Anal. Bioanal. Electrochem., Vol. 5, No. 3, 2013, 316 - 324

Analytical & Bioanalytical Electrochemistry

© 2013 by CEE
www.abechem.com

Full Paper

Hydrogen Generation by Shimalite Ni Catalyst

Ali Ghaffarinejad[1,*], Einollah Magsoudi [2] and Naghmeh Sadeghi [2]

[1]Faculty of Chemistry, Iran University of Science and Technology, Tehran 1684613114, Iran
[2]Department of Chemistry, Islamic Azad University, Firoozabad Branch, P.O. Box 74715117, Firoozabad, Fars, Iran

*Corresponding Author, Tel.: +98-21-77240516; Fax: +98-21-77491204
E-Mails: Ghaffarinejad@iust.ac.ir, Ghaffarinejad@gmail.com

Received: 6 March 2013 / Accepted: 13 April 2013 / Published online: 30 June 2013

Abstract- Platinum is a suitable electrode for electrochemical production of hydrogen, but it is expensive and its resource availability very limited. Shimalite Ni is a catalyst for reduction in gas chromatography, which commonly used for methane conversion of carbon monoxide, carbon dioxide, formaldehyde, and so on. In this study carbon paste electrode was modified by the proposed catalyst and the modified electrode was used for electrochemical hydrogen evolution in acidic media. Some parameters including oil and catalyst percentage in the paste, pH and supporting electrolyte type were examined. The best conditions and composition was 13% catalyst, 20% paraffin oil and 1.5 M H_2SO_4. Due to the low cost and high performance of this catalyst, it can be considered a good candidate for production of hydrogen without using Pt. Also against very reports, in this study by applying successive potential cycles on the modified electrode surface, the performance of the electrode improves.

Keywords- Hydrogen Production, Shimalite Ni, Carbon Paste Electrode, Electrolysis

1. INTRODUCTION

Hydrogen is one of the most promising candidates for "the fuel of the future" [1,2]. Unlike the fossil fuels, the combustion products of hydrogen are free from pollution. In addition, hydrogen is becoming more important as an energy source for fuel cells, so it is essential to develop active and efficient catalysts for H_2 production.

There are various methods for hydrogen production including steam reforming, gasification, electrolysis [3], hydrolysis [4], thermal catalysis, thermochemical [5], photocatalysis [6,7], and photoelectrocatalytic [8]. In the electrochemical method, platinum is regarded as an ideal catalyst for hydrogen production from aqueous solutions. According to some analyses [9,10], the present available sources of Pt are to cover only 20% of automotive industry needs. Therefore, the search for new methods to reduce loaded Pt or replace other materials in the hydrogen evolution reaction (HER) has been a topic of current interest [11,12].

Shimalite Ni is a catalyst for gas chromatography which, according to its MSDS (No. 10003E-GC), contains 13.5% Ni and 85.5% diatomaceous earth [13]. It is catalytic particles, which has the thin layer of the metallic nickel structure on the diatomaceous earth particle surface for the reduction. It is effective as a reducing agent to convert the material, which does not have the sensitivity for hydrogen flame ionization detector (FID) such as carbon dioxide (CO_2) and carbon monoxide (CO) into methane (CH_4) [14,15]. The analysis of oven-dried crude ore blocks of diatomaceous earth (or diatomite) typically shows 80% to 90% (sometimes 95%) silica (SiO_2) plus alumina (2% to 4% attributed mostly to clay minerals) and hematite (0.5% to 2%), with an analytical ignition loss of 4% to 6%. Apparent block density is 320 to 640 grams per liter with 80% to 90% voids [16]. Therefore this catalyst contains Ni, SiO_2, Fe_2O_3 and alumina; four species that have been widely used for hydrogen generation [17-21].

Due to the spontaneous presence of these species in Shimalite Ni, and the porosity of the diatomite, in this study the proposed catalyst was used for electrochemical hydrogen production in acidic media.

2. EXPERIMENTAL

2.1. Apparatus

Electrochemical studies were carried out using a Metrohm computer-controlled electroanalyzer model of 797 VA Computrace. The instrument software for signal analyzing was 797 VA Computrace (version 1.2). The three-electrode system consists of the bare or modified carbon paste electrode as working electrode, Ag/AgCl (3 M KCl) as a reference electrode and a Pt wire as a counter electrode. The body of the working electrode was a Teflon cylinder (2.0 mm i.d.), which was tightly packed with carbon paste. A stainless steel rod was inserted into the Teflon tube containing carbon paste to establish the electrical contact [22].

X-ray diffraction (XRD) studies were performed at room temperature (25 °C) by an X-ray diffractometer model of Bruker D8 advance, with a Cu (Kα) radiation source (λ=1.5418 Å) generated at 40 kV and 25 mA. The step time was 0.05° s^{-1} and 5°≤2θ≤100°.

2.2. Materials and solutions

Shimalite Ni catalyst was purchased from Shimadzu. Acetic acid, orthophosphoric and sulfuric acids were obtained from Merck. Paraffin oil with spectroscopic grade (Uvasol®) and graphite fine powder (extra pure, particle size ≤50 μm), which were used for paste preparation, were obtained from Merck.

All materials and reagents were analytical grade and were used without further purification. All solutions were prepared with deionized water.

2.3. Preparation of bare and modified carbon paste electrode

Carbon paste electrode (CPE) was prepared by carefully hand mixing the graphite powder with paraffin oil (70:30) to obtain a uniform paste. This paste was packed into the end of the Teflon cylinder hole, and then polished with smooth paper.

For preparing the modified carbon paste electrode (MCPE), Shimalite Ni (13%), graphite powder (67%) and paraffin oil (20%) were mixed well for about 10 min to obtain a uniform modified paste. This modified paste was packed into the end of the Teflon cylinder hole, and then polished with smooth paper. For removing O_2, before each measurement, the solution in the electrochemical cell was purged with a flow of N_2 inert gas for 10 min, and during the measurements, this flow was established on top of the solution. For removing H_2 bubbles on the working electrode surface, during all measurements the electrode was rotated.

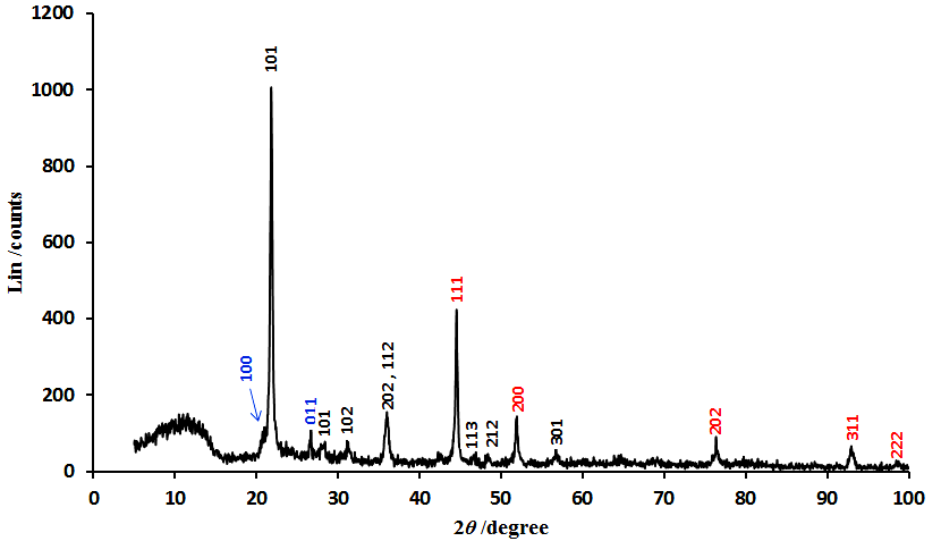

Fig. 1. XRD pattern of the Shimalite Ni catalyst, marks □, * and ■ are respectively related to quarts, SiO_2 (Cristobalite) and Ni (cubic) peaks. (Step time: 5^o s^{-1})

2.4. XRD study of the Shimalite Ni

In order to obtain more information about the catalyst composition, the X-ray diffraction method was used. Fig. 1 shows the XRD pattern of the Shimalite Ni catalyst. The results show that the main constituents of this catalyst are Ni (cubic), SiO_2 (Cristobalite, with a tetragonal crystalline structure) and quartz (with hexagonal crystalline structure). The related peaks are marked in this figure. The peaks related to alumina and hematite is not obvious, which may be due to their very low quantity in the catalyst.

3. RESULTS AND DISCUSSION

3.1. HER on CPE

The over voltage of hydrogen evolution on the CPE is very high. Fig. 1 shows the voltammograms of CPE in various pHs. As illustrated in this figure by increasing hydronium concentration (decreasing pH), the HER current density is increased, but the over voltage is still high. Therefore in this study Shimalite Ni, which has four HER catalyst materials together, was used for reducing this overvoltage and increasing current density.

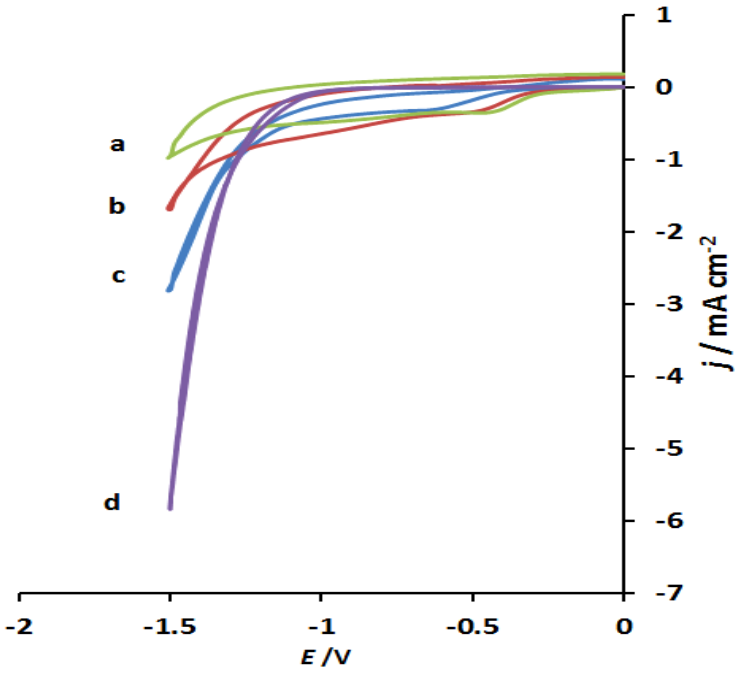

Fig. 2. HER voltammograms on bare CPE in: (a) PBS (pH=9.7), (b) PBS (pH=7.0), (c) PBS (pH=2.7) and (d) 2 M H_2SO_4 (scan rate: 100 mV s^{-1})

3.2. HER on MCPE

To obtain better conditions for HER on the Shimalite Ni modified CPE, the effect of some parameters should be investigated and optimized.

3.2.1.pH and electrolyte effect

Initially the effect of pH and electrolyte on HER was investigated in phosphate buffer solutions (pH=2.2, 7.0 and 9.0), 1 M KOH and various concentrations of sulfuric acid (0.5, 1.0, 1.5 and 2.0 M). The modified electrode contains 13% catalyst and 20% oil. In each solution, in the potential range of 0 to -0.8 V successive CVs with a scan rate of 100 mV s^{-1} were applied on the electrode surface. Fig. 2 illustrates the last CV of HER for each solution.

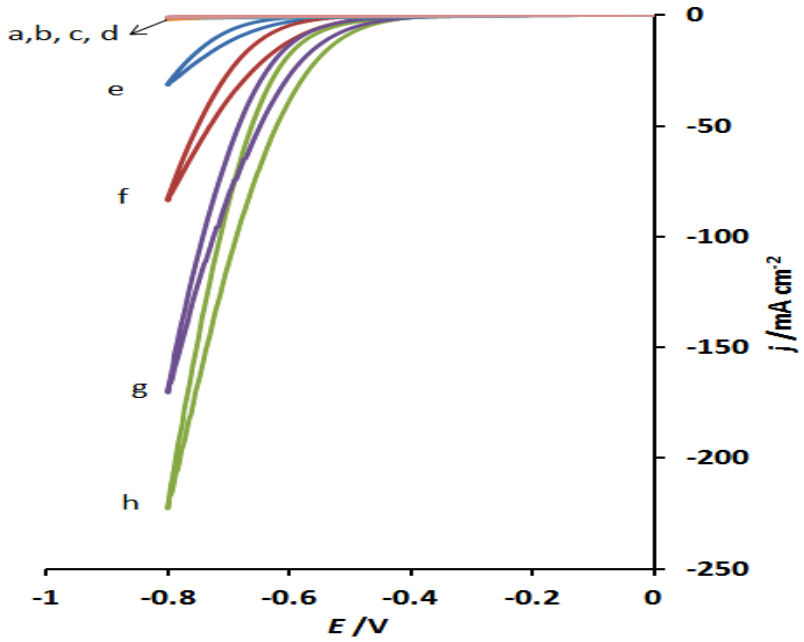

Fig. 3. Cyclic Voltammograms of HER on MCPE (13% catalyst and 20% oil) at different pH and supporting electrolyte; a) 1 M KOH, b) PBS 9, c) PBS 7.0, d) PBS 9.0, e) 0.5 M H_2SO_4 , f) 1 M H_2SO_4, g) 1.5 M H_2SO_4 and h) 2.0 M H_2SO_4.(scan rate=100 mV s^{-1})

As illustrated in this figure, among these solutions the best result is for 1.5 M H_2SO_4. With this solution, the onset potential for hydronium reduction is smaller than other media (about -0.4 V) and its current density is larger; thus compared to other examined solutions the HER performance is the best, and therefore this solution was used for the rest of the experiment.

3.2.2. Catalyst percentage

The amount of catalyst has an important effect, therefore in this experiment the paraffin value was fixed at 20%, and the extent of catalyst was changed (5, 10, 13 and 15% catalyst)

and its effect on the HER performance in 1.5 M H_2SO_4 was examined. For this reason several successive CVs were applied on each modified electrode until a relatively stable signal was obtained. The results of these experiments are shown in Fig. 3. In this figure the last CV for each of MCPEs are illustrated. Even though the 15% has the larger current density, its signal stability is poor. Therefore, for the remainder of the experiments the 13% catalyst, with respect to the smaller catalyst percentages having larger current density, smaller HER onset potential and reasonable stability, was chosen.

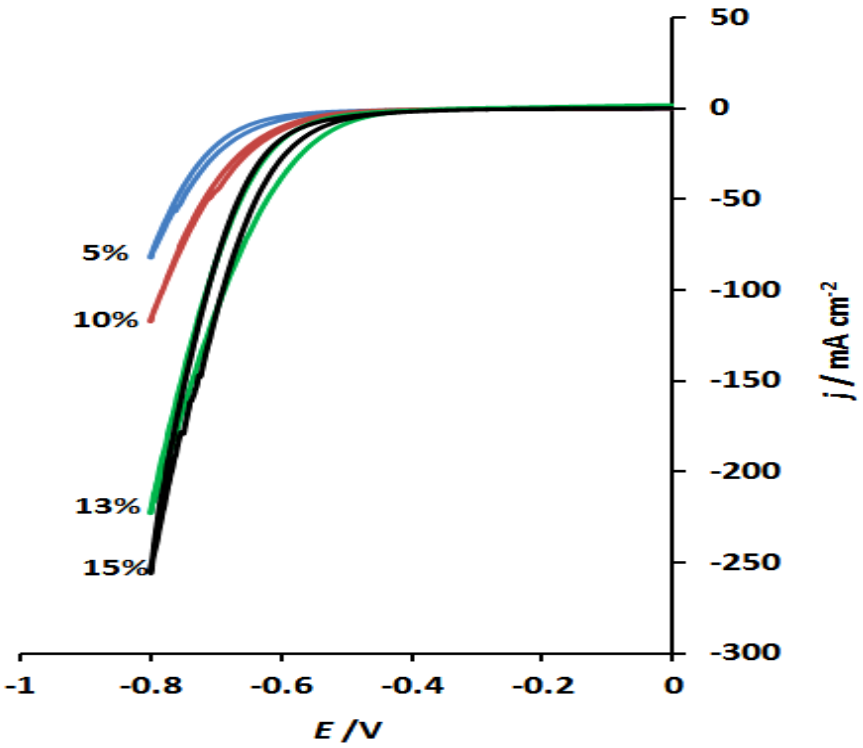

Fig. 4. Cyclic Voltammograms on MCPE with different percent of Shimalite Ni catalyst in H_2SO_4 (1.5 M), scan rate: 100 mV s^{-1}

3.2.3. Oil (binder) amount effect

Since the binder is nonconductive, the amount of paraffin oil affects the electrode performance. Fig. 4 shows the CVs of MCPE with 13% catalyst and various amount of binder (5, 10, 20 and 30%) in 1.5 M H_2SO_4. Among these binder percentages, the 20% has the best HER current density and potential.

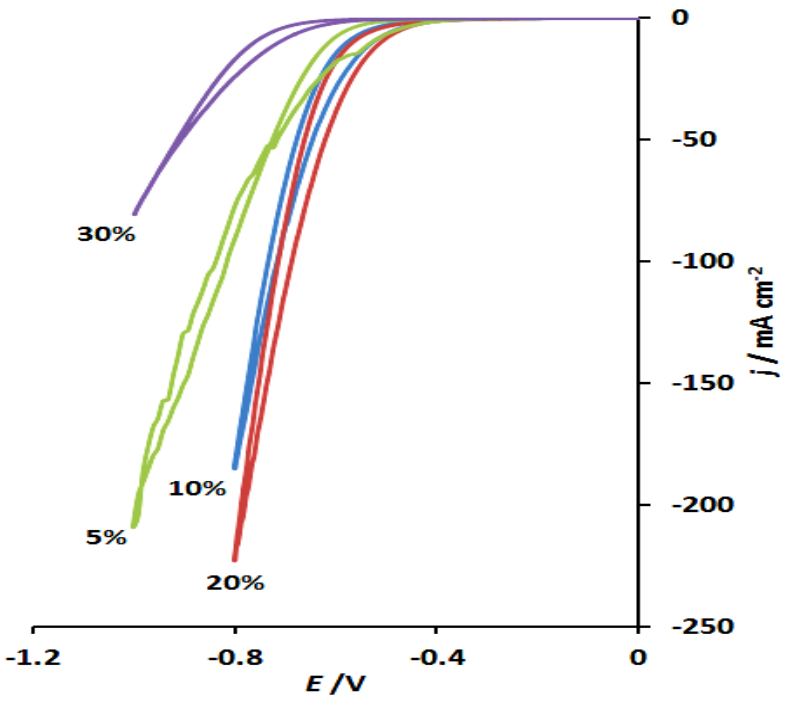

Fig. 5. Effect of oil percent on the HER performance of MCPE with 13% catalyst in H_2SO_4 (1.5 M) and scan rate of 100 mV s^{-1}

3.2.4. Electrode stability

One of the most important properties of the electrode used for hydrogen generation is its stability. For this reason with the selected composition and conditions, 220 successive CVs were applied on the electrode surface. The results of this experiment are illustrated in Fig. 5, which shows that during application of these CVs, hydrogen generation not only does not reduce, but improves considerably (the HER onset potential is decreased and its related current density is increased).

As has been described in the literature the associated mechanism for HER on Ni in sulfuric acid media involves three steps [23] the electro-adsorption of hydrogen at the electrode surface (Volmer reaction), followed by an electrochemical desorption of H_2 (Heyrovsky reaction), and/or a chemical desorption of H_2 (Tafel reaction).

$$M + H^+ + e \leftrightarrows MH_{ads} \qquad \text{Volmer}$$

$$MH_{ads} + H^+ + e^- \leftrightarrows H_2 + M \qquad \text{Heyrovsky}$$

$$2MH_{ads} \leftrightarrows H_2 + 2M \qquad \text{Tafel}$$

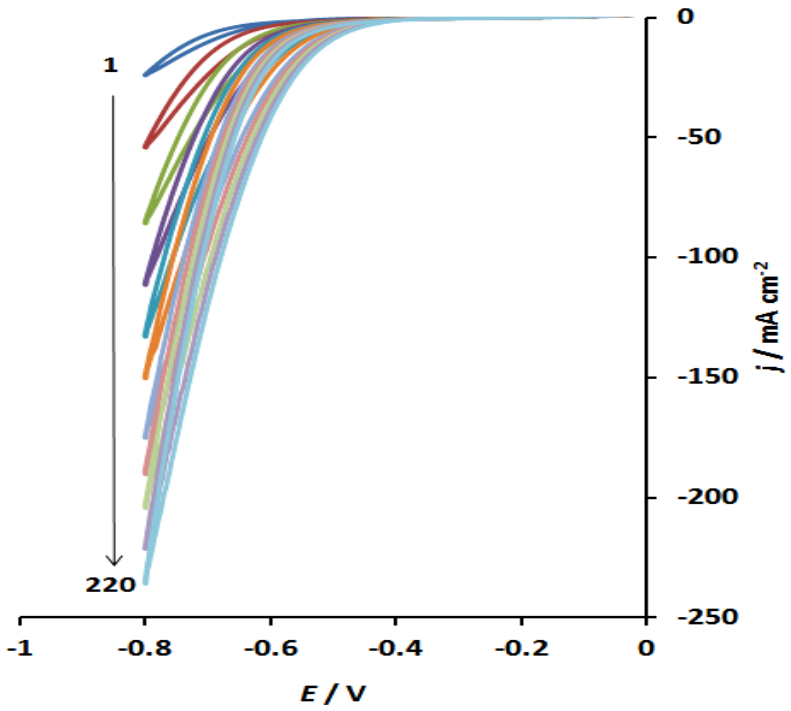

Fig. 6. Successive CVs on the MCPE surface with the scan rate of 100 mV s^{-1} at the selected conditions (13% catalyst, 20% oil, 1.5 M H_2SO_4). Only the 1st, 22, 44, 88, 110, 132, 154, 176, 198 and 220th CVs are presented

4. CONCLUSION

Shimalite Ni catalyst contains Ni, Al_2O_3, SiO_2 and Fe_2O_3, four materials that have been used for hydrogen production. When the CPE is modified with Shimalite Ni, the overvoltage of hydrogen reduction becomes low and its current density increases. Also applying successive CVs on the electrode surface does not reduce the performance of the electrode for HER. In contrast, by applying successive CVs the overvoltage reduces, and the current density for HER increases. In conclusion, according to the ease of preparation, low cost and favorable performance of the proposed modified electrode, this can be an acceptable candidate for electrochemical hydrogen production.

Acknowledgments

We gratefully acknowledge the support of this work by the research councils of Iran University of Science and Technology and Islamic Azad University of Firoozabad.

REFERENCES

[1] S. Dunn, Int. J. Hydrogen Energ. 27 (2002) 235.

[2] I. Dincer, Int. J. Hydrogen Energ. 27 (2002) 265.

[3] J. Jia, X. Li, and G. Chen, Electrochim. Acta 55 (2010) 8197.
[4] B. H. Liu, and Z. P. Li, J. Power Sources 187 (2009) 527.
[5] C. Zamfirescu, I. Dincer, and G. F. Naterer, Int. J. Hydrogen Energ. 35 (2010) 4839.
[6] S. Shen, L. Guo, X. Chen, F. Ren, and S. S. Mao, Int. J. Hydrogen Energ. 35 (2010) 7110.
[7] P. A. Mangrulkar, M. V. Joshi, S. P. Kamble, N. K. Labhsetwar, and S. S. Rayalu, Int. J. Hydrogen Energ. 35 (2010) 10859.
[8] C. K. Halford, and R. F. Boehm, Exp. Therm. Fluid Sci. 35 (2011) 180.
[9] K. Lee, J. Zhang, H. Wang, and D. P. Wilinson, J. Appl. Electrochem. 3 (2006) 507.
[10] M. Arita, Fuel Cells 2 (2002) 10.
[11] M. R. Gennero, J. Electroanal. Chem. 448 (1998) 87.
[12] J. B. Raoof, R. Ojani, S. Asghari Esfeden, and S. Rashid Nadimi, Int. J. Hydrogen Energ. 35 (2010) 3937.
[13] Shimalite Ni MSDS No. 10003EGC, www.ssi.shimadzu.com.
[14] C. L. Roehm, and N. T. Roulet, Global Biogeochem.Cy. 7 (2003) 29.
[15] Gas chromatography catalog, SHINVA CHEMICAL INDUSTRIES Ltd. http://www.winlab.com.au/Chromatography/Shinwa_GasChromotographyCatalog.pdf, Accessed 23 November (2012).
[16] Antonides LE, Diatomite. http:// minerals. usgs. gov/ minerals /pubs /commodity /diatomite/250397.pdf. Accessed 20 July (2012).
[17] E. A. Sánchez, M. A. D'Angelo, and R. A. Comelli, Int. J. Hydrogen Energ. 35 (2010) 5902.
[18] P. C. Chen, Y. M. Chang, P. W. Wu, and Y. F. Chiu, Int. J. Hydrogen Energ. 34 (2009) 6596.
[19] R. Muangrat, J. A. Onwudili, and P. T. Williams, Appl. Catal. B 100 (2010) 143.
[20] A. Boudjemaa, S. Boumaza, M. Trari, R. Bouarab, and A. Bougueliac, Int. J. Hydrogen Energ. 34 (2009) 4268.
[21] J. Liu, H. Watanabe, M. Fuji, and M. Takahashi, Electrochem. Commun. 11(2009) 107.
[22] A. Abbaspour, and A. Ghaffarinejad, Electrochim. Acta 53 (2008) 6643.
[23] H. El Alami, J. Creus, and X. Feaugas, Electrochim. Acta 51(2006) 4716.

Copyright © 2013 by CEE (Center of Excellence in Electrochemistry)
ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY (http://www.abechem.com)
Reproduction is permitted for noncommercial purposes.