Electro-Oxidation of Methanol on TiO₂ Nanotube Supported Platinum Electrodes

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TiO₂ nanotubes have been synthesized using anodic alumina membrane as template. Highly dispersed platinum nanoparticles have been supported on the TiO₂ nanotube. The supported system has been characterized by electron microscopy and electrochemical analysis. SEM image shows that the nanotubes are well aligned and the TEM image shows that the Pt particles are uniformly distributed over the TiO₂ nanotube support. A homogeneous structure in the composite nanomaterials is indicated by XRD analysis. The electrocatalytic activity of the platinum catalyst supported on TiO₂ nanotubes for methanol oxidation is found to be better than that of the standard commercial E-TEK catalyst.

Keywords: TiO₂ Nanotubes, Template Synthesis, Catalyst Support, Methanol Oxidation.

1. INTRODUCTION

Fuel cells operating by the electrochemical oxidation of hydrogen or methanol, as fuels at the anode and reduction of oxygen at the cathode are attractive power sources due to their high conversion efficiencies, low pollution, light weight, and high power density. While methanol offers the advantage of easy storage and transportation in comparison to hydrogen oxygen fuel cell, its energy density (~2000 Wh/kg) and operating cell voltage (0.4 V) are lower than the theoretical energy density (~6000 Wh/kg) and the thermodynamic potential (~1.2 V).^{1,2} However, the fuel cells could not reach the stage of commercialization due to the high cost which are mainly associated with the noble metal loaded electrodes as well as the membrane. In order to reduce the amount of Pt loading on the electrodes, there have been considerable efforts to increase the dispersion of the metal on the support. Pt nanoparticles have been dispersed on a wide variety of substrates such as carbon nanomaterials,^{3,4} Nafion membranes,^{5,6} polymers,^{7,8} polymer-oxide nanocomposites,⁹ three-dimensional organic matrices,¹⁰ and oxide matrices.^{11–18} Most often the catalyst is dispersed on a conventional carbon support and the support material influences the catalytic activity through metal support interaction. Dispersion of Pt particles on an oxide matrix can lead, depending mainly on the nature of support, to Pt supported oxide system that shows better behaviour than pure Pt. On the other hand, if the oxide is not involved in the electrochemical

reactions taking place on the Pt sites, it might just provide a convenient matrix to produce a high surface area catalyst.^{17,18}

Titanium dioxide is an attractive system for electrocatalysis, since if used as the support for metallic catalysts or electrocatalysts, it may enhance their catalytic activity on the basis of strong metal support interaction (SMSI).^{23,24} TiO₂ is an effective photocatalysts for oxidation of methanol.¹⁹ Pt/TiO₂ is stable in acidic or alkaline medium, which has higher active surface area than Pt and shows high activity for oxygen reduction.^{15,20,21} There are several articles, which deal with the methanol oxidation reaction on TiO₂ supported Platinum catalyst.^{17,18} Titanium mesh supported electrodes showed high activity on the methanol oxidation, therefore appears to be a promising alternative to carbon-supported catalysts.²² More important in the present case, Pd/TiO₂ nanotube has been recently shown to act as a good catalyst for the oxidation of methanol.²³

The present report focuses on the efforts undertaken to develop unconventional supports based on platinum catalysts for methanol oxidation. The catalyst supported on metal oxide nanotubes yields a better dispersion and shows better catalytic activity. TiO₂ nanotubes of the anatase form have been synthesized by sol gel method using anodic aluminium oxide (AAO) as the template. TiO₂ nanotubes were used to disperse the platinum particles effectively without sintering and to increase the catalytic activity for methanol oxidation. The tubular morphology and the oxide nature of the support have influence on the dispersion as well as the catalytic activity of the electrode. Titanium dioxide is also known to have strong metal

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support interaction with Pt particles. The present communication, deals with the preparation of highly dispersed platinum supported on TiO₂ nanotubes, the evaluation of the catalytic activity for the methanol oxidation of the electrodes and a comparison with the catalytic activity of conventional electrodes.

2. EXPERIMENTAL DETAILS

2.1. Materials

All the chemicals used were of analytical grade. Titanium isopropoxide (Aldrich) and 2-propanol (Merck) were used as received. Hexachloroplatinic acid was obtained from Aldrich. 20 wt% Pt/Vulcan carbons were procured from E-TEK. 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.

2.2. Synthesis of Pt/TiO₂ Nanotubes

Titanium isopropoxide (5 mL) was added to 25 mL of 2-propanol (mole ratio [Ti⁴⁺]/[2-propanol] = 1:20). The solution was stirred for 3 h at room temperature (298 K). The alumina template membrane was dipped into this solution for 2 min. After removal from the solution, vacuum was applied to the bottom of the membrane until the entire volume of the solution was pulled through the membrane. The membrane was then air-dried for 60 min at 303 K, and then placed in a furnace (in air) with a temperature ramp of 2 °C min⁻¹ to 873 K for 2 h. The temperature was then decreased at a ramp rate of 2 °C min⁻¹ to room temperature (303 K).²⁴ The TiO₂/alumina composite obtained (before the dissolution of template membrane) was immersed in 73 mM H₂PtCl₆ (aq) for 12 h. After immersion, the membrane was dried in air and the ions were reduced to the corresponding metal(s) by exposure to flowing H₂ gas at 823 K for 3 h. The resulting composite was immersed into 3 M aqueous NaOH for several minutes to dissolve the alumina template membrane. This procedure resulted in the formation of Pt nanocluster loaded TiO₂ nanotubes.

2.3. Preparation of Working Electrode

Glassy Carbon (GC) (Bas Electrode, 0.07 cm²) 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 nanotubes were dispersed ultrasonically in water at a concentration of 1 mg ml⁻¹ and 20 μl aliquot was transferred on to a polished glassy carbon substrate. After the evaporation of water, the 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.

2.4. Characterization Methods

The scanning electron micrographs were obtained using JEOL JSM-840 model, working at 15 keV after the removal of alumina template. For transmission electron microscopic studies, the nanotubes dispersed in ethanol were placed on the copper grid and the images were obtained using Phillips 420 model, operating at 120 keV. The X-ray diffraction patterns were obtained on a Philips PW 1820 diffractometer with Cu K_α (1.54178 Å) radiation.

2.5. Electrochemical Measurements

The catalyst was electrochemically characterized by cyclic voltammetry (CV) using an electrochemical analyzer (Bio-analytical Sciences, BAS 100). A common three-electrode electrochemical cell was used for the measurements. The counter and reference electrodes were a platinum plate (5 cm²) and a saturated Ag/AgCl electrode respectively. The CV experiments were performed using 1 M H₂SO₄ solution in the presence of 1 M CH₃OH 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 before the electrochemical measurements.

3. RESULTS AND DISCUSSION

The scanning electron microscopic (SEM) image of the TiO₂ nanotubes obtained after dissolving the 200 nm alumina template membrane is shown in Figure 1. It can be

Fig. 1. SEM image of TiO₂ nanotubes obtained by sol gel method calcined at 650 °C for 2 h.

Fig. 2. TEM images of (a) TiO₂ nanotubes obtained by sol gel method calcined at 650 °C for 2 h (b) Pt filled TiO₂ nanotubes.

seen from the figure that an ordered array of nanotubes with uniform diameter and length is formed. The open end and the hollow nature of the TiO₂ nanotubes is also confirmed by transmission electron microscopy (TEM) image as shown in Figure 2a. The outer diameter of the nanotubes is ca. 200 nm, retaining the size and near cylindrical shape of the pores of the aluminium oxide template membrane. The TEM image of a Pt/TiO₂ nanotube electrode is shown in Figure 2b, which shows that the Pt particles are highly dispersed on the TiO₂ nanotube support. The Pt particle size was found to be around 3–4 nm while their crystal structure is confirmed by the XRD method. The optimal Pt particle size for reactions in the H₂/O₂ fuel cell is around 3 nm.²⁵ The importance of the Pt particle size on the activity for methanol oxidation is due to the structure sensitive nature of the reaction and the fact that particles with different sizes will have different dominant crystal planes and hence the different intercrystallite distances, which might influence methanol adsorption. The commercial Pt/C has a high specific surface area but contributed mostly by micropores less than 1 nm and are therefore more difficult to be fully accessible. It has been reported that the mean value of particle size for 20% Pt/Vulcan (E-TEK) catalyst was around 2.6 nm.²⁶ The TiO₂ nanotube matrix of anatase form can provide hydroxide ions to remove CO poisoning. Methanol oxidation studies on the prepared electrode have been carried out using cyclic voltammetry.

The XRD patterns of the Pt/TiO₂ nanotubes as well as P-25 are shown in Figure 3. Rutile and anatase were seen by XRD in P25 titania, but rutile was not seen in the TiO₂ nanotubes. The diffractograms of the synthesized TiO₂ nanotubes mainly belong to the crystalline structure of anatase TiO₂. XRD pattern of the TiO₂ nanotubes evidenced the presence of anatase as the main phase. After Pt deposition, the colour of the TiO₂ nanotubes changed to dark gray and during reduction of Pt, oxide reduction takes place and new diffraction peaks are formed. The presence of Pt could be observed at diffraction angle of 39.8° indexed to (111) plane of metallic Pt. However the peak intensity is relatively weak, presumably due to the combination of its low content and small particle size.

Fig. 3. X-ray diffraction patterns of (a) Degussa TiO₂ as a reference, (b) TiO₂ nanotube, and (c) Pt/TiO₂ nanotube.

In order to evaluate the electrocatalytic activity of the Pt/TiO₂ nanotube electrodes for the oxidation of methanol, cyclic voltammetric studies were carried out in 0.5 M H₂SO₄ and 1 M CH₃OH. During the anodic scan, the current increases due to dehydrogenation of methanol followed by the oxidation of absorbed methanol residues and reaches a maximum in the potential range between 0.8 and 1.0 V versus Ag/AgCl. In the cathodic scan, the re-oxidation of the residues is observed. On the whole, the behaviour of the Pt/TiO₂ nanotube electrodes was found to be similar to that of Pt. This suggests that the electrooxidation reaction takes place on the Pt nanoparticles, dispersed on the TiO₂ nanotube, involves basically the same reaction mechanism.

Fig. 4. Cyclic voltammogram of (a) pure Pt, (b) Pt/C, and (c) Pt/TiO₂ nanotube in 0.5 M H₂SO₄/1 M CH₃OH run at 50 mV/s (area of the electrode = 0.07 cm²).

Table I. Electrocatalytic activity of various catalysts for methanol oxidation.

Electrocatalyst	Specific activity (mA cm ⁻²)	Mass activity (mA mg ⁻¹ Pt)
Bulk Pt	0.167	—
Pt/C	1.3	3.25
Pt/TiO ₂ nanotube	13.2	33

The results of the voltammetric curves for the oxidation of methanol obtained with the Pt/TiO₂ nanotube, Pt and Pt/C (E-TEK) electrodes are shown in Figure 3. The Pt/TiO₂ nanotube shows a higher current density of 13.2 mA/cm² compared to Pt/C (E-TEK) electrodes (1.23 mA/cm²). The specific activity and the mass activity for the different electrodes are given in Table I. The results show that the high electrocatalytic activity for methanol oxidation for Pt/TiO₂ nanotube electrode. It is evident that the mass activity observed with the Pt supported TiO₂ nanotubes shows around ten-fold increase in current than Pt/C (E-TEK) electrode. The Pt/TiO₂ nanotube catalyst had a better electrocatalytic activity for methanol oxidation when compared with that of bulk Pt and Pt/C (E-TEK) catalysts. This higher catalytic activity can be mainly attributed to remarkably platinum active reaction sites on the nanotube oxide matrix and the role of the TiO₂ nanotube facilitates as a path for methanol (CH₃OH) as a fuel and Protons (H⁺) produced during an electrochemical reaction.

It is possible that TiO₂ nanotube functions in the same way as Ru does in Pt-Ru/C catalysts because hydroxide ion species could easily form on the surface of the TiO₂ nanotubes. The formation of hydroxide ion species on the surface of the TiO₂ nanotubes transforms CO like poisoning species on Pt to CO₂, leaving the active sites on Pt for further electrochemical reaction has been shown in Figure 5.^{27, 28} The participation of the TiO₂ nanotube support the high dispersion of Pt particles on TiO₂ nanotube electrode, OH groups generated near the Pt-oxide interface promote CO removal, and strong metal support interaction (SMSI) could be a reason for enhanced electrocatalytic activity of methanol oxidation.^{29, 30}

Fig. 5. A possible mechanism for the removal of CO poisoning intermediates during methanol oxidation over TiO₂ nanotube supported Pt catalysts.

4. CONCLUSIONS

The Pt was deposited on TiO₂ nanotubes in order to study the effect of the properties of the support for methanol oxidation reaction. The Pt/TiO₂ nanotube catalyst exhibits a high electrocatalytic activity for methanol oxidation compared to the commercial E-TEK catalysts. Overall, the relative activities are of the order Pt/TiO₂ nanotubes > E-TEK > pure Pt. The observed improved catalytic activity of Pt/TiO₂ nanotube catalysts can be due to oxidation of CO to CO₂ by the surface hydroxyl groups of TiO₂ nanotube support which otherwise poison the active Pt sites. The electronic interaction between TiO₂ support and the Pt particles could also be another factor contributing to the observed higher activity. Further study on the detailed mechanism and stability of the TiO₂ nanotube supported catalysts are now under progress.

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