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Large-area metal foams with highly ordered sub-micrometer-scale pores for potential applications in energy areas

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ABSTRACT

Nanoporous metallic foams with an exceptionally high specific surface area can be a perfect solution for advanced energy applications. There have been an increasing number of recent efforts to achieve nanoporous metallic foams, but the latest research has paid much attention to the processing and characterization of noble nanoporous metallic foams (Pt and Au) through the conventional dealloying technique. This study proposes a new and innovative method of processing non-noble nanoporous (sub-micrometer-scale) metallic foams: a technique that combines the conventional electroless plating and three-dimensional proximity-field nanopatterning. Copper and nickel foams with sub-micrometer-scale pores are processed and characterized in this study.

1. Introduction

Thus far, the development of nanoporous structures with high specific surface area for use in energy or functional applications has been traditionally confined to nanoporous organic or inorganic materials. The fabrication of nanoporous metallic materials is considered difficult, probably because of the challenges associated with the fabrication of nanoporous metallic materials. Indeed, at the nanoscale they may suffer from poor stability, and poor oxidation and corrosion resistance. Despite these difficulties, sustained research efforts are being devoted to utilize the promising potentials of nanoporous metals in advanced functional applications, such as high-efficiency heat-exchanger substrates, catalysts, sensors, actuators, and microfluidic flow controllers [1–4]. More interestingly, nanoporous metallic electrodes can allow very efficient and rapid electrochemical reactions, owing to their high specific surface area and uniform distribution of pores [5]. For the same reason, they are also considered excellent substrate materials for catalysts [6]. Furthermore, nanoporous metallic structures are considered to exhibit better mechanical properties and long-term operational reliability than their polymer or ceramic counterparts. In particular, nanoporous metallic structures exhibit excellent specific strength and fracture toughness, high thermal and electrical conductivities, and relatively high melting temperature.

Herein, we propose a novel method for fabricating nanoporous Cu and Ni foams with precisely controlled pores by a modified electroless plating technique using a proximity-field nanopatterned (PnP) polymer template. Unlike the conventional dealloying methods, the technique proposed in this study enables highly ordered distribution of the submicron pores in both Ni and Cu foams. Furthermore, the PnP technique allows the fabrication of large-area nanoporous polymer template, which is beneficial for the industrial-scale production of submicron-scale Ni and Cu foams. In addition, the PnP technique facilitates the direct fabrication of nanoporous Ni and Cu foams of several tens of microns in thickness, without requiring any additional material machining or shaping process. This is especially important from practical perspective, as the metallic foams must be prepared in the form of a thin film of thickness from tens to hundreds of microns in order to be used as electrodes in energy areas such as batteries, die-sensitized solar cells, or fuel cells, as schematically illustrated in Fig. 1.

2. Material and methods

In the typical process, a photopolymer (SU-8, Microchem, Newton, MA) layer of 10 μm in thickness was spin-coated onto a glass substrate. The photopolymer-coated glass substrate was subsequently heated at a temperature of 60–90 °C, to evaporate

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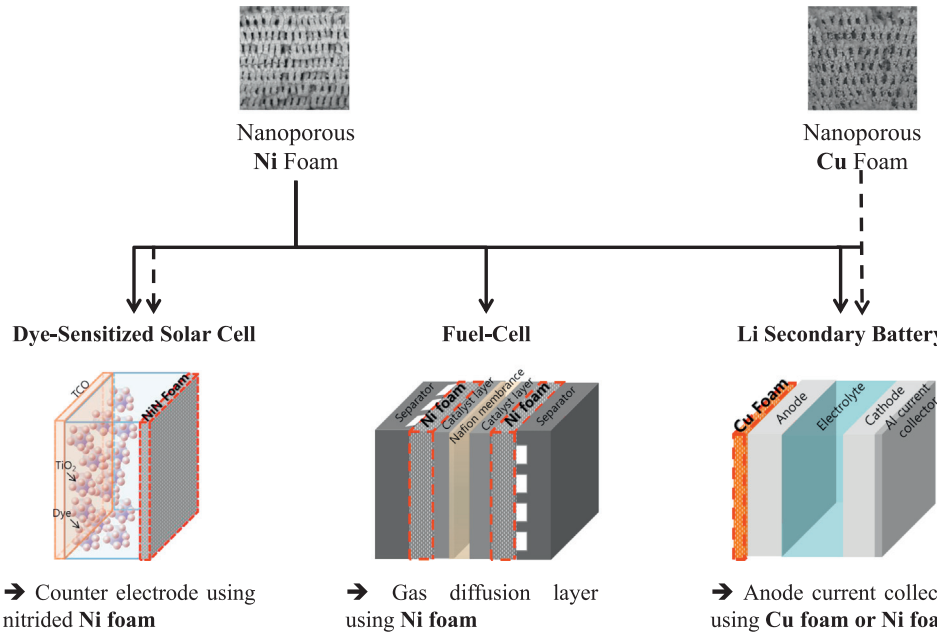

Fig. 1. Schematic illustration of potential applications in energy areas for Cu and Ni foams fabricated in this study.

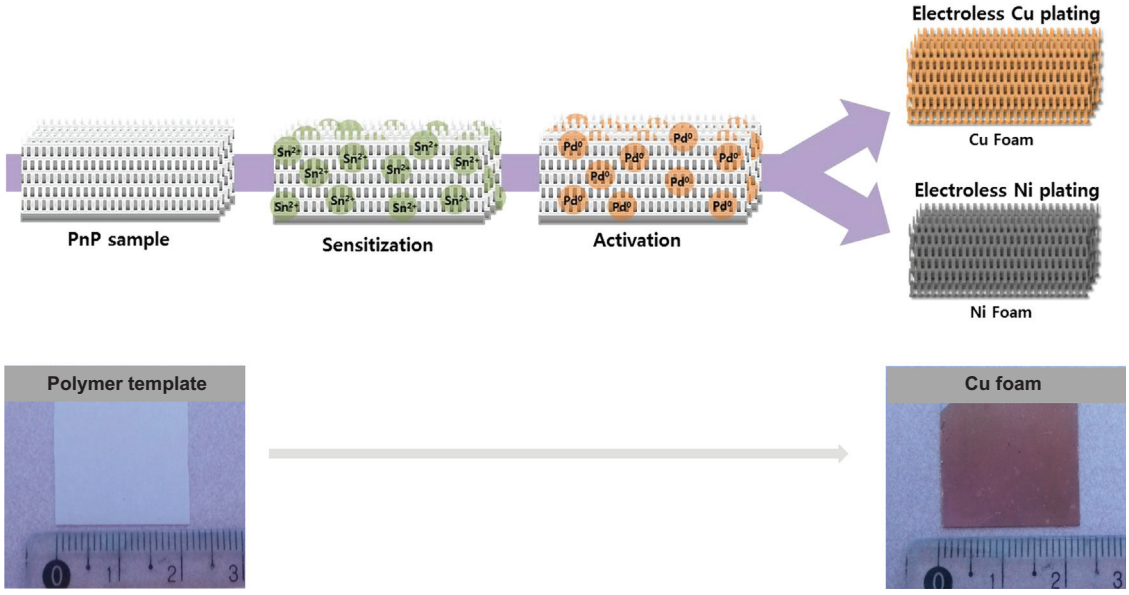

Fig. 2. Schematic illustration of the steps involved in the novel electroless plating method used for the fabrication of Cu and Ni foams with submicron pores. Shown in the micrographs are the pristine polymer template and the polymer template electroless-plated with Cu.

the solvent used in the process. Following that, a conformal transparent phase mask was placed on the polymer template and irradiated using an Nd:YAG microchip laser (wavelength: 355 nm, 500 mW) for selective exposure. A selective curing reaction of the polymer was carried out at a temperature of 50–60 °C. The polymer was then developed using a propylene glycol methyl ether acetate (PGMEA) solvent for 30 min. More details of this process are described elsewhere [6,7]. Prior to electroless plating of the metal, the non-conductive polymer template thus obtained needs to be 'activated' by an appropriate pre-treatment process (Fig. 2). The surface of the polymer template was made catalytically active to the metal by dipping the template in a pre-treatment solution composed of dilute tin chloride ($SnCl_2$) and palladium chloride ($PdCl_2$) solutions. In the pre-treatment process, the polymer template was dipped in 10.0 g/L of tin chloride ($SnCl_2 \cdot H_2O$) and 40.0 ml/L of hydrochloric acid (HCl, 35%) at 30 °C for 3 min. Following that, the polymer template was dipped in 2.0 g/L of palladium chloride ($PdCl_2$) and 16.3 ml/L of hydrochloric acid (HCl, 35%) at 40 °C for 5 min. The dipping of the polymer template in the pre-treatment solutions was carefully carried out under ultrasonic conditions. The electroless solution bath used for Cu plating was composed of 6.4 g/L of Cu sulfate ($CuSO_4 \cdot 5H_2O$), 70.0 g/L of ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$), 18.0 g/L of glyoxylic acid (CHOCOOH), and 0.5 g/L of polyethylene glycol. The pre-treated nanoporous polymer template was immersed in a Cu plating bath (pH ~12.5) at a temperature of 70 °C. Similarly, the electroless solution bath for Ni plating was composed of 21.3 g/L of Ni sulfate ($NiSO_4 \cdot 6H_2O$), 25.3 g/L of sodium hypophosphite monohydrate ($NaPO_2H_2$), 32.9 g/L of lactic acid ($C_3H_6O_3$), and 2.2 g/L of propionic acid

(C_2H_5COOH). The pre-treated nanoporous polymer template was immersed in the Ni plating bath (pH ~4.1) at a temperature of 80 °C. In particular, ultrasonic agitation was performed during both the pre-treatment and electroless plating, in order to ensure that the plating solution circulates rigorously and becomes sufficiently available inside the polymer template. Atomic force microscopy (AFM, XE-100, Park System Corp., Republic of Korea) was used in non-contact mode to examine the surface morphology of the plated Cu foam. The porosity was determined by analyzing the SEM images. The degree of continuity (C_S) of the nanoporous Cu foam strut structure was assessed metallographically using the continuity parameters N^{SS} and N^{SP}, which were determined using simple intercept measurements by drawing ten random lines of unit length on the SEM images.

3. Results and discussion

Among the various deposition methods proposed for the fabrication of metal films, we particularly used the electroless plating method to deposit Ni and Cu coatings from a solution of metallic salts and reducing agents, because the chemical and autocatalytic nature of the electroless plating process results in the deposition of thin uniform layers onto the substrates, irrespective of their shape [8].

Fig. 3 shows the scanning electron microscopic (SEM) images of the nanoporous polymer template, and the nanoporous Cu and Ni foams prepared by the novel multi-step electroless plating process. As can be seen from the SEM images shown in Fig. 3(a) and (d), the nanoporous polymer template is composed of 3D, orderly-spaced pores with the mean diameter of 424 ± 26. Similarly, the successful deposition of Cu (Fig. 3(b) and (e)) and Ni (Fig. 3(c) and (f)) onto the nanoporous polymer template could also be confirmed from the corresponding SEM images. The highly controlled pores have a uniform pore shape and size ranging from 321 to 330 nm in diameter, with a fairly thin and uniform plating thickness (45–51 nm, Table 1). Surface roughness is measured quantitatively by using AFM, and the corresponding AFM images for the Cu coating are shown in Fig. 4. The average surface roughness (R_a) of the Cu foam is 12.7 ± 7.8 nm, which is comparable to R_a value of ~15 nm reported previously [9]. The elemental analysis, as determined by using energy dispersive X-ray spectroscopy, is shown in Fig. 3. Major peaks of Cu and Ni are observed in Cu and Ni foams, respectively, with trace amounts of carbon and oxygen. The phosphorus (P) detected in the nanoporous Ni foam is attributed to the unavoidable presence of the reducer, $NaPO_2H_2$. These pore sizes on the order of a few hundreds of nanometers in the submicron Cu and Ni foams are likely to be quite reasonable for use in energy applications, e.g. a battery anode, because they can allow the foams to have a large specific surface area for the catalytic reaction application and still provide sufficient room for the successful subsequent deposition of an additional 'active' material.

For effective use as a thin-film electrode component, it is very necessary to maintain reliable mechanical integrity during long-term operation. From this standpoint, the uniquely aligned, ordered strut structure of the nanoporous Cu and Ni foams fabricated in this study is highly advantageous, as they provide exceptionally good strut continuity, compared to other types of nanoporous metallic foams fabricated by the conventional dealloying process [10]. In order to substantiate this further, we estimated the degree of

Table 1
Comparison of characteristics of PnP polymer template, and electroless-plated submicron Cu and Ni foams.

Material	Pore size (nm)	Plating thickness (nm)	Porosity (%)
Polymer template	424 ± 26	N.A.	57.5 ± 0.6
Electroless-plated Cu	321 ± 33	51 ± 8	35.8 ± 3.7
Electroless-plated Ni	330 ± 56	45 ± 17	46.5 ± 0.9

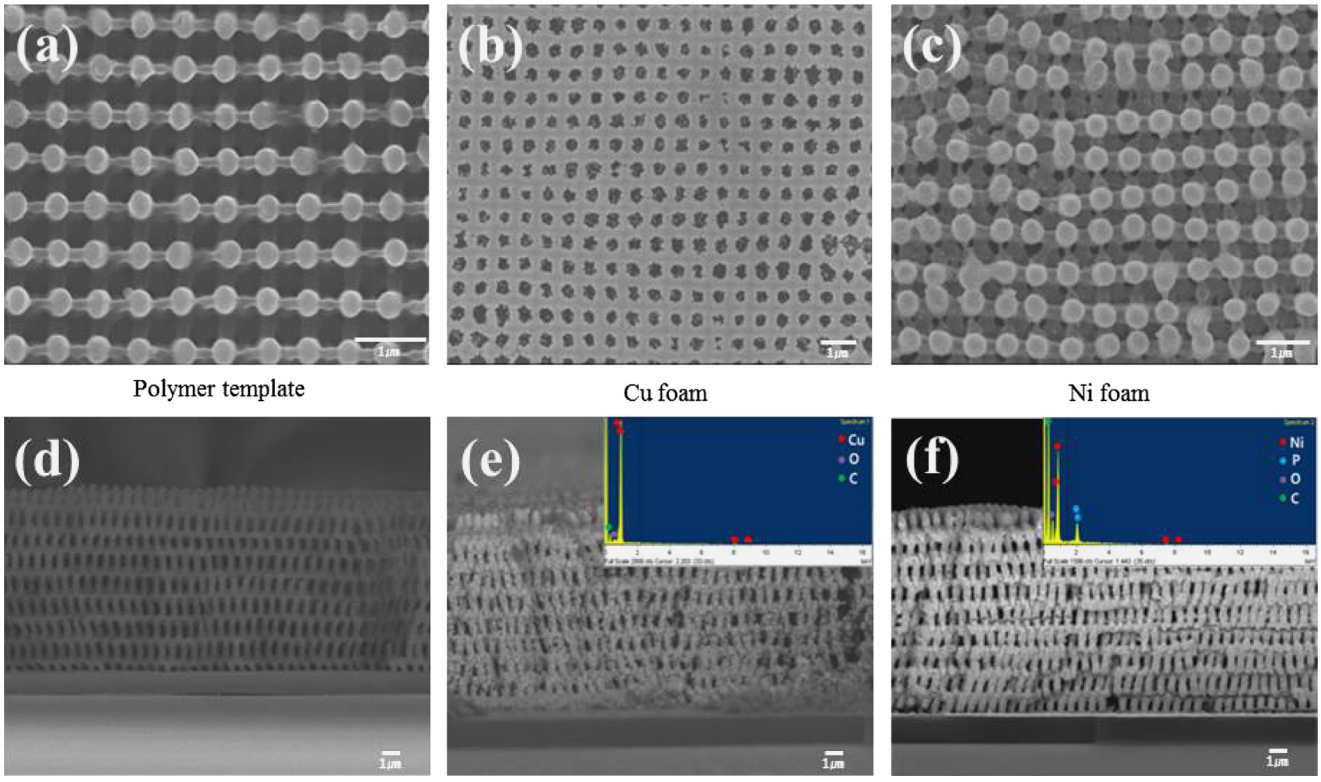

Fig. 3. Top and cross-sectional SEM images of electroless-plated Cu and Ni nanofoams: (a, d) PnP polymer template, (b, e) submicron Cu foams, and (c, f) submicron Ni foams.

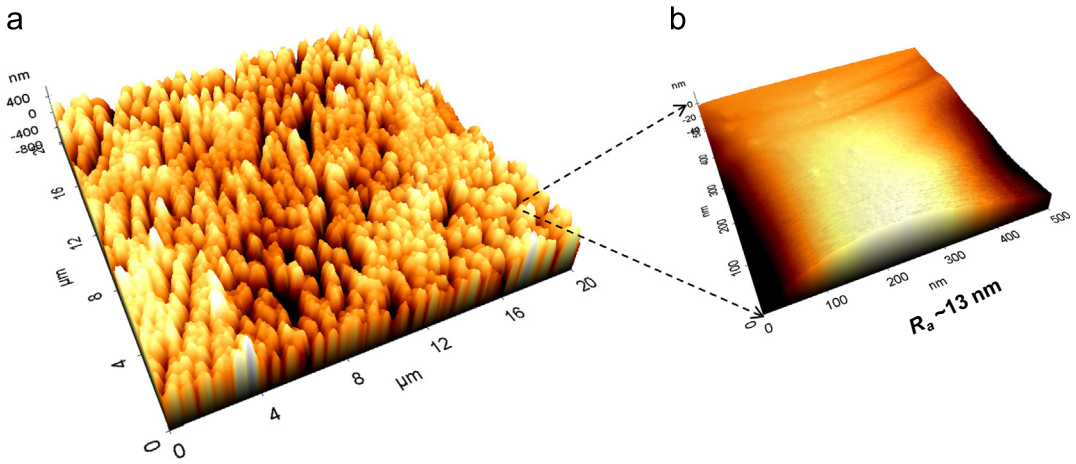

Fig. 4. AFM images of (a) the top morphology of the nanoporous Cu foam taken at a low magnification and (b) the smooth surface of a zoomed-in Cu strut with an average surface roughness (R_a) ~13 nm.

strut continuity of the nanoporous Cu foam specimen, by measuring the contiguity, C_S. According to Fan's approach [11,12]

$$C_S \approx \frac{2N^{SS}}{2N^{SS}+N^{SP}} \quad (1)$$

where N^{SS} and N^{SP} are the numbers of intercepts of the strut/strut and strut/pore interfaces, respectively, within a random line of unit length in the examined SEM images shown in Fig. 3. The strut contiguity of the nanoporous Cu foam is found to be highly continuous (C_S~0.8), as compared to those of the typical semi-continuous nanoporous Cu foams fabricated by the conventional dealloying process (C_S~0.3 to 0.4) [10]. This highly ordered and continuous strut structure can be beneficial in providing reliable mechanical integrity by improving the strength and ductility of the overall foam strut structure with the increased degree of strut connectivity.

4. Conclusions

In summary, a nanoporous template with highly ordered pore structure was fabricated on a photoresist SU-8 polymer by using a proximity-field nanopatterning technique. Subsequently, Cu and Ni foams with pore size on the order of a few hundred nanometers were successfully fabricated onto the nanoporous polymer template through a novel electroless plating process. SEM observation clearly confirms that the Cu and Ni coatings were uniformly deposited throughout the polymer template, with a consistent thickness of ~50 nm. It is expected that the submicron Cu and Ni foams fabricated in this study may be used as promising electrode materials, owing to their highly ordered pores and large surface area.

Acknowledgments

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