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PURITY INVESTIGATION OF HYDROGEN PRODUCED BY HYDROLYSIS OF SODIUM BOROHYDRIDE VIA PHOSPHORIC ACID PROCESS**Sadig Kuliye^{a,*}, Sevgi Fettah^a and Bora Timurkutluk^{b,c}**

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Abstract

In this study, H₂ gas produced by the hydrolysis of sodium borohydride (SBH) in an alkaline medium via phosphoric acid catalyst for PEM fuel cell applications was analyzed. The purity of H₂ gas investigated by electrocatalytic method. High purity 0.5M H₂SO₄ solution with immersed smooth surface Pt electrodesaturated with H₂ gas produced by hydrolysis process. By considering the results of electrochemical pulse techniques and CV (cyclic voltammetry) methods on the smooth surface of Pt electrode, the purity degree of gaseous H₂ determined.

Keywords: *sodium borohydride, catalytic hydrolysis, Pt electrode, H₂SO₄ electrolyte, H₂ gas, pulse techniques, CV.*

1. Introduction

A great deal of research and investments have been made on the hydrogen production and its storage; hydrogen has usage of *wide spread area such as in fuel cells* to generate electricity and it is the cleanest energy source around the world [1, 2]. Hydrogen can be produced from various sources by different methods [3, 4]. Depending on the production method, hydrogen gas may include some impurities such as H₂S, SO₂, NH₃, CO, CO₂ and B₂H₆ [5-9]. Pt based metals widely used as anode catalyst materials in PEM fuel cell which is one of the most common type among other fuel cell types. However, Pt-based catalysts are vulnerable to poisoning by these impurities resulting in a significant degradation of the cell performance and limited service life. For example, it is well known that Pt surface is more easily poisoned by gases such as H₂S, CO, and NH₃ [10, 11]. Beside, a variety of organic compounds, such as alcohols, aldehydes, organic acids, nitrogenous organic compounds and aromatic compounds can be adsorbed simply on the Pt

surface [12, 13]. Therefore, catalysts for PEM fuel cells has to be activated after the catalysts poisoned [14-17].

Hydrogen gas as a fuel for PEM fuel cells fed to anode side for this reason the controllability of purity degree of hydrogen gas is crucial for PEM fuel cells. Future uptake of hydrogen as a fuel is crucially dependent on the availability of hydrogen at a sufficient purity degree because impurities at even trace levels can severely affect the performance of PEM fuel cells. These purity requirements listed in the draft documents of International Standards ISO/DIS 14687-2 and ISO/WD 14687-3[8] indicating the methods essential for the purification of hydrogen gas derived from fossil fuels or biofuels since it may possess sulfur compounds, ammoniac, CO etc.

As known, gas chromatography is a well-known and the most appropriate analysis method for the determination of mixtures in gas content. The detection limit may alter depending on detectors of chromatograph equipped for the gas analysis. For instance,

Thermal Conductivity Detector (TCD) has universal-sample usage for 500 pg/ml while Photo Ionization Detector (PID) for vapor and gaseous compounds from 0.002 to 0.02 µg/L [9]. Gas chromatography identifies traces of variety of compounds in hydrogen gas. However, this method makes it impossible to reveal effect of all compounds identified during measurement of PEM fuel cell performance. Moreover, principle of GC analysis may require a specific column for the determination of each material.

The production of H₂ from various hydrides and the use of H₂ in fuel cells is the focus of attention of researchers for decades. It is possible to separate hydrogen from hydrides by means of thermal and catalytic methods [18, 19]. Sodium borohydride is known to have better hydrogen storage by compared to metal hydrides and much more advantageous than other hydrides. The hydrogen content of its molecular structure is approximately 10.8%. The hydrolysis of sodium borohydride with water makes the quantity of hydrogen redouble. Since hydrogen is also separated from water, the quantity of hydrogen obtained will redouble in the following reaction:



In general, if aqueous solution of NaBH₄ is used, H₂O hydrolysis continues even at very low rates. In order to prevent hydrolysis, alkaline solutions of NaBH₄ are generally used. Hence, a variety of catalysts in solid and liquid phases have been developed in order to obtain that H₂ production either from solid sodium borohydride or its alkaline solutions is under control at a desired rate yielding adequate quantity of H₂ whenever necessary.

Partake of a large number of sources referred in the literature conclude that boranes that poison Pt catalysts number of catalysts into hydrolysis process of NaBH₄ is also referred in the literature [19]. Also, various hydrogen catalysts were reported that they act as hydrogen generators [20-23]. Furthermore, patent studies about hydrogen generators using various hydrolysis catalysts have been intensively continued [20-23]. Generated from hydrolysis of NaBH₄, H₂ is usually used in PEM fuel cells as a fuel. The degree of purity of obtained H₂ may vary due to the type of the

catalyst used in the hydrolysis process specific temperature and concentration of the solution and the rate of H₂ production. A few, may be produced as a result of the hydrolysis process [24]. Due to the high reductive characteristics of BH₄⁻, different intermediate compounds could be formed depending on the nature of hydrolysis catalysts.

The polarization of Pt electrode in an acidic medium contains various processes on the surface of electrode within a certain voltage range. Regions where these processes occur are referred as hydrogen region, double layer region and oxygen region [25]. In these regions, electro-catalytic properties of smooth platinum electrode are similar to surface changes of anode electro-catalysts used in PEM fuel cells under certain conditions. Therefore, PEM anode catalysts' interaction with H₂ gas may be identically interact with H₂ with surface of smooth platinum electrode in sulfuric acid medium.

Effect of produced H₂ gas on the smooth polycrystalline platinum electrode surface analyzed in the study where phosphoric acid solution is used as a hydrolysis catalyst. Furthermore, the purity of produced H₂ gas (produced by electrolysis method) and commercial H₂ gas are compared to these methods. On the other hand, degree of poisoning of smooth Pt electrode due to impurities in H₂ gas mixtures obtained through hydrolysis process considered as a measure of purity for H₂. It is possible to identify degree of poisoning of Pt surface due to the mixtures H₂ gas may contain when no gas (mainly H₂) previously been accumulated on the Pt intensive catalyst that used in PEM fuel cells. It is also possible to determine degree of purity of H₂ under the operating conditions of Pt anode catalyst used in PEM fuel cells. The primary advantage of the suggested concept is based on poisoning of Pt electrode some molecules produced in the process of catalytic hydrolysis of NaBH₄ that H₂ gas may contain. These compounds can be produced as an intermediate or a byproduct due to the effect of reagents used in the hydrolysis reaction. To take into consideration that poisonous molecules for smooth Pt electrode are also

poisonous for the anode catalyst of PEM fuel cells.

2. Experimental

H₂ gas at a certain flow rate can be produced by adding a liquid catalyst to NaBH₄ alkaline solution (4-20%) in a specially designed reactor. In this study, different concentrations of catalyst (25-60% pure H₃PO₄) were considered. To purify hydrogen produced by the hydrolysis reaction from alkaline solution and vapor passed through deionized water trap (has a weak acidic property) in a flow meter, the high purity 0.5M

H₂SO₄ solution at a certain volume (15ml) in an electrochemical cell was fed at 20 ml / min H₂ flow through solution before measurements were made. The total volume of gas flow through the cell was set to 100 ml. Electrochemical cell experiments were performed at 25 °C. To consider the electrochemical cell consists of a Pt disk electrode (D=0.2 mm) as an indicator electrode. The experimental set up is shown in Figure 1.

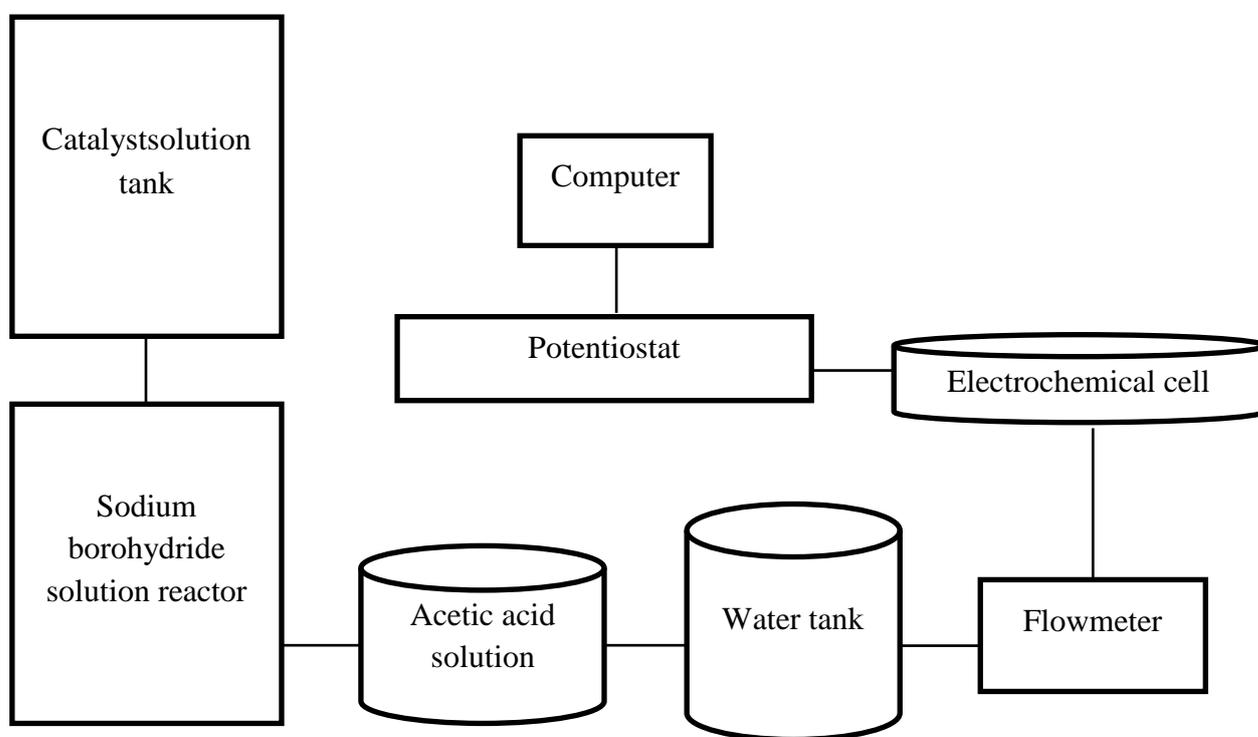


Fig.1. A block diagram of the experimental set up

Moreover, spirally platinum wire (L= 3 cm and D=0.2 mm) was used as an auxiliary electrode. H₂ electrode identified as a reference electrode (reference Pt/Pt electrode immersed in the 0.5 M H₂SO₄ solution, and H₂ gas was continuously fed to the reference

electrode cell at 1 bar pressure). Electrochemical programs were applied to the cell by using IVIUM mark potentiostat. Potential values (E_r) suitable for reference electrode values are shown in Fig 2.

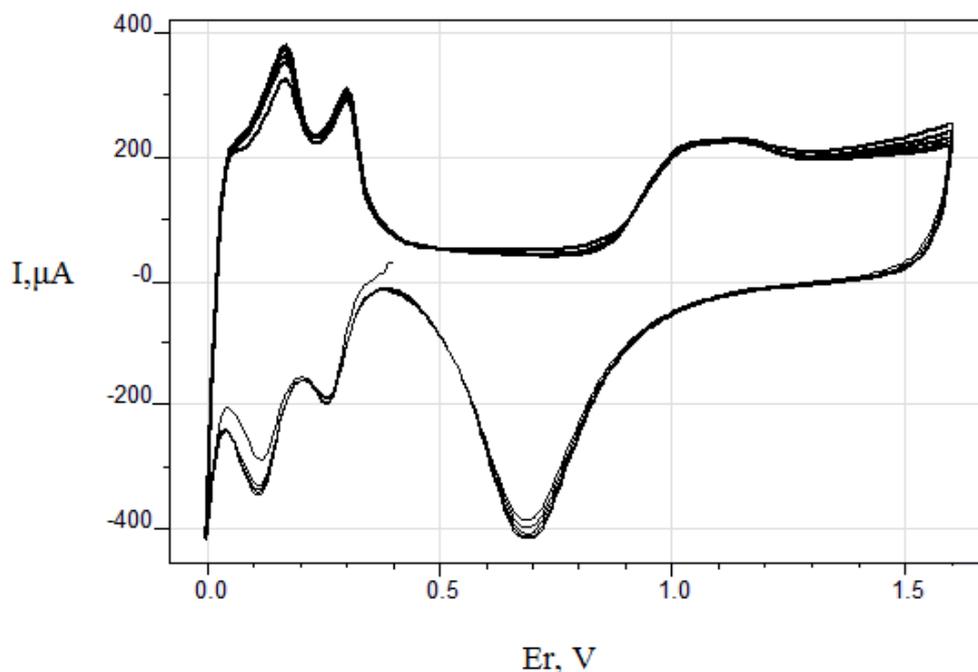
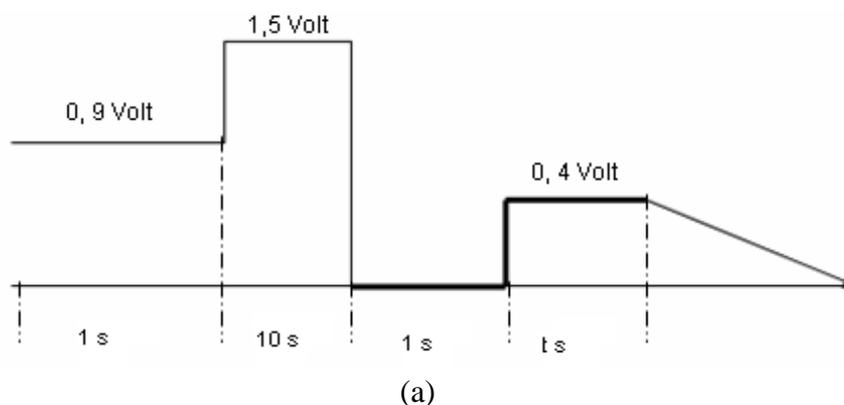


Fig 2. CV of electrochemical activation of Pt electrode in 0.5M H₂SO₄ solution. Starting potential=0.4 V and $dE/dt = 5 \text{ V/s}$

After the activation process, solution in the cell (electrolyte) was renewed via oxygen flow through pure nitrogen gas. The surface of the electrode examined by using three different programs are shown in Fig.3. The first program is applied to the Pt indicator electrode to determine the purity of the electrolyte; the purity of hydrogen gas generated via hydrolysis of SBH and the purity of industrial hydrogen gas. Effect of the impurities on the Pt indicator electrode at 0.4 V constant voltage determined in accordance with the first program. The second program is applied to the

indicator electrode in order to investigate level of poisoning of PEM fuel cell anode fed by hydrogen from the hydrolysis of SBH. The third one, on the other hand, is performed for anodic oxidation of the chemisorbed particles on the electrode surface which was subjected to hydrogen flow from the hydrolysis of SBH followed by the hydrogen desorption on the indicator electrode surface. The same program is also used for the oxidation of the previously chemisorbed particles in the presence of renewed electrolyte.



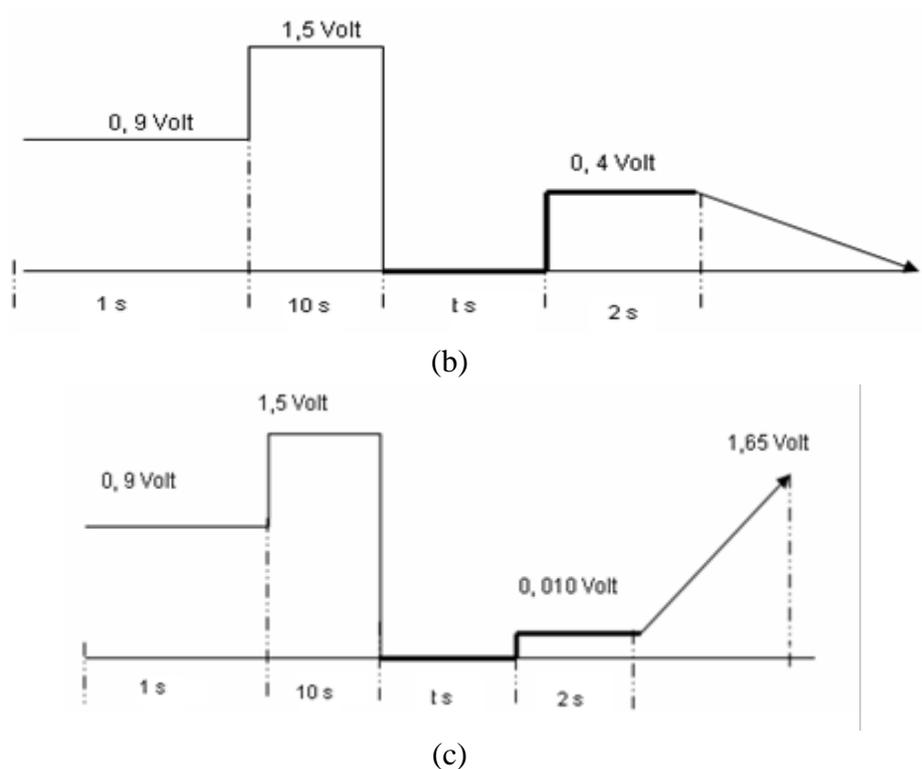


Fig 3. (a) Programme for studying the electrode surfaces and purity of background electrolyte (program 1); (b) program for the studying surface changing at potential $E_r = 0.0V$ (programme 2) and (c) programme for studying the chemisorbed particles at $E_r = 0.0V$ (programme 3)

Results of electrochemical experiments shows that it help to control the purity of hydrogen produced by catalytic hydrolysis method. To

compare obtained result with the same experiments were conducted with commercial electrolytic hydrogen.

3. Results and Discussion

3.1 Determination of electrolyte impurity ratio

Results indicate that impurity of the electrolyte is found to be strongly affected. The purity of background electrolyte before each experiment was controlled via indicator cathodic and anodic potentiodynamic electrode pulses for poisoning effect of impurities on the surface of the electrode. The purity of electrolyte determined by indicator electrode program 1, that the surface of the Pt indicator electrode is very sensitive to impurities in acidic medium under a potential range between $E_r = 0.35-0.75V$. These methods for determination of indicator electrode activity and acidic electrolyte solution purity were

frequently referred in the literature [9, 10]. Before controlling the electrolyte purity, the indicator electrode was activated by using CV in the potential range of 0.0-1.65 V (Fig 2) and then program 2 was applied to establish the purity of solution (I/E_r curves from $E_r = 0.4 V$ potential were taken after 1-300 sec). From these two synchronizing curves given in Fig.4, the difference of charge for adsorption of monolayer hydrogen atoms was characterized via surface state of electrode. This decrease is proportional to the impurities in the electrolyte and could be calculated as $\Delta Q (H) / Q (H_0) = 0.048$.

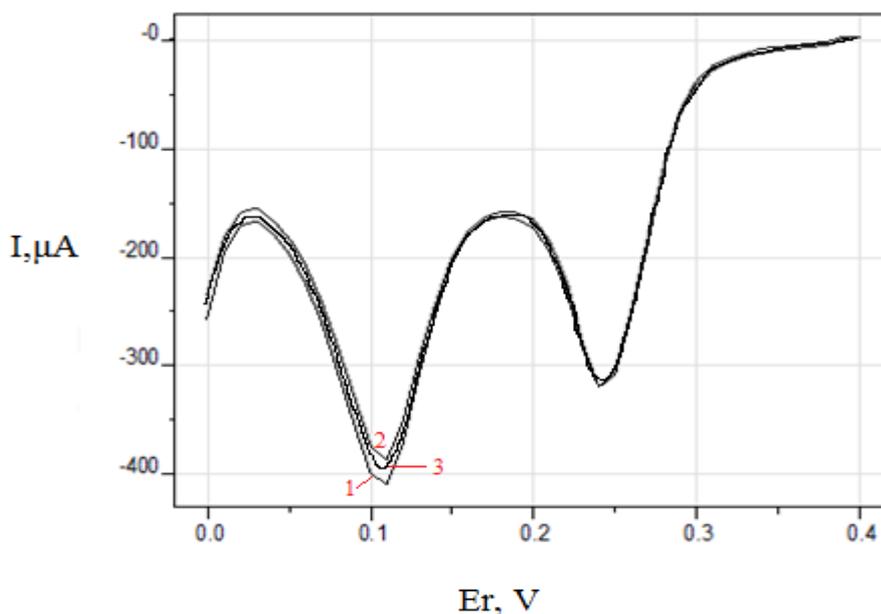


Fig.4. Testing of purity supporting electrolyte and commercial hydrogen gas usage of program 1: $E_r = 0.4V$; 1- $t = 1\text{ sec}$, 2- $t = 300\text{ sec}$; 3- curve restarted after passing through cell 100ml commercial H_2 gas ($V = 20\text{ ml/min}$).

3.2. Tests on commercial hydrogen

After commercial hydrogen gas with a certain flow (20 ml / min) flow through the cell for 300 sec, poisoning ratio of the electrode assessed. In this case, poisoning degree of the electrode surface is the same as

one of the surface electrodes as measured in the first group of tests (Fig 4: curve 3). One can see that commercial hydrogen has higher purity than produced hydrogen by hydrolysis of SBH.

3.3. Analysis of the purity of the hydrogen produced in the hydrolysis process in an alkaline medium of SBH

H_2 gas produced by hydrolysis of SBH introduced to the electrochemical cell and the electrolyte saturated with this gas. At the operation temperature of 298.15 K, the solubility of H_2 gas in water is approx. 0.00155 g/kg [26]. Therefore, the electrolyte solution in the cell contains saturated hydrogen gas with soluble impurity. After H_2 gas produced by hydrolysis of SBH flow through electrolyte, changes in the electrolyte solution of electrode surface analyzed by using program 1 and obtained results are shown in Fig.5. In this case, the hydrogen adsorption charge $Q(H)$ compared with the hydrogen

adsorption charge of pure electrolyte $Q(H_0)$ as follows [12, 13]:

$$\frac{[Q(H_0) - Q(H)]}{Q(H_0)} \geq 0.60. \quad (2)$$

This result determines the impurity of H_2 gas to indicate that despite gas flow through water trap containing weak acidic solution, processing was significantly affected by the purity of the H_2 gas.

On the other hand, as shown in Fig5, the poisoning of hydrogen adsorption centers varies adsorption energy for hydrogen atoms have the same order.

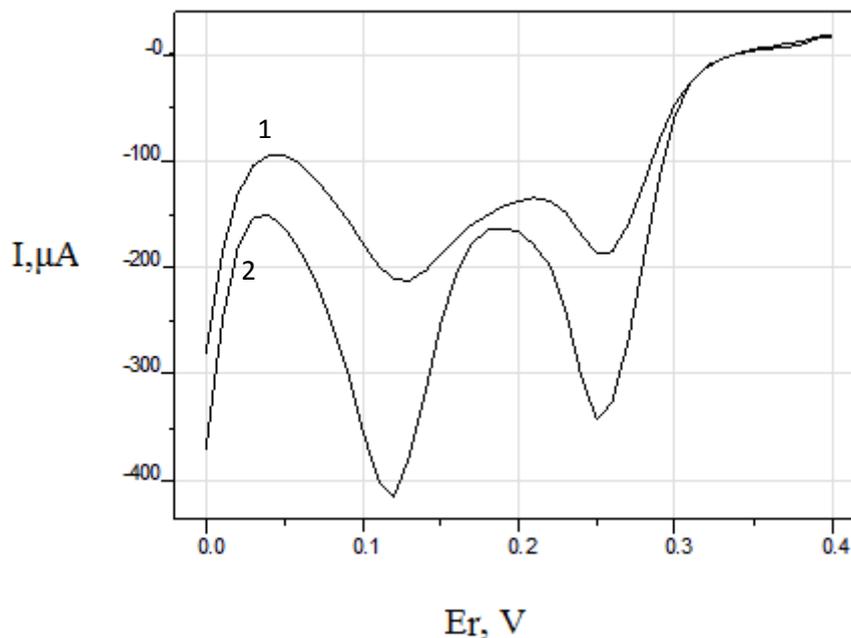


Fig 5. Test for poisoning of the electrode surfaces after saturating electrolyte H_2 gas produced by hydrolysis of SBH. 1-pure electrode surface, 2- in 300sec at constant $E_r=0.4V$ in the saturated H_2 electrolyte.

Take into consideration that potential of the anode catalysts in PEM fuel cell at the open circuit condition at 1 bar hydrogen pressure reaches approximately 0.0V. Poisoning degree of the surfaces by produced hydrogen at this potential taking attention of many researchers. Therefore, the changes on the surface of the indicator electrode analyzed by using program 3. After conduction of activation stages on the electrode surface, the surface adsorption determine dat 0.0 V potential. The surface adsorption was repeated for several times at this potential. Then, the electrode potential changed for 1 sec. Furthermore, anodic potio-dynamic pulses were applied between 0.01 V to 1.65 V. These results are presented on Fig 6. It shows that the surface blocked by adsorbed particles and thus adsorption of hydrogen was diminished. As compared to 0.4 V, the electrode surface was found to be less poisoned at 0.0V potential at this value $-\Delta Q(H) / Q(H_0) \leq 0.20$. In this case, the low

energy of hydrogen adsorption centers proven more sensitive to poisoning.

However, the adsorbed particles have changed the characteristic of anodic I / E_r curves different from in 0.3-0.5 V and 1.15-1.65 V ranges. The oxidation of adsorbed particles was observed in wide potential range 1.15-1.65V without forming an anodic peak. To show adsorption characteristic of the surface adsorbed species (physical or chemical), the electrolyte in the cell was replaced by a new type of electrolyte that pre-purified from oxygen after the adsorption. The solution was renewed at 0.0 V constant potential. Then, the consecutive potio-dynamic pulses were applied on the electrode at 0.01-1.65 V potential range (Fig 7). To compare by previous results (Fig 6), there were no changes in double layer range of potential were seen. In addition, a weak anodic peak was observed at 0.9-1.1 V. At the same time, the value of oxidation (ΔQ_A) was found to decrease at 1.2-1.65 V.

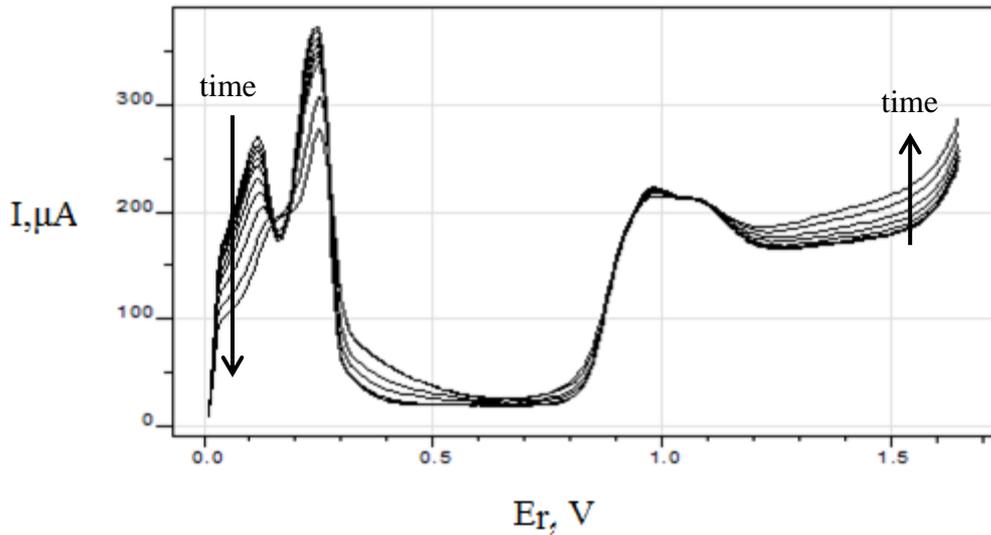


Fig 6. Electro-oxidation of preliminary adsorbed particles at $E_r = 0.0$ V at different adsorption time: 1: 10sec; 2:20 sec; 3:50 sec; 4:100 sec and 5:300 sec. under pulse program 3

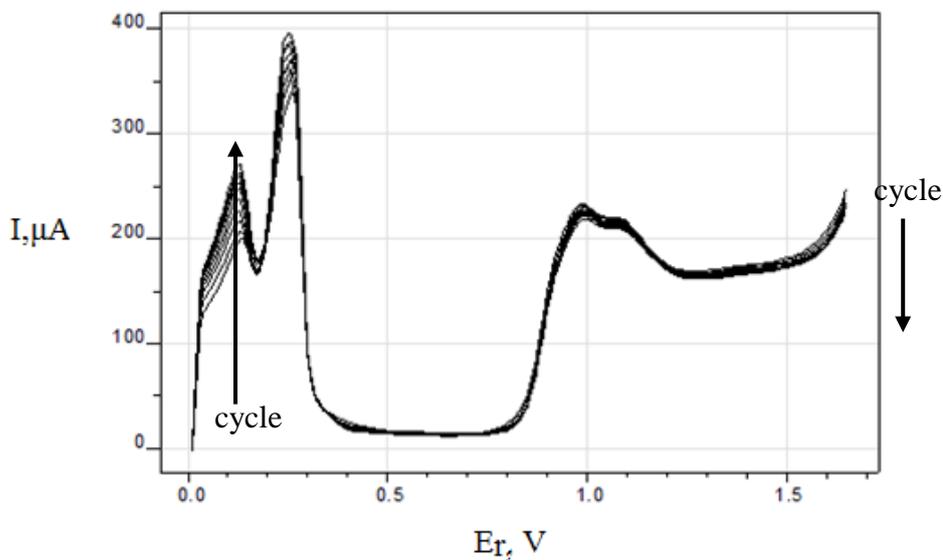


Fig 7. Electro-oxidation of preliminary adsorbed particles at $E_r = 0.0$ V, $t = 300$ sec in renewed electrolyte solution for pulse program 3

4. Conclusion

Sodium Borhydrid is very good reducing agent can form various intermediate compounds that depends on the characteristics of hydrolyzing catalyst used. When H_3PO_4 used as hydrolyzing catalyst of the alkaline solution, obtained hydrogen gas contains impurities. These impurities could not be removed by water trap containing week acidic solution to

take into account that H_2 gas contains impurities poisoning Pt electrode for a very short period of time. So, H_2 gas occurred by the hydrolysis reaction of SBH by H_3PO_4 before use in PEM fuel cell sand should be purified by the specific method. The results are summarized below:

- 1 - Weak and stronger surface adsorbed particles are occurred after adsorbing at 0.0 V;
- 2 - Weakly (physical adsorption) adsorbed particles are cleaned from electrode surfaces in the replacing background solution;
- 3 - Strongly adsorbed particles can be desorbed from the surfaces by using consecutive anodic pulses.

References

1. Song Ch. Overview of Hydrogen Production Options for Hydrogen Energy Development, Fuel-Cell Fuel Processing and Mitigation of CO₂ Emission. *Proc. 20th International Pittsburgh Coal Conference*, Sept 15-19, 2003, Pittsburgh, PA, USA, Paper No. 40-3 (Hydrogen from Coal).
2. Stainberg M., Cheng H.C. Modern and Prospective Technologies For Hydrogen Production From Fossil Fuels. *International J. Hydrogen Energy*, 1989; 14, pp. 797-820.
3. Sunde S. Electrolysis for Hydrogen Production, Haldor Topsøe Catalysis Forum Hornbæk, Denmark, August 24 – 25, 2006. [http://www.topsoe.com/sitecore/shell/Applications/~media/PDF%20files/Topsoe Catalysis Forum/2006/Sunde.ashx](http://www.topsoe.com/sitecore/shell/Applications/~media/PDF%20files/Topsoe%20Catalysis%20Forum/2006/Sunde.ashx)
4. Bagotsky V.S. Fuel Cells Problems and Solutions, John Wiley & Sons, Inc. 2nd Edn. 2012, 320 p.
5. ISO14687:1999E, Hydrogen Fuel product Specification. <http://www.npl.co.uk/upload/pdf/new-methods-for-hydrogen-purity-analysis.pdf>
6. John Kotz, Paul Treichel, John Townsend. Chemistry and Chemical Reactivity - 2014 - Sciences, p.551.
7. Sankaran Murugesan, Vaidyanathan (Ravi) Subramanian. Effect of acid accelerators on hydrogen generation from solid sodium borohydride using small scale devices. *J Power Sources*. 2009, 187, pp.216-223.
8. Abdul-Majeed WS, Serdaroglu CM, Zimmerman WB. Application of liquid nitrogen cold trap for purification of hydrogen gas stream generated from NaBH₄. *J Chem. Chem Eng.* 2012, 6(5):425-434.
9. http://chemwiki.ucdavis.edu/Analytical_Chemistry/InstrumentalAnalysis/Chromatography/GasChromatography.
10. Rockward T., Urdampilleta I., Uribe F.A., Brosha E., Pivovar B., Garzon F. The Effects of Multiple Contaminants on Polymer Electrolyte Fuel Cells. *ECS Transactions* 2007; 11 (1), pp. 821-829.
11. Garzon F., Rockward T., Urdampilleta I., Brosha E.L., Uribe F.A. The impact of Hydrogen Fuel Contaminates on Long-Term PEMFC Performance. *ECS Transactions*, 2006; (1), pp.695-705.
12. Kazarinov V.E., Bagotsky V.S., Vasiliev Y.B., Khazova O.A. Electrochemical Methods For Determination of Organic Impurities And Cations Of Certain Metals In Natural, Drinking And Sewage Water. *Journal of Applied Electrochemistry*. 1988; 18(3), pp.347-356.
13. Fichicioglu F., Kuliyevev S.A., Kadirkan F. Electrochemical Studies of the Adsorption of Aniline on Smooth Polycrystalline Platinum Electrode. *J. Electroanalytical Chemistry* 1996; 408(1-2), pp.231-236.
14. Wilkinson D.P., Clarence Y.F., Allan D.E., Johannes E.P. Method And Apparatus For Operating An Electrochemical Fuel Cell With Periodic Fuel Starvation At The Anode, US Patent 6,096,448; 2000.
15. He C., Qi Z., Kaufman A. Electrochemical Method to Improve the Performance of H₂/air PEM Fuel Cells And Direct Methanol Fuel Cells, US Patent 6,730,424; 2004.
16. Uribe F.A. et al. Cleaning (de-poisoning) PEMFC electrodes from strongly adsorbed species on the catalysis surface. US Patent application publication, US 2006/0249399 A1
17. Janga J.M., Parka G.G., Sohna Y.J., Yima S.D., Kima C.S., Yang T.H. The Analysis on the Activation Procedure of Polymer Electrolyte Fuel Cells. *Journal of Electrochemical Science and Technology* 2011; 2 (3): pp.131-135.

18. Hout J., Bravnsbaek D., Zang J. et al. Mechanochemical Synthesis of Hydrogen Storage Materials, *Progress In Materials Science*. 2013; 58, pp.30-75.
19. Demirci U.D., Akdim O., Andrieux J., Hannauer J., Chamoun R., Miele P. Sodium Borohydride Hydrolysis as Hydrogen Generator: Issues, State of the Art and Applicability Upstream from a Fuel Cell, *Fuel Cells* 2010; 10, pp.335-350.
20. Amendola C.S., Sharp-Goldm S.L., Janjua M.S., Spencer N.S., Kelly M.T., Petillo P.J., Binder M. A safe, Portable, Hydrogen Gas Generator Using Aqueous Borohydride Solution and Ru catalyst. *International Journal of Hydrogen Energy*, 2000; 25, pp.969-975.
21. Hanxi Y., Hua D., Xinping A., Spenqing F.Z., Shuomingshu G. Process and Equipment for The Production of H₂, Patent of China No 20030827
22. Osenar P. Advancement in Sodium Borohydride Fueling Subsystems for Portable applications Small Fuel Cells For Portable Applications, in 8th Annual International Symposium "Small Fuel Cells 2006", April 2-4, 2006, Washington, USA.
23. Sarata T. Small Scale Passive Type PEMFC Using Chemical Hydrides in in 8th Annual International Symposium "Small Fuel Cells 2006", April 2-4, 2006, Washington, USA.
24. Ladovski A.B., Portativniye Istochniki Toka Na Osnove Toplivnikh Elementov. Sbornik Konkursnikh Rabot Molodikh Spesialistov V Ramkakh Mejdunarodnoy Molodejnoj Konferensii. Shkola Seminar Molodikh Uchenix v Oblasti Vodородnikh tekhnologiy dlya proizvodstva energii. Moskva, 2006, pp.182-186.
25. Bard A.J., Faulkner L.R. Electrochemical Methods, Fundamentals and Applications; 2nd ed.; John Wiley and Sons, INC: New York, 2001, 864 p.
26. http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html, accessed: February 2015.

ИССЛЕДОВАНИЕ ЧИСТОТЫ ВОДОРОДА, ПОЛУЧЕННОГО В ПРОЦЕССЕ ГИДРОЛИЗА БОРОГИДРИДА НАТРИЯ С ИСПОЛЬЗОВАНИЕМ ФОСФОРНОЙ КИСЛОТЫ

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Работа посвящена исследованию чистоты водорода, полученного при гидролизе боргидрида натрия в щелочной среде с использованием фосфорной кислоты, для применения его в полиэлектролитном топливном элементе. При этом чистота водорода исследуется электрокаталитическим методом: высокочистый 0.5 М H₂SO₄ раствор с погруженным гладким Pt электродом насыщается газообразным H₂, полученным в процессе гидролиза. По результатам электрохимических импульсных методов и методов CV (циклической вольтамперометрии) на гладкой поверхности Pt электрода, определяется чистота газообразного водорода.

Ключевые слова: боргидрид натрия, каталитический гидролиз, платиновый электрод, электролит, водород, циклическая вольтамперометрия.

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