

Copper Foam Structures with Highly Porous Nanostructured Walls

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A variety of copper foams with highly open porous walls have been successfully sculptured using the gas evolved in an electrochemical deposition process. The pore sizes and wall structures of the foams are tunable by adjusting the deposition conditions. In particular, the reduction in pore size is a result of lowering hydrophobic force of the generated hydrogen gas by adding bubble stabilizer (e.g., acetic acid) that suppresses the coalescence of bubbles, while the decrease in branch size in the foam wall is a consequence of the catalytic effect of chloride ions (added to the deposition bath) on the copper deposition reaction. For example, the size of the surface pore of a 100- μm -thick foam was reduced from 50 to about 25 μm by adding 0.1 M acetic acid to the deposition bath. With the addition of 1–50 mM HCl, the size of the copper branches was dramatically reduced; in particular, the average size of the elementary branches in the foam wall was reduced from 300 to 50 nm, forming nanostructured porous electrodes ideally suited for electrochemical and catalytic applications.

Introduction

Three-dimensional (3-D) nano-structured architectures have been explored for a new generation of advanced devices such as sensors,^{1,2} supercapacitors,³ batteries,⁴ and fuel cells⁵ because of their great potential for rapid electrochemical reactions arising from the extremely large specific surface areas for charge and mass (gas) transport. To date, various concepts have been explored to construct 3-D structures, including a sol–gel-derived 3-D network of nanoscale particles (aerogel/ambigel),⁶ a 3-D (hierarchically-) ordered macroporous (3DOM) solid with an inverted opal structure created by a combination of sol–gel chemistry and templating,^{7,8} and on-chip 3-D arrays based on microelectronics and microelectromechanical systems (MEMS) technology.^{9,10} However, fabrication of materials with specific functionalities in an efficient 3-D architecture is still a great challenge.

Recently, we have reported a new way of producing unique self-supported 3-D foams of metals (such as copper and tin) with highly porous ramified (dendritic) walls.¹¹ This simple but very effective technique involves electrochemical deposition accompanying hydrogen evolution, which has been deliberately suppressed in typical electro-deposition processes to produce dense metallic components. In this process, hydrogen bubbles function as a dynamic template for metal deposition, resulting in 3-D foams having very unique pore size distribution. In fact, the conventional 3-D nano-structured materials with uniform pore size is not ideally suited for fast electrochemical reactions because the small pores near the top surface may restrict the transport of electroactive species (gas/ion) to the inner space of the structure, leading to low utilization of the whole surface area due to mass transfer limitations. In contrast, the pore size of our foam structures increases with the distance away from the substrate to facilitate fast transport of electroactive gas (or ion) through the porous electrodes. This graded structure is ideally suited for electrodes in fuel cells, batteries, and sensors where fast transport of electroactive species is essential to sustained operation.

While the potential of 3-D foam structures is very attractive, the key issues for practical applications of these structures still remain, including the control of the microstructure (such as pore size and wall density) of foam structures for better utilization of the internal surfaces as well as fabrication of new materials with similar structures for a specific functional device. In this article, we report our recent results on the structurally modified 3-D foam structures of copper in an effort to tailor the size of the large pores in the foam as well as the size of the branches in the foam wall, which is

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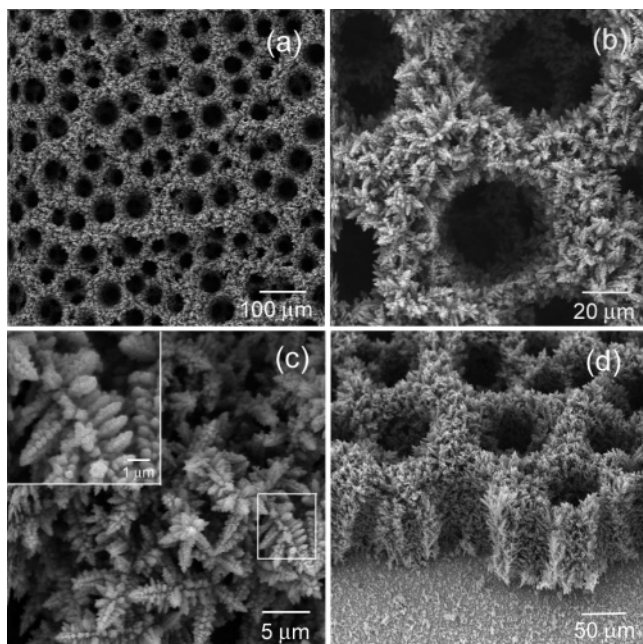


Figure 1. (a–c) Top and (d) cross-sectional views of 3-D foam structures of copper, electrodeposited for 20 s in the electrolyte of 0.4 M CuSO_4 + 1.5 M H_2SO_4 at an applied cell current density of 3 A/cm^2 .

critical to achieving optimal packing density and specific surface area for a particular application.

Experimental Section

High-purity copper (Alfa Aesar, 99.8%), cleaned with acetone and dilute hydrochloric acid, was used as the substrate (cathode) for copper deposition. A platinum electrode was used as the counter electrode (anode). The distance between anode and cathode was kept at 2 cm. For copper deposition, a constant current (as high as 3 A/cm^2) was applied to the cell using a Solartron 1285 potentiostat. To investigate the effect of the electrolyte on the morphology and microstructures of the deposits, various combinations of CuSO_4 (0.2–0.8 M), H_2SO_4 (0.1–1.5 M), CH_3COOH (0.03–0.5 M), and HCl (1–50 mM) were employed. First, the electrolytes containing only the essential salts for copper foam formation, i.e., CuSO_4 and H_2SO_4 , were tested in different concentrations and deposition times. Next, different concentrations of CH_3COOH were added to 0.4 M CuSO_4 and 1.5 M H_2SO_4 to stabilize the evolved hydrogen bubbles. Finally, various concentrations of HCl were added to 0.4 M CuSO_4 and 1.5 M H_2SO_4 as a catalyst of the copper deposition process. Deposition was performed in a stationary electrolyte solution (without stirring or N_2 bubbling) at room temperature.

Results and Discussion

Figure 1 depicts some typical 3-D foam structures of copper created by electrodeposition for 20 s in an electrolyte of 0.4 M CuSO_4 and 1.5 M H_2SO_4 . Hereafter, we call the electrolyte of this composition “baseline deposition bath”. It can be seen that the foam walls are composed of numerous small-ramified deposits, similar to those reported in a recent communication.¹¹ Nevertheless, the size of the surface pore ($\sim 50 \mu\text{m}$), as seen in Figure 1a, is too large, leading to low volumetric (mass of copper/superficial volume of the copper foam) and areal (mass of copper/superficial surface area of the substrate) densities. Moreover, the sizes of the branches and sub-branches are relatively large (0.3–1 μm),

resulting in relatively low specific surface area of copper deposits. To increase the specific surface area, and hence enhance the effectiveness/activity of the porous electrodes, it is necessary to reduce the sizes of the pores in the foam and the branches in the foam wall.

Reducing Pore Size of the Foam. To reduce the feature size of the pore, two approaches have been adopted. First, it is proven that the creation of the foam structure is caused by the competitive reaction of copper deposition and hydrogen evolution.¹¹ This implies that either reducing H_2 evolution rate (by reducing the concentration of the sulfuric acid) or increasing copper deposition rate (by increasing the concentration of the copper salts) might be an effective way to reduce the pore size of the foam.

Shown in Figure 2a and b is the dependence of the surface pore size and thickness, respectively, on the concentrations of copper salt. It is noted that both the surface pore size and the thickness of the deposits increased with the concentration of copper salt. To examine whether there is any morphological change, let us take a closer look at two different deposits, sample A (20-s deposition in 0.8 M CuSO_4) and sample B (40-s deposition in 0.4 M CuSO_4). Interestingly, samples A and B, which have the same thickness (Figure 2b), have the same surface pore size (Figure 2a). This is consistently observed in other samples (e.g., samples a, b, and c in Figure 2). Moreover, it was found that the change in wall structure, i.e., morphology of the branches, with copper salt content was quite trivial. These results suggest that the increase in copper salt simply increases the copper deposition rate, with very little effect on the pore size and wall structure of the foam.

On the other hand, the surface pore size and foam thickness were unchanged when the concentration of sulfuric acid was changed from 0.5 to 1.5 M (data are not presented here). This implies that only part of the evolved H_2 (from the substrate) actually participates in the foam formation process, and the decrease in the amount of evolved H_2 does not influence the overall foam structure (i.e., the surface pore size and thickness).

Nevertheless, the over-growth (nonuniformity) of the foam wall was sporadically observed throughout the foam surface at relatively low acidity. The nonuniformity of the foam wall is most likely due to the reduced amount of H_2 bubbles (from the freshly formed Cu deposits), which play a critical role in uniform growth of the branches in the foam wall. When the concentration of sulfuric acid is sufficiently low ($< 0.1 \text{ M}$), a well-defined 3-D foam structure was no longer created as a result of insufficient amount of H_2 bubbles. The above results imply that the decrease in acidity has no desirable effect on the pore structure of the foam.

The other approach to achieving reduced pore size of the foam is to decrease the size of the template, i.e., the evolved H_2 bubbles. As a matter of fact, the large surface pore of the foam is caused by the coalescence of the evolved H_2 bubbles during the copper deposition process. While the differences in bubbling behavior between some specific solution systems have been frequently reported,^{12–14} the effects of various factors on bubble

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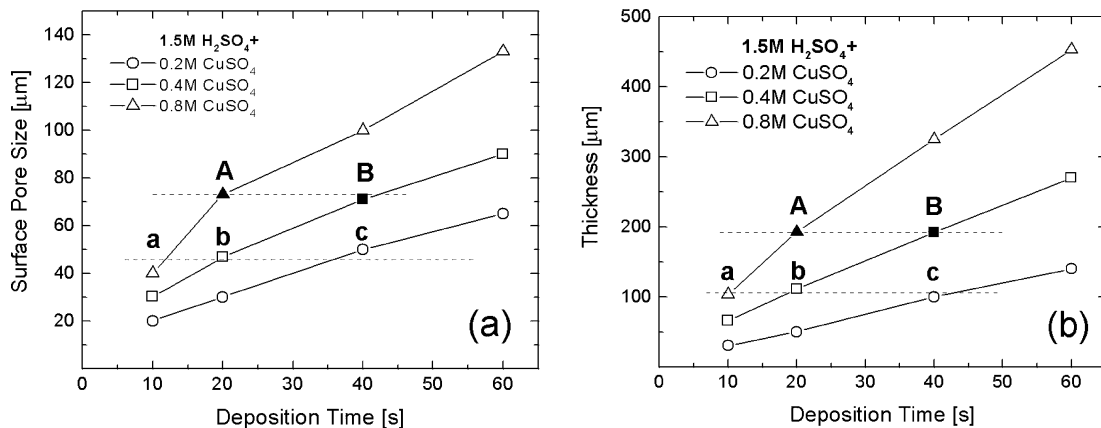


Figure 2. Variation of (a) surface pore size and (b) thickness of the copper electrodeposits with deposition time at different concentrations of CuSO₄.

coalescence are yet to be clarified. Among the possible explanations of bubble stabilization effect, the concept of hydrophobic force appears to be most reasonable because the bubble coalescence is typically a long-range ordering process.¹² It is believed that the bubble coalescence is driven by the long-range hydrophobic force of bubbles sufficient to overcome the hydrodynamic repulsive force due to the need to expel water molecules from the film between the bubbles.¹² Thus, how to decrease the hydrophobic force of bubbles is a key issue to suppress bubble coalescence and thus to make smaller H₂ bubbles (template) for the foam formation. In recent publications on the inhibition of bubble coalescence in aqueous solutions,^{12,13} it has been suggested that the rate of bubble coalescence is closely related to the effect of electrolytes on hydrophobicity of bubbles (or the gas within them). Although there is little widespread consensus on the details of the hydrophobic force and interactions, a variety of additives have been empirically suggested to suppress the bubble coalescence or to stabilize the bubble.^{12–14} Among them, we selected acetic acid (CH₃COOH) as the bubble stabilizer because it involves no metallic ions which might be co-deposited¹⁵ and then contaminate the copper deposits. More importantly, acetic acid is known to have a strong bubble-stabilizing effect even in a very small amount,¹² enabling us to minimize the possible detrimental effect of the bubble stabilizer on the ramification process.

Shown in Figure 3 are the 3-D foam structures of copper electrodeposited for 20 s in the baseline deposition bath with the addition of 0.1 M CH₃COOH. Clearly, the surface pore size and foam wall width were decreased by about 50% (Figure 3a and b) whereas the thickness of the deposit layer was decreased by only about 20% (Figure 3c), as compared to that without acetic acid (Figure 1a, b, and d). It is also noted that the essential features of the porous structure remain the same (Figure 3d) although the feature size of the surface pore is reduced. The areal surface pore densities (number of the surface pores per cm²) of the samples created without (Figure 1a) and with acetic acid (Figure

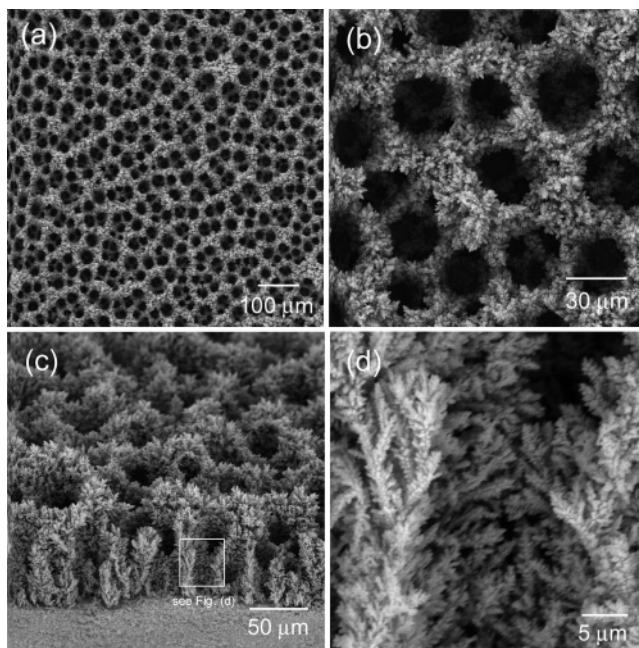


Figure 3. (a, b) Top and (c, d) cross-sectional views of 3-D foam structures of copper electrodeposited for 20 s in the electrolyte of 0.4 M CuSO₄ + 1.5 M H₂SO₄ + 0.1 M CH₃COOH at an applied cell current density of 3 A/cm².

3a) were roughly estimated to be 1.85×10^4 and 8.27×10^4 cm⁻², respectively, by quantitative analysis of the micrographs. These results strongly indicate that the addition of acetic acid has a significant effect on suppressing the coalescence of H₂ bubbles and thus reducing pore size and increasing pore density of the foam with very little effect on other microscopic features.

Figure 4a and b summarize the effect of the addition of acetic acid on the surface pore size and foam layer thickness, respectively. The variation of foam structure (i.e., surface pore size and foam thickness) with the concentration of acetic acid showed a trend similar to that described in the micrographs shown in Figure 3. When the acetic acid content is less than 0.1 M, the surface pore size is much more sensitive to the content of acetic acid than the foam thickness. When the concentration of acetic acid is greater than 0.1 M, however, it has little effect on the pore structure. For example, sample A' (20-s deposition in 0.1 M CH₃COOH) and sample B' (40-s deposition in 0.2 M CH₃COOH) have the same thickness (Figure 4b) and the

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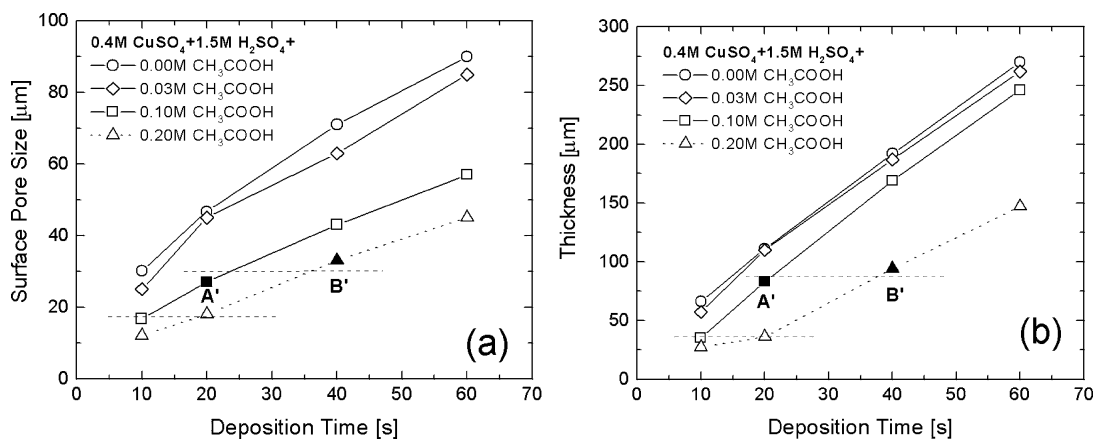


Figure 4. Variation of (a) surface pore size and (b) thickness of the copper electrodeposits with deposition time at different concentrations of CH_3COOH .

same surface pore size (Figure 4a), indicating that acetic acid (more than 0.1 M) just retards the foam formation without changing significantly the morphology of the foam.

Control of the Branch Size in the Foam Wall. It is well-known that small amounts of additives in the plating bath may have a dramatic impact on the morphology of the deposits. According to the literature, alkaline sulfate and chloride might be particularly effective in reducing the branch size of the copper foam. The influence of a supporting electrolyte (e.g., alkaline sulfates) on the shape of copper deposits has been widely studied in the past decade as a model system of nonequilibrium pattern formation.^{16–20} In this case, cuprous oxide rich highly ramified deposits with high space filling capability, i.e., the so-called fingerlike aggregates, could be created by adjusting the content of alkaline sulfates and applied cathodic voltage.^{16–19} The investigation on the effect of sodium sulfate (5 mM to 0.5 M) on shape evolution of our copper foam structure (data are not presented here), however, seems to suggest otherwise: there was no effect of sodium sulfate on the morphology of the foam. Considering that the hydrodynamic instability of the interface between the copper-depleted layer and the bulk solution (due to cuprous oxide on the copper growing tip) is responsible for the fingerlike highly ramified aggregates,^{18,21} the negligible effect of sodium sulfate on our ramified wall structure is most likely due to the inhibition of the development of the intermediate cupric hydroxide or cuprous oxide on the growing tip of the deposit in a highly acidic deposition bath.

On the other hand, due primarily to industrial interest (e.g., electrodeposited copper for the applications as ultrascala integrated interconnects and circuitry), a number of studies have been carried out in an effort to dramatically improve the quality of the copper electro-

deposits.^{22–27} In particular, sulfuric copper electrolyte with additives of chloride ions, poly(ethylene glycol), and/or bis(3-sulfopropyl) disulfide is proven to have a significant beneficial effect on the formation of void-free, seamless “bright” copper deposits, although the synergistic effect of those additives is still unclear.²⁸ Among these additives, chloride ions attract particular attention as a single additive in this work due to its strong depolarization power of the solution: a number of studies have reported that the copper deposition (reduction) reaction is accelerated or catalyzed by chloride ions.^{28–31} And it has been theoretically substantiated, based upon ab initio molecular orbital theory, that a trace amount of chloride ion in the solution would change the reaction mechanism for the electron transfer from outer-sphere reaction (water–water bridge) to inner-sphere reaction (chloride bridge), resulting in much higher exchange current density of the $\text{Cu}^{2+}/\text{Cu}^+$ reaction step.³⁰ Under the circumstances, it is very interesting to investigate how the catalytic effect of chloride ions influences the wall structure of the copper foam which is created in an extreme condition of fast copper deposition accompanying vigorous H_2 evolution.

Shown in Figure 5 are the 3-D foam structures of copper electrodeposited for 20 s in the “baseline deposition bath” with the addition of (a, b) 1 mM, (c, d) 10 mM, and (e, f) 50 mM HCl. It is noted that the morphology of the foam wall changed dramatically with concentration of chloride ions. As the chloride ions were added, the agglomeration of the branches, which char-

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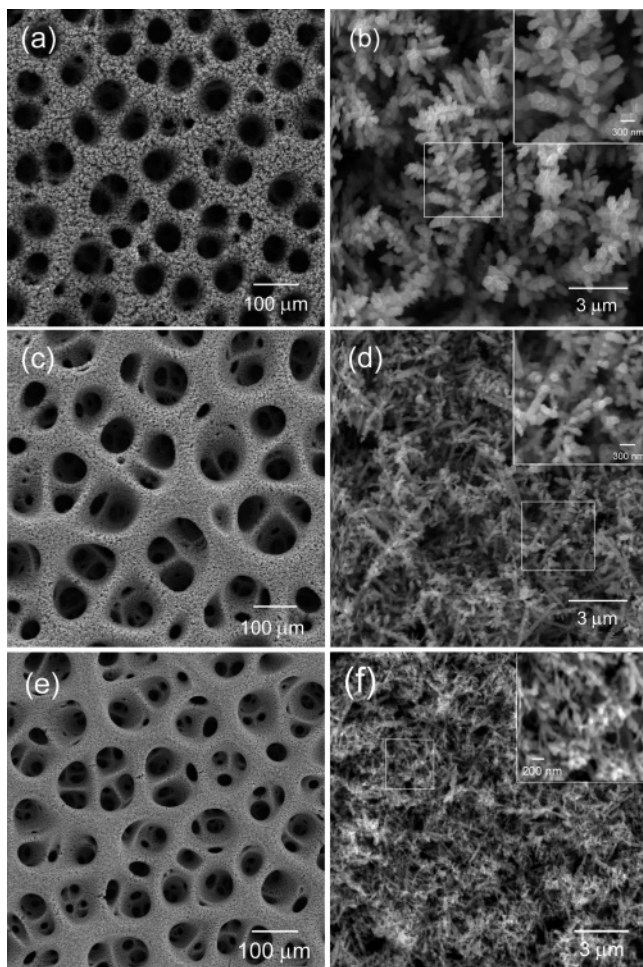


Figure 5. Typical SEM micrographs of copper electrodeposited for 20 s in the electrolyte of 0.4 M CuSO_4 + 1.5 M H_2SO_4 + 1 mM (a, b), 10 mM (c, d), and 50 mM HCl (e, f) at an applied cell current density of 3 A/cm^2 .

acterizes the deposits created in the base deposition bath (Figure 1), was suppressed and, at the same time, the overall wall structure became much denser. With the addition of 50 mM HCl, the branch size was reduced to <50 nm without any apparent branch agglomeration. Interestingly, the essential porous feature of the foam walls remains the same even after the addition of chloride ions.

Although the detailed formation mechanism of this unique structure is yet to be determined, the effect of deposition condition on the microstructures of the foam can be understood as follows. (1) For the copper deposition, we adopted extremely high cathodic current density (as high as 3 A/cm^2) in an electrolyte with high acidity. Here, the high cathodic polarization is a sufficient condition for nonequilibrium (or instable) copper deposition (which is intrinsic to diffusion-limited growth of copper), leading to ramification.^{32,33} (2) The use of a highly acidic deposition bath ensures vigorous H_2 evolu-

tion on the surface of newly generated copper branches during deposition, possibly creating a local turbulence of electrolyte around the copper deposits and thus disrupting continuous growth of it. (3) Finally, the addition of chloride ions accelerates the deposition reaction and hence the foam wall is more effectively filled with the copper deposits, as compared to without chloride ions. Under the circumstances, the copper foam with highly open porous nanostructured wall could be a consequence of the combination of ramification (roughening) effect under the extreme deposition condition and the catalytic (accelerating and thus possible brightening) effect of chloride ions. This further indicates that the addition of chloride ion is effective to disturb the ramification process or to modify the growth habit of the copper.

Elemental analysis using energy-dispersive X-ray spectroscopy (EDS) showed that there was no detectable amount of chlorine in the deposits created in the electrolytes containing 1–50 mM HCl. This is consistent with the previous suggestion that all chlorine is present as a soluble species at a cathodic over-voltage higher than 146 mV (vs Cu/Cu^{2+}) when the chloride content is less than 50 mM.³⁴ The cathodic polarization during the copper foam formation in this work was determined to be as high as >3 V (vs Cu/Cu^{2+}) through a three-electrode electrochemical cell using copper as the reference electrode.

Conclusions

The pore sizes and wall structures of electro-deposited copper foam have been successfully controlled with the addition of bubble stabilizer (acetic acid) and reaction catalyst (chloride ions), respectively, to the deposition bath. This represents a novel way of creating porous foam structures with much finer microscopic features and larger surface area as compared to those prepared without the additives. The porous copper foams are being tested for construction of nanocomposite anodes (consisting of Cu and CeO_2) for solid oxide fuel cells. Further, the porous copper foam can be used as 3-D current collector of negative electrodes in high-performance lithium batteries. Finally, the porous copper foam may be used as 3-D templates for preparation of other functional materials in nanostructured forms.

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