Short Articles

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Hydrogen Gas Diffusion Electrode Prepared from Porous Carbon Spheres Dispersed with Pd–Ag Alloy Nanoparticles

Masataka Horigome, David A. Pacheco Tanaka, Margot A. Llosa Tanco, Waki Yukita, Kiyoshi Kobayashi, and Toshishige M. Suzuki*

National Institute of Advanced Industrial Science and Technology (AIST), Research Center for Compact Chemical Process, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551

Received June 5, 2007; E-mail: tm-suzuki@aist.go.jp

Hydrogen gas diffusion electrodes were prepared from porous carbon spheres dispersed with Pd–Ag alloy nanoparticles with various Pd/Ag ratios. The performance of the electrodes evaluated by observing the polarization characteristics in the electro-oxidation of hydrogen markedly depended on the ratio of Pd and Ag in the alloy.

Palladium (Pd) and palladium–silver (Pd–Ag) alloy have attracted attention due to the potential applications as hydrogenation catalysts,[1] in hydrogen permeable membranes,[2] and electrode materials.[3] Particularly, remarkable performances in terms of catalytic and electro-catalytic activity have been demonstrated by high dispersion of nano-sized Pd particles in the support matrix.[4] Recently, metal-dispersed carbon composite spheres have been obtained by calcination of metal ion loaded ion-exchange resin in an inert atmosphere.[5] However, most of the precedent works have been limited to a single metal system, and binary alloy systems are scarce.

In our preliminary study, we have prepared porous carbon composite dispersed with Pd–Ag alloy nanoparticles by using a Pd^{II} and Ag^{I} loaded chelating resin as the precursor.[6] In the present paper, we prepared a hydrogen gas diffusion electrode from the Pd–Ag alloy dispersed carbon composite. The performance of the electrodes was evaluated by observing the polarization characteristics in the electro-oxidation of hydrogen in H_2SO_4 and discussed with respect to the Pd/Ag ratio of the alloy and the porous structure of the electrodes.

Pd^{II} and Ag^{I} of desired ratio were simultaneously retained in the chelating resin by treatment with an aqueous metal ion mixture. Subsequent calcinations of the resin at 900 °C under N_2 and then reduction with H_2 yielded unique binary alloy nanoparticles dispersed in a porous carbon matrix. Thermal gravimetric analysis (TGA) of the metal ion loaded chelating resin under N_2 showed a marked mass loss at 200 °C due to carbonization of the polymer which finally reached about 27 wt % of the original resin mass upon by heating to 900 °C. Crystalline Pd–Ag alloy was obtained by calcinations of
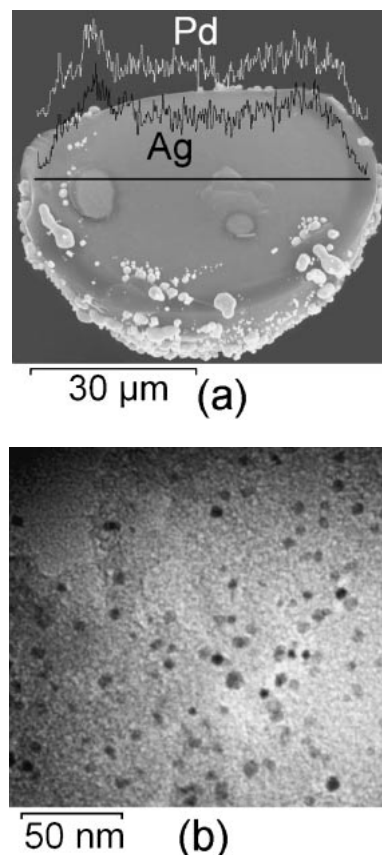

Fig. 1.   (a) Cross sectional SEM image and EDX line profile of the carbonized resin indicating the Pd and Ag distribution along the diameter of hemisphere (Pd–Ag (60:40)). (b) TEM image of the carbonized resin (Pd–Ag (60:40)). Dark particles indicate the alloy nanoparticles.

the resin since palladium and silver are miscible at any atomic ratio.[7,8] We confirmed the complete alloying of the palladium and silver by X-ray diffraction analysis.[6] Composition of Pd and Ag in the alloy was confirmed by complete degradation of the carbonized alloy composite followed by ICP-AES analysis.

According to the SEM image, the carbonized alloy composites were spherical in shape, but were approximately 1/3 size of the initial chelating resin beads. EDX analysis along the cross section of a carbonized bead (Fig. 1a) showed that Pd and Ag were uniformly distributed throughout the carbon matrix. Transmission electron microscopy (TEM) confirmed that nano-sized alloy particles were finely dispersed (Fig. 1b).[6] Noteworthy, the size distribution was rather narrow with average of around 10 nm in diameter. The carbonized products were highly porous as given in the numerical data of porosity (Table 1). The surface area and pore volume gradually decreased with an increase in the silver content in the alloy. One plausible interpretation is the difference in the catalytic activity by changing the alloy composition. An alloy with a high Pd content may enhance the carbonization that accompanies rapid gas evolution, leaving more space.

A double-layered working electrode was fabricated by sandwiching a silver wire net (indicated as a solid line in Fig. 2a) between the catalyst layer and the gas diffusion layer.[9] The

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Table 1. Specific Surface Area and Porosity Data of the Pd–Ag Alloy Dispersed Carbon Composites

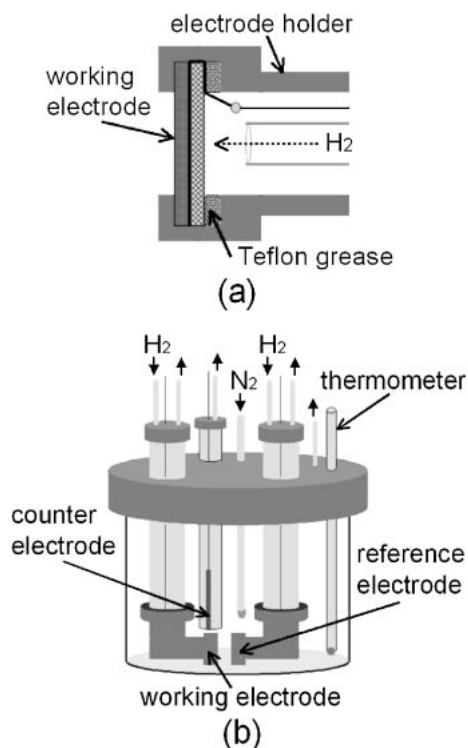|	Specific surface area /$m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$	Average pore diameter /nm
Pd–Ag (100:0)	310	0.20	2.6
Pd–Ag (70:30)	300	0.20	2.6
Pd–Ag (60:40)	240	0.14	2.4
Pd–Ag (50:50)	220	0.12	2.2

Fig. 2. (a) Schematic drawing of the electrode installed in the holder. (b) Configuration of the half cell setup.

catalyst layer was prepared by mixing Pd–Ag alloy dispersed carbon spheres and polytetrafluoroethylene (PTFE) with 90:10 wt % ratio, and the gas diffusion layer (hatched layer in Fig. 2a) was prepared from 30% PTFE and 70% graphite powder. Hydrophobic PTFE in the gas diffusion layer prevent the electrolyte solution from leaking out of the system. The electrode installed in the holder and the configuration of the cell system are depicted in Figs. 2a and 2b, respectively, where the working and the reference electrodes are faced each other with a 1 cm separation, and a Pt screen was used as a counter electrode. Hydrogen gas was supplied to both working and reference electrodes under atmospheric pressure with a flow rate of 50 $cm^3 min^{-1}$. All electrochemical experiments were carried out at 35 °C in a Pyrex glass vessel filled with 1 M H_2SO_4 (300 mL) as the electrolyte. Electrochemical steady polarization measurements were performed under potential regulation.[9]

The performance of the electrodes was evaluated by observing the polarization characteristics of the electro-oxidation of hydrogen (Eq. 1).[10] Hydrogen gas supplied from the rear face
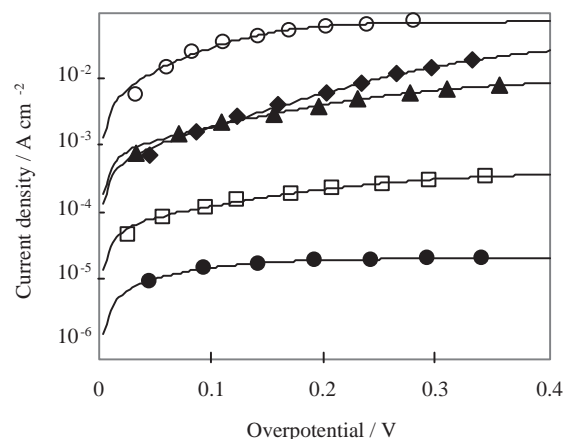

Fig. 3. Typical polarization curves of hydrogen electro-oxidation for a series of electrodes (1 M H_2SO_4, 35 °C). ○: Pd–Ag (60:40), ◆: Pd–Ag (100:0), ▲: Pd–Ag (80:20), □: Pd–Ag (40:60), ●: Pd–Ag (50:50).

Table 2. Fitted Parameters Derived from the Polarization Curves of Hydrogen Electro-Oxidation

	i_0 /$mA cm^{-2}$	iL /$mA cm^{-2}$	α_a	RMSE[a] /$mA cm^{-2}$
Pd–Ag (100:0)	0.67	38	0.17	0.2
Pd–Ag (80:20)	1.0	12	0.14	0.1
Pd–Ag (70:30)	1.4	47	0.18	0.6
Pd–Ag (60:40)	6.2	75	0.29	2.0
Pd–Ag (50:50)	0.011	0.052	0.11	0.0010

a) Root mean square error of the fitting.

of the working electrode diffuses into the catalyst layer and dissociates into protons on the catalytic surface, according to the Eq. 1.

$$H_2 \rightarrow 2H^+ + 2e^-. \tag{1}$$

Figure 3 shows the current density vs. overpotential curves for the electrodes prepared from the carbonized alloy composites of various Pd/Ag ratios. Reproducibility of the polarization data was confirmed by comparing the data to those obtained using two separately manufactured electrodes. The fitted lines were calculated according to the theoretical model expressed in Eq. 2.[9,10] Here, we considered the contribution of mass transfer, i.e., hydrogen diffusion process, in the electrode reaction as denoted iL term.

$$i(\eta) = \frac{\exp(\alpha_a n f \eta) - \exp(-(1 - \alpha_a) n f \eta)}{1/i_0 + \exp(\alpha_a n f \eta)/iL}. \tag{2}$$

The parameters and their units are as follows: i: current density (A cm^{-2}), η: overpotential (V), α_a: transfer coefficient, i_0: exchange current density (A cm^{-2}), iL: limiting current density (A cm^{-2}), n: number of electrons, F: Faraday's constant (9.648×10^4 C mol^{-1}), f: F/RT (V^{-1}).

We fixed $n = 2$ in this equation since two electrons are involved in the present electrochemical reaction. A well fitted curve to the experimental data was obtained with this assumption. The calculated parameters, i.e., exchange current density (i_0), limiting current density (iL), and transfer coefficient (α_a), are summarized in Table 2.

As seen from Fig. 3, the current density increased significantly with an increase in the silver content up to 40% and suddenly decreased with a Ag content of more than 60%. Thus, the performance of the Pd–Ag (60:40) electrode is one order of magnitude larger than that of a pure Pd electrode, but markedly less when the Ag content is more than 60%. In general, the performance of an electrode depends on the activity of catalysis and the structural parameters including surface area and micro and macro channel network of the electrode.[10] The catalytic activity is correlated to i_0 value, whereas iL is controlled by the diffusion of reactants in the electrode.[10] Diffusion of reactants has been considered in connection with the macro and micro structure of the electrodes. As has been shown in Table 1, specific surface area and pore volume of the alloy–carbon composite gradually decreased with an increase in the silver content in the alloy. The macropore volume determined by mercury porocimetry was similar among electrodes prepared under the same condition. Thus, macro and micro structural parameters do not directly correlate to the observed electrode performances. Hence, we attributed the remarkable composition dependency of the current density to the catalytic activity of Pd–Ag alloy.

Transport of hydrogen proceeds by dissociation and diffusion of hydrogen in the Pd–Ag alloy particles, and the activated hydrogen migrate through micro pore toward particle/electrode interface. The activation energies of hydrogen diffusion are following order: Pd–Ag (77:23) < Pd (100) < Pd–Ag (50:50).[11] In accord with this, hydrogen permeance in bulk Pd is known to increase by alloying with 20–30 wt % Ag and to decrease at a much higher Ag content.[2,8] Furthermore, according to the data of Sakamoto and co-workers,[12] heat of hydrogen dissolution (ΔH) for pure palladium ($-17.07\,\mathrm{kJ\,mol^{-1}}$) decreases with an increase in the silver content in the alloy, reaching a minimum value of $-23.4\,\mathrm{kJ\,mol^{-1}}$ at a Pd–Ag ratio of 60:40 and then increase rapidly reaching a value of $-12.16\,\mathrm{kJ\,mol^{-1}}$ at a Pd–Ag ratio of 50:50. They interpreted this phenomenon by the change in the more mobile Fermi electron concentration when palladium is replaced with silver in the alloy. Alloying of palladium with silver also alters the electroconductivity since silver is more electro-conductive than palladium. Thus, the striking enhancement in the electrode activity at a Pd–Ag ratio of 60:40 can be attributed to the favorable matching of solubility and diffusivity of hydrogen in the alloy and also an increase in the electro-conductivity by alloying with Ag.

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