Electrodeposited Nickel-Boron Thin-Film Ethanol Sensor

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Electrodeposited nickel-based ethanol sensor was constructed by thin-film technique. The sensing layers of nickel-boron films were prepared at constant cathodic current density of 1.5 mA cm⁻² in 0.91 M Ni₂SO₄, 0.19 M NiCl₂, and 0.49 M H₃BO₃ aqueous solution. Amperometric response of this miniaturized sensor was higher than that of the traditional bulky electrodes. The microfabricated electrodeposited nickel-boron electrode exhibits good electrochemical performance in terms of response time (90% = 9 s), linearity (100–600 ppm, r² = 0.998), and sensitivity (6.1 µA ppm⁻¹ cm⁻²). This sensor also shows a high selectivity to ethanol over malic, citric, ascorbic, and acetic acids. The optimal operating conditions of these ethanol sensors were 80°C of electrodeposition temperature and 20 min of electrodeposition time.

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Manuscript submitted September 2, 2005; revised manuscript received February 17, 2006. Available electronically April 19, 2006.

The development of a convenient method for the detection of ethanol has always been in great demand in the biotechnology and chemical industry. Ethanol assays are widely applied in breathalyzers, fermentation, medicine, food, and cosmetics. Several analytical methods have been proposed for the detection and quantification of ethanol, such as gas/liquid chromatography, spectroscopy, electrochemical analysis, and sensors. Among these, ethanol sensors may be the most promising method because of their convenience, simplicity, and accuracy.

Generally, electrochemical sensors have higher selective sensing characteristics than others. Enzyme modified electrodes with either alcohol dehydrogenase (ADH) or alcohol oxidase (AOX) are commonly used to determine ethanol concentration. However, enzyme modified electrodes should work at near-physiological conditions and suffer from the loss of bioactivity at room temperature. In addition to enzymes, other materials such as metal or metal oxide modified electrodes have been developed.

The sensing layers such as electrodeposited Co–Ni modified Pt electrode, co-electrodeposited Pt–WO₃ modified Au electrode, [Ni/Al–Cl] hydrotalcite-like clay modified glassy carbon (GC) electrode, and CuO modified Cu electrode have been studied. Each of them has its own outstanding property in the sensing performances. However, these sensors still have some shortcomings, such as the lifetime of Co–Ni modified Pt electrode is only 3 days and Pt–WO₃ modified Au electrode suffers long-term dissolution of WO₃.

In this study, an electrodeposited Ni–B electrode was used to sense ethanol because Ni-based electrodes have been shown to give a good performance and sensitivity. The sensor was constructed with an electrodeposited Ni–B film on microfabricated Pt/Ti thin film on an alumina substrate as the working electrode in liquid system to monitor ethanol. The electrochemical behaviors of the traditional bulk electrode and miniaturized electrode were compared. The characteristics of this developed ethanol sensor, such as sensing range, sensitivity, response time, selectivity, and reproducibility, were also explored.

Experimental

Reagent.—Rectangular alumina strips (8 × 25 × 0.635 mm) were purchased from Lei Ke Company, Taiwan. The nickel sulfate hexahydrate, nickel chloride-6-hydrate, and boric acid are GR grades of Showa (Japan), Riedel-deHaën (Germany), and Alfa Aesar (USA), respectively. Furthermore, ethanol and potassium hydroxide are GR grades of Riedel-deHaën. All aqueous solutions were prepared with deionized (DI) water purified to a resistivity of at least 18.3 MΩ cm by a water system (Mili-RO 60, Japan).

Sensing electrodes preparation.—A miniature-size ethanol sensor was fabricated by using thin-film techniques as described elsewhere and its structure is shown in Fig. 1. The pairs of platinum interdigitated electrodes were formed by a magnetron d-c sputtering device and photore sist pattern mask on the alumina substrate. The inner layer of Ti film was deposited in order to improve the adhesion between Pt and the substrate. Nickel-boron films were prepared by cathodic deposition of nickel in 0.91 M NiSO₄, 0.19 M NiCl₂, and 0.49 M H₃BO₃ aqueous solution at various temperatures and deposition time on Pt/Ti on Al₂O₃ substrate. All electrochemical synthesis processes were controlled galvanostatically at constant cathodic current density of 1.5 mA cm⁻². A platinum plate and Ag/AgCl (in saturated KCl) were employed as the counter and reference electrodes, respectively, in the deposition cell. The prepared film was partially sealed with a Teflon tape to define 0.15 cm⁻² geometry areas of working electrode. A conventional large-size electrodeposited Ni–B modified Pt foil electrode (1 × 1 cm² geometry area) was prepared in the same electrodeposition conditions for comparison.

Electrode characterization.—The electrochemical properties of the electrodes were performed by cyclic voltammetry and chronoamperometry using an EG&G 273A potentiostat with m270 Electrochemical Analysis System. The surface morphology was examined by scanning electron microscope (SEM, S-2500, Hitachi). The structure of the electrodeposited Ni–B electrode was characterized using an X-ray diffractometer (XRD, Rint-2200, Rigaku) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS, Fison, ESCA210) was used to analyze the surface composition (ration of B to Ni).

Sensing procedure.—A three-electrode electrochemical cell was used as the sensing system. Aqueous solution containing 0.1 M KOH as electrolyte was added into a Pyrex flask. The electrodeposited Ni–B/Pt/Ti (0.15 cm²) and sputtered Pt/Ti (0.15 cm²) films on the same material of the Al₂O₃ substrate were used as working electrode and counter electrode, respectively. An EG&G 273A potentiostat with m270 Electrochemical Analysis was used to control potential and record the corresponding current. All potentials were referred to the reference electrode, Ag/AgCl (in saturated KCl) aqueous solution. After choosing the properly applied potential at which the mass transfer of ethanol to electrode surface was the rate-determining step, the sensing process could be carried out. When the background current was stable, the desired amount of testing ethanol was injected into the flask and the amperometric response current of the working electrode was recorded.

Results and Discussion

Characteristics of the electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrodes.—The crystalline structure and the surface morphology of the produced electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode were characterized by XRD and SEM. The XRD measurements on the electrodeposited Ni–B films prepared at vari-
ous temperatures in the range from 40 to 80°C for 30 min are shown in Fig. 2. It was found that the crystalline Ni$_3$B phase was well formed according to the PCPDFWIN-power diffraction file. The crystal structure was orthorhombic when the electrodeposition temperature was in the range from 40 to 80°C.

The surface morphologies of the electrodeposited Ni–B films with various electrodeposition temperatures are shown in Fig. 3. These photographs reveal that the surface morphology of electrodeposited Ni–B films is strongly dependent on the electrodeposition temperature. The Ni–B deposit exhibited a pyramid-like structure consisting of thousands of small particles with an average size of less than 60 nm. As the electrodeposition temperature increased, the grain size of crystalline increased, which was consistent with the observation XRD patterns.

Comparison of electrochemical behaviors of traditional bulky and miniaturized electrodes.— Cyclic voltammograms were carried out in 0.1 M KOH with or without ethanol, both on a conventional electrodeposited Ni–B modified Pt foil and on a miniaturized electrodeposited Ni–B/Pt/Ti on Al$_2$O$_3$ substrate electrode to compare their electrocatalytic behaviors. For the electrodeposited Ni–B modified Pt foil electrode (Fig. 4a), the anodic peak exhibited at 570 mV (vs Ag/AgCl) while the cathodic peak appeared at 455 mV (vs Ag/AgCl) in the absence of ethanol. Oxygen evolution took place at 600 mV (vs Ag/AgCl). With repetitive additions of ethanol, the oxidation peak increased continuously in the range from 550 to 600 mV (vs Ag/AgCl). For the electrodeposited Ni–B/Pt/Ti on Al$_2$O$_3$ substrate electrode (Fig. 4b), the anodic peak exhibited at 465 mV (vs Ag/AgCl) and the cathodic peak was located at 350 mV (vs Ag/AgCl). The discrepancy in the redox peak potential between a conventional electrodeposited Ni–B/Pt/Ti on Al$_2$O$_3$ substrate electrode and a miniaturized electrodeposited Ni–B/Pt/Ti on Al$_2$O$_3$ substrate electrode may be attributed to the different structures of Ni$_3$B as well as NiOOH. Bode and co-workers$^{15}$ first discovered the existence of two forms of Ni(OH)$_2$, including an anhydrous form of $\beta$-Ni(OH)$_2$ and a hydrated form of $\alpha$-Ni(OH)$_2$. In general, the anodic oxidation peak of $\beta$-Ni(OH)$_2$ is more positive than that of $\alpha$-Ni(OH)$_2$ and the oxidation state of $\gamma$-NiOOH is higher than that of $\beta$-NiOOH.$^{16,17}$ Furthermore, $\gamma$-NiOOH has higher electroactivity for ethanol oxidation than $\beta$-NiOOH.$^{15}$ It seems that the redox pair of $\beta$-Ni(OH)$_2$/$\beta$-NiOOH was formed on the surface of a conventional electrodeposited Ni–B modified Pt foil electrode, while $\alpha$-Ni(OH)$_2$/$\gamma$-NiOOH was generated on the surface of a miniaturized electrodeposited Ni–B/Pt/Ti on Al$_2$O$_3$ substrate electrode. The higher reversible redox capacity and larger anodic current density for ethanol oxidation of an electrodeposited Ni–B/Pt/Ti on Al$_2$O$_3$ substrate electrode also supports this suggestion.

NiOOH acts as an electrocatalyst in alkaline for alcohol oxidation, as proposed by Fleischmann et al.,$^{20}$ due to the observation that alcohols were oxidized at a potential which coincided exactly with that where NiOOH was produced and on the disappearance of the NiOOH reduction peak in the negative sweep. However, this assumption has been questioned by other authors,$^{21-23}$ who observed the unchanged current of Ni(OH)$_2$ oxidation and NiOOH reduction in the presence of alcohol while a new peak at positive potential corresponded to alcohol oxidation. Tarasewicz$^{24}$ supposed that methanol penetrated a nickel oxide film and was oxidized by the OH$^-$ ions trapped in the film. However, El-Shafei$^{25}$ suggested that the appearance of two anodic peaks in the presence of methanol is due to the slowness of the catalytic reaction between methanol and NiOOH compared with the redox reaction of NiOOH/Ni(OH)$_2$. These different electrochemical behaviors for ethanol oxidation are individually observed at a conventional electrodeposited Ni–B modified Pt foil and a miniaturized electrodeposited Ni–B/Pt/Ti on
Al₂O₃ substrate electrodes, respectively. It indicated that the interaction between the ethanol and NiOOH may be influenced by the structure of NiOOH. Additionally, the \( \text{Ni}^{2+}/\text{H}_2\text{O} \)-Ni\text{OH}/\text{H}_2\text{O}_{2}/\text{NiOOH} \) media-\( \text{tor} \) formed on the surface of a miniaturized electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode could catalyze the oxidation of ethanol efficiently.

\[ \text{Determination of potential window.} \] — The linear sweep voltammetry technique is applied to obtain the limiting current as shown in Fig. 5. The Ni–B sensing film was prepared with 2.24 Ni²⁺/H₂BO₃ mole ratio at an electrodeposition temperature of 80°C for 20 min. The applied potential range was from 450 to 700 mV (vs Ag/AgCl) and the scan rate was 0.1 mV s⁻¹. When the potential increased from 450 to 560 mV (vs Ag/AgCl), the response current increased from 40 to 325 \( \mu \text{A} \). The response in this potential range was controlled by both kinetic and mass-transfer mechanisms. Further increasing the sensing potential from 560 to 620 mV (vs Ag/AgCl) resulted in a constant response current of about 347 \( \mu \text{A} \); thus, the reaction was controlled by the mass transfer at this potential range. This potential region is called the limiting current region and 347 \( \mu \text{A} \) was observed to be the limiting oxidation current of 600 ppm. The potential at 560 mV (vs Ag/AgCl) was chosen as the applied potential for sensing ethanol concentrations in this study.

\[ \text{Chronoamperometry.} \] — A typical current-time response of the prepared electrode at the applied potential 560 mV (vs Ag/AgCl) both on a conventional electrodeposited Ni–B modified Pt foil electrode and a miniaturized electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode is shown in Fig. 6. After the background current was stable, 0.1 mL of ethanol solution (2.45 mL ethanol in 100 mL) was added to 0.1 M KOH electrolyte. While the system reached its steady-state value, successive additions of the ethanol solution were injected into the electrolyte. The ethanol concentration after each addition step increased 100 ppm and the anodic current rose to reach a stable value. The response current for ethanol oxidation on a miniaturized electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode...
sensing conditions: same as Fig. 6.

Figure 7. Plot of response current against ethanol concentration both on a miniaturized electrodeposited Ni–B/Pt/Ti on Al2O3 substrate and a conventional electrodeposited Ni–B modified Pt foil electrodes. Preparation and sensing conditions: same as Fig. 6.

is much higher than that on an electrodeposited Ni–B modified Pt foil electrode. The response times (reaching 90% of the maximum response) were 9 and 21 s on a miniaturized electrodeposited Ni–B/Pt/Ti on Al2O3 substrate electrode and a conventional electrodeposited Ni–B modified Pt electrode, respectively.

The steady-state values of the response current in Fig. 6 were plotted against the concentration of ethanol as shown in Fig. 7. The linear range of ethanol concentration spanned between 100 and 600 ppm. The sensitivities for a miniaturized electrodeposited Ni–B/Pt/Ti on Al2O3 substrate electrode and a conventional electrodeposited Ni–B modified Pt electrode are 6.1 and 0.3 μA ppm⁻¹ cm⁻², respectively. The great sensitivity of a miniaturized electrodeposited Ni–B/Pt/Ti on Al2O3 substrate electrode is also higher than that previously cited.⁹–¹⁰

Effect of electrodeposition temperature.— The effect of electrodeposition temperature taken to prepare the electrodes on the boron content and the sensitivity of an electrodeposited Ni–B electrode was studied as shown in Fig. 8. As the electrodeposition temperature increased from 40 to 80°C, B/Ni weight ratio increased from 0.13 to 0.18 and the sensitivity of ethanol sensor increased from 0.87 to 5.73 μA ppm⁻¹ cm⁻². Previous observations of electrode characterizations show that increasing the electrodeposition temperature would decrease the surface areas of the electrodeposited Ni–B films. However, the best sensitivity with an electrodeposition temperature of 80°C was obtained where the surface area is smallest. This indicated that the effect of the surface area on sensitivity was insignificant. An increase of the sensitivity at higher temperature may arise due to the increased boron content that could cocatalyze the anodic oxidation of ethanol efficiently. As we were more interested in obtaining the highest sensitivity, 80°C electrodeposition temperature was selected for further studies.

Figure 8. Effect of electrodeposition temperature on the sensitivity of ethanol sensing and the B/Ni weight ratio on the film. Preparation conditions: 0.91 M NiSO₄, 0.19 M NiCl₂, and 0.49 M H₃BO₃ aqueous solution, 80°C electrodeposition temperature. Sensing conditions: KOH electrolyte: 0.1 M; ethanol concentration: 600 ppm; applied potential: 560 mV (vs Ag/AgCl); stirring rate: 560 rpm; temperature: 25°C.

Effect of electrodeposition temperature.— The effect of electrodeposition time used for preparing the electrodes on the sensitivity and the response time of the ethanol sensor is studied as shown in Fig. 9. The sensitivity of the ethanol sensor increased from 2.67 to 6.1 μA ppm⁻¹ cm⁻² by increasing electrodeposition time from 10 to 20 min, and further increasing the electrodeposition time from 20 to 50 min caused the sensitivity to decrease from 6.1 to 2 μA ppm⁻¹ cm⁻². Additionally, increasing the electrodeposition time from 10 min to 50 min increased the response time from 6.3 to 18 s. The results showed that the sensitivity reached a maximum value of 6.1 μA ppm⁻¹ cm⁻² at 20 min of electrodeposition time, whereas the fast response time was 6.3 s at 10 min of electrodeposition time. Because the effect of electrodeposition time on the sensitivity and the response time of the ethanol oxidation would be directly involved with the thickness of the Ni–B films, the corresponding thicknesses of Ni–B films and anodic peak current of Ni(OH)₂ oxidizing to NiOOH of electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrodes are listed in Table I.

As the electrodeposition time increased from 10 to 50 min, the thicknesses of Ni–B films increased from 1.01 to 8.8 μm, and the anodic peak current of Ni(OH)₂ oxide to NiOOH decreased from 545.6 to 447.8 μA. It was at once evident that, though linearity was shown between the electrodeposition time and the thicknesses of Ni–B films, the formation of NiOOH did not grow proportional to the electrodeposition time continuously. Wohlfahrt-Mehrens et al. verified that the nickel hydroxide was predominately an ionic conductor. This means that the electrochemical reaction must occur underneath the ionic conductor at the Ni(OH)₂/Pt surface, whereas...
the chemical reaction occurred at the interface of electrolyte and Ni(OH)₂. If the thicknesses of Ni(OH)₂ film were too thick, the conductivity of the film would be poor and decrease the current of Ni(OH)₂ oxidizing to NiOOH. That also causes the increase of diffusion resistance and results in decrease of the sensitivity and increase of the response time.

Selectivity studies.—— Some acids may be present as the ethanol sensor is to be used in medical or brewing applications. Therefore, the following acids were tested as potential interfering species: malic acid, citric acid, ascorbic acid, and acetic acid. A comparison of sensitivities on various interfering analytes is shown in Fig. 10. The results show that the electrodeposited Ni–B/Pt/Ti on Al₂O₃ exhibits a very high selectivity toward ethanol. The sensitivity of this sensor for ethanol oxidation was five times larger than that for the oxidation of ascorbic acid. No obvious response currents were obtained for malic acid, citric acid, and acetic acid. These observations indicate this sensor is suitable for medical or brewing applications.

Reproducibility test.— The reproducibility of successive measurements with a single sensor is shown in Fig. 11. The electrodeposited Ni–B/Pt/Ti on Al₂O₃ electrode used for this test was prepared at 80°C for electrodeposition temperature with 30 min of electrodeposition time. The selectivity of the electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrodes prepared at different electrodeposition times is shown in Fig. 11. The electrode-test for an electrode used 21 times showed that the sensitivity of the prepared Ni–B films depended on the B/Ni weight ratio, from 100 to 600 ppm with relatively fast response time. The sensitivity decreased to 3.65 A ppm⁻¹ cm⁻² after 31 repeat tests. The fluctuating sensitivity during successive measurements indicated the instability of the electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode. The instability may result from the phase transformation of NiOOH. When an electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode was immersed in KOH solution, α-Ni(OH)₂ was formed. After applying the proper potential, γ-NiOOH was generated and efficiently electrocatalyzed the ethanol oxidation. However, α-Ni(OH)₂ is not stable and it spontaneously dehydrates in concentrated alkali to β-Ni(OH)₂.¹⁵ The electrocatalytic activity of β-NiOOH for ethanol oxidation is poorer than α-NiOOH, resulting in the decrease of sensitivity. Although β-Ni(OH)₂ is more stable than α-Ni(OH)₂, β-NiOOH is converted to γ-NiOOH while the electrode is overcharged.¹⁵ Therefore, the transformation between the γ-NiOOH and β-NiOOH phases would lead to different response currents for ethanol oxidation. In order to solve the phase transformation of NiOOH, the more modified nickel electrodes will be explored further. Al-substituted nickel hydroxide²⁶ and zinc-substituted nickel hydroxide²⁶ are reported to effectively stabilize α-Ni(OH)₂/γ-NiOOH and β-Ni(OH)₂/β-Ni–OOH, respectively, in battery applications. These metal-substituted nickel hydroxide electrocatalysts might be a good way to solve the stability problem.

Conclusions

A miniaturized electrodeposited Ni–B/Pt/Ti on Al₂O₃ electrode was produced using thin-film microfabrication technology. This sensor exhibits high sensitivity to ethanol concentration in the range from 100 to 600 ppm with relatively fast response time. The sensitivity of the prepared Ni–B films depended on the B/Ni weight ratio, electrodeposition time, and the structure of NiOOH. The best sensitivity of this sensor was about 6.1 A ppm⁻¹ cm⁻², and the optimal operation conditions of the electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode were 80°C of electrodeposition temperature and 20 min of electrodeposition time.

Acknowledgments

The support of the National Science Council of the Republic of China (NSC 90-2214-E-006-001), Ministry of Education (EX-91-E-FA09-5-4), and National Cheng-Kung University is gratefully acknowledged.

<table>
<thead>
<tr>
<th>Electrodeposition time (min)</th>
<th>Electrodeposition thickness (µm)</th>
<th>Anodic peak current of Ni(OH)₂ oxide to NiOOH (µA)</th>
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<td>50</td>
<td>8.8</td>
<td>447.8</td>
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Figure 10. The selectivity of the electrodeposited Ni–B/Pt/Ti on Al₂O₃ substrate electrode for ethanol, malic acid, citric acid, ascorbic acid, and acetic acid. Preparation conditions: electrodeposition temperature: 80°C; electrodeposition time: 30 min. Sensing condition: KOH electrolyte: 0.1 M; applied potential: 560 mV vs Ag/AgCl; stirring rate: 560 rpm; temperature: 25°C.

Figure 11. The reproducibility of successive measurements repeated 31 times with a single sensor. Preparation conditions: electrodeposition temperature: 80°C; electrodeposition time: 30 min. Sensing condition: KOH electrolyte: 0.1 M; ethanol concentration: 600 ppm; applied potential: 560 mV vs Ag/AgCl; stirring rate: 560 rpm; temperature: 25°C.
National Cheng Kung University assisted in meeting the publication costs of this article.

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