscopy (HR-TEM) investigations were carried out using a JEM-3000F (JEOL, Japan). At first, samples were ultrasonicated in ethanol for 30 min and then deposited on a Cu grid covered with a continuous film of carbon. The grid was dried in a vacuum oven at 50 °C for an over-night.

2.4. Measurement of XRD

X-ray diffraction (XRD) analysis was carried out using a M18XHF-SRA (MAC Science Co.) which was operated with a Cu Kα source at 50 kV and 200 mA and at a scan rate of 5°/min.

2.5. Electrochemical measurements for methanol electro-oxidation

Electrochemical measurements were carried out with a computer-controlled electrochemical analyzer (100 B/W, BAS). A three-electrode cell which consisted of a glassy carbon working disk, a Pt foil counter electrode, and an Ag/AgCl reference electrode were used. All potentials of the electrochemical measurement were converted to a potential in normal hydrogen electrode (NHE) scale. The working electrode was prepared on the glassy carbon electrode by the following method. A suspension containing 10 mg of the catalyst and 0.1 mL of 5 wt.% Nafion® solution (Aldrich) in the mixture of *iso*-propyl alcohol and water was ultrasonically dispersed for 30 min, and then 10 μL of the slurry was pipetted onto the polished surface of the glassy carbon disk electrode. After the solvent is completely evaporated in a vacuum oven for a day, electrochemical measurements were conducted. The electrolyte was a 1 M H_2SO_4 solution or a mixture of 1 M CH_3OH and 1 M H_2SO_4 solution. The activity was measured by applying a sweep at a scan rate of 20 mV/s at 25 °C. All activity measurements were carried out at least in duplicate with a freshly prepared electrode for each measurement.

The electrochemical surface area was estimated using CO stripping voltammetry.

CO adsorption was achieved at 0.1 V versus NHE in a CO-saturated solution for 10 min, and then the electrolyte was purged with nitrogen for 30 min to remove dissolved CO.

2.6. Fabrication of MEAs and operation of unit cell

The anode electrodes were prepared using home-made catalysts by spraying procedure. A homogeneous suspension composed of PTFE and Acetylene Black powder (Denka, Japan) was sprayed onto the carbon cloth (E-TEK, USA) to form a gas diffusion layer. Then catalyst slurry composed of catalysts, Nafion® solution (Aldrich, 5 wt.% in water/aliphatic alcohols), and *iso*-propyl alcohol was sprayed onto the prepared diffusion layer. The ratio of metal to dry Nafion® for the slurry was 10:3 or 10:2 (weight of solids). The cathode electrodes were prepared by the same method using Pt/C catalyst (E-TEK, 60 wt.%). Pt loading was adjusted to 3 mg/cm^2 in the cathode electrode and Pt–Ru loading was 5 mg/cm^2 in the anode electrode. The MEAs for a single cell test were prepared by hot-pressing the electrodes with a Nafion® 117 membrane at 135 °C for 3 min at 200 kg/cm^2. The geometric area of the single cell was 1 cm^2.

An aqueous solution of 2 M methanol was fed to the anode at a rate of 2 cm^3/min and air was fed to the cathode at a rate of 1000 cm^3/min. Both reactants were passed through a heater maintained at 40 °C, while the cell temperature was maintained at 80 °C. The operation of the cell was performed at atmospheric pressure on both sides. Current voltage curves were measured galvanostatically with an electronic load.

3. Data and results

Representative TEM images of the nanocomposites, as displayed in Fig. 1, revealed metal particles having 2–3 nm except Fig. 1(a). Ketjen Black supported catalysts (Fig. 1(c) and (d)) showed homogeneous dispersion of metal particles. However, Fig. 1(a) shows that nanoparticles are agglomerated because the surface area of Acetylene Black is too small to prepare 80 wt.% catalyst. It is observed that the decrease of specific area in carbon supports and increase of metal loading in the same supports induce agglomeration of particles. The 90 wt.% catalyst has less than a half of the carbon support to accommodate the same metal content on the carbon surface compared with 80 wt.% catalyst, i.e. 90 wt.% metal on 10 wt.% supporting material versus 80 wt.% metal on 20 wt.% supporting material. Measured specific surface areas are 66, 250 and 845 m^2/g for Acetylene Black, Vulcan XC-72, and Ketjen Black, respectively.

XRD patterns of the supported catalysts are shown in Fig. 2. The diffraction peak at $2\theta \approx 25°$ observed in all the XRD patterns is due to (0 0 2) plane of the amorphous activated carbon