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Modified polyol method for a highly alloyed PtRu/C electrocatalyst: Effect of hot injection of metal precursor and NaOH

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HIGHLIGHTS

- Showing the effect of mixing metal ion and hydroxide ion on alloying degree of PtRu nanoparticles.
- Success of synthesis of highly alloyed PtRu nanoparticles using ethylene glycol in an hour.
- Finding an optimum NaOH concentration and. temperature.
- Oxidation of pure ethylene glycol via RDE with a salt bridge.

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ABSTRACT

In this study, two modified polyol methods (I and II) were proposed to improve the alloying degree of PtRu nanoparticles. A 20 wt% PtRu/C catalyst was successfully synthesized using modified polyol method I, in which a metal precursor-ethylene glycol (EG) solution was injected into a hot NaOH-EG solution. The alloying degree of PtRu/C reached 56% with modified polyol method I. In modified polyol method II, the metal precursor- and NaOH-EG solutions were simultaneously injected into a hot EG solution, and an alloying degree of 84% was achieved by preventing the original precursor salt from becoming a metal hydroxide under high pH. The catalysts prepared by each modified method were characterized using XRD, HR-TEM, cyclic voltammetry, CO stripping, and chronoamperometry. The results showed that the catalysts prepared by the modified polyol methods had highly alloyed surfaces that exhibited strong CO tolerance and enhanced activity. The electrochemical activities of the developed catalysts for methanol oxidation were higher than that of commercial PtRu/C in terms of the mass-normalized current density.
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1. Introduction

Low catalytic activity and CO poisoning of Pt during methanol oxidation cause various complications in the selection of an appropriate catalyst [1–4]. The carbon-supported PtRu electrocatalyst is the most effective anode catalyst for methanol oxidation [5,6]. Many researchers reported explanations for the enhanced electrocatalytic activity of PtRu [7–9]. Watanabe et al. suggested the bifunctional mechanism to explain the enhancement [8]. Badu et al. investigated differences of the orbital structure of Pt black and PtRu alloy. The results indicate that "Ru enhancement" is valid despite Ru scarcity on the surface. Roth et al. observed OH and CO adsorbed on the active sites which visualized by *in-situ* XAS. They concluded that bifunctional mechanism and an electronic effect are valid explanations [7]. Additionally, CO-like intermediate species can be oxidized to CO_2 by OH groups formed on neighboring Ru under relatively low potentials. Therefore, contact between Pt and Ru on the atomic scale is important to optimize this effect. Although amorphous hydrous ruthenium oxide ($RuO_x \cdot xH_2O$) has been reported to be more active than metallic Ru [10,11], PtRu alloys maximize the effectiveness of the bifunctional mechanism because of the relatively uniform distributions of Pt and Ru sites

Abbreviations: EG, ethylene glycol; RDE, rotating disk electrode; MOR, methanol oxidation reaction; NHE, normal hydrogen electrode; EAS, electrochemical surface area.

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[12–15].

Various preparation methods have been investigated to synthesize catalysts with well-dispersed, nano-sized metal particles [16–18]. The polyol method in which ethylene glycol (EG) is used as the reducing agent and solvent is one of the most promising methods to achieve this goal [19,20]. Bock et al. [21] reported that the glycolates produced by EG oxidation stabilize metal colloids and that the size of the resulting metal particles can be controlled by the pH of the solution. However, in the preparation of PtRu catalysts through EG reduction, problems arise because Pt and Ru ions cannot be reduced simultaneously [21–23] because the reduction of Ru ions is more difficult than that of Pt ions. Thus, it is necessary to minimize the difference in the reduction times of the two precursor salts to successfully obtain PtRu alloys. Lee et al. reported that $PtCl_6^{-2}$ and $RuCl_3$ salts should be reduced at a temperature above 190 °C to decrease the difference in the reduction rates of the two metal ions [23]. However, in the conventional polyol method, reduction is complete before the nominal temperature, 160 °C, is reached. Therefore, the real reaction temperature is lower than the nominal temperature [21].

Furthermore, a high EG pH value (pH > 11), which is required to prepare small nanoparticles via the polyol method, is not suitable for Ru reduction because undesirable Ru precipitates appear at high pH [24]. Sarma et al. [25] reported that the pH of the reacted EG solution containing the Pt and Ru precursor salts reached 11, leading to the reduction of Pt^{4+} to Pt^{2+}, which corresponds to $[PtCl_4]^{2-}$, while $RuCl_3$ became $[Ru(OH)_6]^{3-}$. Thus, in this study, we investigate effective preparation methods for PtRu catalysts using EG. To achieve this, we modified the conventional polyol method and injected the EG solution containing the Pt and Ru precursor salts at a temperature of 190 °C. In addition, the pH of the injected precursor solution was not adjusted to avoid altering the forms of the Pt and Ru precursor salts.

2. Materials and methods

2.1. Preparation of PtRu/C by the conventional polyol method

The calculated amount of carbon support was dispersed in 30 mL of EG using ultra-sonic vibration and stirring. Then, 1 g of $H_2PtCl_6 \cdot 5.7H_2O$ (Kojima Chemicals) and 1 g of $RuCl_3 \cdot xH_2O$ (Sigma-Aldrich) were dissolved in 100 mL and 50 mL of EG (Acros Organics), respectively. Subsequently, 1.7 mL of $H_2PtCl_6 \cdot 5.7H_2O$ in EG and 0.4 mL of $RuCl_3 \cdot xH_2O$ in EG were added to the solution containing the dispersed carbon. To increase the pH of the mixture to 6, a solution of NaOH in EG (0.25 M) 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) in EG was added to the mixture to adjust the pH below 2 [26]. The synthesized catalyst was filtered, washed with distilled water, and dried in a vacuum oven for 24 h. The obtained catalyst was post-treated in 10% H_2/N_2 at room temperature for 1 h. The catalyst prepared using the conventional polyol method was denoted as PR-C. The metal-loading amount of PtRu/C was fixed at 20 wt%.

2.2. Preparation of PtRu/C by modified polyol method I

The calculated amount of carbon support was dispersed in 30 mL of EG using ultra-sonic vibration and stirring. Subsequently, the designated volume of 0.25 M NaOH-EG solution was added. After stirring for several minutes, the homogeneous NaOH-EG solution was heated to the designated temperature in an oil bath with N_2 purging and refluxing. When the solution reached 190 °C, 2.1 mL of premixed H_2PtCl_6 and $RuCl_3$ in EG was injected. The composition of this solution was the same as that used for the conventional method. Subsequently, the mixture was refluxed for 1 h in an oil bath with N_2 purging. Subsequently, the synthesized catalysts were subjected to the same post-processing as those synthesized via the conventional polyol method. The catalysts prepared via modified polyol method I were denoted as PR-I.

2.3. Preparation of PtRu/C by modified polyol method II

The calculated amount of carbon support was dispersed in 30 mL of EG using ultra-sonic vibration and stirring. Then, the EG-solution was heated to 190 °C in an oil bath with N_2 purging and refluxing. When the solution reached 190 °C, 8 mL of premixed EG solution containing 10 mg of PtRu with a molar ratio of 1:1 and the calculated concentration of NaOH-EG solution were injected using syringes at a rate of 1.6 mL per min. Subsequently, the mixture was refluxed at 190 °C for 1 h in an oil bath with N_2. Subsequently, the synthesized catalysts were subjected to the same post-processing as those synthesized using the conventional polyol method. The catalysts prepared through modified polyol method II were denoted as PR-II. The metal-loading amount of PtRu/C was fixed at 20 wt %.

2.4. Physical characterization of the catalyst

The XRD (Rigaku D/MAX 2500) measurement was performed with a Cu Kα radiation source (λ = 0.1541 nm) operated at 40 kV and 200 mA. To identify phases and estimate particle sizes, the catalysts were scanned from 20° to 90° at a scanning rate of 4° min^{-1}. The microstructures of the prepared samples were identified by a high-resolution TEM (HR-TEM, JEM-3010, JEOL) operated at an accelerating voltage of 300 kV. Elemental analysis was achieved using inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a PerkinElmer Optima-4300 DV.

2.5. Electrochemical measurements

Catalytic activity tests were performed using cyclic voltammetry (CV) in a three-electrode cell system with a potentiostat (PGSTAT302, Autolab). A glassy carbon electrode (MF-2012, BAS Inc.) was used as the working electrode. A Pt wire electrode (MW-1032, BAS Inc.) and an Ag/AgCl electrode (MF-2052, BAS Inc.) were used as the counter and reference electrodes, respectively. The catalyst ink was prepared by mixing the catalyst with 5% Nafion solution (1100 EW, DuPont) in isopropyl alcohol. The amounts of catalyst and Nafion were adjusted to a catalyst:Nafion weight ratio of 3:1. The prepared catalyst ink was loaded onto the polished glassy carbon and dried at room temperature. Before performing the electrochemical measurements, the catalysts were pre-treated by potential cycling. CV tests were conducted within a 0.5–1.4 V potential range (vs. NHE) with a scan rate of 20 mV s^{-1} at 25 °C. The methanol oxidation reaction (MOR) activity measurement was performed by potential cycling over 0–1.2 V at a scan rate of 20 mV s^{-1} at 60 °C. An aqueous solution of 0.5 M H_2SO_4 with 2 M CH_3OH was used as the electrolyte. CO-stripping tests were conducted in 0.5 M aqueous H_2SO_4. The adsorption of CO onto the catalyst was achieved by CO purging at an electrode potential of 0.1 V (vs. NHE). Additionally, residual CO in the solution was removed by N_2 purging while holding the electrode potential at 0.1 V. Subsequently, CO-stripping voltammograms were obtained in a 0.1–1.0 V potential range (vs. NHE) with a scan rate of 20 mV s^{-1}. Linear sweep voltammetry was adopted to measure the variation of the EG oxidation rate with NaOH concentration using an agar salt bridge containing 1 M KCl and a rotating disk electrode (RDE), with a rotating speed of 1600 rpm and a scan rate of

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