Design of Highly Uniform Platinum and Palladium Nanoparticle Decoration on TiO_2 Nanotube Arrays: An Efficient Anode to the Electro-Oxidation of Alcohols

M. G. Hosseini, M. M. Momeni

Abstract

We explore electro-catalytic properties of a system consisting of platinum and palladium nanoparticles dispersed over a nanotubular self-organized TiO_2 matrix. These electrodes prepared by electroess and micro-emulsion of palladium and palladium nanoparticles on to TiO_2 nanotubes, respectively. Titanium oxide nanotubes were fabricated by anodizing titanium foil in ethylene glycol (EG) fluoride-containing electrolyte. The morphology and surface characteristics of Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes were investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively. The results indicated that platinum and palladium nanoparticles were homogeneously deposited on the surface of TiO_2 nanotubes. The nanotubular TiO_2 layers consist of individual tubes of 70-90 nm diameters. This nanotubular TiO_2 support provides a high surface area and it significantly enhances the electro-catalytic activity of Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes for alcohols oxidation. The electro-catalytic activity of Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes in the alcohols electro-oxidation was studied by electrochemical methods. The results indicate that Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes improve the electro-catalytic activity for alcohols oxidation greatly and confirmed the better electro-catalytic activity and stability of these new electrodes. So, the Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes have a good application potential to fuel cells.

Keywords: Fuel cells; TiO_2 nanotubes; Palladium nanoparticle; Platinum nanoparticle; Alcohols electro-oxidation

1. Introduction

Fuel cells operated with the electrochemical oxidation of hydrogen or alcohols, as fuels at the anode and the reduction of oxygen at the cathode are attractive power sources due to their high conversion efficiencies, low pollution, light weight and high power density. Alcohols offer the advantage of easy storage and transportation when compared to hydrogen oxygen fuel cell [1, 2]. However, the fuel cells could not reach the stage of commercialization due to the high cost which was mainly associated with the noble metal loaded electrodes. In order to reduce the amount of noble metal loading and also for enhancement of electro-catalytic activity of electrodes, there have been considerable efforts to increase the dispersion of the metal particles on the support. Recent studies have shown that the co-immobilization of the metal nanoparticles in a porous matrix improves the electro-catalytic activity to a great extent [3-13]. In the present work, we prepared a promising alcohol electro-catalyst based on the co-immobilization of palladium and platinum nanoparticle on titanium dioxide nanotube arrays and compared it with flat palladium and platinum electrode in terms of the electrochemical activity and stability for alcohols oxidation using cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). This study provides a promising route for the simple, facile and cost-effective synthesis of Pd-TiO_2/Ti and Pt-TiO_2/Ti catalysts. The results indicate that Pd-TiO_2/Ti and Pt-TiO_2/Ti catalysts as a promising support material improve the excellent electro-catalytic activity for alcohols oxidation greatly. So the Pd-TiO_2/Ti and Pt-TiO_2/Ti catalysts have a good application potential to fuel cells.

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2. Experimental procedure

2.1. Chemicals, Solutions and Equipment

NaOH, Methanol, Ethanol and formic acid were from Merck and used as received. All other chemicals were of analytical grade and used without further purification. All electrochemical experiments were carried out at room temperature. Distilled water was used throughout. The electrochemical experiments were performed in a three-electrode cell arrangement. A platinum sheet of the geometric area of about 20 cm2 was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel reference electrode (SCE). Electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical system run by Powersuite software. All experiments were carried out at room temperature.

2.2. Preparation of TiO_2 nanotubes

Self-organized, vertically oriented and uniformly distributed TiO2 nanotubes arrays on a pure titanium substrate were prepared by anodizing of pure titanium sheet in a non-aqueous fluoride-containing electrolyte. Titanium discs were cut from a titanium sheet (purity %99.99, 1 mm thickness) and mounted using polyester resin. Titanium samples were degreased by sonicating in acetone and ethanol followed by rinsing with distilled water. Anodic films were grown from titanium by anodizing in an ethylene glycol electrolyte containing 25×10-4 %W/V NH4F at a constant voltage of 40 V using a platinum sheet as counter electrode.

2.3. Preparation of Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes

After anodizing of titanium, the samples were ultrasonically cleaned in distilled water for 5-10 min to remove surface contaminants. Palladium nanoparticles were deposited on the nanotubes by electroless method. Activating, reducing and plating bath recipes are presented in Table 1. All processes performed in an ultrasonic bath. Electroless deposition of palladium on TiO_2/Ti electrodes was performed in various times and finally it was observed that five minute is the optimum time, resulting in highest current values. After the electroless plating, the samples were rinsed, dried and subjected to the characterization.

Table 1. The chemical composition and operating conditions of electroless plating bath

Solution	Component	Quantity	Condition
Sensitizing	$SnCl_2$ HCl	4.5×10^{-3} mol l^{-1}	2 min at 273K
Activating	$PdCl_2$ HCl	5.9×10^{-4} mol l^{-1}	2 min at 273K
Electroless-plating bath	$PdCl_2$ ethylenediamine $N_2H_4\cdot H_2O$	1.0×10^{-2} mol l^{-1} 4.8 g l^{-1} 11 g l^{-1}	5 min at 323K

Platinum nanoparticles were produced in a water-in-oil microemulsions consisting of n-heptane as the continuous oil phase, AOT as the surfactant and the aqueous solutions of metal precursor or reducing agent. The metal precursor and reducing agent containing microemulsions were prepared by mixing the desired amounts of the proper chemicals to obtain microemulsions with 15wt% of surfactant (AOT) and following molar ratios of [H2O]/[AOT] = 8, and aqueous phase concentrations of [NaBH4]/[Pt]=7.5, [Pt] = 0.8 M. For preparation of Pt/TiO_2 nanotubes electrodes, at the first, the TiO_2 nanotube samples were ultrasonically cleaned in distilled water for 5-10 min to remove surface contaminants and then were immerged in a solution containing tow mentioned mixture. Acetone was used to break the micro-emulsion and precipitate out the platinum nanoparticles on the TiO_2 nanotubes. Finally, Pt-TiO_2 nanotubes electrodes were washed sequentially with n-heptane, acetone and hot distilled water to remove all remaining chemicals.

2.4. Surface morphology of electrodes

For characterizing Morphology, alignment and composition of the TiO2 nanotubes array and Pd and Pt coating on TiO2 nanotubes substrates, a scanning electron microscope (Model XL30, Philips, Netherlands) was employed with an accelerating voltage 15 kV.

To identify the element composition, an energy dispersive X-ray (EDX Genesis fitted to the Philips SEM XL30) was employed with an accelerating voltage 16 kV.

3. Results and discussions

3.1. Characterization of the electrodes morphology

Scanning electron microscopy (SEM) images of a typical TiO_2 nanotubes array, palladium and platinum nanoparticles on these TiO_2 nanotubes were investigated and results are shown in figures1(a-f), respectively. As can be seen in figure 1(a, b) these TiO_2 nanotubes are well-aligned and organized into a highly oriented array. It can be seen from figure 1(a, b) that the average diameters of these nanotubes are about 70-90 nm. Figures 1(c, d) and 1(e, f) show the nanotubes after loading with palladium and platinum nanoparticles using electroless and microemulsion, approach. It can be seen that the palladium and platinum nanoparticles are distributed in an almost homogeneous manner on the surface of the TiO_2 nanotubes. Figure 2 shows the energy dispersive X-ray spectrum of palladium and platinum on the titanium dioxide nanotubes. Energy dispersive spectroscopy (EDS) results confirm the presence of palladium particle in the surface.

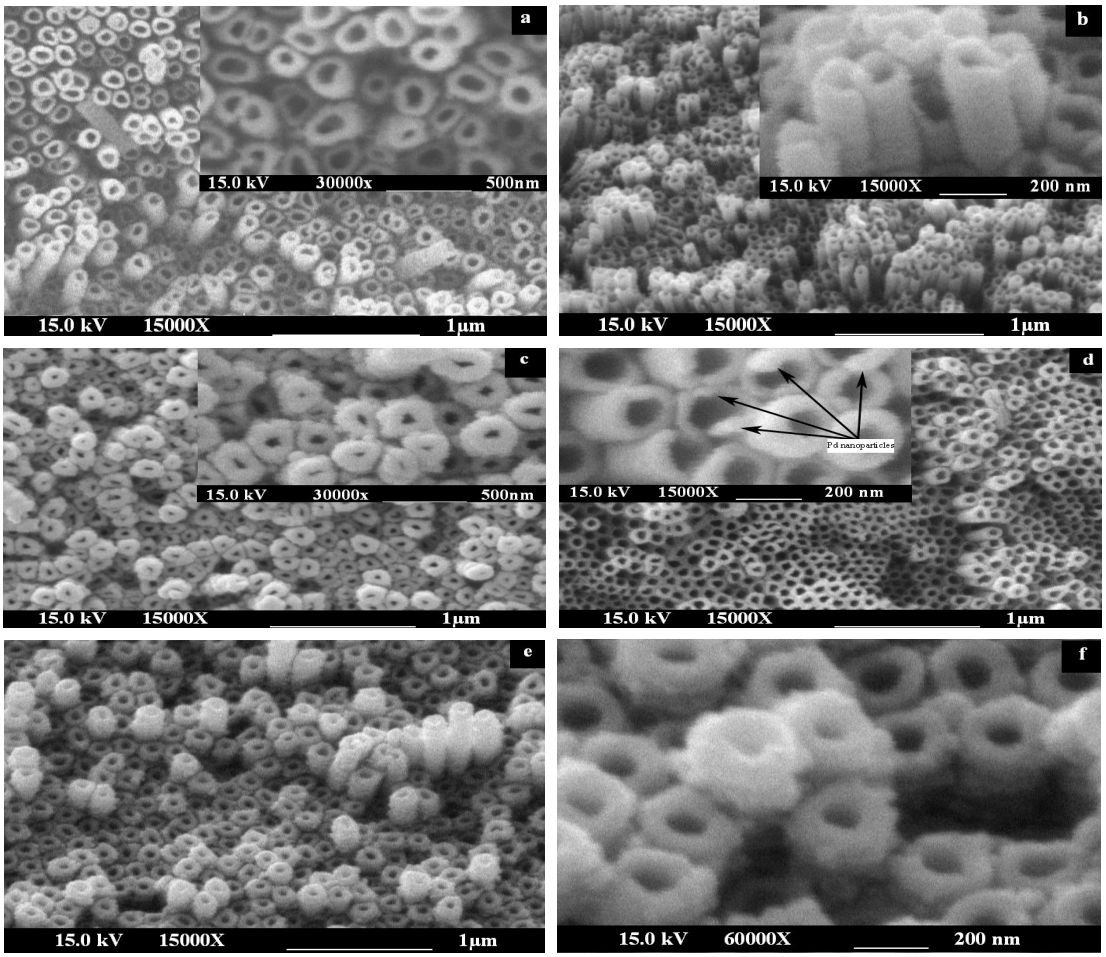

Fig. 1. (a, b) The surface morphology of TiO_2 nanotube arrays on a pure titanium substrate prepared by anodizing of titanium with low and (Insets) high magnification. a: top view, b: tilt view. (c, d) The surface morphology of palladium coating on TiO_2 nanotube arrays with low and (Insets) high magnification. c: top view, d: tilt view. (e, f) The surface morphology of palladium coating on TiO_2 nanotube arrays.titanium dioxide nanotubes.

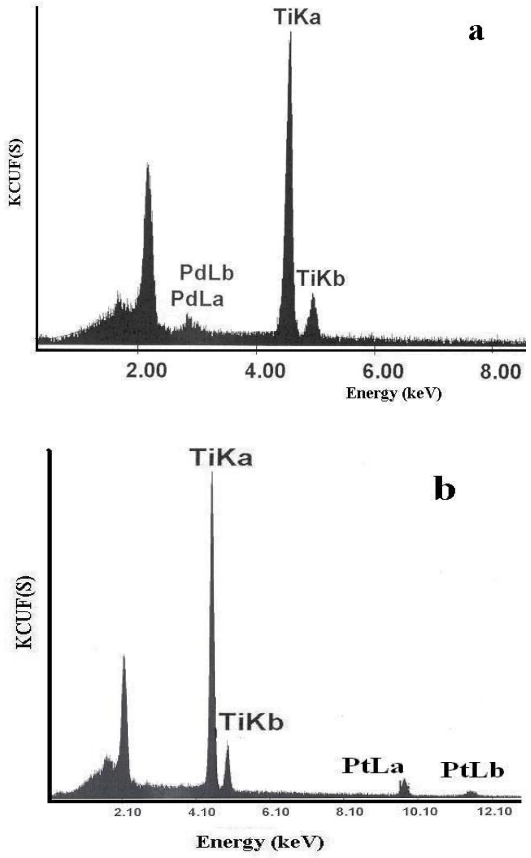

Fig. 2. EDX of TiO_2 nanotubes (a) after palladium nanoparticles loading and (b) after platinum nanoparticle loading.

3.2. Electro-catalytic activity of Pt-TiO_2/Ti, Pt-TiO_2/Ti, pure palladium and platinum electrodes for methanol electro-oxidation

In order to compare Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes with flat palladium and platinum electrodes, the cyclic voltammetry method was used to estimate the electro-catalytic behavior of these electrodes. Figures 3-5 present cyclic voltamograms of flat palladium, flat platinum, Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes in methanol, ethanol and formic acid aqueous solutions.

Figure 3 presents CVs of flat palladium and Pd-TiO_2/Ti electrodes in 1.0 M KOH + 0.5 M methanol aqueous solutions, at a scan rate of 100mV s1. From figure 3 (curve b), two peaks of methanol oxidation could be observed, and the peak potentials were -0.20 and -0.40V for the forward and back ward scans, respectively. The current density for methanol oxidation on Pd-TiO_2/Ti electrode is greater than that observed for flat palladium

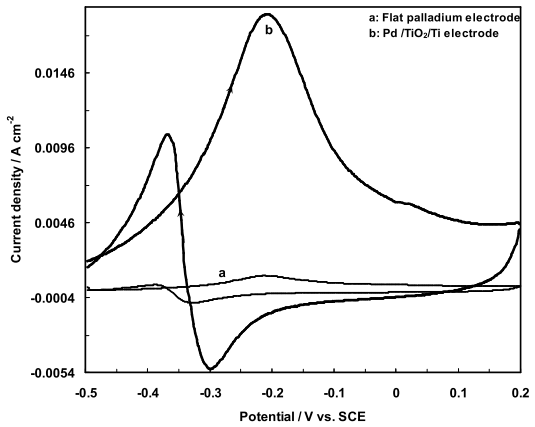

Fig. 3. Cyclic voltammograms for a flat palladium electrode (a) and Pd-TiO_2/Ti electrode (b) in a 1.0 M KOH + 0.5 M methanol aqueous solution at 25 °C with a scan rate of 100 mV s^{-1}.

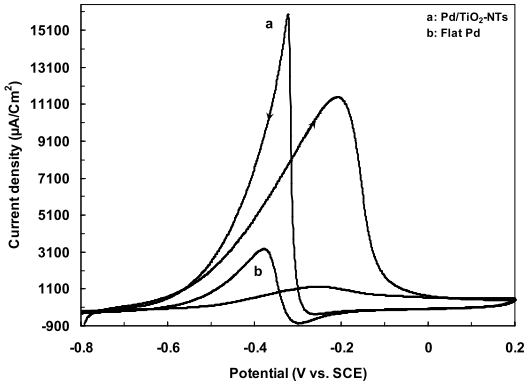

Fig. 4. Cyclic voltammograms for flat palladium and Pd-TiO_2/Ti electrodes in 1.0 M NaOH + 0.05 M ethanol aqueous solution at 25 °C with a scan rate of 100 mV s-1.

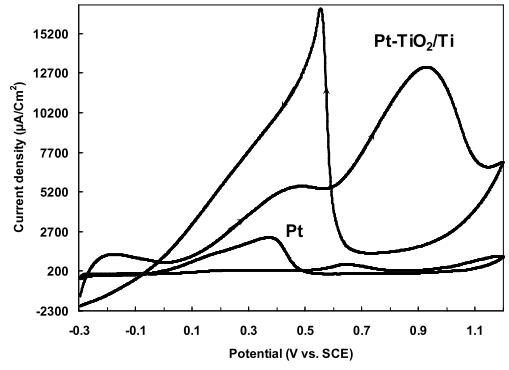

Fig. 5. Cyclic voltammograms for flat platinum and Pt-TiO_2/Ti electrodes in 0.1 M H2SO4 + 0.1 M formic acid aqueous solution at 25 °C with a scan rate of 100 mVs^{-1}.

electrode. This result may also be attributed to the larger geometrical area of the Pd-TiO_2/Ti electrode. Also, the current density for ethanol and formic acid oxidation on Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes is greater than that observed for flat palladium and platinum electrodes. This result can be attributed to the larger geometrical area of the Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes.

4. Conclusions

Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes with highly porous structure and excellent electro-catalytic property have been successfully fabricated by a two-step process consisting of anodizing titanium followed by deposition of palladium and platinum nanoparticles. The morphology and surface analysis of Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes were investigated by scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. The results indicated that TiO_2 layers consist of individual tubes of about 70-90 nm diameters and palladium and platinum nanoparticles are well-dispersed on the surface of TiO_2/Ti support. The electro-catalytic activity of the Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes for alcohols oxidation was evaluated by various electrochemical methods. The Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes showed much higher currents of alcohols oxidation than the flat palladium and flat platinum electrode, respectively.

This study provides a promising route for the simple, facile and cost-effective synthesis of Pd-TiO_2/Ti and Pt-TiO_2/Ti electrodes.

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