NANOSTRUCTURED NI-Cu FOAM ELECTRODEPOSITED ON A COPPER SUBSTRATE APPLIED AS SUPERCAPACITOR ELECTRODE

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Abstract

The applicability of nickel-copper metallic foams as a current collector was investigated for supercapacitor. A comprehensive characterization of Ni-Cu based foam was studied and the analysis of their structural, chemical, and electrochemical properties was evaluated. Structural characteristics and electrochemical methods were used to examine the surface morphology, and surface-chemical composition of the materials. The foams deposited at the time deposition of 180s exhibited dual-porosities (macro and mesopores) with pores ranging from13 to 16 μ m and the branch size ranged from 25 to 50 nm. Ni-Cu foam electrodes are employed as current collector for supercapacitor. Their usefulness as current collector was evaluated by well-defined experimental conditions using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge and discharge (GCD) techniques. The outcome of these experiments demonstrated that the Ni-Cu foams which was synthesized at the time deposition of 180s had pseudocapacitive behavior. The best value for specific capacitance which was calculated from GCD was (536 F/g at 1 mA/cm²) for the Ni-Cu foams deposited at 2 A/cm² for 180 s. The Ni-Cu foam sustained a current density of 15 mA/cm² after 2000 cycles without significant loss of supercapacitor activity.

Keywords: Ni-Cu foam; Supercapacitor; Hydrogen bubble template

1 Introduction

Nano metallic foams (NMFs) with cellular and three dimension structures of interconnected pores with nanoramified walls are formed from metallic particles, filaments, or other morphologies which makes them attractive for applications such as catalysis, sensors, and electrodes for energy storage devices [1]. These materials usually demonstrate wide pore size distribution and porosities above 50 % due to its specific surface area. Metallic foams with highly porous nanostructured walls exhibit properties that are trait of metals, such as thermal conductivities, excellent ductility and malleability and good electrical behaviors that are trait of more advanced nanomaterials, like aerogels, which embrace a decreased density and an increased surface area, making NMFs as an uppermost choice for porous electrodes such as supercapacitor. Dealloying of metallic alloys and hard-template processes are of the most used methods for producing highly-porous networks. The former works are based on removing one of the metals, and the latter one performs by depositing a metal in the template vacancies followed by eliminating the template [1]. Electrodeposition is another procedure which is used for fabricating NMFs. In this method, hydrogen bubbling, arising from the metal deposition, results in the formation of a dynamic template. Therefore, it imparts appropriately-tailored structures to

self-supported nanoramified foams and, consequently, leads to an improved process for mass and charge transfer. Electrodeposition of NMFs on metallic substrates, which are highlyelectrically conductive can be used for making supercapacitor (SC) electrodes. During the electrodeposition from aqueous solutions and deposition of transition metals, the hydrogen gas releases, which is derived from extensively-negative potentials. The concurrence of hydrogen formation and electrodeposition may result in creating porous metallic foams [2]. Studies on copper and tin foams and NMFs show that the morphology of electrodeposited NMFs are significantly affected by the controlling parameters of deposition and electrolyte composition [3-5]. Hydrogen evolution is affected by different factors in copper foam production such as overpotential and H₂SO₄ and Cu (II) concentrations. Addition of additives to electrolyte for preventing the coalescence of hydrogen bubbles controls the size of porosities and it has catalytic effects on copper deposition. For example, adding chlorine ion-containing materials reduces the size of dendritic branches in foam walls [6]. As previously reported, most studies have been focused on the formation of copper foam [5]. In addition, the electrochemical deposition method and the hydrogen bubble templates for the formation of tin [2], silver [7], palladium [8] and gold [9] foams have also been used. In other words, few studies have been focused on the construction of metal foams containing transition metals. In many foam-related work, supercapacitor applications have not been applied and its electrochemical studies are limited. In current study, the effect of different deposition parameters on electrodeposited nanoporous Ni-Cu foams by hydrogen bubble template on copper substrates were investigated, and their performance as electrodes for SCs was evaluated.

2 Experimental procedures

2.1 Chemicals and synthesis of nickel-copper foam

High-purity copper (Alfa Aesar, 99.8%, $1 \times 1 \text{ cm}^2$) was abraded with grit SiC papers, cleaned with acetone and dilute hydrochloric acid, and used as a substrate (cathode) for copper deposition. A platinum electrode ($2 \times 2 \text{ cm}^2$) was used as a counter electrode (anode). The distance between anode and cathode was kept at 1.5 cm. For Ni-Cu deposition, a constant current (2 A/cm²) was applied to the cell using a Solartron 1278 potentiostat. Ni-Cu foams were electrodeposited from an electrolyte solution containing 0.5M NiSO₄.7H₂O, 1.5M H₂SO₄, 1M HCl and 0.01M CuSO₄.5H₂O. The deposition time was selected to be between 30 to 180 seconds for electrolyte.

2.2 Structural and morphological characterization & electrochemical measurements

The morphologies and chemical composition of the deposited films were analyzed using a scanning electron microscope (CamScan- MV2300) equipped with an energy-dispersive X-ray spectrometer (HORIBA 7593-H EMAX, Japan). The nitrogen adsorption–desorption technique (ASAP 2020 Physisorption Analyzer) was used to measure specific surface area (BET). The electrochemical performance of Ni-Cu foams were evaluated by CV and GCD using a 3-electrode cell configurations connected to a Solartron 1278 potentiostat. The metallic foam, a platinum plate, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. All the measurements were carried out in 6 M KOH electrolyte at room temperature. The EIS data were obtained at the open-circuit potential using a Solarton Potentiostat/Galvanostat over the frequency range of 10 mHz to 100 kHz using 5 mV amplitude of sinusoidal voltage.

3 Results and discussion

3.1 Morphology and structure of Ni-Cu foams

Fig. 1(a-e) showed the SEM images of Ni–Cu films grown by electrodeposition at a constant current density of 2A/cm² for 30-180 s. At a deposition time of 30 s (Fig. 1a), the film was porous but no interconnected pores were observed. However, in some locations, more developed dendrites were observed. The morphology was completely different from that of the foams deposited at the other times. As the deposition time increased (Figs. 1b, c) a three-dimensional foam consisted of numerous small dendritic walls was formed showing continuous pores ranging from 6 to 10 µm. The feature size for copper branches was from 350-500 nm (inset of Figs. 1b, 1c). In Figs. 1(d,e) foam frameworks with pores ranging from 13 to 16 µm and nanoramified walls were uniformly created. The branch sizes at the deposition times of 120 to 180 were from 50 to 300 nm and 25-200 nm respectively. However, the size of surface pore (Figs.1 (d,e)) was similar, but the sizes of branches and sub branches shown in Fig.1e was reduced, leading to high volumetric (mass of copper/superficial volume of the copper foam) and areal (mass of copper/superficial surface area of the substrate) densities. As a result, the optimal time deposition of copper-nickel foam was 180s. At deposition time more than 180 seconds, the thickness of the foam was increased and the adhesion was decreased. As a result, the deposition time of 180s was chosen as the optimum deposition time. Insets of Figs. 1(b-e) showed the isotherm curves matching to type IV, where hysteresis loops were detected in the range of 0.5 - 1.0 P/P_0 , indicating the foams had mesoporous structures. The highest surface area in the Ni-Cu foam found to be 39.26 m^2/g at the deposition time of 180 s. At a higher time, the active sites was reduced, and hence the surface area was decreased. Sectional images (Figs. 2a, 2d and 2g) showed that the wall thickness was made of numerous intertwined packed nanodendrites. The thickness of the Ni–Cu foam electrodeposited for 60 s (14.28µm, Fig. 2a) was the half of that for the time deposition of 120s (26.74 mm). An increase in the rate of foam thickness was reduced with the deposition time, as observed in the cases of 180s (34.28µm). As the foam thickness was increased, the nonuniformity of the foam (wall) structure became more remarkable due to an increase in bubble attack. The EDS spectrum and mapping of the Cu-Ni foams was shown in Figs. 2 (b, c, e, f, h and i).



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Fig. 1 SEM views of 3D Ni-Cu foams electrodeposited at 2A/cm² for the deposition times of (a) 30, (b) 60, (c) 90, (d) 120 and (e) 180s on copper substrate. Insets showed higher Magnifications. Insets also showed N₂ adsorption-desorption isotherms and specific surface area at different deposition times



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Fig. 2 SEM images (a) cross section (b) elemental distribution maps (c) EDS spectrum of Ni– Cu electrodeposited at 2 A/ cm² for 60s. (d) Cross section (e) elemental distribution maps (f) EDS spectrum of Ni–Cu electrodeposited at 2 A/ cm² for 120s. (g) cross section (h) elemental distribution maps (i) EDS spectrum of Ni–Cu electrodeposited at 2 A/cm² for 180s

This proved that phase separation was occurred during the electrodeposition. In other words, the amount of Ni and Cu in the dendrites changed in the direction away from the substrate. It resulted to a faster consumption of nickel ions than that of copper ions, due to the generation of a nickel rich phase around the substrate, and the displacement of nickel by copper in the electrolyte. The tendency towards phase separation was considered to be associated with the degree of mutual solubility of Ni and Cu elements. The miscibility gap in the composition range created a driving force for phase separation. Deposition of Cu-Ni and tendency towards phase separation was mostly proceeded according to the following reactions:

$$\mathbf{C}\mathbf{u}^{2+} + 2\mathbf{e}^{-} \to \mathbf{C}\mathbf{u} \tag{1.}$$

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{2.}$$

$$\mathrm{H}^{2} + \mathrm{e}^{-} \rightarrow \frac{1}{2} \mathrm{H}_{2} \tag{3.}$$

$$H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$$
(4.)

In accordance to the reactions (1) and (2), Ni and Cu discharges took place from Ni and Cu ions. At the same time, a large part of current was applied for the reduction of protons in solution (eq. 3) (together with water reduction (eq. 4)). Moreover, Ni²⁺ was reduced much slower than Cu²⁺, leading to the formation of low density large Cu islands during stages of reduction process. When the surface was reduced in Cu ions, Ni nucleation was promoted in the nearby areas of Cu islands [10, 11]. Another reason could be due to the fact that Ni atoms segregate to form Ni-rich magnetic clusters, compared to the Cu–Ni solid solution, the free energy of the nickel-copper foams becomes lower [12, 13].

3.2 X-ray diffraction studies (XRD) of Cu-Ni foams

The diffractogram patterns in 39 to 56° ranges were obtained for the Ni-Cu foams electrodeposited at $2A/cm^2$ and at the deposition times of 60, 90, 120 and 180 s as shown in Fig. 3. It was feasible to identify four peaks for Ni (111), Ni (200), Cu (200) and Cu (111) reflections

of fcc structure. The position of Ni (111) reflection was shifted toward lower angles with respect to the standard position. In addition, as the time of deposition was increased, the relative intensity for the reflections of Ni phase was decreased, which implied the presence of smaller volume segment of the Ni rich phase. The reason for not seeing the copper and copper oxide peaks in 180 s was that the depth of the X-ray diffraction was less than the thickness of the coating at 180 s. Therefore, these phases were not observed. The width of the XRD peaks was matched to the Ni phase which was larger for deposition time of 180s which resulted that the size of Ni crystallite was smaller. The lattice parameters for these foams were given in **Table 1**.



Fig. 3 XRD pattern of Ni–Cu foams deposited at 2 A/cm² for different deposition times

Table 1	XRD parameters for Ni-C	ı foams	deposited	at 2	A /cm ²	for	different	deposition	times
	calculated for major peaks								

Deposition time (s)	Lattice parameters (Ni) (A°)
60	3.520
90	3.519
120	3.518
180	3.514

3.3 Supercapacitor electrochemical characterization

To evaluate the electrochemical capacitances of the electrodes EIS measurements were performed. The Nyquist plots were obtained for various Ni-Cu foam electrodes fabricated at different electrodeposition time as depicted in **Fig. 4**. Each Nyquist diagram featured a straight line in the low-frequency region and a small arc in the high-frequency region. The power density of supercapacitors depends strongly on the equivalent series resistance (ESR), which was obtained from the X-intercept (real impedance part (Z')) of the Nyquist plot at the high-frequency range. A decisive factor in determining the rate of charging and discharging processes in a conventional supercapacitor application was the magnitude of the ESR value, which was obtained by fitting the impedance data. The ESR values were extracted from fitting EIS data (using Zsimp win software) for Ni-Cu foam electrodes which revealed that the electrodes fabricated at deposition time of 180s had the small ESR value (14.3 Ω).The diameter of arc in the high-frequency region was ascribed to be the double-layer capacitance (C_{dl}) in parallel with

the charge transfer resistance (R_{ct}) at the contact interface between electrode and electrolyte solution [14]. The radius of semicircle for Ni-Cu foam electrodes electrodeposited at 180s was smaller than that of Ni-Cu foam which was electrodeposited at other times. This suggested a lower charge transfer resistance for Ni-Cu foam due to the introduction of active sites. The line at lower frequency region was closely related to diffusion resistance of electrolyte into electrode pores and the proton diffusion in the host material, which was a good indication of capacitive nature for porous electrodes. The almost vertical shape of this straight line indicated the swift diffusion of ions from the bulk of the electrolyte and the adsorption onto the electrode surface. Moreover, the ascending trend of straight line slope by increasing time revealed a decrease in the Warburg resistance. Actually, the open space between ultrathin layers worked as a reservoir for ions and a pathway for penetration of electrolyte within the electrode. 3D Ni-Cu foam nanodendrites constructed 3D network which made the ions to have a full access to electrolyte, and thus optimizing electrochemical accessibility. Furthermore, Ni-Cu foam grown on copper substrate served as highly conductive pathways for fast electron transport [15].



Fig. 4 Nyquist plots for Ni-Cu foam composite under different times of electrodeposition

CV was used to evaluate the electrochemical properties of Ni-Cu foams in KOH electrolyte and to relate such acquired insight to their chemical composition and surface characteristics. CV profile for Ni-Cu foams in the potential range of 0 to 0.5 V showed the following anodic (5-7) and cathodic (8.) features:

$$Ni + 2OH^{-} \rightarrow \alpha - Ni(OH)_{2} + 2e^{-}$$
(5.)

$$\alpha - \text{Ni}(\text{OH})_2 \rightarrow \beta - \text{Ni}(\text{OH})_2 \tag{6.}$$

$$\beta - \text{Ni}(\text{OH})_2 + \text{OH}^- \rightarrow \text{Ni}(\text{OH} + \text{H}_2\text{O} + 2\text{e}^-$$
(7.)

$$NiOOH + H_2O + 2e^- \rightarrow \beta - Ni(OH)_2 + OH^-$$
(8.)

The appearance of redox peaks for CV curves reflecting fine reversibility of redox reaction and good power property (**Fig. 5a**). The oxidation process of NiOOH to Ni(OH)₂ caused the anodic peak (positive current density), and the reverse reduction process to lead to the cathodic peak (negative current density). As the scan rate was raised from 5 to 100 mV/s, both reduction and

oxidation peak currents were increased in the peak potentials without remarkable changes in the shape of the CV curves, disclosing the fast redox reactions for electrochemical energy storage system.

To calculate average specific capacitance from CV measurements equation (9) was used:

$$C = \int I dV / v m \Delta V$$

Where I depicted the voltammetric current, m the total mass of the solid electrode material, vpotential scan rate and V voltage in one sweep subdivision. Inset of Fig. 5b presented the variation of specific capacitance with scan rate which was obtained for Ni-Cu foam, indicating C_{sp} values decreased gradually with an increase in scan rate. The highest C_{sp} values obtained for Ni-Cu foam at scan rates of 5, 10, 25, 50 and 100 mV/s were 510, 436, 324, 245 and 183 F/g, respectively. The extracted peak current values from CV curves were plotted against the square root of scan rate (Fig. 5b) which revealed the linear variation of anodic and cathodic peaks versus $v^{1/2}$. This indicated that the electrochemical deposition process was controlled by diffusion. It was observed that the nickel-copper foam experienced a redox process with low current intensities in 6M KOH, which was closely related to the reversible reaction of Ni(OH)₂/NiOOH which took place on the Cu surface. Copper was experienced reactions of Cu^{2+}/Cu^{3+} , but its response was not seen in the CV curve. The reason for not observing copper peaks was the formation of a protective nickel hydroxide film that prevented copper oxidation reactions in nickel-copper foam [16]. To further evaluate the specific capacitance and comprehend the rate capability of Ni-Cu foam electrode, the GCD measurements were performed at various current densities. Inset of Fig. 6a showed the specific capacitance values obtained for Ni-Cu foam in potential range of 0-0.5 V (vs. SCE) at different current densities. The specific capacitance derived from GCD curves was also calculated by the following equation:

 $C = ldV/m\Delta V$

0.10

0.06 0.04

0.00

-0.04

-0.06

-0.08

0.0

0.1

0.2

0.3

(V/cm²) 0.02

0.08 (a)

in which *I* is the discharge current, Δt is the time for a complete discharge, m is the mass of the total solid electrode material, and ΔV represents the potential change after a complete discharge.

-0.02

-0.03

-0.04

-0.05

-0.06

-0.07

0

2

4

ipe(A/cm²)

0=5 mV/s 0=10 mV/s

0=25mV/

0=50 mV/s 0=100 mV/s

0.5

0.4

(b)



The specific capacitances of 536, 426, 301, 229 and 186 F/g were obtained for Ni-Cu foam at 1, 2,5,10 and 15 mA/cm². Notably, an increase in current density resulted in a gradual decrease in

10

12

(10.)

(9.)

discharge C_{sp} values, probably due to the resistance of Ni-Cu foam and the deficient redox reaction at a higher current density [17]. Cyclic stability evaluation of the deposited film was taken by GCD test at a constant current density of 15 mA/cm² for 2000 cycles (Fig. 6b). Furthermore, maintaining ~92.8 % of capacitance when the discharge rate was 15 mA/cm² demonstrated the excellent performance of the electrodes. In inset of Fig.6b, the columbic efficiency did not decrease after 2000 cycles, signifying that the charge-discharge procedures were highly reversible. Significant improvement in capacitance retention was obtained by its unique structure. Porous channels and regular dendritic networks formed on Ni-Cu foam created plenty of electroactive sites for redox reactions [18]. On the other hand, the porous structure films allowed easy access to the electrolyte, which shortened the ion transfer pathways, and thus enhanced the diffusion kinetics. Therefore, the special architecture of Ni-Cu foam facilitated its utilization in supercapacitors, especially at high rates. A high specific capacitance was obtained at a current density of 1 mA/cm², which was better than those of the electrodes made from Cu-Fe foams. CuO on copper foam and Cu-Ni foam reported in **Table 2** [16, 19, 20].



Fig. 6 GCD curves of Ni-Cu foams; (a) the effect of applied charge-discharge current; Inset: specific capacitance of the Ni-Cu foams as a function of current density (b) the cycling stability of copper foams deposited at 2 A/ cm² during 180 s; Inset: corresponding columbic efficiency of Ni-Cu foam during cycling test

Table 2 A compari	ison of specific cap	pacities between Ni	i-Cu foams develop	ped in this study and
literature d	lata			

Electrode material	Specific capacitance (F/g)	Reference
Ni-Cu Foam	105 at 1mA/cm ²	[16]
Cu-Fe Foam	297 at 1mA/cm ²	[19]
CuO on Copper Foam	212 at 0.41mA/mg	[20]
Ni-Cu Foam	536 F/g at 1 mA/cm ²	This work

4 Conclusions

In order to make nanostructured Ni-Cu foam, cathodic electrochemical method and dynamic template of hydrogen bubble combined together. The pore sizes and wall structures of electrodeposited Ni-Cu foam were successfully controlled by the deposition time to the deposition bath. This represents a novel way of creating porous foam structures with much finer microscopic features and larger surface areas, compared to other articles. The Ni-Cu foams presented a pseudocapacitive behavior, charge storage arising from reversible redox reactions of the Ni-Cu phase. A maximum specific capacitance value of 536 F/g at 1 mA/cm² was obtained

for the foams deposited at 2 A/cm² during 180 s. The cyclic stability of the resulting foam was appropriate, showing a capacitance retention of 92.8 % after 2000 cycling tests. Given the simple, low cost and environmentally-friendly fabrication process used in this article, the electrodes made from the Ni-Cu foam may become an ideal candidate for future use.

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