Hierarchical nanoporous metal/metal-oxide composite by dealloying metallic glass for high-performance energy storage

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Abstract

A free-standing nanoporous YNiCo metal/metal-oxide composite with hierarchical porosity is fabricated by chemically dealloying Al₈₅Y₆Ni₆Co₃ metallic glass in alkaline solutions. The mixed core-shell-like metal/metal-oxide structure formed during dealloying due to the active properties of these metals. Time-dependent etching experiments suggest that the formation of large and small pores occur simultaneously, which may be related to the different dissolution rate of Al at different sites. The nanoporous composite with a highly conductive metal core exhibits a high areal capacitance. Moreover, this strategy can be extended to fabricate other nanoporous composites considering that the composition of metallic glass can be easily tuned.

Keywords: A. Nanoporous metals; B. Dealloying; C. Hierarchical structure C. Supercapacitor

1. Introduction

Nanoporous metals have attracted growing research interests in both potential applications and theoretical studies owing to their unique physicochemical properties such as interconnected interior voids, large surface areas, high catalytic activities, etc. [1-4] A general route towards nanoporous metal involves the deposition of a shell of designed metal on removable templates. The use of the templates in principle allows one to manipulate the morphology and pore size by controlling the templates. However, the templating method is relatively complex, which requires multi-step treatment. Recently, dealloying (i.e., selective removal of one active component from an alloy) has been demonstrated to be a good strategy to fabricate nanoporous metals with three dimensional (3D) ligament-pore structure due to the simplicity and high efficiency [2, 3, 5-8]. To prepare uniform nanoporous metals by dealloying, it is essential to design suitable precursors, which satisfy two basic requirements: homogeneous single phases and a large electrochemical potential difference between the alloy components [9]. Since dealloying is essentially an etching process under relatively harsh conditions, the dealloying strategy is usually limited to produce nanoporous noble metals such as Pt, Pd, Au, Ag and their alloys due to their high chemical stability [1, 2, 10]. Driven by low-cost practical applications such as electrochemical energy storage, developing economic nanoporous transition metals, such as nickel, has been the topics of recent studies [11-15]. For example, uniform nanoporous Ni and NiCu alloy have been prepared recently as supercapacitor electrodes by dealloying single-phase NiMn and NiCuMn alloy [11, 12]. Besides Mn-based precursors, Al-based precursor should also be a good choice for the fabrication of nanoporous active metals because the dealloying Al-based precursors can be carried out in alkaline solutions where many other active metals can be preserved. One successful example is Raney nickel which is

prepared by dealloying NiAl alloy in alkaline solutions [16]. However, the Al-based alloys often contain many intermetallic phases [17], which is not favorable for the fabrication of uniform and monolithic nanoporous metals for energy-storage electrodes.

The limited single-phase crystalline Al alloys inhibit the development of dealloyed nanoporous metals. Compared with crystallized precursors (i.e., alloys), metallic glasses with multicomponent (i.e., containing 2~6 elements) show monolithic and isotropic phase with a homogeneous composition and structure down to nanoscale [18, 19]. Due to the metastable far-from-equilibrium nature, the composition of metallic glasses can be tuned continuously in a wide composition range. Thousands of metallic glasses have been fabricated in different alloy systems [20]. These combined properties of metallic glasses provide a promising route to obtain nanoporous metals with uniform microstructure by dealloying. The use of metallic glasses as precursors to fabricate nanoporous noble metals, such as Pd, Au and Cu, has been demonstrated in previous work [21-25]. However, the fabrication of technically important but chemically active metals, such as Ni and Co by dealloying metallic glasses for electrochemical energy storage, is still a challenging target. In this work, we fabricated nanoporous $\text{Y}_{40}\text{Ni}_{40}\text{Co}_{20}$ (np-YNiCo) by dealloying an $\text{Al}_{85}\text{Y}_6\text{Ni}_6\text{Co}_3$ metallic glass (MG). As a binder-free supercapacitor electrode, the as-prepared np-YNiCo with a conductive ligament network and naturally formed metal oxide films exhibits a high and stable capacitance.

2. Experimental

Pure metals with high purity (>99.9 wt.%) were designed with the nominal composition of $\text{Al}_{85}\text{Y}_6\text{Ni}_6\text{Co}_3$ (at.%) and melted in BN crucible using an induction-melting furnace. The master alloy was remelted in a quartz tube and subsequently injected onto a rotating Cu wheel to obtain metallic glass ribbon with a thickness of about 20 μm . The dealloying of the metallic glass precursor was carried out in NaOH aqueous solutions with different concentrations at room temperature. After dealloying, the samples were rinsed with deionized water.

The crystal structure of the precursor alloys and dealloyed samples were characterized by X-ray diffraction using a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation. The microstructures of the dealloyed samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2010F) and scanning electron microscopy (SEM, JEOL JSM-6700). Chemical analysis was performed by an energy-dispersive X-ray spectrometer (EDS, Oxford INCA x-sight). Electrochemical tests were carried out at room temperature using an electrochemical workstation (Iviumstat Technology) in a three-electrode cell with a Pt foil as counter electrode and Ag/AgCl (Cl^- concentration inside of the electrode is 4 M) as the reference electrode. For capacitive performance measurements, 1 M KOH was chosen as the electrolyte. The working electrode is the dealloyed sample with two sides and the dealloyed part is naturally connected with the undealloyed part which is in contact with the conducting wires of the workstation. The nominal area of the samples immersed into the electrolyte for electrochemical tests was controlled to be $\sim 16 \text{ mm}^2$.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the $\text{Al}_{85}\text{Y}_6\text{Ni}_6\text{Co}_3$ MG precursor before and after dealloying. The precursor only exhibits one broad diffraction peak between 30° and 45° , demonstrating the glassy nature. Scanning electron microscopy (SEM) image (Fig. 2a) shows that the MG has a smooth surface without any microstructural features, such as grain boundaries in polycrystalline crystals. EDS analysis (Fig. S1 in Supporting Information) shows that the atomic composition of the precursor is in good agreement with the nominal composition of the glass, which is around $\text{Al}_{85}\text{Y}_6\text{Ni}_6\text{Co}_3$. The NaOH concentration has a significant effect on the dealloying process. The MG is stable in a low concentration of NaOH solution (e.g., 0.1 M) but can be dealloyed to form a bimodal nanoporous structure when the NaOH concentration is increased to 1 M. Fig. 2b shows the plane-view SEM image of the MG after 5 h dealloying in 2 M NaOH aqueous solution. From the low-magnification image, uniform bicontinuous ligament-pore structure with pore size of

~15 nm can be observed. The zoom-in image in Fig. 2c shows that within each ligament, small pores with sizes of 3-5 nm are formed, suggesting the bimodal porosity of the nanoporous structure. The section-view SEM image (Fig. 2d) shows that the formed nanoporous structure is across the whole sample, indicating that the MG has been dealloyed completely. This conclusion is further supported by the EDS result which shows that Al content is less than 10 at.% after 5 h dealloying. No significant ratio change for the other three components indicates that the alkaline environment is suitable for the selective etching of Al and for the formation of nanoporous active metals. After dealloying, the XRD pattern (Fig. 1) changes greatly. The diffraction peaks can be ascribed to both Ni/Co metal and Y, Ni, Co metal oxides. Due to the active properties of nanostructured Y, Ni and Co, it is reasonable to assume that the metallic Ni and Co should exist in the ligament core and passivated by the surface metal oxides [11]. On the other hand, according to the dealloying theory, the Al residue should also exist in the core, which is similar to the distribution of Ag residue when dealloying AuAg alloy [26]. The broad feature of these peaks indicates that the formed crystals are nanoscale. The diffraction peaks become more prominent when the dealloyed sample was annealed at 400 °C for 1 h under N₂ atmosphere due to the growth of the crystals (Fig. 1).

The hierarchical nanoporous structure was further characterized by transmission electron microscopy (TEM) and scanning TEM (STEM). From the TEM images (Fig. 3a and b), both large and small pores with bright contrast can be clearly observed, which confirms the bimodal porosity of the dealloyed nanoporous metal/metal-oxide composite. The STEM image (Fig. 3c) shows that a large amount of wrinkle/whisker-like structure formed on the ligament surface, which is due to the growth of metal oxides on the active metal ligament surface in the alkaline solution. The large amount of wrinkle-like metal oxides also makes the big pore semi-transparent in the TEM image. HRTEM image in Fig. 3d shows that each wrinkle-like structure contains many small crystals. The small crystal size observed from HRTEM is in agreement with the result from XRD which shows

very broad diffraction peaks from the dealloyed sample. The polycrystal nature of the wrinkle structure is further confirmed by selected-area electron diffraction (SAED, [inset in Fig. 3a](#)).

To understand the formation process of the nanoporous composite with bimodal porosity, time-dependent experiment was carried out. After only 5 min dealloying, as shown in [Fig. 4](#), uniform etching pits can be observed on the MG surface which may be due to the selective etching of active Al in a certain way. These etching pits exhibit different depth. The deepest part should form the final big pores. At the same time, a small number of small pores (less than 10 nm) have already been formed. After 15 min dealloying, the number of small pores increased. After 1 h, large pores around 20 nm can be observed with the small pores within the ligaments of large pores. As the etching time further goes, the large pores become well-developed from the original etching pits probably due to the continuous etching of the residual elements while the size of the small pores seems unchanged. These observations suggest that the large and small pores are formed simultaneously during the dealloying process. [Since the Al content is very high \(~85 at.%\), the initial dealloying would start from the sites where Al atoms are aggregated. The fast removal of Al would cause the diffusion of Ni, Co, and Y atoms and formation of big alloy ligaments and pores. The alloy ligaments should still contain a small amount of Al due to the initial Al distribution and/or Al residue. The slow dissolution of these Al in the big alloy ligaments would generate the small pores within the big ligaments. Moreover, during the formation of small pores, the oxidation of these active metals \(Ni, Co and Y\) would form oxide whiskers, resulting in the final hierarchical porous structure.](#)

To demonstrate the unique advantage of MGs as precursors for dealloying, a crystallized $\text{Al}_{85}\text{Y}_6\text{Ni}_6\text{Co}_3$ alloy (obtained by annealing the MG ribbon at 500 °C for 30 min under the protection of high purity Ar) has also been studied. XRD analysis ([Fig. S2](#)) shows that the crystallized precursor contains multiple phases including pure Al, Al_3Y , Ni_3Y , etc. SEM images in [Fig. S3a and](#)

S3b show that the surface of the crystallized precursor is very rough, which should be caused by the crystallization and formation of different intermetallics. When dealloyed in 2.0 M NaOH aqueous solution, it was found that the dealloying rate is very fast compared with that of the MG precursor and after ~30 min, the bubbling stops. XRD analysis shows that only pure Al phase is removed by the etching process, while the Al_3Y and Ni_3Y phases remain (Fig. S2). The etched sample shows coarse porous structure, formed by the removal of pure Al phase (Fig. S3c-e), and does not have a good supercapacitor performance due to the small effective surface area. EDS result (Fig. S3f) shows that after the etching, the Al content is about ~46 at.% because of the existence of Al_3Y phase which is consistent with the XRD measurements. These results further demonstrate the importance of the amorphous structure of Al alloys for the formation of uniform nanoporous structure.

The hierarchical nanoporous metal/metal-oxide structure is expected to have a wide range of applications because nanostructured metal oxides are important functional materials and the NiCo metal core provides a high conductivity. Herein, the nanoporous composite is evaluated as a binder-free electrode for electrochemical supercapacitors. Fig. 5a shows the cyclic voltammetry (CV) curves of the nanoporous composite electrode with various sweep rates ranging from 2.5 to 20 mV s^{-1} . The shape of the CV curves clearly reveals the pseudocapacitive characteristics. Specifically, a pair of redox peaks can be observed within the potential range from 0.1 to 0.5 V for all sweep rates, which is mainly related to the Faradic redox reactions of Ni and Co oxides and/or hydroxides [27-31]. It is observed that the peak potential difference is only ~0.4 V even when the scan rate is increased to 20 mV s^{-1} , indicating good reversibility of the redox reaction, which should be due to the low electric resistance of the nanoporous electrode.

From the charge/discharge curves (Fig. 5b), it can be observed that the potential plateaus are around 0.2–0.3 V, which is consistent with previous results [32]. The areal specific capacitance is

calculated by the formula, $C = I\Delta t/S\Delta V$, where I is the discharge current, Δt is the discharge time, ΔV is the potential range and S is the area of the electrode. The calculated areal specific capacitance as a function of charge/discharge current densities is plotted in Fig. 5c. The specific capacitance is as high as 1.12, 1.09 and 0.96 F cm⁻² at the current density of 2, 5 and 10 mA cm⁻², respectively. These results are better or comparable with the previously reported values for such free-standing pseudocapacitive electrodes, such as Co₃O₄/MnO₂ nanowires/nanosheet structured electrode (~0.56 F cm⁻² at 11.24 mA cm⁻²) [33], NiCo₂O₄ nanoneedle electrode (0.99 F cm⁻² at 5.56 mA cm⁻²) [32], Co₃O₄-NiO core-shell nanowire electrode (1.35 F cm⁻² at 6 mA cm⁻²) [34], and MnO₂-NiO core-shell nanoflake electrode (0.35 F cm⁻² at 9.5 mA cm⁻²) [35]. More literature results are summarized in Table 1. The cycling stability of the nanoporous composite is evaluated by the repeated charge/discharge cycling at a current density of 5 mA cm⁻² (Fig. 5d). The specific capacitance is ~1.1 F cm⁻² in the first cycle and then gradually increased to ~1.2 F cm⁻² at the ~1000th cycle. The increase in capacitance may be due to the continuous growth of Ni/Co oxides/hydroxides. After 2000 cycles, the capacitance remains constant, which is better than that of free-standing NiCo₂O₄ nanoneedle (10.6% loss after 2000 cycles) [32] and NiCo₂O₄/graphene composites (6.2% loss after 3000 cycles) [36]. The calculated volumetric capacitance is ~560 F cm⁻³ at 2 mA cm⁻², which is even higher than recently reported values achieved from nanoporous Ni/Ni(OH)₂ (344 F cm⁻³) [11] and Ni/Mn mixed hydroxides (505 F cm⁻³) [13] electrodes.

The good electrochemical performance could be related to the following structural features. First, the small diameter of the ligaments leads to a high surface area which undoubtedly contributes to the high capacitance. Secondly, the well-defined bimodal nanoporous structure leads to the separation of surface metal oxides from each other and makes most of the oxide surface easily accessible by the electrolyte. This will give high capacitance and enhanced electrochemical kinetics relative to conventional film electrodes. Thirdly, the direct growth of nanostructured Ni/Co metal

oxides/hydroxides on conductive metal ligaments ensures good mechanical adhesion, and more importantly, good electrical conductivity.

4. Conclusions

In summary, nanoporous YNiCo metal/metal-oxides composite with hierarchical porosity has been fabricated by one-step dealloying AlYNiCo metallic glass in an alkaline solution. Due to the active chemical properties of Y, Ni, and Co, mixed metal oxides formed simultaneously during the etching process forming a core-shell-like nanoporous composite. Remarkably, when used as a binder-free electrode for supercapacitor, the nanoporous composite exhibits greatly high electrochemical performance with a high capacitance normalized with area (volume) and excellent cycling stability compared to other binder-free electrodes. The fabrication strategy proposed here is not only facile but also suitable for large-scale production and provides a good opportunity for fabrication of various kinds of functional nanoporous metals which may be useful in sensing, catalysis, energy storage, etc.

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Table 1. Comparison of the capacitance of the hierarchal nanoporous metal/metal-oxide composite with literature results.

Electrode	Electrolyte	Performance	Ref.
Hierarchical np-YNiCo metal/metal-oxide	1 M KOH	1.12-0.96 F cm ⁻² at 2-10 mA cm ⁻²	This work
NiCo₂O₄ nanoneedle	--	0.99 F cm ⁻² at 5.56 mA cm ⁻²	[32]
MnO₂/Co₃O₄ core/shell hybrid array	1 M LiOH	0.71-0.4 F cm ⁻² at 4-44.7 mA cm ⁻²	[33]
MnO₂-NiO tubular arrays	1 M LiOH	0.4-0.22 F cm ⁻² at 5-25 mA cm ⁻²	[35]
Ni-NiO core-shell inverse opal	1 M KOH	9-7.8 mF cm ⁻² at 5-500 mV s ⁻¹	[37]
CNT-Ni hybrid arrays	6 M KOH	0.901-0.722 mF cm ⁻² at 0.69-27.2 mA cm ⁻²	[38]

Figure 1. XRD patterns of AlYNiCo MG ribbon (black), as-dealloyed np-YNiCo in 2 M NaOH (red) and annealed np-YNiCo at 400 °C for 1 h (green).

Figure 2. SEM image of the AlYNiCo precursor (a); SEM images of the np-YNiCo obtained by dealloying in 2 M NaOH solution (b: low magnification plane-view image; c: high magnification plane-view image; d: section-view image); SEM images of the np-YNiCo obtained in 1 M NaOH aqueous solution (e: plane-view image; f: section-view image).

Figure 3. TEM (a, b) SAED (inset in (a)) and STEM (c) image of the np-YNiCo. (d) HRTEM image of the wrinkle.

Figure 4. SEM images (different magnifications) of the metallic glass after dealloying in 2 M NaOH for different time (a and b: 5 min; c and d: 15 min; e and f: 60 min).

Figure 5. CV curves of np-YNiCo at different scan rates (a). Charge-discharge curves (b) and the area specific capacitance (c) of np-YNiCo as a function of current density. The area specific capacitance as a function of cycle number at a constant current density of 5 mA cm^{-2} (d). The electrolyte is 1 M KOH aqueous solution.