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Effects of ultrasonics on the properties of continuous nickel foam

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Abstract

Environmental pollution and high cost are two typical problems when vacuum gas deposition or electroless nickel conductive technology is applied to the production of continuous nickel foam. To solve these problems, conductive colloid coating technology is usually used. But the continuous nickel foam obtained via this method has drawbacks, such as low tensile strength and elongation, high deposit thickness ratios (DTRs), inhomogeneous surface density distribution and inhomogeneous morphology. In this work, ultrasonic treatment was applied to certain production stages to investigate the effects on the properties of continuous nickel foam mentioned above. It was found through the comparison of the results obtained that using ultrasonic waves can significantly improve the structures and performances of continuous nickel foam.

1. Introduction

Continuous nickel foam is a material with high porosity (above 95%), high specific surface area and tensile strength, an aperture size of (200–600 μm) and uniform mass distribution. It can be easily filled with active materials. Compared with a sintered plate [1], a continuous nickel foam plate can be made with 50% less nickel and, when used in batteries, can increase battery capacity by 40%. Therefore, continuous nickel foam has become an ideal electrode material for high energy MH/Ni and Cd/Ni batteries [2–6].

To date, increasing attention has been focused on the production techniques for continuous nickel foam [7–19], most of which involve the conductive treatment of foams and electrodeposition. The widely known approaches for foam conductive treatment are electroless nickel plating, vacuum gas deposition and conductive graphite colloid coating. Electroless plating provides the most homogenous result. However, this method is complex and can pollute the environment. The vacuum gas deposition technique is costly. The conductive graphite colloid coating technique is an attractive alternative due to its simplicity, low cost and efficiency. However, the continuous nickel foam produced via this technique has low tensile strength, low elongation, high deposit thickness ratios (DTRs) and inhomogeneous surface density. Therefore, improving the uniformity of the structure [18] and the performance of nickel foam formed by using the conductive graphite-based colloid coating technique is a key goal. In this work, the ultrasonic treatment was used in the conductive graphite-based colloid coating stage and in the nickel electrodeposition stage. As a result, the performance and the structure of the continuous nickel foams were improved significantly without risk of environmental pollution.

2. Experimental

The main process for producing nickel foam via the electrodeposition technique includes foam conductive treatment, electrodeposition and heat treatment. The details of the procedures and the production conditions applied in this experiment are shown in Table 1.

The four kinds of techniques employed in this research are described in Table 2. The equipment, including an ultrasonic wave generator used to apply the conductive colloid coating and the nickel electrodeposition, is shown in Figure 1(a and b).

The polyurethane foam used was made by Inoac of Japan (MF-50LE, with a foam thickness of 1.7 mm). The conductive graphite colloid (TG-10) used was made by Tianrun company from Shenyang, China. A set of samples was prepared via four different techniques (see Table 2). The thickness of the nickel foam was 1.7 mm, and the surface density was (450 ± 30) g m^{-2}.

The tensile strength and the elongation were tested with an Instron-5569 electronic multi-functional material testing machine. The samples were 1.6-mm-thick strips with the dimension of 30 mm × 230 mm. At 25 °C, the initial clamped length of the sample strips

Table 1. The production procedures and conditions of the continuous nickel foams

Procedure	Solution composition and operation conditions
Conductive treatment	Graphite conductive colloid Ultrasonic waves, frequency = 28 kHz[a]
Nickel electrodeposition	$NiSO_4 \cdot 6H_2O$ 250–300 g l^{-1} $NiCL_2 \cdot 6H_2O$ 30–50 g l^{-1} H_3BO_3 30–50 g l^{-1} pH 3.5–4.5 T 45–55 °C Ultrasonic waves, frequency = 28 kHz[b]
Metallurgical heat treatment	
Pyrolysis	550–650 °C, 10–30 min in air
Reduction	900–950 °C, 20–30 min in ammonia decomposition gas

[a] Used only in techniques III and IV; [b] Used only in techniques II and IV.

was 100 mm, and they were subjected to an elongation speed of 20 mm min^{-1}.

The surface morphology and DTRs were observed and analyzed via an S-570 scanning electron microscope (SEM).

The conductive layer surface density distribution data of the nickel foams were measured by means of an analytical balance. Fifty samples (each 80 mm × 80 mm), were cut from each for each of the four kinds of continuous nickel foam and were weighed individually. The deviations of mean values from the standard value were calculated. The composition of the continuous nickel foam made via technique IV was analyzed with a TJA IRIS Advantage ICP Spectrometer.

The graphite matrix was first coated with conductive graphite colloid and then tested using a Model 273 potentiostat (EG & G Princeton Applied Research). The cathode polarization curves in the Watts nickel solution were recorded in order to investigate the deposition behavior of Ni^{2+} ions on the conductive graphite colloid.

3. Results of experiments

3.1. *Surface morphology of conductive foams*

The conductive treatment is one of the most important stages in the process of continuous nickel foam production. In this work, the ultrasonic treatment was introduced in the coating stage of conductive graphite colloid (techniques III and IV) to investigate the effects of ultrasonics on the uniformity of conductive foams obtained via the conductive treatments. Figure 2(d–f) shows the SEM photographs of the conductive foam modified by the ultrasonic treatment. The conductive foam produced without ultrasonic treatment (SEM pictures are shown in Figure 2(a–c)), had many sites filled with white clusters (indicated by arrow A in Figure 2(c)) where the conductivity was low or even zero. Compared with these conductive foams, those obtained by using the ultrasonic treatment had the much smaller round-shaped clusters as shown in Figure 2(f). Therefore, ultrasonic waves can improve the uniformity of conductive colloid coatings.

3.2. *Performance of continuous nickel foam*

In order to explore the optimal production technique for producing continuous nickel foam, various samples were prepared using the different electrodeposition techniques shown in Table 2, and their characteristics were measured.

3.2.1. *Tensile strength and elongation*

Table 3 shows the test results of tensile strength and elongation of the continuous nickel foams prepared via the four different techniques.

Table 2. Fours different techniques used in this work for producing the continuous nickel foams

Technique	Conductive treatment stage	Conductive layer surface density/g m^{-2}	Electrodeposition stage	Sample
I	Coating conductive colloid without ultrasonic treatment	5	Nickel electrodeposition without ultrasonic treatment	1
II	Coating conductive colloid without ultrasonic treatment	5	Nickel electrodeposition with ultrasonic treatment	2
III	Coating conductive colloid with ultrasonic treatment	5	Nickel electrodeposition without ultrasonic treatment	3
IV	Coating conductive colloid with ultrasonic treatment	5	Nickel electrodeposition with ultrasonic treatment	4

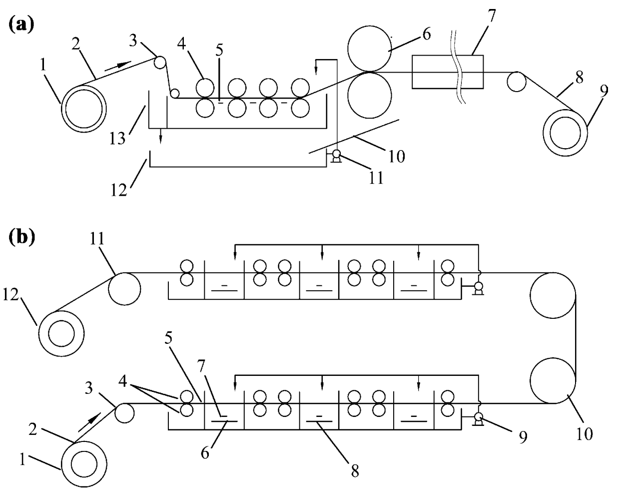

Fig. 1. (a) Equipment for the coating conductive graphite colloid on the continuous foam; 1 – Unreeling roller; 2 – foam; 3 – deflecting roller; 4 – colloid roller; 5 – ultrasonic wave generator; 6 – wipping roller; 7 – tunnel oven; 8 – conductive foam; 9 – wind up roller; 10 – baffle; 11 – pump; 12 – collide storage tank; 13 – collide coating tank; and (b) Equipment for the nickel electrodeposition on the continuous foam. 1 – Unreeling roller; 2 – conductive foam; 3 – deflecting roller; 4 – cathode conductive roller; 5 – small plating bath; 6 – anode; 7 – ultrasonic wave generator; 8 – big plating bath; 9 – pump; 10 – defleting roller; 11 – deflecting roller; 12 – wind up roller.

Figure 3 shows the stress–strain curves of the continuous nickel foams prepared via the conductive colloid technique without using the ultrasonic treatment (technique I) and prepared via the improved conductive colloid technique with ultrasonic treatment (technique IV).

From the results displayed in Table 3 and Figure 3, it can be seen that techniques II–IV (all of which include ultrasonic treatment) are more effective than technique I in improving the tensile strength and elongation of the nickel foam. The tensile strength and elongation of the continuous nickel foam were gradually enhanced from technique I through technique IV (i.e. technique IV produced the best results).

3.2.2. *DTR*

DTR is one of the important criteria in evaluating the quality of continuous nickel foam. In this work, pictures of the structure of the different continuous nickel foams samples were taken with a scanning electron microscope (see Figure 4), and the DTR data, as shown in Table 4, of the different samples was calculated. From the data in Table 4 it can be found that the DTRs of the continuous nickel foams were reduced by using ultrasonic treatment in the production process.

3.2.3. *Surface density*

In general, the surface density of continuous nickel foam will fluctuate because of the inhomogeneity of the continuous plastic foam structure and the electrodeposition process itself. This fluctuation will affect the filled quantity of electrode active materials and the ossification state of electrodes after pressurization, which results in the fluctuation of tensile strength, elongation, and flexibility as well as the electrode rupture resistance during the preparation of electrodes. The homogeneous surface density is a pre-requisite for improving the uniformity of batteries, and it determines the battery performance.

The surface density distribution data of the continuous nickel foam prepared via the four different techniques is also shown in Table 4. It can be seen that the surface density distribution of the foam produced via the different techniques, was improved measurably from sample 1 (produced with technique I) to sample 4 (produced with technique IV).

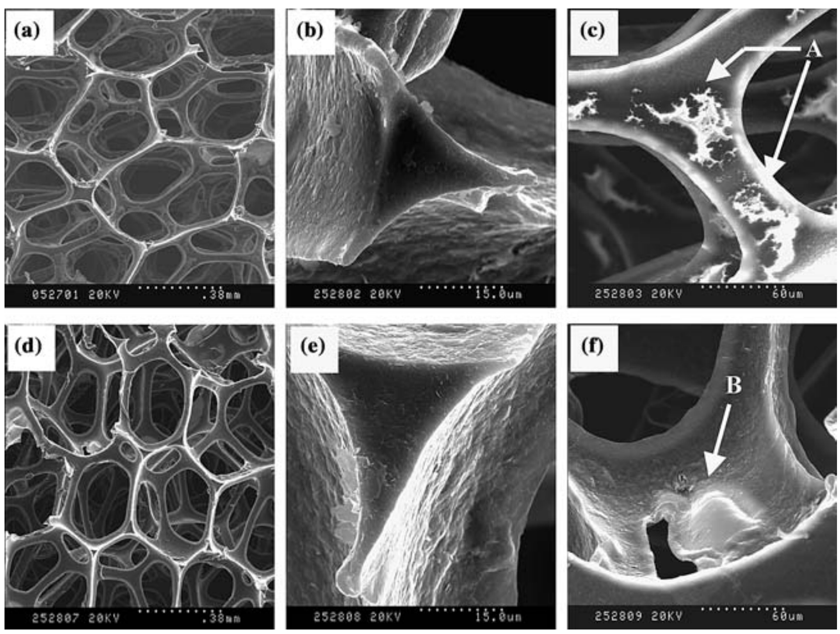

Fig. 2. SEM Photographs of the conductive foam treated with conductive colloid without ultrasonic treatment (a) integer; (b) rib head; (c) insulate section, and with ultrasonic treatment; (d) integer; (e) rib head; (f) insulate section.

Table 3. Test results of tensile strength and elongation of the continuous nickel foams produced by means of different techniques

Technique	Sample	Tensile strength/Mpa		Elongation/%	
		Longitudinal	Transverse	Longitudinal	Transverse
I	1	1.25	1.00	4.17	8.70
II	2	1.50	1.18	5.06	10.50
III	3	1.68	1.38	6.12	14.60
IV	4	1.81	1.56	8.90	15.05

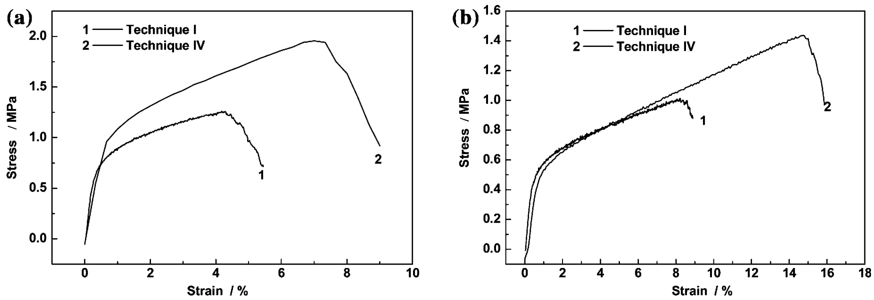

Fig. 3. Stress–strain curves of continuous nickel foams made via technique I and technique IV (a) longitudinal; (b) transverse.

3.3. *Surface morphology*

To investigate the effects of ultrasonic treatment on the surface morphologies and the structure of the continuous nickel foam, SEM was used to observe the integral and local morphologies of four types. From Figure 5, it can be seen that each of the four types has a three dimensional (3D) network. The 3D structure of the foam made via technique (Figure 5(a-1–a-3)) is non-homogeneous with many large rectangular holes in the ribs while the 3D network structure of the foam made by means of technique I through technique IV shows increasing uniformity, and a decreasing number of holes in the ribs. These holes become smaller, and the shape becomes round. The 3D network structure in sample 4 is the most homogeneous with the fewest number of holes in the ribs. Therefore, the 3D network structure can be improved by using ultrasonic treatment.

3.4. *Composition analysis*

The composition of the foam made via technique IV was analyzed by a TJA IRIS Advantage ICP spectrometer and is shown in Table 5. It was found that the composition of the foam could meet the requirement for battery production.

4. Analysis and discussion

4.1. *Technique of coating graphite conductive colloid*

The mechanism of ultrasonic-catalysis is not related to the direct interaction between ultrasonic waves and molecules, but is related to the acoustic cavitation process namely, the formation, the vibration, the growth and the collapse of cavities in liquid. When cavities collapse, the local temperature may be above 5000 K and the local pressure will be 5×10^7 Pa. Meanwhile, the rate change of the temperature is about 10^9 K s^{-1} and intense shock waves and jet currents at a speed of 400 km h^{-1} occur. Under such conditions, some chemical reactions occur that do not happen under normal

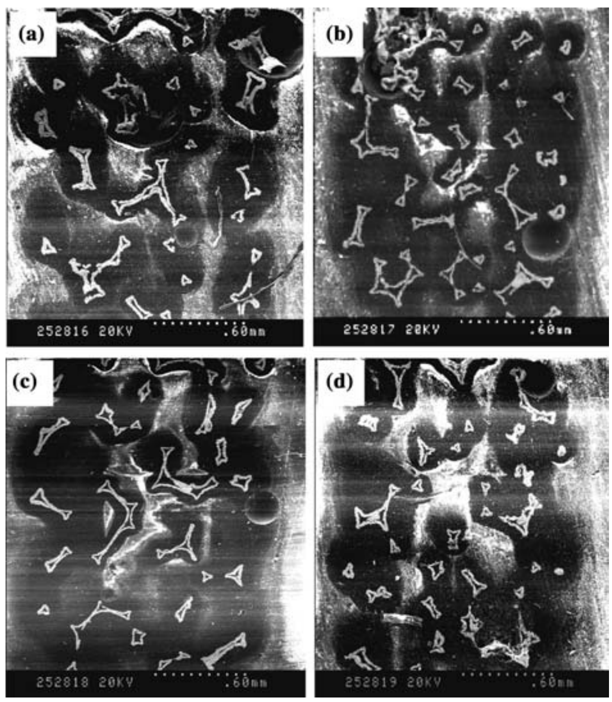

Fig. 4. Section microstructure of nickel foams made by means of different techniques. (a) prepared through technique I ; (b) prepared through technique II; (c) prepared through technique III ; (d) prepared through technique IV.

Table 4. DTR, surface density distribution of the continuous nickel foams made via different techniques

Technique	I	II	III	IV
DTR	1.50	1.50	1.39	1.36
Surface density of nickel foam/g m^{-2}	420 ± 38.0	420 ± 31.0	420 ± 29.0	420 ± 24.7

conditions. Based on the hot spot theory, when air bubbles collapse under a heat-insulated condition, the high temperature and pressure will activate the materials around the hotspot. During the preparation of the graphite conductive colloid coating process, ultrasonic waves can improve the activity of foam and graphite particles, and can also make conductive graphite colloids more uniform and more continuous. Therefore, if coated in such a conductive graphite colloid, a more uniform and more continuous nickel foam through electrodeposition can be obtained. This is supported by the results shown in Figures 2 and 3. By comparing the photographs in Figures 2 and 5, it can be found that the integral morphology of continuous nickel foam is

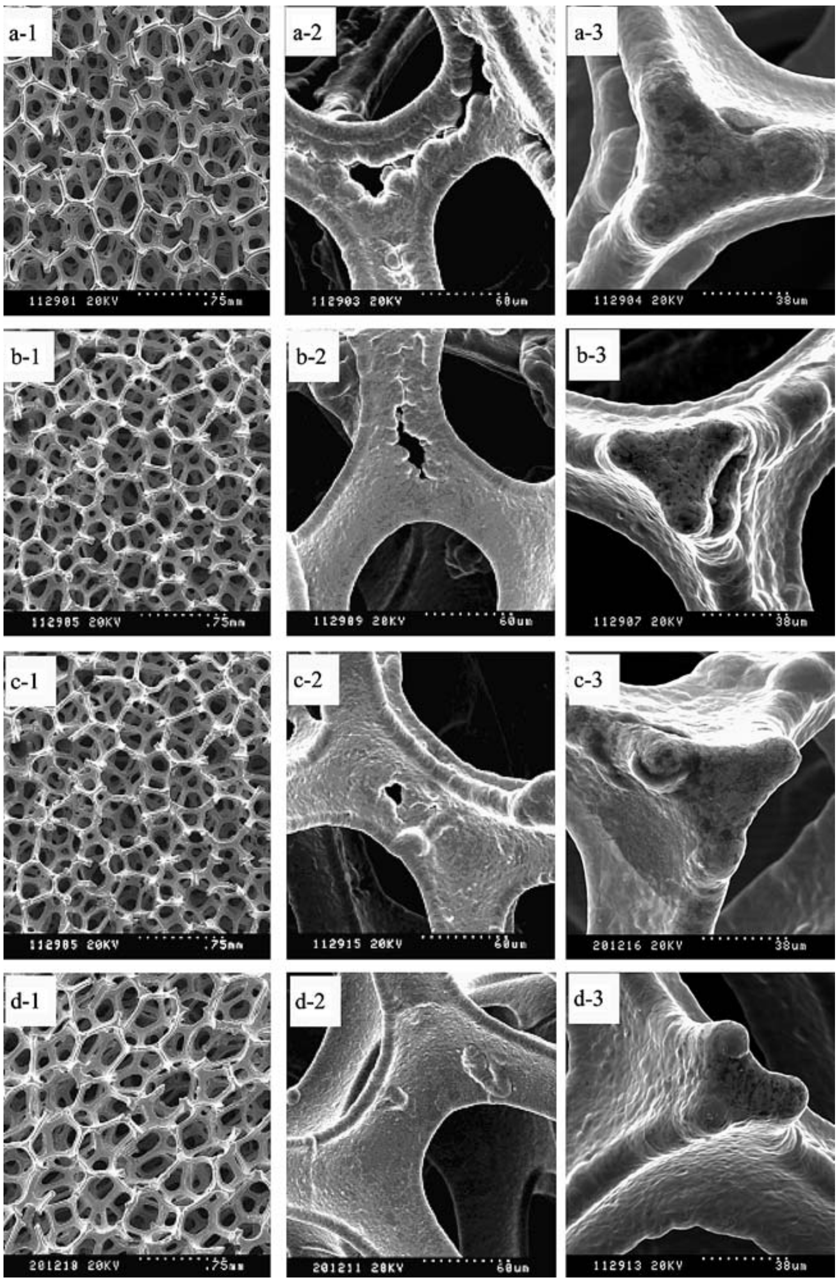

Fig. 5. SEM pictures of continuous nickel foams (sample 1) (a-1) integral; (a-2) rib; (a-3) rib head, (sample 2) (b-1) integral; (b-2) rib; (b-3) rib head, (sample 3) (c-1) integral; (b-2) rib; (c-3) rib head, (sample 4) (d-1) integral; (d-2) rib; (d-3) rib head.

Table 5. The composition of the continuous nickel foam made via technique IV

Element	C	Si	S	Fe	Cu	Co	Ni
Content/wt %	0.020	0.002	0.0012	0.013	0.002	0.017	Remainder

correlated with the number of the holes in the ribs as well as the uniformity of the conductive graphite colloid. Hence, compared with techniques I and III produces continuous nickel foam which is more uniform and more continuous, with better tensile strength, better elongation, a lower DTR and a higher surface uniformity. The same conclusion can be drawn from the results in Tables 3 and 4.

4.2. *Techniques of nickel electrodeposition*

The reduction process of Ni^{2+} ions (not including the mass transfer step) usually includes the following steps [20]: (1) rearrangement of the water molecule around Ni^{2+} ions in the surface liquid layer of an electrode, which results in the rising of the void valence electron energy level of Ni^{2+} ions to the Fermi energy level of the electrode; (2) electron transition between electrodes and Ni^{2+} ions to form partially-hydrated Ni adsorbed atoms; (3) loss of the rest of the hydration layer on Ni atoms to form Ni atoms in the metal crystal lattice.

The cathode polarization curves of the graphite matrix in the Watts nickel solution are shown in Figure 6 (cathode scanning was started from the open circuit potential). Even before the equilibrium potential $\varphi_e^{Ni^{2+}/Ni} = -0.2478$ V of nickel was reached, the cathode current could reach a value higher than zero, which showed that nickel has the characteristics of under-potential deposition. Using an ultrasonic-treatment technique, the characteristic of under-potential deposition of nickel on a graphite backing material is enhanced, an advantage in the initial deposition of nickel.

At the same time, using ultrasonic treatment makes more water molecules around the Ni^{2+} ions rearranged on an electrode surface, and causes the energy level of void valence electrons of Ni^{2+} ions to rise closer to the Fermi energy level of the electrode, which results in the formation of more adsorbed Ni atoms. Thus, the nickel uniformity during early deposition and later deposition on conductive foam will be enhanced. Meanwhile, the intense agitation caused by ultrasonic waves makes the diffusion and transmission of Ni^{2+} ions easier in a porous electrode, which helps to increase the uniformity of the foam along the thickness direction. The nickel foam prepared via this technique will be more continuous and more compact. Therefore, compared with that obtained via technique I , the foam made by means of techniques IV and II had high tensile strength and elongation. The fact that the properties of the continuous nickel foam produced via technique III were better than those of the nickel foam made by means of technique II proves that the uniformity and distribution of conductive particles on foam play an important role in the formation of uniform and continuous foam.

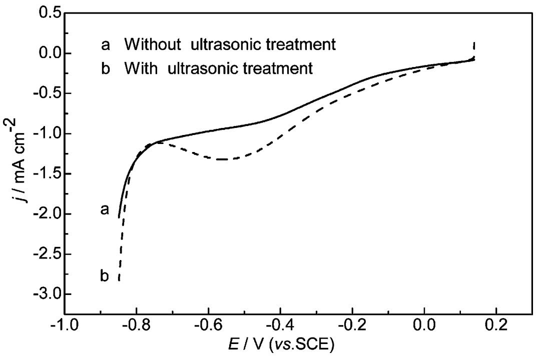

Fig. 6. Effects of ultrasonic waves on the cathode polarization curves of nickel.

5. Conclusions

1. The conductive graphite layer will be more uniform and more continuous when ultrasonic treatment is applied during the preparation of the conductive graphite-based colloid used in nickel foam production.
2. The ultrasonic treatment improves the uniformity of early deposition and later deposition of nickel on the conductive graphite layer.
3. Using ultrasonics can improve the tensile strength, and elongation, lower the DTRs and increase the surface density uniformity of continuous nickel foam.

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