Enhancement of Electroactivity of Platinum-Tungsten Trioxide Nanocomposites with NaOH-Treated Carbon Support toward Methanol Oxidation Reaction

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Abstract

Platinum-tungsten trioxide nanocomposite electrocatalysts on carbon black support (Pt-WO3/C) are synthesized and their electrocatalytic performances toward methanol oxidation reaction (MOR) are investigated in this study. Tungsten trioxide, which derived from the hydrolysis of tungsten hexachloride (WCl6) in dimethylformamide (DMF) solution, is firstly deposited onto pristine or NaOH-treated Vulcan XC-72 carbon black support to obtain tungsten trioxide/carbon black (WO3/C or WO3/Cs) nanocomposites, and then Pt nanoparticles are decorated onto these nanocomposites by polyol method to obtain Pt-WO3/C or Pt-WO3/Cs electrocatalysts. XRD and TEM characterizations are performed to examine the WO3 structures and the size distributions of the Pt nanoparticles. The effects of WO3 loading, annealing temperature and the NaOH-treatment of carbon black support on MOR mass activity and CO-tolerance ability of the electrocatalysts are investigated. The electrocatalyst (PtW(0.08)Cs200) with the WO3/Cs nanocomposite derived from a DMF solution containing 0.08 M WCl6, using NaOH-treated XC-72 carbon black as the support and annealed at 200 ºC, achieves the highest MOR activity among all the electrocatalysts synthesized in this study. The MOR performances of PtW(0.08)Cs200 is superior to that of the commercial E-TEK Pt(20 wt%)/C and E-TEK PtRu(20 wt%)/C electrocatalysts under the same test conditions.

Keywords: methanol oxidation reaction; electrocatalyst; nanocomposite; tungsten trioxide.

1. Introduction

It is known that the intermediate species generated during MOR, especially carbon monoxide, can rapidly poison the active Pt sites and impair their MOR efficiency. Bimetallic alloy of Pt with other metal,
such as PtRu [1] and PtSn [2], or the addition of transition-metal oxide as a co-catalyst with Pt, such as Pt-TiO$_2$ [3] and Pt-WO$_3$ [4-8], could reduce the CO-poisoning effect and therefore enhance the MOR performance of the electrocatalysts. In order to have effective interactions between Pt and WO$_3$ nanoparticles on carbon black support to enhance the MOR performance, WO$_3$ nanoparticle should have similar size as Pt nanoparticle. According to the literature research, very few attempts have been made using WCl$_6$ for the preparation of Pt-WO$_3$ nanocomposite electrocatalyst [9] especially on carbon black support. In this study, WO$_3$/carbon black nanocomposites were firstly synthesized from the hydrolyzation of WCl$_6$ in dimethylformamide (DMF) solution, and Pt nanoparticles were then deposited onto the nanocomposites by polyol method using ethylene glycol (EG) as both the reducing agent and solvent to obtain Pt-WO$_3$/C electrocatalysts. Vulcan XC-72 carbon black with or without NaOH treatment was employed as the support for the electrocatalysts. Influence of the preparation parameters of WO$_3$/C nanocomposite and carbon black support on the morphology, MOR performances and CO-tolerance ability of the Pt-WO$_3$/C electrocatalysts were investigated.

2. Experimental

Preparation of the WO$_3$/C nanocomposites. - WO$_3$ nanoparticles were firstly prepared by controlled hydrolysis of WCl$_6$ in dimethylformamide (DMF), and then were adsorbed onto carbon black support to obtain WO$_3$/C nanocomposites. A desired amount of tungsten hexachloride was dissolved in 10 mL of DMF to obtain a WCl$_6$/DMF solution. 0.25 g of Vulcan XC-72 carbon black was uniformly dispersed in 50 mL of DMF by sonication for 15 min. The WCl$_6$/DMF solution was added dropwise into the carbon black/DMF solution at a speed of 1 drop/s under stirring. Then, deionized water was dropwisely added into the above mixture. The mixture was stirred for 1 h and then stored at room temperature for 1 day. The precipitate was centrifuged, washed twice with ethanol and deionized water. The collected precipitate was then annealed at 200 °C or 450 °C for 2h under air and the WO$_3$/C nanocomposite was obtained. Preparation of the Pt-WO$_3$/C electrocatalysts. - 25 mg of H$_2$PtCl$_6$ was dissolved in 1 mL EG. 40 mg of WO$_3$/C nanocomposites was evenly dispersed in 50 mL EG by sonication for 15 min. The H$_2$PtCl$_6$/EG solution was then added dropwisely into (WO$_3$/C)/EG solution under stirring. The pH of the solution was adjusted to 11 by adding EG solution containing 0.5 M NaOH. The above mixture solution was refluxed at 120 °C for 2 h under continuous stirring. After cooled to room temperature, the mixture was filtered and washed thoroughly by deionized water and ethanol, then dried at 100 °C for 2 h under argon atmosphere and the Pt-WO$_3$/C electrocatalyst was obtained. Preparation of NaOH-treated carbon black. - 2 g of Vulcan XC-72 carbon black was dispersed in 200 mL 1.0 M NaOH aqueous solution and stirred for 4 days. The mixture solution was centrifuged and the collected precipitate was dried at 80 °C for 2h in air. The obtained NaOH-treated carbon black was denoted as C$_s$.

A conventional three-electrode system employing a Ag/AgCl electrode as the reference electrode and a Pt coil as the counter electrode was used for electrochemical experiments. A glassy carbon electrode (GCE) with a diameter of 3 mm was used for the preparation of the working electrode. 2 mg of the as-prepared electrocatalyst was ultrasonically dispersed in a solution which consisted of 1 mL deionized water, 1 mL ethanol, and 0.1 mL 5% Nafion(aq.) to form an electrocatalyst ink. 1.5 μL of the ink was pipetted onto the polished GCE and dried at room temperature under atmosphere. Cyclic voltammetry (CV), CO-stripping and chronoamperometry (CA) experiments were performed by a CHI-760D electrochemical workstation.

3. Results and Discussion

Cyclic voltammograms of the electrocatalysts in a 0.5 M H$_2$SO$_4$ deaerated aqueous electrolyte
containing 1.0 M methanol are shown in Fig. 1(a) ~ 1(c). The averaged peak MOR activities of these electrocatalysts at potential around 0.65 V (vs. Ag/AgCl) were plotted against their corresponding WCl₆ concentrations used during the synthesis procedure in Fig. 1(d). The MOR activity of the electrocatalyst was improved by replacing the pristine carbon black with NaOH-treated carbon black as the support (PtW(0.06~0.14)Cs450 series), and the PtW(0.12)Cs450 revealed a higher MOR activity among these electrocatalysts. A further enhancement in the MOR activity was achieved by changing the annealing temperature. As shown in Fig. 1(d), the PtW(0.08)Cs200 achieved the highest peak MOR activity among all the electrocatalysts. It is noted that for the electrocatalysts using NaOH-treated carbon black support, their average MOR activities were all higher than that of the E-TEK Pt(20 wt%)/C.

Figure 1. Cyclic voltammograms of (a) PtW(0.08~0.14)C450 series, (b) PtW(0.08~0.14)Cs450 series, and (c) PtW(0.08~0.14)Cs200 series electrocatalysts in deaerated 0.5 M H₂SO₄ aqueous solution containing 1.0 M methanol. The scan rate was 50 mV s⁻¹. (d) Comparison of the peak MOR activity of the electrocatalysts at potential around 0.65 V (vs. Ag/AgCl).

The electrochemical active surface area (ECSA) of a Pt-based MOR electrocatalyst can be estimated by integrating the area under its CV curve in the hydrogen absorption region, and the ECSA of the electrocatalysts synthesized in this study are listed in Table 1. The estimated ECSA of PtW(0.10)C450, PtW(0.12)C450 and PtW(0.08)C200 were all higher than that of the E-TEK Pt(20 wt%)/C and suggested that the presence of more electroactive sites for MOR in these electrocatalysts.

Figure 2. TEM images of (a) PtW(0.10)C450, (b) PtW(0.12)C450 and (c) PtW(0.08)C200 electrocatalysts.

Typical TEM images of the electrocatalysts with different annealing temperatures of WO₃/C or WO₃/Cs are shown in Fig. 2. Uniform spatial distribution of Pt nanoparticles was observed in all cases. Comparatively lesser WO₃ aggregations were observed if the annealing temperature of WO₃/C nanocomposite was 200 °C (Fig 4(c)). The average Pt nanoparticle sizes were ~ 3 nm for all the electrocatalysts. CO-stripping voltammograms of the electrocatalysts are shown in Fig. 3(a). The PtW(0.08)C200 electrocatalyst showed a lower CO-stripping onset potential around 0.601 V (vs. Ag/AgCl), which suggested a better Pt-surface-attached CO removing ability than that of the E-TEK Pt(20 wt%)/C electrocatalyst. CO-tolerance ability of an electrocatalyst was examined by CA experiment. As shown in Fig. 3(b), CO-tolerance abilities of the PtW(0.10)C450, PtW(0.12)C450 and PtW(0.08)C200 electrocatalysts were all enhanced as verified by comparing the MOR activity at 1000 s with that of the E-TEK PtRu(20 wt%)/C and Pt(20 wt%)/C.
0.55 0.60 0.65 0.70 0.75
0 100 200 300 400

0 100 200 300 400

0 100 200 300 400

Figure 3. (a) CO-Stripping voltammograms of the PtW(0.10)C450, PtW(0.12)C450, PtW(0.08)C200 and E-TEK Pt(20 wt%)/C electrocatalysts in 0.5 M H2SO4 aqueous solution. The scan rate was 50 mV s⁻¹. (b) Chronoamperometry of the PtW(0.10)C450, PtW(0.12)C450, PtW(0.08)C200 and E-TEK Pt/C electrocatalysts in aqueous electrolyte containing 1.0 M methanol and 0.5M H2SO4. The applying potential was 0.5 V (vs. Ag/AgCl).

4. Conclusions

The PtW(0.08)C200 electrocatalyst exhibited the highest MOR activity and the best CO-tolerance ability confirmed by CV, CA and CO-stripping experiments among all the electrocatalysts prepared in this study. Electrocatalysts employing NaOH-treated Vulcan XC-72 carbon black as the support achieved average ly higher MOR mass activities than those using pristine XC-72 carbon black support. It is deduced that both the interaction between Pt and amorphous WO3 as well as the NaOH-treatment of the carbon black support play pivotal roles in promoting the MOR performance and the CO-tolerance ability of a Pt-WO3/C electrocatalyst.

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References


Biography

Dr. Cheng-Lan Lin is an assistant professor of Department of Chemical and Materials Engineering at Tamkang University, Taiwan. His research interests include electrochemistry, fuel cell electrocatalysts, electrochromic materials and devices, and organic/inorganic hybrid materials.