# Investigation of glucose electro-oxidation on Co and CoB alloy coatings modified with Au nanoparticles

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<sup>2</sup> Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko St. 24, 03225 Vilnius, Lithuania The electrochemical oxidation of glucose was investigated on the Co and CoB alloy coatings, which were deposited on the copper substrate (Cu) and subsequently modified with a small amount of Au nanocrystallites. The catalysts were prepared via a simple electroless Co deposition method followed by a spontaneous Au galvanic displacement from the Au(III)-containing solution. The activity of Co and CoB alloy coatings modified with Au crystallites towards the oxidation of glucose was examined by the cyclic voltammetry method.

It has been determined that the Co and CoB alloy coatings, which were modified with a small amount of Au crystallites, exhibit a significantly higher activity for the oxidation of glucose as compared to that of bare Au, Co and CoB alloy catalysts. The process of glucose oxidation is significantly shifted to a more negative potential domain at the both Co/Cu and CoB/Cu catalysts modified by Au nanocrystallites, indicating the higher activity of those catalysts as compared to that of the unmodified Co/Cu and CoB/Cu catalysts and the bare Au electrode. It was found that ca. 22 and even 67 times higher glucose oxidation current density values have been obtained at the AuCo/Cu and AuCoB/Cu catalysts, respectively, as compared to those for the unmodified Co/Cu.

Keywords: cobalt, boron, gold, nanoparticles, glucose, oxidation

# INTRODUCTION

Among renewable energy sources, direct glucose fuel cells (DGFCs) have been examined most extensively due to their intrinsic high efficiency, environment-friendly and silent operation, good stability, considerable durability and simple structure. Great efforts have been devoted to the investigation of glucose application as a fuel over the past decades [1–14]. Glucose is an ideal renewable fuel since it is easily available, cheap and abundant in nature, non-flammable, odourless, non-toxic, environmentally benign and safe, easy to produce and handle. These properties make glucose an appealing fuel for various uses, especially for bio-fuel cells as the next generation

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energy source [15–20], biosensors [21–28], biological implants and pacemakers [18], new photonic materials [29], food industry [30] and so forth.

Operating of a direct glucose fuel cell is based on the reactions occurring at the anode and cathode, e.g. oxidation of glucose (Eq. (1)) and reduction of oxygen (Eq. (2)) [19]:

At the anode  

$$C_6H_{12}O_6 + 24OH^- \rightarrow 6CO_2 + 18H_2O + 24 e^-;$$
 (1)

At the cathode  $6O_2 + 12H_2O + 24 e^- \rightarrow 24OH^-$ ;

Overall process  
$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 18H_2O.$$
 (3)

Theoretically, glucose can be completely oxidized to carbon dioxide and water, releasing 24 electrons per molecule of glucose according to Eq. (1) [19]. Currently, only in a biological system, the complete glucose oxidation, generating 24 electrons, can be achieved. In real conditions glucose oxidation will mainly occur through a process generating two electrons [7, 19]. On a noble metalbased catalyst glucose is electrochemically oxidized to gluconolactone and gluconic acid by releasing two electrons. Thus, in practice the corresponding fuel cell reactions are as follows [8, 10, 19]:

Anode

$$C_6H_{12}O_6 + 2OH^- \rightarrow C_6H_{12}O_7 + H_2O + 2e^-, E_a = 0.853 V; (4)$$

Cathode  $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-, E_c = 0.403 \text{ V};$  (5)

Overall  

$$C_6H_{12}O_6 + 1/2O_2 \Rightarrow C_6H_{12}O_7, E_0 = 1.256 \text{ V.}$$
 (6)

The studies on the electro-oxidation of sugars throughout the last few decades show that noble metal catalysts based on platinum and gold could potentially oxidize monosaccharides such as glucose, mannose and fructose [6, 17, 21, 31–34]. Various catalytic materials like noble metals have been proved to be highly efficient anode catalysts for fuel cells because of their long-term stability and biocompatibility. Recently, some reports showed a promise in the current increase in nonbiological glucose fuel cells by using noble metal catalysts such as Pt, Au, Ru, Ag and Pd. Among them, Au appears as rather viable for its ability to convert different types of aldoses (e.g. glucose, lactose, maltose, xylose, arabinose) to their corresponding aldonic acids (e.g. gluconic acid) [6, 3, 8, 19]. However, platinum is still the most extensively and successfully used catalyst for the electrooxidation of glucose. The Pt and Pt-based catalysts exhibit a high activity, but show a low selectivity for the oxidation reaction of glucose. Moreover, the mentioned catalysts are rather expensive, which limits their wide und multi-functional applications in various fields of industry. One more disadvantage is the presence of carbon monoxide (CO) and other intermediates that are formed during the oxidation of glucose because they easily poison the traditional Pt and Pt-based catalysts used in the oxidation process. For those reasons alternative metals have been widely considered. Among them, Au [4, 5, 12, 13, 35–41], Ag [43] and Pd [44, 45] were investigated for anodic activity studies of DGFC. Au is of special interest since it displays a rather high catalytic activity towards the oxidation of glucose in neutral media due to the lower price as compared to that of the Pt or Pt-based catalysts, furthermore, is more stable and minimally prone to be poisoned during the oxidation of glucose. On the other hand, interest in Au lies not only for its use as a catalyst for glucose oxidation in the neutral media, but in an alkaline also. It has been noted that the rate of the electro-oxidation of glucose on Au is higher in an alkaline environment than that in an acidic or neutral one and occurs at more negative potentials as compared to the other metals [37, 38, 46]. Therefore, the mechanism of glucose electrooxidation has been intensively studied in detail at different solution pH values, concentrations and by using different techniques [23, 28, 31, 39, 40-42]. However, up till now the studies do not agree unambiguously neither on the peak nor wave assignments in CV curves for glucose oxidation at Au. The glucose oxidation process is rather complex regarding numerous by-products that can be formed. It significantly depends on a lot of various factors, including the catalyst nature, surface structure and energy, particle size, support selected, potential applied and others [25].

Despite the mentioned advantages for noble metals catalysts, including Au, the necessity of more efficient, cost-effective and durable alternatives has led to further research. To overcome difficulties related to the high cost of the catalyst enormous efforts have been focused on the development of non-precious and efficient catalysts for electrooxidation or detection of glucose. Transition metals, as cheaper alternatives to replace the noble catalysts such as Cu [47], Mn [48], Co [49, 50] and Ni [26, 27, 51, 52], have been shown to possess a good electrocatalytic activity and sensitivity towards the oxidation of glucose in an alkaline medium. Their properties have been thoroughly reviewed in [22]. Among them, Co is appreciated for its environmentally friendly nature, relatively low cost, intriguing electronic, electrochemical and electrocatalytic properties and therefore seems to have a great potential in the applications for catalysts, electrochemical sensors, Li-ion rechargeable batteries, etc. Based on the Co metal, a number of double- or multiplecomponent systems containing only the non-precious transition metals, such as bimetallic MCo (M = Cu, Fe, Ni, Mn) [53], Co-Cu alloy [54], Ni-Co [14], Ni/Cr/Co [55] and NiCo<sub>2</sub>O<sub>4</sub>@Polyaniline core-shell system [56], have been developed and showed a significantly higher response for the oxidation of glucose as compared to that obtained at the pure metals. Coupling transition metals together enabled to gain the desirable effect in reducing the price as compared to the precious catalyst also.

However, a strong demand for efficient catalysts with excellent characteristics that could equal those of the noble metals forces an investigator to recall back those systems containing the precious elements in their composition. Decoration of transition metals by small amounts of the noble metal has been shown to be advantageous strategy, since it satisfies cost-efficient requirements for the catalyst, on the one hand, and promotes the oxidation reaction rate due to the synergistic effect of the metals, on the other hand. Recent electrochemical studies suggest that the noble metal-based binary electrocatalysts like Pt-Ni [57], Pt-Cu [58, 59] and Au-Co [60, 61] definitely perform the apparently improved catalytic activity and stability as compared to those of monometallic catalysts, lower the price of the catalyst and therefore are highly preferred.

In our previous study it was found that the gold-cobalt and gold-cobalt-boron catalysts deposited on the copper surface (denoted as AuCo/Cu and AuCoB/Cu) show a high electrocatalytic activity for the oxidation of sodium borohydride in an alkaline medium [62]. Based on a strong demand for efficient and relatively inexpensive catalysts, in this study we investigated the oxidation of glucose on the same low Au loading containing AuCo/Cu and AuCoB/Cu catalysts. Furthermore, for the preparation of the AuCo/Cu and AuCoB/Cu catalysts a simple two-step process, which involves electroless cobalt plating followed by a spontaneous Au galvanic displacement from the Au(III)-containing solution, was used as in Ref. [62]. The use of a simple and low-cost approach for the preparation of the efficient catalysts is a promising way to fabricate relatively inexpensive catalysts.

### **EXPERIMENTAL**

### Chemicals

HAuCl<sub>4</sub> · 3H<sub>2</sub>O (99.99%, ≥49.0%), C<sub>4</sub>H<sub>8</sub>ONH<sup>·</sup>BH<sub>3</sub> (morpholine borane, 97%), NH<sub>2</sub>CH<sub>2</sub>COOH (glycine, 99%) and C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> · H<sub>2</sub>O (D-(+)-glucose, 99.5%) were purchased from Sigma-Aldrich Supply. HCl (36%), NaOH (98.8%) and CoSO<sub>4</sub> · 7H<sub>2</sub>O (99.5%) were purchased from Chempur Company. All chemicals were of analytical grade. Deionized water with the resistivity of 18.2 MΩ cm<sup>-1</sup> was used to prepare all the solutions.

### **Fabrication of catalysts**

The Co and CoB catalysts and those decorated with a small amount of Au crystallites (termed as the Co, CoB, AuCo and AuCoB catalysts) were the same as described in our previous study [62]. Briefly, the Co and CoB alloy coatings were deposited on the Cu surface using morpholine borane as a reducing agent. The pure Co coatings were obtained using a cobalt plating bath containing  $0.05 \text{ M CoSO}_4$ , 0.05 M morpholine borane and 0.2 M glycine. In order to obtain the CoB alloy coatings, the plating solution of the same composition was used, but without glycine. In both cases the plating bath operated at pH 7 at 30°C temperature. The duration of electroless Co and CoB alloy coatings deposition on the copper surface corresponded to 30 and 100 min, respectively. The thickness of the pure Co and CoB alloy coatings was determined gravimetrically and was equal to ca. 1 µm.

Au nanoparticles were deposited on the prepared Co/Cu and CoB/Cu electrodes by their immersion into a 1 mM HAuCl<sub>4</sub> solution (pH 1.8) at 30°C temperature for 30 s. The surface-to-volume ratio was 2 dm<sup>2</sup> l<sup>-1</sup>. After plating, the samples were taken out, thoroughly rinsed with deionized water and dried in air at room temperature. Then, the prepared catalysts were used for the electrooxidation of glucose measurements without any further treatment.

#### **Electrochemical measurements**

A conventional three-electrode cell was used for electrochemical measurements. The pure Au, Co/ Cu, CoB/Cu, AuCo/Cu and AuCoB/Cu catalysts with a geometric area of 2 cm<sup>2</sup> were employed as working electrodes, an Ag/AgCl/KCl<sub>est</sub> electrode was used as a reference and a Pt sheet was used as a counter electrode. An Au-sputtered quartz crystal plate with a geometric area of 0.636 cm<sup>2</sup> was used as a bare gold electrode. All electrochemical measurements were performed with a Zennium electrochemical workstation (ZAHNER-Elektrik GmbH & Co.KG). Cyclic voltammograms (CVs) were recorded at a potential sweep rate of 50 mV s<sup>-1</sup> from the stationary  $E_{c}$  value in the anodic direction up to 0.7 V vs SHE in a 0.1 M NaOH solution containing 0.1 M glucose at 30°C temperature. The electrode potential is quoted versus the standard hydrogen electrode (SHE). The presented current densities are normalized with respect to the geometric area of catalysts.

All solutions were deaerated by argon for 15 min prior to measurements.

### **RESULTS AND DISCUSSION**

Herein we investigated the gold–cobalt and gold– cobalt–boron catalysts deposited on the copper substrate for their glucose oxidation performance, whereas in our previous study those catalysts were identified as effective enough electrocatalysts for the oxidation of sodium borohydride in an alkaline medium [62]. The AuCo/Cu and AuCoB/ Cu catalysts were prepared by a two-step process, which involves electroless cobalt plating followed by a spontaneous Au galvanic displacement from the Au(III)-containing solution [62]. The electroless Co or CoB layers were used as the underlayers for the deposition of Au nanoparticles onto the copper substrate. As was described in our work [62], the electroless Co layer was deposited on the copper substrate using a cobalt plating bath with or without glycine and morpholine borane as a reducing agent. When the electroless cobalt plating was performed without glycine, the obtained Co coatings contained ca. 10.4–13.0 at.% B, whereas cobalt plating was performed in the presence of 0.2 M glycine, practically pure Co coatings were obtained [62].

Au nanoparticles were deposited on the asprepared Co/Cu and CoB/Cu catalysts by their immersion into the Au(III)-containing solution at 30°C temperature for 30 s [62]. It was found that the Au nanoparticles in size of 6–50 nm were successively deposited on the surface of Co/Cu and CoB/Cu.

The activity of the prepared AuCo/Cu and Au-CoB/Cu catalysts for the oxidation of glucose in an alkaline medium was evaluated using cyclic voltammetry and compared to that of the bare Au, Co/Cu, and CoB/Cu catalysts. Figure 1 presents typical CVs for the bare Au electrode recorded in the 0.1 M NaOH solution (a dashed line) and in that containing 0.1 M glucose (a solid line) in the potential region ranging from -0.7 to 0.7 V at a scan rate of 50 mV s<sup>-1</sup> at 25°C temperature.

A pair of redox peaks corresponding to the formation and reduction of an oxide layer on the Au electrode surface in the 0.1 M NaOH solution



Fig. 1. CVs of the Au electrode recorded in the 0.1 M NaOH solution (a dashed line) and that containing 0.1 M glucose (a solid line) at 50 mV s<sup>-1</sup>

is observed in the potential region from 0.45 to 0.7 V and from 0.2 to 0.45 V, respectively (Fig. 1, a dashed line). Both peaks involve continuous redox reactions and can be represented by the following sequence as Au  $\leftrightarrow$  AuOH  $\leftrightarrow$  Au<sub>2</sub>O<sub>3</sub> [28]. Meanwhile, the region of more negative potentials is related to the early oxidation of gold surface by Eq. (7) [41, 63]:

$$\operatorname{Au} + \operatorname{OH}^{-} \rightarrow \operatorname{AuOH}_{\operatorname{ad}} + e^{-}.$$
 (7)

It is considered that adsorbed AuOH<sub>ad</sub> formed by chemisorption of OH<sup>-</sup> anion plays a decisive role in the oxidation of glucose, especially in an alkaline media, where the chemisorption process is more pronounced [38, 39]. It should be noted that the intensity of the oxidation peaks on the Au electrode significantly depends on the presence of specific crystallographic planes on the gold surface [31, 39]. The addition of glucose into the system results in an apparently changed shape of the CV curve followed by significant increases in current density (Fig. 1, a solid line). The obtained voltammetric data for the polycrystalline Au electrode in the presence of 0.1 M glucose, as compared to those presented in Refs. [31, 37, 39-41], show that the CV curve does not undergo radical transformations, moreover, is similar in shape and coincides well with those observed earlier. Three characteristic oxidation peaks labelled as A1, A2 and A3 are observed in the CV curve on the positive-going sweep, and another two labelled as **B1** and **B2** are revealed on the negative-going sweep (Fig. 1, a solid line). Generally, two well-distinguished anodic peaks A1 and A2, one at lower potential values located at ca. -0.1 V and another one at more positive potential values at ca. 0.4 V, are attributed to the oxidation of adsorbed glucose to gluconolactone [31, 40, 41] and to further oxidation of gluconolactone to gluconate [28, 39, 40, 42], respectively. The third poorly expressed peak A3 is related to the formation of a gold oxide layer, which leads to the decrease of AuOH and, therefore, current density falls down. In our case a good correlation is observed between the glucose oxidation potential  $E_{\rm onset}$  of ca. –0.4 V and that for the generation of  ${\rm AuOH}_{\rm ad}$  in an alkaline media. Consequently, it is reasonable to presume that the presence of AuOH<sub>ad</sub> promotes the oxidation process of adsorbed glucose. In the backward

scan, the pronounced peaks **B2** and **B1** are observed at potential values of ca. 0.50 and 0.05 V, respectively. They may be attributed to the oxidation of intermediate species formed during the oxidation of glucose and to the oxidation of glucose on the renewed gold surface after the gold oxide layer reduction (Fig. 1), respectively [28, 31, 39].

An analysis of the maximum current density values of each process occurring in the potential region of anodic peaks A1 and A2 shows that they are almost of the same magnitude and point to the fact that the gold surface is almost equally active to the oxidation of glucose and gluconol-actone since the presence of a sufficient amount of active AuOH<sub>ads</sub> is available for the oxidation process in the appropriate potential regions.

The oxidation of glucose on the CoB/Cu, Co/Cu, AuCoB/Cu, and AuCo/Cu catalysts was investigated by recording cyclic voltammograms in a 0.1 M glucose + 0.1 M NaOH solution at 25°C temperature by sweeping the electrode potential from ca. -0.7 to 0.7 V vs SHE at a potential scan rate of 50 mV s<sup>-1</sup> (Fig. 2). Figure 2a shows the first cycles of continuous CVs for the CoB/Cu (1) and Co/Cu (2) electrodes, which demonstrate a different behaviour at low potentials (ca. -0.4 V) in the region of anodic peak **A0**, but almost the same one at more positive potentials (ca. 0.4 V) in the region of anodic peak **A1**.

In the backward scan the reduction peak **C** is seen for the Co/Cu catalyst in the CV. Following the data in literature [64, 65], anodic peak **A0** could be related to the formation of Co oxide and hydroxide in an alkaline solution according to the following reactions:

 $\text{Co} + 2\text{OH}^- \rightarrow \text{Co(OH)}_2 + 2e^-, E^\circ = -0.918 \text{ V}, (8)$ 

Co + 2OH<sup>-</sup> → CoO + H<sub>2</sub>O + 2e<sup>-</sup>, 
$$E^{\circ} = -0.892$$
 V. (9)

During the anodic scan the Co surface undergoes the oxidation process by the sequence  $CoO \rightarrow Co_3O_4 \rightarrow Co_2O_3$  [66]. Therefore, at low potentials the current response of glucose oxidation at peak **A0** could be reasonably related to the presence of lower valency Co oxide species, meanwhile at higher potentials of ca. 0.4 V the nature of anodic peak **A1** could be related to the presence of Co<sub>3</sub>O<sub>4</sub> species, which catalyze the oxidation of glucose [67]. Since the glucose oxidation



**Fig. 2.** CVs for CoB/Cu (a, 1), Co/Cu (a, 2), AuCoB/Cu (b, 1) and AuCo/Cu (b, 2) recorded in a 0.1 M glucose + 0.1 M NaOH solution at 50 mV s<sup>-1</sup>

to gluconolactone occurs through the two-electron electrochemical reaction, the mechanism of the electrochemical oxidation of glucose catalyzed by  $Co_3O_4$  could be explained by the  $Co_3O_4$  oxidation to CoOOH, followed by further oxidation of CoOOH species to  $CoO_2$ , which oxidize glucose to generate gluconolactone and CoOOH by Eqs. (10–12) [60, 68]:

$$\operatorname{Co}_{3}\operatorname{O}_{4} + \operatorname{OH}^{-} + \operatorname{H}_{2}\operatorname{O} \leftrightarrow 3\operatorname{CoOOH} + e^{-},$$
 (10)

$$CoOOH + OH^{-} \leftrightarrow CoO_{2} + H_{2}O + e^{-}, \qquad (11)$$

$$2\operatorname{CoO}_2 + \operatorname{C_6H_{12}O_6} \leftrightarrow 2\operatorname{CoOOH} + \operatorname{C_6H_{10}O_6}. (12)$$

The comparison of the glucose oxidation currents on the Co/Cu and CoB/Cu catalysts indicates that almost four times higher current density values are obtained for the Co/Cu catalyst at the main glucose oxidation potential of ca. 0.4 V at anodic peak A1 (Fig. 2a). Thus, the Co/Cu catalyst is more favourable for the oxidation of glucose when compared to the CoB/Cu catalyst, moreover, it significantly yields to the bare Au catalyst (Fig. 1) resulting in ten times lower glucose oxidation current densities. For that reason (based on the goal of achieving a more enhanced oxidation process of glucose in the presence of Au species) the aforementioned catalysts were treated to further modification (galvanic displacement) by a small amount of Au nanoparticles - the final Au loadings were 11.6 and 14.3  $\mu g_{Au}$  cm<sup>-2</sup> in the prepared AuCo/Cu and AuCoB/Cu catalysts, respectively.

Electrocatalytic activity of the AuCo/Cu and AuCoB/Cu catalysts was investigated with respect to the oxidation of glucose in alkaline media. The CV curves of the Co/Cu and CoB/ Cu electrodes modified by small amounts of Au crystallites are presented in Fig. 2b. Comparing the activities of the AuCoB/Cu (1) and AuCo/ Cu (2) catalysts (Fig. 2b) towards the oxidation of glucose with that of bare CoB/Cu (Fig. 2a, 1) and Co/Cu (Fig. 2a, 2), it is clearly seen that only one broad anodic peak A is recorded on the AuCoB/Cu (1) and AuCo/Cu (2) catalysts. Typical two well-distinguished anodic peaks A1 and A2 for glucose oxidation at the bare Au electrode disappear transforming into one broadly spread peak. This suggests that the oxidation processes of glucose and gluconolactone occur consecutively or very quickly [42]. The location of the overall anodic peak A for both catalysts is shifted into a more negative potential region. Anodic peak A for the AuCoB/Cu catalyst is centered at ca. 0.3 V, while for the AuCo/Cu catalyst it is emerged at ca. 0.15 V. Nevertheless, the overall oxidation peak for glucose oxidation at AuCo/Cu is shifted to more negative potential values by ca. 0.15 V as compared with that at the AuCoB/Cu catalyst, but higher glucose oxidation current density values are obtained at the latter catalyst. Moreover, glucose oxidation starts as soon as a negative potential scan is applied for the both catalysts. This indicates a higher activity of those catalysts for the oxidation of glucose. Additionally,

an unmodified Co catalyst demonstrates a higher electrocatalytic activity for the oxidation of glucose as compared to that of the CoB alloy catalyst, meanwhile, decoration of the mentioned catalyst by Au nanoparticles results in a higher activity of the AuCoB catalyst than compared to that of the AuCo catalyst (Fig. 2).

Figure 3a presents the first positive-going scans recorded on the CoB/Cu (1), Co/Cu (2), AuCo/ Cu (4), AuCoB/Cu (5) and bare Au (3) catalysts in an alkaline glucose solution. Bar columns of anodic current peak densities for the same catalysts are given in Fig. 3b. It is clearly seen that the modification of the Co and CoB alloy coatings by Au nanoparticles results in a significantly higher electrocatalytic activity of the AuCo/Cu and AuCoB/Cu catalysts for glucose oxidation as compared to that of the unmodified Co/Cu and CoB/Cu and bare Au (Fig. 3a). A tremendous increase in the glucose oxidation current densities is observed for the AuCo/Cu and AuCoB/Cu catalysts as compared to the both CoB/Cu and Co/Cu catalysts, respectively. In addition, ca. 22 and even 67 times higher glucose oxidation current densities are obtained at the AuCo/Cu and AuCoB/Cu catalysts as compared to those for the unmodified CoB/Cu and Co/Cu (Fig. 3b). Moreover, ca. 1.6 and 3.6 times greater glucose oxidation current densities are observed at the AuCo/Cu and Au-CoB/Cu catalysts, respectively, compared to those for bare Au as depicted in Fig. 3a. On the other hand, the  $E_{\text{onset}}$  potential for glucose oxidation at AuCo/Cu and AuCoB/Cu is shifted by ca. 0.2 and 0.4 V, respectively, to more negative potential values as compared with that for the bare Au electrode. These results indicate that the deposition of a small amount of Au nanoparticles on the Co/ Cu and CoB/Cu significantly improves the performance of the both CoB/Cu and Co/Cu catalysts for the oxidation of glucose, compared to that of the bare Au.

Furthermore, to evaluate the activity of the AuCo/Cu and AuCoB/Cu catalysts, the glucose oxidation current density values were normalized by the Au loadings for each catalyst to represent the mass activity. The obtained data are shown in Fig. 3c. It is clearly seen that the higher mass activity for glucose oxidation shows the Au-CoB/Cu catalyst (ca. 1297 mA  $mg^{-1}_{Au}$ ) as compared with that of AuCo/Cu (984 mA  $mg^{-1}_{Au}$ ).



**Fig. 3.** (a) Anodic scans for CoB/Cu (1), Co/Cu (2), Au (3), AuCo/Cu (4) and AuCoB/Cu (5) recorded in a 0.1 M glucose + 0.1 M NaOH solution at 50 mV s<sup>-1</sup>. (b) Bar columns of anodic current peak density values for the same catalysts. (c) Bar columns of anodic current peak density values normalized by the Au loadings for AuCo/Cu and AuCoB/Cu

In conclusion, a higher activity of the Co/Cu and CoB/Cu catalysts modified with a small amount of Au nanoparticles may be related with the beneficial effect of smaller Au nanoparticles, deposited on Co/Cu and CoB/Cu from the Au(III)-containing solution. Furthermore, the enhancement of the catalytic abilities of the AuCoB/Cu and AuCo/Cu catalysts can be attributed to a higher number of the active sites on the catalyst surface as a result of the Au nanoparticles and CoB/Cu or Co/Cu interaction in the catalyst composition, which leads to higher activities for the oxidation of glucose as compared to those for the unmodified CoB/Cu and Co/Cu catalysts.

#### CONCLUSIONS

The AuCo/Cu and AuCoB/Cu catalysts with low Au loadings were prepared by a simple electroless Co deposition method followed by a spontaneous Au galvanic displacement from the Au(III)-containing solution. The electrocatalytic activity of the prepared catalysts for the oxidation of glucose was examined using cyclic voltammetry.

The prepared AuCo/Cu and AuCoB/Cu catalysts with the Au loadings of 11.6 and 14.3  $\mu g_{Au}$  cm<sup>-2</sup>, respectively, demonstrate a significantly higher electrocatalytic activity towards the oxidation of glucose as compared to those at the bare Au or Co/ Cu and CoB/Cu. Moreover, the process of glucose oxidation is significantly shifted to a more negative potential domain after the both Co/Cu and CoB/ Cu catalysts undergo modification by Au nanoparticles, indicating the higher activity of those catalysts as compared to that of the unmodified Co/Cu and CoB/Cu catalysts and bare Au electrode. It was found that ca. 22 and even 67 times higher glucose oxidation current densities have been obtained at the AuCo/Cu and AuCoB/Cu catalysts, respectively, as compared to those for the unmodified CoB/ Cu and Co/Cu. In addition, the prepared AuCo/Cu and AuCoB/Cu catalysts seem to be a promising anode material for direct glucose fuel cells.

> Received 5 December 2018 Accepted 11 December 2018

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## ELEKTROCHEMINĖS GLIUKOZĖS OKSIDACIJOS TYRIMAS ANT Co IR CoB LYDINIO DANGŲ, MODIFIKUOTŲ Au NANODALELĖMIS

#### Santrauka

Elektrocheminė gliukozės oksidacija buvo tirta ant Au nanodalelėmis modifikuotų Co ir CoB lydinio dangų, nusodintų ant Cu pagrindo. Co ir CoB lydinio dangos ant Cu pagrindo nusodintos cheminiu būdu, reduktoriumi naudojant morfolino boraną. Au nanodalelės buvo nusodinamos ant Co/Cu ir CoB/Cu katalizatorių, juos įmerkiant į 1 mM HAuCl<sub>4</sub> 30 °C tirpalą 30-iai sekundžių. Gautų katalizatorių aktyvumas gliukozės oksidacijos reakcijai buvo tirtas taikant ciklinės voltamperometrijos metodą.

Nustatyta, kad AuCo/Cu ir AuCoB/Cu katalizatoriai pasižymi didesniu elektrokataliziniu aktyvumu gliukozės oksidacijai nei gryni Au, Co/Cu ir CoB/Cu katalizatoriai. Be to, gliukozės oksidacija ant AuCo/Cu ir AuCoB/Cu katalizatorių prasideda neigiamesnėje potencialų srityje, palyginti su gliukozės oksidacijos pradžia ant nemodifikuotų Co/Cu ir CoB/Cu katalizatorių ar gryno Au katalizatoriaus. Išmatuotos gliukozės oksidacijos srovės tankio vertės ant AuCo/Cu ir AuCoB/Cu katalizatorių yra, atitinkamai, apie 22 ir 67 kartus didesnės, palyginti su gautomis ant Co/Cu ir CoB/Cu katalizatorių.