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ORIGINAL PAPER

Influence of ammonia concentration on anodic deposition of nickel oxide

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Abstract Nickel oxide was prepared by anodic deposition in a basic solution comprising nickel chloride, ammonium chloride and ammonia. The influence of ammonia was investigated using galvanostatic reduction techniques and cyclic voltammetry (CV). It was found that the oxidization peak potentials shift positively with decreasing ammonia concentration, while the oxidization peak currents firstly increase with decreasing ammonia concentration and then decrease when the ammonia concentration is lower than 1.67 mol L^{-1}. This is mainly attributed to the fact that the equilibrium concentration of $Ni(OH)_{2(aq)}$ varies with the ammonia concentration. A potential plateau at about 0.75 V was observed in galvanostatic reduction curves for nickel oxide, and the length of the potential plateau in solution with 1.67 mol L^{-1} ammonia concentration was longer than that in the other solutions, which agreed well with the CV results.

Keywords Nickel oxide · Anodic deposition · Ammonia · Cyclic voltammetric · Galvanostatic reduction

1 Introduction

Nickel oxides have received great attention in technological applications of batteries, electrochromic devices, water electrolysis, electrosynthesis and fuel cells. These oxides can be prepared either using physical methods such as vacuum deposition and sputtering [1–2] or using chemical methods, e.g. sol-gel process and electrochemical deposition etc [3–8]. As a result of high cost and energy consumption, however, the physical methods cannot be easily scaled-up for industrial application. For the sol-gel process, it is usually complicated and not easily controlled. For the electrodeposition of oxides based on ion-group metals it is more convenient and inexpensive than the above-mentioned methods. As a result it has become an attractive method.

The typical bath for the electrodeposition of nickel oxides is neutral or alkaline. For example, NiO_x was prepared by anodic deposition in a solution containing nickel ammine complex [9]. In addition a nickel oxide was generated by electrochemical deposition from a $NiSO_4$ solution with pH value of 12.5 containing glycine [6]. And it was also prepared by potentiostatic electrodeposition in a nickel ammine complex solution of pH 9 containing KOH or $(CH_3)_4NOH$ as alkaline electrolyte [10]. In these papers, the properties, morphology, texture and composition of the corresponding deposited nickel oxides have been described. Until now, however, the influence of alkaline electrolyte such as ammonia has not been investigated systematically. In the previous work, the authors have proposed an anodic deposition method to prepare trivalent nickel oxide in a nickel ammine complex solution [11]. In this work, trivalent nickel oxide was prepared using the above-mentioned method and the influence of the ammonia concentration on anodic deposition of nickel oxide was also investigated.

2 Experimental

All chemicals were analytical grade and the solvent was double-distilled water. A RuO_2/Ti electrode (1 × 1 cm^2), a platinum electrode and a saturated calomel electrode

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were used as working, counter and reference electrodes, respectively. Firstly, the working electrode was soaked in Na_2SO_3 and HCl solution for one minute, and then degreased with anhydrous ethanol. Electrolyte solutions of the nickel ammine complex ($Ni(NH_3)_i^{2+}$(i = 1,2,...,6)) were prepared by the addition of an aqueous NH_3H_2O solution(28%) to a solution containing 1 mol L^{-1} $NiCl_2$ and 1 mol L^{-1} NH_4Cl to give ammonia composition of 1 mol L^{-1}, 1.33 mol L^{-1}, 1.67 mol L^{-1}, 2 mol L^{-1}, 2.2 mol L^{-1}, respectively.

The nickel oxide was deposited by oxidization for 10 min using a CHI660 electrochemical working station at potentials corresponding to the different oxidization peak potentials in the CV curves at various ammonia concentrations, and the galvanostatic reduction curves for nickel oxide were measured subsequently after the electrolysis. In this paper all potentials are referred to the saturated calomel electrode (SCE).

3 Thermodynamic analysis

Equilibrium diagrams in Ni(II)-NH_3-NH_4Cl-H_2O system at 25 °C were analyzed according to the principle of simultaneous equilibrium. In such a complicated system, there are at least eleven complex species, i.e. $Ni(NH_3)_i^{2+}$ (i = 1,2,...,6), $Ni(OH)_n^{2-n}$ (n = 1,2,...,4), $NiCl^+$. The concentration equilibrium constants of the nickel complex formation reactions are listed in Table 1 [12–15]. To simplify the calculation, the solutions are assumed to be ideal.

The mass balances of the main species in the solution are as follows:

$$[Ni]_T = [Ni^{2+}] + \Sigma[Ni(NH_3)_i^{2+}](i = 1,2,\ldots,6) + \Sigma[Ni(OH^-)_n^{2-n}](n = 1,2,\ldots,4) + [NiCl^+] \quad (1)$$

$$[N]_T = [NH_3] + \Sigma i \cdot [Ni(NH_3)_i^{2+}](i = 1,2,\ldots,6) + [NH_4^+] \quad (2)$$

$$[Cl^-]_T = [Cl^-] + [NiCl^+] \quad (3)$$

The balance of the electric charges is

$$[Ni^{2+}]_T + [NH_4^+] + [H^+] = [Cl^-] + [OH^-] \quad (4)$$

In these equations, $[M]_T$ denotes the total concentration of M and [M] is the free state concentration of M.

The values of $[Ni]_T$, $[N]_T$, $[Cl]_T$ are known. As a result, the other four unknown parameters i.e. $[Ni^{2+}]$, $[NH_3]$, $[Cl^-]$, $[OH^-]$ can be calculated from the equations (1)–(4) using the equilibrium constants in Table 1.

The effect of the ammonia content on the equilibrium concentration of $Ni(OH)_{2(aq)}$ is shown in Fig. 1. The $Ni(OH)_{2(aq)}$ equilibrium concentration does not change monotonically. There is a concentration peak emerging at the ammonia composition of 2 mol L^{-1} in the solution. The relationship between $[Ni(OH)_{2(aq)}] \times [OH^-]$ and the ammonia concentration is given in Fig. 2. A peak can also be observed in the curve. The value of $[Ni(OH)_{2(aq)}] \times [OH^-]$ firstly increases with increasing ammonia concentration and then decreases when the ammonia concentration is larger than 3.3 mol L^{-1}.

The real activities of OH^- in electrolytes with 1, 1.3, 1.6, 2, and 2.3 mol L^{-1} NH_3H_2O were tested with a liquid pH meter, and the pH values were 7.07, 7.21, 7.38, 7.53, 7.71 respectively, which agree well with the theoretical calculation values, 6.98, 7.11, 7.24, 7.40, 7.52.

Table 1 Concentration equilibrium constants in the Ni(II)-NH_3-NH_4Cl-H_2O system

System	Equilibria	lgK
Ni(II) - NH_3	$Ni^{2+} + NH_3 \rightarrow Ni(NH_3)^{2+}$	2.75
	$Ni^{2+} + 2NH_3 \rightarrow Ni(NH_3)_i^{2+}$	4.95
	$Ni^{2+} + 3NH_3 \rightarrow Ni(NH_3)_3^{2+}$	6.64
	$Ni^{2+} + 4\,NH_3 \rightarrow Ni(NH_3)_4^{2+}$	7.79
	$Ni^{2+} + 5NH_3 \rightarrow Ni(NH_3)_5^{2+}$	8.50
	$Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_6^{2+}$	8.49
H^+ - NH_3	$NH_3 + H^+ \rightarrow NH_4^+$	9.27
Ni(II) - OH^-	$Ni^{2+} + OH^- \rightarrow Ni(OH)^+$	3.58
	$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_{2(aq)}$	8.10
	$Ni^{2+} + 3OH^- \rightarrow Ni(OH)^-{}_3$	11.2
	$Ni^{2+} + 4OH^- \rightarrow Ni(OH)^{2-}{}_4$	11.9
Ni(II) - Cl^-	$Ni^{2+} + Cl^- \rightarrow NiCl^+$	0

4 Results and discussion

4.1 Cyclic voltammogram research

A typical cyclic voltammogram obtained for nickel oxide growth on a RuO_2/Ti electrode between 0.6 and 1.0 V is presented in Fig. 3. As is characteristic of the electrodeposited nickel oxide, the anodic current peaks A1 centers at about 0.89 V and the cathodic current peak C1 centers at about 0.75 V. The A1/C1 redox peaks characterize the Ni(II)/Ni(III) transition [16–18]. Another anodic current peak A2, appearing at higher potential, corresponds to nitrogen evolution [19].

The anodic peak current A1 increases with scan number, and is similar to the case of the cathodic current peak C1. On the negative sweep the cathodic current peak at about

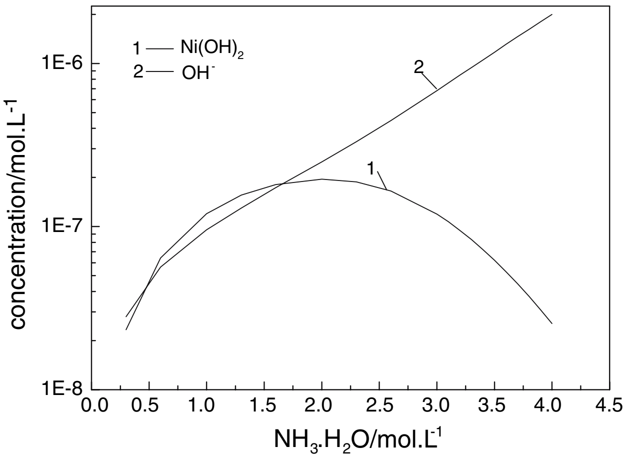

Fig. 1 Relationships between [$Ni(OH)_{2(aq)}$] and [NH_3• H_2O], [OH^-] and [NH_3• H_2O]

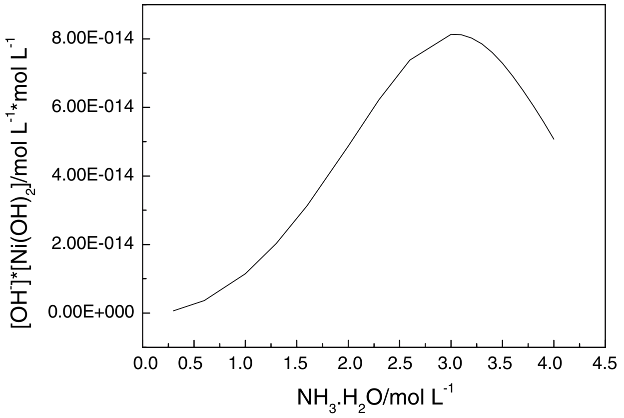

Fig. 2 Relationship between [$Ni(OH)_{2(aq)}$] × [OH^-] and [NH_3• H_2O]

0.75 V is obviously divided into two current peaks C11 and C12. As has been reported in the literature [20–22], nickel hydroxide may exist in at least two different crystallographic forms α-$Ni(OH)_2$ and β-$Ni(OH)_2$, hydrous and anhydrous, respectively. In addition, the oxidization of nickel hydroxide gives two other varieties of oxyhydroxides, β-NiOOH and γ-NiOOH. This explains the existence of two separate cathodic reduction peaks during the negative sweep.

The sixth cyclic voltammogram at different ammonia concentrations is shown in Fig. 4. It can be seen that the oxidization peak potential shifts positively with decreasing ammonia concentration. This is mainly due to the variation of $Ni(OH)_{2(aq)}$ and OH^- equilibrium concentration, which is influenced by the change in ammonia concentration in solution. The oxidization reaction occurring on the RuO_2/Ti electrode is as follows [23]:

$$Ni(OH)_{2(aq)} + OH^- - e \Leftrightarrow NiOOH + H_2O \qquad (5)$$

The equilibrium potential can be expressed as follows:

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{NiOOH}}{a_{Ni(OH)_{2(aq)}} \cdot a_{OH^-}} \qquad (6)$$

where E^0 is the standard electrode potential, αNiOOH, $\alpha Ni(OH)_2$, αOH^- are the activities of NiOOH, $Ni(OH)_2$, OH-, respectively. For simplification, it is assumed that the mechanism of the electrochemical reaction and related parameters remain unchanged since the variation of the ammonia content is limited. Moreover, the activity of solid production NiOOH formed on the electrode surface is assumed to be 1. Thus, the following equation can be obtained:

$$\Delta E = E - E' = \frac{RT}{nF}\ln\frac{a'_{Ni(OH)_{2(aq)}} \cdot a'_{OH^-}}{a_{Ni(OH)_{2(aq)}} \cdot a_{OH^-}} \qquad (7)$$

Eq. (7) implies that the oxidization peak potential depends on the value of [$Ni(OH)_{2(aq)}$] × [OH^-]. As shown in Fig. 2, the value of [$Ni(OH)_{2(aq)}$] × [OH^-] increases with increasing ammonia concentration from 1 to 3.5 mol L^{-1}. As a result the oxidization peak potential shifts negatively with increasing ammonia concentration.

In Fig. 4 it is clear that the oxidization peak current firstly increases with decreasing ammonia concentration followed by a decrease when the ammonia concentration is lower than 1.67 mol L^{-1}. This may be related to the change in the $Ni(OH)_{2(aq)}$ equilibrium concentration in the electrolyte when decreasing the ammonia concentration. For a simple irreversible charge transfer reaction the current of a linear potential scan is a function of time[24],

$$i = nFAC(\pi Db)^{1/2}\chi(bt) \qquad (8)$$

$$b = \alpha nFv/RT \qquad (9)$$

where n is the number of electrons transferred, A the area surface, D the diffusion coefficient, C the concentration of $Ni(OH)_{2(aq)}$ in the bulk of the solution, α the transfer coefficient, v the scanning rate. The parameter $\pi^{1/2}\chi(bt)$ has a maximum of 0.496, thus the peak current may be expressed as follows,

$$i_p = 2.99 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} \alpha^{1/2} c$$

Considering that the concentration of ammonia changes over a small range it can be assumed that the electrochemical reaction mechanical and the other parameters remain constant, thus:

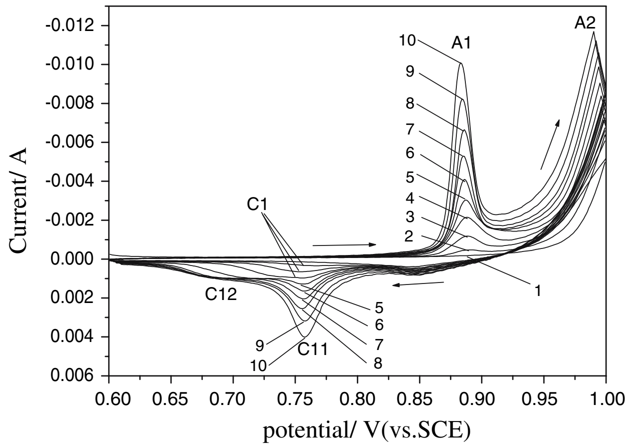

Fig. 3 Cyclic voltammogram of nickel oxide growth on RuO_2/Ti electrode in a solution with 1 mol $L^{-1}NiCl_2 \cdot 6H_2O$, 1 mol L^{-1} NH_4Cl and 2 mol L^{-1} $NH_3 \cdot H_2O$ Scan rate: 5 mV s^{-1}. Temperature: 25 °C

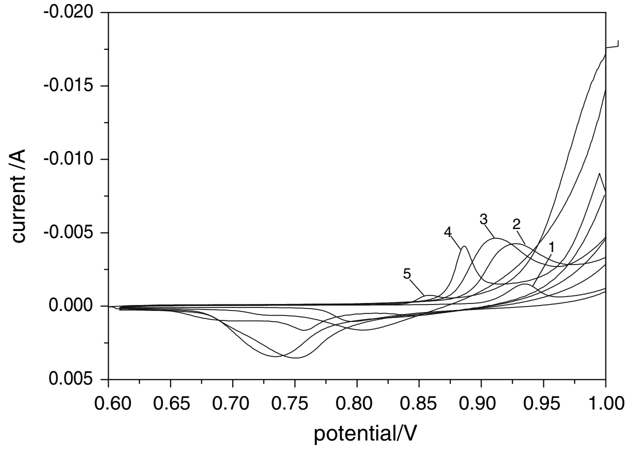

Fig. 4 Sixth cyclic voltammogram at various $NH_3 \cdot H_2O$ concentrations Scan rate: 5 mV s^{-1} Temperature: 25 °C. $NH_3 \cdot H_2O$: 1–1.00 mol L^{-1}, 2–1.33 mol L^{-1}, 3–1.67 mol L^{-1}, 4–2.00 mol L^{-1}, 5–2.20 mol L^{-1}

$$i_{p1}/i_{p2} = C_1/C_2 \tag{10}$$

This means that the peak current changes linearly with the $Ni(OH)_{2(aq)}$ concentration. It is known that the equilibrium concentration of the $Ni(OH)_{2(aq)}$ increases at first and then decreases with increasing ammonia concentration (see Fig. 1). As a result it can be concluded that the peak current variations will show a similar tend when changing the ammonia concentration, which is indeed observed in our experiments (see Fig. 4).

4.2 Galvanostatic reduction curves

Fig. 5 shows the galvanostatic reduction curves for nickel oxide, formed at potentials of 0.926, 0.919, 0.903, 0.875 and 0.848V respectively, corresponding to the different oxidization peak potentials at ammonia concentrations of 1.00, 1.33, 1.67, 2.00 and 2.20 mol L^{-1}. Different characteristics are observed in the various galvanostatic reduction curves for nickel oxide. Compared with other solutions, the potential plateau at about 0.75 V in the solution with 1.67 mol L^{-1} ammonia is longer, indicating that the amount of product, Ni(III), is the largest in the solution with 1.67 mol L^{-1} ammonia. This result is consistent with the CV observations.

In Fig. 5, it is also observed that in the system containing 1.67 mol L^{-1} ammonia concentration, besides the potential plateaus at about 0.75 V, another weak potential plateau at about 0.65 V is seen. Hu and Cheng [25] have found that the galvanostatic reduction curve for nickel oxide is significantly influenced by its thickness and/or structure, which is a function of the electrochemical oxidization methods and oxidization potentials. In light of this, the two potential plateaus may be related to the reduction of various nickel oxides.

5 Conclusion

Nickel oxide species can be anodically electrodeposited directly from a nickel ammine complex solution with ammonia as an alkaline electrolyte. The effects of ammonia on the electrodeposition process can be summarized as follows: (1) The concentration of ammonia has a significant impact on both the potential and current of the oxidation peak. With decreasing ammonia concentration, the oxidization peak potential of nickel oxide shifts positively.

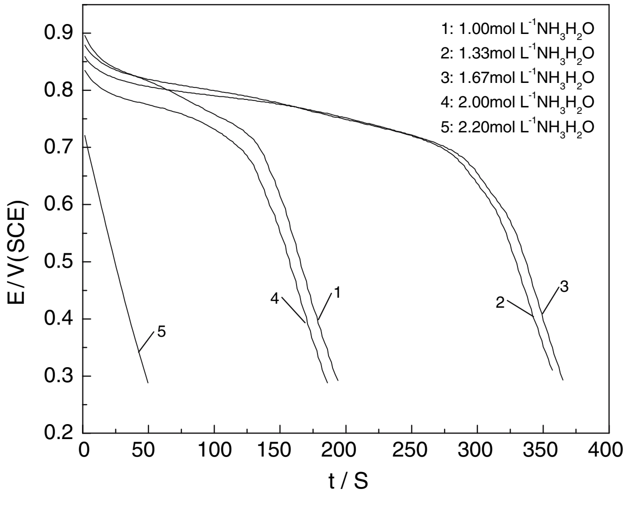

Fig. 5 Galvanostatic reduction curves for nickel oxide prepared at respective oxidation peak potentials, 1: 0.926; 2: 0.919; 3: 0.903; 4: 0.875; and 5: 0.848 V Temperature: 25 °C, oxidization time: 10 min, discharge current: 0.2 mA, electrode area: 1 cm^2

The oxidization peak current, however, increases with decreasing ammonia concentration initially, but then decreases when the ammonia concentration is lower than 1.67 mol L^{-1}. These observations can be attributed to the variation of $Ni(OH)_{2(aq)}$ equilibrium concentration, which depends on the ammonia concentration; (2) A potential plateau at about 0.75 V is observed in the galvanostatic reduction curves for nickel oxide, and the reduction potential plateau for the nickel oxide prepared in solution with 1.67 mol L^{-1} ammonia concentration is longer than that in other solutions.

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