

Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/he

A novel photoelectrochemical cell with self-organized TiO₂ nanotubes as photoanodes for hydrogen generation

Yongkun Li^{a,b}, Hongmei Yu^{a,*}, Wei Song^a, Guangfu Li^{a,b}, Baolian Yi^a, Zhigang Shao^a

^a Laboratory of Fuel Cells, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

^b Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:

Received 28 May 2011

Received in revised form

27 July 2011

Accepted 7 August 2011

Available online 10 September 2011

Keywords:

Photoelectrochemical cell

Electrochemical anodization

TiO₂ nanotubes

Water splitting

Hydrogen production

ABSTRACT

A photoelectrochemical (PEC) cell with an innovative design for hydrogen generation via photoelectrocatalytic water splitting is proposed and investigated. It consisted of a TiO₂ nanotube photoanode, a Pt/C cathode and a commercial asbestos diaphragm. The PEC could generate hydrogen under ultraviolet (UV) light-excitation with applied bias in KOH solution. The Ti mesh was used as the substrate to synthesize the self-organized TiO₂ nanotubular array layers. The effect of the morphology of the nanotubular array layers on the photovoltaic performances was investigated. When TiO₂ photocatalyst was irradiated with UV-excitation, it prompted the water splitting under applied bias (0.6 V vs. Normal Hydrogen Electrode, NHE). Photocurrent generation of 0.58 mA/cm² under UV-light irradiation showed good performance on hydrogen production.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Photoelectrochemical (PEC) water splitting has attracted significant attention in the past decades as a promising renewable energy source due to their low production cost and simple manufacturing process [1–7]. Since the early 1970s, Fujishima and Honda reported a single-crystalline TiO₂ semiconductor photoanode for photoelectrocatalytic decomposition of water under UV-excitation and an external bias for the first time [8], great efforts have been devoted to the development of photocatalytic hydrogen production technologies [9–14]. However, the practical applications are still difficult. The main difficulties can be attributed to the lack of effective photocatalysts and efficient photoelectrocatalytic reactors [15]. In photoelectrochemical water splitting for hydrogen generation, the ITO (indium-tin oxide)/FTO (F-doped SnO₂) glass or metal substrate-based photoanode and the Pt

cathode are used and immersed in an aqueous solution especially in alkaline solutions [16–21]. Porous material, such as glass frit, is used as the separator in the cell compartment. The drawback is that such a cell design is only suitable for small scale experiments, and the use of three-electrode or two separated electrodes in an undivided cell, or in a one-compartment cell, can be very problematic due to less effective separation of the generated hydrogen and oxygen. The gaseous mixture is hazardous and brings collecting problems.

Recently, Kamat and co-workers have reported a hybrid fuel cell based on the polymer membrane electrode assembly (MEA) consisting of a P-25 TiO₂ photoanode, a Pt cathode, and a proton exchange membrane for the hydrogen production, and there have other literatures about the new PECs' structure for hydrogen generation [9,22]. However, the photocatalyst casted onto the carbon paper or carbon cloth would be peeled easily after long time run. Therefore, it is not suitable for long-

* Corresponding author. Tel.: +86 411 84379051; fax: +86 411 84379185.

E-mail address: hmyu@dicp.ac.cn (H. Yu).

term water splitting operations. Whereas, the TiO₂ nanotube arrays incorporated with the Ti meshes will avoid this issue. Furthermore, the ions can be transferred easily from the anode to the cathode through the openings of the Ti meshes while it is difficult for Ti foils. In the Ti meshes substrate system, the ions transfer distance is short, that the ions transfer to the counter electrode faster. Besides, the growths of titanium oxide tubes on the Ti foil/meshes will strength the adhesion of TiO₂ nanotube arrays to the substrate. This can be a great opportunity for their use in electrically enhanced photo processes in which the electrical contacts are crucial to obtain high efficiency [23].

In this paper, a novel PEC cell with an innovative design is proposed and investigated. The core of the PEC cell is an MEA incorporated with Ti mesh as the substrates of the photoanode and Pt/C carbon paper as the cathode. The MEA serves as a compact but effective reactor for water splitting as well as an effective gas separator. A self-organized TiO₂ nanotube arrays around the whole Ti mesh with high stabilities in alkaline environments is employed as the photoanode. Besides, a detailed investigation of this photoanode applying on photoelectrolysis of water under illumination of UV light is carried out. As for this type of PEC cell, the driving force for the water electrolysis is the applied potential and light source. In this way, gases generated at each electrode can be separated, and the utilization of light can be improved in comparison with the traditional three-arm reactor.

2. Experimental section

2.1. Materials

All chemical reagents were commercially available, including ethylene glycol, ammonium fluoride (NH₄F, AR). The purity of the titanium meshes was 99.8%. A commercial Pt/C electrode (Pt/C anchored on the Toray TGP-H-60 carbon paper, Sunrise Power Co. Ltd.) with Pt loading of 0.4 mg/cm² was used as the cathode, and asbestos (pore diameter 160 nm, thickness 0.5 mm, SiChuan, China) was used as the diaphragm. The electrolyte was KOH solution (1 M, pH ≈ 13.6).

2.2. Photoanode preparation

Ti meshes (0.2 mm thick, 99.8% metal basis, Dexmet Co. Ltd.) with 58% porosity were used as starting material to obtain the TiO₂ photoelectrodes. Prior to anodization, the Ti mesh was ultrasonically cleaned and degreased in acetone and ethanol successively, followed by rinsing with deionized water and drying in an air stream. Anodization was performed in a two-electrode configuration with titanium mesh as the working electrode under constant potential (30 V) at room temperature (20 °C). A rectangle-shaped carbon electrode (thickness 2 mm, area 4 × 4 cm²) served as the cathode. The distance between the two electrodes was kept at 4 cm in all experiments. A direct current power supply (HY 1791-20S, YaGuang Electronics Co. Ltd.) was used as the voltage source to drive the anodization. The Ti mesh was anodized in the electrolyte (pH ≈ 6.2) with a mixture of ethylene glycol (97.5 wt%), H₂O (2 wt%) and NH₄F (0.5 wt%). During the first 2 min of the anodization, little

bubbles were generated out of the surface of the titanium mesh and afterward less gradually. The colour of the titanium mesh changed from white to light purple and finally brown. In order to achieve different morphologies of nanotubular array layers, anodization time ranged from 4 h to 10 h. After oxidation, the anodized samples were properly rinsed with deionized water to remove the occluded ions, and then dried in an air oven. A subsequent annealing treatment, performed at 450 °C (heating rate of 2 °C/min) in air, was needed to transfer the amorphous structure into crystalline anatase.

2.3. Measurements

A field emission scanning electron microscope (FESEM; Hitachi, S-4800) was used to analyze the morphology of the nanotubes and X-ray diffraction (XRD) measurements were carried out by using an X'pert PRO (PAN-alytical) with a Cu K α tube. Photoelectrochemical features of TiO₂ photoelectrode were tested in a three-arm reactor, in which the TiO₂ sample worked as the anode, a platinum grid worked as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode; all the values of potential in the text were referred to SCE. The light source was an 8 W Deuterium lamp; 1 M KOH solution was employed as the electrolyte. The effective photoactive area of the cell was 1.3 cm². A computer-controlled potentiostat (CHI760, CH Instruments Co. Ltd., China) was employed to control the external bias and to record the photocurrent. The samples were anodically polarized at a scan rate of 5 mV/s under the illumination, and the photocurrent was recorded.

2.4. Photoelectrochemical generation of hydrogen from water

In our early patent [24], a PEC cell was described as Fig. 1. With the anode (TiO₂ nanotube) and the cathode (Pt/C carbon paper) on two sides of the asbestos diaphragm, the membrane electrode assembly (MEA) was pressed between two stainless steel flow-field plates. There were parallel channels flow at the cathode side, and an open chamber with a 24 cm² quartz window at the anode side, which allowed the photocatalyst surface exposed to the light. Rubber rings were positioned in the cell as the sealing. A potentiostat (PARSTAT 2273,

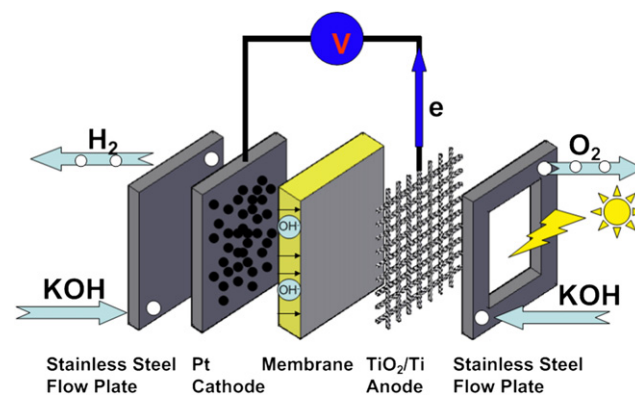


Fig. 1 – Schematic diagram of the photoelectrolysis cell for hydrogen generation.

Download English Version:

<https://daneshyari.com/en/article/1275644>

Download Persian Version:

<https://daneshyari.com/article/1275644>

[Daneshyari.com](https://daneshyari.com)