

European Materials Research Society Bilateral Conference on Energy 2011

Study of Photo-cathode Materials for Tandem Photoelectrochemical Cell for Direct Water Splitting

Haixiang Zhang^a, Shujuan Huang^a, Gavin Conibeer^{a*}

^a*School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney 2052, Australia*

Abstract

Hydrogen production using water splitting, based on a photoelectrochemical (PEC) process, has attracted considerable attention since the introduction of TiO₂ photo-electrodes. A tandem PEC cell, with photo-voltages added from two photo-electrodes, is a possible solution to generate voltage high enough to split water while absorbing more light from a greater part of the solar spectrum.

This paper studies some of the potential semiconductor materials that may be suitable for photo-cathode for the tandem PEC cells. The effect of electrolyte pH in changing the photo-cathode material electrochemical properties is analyzed and the effect of semiconductor corrosion property is discussed in this paper. The paper concludes by presenting the results of several semiconductors that have been tested.

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Keywords: water splitting; Tandem Photoelectrochemical cell; photo-cathode; pH effect; corrosion

1. Introduction

The direct photoelectrolysis of water, using photo-electrochemical (PEC) cell to split water into H₂ and O₂ under illumination from the sun, is not only an innovative way of generating fuel from a renewable energy source but also a new solution for storing solar energy. Ever since Fujishima and Honda[1] introduce TiO₂ photoelectrode, many semiconductor materials have been studied[2-8]. However only very few large band gap materials can generate enough photo-voltage to cleave water on their own, because the cleavage requires more than 1.4V or even up to 1.9V, including the redox potential of water (1.23V) and unavoidable over-potentials[9, 10]. Materials such as SrTiO₃ (3.7eV) and KTa₂O₃ (3.5eV) can generate sufficient photo-voltages, but the efficiency is very low (<1%) due to the large band gap absorbing almost no photons in the solar spectrum.

A tandem PEC cell, with photo-voltages added from two photo-electrodes, is a possible solution to generate voltage high enough to split water while absorbing more light from a greater part of the solar spectrum. As it

* Corresponding author. Tel.: +61-2-9385-7858 ; fax: +61-2-9385-9666.
E-mail address: g.conibeer@unsw.edu.au.

combines the voltage obtained from illumination of the two photo-electrodes, each half-cell might only need to provide approximately 0.7V to cleave water. Similar approaches have been applied in a tandem device with two discrete PEC cells by Conibeer et al[10] and Graetzel et al [11]. Another advantage of this tandem cell concept is increased overall cell efficiency, due to the two band gaps used and the greater fraction of the spectrum utilized. The theoretical efficiency of tandem cell could reach 12-20%, which is higher than the theoretical efficiency of 7% for the single photo-electrode PEC cell[12, 13]. Moreover, these tandem device concepts are based on thin film materials and technology, which can reduce the cost of the cell.

Many issues concerning tandem photoelectrochemical remain to be solved, before it can become a promising solution for photoelectrolysis of water direct from sunlight illumination. The first problem is what kind of material should be used as photo-electrodes. A couple of metal oxide materials, such as WO_3 (2.7eV) [6]; Fe_2O_3 (2eV)[14]; ZnO (3.3eV); TiO_2 (3.2eV)[8] are possible metal oxide materials for photo-anodes. Semiconductor materials are also a good candidate as photo-cathode material, such as 3C-SiC(2.4eV)[2], a-SiC[15]. This paper mainly focuses on the study of a photo-cathode half-cell and the p-type materials that can be use for the photo-cathode. Electrolyte is one of the important features in a PEC system. Conductivity and energy level dominate the efficiency by limiting the current and the pH will change the line-up of the redox potential. Hence, pH effect is the second problem discussed in this paper. The third barrier discussed in this paper is the stability of the material. Khaselev et al[16] reported a p-GaInP₂/TJ/GaAs photoelectrode can work as a self-biased photoelectrochemical cell with a 12.4% efficiency. However, the stability is poor and still awaits to be improved. A Tafel Plot technology and Faraday's law is used in this paper to study the corrosion properties of selected p-type photo-cathode materials[17-19].

2. Experimental

Amorphous silicon rich silicon carbide (SiC_x) photoelectrode were fabricated by magnetron co-sputtering machine (AJA International, ATC-2200). 90nm SiC_x monolayer film were prepared on p-type Si (100) wafer. Nitrogen doped hexagonal modification SiC (6H-SiC) studied in this paper. P-type Si (100) wafer with different doping density, highly doped (0.001! /sq.) moderate doped (8! /sq.) and light doped (50! /sq.), are also studied.

Electrochemical experiments were implemented using an AUTOLAB potentiostat. Initial experiments were performed as a half-cell measurement for the photo-cathode material. The chemical cell of electrochemical C-V profilers (ACCENT, PN4300PC) is used as a reactor. Reacting surface area is 0.1 cm^2 . The photoelectrochemical measurements were carried in a three-electrode cell with a Pt counter electrode, Ag/AgCl reference electrode, and photo-cathode material as working electrode. General Purpose Electrochemical System software (AUTOLAB, GPES 4.9) provided a fully computer controlled electrochemical measurement system and corrosion analysis. A Xenon lamp is used in the illuminated measurements.

The solution used in the test was 0.5M Sodium Sulphate (Na_2SO_4). The analytical grade of powdered Sodium Sulphate ($M_{\text{Na}_2\text{SO}_4}=142.04\text{g/mol}$) was used. Both pH=3 and pH=11 solutions were prepared in this project to examine the potential photo-cathode materials. Sodium Hydroxide (NaOH) was added to the pH7 0.5M Sodium Sulphate to make an alkaline solution; Sulphuric Acid (H_2SO_4) was added to make the electrolyte acidic. Hence, for the Na_2SO_4 electrolyte, only the H^+ and OH^- ions are added without introducing any other impurity ions.

3. Results and Discussions

3.1 Photo-voltage of Different Materials and pH effects

By comparing the onset of the electrolysis reaction, an increase in the current with respect to voltage is observed as electrolysis occurs when illuminated, which increases the ionic current in the electrolyte. The expectation is that illumination will reduce the required external voltage for onset of electrolysis. This difference in the onset voltage is termed the 'photo-voltage'[7, 10], Figure 1 (a) demonstrated the photo-voltage for Si((8! /sq) sample in pH 7 solution.

Table 1 summarized the results for different semiconductor's photo-voltage in different pH value Na_2SO_4 solution. Figure 1 (b) is the plot for this summarized result. It's interesting to find out that Si wafer with heavily doping doesn't give any result in the photo-voltage. This could be explained as probably due to the band alignment of heavily doped Si wafer being inappropriate to line-up with the water redox potentials. For a photoelectrochemical cathode, the split Quasi-Fermi level should higher than the evolution potential of H_2/H^+ . Since Si (0.001! /sq) wafer is a heavily doped p-type material, the Fermi level is closer to the valence band, which make the split Quasi-Fermi

level lower than the evolution potential of H_2/H^+ . Therefore, the photoelectrolysis reaction can't start. As figure 1 (b) illustrated, the photo-voltage of Si (8! /sq) and Si (50! /sq) wafer decreased as the solution become more alkaline. Takes laterally comparative analysis for these Si wafer with different doping level, we can tell that changing the pH has the same effect as varying the doping level of the semiconductor.

The photo-voltage observed for SiC is not as good as expected. There are two possible reasons for this. Either the n-type SiC wafer used as a photo-anode was not well aligned with the electrolyte redox potential. Or the Xenon lamp may not be able to provide sufficient light above the band gap of 6H-SiC wafer at 3.0eV. For n-type N_2 doped 6H-SiC wafer, the photo-voltage increase as the solution become more alkaline. Therefore, we can draw a conclusion that the p type material prefer an acidic environment and n type material prefer alkaline ambient.

The photo-voltage obtained for Si/SiC is very strange. The photo-voltage increases as the solution either become more acidic or basic. Although Si/SiC film is deposited on Si (0.001! /sq), it was expected to work as an intrinsic film. However, the result was against this estimation. Reasons for this phenomenon will need further study for Si/SiC wafer.

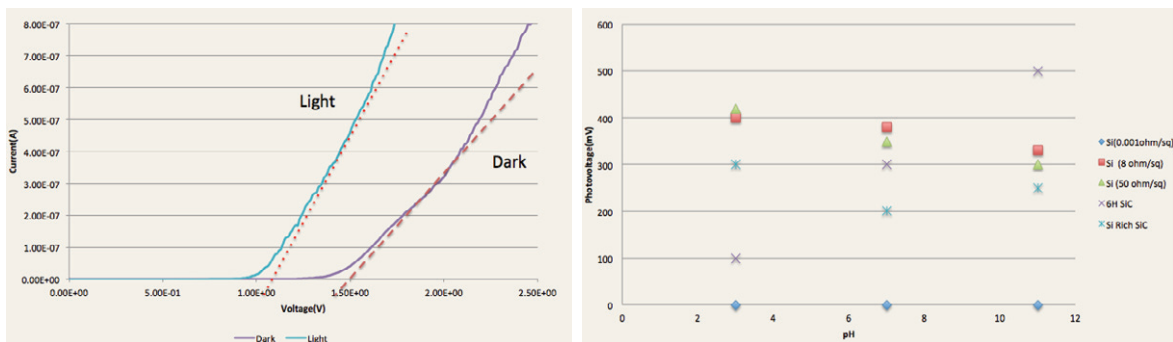


Figure 1 (a) Photo-voltage for Si (8! /sq) in pH7

(b) semiconductor's photo-voltage in different pH

Table 1 Summarized results for Different semiconductor's photo-voltage in different pH value Na_2SO_4 Solution

Material	pH 3	pH 7	pH 11	Parasitic reactions
Si (0.001! /sq)	0	0	0	N/A
Si (8! /sq)	400mV	380mV	330mV	Oxidation
Si (50! /sq)	420mV	350mV	300mV	Oxidation
Si Rich SiC	300mV	200mV	250mV	Dissolution
6H SiC	100mV	300mV	500mV	Dissolution

3.2 Corrosion Study

Since the photoelectrochemical cell was immersed in aqueous environment when operated, the stability is an important factor when selecting the photo-electrode material. There are mainly two types of corrosion study methods: linear polarization resistance (LPR) and Tafel plot (TP) technique. The main difference between these two methods is that TP has larger change of potential up to $\pm 250mV$ when LPR must kept less than $\pm 25mV$. Also TP technology allow to calculate the corrosion rate using straightforward substitution of Tafel slope value (! c and ! b) as shown in equation (1):

$$i = i_{corr} [e^{S_1(E-E_{corr})} - e^{S_2(E-E_{corr})}] \quad (1)$$

Where S_1 =slope of the anodic branch= $2.303/ ! c$; S_2 =slope of the cathodic branch= $2.303/ ! b$ E_{corr} =corrosion potential I_{corr} =corrosion current in Ampere E =potential at any time i =current at any time

The corrosion rate can be obtained by using Faraday's Law as:

$$Corrosion\ rate = m/t = (M_{wt} \times I) / (n \times F) \quad (2)$$

m = mass deposited/released (g); M_{wt} = atomic or molecular weight (g/mol); I = current passed (Amps); t = time current/potential applied (seconds); n = electrons transferred in the half-cell reaction; F = Faraday constant (96485 C/mol). This is the number of charges that must be passed to reduce or oxidize one mole of a compound.

In this paper, Tafel plot technique and Faraday's Law were used to determine the corrosion of selecting photo-cathode material. Table 2 presented the electrochemical corrosion rate for different material in different pH solution. The corrosion current for illuminated situation is larger than the dark measurement without doubted. When comparing the corrosion rate for different material in the same pH solution, n-type 6H SiC turns out to be the most unstable material, followed by Si/SiC and Si (50! /sq).

Table 2 Electrochemical corrosion parameters of different material in different pH solution

pH	Si (8! /sq)		Si (50! /sq)		Si Rich SiC		6H SiC	
	Dark	Illuminate	Dark	Illuminate	Dark	Illuminate	Dark	Illuminate
3	3.51E-01	6.69E+00	9.87E-03	1.64E-01	7.65E+00	7.98E+00	2.41E+00	1.94E+01
7	2.78E-01	1.58E+00	8.10E-03	3.96E+00	3.49E+00	2.32E+01	1.50E+00	4.57E+01
11	1.09E-01	1.58E-01	1.25E-01	9.67E-01	2.36E+00	1.02E+01	4.14E-01	2.28E+01

Corrosion rate is in $\mu\text{m}/\text{year}$.

Table 2 also showed that, the corrosion rate of Si (8! /sq) wafer increased as the pH decreased. Therefore, a trade off between enhances the photo-electrochemical reaction for p-type Si (8! /sq) in acidic environment versus the optimum corrosion rate in a basic situation. However, rest of the materials has a random distribution of the corrosion rate related with the pH variation. Hence the relation between pH and corrosion rate still need further study.

4. Conclusions

The research on photo-cathodes for a photo-electrolysis cell is aimed at the possibility of direct water splitting under sunlight. The main challenge for photo-electrode materials used in PEC cells is to generate a sufficient photo-voltage whilst maintaining excellent resistance to corrosion under photo-illumination in an aqueous electrolyte.

The data on a p-type Si photo-cathode shows that Si is able to give a promising photo-voltage, even though it is still not enough for a photo-cathode. Silicon has a varying response with pH, as is expected from the relationship between doping and acidity. However, an anodic decomposition reaction is observed for the Si cathode.

Si rich SiC wafer result is not convincing in this paper and the electrochemical property to use as a photo-electrode still need further study.

In theory, SiC is a promising material for a photo-electrode. The Si-C bond is very strong, making SiC a reliable anti-corrosion material in an aqueous electrolyte. However, the corrosion study in this paper proved that the stability for 6H-SiC is not as good as estimation. Although the n-type 6H-SiC doesn't give an inspiring result in this paper, 500mV photo-voltage was observed in pH 11 electrolyte.

Acknowledgments

The author delivers his deepest gratitude to other members of Third Generation Group at the ARC Photovoltaic Centre of Excellence for their contribution to this paper. The author also acknowledges the assistance in electrochemical measurements provided by Jungho Yun, Yun Hau Ng and Prof. Rose Amal from the School of Chemical Sciences, UNSW.

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