

Preparation of platinum-doped hollow spheres and their electrocatalytic activity in water electrolysis

Hong Rok Kim, Jayeeta Chattopadhyay, Jae Ik Son, and Daewon Pak[†]

Graduate School of Energy and Environment, Seoul National University of Technology,
172 Gongneung-2 dong, Nowon-gu, Seoul 139-743, Korea

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Abstract—Pure TiO₂ hollow spheres were prepared by using poly(styrene-methacrylic acid) latex particles as template; thereafter, titania hollow spheres were coated by platinum with an appropriate amount of chloroplatinic acid solution to obtain Pt/TiO₂ catalysts. The morphology and structure of nonstructural Pt/TiO₂ hollow spheres were characterized by BET, XRD, TGA, SEM and TEM analysis. In the samples, a remarkably uniform layer of Pt consisting of particles from 5 to 70 nm in size was formed over TiO₂ hollow spheres. We found the electrocatalytic nature of the samples by cyclic voltammetric experiment in acidic solution. The anodic peak current density of 20 wt% Pt-loaded TiO₂ hollow particles was observed 2.5 times higher than that of 5 wt% Pt/TiO₂ in the same experimental condition. Also, the anodic current density of 20 wt% Pt/TiO₂ hollow spheres calcined at various temperatures followed the order: 400 °C ≈ 500 °C > 600 °C. The electrocatalytic activity of the Pt-loaded TiO₂ hollow spheres depends on the amount of atomic platinum present in the sample; a higher concentration of platinum results in a larger current density value in anodic sweep, resulting in more oxygen production during electrolysis. Pt/TiO₂ hollow sphere catalysts have also shown long term electrocatalytic stability in acidic media.

Key words: Hollow Sphere, Pt-doped TiO₂, Cyclic Voltammetry, Electrocatalysis

INTRODUCTION

Electrochemical technology is playing an increasingly important role in modern society and especially in the chemical industry. One of the major reasons for the shift in interest towards electrochemical technology is the need for clean and efficient energy sources, especially for transport systems [1]. Water electrolysis represents a most important process, which offers the way to convert electrical energy to chemical energy as hydrogen and oxygen production. The key components of all electrochemical cells are electrodes and separators. In almost all the cases where process economics require the optimization of cell performance, electrodes and/or electrocatalysts of noble metals or their oxides are the components of choice in water electrolysis for hydrogen and oxygen production irrespective of their high cost. But the major problem in hydrogen and oxygen production from water electrolysis is high energy consumption, mainly due to the high production and investment cost. In recent days, researchers have considered the following ways to improve product selectivity and/or to minimize overpotentials during preparation of electrocatalysts: minimization of the platinum metal loading; alloying of platinum with transition metals to improve catalytic activity (Pt-Co, Pt-Ni, Pt-Fe, Pt-Ru, Pt-Pd, Pt-Rh and Pt-Sn catalysts) [2-4]; and use of mixtures of oxides to enhance electrode stability. Now-a-days, electrodes based on dispersed precious metal on an inert high-surface area substrate (most commonly formulated from carbon powder) are one of the workhorses of electrochemical technology [5]. However, precious metals like platinum are often found to corrode significantly in a long time-scale pilot

plant operation [6].

TiO₂ has been widely studied as a semiconductive oxide for its special photoelectric properties [7-10]. Additionally, it is very stable in acidic solution, and TiO₂ electrode has been reported as the support of Pt [5] or Pt-Ru [11]. Platinized titanium anodes have certainly found applications in electrochemical technology. They have been used in the electrosynthesis of inorganic compounds, including persulfates and perchlorates, in electrochlorination plants and electrochemical processes, for example, for chromium and gold. At the same time, titania hollow spheres have received enormous attention in recent years due to their excellent properties as a photocatalyst and wide range applications [12,13]. Coated titania particles are also very useful as catalysts [14]. The submicrometer-sized titania hollow spheres with tunable shell thickness, surface area, and void volume by employing sulfonated polystyrene (PS) latex particles as a template can show excellent electrochemical property when they are doped by dispersed precious metals. Herein, we prepared various Pt-doped TiO₂ hollow spheres having 5, 10, 15 or 20 wt% of Pt and calcined at various temperatures (400, 500 and 600 °C) by using PS latex as template material. The structure and morphology of samples have also been studied. The electrochemical activity for water electrolysis was investigated by using cyclic voltammetry (CV) at 20 °C in H₂SO₄ solutions. The effects of platinum loading on the titania spheres and of calcination temperature on electrochemical activity have also been evaluated.

EXPERIMENTAL METHODS

1. Preparation and Characterization of Pt/TiO₂ Hollow Sphere Catalysts

Pure TiO₂ hollow spheres were prepared by using poly(styrene-

[†]To whom correspondence should be addressed.

E-mail: daewon@snu.ac.kr

methacrylic acid) (PSA) latex particles, the surface of which contained carboxylic groups, as template. The PSA latex spheres with diameter of about 450–550 nm were obtained by the method reported in the literature [15]. The pure TiO_2 hollow spheres were prepared by using $\text{Ti}(\text{SO}_4)_2$ as a precursor of titania. By using PSA for core particles and cetyltrimethylammonium chloride (CTACl) as a surfactant, pure TiO_2 hollow spheres were prepared. The detailed synthesis method has been described in our previous work [16]. After the preparation of pure TiO_2 hollow sphere particles, 5, 10, 15 or 20 wt% of platinum was loaded over those spheres. In the preparation of Pt-doped TiO_2 hollow sphere particles, the following method was used: appropriate amount of pure TiO_2 was added into 32 ml of DI water under vigorous stirring followed by the addition of 0.8 ml of HCl, 1.98 ml of CTACl, and requisite amount of chloroplatinic acid solution. The mixture was then aged at 70 °C for 12 h, then cooled, centrifuged, and washed with DI water in the same manner as used in the preparation of pure TiO_2 particles. The obtained sample was heated at a rate of 1 °C min^{-1} and calcined at various temperatures of 400, 500 and 600 °C in air for 4 h.

The catalysts were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET) surface area analysis. Their morphology was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis. X-ray diffraction patterns of the catalysts were measured on a D/MAX-3C equipment of Rigaku Denki Co. Ltd. by using Cu $K\alpha$ radiation and a fixed powder source (30 KV, 15 mA). The scan rate was 2° (2θ)/min. Thermogravimetric investigation was performed with a Shimadzu TGA-50H apparatus up to 700 °C with a heating rate of 10 °C min^{-1} under air atmosphere (30 ml min^{-1}). SEM and TEM have been performed by using JSM-6400 and JEM-2010, respectively.

2. Electrochemical Characteristics of Catalysts

The catalyst ink was prepared by mixing the catalyst powder, Nafion solution (Dupont, 5% solution, equivalent to 110 g/mol) and solvent (mixture of water and isopropyl alcohol) under sonication for 20 min. The catalyst ink was cast onto waterproof carbon cloth (1 cm×1 cm) and dried at 70 °C in air to remove solvent (water and alcohol). The casting process was followed repeatedly to load approximately 2 mg of catalyst onto the carbon cloth.

Cyclic voltammetric measurement was carried out in a three-electrode cell with Potentiostat/Galvanostat (WonATech, WPG100). Ag/AgCl electrode and Pt plate (1 cm×1 cm) were used as reference and counter electrodes, respectively. A H_2SO_4 solution of 0.01 N concentration was used as electrolyte in the experiment. The cyclic voltammetry data were recorded in the potential range of 0 to 2 V

vs. Ag/AgCl electrode with a scan rate of 100 mV s^{-1} .

RESULTS AND DISCUSSION

The BET specific surface area results of the electrocatalysts used in this study are summarized in Table 1. The sample of 20 wt% Pt/ TiO_2 calcined at 400 °C shows a specific surface area of 163.3 $\text{m}^2 \text{g}^{-1}$.

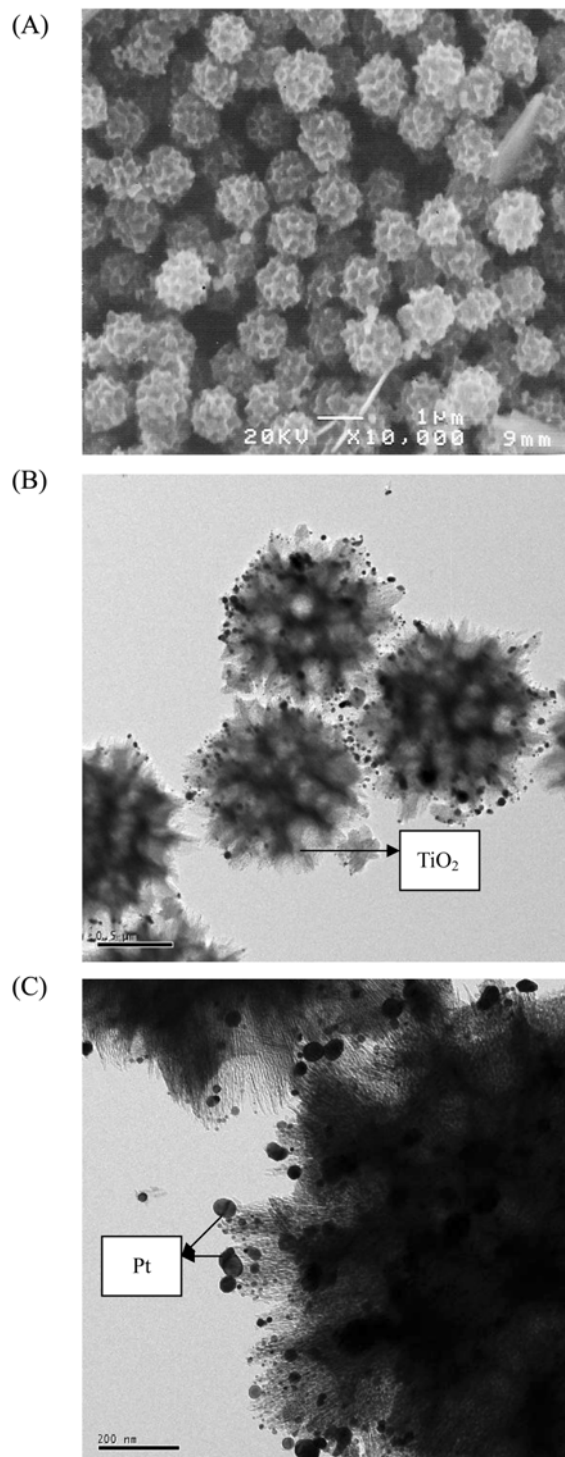


Fig. 1. SEM (A) and TEM (B and C) images of 20 wt% Pt-doped TiO_2 hollow spheres calcined at 400 °C.

Table 1. Summary of BET surface area results of the electrocatalysts used in this study

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)
5 wt% Pt/95 wt% TiO_2 (400 °C)	197.8
10 wt% Pt/90 wt% TiO_2 (400 °C)	215.2
15 wt% Pt/85 wt% TiO_2 (400 °C)	206.7
20 wt% Pt/80 wt% TiO_2 (400 °C)	163.3
20 wt% Pt/80 wt% TiO_2 (500 °C)	125.0
20 wt% Pt/80 wt% TiO_2 (600 °C)	60.4

But when the calcination temperatures increase to 500 and 600 °C, the catalysts show diminished BET surface areas of 125 and 60.4 m² g⁻¹, respectively. The surface area reduction may occur due to the removal of organic matters during the calcination process. At the same time, with increase of the Pt loading in the doped samples, BET surface area value drops considerably in 20 wt% Pt/TiO₂ catalyst.

Fig. 1(A), (B) and (C) show SEM and TEM images of the Pt-doped TiO₂ hollow spheres calcined at 400 °C with 20 wt% content of Pt. The diameter of Pt/TiO₂ hollow spheres was in the range of 900-1,000 nm. From the TEM image, it is obviously observed that a remarkably uniform layer of Pt consisting of Pt particles averaging from 5 to 70 nm size was formed over TiO₂ hollow spheres. The Pt loading above 20 wt% on TiO₂ could not produce hollow spheres.

Thermal scans of 20 wt% Pt/TiO₂ hollow spheres without heat treatment were carried out from 25 to 700 °C by the TGA method. As shown in Fig. 2, a weight loss between 210 °C and 257.6 °C can

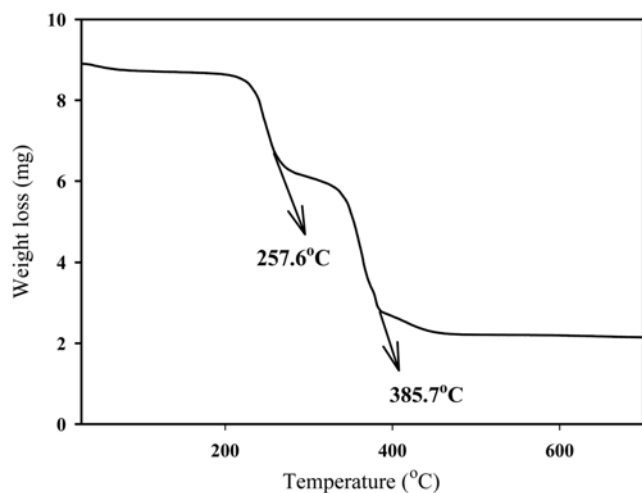


Fig. 2. Thermogravimetric curve of 20 wt% Pt-doped TiO₂ hollow spheres calcined at 400 °C.

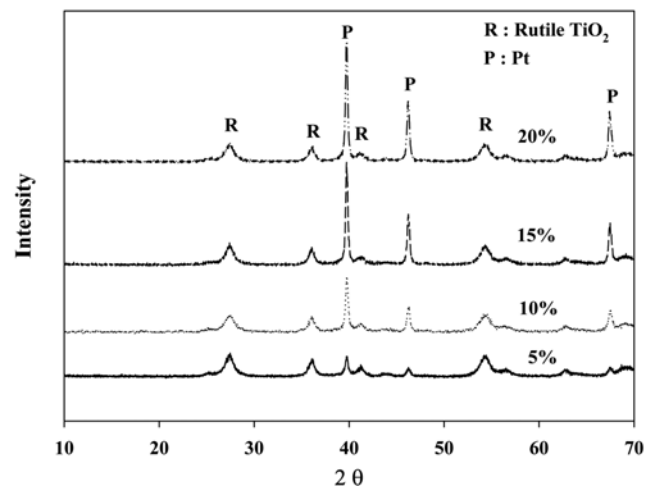


Fig. 3. XRD patterns of Pt/TiO₂ hollow spheres of various Pt content calcined at 400 °C.

be assigned to the desorption of water. In the region between 350 °C and 450 °C, there was weight loss related to the burning out of organic residues such as PSA latex and surfactant CTACl. From the TGA data it was also found that the total mass percentage of removed matter is about 76% in the 20 wt% Pt/TiO₂ hollow sphere sample.

X-ray diffraction patterns of mixed oxides of various Pt/Ti ratios are presented in Fig. 3; the samples were treated at 400 °C before XRD analysis. The results illustrate that a rutile crystal phase known as a stable matter in strong acidic or basic solution is present in the prepared samples without showing any other crystalline peak such as for anatase phase. The diffraction peaks around 40°, 46°, and 68° were ascribed to (111), (200), and (220) planes of the face-centered cubic (fcc) crystal of nanoparticles, which represents the metallic platinum phase [17]. Fig. 4 shows the X-ray diffraction patterns of 20 wt% Pt/Ti samples calcined at various temperatures. The peak intensity for platinum phase increased with the rise of calcination temperature, indicating the critical growth of platinum in the cata-

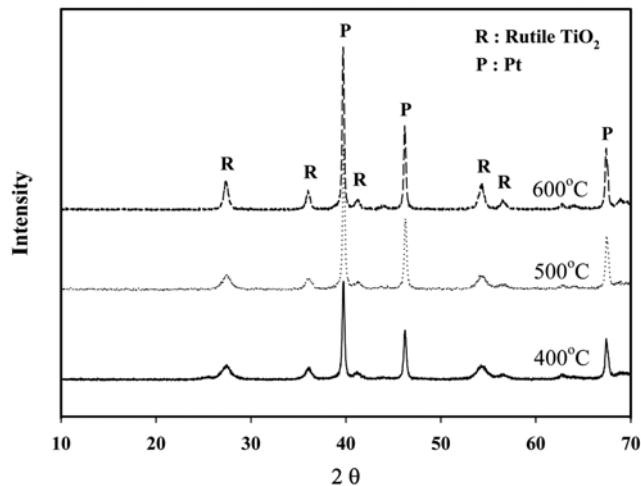


Fig. 4. XRD patterns of 20 wt% Pt doped TiO₂ hollow spheres calcined at various temperatures.

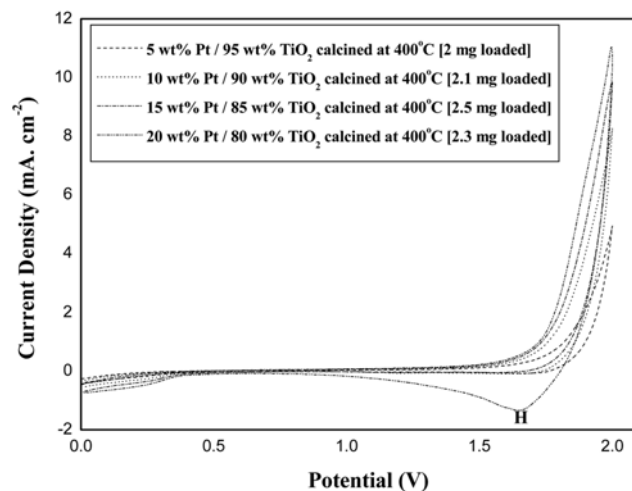


Fig. 5. CV curves of Pt/TiO₂ hollow spheres of various Pt content calcined at 400 °C.

lysts.

Fig. 5 shows the comparison of the potentiodynamic cyclic voltammetric curves for Pt/TiO₂ hollow spheres having various compositions of Pt after heat treatment of the samples at 400 °C. The electrochemical behaviors of the prepared samples are similar in all cases except for 20 wt% Pt/TiO₂ hollow spheres. It can be seen that the anodic sweep began approximately at 1.75 V and reached a peak current density at around 2.0 V. The current density of 20 wt% Pt/TiO₂ is significantly higher than that of others at potentials above 1.5 V, which was about 11 mA cm⁻² at 1.9 V. The current density of 5 wt% Pt/TiO₂ is 2.5 times lower than that of 20 wt% Pt/TiO₂. But during the cathodic sweep, only a single peak (H) was observed at around 1.85 V in 20 wt% Pt/TiO₂ hollow sphere catalyst. This observation indicates that the oxygen adsorption-desorption potential has been influenced by the second metal added in considerable amount, and affects the oxide reduction potential value and the charge passed due to oxygen adsorption, resulting in the enhancement of the active sites, as has been reported by some researchers [18].

In the present work, oxygen and hydrogen are adsorbed to a great extent on the large surface of hollow spheres and also may adsorb into the void sphere structure of the catalysts. Generally, on an interface of metal oxides/aqueous solution interface, surface species are either H⁺, adsorbed on O²⁻ ions, or OH⁻ adsorbed on metal ions; H⁺ species are present mostly in acidic solutions. It is known from the literature that titania is oxygen deficient in nature; therefore, it can create oxygen vacancies on the catalyst surface. Generally, these oxygen vacancies are resulting in the oxygen adsorption and diffusions. These adsorption processes create charge shifting and alteration at the local electronic structure. On the other hand, during the cathodic potential sweep metal ions are present in their reduced form on the surface of hollow spheres, and influenced themselves in cyclic voltammetry. At the same time, the reduction of metal oxides creates more vacancies on the catalyst surface. Therefore, adsorbed oxygen molecules always compete for reduced metal ion sites, and the molecules may be unsymmetrical, with only one oxygen atom bonded to the surface, resulting in the reduction of oxygen. This oxygen reduction phenomenon therefore precedes the hydrogen evolution

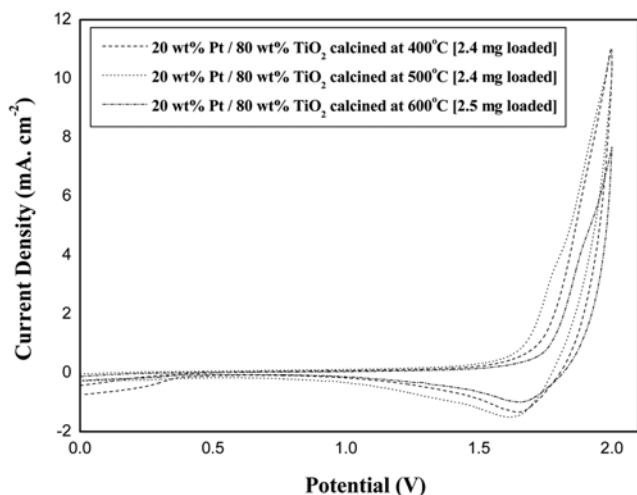


Fig. 6. CV curves of 20 wt% Pt-doped TiO₂ hollow spheres calcined at various temperatures.

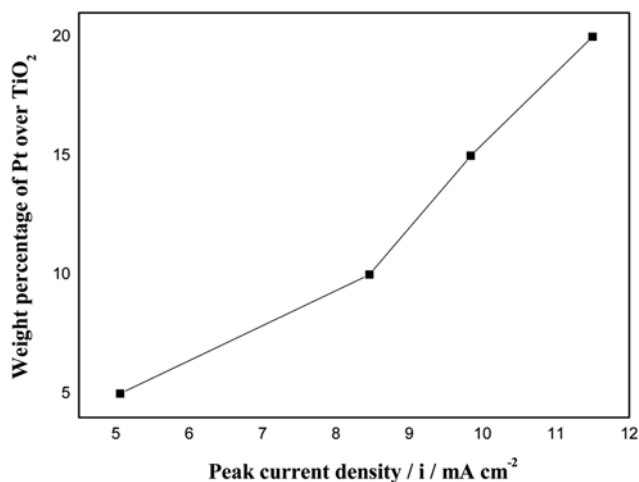


Fig. 7. Peak current density of Pt-doped TiO₂ catalysts vs. various Pt loading in the samples.

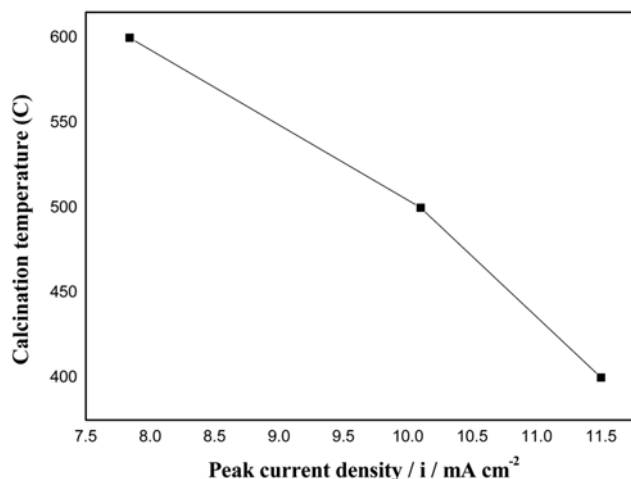


Fig. 8. Peak current density of 20 wt% Pt-doped catalysts vs. different calcination temperatures.

during the process.

The oxygen evolution and reduction processes take place only in the presence of 20 wt% Pt/TiO₂ during the electrolysis process, whereas only oxygen has been evolved in the case of other catalysts. The cyclic voltammogram curves of 20 wt% Pt/TiO₂ hollow spheres calcined at various temperatures are shown Fig. 6. The results are presented in Fig. 7, including the anodic peak current densities of the Pt-doped TiO₂ catalysts of various loading of platinum. Similarly, Fig. 8 represents the peak current density values during anodic sweep for 20 wt% Pt-loaded titania catalysts calcined at different temperatures. The peak current density of the 20 wt% Pt/TiO₂ catalysts follows the order of calcination temperature: 400 °C ≈ 500 °C > 600 °C. It may be due to the removal of increased amount of carbon at higher calcination temperature. The BET results are also showing good agreement with this incident. From Fig. 7 it is also clear that the peak current density was increased dramatically with more loading of Pt in the catalysts.

20 wt% Pt-doped TiO₂ hollow sphere sample (calcined at 400 °C) was subjected for long time test to evaluate the electrochemical sta-

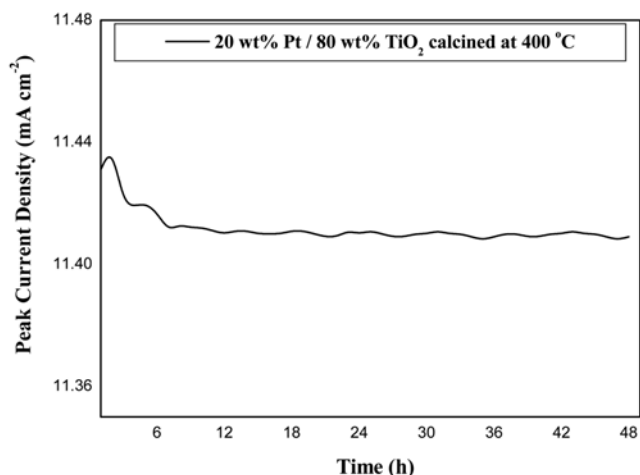


Fig. 9. Stability test of 20 wt% Pt-doped TiO_2 catalyst calcined at $400\text{ }^\circ\text{C}$: A plot of Time vs. Anodic peak current density.

bility of the electrocatalysts at potentiostatic condition. Cyclic voltammograms were performed every after 1 hr for 48 hrs continuously, and the anodic peak current density values were plotted against time in Fig. 9. This stability test has shown the stable values of peak current density all along the experiment, which reveals the stable electrocatalytic nature of Pt-doped titania hollow sphere catalysts in acidic media during water electrolysis. Actually, the stability of an electrocatalyst during electrolysis process depends on many factors. In the present study, the adhesive quality of hollow sphere structure of catalysts might influence their sticking with a carbon cloth for a long time. At the same time, the presence of rutile TiO_2 phase in the catalysts enhances the stability of the samples in acid solution, as it is known as a stable matter in acidic or basic solution.

CONCLUSIONS

Pt/TiO_2 hollow spheres were prepared by using poly(styrene-methacrylic acid) latex particles as template. The diameter of the hollow spheres was in the range of 900-1,000 nm. The TEM showed the formation of a uniform layer of Pt over TiO_2 hollow spheres. In the catalysts, rutile crystal phase was observed as a stable matter in the XRD analysis which showed no crystalline peak for anatase phase. At the same time, peak for platinum phase became more intense with increase in the calcination temperature, indicating the critical growth of platinum in the samples. The CV curves presented that 20 wt% Pt-doped TiO_2 sample (calcined at $400\text{ }^\circ\text{C}$) has remarkably high anodic peak current density of 11 mA cm^{-2} at 1.9 V in comparison with the others, which resulted in the evolution of oxygen gas during anodic sweep. Similarly, one small peak also appeared around 1.6 V in the cathodic sweep of voltammogram in each of the CV curves of 20 wt% Pt-doped titania catalysts calcined at various temperatures; this peak indicates the reduction of oxygen. This oxygen reduction phenomenon therefore precedes the hydrogen

evolution during the process. At the same time, the current density of the 20 wt% Pt/TiO_2 catalysts follows the order of the calcination temperature: $400\text{ }^\circ\text{C} \approx 500\text{ }^\circ\text{C} > 600\text{ }^\circ\text{C}$. Generally, at higher calcination temperatures organic matters are removed from the spheres, creating cracks on the titania sphere resulting in the entering of platinum particles into spheres, which induces the reduction of specific surface area of Pt/TiO_2 catalysts. Thus, the cyclic voltammetry results described in the present work proved that Pt/TiO_2 hollow spheres have good electrocatalytic properties in oxygen evolution reaction during the electrolysis of water in acidic medium. At the same time, Pt-doped titania catalysts have shown long-term electrocatalytic stability during the water electrolysis process.

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