



Cellular Ni sheet created by a simple oxidation-reduction process for enhanced supercapacitor performance



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ABSTRACT

In this article, we propose a simple redox process to *in-situ* create a cellular architecture on Ni solid sheet by the direct oxidization (O_2) and subsequent reduction (H_2) at 750 °C. Nanocrystalline $Ni(OH)_2$ is fabricated on the micro-porous Ni sheet (MPNS) using cathodic electrodeposition method to form a MPNS- $Ni(OH)_2$ electrode for supercapacitor. The obtained results indicate that the created micro-porous architectures expand the contact interfaces between the $Ni(OH)_2$ and Ni substrate and enhance its supercapacitor performance and cyclic stability.

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1. Introduction

Porous metals with cellular structure have attracted considerable attention for a diverse range of applications in catalysis, sensing, and bio-detection due to their large surface-to-volume ratios and excellent thermal and electrical conductivity [1]. Several chemical and physical approaches, such as direct foaming of liquid metals [2], sintering of metal powder slurry [3], electrodeposition [4], template method [5,6] and dealloying [7–11], have been proposed to fabricate various useful porous metals. Among them, developing low-cost porous transition metals for practical application, such as Ni and Cu, have been the recent topics of intense studies [12–14]. Until now, template and dealloying are two kinds of common methods to fabricate cellular Ni metals with smaller micro/nanoporous structure. For example, Ni foams with different porosities have been prepared by using porous templates [15]; commercial Raney Ni by the alkali leaching of Al from Ni–Al

alloy has been used as an industry powder catalyst for more than 80 years [12]. Recently, Ni–Mn [12,13], Ni–Cu [16,17], Ni–Al [18] and Ni–Zn [19] alloys as the precursors have been used to fabricate various nonporous Ni by chemical and electrochemical dealloying.

One of important application for these formed porous metals is as promising conducting substrates for supercapacitor based on metal oxides/hydroxides electrodes (such as MnO_2 , Co_3O_4 and $Ni(OH)_2$) [12,14,19–21]. These metal oxides/hydroxides with variable valence, showing high capacitance for storing electrical charge, have been widely used as electrode materials in pseudocapacitors [1,18,22–24]. However, the main drawback of these metal oxides/hydroxide electrode is their poor electrical conductivity, limiting their performance. It has been proved that the preparation of these metal oxides/hydroxide active materials on highly conductive porous metal substrates is a better strategy to fabricate high-performance binder-free supercapacitor. For examples, Wang et al. fabricated hierarchical nanoporous Ni by chemically dealloying gadiluted $Ni_{15}Al_{85}$ precursor, which was then electrochemically oxidized to form a p-Ni/ $Ni(OH)_2$ core/shell-like np-composite [18]. The hierarchical nanoporous metal/metal hydroxides composite exhibited a high areal capacitance ($\sim 4.76 \text{ Fcm}^{-2}$). Guo et al. fabricated 3-dimensional porous crack nickel (3-DPCNi)

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by electrodeposition of Zn-Ni alloy on Ni foam substrate, followed by chemically dealloying process [19]. Nanocrystalline MnO₂ was deposited on the 3-DPCNi to form hybrid electrodes, exhibiting high specific capacitance of the constituent MnO₂ at a high mass loading of 2.5 mg/cm² (~682.8 F/g).

However, it should be noted that these existing technologies for porous Ni metals are almost related to introduction of the second components and multiple process steps, which are generally complex and time-consuming. For example, porous inorganic and polymeric production for template method, metal components (Cu, Mn, Al and Zn), and alloying/dealloying process for dealloying technology. Furthermore, it is difficult to form a uniform cellular structure of pure Ni metal in comparison with the precious metal (Au and Pt) for dealloying process on a large scale due to its poor pore formation ability and low chemical ability [12]. Therefore, there is a continued interest in the discovery of cost-effective ways to make clean porous Ni metals.

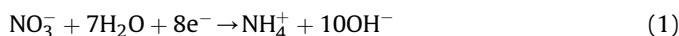
In fact, Ni-based cermet (such as Ni-(ZrO₂)_{0.92}(Y₂O₃)_{0.08}) (Ni-YSZ) is the most commonly used anode material of solid oxide fuel cell (SOFC) operating at elevated temperatures of 600–1000 °C [25,26]. An interesting phenomenon was pore formation in the Ni grains when the Ni-cermet anodes (Ni-YSZ) expected redox treatment under successive O₂ and H₂ atmosphere [27–29]. During oxidation process, some small internal pores were produced on the Ni grains mainly due to different diffusion coefficients between Ni²⁺ and O²⁻ in the nickel oxide like a pseudo Kirkendall effect [28]. During reduction the porosity further increased owing to the volume reduction of ~41% of nickel oxide to metallic nickel [27].

In this work, based on the finding of porosity of Ni during the reduction and oxidation (redox) process, we proposed a novel and cost-effective pathway to *in-situ* create cellular structure efficiently on a Ni sheet through the simple oxidation-reduction (redox) process. This process is mainly related to the interaction between gas reactants (O₂ and H₂) and Ni solid precursor, which is in a clean reaction environment without any other chemical element. Furthermore, Ni(OH)₂ is coated on the surface of micro-porous Ni sheet (MPNS) by cathodic electrodeposition method to form a MPNS-Ni(OH)₂ electrode for supercapacitors, which was used to further verify the application of MPNS as a promising supercapacitor substrate. The obtained results indicate that the created cellular structure in micro-meter diameter can expand the contact interfaces between the Ni(OH)₂ and Ni substrate, resulting in an enhanced capacitance and stability.

2. Experimental

Nickel sheets (99.9%, 0.05 mm thickness, Qingyuan Metal Materials, China) were used as the primary raw material in this work. To create the micro-porous architectures on these Ni sheets, they were firstly put in the center of an open quartz tube (~22 mm in an inner diameter) and oxidized to NiO in pure O₂ (100 sccm) for 1 h at 750 °C. Pure argon with a flow rate of 100 sccm was fed in order to blow away the remaining O₂ out of the tube in 30 min. Afterward, the high purity H₂ (100 sccm) was then fed into the tube to implement the reduction process of the formed NiO. Finally, these samples were cooled to room temperature under H₂ atmosphere and a micro-porous Ni sheet (MPNS) was obtained through this simple redox process.

A piece of MPNS (1 × 1 cm²) was washed with acetone, ethanol and deionized water for several times to ensure its surface was well cleaned before use. Nickel hydroxide (Ni(OH)₂) film was fabricated on the MPNS by the cathodic electrodeposition process in a 0.1 M nickel nitrate solution and 0.075 M sodium nitrate solution. Cathodic electrodeposition of the Ni(OH)₂ by the principle of work is as follows:



The electrodeposition was conducted at a current density of 1 mA/cm² for 4 min at room temperature (~25 °C) in a three-electrode configuration with a platinum counter electrode and an Hg/HgO reference electrode. The mass loading of Ni(OH)₂ was 0.14 mg via charge flow throughout the electrodeposition process based on the assumption of 100% current efficiency. Almost the same amount of Ni(OH)₂ was also deposited on a fresh Ni sheet (NS) to fabricate a comparable electrode.

The phase of the samples was characterized by X-ray diffraction (XRD, Rigaku D/max2200, Japan) using a Cu K α radiation. The morphologies of these samples were examined by scanning electron microscopy (SEM, Hitachi SU800, Japan). Electrochemical measurements were performed in a typical three-electrode glass cell with a Pt counter electrode and an Hg/HgO reference electrode. 1.0 M KOH solution was employed as electrolyte. Cyclic voltammetry (CV) of the NS/MPNS-MnO₂ electrodes was conducted in a potential range of 0–0.6 V at various scan rates ranging from 2 to 50 mV/s using an electrochemical station (Shanghai CH Instrument CO. CHI604C, China). The galvanostatic charge/discharge (GCD) tests were performed in a potential range of 0–0.5 V using the Neware equipment (Shenzhen, China).

3. Results and discussion

Fig. 1(a) is the scanning electron microscope (SEM) image of fresh Ni sheet, which shows a smooth surface. Whereas, after the oxidation treatment by O₂ at 750 °C a number of particles grew out of the surface of the Ni sheet, suggesting the formation of NiO grains (Fig. 1(b)). This was supported by the color change of Ni sheet from the original bright white to dark. As the Ni sheet was exposed to H₂ for 2 h at 750 °C, it was interesting to find that these extrusive NiO grains disappeared and some visible pores were observed on the surface of Ni sheet (Fig. 1(c)). The thickness of the porous layer on the top of the Ni sheet was ~3.4 μm (Fig. 1(d) and (e)), implying that here the redox process can be considered to be a surface treatment and inner part of the Ni sheet was not vulnerable to the redox reactions due to the formation of dense oxidation film during oxidation process. Thus, the inner metal solid maintained remarkable mechanical integrity and robustness of the MPNS, while the outside porous layer provided high surface area for deposition of Ni(OH)₂.

The average diameter of these formed pores was ~1.3 μm (in the range of ~0.5–3.4 μm) (Fig. 2(a)). The similar phenomenon was observed on Ni-YSZ anode of SOFCs that smaller pores (~50 nm) were formed associated with the reduction of NiO to Ni by H₂ at 700 °C [27]. It can be seen that the formed pores on Ni sheet were as large as several microns, which was much larger than those on Ni particles in Ni-YSZ anode. This phenomenon is related to the microstructure difference between the Ni sheet and Ni-YSZ anode. For Ni sheet Ni grains on the surface were connected continuously, meaning that a continuous coarsening of Ni atom could take place and a pore could grow up to micron-scale during a reduction process. While in Ni-YSZ anode, Ni particles are separated by YSZ particles and may be connected weakly, thus only nano sized pores can formed in a reduction process. The XRD patterns (Fig. 2(b)) and energy dispersed X-ray (EDX) analysis (Fig. 2(c)) of the porous Ni sheet exhibited that it consisted of pure Ni and there were no other phase formed after the redox treatment process. The gold peaks detected by EDX originated from the gold coating for SEM characterization. The results indicated a fully clean cellular architecture

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