DOI: 10.6060/ivkkt.20206302.6069

ИССЛЕДОВАНИЕ СИНТЕЗА И ХАРАКТЕРИСТИКИ ЭЛЕКТРОКАТАЛИЗАТОРА, СОДЕРЖАЩЕГО ПЛАТИНУ, ПАЛЛАДИЙ, НИКЕЛЬ ДЛЯ РЕАКЦИИ ВЫДЕЛЕНИЯ ВОДОРОДА В ЩЕЛОЧНОЙ СРЕДЕ

Нгуен Тхи Кам Ха, Хиун Тхы Лан Фыонь, Нгуен Хый Тхо, Нгуен Ван Тхык

Нгуен Тхи Кам Ха, Нгуен Хый Тхо, Нгуен Ван Тхык*

Химический Факультет. Университет естественных наук, Ханойский Государственный Университет, 19 Ле Тхан Тонг, Хоан Кием, Ханой
E-mail: nguyencamha74@gmail.com, thochemist@gmail.com, nguyenvanthuc@vnu.edu.vn*

Хиун Тхы Лан Фыонь

Хиньонский Университет, 170 Ан Дыонь Выонг, Хиньон, Бьин Динь
Химический Факультет. Университет естественных наук, Ханойский Государственный Университет, 19 Ле Тхан Тонг, Хоан Кием, Ханой
E-mail: huynhthilanphuong@qnu.edu.vn

В данной работе были успешно синтезированы методом электроосаждения несколько видов электрокатализатора на основе платины, палладия, никеля со стеклоуглеродным электродом (GC), а затем полученные материалы были применены для процесса электролиза воды в щелочных средах. Морфология поверхности материалов была исследована методом сканирующей электронной микроскопии (SEM). Кроме того, для определения содержания каждого металла в биметаллических материалах был использовал метод энергодисперсионной рентгеновской спектроскопий (EDS). Результат показал, что количество благородных металлов умеренно уменьшилось, в то же время как каталитическая активность была немного выше, чем у чистых металлических электродов. Измерение вольтамперометрий с линейной разверткой потенциала (LSV) проводилось в растворе KOH 1M, чтобы найти перенапряжение реакции выделения водорода (HER). Кроме того, в данной работе для определения обратимой емкости материалов электродов использовали метод циклической вольтамперометрии (CV) в растворе, содержащем 0,01M $K_3[Fe(CN)_6]$ – 0,01M $K_4[Fe(CN)_6]$ - 0,1M KOH. Измерения вольтамперометрий с линейной разверткой потенциала подтвердили, что активность новых катализаторов выше, чем у чистых металлических материалов. Бинарный катализатор (Pt-Ni/GC) может заменить платину для реакции выделения водорода в щелочной среде. Примечательно, что замена атомов платины атомами палладия и никеля и сочетание их хороших свойств приводит к улучшению каталитической активности, и в то же время к снижению стоимости катализатора. Еще раз, на основе электрохимических параметров можно открывать новую перспективу для процесса производства водорода.

Ключевые слова: реакция выделение водорода, платина, палладий, никель, электрокатализатор

STUDY ON SYNTHESIS AND CHARACTERIZATION OF ELECTROCATALYST CONTAINING PLATINUM, PALLADIUM, NICKEL FOR HYDROGEN EVOLUTION REACTION IN ALKALINE MEDIUM

Nguyen Thi Cam Ha, Huynh Thi Lan Phuong, Nguyen Huu Tho, Nguyen Van Thuc

Nguyen Thi Cam Ha, Nguyen Huu Tho, Nguyen Van Thuc*

Faculty of Chemistry, VNU-University of Science, 19 Le Thanh Tong, Hoan Kiem Hanoi, Vietnam
E-mail: nguyencamha74@gmail.com, thochemist@gmail.com, nguyenvanthuc@vnu.edu.vn*

Huynh Thi Lan Phuong

Faculty of Chemistry, VNU-University of Science, 19 Le Thanh Tong, Hoan Kiem Hanoi, Vietnam
Faculty of Chemistry, Quy Nhon University, 170 An Duong Vuong, Quy Nhon, Binh Dinh, Vietnam
E-mail: huynhthilanphuong@qnu.edu.vn

Several kinds of electrocatalyst based on platinum, palladium, and nickel with glassy carbon substrate were successfully synthesized by electrodeposition method, and then applied for water electrolysis in alkaline media. Surface morphology of materials was investigated with scanning electron microscopy method. Energy-dispersive X-ray spectroscopy was used to find the content of each metal in bimetallic materials. The result showed that the number of noble metals was moderately decreased while the catalytic activities were slightly better than pure metal electrodes. Linear sweep voltammetry measurement was taken in KOH 1M solution to find the overvoltage of hydrogen evolution reaction and cyclic voltammetry method in 0.01M $K_3[Fe(CN)_6]$: 0.01M $K_4[Fe(CN)_6]$ in 0.1M KOH was used to determine the reversible capacity of material electrodes. The linear sweep voltammetry measurements confirmed that the activities of new catalysts are higher than the origin materials. The binary catalyst of Pt-Ni can replace platinum for hydrogen evolution reaction in alkaline medium. Notably, the replacement of platinum atoms with palladium and nickel atoms, and the combination of good properties of them leads to improve the catalytic activity, and in the same time to decrease the catalyst cost. Once again, the electrochemical parameters open up a new prospect for the hydrogen produce.

Key words: hydrogen evolution reaction, platinum, palladium, nickel, electrocatalyst

Для цитирования:
Нгуен Тхи Кам Ха, Хиун Тхы Лан Фыонь, Нгуен Хый Тхо, Нгуен Ван Тхык Исследование синтеза и характеристики электрокатализатора, содержащего платину, палладий, никель для реакции выделения водорода в щелочной среде. *Изв. вузов. Химия и хим. технология*. 2020. Т. 63. Вып. 2. С. 52–58

For citation:
Nguyen Thi Cam Ha, Huynh Thi Lan Phuong, Nguyen Huu Tho, Nguyen Van Thuc Study on synthesis and characterization of electrocatalyst containing platinum, palladium, nickel for hydrogen evolution reaction in alkaline medium. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* [Russ. J. Chem. & Chem. Tech.]. 2020. V. 63. N 2. P. 52–58

INTRODUCTION

In the last two decades, because of rising the oil price and the growing concern of climate change, the interested in renewable energy sources have been dramatically grown up. One way of stabilizing the energy supply is to diversify sources of energy that can be produced when there were a supplementary of renewable energy and used when it is deficient in renewable energy. There is multiple choices for renewable energy sources such as sun, wind, biomass, etc. However, sun and win do not provide stable supply and can be used for the small scale production only.

Up to now, hydrogen is the most promising candidate for energy carrier [1] since the energy can be stored in the form of chemical energy and transformed into electrical energy in fuel cells (FCs) [2]. The use of hydrogen in FCs does not damage the environment because of the only by-product is water.

There are many methods to produce hydrogen [3]. In recent time, the most popular technique is based on fossil fuels, from natural gas, we can steam reforming, partial oxidation or autothermal reforming to get the H_2. Another way, from coal, a variety of gasification processes also be used to produce H_2 [3]. Although this source can produce a huge amount of hydrogen, the quality of the product is not good. In addition, this source still depends on fossil fuels, which we need to replace.

From the late 1920s, water electrolysis was the first technology used to produce pure hydrogen [3]. This method has many advantages compared with the others: first, it has a simple principle, we only need to apply direct current (DC) to the water, if the energy is large enough, the O-H bond can be broken to form H_2 and O_2. However, this technology has large trouble that is the O-H bond is one of the most stable single bonds, and we need a high current to split it. To reduce this energy, we need to use a catalyst with some special parameter. Jaccaud et al [4] summarized which are the properties of an ideal electrocatalytic cathode need: a) low hydrogen overvoltage, b) no change potential in time, c) good chemical and electrochemical stability: long lifetime and no release of process-toxic products, d) high adhesion to the support, e) low sensitivity to poisoning by impurities, f) low sensitivity to current shut down (short-circuit) or modulation, g) no safety or environmental problems in the manufacturing process, h) easy to prepare at a low cost/lifetime ratio. Therefore, considering the strict criteria to be satisfied, choosing the most appropriate electrode material is not an easy task. In recent times, there have been many studies with the aim of improving the efficiency for hydrogen evolution reaction (HER) in different environments [5-8].

Up to now, many research that the best catalyst for HER is Pt [9-10] Nevertheless, the cost of Pt is very expensive and the source of this is limited, the problem is how to reduce the content of Pt in the composition of catalyst but the catalytic activity is unchanged or better than using pure Pt catalyst. The modified Pt and composite material, containing Pt have been studied and applied to the HER [11-13].

For the alternative choice of the catalyst of water electrolysis, Pd is one of the candidate base on the low overvoltage [14]. Pd, either in its pure form or as part of bimetallic systems, has been widely investigated as electrode material. Most studies have focused on the interaction between Pd and hydrogen. During the last decades, interest in these systems peaked several times, such as in the 1970s, due to the discovery of superconducting properties of PdHx, or at the end of the 1980s, when the possibility of cold fusion was announced. The latter turned out to be one of the major fiascos in science. Anyway, these facts demonstrate the passions that this system can awaken, and, independent of how serious the motivations were, it is a widely investigated system [15]. Although Ni is non-noble metals, it has one of the most interesting candidates for HER [2, 16-19], because of the high conductivity. However, the major problems encountered with using this metal alone as a cathode are its low catalytic activity or low resistance to intermittent electrolysis. Therefore, Ni has always been used in the form of alloy to increase its catalytic activity. Due to excellent resistance to corrosion of Ni in hot concentrated alkaline solutions [20], we favor using alkaline media than acidic media in this study.

This process can be played in acidic media, but it is not good for some kind of electrode because of the stripping non-noble metal. Alkaline media is the better choice for application for FCs because it avoids the corrosion problems which is caused by acid electrolytes [21].

From views of above, the goal of this research is to synthesize novel materials, which can be used as a cathode for HER by depositing Pt, Pd, Ni in GC substrate to form bimetallic catalysts with high catalytic activities andgood corrosion resistance.

EXPERIMENTAL

Chemical: Na_2PdCl_4 (Aldrich), K_2PtCl_4 (Aldrich), $NiSO_4.6H_2O$ (Merck), $C_3H_5(OH)_3$ (Merck), KOH (Merck), H_2SO_4 (Merck), H_3BO_3 (AR - China), NaCl (AR - China).

Preparation of electrode materials:

Glassy carbon electrode (GC) was polished using sandpaper C-2000 and was washed several times with distilled water. After that, the electrode was cleaned by ultrasonic device, using solution HNO_3 1M for 2-5 min, continues to be polished and cleaned. Then the electrode was treated under cyclic voltammetry condition in the solution of H_2SO_4 0.1 mol/l from -1.8 V to 1.8 V, scan rate 50 mV/s, until the reproducible cyclic voltammogram was obtained. Normally, it takes 5-10 cycles. This step is implemented to ensure removing organic compounds. Then it is washed carefully with water several times and conducts the electrolysis process. Conditions for each electrode material are shown in Table 1.

Table 1

Condition for electroplating process

***Таблица 1*. Условия для процесса электроосаждения**

Type of materials electrode	Component of electrolyte solution	Value of electrolysis potential(V)
Pt/GC	K_2PtCl_4 1mM in H_2SO_4 1M	0.20
Pd/GC	Na_2PdCl_4 1mM in H_2SO_4 1M	0.25
Ni/GC	$NiSO_4$ 1M in buffer solution containing H_3BO_3 (15 g/l), NaCl (30 g/l).	-0.69
Pt-Ni/GC	K_2PtCl_4 1mM, $NiSO_4$ 60mM in buffer solution containing H_3BO_3 (15 g/l), NaCl (30g/l).	-0.28
Pd-Ni/GC	Na_2PdCl_4 1mM, $NiSO_4$ 60mM in buffer solution containing H_3BO_3 (15g/l), NaCl (30g/l).	-0.22

In the case of *co*-deposit to get bimetallic electrode (Pd-Ni/GC and Pt-Ni/GC), the mechanism of electroplating of two components is more complicated. There are two possible processes can take place: two components will be reduced and deposited together onto the substrate, or we apply a potential which lets Ni deposited the first, and then Pt ion will react with Ni at the same moment. Because Ni and Pt have depositing potential far to each other, so we choose first method. And we run the process of electrodeposition by follow condition. We choose decomposition potential which is more favor with the electroplating process of K_2PtCl_4. Selecting a high concentration of Ni^{2+} and a favorable concentration of pH for Ni precipitation.

Characterization and electrochemical measurements

The morphology of the film surface was studied by an SEM-JEOL-JSM 5410LV scanning electronic microscope (SEM), 10 kV, working distance 8-19 mm, maximum zoom × 200.000 times. For the bimetallic catalysts, the content of each metal was investigated by Energy dispersive X-ray spectroscopy (EDS) method.

All the electrochemical measurements were conducted in a system three-electrode cell (Autolab 30

– Netherlands), with an AgCl/Ag (in 3M KCl) reference electrode (RSE), a Pt wire counter electrode and a working electrode. Electrochemical behavior of the materials for HER catalysis was studied with the methods of linear sweep voltammetry in KOH 1M with scan rate 50mV/s. Besides that the electron exchange capacity of the film was investigated by cyclic voltammetry method in $K_3[Fe(CN)_6]$ 0.01M: $K_4[Fe(CN)_6]$ 0.01M in KOH 0.1M (Ferri/Ferro system).

RESULT AND DISCUSSION

Morphology of the surface and composition electrodes

By comparing the SEM images of materials before and after deposit metal on GC surface (Fig. 1) we can recognize that there is a lot of change in morphology of it. Initially, the GC surface is very smooth and sleek, after depositing, there are many particles with different size in this surface. In the case of modified Pt/GC and Pd/GC electrode, as can be seen, the particles are uniformly distributed with a size approximately 100 nm scale. In the image of Pt/GC, the boundary of the Pt particles is more clearly. From this information, we easily see that the amount of noble metal was significant decrease compared with pure metal Pt electrode but the catalytic activity, which we will discuss in the next part, is remain unchanged. Case of depositing Ni is slightly different, the surface of the material is eschar with the size in µm scale. This difference can be explained by the change in the concentration of electrolyte. Besides that the nature of the material also is one of the suitable reason. When comparing with the result of the modified bimetallic electrode, we can see another picture. Although we still receive materials with very small in particles size (Pt-Ni/GC, Pd-Ni/GC), in this case, the average particle size is about less than 100 nm, and smaller than a case of Ni. The SEM images point out the homogenous structure, means Pt and Pd existed in alloy form with Ni. From this data, we can initially confirm the metal particles had been successfully deposited on the GC surface in both cases.

In the case of the bimetallic electrode, to investigating the content of each metal we use the EDS spectrum. The results about the amount of each metal in the composition of Pd-Ni/GC electrode and Pt-Ni/GC electrode are shown in Fig. 2, respectively.

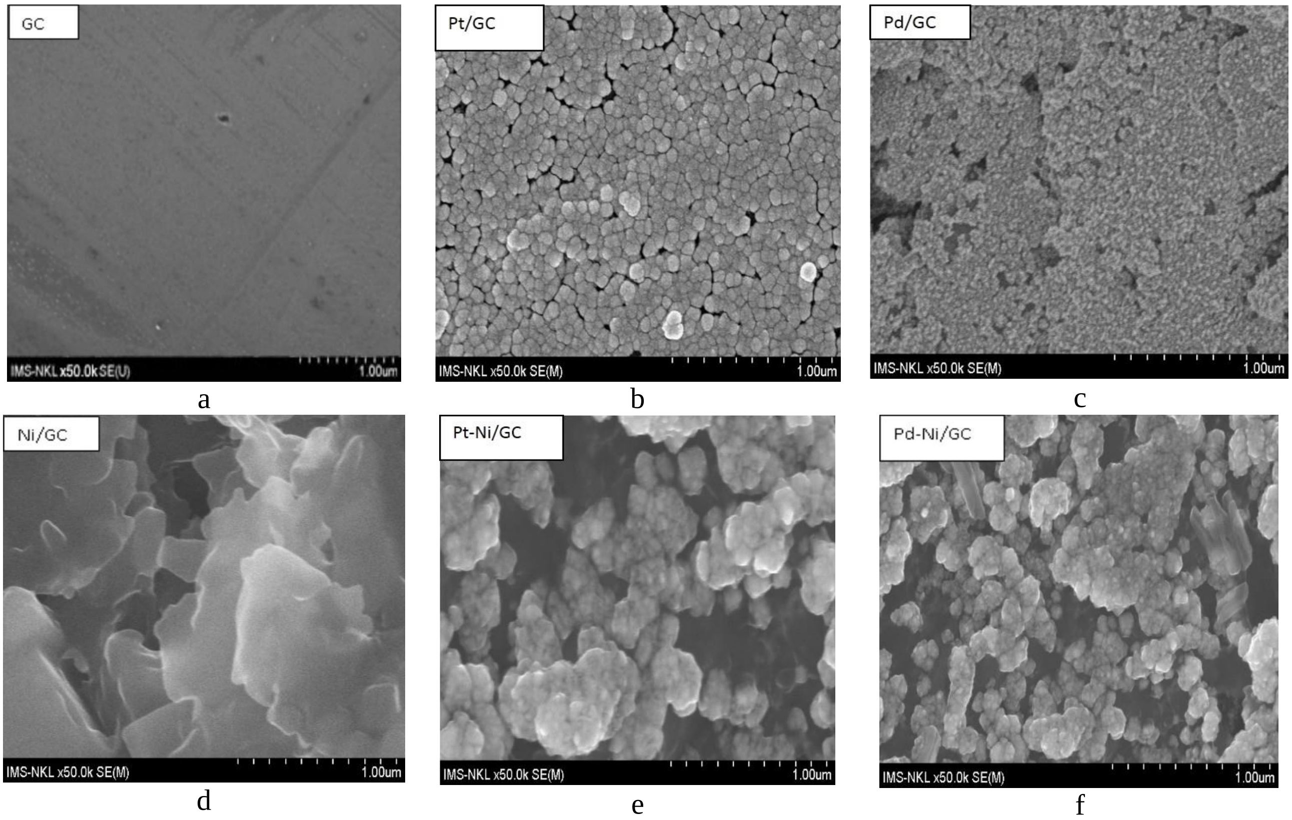
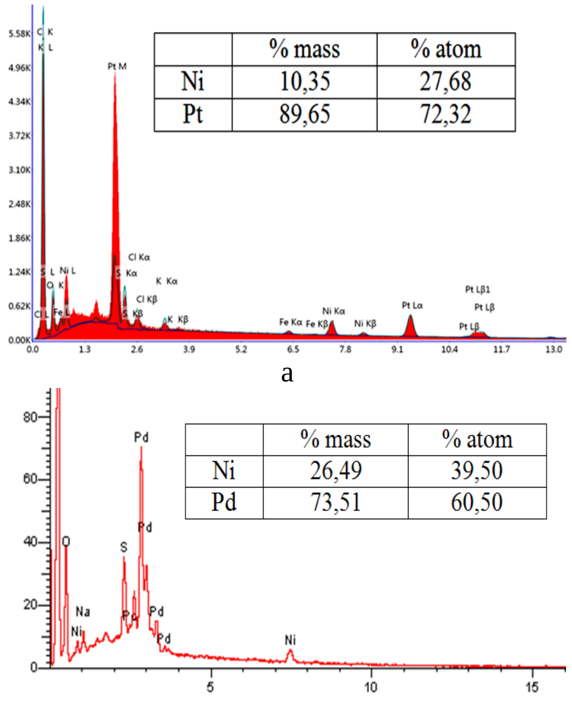


Fig. 1. SEM images of GC (a), Pt/GC (b), Pd/GC (c), Ni/GC (d), Pt-Ni/GC (e) and Pd-Ni/GC (f) electrodes surface
Рис. 1. Электронные микрофотографии поверхности электродов GC (a), Pt/GC (b), Pd/GC (c), Ni/GC (d), Pt-Ni/GC (e) и Pd-Ni/GC (f)



	% mass	% atom
Ni	10,35	27,68
Pt	89,65	72,32

a

	% mass	% atom
Ni	26,49	39,50
Pd	73,51	60,50

b

Fig. 2. EDS spectrum of Pt-Ni/GC (a) and Pd-Ni/GC (b) electrodes

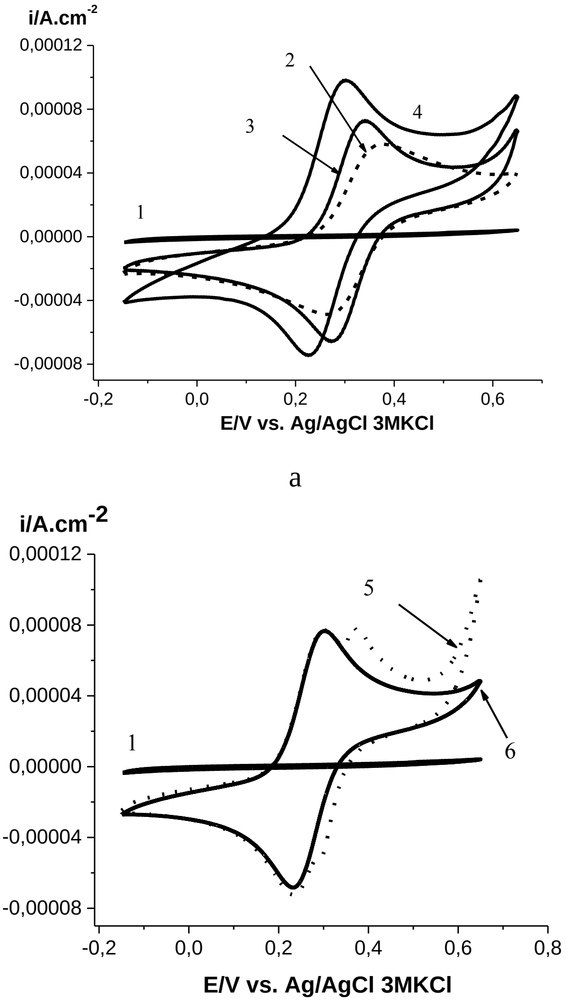
Рис. 2. Энергодисперсионные рентгеновские спектры Pt-Ni/GC (a) и Pd-Ni/GC (b) электродов

In the EDS spectrum (Fig. 2) show the appearance of metals characteristic energy levels with corresponding components on the surface of the material (attached tables). The results reconfirm the co-deposition of the two metals on the GC. EDS results obtained show metal components in composite materials that are different from the salt concentration ratio of the two metals initially. This can be explained by the electrolysis mode selection priority to the discharge of Pt and Pd metal.

Study the electron exchange capacity of membrane

To evaluate the electron exchange capacity of new materials, the electrodes were measured in a mixture of $K_3[Fe(CN)_6]$0.01M, $K_4[Fe(CN)_6]$ 0.01M in KOH 0.1M (Ferro/Ferri system) by the cyclic voltammetry method. Fig, 3 shows the result of this measurement.

From the Figure and Table above, we can see that the equilibrium voltage of Pt/GC is highest, the second value is Ni/GC, then Pd/GC, the bimetallic electrodes have smaller value so that the Pt/GC electrode is the most reversible. But Ni/GC has the highest current density so that is the best conductivity. This order can be explained by the amount of metal on the surface electrode because the concentration of Ni^{2+} solution is much higher than the $PtCl_4^{2-}$ and $PdCl_4^{2-}$ solution. However, the catalytic activities of Pt/GC and Pd/GC are higher than that of Ni/GC. This result once again confirms that the HER not only is an electrochemical reaction but also is catalyzed by the cathode. Moreover, due to differences in ΔE value between the modified monometallic electrode and bimetallic electrode, once again we can confirm that the co-electrodepositing of 2 metals on the GC surface is successful. Due to ΔE value, the reversible capacity is increased by the following order: Pd-Ni/GC → Pt-Ni/GC → Pd/GC → Ni/GC → Pt/GC.



a

b

Fig. 3. Cyclic voltammogram of modified monometallic electrodes (a) and bimetallic electrodes(б) in mixture of 0.01M $K_3[Fe(CN)_6]$0.01M, 0.01M $K_4[Fe(CN)_6]$, 0.1M KOH at a scan rate of 50 mV/s. Respectively of 1 (GC); 2 (Pt/GC); 3 (Pd/GC); 4 (Ni/GC); 5 (Pt-Ni/GC); 6 (Pd-Ni/GC)

Рис. 3. Циклические вольтамперограммы модифицированных монометаллических электродов (а) и биметаллических электродов (б) в смеси 0,01M $K_3[Fe(CN)_6]$- 0,01M $K_4[Fe(CN)_6]$ – 0,1M KOH при скорости сканирования 50 мВ/с

Table 2

The potential difference between reduction peak and oxidation peak of novel material electrodes in Ferri/Ferro system

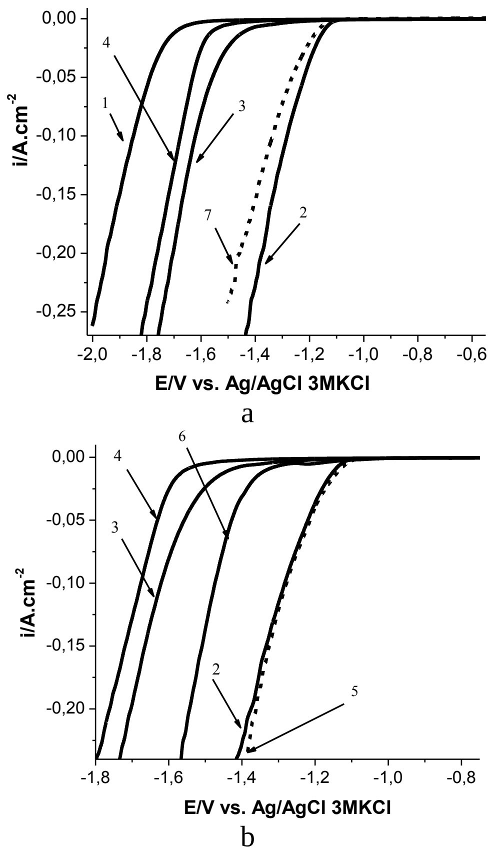
Таблица 2. Разность потенциалов между восстановительным и окислительным пикам металических электродов в ферро-ферри-системе

Electrode	ΔE(V)
Pt/GC	0.112
Pd/GC	0.068
Ni/GC	0.076
Pt-Ni/GC	0.059
Pd-Ni/GC	0.045

Catalytic activity analysis of material

The most important property of these materials is the overvoltage for HER, due to this value, we can find the best model to apply for fuel cells. In this study, the overvoltage of the novel materials is conducted by taking the linear sweep voltammetry method in 1M KOH solution (to get longer lifetime for electrodes to contain Ni in their composition). Fig. 4 shows the result of this experiment.

As can be seen from the figure above the overvoltage of HER in (a), which is controlled by the Pt/GC electrode is approximately to the pure Pt electrode. This is a piece of very interesting information because the modified electrode is much cheaper than Pt bulk electrode (base on the content of Pt). For the case of Pd/GC, Ni/GC the overpotential is very different from GC electrode, this is once again confirmed that precipitation of particles of Pd, Ni on the surface of glassy carbon electrode. Although Pd, Ni has good catalytic activity, they not as good as Pt. In spite of the high conductivity, it has higher overvoltage than the others. The most suitable reason for this phenomena is that the overvoltage is depended on another property of electrode that is the adsorptivity of materials. This interpretation was proof by mechanism, given by N. Krstajić et al [22]. Table 3 shows the full expression of this.



a

b

Fig. 4. Polarization curves of modified monometallic electrodes (a) and bimetallic electrodes(б) in 1M KOH at a scan rate of 50 mV/s. Respectively of 1 (GC); 2 (Pt/GC); 3 (Pd/GC); 4 (Ni/GC); 5 (Pt-Ni/GC); 6 (Pd-Ni/GC) ; 7 (Pt-pure)

Рис. 4. Поляризационные кривые монометаллических электродов (a) и биметаллических электродов (б) в 1M KOH при скорости сканирования 50 мВ/с

Table 3

Stoichiometric equations and rates for three basic steps of the HER

***Таблица 3.* Стехиометрические уравнения и скорости для трех основных ступеней реакции выделения водорода**

Name of the step	Stoichiometric equation	Theoretical rate law
Volmer	$M + H_2O + e^- \rightarrow MH_{ads} + OH^-$ (1)	$v_1 = k_1(1-\theta_H) - k_{-1}\theta_H$ (4)
Heyrovsky	$MH_{ads} + H_2O + e^- \rightarrow M + H_2 + OH^-$ (2)	$v_2 = k_2\,\theta_H - k_{-2}(1-\theta_H)$ (5)
Tafel	$2MH_{ads} \rightarrow 2M + H_2$ (3)	$v_3 = k_3\,\theta_H^2 - k_{-3}(1-\theta_H)^2$ (6)

Note: M represents the materials, which are used to making cathode of systems

Примечание: M – материал, который использовался для катода

Due to the high conductivity of Ni and Hydrogen adsorptivity of Pt, the combination of two metals has been studied. In the case of Pt-Ni/GC electrode (b), the first thing we can say about is the synthesized material has good catalytic activity for electrolysis of water in KOH solution. The overvoltage is approximately as on a Pt/GC electrode. That means the energy need for procedure H_2 is lower. It also confirms that our material has both Ni and Pt. The current of binary catalyst is higher than Pt or Ni. From that result, somehow we can conclude that the binary catalyst has better performance to electrolysis of water. Moreover, when we combine two metal the content of Pt decrease compare with Pt/GC, so this makes the product is more economical. These properties can be explained by the change of structure when 2 metal co-precipitated when Ni has been changed it increases activity by the bimetal effect. Although the difference between Pt/GC and Pt-Ni/GC electrode is not clear, the case of Pd/GC, Ni/GC, and Pd-Ni/GC has a better view with overvoltage of the bimetallic electrode is significantly lower than the modified monometallic electrode. In addition, the better activity will lead to the new solution for the problem of overvoltage of HER in case of water electrolysis. In the future, we can combine more transition metals with specific properties such as conductivity, or adsorption activity, etc. to get better materials for this problem.

CONCLUSION

Several novel materials, which support for electrolysis alkaline solution to produce H_2, were successfully synthesized by electroplating method. Some important properties, including exchange capacity and catalytic activity, were evaluated by electrochemical techniques like CV, LSV. The LSV measurements confirmed that the activities of new catalysts are higher than the origin materials. The binary catalyst of Pt-Ni can replace platinum for hydrogen evolution reaction in alkaline medium. Notably, the replacement of platinum atoms with palladium and nickel atoms, and the combination of good properties of them leads to improve the catalytic activity, and in the same time to decrease the catalyst cost. These results are very interesting for the development of electrolysis of water.

REFERENCES
ЛИТЕРАТУРА

1. **Dresselhaus I., Thomas M.S.** Alternative energy technologies. *Nature*. 2001. V. 414. P. 332–337. DOI: 10.1038/35104599.
2. **Nikolic V.M., Maslovara S.L., Tasic G.S., Brdaric T.P., Lausevic P.Z., Radak B.B., Marceta Kaninski M.P.** Kinetics of hydrogen evolution reaction in alkaline electrolysis on a Ni cathode in the presence of Ni-Co-Mo based ionic activators. *Appl. Catal. B Environ*. 2015. V. 179, P. 88–94. DOI: 10.1016/j.apcatb.2015.05.012.
3. International Energy Agency. Hydrogen Production and Storage. R&D Priorities and Gaps. Hydrog. Implement. Agreem. 2006. V. 13. P. 392.
4. **Jaccaud M., Leroux F., Millet J.C.** New chlor-alkali activated cathodes. *Mater. Chem. Phys.* 1989. V. 22. P. 105–119. DOI: 10.1016/0254-0584(89)90033-3.
5. **Eftekhari A.** Electrocatalysts for hydrogen evolution reaction. *Int. J. Hydrogen Energy*. 2017. V. 42. N 16. P. 11053-11077. DOI: 10.1016/j.ijhydene.2017.02.125.
6. **Kuzminykh M.M., Panteleeva V.V., Shein A.B.** Cathodic hydrogen evolution on iron disilicide. II. Acidic solution. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2019. V. 62. N 2. P. 59-64. DOI: 10.6060/ivkkt.20196202.5750.
7. **Shi Y., Zhang B.** Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. *Chem. Soc. Rev.* 2016. V. 45. P. 1529–1541. DOI: 10.1039/C5CS00434A.
8. **Kuzminykh M.M., Panteleeva V.V., Shein A.B.** Cathodic hydrogen evolution on iron disilicide. I. Alkaline solution. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2019. V. 62. N 1. P. 38-45. DOI: 10.6060/ivkkt.20196201.5745.
9. **He Z., Wei J., Chen Y., Santos E., Schmickler W.** Hydrogen evolution at Pt(111)- activation energy, frequency factor and hydrogen repulsion. *Electrochim. Acta*. 2017. V. 255. P. 391-395. DOI: 10.1016/j.electacta.2017.09.127.
10. **Ojani R., Valiollahi R., Raoof J.B.** Comparison between graphene supported Pt hollow nanospheres and graphene supported Pt solid nanoparticles for hydrogen evolution reaction. *Energy*. 2014. V. 74. P. 871-876. DOI: 10.1016/j.energy.2014.07.062.
11. **Kelly T.G., Lee K.X., Chen J.G.** Pt-modified molybdenum carbide for the hydrogen evolution reaction: From model surfaces to powder electrocatalysts. *J. Power Sour*. 2014. V. 271. P. 76-81. DOI: 10.1016/j.jpowsour.2014.07.179.
12. **Greeley J., Thomas F.J., Jacob B., Ib Chorkendorff, Jens K.N.** Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. *Nature Mater*. 2006. V. 5. P. 909–913. DOI: 10.1038/nmat1752.
13. **Sukanta C., Chinnakonda S.G, Retna R.C.** Polymer-based hybrid catalyst of low Pt content for electrochemical hydrogen evolution. *Int. J. Hydrogen Energy.* 2017. V. 42. N 36. P. 22821-22829. DOI: 10.1016/j.ijhydene.2017.07.152.
14. **Wang M. Wang Z., Gong X. Guo Z.** The intensification technologies to water electrolysis for hydrogen production - A review. Renew. *Sustain. Energy Rev.* 2014. V. 29. P. 573–588. DOI: 10.1016/j.rser.2013.08.090.
15. **Quaino P., Santos E.** Hydrogen evolution reaction on palladium multilayers deposited on Au(111): A theoretical approach. *Langmuir*. 2015. V. 31. P. 858–867. DOI: 10.1021/la503881y.
16. **Li Y., Zhang X., Hu A., Li M.** Morphological variation of electrodeposited nanostructured Ni-Co alloy electrodes and their property for hydrogen evolution reaction. *Int. J. Hydrogen Energy*. 2018. V. 43. P. 22012-22020. DOI: 10.1016/j.ijhydene.2018.10.038.
17. **Nikolic V.M., Maslovara S.L., Tasic. G.S., Brdaric T.P., Lausevic P.Z., Radak B.B., Kaninski M.P.M.** Kinetics of hydrogen evolution reaction in alkaline electrolysis on a Ni cathode in the presence of Ni-Co-Mo based ionic activators. *Appl. Catal. B: Environ.* 2015. V. 179. P. 88–94. DOI: 10.1016/j.apcatb.2015.05.012.
18. **Hong S.H., Ahn S.H., Choi J., Kim J.Y., Kim H.Y., Kim H.J., Kim H., Kim S.K.** High-activity electrodeposited NiW catalysts for hydrogen evolution in alkaline water electrolysis. *Appl. Surf. Sci.* 2015. V. 349. P. 629–635. DOI: 10.1016/j.apsusc.2015.05.040.
19. **Shamsul Huq A.K.M., Rosenberg A.J.J.** Electrochemical behavior of nickel compounds: I. The hydrogen evolution reaction on NiSi, NiAs, NiSb, NiS, $NiTe_2$, and their constitu ent elements. *Electrochem. Soc.* 1964. V. 111. N 3. P. 270-278. DOI: 10.1007/BF02849200.
20. **Safizadeh F. Ghali E. Houlachi G.** Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions - A Review. *Int. J. Hydrogen Energy.* 2015. V. 40. P. 256–274. DOI: 10.1016/j.ijhydene.2014.10.109.
21. **LeRoy R.L.** Industrial water electrolysis: Present and future. *Int. J. Hydrogen Energy.* 1983. V. 8. P. 401–417. DOI: 10.1016/0260-3199(83)90162-3.
22. **Krstajić N., Popović M., Grgur B., Vojnović M., Šepa D.** On the kinetics of the hydrogen evolution reaction on nickel in alkaline solution - Part I. The mechanism. *J. Electroanal. Chem.* 2001. V. 512. P. 16–26. DOI: 10.1016/S0022-0728(01)00590-3.

Поступила в редакцию (Received) 06.06.2019
Принята к опубликованию (Accepted) 23.12.2019