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Investigation of the hydrogen evolution on Ni deposited titanium oxide nano tubes

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ABSTRACT

Titanium oxide nano tubes (TiOx) were prepared by the electrochemical anodizing method from at different process time and different potential in 0.1 M HF solution. Their morphologies were determined with surface photographs and scanning electron microscopy (SEM) images. Ni nano particles were deposited in conductive TiOx nano tubes arrays via pulsed electrodeposition method. Their catalytic activity towards the hydrogen evolution reaction (HER) was assessed by recording cyclic voltammetry technique, cathodic current–potential curves, hydrogen gas volumes and electrochemical impedance spectroscopy techniques. The highest HER activity thought the studied is observed on the $TiOx_{(30)}$-Ni.

1. Introduction

All the world's energy needs are increasing rapidly. Hydrogen is considered as an ideal energy source. It has advantages such as a high energy density, environment friendliness and safely and one of the most promising energy carrier for the future [1–3]. An important technique of producing hydrogen is the electrolysis of water. Although electrolysis of water would be preferred to produce for high-quality hydrogen, this technique is costly [4,5].

The most important parameter limiting the hydrogen evolution reaction (HER) is the cathode material. The electrode materials should have high catalytic activity such as noble metals with low overpotential but these metals are very expensive for industrial applications. The properties of an ideal electrode for HER have a large active surface area, electrochemical stability, good electrical conductivity, low overpotential, selectivity, low cost and ease of use [5]. Ni, Co and Fe based alloys have been successfully employed to fabricate HER cathodes in an alkaline electrolyte. Many researchers have utilized it to analyze the performance of hydrogen production systems and obtained some significant results [6–8]. For example; Kaninski and co-workers [9] studied electrocatalytic activity of Ni electrode for the HER in alkaline solution. They electrodeposited Co and V species on Ni support electrode. Electrolysis at the constant hydrogen production rate was shown that in the case of the Ni–Co cathode, decrease of the energy input was in order of 10%–15% compared to Ni. This decrease was slightly lower for the Ni–Co–V.

It is reported that titanium oxide tube which have large surface area, the ease of preparation, eco-friendliness, good chemical inertness and the strong oxidizing power of the photogenerated holes [10–13]. This material is demonstrated a number of important applications including gas sensors [14], solar cells [15], photo-catalysts [16] and electro-catalyst [17].

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Although there are many studies related to titanium oxide nano tubes, these are interesting oxidation reactions [18,19]. The effects of TiOx-Ni coatings for the HER have not been reported yet.

Electrocatalytic activities of TiOx and TiOx-Ni electrodes as catalysts of alkaline electrolysis for hydrogen production are studied help with cyclic voltammetry technique and current–potential curves. For this purpose, titanium oxide nanotubes are produced in different potentials and measured these oxide conductivities. Electrocatalytic activities for the HER of TiOx and TiOx-Ni electrodes are compared with each other.

2. Experimental

2.1. *Preparation of the titanium oxide tubes and anodizing process*

A cylindrical titanium with 0.785 cm^2 of the surface area (Ti, 99.9%) rods cut to 2 cm length of titanium rod, used as working electrode. The electrical conductivity was provided by a copper wire. The surface of electrode was smoothed by emery paper down to 1200 grade. Then, it was cleaned by acetone/ethanol mixture and pure water. Titanium oxide nano tubes (TiOx) were prepared by electrochemical anodizing method with two electrode technique help with Matrix power supply (MPS-3003L-3) instrument. A platinum sheet (with 2 cm^2 surface area) was used as the counter electrode. Anodized was accomplished at different concentrations of HF solution. For this purpose 0.1–1.0 M HF solutions were used. The tests show that electrode surface corroded with increasing concentration of HF. For this reason, 0.1 M HF solution was used for the anodized process. Ti rod was anodized at different process time (5, 15, 30, 45, 60 min) in 0.1 M HF solution. In order to determine the convenient anodizing voltage, potentiodynamic polarization was applied cyclic scan between 0 and 30 V with 1 V min^{-1} scan rate. The appropriate anodizing time was determined as 30 and 45 min.

2.2. *Deposition of nickel*

The electrodeposition of nickel was performed by galvanostatically using IVIUMSTAT Electrochemical Interface (with serial number AO6063) with a three-electrode configuration. In this system, TiOx was used as working electrode, nickel as counter electrode and an Ag/AgCl (3 M KCl) electrode was used as the reference electrode. The bath composition was 30% $NiSO_4 \cdot 7H_2O$, 1% $NiCl_2 \cdot 6H_2O$, 1.25% H_3BO_3. The constant current density of 5 mA cm^{-2} was applied during 67 s. The 100 μg Ni was deposited per cm^{-2} of TiOx electrode surface, which was calculated via Faraday's laws.

2.3. *Techniques and instrumentation*

The electrochemical measurements were carried using by CHI 660D A.C. electrochemical analyzer (R0633) at room temperature, open to atmosphere. A platinum sheet (with 2 cm^2 surface area) was used as the counter electrode and Ag/AgCl (3 M KCl) electrode was used as the reference electrode for electrochemical analysis such as cathodic polarization curves, cyclic voltammetry and impedance measurements. The electrolyte in all measurements was 1 M KOH aqueous solution. The polarization curves were potentiodynamically obtained in the potential ranges between the 0.9 V and −2.0 V with a scan rate of 0.005 V s^{-1}. The cyclic voltammetry measurements were obtained in the potential ranges between −1.7 V and 0.8 V with a scan rate of 0.1 V s^{-1}. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and low limit of 0.01 Hz. The amplitude was 0.005 V. The EIS study was performed using a Zview software was used to analyze the data.

Conductivity values of electrode were determined help with Four Point Probe Measuring System (FPP 470) at 293 K. The surface morphologies of electrodes were examined by SEM. The SEM images were taken using a Carl Zeiss Evo 40 SEM instrument at high vacuum and 10 kV EHT.

2.4. *Hydrogen gas production measurement*

The hydrogen gas volume is determined by conventional three electrode set up in 1 M KOH solution. The platinum electrode and Ag/AgCl is used as anode and reference electrode, respectively in the electrolysis system. The bare Ti, TiOx and TiOx-Ni electrodes are used as cathode. A burette is filled with the same electrolyte, it is inverted over the cathode constant −1.8 V is applied to the system. The filled hydrogen gas in burette is measured over 30 min.

3. Results and discussion

3.1. *Preparation of TiOx nano tubes*

Titanium oxide electrodes prepared in 0.1 M HF solution by anodizing process (Fig. 1). As seen from Fig. 1 the current values of the system increase with increasing potential value on 0–10 V potential range at forward scan. In this case explained with ions formed (Ti^{2+}, TiO_2^{2+}, Ti^{3+}) by oxidation of Ti that made up the composite with F^- ions [20]. Dissolution is continued with effect of F^- ions and applied anodic potential following equations [21];

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad (1)$$

$$Ti(OH)_4 + 6F^- \rightarrow 4OH^- + TiF_6^{2-} \quad (2)$$

Current is maximum in the range of 10–25 V anodizing potential. In this potential region, the higher dissolution rate in the surface. This potential region is the most appropriate for anodized method for establishment of a controlled oxide layer. Because the surface in this region is completely opened and cleaned by the effect of solution and the new surface layer (TiO_2, $Ti(OH)_4$) will be created depending on the period of application. This oxide layer is not have been enough stability in acidic solution [20]. At the reverse scan, the current values increased by up to 10 V due to pores on the surface and the current value decrease with potential from 0 V to 10 V. The most appropriate application potentials for the anodized process, 10, 17.5 and 25 V, respectively. Wang et al. [17] applied in a similar potential (20 V) due to produce the TiOx nanotubes