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# Enhanced supercapacitor performance by fabricating hierarchical nanoporous nickel/nickel hydroxide structure

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## ABSTRACT

Hierarchical nanoporous Ni with both nanopores (less than 10 nm) and big pores/channels (hundreds nm) was fabricated by chemically dealloying a diluted Ni<sub>15</sub>Al<sub>85</sub> precursor in 1.0 M NaOH aqueous solutions. Due to the active property of nanoscale Ni, the Ni nano-ligaments can be easily converted to Ni/Ni(OH)<sub>2</sub> core-shell-like nano-composite by electrochemical oxidation. Compared with uniform nanoporous Ni, the hierarchical nanoporous Ni provides more void space and allows the formation of more active Ni hydroxides inside. Consequently, the hierarchical nanoporous metal/metal hydroxides composite exhibits a high areal capacitance ( $\sim 4.76 \text{ F cm}^{-2}$ ) with good rate performance and cycling stability.

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## 1. Introduction

Electrochemical supercapacitors are considered to be one of the most promising energy storage devices due to their high power density and long lifespan [1]. Transition metal oxides (e.g., MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO, etc.) have attracted much research interest due to their high theoretical capacitance from surface reversible redox reactions (pseudo-capacitance) [2,3]. However, these transition metal oxides usually suffer from poor electrical conductivities which limit their performance, especially at high rates [2].

To solve these problems, recently, the growth of metal oxides on conductive free-standing substrates has been demonstrated to be a better strategy to fabricate binder-free supercapacitor electrodes compared with the traditional slurry-coating method [4]. This design makes the active metal oxides possess a better conductivity and also makes additives and binders completely unnecessary. So far, various metal oxides have been deposited or in situ formed on conductive substrates such as 3D Ni or Cu foam [5–7]. Although high mass specific capacitances have been achieved in most of these works (only the mass of deposited metal oxides is counted), their areal (volume) specific capacitance is still too low due to the large pore size of Ni foam (several hundred micrometers). Considering the practical applications, enhancing

the utilization rate of the limited volume in a portable electronic device is quite important. To achieve a high areal (volumetric) capacitance, quite recently, we prepared a high-surface-area nanoporous Ni (np-Ni) by dealloying a Ni<sub>30</sub>Mn<sub>70</sub> alloy [8,9]. However, when used as a binder-free supercapacitor electrode, the uniform nanoporous electrode only exhibited an areal capacitance of  $\sim 1.2$ – $2.1 \text{ F cm}^{-2}$  due to the small pore size ( $\sim 10 \text{ nm}$ ) and limited void space for active Ni oxides/hydroxides formation.

During dealloying to prepare nanoporous metals, a single phase precursor would lead to a uniform nanoporous structure after complete dealloying. However, if the precursor contains two phases and one phase can be completely removed and the other can be selectively dealloyed, dealloying this precursor would produce hierarchical nanoporous structure with both big pores/channels (formed by the complete removal of one phase) and small nanopores/ligaments (formed by the dealloying of the other phase). Normally, the formation of more void space is considered as a negative phenomenon, which would affect the mechanical properties of the nanoporous metals. However, in this work, by microstructure design, we fabricate a hierarchical np-Ni with both large pores/channels and small nanoscale ligaments/pores by dealloying a diluted Ni<sub>15</sub>Al<sub>85</sub> precursor. Importantly, we demonstrate that the large pores/channels with a diameter of hundreds of nanometers can provide sufficient space for the growth of more thin oxide/hydroxide nanosheets (in situ formed from the highly active nanoscale Ni ligament), resulting in an enhanced capacitance.

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## 2. Experimental

$\text{Ni}_{15}\text{Al}_{85}$  thin films with a thickness of  $\sim 28 \mu\text{m}$  were prepared by a melt-spinning method using pure Ni and Al ( $> 99.9 \text{ at}\%$ ). Nanoporous Ni was prepared by chemical dealloying in 1.0 M NaOH aqueous solution for 24 h at room temperature. After dealloying, the np-Ni was electrochemically oxidized by continuous cyclic voltammetry (CV) cycling from  $-0.2$  to  $0.6 \text{ V}$  vs SCE at  $10 \text{ mV s}^{-1}$  for 300 cycles in 1.0 M KOH aqueous solution to prepare the np-Ni/ $\text{Ni}(\text{OH})_2$  composite.

The samples were characterized by X-ray diffraction (XRD) using a Cu  $K\alpha$  radiation, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDS). Electrochemical tests were performed on an electrochemical workstation (CHI 660e) in a three-electrode cell with a Pt foil served as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. For capacitive measurements, 1.0 M KOH was chosen as the electrolyte. Three thin film were bound together to enhance the mechanical properties. The nominal area of the samples immersed into the electrolyte was  $\sim 0.2 \text{ cm}^2$ . The areal specific capacitance ( $C$ ) was calculated by:  $C = I\Delta t / S\Delta V$ , where  $I$  is the current,  $\Delta t$  is the discharge time,  $\Delta V$  is the voltage range and  $S$  is the nominal area of the free-

standing electrode.

## 3. Results and discussion

The composition of the  $\text{Ni}_{15}\text{Al}_{85}$  alloy precursor was controlled by the feeding ratio of the pure Ni and Al. XRD analysis shows that the precursor mainly contains two phases (Fig. 1a). One is face-centered cubic (FCC) pure Al phase which can be completely removed during the corrosion and the other is  $\text{NiAl}_3$  phase which can be selectively dealloyed. After the dealloying, the XRD pattern shows that both the pure Al phase and the  $\text{NiAl}_3$  phase disappear (Fig. 1b). The new diffraction peaks formed can be ascribed to FCC Ni and Ni oxides formed by the in situ oxidation of the nanoscale Ni. Figs. 2a and 2b show low magnification SEM images of the dealloyed np-Ni. It can be observed that the np-Ni exhibits interconnected big pores/channels with diameter of hundreds nanometers. The 3D uniform porous structure also suggests that these pure Al phase are very uniformly distributed in the precursor. As shown in a typical TEM image in Fig. 2c, the clear contrast of the dark ligaments and bright pores are uniformly distributed, confirming that the solid Ni part possesses ultrafine nanoporous ligament-pore structure with a ligament size of less than 10 nm.

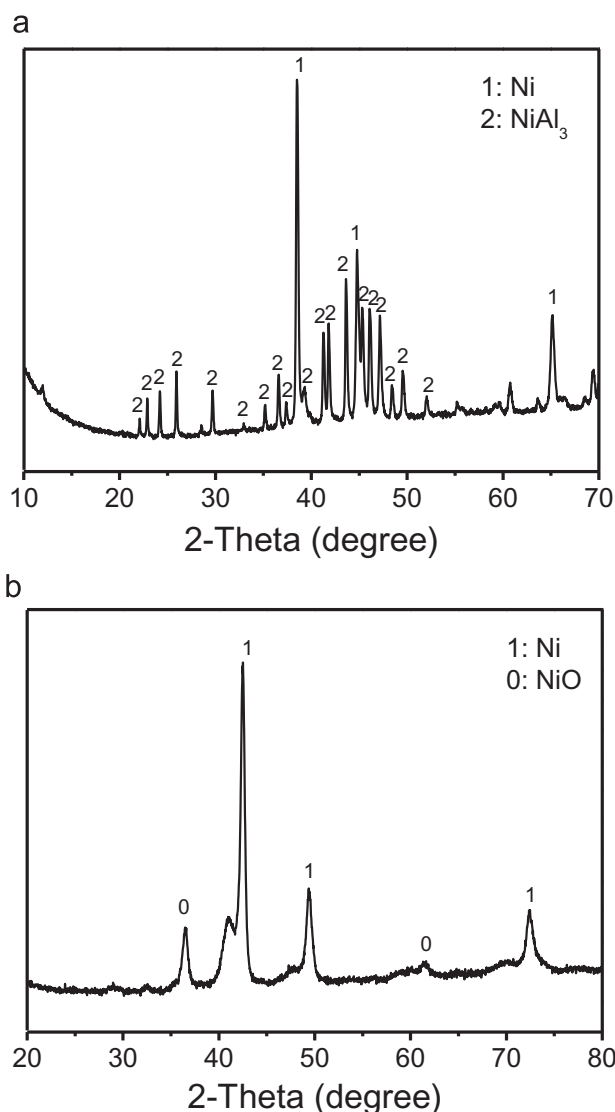


Fig. 1. XRD patterns of the  $\text{Ni}_{15}\text{Al}_{85}$  precursor before (a) and after (b) dealloying.

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