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Facile synthesis of platinum alloy electrocatalyst via aluminum reducing agent and the effect of post heat treatment for oxygen reduction reaction

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ABSTRACT

We have synthesized carbon-supported Pt and PtM (Au, Pd) nanoparticles (NPs) by using an aluminum (Al) metal foil as a reducing agent and conducted post heat treatments to investigate the relationship between oxygen reduction reaction (ORR) activity and surface crystalline/electronic structures of electrocatalysts. The as-prepared Pt and PtM (Au, Pd) NPs received the post heat treatment to induce structural modifications to improve ORR activity. From structural characterizations, well-synthesized carbon-supported Pt and PtM (Au, Pd) NPs were confirmed and the post heat treatment has the effect of inducing the alteration of surface crystalline structure and results in higher ORR activity. Furthermore, based on electrochemical characterizations, it is proved that after the heat treatment, the surface reconstruction brought about the increased fraction of Pt (111) and electrochemical active surface area of PtAu/C CO sample. And, the downshift of Pt d-band center of PtPd/C CO sample, which decreases the affinity of Pt to oxygen species, occurred resulting in more favorable kinetics of ORR.

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Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are environment-friendly energy conversion devices for mobile and stationary power supply, due to their high energy conversion efficiency compared to internal combustion engines

and no emission of pollutants such as CO₂, NO_x gas and hydrocarbon materials [1–7]. However, the commercialization of PEMFCs has been delayed because of the high manufacturing price of Pt electrocatalyst. Commonly, large amount of Pt nanoparticles (NPs) is used to compensate for the slow kinetic reaction with oxygen at the cathode, so called oxygen reduction reaction (ORR). To lower the manufacturing price of

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PEMFCs while maintaining high catalytic activity of ORR, many studies have been conducted on alloying Pt with other transition metals (Ni, Co, Fe and etc.), Pt shell - cheap transition metal core structure and structural modifications of Pt and Pt alloy NPs [8–23]. However, to obtain these types of electrocatalysts, complex synthetic processes that demand to be carried out in high temperature or a certain gaseous atmosphere with unstable and toxic materials like metal hydride reducing agents or noxious organic solvents have been used [8,17–20]. Simple, efficient, and environment-friendly synthetic processes have recently been tried using pure metal elements as reducing agents, in which no toxic chemicals and no organic solvents are needed [24–28].

In this research, we prepared carbon-supported Pt and PtM (Au, Pd) NPs by using an aluminum (Al) metal foil as an effective reducing agent and NPs were analyzed through physical, chemical, and electrochemical methods. Additionally, the post heat treatment of various conditions was conducted to elucidate the relationship between ORR activity and crystalline/electronic structures of electrocatalyst. This work proposes an easy, safe, and affordable synthetic method of electrocatalysts syntheses.

Experimental section

Preparation of electrocatalysts

Synthesis of carbon-supported Pt and PtM (Au, Pd) NPs

Materials for the synthesis are as follows; carbon black (Vulcan XC-72R, Cabot), DI water (18.2 M Ω cm, Millipore), and sodium citrate have been used as support, solvent, and surfactant, respectively. The carbon black and sodium citrate were dispersed into the DI water by using a magnetic stirrer and an ultrasonic bath for 1 h. After mixing, precursors including chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), gold (III) chloride trihydrate (HAuCl₄·3H₂O) or sodium tetrachloropalladate (II) (Na₂PdCl₄) were added to the solution and stirred for 1 h. In the final step, Al metal foil as a reducing agent was added and stirred for 24 h to end the reduction reaction completely. During this process, Al metal foil was torn into small pieces (~1 cm² area each) by hands with ease and simply added to the solution immediately. The solution was then filtered, washed with DI water, and dried in a vacuum desiccator for more than 6 h. To eliminate Al metal foil residues generated during the synthesis, the additional acid treatment was conducted in 0.5 M HClO₄ solution for 12 h and the secondary filtering step with DI water was conducted. The nominal atomic ratio of Pt to M (Au, Pd) was fixed as 3:1. All chemicals were purchased from Sigma–Aldrich and used as received.

Post heat treatment of carbon-supported Pt and PtM (Au, Pd) NPs

The structural modification of carbon-supported Pt and PtM (Au, Pd) NPs was induced through the post heat treatment under various conditions. At first, every sample was heat-treated at 150 °C for 2 h under H₂/Ar (the mixture of 5% H₂ and 95% Ar) atmosphere to reduce their surface further, which was largely contaminated and oxidized during the synthesis due to the existence of excessive surfactant and the effect of

additional acid treatment on their surface. In sequence, there were two different heat treatment conditions; i) to induce a fully ordered structure, NPs received heat treatment at 500 °C for 1 h under H₂/Ar, ii) to segregate Pt atoms to their surface for the additional increase in ORR activity, the heat treatment was conducted at 150 °C for 1 h under CO (99.9%) atmosphere. NPs in this study were denoted as Pt/C or PtM (Au, Pd)/C ASP, H₂, 500 or CO according to the conditions of the heat treatment.

Characterization of carbon-supported Pt and PtM (Au, Pd) NPs

The crystalline structure of carbon-supported Pt and PtM (Au, Pd) NPs was examined by X-ray diffraction (XRD) using Rigaku D/MAX 2500 operated with a Cu K α radiation (40 kV, 200 mA). The size and morphology of carbon-supported Pt and PtM (Au, Pd) NPs were confirmed by transmission electron microscopy (TEM) using JEM 2100F (JEOL) and their chemical compositions were further analyzed by energy-dispersive X-ray spectroscopy (EDX) with Tecnai F20 (FEI). Samples were prepared by placing a drop of electrocatalyst solution onto a carbon-coated holey copper grid that had subsequently been dried in an oven for more than 12 h. The X-ray photoelectron spectroscopy (XPS, Thermo Sigma Probe) measurement was conducted with Al K α as the X-ray beam source. All spectra were calibrated by C 1s at 285 eV as a reference. The peaks for each sample were deconvoluted by using XPSPEAK 4.1 software. The inductively coupled plasma-atomic emission spectral (ICP-AES, Shimadzu JP/ICPS-7500) analysis was conducted for quantitative analysis of the chemicals.

Electrochemical measurements of carbon-supported Pt and PtM (Au, Pd) NPs

The NPs ink was prepared by mixing samples of carbon-supported Pt or PtM (Au, Pd) NPs with DI water (18.2 M Ω cm; Millipore), 5 wt% Nafion ionomer solution as a binder, and isopropyl alcohol (IPA) (Sigma–Aldrich). The sample of this slurry was pipetted and dropped onto a glassy carbon rotating disk electrode (geometric surface area is 0.196 cm²). Electrochemical measurements were carried out using an Autolab potentiostat (PGSTAT101) with a conventional three-electrode electrochemical cell comprised of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). All electrochemical measurements are quoted with respect to the reversible hydrogen electrode (RHE) and were conducted at 293 K. After the electrochemical cell was purged with Ar for 30 min, cyclic voltammogram (CV) was obtained in the potential range from 0.05 to 1.05 V vs RHE with a scan rate of 20 mV s⁻¹ in 0.1 M HClO₄ under Ar purging. ORR polarization curves were obtained using a rotation disk electrode (RDE, Pine Research Instrumentation) at 1600 rpm, in the range from 0.05 to 1.05 V vs. RHE with a scan rate of 5 mV s⁻¹ in 0.1 M HClO₄ under an O₂ flow. ORR polarization curves and the corresponding activities were reported after the iR-compensation [19,29]. CO_{ad} oxidation and N₂O reduction analyses were conducted using CV at potentials of 0.05–1.05 V and 0.05–0.7 V vs. RHE at a scan rate of 20 and 50 mV s⁻¹. For CO_{ad} oxidation, CO gas was purged for 15 min to adsorb CO molecules onto Pt and PtM (Au, Pd) NPs

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