PALLADIUM-NANOSTRUCTURES ON PLATINUM-BLACK CATALYSTS INTEGRATED INTO A MICROFABRICATED SI-BASED MICROFUEL CELL

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ABSTRACT

In this work, we investigate the effect of the structure and composition of the catalyst on the electro-oxidation of formic acid, first in an electrochemical cell and then in a microfabricated silicon-based membrane electrode assembly (silicon-MEA). The silicon-MEAs consist of two grids that serve as the catalyst support and current collector, and they guide the flow of fuel/oxidant to the anode/cathode and carbon dioxide away from the anode. Different dendritic Pt-black catalyst support structures were fabricated by varying electrodeposition conditions. Bimetallic Pt/Pd catalyst tailored to formic acid-DI water fuel mixtures were obtained by spontaneous deposition on high surface area Pt structures. These Pt/Pd catalyst structures increase the activity towards electro oxidation of formic acid by up to an order of magnitude over long times. In addition, the initial silicon-MEAs with Pt/Pd catalyst grids exhibit doubled power density in fuel cell testing.

INTRODUCTION

Research and commercialization of Proton Exchange Membrane Fuel Cells (PEMFC) are gaining momentum as a "clean" energy source. While hydrogen and methanol are typically used as the fuels, recently formic acid has been shown to be a promising alternative for powering MEMS devices at ambient temperatures [1]. Compared to hydrogen it is easier to store, and formic acid has faster kinetics and exhibits less tendency for crossover across the proton exchange membrane than methanol [1]. Microfuel cells for use in portable applications in particular benefit from formic acid, since the fast kinetics of dissociating H^+ ions at room temperature eliminates the necessity to introduce additional heating elements, which reduce the overall performance of the fuel cell system. Kelley *et al.* have reported a miniaturized fuel cell with performance comparable to large-scale fuel cells [2]. Recently, we have been successful in miniaturizing silicon MEAs using MEMS type microfabrication techniques [3]. This method facilitates the integration of key components of MEAs including microchannels, current collector, and catalyst on a single chip. In comparison to traditional MEAs in which the catalyst is painted as a layer onto the Nafion membrane, the silicon grids with Pt-catalyst structures presented here offer the advantages of: (1) rapid diffusion/transport of fuel towards the catalyst structures; (2) easy removal of CO_2 from the catalyst/fuel interface to the outside world; and (3) low-resistant contact between the catalyst structures and the Nafion membrane.

In the work presented here, we describe the deposition of high surface area Pt/Pd catalyst structures with dendritic morphologies on silicon-grid MEAs. Electrochemical studies have recently shown that Pt/Pd bimetallic catalysts obtained by spontaneously Pd on Pt nanosphere particle catalysts perform well in the electro-oxidation of formic acid, yielding

significantly higher currents at a given potential [4]. Unfortunately, nanoparticle Pt/Pd catalysts are usually contained in a Nafion®-based ink that is painted onto the Nafion PEM, which is not compatible with MEMS fabrication techniques for the MEA. Therefore, we have developed a spontaneous deposition method to deposit Pd onto high surface area electrodeposited Pt catalyst structures that is compatible with our silicon-based MEAs to improve the performance of the formic acid fuel cells.

EXPERIMENTAL DETAILS

1. Microfabrication of silicon MEAs

Silicon-based membrane electrode assemblies (MEAs) were prepared using various microfabrication processes. Briefly, a double-sided <100> oriented polished wafer was covered on the front side with a 1000 Å Au layer and patterned into a circular mesh with 100 μm square holes by photolithography followed by liftoff. Next, the front/back side was covered with a polyimide layer that was further patterned using photolithography, followed by deep reactive ion etching to yield the silicon-based grid with 100 μm square holes. After catalyst deposition (see section 2) two of these grids, which serve both as the current collector and catalyst support, are bonded to a Nafion membrane to yield a silicon-based MEA shown in Figure 1. A detailed description on the fabrication of the silicon-MEA can be found elsewhere [3,5].

2. Synthesis of catalyst structures

2.1 Preparation of Pt catalyst structures

High surface area Pt-black was deposited onto the Au-covered silicon grids by electrodeposition using a plating bath made with 120 ml of water, 5g of chloroplatinic acid (H_2PtCl_6).

Figure 1. (A) Schematic diagram of silicon-based MEA. (B) Photograph of Membrane Electrode Assembly (MEA) prepared by silicon MEMS fabrication processes, with a mesh of 50 μm thick and 150 μm width, and 100 μm square holes to facilitate gas diffusion to the electrode.

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6H₂O), and 30 g of lead acetate (Pb(C₂H₃O₂)₂) [6]. Figure 2 shows two SEM micrographs of the dendritic structures that can be electroplated with this bath. In the present study, we investigate the effect of structure on the catalytic activity of the Pt during formic acid electro-oxidation.

We varied the morphology of the catalyst electrode structures using the following deposition conditions.

1. Flat, shiny Pt deposited by e-beam evaporation.
2. Pt-black electrodeposited at constant voltages of 2, 5 and 10 V using Pt foil as the counter electrode.
3. Pt-black electrodeposited at a constant current of 250 mA.

2.2 Spontaneous deposition of Pd onto Pt catalyst structures

The rate of electro-oxidation of formic acid typically increases on bimetallic Pt/Pd catalysts up to an optimum coverage of dispersed Pd before decreasing with further increase in Pd coverage [4]. Therefore, we deposited Pd islands on the Pt catalyst structures by spontaneous deposition using the process that was reported to maximize the electro-oxidation rate [4]. The electrodes with Pt catalyst structures were first cleaned electrochemically in 0.1 M H₂SO₄ by cycling between 0 and 1.5 V vs. RHE. Then the electrodes were placed in a 5 mM palladium nitrate + 0.1 M H₂SO₄ solution for 5 min, followed by thorough rinsing with Milli-Q water. These electrodes were electrochemically annealed by cycling five times between 0 and 0.95 V in 0.1 M H₂SO₄. This spontaneous deposition procedure was repeated five times to yield Pd decorated Pt catalyst structures on the silicon grids. Note, however, that the resulting structures are of Pd on a various dendritic Pt structures, which for cases (2) and (3) described above are different from the structures previously reported in reference [4]. The inset of Fig. 2 shows a cartoon of one Pt dendrite decorated with Pd adatom islands.

3. Electrochemical Characterization

3.1 Cyclic Voltammetry (CV)

All silicon grids with catalyst structures were cleaned in a 0.1 M H₂SO₄ solution by cycling from 0.0 to 1.5 V vs. RHE at a scan rate of 500 mV/s. Next, cyclic voltammograms of these electrochemically cleaned silicon grids with catalyst structures

Figure 2. SEM micrographs of dendritic catalyst structures, with cartoon of a decorated Pt dendrite.

were recorded in a 0.1 M H₂SO₄ solution in the presence of 0.1 M formic acid between 0.05 and 1.25 V vs. RHE at a scan rate of 50 mV/s.

3.2 Chronoamperometry (CA)

The voltage potential is varied in steps between 0.95 V and 0.01 V to the silicon grids with Pt structures for 1 s and repeated 4 times to ensure complete removal of surface-bound CO. After the cleaning steps the silicon-based electrodes were held at 0.2 V and 0.3 V vs. RHE for 600 s and the current was recorded as a function of time.

3.3 Fuel Cell Test Apparatus

Figure 3 shows a diagram of the test fixture for the silicon-based MEA. The silicon-based MEA is clamped between two PTFE casings, which contain electrical contacts as well as fluidic inlets and outlets. 10 M formic acid was fed into the anode chamber at a flow rate of 1 ml/min and oxygen gas was fed into the cathode chamber at 10 sccm. I-V curves were obtained by applying different potentials to the cell and recording the current at these different potentials. The obtained current values were normalized to the geometric surface area (0.44 cm²) of the silicon-based MEA.

Figure 3. Schematic of silicon-MEA test fixture (FA: Formic Acid).

RESULTS AND DISCUSSION

In the present study, we performed an initial investigation of the effect of structure on the catalytic activity of the Pt/Pd during formic acid oxidation. The structure affects both the total surface area and the average size and density of the dendrites that grow out from the bush-like configuration shown in Fig. 2. Figure 4 shows SEM micrographs of the different Pt catalyst structures. Deposition of Pt via evaporation resulted in a uniform covering of the microfabricated grids (Fig. 4A). Figures 4B-D shows the dendritic-morphology of Pt catalyst structures grown at different constant potentials. At, lower potentials (2V, Fig. 4B) lower surface coverage and a non-uniform deposition of Pt is observed, which can be explained by Ostwald ripening of the electrodeposited structure. This mechanism proposes that the growth of larger crystals occurs at the expense of smaller ones [7]. Deposition at higher potentials (5V, Fig. 4C, and 10V, Fig. 4D) results in a higher surface coverage of uniformly distributed dendritic structures. Figure 4E shows Pt-black catalysts structures deposited at constant current conditions. These different Pt black catalysts structures shown in Figs. 4A-E will exhibit different performance when integrated in a silicon-MEA, due to differences in surface area as well as differences in the nature of the contact between these dendritic structures and the Nafion membrane. Catalyst structures that are uniform in height are expected to lead to better contact.

Figure 4. SEM micrographs of Pt catalysts on Au surface are shown here. A corresponds to evaporated Pt, B, C and D correspond to Pt structures electrodeposited at a constant voltage of 2, 5 and 10 V respectively, and E represents the morphology of Pt structure electrodeposited at a constant current of 250 mA.

1. Electrochemical Characterization

1.1 Cyclic Voltammetry (CV)

The cyclic voltammogram (CV) of silicon grids with Pt catalyst structure (Figure 4D) is shown in Figure 5a. The CV data shows two peaks at 0.65 V (all potentials vs. RHE) and 1 V during the scan, and one peak at 0.9 V on the reverse sweep. Lu *et al.* suggest that the first anodic peak corresponds to formic acid oxidation to CO_2 on Pt surface sites uncovered by CO, while the second peak corresponds to the oxidation of CO on Pt sites and increased formic acid oxidation resulting from the release of CO from the Pt surfaces [4]. The peak appearing at 0.9 V during the cathodic sweep can again be attributed to the oxidation of formic acid to CO_2 , which extends to 0.3 V. Figure 5b shows the cyclic voltammogram of silicon grids with

Figure 5. Cyclic Voltammograms of silicon based Pt-black electrodes in 0.1 M Formic Acid + 0.1 H_2SO_4 (a) without and (b) with Pd-atoms.

Pd-modified Pt catalyst. The peaks on the positive-going sweep appear at 0.45 V and 0.8 V, while on the negative-going sweep a peak appears at 0.75 V. These results indicate that the Pt electrodes decorated with Pd have a higher intrinsic activity for formic acid oxidation than pure Pt electrodes. This increase in activity for transient formic acid oxidation is carried over into an increased activity for steady-state formic acid oxidation, as reflected in the chronoamperometry results (see below).

1.2 Chronoamperometry (CA)

Figure 6. Chronoamperometric data of Pt-black electrodes with and without Pd in an aqueous solution of 0.1 M formic acid + 0.1 M H_2SO_4 . The lines (a,b) and (c,d) correspond to electrodes without and with Pd ad-atoms, respectively. Profiles (a) and (c) are measured at 0.2 V vs. RHE, while (b) and (d) are obtained at 0.3 V vs. RHE.

Figure 6(a-d) show the chronoamperometric plots corresponding to formic acid oxidation on Pt electrodes with and without Pd. At a given potential, the steady-state currents from the Pd/Pt bimetallic catalysts structures are significantly higher in comparison to plain Pt electrodes, reflecting an increased intrinsic activity for formic acid oxidation on Pd islands, as well as a decreased susceptibility to CO poisoning. Indeed, FTIR experiments on Pt(111) modified by Pd show no CO formation on Pd islands during formic acid oxidation [8]. However, Pd islands are not necessarily immune to poisoning during formic acid oxidation. Several reports have demonstrated deactivation of Pt/Pd electrocatalysts during formic acid oxidation, an effect that has been attributed to the presence of interfacial CO_2 [4,9], adsorbed formic acid, formate, or other reaction intermediates [4] or adsorbed OH and anions [8]. Nevertheless, the improved steady-state activity of Pd-modified Pt, as demonstrated in the chronoamperometry results, clearly demonstrates that Pd-modified Pt catalyst structures can serve as better catalysts for formic acid oxidation.

1.3 Fuel Cell Testing

Figure 7 shows the I-V curves and performance for silicon based fuel cells with and without Pd. The current densities and the power densities are significantly higher (~2 times) for the silicon-MEA tested that has Pt/Pd bimetallic catalysts structures, as opposed to Pt only catalyst structures. These electrochemical studies clearly indicate that the Pt/Pd bimetallic catalyst structures enhance formic acid electro-oxidation, allowing formic acid oxidation to occur at a lower anode overpotential, and thus increasing the cell potential at a given current density (Figure 7), similar to fuel cells developed with nafion ink catalysts [1]. The spontaneously deposited Pd structures on the electroplated Pt-black, therefore, gains the advantages of the Pt/Pd bimetallic catalyst, without the issue of requiring ink in the fabrication.

Figure 7. The I-V curves for silicon based fuel cells (a) without Pd and (b) with Pd are shown. Power density curves (c) without Pd, and (d) with Pd.

CONCLUSIONS

Silicon based MEAs comprised of microfabricated grids with Pt or Pt/Pd catalysts structures show promise for application in microfuel cells. Unlike in traditional polymer electrolyte membrane fuel cells in which the catalyst is deposited as an ink, the morphology of the catalyst structures studied here can be precisely controlled by varying electrodeposition conditions. Electrochemical analysis shows that silicon-grid with Pt/Pd bimetallic catalyst structures increases the activity towards electro oxidation of formic acid by up to an order of magnitude over long times. In addition, the initial silicon-MEAs with Pt/Pd catalyst grids exhibit doubled power density in fuel cell testing. In sum, these silicon-MEAs show promise towards integrated, all-silicon microfuel cells.

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