การพัฒนากระบวนการโฟโตอิเล็กโตรคะตะไลติกสำหรับเพิ่มปริมาณออกซิเจนในระบบตู้เลี้ยงปลา

Development of a Photoelectrocatalytic Process for an Increase Dissoslved Oxygen in an Aquarium Container

ธวัชชัย จุฑามาศ ประภัสสร มีเครือบ สุรางคนา ไหมจุ้ย และ ฉัตรชัย พลเชี่ยว*

*ภาควิชาเคมี คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยเทคโนโลยีราชมงคลธัญบุรี

Tawachai Juthamas, Prapassorn Meekluab, Surangkana Maijui and Chatchai Ponchio*

*Department of Chemistry, Faculty of Science and Technology, Rajamangala University Technology Thanyaburi,

บทคัดย่อ

งานวิจัยนี้ได้พัฒนาเทคนิคใหม่สำหรับผลิตก๊าซออกซิเจนในตู้เลี้ยงปลา โดยอาศัยหลักการพัฒนาการเกิดปฏิกิริยาออกซิเดชันของน้ำภายใต้กระบวนการโฟโตอิเล็กโตรคะตะไลติกเพื่อเพิ่มปริมาณออกซิเจนที่ละลายได้ในน้ำ (ค่าดีโอ) ในตู้เลี้ยงปลา จุดประสงค์หลักของงานวิจัยนี้คือเพื่อเพิ่มอัตราการส่งผ่านอิเล็กตรอนจากขั้วไฟฟ้าทำงาน (อยู่ในส่วนของตู้เลี้ยงปลา) ไปยังขั้วไฟฟ้าช่วย (อยู่ในส่วนตัวรับอิเล็กตรอน) ซึ่งทั้งสองส่วนจะถูกแยกออกจากกัน และเชื่อมต่อด้วยสะพานเกลือ ศึกษาผลของชนิดและปริมาณตัวรับอิเล็กตรอนในระบบโฟโตอิเล็กโตรคะตะไลติก โดยใช้ขั้วไฟฟ้าสารกึ่งตัวนำผสมของ FTO/WO_3/$BiVO_4$ เป็นขั้วไฟฟ้าทำงาน ผลการศึกษาพบว่าสารละลายที่ใช้เป็นตัวรับอิเล็กตรอนของ Fe^{3+} ที่ความเข้มข้น 0.10 โมลาร์ได้ประสิทธิภาพสูงสุดในการผลิตก๊าซออกซิเจน นอกจากนี้สะพานเกลือที่ทำจากสารละลายอิ่มตัวของ NaCl สามารถส่งผ่านอิเล็กตรอนได้ใกล้เคียงกับระบบที่ไม่มีการแยกเป็นรอยต่อ ในการศึกษาใช้เทคนิคไซคลิกโวลแทมเมตรี และ โครโนแอมเพอร์โรเมตรีสำหรับศึกษาปฏิกิริยารีดอกซ์ที่ผิวของขั้วไฟฟ้าและประสิทธิภาพการผลิตออกซิเจนภายใต้สภาวะเร่งของแสงช่วงตามองเห็น นอกจากนี้ยังได้นำแผ่นเซลล์สุริยะมาใช้ในส่วนของการเพิ่มศักย์ไฟฟ้าซึ่งได้ผลการผลิตออกซิเจนสูงเหมาะสำหรับการประยุกต์ใช้ในระบบตู้เลี้ยงปลา

คำสำคัญ : โฟโตอิเล็กโตรคะตะไลติก การผลิตออกซิเจน อัตราการส่งผ่านอิเล็กตรอน

Abstract

A new technique for oxygen production in an aquarium container was developed by improving water oxidation reaction under photoelectrocatalytic (PEC) process in order to increase dissolved oxygen (DO) in an aquarium container. The aim of work is to increase rate of electron transfer from working electrode (in an aquarium container part) to counter electrode (accepting electron part). Both electrodes were separated and connected by salt bridge. The types and amount of accepting electron agents were studied under photoelectrocatalytic process by using FTO/WO_3/$BiVO_4$ as working electrode. The accepting electron solution of 0.10M Fe^{3+} (aq) shows the highest efficiency for oxygen evolution. In addition, saturated NaCl as salt bridge presents similar electron transfer rate to non-junction system. Cyclic voltammetry and chronoamperometry were used to study redox reaction at electrode surface and the efficiency of oxygen production under the effect of visible light irradiation. In addition, solar cell was included in order to apply potential resulting in high oxygen production and suitable for an application in aquarium container system.

Keywords : Photoelectrocatalytic; Oxygen evolution; Electron transfer rate

***Corresponding author.** E-mail:CHATCHAI@rmutt.ac.th or c_ponchio@hotmail.com

Introduction

The ambient concentration of oxygen dissolved (DO) in water is very important for the respiration of aquatic animals. There are reduces by the effect of aquatic animals and plants respiration and the decomposition of organic matter. The continuous put in oxygen gas in to water is necessary for all life in water. In the aquarium container business are using air pumps or water fall system in order to substitute O_2 gas from air to dissolve in water. However, these processes are showing the drawback of high cost for instrument and electricity. Many works have interested a low cost technique for produce O_2 gas by water oxidation reaction under the photoelectrocatalytic process on the surface of semiconductor (Xiaoming (2009), Mishra (2007) and Nelson (2006). However, the previous works have presented low efficiency for O_2 production due to the slow electron transfer process effect and using only in ultraviolet region. Therefore, this work has been interesting to develop the photoelectrocatalytic technique for increases DO content by improve the electron transfer rate between electrode for applicable in visible light region. Moreover, to save cost and practical in use the solar cell was included in order to bias the potential of PEC system. This alternative technique is useful for the aquarium container business to save cost, energy and suitable to apply for produce O_2 with other system.

Materials and Methods

2.1 Electrode fabrication and experimental set up

The $WO_3/BiVO_4$ electrode as working electrode was fabricated by spin coating technique on fluorine doped tin oxide (FTO) substrate as shown in the previous work (Chatchai (2009)). The precursor of $BiVO_4$ and WO_3 were prepared in concentration of 0.05 M and 0.10 M, respectively. The WO_3 solution was deposited on FTO at first and followed by 5 layers of $BiVO_4$ and then calcinations at 550°C for 1 h in air. The edges of the electrodes were covered with epoxy resin to confine the irradiation area to 1 cm^2. For study the reaction, Ag/AgCl use as reference electrode and Pt wire as counter electrode by using NaCl as electrolyte solution. A 60 W tungsten lamp was used as light source for visible light irradiation. A beaker 250 ml was used as aquarium container in this experiment for primary study. The solar cell size of 2x5 cm was used as bias potential unit. DO meter was used to determine the dissolved oxygen in the aquarium part.

2.2 Study the effect of salt bridge system

Saturated NaCl and KCl were studied as salt bridge on the filter paper substrate in order to connect the separating system of a working electrode (in an aquarium part) and counter electrode (in an accepting electron part). Various concentrations of each accepting agent, Fe^{3+}(aq), Cu^{2+}(aq) and Na^{+}(aq) were also studied. The photocurrent by the photoelectrocatalytic (PEC) reaction was studied by applied the potential of 0.3V and 1.0V (vs. Ag/AgCl) under visible light irradiation. Moreover, the pH change in an aquarium unit was studied during the reaction process. The experimental set-up shows in figure 1 to clarify the system of PEC reaction cell.

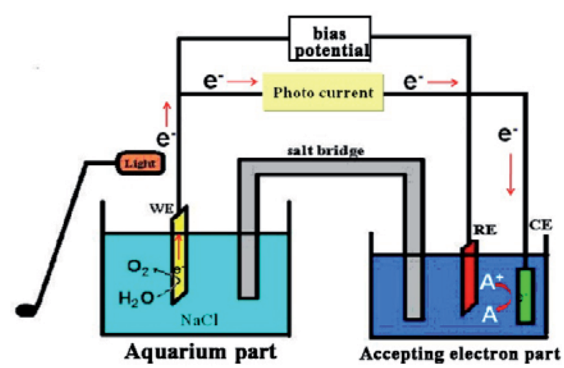


Figure 1 Experimental set-up for study the O_2 production by PEC process, WE: Working electrode ($WO_3/BiVO_4$), RE: Reference electrode (Ag/AgCl), CE: Counter electrode (Pt wire) and A: Accepting electron agents.

2.3 Study of the oxygen production

Figure 1, the DO value in the aquarium part was monitored in order to study the efficient of PEC for oxygen production. N_2 gas was introduced for 1h for setting the DO value to zero at the initial step. In addition, the solar cell (size 2x5 cm) was included to bias potential for saving cost of the system. Oxygen production was compared between PEC system and air pump system by monitoring DO contents.

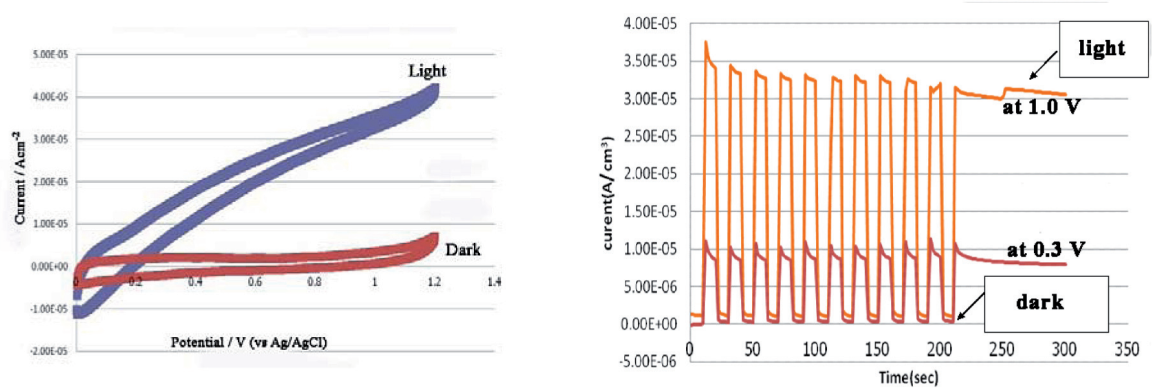
Results and Discussion

3.1 The photoelectrocatalytic activity study

The photoelectrocatalytic activity was studied under applied potential and visible light irradiation. Figure 2A shows the anodic photocurrent of WO_3/$BiVO_4$ electrode significantly enhanced as compared to dark condition. It clearly represents high efficiency of O_2 production from water oxidation under visible light irradiation. Figure 2B shows that WO_3/$BiVO_4$ electrode presents high photocurrent in the solution of 0.1M NaCl and increasing with applied potential from 0.3V to 1.0V. It is corresponding with the good photoelectrocatalytic activity of working electrode for O_2 production in both low (at 0.3V) and high (at 1.0V) bias potentials under visible light irradiation.

3.2 The Effect of salt bridge and accepting electron agents

As shown in section 3.1, WE and CE were studied in the same container. This section, WE and CE were separated in order to study the effect of accepting electron agents for improves electron transfer rate and practical in use for aquarium container.In the real application, WE and CE have to be separated for introduce the accepting electron (NaCl, $CuCl_2$, $FeCl_3$) at CE for enhancing the electron transfer rate from WE to CE. Moreover, the accepting electron solution may affect to fish health. Therefore, the system was separated between WE and CE and connected by salt bridge. The result shows that saturated NaCl presents higher photocurrent than KCl. However, the current is lower than without salt bridge system about 1μAcm^{-2}. Decreasing of photocurrent under salt bridge system may result from the effect of electrode distance between WE and CE and the resistant effect of salt bridge. Figure 3 shows the effect of accepting electron agents to the separation of electrons from counter electrode. An increase in the photocurrents was found when the concentration of all accepting agents are varied from 0.01 - 0.1M and become stable at the concentration between 0.1 - 0.5M which higher than non including accepting electron. It represents that the accepting agents could enhance the electron transfer rate from



(A) (B)

Figure 2 (A) Cyclic voltammogram of WO_3/$BiVO_4$ electrode, scan rate 100 mVs^{-1} (B) Chronoamperographs of WO_3/$BiVO_4$ electrode at different bias potentials of 1.0V and 0.3V vs Ag/AgCl in 0.1M NaCl aqueous solution under periodical visible light illumination.

WE to CE in order to improve water dissociation at WE for O_2 production at aquarium part. Using an aqueous Fe^{3+}as accepting current showed the highest photocurrent compared with Cu^{2+} and Na^+ for all concentrations. The highest photocurrent of Fe^{3+}(aq) is the result of higher reduction potential of Fe^{3+}(0.77V) compared to Cu^{2+}(0.34V) and Na^+(-2.71V) respectively (Skoog(2004)). Therefore, 0.1 M Fe^{3+}(aq) was selected as an accepting electron agent for this PEC system. In addition, pH value was monitored during PEC process in the aquarium part. The pH value was studied from 6.0 to 5.5 when PEC processingtime is 120 min. Decreasein pH value is resulted from the effect of H^+ production by water oxidation process (Lorna (2010)). However, for the application in aquarium system, it may be practical due to H^+ from PEC process could be neutralized by NH_3 generated from waste excretion of aquatic animals.

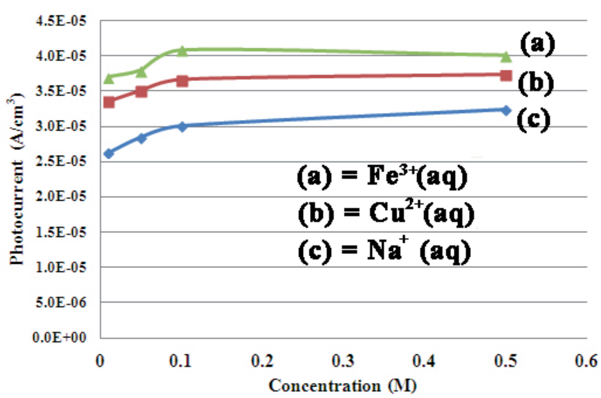


Figure 3 correlations between photocurrent from water oxidation and different accepting agents under the bias potential of 1.0 V vs Ag/AgCl

3.3 O_2 production study

Dissolved oxygen (DO) parameter was selected to study the efficiency of O_2 production by PEC system in aquarium part compared with air pump system. Figure 4 shows increasing of DO value with the function of time process of PEC and air pump systems. At initial time, air pump system shows rapid DO increasing and became stable after 30 min due to the saturated of O_2 dissolved in water. Both systems, without and with solar cell including with PEC technique, shows an enhancing of DO value and continuous increasing with time progress. This result represents that the PEC system including with solar cell as bias potential unit could produce O_2 to increase DO in aquarium system without cost of electrical consumption.

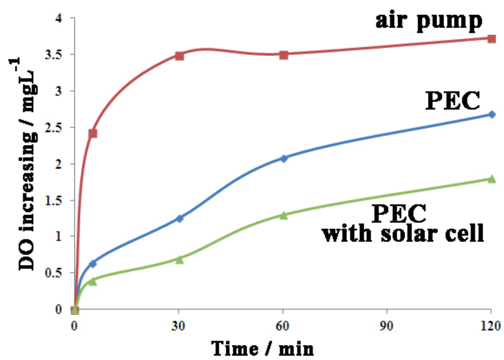


Figure 4 DO value increasing in the function of time process comparison between air pump, PEC and PEC with solar cell systems.

Conclusion

The $WO_3/BiVO_4$ electrode shows high photoelectrocatalytic activity to produce O_2 under visible light irradiation. The maximum efficiency of electron transfer rate was improved by using 0.1M Fe^{3+}(aq) as accepting electron from counter electrode. In this system, WE and CE were separated and connected by saturated NaCl as a salt bridge. The electron transfer rate of this system is closely to non-junction system. This photoelectrocatalysis technique represents the efficiency for increase in DO value and decrease in cost of consumption which suitable for aquarium system application.

Acknowlegements

This research was partial financial supported by Rajamangala University of Technology Thanyaburi (RMUTT) scholarship.

References

Chatchai, P.,, Murakami, Y., Kishioka, S.,, Nosaka, A. Y., & Nosaka, Y., (2009). Efficient photocatalytic activity of water oxidation over $WO_3/BiVO_4$ composite under light irradiation, *Electochimica Acta, 54,* 1147-1152.

Lorna, J. M., Wan, R W. D., Mohammad, B. K., (2010). An overview of photocells and photoreactors for photoelectrochemical water splitting, *International Journal of Hydrogen Energy, 35*, 5233-5244.

Mishra, P.R., Shukla, P. K., & Srivastava, O.N. (2007). Study of modular PEC solar cells for photoelectrochemical splitting of water employing nanostructured TiO2 photoelectrodes, International *Journal of Hydrogen Energy. 32*, 1680-1685.

Nelson, A. K., Thomas, L. G., (2006). Design and characterization of a robust photoelectrochemical device to generate hydrogen using solar water splitting, *InternationalJournal of Hydrogen Energy. 31*, 1658-1673.

Skoog, D. A., West, D. M., Holler, F. J., Crouch, S. R., (2004). *Fundamental of Analytical Chemistry*, Thomson Brooks/cole, 8thUSA.

Xiaoming, H., Robert, F. B., (2009). Direct Solar Water Splitting Cell using Water, WO3, Pt and Polymer Electrolyte Membrane. *Energy, 34*, 1454-1457.