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Short communication

Relationship between apparent electrical-conductivity and preparation conditions for nickel foam

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1. Introduction

Nickel foam is a typical high-porosity metallic material, which is generally produced by electrodeposition [1–4]. This foam often has a porosity greater than 90% and can be used for battery electrode matrixes [1, 3, 4] and electrochemical process cathodes [2, 5–12]. For Cd–Ni and Ni–H batteries, it greatly increases the specific capacity and the specific energy for the electrode [13]. As an electrochemical process cathode, it increases the specific surface area and notably improves cell performance [11, 12].

The electrical resistance of the electrode matrix directly affects the availability of the active matter. Thus, nickel foam will affect the specific capacity, the specific energy and the working voltage of the whole battery [1]. During the electrochemical reaction it will affect the reaction rate [9, 10]. Based on the technology of electrodeposition, the influence of preparation conditions upon the electrical conductivity of the nickel foam was investigated. This work provides basic information for optimizing the technology and for improving the electrical performance of the products.

2. Experimental technique

The nickel foam was produced by electrodeposition, which includes cleaning the organic skeleton, making the skeleton conductive, electrodepositing nickel metal on the skeleton and then removing the skeleton with reductive sintering. A polyurethane sponge sheet about 2 mm thick was used as the organic skeleton, with a graphite-based conductive colloid coating, or chemically plating with nickel metal to make the skeleton conductive. The commonly produced conductive colloid consists of a graphite micropowder and an organic solvent, which can be diluted by aqueous ammonia. The composition of the chemical plating solution was $NiSO_4 \cdot 6\,H_2O$ (25 g dm^{-3}) + $Na_4P_2O_7 \cdot 10\,H_2O$ (50 g dm^{-3}) + $NaH_2PO_2 \cdot H_2O$ (25 g dm^{-3}) + H_2O, which is used at about 30 °C with pH 10 ~ 11. A common electroplating technique was used for electrodeposition, with an apparent current density of about 400 A m^{-2}. This value is one-tenth to one-hundredth that used for general plating. The specific composition of the applied plating solution was $NiSO_4 \cdot 6\,H_2O$ (200 g dm^{-3}) + NaCl (8 g dm^{-3}) + H_3BO_3 (30 g dm^{-3}) + Na_2SO_4 (60 g dm^{-3}) + $MgSO_4$ (50 g dm^{-3}) + H_2O, at about 25 °C with pH 5.0 ~ 5.5. The thickness of the Ni-plating layer was controlled by the electroplating time. The last step, the removal of the organic skeleton by sintering heat treatment, can be done in two ways. One technique was the two-step method of first burning the organic skeleton in air and then sintering in a reducing atmosphere (NH_3-decomposition atmosphere). The other was the one-step method of direct sintering in the reducing atmosphere, which resulted in pyrolysis of the organic skeleton. The specific technological conditions are listed in Table 1.

3. Experimental results

Nickel foams were obtained with thicknesses in the range 2–3 mm. The electrical conductivity was measured using a double circuit bridge at 20 °C. Four samples with the same porosity were measured at the same conditions, with the mean values given in Table 2.

The surface morphology and the internal structure of the wire body of the nickel foam were observed using SEM and OM, and their phase composition was analysed using XRD. Figure 1 shows their surface morphologies at the different stages of preparation, and Figures 2 and 3 show the cross sections for the two methods used to make the skeleton conductive.

The surface morphologies, the internal structures and the relative XRD analysis results all show that although product 2 was oxidized when burnt in air, its oxide scale was then fully reduced during sintering in the

Table 1. Techniques for producing nickel foams

Technique	Conductive treatment	Removing organic skeleton		Product
		At 600 °C in air	Reductive sintering	
1	Conductive colloid soaking	–	980 °C/40 min	1
2	Conductive colloid soaking	for 4 min	980 °C/40 min	2
3	Chemical plating	–	980 °C/40 min	3
4	Chemical plating	–	850 °C/40 min	4
5	Chemical plating	for 4 min	850 °C/40 min	5

NH_3-decomposition atmosphere. The resulting product has a perfect, compact crystal grain for the nickel layer and a good surface condition (Figure 1(a)), which are the same as the corresponding morphology (Figure 1(b)) for the nickel layer obtained from direct pyrolysis-sintering in the NH_3-decomposition atmosphere after electroplating. No graphite C used for the conductive treatment was found inside the Ni layer in techniques 1 and 2 (see Figure 2). Also, no indication of the Ni_3P phase was found precipitating in the Ni layer in techniques 3 and 4 (see Figure 3).

4. Discussion

4.1. *Comparison for different technologies*

The electrical conductivity is closely dependent on the porosity for porous metals. It is difficult to prepare products with the same porosity to compare the different technologies, because the porosity can only be controlled within some range during manufacturing. Since the porosity is very high, the electrical conductivity changes greatly with small change in porosity. Hence, when analysing the effects of the different production methods on the electrical conductivity of the nickel foam, the effect of porosity should be eliminated. Therefore, a parameter must be found which only reflects the effect of the preparation condition.

The electrical resistivity for high porosity materials can be predicted using [14]:

$$\rho = K[1 - 0.121(1-\theta)^{1/2}]\frac{3}{(1-\theta)}\rho_0 \tag{1}$$

which can be rewritten as

$$\lambda = k\frac{(1-\theta)}{3[1 - 0.121(1-\theta)^{1/2}]\rho_0} \tag{2}$$

Table 2. Results of tests and analysis

Technique	Product	Porosity/%	Conductivity /K S m^{-1}	*k* value	Mean *k*	Relative deviation*/%
1	1 [14]	88.60 ~ 98.84	51.1 ~ 628.6	0.893 ~ 1.198	1.05	8.6
		90.02	579.1	1.146		
		93.22	395.9	1.161		
		93.95	350.6	1.154		
2	2	94.67	292.4	1.095	1.15	2.2
		94.94	281.2	1.110		
		97.14	169.9	1.195		
		97.57	140.9	1.168		
3	3	97.95	51.9	0.512	0.51	
4	4	98.07	47.3	0.495	0.50	
5	5	97.82	59.0	0.546	0.55	

* Mean absolute value

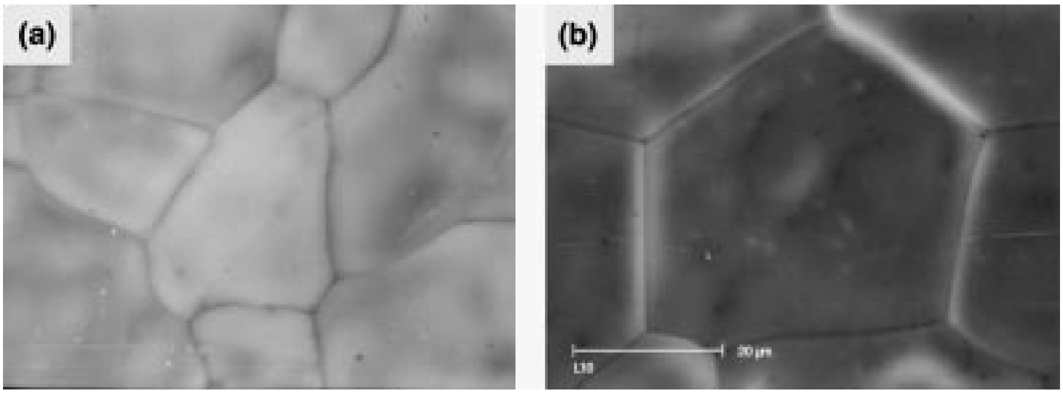

Fig. 1. Wire surface morphology of the nickel foam with thermal treatment by reductive sintering at 980 °C for 40 min after oxidation in air at 600 °C for 4 min (a) and by direct pyrolysis-sintering after electroplating (b).

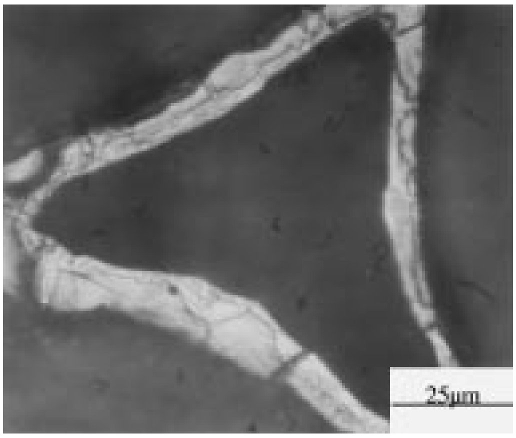

Fig. 2. Cross section of the Ni-wire of the nickel foam with the skeleton made conductive by coating with graphite-based conductive colloid.

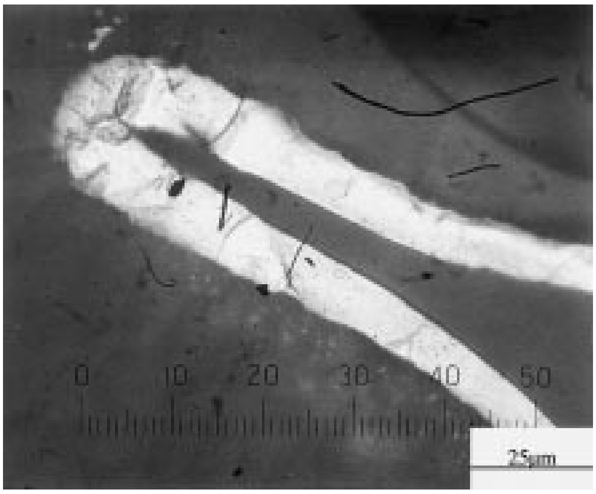

Fig. 3. Partial cross-section of the Ni-wire of the nickel foam with the skeleton made conductive by chemical plating with Ni.

where ρ and λ are the electrical resistivity and conductivity of the porous material, ρ_0 is the resistivity of the corresponding compact material, θ the total porosity of the porous metal, and both K and k are constants determined by the preparation technology and the material type. The values of K or k reflect the influence of the different conditions on the electrical resistivity or conductivity of the nickel foam. For products with the same porosity, larger values of k indicate higher electrical conductivities. Thus, the k value expresses the effect of the different manufacturing conditions on the electrical conductivity.

Using $\rho_0 = 68.44$ nΩ m [15] in Equation 2, the values of k corresponding to the data in Table 1 are listed in Table 2.

Table 2 shows that the values of k for techniques 3–5 are obviously smaller than those for techniques 1 and 2. Therefore, the electrical conductivity of the product made by chemically plating nickel on the skeleton was distinctly less than that of the product with the same porosity made by the conductive colloid.

4.2. *Technology analysis*

Alkaline plating solution with hypophosphorous salt as the reductive agent was used for the chemical plating of nickel [16]. The Ni–P alloy plating layer, about 3 μm thick, contained about 5% P [17]. If this Ni–P alloy layer is thermally treated, Ni_3P will precipitate within the Ni solid solution which will strengthen the layer [16, 18]. However, after more nickel was electroplated and after the reductive treatment for 40 min, the XRD showed only one phase of Ni solid solution, with no indications of Ni_3P by observing the cross-sectional microstructure of the nickel layer. The results infer that, since the P content in the entire nickel layer was very low and completely diffused throughout the entire Ni layer during the long heat treatment, a homogeneous Ni solid solution was formed. The relative size between two atomic radii of Ni and P would cause the replacement solid solution to form.

It should be pointed out that if the phase content in the layer is too small, XRD may not reveal the content, but the effects should be revealed in the large-time metallurgical structure. However, neither method showed that the Ni layer contained the Ni_3P phase.

The chemically plated nickel layer was a supersaturated crystalline solid–solution of the Ni–P alloy, which was then transformed into a homogeneous replacement solid solution during the sintering. Within the metal crystal, each Ni atom contributes two electrons as free electrons and presents a $+2$ valence, while each P atom would obtain three electrons and presents a -3 valence. Consequently, the Ni–P solid solution has a smaller free electron density than a simple Ni crystal, and its electrical conductivity decreases correspondingly. In addition, since the little P atoms replace some Ni atoms in the crystal lattice, some lattice distortion may take place. More importantly, some crystal lattice-point voids occur to maintain the electrical balance, which makes the conduction band of the crystal narrower and the electrical transfer of free electrons more difficult than in a simple Ni crystal.

Carbides cannot form between Ni and C and the solubility of C in Ni is very small. Therefore, when using the graphite-base conductive colloid for the conductive treatment, if the graphite layer was not removed, it remained on the internal surface of the electroplated Ni wire as a thin independent layer. Thus, the whole porous body could be regarded as a composite. This composite will have a smaller electrical conductivity than the foam body consisting of only Ni atoms with the same porosity, for graphite has a smaller electrical conductivity than nickel metal. However, the C layer was not found when using techniques 1 and 2 by either XRD or the cross-sectional metallographic observation (see Figure 2). This is possibly because C can react with H_2 to form gaseous hydrocarbons such as CH_4 and C_2H_6, which are then removed in the reducing atmosphere through NH_4-decomposition '$N_2 + 3H_2$'. When the organic skeleton is burnt in air, C also reacts with O_2

to form CO_2. If the conductive layer is very thin and the amount of graphite is very small, the gasification process completely removes the graphite from the porous body and leaves the foam body with only electroplated Ni.

The data in Table 2 show that the product formed by burning in air at 600 °C for 4 min before the reductive heat treatment seems to have a slightly larger k than that produced by direct reductive pyrolysis-sintering for 40 min. The larger k may occur because nonmetallic inclusions such as S within the electroplated Ni layer were eliminated by oxidation into the gaseous phase during burning in air. Therefore, the electrical conductivity of the porous material was slightly improved. Since the burning time in air was short and the sintering reductive time was long, both the surface and the crystal boundary of the metal crystal grain after oxidation were thoroughly treated reductively. Thus, cavity flaws were completely closed, and the crystal grain well grown, with the whole crystal structure well integrated. No oxides were found in the nickel foam from the air burning in the layer either by XRD, by cross-section metallurgical microstructure observation using OM or by surface observation using SEM. The wire surface condition was good (Figure 1(a)) and was the same as that for the products produced through direct pyrolysis-sintering in the reductive atmosphere after electroplating (Figure 1(b)).

Therefore, with the electrodeposition method for producing nickel foams, if the product is to have a relatively high electrical conductivity, the recommended optimal process is: use the graphite-base conductive colloid to make the skeleton conductive rather than chemically plating with Ni, then burn organic skeleton in air after electroplating and sinter the porous body in a reducing atmosphere.

5. Conclusions

(i) When nickel foam is produced using the electrodeposition process, burning the skeleton in air at 600 °C for 4 min before sintering in a NH_3 decomposition atmosphere at 980 °C for 40 min may slightly increase the electrical conductivity of the product. However, the increase may not be clear because of the measurement inaccuracies.

(ii) The result for technique 1 showed that reducing the sintering temperature from 980 to 850 °C while keeping the other conditions unchanged did not influence the electrical conductivity of the product.

(iii) During the conductive treatment, the graphite-base conductive colloid coating resulted in a much higher electrical conductivity than chemically plating with nickel.

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