

## Preparation of Ni nanoparticles plating by electrodeposition using reverse microemulsion as template

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**Abstract:** Ni nanoparticles plating was prepared in reverse microemulsion. The deposition was carried out through the Brownian motion of water pools in the reverse microemulsion and the adsorption of water pools on the electrode surface. Effects of electrolytic parameters on the size of Ni particles were studied. The performances of hydrogen evolution and hydrogen storage of the Ni nanoparticles plating electrode were also investigated. The results indicate that the size of Ni nanoparticles decreases with the increase of  $\text{Ni}^{2+}$  concentration and the decrease of current density. The electrochemical activity of Ni nanoparticles plating electrode is much higher than that of bulk Ni electrode.

**Key words:** Ni nanoparticles; reverse microemulsion; electrodeposition; electrolytic parameters

### 1 Introduction

Nanoparticles show good application perspective in electricity, optics, catalysis and biosensor due to their unique physical and chemical properties [1–3]. Reverse microemulsion is defined as a transparent, thermodynamically stable system where water pools stabilized by surfactant disperse in continuous oil phase [4–6]. The diameter of dispersive phase in reverse microemulsion is 10–100 nm. The nano-water pools in reverse microemulsion provide a good microenvironment for preparation of nanoparticles. The size and morphology of the resultant nanoparticles can be controlled by adjusting the size of nano-water pools [7–8]. In electrochemical reaction system, aqueous solution, organic solution or melted salt is often used as electrolyte. And the obtained plating is usually bulk metal or alloy layer. However, it is difficult for reverse microemulsion to construct electrochemical system due to very low electric conductivity of reverse microemulsion whose continuous phase is oil. ZHOU et al [9–10] presented that the electric conductivity of reverse microemulsion can be improved by adding high concentration HCl into the water phase. In this work, reverse microemulsion with high electric conductivity was used as the electrolyte, and Ni nanoparticles plating was prepared by electrodeposition. Moreover, influences

of electrolytic parameters on the morphology and performance of Ni nanoparticles plating were investigated.

### 2 Experimental

#### 2.1 Reagents

Ni sulfate, *n*-hexane, *n*-hexanol, *p*-octyl polyethylene glycol phenyl ether (TritonX-100), hydrochloric acid, sodium hydroxide, sulfuric acid, ethanol and acetone were used. All chemical reagents used are analytical grade. All solutions were prepared with double distilled water.

#### 2.2 Preparation and characterization of reverse microemulsion

After mixing 10 mL TritonX-100, 20 mL *n*-hexanol and 20 mL *n*-hexane as the oil phase, 3.2 mL aqueous solution (9.375 mol/L HCl + 0.065–0.286 mol/L  $\text{NiSO}_4$ ) was added under stirring, and a transparent microemulsion was obtained. Then the microemulsion was centrifuged by a high-speed centrifuge (Eppendorf Centrifuge 5804 R, Germany) with a speed of  $1 \times 10^4$  r/min at 5 °C for 5 min. The microemulsion was still transparent without any phase separation, indicating that the microemulsion used was quite stable. The structure of microemulsion was characterized by a dynamic light scattering equipment (ALV/CGS-5022F, ALV/Laser

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### 2.3 Preparation of Ni nanoparticles plating electrode

Electrodeposition of Ni nanoparticles was carried out in a two-electrode cell from a reverse microemulsion with a direct current electrical source. The working electrode was a Ni electrode with a surface area of  $0.2 \text{ cm}^2$ . A platinum foil was used as the counter electrode. Prior to use, the working electrode was first polished with alumina emery paper. Then, it was washed with alcohol, acetone and double distilled water, respectively.

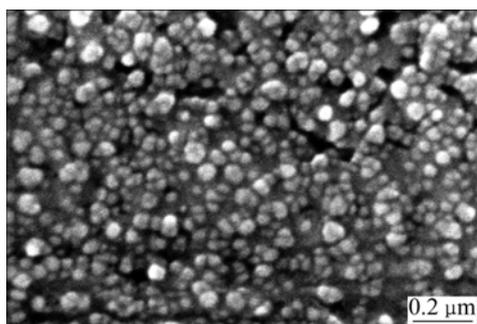
### 2.4 Measurements of morphology and electrochemical property of Ni nanoparticles plating electrode

The morphology of Ni nanoparticles plating was observed using scanning electron microscopy (SEM, JSM-5600LV, JEOL Company, Japan). The electrochemical property of Ni nanoparticles plating was investigated by linear polarization (scan rate:  $10 \text{ mV/s}$ ) and cyclic voltammetry (scan rate:  $50 \text{ mV/s}$ ) using a CHI model 660B electrochemical workstation (Shanghai Chenhua Instrument Factory, China). In the electrochemical measurement, the working electrode was a Ni nanoparticles plating electrode. A platinum foil and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively.

## 3 Results and discussion

### 3.1 Preparation of Ni nanoparticles plating

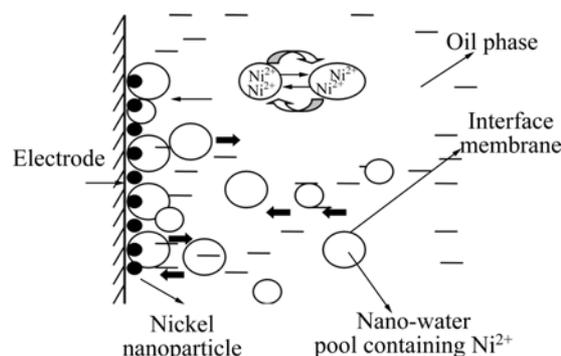
Fig.1 shows SEM image of the Ni nanoparticles plating obtained from a reverse microemulsion containing  $0.125 \text{ mol/L NiSO}_4$  in water phase. It can be observed from Fig.1 that the plating is composed of Ni particles with diameter of about  $50 \text{ nm}$ , and the nanoparticles on the electrode surface accumulate together. This presents that Ni nanoparticles plating obtained from reverse microemulsion is incontinuous,



**Fig.1** SEM image of Ni nanoparticles plating obtained from reverse microemulsion at  $\text{Ni}^{2+}$  concentration of  $0.125 \text{ mol/L}$  and current density of  $10 \text{ mA/cm}^2$

and hence the electrodeposition process in reverse microemulsion is obviously different from that in conventional homogeneous solution.

The surfactant-stabilized nano-water pools in reverse microemulsion are unique nanosized reactors. The average hydrodynamic radius of the reverse microemulsion is  $17.1 \text{ nm}$  with a distribution from  $3.2$  to  $87.1 \text{ nm}$ . Fig.2 shows the cathodic reduction process of  $\text{Ni}^{2+}$  at the electrode/reverse microemulsion interface. The nano-water pools containing  $\text{Ni}^{2+}$  collide with the electrode continuously because of their Brownian motion. Moreover, due to the interaction between the surfactant film and the electrode/reverse microemulsion interface, some water pools also adsorb at the interface. When the equilibrium between the adsorbed water pools and those colliding with the electrode is set up, a layer of homeostatic adsorbed water pools forms. Because  $\text{Ni}^{2+}$  can only dissolve in the water phase, the distribution of  $\text{Ni}^{2+}$  in the reverse microemulsion is incontinuous and ununiform. Thus, only  $\text{Ni}^{2+}$  in the water pools adsorbed at the interface can be reduced to Ni, which exhibits nanosized particle due to the size effect of nano-water pool [11–12]. The organic compound especially surfactant around the nano-water pool adsorbs on the surface of Ni nanoparticles and inhibits further growth of Ni particles. Subsequently, the reduction of  $\text{Ni}^{2+}$  in another nano-water pool occurs. Go round and round, Ni nanoparticles plating forms on the electrode surface eventually.

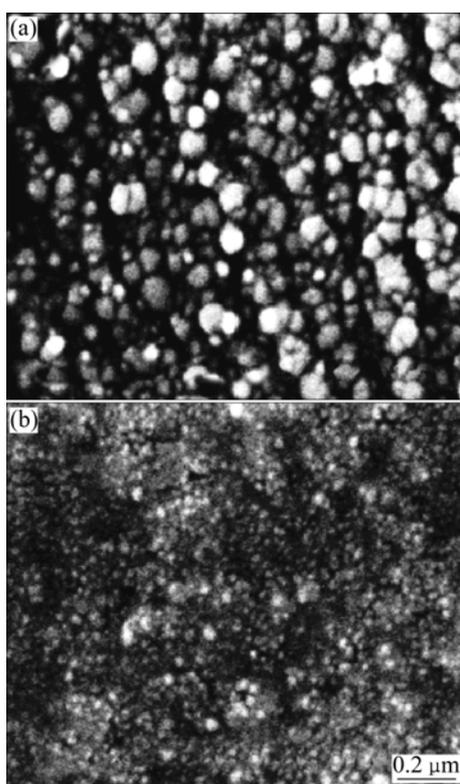


**Fig.2** Sketch map of cathodic reduction process of  $\text{Ni}^{2+}$  at electrode/reverse microemulsion interface

### 3.2 Influences of $\text{NiSO}_4$ concentration on morphology and electrochemical activity of Ni nanoparticles plating

Fig.3 shows SEM images of the Ni nanoparticles plating obtained from reverse microemulsion containing different  $\text{Ni}^{2+}$  concentrations. It can be observed from Fig.3 that when  $\text{Ni}^{2+}$  concentration of the water phase is  $0.065 \text{ mol/L}$ , the diameter of the Ni nanoparticles is about  $90 \text{ nm}$ . When  $\text{Ni}^{2+}$  concentration increases to  $0.286 \text{ mol/L}$ , the diameter of the Ni nanoparticles decreases to about  $30 \text{ nm}$ . This presents that  $\text{Ni}^{2+}$

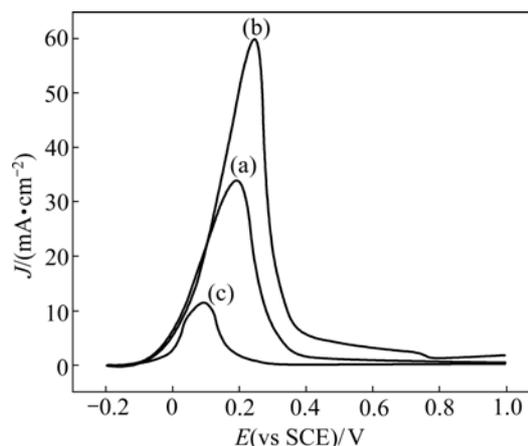
concentration of the water phase markedly affects the size of Ni nanoparticles. For the electrode reaction of  $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$ , the change of  $\text{Ni}^{2+}$  concentration will lead to the change of exchange current density and limit diffusion current density of the electrode reaction. On account of the special structure of reverse microemulsion,  $\text{Ni}^{2+}$  ions participating in the electrodeposition process are almost from the water pools. When  $\text{Ni}^{2+}$  concentration of the water pools is low,  $\text{Ni}^{2+}$  concentration will decrease constantly with the consumption of  $\text{Ni}^{2+}$  during the electrodeposition process. The controlling step of the electrode reaction will convert to concentration polarization step from electron exchange step and the overvoltage will mainly result from concentration polarization. The crystals of the Ni nanoparticle plating formed are large. So, the diameter of Ni nanoparticles obtained from the microemulsion containing 0.065 mol/L  $\text{Ni}^{2+}$  is larger than that obtained from the microemulsion containing 0.286 mol/L  $\text{Ni}^{2+}$ .



**Fig.3** SEM images of Ni nanoparticles platings obtained from reverse microemulsion containing different  $\text{Ni}^{2+}$  concentrations at current density of 10 mA/cm<sup>2</sup>: (a) 0.065 mol/L; (b) 0.286 mol/L

Fig.4 shows the anodic polarization curves of bulk Ni electrode and the Ni nanoparticles plating electrodes obtained from reverse microemulsion containing different  $\text{Ni}^{2+}$  concentrations in 0.5 mol/L  $\text{H}_2\text{SO}_4$ . The passive peaks of Ni can be observed at about 0.2 V. Because the apparent areas of the three electrodes are equal, the real areas of the electrodes can be evaluated

according to the value of the passive current density. It can be deduced from Fig.4 that the electrochemical activity of the Ni nanoparticles plating electrodes is higher than that of the bulk Ni electrode. Moreover, the activity of the Ni nanoparticles plating increases with the decrease of the size of Ni nanoparticles. This is attributed to the fact that the Ni nanoparticles plating electrode has larger specific surface areas than the bulk Ni electrode. And the smaller the size of Ni nanoparticles, the larger the specific surface area of the electrode.



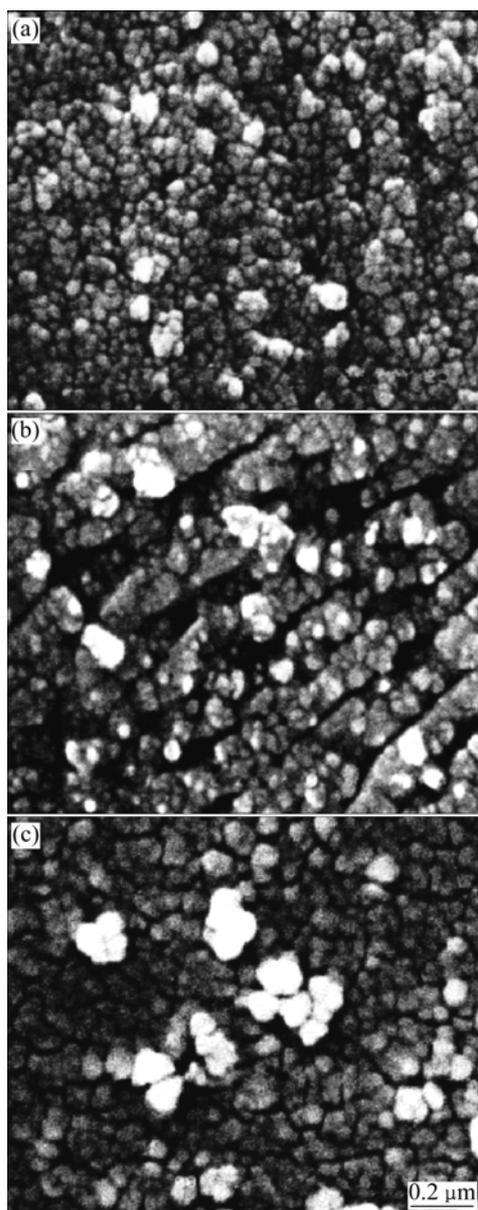
**Fig.4** Anodic polarization curves of bulk Ni electrode and Ni nanoparticles plating electrodes obtained from reverse microemulsion containing different  $\text{Ni}^{2+}$  concentrations in 0.5 mol/L  $\text{H}_2\text{SO}_4$ : (a) 0.065 mol/L; (b) 0.286 mol/L; (c) Bulk Ni

### 3.3 Influences of current density on morphology and electrochemical activity of Ni nanoparticles plating

The electrochemical kinetic rule of Ni deposition can also be changed by changing the deposition current density under the same  $\text{Ni}^{2+}$  concentration. Fig.5 shows SEM images of Ni nanoparticles platings prepared at 5, 15 and 25 mA/cm<sup>2</sup>. It can be seen that the smaller the current density, the smaller the size of Ni nanoparticles and the more uniform of the Ni nanoparticles plating. When the current density is 25 mA/cm<sup>2</sup>, the diameter of Ni nanoparticles reaches about 70 nm. This may result from the mass transfer characteristic of reverse microemulsion. In reverse microemulsion, the water pools are very small and hence convection transfer is approximately zero. The reaction particles in the water pools reach the electrode surface only by diffusion, liquid phase transfer is the controlling step at large current density, and hence the crystals of the plating become large.

### 3.4 Hydrogen evolution and hydrogen storage performances of Ni nanoparticles plating

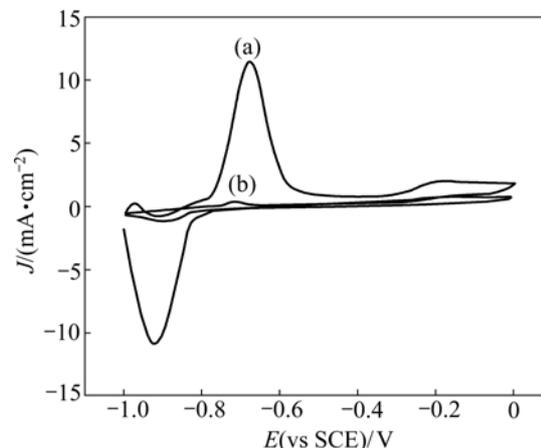
The cyclic voltammetric curves of the Ni nanoparticles plating electrode and bulk Ni electrode in



**Fig.5** SEM images of Ni nanoparticles platings obtained at  $\text{Ni}^{2+}$  concentration of 0.125 mol/L and different current densities: (a) 5  $\text{mA}/\text{cm}^2$ ; (b) 15  $\text{mA}/\text{cm}^2$ ; (c) 25  $\text{mA}/\text{cm}^2$

7 mol/L NaOH are shown in Fig.6. Hydrogen evolution can be observed obviously at potential from  $-0.90$  to  $-0.95$  V during the negative sweeping. Anodic oxidation peaks emerge at potential from  $-0.70$  to  $-0.60$  V during the positive sweeping, which may be corresponding to the anodic oxidation of hydrogen atoms adsorbing on the electrode surface during the negative sweeping [13–14]. Comparing curve (a) with curve (b), it can be seen that both the cathodic reduction peak current of  $\text{H}^+$  and the anodic oxidation peak current of absorbed H on the Ni nanoparticles plating electrode are almost 9 times higher than those on the bulk Ni electrode. This reveals that the electrochemical activity of the Ni nanoparticles plating electrode for redox of hydrogen is much higher than that

of the bulk Ni electrode. The electrochemical reaction of the Ni nanoparticles plating electrode in 7 mol/L NaOH is controlled by adsorption/oxidation processes. Moreover, it can be deduced that the Ni nanoparticles plating electrode has potential value in hydrogen storage.



**Fig.6** Cyclic voltammograms of Ni nanoparticles plating electrode and bulk Ni electrode in 7 mol/L NaOH: (a) Ni nanoparticles plating electrode; (b) Bulk Ni electrode

## 4 Conclusions

(1) Ni nanoparticles plating is prepared using reverse microemulsion as template.

(2) The higher the  $\text{Ni}^{2+}$  concentration of the water phase and the smaller the deposition current density, the smaller the size of Ni nanoparticles.

(3) The Ni nanoparticles plating electrode has higher electrochemical activity than the bulk Ni electrode. There are two redox peaks for the Ni nanoparticles plating electrode in 7 mol/L NaOH, indicating good hydrogen evolution and hydrogen storage performances of the electrode.

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