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Electrocatalytic activity and electrochemical hydrogen storage of Ni-La alloy prepared by electrodeposition from aqueous electrolyte^①

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[Abstract] Ni-La alloy coating was prepared by electrodeposition. The effect of cathodic current density on the La content of the alloy coatings was discussed. It is found that the content of La in the alloy increases with increasing the cathodic current density. The microstructures and codeposition mechanism of Ni-La alloy coatings were investigated by means of X-ray diffraction (XRD) and cyclic voltammetry (CV). The results demonstrate that the Ni-La alloy is FCC and codeposited by the induced mechanism. The hydrogen evolution reaction (HER) on the electrodeposited Ni-La alloy electrodes in alkaline solution was evaluated by Tafel polarization curves. It is found that La-Ni alloy coating exhibits much higher exchange current density for HER than pure Ni electrode, and that the exchange current density increases with increasing the La content of alloys. The good electrocatalytic activity for HER of this Ni-La alloy is attributed to the synergism of the electronic structure of La and Ni. The electrodeposited La-Ni alloys have a certain electrochemical hydrogen storage capacity of 34~143 mAh/g, which increases with increasing the La content of alloys.

[Key words] Ni-La alloy; electrodeposition; hydrogen evolution reaction; hydrogen storage

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1 INTRODUCTION

Rare earth-Ni based alloys have been widely used as the negative materials in Ni/MH batteries^[1~4] and as hydrogen evolution cathode for water electrolysis^[5~7], because of their high hydrogen storage capacity and good electrocatalytic activity for hydrogen electrode reaction. It was reported that the LaNi₅ type hydrogen alloys electrodes have a very high electrocatalytic activity for the HER in alkaline solution, almost comparable with those of platinum and palladium electrodes^[8]. Therefore, the rare earth-Ni system hydrogen storage alloys have presented interesting and promising characteristics as cathodes for HER. More recently, it was reported that the nickel composite coating with rare earth based hydrogen storage alloy particles were prepared by the composite plating^[5~7]. It was found that this composite coating exhibited a very high electrocatalytic activity and good stability for alkaline water electrolysis.

Electrodeposition has been widely introduced to prepare many kinds of Ni-based alloys. In this paper, the Ni-La alloy coating was prepared by electrodeposition, and characterized by XRD. The effect of cathodic current density on the La content of the alloy and the mechanism of La codeposition with Ni were investigated. The hydrogen evolution reaction on the Ni-La alloy coating electrode was evaluated by Tafel

polarization curves, and the synergism of the electrocatalytic activity for HER of Ni-La alloy electrodes was investigated. In addition, the hydrogen storage property of Ni-La alloy was tested.

2 EXPERIMENTAL

Bath compositions and plating conditions are as follows:

| | |
|------------------|------------------------------|
| La ³⁺ | 0.07~0.11 mol/L |
| Ni ²⁺ | 0.09~0.12 mol/L |
| Complex agent | 0.08~0.12 mol/L |
| Additive | 30~50 mL/L |
| pH | 7.0~8.0 |
| Temperature | 40~50 °C |
| Current density | 3 500~7 000 A/m ² |

Ni-La alloy coating was plated on Cu substrate at different current densities. The components of Ni-La alloy coating was analyzed by the atomic absorption spectrophotometry (AAS) using XWY-401 atomic absorption spectrometer and by spectrophotography using 752 type ultraviolet-visible spectrometer. XRD patterns were recorded with Model 2038 X-ray diffractometer. The mechanism of Ni-La codeposition was investigated by a cyclic voltammetry at the range of -1.3~0.6 V (vs SCE) and a scan rate of 50 mV/s, in which a glassy carbon electrode of 0.2 cm² was used as a work one, a Pt foil used as a

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counter electrode, a saturated calomel electrode (SCE) used as a reference.

Hydrogen evolution reactions on the Ni-La coating and pure Ni electrodes were performed in 25% (mass fraction) NaOH solution at 303 K by using H-shape glass electrolytic cell, in which a Pt foil was used as a counter electrode, Hg/HgO (1 mol/L KOH) as a reference. The kinetics for HER were evaluated by Tafel polarization curves. The Ni-La alloy was peeled from the substrate and mechanically pulverized, then mixed with fine copper to press a testing electrode. The electrode was charged at a constant current density of 50 mA/g for 8 h in 6 mol/L KOH, and discharged to -0.600 V at the same current density, in which a sintered nickel hydroxide was used as a counter electrode, Hg/HgO as reference electrode.

3 RESULTS AND DISCUSSION

3.1 Compositions and microstructure of electrodeposited Ni-La alloy coatings

The effect of cathodic current density on the La content of Ni-La alloy is shown in Table 1, in which one can find that the La content obviously increases with increasing the current density. XRD patterns of the Ni-La alloy coatings are shown in Fig. 1. It is found that the crystal structure of Ni-La alloys in this work still belongs to the face centered cubic (FCC), which is similar to that of nickel. Because the atomic radius of La is larger than that of Ni, the lattice parameters of Ni-La alloys are slightly larger than that of pure Ni ($a = 0.352377$ nm) as shown in Table 1.

Table 1 Effect of current density on La content and lattice parameters of Ni-La alloy

| Current density ($\text{A} \cdot \text{cm}^{-2}$) | La content (mole fraction) / % | Lattice parameter / nm |
|--|-----------------------------------|---------------------------|
| 3 500 | 2.54 | 0.352 519 |
| 5 000 | 6.67 | 0.352 659 |
| 7 000 | 11.0 | 0.353 077 |

It is well known that rare earth metals are difficult to deposit individually in aqueous solution, but can be co-deposited with nickel on Ni-based alloy by electroplating and electroless^[9,10]. In general, the mechanisms of the alloy codeposition are divided into the following five categories: regular codeposition, irregular codeposition, equilibrium codeposition, anomalous codeposition and induced codeposition. As shown in the CVs of Fig. 2, in the case of the bath containing La ion without Ni ion, no electrode reaction takes place in the potential scan range, indicating that the La can't be individually deposited. For the bath containing Ni ion without La ion, when the potential negatively sweep near about -1.10 V (vs SCE), the cathodic current obviously increases be-

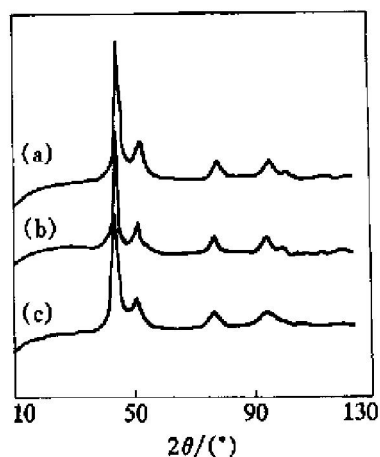


Fig. 1 XRD patterns of Ni-La alloy electrodeposited at different current densities (a) -3500 A/m^2 ; (b) -5000 A/m^2 ; (c) -7000 A/m^2

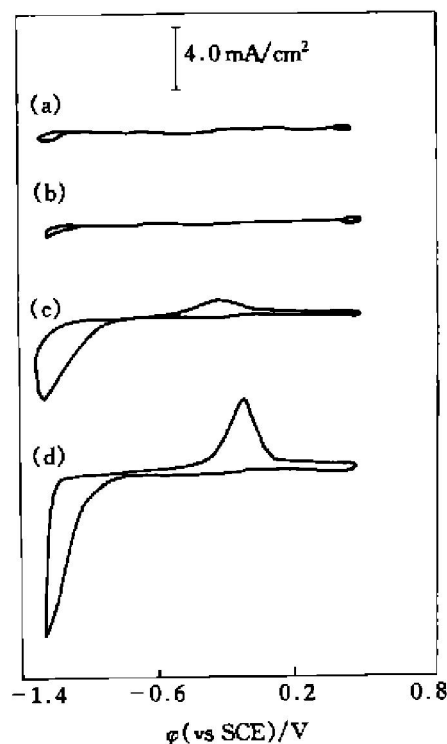


Fig. 2 Cyclic voltammograms at different solutions (a) —Blank; (b) —Bath only containing La^{3+} ; (c) —Bath only containing Ni^{2+} ; (d) —Bath containing La^{3+} and Ni^{2+}

cause of the deposition of nickel. An anodic peak attributed to the dissolution of metallic nickel at -0.22 V (vs SCE) can be observed. In the case of the bath containing nickel ion and La ion, when the potential negatively sweeps near -1.10 V (vs SCE), the cathodic current begins to markedly increase, as a result of the codeposition of Ni and La. An anodic peak of the co-dissolution of Ni-La at -0.05 V (vs SCE) is found, which is more positive than that in Fig. 2(b). It was reported by Jovic et al^[11] that the phase structure of the electrodeposited alloy was determined by means of anodic stripping voltammetry. They claimed that all the alloying components are dis-

solved at the same time during the anodic stripping of the solid solution alloy, and so an anodic peak should be found in the cyclic voltammogram. Compared with that of pure metal, the anodic peak potential should shift in a positive direction because of the interaction of the alloying elements with each other. As shown in Fig. 2, the anodic peak potential for Ni-La alloy is more positive than that for Ni coating. Therefore, it can be concluded that La is codeposited with Ni by induced mechanism and forms a substitutional solid solution.

3.2 Hydrogen evolution reactions on Ni-La alloy electrode

Fig. 3 shows the Tafel polarization curves for the hydrogen evolution reaction on the Ni-La alloys and pure Ni electrode in 25% (mass fraction) NaOH solution at 303 K. Tafel slopes and exchange current densities for HER calculated from the Tafel curves are summarized in Table 2. It is clear from Table 2 that Ni-La alloy electrodes have much higher exchange current density than pure Ni electrode, and the exchange current density increases with increasing the content of La in Ni-La alloys. On the other hand, it can be found from Table 2 that the Tafel slopes for HER on Ni-La alloys are close to that for Ni electrode and independent of the content of La. Machida et al.^[12,13] reported that the Ni site is responsible for

HER on Ni-based alloys of Ni-Ti, Ni-Zr, Ni-V and Ni-La, and so the Tafel slopes for HER on these Ni-based alloys are close to that of Ni electrode.

It is accepted that the properties of HER on the alloy electrode depend on the mother metal as well as the alloying elements. It was reported that the alloys of the transition elements such as Ni-Ti, Ni-V, Ni-Mo, Ni-Zr and Ni-La have higher activity for HER than pure metals because of the electronic interaction of the mother metal and alloying element^[12~15]. Two main strategies were reported to explain the electrocatalytic synergism of the transition metal alloys. One is the hypo-hyper- δ -electronic interactive effect of transition element alloys reported by Jaksis^[16]. According to Jaksis, the combination of hypo-hyper- δ -electronic transition elements results in rather strong bonding effectiveness, and so enhances the activity for HER. Ni is a typical hyper- δ -electronic element ($3d^8 4s^2$), and La is a typical hypo- δ -electronic element ($5d^1 6s^2$). Tamura et al.^[8] and Machida et al.^[12,13] reported that the LaNi₅ and Ni-La alloy electrodes have much higher electrocatalytic activity for HER than pure Ni and La metal, and attributed this fact to the hypo-hyper- δ -electronic synergism of La and Ni. The other is the charge transfer between the based metal and the alloying element reported by Ezaki^[17]. According to Ezaki, when the alloying element is less electronegative than the mother metal, the charge transfers from the alloying element to the mother metal, and so the excess electrons are located near the based metal. In this case, the water molecular is more easily discharged on the based metal site, hence, the based metal is responsible for HER, vice versa. In this work, La is positioned on the left side of Ni in the periodic table, and less electronegative than Ni. So the charge transfers in the direction from La to Ni. The excess electrons are located near the nickel atoms, resulting in good electrocatalytic activity for HER on Ni-La alloy. Because the Ni is responsible for HER, the Tafel slopes of HER on Ni-La alloys are close to that of the nickel electrode and independent of the content of La. In addition, the more the content of La in the alloy, the more excess electron near nickel atoms and the higher electrocatalytic activity for HER in this work.

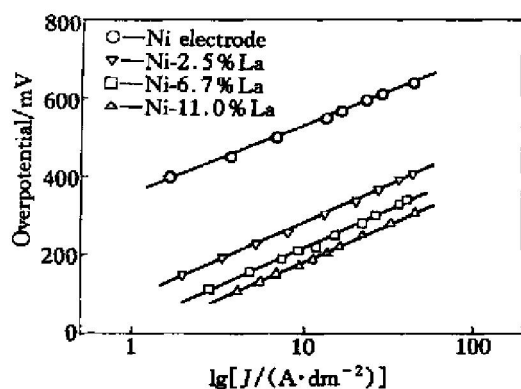


Fig. 3 Tafel polarization curves of hydrogen evolution reactions on electrodeposited Ni-La alloys and pure Ni electrodes in 25% NaOH solution at 303 K

Table 2 Kinetic parameters of HER on Ni-La and Ni electrode from Tafel polarization curves

| Electrode | Tafel slope /(mV·dec ⁻¹) | Exchange current density/(A·dm ⁻²) |
|-------------|---|---|
| Ni | 172 | 8.87×10^{-3} |
| Ni-2.5% La | 193 | 0.354 |
| Ni-6.7% La | 197 | 0.802 |
| Ni-11.0% La | 194 | 1.19 |

3.3 Electrochemical hydrogen storage property of electrodeposited Ni-La alloy

The discharge curves of Ni-La alloys with different La contents are shown in Fig. 4. It can be found from Fig. 4 that the discharge capacity of electrodeposited Ni-La alloy obviously increases with increasing the La content. The electrochemical capacity of hydrogen storage of Ni-La alloys is 34 mA·h/g for Ni-2.5% La (mole fraction), 92 mA·h/g for Ni-6.7% La and 143 mA·h/g for Ni-11.0% La. At

though it is much less than the capacity of LaNi_5 alloy ($372 \text{ mA} \cdot \text{h/g}$) and it seems to be insufficient for the hydrogen storage, but it can inhibit the degradation of the activity for HER. It is well known that Raney-Ni has been widely used for water electrolysis. However, its activity for HER is easily lost after intermittent operation, especially after a long period. More recently, HU^[5] reported that the Ni-based composite electrode with hydrogen storage alloy was employed as new cathodic material for water electrolysis. The hydrogen storage alloy particles can absorb hydrogen in electrolysis process and release the absorbed hydrogen during intermittent operation, which can improve the stability of the electrode for HER.

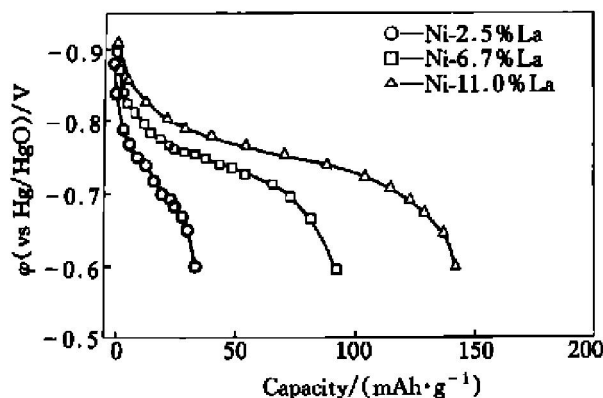


Fig. 4 Discharge curves of electrodeposited Ni-La alloys electrodes

4 CONCLUSION

Ni-La alloys with different La contents were prepared by electrodeposition in aqueous solution. It is found that the La content in Ni-La alloy obviously increases with increasing cathodic current density. According to the results of CV and XRD, the La is codeposited with Ni by induced mechanism and forms a substitutional solid solution alloy.

The Ni-La alloy electrode exhibits much higher exchange current density for HER in alkaline solution than pure Ni, in addition, the exchange current density increases with increasing the La content. The good activity for HER of Ni-La alloy electrode can be attributed to the synergism of the electronic structure of La and Ni. In addition, the electrodeposited Ni-La alloy has a certain hydrogen capacity, which increases with increasing the La content. Although the capacity is too low for hydrogen storage, it facilitates to improve the stability of Ni-La electrode for water electrolysis.

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