

Full Paper

Electroless Deposition of the Ni Nanoparticles on the Graphite Electrode for Glucose Oxidation

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Abstract- Battery graphite rod was modified with Ni nanoparticles with a new electroless procedure and the performance of the proposed electrode was evaluated as a non-enzymatic anode for electrocatalytic oxidation of glucose in alkaline media. Glucose fuel cells that use enzymes or microorganisms catalysts are limited by their extremely low power output and rather short durability. The structure and morphology of the electrode surface were examined with X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) techniques. Voltammetric and amperometric studies indicated that the onset potential of the glucose oxidation is low (~ 0.3 V) and the electrode stability is good. In addition to these advantageous, due to easily preparation and low cost, it will be used probably in glucose fuel cells as an anode.

Keywords- Electroless deposition, Glucose oxidation, Graphite electrode, Nickel nanoparticles

1. INTRODUCTION

Electrocatalytic processes related to sugars oxidation are of great interest in many areas, as medical applications, wastewater treatment, biological fuel cells and food industry [1-6]. The investigation of glucose electrochemical oxidation began in 1960s [7] and remained as a very active research field. Bagotzky and Vassilyev [8] reported first time the electro-oxidation behaviour of glucose in an acidic medium. At about the same time, Bockris et al. [9] studied this reaction at high temperatures and in alkaline solutions.

Oxidizable metal electrodes Ni [10-12], Au [13], Pt [14] and Cu [15] provide simple way for the catalytic oxidation of carbohydrates at constant applied potentials. Non-enzymatic glucose fuel cells will probably replace by lithium batteries, because of long-term stability and adequate power density [16]. In this type of fuel cells one of the common electrodes is Pt, which is expensive, its current resource is limited [17] and shows serious self-poisoning in the glucose oxidation [18]. Therefore it is better reduce the loaded Pt or replace it with other catalyst that eliminate the proposed disadvantageous. Among these replacements Ni is one of the most common materials, and there are several reports which have been used Ni [19-21] or its compounds for electrocatalytic glucose oxidation [22-24]. In a report Au, Ni and Cu microelectrodes activated by microwave for glucose oxidation in alkaline media, give the best results as for Ni microelectrode [25]. Tomita et al. [26] introduced a thin flat film consisting of a 0.8% mixture of nickel nanoparticles in disordered graphite-like carbon (Ni-NDC) prepared by a one-step radio frequency sputtering method below 200 °C. The Ni nanoparticle size was 3 nm, and the film consisted of a mixture of Ni, NiO, Ni₂O₃ and Ni(OH)₂. This electrode was used in an electrochemical detector for detection of sugars by HPLC. In another report [27] Ni nanowire array was used for ultrasensitive detection of glucose, which the nanowires were generated by Ni-electrodeposition in pores of a polycarbonate membrane followed by chemical etching of the template. Wang et al. used an ultralong Ni nanowire modified GCE as a glucose sensor [28]. Liu and co-workers [29] dispersed simultaneously spherical nanoparticles of Ni and NiO on the carbon nanofibers, and used as a glucose sensor in alkaline solution. Electrodeposition of Ni on GC electrode studied by Danaee et al. [30], and the kinetics of glucose electrocatalytic oxidation on this modified electrode in alkaline solutions was postulated. In another work [31] GC electrode was modified with graphene-nickel/nickel oxide composite, and was used as a sensor for glucose oxidation in alkaline media.

In the most of reports, which have used Ni or Ni containing catalysts for electrocatalytic oxidation of glucose, the best result have obtained in the alkaline solutions [32,33]. In alkaline solutions Ni should be pre-oxidized to form oxide film, which initiate electron transfer by a surface-bound in redox couple Ni²⁺/Ni³⁺ [21,34].

All previous reports have used a complicated procedure or relatively expensive substrate for Ni deposition. In this study for the first time Ni-nanoparticles (Ni-NP) were deposited on

the graphite electrode (GE) with an electroless procedure, and used as a modified electrode for glucose oxidation.

2. EXPERIMENTAL

2.1. Materials

D(+)-Glucose, Nickel(II) sulfate hexahydrate, ammonium sulfate, sodium hydroxide, tin(II) chloride and sodium dodecyl sulfate all were of analytical grade, and purchased from Merck (Germany), and used without further purification. Palladium(II) chloride (59%), formaldehyde and sodium hypophosphite were purchased from Merck (Germany). All solutions were prepared with de-ionization water.

2.2. Instruments

All electrochemical measurements were done with a potentiostat-galvanostat (SAMA 500, Iran). The software of this device was SAMA 500. The three-electrode system consisted of the bare or modified graphite rod as working electrode, Ag|AgCl (3 M KCl) as reference electrode and Pt wire as a counter electrode. The graphite rod (4 mm diameter) was prepared from Sony[®] commercial dry cell batteries. For a reproducible surface, the rod was covered tightly with a Teflon tube and was polished with fine emery papers.

The surface morphology was studied by a Philips scanning electron microscopy (SEM) model VEGA TESCAN (Czech Republic).

X-ray diffraction (XRD) studies were performed at room temperature (25°C) by Philips X-ray diffractometer model PW1800. The model of energy dispersive analysis instrument was TESCAN VEGA-XMU.

2.3. Preparation of electrodes modified with Ni-NP

Ni-NPs were deposited on the graphite electrode (NiNP-GE) with an electroless procedure. First graphite electrode was polished by emery papers with different grades. Organic pollutants were removed by cleaning with acetone, in ultrasonic bath, for 10 min, thereafter washed with deionized water.

By two-step pretreatment [35], sensitization and activation, Ni-NP coated graphite was prepared. As sensitizer and activator the stannous chloride/hydrochloric acid and palladium chloride/hydrochloric were used. First the electrode was dipped in 40 mL aqueous solution, containing 0.4 g SnCl₂+1.6 mL concentrated HCl, then was washed with deionized water, thereafter dipped in 40 mL solution containing 0.01 g PdCl₂+5 drops HCl+H₂O. Every experiment carried out for 30 min at 367 K. After activation, the graphite electrode was washed and entered in the nickel-plating bath at 358 K with the stirring speed of 200 rpm. The bath composition contained nickel (II) sulphate (42 g L⁻¹), formaldehyde (15 mL L⁻¹) as

reducing agent, sodium dodecyl sulphate (2 gL^{-1}) as stabilizer and ammonium sulphate (66 g L^{-1}) as buffering agent.

3. RESULTS AND DISCUSSION

3.1. XRD and SEM analysis

The morphology of the Ni-NP modified graphite electrode (NiNP-GE) was studied by SEM. The images of this study in two magnifications are shown in Fig. 1 (A, B). As the figure shows the Ni particles are produced in nano scale.

Also the energy dispersive x-ray analysis (EDX) was carried out, which the result is shown in Fig. 1(C). As this figure illustrates only pure Ni particles were deposited on the graphite rod.

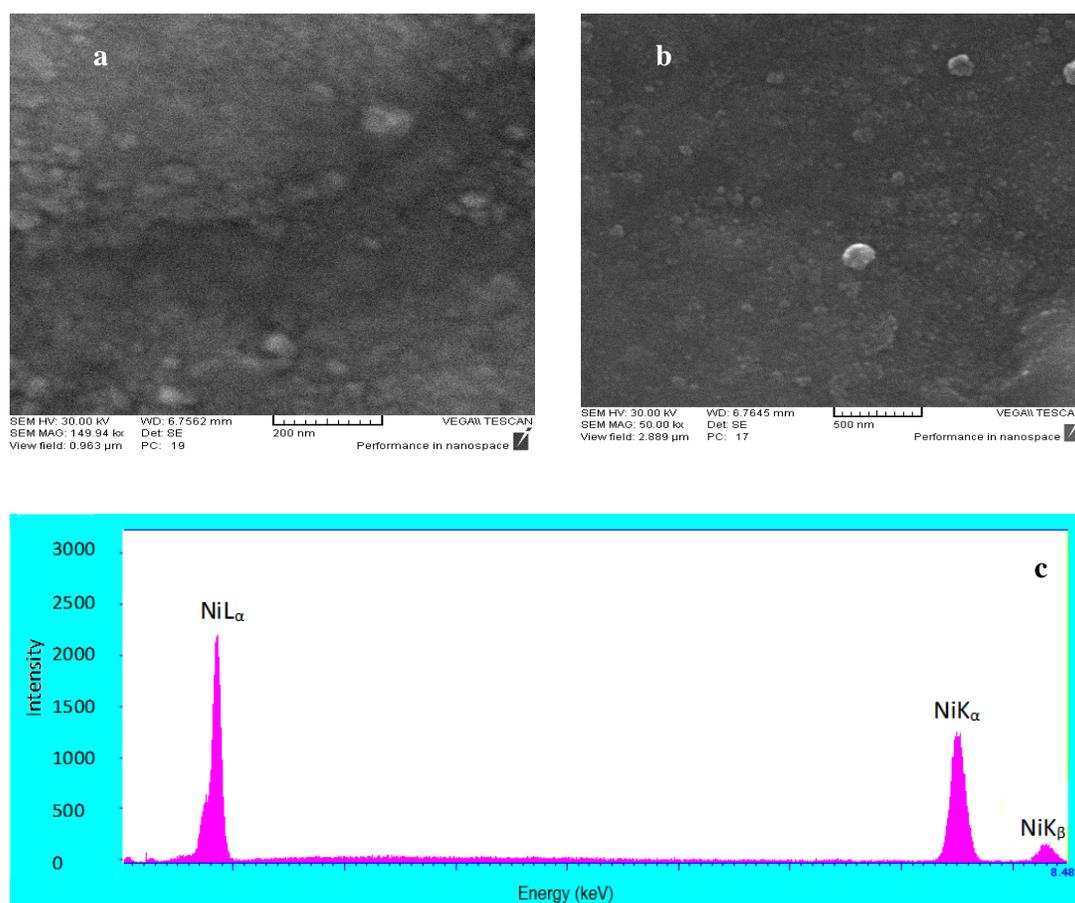


Fig. 1. SEM images of electroless coating of Ni-NPs on GE with two magnifications (a,b), and energy dispersive spectrum of a Ni-NP coated graphite electrode (c)

The surface composition was investigated by XRD technique (Fig. 2). In this figure the peaks related to Ni and carbons are marked. As it shows the Ni-NPs are pure, without any impurity in the coating.

As Fig.1 shows, the Ni particles are smaller than 100 nm therefore the Scherrer equation [36](Eq. 1) was used for estimating the nanoparticle size.

$$\tau = K\lambda / \beta \cos\theta \quad (1)$$

τ : mean size of the crystalline (nm)

K : dimensionless shape factor value close to unity

λ : X-ray wavelength (nm)

β : line broadening at half the maximum intensity (FWHM) (radians)

θ : Bragg angle (degree).

Using this equation the average crystalline size of the particles is 23.3 nm.

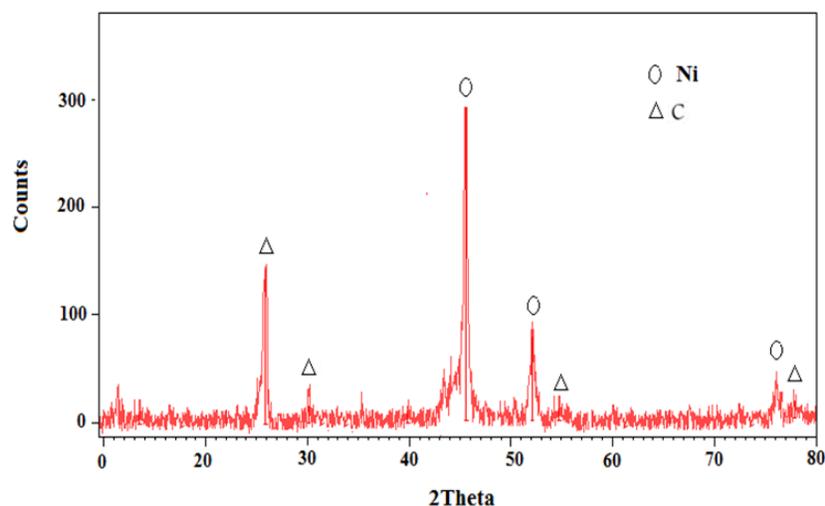


Fig. 2. XRD pattern of electroless coating of Ni-NPs on GE

3.2. Electrochemical studies

The effect of supporting electrolyte and pH was studied with cyclic voltammetry method. Fig. 3 shows the voltammograms of the modified electrode at various pHs (3, 5, 7, 11 and 14) and at different supporting electrolytes (phosphate, acetate and carbonate buffers and sodium hydroxide). As the figure shows at the lower pHs the redox peaks related to oxidation and reduction of Ni atoms on the electrode surface is very lower than 1 M NaOH solution. Since for the rest of experiments, this solution was used as the supporting electrolyte.

The electrochemical responses of the NiNP-GE and GE were obtained in 1 M NaOH solution. Fig. 4. shows cyclic voltammograms of NiNP-GE and GE in 1 M NaOH, with the 0.1 Vs^{-1} scan rate, in the potential range of 0 – 0.8 V. It shows any redox peaks for GE in the range of 0–0.8 V, but two redox peaks, related to $\text{Ni}^{2+}/\text{Ni}^{3+}$ on the NiNP-GE are observed.

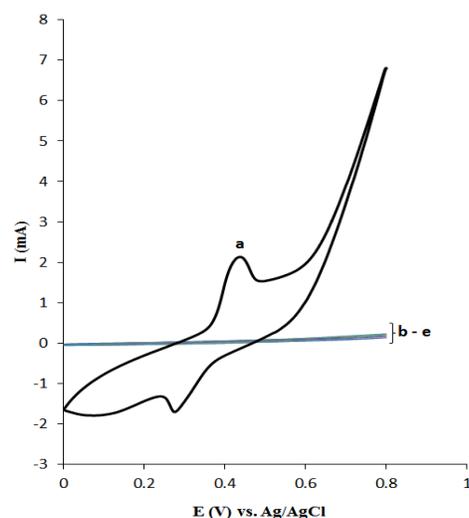


Fig. 3. Cyclic voltammograms (0.1 Vs^{-1}) of the NiNP-GE at different solutions. a) 1 M NaOH, b) phosphate buffer (pH 3), c) acetate buffer (pH 5), d), phosphate buffer (pH 7), d) carbonate buffer (pH 7) and phosphate buffer (pH 11)

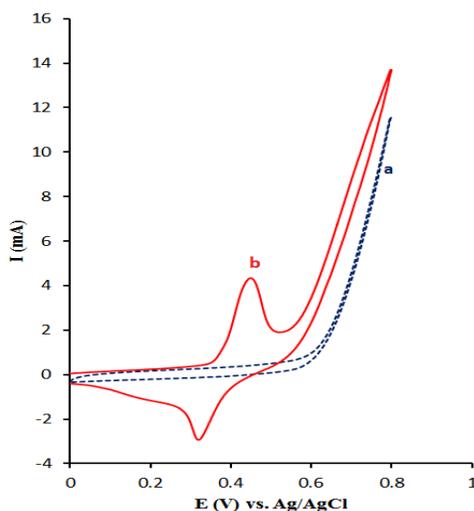


Fig. 4. Cyclic voltammograms (0.1 Vs^{-1}) of GE (a) and NiNP-GE (b) in 1 M NaOH in the potential range of 0 to 0.8 V.

Fig. 5 illustrates the responses of the NiNP-GE and GE in 1 M NaOH solution, containing 0.1 M of glucose, at the potential range of 0 to 0.8 V. It shows any peak related to glucose

oxidation on GE, but on the NiNP-GE the glucose oxidation is catalysed. Comparing of two cyclic voltammograms in Fig. 5 related to glucose oxidation and reduction reactions on NiNP-GE, shows that the peak heights have increased, which implies that in addition of glucose oxidation, the product of this reaction is catalysed by these nanoparticles.

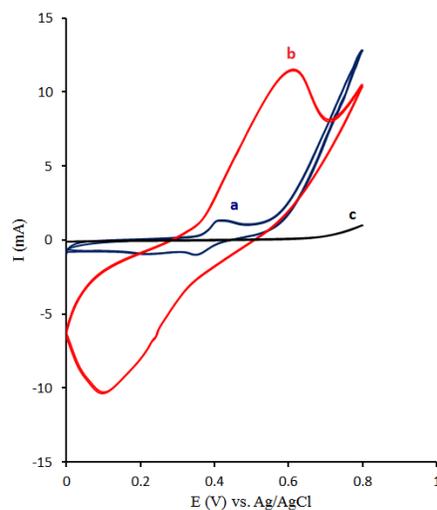


Fig. 5. Cyclic voltammograms of the NiNP-GE in absence (a) and presence of 0.1 M glucose (b) and GE in presence of 0.1 M glucose (c). (Scan rate: 0.1 Vs^{-1} , supporting electrolyte 1 M NaOH)

The cyclic voltammograms of glucose with different concentrations, in 1 M NaOH solution, by NiNP-GE, are illustrated in Fig. 6. The inset of this figure shows the linear relation between I_{pa} and glucose concentration between 2 to 31 mM.

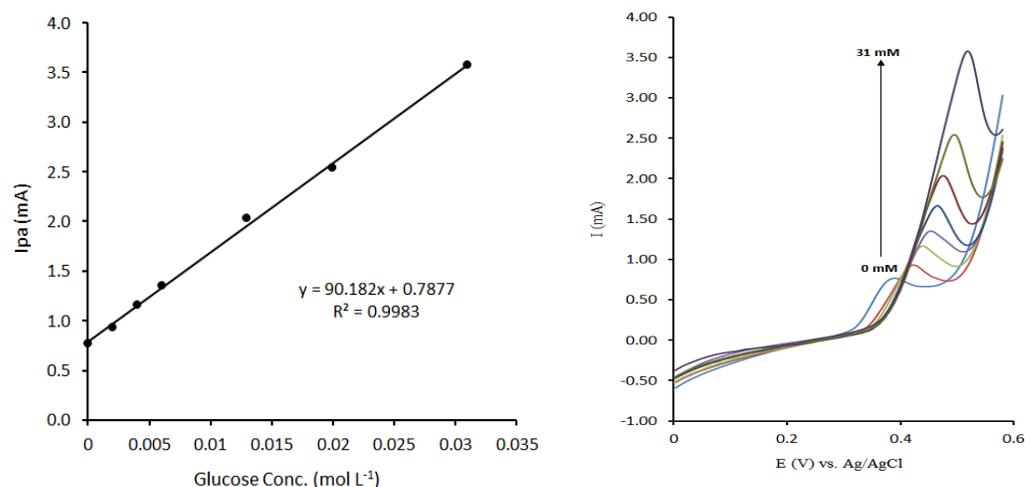


Fig. 6. Cyclic voltammograms at different concentrations of glucose (0, 2, 4, 6, 9, 13, 20 and 31 mM) in 1 M NaOH solution. (For better comparison only the forward scans are shown)

By plotting of the rate equation (2), $\log j$ vs. $\log C$ [37], the slope ($m=0.54$) will give the order of reaction.

$$\log j = \log k + m \log C \quad (2)$$

j : the peak of current density

k : rate constant

C : glucose concentration

m : reaction order.

3.2.1. Scan rate study

For more study, the effect of potential scan rate (v) on the NiNP-GE was investigated. Fig. 7 shows the CVs in 1 M NaOH at different scan rates (0.02, 0.04, 0.05, 0.06, 0.08 and 0.1 Vs⁻¹). Insets of this figure shows a plot of anodic peak currents (I_{pa}) and cathodic peak currents (I_{pc}) vs. v (a and b) and $v^{1/2}$ (c and d).

As insets a and b show, there are linear relations between I_p and v , so it can be concluded that the electrode responses are following from a surface confined mechanism.

Previous studies for the glucose oxidation in alkaline solutions, lead to the following electrocatalytic mechanism on the Ni modified surface [10,30]. By potential scanning toward positive direction Ni (0) converts to Ni (II) and thereafter Ni(III). Finally glucose oxidizes with Ni (III) to gluconate:



The electrocatalytic oxidation mechanism of glucose, on nickel modified surface may be simply described by:



Also the cyclic voltammograms at different scan rates were obtained in 1 M NaOH solution containing 0.1 M of glucose (Fig. 8). The insets of this figure give a linear relation between I_{pa} and $v^{1/2}$, meaning that glucose oxidation follows by diffusion mechanism.

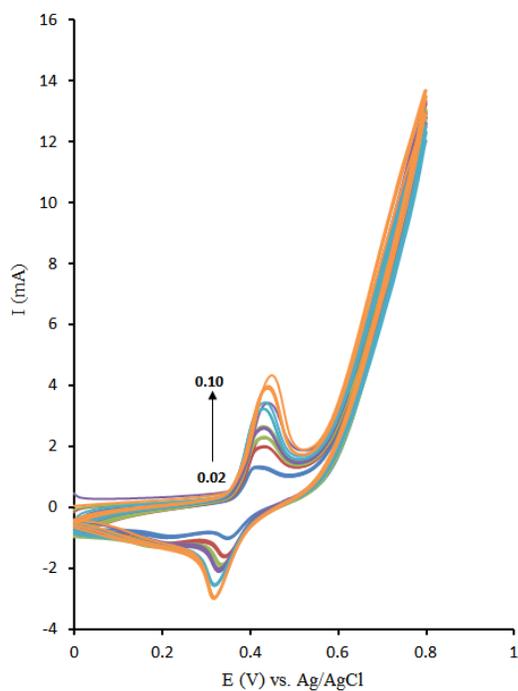
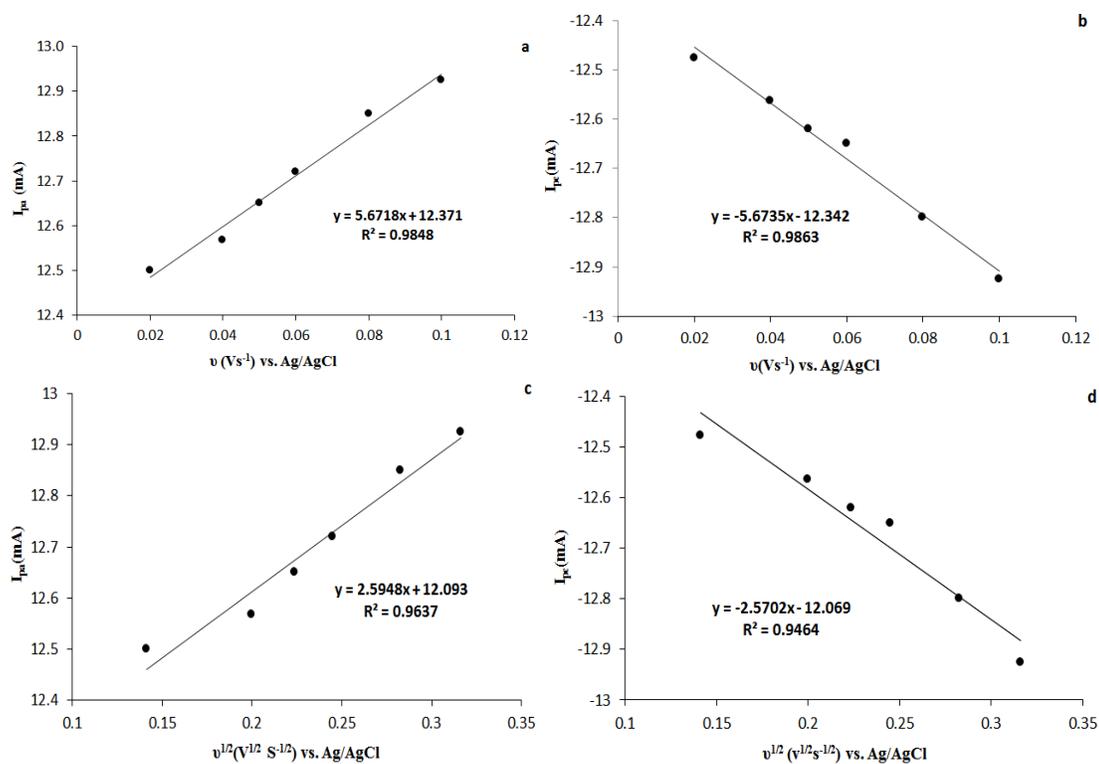


Fig. 7. Cyclic voltammograms on NiNP-GE from 0 to 0.8 V at different scan rates (0.02, 0.04, 0.05, 0.06, 0.08 and 0.1 Vs^{-1}) in 1 M NaOH. Insets a and b: plots of I_{pa} and I_{pc} vs. v ; Insets c and d: plots of I_{pa} and I_{pc} vs. $v^{1/2}$

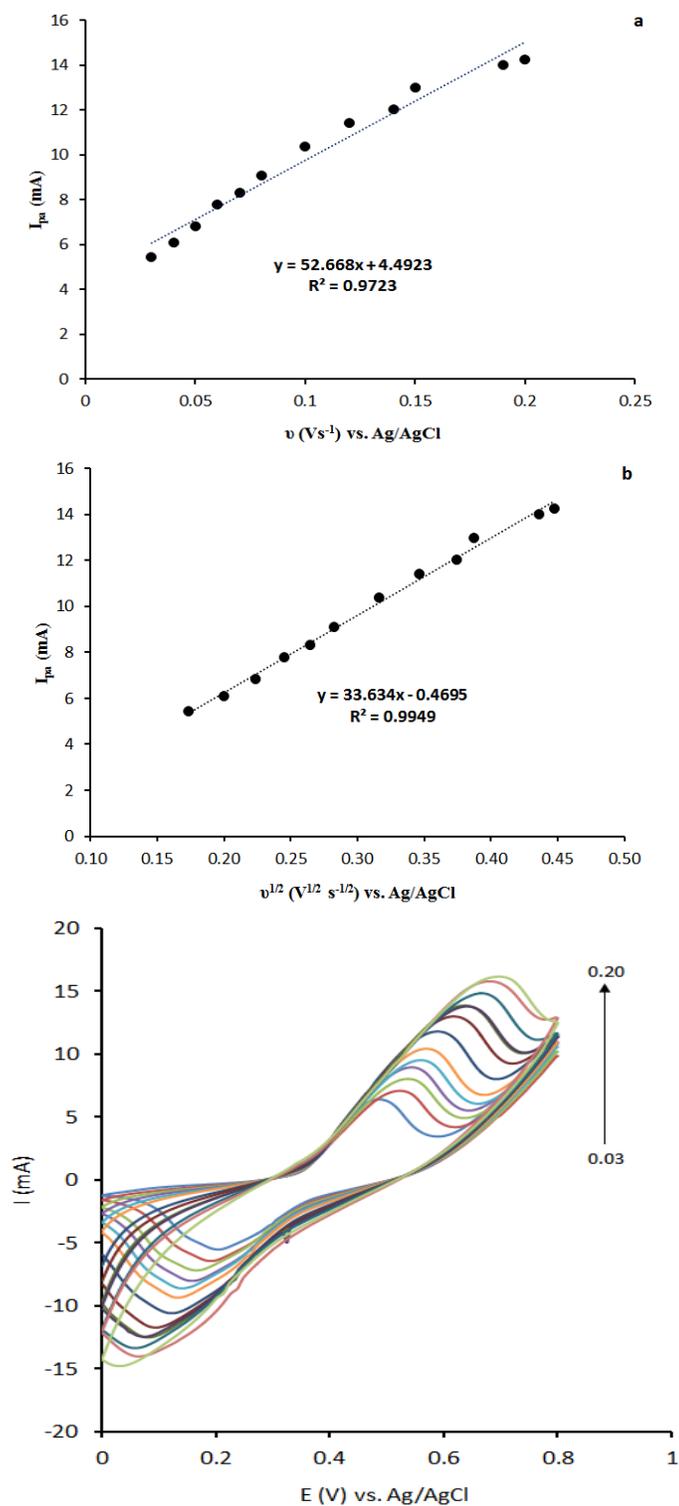


Fig. 8. Cyclic voltammograms of NiNP-GE from 0 to 0.8 V at different scan rates (0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.10, 0.12, 0.14, 0.15, 0.19 and 0.2 Vs⁻¹) in 1 M NaOH solution containing 0.1 M of glucose. Insets a and b are plots of *I*_{pa} vs. *v* and *v*^{1/2}, respectively

3.2.2. Electrode stability and interference study

Fig. 9 illustrates the chronoamperogram of five successive applied potential steps (base potential (E_1) 0.2 V and step potential (E_2) 0.8 V) on NiNP-GE in a stirred solution of 1 M NaOH solution containing 0.1 M glucose. With applying successive potential steps, after each step the electrode response is close to the previous step, and the oxidation product do not influence on the electrode response. Therefore the stability of the electrode response is good, a well characteristic for anode electrode in glucose fuel cells.

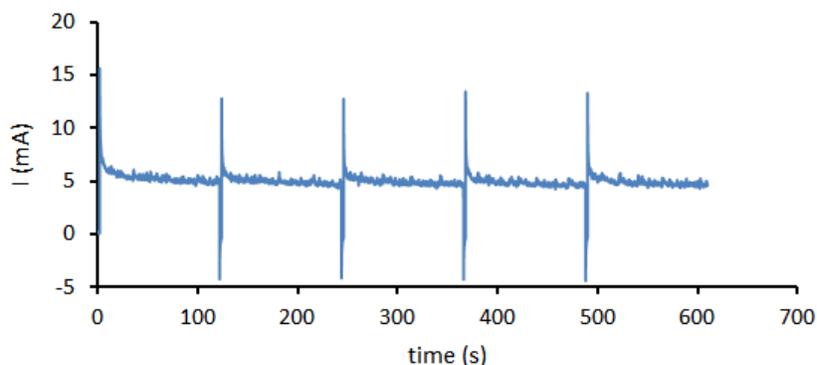


Fig. 9. Chronoamperometry of the NiNP-GE in in a stirred solution of 1 M NaOH containing 0.1 M glucose (base potential (E_1) 0.2 V and step potential (E_2) 0.8 V)

In another study the response of the electrode in the presence of some important biological molecules including ascorbic acid (AA) and uric acid (UA) were examined (data is not shown). Although the oxidation peak of these molecules overlap with the glucose oxidation peak, but this subject is important when we want to determine glucose in the presence of these molecules. The main goal of this study was the introduction of a simple and cheap anode for a glucose fuel cell. Therefore the presence of these molecules is not a problem, unless their oxidation products poison the electrode surface, which in this study there was no poisoning effect for UA and AA.

This work is not the first study which used Ni as electrocatalyst for glucose oxidation in fuel cell. But in the previous reports, the electrode preparation is more complicate or the substrate for Ni deposition is more expensive, therefore the main advantage of our proposed electrode is its simplicity and low cost.

4. CONCLUSION

Graphite rod was modified with nickel nanoparticles with a new electroless method. The performance of this electrode for glucose oxidation was investigated in alkaline solution. The results of the chronoamperometry study showed that the electrode response is stable, and the

electrode is not poisoned with the products of glucose oxidation. This work is not the first study which used Ni as electrocatalyst for glucose oxidation in fuel cell anode. But in the previous reports, the electrode preparation is more complicate or the substrate for Ni deposition is more expensive, therefore the main advantage of our proposed electrode is its simplicity, stability and low cost with an acceptable performance.

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REFERENCES

- [1] M. Tominaga, Y. Taema, and I. Taniguchi, *J. Electroanal. Chem.* 624 (2008) 1.
- [2] Y. Hu, J. Jin, P. Wu, H. Zhang, and C. Cai, *Electrochim. Acta* 56 (2010) 491.
- [3] H. Qiu, and X. Huang, *J. Electroanal. Chem.* 643 (2010) 39.
- [4] M. Tominaga, T. Shimazoe, M. Nagashima, and I. Taniguchi, *Electrochem. Commun.* 7 (2005) 189.
- [5] S. Hui, J. Zhang, X. Chen, H. Xu, D. Ma, Y. Liu, and B. Tao, *Sens. Actuators B Chem.* 155 (2011) 592.
- [6] S. Y. Kwon, H. D. Kwon, and S. H. Choi, *J. Sens.* 2012 (2012) 8.
- [7] H. W. Lei, B. Wu, C. S. Cha, and H. Kita, *J. Electroanal. Chem.* 382 (1995) 103.
- [8] V. S. Bagotzky, and Y. B. Vassilyev, *Electrochim. Acta* 12 (1967) 1323.
- [9] J. O. M. Bockris, B. J. Piersma, and E. Gileadi, *Electrochim. Acta* 9 (1964) 1329.
- [10] C. Zhao, C. Shao, M. Li, and K. Jiao, *Talanta* 71 (2007) 1769.
- [11] M. Morita, O. Niwa, S. Tou, and N. Watanabe, *J. Chromatog. A* 837 (1999) 17.
- [12] M. Fleischmann, K. Korinek, and D. Pletcher, *J. Electroanal. Chem. Inter. Electrochem.* 31 (1971) 39.
- [13] A. Hilmi, and J. H. T. Luong, *Anal. Chem.* 72 (2000) 4677.
- [14] E. Skou, *Electrochim. Acta* 22 (1977) 313.
- [15] L. A. Colon, R. Dadoo, and R. N. Zare, *Anal. Chem.* 65 (1993) 476.
- [16] V. Oncescu, and D. Erickson, *Sci. Rep.* 3 (2013) 1226.
- [17] N. Sato, *Oyo Buturi* 72 (2003) 857.
- [18] C. Jin, and Z. Chen, *Synth. Metal.* 157 (2007) 592.
- [19] D. E. Pissinis, L. E. Sereno, and J. M. Marioli, *J. Electroanal. Chem.* 694 (2013) 23.
- [20] M. Jafarian, F. Forouzandeh, I. Danaee, F. Gobal, and M. G. Mahjani, *J. Solid State Electrochem.* 13 (2009) 1171.
- [21] I. Danaee, M. Jafarian, F. Forouzandeh, F. Gobal, and M. G. Mahjani, *Electrochim. Acta* 53 (2008) 6602.
- [22] A. Ciszewski, and I. Stepniak, *Electrochim. Acta* 111 (2013) 185.

- [23] M. Yousef Elahi, H. Heli, S. Z. Bathaie, and M. F. Mousavi, *J. Solid State Electrochem.* 11 (2007) 273.
- [24] L. Zheng, J. Q. Zhang, and J. F. Song, *Electrochim. Acta* 54 (2009) 4559.
- [25] M. A. Ghanem, R. G. Compton, B. A. Coles, A. Canals, A. Vuorema, P. John, and F. Marken, *Phys. Chem. Chem. Phys.* 7 (2005) 3552.
- [26] T. You, O. Niwa, Z. Chen, K. Hayashi, M. Tomita, and S. Hirono, *Anal. Chem.* 75 (2003) 5191.
- [27] A. de la Escosura-Muñiz, M. Maltez-da Costa, C. Sánchez-Espinel, B. Díaz-Freitas, J. Fernández-Suarez, Á. González-Fernández, and A. Merkoçi, *Biosens. Bioelectron.* 26 (2010) 1710.
- [28] J. Wang, W. Bao, and L. Zhang, *Anal. Method.* 4 (2012) 4009.
- [29] Y. Liu, H. Teng, H. Hou, and T. You, *Biosens. Bioelectron.* 24 (2009) 3329.
- [30] I. Danaee, M. Jafarian, F. Forouzandeh, and F. Gopal, *Int. J. Chem. Kinet.* 44 (2012) 712.
- [31] X. Lü, Z. Wu, J. Shen, J. Feng, Y. Wang, and Y. Song, *Int. J. Electrochem. Sci.* 8 (2013) 2220.
- [32] K. C. Lin, Y. C. Lin, and S. M. Chen, *Electrochim. Acta* 96 (2013) 164.
- [33] J. Chen, C. X. Zhao, M. M. Zhi, K. Wang, L. Deng, and G. Xu, *Electrochim. Acta* 66 (2012) 133.
- [34] S. Park, H. Boo, and T. D. Chung, *Anal. Chim. Acta* 556 (2006) 46.
- [35] Q. Li, G. Z. Zeng, W. F. Zhao, and G. H. Chen, *Synt. Metal.* 160 (2010) 200.
- [36] R. Jenkins, and R. L. Snyder, *Introduction to X-Ray Powder Diffractometry*, John Wiley & Sons (1996).
- [37] M. A. Abdel Rahim, R. M. Abdel Hameed, and M. W. Khalil, *J. Power Sourc.* 134 (2004) 160.