



## Electrochemical dealloying using pulsed voltage waveforms and its application for supercapacitor electrodes



Jie Zhang<sup>a,b,c</sup>, Yawen Zhan<sup>a,b,c</sup>, Haidong Bian<sup>a,c</sup>, Zhe Li<sup>a,b,c</sup>, Chun-Kwan Tsang<sup>a,b,c</sup>, Chris Lee<sup>a,b,c</sup>, Hua Cheng<sup>a,b,c</sup>, Shiwei Shu<sup>c</sup>, Yang Yang Li<sup>a,c,d,\*</sup>, Jian Lu<sup>b,e</sup>

<sup>a</sup> Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

<sup>b</sup> Department of Mechanical and Biomedical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

<sup>c</sup> Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

<sup>d</sup> City University of Hong Kong Shenzhen Research Institute, 8 Yuexing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen, China

<sup>e</sup> Centre for Advanced Structural Materials, City University of Hong Kong Shenzhen Research Institute, 8 Yuexing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen, China

### HIGHLIGHTS

- A novel dealloying method using pulsed voltage waveforms is invented.
- It can lower the compositional threshold for dealloying to take place.
- It can more thoroughly remove the more reactive metal component, producing a porous metal of higher purity and higher porosity.
- It can lead to thinner ligaments.
- It can enable supercapacitor electrodes with better performance.

### ARTICLE INFO

#### Article history:

Received 10 September 2013

Received in revised form

14 November 2013

Accepted 16 November 2013

Available online 28 November 2013

#### Keywords:

Dealloying

Pulsed voltage

Electrodeposition

Nanoporous metal

Supercapacitor

### ABSTRACT

Dealloying is an important industrial technique for generating nanoporous metallic structures by selectively leaching out the more reactive metal component from an alloy material. A constant voltage is often applied to facilitate the dealloying process. Here we report the first study on dealloying with the application of a voltage waveform—specifically, pulsed voltage waveforms are applied for dealloying Ni–Cu alloys. It is found that pulsed dealloying voltage waveforms can exert a strong impact on the dealloying process by 1) significantly lowering the compositional threshold of the more reactive metal component for the dealloying reaction to take place, 2) more thoroughly removing the more reactive metal component and thus producing a porous metal of higher purity and higher porosity (volume fraction of voids), and 3) greatly affecting the morphology of the generated porous metal structure (e.g., leading to significantly thinner ligaments). The nanoporous metallic materials obtained by the pulsed voltage waveform enable supercapacitor electrodes of significantly better performance than the counterpart dealloyed with a constant voltage.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

Nanoporous metals are intensively investigated for their importance in a wide range of applications. Among the different techniques for fabricating nanoporous metals, dealloying is a convenient industrial technique that is commonly used to generate nanoporous metals by selectively dissolving the more reactive

metal component from an alloy system, often with the aid of an electric field [1,2]. Various kinds of nanoporous metals (such as Ni, Au, Ag, Cu, and Pt) have been fabricated using the dealloying method, and applied for different applications [3–14] such as: sensors, catalysts, photonic materials, batteries, supercapacitors, etc. For example, dealloyed nanoporous Ni has lately attracted much attention for its applications in photonic materials, [10] electrochemical capacitors, [6] and electrocatalysts for hydrogen evolution [15]. Furthermore, dealloying is being applied to ever-expanding material systems. Dealloying process in intermetallics and multi-phase alloy films, [16,17] tough nanoporous metals by controlled electrochemical dealloying, [18] and selective etching of

\* Corresponding author. Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong.

E-mail addresses: [yangli@cityu.edu.hk](mailto:yangli@cityu.edu.hk) (Y.Y. Li), [jianlu@cityu.edu.hk](mailto:jianlu@cityu.edu.hk) (J. Lu).

the more noble component of an alloy, [19] have all been demonstrated. Additionally, alternating dealloying and electroplating treatments have been utilized for generating interesting porous metallic materials [20]. One of the major challenges present for the current dealloying technology is on how to control the morphology and composition of the generated porous materials. To address this challenge, the effects of different dealloying parameters, such as the etchant concentration, dealloying time, and dealloying temperature, have been studied [1,21]. Nevertheless, little attention has been paid to understand the impact of modulated anodization voltages.

Here we report the first study on dealloying with the application of a voltage waveform. To introduce our motivation, a brief introduction of the dealloying mechanism is necessary. Previous studies [22] have shown that, for binary alloys, after the more reactive metal atoms are dissolved at alloy/electrolyte interface, the more inert metal atoms at alloy/electrolyte interface undergo an atom rearrangement process and form clusters, exposing more the underlying more reactive metal atoms. The concurrent processes of chemical dissolution of the more reactive atoms and atom rearrangement of the more inert atoms allow the dissolution front to proceed and eventually penetrate throughout the whole alloy. In other words, dealloying is resulted from the dynamic interplay between atom rearrangements of the more inert metal species and the chemical etching of the more reactive metal species. Conversely, it is well-known that the chemical etching rates of metals can be easily controlled by adjusting the bias applied. Therefore, one should be able to affect the dealloying process by adjusting the bias applied. To verify this hypothesis, we dealloyed Ni–Cu alloys with pulsed voltage waveforms to generate nanoporous Ni. It was found that dealloying under a pulsed electric field provides a simple but powerful method to conveniently control the structures and compositions of the porous metals generated (e.g., more thoroughly dealloyed nanoporous metal with higher porosity and higher purity can be easily achieved) and to effectively lower the Dealloying Threshold (*DT*), defined here as the compositional threshold of the more reactive metals required for dealloying to take place throughout the alloy.

Moreover, this novel dealloying method proves to be particularly effective for treating alloys electrodeposited with surfactants. In order to eliminate voids and generate smoother films with finer grains, surfactants are often added into electroplating bath [23,24], however, the alloy films thus obtained are often found difficult to dealloy. Here we demonstrate that dealloying with pulsed voltage waveforms is a particularly powerful method to address this difficulty.

Finally, when used as the supercapacitor electrode materials, porous Ni fabricated using this novel dealloying method displays significantly higher specific capacitance than the conventionally dealloyed counterpart.

## 2. Experimental

### 2.1. Electrodeposition of Ni–Cu

A three-electrode cell controlled by a potentiostat (HEKA, PG 310) is used with indium tin oxide-coated glass (CSG PVTech Co., Ltd., 1.0 cm × 1.0 cm) as the working electrode, a platinum ring as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All the electrochemical experiments are carried out at room temperature (~20 °C) and all the potentials in this paper are reported in reference to the SCE (0.244 V vs. the standard hydrogen electrode). Electrodeposition is performed in an aqueous electrolyte: 0.5 M nickel (II) sulfamate tetrahydrate (Aldrich, 98%), 0.005 M copper (II) sulfate pentahydrate (Riedal–

Dehaën), and 0.6 M boric acid (Riedal–Dehaën). The pH value of the electrolyte is measured to be 3.83. For experiments with surfactants added in the electrolyte, 3 μg mL<sup>-1</sup> of saccharin (International Laboratory USA) is added into the electrolyte. All chemicals are of analytical grade and used without further purification. The Ni–Cu films are typically deposited at –0.820 V for 130 min.

### 2.2. Dealloying

After the Ni–Cu film is deposited, the film is anodically etched at the room temperature in the same electrolyte used for electrodeposition. Pulse dealloying is carried out with the voltage periodically modulating between  $V_1$  and  $V_2$  for time durations of  $t_1$  and  $t_2$ , respectively, for an overall period of time of  $t_{\text{dealloy}}$ . Unless otherwise stated,  $V_1 = 0.5$  V,  $t_1 = 1$  s,  $V_2 = 0.06$  V,  $t_2 = 5$  s, and  $t_{\text{dealloy}} = 30$  min (typically the dealloying current drops to essentially zero within this period). For comparison, dealloying is also performed at a constant voltage (ConstV) of 0.5 V for 30 min.

### 2.3. Characterizations

The scanning electron microscope (SEM, JEOL JSM-820) equipped with the energy dispersive X-ray spectrometer (EDX) (Oxford INCA 7109) is used to examine the film morphology and composition. The X-ray diffraction (XRD) patterns are collected using an X-ray diffractometer (Rigaku SmartLab). The cyclic voltammetry (CV) measurements are conducted on the as-electrodeposited (not dealloyed) Ni–Cu films in the electrolyte used for electrodeposition and dealloying. The voltage is scanned between 0.5 V and –0.75 V at a rate of 50 mV s<sup>-1</sup> with a potentiostat (PAR Verastat 3).

### 2.4. Electrodeposition of Ni<sup>III</sup>O(OH)

Ni<sup>III</sup>O(OH) is electrodeposited at 0.9 V in a solution of nickel (II) sulfate (0.5 M, Aldrich, ACS reagent) and ammonium hydroxide solution (0.5 M, Riedal–Dehaën, ACS reagent), following the previously reported method [25]. The amount of charge passed during the electrodeposition of Ni<sup>III</sup>O(OH) is set at 0.2 C cm<sup>-2</sup>. The actual mass of Ni<sup>III</sup>O(OH) deposited is measured by an analytical balance (METTLER AT250 with the resolution of 0.01 mg and the readability (standard deviation) of 0.02 mg). After deposition, the sample is rinsed with deionized water and ethanol separately and then dried under N<sub>2</sub>.

### 2.5. Electrochemical measurements for supercapacitor applications

Electrochemical measurements for supercapacitor applications are performed at room temperature with a potentiostat (PAR Verastat 3). A three-electrode system is used with the SCE as the reference electrode, a platinum foil (2 cm × 2 cm) as the counter electrode, and the sample as the working electrode. The electrolyte used is an aqueous solution of 1 M KOH. Cyclic voltammetry measurements are performed between –0.5 V and 0.5 V with a scan rate of 5 mV s<sup>-1</sup>. Cyclic chronopotentiometric profiles are measured at a current density of 1.5, 3, 7.5, 15, 30 A g<sup>-1</sup>, and the cycling stability is tested with a constant current density of 7.5 A g<sup>-1</sup> for 1000 cycles.

## 3. Results and discussion

The voltage value of the pulsing steps is determined from the cyclic voltammogram measurement (Fig. S1) of the as-deposited Ni–Cu film: the pulse bias is set to be 0.06 V based on the observation that at 0.06 V a very low current was generated. Minimum current flow is desired for the pulsing steps in order to eliminate

Download English Version:

<https://daneshyari.com/en/article/7737486>

Download Persian Version:

<https://daneshyari.com/article/7737486>

[Daneshyari.com](https://daneshyari.com)