Preparation of a Novel Ni-In Alloy Electrode and its Electrocatalytic Activity

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Nickel electrode, indium electrode and two kinds of Ni-In alloy electrodes (A-type and B-type) were prepared by electrodeposition method and their voltammetric behaviours were investigated in a 0.2 mol/L NaOH solution. The electrocatalytic activities of glucose on these electrode surfaces were also examined. The results of electrochemical experiments indicated that the Ni electrode and Ni-In alloy electrodes had catalysis effect on glucose oxidation in an alkaline solution. The A-type Ni-In alloy electrode, prepared in an electrolyte at a 5:1 Ni^{2+}/In^{3+} mole ratio, had the best electrocatalytic activity. There was a liner relationship between glucose oxidation peak current and its concentration in the range of 1-10 mmol/L. The A-type Ni-In alloy electrode in alkaline solution was steady and it preferably resisted surface poisoning. This alloy electrode can be used as a high catalytic activity electrode of glucose sensor and glucose fuel cell.

Key Words: Ni-In alloy electrode, Cyclic voltammetry, Electrocatalytic, Glucose.

INTRODUCTION

Alloy electrodes have many special electrochemical functions and they are especially useful in electrocatalysis oxidation and electrochemical determination of organic and biologic molecules[1-4]. In recent reports, the alloy electrodes with better electrocatalysis activity usually prepared by noble metals or their oxide particles[5-8]. Nickel and their alloys are important engineering materials used widely in many fields because of their special properties such as magnetic, heat-conductive and electrocatalytic properties[8-10]. Compared with noble metals, nickel is cheaper, so it draws more and more attentions from worldwide electrochemical researchers. However, the studies on Ni alloy electrodes are mainly about applications of which used as electrocatalyst for the hydrogen and oxygen evolution reaction and these alloy electrodes are mostly Ni-Co, Ni-S-Co, Ni-rare earths, Ni-Mo, *etc.*[11-14]; while there are few studies on Ni alloy electrodes applied in glucose electrocatalysis oxidation and used as catalytic activity electrodes. Indium has better stability and capability of restraining hydrogen evolution in alkaline medium so that it is usually used as cathodal additive and current collector of the alkaline battery[15-19].

Eletrocatalysis for the oxidation of glucose is of importance to the development of the glucose sensor and glucose fuel cell[20-24]. The reaction equation of glucose electrocatalysis oxidation[25,26] in alkaline solution is

$$C_6H_{12}O_6 \xrightarrow{[O]/[OH^-]} C_6H_{12}O_7.$$
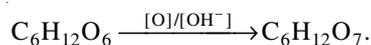
The electrocatalysis activity of metal nickel will increase when some metal ions or metal oxides are added in[27,28]. In this study, we prepared two kinds of Ni-In alloy electrodes (A-type and B-type) and discussed about their cyclic voltammetric behaviours in alkaline medium and electrocatalytic activities for glucose oxidation. We also investigated the stability of these alloy electrodes and the influence of glucose concentration on glucose oxidation peak current and the results are satisfactory.

EXPERIMENTAL

All electrochemical measurements were carried out in a conventional three-electrode cell controlled by CHI 650 electrochemical workstation (Shanghai Chenhua Instruments, China). The nickel electrode, indium electrode and Ni-In alloy electrodes were used as working electrodes. A platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. All potentials mentioned in this paper were referred to this reference electrode. The working electrodes were washed clean before the experiments by CQ50 ultrasonicator (Shanghai ultrasonic Instruments, China). The component of Ni-In ally was determined by PV9100 energy dispersive X-ray analyzer (EDAX Instruments, USA). $In_2(SO_4)_3 \cdot 5H_2O$ (purity > 99.99 %) and $NiSO_4 \cdot 6H_2O$ (purity > 99.99 %) was purchased from Tianjin Guangfu fine chemical research institute (Tianjin, China). Unless otherwise

stated, all chemicals and reagents used were of analytical reagent grade and all the chemicals and reagents were used without further purification. All solutions were prepared using redistilled water and deoxygenated by bubbling N_2 throughout the experiments.

Fabrication of electrodes: The substrate electrode of electrodepositing was a copper pole with $0.3 \, cm^{-2}$ working surface acreage. Before each electrodeposition experiment, the copper pole was polished and washed under running water at first, then ultrasonically cleaned with acetone and distilled water for 10 min in turn, at last it was aired naturally for the future use. All the experiments were carried out under room temperature and the solutions of 1 mol/L NaOH and 1 mol/L H_2SO_4 were used to regulate the pH value of electrolytes.

The preparation conditions of four different working electrodes are as follows: **(1) Ni electrode:** The plating solution was composed of $NiSO_4 \cdot 6H_2O$ of 16 g/L and citric acid of 20 g/L and the plating time was 5 min and the electric current density was 2 A/dm². **(2) In electrode:** The plating solution was composed of $In_2(SO_4)_3 \cdot 5H_2O$ of 18 g/L, H_2SO_4 of 25 mL/L and Na_2SO_4 of 10 g/L and the plating time was 10 min and the electric current density was 5 A/dm². **(3) A-type Ni-In alloy electrode:** The plating solution were composed of different mole proportions of Ni^{2+} and In^{3+} and the mole proportions were 1:1, 3:1, 5:1, 7:1 with trisodium citrate of 10-20 g/L, respectively. The pH value of above electrolytes adapted to 3 and the plating time was 10 min and the electric current density was 2 A/dm². **(4) B-type Ni-In alloy electrode:** This kind of electrodes were got by first electroplating in Ni electrolyte for 5 min and then in In electrolyte for 5 min and the electric current density was 2 A/dm².

RESULTS AND DISCUSSION

Voltammetric behaviours of electrodes in alkaline medium: Typical cyclic voltammograms (CVs) of four different electrodes in a 0.2 mol/L NaOH solution are shown in Fig. 1 (curve a: In electrode; curve b: Ni electrode; curve c: A-type Ni-In electrode; curve d: B-type Ni-In electrode). From curve a, it can be showed that oxidation peak (O1) occured at -0.38 V and reduction peak (R1) occured at -0.7 V, which corresponded to oxidation of In and reduction of oxidated In(III) in alkaline solution. There was no obvious hydrogen evolution peak because hydrogen was difficult to separated out on In surface with comparatively larger over-potential in alkaline medium[16-19]. From curve b, it is shown that the first oxidation peak (O2) occured around -0.4 V and the second faint oxidation peak (O3) occured around -0.2 V; that's probably because Ni was at first oxidated into Ni(II) and then further oxidated into Ni(III); however Ni(II)/Ni(III) has electrocatalytic activity[4,25]. In addition, two reduction peaks (R2 and R3) occured around -0.45 and -0.85 V, respectively which illustrated that reduction process of Ni(III) went through two steps corresponding to Ni(III) → Ni(II) → Ni. Compared curve c with curve b, the oxidation peak and reduction peak of A-type Ni-In electrode were kind of bigger compared to Ni electrode; but the oxidation peak current of O4 became about ten times bigger than that of O2, which showed after adding in In, electrocatalytic activity of Ni increased greatly; meanwhile,
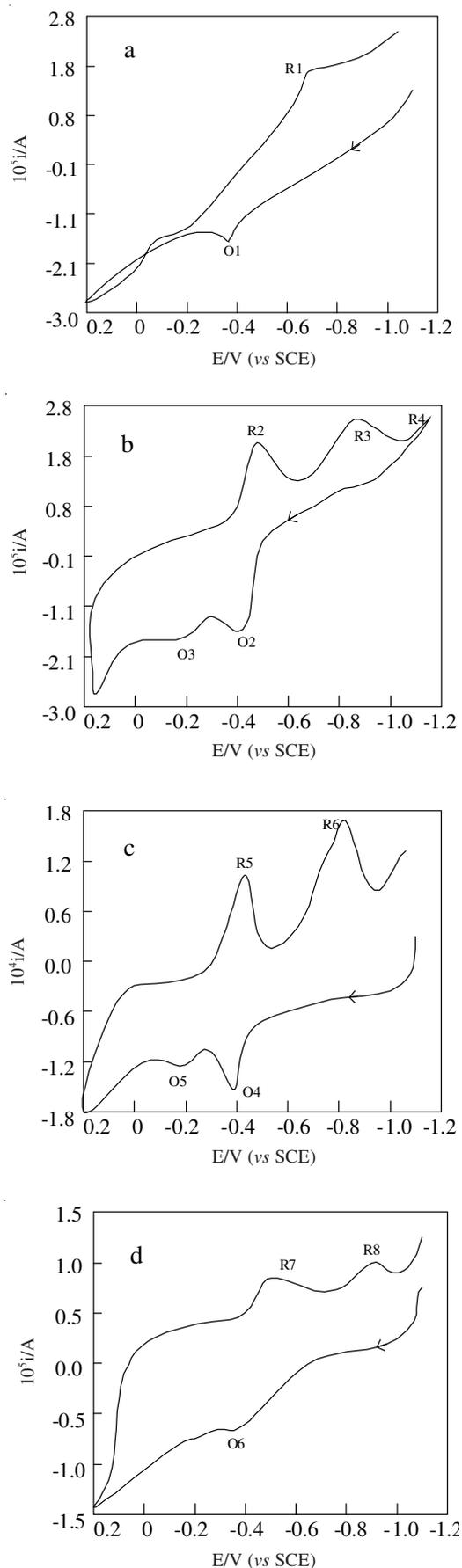
Fig. 1. Cyclic voltammograms of four electrodes in a 0.2 mol/L NaOH solution (curve a: In electrode; curve b: Ni electrode; curve c: A-type Ni-In electrode; curve d: B-type Ni-In electrode)

without hydrogen evolution peak, it was helpful to improve the longevity and stability of this kind of Ni-In electrodes due to the contributions of In[18,19]. Compared curve d with curve c, it can be known that oxidation peak and reduction peak of B-type Ni-In electrode were smaller, so its electrocatalytic activity was lower. It can be seen through the above analysis, Ni electrode and A-type Ni-In electrode have comparatively higher electrocatalytic activity in alkaline medium and A-type Ni-In electrode has the highest electrocatalytic activity.

Electrocatalytic activities of electrodes: Fig. 2 shows cyclic voltammograms of four electrodes for In electrode, Ni electrode, A-type and B-type Ni-In electrodes in a 0.2 mol/L NaOH containing 10 mmol/L glucose. From the curve a in Fig. 2, it can be seen that In electrode didn't have any catalytic activity for glucose oxidation under the present experimental conditions. Compared with the curve b in Fig. 1, the basic shape of curve b in Fig. 2 hasn't changed, the current of first oxidation peak increased a little and the currents of R1 and R2 decreased a little. Curve d in Fig. 2 represents for the catalytic activity of B-type Ni-In electrode for glucose oxidation, the current of oxidation peak was smaller than that of Ni electrode, it was further shown that the catalytic activity of B-type Ni-In electrode was weaker. Compared curve c in Fig. 2 with curve c in Fig. 1, currents of redox peaks of A-type Ni-In electrode increased obviously. The first oxidation peak current increased more than one time, which showed that glucose could be oxidated to a great extent on this Ni-In electrode so it make the oxidation current increase and this kind of alloy electrodes can be used as high catalytic activity electrodes of the glucose sensors and glucose fuel cells.
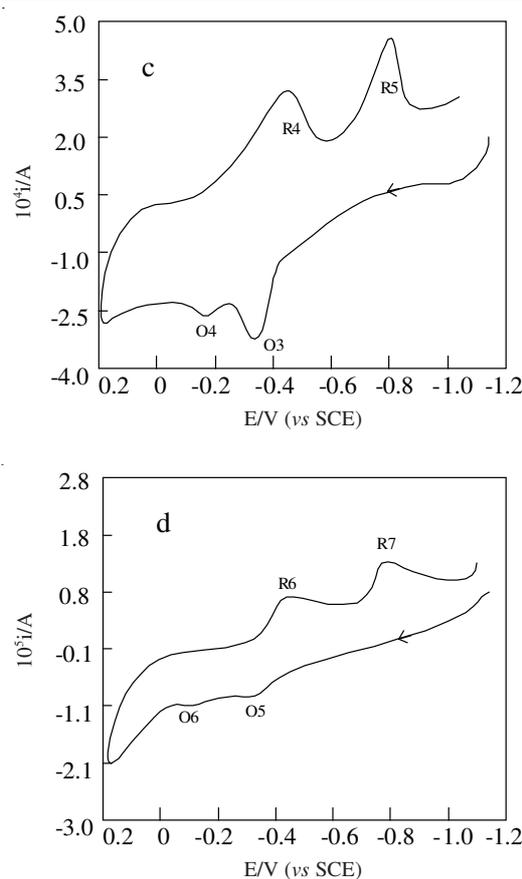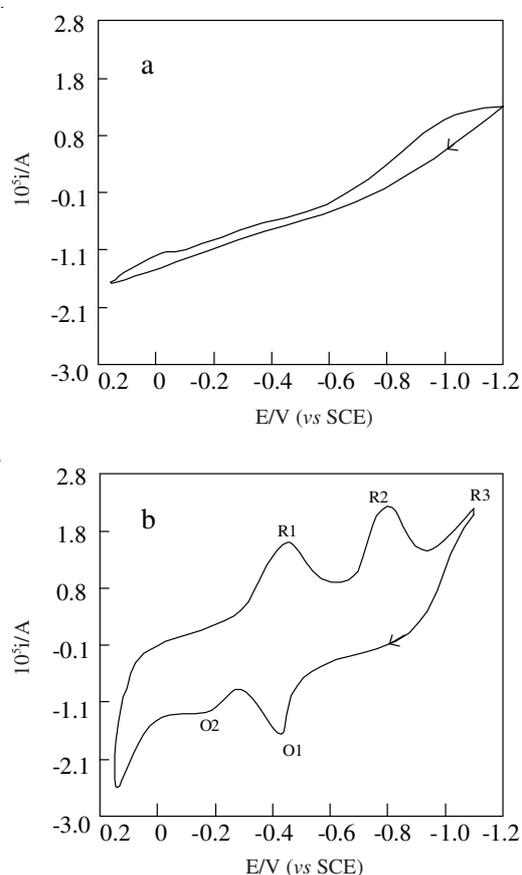
Fig. 2. Cyclic voltammograms of four electrodes in a 0.2 mol/L NaOH containing 10 mmol/L glucose (curve a: In electrode; curve b: Ni electrode; curve c: A-type Ni-In electrode; curve d: B-type Ni-In electrode)

Current-time curves: Fig. 3 illustrates current-time curves of Ni electrode and Ni-In electrodes in a 0.2 mol/L NaOH solution containing 10 mmol/L glucose. According to voltammograms of Fig. 2, the oxidation potentials of glucose on Ni electrode and Ni-In electrode surfaces were between -0.4 ~ -0.3V, so -0.3 V was chosen to be the step potential for
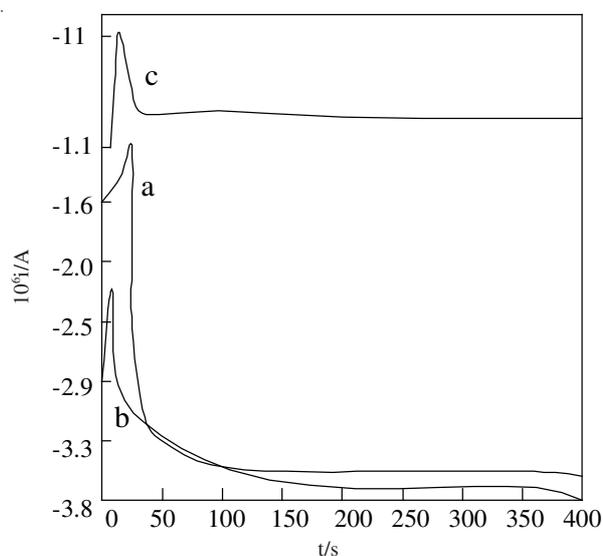
Fig. 3. Current-time curves of three electrodes in a 0.2 mol/L NaOH solution containing 10 mmol/L glucose (curve a: Ni electrode; curve b: B-type Ni-In electrode; curve c: A-type Ni-In electrode)

the present experiment corresponding to the electrocatalytic oxidation reaction of glucose. It is shown in Fig. 3 that the currents came to their maximums within 50 s, then kept stable, which showed that oxidation speed of glucose was faster under the catalysis of Ni and a homeostasis achieved rapidly. Further compared the curves in Fig. 3, it was found out that curve c became stable within 40 s and the current kept stable with time went along; while the currents of curve a and curve b dropped dramatically within 50 s, later the currents still decreased slowly. In addition, compared to curve a and curve b, the steady current of curve c was several times higher than those of them, which showed that glucose could be oxidated fastest and most effectively on the surface of A-type Ni-In electrode and soon achieved stable diffusing-control current. The electrocatalytic activity of A-type Ni-In electrode was the highest and this result was the same to the above one.

Influence of A-type Ni-In electrode component on its catalytic activity: The A-type Ni-In alloy electrode was manu-factured in mixed plating solution by electrodepositing. The components of this alloy electrode had great effect on its catalytic activity. Table-1 lists the effects of Ni^{2+}/In^{3+} mole ratio on electrocatalytic activities of this kind of Ni-In alloy electrodes, among which I_p denoted the first oxidation peak current of alloy electrode in a 0.2 mol/L NaOH solution; I_p' denoted the first oxidation peak current of the alloy electrode in a 0.2 mol/L NaOH solution containing 10 mmol/L glucose. It was concluded from the table that compared with Ni electrode, A-type Ni-In electrode had higher catalytic activity on glucose; at the same time, with the increase of Ni^{2+} in plating solution, the oxidation peak current of glucose increase as well. When the ratio of Ni^{2+}/In^{3+} mole became 5:1, the oxidation peak current reached the highest and then decreased, all of which showed the alloy electrode had best catalytic activity when made under the condi-tion that Ni^{2+}/In^{3+} mole ratio was 5:1. The result of chemical composition analysis obtained by EDX revealed the A-type Ni-In ally electrode (Ni^{2+}/In^{3+} 5:1) contains 84 % Ni and 16 % In (weight per cents).

TABLE-1
EFFECT OF Ni^{2+}/In^{3+} MOLE RATIO ON ELECTROCATALYTIC ACTIVITY OF A-TYPE Ni-In ELECTRODE

$n(Ni^{2+}):n(In^{3+})$	$10^5\ I_p\ (A)$	$10^5\ I_p'\ (A)$	Increase ratio (%)
1:0	0.910	1.396	53.41
1:1	1.689	2.928	73.36
3:1	3.360	6.237	85.63
5:1	15.85	33.58	111.9
7:1	4.866	8.118	66.83

Relationship between glucose concentration and its oxidation current: In the 0.2 mol/L NaOH solution, there was a good liner relationship between glucose concentration and its oxidation current in the range of 1-10 mmol/L and the detection limit was 0.01 mmol/L. In addition, when glucose concentration was between 10-15 mmol/L, the increase of oxidation current became slower. After 15 mmol/L, there was little change of the current; which might because catalytic activity locations on electrode surface were fully occupied by glucose molecules and reached their highest catalytic ability.

Stability of the A-type Ni-In alloy alloy electrode: Fig. 4 depicts cyclic voltammograms of an A-type Ni-In alloy electrode
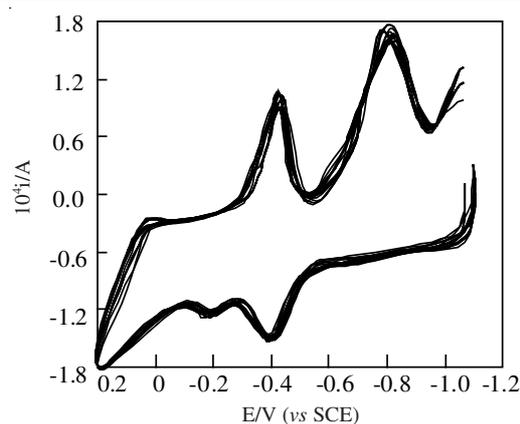
Fig. 4.   Cyclic voltammograms of A-type Ni-In alloy electrode in 0.2 mol/L NaOH solution

scanned in a 0.2 mol/L NaOH solution for 30 times. It can be seen from the figure that there was no change on the shape of redox peaks, moreover, peak current and peak potential held stably, which showed that this type of alloy electrode was steady in alkaline solution. There was no surge phenomenon of glucose oxidation seen from potential-time curve of Fig. 5, which also showed the A-type Ni-In alloy electrode was steady in alkaline solution and better resisted surface poisoning so it can be used as a high catalytic activity electrode.
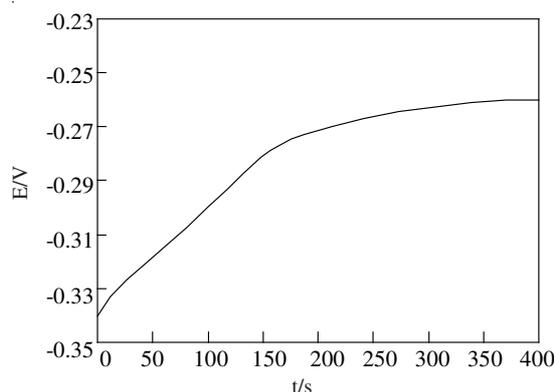
Fig. 5.   Potential-time curve of A-type Ni-In alloy electrode in 0.2 mol/L NaOH solution

Conclusion

In this study, we prepared four types of electrodes by electrochemical methods. Among these electrodes, A-type Ni-In alloy electrode, which prepared in an plating solution at a 5:1 Ni^{2+}/In^{3+} mole ratio, showed best electrocatalytic activity on glucose electro-oxidation. There was a liner relationship between glucose oxidation peak current and its concentration in the range of 1-10 mmol/L. The A-type Ni-In alloy electrode in alkaline solution was steady and it preferably resisted surface poisoning. This alloy electrode should be used as a high catalytic activity electrode of glucose sensor and glucose fuel cell.

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