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Fabrication of TiO_2 Cathodes by Anodic Oxidation for Hydrogen Generation from Electrolysis of Water

*İ. Koyuncu and E. Kahraman
Yıldız Technical University, Department of Chemistry, Campus of Davutpaşa, 34210, İstanbul, Turkey.
Email: ikoyuncul@yahoo.com

ABSTRACT
In this investigation, titanium oxide plates were used as cathode for hydrogen production in the aqueous solutions of sulfuric acid, potassium hydroxide, acetic acid and ammonia hydroxides electrolytes separately. Gaseous hydrogen was produced at the cathode and oxygen at the anode. For this purpose, titanium plates were fabricated in acid solution by anodic oxidation. Microstructure of TiO_2 nanorod observation was conducted with scanning electron microscopy (SEM). The effects of operating conditions and the electrochemical test parameters, such as electrolytes concentration, temperature, and cell voltage were investigated. Also the performance of TiO_2 cathode was compared to zirconium oxide and graphite electrodes. The results show that the highly rated, hydrogen production performance on TiO_2 cathode has better than the other electrodes. The maximum rate of hydrogen production is by TiO_2 cathode 8.18 ml/ (h. cm^2). The cell efficiency for water electrolysis was reached 95% using titanium oxide electrode in 1.5 M H_2SO_4.

Keywords: hydrogen, electrolytic oxidation, titanium oxide

1. INTRODUCTION
Hydrogen is generated by many methods, using reforming of fossil fuels[1-3], photo electrolysis from water splitting[4,5], thermo chemical processes[6-13] biophotolysis[14-18], magnetolysis[19-21], radiolysis[22-24], etc.

Development of photoactive structures has been used to production of hydrogen from water splitting. TiO_2 is regarded as one of the most useful photocatalysts due its broad functionality, long-term stability and non-toxicity, since its properties were first reported by Honda and Fujishima[25]. The TiO_2 different in morphology has been investigated for hydrogen generation[26-29]. The authors have employed anodic oxidation to immobilize TiO_2 on the surface of titanium and its allows. It has been demonstrated that the rutile-structured TiO_2, when prepared in the high concentration sulfuric acid electrolyte. TiO_2 is a semiconductor with a wide band gap (anatase, 3.2 eV; rutile, 3.0 eV) and acts as a photocatalyst only under UV light. However natural solar light contains only a few percent of its total energy in this region[30-33]. In order to activate the photocatalysts to visible light, it is necessary to change the electronic structure to give a band gap which corresponds to visible light. Doping is an effective method of modifying the electronic structure of TiO_2, and metal doping has been extensively reported[34-49].

In the present study, we were prepared titanium oxide electrodes by anodic oxidation in a sulfuric acid electrolyte. The anodic oxidation for titanium plate was doped by the composition of various electrolytes. Thus was controlled band gap of the oxide. The cathode electrodes are fabricated with TiO_2, ZrO_2 and graphide nanorods.

2. EXPERIMENTAL

2.1 *Preparation and characterization of TiO_2 electrodes*
The lab-made electrochemical cell that has two separate compartments connected each other was manufactured for hydrogen generation. Potentiostat and two electrodes were used for electrolysis. Voltage was supplied to the electrodes by DC power source. Titanium plates with dimensions of 2.0 cm × 5.0 cm × 0.1 cm were prepared. It was polished using SiC grinding paper and rinsing in ethanol and drying in air. Pt electrode was used, 1.5 cm long and 0.25 cm in diameter, as cathode. The distance between electrodes was set as 5.0 cm. The anodic oxidation was made in a sulfuric acid ranging from 0.5 to 3.0 mol l^{-1} with a current density of 50 mA/cm^2 for 1.0 h. With applied voltage between the titanium plates and Pt were made an anodic oxidation.

The anodisation voltage was applied from 1.00 to 10.00 V in the electrochemical bath. The solution temperature was kept at 25°C and stirred with a stirring bar. The anodized oxide titanium was rinsed with distilled water and then dried at room temperature, Microstructure observation was conducted with scanning electron microscopy (Jeol JSM 5410 LV,) at an operating voltage of 20 kV and 500 nm.

2.2 *Electrochemical measurements*

2.2.1 *Effect of electrolytes on anodic oxidation*
The test solutions were prepared with potassium hydroxide, acetic acid and ammonia hydroxides as electrolyte concentration of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 M. The titanium plate was made the anodized oxide with applying 10 V. The temperatures of solutions were controlled by digital hot plate with stirrer. The SEM images of nanorods grown on three different electrolytes are shown below in Fig-1.

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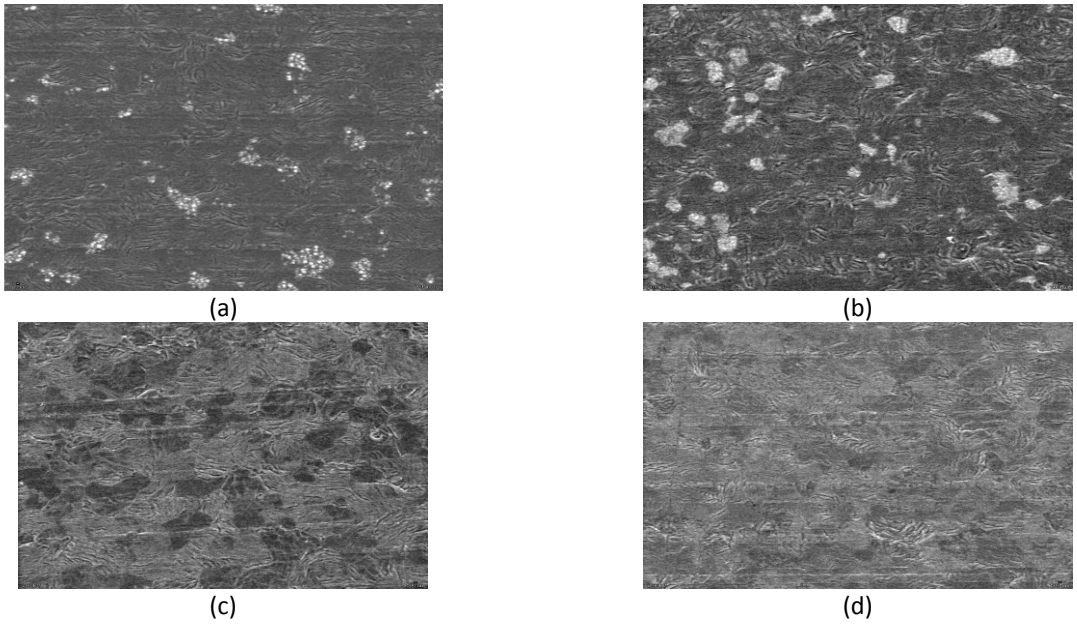

Fig-1: SEM images of anodic oxides prepared in an electrolytes of (a) sulfuric acid, (b) potassium hydroxide, (c) ammonia hydroxides and (d) acetic acid at, their concentration of 1.5 M

2.2.2 *The production of Hydrogen*

The anodized oxide titanium was used for cathode electrode and a Pt electrode was used as an anode. The generation of hydrogen was made in a sulfuric acid electrolyte ranging from 0.5 to 3.0 M with a current density of 50 mA/cm^2 for 90 min. All the hydrogen gas evolving at the cathode was collected in the burette displacing the electrolyte level. The production rate of H_2 of cathode surface was found to the current density supplied to the cathode.

2.2.3 *Effect of electrolyte on hydrogen production*

Effect of electrolyte was investigated. For this purpose, test solutions were prepared with potassium hydroxide, acetic acid and ammonia hydroxides range of 1.0 to 3.0 M concentration. The anode of Pt electrode and cathode of the anodized oxide titanium plate was used.

2.2.4 *Gas collection*

Gaseous hydrogen was produced at the cathode and oxygen at the anode. Gas generated by cathode under constant voltage for 90 min of electrolysis was collected with an electrolyte replacement device. An electrolyte was used 10 vol% pyrogallol, as. Collected gas in the burette was displaced the electrolyte. The volume of hydrogen gas was measured by reading the electrolyte level in the burette at regular intervals.

2.2.5 *Comparison of cathode electrodes*

The rate of hydrogen production was made of two kinds cathodes. One of them zirconium plate was prepared to dimensions of 2.0 cm × 5.0 cm × 0.1 cm. It was polished using SiC grinding paper and rinsing in ethanol and drying in air. The anodic oxidation was made in a sulfuric acid electrolyte for 1.5 M with a current density of 50 mA/cm^2 for 90 minute. The voltage was applied to 10 V into the electrochemical bath. The solution temperature was kept at 25^{o}C and stirred with a stirring bar. The anodized oxide zirconium was used for a cathode and a Pt was used as anode for the production of hydrogen.

Other was selected graphite as cathode. It was prepared dimensions of 2.0 x 5.0 x 1.0 cm and then cleaned by ethanol and deionized water.

All the tests were performed with same conditions. Hydrogen generation rate and its efficiency were investigated with ZrO_2 and graphite electrodes.

3. RESULT AND DISCUSSION

3.1 *The effect of electrolytes on anodic oxidation*

At the beginning of anodisation, the voltage was limited. When voltage was increased stepwise, was reached anodisation voltage. More pore structure was observed increased voltages. The oxide layer was produced at 10 V.

The color of the anodized surface was varied with the concentration of sulfuric acid in the electrolyte. The color of the anodized surface was changed to dull gray in the electrolyte of 0.5 M sulfuric acid aqueous solution. Dull violet and dark violet colors were observed in 1.0 M and 3.0 M sulfuric acid aqueous solution, respectively. The pores increased with increasing sulfuric acid concentration. The surface roughness was increased with increasing of acid concentration. The sulfur was doped into anodic oxide[50]. The amounts of doped sulfur can be controlled with the sulfuric acid concentration in the electrolyte.

Effect of electrolytes on anodized oxide of titanium plate was investigated. The tests were made potassium hydroxide, acetic acid and ammonia hydroxides solutions of concentration from 0.5 M to 3.0 M. The SEM observation (Fig-1) shows the microstructures in the anodized oxides prepared in above solutions for concentration of 1.5 M. At the potassium hydroxide concentration of 3 M, it was observed increase of at the pores on the surface. As increased of concentration of ammonia decrease the pore on electrode surface. Using an electrolyte acetic acid was almost observed no change. The porous structures were provided exit paths for the gas generated at the electrodes. The excess oxygen in the inter spaces of the p-type oxide semiconductor was received electrons from neighboring metal ions and become O^- (or O^{2-}), with a positive hole getting associated with this metal ion. The holes oxidize water and oxygen is evolved. The transfer of electrons from the particle surface to water, so that hydrogen is evolved. The reaction is

$$2h^+ + H_2O \rightarrow 2H^+ + ½\ O_2$$

The protons move towards the cathode where they combine with electrons to generate hydrogen gas. Another approximation is the transfer of electrons from the particle surfaces to water, so that hydrogen is evolved according to the reaction[51].

$$2e^- + 2H_2O \rightarrow 2OH^- + H_2$$

3.2 *The relationship between cell voltage and current density*

The overpotentials were reduced to increase the optimum current density. The electrode overpotantial was minimized by selecting TiO_2 electrode that is high electro catalytic activity. The relationship between cell voltage and current density was given in Figure 2 for 1.5 M H_2SO_4 and 1.5 M KOH. The electrolysis cell's I-V results were observed to depend on the electrolyte concentration. It is seen that, at the cell voltage ranging from 0 to 10 V, current density of an alkaline electrolyte (KOH) is lower than from acidic electrolyte (H_2SO_4). When the applied voltage was increased, the current increased so that hydrogen generation rate increases. It is seen that the current density increased with concentration of H_2SO_4, as well. The current density was 0.226 mA/cm^2. 1.5 M H_2SO_4 exhibited the highest current and was more suitable than others electrolyte. Therefore, 1.5 M H_2SO_4 electrolyte was used the water splitting.

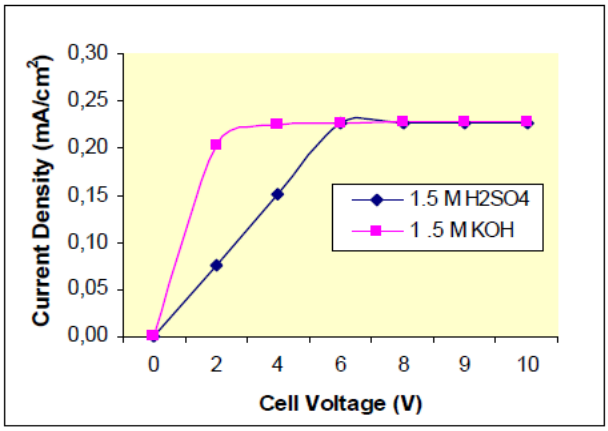

Fig-2: The relationship between cell voltage and current density in 1.5 M H_2SO_4 and 1.5 M KOH solutions

3.3 *Operating time*

Fig-3, shows that I-t curves at 1 V for 1.5 M H_2SO_4 and 1.5 M KOH electrolytes. It is seen from Fig-3. The current density was increased with increasing time. However, after the 90 minutes, current density was almost at the same level. So, at this experiments were used for electrolysis time 90 minutes.

For the first 30 minutes every two electrolytes is almost no generation of hydrogen at the cathode. After 30 minutes electrolysis in electrolytes, the gas of anode and cathode was collected, and current density was calculated the amount hydrogen for 90 minutes both of acidic and alkaline electrolytes was calculated as 25.6 mg and 20.4 mg, respectively.

The production rate of H_2 on cathode surface was found to be directly proportional to the current density supplied to cathode. Average current density was obtained for each electrolyte by the current-time curves.

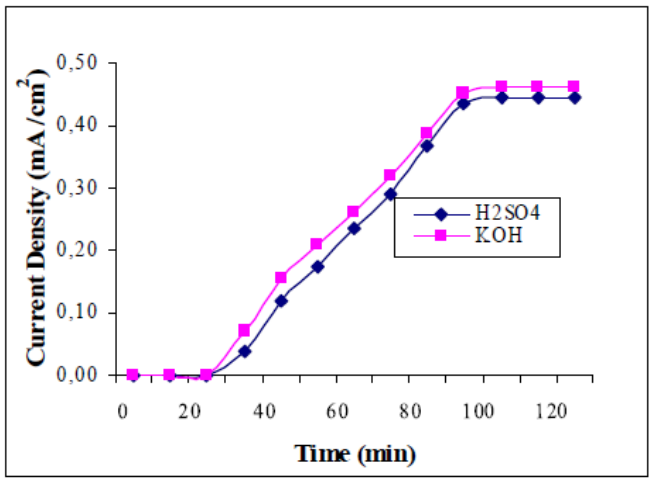

Fig-3: The relationship between current and time at 1 V for 1.5 M H_2SO_4 and 1.5 M KOH electrolytes

3.4 *The effect of electrolytes on the efficiency of hydrogen production*

For hydrogen production from water, the conductivity of water was increased by the addition of acids and alkalis. By offering high ionic concentrations, electrical resistance was decreased. The effects of sulfuric acid, potassium hydroxide, acidic acid and ammonia hydroxide on cathode hydrogen evaluation were investigated. The hydrogen production rate was affected the electrolyte concentration. Fig.4 shows that the electrolytic cell efficiency for water splitting in various electrolytes concentration. It is seen that, by increased the ammonia concentration from 0.5 to 3.0 M, decreased the electro activity of the electrode for hydrogen evolution reaction, so that decreased in cathode current density. The cell efficiency was increased in 1.0 M KOH aqueous solution. By increasing concentration of KOH was decreased the electrolytic cell efficiency. Changing concentration of acidic acid was not effected on the electrolytic cell efficiency. Results of shows that produced of H_2 were achieved by efficiency of 95% in 1.5 M H_2SO_4.

The production rate of H_2 of cathode surface was found to be kind of electrolytes is that due to ion conduction in the electrolyte.

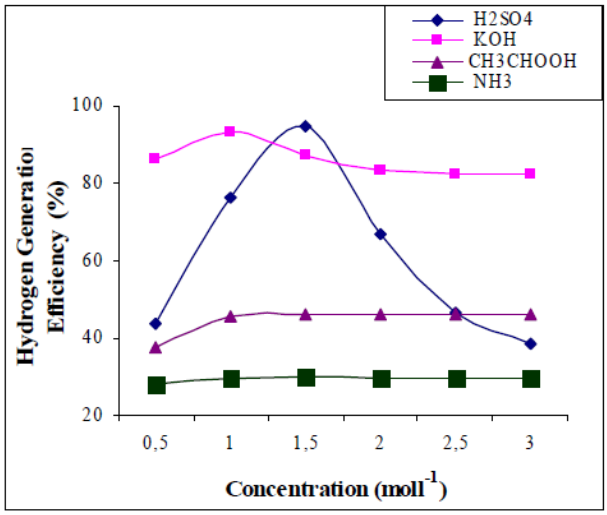

Fig-4: The electrolytic cell efficiency for water splitting in various electrolytes as H_2SO_4, KOH, NH_4OH and CH_3COOH range of concentration 0.5 to 3.0 M

3.5 *Comparison of cathode electrodes*

Hydrogen generation was made using zirconium oxide and graphite electrodes as cathode, also. The results are given in Figure 5 and Figure 6 for zirconium oxide and graphite electrodes, respectively.

Efficiency of the hydrogen was found 88.56%, 75.04%, 51.28%, and 32.05% using electrolytes of sulfuric acid, potassium hydroxide, acetic acid and ammonium, for zirconium oxide as electrode, respectively

Efficiency of the hydrogen was found 3.74%, 2.96%, 2.17%, 2.38%, using electrolytes of sulfuric acid, potassium hydroxide, acetic acid and ammonium for graphite electrode, respectively.

Compared with these electrodes of titanium oxide electrode, the efficiency of hydrogen was found 95 % for sulfate acid, 87.32%, for potassium hydroxide. The results are given in Figure 7.

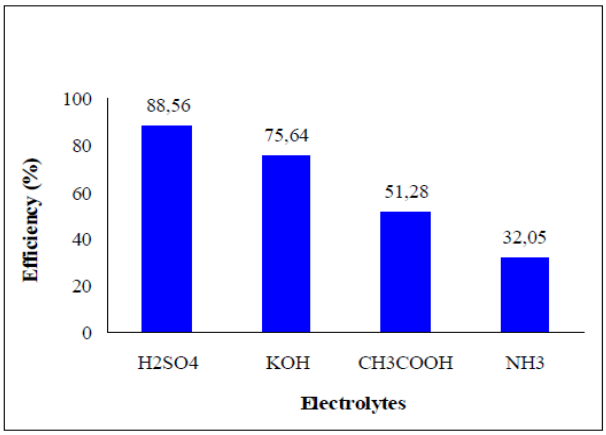

Fig-5: Comparison of the efficiency (%) of hydrogen for zirconium oxide electrode

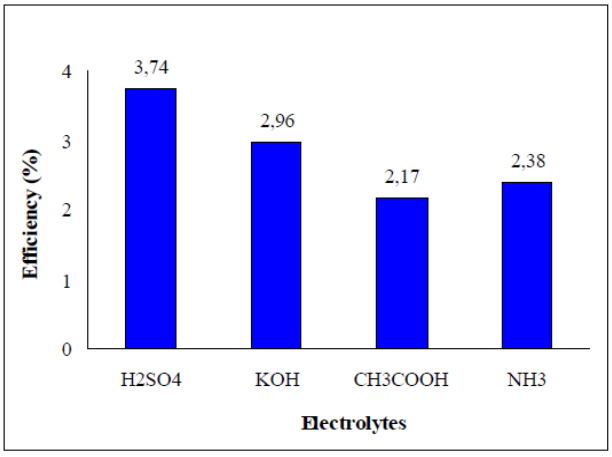

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Fig-6: Comparison of the efficiency (%) of hydrogen for graphite electrode

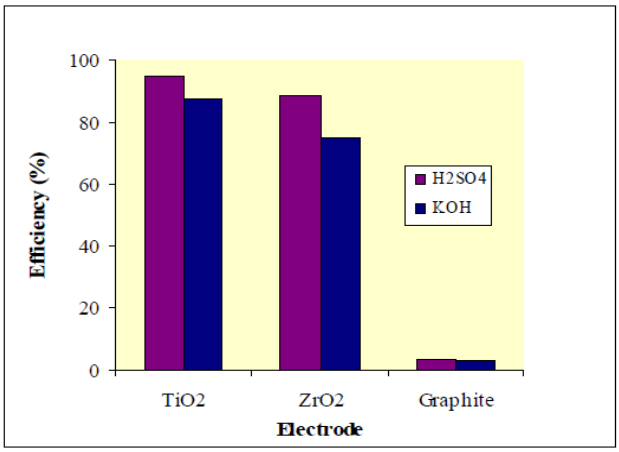

Fig-7: Compared to three electrodes titanium oxides, zirconium oxides and graphite in sulfate acid and potassium hydroxide

4. CONCLUSION

In this study, we have developed electrochemical hydrogen production using the semiconductor cathode in strong acidic electrolyte. The anodic oxidation for titanium plates were made by various concentrations of acid and alkaline electrolytes. The best realized electrolyte for anodic oxidation become in 1.5 M H_2SO_4. TiO_2 electrode was used as cathodes for acidic electrolytes, because of has high catalytic activity with high corrosion resistance. It has been shown to be electrolyzed high-performance. Optimum stabilities of TiO_2 were obtained with an anodisation voltage of 10 V. The conductivity of this electrolyte was decreased with increasing temperature therefore operating temperature was kept 25^oC.

The various electrode materials were investigated ZrO_2 and graphite for hydrogen production. The best efficiency for photoelectrolysis of water was detected in TiO_2.

Compared with these electrodes to TiO_2, hydrogen production rate was increased by 95%. The maximum rate of hydrogen production was reached 8, 18 ml/h x cm^2 by using the n-type TiO_2 electrode.

5. ACKNOWLEDGEMENTS

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