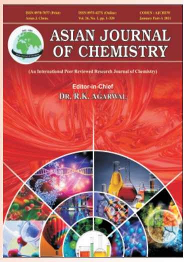
Estd. 1989
Asian Journal of Chemistry

Asian Journal of Chemistry; Vol. 26, No. 22 (2014), 7591-7596

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16914



Hydrogen Evolution from Water in Presence of Diethylamine Acetate and 1-Butyl-3-methyl Imidazolium Tetrafluoroborate Ionic Liquids as Electrocatalysts on Different Electrode Materials

L.Q. LONG[1], H.D. HUNG[2], V.T.T. HA[1], P.T.H. YEN[1], P.H. PHONG[1] and L.Q. HUNG[1,*]

[1]Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
[2]Hanoi University of Science, Vietnam National University, 19 Le Thanh Tong, Hoan Kiem, Hanoi, Vietnam

*Corresponding author: Fax: +84 43 8361283; Tel: +84 43 8362008; E-mail: hunglq@ich.vast.ac.vn; hunglq114@yahoo.com

Received: 23 December 2013; *Accepted*: 10 April 2014; *Published online*: 6 November 2014; AJC-16190

This report presents the investigation of electrochemical generation of hydrogen from water in the presence of the ionic liquids diethylamine acetate ([DEA][Ac]) and 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF$_4$]) on different electrode materials such as brass, stainless steel, carbon steel and carbon nanotube paste. Electrochemical properties were investigated using cyclic voltametric, potentiostatic and galvanostatic techniques. The best concentration in water of both ionic liquids studied was obtained at 10 vol. % in cases of brass and stainless steel and for CT$_3$ in solution containing [DEA][Ac]. Efficiencies of hydrogen evolution were determined to be between 94 and 99 %. The materials displayed high stability during the electrolysis process, especially for stainless steel.

Keywords: Ionic liquid, Hydrogen evolution, Water electrolyte.

INTRODUCTION

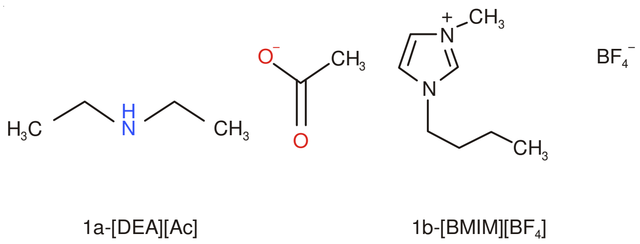
The important roles of hydrogen as an energy source and as a convenient agent for energy storage, transport and manipulation have received significant attention over the last decade[1-7]. Research indicates that fossil fuels are energy sources intrinsically associated with environmental impacts; they generate a large amount of contaminants including CO$_2$, which are the main problem of global warming and the major cause of climate change. Hydrogen is one of several promising clean fuels with future potential as a substitute for conventional fuels such as oil, coal and natural gases. The high values of combustion energy and the large difference in redox potentials in fuel cells contribute to a very clean final product (H$_2$O) producing the advantages of hydrogen as a reduction fuel. Therefore, hydrogen generation is receiving more and more interest by scientists and is considered as an ideal alternative to fossil fuels in the future because the energy derived from hydrogen *via* combustion or *via* fuel cells is non-polluting[8]. Hydrogen can be produced by several methods and the relative convenience of these methods has been the subject of many publications[9-11]. One of these methods is the direct electrolysis of water[10-11]. Classical alkaline electrolytic cells, filled with potassium or sodium hydroxides, operating at moderate temperatures (65-80 °C) enable the production of gaseous hydrogen with an overall efficiency in between 60 and 100 %. The cost of this production depends basically on the price of the energy necessary to perform the electrolysis and to keep the cell at the operation temperature. Among the industrial methods of hydrogen production, three processes have gained prominence: eforming, photoconversion and electrolysis. Because of environmental advantages, electrolysis is receiving considerable attention by many researchers using ionic liquid (IL) as electrolytes/catalysts. Ionic liquids are organic compounds that are liquid at room temperature and conduct electricity[12-14]. Ionic liquids have been shown to be potential alternatives to the electrolytes currently employed in industrial electrolysis systems, taking into account that they are chemically inert, their vapor pressure is extremely low and they have no deleterious effects on the environment[11]. To date, imidazolium-based ionic liquids with tetrafluoroborate anions have been the focus of numerous publications that describe their physicochemical properties, phase equilibria and direct application studies[15]. Imidazolium-based ionic liquids have been shown to be an ionic liquid with interesting properties such as high conductivity and chemical and electrochemical stability[14-17].

De Souza *et al.*[10] investigated dialkylimidazolim ionic liquids as electrolytes, using Pt as the working electrode and obtained the efficiencies of more than 94.5 %. In 2007, this group also studied[11] the 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) as an ionic liquid, using Pt, Ni, stainless steels (SS) and low carbon steel (LCS) as different working electrodes with overall hydrogen production efficiencies between 82 and 98 %. Nguyen *et al.*[9] used the hyperthermophilic eubacterium, *Thermotoga neapolitana*, to produce hydrogen from cellulose pretreated by ionic liquid[9]. Pool *et al.*[18] used the highly acidic ionic liquid dibutylformamidium *bis*(trifluoromethanesulfonyl)amide for electrocatalytic H_2 evolution by $[Ni(P_2N_2)_2]^{2+}$ complexes.

In the scope of this paper, two ionic liquids *i.e.*, diethylamine acetate ([DEA][Ac]) and 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]) were tested as electrolytes for hydrogen production electrolyzed on various kinds of working electrodes: brass, stainless steel and carbon steel.

EXPERIMENTAL

Diethylamine acetate [DEA][Ac] (**Scheme-Ia**) and 1-butyl-3-methyl imidazolium tetrafluoroborate [BMIM][BF_4] (**Scheme-Ib**) ionic liquids were received from Kakiuchi's Laboratory (Kyoto University, Japan) as a gift. They were used without further purification.



Scheme-I: Structures of studied ionic liquids

Electrochemical procedure: The electrolysis solutions varying from 1 to 25 %. were prepared by dissolving the ionic liquids in ultra pure water. The production of hydrogen from water electrolysis was performed using a system fabricated in our laboratory at the Vietnam Academy of Science and Technology, Hanoi, Vietnam (VAST). The system used the principle of a Holfmann'cell, shown in Fig. 1, equipped with a working electrode, platinum as quasi-reference electrode and platinum wire as an auxiliary electrode. The potential measurement was performed relative to a Pt quasi-reference electrode. The three electrode system was connected to a custom-made multifunction potentiogalvanostat also manufactured at Vietnam Academy of Science and Technology. It was equipped with 12 byte analog-digital converter (ADC) and the signal was amplified by two operational amplifiers with an active filter. Noise was reduced by an active filter and a custom-written noise reduction algorithm. Overall, it provided current resolution down to 0.008 nA, valuable for sensitive measurements. The data acquisition was performed using custom-written software.

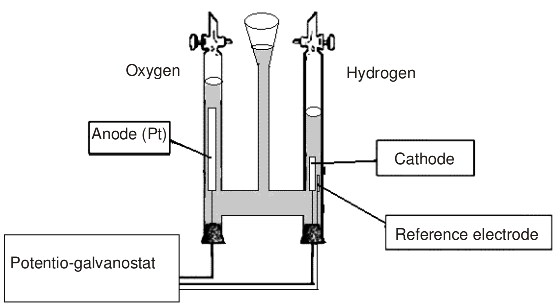


Fig. 1. Experimental arrangement of Hofmann's cell system

The working electrodes were made from different materials such as brass, stainless steel, carbon steel, graphite and carbon nanotube paste. The areas of these electrodes were measured as follows: brass: 1.56 cm^2, stainless steel 1.36 cm^2 and carbon steel 2 cm^2, graphite 0.754 cm^2 and carbon nanotubes paste electrode estimated as 0.1963 cm^2.

Preparation of graphite and carbon nanotubes (CNT) paste electrode: The graphite powder and CNT paste electrodes were prepared following reported procedure in previous papers[19,20]. Seventy percent graphite (Japan) or CNT (made in Institute of Materials Sciences-VAST) was ground in 30 % paraffin oil (Wake, Japan) in an agate mortar by hand mixing for about 0.5 h to get a homogenous paste of graphite and CNT, respectively. The mixtures were then tightly packed into one end of a teflon tube (5 mm internal diameter) and a gold wire was inserted through the opposite end for electrical contact. The surface of the graphite and CNT paste electrode were manually smoothed by polishing on clean paper and were then rinsed with distilled water before use without any electrochemical pretreatment. They were used immediately after preparation.

A computerized potentiogalvanostat PGS-HH5 fabricated in our laboratory was used to perform all electrochemical measurements such as: cyclic voltametric to determine the convenient potential applied between the working and reference electrode as well as the chronoamperometry for the determination of the efficiency of electrolysis decomposition of water into H_2 and O_2 in electrolytes containing [DEA][Ac] or [BMIM][BF_4].

The current densities (j = 1/A) were calculated from the measured intensity (I) and the surface (A) of the electrode exposed to the medium. The efficiency of the electrolysis processes was determined from the consumed charge data (Q) and from the volume of hydrogen produced in the cathodic compartment of the cell during the electrochemical reaction. With the Holfmann's cell the hydrogen volumes were measured directly and their values used to calculate the efficiency (η %) by the following equations:

$$\eta\,\% = 100 \times \frac{V^{R}_{H_2}}{V^{T}_{H_2}} \quad (1)$$

where $V^{R}_{H_2}$ is the measured volume of hydrogen and $V^{T}_{H_2}$ is the theoretical one calculated by

$$V^{T}_{H_2} = \left(\frac{Q}{2F}\right)\left(\frac{RT}{2\alpha}\right) \quad (2)$$

Consumed charge Q was determined by integration of chronoamperometric curve (i-t) measured at constant potential (potentiostatic regime) (Fig. 5). This calculation was completed using a computer subroutine program included in the special software named PGSTAT.EXE written by the authors.

RESULTS AND DISCUSSION

Water electrolyses were performed in a Hofmann's cell (Fig. 1) equipped with different working electrode materials such as brass, stainless steel and carbon steel using counter electrodes made from platinum, aqueous solutions of ionic liquids ([DEA][Ac] or [BMIM][BF_4]) at different concentrations and operating at different imposed cathodic potentials.

In the cathodic compartment of the cell, water is reduced at the working electrode leading to the production of hydrogen:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

whereas in the anodic compartment oxygen is produced through water oxidation:

$$H_2O \rightarrow 2H^+ + (1/2)\,O_2 + 2e^-$$

Cyclic voltammetric investigation of different working electrode materials in [BMIM][BF_4] and [DEA][Ac]: The cyclic voltametrics (data not shown) of the pure ionic liquids [BMIM][BF_4] and [DEA][Ac] and with the addition of 75 % water (25 % IL) were recorded. It is shown that in pure ionic liquid, the obtained current density (*j*) is neglicable, lower than -0.1 mAcm^{-2} in the potential range of -0.5 and -2 V. This proves that ionic liquids are highly stable in the potential range studied. With the addition of water (1-25 %), high current density values were observed indicating that the current was obtained mainly by the electrolysis of water, indicating that these ionic liquids are suitable electrolytes for hydrogen production.

Before the electrolysis experiments were performed, the potential range of the hydrogen evolution reaction needed to be determined. Hence, the cyclic voltammetry (CV) technique was carried out in a conventional electrolyte cell with Pt as counter electrode and a quasi-reference electrode made of Pt as well as, different materials: brass, stainless steel and low carbon steel were used for the working electrode. The solution with 10 % [BMIM][BF_4] served as the medium with a sweep rate of 300 mV/s. Fig. 2 shows the cyclic voltametric curves of stainless steel with 1, 10 and 25 % of [BMIM][BF_4] in distilled water. In this ionic liquid solution, potential ranges noted varied by ionic liquid concentration as well as by working materials. Values of -5 V for stainless steel and -2 V for brass and CT_3 were found to be equal.

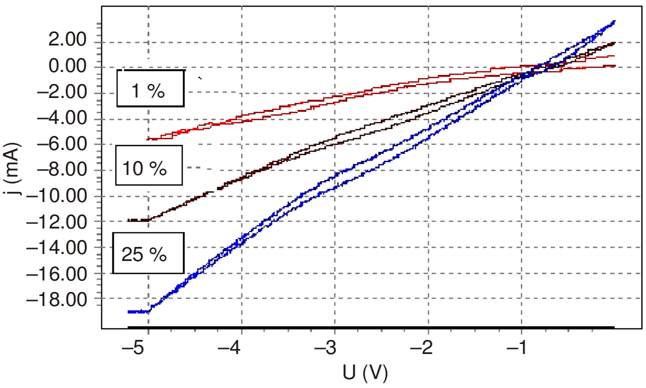


Fig. 2. Cyclic voltametric curves of stainless steel in the solutions with different concentration of [BMIM][BF_4]

Fig. 3 shows the cyclic voltametric curves of the electrolysis water reaction using stainless steel as the working electrode in solutions of [DEA][Ac] of 1, 10 and 25 %. In the case of stainless steel, we can observe that the hydrogen evolution occurs significantly at -1.4 V to -5 V. The current intensity obtained at -5 V is 20 times larger when the concentration increases from 1 to 25 %. The current intensities are proportional to the concentration of [DEA][Ac] which plays a role as electrolyte/catalyst of the reaction.

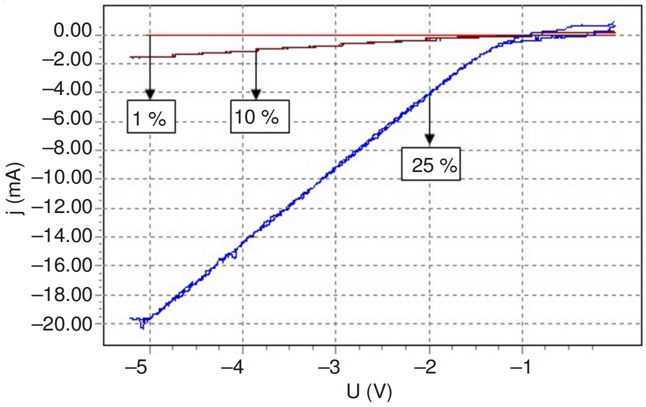


Fig. 3. Cyclic voltametric curves of stainless steel in the solutions with different concentration of [DEA][Ac]

Similar experiments were performed with brass and low carbon steel as working electrodes. The potential ranges of cyclic voltametric experiments for low carbon steel and brass are 0- 2 V and 0-3 V, respectively. Based on cyclic voltametric results, the suitable potential ranges for chronoamperometry experiments for the determination of the efficiency of hydrogen reduction were chosen. In both studied ionic liquids solutions, depending on the working materials, potential ranges found varied from -1.6 to -5 V for stainless steel and -1.6 to -2 V for brass and CT_3.

Chronoamperometry curves of water reduction in two ionic liquids: Fig. 4 shows chronoamperometric curves of the brass electrode, with 10 % (v/v) ionic liquids at -1.6 V, during electrolysis of 1800s. Shortly after the start, the current decreased according to the Cottrell equation[21] then increased gradually until it reached stability in the period of 200s (Fig. 4). This stabilization period is explained as being a consequence of the surface stabilization of the electrodes. The stability of the cathodic current also indicates that in such conditions there is no occurrence of side reactions, which could affect the active sites on the electrode surfaces.

The difference between the current densities of [BMIM][BF_4] and [DEA][Ac] could be explained by the physical properties of these ionic liquids, such as their viscosity at low water content[14,19].

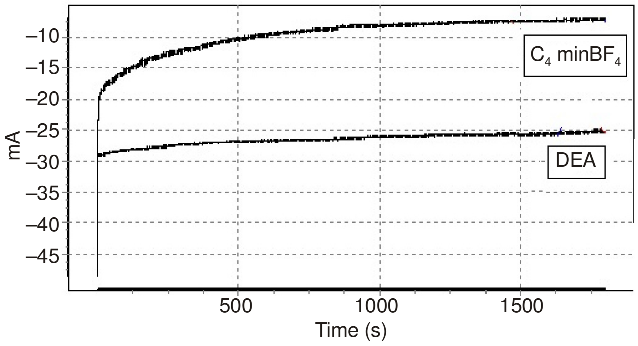


Fig. 4. Chronoamperometry of brass at applied potential -1.6 V in [DEA][Ac] and [BMIM][BF_4] 10 % solution

Determine the best experimental conditions for hydrogen production by electrolysis H_2O in two ionic liquids: After completing the cyclic voltametric experiments, the suitable potentials for the chronoamperometry corresponding with each working electrodes were applied. The influences of applied potentials, concentrations and materials of the electrode to the efficiency of hydrogen evolution were also investigated.

Determination of the best water reduction potential: Fig. 5 shows the effect of chronoamperometric applied potentials on the consumed charge. Brass, stainless steel and low carbon steel used as working electrodes (WE), Pt as counter electrode in 25 % ionic liquid solutions.

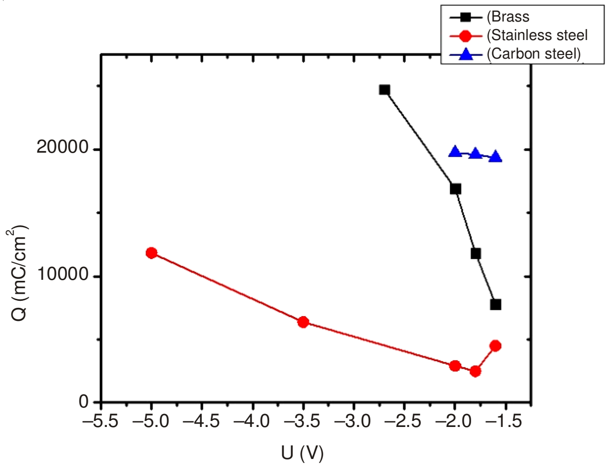


Fig. 5. Dependence of consumed charge on applied potentials in [BMIM][BF_4]

From Fig. 5, it can be seen that increases in negative values of the applied potentials result in larger current densities. With brass as working electrode, |Q| reaches the maximum value of 25 C/cm^2 at -2.7 V, while with stainless steel and low carbon steel, obtained Q are 12 C/cm^2 (at -5 V) and 20 C/cm^2 (-2 V), respectively. The same results were also obtained if the ionic liquid is [DEA][Ac]. Hence, in order to investigate the other parameters, those potentials were chosen for the following experiments.

Determination of the best concentration of ionic liquids: The dependence of the concentration of ionic liquids on the efficiency of the electrolysis process at room temperature is shown in Fig. 6. A -5 V potential was applied on stainless steel in [BMIM][BF_4] and [DEA][Ac] at different concentrations during 15-30 min of electrolysis.

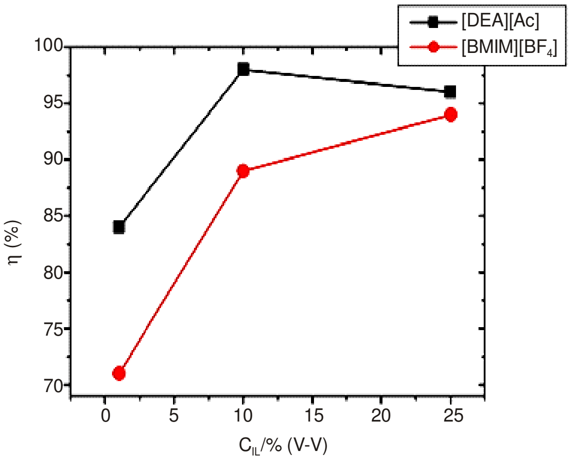


Fig. 6. Dependence of electrolysis efficiency on stainless steel with various concentrations of ionic liquids

It was found that the efficiency (η %) increases from 71 to 89 % when the concentration of [BMIM][BF_4] increases from 1 to 10 %. At 25 %, the value of h increases gradually to 94 %. Similarly, when the ionic liquid used is [DEA][Ac], η % increase from 84 to 98 % then slowly decreases to 96 %. Many reasons can be offered to explain this phenomenon, but the main contribution is probably the variation of the viscosity. At low ionic liquid concentration, the conductivity is low thus η(%) is smaller. Increasing the amount of water decreases the viscosity and enhances the ionic transport, which leads to the observed enhancement of η %[14,19]. However, at the higher concentration (> 25 %) the viscosity of ionic liquid slows down the capacity of hydrogen evolution. Therefore we conclude that 10 % of ionic liquid in water is the suitable ratio for the electrolysis reaction.

Primary investigation on CNT paste electrode: An attempt using CNT paste electrode was made in order to investigate the effect of electrode areas on the efficiency of water electrolytes with ionic liquids. As shown on cyclic voltam-mograms of graphite (1) and CNT paste electrodes (2) in 1 % [BMIM][BF_4] solution (Fig. 7a), although the presence of paraffin oil in CNT paste electrodes increases the Ohmic resistance and reduces actual working areas of electrode, the CNT paste electrode still provides higher current density (2 in Fig. 7a). This observation can be explained by the higher electrochemical activity of individual CNT particles contacting with electrolyte solution on the surface of the electrode. The same effect was found in their current-time curves (Fig. 7b).

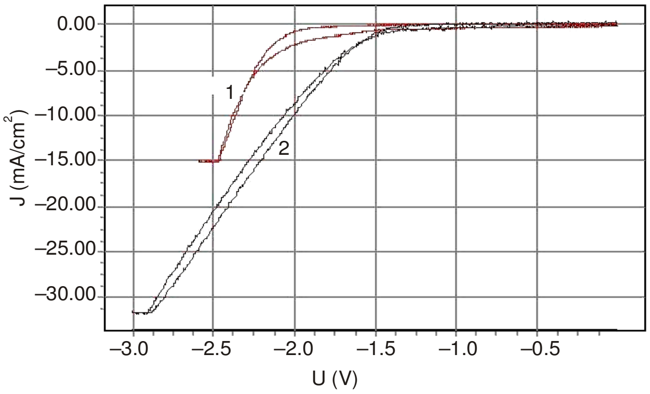


Fig. 7a. Cyclic voltammograms of graphite (1) and CNT paste (2) electrodes in 1 % [BMIM][BF_4] solution

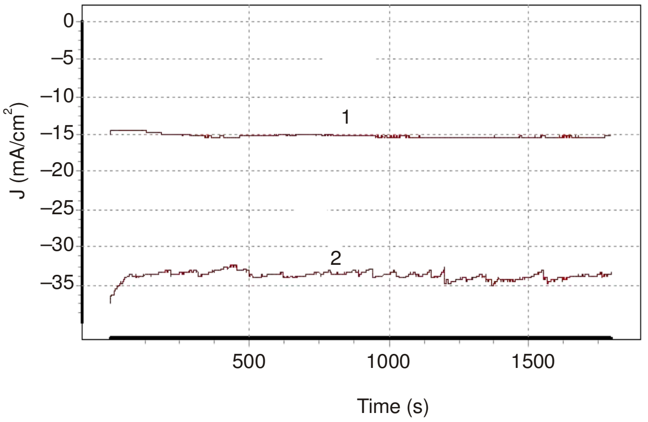


Fig. 7b. Chronoamperometic curves of graphite (1) and CNT paste (2) electrodes in 1 % [BMIM][BF_4] solution

The maximum electrolyte efficiencies on CNT paste electrodes was found in 1 % [BMIM][BF_4] solution at -2.5 and -2 V equal to 94 and 95 %, respectively. At the same time, maximum electrolyte efficiencies found on the graphite electrode in 1 % [BMIM][BF_4] solution at -2 and -1.8 V were equal to only 82 and 79 %, respectively.

Determination of the best material for working electrode: Carbon nanotube is chemically stable and provides rather high electrochemical activity (higher than that on graphite electrode). However CNT only functions as a working electrode in the form of a paste electrode, which in practice is not applicable for water electrolytes. For these reasons, both CNT paste and graphite electrodes were not chosen for further study. Using the results of ionic liquids' concentrations as above and the appropriate reduced potential, we continued to study which is the best material to produce a working electrode (WE) with high electrolyte efficiency *i.e.*, brass, stainless steel or low carbon steel. Obviously the standard quality is based on the overall efficiency of the electrolysis reaction and the stability of electrodes. Fig. 8 shows the comparison between these electrodes in the solutions of [DEA][Ac] at 1, 10 and 25 % and the applied potential is -2 V.

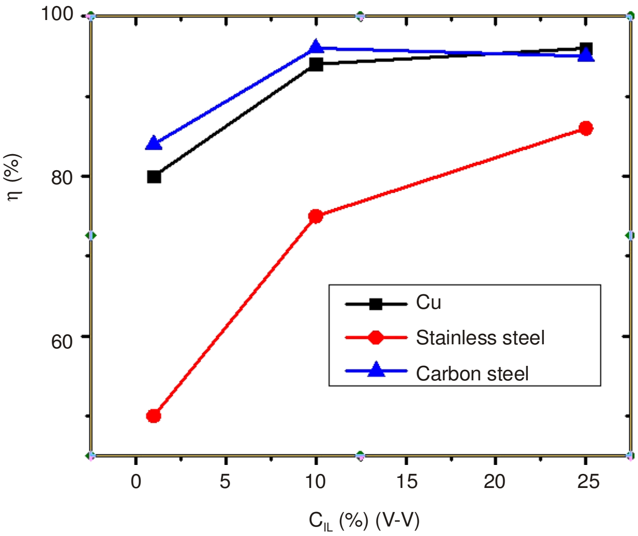


Fig. 8. Effect of the materials of working electrode in different [DEA][Ac] solutions to efficiency η(%)

From Fig. 8, the highest efficiencies were obtained by using carbon steel as the working electrode. If the concentration chosen is 10 %, the received efficiencies of brass, stainless steel and low carbon steel are 94, 75 and 96 %, respectively. Moreover, the stainless steel needs more applied negative potential to obtain the higher efficiency, whereas the brass electrode has low stability. Among those electrodes, carbon steel is considered as the best material to produce a working electrode with the high efficiency of about 96 % at an applied potential of -2 V. However, stainless steel shows more stability during electrolysis. At a more negative potential, its efficiency becomes similar with that noted using CT_3.

Table-1 shows the best efficiencies obtained from optimized electrolysis conditions. The highest value is 99 % with CT_3 in 10 % of [DEA][Ac].

Conclusion

It has been shown that hydrogen production can occur efficiently from the reduction of water in the presence of low concentrations of ionic liquids using different electrode materials. The best concentration of the ionic liquids studied were obtained at 10 vol. % of ionic liquid in water for brass and stainless steel for both ionic liquids and for CT_3 in [DEA][Ac] with hydrogen evolution efficiencies between 94 and 99 %. The materials studied generally had high stability during the electrolysis process, especially in the case of stainless steel. However, there is the possibility of decomposition of [BMIM][BF_4] in water to form F^- in aqueous solution, which may cause corrosion of the metal electrodes used during the electrolysis. That potential problem will be addressed in future studies.

ACKNOWLEDGEMENTS

This research was funded by Viet Nam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03-2010.46. The authors thank Prof. Kakiuchi Takashi (Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University) for providing ionic liquids as gifts.

REFERENCES

1. R.F. Service, *Science*, **296**, 1222 (2002).
2. R.S. Greeley, *Science*, **295**, 1235 (2002).
3. B.C.H. Steele and A. Heinzel, *Nature*, **414**, 345 (2001).
4. S.M. Haile, D.A. Boysen, C.R.I. Chisholm and R.B. Merle, *Nature*, **410**, 910 (2001).
5. R. Ferrigno, A.D. Stroock, T.D. Clark, M. Mayer and G.M. Whitesides, *J. Am. Chem. Soc.*, **124**, 12930 (2002).
6. D.L. Wood III, J.S. Yi and T.V. Nguyen, *Electrochim. Acta*, **24**, 3795 (1998).
7. M.A. Susan, A. Noda, S. Mitsushima and M. Watanabe, *Chem. Commun.*, **8**, 938 (2003).
8. P.A.M. Claassen, J.B. van Lier, A.M. Lopez Contreras, E.W.J. van Niel, L. Sijtsma, A.J.M. Stams, S.S. de Vries and R.A. Weusthuis, *Appl. Microbiol. Biotechnol.*, **52**, 741 (1999).

TABLE-1
EFFICIENCIES OF HYDROGEN PRODUCTION IN VARIOUS IL SOLUTIONS USING DIFFERENT WORKING ELECTRODES

Ionic liquid (IL)	Concentration of IL (%)	η(%)/Material				
		Brass	Stainless steel	CT_3	CNT paste	Graphite
[BMIM][BF_4]	1	98	83	94	94	82
	10	98	97	98	95	79
	25	90	94	96	-	-
[DEA][Ac]	1	80	84	84	80	69
	10	94	98	99	82	72
	25	97	96	95	-	-

9. T.-A.D. Nguyen, S.J. Han, J.P. Kim, M.S. Kim, Y.K. Oh and S.J. Sim, *Int. J. Hydrogen Energy*, **33**, 5161 (2008).
10. R.F. De Souza, J.C. Padilha, R.S. Gonçalves and J. Rault-Berthelot, *Electrochem. Commun*., **8**, 211 (2006).
11. R.F. De Souza, J.C. Padilha, R.S. Gonçalves, M.O. de Souza and J. Rault-Berthelot, *J. Power Sources*, **164**, 792 (2007).
12. Y. She, Y. Tang, H. Liu and P. He, *Chem. Cent. J*., **4**, 17 (2010).
13. H. Liu, Y. Liu and J. Li, *Phys. Chem. Chem. Phys*., **12**, 1685 (2010).
14. C. Zhao, G. Burrell, A.A. Torriero, F. Separovic, N.F. Dunlop, D.R. MacFarlane and A.M. Bond, *J. Phys. Chem. B*, **112**, 6923 (2008).
15. M.G. Freire, C.M.S.S. Neves, I.M. Marrucho, J.A.P. Coutinho and A.M. Fernandes, *J. Phys. Chem. A*, **114**, 3744 (2009).
16. J.D. Wadhawan, U. Schröder, A. Neudeck, S.J. Wilkins, R.G. Compton, F. Marken, C.S. Consorti, R.F. de Souza and J. Dupont, *J. Electroanal. Chem*., **493**, 75 (2000).
17. U. Schroder, J.D. Wadhawan, R.G. Compton, F. Marken, P.A.Z. Suarez, C.S. Consorti, R.F. de Souza and J. Dupont, *New J. Chem*., **24**, 1009 (2000).
18. D.H. Pool, M.P. Stewart, M. O'Hagan, W.J. Shaw, J.A.S. Roberts, R.M. Bullock and D.L. DuBois, *Proc. Natl. Acad. Sci. USA*, **109**, 15634 (2012).
19. A. Safavi, N. Maleki, S. Momeni and F. Tajabadi, *Anal. Chim. Acta*, **625**, 8 (2008).
20. J.P. Feng, W. Jian and Y.Y. Bin, *Chin. Sci. Bull*., **15**, 1781 (2012).
21. A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, John Wiley & Sons, Inc., p. 163 (2001).