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Composition-tuned porous Pd-Ag bimetallic dendrites for the enhancement of ethanol oxidation reactions

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ABSTRACT

Porous Pd-Ag bimetallic dendrites of various compositions were prepared using a galvanic replacement reaction between Ag dendrites and $Pd(NO_3)_2$, in which the compositional variation could be effectively controlled by adjusting the concentration of $Pd(NO_3)_2$. The structural and morphological results revealed that the Ag-rich bimetallic dendrites had hollow structures with porous surface layers, whereas the Pd-rich bimetallic dendrite structures collapsed into large aggregates composed of Pd fragments. The electrochemical measurements for the ethanol oxidation revealed that in terms of electrocatalytic activity, the $Pd_{40}Ag_{60}$ bimetallic dendrites were superior to the other Pd-Ag catalysts. This could be attributed to the geometric and electronic effects of the porous Pd-Ag bimetal dendritic structure.

1. Introduction

Fuel cells are widely recognized as very attractive devices in that they are able to obtain electric energy directly from the combustion of a chemical product. Low temperature fuel cells, which generally involve a proton electrolyte membrane, can be used for various power applications. Alcohols and mainly methanol are widely proposed as possible fuels for mobile applications such as electric vehicles. For direct methanol fuel cell applications, the direct oxidation of methanol in fuel cells has been widely investigated [1]. However, methanol has long been considered a toxic product, and it has also been associated with possible environmental problems in relation to its large miscibility to water. Direct ethanol fuel cells (DEFCs), as eco-friendly energy conversion devices, have attracted a great deal of attention since ethanol is less toxic and has a higher theoretical energy density (8.01 kW h/kg) than methanol (6.09 kW h/kg) [2–8]. However, at present, DEFC development is still lacking due to slow anode kinetics and catalyst poisoning brought about by the carbonaceous species [6,9].

A superb electrocatalyst needs to achieve high levels of electrocatalytic activity while simultaneously being cost effective in order to be suitable for practical applications. In previous research, platinum appeared to be a promising catalyst as it had the highest catalytic activity among anode catalysts for the electro-oxidation of alcohols in a fuel cell [10]. Unfortunately, the surface of the Pt was usually heavily poisoned by the strong adsorption of carbonaceous products during the oxidation of fuels, resulting in a deterioration of catalytic performance [11]. Pd-based catalysts have been considered as promising candidates for use in DEFCs due to their superior activity for ethanol oxidation reactions (EORs) in alkaline media [8,12–15]. It has also been well established that the catalytic activity and stability of Pd-based catalysts could be further improved by alloying the catalysts with another metal. In view of the *d*-band theory, Ag would be the most desirable alloying material due to the large difference (Ag: -4.30 eV *vs.* Pd: -1.83 eV) in *d*-band centers [16]. Hence, catalytic activity could be effectively enhanced by tailoring the electronic redistribution (i.e., compositional variation).

To design Pd-Ag bimetallic catalysts with several functionalities (porous, dendritic and composition-tuned) in one object, improved synthetic methods are needed to control the composition, morphology and architecture. Generally, synthesizing Pd-Ag alloys is achieved via galvanic replacement using a polymeric or halogenic precursor [17–20]. However, when carrying out galvanic replacement using these precursors, complex processes such as washing and/or etching to eliminate insoluble compounds (AgCl) are

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inevitable. In addition, it is difficult to control the composition precisely in the presence of an etchant. Therefore, achieving a synthetic route for composition-tuned Pd-Ag catalysts remains a grand challenge.

In this paper, porous Pd-Ag bimetallic dendrites were synthesized via a galvanic replacement reaction between an Ag template and $Pd(NO_3)_2$ without any additional processes such as washing and/or etching. In addition, the composition was controlled by adjusting the concentration ratio of $Pd(NO_3)_2$ to Ag dendrite. Subsequently, the catalytic activity toward the EOR was evaluated for DEFC applications.

2. Experimental

2.1. Synthesis of Ag dendrites via discharge in water

The plasma-induced reduction method for the synthesis of Ag dendrites in this paper was described in detail in a previous publication [21,22]. Silver nitrate ($AgNO_3$) was added as a precursor into deionized water to prepare an $AgNO_3$ solution. The plasma reactions in the $AgNO_3$ solution were conducted in a Teflon vessel with an inner diameter and height of 80 mm. A plasma discharge was generated across the electrodes using a bipolar pulsed power supply (Kurita, Seisakusyo Co. Ltd), which consisted of a pulse generator connected to a high voltage amplifier. 2.4 kV with a bipolar pulsed DC (pulse width: 2 μs, frequency: 25 kHz) was applied to inter-electrodes (gap distance: 1 mm) for 60 min.

2.2. Synthesis of porous Pd-Ag dendrites and porous Pd via galvanic replacement reaction

After the Ag dendrites were synthesized, the N_2 gas was purged into the solution containing Ag dendrites for 60 min to eliminate the dissolved oxygen. Then, porous Pd-Ag bimetallic dendrites were prepared at 90 °C via the replacement reaction between the Ag dendrites and $Pd(NO_3)_2$. At this time, to obtain different Pd-Ag compositions, the Ag (27 mg) to Pd (0.33–1.5 mM, 250 ml) molar ratio was controlled, *i.e.*, 3:2, 1:1, 1:2 and 1:3 Pd/Ag molar ratios were selected. As a reference sample, porous Pd dendrites were synthesized using the same synthetic method (via a 3:2 Pd/Ag molar ratio), except for the additional etching process, which was conducted using HNO_3 to remove the Ag atoms from the Pd-Ag structure.

2.3. Characterization of Pd-Ag dendrites

Elemental compositions were acquired using an inductively coupled plasma mass spectrometer (ICP-MS, ELAN-6100, Perkin-Elmer SCIEX). The crystalline structures were recorded with an X-ray diffractometer (XRD, SmartLAB, Rigaku). High-resolution transmission electron microscopy (HR-TEM) was performed on a JEOL JEM-ARM200F at an accelerating voltage of 200 kV. Elemental distribution mapping was conducted using energy-dispersive X-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Fisher Scientific K-ALPHA XPS with monochromatic Al Kα radiation (hν = 1486.6 eV).

2.4. Electrochemical measurements

Electrochemical characterizations were conducted using cyclic voltammetry (CV) and chronoamperometry (CA) with a three-compartment electrochemical glass cell and a potentiostat (VersaSTAT III, PAR) at room temperature. The working electrode was prepared by depositing porous Pd and Pd-Ag dendrites on Vulcan XC-72 by pipetting 25 μl of catalyst aqueous solution (1.44 mg $_{\text{metal}}$ and 5.76 mg $_{\text{Vulcan XC-72 carbon}}$ in 2.5 ml ethanol) on a glassy carbon electrode with a diameter of 5 mm. Before carrying out the cyclic voltammetry and chronoamperometry tests, the activation process was conducted in a 0.5-M NaOH N_2-saturated alkaline media at a scan rate of 500 mV/s until the reproducible curves were obtained. After an activation step, CV measurements were conducted in the same aqueous solution at a scan rate of 50 mV/s. The catalytic oxidation of the ethanol experiments was performed in a 0.5 M NaOH solution containing 1.0 M of C_2H_5OH at a scan rate of 50 mV/s. All of the cyclic voltammograms were recorded between the potential range of −0.926 and 0.274 V. The CA curves were recorded under a constant potential of −0.1 V vs. Hg/HgO.

3. Results and discussion

The composition of the Pd-Ag bimetallic dendrites was adjusted by varying the ratio of the concentrations of Ag dendrites and Pd precursors in the synthesis. The Pd-Ag compositions, as measured from the ICP-MS, were $Pd_{59}Ag_{41}$, $Pd_{52}Ag_{48}$, $Pd_{40}Ag_{60}$ and $Pd_{34}Ag_{66}$, as denoted in Table 1. The Pd content in the Pd-Ag dendrites increased proportionately with increasing the concentration of $Pd(NO_3)_2$.

Fig. 1a and b shows the XRD patterns and enlarged peaks for the (111) plane of the Pd-Ag bimetallic dendrites with different compositions. The XRD peaks of the Pd-Ag dendrites can be assigned to the {111}, {200} and {220} diffractions of a pure phase of the face-centered cubic (FCC) structures, in which the peaks are located between the corresponding standard peaks of pure Pd (JCPDS #01-1201) and Ag (JCPDS #01-1164), suggesting the formation of Pd-Ag alloyed structures. Furthermore, the experimental values based on the lattice parameters calculated from the XRD and the composition measured by the ICP-MS agreed well with the theoretical values obtained based on Vegard's law [23], suggesting that the Pd-Ag binary systems formed a solid solution (Fig. 1c). Interestingly, the peak broadening was observed with compositional variation. As the Pd/Ag molar ratio increased, the peaks became broader, indicating that the crystalline size of the Pd-Ag nanostructures gradually decreased. In order to verify this, the mean crystalline sizes for the (111) plane of the Ag, Pd-Ag and Pd nanostructures were calculated using the Scherrer formula, as listed in Table 1. $Pd_{59}Ag_{41}$, which had a high Pd content, exhibited the largest crystalline size at 30.1 nm, while $Pd_{34}Ag_{66}$, which had a low Pd content, showed the minimum size at 10.2 nm. As a result, it was confirmed that the crystalline size of the Pd-Ag bimetallic dendrite changed during the galvanic replacement reaction. Possible reasons for this will be discussed in the microscopy section below.

Fig. 2 presents the representative TEM images of the as-synthesized Ag, Pd and Pd-Ag dendrites. Before the replacement reaction, the Ag dendrites with hierarchical structures had a long main stem with many well-aligned side branches (Fig. 2a). After the completion of the replacement reaction (using the 1:3 Pd/Ag ratio), the $Pd_{34}Ag_{66}$ revealed that similar dendritic structures had been obtained. However, the surface of the dendrites became bumpy and developed a porous structure (Fig. 2b, c). These phenomena could be explained by the fact that each Pd atom was formed at the expense of two Ag atoms in the reaction. The formation mechanism for the porous Pd-Ag dendrites relied on the stoichiometric relationship shown in Eq (1).

$$2Ag_{(s)} + Pd^{2+}{}_{(aq)} \rightarrow Pd_{(s)} + 2Ag^{+}{}_{(aq)} \quad (1)$$

Based on the reaction in Eq. (1), only one Pd atom was generated for every two Ag atoms that were oxidized because the standard reduction potential of the Pd^{2+}/Pd was higher than that of the Ag^{+}/Ag. Consequently, the rapid galvanic replacement reaction created