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Authors: T. Maiyalagan, B. Viswanathan

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Catalytic activity of Pt /WO₃ nanorod electrodes towards electro-oxidation of methanol

T. Maiyalagan and B. Viswanathan*
National Center for Catalysis Research
Department of Chemistry,
Indian Institute of Technology Madras,
Chennai 600 036, India

Abstract

WO₃ nanorods have been synthesized using Anodisc alumina membrane as template and platinum nanoparticles have been supported on the WO₃ nanorods. WO₃ nanorods as Platinum catalyst supports were characterized by electron microscopic technique and electrochemical analysis. Methanol oxidation on the prepared electrode was studied using cyclic voltammetry and chronopotentiometry. Pt/WO₃ nanorods film on glassy carbon electrode shows higher electro-catalytic activity for the oxidation of methanol. High electro-catalytic activities and good stabilities could be attributed to the synergistic effect between Pt and WO₃, avoiding the electrodes being poisoned.

Keywords: Pt nanoparticles; WO₃ nanorods; Template synthesis; Alumina template; Catalyst support; Methanol Oxidation

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* bvnathan@iitm.ac.in Ph: +91-044-22574200, Fax: +91-44-22574202

1. Introduction

Platinum supported on metal oxides has received attention in recent years, mainly because of its potential utility in anodes in direct methanol fuel cells [1-8]. Most often the catalyst is dispersed on a conventional carbon support and the support material influences the catalytic activity through metal support interaction. In order to achieve better dispersion of the metal, as well as to derive maximum activity from the dispersed metal sites, one has to adopt some innovative strategies. A strategy is to preferentially promote the oxidation of the intermediate species (partial oxidation products of methanol like CO and other partially dehydrogenated species) on other sites so that the noble metal sites are still available and free for the electrochemical oxidation of the fuel [9,10]. However, it is essential that the additional components employed for the reaction of the inhibiting intermediates, should not only be contributive to the overall desired electrochemical reaction but also not render any additional impedance to the activity of the electro-catalyst as well as not lead to the loss of electrochemical energy converted. This means that the role of the support (mainly oxides for the preferential oxidation of partial combustion products) should be cumulative and not additive. The role of tungsten oxide nanorods is examined as supports for noble metals for possible application as fuel cell anodes.

Tungsten oxide is a well-known multifunctional material, especially for fuel cell applications [11]. Tungsten oxide nanorods have been utilized as support for the following reasons: Platinum catalysts supported on tungsten oxide have been extensively studied as active catalysts for the electro-oxidation of methanol [12].Tungsten oxide can form hydrogen bronze (H_xWO_3) that effectively facilitates the dehydrogenation of

methanol, though these catalysts exhibit high performance, tungsten oxide undergoes dissolution in acid medium and thus reduces the electrocatalytic activity. The stability of tungsten oxide in acid medium can be improved by suitably adjusting the conditions of its preparation. Application of the tungsten oxide matrix should increase the electrochemically active surface area and facilitate charge (electron, proton) distribution [13]. Moreover, the OH_{ads} groups on tungsten oxide surface may induce oxidation of the poisoning CO intermediate [14]. The present study aims at fabrication of electrocatalytic system with optimized reactivity towards electrooxidation of methanol. On the whole, the system is multifunctional in terms of promoting oxidation of methanol.

In this communication, the preparation of Pt nanoparticles supported on the surface of WO_3 nanorods and the electro-catalytic activity for the methanol oxidation of these composite electrodes are compared with the activity of conventional electrodes. The results indicated that the as-obtained Pt/WO_3 nanorod catalysts have an excellent electro-catalytic activity for methanol oxidation than the commercial Pt/C catalyst.

2. Experimental

2.1 Materials

All the chemicals used were of analytical grade. (Sisco Research Laboratories, India), Phosphotungstic acid and concentrated HF (both from Merck) were used. Hexachloroplatinic acid was obtained from Aldrich. 20 wt % Pt/Vulcan carbons were procured from Jhonson Mathey. Methanol and sulphuric acid were obtained from Fischer chemicals. The alumina template membranes (Anodisc 47) with 200 nm diameter pores were obtained from Whatman Corp. Nafion 5 wt % solution was obtained from Dupont and was used as received.

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2.2 Synthesis of WO$_3$ nanorods

10 g of Phosphotungtstic acid (H$_3$PW$_{12}$O$_{40}$) was stirred in a 30 ml of methanol solution. The resulting colloidal suspension was infiltrated into the membrane under vacuum by wetting method [15]. The same procedure was repeated 1 to 8 times. The upper surface of the membrane was then polished gently by sand paper (2500 grit) and dried at 95^0 C for 1 h. The formation of WO$_3$ nanorods inside alumina template (WO$_3$ /AAO) was further achieved by programmed temperature thermal decomposition from 95 to 500 ^{0} min^{-1} and finally calcinated at 873 K for 3 h in air. The removal of the AAO template was performed by dissolving alumina template in 10 %(v/v) HF. The WO$_3$ nanorods product was washed with a copious amount of deionized water, to remove the residual HF and dried at 393 K.

2.3 Preparation of Pt/WO$_3$ nanorods composites

Platinum nanoclusters were loaded on the WO$_3$ nanorods by conventional impregnation methods [16]. Platinum was loaded on the nanorods as follows: 5 ml of 73mM aqueous hexachloroplatinic acid (H$_2$PtCl$_6$) was mixed with 100 mg of WO$_3$ nanorods by stirring at room temperature. The mixture was then evaporated to dryness and the resulting material was then reduced in hydrogen atmosphere at 623 K for 3h to give Pt/WO$_3$ nanorods.

2.4 Preparation of working electrode

Glassy carbon (GC) (BAS Electrode, 0.07 cm^2) was polished to a mirror finish with 0.05 μm alumina suspensions before each experiment and served as an underlying substrate of the working electrode. In order to prepare the composite electrode, the nanorods were dispersed ultrasonically in water at a concentration of 1mg ml^{-1} and 20 μl aliquot was transferred on to a polished glassy carbon substrate. After the evaporation of water, the

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resulting thin catalyst film was covered with 5-wt% Nafion solution. Then, the electrode was dried at 353 K and used as the working electrode.

2.5 Characterization Methods

The scanning electron micrographs were obtained using JEOL JSM-840 model, working at 15 keV. The nanorods were sonicated in acetone for 20 minutes and then were dropped on the cleaned Si substrates. The AFM imaging was performed in air using the Nanoscope IIIA atomic force microscope (Digital Instruments, St. Barbara, CA) operated in contact mode. For transmission electron microscopic studies, the nanorods dispersed in ethanol were placed on the copper grid and the images were obtained using Phillips 420 model, operating at 120 keV.

2.6 Electrochemical Measurements

All electrochemical studies were carried out using a BAS 100 electrochemical analyzer. A conventional three-electrode cell consisting of the GC (0.07 cm^2) working electrode, Pt plate (5 cm^2) as counter electrode and Ag/AgCl reference electrode were used for the cyclic voltammetry (CV) studies. The CV experiments were performed using 1 M H$_2$SO$_4$ solution in the absence and presence of 1 M CH$_3$OH at a scan rate of 50 mV/s. All the solutions were prepared by using ultra pure water (Millipore, 18 MΩ). The electrolytes were degassed with nitrogen gas before the electrochemical measurements.

3. Results and Discussion

The XRD pattern for the as-synthesized tungsten oxide nanorods and platinum loaded tungsten oxide nanorods are given in Fig 1.a and 1.b respectively. The diffraction peaks and the peak intensities of the tungsten oxide nanorods are in good agreement with the diffraction peaks of crystalline monoclinic phase of WO$_3$. XRD patterns of Pt/WO$_3$ nanorods are shown in Fig. 1.b. The presence of Pt (111), Pt (200) peaks are

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found in Fig 1.b. Furthermore, the major diffraction peaks of Pt nanoparticles can be observed.

The morphology of tungsten oxide nanorods was studied with SEM, AFM, transmission electron microscopy (TEM) images on a Philips CM12/STEM instrument. The scanning electron microscopy (SEM) image presented in Fig 2.a shows rod like morphology of the product. Further AFM image confirms the rod like morphology in Fig 2.b representing low magnification. The morphology of the nanorods can be confirmed with TEM micrographs shown in Fig 3. (a, b). The dimensions of the nanorods are matched with the outer diameter of the template used. The diameter of the nanorods was found to be around 200 nm. The WO_3 nanorods have been utilized as support for the Pt deposition. The presence of Pt on WO_3 nanorods can be seen from Fig 3.b and it is clear from the micrograph that the Pt is well dispersed all over the surface of the nanorods. The size of the Pt nanoparticles is in the range of 3-4 nm. The optimal Pt particle size for reactions in the H_2/O_2 fuel cell is 3 nm [17]. The Fig 4. taken from the EDX shows the presence of Pt in WO_3 nanorods. The complete removal of fluorine and aluminum has also been confirmed.

The electrochemical behavior of WO_3 nanorods was studied in 1 M H_2SO_4 as shown in Fig 5. b. The cyclic voltammogram shows an anodic peak current at -0.07 V and it is due to the formation of tungsten bronzes by hydrogen intercalation in the tungsten trioxide. The electrochemical response due to W is seen at -0.1 V in the forward scan, which matches with the peak reported in literature [18]. Further, the stability of tungsten trioxides in sulphuric acid medium was evaluated by carrying out the cyclic voltammetry by repeating voltammetric cycles in 1 M H_2SO_4. Cyclic voltammetry of the

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WO_3 nanorods shows higher stability compared to the bulk WO_3. There is gradual decrease in current for subsequent cycles showing the less stability of bulk WO_3. After the second cycle in WO_3 nanorods, there is no decrease in the currents produced upon repeated cycling. This shows good stability of WO_3 nanorods compared to bulk WO_3 in sulfuric acid medium.

The electrochemical activity of platinum loaded WO_3 nanorods for methanol oxidation was studied using cyclic voltammetry in the presence of 1M H_2SO_4 and 1M CH_3OH. Fig 6.a shows the electrochemical oxidation of methanol by Pt loaded on WO_3. (Voltammogram obtained after the peak attaining a constant peak current). For comparison, methanol oxidation was also carried out with commercial 20% Pt/C (Jhonson Mathey). Fig 6.c shows the cyclic voltammetry of WO_3 nanorods in 1M H_2SO_4 and 1M CH_3OH. Like Ru, WO_3 has no activity for methanol oxidation in acid solution. The unsupported WO_3 nanorods showed no activity towards methanol oxidation. As is shown in Fig 6. a, two oxidation peaks are observed, which belong to the oxidation of methanol and the corresponding intermediates [10].

The methanol oxidation peak potential is lower for Pt/WO_3 nanorods than for Pt/C indicating the better performance of Pt particles supported on WO_3 nanorods. For a lower platinum loading, the WO_3 nanorods show enhanced activity than the commercial catalyst. The specific activity (mA cm^{-2}) of the platinum supported on WO_3 nanorods is almost two times higher than that of the commercial 20% platinum on carbon support (Table 1). The higher activity of Pt/WO_3 can be attributed to the stabilization of Pt nanoparticles and dispersion on the WO_3 nanorods. It can be supposed from the cyclic

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voltammogram that the Pt/WO$_3$ nanorods electrode is relatively endurable for intermediate production.

According to Yoshiike and Kondo [19, 20] H$_2$O molecules are physisorbed but also chemisorbed on WO$_3$. The oxophilic nature of WO$_3$ would help in adsorbing the intermediates and thereby, keeps the surface of platinum clean. It is not possible in the case of Pt supported on carbon. The advantages of using Pt/WO$_3$ electrode are (1) keeping the Pt site clean for chemisorption of methanol by the formation and oxidation of hydrogen tungsten bronzes during dehydrogenation of methanol on the surface of Pt/WO$_3$ electrode.

$$WO_3 \ + xPt\text{-}H \ \longrightarrow \ HxWO_3 \ + \ xPt$$

$$HxWO_3 \ \longrightarrow \ xH^+ \ + xe^- \ + WO_3$$
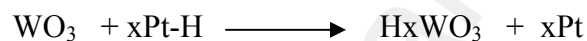
and (2) oxidizing the poisons such as CO, since water adsorbed on WO$_3$ surface can interact with CO adsorbed on Pt at the neighbouring site. Such bronzes show better catalytic activity than Pt-Ru based electrocatalyts [21, 22].

The stability of electrode for methanol oxidation was evaluated by chronoamperometry Fig 7. compares the chronopotentiometric results of methanol oxidation in 1 M H$_2$SO$_4$ and 1 M CH$_3$OH at 0.6 V. Pt/WO$_3$ nanorods electrode not only showing higher initial activity but also revealing more stability than Pt/C electrode (Fig. 7.). The probable reason could be the lower polarisation potential. At this potential, the leaching of W would not have had a pronounced effect on the stability of the electrode for methanol

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oxidation [23]. Also, the oxophilic nature of WO$_3$ is beneficial to producing hydroxyl groups on the catalyst surface, which promotes the oxidation of adsorbed CO [24, 25].

4. Conclusion

In conclusion, a simple template synthesis has been described for preparing WO$_3$ nanorods by a direct calcination of Phosphotungtstic acid in the channels of the alumina template. The size of nanorods is around 200 nm matches with the diameter of the template used. The methanol oxidation activity of platinum supported on WO$_3$ nanorods has been studied and compared with that of the commercial catalyst. Pt/WO$_3$ nanorods exhibited higher methanol oxidation activity than the commercial Pt/C catalyst by a factor of two. Platinum supported on such nanorods is found to be stable for several cycles in an electrochemical environment. Enhancement in the electro-catalytic activity is due to spill-over effect in methanol oxidation and the role of tungsten oxide nanorods are examined for use as supports for noble metals for possible application as fuel cell anodes.

Acknowledgements

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List of Figure captions

Fig. 1. XRD patterns of (a) Pt/WO_3 nanorods and (b) WO_3 nanorods

Fig. 2. (a) SEM Micrograph of the WO_3 nanorod and (b) AFM micrograph of the nanorod

Fig. 3. TEM images of the nanorods (a) WO_3 nanorods (b) Pt/WO_3 nanorods

Fig. 4. EDX pattern of Pt/WO_3 nanorod electrode

Fig. 5. Cyclic voltammogram for (a) bulk WO_3 (b) WO_3 nanorods in 1 M H_2SO_4 at scan rate of 50 mV s^{-1} at 298 K

Fig. 6. Cyclic voltammograms of (a) Pt/WO_3 nanorods (b) Pt/C (Johnson Mathey) (c) WO_3 nanorods in 1 M H_2SO_4/1 M CH_3OH run at 50 mV/s

Fig. 7. Current density versus time curves at (a) Pt/ WO_3 nanorods (b) Pt/C Johnson Mathey) measured in 1 M H_2SO_4 + 1 M CH_3OH. The potential was stepped from the rest potential to 0.6 V vs. Ag/AgCl

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Table 1. **Electro-catalytic activity of Pt/WO$_3$ nanorods and Pt/C for methanol oxidation**

Electrocatalyst	Pt loading μg/cm^2	Specific activity mA/cm^2
Pt/C	20	29.5
Pt/WO$_3$ nanorods	20	62.0

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

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Fig. 5.

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Fig. 6.

Fig. 7.

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