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Preparation of Porous Carbon Spheres Dispersed with Pd–Ag Alloy Nanoparticles

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Porous carbon spheres dispersed with Pd–Ag alloy nanoparticles have been prepared by simultaneous complexation of Pd^{II} and Ag^{I} onto the chelating resin and subsequent thermal treatment, and the obtained alloy–carbon composites were examined as the electrode material in electrooxidation of hydrogen.

Recently, wet chemical process using appropriate organic templates for loading of metal precursor has attracted increasing attentions as the simple and promising procedure for the preparation of porous metal spheres.[1] The general method for the preparation of porous metals is to soak the organic template in the corresponding metal solution, and then the template is removed by firing in the presence of O_2, while metal-dispersed carbon composites are formed by carbonization of organic component in an inert atmosphere.[2] The use of ion-exchange resins as metal template has advantages to allow high dispersion of metal particles and easy control of morphology and size of the matrix.[2d] Furthermore, when two or more metal ions are loaded on the resin beads, binary or multicomponent metal alloys can be dispersed on the spherical carbon support. However, most of the precedent works have been limited to single metal systems.

Palladium–silver binary alloy systems have been studied, particularly in conjunction with hydrogenation/dehydrogenation catalysis,[3] hydrogen permeable membranes,[4] and as the electrode materials.[5] The physicochemical properties, for example, solubility and diffusion coefficient of hydrogen and critical temperature of α–β crystal phase transition substantially change by controlling the atomic ratio of Pd–Ag alloy.[6] As the consequence, hydrogen permeability, catalytic activity, and mechanical strength of alloys are remarkably affected by the Pd/Ag ratio. In this study, we have prepared novel carbon spheres dispersed with a series of Pd–Ag alloy nanoparticles. The chelating resin (CMA resin) bearing diethylenetriamine-*N*,*N*,*N*′,*N*′-tetraacetic acid group (Figure 1)[7] was used as the template for simultaneous loading of Pd^{II} and Ag^{I} from aqueous solution. The alloy–carbon spheres were examined as the electrode material in the electrooxidation of hydrogen.

The CMA resin can strongly retain Pd^{II} and Ag^{I} but with different binding ability. Therefore, we fed the mixture of the two metal ions with only small excess to the ligand capacity so that both of the metal ions were simultaneously retained onto the resin. According to the ICP atomic emission spectral analysis of metals the Pd/Ag ratio in the CMA resin was in fairy good agreement with that present in the feed solution (Supporting Information).[8] After complex formation with Pd^{II} and Ag^{I}, the chelating resin beads were calcined at 900 °C under N_2, and finally the metal species was reduced by H_2 at 1050 °C for 3 h. During this procedure, the chelating resin beads were carbonized and appeared dark gray keeping the initial spherical morphology. Thermal gravimetric analysis of the metal ion loaded chelating resin (Pd–Ag (40:60), the ratio of the wt % of metal component in the alloy) under N_2 showed that a marked mass loss starts at 200 °C associated with the decomposition of the polymer. Finally, the residual mass reached about 27% to that of the precursor by heating up to 900 °C.

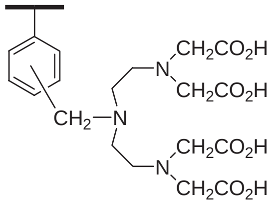

Figure 1. Ligand structure of the CMA resin. The resin matrix is composed of styrene-2%-divinylbenzene copolymer beads.

It is noted that, crystalline alloys of any Pd/Ag ratio can be formed by the thermal treatment since palladium and silver are miscible each other with any atomic ratio. Figure 2 shows the correlation between X-ray peak location and the atomic ratio of Pd/Ag. The intense diffraction peak at $2\theta = 40.14°$ assignable to pure palladium regularly shifts to lower angle associated with the increase of silver content in the alloy.[6] The observed peak positions are rather in good agreement with the solid line, which was drawn by connecting the peak of pure palladium and that of silver. Since palladium and silver are simultaneously retained in the chelating resin, alloying by mutual diffusion of atoms must favorably progress.

The SEM image (Figure 3a) of the carbonized alloy (Pd–Ag (40:60)) shows the spherical shape but approximately 35% reduction of the size from the initial template beads. EDX analy-

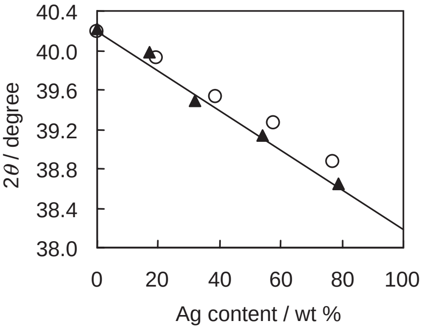

Figure 2. Shift of X-ray diffraction peak at $2\theta = 40.14°$ for palladium as a function of silver content (wt %) in the alloys. The solid line was drawn by connecting the peaks of pure palladium and silver. (O): carbonized resin dispersed with alloy particles, (▲): hollow alloy spheres prepared in the presence of O_2.

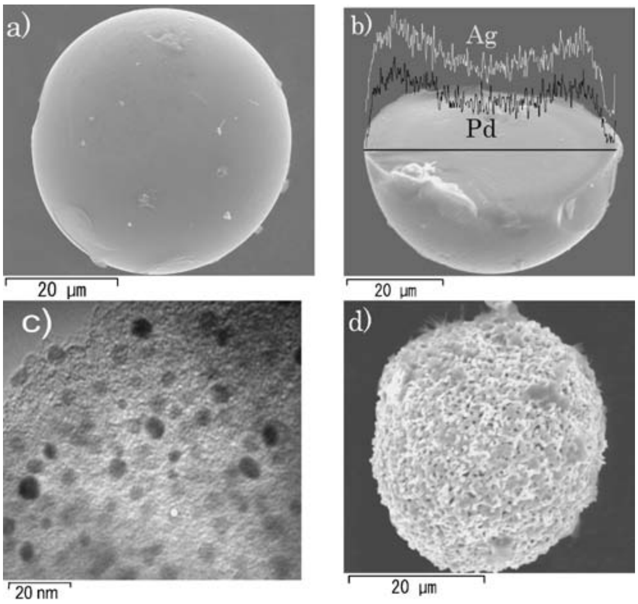

Figure 3. a) SEM image of the carbonized resin sphere (Pd–Ag (40:60)). b) Cross sectional SEM image and the EDX line profile of the carbonized resin indicating the Pd and Ag distribution. c) TEM image of the carbonized resin (Pd–Ag (80:20)). d) SEM image of hollow alloy sphere (Pd–Ag (40:60)).

sis along the cross section revealed that palladium and silver are distributed homogeneously in the carbon matrix (Figure 3b). Since the CMA resin is soft gel owing to low cross-linkage (2% divinylbenzene) of polymer matrix, both metal ions can be accommodated throughout the bead. Transmission electron microscopy (TEM) given in Figure 3c confirmed the formation of nanosized particles (10 nm or less) of alloy. Despite macropores are not observed, the carbonized product showed the specific surface area of more than $225\,m^2\,g^{-1}$ (Pd–Ag (40:60)) because of the presence of mesopores (mean pore diameter, 3.7 nm) in the carbon matrix. In contrast, when the metal-loaded precursor was fired under O_2 atmosphere at 600 °C, organic moiety was completely removed leaving hollow alloy spheres with apparent macropores (Figure 3d).

Hydrogen gas diffusion electrode was fabricated from the mixture of the alloy–carbon spheres and polytetrafluoroethylene (PTFE). The performance of the electrodes was evaluated by the polarization characteristics in the electrooxidation of hydrogen ($H_2 = 2H^+ + 2e^-$)[9] performed in 1 M sulfuric acid at 35 °C. Figure 4 shows the exchange current density[10] of the reaction vs. Pd/Ag ratios in the electrode. The exchange current density was estimated by the parameter fitting of the current density vs. overpotential curves. Noteworthy, the exchange current density increased significantly by alloying with silver at the metal ratio of Pd–Ag (60:40). It is known that addition of silver increases hydrogen solubility but decreases the hydrogen diffusivity.[4,6] Alloying of palladium with silver also alters the electro-conductivity since silver is more conductive than palladium. Thus, the enhanced activity of the alloy electrode (Pd–Ag (60:40)) may be attributed to the matching of conductivity, hydrogen solubility and hydrogen diffusivity in the alloy.[11] In analogy with this observation, the Pd–Ag (75:25) alloy membrane can transport hydrogen more quickly than pure palladium.[4]

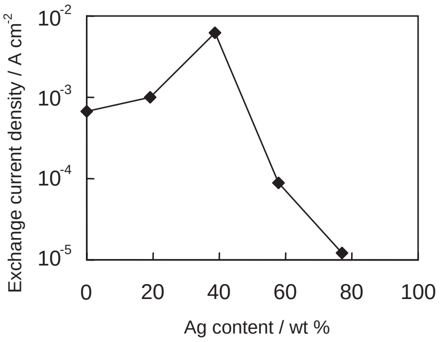

Figure 4. Exchange current density of the hydrogen oxidation reaction (1 M H_2SO_4, 35 °C) as the function of silver content in the carbonized alloy electrodes.

In summary, we have successfully fabricated carbon composite spheres in which Pd–Ag alloy nanoparticles of desired ratio are dispersed by simultaneous complexation of Pd^{II} and Ag^{I} and subsequent thermal treatment under N_2. We have demonstrated that the present alloy–carbon composite spheres were useful as the electrode material in hydrogen oxidation reaction. In particular remarkably higher performance of electrode was attained by alloying with silver at the metal ratio of around Pd–Ag (60:40).

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8 The data of Pd/Ag ratio in the chelating resin vs. that present in the feed solution is displayed in the Supporting Information. Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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