"Platinum Nanostructures by Template Wetting Nanofabrication and Their Use in a Miniature Fuel Cell Membrane Electrode Assembly"

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Template wetting nanofabrication was used to fabricate platinum nanotubes in a porous alumina template membrane. The resulting high surface area platinum nanostructures were characterized electrochemically using cyclic voltammetry and chronoamperometry for both methanol and formic acid oxidation reaction. Performance compared favorably to a commercial platinum black catalyst in terms of surface area and activity. Leaving the nanotubes partially imbedded in the alumina template allows for a convenient means of incorporating this catalyst into a membrane electrode assembly. A simple MEA was thus fabricated utilizing platinum nanotubes embedded in a porous alumina membrane as both the anode and cathode. This was utilized in a small direct formic acid fuel cell and current voltage characteristic measured.

Introduction

Expensive noble metals are the leading anode catalysts for hydrogen PEM fuel cells, direct methanol fuel cells, and direct formic acid fuel cells. Pt and Pt based metals are generally used as fuel cell catalysts due to having the greatest activity towards methanol electro-oxidation and formic acid electro-oxidation. Due to the extremely high cost of precious metals, there is a great need to develop better structures of these materials that would increase the active surface area and reduce the loading of these expensive metal catalysts. Nanoparticles and other high surface area surface area structures can help meet this need. This work will demonstrate that platinum

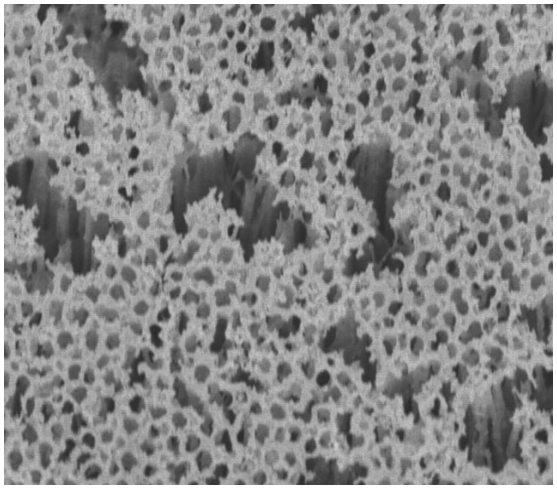

Figure 1: SEM image of 100 nm platinum nanotubes imbedded in an alumina template

nanotubes imbedded in an alumina support can increase surface area while reducing the loading of the precious metal as a fuel cell catalyst. Also, the platinum nanotubes/alumina template catalyst can be easily incorporated in a membrane electrode assembly for utilization in a miniature fuel cell.

Fabrication

100 and 200 nm diameter platinum nanotubes were made using template wetting nanofabrication. A solution of a platinum precursor and a surface tension reducing agent was placed drop-wise onto the surface of porous alumina templates consisting of 100 and 200 nm diameter pores. The solution entered the pores of the alumina template and wetted the walls of the pores. After heating the templates, the platinum precursor was reduced to form platinum metal. The templates were then etched to release the platinum nanotubes. The templates were etched just long enough for the platinum nanotubes to remain upright without collapsing onto each other as shown in figure 1.

Experimental

Electrochemical Characterization

Cyclic voltammetry and chronoamperometry were performed on the platinum nanotube templates. These tests were done using a potentiostat and a 3-electrode set-up (working electrode, Pt wire counter electrode, saturated calomel reference electrode). The electrolyte solutions were 0.1M formic acid + 0.1M sulfuric acid and 0.1M methanol + 0.1M sulfuric acid. The platinum nanotube working electrode was made byattachint the template onto a glassy carbon electrode using a graphite adhesive. A platinum black working electrode was made for comparison to the platinum nanotube templates. This electrode was made by depositing a known amount of platinum black in solution with nafion and water to the tip of a glassy carbon electrode and let dry. The platinum electrodes were used as the working electrode, platinum wire was used as the counter electrode, and a saturated calomel electrode was the reference electrode, however the data is reported versus a standard hydrogen electrode. Surface area of the Pt nanotube templates and the platinum black templates were measured using cyclic voltammetry.

Button Fuel Cell

A small air-breathing button fuel cell with a fuel reservoir constructed out of Teflon® was made. The membrane electrode assembly consisted of Nafion® 117 as the proton electron membrane and the platinum nanotubes on both of sides of the membrane for use as the anode and the cathode for the fuel cell. Two pieces

of aluminum were machined for use as current collectors and were positioned on the fuel cell in contact with the anode and cathode Pt nanotube catalyts.

5. Results

Cyclic Voltammetry

Cyclic voltammetry was carried out at a scan rate of 60 mV/s. Fig. 2 shows CV scans of the 100 nm and 200 nm Pt nanotube catalyst compared with a 10 mg/cm^2 loaded Pt black catalyst run in a 0.1M HCOOH + 0.1M H_2SO_4 solution. Fig. 3 represents the CV scans of the samples run in a 0.1M CH_3OH + 0.1M H_2SO_4 solution.

In the formic acid solution, the CV plots of all three are very similar in appearance, which shows that the 100 and 200 nm Pt nanotubes, when imbedded in the alumina template, generate comparable reaction kinetics towards formic acid elecro-oxidation to that of platinum black. The plots show two anodic peaks at ~0.55V and ~0.9V and a large cathodic peak at the same spot as the first anodic peak (about 0.55V). These peaks are similar to that of

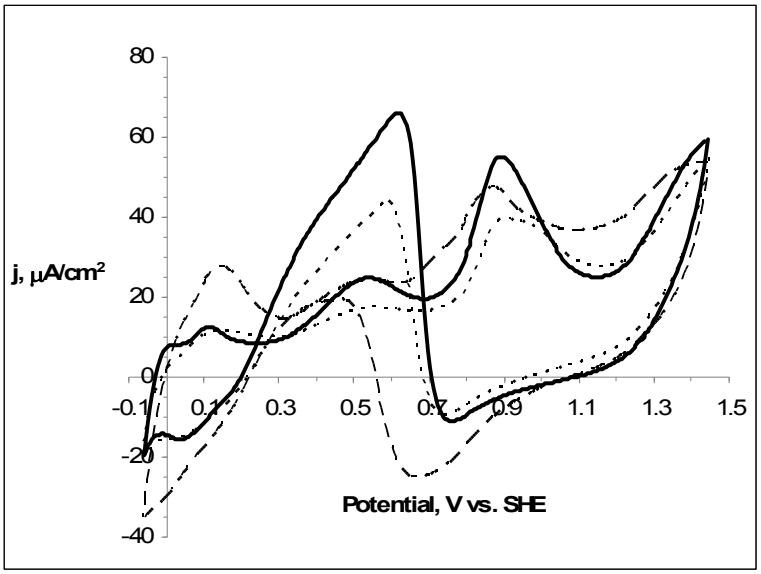

Figure 2: Cyclic voltammetry scans of the 200 nm Pt nanotubes (—), 100 nm Pt nanotubes (····), and Pt Black (— —) in 0.1M HCOOH + 0.1M H_2SO_4. The current densities are normalized to the true surface area of the Pt catalyst. The loading for Pt Black is 10mg/cm^2.

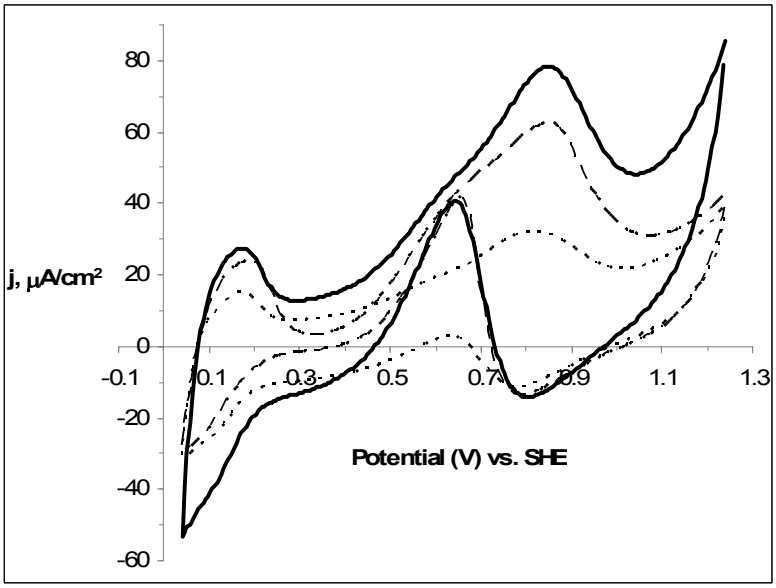

Figure 3: Cyclic voltammetry scans of the 200 nm Pt nanotubes (—), 100 nm Pt nanotubes (····), and Pt Black (— —) in 0.1M CH_3OH + 0.1M H_2SO_4. The current densities are normalized to the true surface area of the Pt catalyst. The loading for Pt Black

peaks found in CV plots from previous studies on Pt nanoparticle-based catalysts for the electro-oxidation of formic acid.
In the methanol solution, The CV plots of all three are also very similar. The peaks for the nanotube catalysts match up with that of the peaks for the Pt black catalyst. This shows that the reaction kinetics towards methanol electro-oxidation for the platinum nanotubes imbedded in the alumina template are similar to that of the commercially used Pt black. The anodic peak at ~0.8V and the cathodic peak at ~0.6V are similar to that of peaks seen in the literature for Pt-nanoparticle-based catalysts in methanol.

Chronamperometry

For removal of surface-bound CO, potential steps between 0.708 and -0.241 V vs. SCE were applied for 1 s and repeated four times. After these cleaning steps, the electrode was held at a potential 0.0 V vs. SCE for 1 second and then stepped to a potential of 0.158 V vs. SCE (=0.4V vs. SHE) and held for 1000 seconds. The current measured while holding the voltage constant at 0.4V vs. SHE was recorded as a function of time. In the formic acid solution, the 100 nm and 200 nm Pt nanotubes both produce at constant current density of ~6 $\mu A/cm^2$ around 20 seconds. The Pt black begins to level off around 75 seconds into the run where it produces a current density of ~4 $\mu A/cm^2$. In the methanol solution, the 200 nm Pt nanotubes performed the best giving a current density of ~5 $\mu A/cm^2$ while the 100 nm Pt nanotubes and the Pt black had a current density of ~2 $\mu A/cm^2$. From this experiment, it is shown that the platinum nanotubes compare favorably with the Pt black in terms of production of current over time.

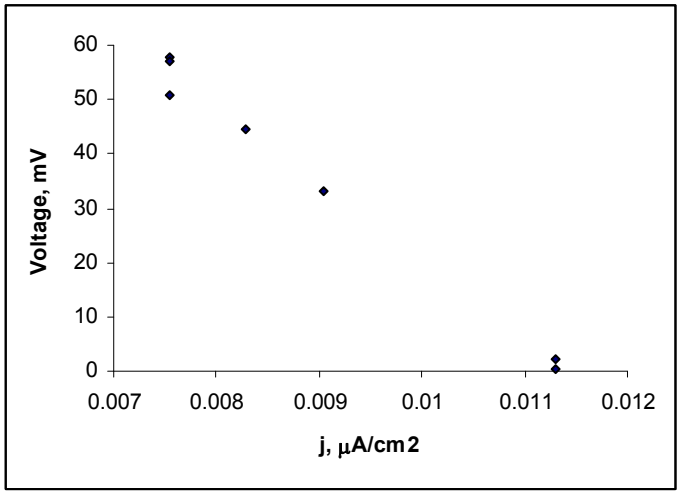

Figure 4: Current -Voltage polarization plot of the button fuel cell. The fuel used was 0.1M formic acid, the anode and cathode are 200 nm Pt nanotubes imbedded in an alumina template, and the

Fuel Cell Polarization Curve

The MEA, consisting of 200 nm Pt nanotubes imbedded in an alumina template as the anode and the cathode and Nafion® 117 as the membrane, was set up and incorporated into the button fuel cell. A variable resistor was connected to the fuel cell to control the resistance. 0.1M formic acid was inserted into the fuel

reservoir of the fuel cell and the voltage vs. current was recorded. This can be seen in Figure 4. The current is reported as current density with the area of the nominal area of the catalysts being 1.33 cm^2. The fuel cell was kept at room temperature. The results show that by using the imbedded Pt nanotubes, a typical I-V polarization curve is observed. The low current and voltage can be assumed to be caused from design error.

Discussion

100 and 200 nm diameter platinum nanotubes were fabricated inside an alumina template. This nanostructural catalyst was then utilized as a membrane electrode assembly for use in a direct formic acid fuel cell. Electrochemically, the nanotubular platinum catalysts performed favorably compared to Pt black for both cyclic voltammetry and chronoamperometry. The voltage and the current obtained from the direct formic acid fuel cell when using the nanotubular platinum catalysts were shown to be quite low. This can be assumed to be due to the design of the fuel cell. A better design for the fuel cell is needed to reduce leaking and cross-over effects. From this research, it can be taken that the platinum nanotube catalysts that were fabricated can be a viable catalysts for direct formic and direct methanol fuel cells.