

Highly Ordered Pd Nanowire Arrays as Effective Electrocatalysts for Ethanol Oxidation in Direct Alcohol Fuel Cells

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Direct alcohol fuel cells (DAFCs) based on liquid fuels have attracted enormous attention as power sources for portable electronic devices and fuel-cell vehicles owing to the much higher energy density of liquid fuels than gaseous fuels such as hydrogen (e.g., the energy densities of ethanol and methanol are 6.34 kWh L^{-1} and 4.82 kWh L^{-1} , respectively, as compared to 0.53 kWh L^{-1} for gaseous hydrogen at 20 MPa.^[1] Among various liquid fuels, ethanol is particularly attractive because it is less toxic than methanol and can be produced in large quantities from agricultural products. Ethanol is also the major renewable biofuel from the fermentation of biomass.^[2] Pt and Pt-based catalysts such as PtRu/C have been extensively investigated as electrocatalysts for the electrooxidation of liquid fuels such as methanol and ethanol.^[1b,3] However, the high cost and limited supply of Pt constitute a major barrier to the development of DAFCs. We studied recently Pt-free electrocatalysts for the electrooxidation reactions of ethanol and methanol, and the results revealed that Pd is a good electrocatalyst for ethanol oxidation in alkaline media.^[4]

Metal nanowire arrays (NWAs) have attracted much attention and interest owing to their excellent physical and chemical properties and have been extensively investigated for applications such as high-density magnetic recording devices^[5] and sensors.^[6] Ordered nanowire or nanotube arrays have also been applied for methanol oxidation and H_2O_2 electrocatalytic reduction because of their high active surface area.^[7] Among various techniques to synthesize NWAs, the anodized aluminum oxide (AAO) template method is probably the simplest and most versatile approach to creating highly ordered metal NWAs with uniform and tunable porous structure and good mechanical and thermal stability.^[8] Electrodeposition has been shown to be an efficient method for the growth of uniform and continuous metallic nanowire arrays.^[9] Despite

the exceptional physical, chemical, and electrical properties of metal NWAs, there is little information on the electrocatalytic properties of Pd NWAs. Here, we report the fabrication of highly ordered Pd NWA electrodes by the AAO template-electrodeposition method, and the results show that Pd NWAs are highly active for ethanol oxidation in alkaline media, demonstrating the potential of applying Pd NWAs as effective electrocatalysts for DAFCs.

Figure 1 shows typical scanning electron microscopy (SEM) images of Pd NWAs after the AAO template has been fully dissolved. The Pd nanowires (NWs) are highly ordered with uniform diameter and length. The average length and diameter of the Pd NWs are ca. 800 and ca. 80 nm, respectively. The NWs are uniform, well isolated, parallel to one another, and standing vertically to the electrode substrate surface. The hexagonal shape of the Pd NWs is due to the AAO porous structure during anodization.^[10] The X-ray diffraction (XRD) pattern (inset in Fig. 1a) indicates that the Pd NWAs exhibit a typical face-centered cubic (fcc) lattice structure. The strong diffraction peaks at 40.10° , 46.49° , and 68.08° correspond to the (111), (200), and (220) facets of Pd. This indicates that Pd NWAs have been successfully fabricated.

Figure 2a shows cyclic voltammograms (CVs) of ethanol oxidation in a $1.0 \text{ M KOH} + 1.0 \text{ M C}_2\text{H}_5\text{OH}$ solution on a Pd film electrode (curve a, Pd loading: 1.10 mg cm^{-2}), a Pd NWA electrode (curve c, Pd loading: 0.24 mg cm^{-2}), and an E-TEK PtRu/C electrode (curve b, Pt loading: 0.24 mg cm^{-2}). The cyclic voltammograms of the Pd film, E-TEK PtRu/C, and Pd NWA electrodes in 1.0 M KOH solution without ethanol are shown in Figure 2b. In the CVs obtained in 1.0 M KOH electrolyte solution, the anodic peaks appearing between -0.73 and -0.53 V versus Hg/HgO on Pd and -0.8 and -0.5 V versus Hg/HgO on Pt originate from the desorption of atomic hydrogen on the electrocatalysts (Fig. 2b). Thus the area of H desorption after the deduction of the double layer region on the CV curves represents the charge passed for the H desorption, Q_H , and is proportional to the electrochemically active area (EAA) of the electrocatalysts.^[11] The value $Q_H = 10.6 \text{ mC cm}^{-2}$ for the Pd NWA electrode is much higher than 3.4 mC cm^{-2} for the Pd film electrode and 4.6 mC cm^{-2} for the E-TEK PtRu/C electrode. This shows that the Pd NWA electrode has high EAA, most likely due to the well-defined and uniform porous structure of the nanowires in the arrays (Fig. 1). Such well-defined nanowire structure enhances the active sites for the electrooxidation reaction of ethanol.

The high electrocatalytic activity of the Pd NWA electrode is also indicated by its superior performance for the electroox-

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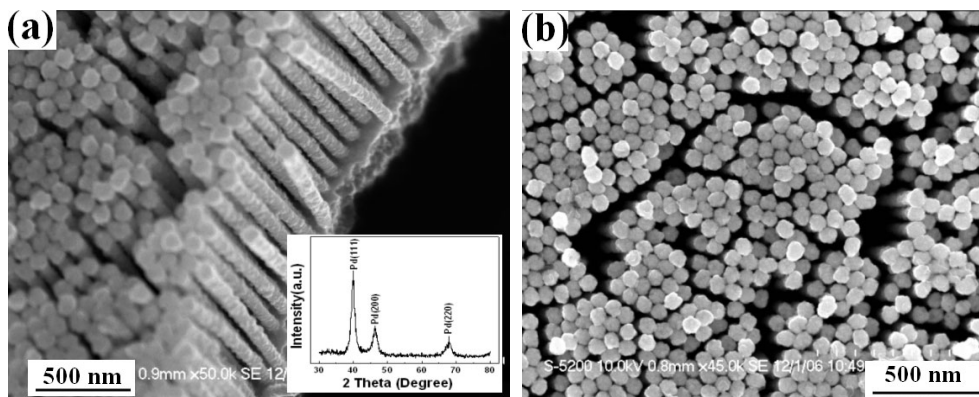


Figure 1. SEM images of a) cross section and b) surface of Pd NWAs. Inset in (a): XRD pattern of Pd NWAs.

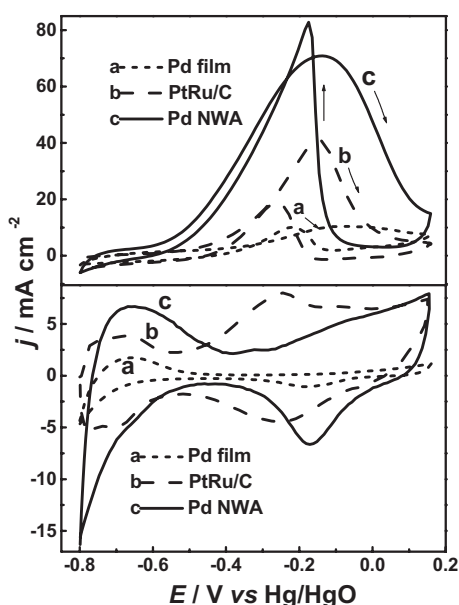


Figure 2. CVs measured on a Pd film electrode (curves a, Pd loading: 1.1 mg cm^{-2}), E-TEK PtRu (2:1 by weight)/C electrode (curves b, Pt loading: 0.24 mg cm^{-2}), and Pd NWA electrode (curves c, Pd loading: 0.24 mg cm^{-2}) in $1.0 \text{ M KOH} + 1.0 \text{ M C}_2\text{H}_5\text{OH}$ (upper panel) and 1.0 M KOH (lower panel) solution at a scan rate of 50 mV s^{-1} .

oxidation reaction of ethanol, as shown in Figure 2a. The onset potential for the ethanol oxidation on the Pd NWA electrode is -0.62 V , which is 150 mV more negative than the -0.45 V observed on the Pd film electrode and 40 mV more negative than the -0.58 V obtained on the conventional E-TEK PtRu/C electrocatalysts. The reduction in the onset anodic potential shows the significant enhancement in the kinetics of the ethanol oxidation reaction. Ethanol oxidation is characterized by well-separated anodic peaks in the forward and reverse scans, similar to that of the methanol oxidation reaction on Pt-based electrocatalysts in acid media.^[12] Thus, the magnitude of the anodic peak current in the forward scan is also directly proportional to the amount of ethanol oxidized at the Pd and

PtRu electrodes. The peak current density is 10 , 41 , and 74 mA cm^{-2} for the reaction on the Pd film, E-TEK PtRu/C, and Pd NWA electrodes, respectively. The anodic peak current on the Pd NWA electrode is 7 times that on the Pd film electrode and almost twice that on the PtRu/C electrode. The significantly negatively shifted onset potential and high anodic peak current for the ethanol electrooxidation reaction on the Pd NWA electrode show that Pd NWA electrodes have much higher electrocatalytic activity than conventional Pd film electrodes. Moreover, Pd NWAs also show a higher activity than E-TEK PtRu/C electrocatalysts for ethanol electrooxidation in alkaline media at the same electrocatalyst loading of 0.24 mg cm^{-2} .

For the ethanol oxidation reaction on the Pd NWA electrode, the anodic oxidation current in the reverse scan is quite sharp in comparison with that observed on Pd film and PtRu/C electrodes. This may be related to the significant oxidation of adsorbed intermediate species on the highly active Pd NWA electrode and implies that ethanol electrooxidation on the Pd NWA electrode may not proceed directly via a total oxidation to CO_2 . However, the reasons for such a sharp auto-oxidation peak in the reverse scan are not clear at this stage.

The electrochemical stability of Pd film, PtRu/C, and Pd NWA electrodes for ethanol electrooxidation was investigated by chronoamperometric experiments at -0.3 V versus Hg/HgO in $1.0 \text{ M KOH} + 1.0 \text{ M C}_2\text{H}_5\text{OH}$ solution at room temperature (Fig. 3). The polarization current for the ethanol electrooxidation reaction shows a rapid decay, similar to the ethanol electrooxidation reaction on the Pt-based electrocatalysts in acid media.^[13] This may indicate a similar poisoning mechanism of the intermediate species during the ethanol electrooxidation reaction on the Pd and PtRu/C electrocatalysts in alkaline media. Breaking the C–C bond for a total oxidation to CO_2 is a major problem in ethanol electrocatalysis. Nevertheless, the current decay for the reaction on the Pd NWAs is significantly slower than that on the Pd film and PtRu/C electrocatalysts. At the end of the 30 min test, the oxidation current on the Pd NWAs is considerably higher than

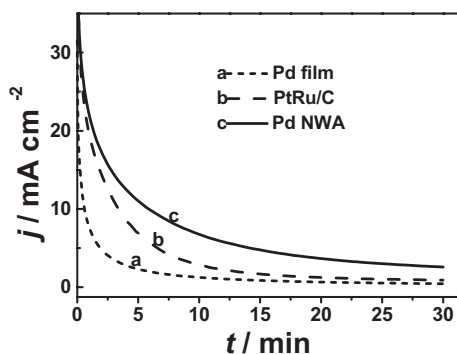


Figure 3. Chronoamperometric curves for ethanol electrooxidation at -0.3 V versus Hg/HgO on a Pd film electrode (curve a, Pd loading: 1.1 mg cm^{-2}), E-TEK PtRu (2:1 by weight)/C electrode (curve b, Pt loading: 0.24 mg cm^{-2}), and Pd NWAs electrode (curve c, Pd loading: 0.24 mg cm^{-2}) in a $1.0 \text{ M KOH} + 1.0 \text{ M C}_2\text{H}_5\text{OH}$ solution.

on the Pd film and E-TEK PtRu/C electrodes. This shows that the nanowire array structure enhances the electrochemical stability of Pd electrocatalysts for the ethanol electrooxidation reaction in alkaline media.

We also examined the effect of the morphology and structure of Pd NWAs on the electrocatalytic activity of the Pd NWA electrodes for the ethanol electrooxidation reaction. Figure 4 shows SEM images of a Pd NWA electrode fabricated with prolonged deposition time. The length of the Pd nanowires was ca. $6 \mu\text{m}$ and Pd loading was 1.80 mg cm^{-2} . The nanowires did not stand perpendicular to the electrode substrate and were bent due to their extra length. The activity of the Pd NWA electrode for the ethanol electrooxidation was also measured by cyclic voltammetry in $1.0 \text{ M KOH} + 1.0 \text{ M C}_2\text{H}_5\text{OH}$ solution. The onset potential is the same as that on the Pd NWA electrode with a Pd loading of 0.24 mg cm^{-2} , while the anodic peak current in the forward scan is 94 mA cm^{-2} , higher than the 74 mA cm^{-2} obtained on the Pd NWAs electrode with a lower Pd loading. However, the mass activity of the Pd NWA electrode with NW length of

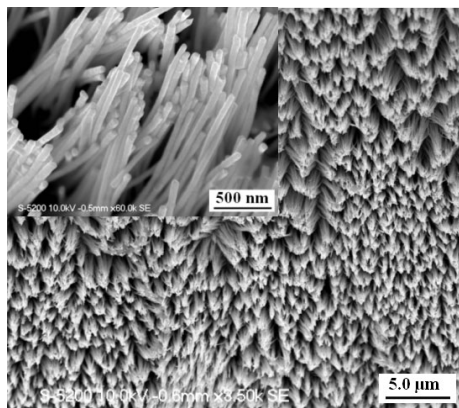


Figure 4. SEM image of the surface of a Pd NWA with an average nanowire length of ca. $6 \mu\text{m}$ (Pd loading: 1.80 mg cm^{-2}). Inset: Enlarged image of the Pd NWA.

$6 \mu\text{m}$ is 52 A g^{-1} , significantly smaller than the 308 A g^{-1} obtained on the Pd NWA electrode with much shorter nanowires of 800 nm . This clearly demonstrates that utilization efficiency and electrocatalytic activity of the Pd NWAs electrode depend strongly on the length and structure of the nanowires. In the case of Pd NWAs with short nanowires (see Fig. 1), the nanometer-sized gaps or pores between the nanowires in the array are straight and short, acting as effective transportation channels to and from the electrode/electrolyte interface for the liquid fuel and products formed during the electrooxidation of ethanol. This appears to be supported by the very high electrocatalytic activity of the Pd NWA electrode with a nanowire length of 800 nm in comparison to that of the conventional Pd film and PtRu/C electrodes (Fig. 2). However, when the nanowires get too long, the channels or gaps between the nanowires are no longer straight due to the bent and collapsed nanowire structure (Fig. 4). This in turn significantly increases the resistance for diffusion of liquid fuel and products to and from the Pd NWA electrodes. This could be the reason for the significantly reduced mass activity of the Pd NWA electrodes with nanowires of $6 \mu\text{m}$.

In summary, highly ordered Pd NWA electrodes have been successfully fabricated by the AAO template-electrodeposition method. The Pd NWAs have high electrochemically active surface areas. The electrocatalytic activity and stability of the Pd NWAs for ethanol electrooxidation are not only significantly higher than that of conventional Pd film electrodes, but also higher than that of the well-established commercial E-TEK PtRu/C electrocatalysts. The Pd NWAs presented in this paper show great potential as excellent electrocatalysts for ethanol electrooxidation in alkaline media in direct ethanol fuel cells.

Experimental

Porous AAO templates were fabricated through a two-step anodization process.^[9a,14] Prior to anodization, high-purity aluminum foils (99.999%) were annealed at 500°C for 2 h in vacuum, followed by degreasing in acetone. Anodization was carried out in $1 \text{ M H}_2\text{SO}_4$ solution for 2 h. The alumina layer formed during the anodization step was removed in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%). Then the aluminum foil was oxidized again at the same conditions for 5 h. The AAO template was etched in a saturated SnCl_4 solution to remove the remaining aluminum. The AAO template was treated again in a 5 wt% phosphoric acid solution at 25°C for 20 min to remove the barrier layer on the other side of the aluminum foil.

A glassy carbon electrode (GCE) was polished and thoroughly cleaned. A piece of as-prepared AAO template was attached to the polished surface of the GCE. Electrodeposition was carried out in an aqueous solution containing $0.5 \text{ g L}^{-1} \text{ Pd}(\text{NH}_3)_4\text{Cl}_2 + 0.8 \text{ g L}^{-1} \text{ Na}_2\text{EDTA}$, where EDTA is ethylenediaminetetraacetic acid. The pH value of the solution was adjusted to 8.5 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. A Pd NWA electrode with a nanowire length of 800 nm was deposited at a potential of -0.6 V (vs. saturated calomel electrode, SCE) for 40 min. Double distilled water was used and solutions were purged with Ar before the experiment. The Pd nanowire array embedded in the porous alumina template was placed in a 2 M NaOH solution for 1 h to completely remove the AAO, followed by washing in distilled water. The electrodeposition of the Pd film electrode was carried out on the GCE under

conditions similar to that for the Pd NWA electrode. For the Pd NWA electrode with a nanowire length of 6 μm , deposition was carried out in 2.0 g L⁻¹ Pd(NH₃)₄Cl₂ + 0.32 g L⁻¹ Na₂EDTA solution at -0.6 V (vs. SCE) for 1 h.

PtRu(2:1 by weight)/C (E-TEK, USA) electrode was fabricated by casting poly(tetrafluoroethylene) (PTFE)-impregnated PtRu/C catalyst ink onto the GCE. The Pt loading was 0.24 mg cm⁻². Electrochemical experiments were performed on a PARSTAT 2273 electrochemical workstation (Princeton, USA) at 25 °C using a standard three-electrode cell. A platinum foil (3.0 cm²) and Hg/HgO (1.0 M KOH) were used as the counter and reference electrodes, respectively. Cyclic voltammograms were obtained in 1.0 M KOH + 1.0 M C₂H₅OH and 1.0 M KOH solutions at room temperature at a scan rate of 50 mV s⁻¹ in the potential range of -0.8 to 0.3 V versus Hg/HgO. Chronoamperometric experiments were carried out at -0.3 V versus Hg/HgO in 1.0 M KOH + 1.0 M C₂H₅OH solution at room temperature. XRD was carried out on a D/MAX2200 diffractometer. SEM analysis was performed using a Hitachi S-5200.

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