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Investigation of Borohydride Oxidation at Ultrafine Gold Layer Supported on Nickel

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The direct borohydride fuel cell has attracted increasing interest because of its potential advantages. So, it is important to find cost-effective catalysts for borohydride oxidation. One of them is nickel, which demonstrates good performance for hydrolysis of sodium borohydride due to its high specific surface area, but it oxidizes in alkaline media. An ultrafine gold layer presents a good protection for nickel. Moreover, gold catalyzes borohydride oxidation. In this work we have investigated the kinetics of instantaneous immersion gold deposition formation on nickel electrode by quartz crystal microbalance (QCM). The electrochemical behaviour of sodium borohydride on different electrodes: nickel, thin immersion gold layer deposited on it and bulk-form gold electrode has been studied by cyclic voltammetry.

Keywords: borohydride oxidation, immersion gold, nickel, quartz crystal microbalance.

INTRODUCTION

One of inorganic reducing agents sodium borohydride ($NaBH_4$) is characterized by interesting options for electrochemical power generation as a source of hydrogen or anodic fuel for direct borohydride fuel cells (DBFC) and batteries. In recent years the direct borohydride fuel cells has attracted increasing interest because of its potential advantages. A sodium borohydride anode is characterized by a high capacity (5.7 Ah g^{-1}) and energy density (9.3 Wh g^{-1} at 1.64 V). Moreover, sodium borohydride is rather safe, chemically stable and easy to transport in its dry state [1].

Our investigation substance nickel has good performance for hydrolysis of sodium borohydride due to its high specific surface area. In addition, it is cost-effective. But there are some problems in nickel electrode application as catalyst for borohydride oxidation in DBFC due to its oxidation in alkaline media. Noble metal gold has been used in the fuel cell for a wide range of applications such as gas phase catalysts, electro-catalysts and electrical connectors. Gold nanoparticles supported on carbon also have been studied aiming at a variety of applications, such as nanotechnology, catalysis in the oxidation of reducers, among them sodium borohydride [2–4]. Gold is an effective catalyst only for borohydride oxidation but not for hydrolysis [5].

In the present study, we investigated the immersion gold layer formation on the nickel electrode by quartz crystal microbalance. Another point was to find a cost-effective catalyst for borohydride oxidation and to protect nickel electrode from its oxidation and dissolution in alkaline media.

EXPERIMENTAL

The details of the quartz crystal microbalance (QCM) set-up employed are described elsewhere [6–8]. AT-cut quartz crystals of 6 MHz frequency (from Intellemetrics Ltd., UK) sputtered by gold from both sides was used in QCM. Their electrochemically and piezoelectric active geometric areas were 0.636 cm^2 and 0.283 cm^2, respectively. For the 6 MHz, AT-cut quartz crystal used in this study, a frequency change of 1 Hz corresponded to 12.26 ng cm^{-2}. This corresponds to the sensitivity of the QCM used 0.081 Hz ng^{-1} cm^2.

Quartz crystals were mounted in-between two silicone rubber o-rings at the bottom of the cell (the working volume of *ca*. 2 ml). All QCM measurements were performed with a precision frequency counter CH 3-64 connected to a PC through the IEEE 488 interface. The measured frequency (the stability ±0.5 Hz) were transferred to the PC every 1.3 s. All experiments were carried out at 20 °C.

Prior to the measurements, a nickel layer was electrodeposited on a gold sublayer onto quartz crystals installed at the bottom of the cell from a solution containing 0.05 mol l^{-1} $NiSO_4$ and 0.32 mol l^{-1} H_3BO_3, pH 4, at a potential of –1.3 V for 5 min. The nickel electrode was immersed into a 1 mmol l^{-1} $HAuCl_4$ solution in order to obtain immersion gold deposition layer on the nickel.

The electrochemical experiments of the anodic oxidation were carried out in a 1.0 mol l^{-1} NaOH solution containing sodium borohydride at a concentration of 0.05 mol l^{-1}, purged by argon. Analytical grade chemicals were used to prepare solutions. The electrochemical behaviour of sodium borohydride on different electrodes: nickel, a gold layer supported on nickel and gold electrode was investigated by cyclic voltammetry. Cyclic voltammetric curves (CVs) were recorded by using standard electrochemical equipment (a programming potentiostat PI-50-1.1, a sweep generator PR-8, two digital voltmeters B7-46/1 (Russia) connected to a PC through the IEEE 488 interface and a three electrodes electrochemical cell). A quartz crystal sputtered by gold working electrode (apparent surface area 0.636 cm^2), a Pt-wire counter electrode and Ag/AgCl/KClsat reference electrode were used. The potential scan rate was 10 mV s^{-1}. All potentials are given versus the SHE.

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RESULTS AND DISCUSSION

The electroplated nickel was chosen as a substrate for the formation of immersion gold layer due to the significant difference between the potentials of Ni/Ni^{2+} and Au^{3+}/Au. The reaction of the gold deposition takes place without another reducing agent:

$$3Ni^0 + 2Au^{3+} \rightarrow 2Au^0 + 3Ni^{2+} . \qquad (1)$$

The formation of ultrafine gold layer on the nickel electrode was studied by QCM. The QCM is basically a mass sensing device with the ability to measure very small mass changes as a fraction of monolayer or single layer of atoms on a quartz crystal resonator in real-time. The immersion gold layer may be equal to monolayer or less. Since nickel is a catalyst for borohydride oxidation, therefore, it is interesting to compare catalytic activities of the nickel substrate and thin immersion gold layer supported on them.

The data of the QCM measurements under open-circuit conditions given in Fig. 1 provide information on the kinetics of immersion gold layer formation and on instantaneous gold deposition rate, found respectively from the integral (Fig. 1, b) and differential (Fig. 1, a) changes of the quartz oscillator's frequency.

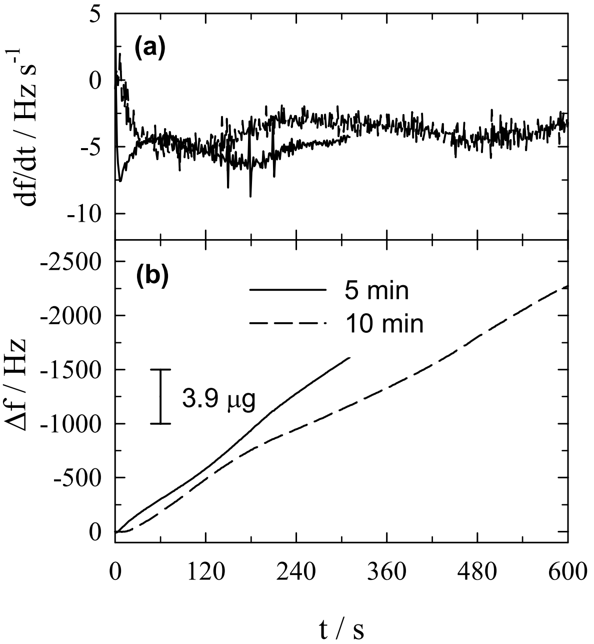

Fig. 1. Dependences of immersion gold deposition on the nickel electrode on time under open-circuit conditions: (a) frequency change rate and (b) change in frequency. The solution contained 1 mmol l^{-1} HAuCl$_4$, t = 20 °C

The coating mass increases with time (Fig. 1, b): 19 µg cm^{-2} and 28 µg cm^{-2} of gold was deposited over 5 min and 10 min, respectively. The data were obtained from the separate experiments.

The results of the electrochemical oxidation of sodium borohydride in 1.0 mol l^{-1} NaOH solution on the nickel electrode, on the gold layer supported on nickel and on a gold electrode are given in Figs. 2 and 3. Eight hydroxide ions are needed for each borohydride ion; therefore, the BH$_4^-$ oxidation reaction strongly depends on the hydroxide concentration. At a lower OH$^-$/BH$_4^-$ ratio, borohydride anions are hydrolyzed in solution, forming BH$_3$OH$^-$ [1]. When 1.0 mol l^{-1} of NaOH is used, the hydrolysis is negligible and the reaction begins after the absorption of BH$_4^-$ on the electrode.

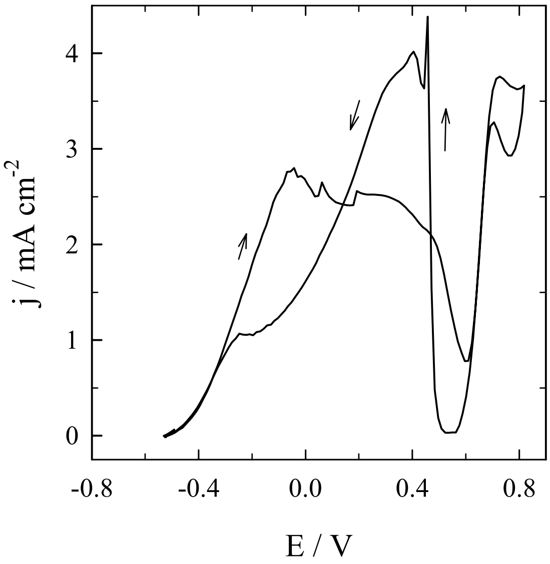

Fig. 2. Borohydride oxidation on the nickel electrode in 0.05 mol l^{-1} NaBH$_4$ and 1.0 mol l^{-1} NaOH solution. The potential scan rate 10 mV s^{-1}, t = 20 °C

Fig. 2 shows the anodic oxidation of borohydride on the nickel electrode. The voltammogram obtained over the potential range –0.5 V to 0.8 V possess a distinct plateau between –0.2 V and 0.4 V in the positive potential scan, showing a mass transport-limited borohydride oxidation current on the Ni electrode. The following decrease in activity of the electrode at 0.4 V may be attributed to the passivation of the electrode surface because of BH$_4^-$ intermediates adsorption. The Ni electrode oxidation and dissolution begins at potentials more positive than 0.6 V. In the reverse scan, an anodic peak at 0.4 V appears, shoving reactivation of the Ni surface. The actual anodic reaction of borohydride on the nickel electrode was proved to be a four-electron process instead of an ideal eight-electron process [9].

Higher anodic oxidation currents were obtained on the gold layer supported on nickel and bulk-form gold electrodes as compared with those of the nickel electrode (Fig. 3). A small quantity of gold (19 µg cm^{-2}) deposited on nickel electrode enhances its catalytic activity for the oxidation of borohydride and protects nickel from dissolution in alkaline media. In a positive-going scan at the potential 0 V, the current is 2.6, 7.0 and 23.0 mA cm^{-2}, respectively, for nickel, gold/nickel and gold electrodes (Fig. 3). The CV of borohydride oxidation on a gold layer supported on nickel electrode (Fig. 3, dashed line) is similar in shape to that recorded for borohydride oxidation on gold electrode (Fig. 3, solid line). The plateau of direct borohydride oxidation is larger in case of oxidation on the bulk-form gold or on the thin gold layer supported on Ni electrode (–0.3 V – 0.5 V) compare with one on the nickel electrode. The outset of borohydride oxidation on the Au supported on Ni or on the gold electrode is observed at more positive potentials. A high peak of anodic current is observed during the reverse scan at 0.5 V (on the gold

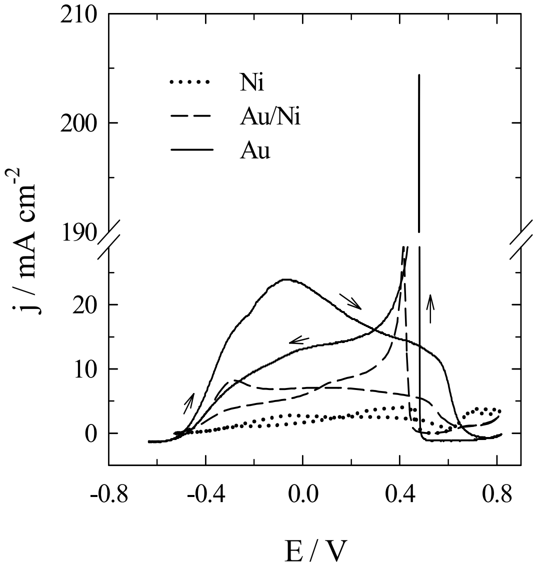

Fig. 3. The oxidation of borohydride on nickel (dotted line), on gold layer supported on nickel (dashed line) and on gold (solid line) electrodes in 0.05 mol l^{-1} NaBH$_4$ solution containing 1.0 mol l^{-1} NaOH. The amount of immersion gold formed in open-circuit conditions was 19 µg cm^{-2}. The potential scan rate 10 mV s^{-1}, t = 20 °C

electrode) and at 0.4 V (on the gold layer supported on nickel electrode) showing slight differences in the behaviour of gold and Au supported on Ni electrodes. The corresponding reverse peak on the Ni electrode is comparatively lower.

CONCLUSIONS

An ultrafine gold layer deposited on nickel by immersion method exhibit a significantly higher electrocatalytic activity for the electro-oxidation of borohydride as compared with that of the nickel electrode and prevent nickel electrode from its oxidation. The immersion gold layer (~19 µg cm^{-2}) deposited onto the nickel electrode behaves in the same way as the bulk-form gold electrode in alkaline media. The amount of immersion gold on nickel surface can be easily controlled by varying conditions of Au(III) solution preparation and gold deposition time.

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