INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 35 (2010) 313–320

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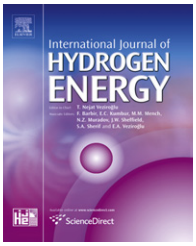

Preparation of Pt/NiO-C electrocatalyst and heat-treatment effect on its electrocatalytic performance for methanol oxidation

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ARTICLE INFO

Article history:
Received 28 August 2009
Received in revised form
6 October 2009
Accepted 9 October 2009
Available online 4 November 2009

Keywords:
Direct methanol fuel cell
Pt catalyst
NiO
Methanol oxidation, Heat-treatment

ABSTRACT

Pt catalyst supported on Vulcan XC-72R containing 5 wt% NiO (Pt/NiO–C) showed larger electrochemical active surface area and higher electrochemical activity for methanol oxidation than Pt catalyst supported on Vulcan XC-72R using polyol method without NiO addition. Prepared Pt/NiO–C electrocatalyst was heat-treated at four temperatures (200, 400, 600, and 800 °C) in flowing N_2. X-ray diffraction and temperature-programmed desorption results indicated that NiO was reduced to Ni in inert N_2 during heat-treatments at temperatures above or equal to 400 °C, while oxygen from NiO reacted with carbon support due to the catalytic effect of Pt. The reduced Ni formed an alloy with Pt, which, according to the X-ray photoelectron spectroscopy data, resulted in a shift to a lower binding energy of Pt 4f electrons. The Pt/NiO–C electrocatalyst heat-treated at 400 °C showed the best activity in methanol oxidation due to the change in Pt electronic structure by Ni and the minimal aggregation of Pt particles.

1. Introduction

Recently, the direct methanol fuel cell (DMFC) has been extensively studied due to its numerous advantages such as low operation temperature, high energy density, and direct use of methanol without additional reforming [1–3]. Prior to the commercialization of DMFC, however, barriers such as low catalytic activity and CO poisoning of Pt during methanol oxidation pose various complications regarding the selection of an appropriate catalyst [4–6]. Increasing the utilization of Pt or adding a second material have been suggested as solutions to these problems [7–11].

Metal oxides, such as CeO_2, MoO_x, TiO_2, and WO_x, have been employed to increase electrocatalytic activity for methanol oxidation [12–15]. In particular, Min et al. [16] reported that a Pt catalyst supported on NiO showed superior electrocatalytic activity for methanol oxidation in acidic solution compared to the catalyst supported on carbon. In addition, modifications to the interaction between Pt and metal oxides are reported to enhance the catalytic activity. For example, Song et al. [17] reported that the electrocatalytic performance of a TiO_2-Pt catalyst was improved by a heat-treatment at 200 °C due to an interaction change between Pt and TiO_2.

It is well known that the activity of an electrocatalyst is dependent on the size and the dispersion of metal particles. Preparation methods have been investigated to synthesize catalyst with well-dispersed and nano-sized metal particles

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doi:10.1016/j.ijhydene.2009.10.037

[18–21]. Polyol method using ethylene glycol as reducing agent and solvent is one of the most promising methods to achieve this goal [22–24]. Bock et al. [25] reported that glycolates produced from the oxidation of ethylene glycol act as a stabilizer for metal colloids and that the size of the resulting metal particles can be controlled by the pH of the solution. Therefore, well-dispersed Pt-based electrocatalyst could be obtained.

In this study, we investigated the effect of NiO addition on the enhancement of Pt catalyst activity for methanol oxidation. The NiO was precipitated onto carbon (NiO–C) prior to the loading Pt onto NiO–C by the polyol method. In addition, Pt catalyst supported on Vulcan XC-72R carbon black containing 5 wt% NiO (Pt/NiO–C) was heat-treated, and the effect of heat-treatment on the methanol oxidation performance of the catalyst was also studied. The prepared Pt/NiO–C was then heat-treated at 200, 400, 600, and 800 °C in flowing N_2. The samples were characterized with several analysis tools including X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). The performances of heat-treated Pt/NiO–C electrocatalysts for methanol oxidation were evaluated and the catalyst with the highest activity was compared to the commercial Pt/C catalyst.

2. Experimental

2.1. *Synthesis of electrocatalyst*

NiO was supported on Vulcan XC-72R (Cabot) by a precipitation method. 20 g of $Ni(NO_3)_2 \cdot 6H_2O$ (Junsei) was dissolved in 330 ml of distilled water. This solution (16.88 ml) was introduced to a suspension of Vulcan XC-72R (5 g) in distilled water. The NiO loading amount was fixed at 5 wt%, an optimum loading amount from our preliminary experiment. pH of 10 was established using ammonia solution (Daejung Chemicals and Metals), and the mixture was stirred vigorously for 3 h. After filtering and washing the precipitation mixture with distilled water, the solid residue was dried in vacuum for 12 h. The dried residue was then calcined at 400 °C for 3 h in air to form NiO–C. Subsequently, Pt was loaded onto the prepared NiO–C using the polyol method. The Pt loading amount of Pt/NiO–C was fixed at 20 wt%. 1 g of $H_2PtCl_6 \cdot 6H_2O$ (Kojima Chemicals) was dissolved in 100 mL of ethylene glycol (Acros Organics). This solution (6.6 mL) was introduced to 0.1 g of NiO–C dispersed in 25 mL of ethylene glycol. To increase the pH of the mixture to 13 or above, 2.5 M NaOH (Daejung Chemicals and Metals) solution was added. Subsequently, the mixture was refluxed at 160 °C for 3 h in an oil bath with N_2 purging to remove any oxygen or organic by-products. After cooling to room temperature, 3 M HCl (Matsunoen Chemicals) aqueous solution was added to the mixture in order to lower the pH to 2 or below. Thus created Pt/NiO–C was filtered, washed with distilled water, and dried in a vacuum oven for 24 h. The dried electrocatalyst was then heat-treated in flowing N_2 for 3 h at 200, 400, 600, or 800 °C. Catalysts thus created were denoted as Pt/NiO–Cx, where x represents the heat-treatment temperature in degrees Celsius. Pt catalyst supported on Vulcan XC-72R (Pt/C) for comparison was synthesized using the same polyol procedure described above with Pt loading also fixed at 20 wt%.

2.2. *Electrochemical measurements*

Electrochemical measurements were performed using cyclic voltammetry (CV) in a three-electrode cell system with a potentiostat (PGSTAT302, Autolab). A glassy carbon electrode (010422, BAS Inc.), polished with 0.05 μm γ-Al_2O_3 (40-6301-016, Buehler) paste and washed with distilled water was used as the working electrode. A Pt electrode (219810, Princeton Applied Research) and an Ag/AgCl (3 M) electrode (MF-2052, BAS Inc.) were used as counter and reference electrodes, respectively. The obtained potentials were referred to normal hydrogen electrode (NHE). The catalyst ink to be tested was prepared by mixing the catalyst with 5% Nafion solution (1100 EW, DuPont) in isopropyl alcohol. The weight ratio of the catalyst to Nafion in the catalyst ink was 3:1. The prepared catalyst ink was loaded onto the surface of the polished glassy carbon, and dried at room temperature. CV tests were conducted within a 0–1.2 V potential range (vs. NHE) with a scan rate of 20 mV s^{-1}. Aqueous solutions of 0.5 M H_2SO_4, with or without 2 M MeOH, were used as electrolytes after N_2 purging to remove dissolved oxygen in the H_2SO_4 aqueous solution. CO stripping test was carried out in aqueous H_2SO_4 solution. After N_2 purging, the adsorption of CO onto the catalyst was carried out by CO purging at 0.1 V (vs. NHE) for 20 min, and residual CO in the solution was removed by N_2 purging. Subsequently, a CO stripping voltammogram was obtained in a 0–1.2 V potential range (vs. NHE) with a scan rate of 20 mV s^{-1}.

2.3. *Characterization*

Powder XRD (D8 ADVANCE, Bruker AXS) with a Cu Kα radiation source was used to determine the crystalline structure of the prepared samples. TEM images were obtained using a transmission electron microscope (JEM-2000EXII, JEOL) operated at a 200 kV accelerating voltage. XPS (AXIS, Kratos) was conducted to determine Ni and Pt states within Pt/NiO–C. TPD was carried out using mass spectroscopy (Prisma QMS200, Pfeiffer Vacuum) as a detector under ultra-high vacuum (5×10^{-9} Torr) with a heating rate of 2 °C s^{-1}.

3. Results and discussion

3.1. *Effect of NiO addition to Pt/C catalyst*

X-ray diffraction patterns for NiO–C, Pt/C, and Pt/NiO–C are presented in Fig. 1. Diffraction peaks at 25°, observed in all three samples are assigned to the (002) plane of the carbon. Intensities of the carbon peaks in Fig. 1(b) and (c) are lower than the intensity shown in Fig. 1(a) due to the presence of metal particles on the surface of the carbon support. Diffraction peaks in Fig. 1(a) at around 37°, 43°, and 63° are assigned to the NiO (111), (200), and (220) planes, respectively. Diffraction peaks in Fig. 1(b) and (c) at around 39°, 46°, and 67° are attributed to the Pt (111), (200), and (220) planes, respectively, indicating a Pt crystallite with face-centered cubic structure.