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Effects of additives on morphology and hydrogen evolution activities of nickel films prepared by electrodepositing

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Nickel thin films with different morphologies were prepared by electrodeposition from solutions with different additives. It is found by observing the nickel film morphology with SEM that the compact nickel films were prepared from solutions containing H_3BO_3 or $C_6H_5Na_3O_7$. And when the solutions contained $(NH_4)_2SO_4$, porous nickel film was prepared. It is shown by investigating the effects of different additives on the nickel deposition process that $(NH_4)_2SO_4$ could significantly reduce the cathode potential in the process of nickel electrodeposition. Meanwhile, $(NH_4)_2SO_4$ could reduce current efficiencies for hydrogen evolution electrode. Cyclic voltammetry for nickel films showed that $(NH_4)_2SO_4$ could significantly increase the roughness factor of nickel films. And the polarization curves of different nickel films for hydrogen evolution in the electrolyte of 1M NaOH show that $(NH_4)_2SO_4$ could significantly increase the activity of hydrogen evolution. Chronoamperometric responses recorded on different nickel films for hydrogen evolution at constant applied potential of -1.6 V show that all the nickel films prepared by electrodeposition have good stability of hydrogen evolution.

Keywords: additive; $(NH_4)_2SO_4$; morphology; electrodeposition; nickel thin film

1. INTRODUCTION

With the decrease of the oil, coal and other fossil fuel resources and the successful application of hydrogen in the chemical engineering, metallurgy, aerospace and other fields, hydrogen as renewable and clean energy resource has been becoming a widespread concern [1-4]. Because of rich raw materials, hydrogen produced by water electrolysis has been extensively studied, and one of the key factors about clean and high-efficiency hydrogen production is the preparation of high-activity hydrogen evolution electrode [5-8]. Influencing electrode hydrogen evolution activities there are two main factors, of which one is electronic configuration of electrodes, and the other is electrochemical active area of electrodes. So the research focus lies in preparing active hydrogen evolution electrode which is of large active surface area and good electronic configuration [9,10]. On the other hand, for porous metal films, which act as a highly active catalytic electrode due to large specific surface area, there are a wide range of applications in fuel cells, capacitors, electrolysis of water, etc. [11,12]. The fabrication technology of the porous metal film by electrodeposition with hydrogen bubbles as template, because of its own simple process and strong practicability, has been increasingly been a hot topic in hydrogen production electrode material [13]. The electrodeposition solution components could affect the electrode reaction, which has large impacts on the morphology of electrodeposited products [14,15]. Because of the negative balance potential of nickel, nickel electrodeposition process is accompanied by the occurrence of hydrogen evolution reaction, so the effects of additive on nickel electrodeposition and hydrogen evolution reaction are more significant [16-18]. Less study has been done concerning the influence of different additives on nickel electrodeposition surface morphology and its hydrogen evolution activity. H_3BO_3 and $(NH_4)_2SO_4$ in the electrodeposition process can generate the discharge ions H^+ for hydrogen production by electrolysis, affect the hydrogen evolution reaction, and maintain the local stability of pH value on the cathode. And both $C_6H_5Na_3O_7$ and NH_4^+ can react with Ni^{2+} to form the complexes affecting the electroreduction process of nickel ion [19]. So this paper focused on the effects of H_3BO_3, $C_6H_5Na_3O_7$, and $(NH_4)_2SO_4$ on the cathodic reaction process in nickel electrolysis, and analyzed the effects of three additives on the composition, structure, surface morphology, surface roughness of nickel thin film prepared by electrodeposition. Finally, the activity and stability of hydrogen evolution for nickel thin film electrodes fabricated were investigated.

2. EXPERIMENTAL

2.1 Nickel thin films prepared by electrodeposition

Nickel thin film prepared by electrodeposition s were fabricated by constant-current electrodeposition in the electroplating bath of the conventional three-electrode system on 760C electrochemical workstation (Chen Hua, Shanghai). To study the influence of additives on onickel thin films morphology prepared by electrodeposition, different additives were added to the base solution of 0.2 M $NiSO_4$ and 1 M Na_2SO_4.

As is shown in Table 1 that No. 1 electrodeposition solution was the electrolyte added with 40 g/L H_3BO_3, No. 2 electrolyte added with 80 g/L $C_6H_5Na_3O_7.2H_2O$, No. 3 electrolyte added with 80 g/L $C_6H_5Na_3O_7.2H_2O$ and 1 M $(NH_4)_2SO_4$, and No. 4 electrolyte added with 1 M $(NH_4)_2SO_4$. A thin copper plate, of which the geometric size is 1 cm × 1 cm and the purity is 99.99%, served as a working electrode, a platinum electrode with large surface area served as a counter electrode, and a saturated calomel electrode (SCE) served as a reference electrode. The basic technological parameters were as follows: the current density is 1 A/cm^2, and the deposition time is 30 s. All the reagents used in the experiment were analytically pure, and all the electrolytes were fabricated by secondary deionized water.

Table 1. Composition of No. 1 ~ No. 4 electrodeposition solutions

Group ID	$NiSO_4$ (M)	Na_2SO_4 (M)	H_3BO_3 (g L^{-1})	$C_6H_5Na_3O_7.2H_2O$ (g L^{-1})	$(NH_4)_2SO_4$ (M)
No. 1	0.2	0.5	40		
No. 2	0.2	0.5		80	
No. 3	0.2	0.5		80	1
No. 4	0.2	0.5			1

2.2 Morphology, microstructure, composition characterization of nickel thin film

The surface morphology of nickel thin film prepared by electrodeposition was observed by FESEM (JEOL JSM-7001F). The chemical composition and crystal structure of nickel thin films were analyzed by X-ray energy dispersive spectroscopy (Oxford Instruments, UK INCA X-MAX) and X-ray diffraction (Rigaku Smartlab (9)). The quality of the working electrode before and after the electrodeposition was measured by weighing method to obtain the quality of electrodeposited nickel, and then the current efficiency of nickel deposition was calculated. Nickel reduction reaction and hydrogen evolution mainly appear on the cathode in nickel electrodeposition process, so the current efficiencies η_{H2} for hydrogen evolution were obtained in line with the formula (1).

$$\eta_{H2}=1-2mF/ItM_{Ni} \quad (1)$$

Where m represents for the mass electrodeposited nickel (g), F for the Faraday constant (96485 C/mol), I for electrodeposition current (A), t for electrodeposition time (s), and M_{Ni} for molecular weight of nickel (g/ mol).

2.3 Electrochemical characterization of nickel thin film

In 6 M KOH solution, surface roughness (real active surface area) of nickel thin films fabricated by electrodeposition are measured by cyclic voltammetry (CV) method. The related principles and equations of test method are as follows: charge-discharge range of double electrode layer capacitance of nickel thin film is experimentally measured from -0.6 V to -0.75 V. Therefore, the sweep range of cyclic voltammetry ranges from -0.6 V to -0.75 V, and the scanning speed is 30 mV s^{-1}. Eq. 2 is used to calculate the electrode capacity obtained by cyclic voltammetry curves, and Eq. (2) is expressed as follows:

$$C=(\int I dV)/(\upsilon V) \quad (2)$$

Where C is electrode capacity (F), υ is sweep speed of cyclic voltammetry (V/s), I is responsive current density (A/cm^2), and V is voltage (V).

The surface roughness R_f of nickel thin film is calculated by Eq. 3

$$R_f=C\times 10^6/20 \quad (3)$$

The linear sweep voltammetry (LSV) tests, with linear sweep range from 0 V to -1.4 V and scanning speed of 30 mV/s, were conducted in 1 M NaOH solution to investigate the hydrogen evolution activity of nickel thin film prepared by electrodeposition. The stability of hydrogen evolution for nickel thin film prepared by electrodeposition was tested by galvanostatic method at operation potential of -1.6V and the test time of 10 hours.

3. RESULTS AND DISCUSSION

3.1 Influence of additives on surface morphology, microstructure, and composition of nickel thin films prepared by electrodeposition

SEM images of nickel thin films prepared by electrodeposition from different electrodeposition solutions as well as insert illustrations for the cathode photos of electrodeposited nickel thin films were given in Fig. 1. It is evident from the SEM image in the figure that when the electrolyte was added with H_3BO_3, the nickel thin film prepared by electrodeposition was compact and smooth, when the electrolyte was added with $C_6H_5Na_3O_7$, the nickel film surface was still relatively compact, accompanied with small protuberance generated, when $C_6H_5Na_3O_7$ and $(NH_4)_2SO_4$ were added at the same time, porous characteristic appeared on the nickel film surface, and when $(NH_4)_2SO_4$ was only added, the porous structure of nickel thin film surface would evolve into significantly larger aperture, deeper hole, and well-developed porous structure.

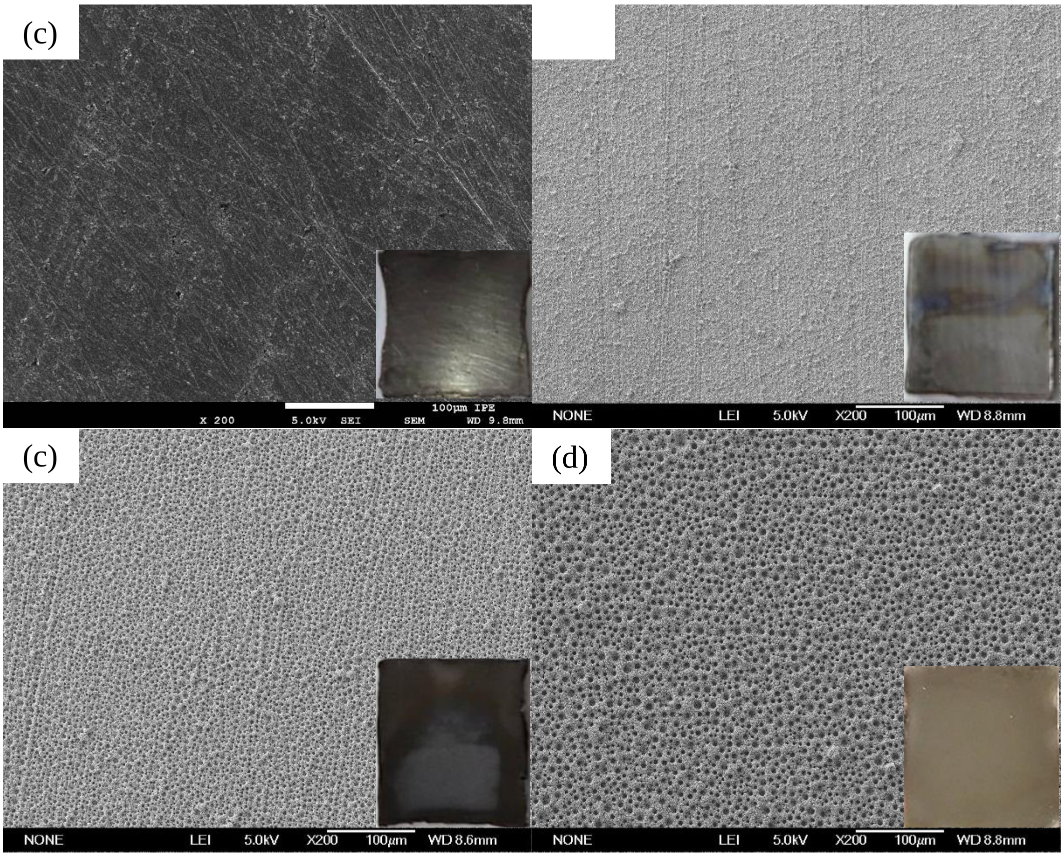


Figure 1. SEM micrographs of nickel thin films prepared by electrodeposition in the electrodeposition solution (a) No. 1, (b) No. 2, (c) No. 3, and (d) No. 4 (corresponding to the Group ID “No. #” shown in Table 1), as well as insert illustrations for the corresponding pictures of electrodeposited nickel films.

Besides that, the nickel thin films prepared by electrodeposition in the electrolyte without $(NH_4)_2SO_4$ were of metallic luster, while the nickel thin films prepared in the electrolyte with $(NH_4)_2SO_4$ became gray and black. Therefore, $(NH_4)_2SO_4$ can promote the production of nickel thin films with porous structure enhancing electrochemical surface activities, while $C_6H_5Na_3O_7$ is capable of inhibiting the porous nickel films formation.

To explore the effects of additives on chemical components of electrodeposition products, X-ray energy spectrum analysis was carried out, and the resulting energy spectrum was shown in Fig. 2 (a), from which it is found all the electrodeposited products were pure Ni. It is illustrated by Fig. 2 (a) that only nickel electrodeposition and hydrogen evolution occurred in the electrodeposition process. To study the effects of crystal structure of the electrode on the activity of hydrogen evolution, the structure of nickel thin films obtained from No. 1 - No. 4 solutions were investigated by XRD test, of which the results were shown in Fig. 2(b) that the structure of four nickel thin films prepared was mainly FCC polycrystalline, without the appearance of amorphous structure.

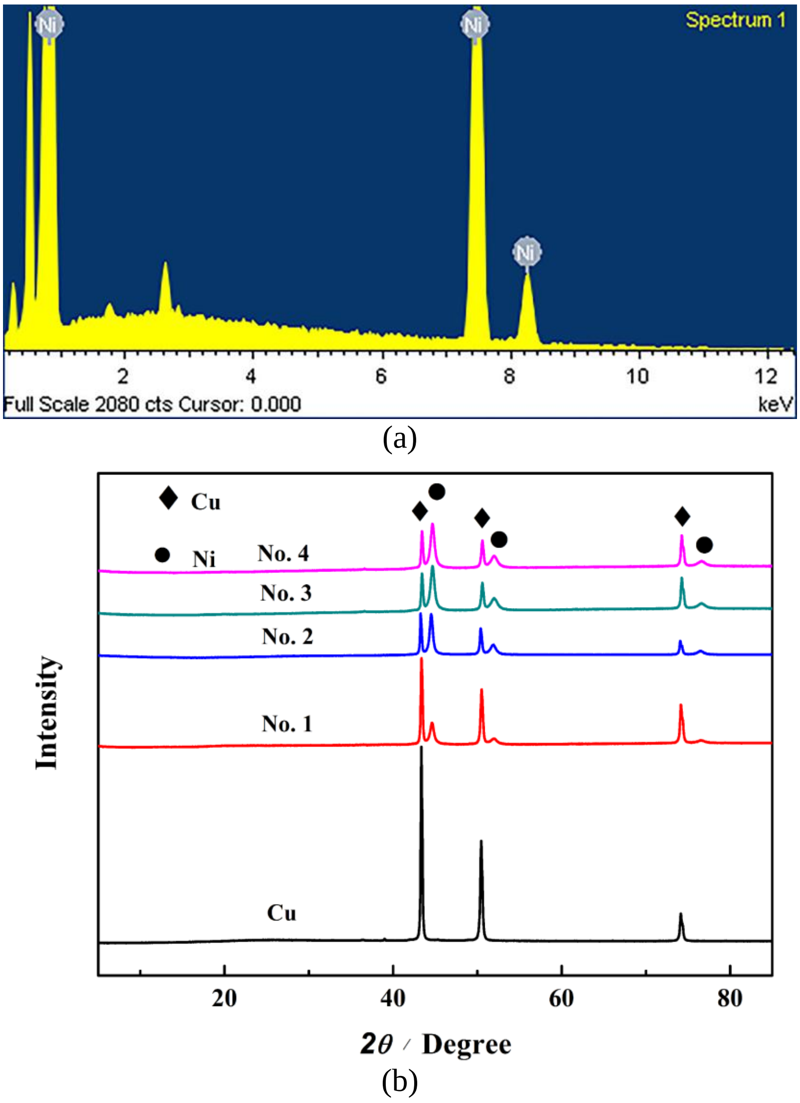


Figure 2. (a) EDS of electrodeposited nickel thin films obtained from No. 1 - No. 4 solutions, (b) XRD of Cu substrate and electrodeposited nickel thin film obtained from No. 1 - No. 4 solutions.

3.2 Effects of additives on the nickel electrodeposition process

Since nickel has lower equilibrium potential, the strong side reaction of hydrogen evolution followed by the electrodeposition process [20]. The variation of cathode surface state on the electrodeposition process could be reflected by potential transient curves, of which the cyclical fluctuations correspond to the nucleation, growth and detachment of hydrogen bubbles on the cathode surface [21]. As can be seen from Figure 3, when the electrolyte was added with $(NH_4)_2SO_4$, the cathode potential decreased, the fluctuation amplitude and cycle of instantaneous potential curve significantly increased, and the fluctuation in potential was more intense, which indicate violent hydrogen evolution occurred at this time. The reasons for this phenomenon is that NH_4^+ can not only generate hydrogen gas by direct discharge, but react with OH^- generated by water electrolysis, thus reducing local pH on the cathode.

Violent hydrogen evolution brought about the disturbances in the electrolyte, reduced the boundary layer thickness of electrode surface, strengthened the nickel mass transfer, and lowered the concentration polarization, consequently reducing cathode potential and accelerating nickel deposition speed. And thus before hydrogen bubble broke out of the electrode plate, porous structure was formed by quick electrodeposition of nickel along hydrogen bubbles. While H_3BO_3 or $C_6H_5Na_3O_7$ was added to the electrolyte, the cathode potential increased, and the fluctuation of transient potential curve was smooth. This illustrates that at this time the hydrogen evolution was not very severe, and the detachment rate of hydrogen bubbles reduced, which resulted in large bubble resistance and nickel ion concentration polarization, so the cathode potential significantly increased.

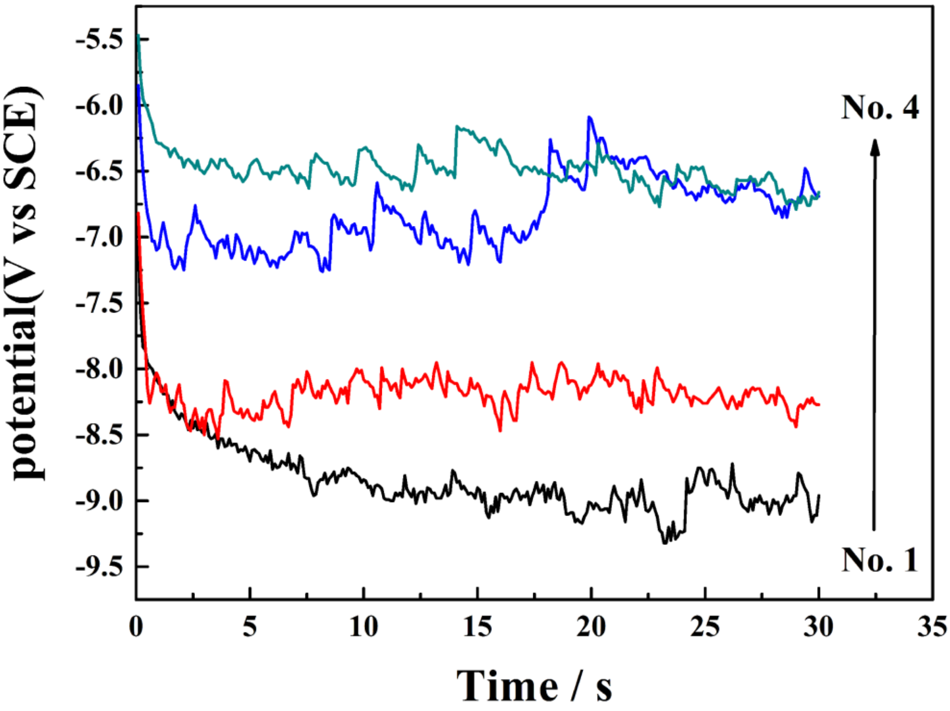


Figure 3. Potential transient curves of nickel deposition by galvanostatic from No. 1 – No. 4 solutions.

Figure 4 shown current efficiencies for hydrogen evolution in four solutions with different additives. It can be found from the figure above that when the electrolyte was added with $(NH_4)_2SO_4$, current efficiency for hydrogen evolution decreased. This is because even though $(NH_4)_2SO_4$ as hydrogen source can be capable of promoting hydrogen evolution, violent hydrogen evolution results in strong stirring action, reducing the boundary layer thickness on the electrode surface and accelerating the mass transfer of nickel, thus increasing the number of nickel reduction electrons, and relatively reducing the number of electrons for hydrogen evolution in the electrodeposition process. So the current efficiencies for hydrogen evolution in the electrolyte added with $(NH_4)_2SO_4$ were lower than those in the electrolyte added with H_3BO_3 or citric acid.

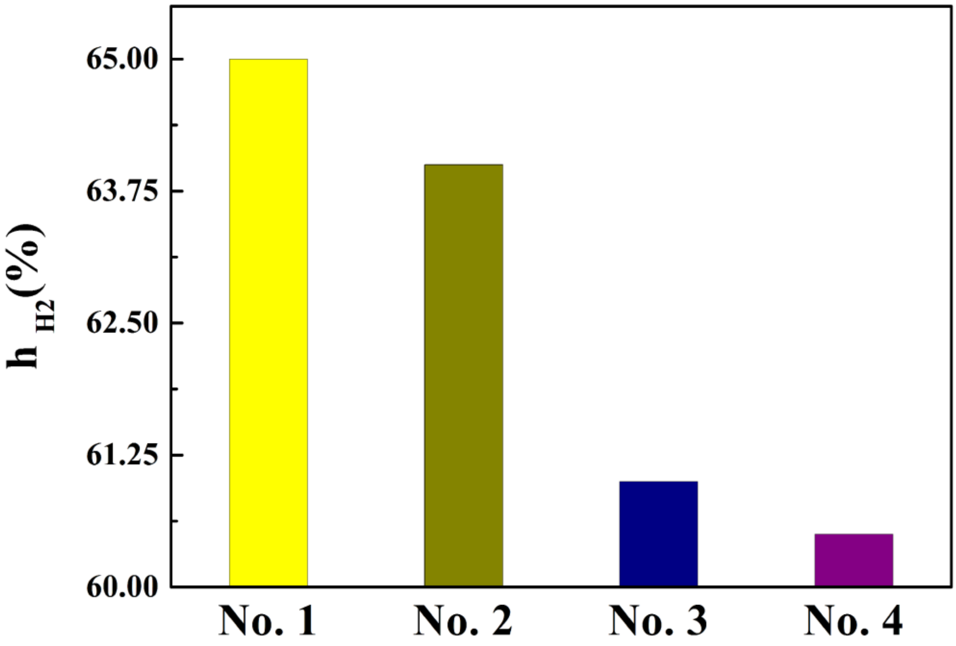
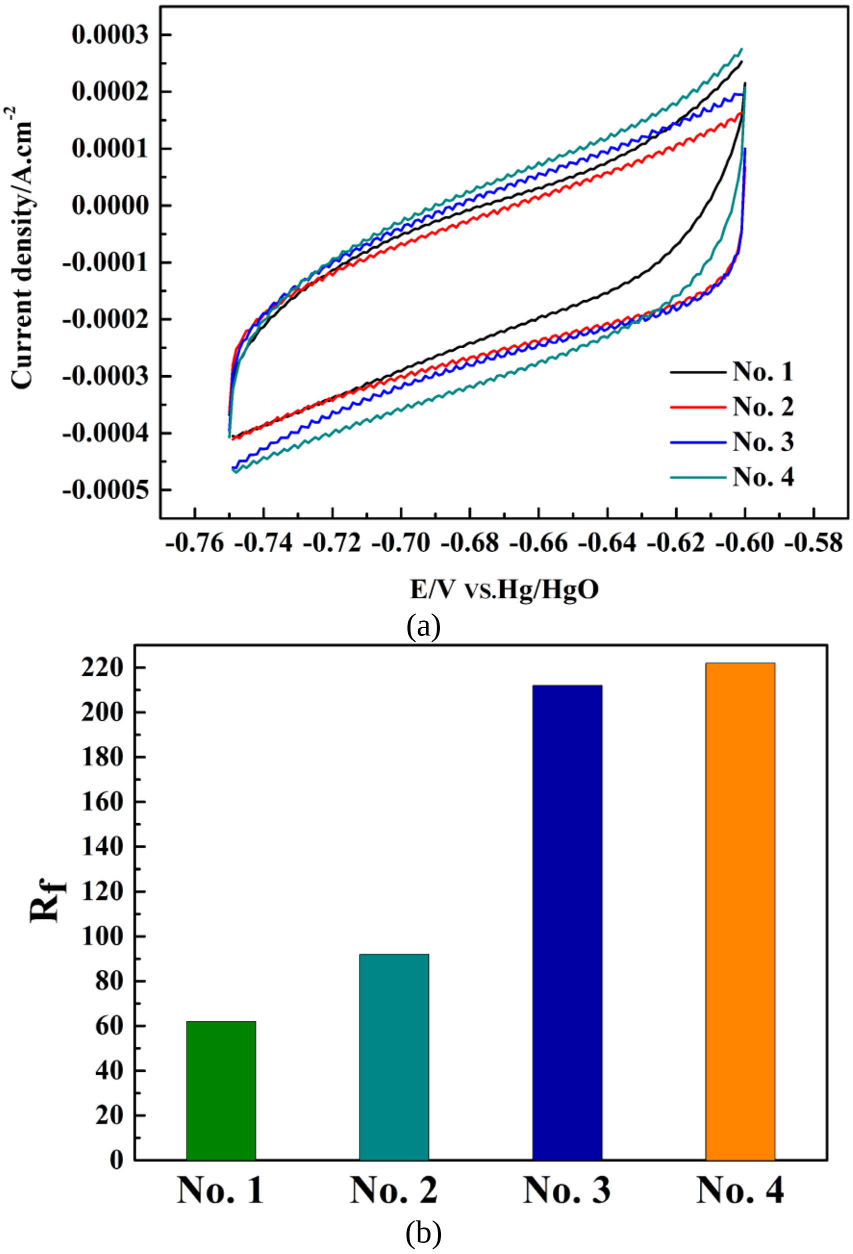


Figure 4. Current efficiencies for hydrogen evolution in different solutions.

3.3 Roughness measurement of nickel thin films and characterization of the activity and stability of hydrogen evolution

High roughness metal plating layer has relatively large electrochemical surface area. There exists a positive correlation between real surface area and hydrogen evolution activities of hydrogen evolution electrode. Electrodeposited nickel films, especially porous nickel film, have higher roughness factor, i.e., have larger real active surface area. In order to analyze the activity of nickel thin film electrodes for hydrogen evolution, it is necessary to investigate the roughness of nickel thin film electrode. Real active surface area of nickel thin film is directly proportional to electrical double-layer capacitor, of which the real value is determined by cyclic voltammetry method. The electric double-layer capacitance of smooth metal is generally considered to be equal to 20 μF/cm [22], and therefore the roughness factor is the ratio of the electric double-layer capacitor of nickel thin film to 20 μF/cm.

Figure 5(a) shows cyclic voltammetry curves of different nickel thin films prepared by electrodeposition in 6M KOH solution, and Figure 5(b) shows the roughness factors of different nickel thin films prepared from No. 1 - No. 4 solutions. As can be seen from the figure that the roughness factors of porous nickel film prepared from both No. 3 and No. 4 solutions added with $(NH_4)_2SO_4$ were higher than 200, and those of compact nickel thin films prepared from No. 1 and No. 2 solutions added with H_3BO_3 and citric acid, respectively, were less than 100. This illustrates $(NH_4)_2SO_4$ can effectively increase the active surface area of nickel thin films. The roughness factor of nickel thin film obtained from No. 3 electrolyte with the simultaneous addition of $(NH_4)_2SO_4$ and $C_6H_5Na_3O_7$ was smaller than that of nickel film obtained by the only addition of $(NH_4)_2SO_4$. Again, none of this is to deny that $C_6H_5Na_3O_7$ is of inhibiting the formation of porous structure and reducing the active specific surface area of nickel thin film.

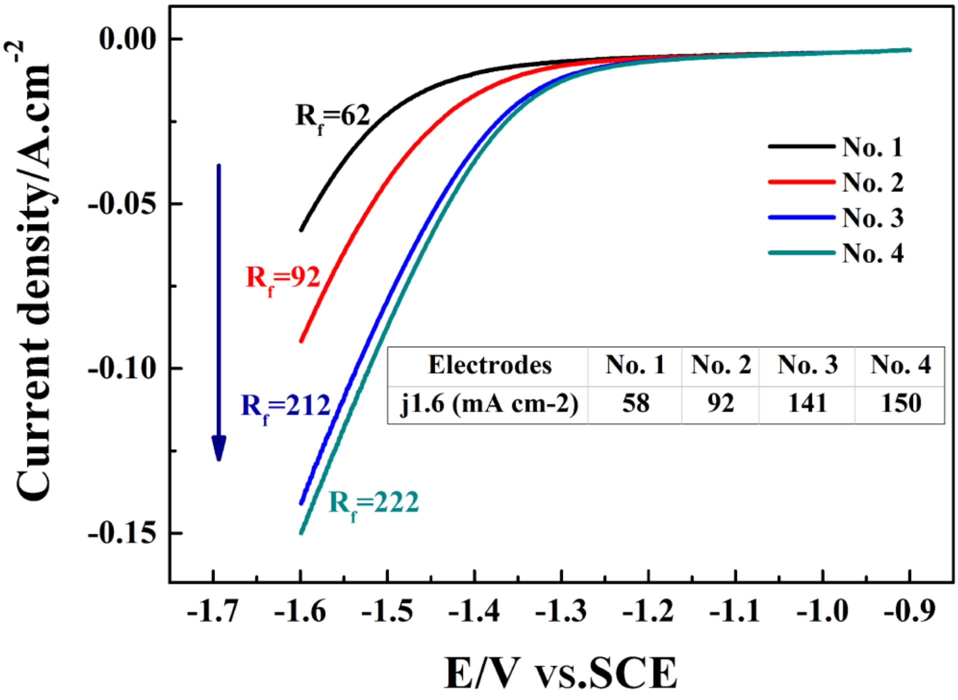


(a)

(b)

Figure 5. (a) Cyclic voltammetry curve in 6 M KOH solution for nickel films electrodeposition from different solutions. (b) The roughness factor of nickel films electrodeposition from different solutions.

To analyze the hydrogen evolution activities for nickel thin film electrode, the electrochemical behaviors of four electrodes prepared were studied by Linear Sweep Voltammetry (LSV) in 1 M NaOH solution, and the experimental results are shown in Figure 6. It is found by polarization curves that the surface roughness factors of No. 3 and No. 4 nickel film electrodes were significantly higher than those of No. 1 and No. 2 electrodes. Also, hydrogen evolution current densities of No. 3 and No. 4 electrodes were significantly higher than those of No. 1 and No. 2 electrodes. The insert table in Fig. 6 illustrates hydrogen evolution current densities of four electrodes under electrode potential of -1.6 V. From the table above it can be seen that under the same electrode potentials, hydrogen evolution current densities increased significantly with the increase of nickel thin film electrode roughness. For instance, as indicated by the facts that the current density of No. 1 electrode with the roughness factor of 62 was 58 mA/cm^2 while that of No. 4 electrode with the roughness factor of 222 increased to 150 mA/cm^2. And the current densities of No. 4 electrode is similar to those measured by Lee [23]. Since the electrode hydrogen evolution activities are mainly determined by active surface area as well as crystal structure, and four nickel films are of the same crystal structure as shown in Fig. 2 (b), the increase of hydrogen evolution activity attributes to the increase of nickel thin films roughness.



Electrodes	No. 1	No. 2	No. 3	No. 4
j1.6 (mA cm-2)	58	92	141	150

Figure 6. Polarization curves of different nickel films for hydrogen evolution, as well as hydrogen evolution current densities illustrated in insert table.

In order to investigate the stability of nickel thin film electrodes for hydrogen evolution, three-electrode system at operation potential of -1.6 V was used for constant potential chronoamperometry, of which the response results are shown in Fig. 7. It is found that as the surface roughness of the electrodes increase, the current densities of hydrogen evolution significantly increase. During 10-hour hydrogen evolution, the current densities of hydrogen evolution for four nickel thin film electrodes are almost unchanged. It is clarified that nickel thin film prepared by electrodeposition has good bonding with the substrate, as well as stable hydrogen evolution activity. Based on the experimental results above, different additives (such as $(NH_4)_2SO_4$, H_3BO_3 or $C_6H_5Na_3O_7$) can improve the hydrogen evolution stability of electrodeposited layer to varying degrees.

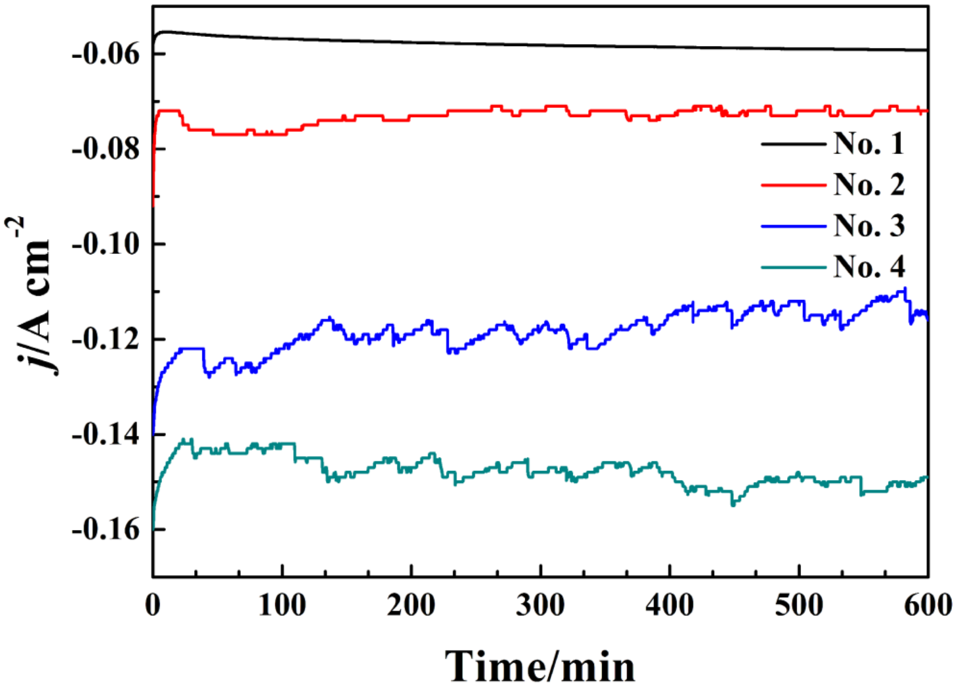


Figure 7. Chronoamperometric responses ($j \sim t$) recorded on different nickel films for hydrogen evolution at a constant applied potential of -1.6 V (VS SCE).

4. CONCLUSIONS

This paper mainly analyzed the influence of additives on morphology, microstructure, composition and electrochemical performance of electrodeposited nickel thin films, as well as nickel electrodeposition process. The results show that additives has great influence of the morphology, structure and hydrogen evolution activity of electrodeposited nickel thin films. H_3BO_3 or $C_6H_5Na_3O_7$ contributed to preparing compact nickel thin films with low roughness, and $(NH_4)_2SO_4$ could help to prepare porous nickel films with high roughness. Also, it is found that $(NH_4)_2SO_4$ could lower the overpotential of nickel deposition, and increase the current efficiencies of nickel deposition, thus promoting the electrodeposition of nickel.

Hydrogen evolution activity tests show that $(NH_4)_2SO_4$ could significantly increase the roughness factor of nickel thin film, prompting the large increase of hydrogen evolution activity of porous nickel film. Hydrogen evolution stability tests show that nickel thin films prepared from different additives had good hydrogen evolution stability. Therefore, the use of some additives (such as $(NH_4)_2SO_4$) in electrolyte is capable of obtaining porous nickel film, enhancing significantly the surface roughness of hydrogen evolution electrode, and obtaining hydrogen evolution electrodes with high activity and high stability.

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