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Influence of Au contents of AuPt anode catalyst on the performance of direct formic acid fuel cell

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Abstract

We reported that various compositions of AuPt nanoparticles synthesized as an anode material for formic acid fuel cell were investigated. Its surface characteristics were systematically analyzed using XRD and TEM and anodic electrocatalytic activity was studied using a linear sweep voltammetry technique in 0.5 M H₂SO₄ + 1 M HCOOH. In addition, the voltage–current curve and power density of home-made AuPt-based membrane–electrode-assembly (MEA) and commercial Pt_{0.5}Ru_{0.5}-based MEA was measured at 60 °C in 9 M formic acid. The maximum power density of Au_{0.6}Pt_{0.4}-based MEA was 30% higher than that of PtRu-based MEA which were 200 mW cm⁻² and 155 mW cm⁻², respectively. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

The electro-oxidation of small organic molecules is very sensitive to the properties of the electrode surface. Thus, these reactions are influenced by the properties of the electrode material, usually a pure metal or an alloy [1,2]. In addition, a surface modified by adatoms often reveals enhanced oxidation properties compared to the pure metal [3].

Among small organic molecules, many researchers have studied the fundamental features of formic acid oxidation. Formic acid oxidation was studied, for example, on polycrystalline [4–10] and single crystal Pt [11–13], rhodium, palladium, and gold [1]. In addition, many efforts have been made to enhance oxidation rates of formic acid on platinum by adding a variety of surface additives (modifiers). Many modifiers such as Ru [14,15], Sn [16–18], Pb [17], As [17], Sb [17,19,20], or Bi [17,19,21,22] have been tested as sources of possible catalytic

0013-4686/\$ – see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2007.12.031 enhancement. In particular, the modification by palladium as a Pt/Pd alloy [23], Pd "decorated" polycrystalline Pt surfaces [10], and Pt single crystals covered with palladium [24,25], have produced an increased reactivity. The single crystal Au(h k l)/Pd [25], and Au/Pd alloy [26] have also been investigated. Enhanced reactivity induced by adatoms has been accounted for by a 'third body effect' [26,27], the third body preventing surface poison (chemisorbed CO) to form on the surface. The chemistry of the Pt/Pd electrolyte interface has also been investigated in relation to anion effects [28], and CO chemisorption [29]. Of late, Sung and co-workers investigated synthesized PtAu alloy as an anodic catalyst in the direct liquid (methanol and formic acid) fuel cell [30], presenting higher activity than that of commercial PtRu, but only one composition of PtAu alloy was investigated.

In this work, we tried to understand the influence of Au on AuPt alloys and did more systematic approach of the effect of Au contents in the electro-oxidation of formic acid. We measured electrocatalytic oxidation activity of formic acid on a various composited AuPt catalysts, which were compared with commercial Pt and PtRu. Their fuel cell performances were also tested applying 9 M formic acid and humidified oxygen. As mentioned

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above, platinum has been attracting considerable attention due to its electrocatalytic characteristics, but its limited resource on the earth is also a considerable issue. On the other hand, Au is more abundant than Pt, and has been known as a catalyst able to enhance oxidation kinetics of formic acid via active intermediate species.

2. Experimental

2.1. Preparation and analysis of Au and AuPt nanoparticles

Unsupported Au, AuPt nanoparticles were prepared by an impregnation reduction method. Metal salts ($H_2PtCl_6 \cdot xH_2O$ and $HAuCl_4 \cdot 3H_2O$) were dissolved in deionized water. After stirring for 1 h, reducing agent (NaBH₄) was injected into the metal salt solution and the solution stirred for 1 h. After completion of the reduction, the precipitated particles were washed three times using deionized water and the resulting materials were freeze-dried using a liquid N₂ atmosphere without any heat-treatment.

X-ray diffraction measurements were made using a Rigaku D/max-IIIA X-ray diffractometer with a scan speed of 0.08° s⁻¹, in the scan range of 20–80 ° using Cu K α as an X-ray source. The size of AuPt nanoparticles was investigated using a transmission electron microscope (Philips (CM200)) operating at a 200-kV accelerating potential.

2.2. Half cell measurements

To investigate the electrocatalytic activity of Pt, PtRu, and AuPt catalysts, half cell tests were carried out. Catalysts sprayed on gas diffusion layer (GDL)/carbon paper were used as the working electrodes (WEs). The geometric area of the WE was 0.2 cm^2 . The Pt plate (99.99%) was used as counter electrode (CE) and silver–silver chloride (Ag/AgCl) saturated KCl was used as reference electrode (RE). Cyclic voltammetric curve between -0.2 V and 1.2 V was recorded in $0.5 \text{ M} \text{ H}_2\text{SO}_4$ and the activity test for formic acid oxidation was performed in $0.5 \text{ M} \text{ H}_2\text{SO}_4$ in the presence of 1 M HCOOH solution. A potentiostat/galvanostat (EG&G 273A) was used for all linear sweep voltammetry (LSV) experiments and the data were transferred to an IBM compatible PC controlled by a GPIB interface.

2.3. Single cell measurements

To compare the different catalysts, such as AuPt, Pt black (Johnson Matthey, Hi-SPEC 1000) and PtRu black (Johnson Matthey, Hi-SPEC 6000) were used as the anodes and Pt black (Johnson Matthey, Hi-SPEC 1000) as the cathode. All electrodes were prepared by dispersing appropriate amounts of unsupported catalysts powder in deionized water, 5% Nafion solution (Aldrich), 2-propanol, and 1-propanol, sonicating the solution for 90 s and catalyst inks were coated on a GDL/carbon paper by spraying at 80 °C. Then, additional ionomer solution was sprayed onto the catalyst layer of each electrode in order to decrease the contact resistance with polymer electrolyte membrane (Nafion 115, DuPont). The catalyst loading for the anode and cathode was approximately 3 mg cm⁻² and

the geometrically active area of the electrode was 10 cm^2 . Membrane–electrode assemblies (MEAs) were prepared by hot pressing with Nafion 115 at a temperature of $140 \,^{\circ}\text{C}$ and a pressure of $30 \,\text{kgf} \,\text{cm}^{-2}$ for $300 \,\text{s}$. Current–voltage curves were measured galvanostatically by using an electronic load (EL-200P, Daegil Electronics).

3. Results and discussion

The characteristics of synthesized AuPt catalysts prepared by the impregnation reduction method were investigated. Fig. 1(a) and (b) shows the XRD patterns of pure Pt, Au and AuPt alloys and those containing a dosage of Au in home-made AuPt nanoparticles, respectively. The peaks in Fig. 1(a) represent



Fig. 1. (a) XRD pattern and (b) portion of Au of synthesized AuPt catalysts, and (c) potential–current plot for Pt, PtRu, and AuPt in $0.5 \text{ M H}_2\text{SO}_4$ (scan rate: 10 mV s^{-1}).

Table 1

Particle size of AuPt catalysts calculated from XRD data using the Debye–Scherrer equation

Ratio of Pt precursor and Au precursor	Portion of Au of the alloy	Particle size (nm)
0.75:1	0.71	2.43
1:1	0.63	1.83
1.25:1	0.60	2.43
1.5:1	0.51	1.30
1.75:1	0.48	1.30
2:1	0.45	2.44

(111), (200), (220) reflection from left to right. The (111)peaks for Pt and Au nanoparticles synthesized by the impregnation reduction method were located at the original peak positions corresponding to their fcc metallic states, respectively. The 2θ of the (111) for AuPt nanoparticles was located between the (111) peaks of Pt and Au nanoparticles. As the proportion of Au was lowered, the diffraction peaks in the AuPt alloy were shifted to higher 2θ values with respect to the same reflections of Pt. Assuming alloy formation between Pt and Au based on a substitutional solid solution, such a shift can be attributed to the difference in atomic size [31]. Therefore, the higher the ratio of Au in an alloy becomes, the more peaks the shift in proportion to the amount of Au added. The amount of Au alloyed can be determined from this since the lattice parameter is linear with the composition of Au. Fig. 1(b) presents the portion of Au in the alloy with the ratio of Pt and Au precursors; it was calculated from the (111) peaks. As shown in Fig. 1(b), the Au portion in AuPt catalysts changes linearly with the ratio of Pt and Au precursors.

Table 1 presents the particle size of synthesized AuPt nanoparticles. The particle size of synthesized nanoparticles can be calculated using Debye–Scherrer equation (1) by fitting the (220) peak:

$$L = \frac{0.94\lambda_{\mathrm{K}\alpha_1}}{\mathrm{B}_{(2\theta)}\cos\theta_{\mathrm{B}}} \tag{1}$$

where L is the average particle size, $\lambda_{K\alpha_1}$ is the X-ray wavelength, $\theta_{\rm B}$ is the angle of the (2.2.0) peak and B₍₂₀₎ is the peak broadening (FWHM). The average size of synthesized AuPt nanoparticles is smaller than 10 nm. The active surface area was calculated assuming the charge for the oxidation of a complete hydrogen monolayer as being $210 \,\mu C \,cm^{-2}$ as derived before for polycrystalline Pt. The active surface area of each electrode was calculated as $270 \pm 30 \text{ cm}^2$. However, for Pt_{0.37}Au_{0.63} a lower active surface area was obtained than for other electrodes. We assume that AuPt nanoparticles are agglomerated as the amount of Au in the AuPt nanoparticles increases. As mentioned above, the (111) peaks for Pt and Au nanoparticles synthesized by impregnation reduction method were located at 39.76° and 38.16°, respectively, having the original peak positions corresponding to their fcc metallic states. The 2θ of Pt_{0.37}Au_{0.63} is 38.72°. The (111) peak of Pt_{0.37}Au_{0.63} was shifted between Pt and Au (111) peaks. Assuming alloy formation between Pt and Au based on a substitutional solid solution, such a shift can be attributed to the difference in atomic size. For example, a Pt atom is larger than a Ru atom and such type of peak shift indicate good alloy formation between Pt and Ru. PtRu (1:1) is known to alloy well. Therefore, we suggest that the structure of PtAu nanoparticles is the crystal structure having fcc metallic state [32].

In order to investigate the real particle size of synthesized AuPt nanoparticles as a function of Pt and Au precursor ratio, tunnelling electron microscopy (TEM) measurements were carried out. They were presented in Fig. 2. As shown in Fig. 2, the particle size of synthesized AuPt is below 10 nm, in good agreement with the XRD data, but most particles are agglomerated into clumps. Interestingly, the higher the amount of Au in AuPt nanoparticles increases, the more AuPt nanoparticles become agglomerated; this might be due to the self-assembling property of Au [33]. Analysis of XRD and TEM data shows that AuPt particles could be controlled on the nano-scale.

Fig. 3 illustrates the linear sweep voltammetry of Pt, PtRu and AuPt alloys for each anode catalyst in $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M}$ HCOOH at room temperature. Current densities in the voltammogram were normalized to the active surface area (see Fig. 1(c)). The oxidation of formic acid on AuPt occurs at the lower overpotential applied and the oxidation current density of AuPt is larger than PtRu and Pt below 0.2 V, which is the most interesting region for catalytic activity in the measurement of formic acid fuel cell performance. The mechanistic origin of the electrocatalytic oxidation of formic acid on AuPt alloys has been explained by the third-body effect [34]. Poisoning does not occur on the Au surface and the Au has a little ability for electro-oxidation of formic acid [35].

Fig. 4 shows the voltage–current curve and power density of a commercial PtRu, home-made AuPt anode and Pt cathode applying humidified oxygen at 60 °C using 9 M formic acid. We observe that the open-circuit voltages of PtRu and Pt_{0.41}Au_{0.59} catalysts are 0.57 V and 0.72 V. In addition, the maximum power density of Pt_{0.41}Au_{0.59} catalyst was higher than that of PtRu which are 200 mW cm⁻² and 155 mW cm⁻², respectively. These findings support the evidence for the higher catalytic activity of AuPt for formic acid oxidation compared to PtRu. As per the results presented above, the AuPt catalyst shows higher formic acid oxidation than Pt and PtRu when the Au portion in the alloy is above 0.59. This indicates that formic acid is relatively rapidly oxidized directly to CO₂ on AuPt catalyst.

The general mechanisms for the electro-oxidation of HCOOH have been proposed by both Capon and Wieckowski [6,7]. The first reaction of HCOOH with Pt involves the one-electron transfer:

$$\text{HCOOH} \rightarrow (\text{COOH})_{\text{ads}} + \text{H}^+ + \text{e}^-$$
(2)

The next step is the decomposition of the unstable intermediate COOH to CO_2 or CO, dependent upon the potential. At potentials within the broad double layer region on Pt, it is most likely that the weakly bound COOH is involved in the main oxidation pathway:

$$(\text{COOH})_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- \tag{3}$$



Fig. 2. TEM images of AuPt catalysts: (a) $Pt_{0.37}Au_{0.63},$ (b) $Pt_{0.40}Au_{0.60},$ and (c) $Pt_{0.53}Au_{0.47}.$



Fig. 3. Potential–current plot for Pt, PtRu, and AuPt in 0.5 M $\rm H_2SO_4$ + 1 M HCOOH (scan rate: 10 mV $\rm s^{-1}$).

Bulk HCOOH may interact with COOH to produce the poison.

$$HCOOH + (COOH)_{ads} \rightarrow (COH)_{ads} + H_2O + CO_2$$
(4)

Competition between reactions (3) and (4) causes the rate of intermediate formation to be an inverse function of the rate of the oxidation reaction.

Pt alone is insufficient for use in a formic acid because $CO/(COH)_{ads}$ poison hinders its catalytic activity. Accordingly, new material is needed to improve activity of formic acid electrooxidation and hinder $CO/(COH)_{ads}$ poison on Pt surface. Au is a poor catalyst; it cannot easily adsorb neither reactant nor intermediates. The addition of Au to Pt can improve $CO/(COH)_{ads}$ tolerance of the Pt surface due to the decrease in the number of surface sites available to $CO/(COH)_{ads}$ adsorption [36]. Also, the electro-oxidation of HCOOH on Au takes place only at high overpotentials and in the presence of oxide [1]. We believe that the activity and performance of AuPt catalyst could be improved because the presence of Au in catalyst prevents $CO/(COH)_{ads}$ poisoning and causes it to be relatively rapidly oxidized directly to CO_2 via a weakly bound reactive intermediate on the AuPt catalyst surface. This occurs although the real surface area of



Fig. 4. Single cell performance of Pt-based Pt, PtRu-based and AuPt-based MEA using 9 M formic acid and oxygen at 60 $^\circ C.$

AuPt catalyst is decreased with increase of the Au portion in the alloy.

4. Conclusions

AuPt catalysts were synthesized by an impregnation reduction method. The synthesized AuPt nanoparticles are generally <10 nm in diameter but many of them agglomerate into clumps. The AuPt catalyst provided a higher activity than that of Pt and PtRu, showing a lower onset potential and large current density and as the proportion of Au in the AuPt particle was increased, the current–potential polarization curve indicated its possible potential as an anodic catalyst in direct formic acid fuel cells.

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