

Experimental of Cathode Plasma Electrodeposition of Nickel

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Experiment was designed to conduct cathode plasma electrodeposition. In the experimental cathode plasma electrodeposition of nickel, ethanol and citric acid at various concentrations along with different electrolytes were adopted to study the effect of electrolyte composition on the deposition rate and surface appearance of a nickel electrodeposition layer. The results revealed that, as the ethanol concentration of an electrolyte increased, the deposition layer of nickel gradually exhibited smoother surfaces as well as uniform, fine structures thereon. In addition, the concentration enrichment of the; in the electrolytes visibly improved the deposition rate of nickel and decreased the particle size of the deposition layer. Besides, when nickel chloride or nickel sulphate were used as the main salts, the deposition rate of nickel was higher, while it was lower when nickel aminosulphonate was used as the main salt. Additionally, the differences in the three types of main salts exerted a slight influence on the surface appearance of nickel electrodeposition layers.

1. Introduction

The principle of cathode plasma electrodeposition is to deposit materials on a cathode where a plasma-sheath layer of high electric field intensity is formed by puncturing a bubble film wrapping the cathode (Allagui et al., 2013). The bubble film is produced at a high voltage by the electrolytic and vapour bubbles generated on the surface of the cathode when the voltage between the cathode and anode in an electrolyser is elevated continuously (Wu et al., 2017). Compared with traditional electrodeposition methods, cathode plasma electrodeposition can improve the deposition rate significantly apart from enhancing the adhesive force and corrosion resistance of the deposition layer (Ouan and He, 2015).

In the experiment investigating cathode plasma electrodeposition of nickel, ethanol was used as the main medium, and electrolytes, at different concentrations, were added to assess the effect of electrolyte composition on the deposition rate and surface appearance of nickel electrodeposition layers.

2. Experimental

Figure. 1 shows the experimental apparatus which was mainly composed of an electrolyser, a supply tank for the main salt solutions, a magnetic stirring apparatus, a flow valve, electrodes, and a high voltage DC power supply. Therein, the flow valve was used to control the velocity of the main salt solutions flowing into the electrolyser, and the magnetic stirring apparatus was used to stir the solution in the electrolyser to improve the diffusivity of the metal ions. The solution containing ethanol, citric acid, and sodium chloride was pre-set in the electrolyser while the main salt solutions were added as the cathode began to discharge.

An electrolyte was used to deposition under the following composition: the main salt solutions 150 g/L, ethanol 50-250 mL/L, citric acid 0-20 g/L and sodium chloride 3-6 g/L. The main salt solutions were used to provide metal ions for deposition, and ethanol was expected to reduce the boiling point of the solution so as to lower the puncture voltage, allowing discharge under a low voltage. In the meantime, through volatilisation, ethanol is capable of decreasing the temperature inside the bubbles around the cathode during discharge. Besides, citric acid was used as a pH modifier, together with the sodium chloride which was used as a conductive agent.

A scanning electron microscope and an electronic scale were separately used to observe the surface appearance of the deposition layer and to weigh the cathode so as to measure any changes therein. The deposition rate can be expressed as $D=\Delta m/t$, where Δm is the mass difference of the cathode before, and after, deposition and t represents the deposition time.

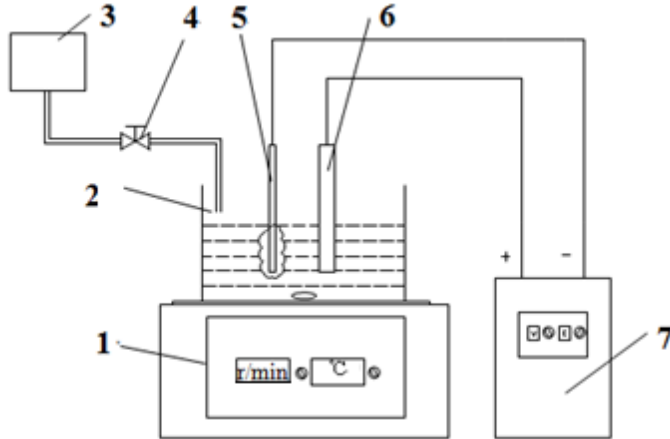


Figure 1: Diagram of experimental apparatus. (1) a magnetic stirring apparatus; (2) an electrolyser; (3) a supply tank for the main salt solutions; (4) a flow valve; (5) cathode; (6) anode; (7) high voltage DC.

3. Results and Discussion

3.1 Analysis of experimental phenomena

Figure 2 shows the discharge process of the cathode surface in the experiment using liquid plasma. After energisation, electrolytic bubbles were firstly generated on the cathode surface, these were scattered and of small diameter, and were incapable of obstructing the currents. As the voltage increased, the liquid around the cathode was heated by the cathode generating rising vapour bubbles which could cling to the cathode, so that the continuous vapour bubbles formed a bubble sheath layer which separated the electrode from the solution. At the same time, the voltage kept increasing, so that the bubble sheath layer was broken down by the discharge. This led to the generation of continuous bubble bunches inside which plasmas were obtained (Chen et al., 2010). With the aid of an applied electrical field of high intensity inside the bubbles, metal ions at the interface of the solution and the bubbles accelerated towards the cathode and were reduced there. At the moment when countless small bubbles in these bubble bunches burst, high temperatures and pressures were generated due to the void effect, which forced the metal ions into the bubbles from where they were deposited faster. Hence, materials are expected to be deposited at a high speed by cathode plasma electrodeposition (Nie et al., 2010).

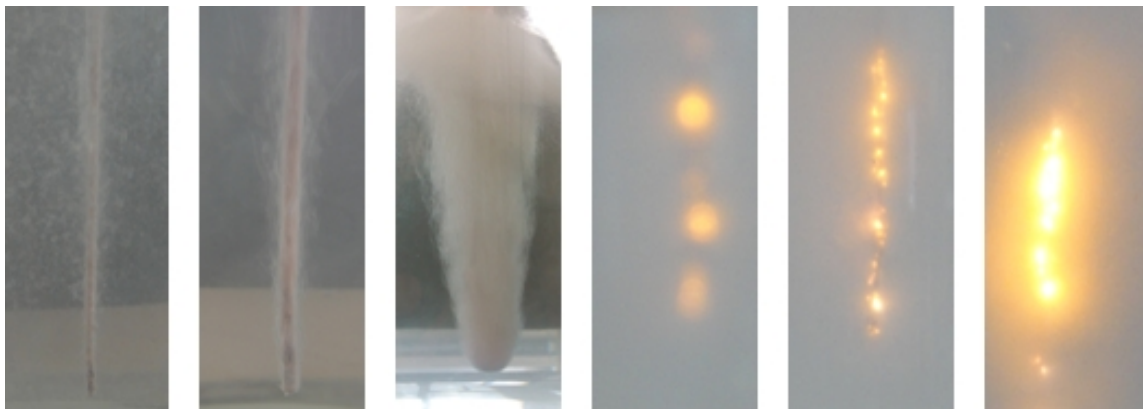


Figure 2: The discharge process of the cathode surface in the experiment using liquid plasma

3.2 The influence of ethanol concentration

Figure 3 shows the effect of ethanol concentration on the deposition rate under the condition of nickel aminosulphonate 150 g/L, citric acid 5 g/L and sodium chloride 3~6 g/L. As ethanol concentration of the electrolyte rose, the discharge voltage gradually decreased, as did the rate of deposition of nickel. That is because, with an essentially constant diameter of the bubble bunches wrapping the cathode, the intensity of the electric field inside the bubbles was directly proportional to the discharge voltage. Moreover, the movement rate of metal ions was dependent on the electrical field intensity, that is, the greater the intensity, the faster the metal ions were when they entered the bubbles and accelerated towards the cathode to be reduced. Therefore, a moderate increase in discharge voltage contributes to the improvement of the rate of diffusion and deposition of metal ions (Yang, et al, 2017).

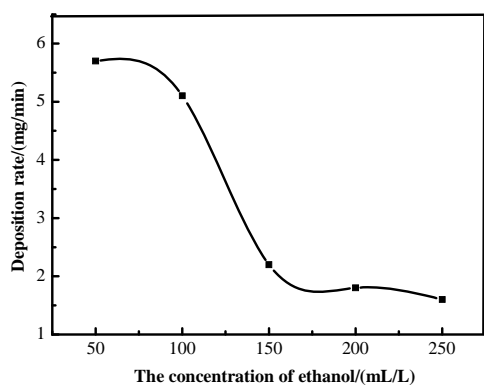


Figure 3: Relationship between the deposition rate and ethanol concentration

Figure 4 shows the surface appearance of the deposition layer under different ethanol concentrations at aminosulphonate 150 g/L, citric acid 5 g/L. The plasma electrodeposition layer presented distinct dendritic growth. With increasing ethanol concentration, the surface of the deposition layer gradually became smooth, where dendrites grew slowly with fine, uniform particles formed. According to dendrite growth theory, the deposition rate determines the expansion in the area of crystals per unit time, that is, the greater the deposition rate, the faster the spread and growth of the crystals. When the adjacent crystals expand and meet, dendrites are expected to be generated, and protrusions thereof cause concentration of current, which results in a more rapid growth rate.

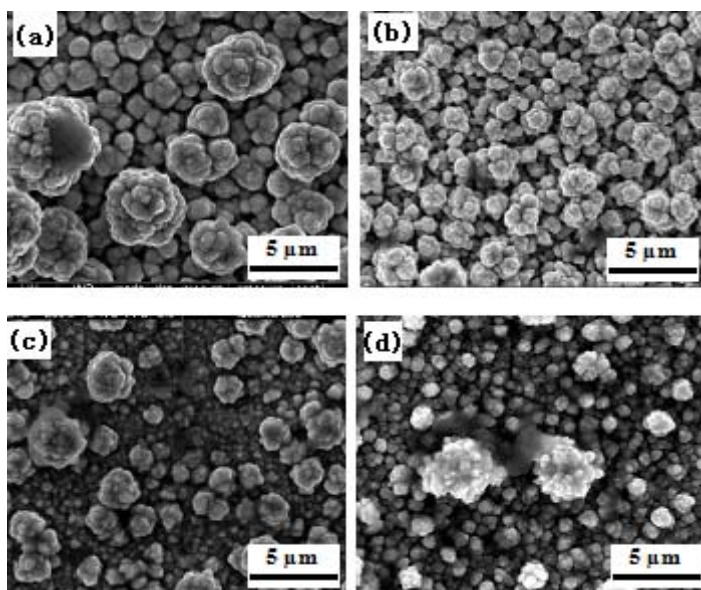


Figure 4: Surface appearance of the deposition layer under different ethanol concentrations (a) 50 mL/L; (b) 100 mL/L; (c) 150 mL/L; (d) 200 mL/L

3.3 The influence of citric acid concentration

Figure 5 shows the effect of citric acid concentration on the deposition rate under the condition of nickel aminosulphonate 150 g/L, ethanol 50 mL/L and sodium chloride 3 g/L. When the concentration of citric acid of the electrolyte was 2 g/L, there was a large amount of floccules and the deposition rate of nickel decreased. As the concentration of citric acid increased, the solution became transparent and clear, along with the considerable acceleration of the deposition of nickel, while with its further addition, no notable change in the deposition rate was found. This indicates that the addition of citric acid makes Ni^{2+} in the solution act as a complex ion instead of a hydrated ion, which can improve the degree of cathodic polarisation so as to accelerate the deposition of nickel. Nevertheless, as the concentration of citric acid continued to increase, the deposition rate no longer varied due to the fixed rate of addition of the main salt solution and the constant concentration of the metal ions inside the electrolyser. In addition, the deposition rate reached 5 mg/min, its highest value, at a citric acid concentration of 5 g/L. Through measurement, the thickness of the deposition layer was greater than 120 μm after 30 min.

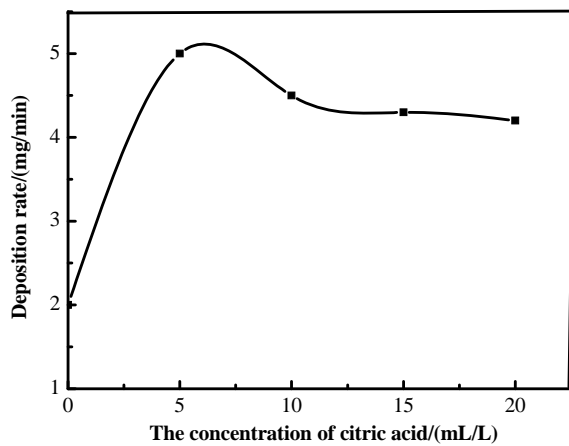


Figure 5: Relationship between the deposition rate and citric concentration

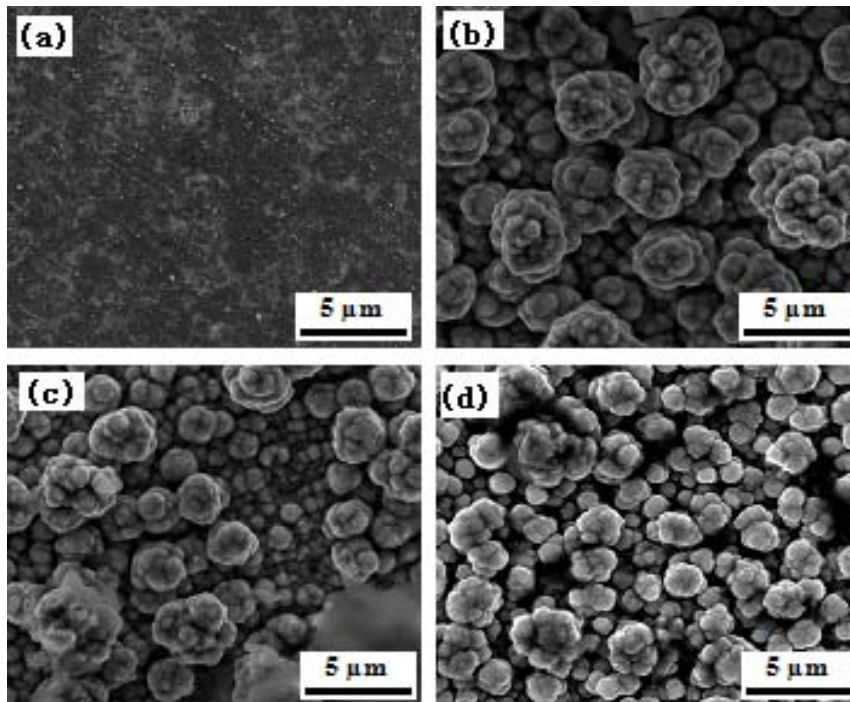


Figure 6: Surface appearance of the deposition layer under different ethanol concentrations. (a) 2 g/L; (b) 5 g/L; (c) 10 g/L; (d) 15 g/L

Figure 6 shows the surface appearance of the deposition layer under different citric acid concentrations, at aminosulphonate 150 g/L, ethanol 50 mL/L and sodium chloride 3 g/L. As the concentration of citric acid increased, the deposition rate, in addition to the quality of the deposition layer, was enhanced significantly: the crystal structure was more compact and even.

3.4 Influence of the type of main salt

Table 1 evinces the relationship between the choice of main salt and deposition rate. In the experiment, nickel aminosulphonate, nickel sulphate, and nickel chloride, were selected as the main salts. The result showed that the deposition rate reached the highest while using nickel chloride as the main salt, followed by nickel sulphate, then nickel aminosulphonate. This was because Cl^- is an anode activator that can restrain the inactivation of the anode so as to reduce the dissolution potential of the nickel plate in the anode and thus accelerate its dissolution. Therefore, increasing the concentration of Ni^{2+} in the solution is expected to facilitate the deposition of nickel.

Table 1: Relationship between the choice of main salt and deposition rate

Type of main salt	Deposition rate $/(mg \cdot min^{-1})$
Nickel aminosulphonate	3.42
Nickel sulphate	45.3
Nickel chloride	2.46

Figure 7 shows the surface appearance of the deposition layer under different type of main salt at nickel aminosulphonate 150 g/L, ethanol 50 mL/L and sodium chloride 3 g/L. The Main salt used had only a slight effect on the surface appearance of the deposition layer on account of the high current density (80 to 100 A/dm^2) or above in the process of cathode plasma electrodeposition. The super-high current density led to crystal growth of dendritic form, and rough surfaces were quickly generated during dendrite growth. As a result, there was no notable variation in the surface appearance of the deposition layer.

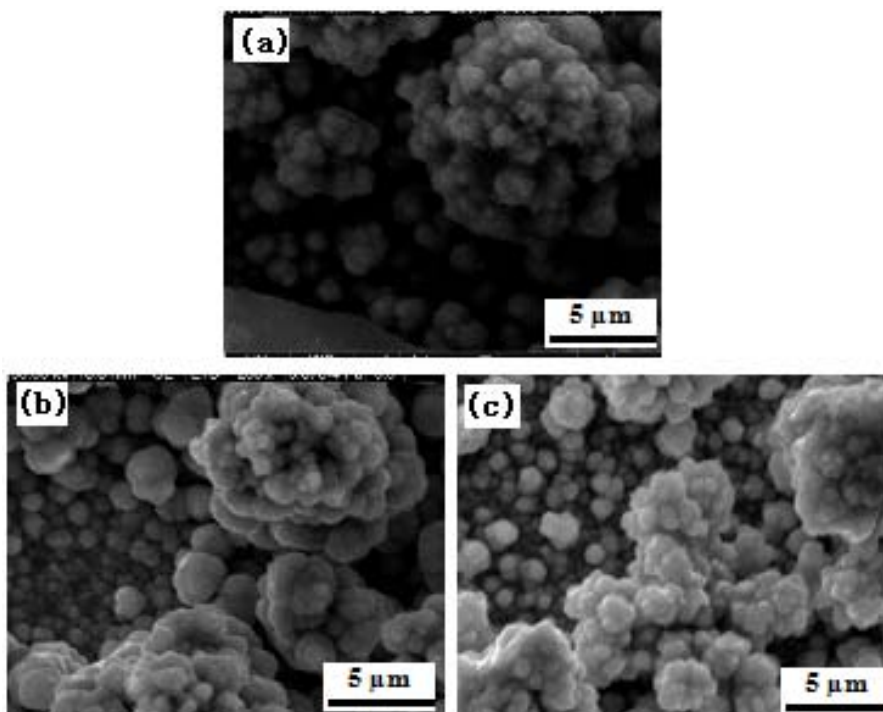


Figure 7: Surface appearance of the deposition layer under different type of main salt. (a) nickel aminosulphonate; (b) nickel sulphate; (c) nickel chloride

4. Conclusions

As the ethanol concentration in the electrolyte increased the surface of the deposition layer of nickel became fine and uniform and its rate of deposition decreased: these effects grew less obviously when the concentration reached a certain level.

When there was little citric acid in the electrolyte, little nickel was deposited; the increase of the concentration of citric acid can accelerate the rate of deposition of nickel; however, under a certain rate of addition of main salt solution, the deposition rate was slightly influenced by the concentration of citric acid when it reached a certain level. Besides, increasing the concentration of citric acid can decrease the size of the particles on the deposition surface.

With nickel chloride, or nickel sulphate, as main salts, the deposition rate of nickel was much higher than that using nickel aminosulphonate. In addition, the three main salts did not exert a strong influence on the surface appearance of the deposition layer.

Acknowledgements

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