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Direct room-temperature synthesis of a highly dispersed Pd nanoparticle catalyst and its electrical properties in a fuel cell

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ABSTRACT

Highly dispersed palladium nanoparticles supported on bacterial cells were successfully prepared by a microbial method using the metal ion-reducing bacterium *Shewanella oneidensis*. Resting cells of *S. oneidensis* reduced soluble palladium(II) to insoluble palladium(0) at room temperature and neutral pH within 60 min when formate was provided as the electron donor. Transmission electron microscopy analysis of a thin section of *S. oneidensis* cells after exposure to a $PdCl_2$ solution revealed that palladium particles approximately 5–10 nm in size were deposited on the bacterial surface and in the periplasmic space. The initial concentrations of soluble palladium(II) and formate in the precursor solution strongly influenced the rate of palladium(II) reduction and the dispersity of biomass-supported palladium particles. The dried biomass-supported palladium was tested as an anode catalyst in a polymer electric membrane fuel cell for power production. The maximum power generation of the highly dispersed biomass-supported palladium particles was comparable to that of a commercial palladium catalyst.

1. Introduction

Supported metal nanoparticle catalysts are used in many commercially important applications, including hydrogenation, dehydrogenation, naphtha reformation, isomerization, hydrocracking, oxidation, automotive exhaust catalysts, and fuel cells. It is generally accepted that the catalytic activity can be improved by decreasing the particle size of the catalyst, which increases the number of reactive sites on the surface. For the application of metal nanoparticles as catalysts, it is desirable to prepare highly dispersed and nano-sized metal particles on a support surface.

Highly dispersed noble metal nanoparticles on a support surface have been prepared by microwave irradiation [1–3], chemical vapor deposition [4], impregnation and reduction of metal precursors in a microporous support [5,6], the colloidal method [7,8], and the microemulsion method [9,10]. These methods generally require an elevated temperature to complete the reduction of soluble noble metals and expensive protective agents such as surfactants to inhibit agglomeration of the nanoparticles and the support material. Any organic stabilizer must then be removed from the catalyst often by heating at a high temperature. Therefore, it is essential to develop a novel nanoparticle catalyst preparation method that uses less toxic precursors (e.g. water as the solvent), fewer reagents and synthetic steps, and a reaction temperature close to room temperature.

Microbial reduction of soluble noble metal ions to insoluble metal has attracted attention as a method to address these issues. The potential of bacteria to reduce metals has been known for over a century and a diverse group of bacteria can use this activity to conserve energy for growth. Microorganisms also have metal resistance and can detoxify metal ions by either reduction and/or precipitation of soluble toxic inorganic ions to insoluble non-toxic metal nanoclusters. Microbial detoxification can occur either by extracellular biomineralization, biosorption, complexation or precipitation, or intracellular bioaccumulation [11,12]. Bioreductive deposition of noble metal ions is attractive as an environmentally friendly method for nanoparticle synthesis because biological systems at room temperature and nearly neutral pH have low energy consumption and are environmentally safe. Recent studies have addressed the microbial preparation of biomass-supported nanoparticles and their application to catalysis. These include dehalogenation of chlorinated aromatics such as polychlorinated biphenyls and benzene hexachloride [13–20], hydrogenation of itaconic acid [21] and 2-pentyne [22], and application to Suzuki–Miyaura and Mizoroki–Heck reactions [23]. In particular, Yang et al. used the sulfate-reducing bacterium *Desulfovibrio desulfuricans* to prepare a biomass-supported Pd catalyst, which performed well in a fuel cell [24]. However, there are some unresolved issues with preparation and catalytic activity of these biomass-supported Pd catalysts. The Pd particles produced by *D. desulfuricans* were relatively agglomerated and exhibited negligible electrical output in the absence of heating at high temperature when applied to fuel cell electrodes. Furthermore, the catalyst contained a potent catalyst poison (H_2S) produced by *D. desulfuricans*, which needed to be removed.

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In comparison, the microbial method using the metal ion-reducing bacterium *Shewanella oneidensis* allowed for preparation of Pd nanoparticles without biogenic H_2S. *S. oneidensis* is one of the most versatile of all known metal reducing species and is known for its ability to reduce Pd(II) ions to insoluble Pd nanoparticles with formate, lactate, or hydrogen gas acting as the electron donor [15,16]. These studies reported the effects of Pd(II) concentration, type of the electron donor (e.g. H_2 or formate) on cell viability, particle size distribution, and catalytic properties in dechlorination. However, no reports have appeared concerning the application of biomass-supported Pd nanoparticles produced by *S. oneidensis* to catalysis in fuel cell electrodes. Herein, we report the preparation of highly dispersed Pd nanoparticles on bacterial cells by the microbial reduction using *S. oneidensis* and their catalytic activity towards the anode electrode in the polymer exchange membrane fuel cell (PEMFC) system. In the microbial reduction, the effects of formate and Pd(II) concentration (more than 1 mol/m^3) on bioreduction rate and Pd nanoparticle preparation were investigated for the first time. Furthermore, X-ray absorption near edge structure (XANES) was employed to determine the oxidation states of the biosynthesized Pd nanoparticles. In the evaluation of catalytic activity, the biomass-supported Pd was directly used for testing in a fuel cell without heating.

2. Experimental section

2.1. Bacterial strain and growth conditions

S. oneidensis strain MR-1 was obtained from the American Type Culture Collection (ATCC 700550) and grown aerobically in trypticase soy broth medium at 30 °C and pH 7.2. After 12 h of batch inoculation, *S. oneidensis* cells were harvested by centrifugation, re-suspended in KH_2PO_4/NaOH buffer (pH 7.0), and pelleted again by centrifugation. This procedure was repeated twice, and the washed cells were subsequently re-suspended in KH_2PO_4/NaOH buffer (pH 7.0). The cell suspension was bubbled with N_2 for 10 min and immediately used for the microbial reduction of Pd(II).

2.2. Preparation of palladium nanoparticles

An anaerobic glovebox was used to carry out the microbial reduction experiments. In a typical reduction experiment at 25 °C, 5 mL of the *S. oneidensis* cell suspension was added to 0.3 mL aqueous $PdCl_2$ and immediately diluted to 15 mL with KH_2PO_4/NaOH buffer (pH 7.0) with continuous stirring. The cell concentration in the mixed solution was held constant at $(6.3 \pm 0.4) \times 10^{15}$ cells/m^3, and the initial concentration of $PdCl_2$ ranged from 1–20 mol/m^3. Formate was provided as the electron donor for microbial reduction, and its initial concentration was varied between 20 to 200 mol/m^3 in different experiments. To follow the time course of the microbial Pd(II) reduction, an aliquot of this mixture was periodically withdrawn and analyzed for Pd. The concentration of Pd in the liquid samples was determined by atomic absorption spectroscopy or inductively-coupled plasma (ICP) spectroscopy. The number of *S. oneidensis* cells in the solution was counted in a Petroff–Hausser counting Chamber (Hausser Scientific, Horsham, PA, USA) with a microscope (BX51, Olympus, Japan).

The *S. oneidensis* cells and biomass-supported particles were observed by transmission electron microscopy (TEM) using a JEOL model JEM-2100F equipped with an EDX attachment (JEOL model JED-2300T). Samples for TEM analysis were prepared on carbon-coated copper TEM grids. The particle size distribution was measured by the microscopic method, in which the geometric mean diameter and geometric standard deviation were evaluated by direct counting of approximately 1000 nanoparticles per sample from TEM photographs using image analysis software (Ruler). Assuming that the particles are spherical, the specific surface area S_W of the biogenic nanoparticles was calculated using the following expression [25]:

$$S_w = \frac{\sum n_i \pi D_i^2}{\sum n_i \pi D_i^3 \rho / 6} \quad (1)$$

where n_i is the number of particles having diameter of D_i, and ρ is the particle density.

Thin sections of *S. oneidensis* cells were analyzed by TEM after exposure to $PdCl_2$ solution at pH 7.0. The cells were prefixed in 2% glutaraldehyde in 30 mol/m^3 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer at 4 °C. After washing with HEPES buffer, they were fixed with 2% osmium tetraoxide in distilled water for 2 h at 4 °C. The cells were then dehydrated at room temperature with ethanol (50–100%). Embedding was carried out using a mixture of resin (Epon 812), hardeners (dodecenyl succinic anhydride and methyl nadic anhydride), and accelerator (dimethylaminomethyl phenol). The mixture was polymerized at 60 °C for 2 days. Ultrathin sections of 80–90 nm were cut using an ultramicrotome, and mounted on a carbon-coated copper TEM grid. The sections were stained with 2% uranyl acetate in distilled water and lead staining solution prior to TEM analysis.

XANES was used to determine the oxidation states of Pd in the *S. oneidensis* cells after exposure to aqueous $PdCl_2$ solution at pH 7.0. XANES involves very little manipulation of the bacteria samples, and provides accurate information on the oxidation states of elements. For XANES analysis, the *S. oneidensis* cells, after exposure to aqueous $PdCl_2$ solution, were harvested by centrifugation, re-suspended in phosphate buffer, and pelleted again by centrifugation. The washed cells were then re-suspended in phosphate buffer. A 2 mL aliquot of cell suspension was loaded into a glass tube (5 cm long) and analyzed for speciation of Pd using XANES. Reference samples were Pd foil (Pd(0)) and 10 mol/m^3 aqueous $PdCl_2$ solution. Measurements were conducted at the BL14B2 line in the Japan Synchrotron Radiation Research Institute (JASRI) in Hyogo, Japan. Palladium K XANES was used to collect spectra of samples in the transmission mode using standard operating conditions of 8 GeV and 100 mA. A silicon (311) double-crystal monochromator with an entrance slit of 1 mm was used for all XANES measurements. Incoming X-ray intensity was monitored with an ion chamber filled with Ar–Kr (75:25, v/v). XANES spectra were collected with a 0.27 eV step size (0.15 s for 1 step) around the K edge of Pd (ca. 24.347 keV). Signals from the ion chamber were averaged to obtain the absorption at each energy level.

2.3. Evaluation of catalytic activity in a fuel cell

The biomass-supported Pd nanoparticles were dried and tested for their catalytic activity as anodes in a PEMFC for power production. After microbial reduction tests, the biomass-supported Pd nanoparticles were harvested by centrifugation, washed with deionized water, and dried at 50 °C for 6 h. Before performing a fuel cell test, the Pd content of the dried biomass was accurately determined by completely dissolving the sample in aqua regia for quantitative analysis using ICP spectroscopy. Four types of biomass-supported Pd catalyst were prepared by altering the initial Pd(II) concentration between 2.5 and 20 mol/m^3.

In a typical fuel cell test using a PEMFC Kit (Techno Xpress Inc.), the biomass-supported Pd catalyst for the anode inks was prepared by mixing the dried biomass-supported Pd nanoparticles with carbon particles, 10 wt.% Nafion solution (1.0 mL), and ultra pure water (0.4 mL). Commercial Pt catalyst (Chemix. Co. Ltd.) was used as the cathode ink for all the tests. In the preparation of the membrane electrode assembly (MEA), anode and cathode inks were uniformly printed onto a Nafion membrane to give a Pd loading of 1.28 mg/cm^2 on the anode and 0.16 mg/cm^2 on the cathode for the H_2/O_2 PEMFC test. After drying the anode and cathode inks, each catalyst layer was