Research Article

Formic Acid Electrooxidation by a Platinum Nanotubule Array Electrode

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One-dimensional metallic nanostructures such as nanowires, rods, and tubes have drawn much attention for electrocatalytic applications due to potential advantages that include fewer diffusion impeding interfaces with polymeric binders, more facile pathways for electron transfer, and more effective exposure of active surface sites. 1D nanostructured electrodes have been fabricated using a variety of methods, typically showing improved current response which has been attributed to improved CO tolerance, enhanced surface activity, and/or improved transport characteristics. A template wetting approach was used to fabricate an array of platinum nanotubules which were examined electrochemically with regard to the electrooxidation of formic acid. Arrays of 100 and 200 nm nanotubules were compared to a traditional platinum black catalyst, all of which were found to have similar surface areas. Peak formic acid oxidation current was observed to be highest for the 100 nm nanotubule array, followed by the 200 nm array and the Pt black; however, CO tolerance of all electrodes was similar, as were the onset potentials of the oxidation and reduction peaks. The higher current response was attributed to enhanced mass transfer in the nanotubule electrodes, likely due to a combination of both the more open nanostructure as well as the lack of a polymeric binder in the catalyst layer.

1. Introduction

Nanostructured materials have long been used in catalysis, usually in the form of metallic nanoparticles on high surface area supports with nanoscale porosity. More recently, one-dimensional metallic nanostructures such as nanowires, rods, and tubes have drawn attention for such electrocatalytic applications, including fuel cells and electrochemical sensors. These types of structures present many potential advantages, including fewer diffusion impeding interfaces with polymeric binders, more facile pathways for electron transfer, and more effective exposure of active surface sites. Such 1D metallic nanostructures have been fabricated by a variety of methods, including template-based methods (wetting [1–4] and electrosynthesis or electrodeposition [5–11]), electrosprining [12], deposition onto nanowire or nanofiber supports [13–15], and others [16–19]. To date, most studies of these nanomaterials have focused on demonstrating the viability of the nanofabrication process and describing fundamental material properties such as morphology, composition, and crystal structure with far less attention paid to their functional properties.

Electrocatalytic studies of 1D metal nanostructures have focused on small organic molecules, in particular those important to fuel cell applications such as methanol [7, 8, 11, 20, 21] and formic acid [19, 22–25]. Often, such studies are only cursory merely demonstrating some degree of electrocatalytic activity with no comparison to a standard catalyst or quantification of kinetic parameters, with the focus being on the fabrication process and other material properties [7]. When electrochemical activity has been the focus, higher current response has typically been reported from 1D nanostructures in comparison to commercial catalysts. The cause of this improved performance has been attributed to different factors, including enhanced catalytic activity of the nanostructured surface, improved CO tolerance, and faster transport in the catalyst layer. Higher catalytic activity has been reported for Pt nanowires made by electrodeposition...
in a polymeric template for methanol electrooxidation [21] and for porous Pt nanowires made by electrodeposition in an alumina template for ethanol electrooxidation [26] in comparison to a commercial Pt black catalyst. In contrast, poorer activity was reported for methanol electrooxidation with PtRu nanowire networks fabricated by electrodeposition in an SBA-15 in comparison to a commercial PtRu black, though with greater power output from a resulting fuel cell attributed to enhanced mass transport of products and reactants in the porous network and reduced the number of interfaces from the lack of a Nafion binder commonly used with Pt black catalysts [11]. Lower activity was also reported for methanol oxidation with Pt nanowires produced via an electrospinning process though with greater CO tolerance than a commercial Pt black catalyst [12].

For this work, platinum nanotubules formed via a simple template-based wetting process, previously demonstrated by Steinhart et al. [1, 3, 27], will be compared with a traditional platinum black catalyst for formic acid electrooxidation. Formic acid was chosen for this study due in part to its promise in direct formic acid fuel cells which have emerged as a key challenger to direct methanol technologies in recent years [28–31] but also due to its long serving role as a model for the electrooxidation for other small organic molecules [32–36].

2. Experimental

2.1. Fabrication of Platinum Nanotubule Array Electrode. Platinum nanotubule arrays were fabricated via template wetting [3] using porous alumina membranes (Whatman, Anodisc, 60 μm thick with either 100 or 200 nm nominal pore diameters containing pore densities of $10^{10}$ and $10^{9}$ pores/cm$^2$, resp.) as templates. The nanofabrication process, illustrated in Figure 1, involved wetting these templates with a solution prepared by mixing platinum (II) 2,4-pentanedionate (Pt(acac)$_2$) (Alfa Aesar) and poly(D,L-lactide) (PDLLA) (Sigma-Aldrich) in a 3:1 ratio in chloroform (Acros Organics, ACS Reagent) to a final concentration of 66.6 mg Pt(acac)$_2$/mL. Using the given nominal pore diameter and density along with the bulk density of platinum and the assumption that all solution entered the pores and that the pores were cylindrical, sufficient solution was pipetted onto the template to form 5 nm thick...
tubule walls. The solution was observed to readily wet the template and allowed to dry in air for 24 hrs, leaving a solid Pt(acac)$_2$/PDLLA film coating the pore walls of the template after solvent evaporation. Residual material on the external surfaces of the templates was removed using a helium plasma etch (200 mTorr, for 10 min) in a Plasma-Therm RIE system. Samples were then annealed in air at 200$^\circ$C for 24 hrs, followed by 1 hr at 350$^\circ$C to reduce the Pt(acac)$_2$ to Pt$^0$ as well as to oxidize and remove the PDLLA [3]. The resulting Pt nanotubes were partially released by selectively etching the alumina template in 25 wt.% KOH(aq) for 2 min followed by rinsing in DI water. These were inspected visually using a Hitachi S-4800 field emission SEM.

Electrochemical characterization of the Pt nanotubule array was carried out by attaching it to a polished glassy carbon electrode (3 mm, encased in Kel-F, CH Instruments) using an alcohol-based conductive graphite adhesive (Alfa Aesar product no. 42466). For comparison purposes, a traditional platinum black material (HiSPEC 1000, Alfa Aesar) was also evaluated. The Pt black was dispersed in DI water and Nafion (5 wt.%, Solution Technology, Inc.) to a final concentration of 2 mg mL$^{-1}$ Pt with 10% Nafion by mass, pipetted onto the same polished glassy carbon surface, and allowed to dry in air at room temperature for 24 hrs.

2.2. Electrochemical Characterization. All electrochemical tests were carried out with a Gamry Instruments PCI4 Potentiostat using a traditional three-electrode cell using a Pt nanotubule array or Pt black working electrode as described above, a platinum wire counter electrode, and an Ag/AgCl reference electrode (CH Instruments), though all potentials in this work are reported relative to the standard hydrogen electrode (SHE). The solutions used in the electrochemical cell were deaerated by bubbling N$_2$ gas and the cell was subsequently blanketed with N$_2$ during the experimental procedure. The Pt catalyst structures were cleaned electrochemically by cycling the potential between 1.5 V and 0.03 V versus SHE (standard hydrogen electrode) at a scan rate of 500 mV/s in a 0.5 M H$_2$SO$_4$(aq) solution (GFS Chemicals, Veritas Grade, double distilled in 18 MΩ deionized water) until a steady-state voltammogram was obtained (approximately 50 cycles) prior to analysis [37, 38]. Active surface area was evaluated using the hydrogen adsorption peaks in the voltammograms from this same solution. Integration of these peaks with respect to time and subtraction of the background double layer charge provides the charge due to hydrogen adsorption [33, 39]. Using a value 210$\mu$C/cm$^2$ for the deposition of a monolayer of hydrogen on a Pt surface allows the surface area to be calculated [39]. To evaluate formic acid electrooxidation kinetics, formic acid (GFS Chemicals, Veritas Grade, double distilled) was added to the 0.5 M H$_2$SO$_4$(aq) supporting electrolyte to a concentration of 0.25 M HCOOH for both cyclic voltammetry and chronoamperometry experiments.

3. Results and Discussion

3.1. Structure and Surface Area. Representative scanning electron micrographs of Pt nanotubules are shown in Figure 2. The template is shown prior to the KOH etching step in Figure 2(a) with the lumen of the nanotubules visible. Figures 2(b) and 2(c) show the exposed nanotubules after the template is partially removed. The high yield of the fabrication process, approximately one tubule per template pore, and the alignment of the tubules are readily apparent in Figure 2(b). As expected, tubule diameter is consistent with the template pore diameter, as shown for tubes made using the 100 nm pore diameter template in Figure 2(c).
The active surface areas of platinum in electrodes made from the nanotubules as well as for a more traditional platinum black described above were evaluated using cyclic voltammetry in 0.5 M sulfuric acid. Representative voltammograms are shown in Figure 3 with the hydrogen adsorption region highlighted. Qualitatively, these appear consistent with the expected form for a platinum electrode with hydrogen adsorption/oxidation and platinum oxide formation/reduction peaks clearly observable [39]. Integration of the hydrogen adsorption peaks to give the charge due to hydrogen adsorption was used to determine surface areas of 19.5 and 14.7 m$^2$/g of Pt for the 100 and 200 nm Pt nanotubules. Total platinum loading based on the total amount of metal in the wetting solution was 0.8 mg/cm$^2$ for these samples. Actual loading should be somewhat lower as some material was removed in the helium plasma etching step of the fabrication process. The platinum black provided a slightly higher surface area of 20.4 m$^2$/g at a loading of 0.5 mg/cm$^2$. This value is somewhat lower than that reported by the manufacturer of 27 m$^2$/g due to the presence of the Nafion binder in the catalyst ink.

3.2. Cyclic Voltammetry. Figure 4 shows representative cyclic voltammograms of the 100 and 200 nm Pt nanotubular catalysts and Pt black catalyst ink for the electrooxidation of formic acid, collected using an 0.25 M HCOOH in an 0.5 M H$_2$SO$_4$ supporting electrolyte. These are in qualitative agreement with the expected form for the electrooxidation of formic acid on a Pt catalyst [33, 37, 40, 41]. The hydrogen adsorption/desorption peaks between 0.05 and 0.4 V versus SHE are suppressed compared to those observed in Figure 3 due to the adsorption of CO [20, 33, 35, 40]. Anodic peaks associated with the oxidation of HCOOH and CO are observed at ~0.5 and ~0.9 V versus SHE, respectively, along with a broad cathodic peak stretching from ~0.7 to 0.4 V due to the oxidation of formic acid after the reduction of the surface Pt oxides [20, 35, 40]. The cathodic scan where the surface has been cleaned of absorbed CO and surface oxides thus represents the real catalytic activity of the Pt surface [40]. Comparing the maximum current of the cathodic formic acid oxidation peak normalized to the active surface area reveals that the 100 nm Pt nanotubules exhibit the highest apparent activity toward formic acid electrooxidation followed by the 200 nm nanotubules and the Pt black ink.

Previous studies have reported improved CO tolerance in 1D metal nanostructures used as catalysts for methanol electrooxidation [7, 11, 12, 15]. As noted previously, the first anodic peak at ~0.5 V versus SHE is due to formic acid oxidation on a surface partially covered by CO, while the large cathodic peak results from the same reaction on a clean Pt surface. The ratio of the maximum current densities of these two peaks provides a measure of the fraction of the catalyst surface not poisoned by CO adsorption and is hence a measure of the CO poison resistance [20, 42]. Values of this ratio, $j_{a1}/j_{c1}$, are 0.27, 0.26, and 0.27 for the 100 nm nanotubules, 200 nm nanotubules, and Pt black catalysts, respectively, indicating no significant difference in CO tolerance between the three catalysts. This is a contrast with results for other types of 1D nanostructures [7, 11, 12, 15].

Figure 5(a) shows cyclic voltammograms for the 100 nm Pt nanotubule electrode at scan rates from 1 to 100 mV/s. The maximum current for the cathodic formic acid oxidation peak was then plotted in Figure 5(b) versus the square root of the scan rate which is expected to be linear for a diffusion controlled reaction, as is expected and observed here. The slope of the best fit line was largest for the 100 nm nanotubule electrode, followed by the 200 nm nanotubules.
Figure 5: (a) Cyclic voltammograms for the electro-oxidation of formic acid (0.25 M HCOOH in 0.5 M H₂SO₄) on the 100 nm Pt nanotube at 1, 10, 50, and 100 mV/s. (b) Cathodic formic acid oxidation peak current versus square root of scan rate for 100 nm Pt nanotube, 200 nm Pt nanotube, and Pt black electrodes. Trendlines represent a linear regression best fit of the data with $R^2$ values of 0.95, 0.96, and 0.97, respectively.

Figure 6: Chronoamperometry data for the 100 and 200 nm Pt nanotube and the Pt black/10 wt% Nafion catalyst in 0.25 M HCOOH in 0.5 M H₂SO₄ at (a) 0.400 and (b) 0.475 V versus SHE. The three plots at each voltage show different time scales to facilitate comparison.
and the platinum black. The larger slope is indicative of a greater apparent diffusivity in the catalyst layer indicating that the increased activity observed is due at least in part to enhanced mass transport. The two anodic peaks showed the same trend when plotted in a similar manner to Figure 5(b). Enhanced mass transfer is consistent with results reported by Choi and Woo [11].

3.3. Chronoamperometry. Chronoamperometry results at 0.400 and 0.475 V versus SHE are illustrated in Figure 6 for the same formic acid solution. These potentials correspond to just after the onset of formic acid electrooxidation and near the peak current observed in the cyclic voltammograms. As is typical, the current declines rapidly after the voltage step is applied due to the accumulation of CO on Pt surface sites until some equilibrium surface coverage is reached. The initial current decline is more rapid for both nanotubule catalysts than for the platinum black. This observation is consistent either with a greater susceptibility to CO poisoning or with enhanced mass transfer of reactants to the surface allowing more rapid CO accumulation. As the \( \frac{j_{\text{a1}}}{j_{\text{c1}}} \) ratio from the CV data discussed previously indicates similar CO tolerance for all three electrodes, the latter conclusion appears more likely. The steady current density at longer times is also observed to be significantly higher for the 100 nm Pt nanotubules and even slightly higher for the 200 nm nanotubules in comparison with the Pt black, consistent with oxidation and reduction peak current trends observed in the cyclic voltammograms. While an enhanced rate constant or reduced CO coverage would yield this result, the data is also consistent with more rapid mass transport which is supported by the previously discussed voltammetry data.

4. Conclusions

Template wetting nanofabrication was successfully used to prepare an array of Pt nanotubules using porous alumina template. The process provided a high yield of nanotubules with geometry consistent with that expected from the porous template used and a high surface area comparable to that of a typical Pt black catalyst ink based on a commercial catalyst. The ease of fabrication and resulting nanotubule array structure should be suitable for a number of sensor or small fuel cell applications. The highest current response for formic acid electrooxidation was observed from the 100 nm nanotubules followed by the 200 nm nanotubules and finally the commercial Pt black catalyst. The Pt nanotubules showed similar susceptibility to CO poisoning and inherent activity toward formic acid electrooxidation to a commercial Pt black. The increased current response was found to be the result of enhanced mass transfer in the open nanotubule array structure with no polymeric binder such as the Nafion commonly used with Pt black.

Conflict of Interests

The authors of this paper do not have any direct financial relation with the commercial identities mentioned in their manuscript that might lead to a conflict of interests.

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