



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

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Hierarchical nanoporous metals with a large surface area and rich 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} .

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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 porosity, 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 in 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 a 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 an 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 an $\text{Ag}_{95}\text{Au}_5$ 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 ($\sim 52 \text{ at.}\%$). After annealing, coarsened Au–Ag ligaments can be further dealloyed to form small pores by removing the remaining Ag. Additionally, bimodal nanoporous structure can also be formed by dealloying two-phase precursors [15] and metallic glasses [16]. It is worth noting that

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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 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. S.1 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

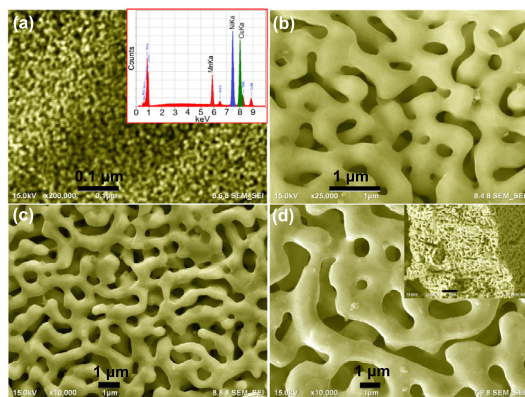


Figure 1. SEM images of nanoporous NiCu before (a) and after annealing under different conditions (800 °C, 5 min (b); 800 °C, 20 min (c); 900 °C, 20 min (d)). Inset in (a) is the EDS spectrum of this sample and inset in (d) is the section-view SEM image with the scale bar of $5\ \mu\text{m}$.

formation of a thin oxide layer due to the active nature of the nanoporous Ni–Cu alloy. The oxygen content is $\sim 2\text{--}3\ \text{at.}\%$, corresponding the formation of $\sim 5\ \text{wt.}\%$ 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 the coarsened nanoporous structure of the nanoporous alloy annealed at 800 °C for 5 min. The average pore/ligament size is $\sim 250\ \text{nm}$, ~ 25 times larger than that of the as-dealloyed sample. Extending the annealing time to 20 min, the pore/ligament size increases to $\sim 500\ \text{nm}$ (Fig. 1c). The pore/ligament size can be further enlarged to $\sim 1000\ \text{nm}$ 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 $35\ \mu\text{m}$ after annealing 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

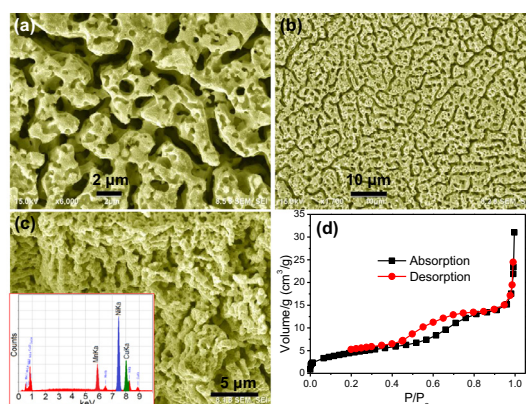


Figure 2. (a) SEM image of the hierarchical nanoporous Ni alloy. (b) Zoom-out SEM image showing the uniformity of hierarchical structure through the entire sample. (c) Cross-sectional SEM image of the hierarchical nanoporous Ni alloy. Inset in (c) shows the EDS spectrum of the hierarchical alloy and (d) the hysteresis curve of N_2 adsorption/desorption isotherm of the hierarchical nanoporous Ni alloy (the X-axis was normalized with the vapor pressure of nitrogen (P_0) at 77.0 K (0.101 MPa)).

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