Chemical Deposition and Electrocatalytic Activity of Platinum Nanoparticles Supported on TiO$_2$ Nanotubes

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Platinum electrocatalysts (Pt-B/TON-N$_2$, Pt-B/TON-air and Pt-H/TON-air) incorporated on annealed titanium oxide nanotubes (TONs) have been successfully synthesized by chemical deposition method using sodium borohydride and hydrazine, reducing agents. TONs were firstly prepared by anodization of pure Ti foil in HF solution followed by annealing in air and N$_2$ atmosphere. The morphology and structure of the electrocatalysts were characterized by scanning (SEM), transmission (TEM) electron microscopies, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and electrochemical techniques. SEM, TEM, XRD and EDX characterization indicate the presence of platinum nanoparticles with diameter less than 50 nm and uniformly incorporated into TON arrays. The electrocatalytic activities results show that the Pt-B/TON-N$_2$ catalyst has higher catalytic activity for the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) compared with Pt-B/TON-air and electrodes prepared using hydrazine as reducing agent because of the better conductivity. In addition, the Pt-B/TON-N$_2$ catalyst exhibits better poison tolerance and two times higher methanol oxidation current density than that reported for Pt/carbon catalyst. This suggests that the Pt-B/TON-N$_2$ catalyst supported on TON-N$_2$ has promising potential applications in electrocatalyst reactions.

Keywords: titanium oxide, nanotubes, Pt nanoparticles, electrocatalysis, reducing agent, electroless.

1. INTRODUCTION

Increasing energy demands, depletion of fossil fuel reserves and environmental pollution have motivated the search for other energy conversion devices with high efficiency and low emissions. The
widespread of fuel cells and subsequent attempts to make the technology economically competitive make more attention to be focused on lowering the cost of the membrane electrode assembly (MEA) and, specifically the catalysts used for the oxygen reduction reaction (ORR). Fuel cells fueled by hydrogen and oxygen; or small organic molecules such as methanol may have the ability to meet these demands [1]. Direct methanol fuel cells (DMFCs) have been considered as the ideal clean fuel cell system for portable electronic devices and transportation applications, as they are superior to other kinds of fuel cells in weight–volume energy densities and working conditions, etc [2]. In an acidic medium, the most efficient catalysts for DMFC is platinum (Pt) based catalysts. The electrocatalytic activity of catalysts for methanol electro-oxidation is dependent on many factors [3]. Of these, is the catalyst support and its surface condition are essential for the catalyst to increase its electrocatalytic activity [4]. In previous studies, a variety of carbon supports have been investigated based on their high chemical stability and good electron conductivity, etc [5].

The catalytic properties of the platinum catalyst depend on the properties of support [7] such as its surface area and electronic properties which are considered important to produce high catalytic activity [8]. One-dimensional catalyst supports, such as titanium oxide nanowires [9], nanoribbons [10], nanotubes and nanorods [11, 12], have attracted considerable attention recently. Titanium oxide nanotubes (TONs) are of particular significance due to their superior physicochemical properties and potential applications in electrocatalysis [13], photocatalysis [14], and energy use including hydrogen storage [15] and lithium batteries [16]. TON arrays have attracted much attention as catalyst support because of their large specific surface area, favorable surface chemistry, good biocompatibility, and allow efficient access for the catalyst materials [17]. For example, the surface chemistry of TONs can be easily modified through coordination with amine and carboxyl groups, and used in detection of electroactive molecules or as biosensors [18, 19]. There are three general approaches for synthesis the titanium oxide nanotubular structures, namely, template-assisted fabrication [20], alkaline hydrothermal synthesis [21], and anodic oxidation or anodization of titanium foil [22]. The advantage of TONs produced by anodization is that they are readily attached onto a titanium substrate and form oriented, aligned perpendicular to the substrate, which offers much improved electron transfer pathways and catalyst accessibility than non-oriented (random mixtures) structure. As a result, this oriented TON has a great potential as electrochemical electrodes for highly sensitive biosensor applications. However, an obstacle preventing TON arrays from wide spread applications is their irreversible electrode reactions. Reduction peaks were commonly observed, but no oxidation peaks can be seen in the reverse potential scan during the cyclic voltammetric measurements due to the low electrical conductivity of titanium oxide [23, 24]. Annealing in different gases is considered to be one possible approach to narrow the band gap and enhance the electrical conductivity [25, 26].

Chemical deposition is among the most straightforward and efficient methods used to fabricate Pt-based nanomaterials [27] with the help of a chemical reducing agent. A variety of reducing agents have been employed to synthesize Pt nanoparticles (NPs) [30, 31]. The most commonly used reducing agents are ethylene glycol [32] and sodium borohydride [33]. Metz et al. [34] synthesized Pt NPs on vertically aligned carbon nanofibers (VACNFs) and Knupp et al. [35] also fabricated Pt nanotubules on aluminum sheets using hydrazine as a reducing agent. Herricks et al. [36] synthesized Pt NPs on carbon nanotubes and carbon nano-fibers using a polyol synthesis method with ethylene glycol as the
reducing agent. Guo et al. [37] used sodium borohydride as a reducing agent and citric acid (CA) as a stabilizing agent to prepare Pt NPs. Wells et al. [38] employed a polyol process with sodium nitrate to control the morphology of the synthesized Pt NPs, where ethylene glycol served as both the reducing agent and solvent.

Recently we developed TONs substrate with improved conductivity by annealing at different temperatures under air atmosphere [39]. In this work we demonstrate the chemical deposition and characterization of Pt NPs (Pt-B/TON-N₂, Pt-B/TON-air and Pt-H/TON-air) loaded on highly conducted TONs support using hydrazine and sodium borohydride as reducing agents. TONs support was pre-annealed in air and N₂ atmosphere at 450 °C which highly improve the electrical conductivity. Also the electrocatalytic activity of the prepared Pt/TONs catalysts was evaluated for the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) and methanol electro-oxidation reaction (MOR) in acidic and alkaline media.

2. EXPERIMENTAL

Ti foil (purity > 99.5% thickness 0.25 mm), dihydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆.H₂O > 99.99%) and PdCl₂ (purity > 99.99%) were purchase from Alfa Aesar. HF (purity 39-43%) from QualiKems, NaBH₄ (purity > 98.0%, WINLAB), NH₂NH₂ ( > 99.0%) and C₂H₄(NH₂)₂ ( > 99.0%) were obtained from PS. H₂SO₄ ( > 98.0%, BDH, AR), CH₃OH (purity > 99.5% , AVONCHEA, AR), NaOH solution 32% in water (Fluka), SnCl₂.2H₂O (Sigma Aldrich, ACS reagent) and HNO₃ (purity >99.0% , BDH, AR). All aqueous solutions were prepared with deionized water produced by Milli-Q (resistance 18.2 MΩ cm, Millipore, Inc.).

Highly ordered TONs substrate were fabricated by electrochemical anodic oxidation of Ti foil according to a method reported in the literature [40]. Ti foils with an area of 20 ×30 mm and thickness of 0.25 mm were used as starting material in order to obtain the TON arrays. All Ti sheets were washed in deionized water and degreased in an ultrasonic bath in isopropanol, acetone and finally washed with DI water followed by air-drying. The anodization was performed at room temperature using two-electrode electrochemical cell with the Ti foil as the anode and a Pt foil as the cathode and the distant between them was maintained at 2 cm. The substrates were prepared by applying anodizing voltage of 20 V using DC power supply (E3612A, Agilent Technologies) in 0.5 wt% HF solution for 20 min. After anodization, samples were washed with deionized water and the as-anodized TONs were subsequently annealed at 450 °C in air or N₂ atmosphere (designated as TON-air and TON-N₂ respectively) for 3 h with heating and cooling rate of 5 °C min⁻¹ to induce anatase crystalization.

Before Pt chemical deposition, TON substrates were firstly sensitized for 30 min in 0.3% (wt) SnCl₂ + 3% (wt) HCl followed by activation in 0.1% (wt) PdCl₂+ 2.0% (wt) HCl solutions respectively. After sensitization and activation of TON arrays, Pt was deposited on TON-air and TON-N₂ by immersing in 25 ml solution containing 0.1 g H₂PtCl₆.4H₂O, 0.1 ml ethylenediamine (C₂H₄(NH₂)₂) and 0.1 g NH₂NH₂ or 0.1 g NaBH₄. The electroless deposition process was performed at 63 °C for 30 min with pH controlled at 13 by adding NaOH solution.
The TON substrates and deposited Pt catalysts were characterized by XRD (Ultima IV, X-ray diffractometer: Rigaku) with Cu-Kα radiation (λ = 0.15418 nm; 40 kV and 40 mA). The morphology of the samples was examined using a high-performance, scanning electron microscope (SEM; JSM-6380LA) fitted with energy dispersive X-ray spectroscopy (EDS) (Vantage 4105, NORAN) and transmission electron microscope (TEM; JEM-1400). The metal loading of Pt deposited on the TON supports was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

The cyclic voltammetry (CV) was performed in a conventional three-electrode single-compartment Pyrex glass cell using a computerized potentiostat/galvanostat (Autolab, PGSTAT30) with NOVA 1.8 software. The reference and the auxiliary electrodes were SCE and pure Pt-foil, respectively. The current was divided by 0.68 cm² the geometric area of working electrode.

3. RESULTS AND DISCUSSION

Figure 1. SEM images for Pt catalysts supported on TONs, (a) Pt-H/TON-air, (b) Pt-B/TON-air, (c) Pt-B/TON-N₂ and (d) cross-sectional view for Pt-B/TON-N₂ electrodes.
Figs. 1 shows the surface morphology of Pt nanoparticles deposited on TONs support annealed in air and N₂ at 450 °C for 3 h and using reducing agent of (a) hydrazine (Pt-H/TON-air), (b) NaBH₄ (Pt-B/TON-air), (c) NaBH₄ (Pt-B/TON-N₂) and (d) shows the cross-sectional for Pt-B/TON-N₂. Homogenously dispersed Pt nanoparticles clearly can be seen on the TON-air and TON-N₂; with some particles located at the rims and inside of highly packed TONs. From the cross section image we can estimate the TONs thickness at about 250 nm.

![Figure 1](image1.png)

Figure 2. (a) TEM image and (b) EDS for Pt-B/TON-N₂ catalyst.

![Figure 3](image2.png)

Figure 3. XRD patterns of Pt-H/TON-air (black); Pt-B/TON-air (blue) and Pt-B/TON-N₂ (red).

Figs. 2 shows the TEM images and EDS analysis of Pt deposited on TONs annealed in N₂ at 450 °C for 3 h using NaBH₄ (Pt-B/TON-N₂). The EDX graph clearly shows that Pt and Ti are the
major elements of composition which confirm the presence of Pt deposited on TONs substrates. It is difficult to measure the Pt particle size from SEM images but from the TEM image in Fig. 2a we can observe the nanoparticles have large size disruption with a diameter less than 50 nm. Fig. 3 shows the XRD pattern of Pt-H/TON-air, Pt-B/TON-air and Pt-B/TON-N₂ catalysts. The diffraction patterns show the presence of Ti, TiO₂ and Pt phases. The sample Pt-B/TON-N₂ show well defined reflections compared with sample Pt-B-air, indicating a different particle size. From the XRD we can conclude that Pt (200) and Pt (220) crystal faces for Pt-B/TON-N₂ are clearly higher than that for Pt-B/TON-air. This indicates that the degree of preferential orientation of Pt (200) and Pt (220) crystal faces are higher in case Pt-B-N₂ catalysts, which may be attributed to the incorporation of boron with Pt deposit on TONs-N₂, support [41]. On the other hand in case of using hydrazine during preparation of Pt-H-air catalyst, the characteristics diffraction peaks of Pt (200) and Pt (220) mostly can’t observe.

Figure 4. CVs at 50 mVs⁻¹ for TON as anodized (black); TON-air (blue) and TON-N₂ (red) in 10 mM Fe(CN)₆³⁻/⁴⁻ + 0.1 M KCl solution.

Fig. 4 shows the CVs at 50 mVs⁻¹ for TONs-as anodized, TONs-air and TONs-N₂ electrodes in 10 mM Fe(CN)₆³⁻/⁴⁻ + 0.1 M KCl. Clearly, the TONs-N₂ electrode shows higher ferri/Ferrocyanide redox peak currents in comparison to the voltammograms obtained for TONs-air and TONs-as anodized electrodes. This can attribute to the greater conductivity and electrochemical active surface area of the TiO₂ nanotubes annealing in N₂ [41].

The electrocatalytic activity of Pt-B/TON-N₂, Pt-B/TON-air and Pt-H/TON-air catalysts towards HER and ORR has been investigated in 0.5 M H₂SO₄ solutions saturated with N₂ or O₂. Fig. 5 shows the cyclic voltammograms at 50 mV s⁻¹ for the Pt-H/TON-air, Pt-B/TON-air and Pt-B/TON-N₂ electrodes in N₂ saturated 0.5 M H₂SO₄ solution in potential region from -0.2 to 0.2 V vs. SCE. For the hydrogen adsorption/desorption features, Pt-B/TON-N₂ shows more resolved peaks and higher current
densities than that for Pt-B/TON-air and Pt-H/TON-air catalysts. This can related to the roughness factor for Pt NPs prepared by NaBH₄ was higher than that prepared by NH₂NH₂ reducing agent, as shown in table 1. This is partly due to the existence of more Pt (200) and Pt (220) surface sites created by the addition of NaBH₄ [42, 43].

![Figure 5](image)

**Figure 5.** CVs at 50 mVs⁻¹ for Pt-H/TON-air (black); Pt-B/TON-air (blue) and Pt-B/TON-N₂ (red) in N₂ saturated 0.5 M H₂SO₄ solution.

Table 1 reports the electrochemical active surface area, roughness factors (Rₚ) and mass loading of Pt catalysts as measure from hydrogen adsorption/desorption charge and ICP analysis respectively. Within the experimental error, ICP analysis shows that the Pt mass loading for the three catalysts is almost the same. However, the Pt-B/TON-N₂ shows higher roughness factor than that for Pt-B/TON-air and Pt-H/TON-air as shown in Table 1.

**Table 1.** Electrochemical active surface area and roughness factors (Rₚ) of Pt NPs on TONs annealed in air and N₂ and deposited by hydrazine and sodium borohydride

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Q_H mC</th>
<th>Surface area (cm²)</th>
<th>Rₚ</th>
<th>Mass loading (g cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-H/TON-air</td>
<td>1.05</td>
<td>5.00</td>
<td>7.35</td>
<td>1.32×10⁻⁵</td>
</tr>
<tr>
<td>Pt-B/TON-air</td>
<td>2.46</td>
<td>11.73</td>
<td>17.25</td>
<td>1.61×10⁻³</td>
</tr>
<tr>
<td>Pt-B/TON-N₂</td>
<td>3.73</td>
<td>17.76</td>
<td>26.11</td>
<td>1.45×10⁻³</td>
</tr>
</tbody>
</table>

Fig. 6 shows the oxygen reduction CVs at 50 mV s⁻¹ for Pt-H/TON-air, Pt-B/TON-air and Pt-B/TON-N₂ catalysts in O₂-saturated 0.5 M H₂SO₄ solution over a potential region from -0.2 to 0.6 V vs. SCE. All the voltammetric profiles show Pt oxide reduction peaks between 0.25 – 0.40 V, which is
the typical potential for oxygen reduction on platinum catalysts in acid solution. Oxygen reduction potential peak is observed at 0.44 V for Pt-B/TON-N₂ while the corresponding value for Pt-B/TON-air and Pt-H/TON-air is observed at 0.38 V and 0.25 V respectively. These results indicate that the Pt-B/TON-N₂ electrode possess higher electrochemical activity for HER and ORR reactions.

![Figure 6](image_url) CVs at 50 mVs⁻¹ for Pt-H/TON-air (black); Pt-B/TON-air (blue) and Pt-B/TON-N₂ (red) in O₂ saturated 0.5 M H₂SO₄ solution.

The electrocatalytic activity of the catalysts was also investigated for methanol oxidation in acidic and basic media. Fig. 7 shows the CVs for the Pt-H/TON-air, Pt-B/TON-air and Pt-B/TON-N₂ catalysts in 1.0 M methanol and 1.0 M KOH. The peak current densities in the forward scan of the Pt-B/TON-N₂, Pt-B/TON-air and Pt-H/TON-air catalysts are measured to be 540, 380 and 250 mA·mg⁻¹ Pt. It is noted that the peak current is enhanced for catalysts prepared by NaBH₄ as reducing agent and TONs annealed in N₂ as a support.

The CV for the Pt-H/TON-air, Pt-B/TON-air and Pt-B/TON-N₂ catalysts in 1.0 M methanol and .5 M H₂SO₄ are shown in Fig. 8 shows. The peak current densities in the forward scan for the Pt-B/TON-N₂, Pt-B/TON-air and Pt-H/TON-air catalysts are 317, 188 and 120 mA·mg⁻¹ Pt respectively. The methanol oxidation current density obtained at Pt-B/TON-N₂ catalyst (317 mA·mg⁻¹ Pt) is higher than that reported for Pt catalyst supported on carbon (159 mA·mg⁻¹ Pt) [44]. Pt-B/TON-N₂ catalyst shows two times increases in methanol oxidation current in compare with Pt/carbon. Also the Pt-B/TON-N₂ shows the highest peak current density in comparison with Pt-B/TON-air and Pt-H/TON-air catalysts. The ratio of peak currents associated with the anodic peaks in forward (I_f) and backward (I_b) scans is generally used to describe the tolerance of a catalyst to intermediates generated during the oxidation of methanol [45].
Figure 7. CVs at 50 mVs$^{-1}$ for Pt-H/TON-air (black); Pt-B/TON-air (blue) and Pt-B/TON-N$_2$ (red) in 0.5 M methanol and 1.0 M KOH solution.

Figure 8. CVs at 50 mVs$^{-1}$ for Pt-H/TON-air (black); Pt-B/TON-air (blue) and Pt-B/TON-N$_2$ (red) in 0.5 M methanol and 0.5 M H$_2$SO$_4$ solution.

A low $I_f/I_b$ ratio indicates poor methanol oxidation to CO$_2$ during the forward scan, and excessive accumulation of carbonaceous intermediates on the catalyst surface [46]. For our Pt-B/TON-N$_2$ catalyst, the value of $I_f/I_b$ is 1.42, which is higher than that for Pt-B/TON-air catalyst (1.30), Pt-
H/TON-air (1.26) and about 1.5 times higher than that reported for Pt/carbon (0.95) [44]. The results of the \( I_d/I_h \) ratio indicate that the Pt-B/TON-N\(_2\) catalysts exhibits better poison tolerance than that of the others catalyst. The exceptional electrocatalytic performance of the Pt-B/TON-N\(_2\) electrode can be attributed to the synergistic effect of Pt NPs and the TON support on CO oxidation [47], and the ordered structures of TONs can provide unidirectional electronic tubes and reduce the grain boundaries [48]. In addition, the greater conductivity and electrochemical active surface area of the TiO\(_2\) nanotubes annealing in N\(_2\) can contribute to catalytic enhancement [49].

4. CONCLUSIONS

In summary, Pt NPs were chemically deposited on pre-annealed TONs support using hydrazine and sodium borohydride reducing agents. The Pt-B/TON-N\(_2\) electrocatalyst shows a uniform and well dispersion of Pt NPs through the TON with particle size less than 50 nm. The Pt-B/TON-N\(_2\) catalyst has higher electrochemical active area and higher catalytic activity for the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) compared with to Pt-B/TON-air and Pt-H/TON-air. Also, the Pt-B/TON-N\(_2\) catalyst exhibits better poison tolerance and two times higher methanol oxidation current density than that reported for Pt/carbon catalyst. This was attributed to the synergistic effect of TON support and Pt NPs and on CO oxidation, the ordered unidirectional structures of TONs tubes and the greater conductivity and electrochemical active surface area of the TiO\(_2\) nanotubes annealed in N\(_2\).

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References

47. CS. Chen, FM. Pan, Appl Catal B-Environ.9 (2009) 663.

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