Research Article

Electrochemical Characterization of Platinum Nanotubes Made via Template Wetting Nanofabrication

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Standard oxidation-reduction reactions such as those of ferrocyanide and ferrocene have long been employed in evaluating and comparing new electrode structures with more traditional configurations. A variety of nanostructured carbon electrodes developed in recent years have been reported to exhibit faster electron transfer kinetics than more traditional carbon structures when studied with these redox reactions. This type of comparison has not been widely explored for nanostructured platinum electrodes that have become increasingly common. In this work, a platinum nanotubule array electrode was fabricated via a simple template-based process and evaluated using the standard ferrocyanide redox reaction. The nanotubule array electrodes were observed to more closely approach ideal reversible behavior than a typical Pt black/Nafion fuel cell electrode or a standard polished Pt disc electrode. The apparent heterogeneous electron transfer coefficient was determined using the Nicholson method and found to be one to two orders of magnitude greater for the nanotubule array electrodes, depending on the diameter of the nanotubules, in comparison with these same two more traditional electrode structures.

1. Introduction

Metal nanowires, rods, tubes, and other so-called “one-dimensional nanostructures” [1–3] have drawn increasing attention due to their unique properties. Among the wide variety of methods reported for fabrication of such nanostructures are template-based methods [2, 4–8], electrospinning [9], deposition onto nanowire or nanofiber supports [10–12], and others [13–15]. One-dimensional carbon and metallic nanostructures have shown promise in electrocatalytic applications, such as in small fuel cells and electrochemical sensors. Beyond their high surface-to-volume ratio, these nanostructures present many potential advantages in electrocatalytic applications, including fewer diffusion impeding interfaces with polymeric binders, more facile pathways for electron transfer, and more effective exposure of active surface sites.

Standard redox reactions such as those of ferrocyanide or ferrocene have long been employed as benchmarks in evaluating various carbon [16] and platinum [17–20] electrode structures, preparation techniques, and surface treatments. While carbon nanotube-based electrodes have been widely

evaluated in this manner [21–25], electrochemical studies of platinum nanostructures have focused on organic molecules important to fuel cells (e.g., methanol and formic acid) [3, 8, 26] or various biosensor applications [1, 27]. Comparison of results for different platinum nanostructures is made challenging by the wide range of testing conditions, though both faster [3, 26] and slower [8] electron transfer kinetics in comparison with commercial catalysts have been reported along with enhanced mass transport [8] in nanostructured catalyst layers.

The focus of this work is to examine electron transfer kinetics of the classic ferrocyanide reaction on a platinum nanotubule array electrode fabricated using a simple template wetting process. The ubiquity and long history of this quasi-reversible, single-electron redox system should enable more meaningful comparison with other electrode structures. The template wetting nanofabrication process used to fabricate the platinum nanotubule array electrodes has been previously demonstrated by Luo et al. [5] The resulting arrays appear similar to those obtained with other template-based processes, though the individual structures are tubular rather than the more common nanowires or rods [2, 6–8, 28] obtained

using electrodeposition process. Electron transfer kinetics will be compared to a standard platinum disc electrode as well as an electrode prepared with a commercial platinum black-based catalyst ink.

2. Material and Methods

2.1. Platinum Nanotubule Array Fabrication. A template wetting process, previously demonstrated by Luo et al. [5] and illustrated in Figure 1, was utilized to fabricate platinum nanotubule arrays. This approach makes use of a porous template, in this case commercially available porous alumina membranes (Whatman, Anodisc, 60 μm thick, 100 or 200 nm nominal pore diameters with pore densities of 10^{10} and 10^9 pores/ cm^2 , resp.), to define the geometry of individual nanotubules. The templates were wetted with a precursor solution prepared of platinum (II) 2,4-pentanedionate ($\text{Pt}(\text{acac})_2$) (Alfa Aesar) and poly(D,L-lactide) (PDLLA) (Sigma-Aldrich) in a 3:1 ratio in chloroform (Acros Organics, ACS Reagent) with a final concentration of 66.6 mg $\text{Pt}(\text{acac})_2/\text{mL}$ (Figure 1(a)). The wetted template was allowed to dry in air for 24 hrs leaving a $\text{Pt}(\text{acac})_2/\text{PDLLA}$ film coating the pore walls of the template, as shown in Figure 1(b). Sufficient solution was used such that if it is assumed that all Pt in solution penetrated the template pores to form tubules with a resulting density equivalent to that of bulk platinum and that all pores were uniform and cylindrical, the tubule walls would be 5 nm thick. This estimate would be conservative as some material was observed on the external surfaces of the template. This however was removed using a helium plasma etch (200 mtorr, for 10 min) in a PlasmaTherm RIE system (Figure 1(c)). An annealing step (Figure 1(d)) in air at 200°C for 24 hrs, followed by 1 hr at 350°C, followed to reduce the $\text{Pt}(\text{acac})_2$ to Pt^0 and to oxidize and remove the PDLLA [5]. Finally, the alumina template was partially removed by etching in a 25 wt% $\text{KOH}(\text{aq})$ for 2 min followed by a DI water rinse to expose the Pt nanotubules as shown in Figure 1(e). A Hitachi S-4800 field-emission SEM was used to visually inspect the nanotube array.

2.2. Electrode Preparation. The Pt nanotubule array was attached to a polished glassy carbon electrode (CH Instruments, 3 mm in Kel-F) using an alcohol-based conductive graphite adhesive (Alfa Aesar product number 42466) to facilitate electrochemical evaluation. Performance of the Pt nanotubule array was compared to that of a polished polycrystalline platinum disc electrode (CH Instruments, 2 mm in Kel-F) and a platinum black-based electrode prepared using a commercial catalyst (HiSPEC 1000, Alfa Aesar). The Pt black-based electrode was prepared by pipetting an ink containing Pt black dispersed in DI water and Nafion (5 wt.%, Solution Technology, Inc.) to a final concentration of 2 $\text{mg}\cdot\text{mL}^{-1}$ Pt with 10% Nafion by mass, a composition typical of fuel cell electrodes, onto a polished glassy carbon electrode surface and allowing it to dry in air at room temperature for 24 hrs [29–33].

FIGURE 1: Template wetting nanofabrication of platinum nanotubules. (a) A porous alumina template is wetted with a solution of platinum (II) 2,4-pentanedionate ($\text{Pt}(\text{acac})_2$) and poly(D,L-lactide) (PDLLA) in chloroform. (b) After evaporation of the solvent, a solid $\text{Pt}(\text{acac})_2/\text{PDLLA}$ film coats template pores. (c) Excess material on the outer surfaces is removed using a helium plasma etch, followed by (d) annealing in air to both reduce the $\text{Pt}(\text{acac})_2$ to Pt^0 and oxidize and remove the PDLLA. (e) Finally, a 2 min etch in 25 wt% $\text{KOH}(\text{aq})$ is used to selectively etch the alumina template and expose the Pt nanotubules.

FIGURE 2: SEM images of (a) an individual 100 nm Pt nanotubule and (b) an array 100 nm Pt nanotubules.

2.3. Electrochemical Methods. A Gamry Instruments PCI4 Potentiostat was used to perform cyclic voltammetry (CV) experiments in a traditional three-electrode cell consisting of the Pt nanotubule array, Pt disc, or Pt black working electrode described above, a platinum counter electrode, and a Ag/AgCl reference electrode (CH Instruments). Deaeration of solutions in the electrochemical cell was accomplished by bubbling N_2 prior to experiments and maintained by subsequently blanketing the cell with N_2 during the experimental procedure. Prior to analysis, the catalyst structures were electrochemically cleaned by immersing in a 0.5 M H_2SO_4 (aq) (GFS Chemicals, Veritas Grade, double distilled in 18 MΩ deionized water) and cycling the potential between 1.5 V and 0.03 V versus SHE (standard hydrogen electrode) at a scan rate of 500 mV/s until a steady-state voltammogram was obtained (approximately 50 cycles) [34, 35]. All potentials here are reported relative to the standard hydrogen electrode (SHE). Cyclic voltammograms collected in this same sulfuric acid solution were used to evaluate the active surface area of the platinum for each respective electrode. Integrating the hydrogen adsorption peaks with respect to time and subtracting double layer charge give the total charge due to adsorbed hydrogen [36–38]. The accepted value of $210 \mu C/cm^2$ for a monolayer of hydrogen on Pt was then used to calculate surface area [36, 39]. Further characterization was then done using the standard ferrocyanide reaction in a 0.1 M KCl electrolyte solution containing 1 mM potassium ferrocyanide (both ACS reagent grade, Sigma Aldrich).

3. Results and Discussion

3.1. Pt Nanotube Structure and Surface Area. Figure 2 shows scanning electron micrographs of representative 100 nm Pt nanotubules. Tubule diameter is consistent with the template pore diameter, as shown for tubules made using the 100 nm pore diameter template in Figure 2(a). The high yield of the fabrication process, approximately one tubule per template

FIGURE 3: Cyclic voltammograms collected in 0.5 M H_2SO_4 (aq) at 15 mV/s of 100 nm and 200 nm Pt nanotubule electrodes and a Pt black/10 wt% Nafion electrode. Surface areas obtained from the highlighted hydrogen adsorption region are shown in the table below the voltammograms.

Catalyst	Loading (mg Pt/cm ²)	Specific area (m ² /g Pt)
Pt black (10 wt% Nafon)	0.5	20.4
100 nm Pt nanotubules	0.8	19.5
200 nm Pt nanotubules	0.8	14.7

pore, is readily apparent in Figure 2(b). It can also be seen that the tubule axes remain aligned with the template pore axes, normal to the flat surface of the template.

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

peaks labeled. Integration of these peaks to give the charge due to hydrogen adsorption was used to determine surface areas which are summarized in the table at the bottom of Figure 3. The active area of the nanotubule-based electrodes approached but remained somewhat lower than that of the commercial platinum black ink. In turn, the active area of the platinum black was somewhat lower than the value reported by the manufacturer (20.4 versus 27 m²/g) due to the presence of the Nafion binder, consistent with results reported by others [40]. For the platinum disc electrode, the nominal area of the 2 mm diameter disc was assumed to be equivalent to the active area.

3.2. Ferrocyanide Electrochemistry. Figure 4 shows cyclic voltammograms in a 0.001 M potassium ferrocyanide (K₄Fe(CN)₆) in a 0.1 M KCl supporting electrolyte using 100 and 200 nm Pt nanotubes and Pt black and Pt disc working electrodes at a scan rate of 10 mV/s. The familiar, nearly symmetrical shape of the data curve for ferrocyanide electrooxidation-reduction is observed. Formal potentials were evaluated from the anodic and cathodic peak potentials, $E_{p,a}$ and $E_{p,c}$, respectively, according to the standard equation $E_0 = (E_{p,a} + E_{p,c})/2$, [41] yielding values of 0.46 V versus SHE for each case (standard deviation of 0.01 V). The peak current ratio ($i_{p,a}/i_{p,c}$) was observed to be unity for all samples over the range of scan rates studied here, characteristic of an ideal reversible electron transfer reaction [41]. A plot of the anodic peak current, $i_{p,a}$, versus the square root of the scan rate, $\nu^{1/2}$, is shown in Figure 5, with the dotted lines representing a least squares fit of the data to a straight line. From the linear dependence of $i_{p,a}$ on $\nu^{1/2}$, it can be concluded that the electrode reaction is diffusion controlled.

Of particular interest is the separation between the anodic and cathodic peak potentials, ΔE_p , which is 0.059 V for an ideal reversible single-electron transfer reaction [41]. For the Pt black/Nafion and Pt disc electrodes, ΔE_p values of 0.089 and 0.084 V, respectively, were observed which increased slightly with scan rate to 0.105 V at 80 mV/s. These values are typical for traditional electrodes and normally considered to represent ideal behavior for all practical purposes. The nanotubule array electrodes, however, were observed to even more closely approach theoretically ideal behavior with ΔE_p values of 0.060 and 0.065 V for the 100 and 200 nm diameter nanotubule arrays, respectively, with this value being invariant over the scan rates examined.

The key kinetic parameter, the apparent heterogeneous electron transfer rate coefficient, k_0 , was calculated using the method of Nicholson [41, 42], as has been commonly done for other nanostructured electrodes [21–25]. Standard values for the diffusivities of the oxidized and reduced species of 7.63×10^{-6} cm²/s and 6.32×10^{-6} cm²/s, respectively, along with a transfer coefficient (α) of 0.5 were used [16]. For the polished Pt disc electrode, a value of 0.009 cm/s for k_0 was obtained, comparable to those reported in the literature, though it should be noted that this value has been observed to be highly dependent on pretreatment and polishing methods used [16]. The Pt black/Nafion electrode yielded a somewhat smaller value of 0.003 cm/s. This is consistent with what

FIGURE 4: Cyclic voltammograms obtained in 0.001 M potassium ferrocyanide (K₄Fe(CN)₆) in a 0.1 M KCl supporting electrolyte at 10 mV/s with ΔE_p illustrated.

FIGURE 5: Randles-Sevcik plot of peak current versus square root of scan rate.

would be intuitively expected as electron transfer should be impeded by both contact resistance between catalyst particles, between the catalyst and the glassy carbon, and by the presence of the Nafion binder. Significantly higher apparent electron transfer rates were observed with the nanotubule-based electrodes. Values for k_0 of 0.13 and 0.026 cm/s for the 100 and 200 nm diameter nanotubule arrays, respectively, were obtained, one to two orders of magnitude greater than observed with the more traditional electrode structures. Similar trends have been reported when comparing carbon nanotube electrode structures to more traditional carbon electrodes (e.g., glassy carbon, carbon pasted, etc.) [21–25]. In carbon, this trend has been attributed to some unique catalytic effect of the carbon nanotubes themselves [24, 25]. Similar trends have also been reported for platinum nanowire arrays with regard to the heterogeneous electron transfer coefficient, though for the electrooxidation of methanol [2, 3, 9, 12, 35].

Similar trends have been reported when comparing carbon nanotube- [21–25] or platinum nanowire- [2, 3, 9, 12, 35] based electrodes to traditional glassy carbon, platinum disc, or other standard electrodes. As noted previously, however, studies of Pt nanostructures have focused on methanol and other organic molecules. Many have attributed these results in carbon nanotubes to some unique catalytic effect of the carbon [24, 25] or platinum nanostructures [2, 9, 12, 35] themselves. This conclusion has commonly been based on an increased heterogeneous electron transfer coefficient, as observed here. However, the Nicholson method used in calculating k_0 assumes semi-infinite diffusion to the electrode surface, which is the case for flat disc electrodes and microelectrodes, but not necessarily for a nanotubule array as studied in this work (or carbon nanotube carpets, platinum nanowire arrays, and other similar structures). Streeter et al. proposed a thin film model for a similar nanoarray electrode structure [43]; however, this model neglects bulk diffusion to the top of the nanoarray. Semi-infinite diffusion would be expected from the bulk electrolyte to the top of the nanoarray structure, while something akin to diffusion in porous media might be expected in the spaces between the nanotubules in the array. The Nicholson method remains valuable for comparing various electrodes; however, due to the aforementioned limitations with nanoarrays, we refer to the heterogeneous electron transfer coefficient as an “apparent” value in this work. The increased k_0 values observed with the platinum nanotubules arrays here may still be due to a catalytic effect, as has been suggested with other nanostructures, and/or due to an apparent mass transfer enhancement. The Randles-Sevcik model derived for semi-infinite diffusion to a flat surface where an ideally completely reversible reaction occurs predicts that the slope of a plot of $i_{p,a}$ versus $\nu^{1/2}$ will be proportional to the diffusivity of the reacting species [41]. As seen in Figure 5, the slope of the $i_{p,a}$ versus $\nu^{1/2}$ fit lines is significantly greater for the nanotubule array electrodes, indicative of an increase in the apparent diffusivity for the ferro/ferricyanide ions as compared to the platinum black/Nafion and platinum disc electrodes.

4. Conclusions

Template wetting nanofabrication was used to prepare Pt nanotubular catalyst structures in a porous alumina membrane. The resulting high surface area Pt nanostructures were characterized electrochemically using the ferro/ferricyanide reaction. Though common with both Pt and carbon electrodes, especially carbon nanotube electrodes, this standard reaction has not previously been used to characterize nanostructured Pt electrodes. The nanotubule electrodes more closely approached ideal, reversible behavior and exhibited a one to two order of magnitude greater apparent heterogeneous electron transfer coefficient than standard platinum disc and platinum black electrodes. While the source of this improvement is not clear at this time, this nanoarray structure shows promise for sensor or small fuel cell applications.

Conflict of Interests

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

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