Hierarchical nanoporous nickel alloy as three-dimensional electrodes for high-efficiency energy storage

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Abstract

Hierarchical nanoporous metals with a large surface area and pore channels are the sought-after nanostructure for many applications. Here we report a two-step dealloying approach to fabricate a hierarchical nanoporous Ni alloy by utilizing the chemical stability difference of the constituent elements in a multicomponent precursor. Due to the large surface area and high electric conductivity, the hierarchical nanoporous Ni alloy exhibits a high specific areal capacitance of $\sim 1.11 \text{ F cm}^{-2}$ and volumetric capacitance of 317 F cm^{-3} .

Keywords: hierarchical structure, nanoporous metal, dealloying, supercapacitor

Dealloyed nanoporous metals with bicontinuous open porosity have shown great promise as a new class of functional materials for a wide range of applications in catalysis, fuel cells, sensors, actuators, energy storage and so forth [1-9]. The chemical and physical properties of nanoporous metals have been found to strongly depend on the characteristic length of the porous materials, namely the nanopore and ligament sizes [10-12]. In general, a smaller pore/ligament size gives rise to a larger effective surface area, higher chemical activity and stronger localized surface plasmon resonance and thus is a desirable nanostructure for catalytic, optical and energy storage applications. However, the small pores inherently impede mass transport and thereby affect reaction kinetics when liquids, solids and gases are involved into the reactions and measurements. In practice, many applications require both small pores for large effective surface area and high chemical/physical activities, and large pore sizes for fast mass exchange. For example, in supercapacitors and batteries, nanoporous metal electrodes are preferred to have large pores (50-100 nm) for rapid ion diffusion and small pores for large internal surface area for charge storage. Therefore, a hierarchical porous structure with both large and small pores is essential for these applications. Two well-regulated methods have been reported to fabricate bimodal nanoporous gold. Ding and Erlebacher developed a dealloying/plating/re-dealloying strategy to create nanoporous gold with a bimodal pore size distribution [13]. In their study, pre-dealloyed nanoporous gold is used as the template for Ag plating. Annealing is applied to form a Ag-Au alloy skin of the metal ligaments. The second leaching of the plated Ag results in the formation of small nanopores in the initial gold ligaments. More recently, Qi and Weissmuller reported a dealloying/annealing/re-dealloying approach to fabricate bimodal nanoporous gold by dealloying a $\text{Ag}_{95}\text{Au}_5$ alloy containing a very low concentration of gold [14]. By controlling the first-step dealloying, the consequential nanoporous alloy contains a high concentration of residual Ag (~52 at.%). After annealing, coarsened Au-Ag ligaments can be further dealloyed to form small pores by removing the remained Ag. Additionally, bimodal nanoporous structure can also be formed by dealloying two-phase precursors[15] and

metallic glasses [16]. It is worth noting that that the bimodal porous structure is only achieved from noble metals, mainly gold and Palladium, because of their easy formation of nanoporous structure and high chemical stability. Although there are growing demands of low-cost nanoporous transition metals for practical applications, hierarchical nanoporous non-noble metals have not been realized so far. This is mainly owing to the poor nanopore formation ability and low chemical stability of transition metals.

In this study we develop a novel approach to fabricate a hierarchical nanoporous Ni alloy by utilizing the chemical stability difference of the constituent elements in a multicomponent precursor alloy in different electrolytes. The hierarchical nanoporous Ni alloy with a large internal surface, high electric conductivity and fast mass transport channels holds a great promise as three-dimensional nanoporous electrodes for the applications of high efficiency energy storage.

The single-phase $\text{Mn}_{70}\text{Cu}_{15}\text{Ni}_{15}$ precursor alloy used in this study is very ductile, similar to the binary $\text{Mn}_{70}\text{Ni}_{30}$ [17, 18], and can be cold-rolled down to $\sim 50\ \mu\text{m}$ (Fig. S1 in Supplementary data), which is the common thickness of current collectors in commercial batteries and supercapacitors. Since both Ni and Mn are unstable in a high concentration acid solution [17], a weak acidic electrolyte of 1 M $(\text{NH}_4)_2\text{SO}_4$ was used for selectively leaching Mn from the $\text{Mn}_{70}\text{Cu}_{15}\text{Ni}_{15}$ alloy (free corrosion) in the first step dealloying. The dealloyed sample has a uniform nanoporous structure with the ligament/pore size of $\sim 10\ \text{nm}$ (Fig. 1a), determined by a fast Fourier transform (FFT) method [19]. The small pore size is mainly caused by the low diffusivity of Ni at the electrode/electrolyte interface [17]. Energy-dispersive X-ray spectroscopy (EDS) analysis shows that the nanoporous alloy contains $\sim 12\ \text{at.}\%$ Mn, $\sim 44\ \text{at.}\%$ Ni and $\sim 44\ \text{at.}\%$ Cu (inset in Fig. 1a), indicating that the nanopore formation is mainly due to the selective leaching of Mn. Since the Ni and Cu ratio keeps the same as that in the precursor alloy, the dissolution of Ni and Cu in the weak acid solution is negligible. A small oxygen peak (at 0.525 KeV) can also be found on the EDS

spectrum, which indicates the formation of a thin oxidelayer due to the active nature of the nanoporous Ni-Cu alloy. The oxygen content is ~2-3 at. %, corresponding the formation of ~5 wt.% oxides out of the total mass of the nanoporous alloy.

The as-dealloyed nanoporous alloy was annealed at high temperatures to enlarge the ligament and pore sizes simultaneously [10]. **Figure 1b** shows that the coarsened nanoporous structure of the nanoporous alloy annealed at 800 °C for 5 min. The average pore/ligament size is ~250 nm, about 25 times larger than that of the as-dealloyed sample. Extending the annealing time to 20 min, the pore/ligament size increases to ~500 nm (**Fig. 1c**). The pore/ligament size can be further enlarged to ~1000 nm after annealing at 900 °C for 20 min (**Fig. 1d**). Therefore, the nanopore/ligament size of the nanoporous Ni alloy can be tailored in a wide range by controlling the heat treatment conditions, similar to the nanoporous noble metals [10, 20, 21]. Although the significant nanopore and ligament growth takes place and there is significant volume shrinkage (the thickness decreased from 50 to 35 μm after annealed at 900 °C for 20 min), the bicontinuous nanoporous structure is well retained in the entire sample as shown in the cross-sectional scanning electron microscope (SEM) image (inset in **Fig. 1d**). Moreover, the annealed samples have a shining color and smooth ligament surface, indicating that the hydrogen/argon protection effectively prevents the oxidation of the nanoporous Ni alloy at high temperatures.

In order to generate a hierarchical nanoporous structure, the annealed samples with large pores and ligaments were subjected to chemical etching in a dilute HNO_3 solution (0.8 M) to selectively leach Cu from the nanoporous alloy. Although Cu has a higher electrode potential and is electrochemically more stable than Ni, the dilute acid solution can preferably dissolve Cu because of the passivation of Ni in the acid electrolyte [22, 23]. The SEM image of **Figure 2a** shows that the secondary pores with smaller sizes are formed within the large Ni alloy ligaments in the coarsened nanoporous Ni alloy annealed at 900°C for 20 min. The zoom-out SEM image (**Fig. 2b**) evidences

that the hierarchical porous structure is formed uniformly through the entire sample. The cross-sectional SEM image (**Fig. 2c**) demonstrates that the hierarchical porous structure remains nearly the same from the center region to surface. After the secondary dealloying, the composition of the hierarchical nanoporous sample is measured to be $\text{Mn}_7\text{Cu}_{28}\text{Ni}_{65}$ (at.%) (the inset of **Fig. 2c**). The reduced Cu/Ni and Mn/Ni ratios, compared to the first-step dealloyed sample, indicate that the formation of small pores in the coarse ligaments mainly arises from the selective dissolution of Cu together with a small amount of Mn. The residual Cu and Mn are most likely to be trapped inside the ligaments due to the passivation of Ni during the corrosion in the acid solution. **Figure 2d** shows the N_2 adsorption/desorption isotherm of the hierarchical nanoporous Ni alloy. The surface area is calculated to be $16.8 \text{ m}^2 \text{ g}^{-1}$ by Brunauer-Emmett-Teller formula. The hysteresis behavior in the N_2 adsorption/desorption curve confirms the existence of secondary small pores. On the basis of Barrett-Joyner-Halenda formula [24], it is estimated that there are two types of small pores, one with the feature size of $\sim 185 \text{ nm}$ and the other of $\sim 6 \text{ nm}$, formed on the coarse Ni alloy ligaments. The hierarchical porosity is likely associated with the different dissolution rates of Mn and Cu. The calculated pore volume is $\sim 31 \text{ cm}^3 \text{ g}^{-1}$ and the porosity is as large as $\sim 71\%$ since the overall sample size (volume) keeps constant during the secondary dealloying. Accompanying with the evolution of nanoporosity, the color of the nanoporous Ni alloy changes from slightly dark after first dealloying to bright white after annealing and then to dark after second dealloying, indicating the strong structure dependence of the optical properties of the nanoporous Ni alloy.

To demonstrate the potential applications of the low-cost hierarchical nanoporous Ni alloy in energy storage and conversion, we preliminarily utilized the sample as free-standing electrodes and current collectors of electrochemical supercapacitors. Electrochemical cyclic voltammetry (CV) characterization shows that the hierarchical Ni alloy has a nearly pure Ni surface with Ni oxidation (forming oxides/hydroxides) and reduction peaks at $\sim 0.45 \text{ V}$ and $\sim 0.20 \text{ V}$, respectively, in a 1 M KOH aqueous solution (**Fig. 3a**), while the redox peaks from Cu and Mn are negligible. In

comparison, the annealed nanoporous alloy with a large pore size (before second dealloying) shows obvious redox peaks from Cu between -0.4 and 0.1 V, demonstrating that the residual Cu and Mn in the hierarchical nanoporous Ni alloy mainly reside in the core of the alloy ligaments. Importantly, the hierarchical sample shows a much larger integration area under the redox peaks, compared to the coarsened nanoporous alloy, suggesting higher charge storage because of the larger internal surface area and the formation of high-capacitance Ni(OH)₂. As shown in the charge/discharge curves (Fig. 3b), there are voltage plateaus at around 0.25-0.35 V during charging and discharging, consistent with the redox reactions of Ni(OH)₂ reported before [25, 26]. The slightly longer charging time than discharging, particularly at low current densities, is probably caused by the *in situ* formation of pseudocapacitive Ni-based oxides/hydroxides in the alkaline solution during charging. XRD analysis (Fig. S2, Supplementary data) shows that, along with Ni(OH)₂ peaks, a small peak at ~36° can also be detected, corresponding to Cu₂O or mixed Cu/Ni oxides due to the high amount of Cu in the alloy. The specific areal capacitance calculated from the discharge curves is shown in Figure 3c. The hierarchical nanoporous Ni alloy can reach a high areal capacitance of ~1.11 F cm⁻² at the current density of 1.25 mA cm⁻², which is about 2-5 times higher than recently reported MnO₂/Co₃O₄ core-shell hybrid arrays (0.71–0.4 F cm⁻² at 4–44.7 mA cm⁻²) [27] and MnO₂–NiO tubular arrays (0.4–0.22 F cm⁻² at 5–25 mA cm⁻²) [28]. With the increase of current density from 1.25 to 20 mA cm⁻², the specific areal capacitance still keeps a high value of 1.05 F cm⁻² (~95% retained), verifying the high-rate capacity performance of the hierarchical nanoporous electrode compared with most reported pseudocapacitive electrodes [3, 25, 29]. The high-rate capacity performance is believed to arise from the fast electron/ion transfer of the highly conductive metal electrode with interconnected large pore channels. Although Ni is much heavier than active carbon, the commercial electrode material, the volumetric capacitance of the hierarchical nanoporous Ni alloy is calculated to be ~317 F cm⁻³, which is also more than 3 times higher than reported pseudocapacitor electrodes and carbon materials, such as NiCo₂O₄/carbon aerogel

1 composite electrode (110 F cm^{-3}) [30] and MnO_2 /carbon electrode (90 F cm^{-3}) [31]. Since there is
2 only ~5 wt.% oxides in the nanoporous alloy, the the specific capacitance per unit oxides can reach
3 about 1900 F/g, which is close to the theoretical value of Ni(OH)_2 . It can be expected that the
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7 capacitive performance of the hierarchical porous electrode can be further improved if high-
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10 capacitance pseudocapacitive materials, such as MnO_2 , are deposited on the internal surface of the
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12 hierarchical nanopores. Our preliminary result also shows that the hierarchical electrode possesses
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14 excellent cycling stability. The capacitance remains to be ~97% after 2000 cycles at the
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16 charge/discharge rate of 10 mA cm^{-2} (Fig. 3d). Again, the high cycling retention is believed to
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18 originate from the high electron/ion conductivity and mechanical stability of the hierarchical porous
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21 structure.
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25 In summary, a hierarchical nanoporous Ni alloy with hierarchical porosity has been successfully
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27 fabricated by dealloying a multicomponent $\text{Mn}_{70}\text{Cu}_{15}\text{Ni}_{15}$ alloy. By utilizing the chemical stability
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29 disparity of Cu, Ni and Mn in different electrolytes, the constituent elements can be selectively
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31 dissolved at different stages of dealloying to form hierarchical nanoporosity. Moreover, the
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33 hierarchical nanoporous Ni alloy shows excellent pseudocapacitive performance with ultrahigh
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35 specific areal capacitance and volumetric capacitance because of the large effective area, high
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37 electric conductivity and fast ion transport. It is worth noting that the dealloying strategy developed
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39 in this study can be easily applied to other alloy systems as a general approach to fabricate
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42 hierarchical nanoporous metals and alloys for applications in sensing devices, catalysis and energy
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44 storage and conversion.
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Supplementary data associated with this article can be found.

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Figure captions:

Figure 1. SEM images of np-NiCu before (a) and after annealing under different conditions (800 °C, 5 min (b); 800 °C, 20 min (c); 900 °C, 20 min (d)). Inset in (a) is the EDS spectrum of this sample and inset in (d) is the section-view SEM image with the scale bar of 5 μm.

Figure 2. (a) SEM image of the hierarchical nanoporous Ni alloy. (b) Zoom-out SEM image showing the uniformity of hierarchical structure through the entire sample. (c) Cross-sectional SEM image of the hierarchical nanoporous Ni alloy. Inset in (c) shows the EDS spectrum of the hierarchical alloy and (d) the hysteresis curve of N₂ adsorption/desorption isotherm of the hierarchical nanoporous Ni alloy (the X-axis was normalized with the vapor pressure of nitrogen (P₀) at 77.0 K (0.101 MPa)).

Figure 3. (a) CV curves of the annealed nanoporous Ni alloy before and after the second dealloying, scan rate: 40 mV s⁻¹. (b) Charge-discharge curves of the hierarchical electrode after the second dealloying. (c) Rate dependence of the specific areal capacitance of the hierarchical electrode at different current densities and (d) the capacitance retention as a function of cycle number at a constant charge/discharge current density of 10 mA cm⁻². The electrolyte is 1 M KOH aqueous solution.

Figure 1.

Figure 2.

Figure 3.