Self-oxidized sponge-like nanoporous nickel alloy in three-dimensions with pseudocapacitive behavior and excellent capacitive performance

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HIGHLIGHTS

- Self-oxidized nanoporous Ni-Co alloy with 3D ultrafine structure is fabricated.
- The product is a battery material in nature but exhibits pseudocapacitive behavior.
- The oxide skin/metallic core composite exhibits pseudocapacitive behavior.
- The good capacitive performance is due to the large surface area and high porosity.

ARTICLE INFO

ABSTRACT

Recent studies clarify that NiO is actually a battery material, rather than the widely considered pseudocapacitive material. Self-oxidized sponge-like nanoporous Ni-Co alloy (ss-npNi) in three-dimensions (3D) is fabricated by dealloying $Mg_{80}Ni_{19.2}Co_{0.8}$ metallic glass ribbon in citric acid and naturally surface self-oxidizing in air. The ss-npNi is found to be a battery material in nature while exhibiting pseudocapacitive behavior. The redox reactions at the peaks are controlled by surface processes with fast charge-transfer, and the pseudocapacitive contribution of the redox current is dominant throughout the whole potential range. The pseudocapacitive behavior originates from the fast charge/discharge processes occurring on the ultrathin metal oxide surface of the three-dimensional conductive ligaments. The ss-npNi exhibits high specific capacitance of $1424\,F\,g^{-1}$ at a current density of $1\,A\,g^{-1}$, enhanced rate capability with $\sim 82.4\%$ retention at a high current density of $40\,A\,g^{-1}$ and excellent cycle stability with $\sim 95.7\%$ retention even after 10000 continuous charge-discharge cycles at $40\,A\,g^{-1}$. This work renders the dealloying method a promising way of endowing battery materials with pseudocapacitive behavior.

1. Introduction

Advanced energy storage devices with high power density, high energy density, long life time and fast charge/discharge process are highly desired for applications such as electric vehicles and electron devices [1]. Among the energy storage devices, batteries and supercapacitors are two of the most important groups. Generally, batteries possess higher energy density but lower power density, shorter life time and slower charge/discharge process than supercapacitors [2]. Therefore, a group of materials combining both the battery and the supercapacitors features are expected to be promising energy storage materials. To date, studies on the supercapacitors mainly focus on carbon-based material [3,4], conductive polymers [5,6], and metal oxides like RuO_2 [1], MnO_2 [7,8] and other oxides like ZnO [9], TiO_2 [10]. In many works, NiO was considered as pseudocapacitive materials

[11–14], due to the strong redox peaks on cyclic voltammetry (CV) curves which were thought to be responsible for pseudocapacitance [15]. Recent studies has clarified that NiO is actually a battery material rather than a pseudocapacitive one [16,17], because NiO does not satisfy the following requirements of an ideal pseudocapacitor: (a) the redox peaks on a CV curve are maintained reversible up to some critical sweep rate [18]; (b) the redox current varies as the sweep rate in a CV test [19]; (c) the phase angle should be 90° in the impedance spectral [18]. In the present work, we fabricated 3D self-oxidized sponge-like nanoporous Ni-Co alloy (ss-npNi), which was found to be a battery material in nature but shows pseudocapacitive behavior. The ss-npNi with open pores and ultrafine ligaments in three dimensions was fabricated by adopting $Mg_{80}Ni_{19.2}Co_{0.8}$ metallic glass ribbon as a precursor for dealloying in $2\,g\,L^{-1}$ citric acid and naturally self-oxidizing in air. The interconnected conductive ligaments, high porosity, high surface

area, and ultrathin metal oxide surface on the ligaments of the ss-npNi is believed to be responsible for the pseudocapacitance. This work presents the possibility of producing advanced energy storage devices by combining battery materials with pseudocapacitive behavior. The capacitive performance of the ss-npNi is also studied.

2. Experimental

The Ni-Co pre-alloy with an atomic ratio of Ni:Co = 24:1 was produced by arc-melting pure nickel (> 99.99 wt%) and cobalt (> 99.99 wt%) in an argon atmosphere. The Ni-Co pre-alloy was then re-melted with pure magnesium (> 99.99 wt%) in a BN covered crucible by high-frequency induction in an argon atmosphere. These processes yielded the alloy with a nominal composition of $Mg_{80}Ni_{19.2}Co_{0.8}$ (at.%). Glassy ribbon with a thickness of ~25 μm and a width of ~1.5 mm were fabricated from the $Mg_{80}Ni_{19.2}Co_{0.8}$ alloy ingot by melt-spinning at a linear velocity of 50 m s^{-1} in an argon atmosphere. The glassy ribbon with one side covered with waterproof tape was immersed in 2 g L^{-1} citric acid aqueous solution for 1.5 h at room temperature for dealloying. After dealloying, the dealloyed part naturally and firmly connected with the undealloyed matrix. The dealloyed ribbon were rinsed with distilled water and dehydrated alcohol, and dried in air.

The microstructure of the as-spun and the dealloyed ribbons were characterized by X-ray diffraction (XRD, Bruker AXS D8) using Co Kα radiation (λ = 1.7902 Å). The microstructure of the dealloyed ribbon were further investigated with a JEOL 7500 F scanning electron microscope (SEM) and a JEM-2100 F high-resolution transmission electron microscope (HRTEM). The composition of the dealloyed ribbon was estimated by an energy-dispersive X-ray analyzer (EDS). The TEM sample was prepared with an ion beam thinner (Gatan PIPS 691). The ligament size was obtained by averaging 100 measurements of the ligaments on the SEM images. The pore size was obtained by subtracting the ligament size from the average of 100 measurements of the centers of the neighboring pores. The uncertainty was the standard deviation. The surface area and pore volume were measured by the Brunauer-EmmettTeller (BET) and Barrett-Joyner-Halenda (BJH) method using a Nova StationA nitrogen adsorption–desorption experimental instrument at 77 K. The X-ray photoelectron spectroscopy (XPS) spectrum was acquired by an ESCALab250 electron spectrometer with a monochromatic Al Kα radiation source. Characterization of the surface was performed at takeoff angles of 15° and 75°. An electrochemical workstation (Princeton VersaSTAT 3) and a three-electrode cell were employed to perform the electrochemical tests in 4 M KOH. The three-electrode cell consisted of the dealloyed ribbon, a platinum counter electrode and a saturated calomel electrode (SCE) connected by a Luggin probe and a slat bridge. For each test, a ribbon with a thickness of H and weight of M was adopted for dealloying. After dealloying, the thickness of the dealloyed layer was h. The values of H and h were measured by the SEM images. The total weight percentage of Ni and Co is 37.7% for $Mg_{80}Ni_{19.2}Co_{0.8}$, and therefore the weight of Ni-Co in the dealloyed layer is $m = M \cdot h/H \times 37.7\%$. When calculating the mass of the electroactive material, all the Ni and Co atoms were assumed to be oxidized to +2 state. Since the Ni atoms take up the overwhelming percentage of the Ni-Co alloy, and the relative atomic mass of Ni (58.7) is very close to that of Co (58.9), the Co atoms are regarded as Ni for simplicity. The weight of the electroactive material is thus m·(58.7 + 16)/58.7. For each test, the typical mass of a dealloyed ribbon is ~3 mg, and the electroactive material areal loading is ~0.4 mg cm^{-2}. The C_s is given by I·t/ΔV, where I, t and ΔV are discharging current density (A g^{-1}), discharging time (s) and discharging potential range (V) during galvanostatic discharging tests, respectively.
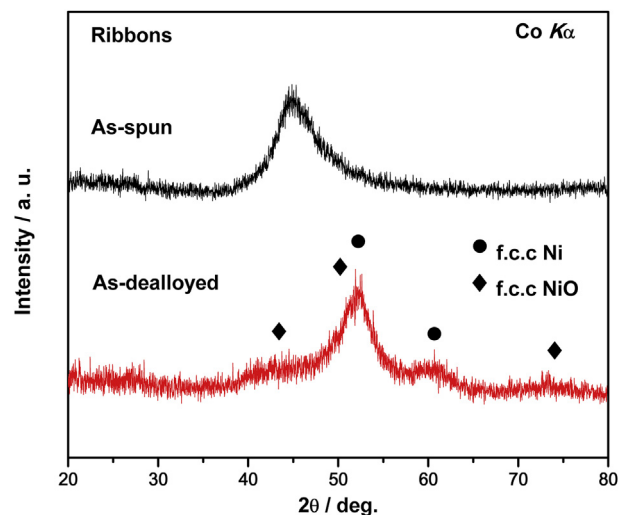

Fig. 1. XRD patterns of $Mg_{80}Ni_{19.2}Co_{0.8}$ metallic glass ribbons before and after dealloying in 2 g L^{-1} citric acid for 1.5 h at room temperature.

3. Results and discussion

3.1. Morphology characterization of the ss-npNi electrode

Nanoporous metals with good conductivity, high surface area and large porosity are good candidates for supporting the pseudocapacitive materials [2,7]. Metallic glasses are ideal precursors to obtain nanoporous metals by dealloying, since the metallic glasses are homogeneous in both microstructure and chemical composition, and free from defects such as segregations and grain boundaries [20]. Fig. 1 shows the XRD patterns of the $Mg_{80}Ni_{19.2}Co_{0.8}$ metallic glass ribbon before and after dealloying in 2 g L^{-1} citric acid for 1.5 h at room temperature. The as-spun ribbon exhibits a broad diffraction hump and no crystalline peaks, confirming its glassy nature. For dealloying, one side of the glassy ribbon was protected from the dealloying solution by covering with waterproof tape and the other side was exposed to the solution for dealloying. The broad peaks on the XRD pattern of the as-dealloyed ribbon correspond to face-centered cubic (fcc) Ni phase, indicating the preferential dealloying of element Mg and the formation of nanocrystalline Ni. The minor Co may be in solid solution with the fcc Ni phase. Fcc NiO is also identified, which may be produced by the naturally surface self-oxidation of Ni.

Scanning electron microscope (SEM) was used to study the microstructure of the dealloyed ribbon. Fig. 2a shows the cross-section of the as-dealloyed side of the ribbon. No cracks or flaws are observed at the boundary of the dealloyed layer and the matrix, which suggests firm binding between two parts. As shown in Fig. 2b–c, the dealloyed layer exhibits sponge-like bicontinuous nanoporosity with interconnected ultrafine ligaments and round open pores in three dimensions. The pore size is 15.5 ± 3.9 nm and the ligament size is 9.7 ± 2.0 nm. The nanoporous structure was studied by N$_2$ absorption-desorption isotherms, as is shown in Fig. S1. The surface area is estimated to be 100.6 m^2 g^{-1} by BET tests and the porosity is evaluated to be 62.4% by dividing the pore volume (0.160 ml g^{-1}) acquired from BJH desorption with the sample volume (0.256 cm^3 g^{-1}). The uniform morphology of the sponge-like nanoporous structure in a large scale, which inherited from the homogeneity of the metallic glass, is confirmed by the low magnification micrograph shown in Fig. 2b.

Fig. 3a–b shows the TEM images of the dealloyed layer. It can be observed that the round open pores are uniformly arranged and exhibit a narrow size distribution, confirming the well-defined nature of the sponge-like structure. The chemical composition of the dealloyed layer determined with EDS are shown in Fig. 3d. In comparison with the atomic percentage of Mg (80 at.%) in the ribbon matrix, the Mg content