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Preparation of Pt deposited nanotubular TiO₂ as cathodes for enhanced photoelectrochemical hydrogen production using seawater electrolytes

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ABSTRACT

The purpose of this study was to develop effective cathodes to increase the production of hydrogen and use the seawater, an abundant resource in the earth as the electrolyte in photoelectrochemical systems. In order to fabricate the Pt/TiO₂ cathodes, various contents of the Pt precursor (0–0.4 wt%) deposited by the electrodeposition method were used. On the basis of the hydrogen evolution rate, 0.2 wt% Pt/TiO₂ was observed to exhibit the best performance among the various Pt/TiO₂ cathodes with the natural seawater and two concentrated seawater electrolytes obtained from single (nanofiltration) and combined membrane (nanofiltration and reverse osmosis) processes.

The surface characterizations exhibited that crystal structures and morphological properties of Pt and TiO₂ found the results of XRD pattern and SEM/TEM images, respectively.

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1. Introduction

In most cases, the production of hydrogen by photocatalytic water splitting was performed using pure water. However, this might not be an ideal solution for producing hydrogen on a large scale, because additional surface water treatment would be required and a large amount of chemicals would have to be injected into the pure water to enhance the efficiency. In addition, mankind will be faced with a water shortage problem in the near future, which will influence entire fields of industry, such as water supply and energy. Therefore, the utilization of seawater has been considered to supplement the limited sources of water available for various purposes as well as the production of hydrogen energy [1,2].

Conventional powder TiO₂ has been criticized as being uneconomical compared to other systems due to the difficulties of immobilization and catalyst recovery after the reaction. However, anodized TiO₂ nanotubular electrodes have recently received considerable attention because of their better performance, due to their higher surface area and photocatalytic activity in comparison with TiO₂ powder. The formation of ordered arrays of vertically oriented TiO₂ nanotubes, with open pores at the top surface and sealed bottoms, through a relatively simple anodization process has been an attracted

approach for many applications. Many researchers have endeavored to fabricate effective nanotubular TiO₂ electrodes and investigate the effect of the chemical composition and pH on the tailoring of the nanotube properties [3–7]. In addition, various procedures for improving the photocatalytic activity of TiO₂ nanotubes on the substrates, such as element doping, noble metal deposition, and surface modification, have been carried out [8–11]. However, most studies on the production of hydrogen based on photoelectrochemical systems were focused on the use of nanotubular TiO₂ electrode as the photoanodes, whereas the number of studies on the use of anodized TiO₂ nanotube arrays as the cathode is relatively small.

In our previous studies [12–15], anodized nanotubular TiO₂ electrodes were used as both the photoanode and cathode immobilized hydrogenase enzyme (from *Pyrococcus furiosus*, 'Pfu') in a photoelectrochemical system using seawater as the feed instead of pure water. In addition, mesh type platinum was used as the cathode in the same system. In comparing these types of cathodes, mesh type Pt and nanotubular TiO₂ immobilized enzyme, the former has a potential problem of scale-up caused by its high cost and the latter exhibits higher efficiency for hydrogen evolution but requires the anoxic conditions and the control of the ambient temperature in the cathodic cell, which needs to be increased up to 70 °C to activate the enzyme.

The purpose of the present work was to develop an electro-deposited Pt/TiO₂ nanotubular cathode to increase the production of hydrogen from natural seawater and seawater concentrated by

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nanofiltration (NF) and reverse osmosis (RO) membranes, and investigate their properties.

2. Experimental

2.1. Materials

Titanium foil (0.25 mm thickness, 99.6% purity, Goodfellow, England) was purchased. All chemical reagents, ethylene glycol ($C_2H_6O_2$, 98%), ammonium fluoride (NH_4F , 99.99%) and chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, 37.5%), were purchased from Aldrich and used without further purification.

The natural seawater was obtained from Busan on the east coast of Korea after pretreatment with a 0.45 μm cartridge filter to remove the particulate matter. The natural seawater and the seawater concentrated by membranes were supplied to the PEC system as the electrolyte for hydrogen production. The membrane experiments were carried out in a bench scale cross-flow flat-sheet testing unit (Osmonics, USA) with commercial polyamide membranes, NF (NF90, Filmtech, USA) and RO (BW30, Filmtech, USA). The natural seawater was pumped using a high pressure pump (M-03 series, Hydra-Cell, USA) into the membrane testing unit. A membrane with an effective area of 139 cm^2 was employed. The detailed characteristics of the natural and concentrated seawater are summarized in Table 1 and in a previous study [13].

2.2. Preparation of Pt/TiO₂ nanotubular electrodes

For the fabrication of the pure TiO₂ nanotubes, titanium foils were cut into pieces (2 cm \times 4 cm) and subjected to potentiostatic anodization in a two-electrode electrochemical cell (100 ml of an electrolyte) that was connected to a DC power supply (BS 32a, LS Industrial System, Korea) using an iron counter electrode with magnetic agitation in an electrolyte consisting of mixed chemicals (0.3 M NH_4F + 2 vol% H_2O + ethylene glycol). The Pt/TiO₂ nanotubular electrodes were prepared by electrodeposition with platinum precursor on the pure TiO₂ nanotube support at room

temperature in the same electrochemical cell system. The electrodepositions were carried out in various concentrations of the precursor solution (0.05–0.4 wt%). The detailed fabrication conditions are summarized in Table 2.

2.3. Apparatus and analysis

The hydrogen evolution experiments were mainly conducted in a two-compartment (anodic and cathodic elements separated by a nanofiltration (NF) membrane and a solar cell panel) reactor. The cylindrical-shaped anodic compartment had a volume of 80 ml (headspace volume of ca. 55 ml) and contained the seawater electrolyte solutions. The cathodic compartment was a water-jacketed, cylindrical-shaped cell (80 ml, headspace volume of ca. 55 ml) with a silicone rubber gasket, which allowed the temperature to be adjusted. Prior to the reaction, the mixture was de-aerated with argon gas for 30 min to remove the oxygen in the water and headspace. The two terminals from a solar cell panel (10 cm \times 10 cm, crystalline silicon) were attached to the photoanode (pure TiO₂ nanotube) and the various cathodes, respectively, in order to apply an external bias to the system. An NF membrane (molecular weight cut-off (MWCO) 200) made of polyamide (SU-210, Toray, Japan) was inserted between the two cells to permit ion transport. A detailed explanation of the reactor is given in previous works [12–15].

The light source used was a 1000 W xenon lamp (Oriol, USA), which was filtered through a 10-cm IR water filter. The irradiated light intensity was ca. 75 ± 5.0 mW cm^{-2} (at 350–450 nm with portable radiometers, UM-10 and UM-400, Minolta Co., Japan), but the light intensity absorbed by the sample seemed to be slightly lower than the irradiated intensity, due to the loss by reflection and absorption at the reactor window and seawater electrolyte. The crystal phase and size were determined by X-ray diffraction (XRD, Miniflex, Rigaku; $k=0.89$, $\lambda=0.15418$ for $CuK\alpha$ X-ray, 30 kV, 15 mA). The structure and morphology of the electrodes were investigated using scanning electron microscopy (SEM, Hitachi S-4700) and transmission electron microscopy (TEM, EM912 Omega, Carl Zeiss, Germany). The hydrogen

Table 1
Major ionic concentration of natural and concentrated seawater electrolytes.

	Seawater I (natural)	Seawater II (concentrated)	Seawater III (concentrated)
Membrane process	N.A. ⁺	NF (NF90)	NF+RO (NF90+BW30)
pH	7.9	8.0	8.1
Total dissolved solids (TDS, mg L ⁻¹)	33,500	46,000	59,260
Sodium (mg L ⁻¹)	10,080	11,709	12,520
Potassium (mg L ⁻¹)	581	655	906
Calcium (mg L ⁻¹)	385	643	650
Magnesium (mg L ⁻¹)	1194	2059	2317
Chloride (mg L ⁻¹)	18,870	28,810	35,240
Sulfate (mg L ⁻¹)	2628	3831	5212

N.A.⁺: not available

Table 2
Fabrication conditions of electrodes in PEC hydrogen production.

Electrode	Anodization (at 25 °C)	Electrodeposition			Annealing conditions		
		Pt (wt%)	Current (A)	Time (min)	Temp (°C)	Time (h)	Ambient (ml min ⁻¹)
I (0 wt% Pt/TiO ₂)	Mixed chemicals (0.3 M NH_4F + 2 vol% H_2O + Ethylene Glycol) at 0.1 A for 1.5 h	N.A. ⁺	N.A. ⁺	N.A. ⁺	500	2	400 (O ₂)
II (0.05 wt% Pt/TiO ₂)		0.05	0.01	5			400 (10% H ₂ /Ar)
III (0.1 wt% Pt/TiO ₂)		0.1					
IV (0.2 wt% Pt/TiO ₂)		0.2					
V (0.4 wt% Pt/TiO ₂)		0.4					

N.A.⁺: not available

produced was analyzed by a gas chromatograph with a thermal conductivity detector (TCD at 260 °C, oven at 40 °C). The column used in the system was a molecular sieve 5 A (Supelco, USA).

The concentrations of the TDS (total dissolved solids), anions (chloride and sulfate), cations (sodium, potassium, magnesium, and calcium) in the seawater electrolytes were determined by means of a portable meter (Orion 5-star plus, Thermo Scientific, Singapore), IC (ICS-90, Dionex corporation, USA) equipped with an AS 14 column, and ICP-OES (Optima 5300DV, Perkin Elmer, Germany), respectively.

3. Results and discussion

Fig. 1 shows the hydrogen evolution rates of the various types of cathodes. Under UV irradiation, hydrogen was produced continuously from the seawater electrolyte by the photocatalytic reaction. In these experiments, pure TiO₂ (electrode I) is commonly used as a photoanode with various cathodes. As shown in the results, the pure Ti metal and pure TiO₂ cathode (electrode I) show the relatively lower hydrogen evolution rates than those of the enzyme immobilized TiO₂ and Pt mesh cathodes. Even though the Pt mesh and enzyme immobilized TiO₂ show better performance, both of these electrodes have disadvantages in that the former is an expensive material and the latter requires additional treatment such as the adjustment of the temperature and the maintenance of anoxic conditions in the cathodic cell during the photocatalytic reaction. For these reasons, various contents of platinum are deposited on nanotubular TiO₂ to overcome the low efficiency of electrode I as a cathode.

Fig. 2 shows the trend of the hydrogen evolution rate for the various contents of Pt/TiO₂ with the natural seawater electrolyte (Seawater I). In this experiment, electrode I (pure TiO₂) is commonly used as the photoanode and electrodes I–V (0, 0.05, 0.1, 0.2 and 0.4 wt% Pt/TiO₂) are used as the cathode in the PEC system. As described in Fig. 2, electrode IV (0.2 wt% Pt/TiO₂) shows the better performance than the other electrodes and the variation of the hydrogen evolution rate is as follows: electrode IV ($205 \pm 15 \mu\text{mol h}^{-1} \text{cm}^{-2}$) > electrode III ($162 \pm 9.8 \mu\text{mol h}^{-1} \text{cm}^{-2}$) > electrode II ($158.7 \pm 5.1 \mu\text{mol h}^{-1} \text{cm}^{-2}$) > electrode V ($156 \pm 10.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$) > electrode I ($103.2 \pm 8.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$).

Fig. 3 shows the XRD pattern of 0.2 wt% Pt/TiO₂ (electrode IV). All the samples are found to be amorphous, while those annealed in dry 10% H₂/Ar ambient supported the formation of a crystalline phase. The diffraction peaks at about $2\theta = 25.4^\circ$ (101), 37.8° (004), 48° (200) and 53° (105), 55.1° (211), 75° (215) can be indexed to the crystal phase of TiO₂ (anatase) [13,15]. Thus, it can be concluded that the anatase phase appeared after annealing at

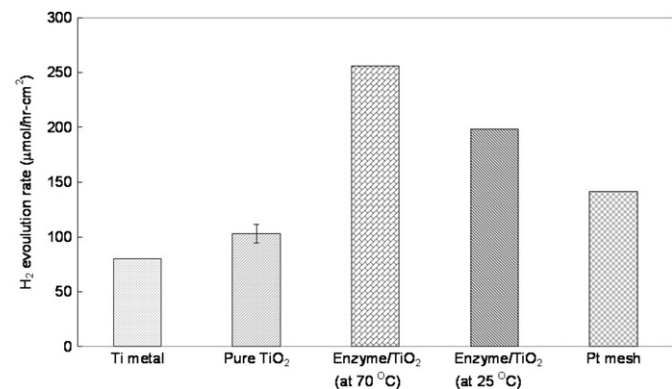


Fig. 1. Comparison of hydrogen evolution rate on cathodes in PEC with seawater electrolyte (anode: electrode I, seawater electrolyte: natural seawater (Seawater I)).

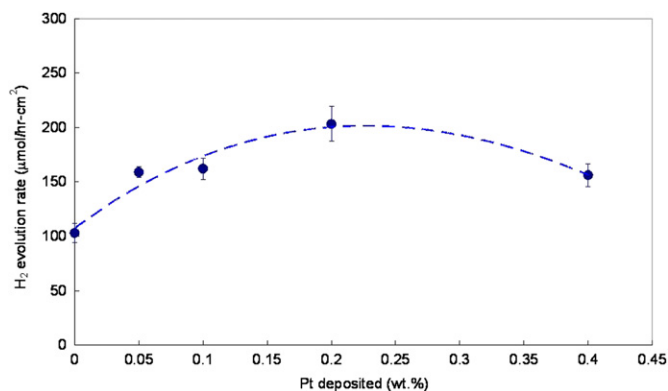


Fig. 2. Effect of various Pt/TiO₂ cathodes on hydrogen evolution rate with seawater (anode: electrode I, seawater electrolyte: natural seawater (Seawater I)).

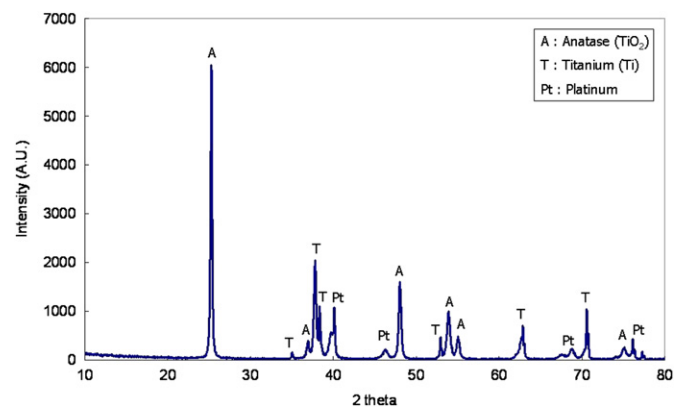


Fig. 3. XRD patterns of the Pt/TiO₂ cathode (electrode IV).

500 °C for 2 h. The other peaks at about $2\theta = 35.1^\circ$ (100), 37.8° (002), 38.4° (111), 52.9° (102), 63° (110) and 71° (107) can be attributed to the Ti substrate [13,15]. The diffraction peaks at about $2\theta = 39^\circ$ (111), 46.5° (200), 68.9° (220) and 76.1° (310) are attributed to the Pt crystal structure [9].

Fig. 4(a) shows the SEM images of Pt/TiO₂ in the top and side views. It is apparent from the images that the TiO₂ layers consist of nanotubular arrays having a length of approximately 7–8 μm, diameter of 70–90 nm and wall thickness of 30–40 nm. In the top and side views, it can be seen that the Pt particles are loaded onto the surface of the TiO₂ nanotubes. As shown in the SEM images, some of the Pt particles on the surface of TiO₂ nanotubes have a size of approximately 50–100 nm and have a tendency to aggregate. However, the most of Pt particles are well dispersed and penetrated into the walls of the TiO₂ nanotubes that have a diameter of less than 5 nm in all of the TEM images (Fig. 4(b)).

After evaluating the production of hydrogen with the various Pt/TiO₂ cathodes and seawater electrolytes, pure TiO₂ (electrode I) and 0.2 wt% Pt/TiO₂ (electrode IV) were used as the photoanode and cathode with two kinds of seawater electrolytes, which are the two types of seawater concentrated by the membranes (Fig. 5). In the membrane experiments, two membranes, NF (nanofiltration) and RO (reverse osmosis), were used to prepare the concentrated seawater electrolytes. Seawater II and III were concentrated by the NF and a combination of NF and RO, respectively. As shown in Table 1, the salinities (total dissolved solids, TDS) of Seawater II and III are higher than that of Seawater I (natural seawater), because the dissolved ions in the seawater are concentrated by the membrane. Especially, Seawater III (ca. 59,260 mg L⁻¹) is more concentrated than Seawater II

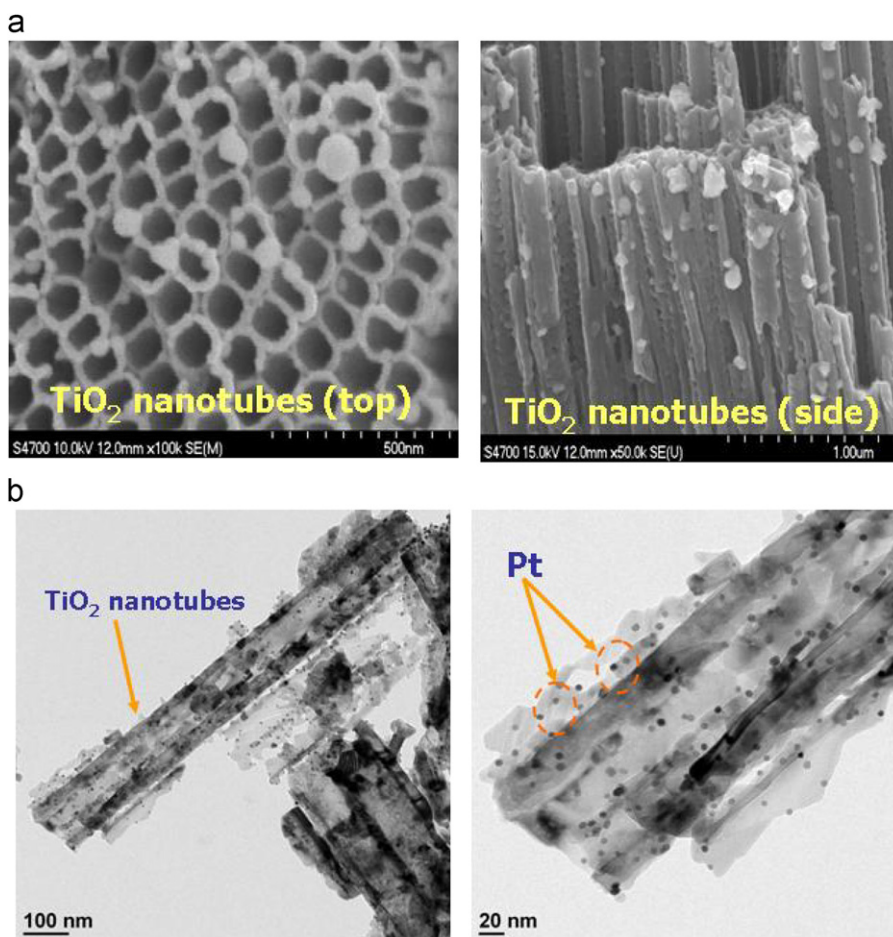


Fig. 4. Images of the selected the Pt/TiO₂ cathode: (a) SEM (top and side views) and (b) HR-TEM (electrode IV).

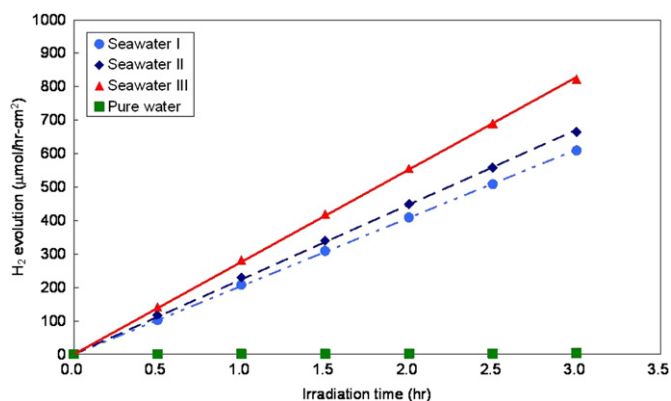


Fig. 5. Time-coursed profiles of hydrogen evolution in PEC with different seawater electrolytes (anode: electrode I, cathode: 0.2 wt% Pt/TiO₂ (electrode IV)).

(ca. 46,000 mg L⁻¹) by the two stage membranes (NF+RO). Fig. 5 shows the amount of hydrogen produced by the various types of seawater electrolytes and pure water as reference in the PEC system. Under UV irradiation, hydrogen was produced continuously from all of the seawater electrolytes by the photocatalytic reaction caused by the dissolved ionic components. As shown in Fig. 5, the hydrogen evolution rate with Seawater III (ca. 277 μmol h⁻¹ cm⁻²) is higher than those obtained with Seawater I (ca. 205 μmol h⁻¹ cm⁻²), Seawater II (ca. 224 μmol h⁻¹ cm⁻²), and pure water (ca. 5 μmol h⁻¹ cm⁻²). In the comparisons of the

hydrogen evolution rate with respect to the various seawater electrolytes, the higher TDS (more concentrated) NF (Seawater II) and NF+RO (Seawater III) concentrates show higher hydrogen production rate than the natural seawater (Seawater I).

4. Conclusions

The conventional platinum mesh and enzyme immobilized TiO₂ were shown the aspects of strength and weakness with respect to the performance as cathodic electrode in photoelectrochemical hydrogen production. To overcome their weak points mentioned above, various types of electrodeposited Pt/TiO₂ electrodes were fabricated for use as the cathode in photoelectrochemical hydrogen production. In addition, the aim of this study was to use the natural and concentrated seawater as the electrolyte in PEC hydrogen production.

The experiments in the PEC were performed with the electrodeposited Pt/TiO₂ cathodes and various seawater electrolytes (natural seawater, concentrated seawaters obtained from NF and NF+RO membranes) under the following common conditions: a pure TiO₂ photoanode and external bias (solar cell) at a reaction temperature of 25 °C.

On the basis of the hydrogen evolution rate, the 0.2 wt% Pt/TiO₂ (ca. 205 μmol h⁻¹ cm⁻²) electrode exhibited the best performance among the various Pt/TiO₂ cathodes with the natural seawater electrolytes. In the comparison of the hydrogen evolution rate with respect to the various seawater electrolytes, the

more concentrated seawater showed higher hydrogen evolution rates than those of the less concentrated seawater.

In consequence, the highest hydrogen evolution rate (ca. $277 \mu\text{mol h}^{-1} \text{cm}^{-2}$) was observed with the 0.2 wt% Pt/TiO₂ (Electrode IV) cathode and the concentrated seawater electrolyte obtained from the combined membrane processes, NF and RO (Seawater III).

For the production of hydrogen from seawater in a PEC system, more detailed studies are needed to ensure the stability and scale-up of the electrode under severe conditions and to examine the use of other metals deposited on pure TiO₂ nanotubes to increase the efficiency of both the anode and cathode.

As is well known, water shortages are anticipated in the future and are likely to have a significant effect on the availability of water for such processes as photocatalysis and electrolysis, as well as for drinking and industrial water. Therefore, this study suggests that seawater could be used as an alternative resource for hydrogen production in PECs. In addition, the use of concentrated seawater (e.g. highly saline seawater from the desalination process) could be beneficial to reduce coastal environmental pollution as well as to produce hydrogen.

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Appendix A. Supplementary Material

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.08.041.

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