

Application of ferrous alloy plated electrode on Raney alloy as a platform to alkaline water electrolysis

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ABSTRACT:

Hydrogen is attracting attention as a next generation energy medium due to the growing awareness of global environmental problems. However, it has not been yet developed the technology capable of producing inexpensive and large amounts of hydrogen in accordance with energy demand. This research aimed to produce the cathode electrode with high performance of hydrogen generation catalytic activity in alkaline water electrolysis, using iron alloy plating of Raney alloy as a platform. Focusing on Ni - Zn alloy as a platform, Ni - Zn alloy plating was applied on a stainless steel substrate. Raney catalyst having a high specific surface area was obtained by dissolving only Zn by alkali immersion of plated Ni - Zn alloy. And iron-based alloy plated electrode having better catalytic activity for hydrogen evolution reaction (HER) than that of Ni was applied on the surface thereof¹⁾. For the evaluation of electrode characteristics, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were tried. Amount of plated Raney Nickel and dissolution of Zinc were varied. Among them the catalytic activity for HER of the plated Raney nickel alloy electrode was improved when the Ni-Zn plating weight was about 120 mg and the KOH immersion time for Zn dissolution was 2 h. HER performance of the Fe-Ni alloy plated Raney nickel was inferior to that of simple Raney nickel because the crevice of Raney nickel had been filled partially by plated Fe-Ni.

Keywords: Alkaline water electrolysis; Raney alloy; plated electrode; Fe-Ni alloy

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I. INTRODUCTION

World energy consumption continues to increase along with economic growth, continuing to increase at an annual average of 2.6% from 1600 GJ in 1965, reaching 5300 GJ in 2013. The main energy source responsible for this huge energy consumption will be fossil fuel. More than 80% of the current world energy demand is covered by natural gas, coal and oil. Disadvantages of the society consuming such a large amount of fossil fuel have emerged as global warming and environmental pollution problems. In order to solve this problem, conversion from fossil fuels to decarbonization and renewable energy, which is a low environmental load, should be a global issue^[1-3].

Hence, hydrogen has been expected as a next-generation energy source. Even when burned, just water is withdrawal, there is no generation of greenhouse gases and harmful gases, and it is a fuel with less environmental burden. Also, due to the growing interest in environmental issues, natural energy power generation such as solar power generation and wind power generation has been actively introduced. Since such a natural energy power generation is influenced by the weather, it is

difficult to stably supply the electric power, so power storage technology is required for stable power supply. By establishing a technology to convert surplus electric power into hydrogen energy and store it, it becomes possible to satisfy the demand and supply of electricity day and night.

However, it has not yet been developed the technology enable to produce inexpensive and massive amounts of hydrogen, which can satisfy energy demands. Therefore, researches on hydrogen production are proceeding actively all over the world. Among them, water electrolysis is the only industrially proven method and process that is indispensable in the hydrogen energy system society. In water electrolysis, high corrosion resistance of the electrode and high catalytic activity directly contributes to improvement of efficiency for hydrogen production and reduction of maintenance cost of the water electrolysis equipment, so its research and development has great significance^[4-14].

Therefore, in this study, we aimed to make the electrode with a high corrosion resistance and high hydrogen generation efficiency by use of iron alloy plating on Raney alloy as the platform for the cathode electrode for alkaline water electrolysis^[15-19]. For the evaluation of the catalytic activity for

hydrogen evolution reaction (HER), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were tried. And the surface treatment of electrodes was evaluated by use of surface analysis methods such as Scanning Electron Microscope (SEM) and Energy dispersive X-ray spectrometry (EDX) in combination.

II. EXPERIMENTAL SECTION

2.1 Method for manufacturing alloy plated electrode

2.1.1 Pretreatment of substrate

Stainless steel (SUS 430) which is relatively inexpensive and has good corrosion resistance was selected as a substrate to be subjected to electroplating treatment. It is general to apply nickel strike plating as a pretreatment to a plating material which is prone to generate an oxide film on the surface like stainless steel. **Table 1** shows the plating conditions for nickel strike. The stainless steel substrate was degreased with acetone and then immersed in concentrated hydrochloric acid for 2 minutes to remove the oxide film. Nickel strike plating was performed under constant current electrolytic method using an electrochemical measurement system (HA 305 Hokuto Denko Co., Ltd.)^[20]. After that, masking was done so that the surface active area was 4 cm² by use of masking tape (N-300 Nitto Denko Co., Ltd.)

2.1.2 Method of manufacturing Ni-Zn and Ni-Zn/Fe-Ni alloy plating electrode

Table 2a and 2b show the bath composition and conditions for Ni - Zn alloy plating^[15-19, 21]. The pH was adjusted with sulfuric acid. Ni - Zn alloy plating was applied to a pretreated stainless steel substrate under constant current electrolysis method using an electrochemical measurement system. Most of the Zn content in the film was dissolved by immersing the prepared Ni - Zn alloy in 7 M KOH at 20 to 25 °C for 2 h or 20 h. **Table 3** shows the bath composition and conditions for Fe - Ni alloy plating. Using the electrochemical measurement system, Fe - Ni alloy plating was applied on the Ni - Zn alloy plating after immersion in KOH under constant current electrolytic method. The plating time was set to 10 min in order to obtaining relatively thin plated film. For the counter electrode, Pt mesh electrode or Ni electrode having sufficiently large surface area with respect to the cathode were used. The purpose of applying Fe - Ni alloy plating is to stabilize the brittle surface by immersion in KOH and to fabricate the Fe - Ni alloy plated surface with better catalytic activity for HER than that of Ni^[5, 22].

2.1.3 Method of manufacturing Ni plating electrode and Fe-Ni alloy plating electrode

Table 4a and 4b show the bath composition

and conditions of Ni plating and Fe - Ni alloy plating. These were prepared as a comparative electrode to Ni-Zn and Ni-Zn/Fe-Ni alloy plated electrode. Ni electroplating and Fe - Ni alloy plating were applied to the pretreated stainless steel substrate under constant current electrolytic method using the electrochemical measurement system. Ni plating was made using a watt bath. For the Fe - Ni alloy plating, the plating time was set to 20 min in order to obtain thick deposited film. For the counter electrode, a Ni electrode having a sufficiently large surface area with respect to the cathode were used.

2.2 Elemental analysis and observation method of coated surface

2.2.1 SEM measurement conditions

The surface of the electrode was observed with a field emission scanning electron microscope (FE-SEM, Hitachi, Ltd.). The surface condition was observed at an accelerating voltage of 15 kV.

2.2.2 EDX measurement conditions

For the purpose of qualitative and quantitative analysis of the surface, the evaluation by an energy dispersive X-ray analyzer, Horiba Co., Ltd.: EMAX-5770) was carried out under the conditions of an acceleration voltage of 20 kV and a probe current of -0.2 nA.

2.3 Method and conditions of electrolysis test

LSV (linear sweep voltammetry) and CV (cyclic voltammetry) were carried out by use of the electrochemical measurement system (HZ - 5000, Hokuto Denko Co., Ltd.) to evaluate the catalytic activity for HER in alkaline water electrolysis. The potential scanning range of LSV was -1000 to -1500 mV vs. SCE within the theoretical hydrogen evolution potential (-1119 mV vs. SCE), and the potential scanning rate was 1 mV/s. The potential scanning range of CV was natural potential \pm 100 mV and the potential scanning speed was 10 mV/s. The surface area of each plated electrode was compared by calculating the electric double layer capacity from the result obtained by CV. An aqueous solution (electrolytic solution temperature: 20 to 25 °C.) of 7 M KOH (industrial flake-form KOH 95.5%: Nippon Soda Co., Ltd.) was used as the electrolytic solution. The cathode electrode area was 4 cm², the counter electrode was Pt mesh electrode with a sufficiently large surface area comparing to the cathode and SCE was used as the reference electrode.

III. RESULTS AND DISCUSSIONS

3.1 Surface analysis of Ni-Zn and Ni-Zn/Fe-Ni alloy plated film

3.1.1 Surface observation by SEM

Fig.1 shows the surface image of Ni - Zn and Ni - Zn / Fe-Ni alloy plated film observed by

SEM. It can be confirmed that the Ni - Zn alloy plating has many cracks after immersion in KOH. Moreover, it can be confirmed that the gap were partially filled by Fe - Ni alloy plating.

3.1.2 Elemental analysis by EDX

Table 5 shows the results of surface element composition analysis of the alloy plated film by EDX. In the case of Ni - Zn alloy plated film, it can be confirmed that the Zn content is sufficiently decreased after immersion in KOH. In addition, it can be confirmed that when Fe - Ni alloy plating was finished, it could be proved that the surfaced had been covered by Fe - Ni plating surface.

3.2 Electrolytic test

3.2.1 LSV and CV; effect of KOH immersion time

Results obtained LSV, CV and obtained specific parameters were shown in **Fig. 2a, 2b** and **Table 6**. In this experiment Ni-Zn alloy plated electrode was prepared under the conditions of **Table 2a**. From the results of LSV, it could be confirmed that the catalytic activity for HER of the Ni - Zn alloy plated electrode after KOH immersion for 2 h was superior to that after KOH immersion for 20 h. From the CV results, it could be confirmed that the electric double layer capacitance of Ni - Zn after KOH immersion time for 2 h was larger than that after KOH immersion for 20 h.

3.2.2 Results of LSV and CV; effect of plating time

Results obtained by LSV and CV were shown in **Fig. 3a, 3b** and **Table 7**. In this experiment Ni-Zn alloy plated electrode was prepared under the conditions of **Table 2b**, and the KOH immersion time was 2 h. Approximately 1 mg of electrodeposition occurred at a plating time of 1 min and it could be suggested that the two third of it was dissolved after immersion in KOH. From the results of LSV, it could be confirmed that the catalytic activity of Ni - Zn alloy plated electrode under plating time of 120 min was better at -1.5 V vs. SCE. In addition, it could be confirmed from the CV result that the electric double layer capacitance of Ni - Zn under plating time of 120 min was larger than others.

3.2.3 LSV and CV; effect of tandem finishing.

The results obtained by LSV and CV were shown in **Fig. 4a, 4b** and **Table 8**. Comparison was made using Ni - Zn, Ni - Zn / Fe - Ni, Ni and Fe - Ni alloy plated electrodes. In this experiment, Ni-Zn alloy plated electrode was prepared under the condition shown in **Table 2b** under the plating time of 120 min, followed by KOH immersion time for 2 h. From the results of LSV, it could be confirmed that

the catalytic activity for HER of the Ni - Zn, Ni - Zn / Fe - Ni alloy plated electrode were superior to others. From the results of CV, it could be confirmed that the Raney alloy plated electrodes had extra-large surface area. From this result, it could be suggested that the electrolytic performance could be significantly controlled by the surface area. In addition, it could be confirmed that Ni - Zn alloy plated electrode had superior catalytic activity for HER and larger surface area than Ni - Zn / Fe - Ni alloy plated electrode. The reason why the electrolytic performance of the Ni - Zn / Fe - Ni alloy plated electrode was inferior to that of Ni-Zn will be attributed to the filling of many cracks caused by KOH immersion by Fe - Ni alloy plating.

IV. CONCLUSION

For the purpose of improvement of the catalytic activity for HER of the plated electrode, a Raney nickel alloy plated electrode having a large specific surface area was served as the platform. In order to solve the problem of the brittleness of Raney nickel plated film, Fe - Ni alloy plating with superior catalytic activity than that of Ni was tried. The catalytic activity for hydrogen evolution reaction of Ni-Zn alloy plated electrode was superior after the KOH immersion time of 2 h. The catalytic activity for hydrogen evolution reaction of Ni-Zn alloy plated electrode was superior in the case of the plating time of 120 min plating, the weight of about 120 mg, and it was considered that the electrolysis performance was improved by prolonging the plating time. However, by Fe - Ni alloy plating on the Ni - Zn plated alloy after immersion to KOH, many cracks induced by KOH immersion had been filled, so the electrolysis performance deteriorated. In order to solve those problem, thin Fe-Ni alloy plating enabled conformal over coating on etched Ni-Zn will be a candidate for better electrode on Ni - Zn.

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Table 1. Bath composition and plating conditions for nickel-strike plating based on wood baths.

Bath Composition	
NiCl₂	1.010 mol/dm³
HCl	1.440 mol/dm³
Plating conditions	
Current density	100 mA/cm²
Plating period	2 min
Bath temperature	22 ~ 25 °C
Counter electrode	Ni plate

Table 2. Bath composition and plating conditions for Ni-Zn alloy plating.

(a) (b)

Bath composition	mol/dm³
NiSO₄ · 6H₂O	0.761
ZnSO₄ · 7H₂O	0.056
H₃BO₃	0.647
Plating conditions	
Current density	25 mA/cm²
Plating period	60 min
Bath temperature	22 ~ 25 °C
pH	1.60 *
Counter electrode	Pt mesh

* Adjusted by H₂SO₄ aq.

Bath composition	mol/dm³
NiSO₄ · 6H₂O	0.761
ZnSO₄ · 7H₂O	0.056
H₃BO₃	0.647
Plating conditions	
Current density	25 mA/cm²
Plating period	60, 90, 120 min
Bath temperature	22 ~ 25 °C
pH	1.93 *
Counter electrode	Pt mesh

* Adjusted by H₂SO₄ aq.

Table 3. Bath composition and plating condition of Fe-Ni alloy plating for the electrodeposition on Ni-Zn alloy plating.

Bath composition	mol/dm ³
FeSO ₄ · 7H ₂ O	0.050
NiSO ₄ · 6H ₂ O	0.099
H ₃ BO ₃	0.243
C ₆ H ₈ O ₆	0.026
Plating conditions	
Current density	25 mA/cm ²
Plating period	10 min
Bath temperature	40 °C
pH	3.11
Counter electrode	Ni plate

Table 4. Bath composition and plating conditions of Ni plating (a) and Fe - Ni alloy plating (b).

Bath composition	mol/dm ³
NiSO ₄ · 6H ₂ O	0.761
NiCl ₂ · 6H ₂ O	0.189
H ₃ BO ₃	0.566
Plating conditions	
Current density	20 mA/cm ²
Plating period	50 min
Bath temperature	60 °C
pH	3.00
Counter electrode	Ni plate

Bath composition	mol/dm ³
FeSO ₄ · 7H ₂ O	0.050
NiSO ₄ · 6H ₂ O	0.099
H ₃ BO ₃	0.243
C ₆ H ₈ O ₆	0.026
Plating conditions	
Current density	25 mA/cm ²
Plating period	20 min
Bath temperature	40 °C
pH	3.11
Counter electrode	Ni plate

Table 5. Composition of Ni-Zn, Ni-Zn (after immersion in KOH) and Ni-Zn/Fe-Ni alloy plated films analyzed by EDX (at %).

	Ni	Zn	Fe	O
Ni-Zn	18.7	81.3	—	0.0
Ni-Zn (after immersion in KOH)	48.1	34.8	—	17.1
Ni-Zn/Fe-Ni	37.6	2.4	45.4	14.6

Table 6. Result of electrolytic test difference in KOH immersion time (2 h, 20 h).

	Hydrogen overvoltage (mV)	Current density (mA cm ⁻²) -1.5 V vs. SCE	Electric double layer capacitance (mC cm ⁻²)
Ni-Zn (2 h)	132	-234	393.59
Ni-Zn (20 h)	109	-196	272.10

Table 7. Result of electrolytic test difference in plating time (60, 90, 120 min).

	Hydrogen overvoltage (mV)	Current density (mA cm ⁻²) -1.5 V vs. SCE	Electric double layer capacitance (mC cm ⁻²)	Plating weight / Weight after KOH immersion (mg)
Ni-Zn (120 min)	116	-247	788.23	117.7 / 41.2
Ni-Zn (90 min)	125	-208	651.89	91.3 / 32.7
Ni-Zn (60 min)	136	-188	514.51	62.1 / 22.6

Table 8. Result of electrolytic test.

	Hydrogen overvoltage (mV)	Current density (mA cm ⁻²) -1.5 V vs. SCE	Electric double layer capacitance (mC cm ⁻²)
Ni-Zn	132	-234	393.59
Ni-Zn/Fe-Ni	109	-196	272.10
Ni	240	-3	0.51
Fe-Ni	283	-27	2.60

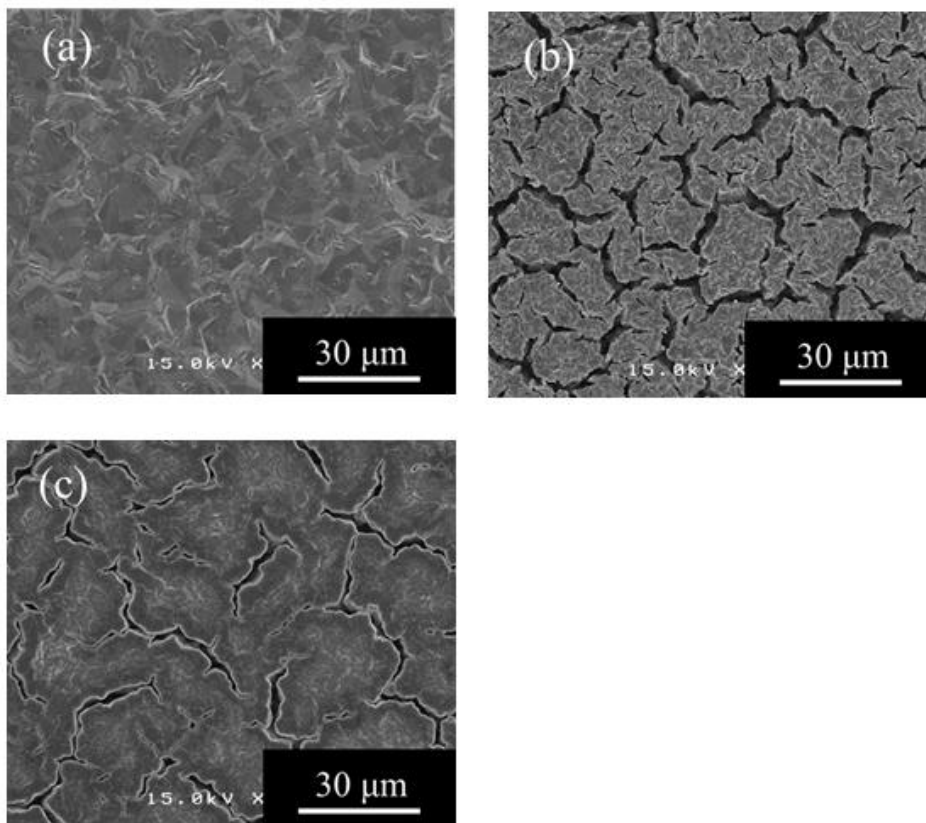


Fig. 1. SEM images of Ni-Zn (a), after immersion in KOH (b), Ni-Zn film on KOH treated Fe-Ni (c).

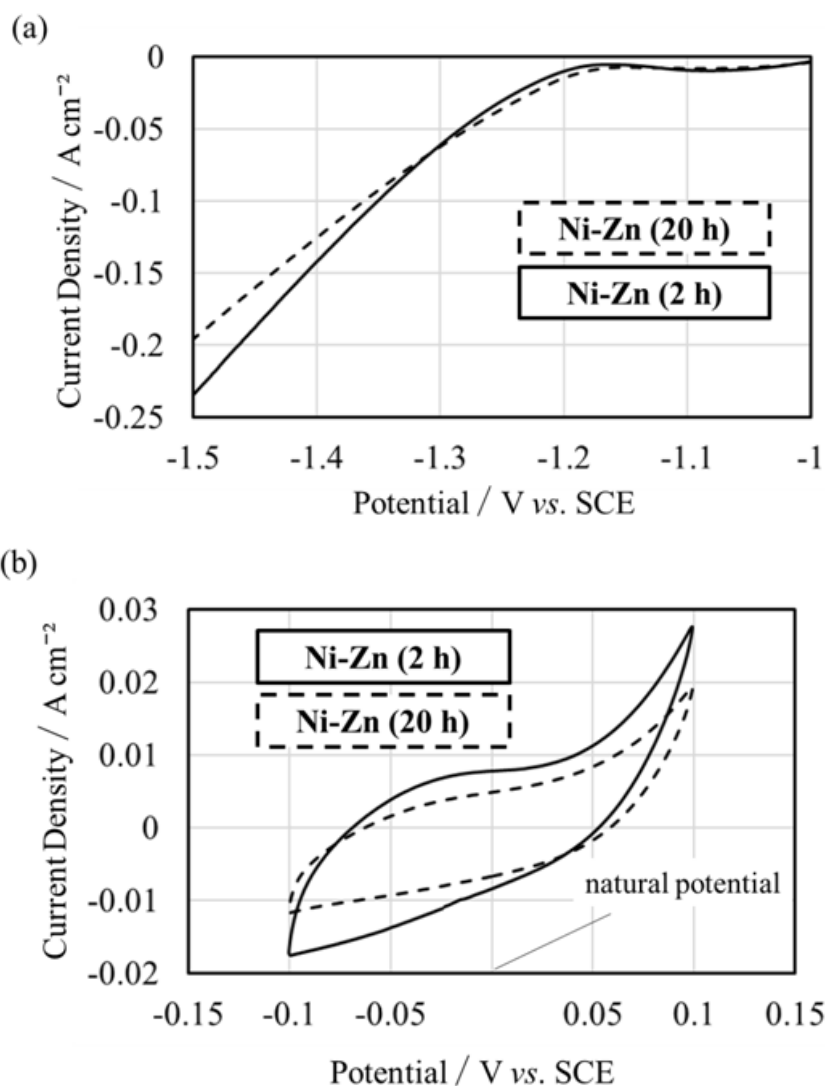
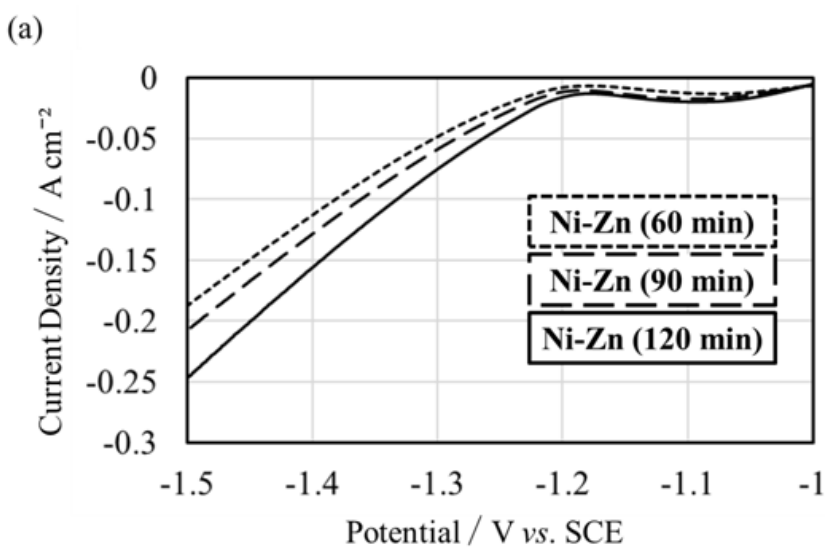


Fig. 2. Electrolytic test effect of KOH immersion time (2 h, 20 h). The current-potential curves (a). Cyclic voltammogram (b).



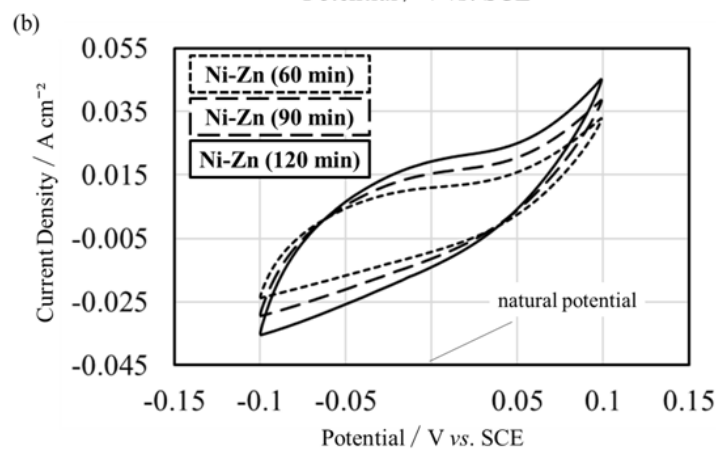


Fig. 3. Electrolytic test effect of plating time (60, 90, 120 min). The current–potential curves (a). Cyclic voltammogram (b).

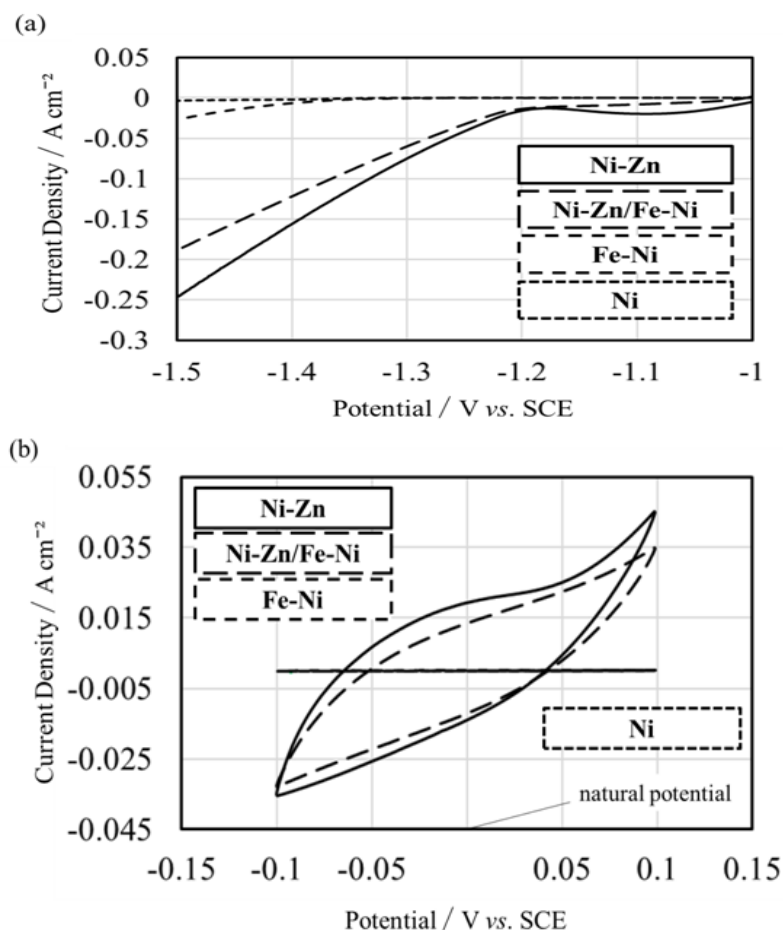


Fig. 4. Electrolytic test effect of tandem finishing. The current–potential curves (a). Cyclic voltammogram (b).

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