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Research Letter

Processing and Electrochemical Property Characterization of Nanoporous Electrodes for Sustainable Energy Applications

Jenny X. He,¹ Shruti Baharani,² and Yong X. Gan^{1,2}

¹Department of Mechanical Engineering, Albert Nerken School of Engineering,
The Cooper Union for the Advancement of Science and Art, New York, NY 10003, USA

²Department of Mechanical, Industrial and Manufacturing Engineering,
College of Engineering, University of Toledo, Toledo, OH 43606, USA

Correspondence should be addressed to Yong X. Gan, yong.gan@utoledo.edu

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Preparation and electrocatalytic reactions of nanoporous materials in biodegradable fluids were studied. Electrochemical etching was conducted to selectively extract metallic elements from alloys to form porous structures. Electrocatalytic properties of the porous electrodes were characterized. Comparative studies on the electrochemical activities of the nanoporous metallic electrodes with bulk metallic wire catalysts were performed. It is found that the current density at the nanoporous electrode is three times higher than that of the bulk electrode.

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1. Introduction

Nanoporous materials may be made via various methods. Chemical etching is an easy way to make nanoporous metals [1–3], while co-evaporation may be used for preparation of nanoporous metal oxides [4]. Nanoporous Au specimens with ligament-like structures were fabricated by dealloying [1]. Smith et al. [2] prepared nanoporous gold films through de-alloying AuAl₂. The nanoporous gold has void densities between 45% and 65%. Zhou et al. [3] proposed another way to fabricate nanoporous gold film. The starting materials are copper and gold alloys thin films obtained through vacuum deposition. The formation of ultra-thin nanoporous gold films from the Au-Cu alloy films involved chemical etching by hydrochloric acid or by nitric acid.

It is well known that preparing nanoporous metals via chemical etching is very difficult to control in view of the reaction kinetics. For example, the change in the concentration of the acids, and the temperature fluctuation in the etchant solutions have significant effect on the ligament morphology, void density and strength of the nanoporous metals. During the process of pore formation, the capillary effect causes surface relaxation and affects the dimension of the nanoporous metals [5]. Another drawback

of chemical dealloying is the environmental pollution due to the frequent use of high concentration, volatile reagents such as concentrated hydrochloric acid and/or nitric acid. One of the objectives of this work is to develop a better controllable dealloying process than chemical etching. Preliminary research results of electrochemical dealloying in low concentration acids to generate nanoporous nickel and gold will be presented. Electrocatalytic properties of the nanoporous Ni and Au in agricultural products for sustainable energy applications will be evaluated.

2. Materials and Experiments

Annealed gold-nickel wire with the composition of Au : Ni = 82 : 18 wt% was purchased from Alfa Aesar, Ward Hill, Md, USA. The diameter of the Au-Ni wire is 0.5 mm. Copper-nickel wire with the diameter of 0.5 mm was also purchased from the same company. The composition of the Cu-Ni wire is Cu : Ni = 55 : 45 wt%. Platinum with the diameter of 0.25 mm and the purity of 99.997 wt% was purchased from Alfa Aesar. Other chemicals such as hydrochloric acid, sulfuric acid, acetone with ACS purities were ordered from Alfa Aesar. Four biodegradable materials

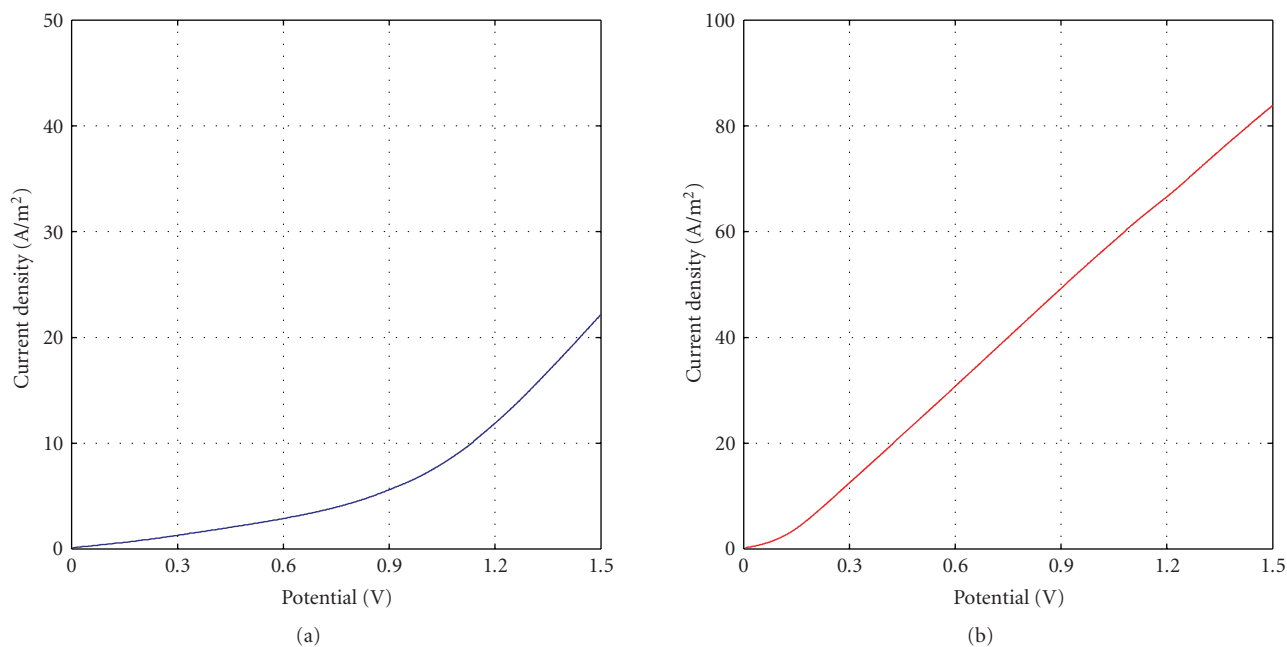


FIGURE 1: Cyclic voltammograms of Ni electrode in grapefruit juice: (a) without pore; (b) with pores.

were used in characterizing the electrocatalytic behaviors of the nanoporous Au and Ni. They are tomato, milk, chocolate drink and grape fruit juice. All these products were purchased from Trade Fair, Forest Hills, USA. A three-electrode system was set up for both electrochemical dealloying and electrocatalytic property characterization. The electrodes are connected with a CHI600B Electrochemical Analyzer. The three electrodes are the Ag/AgCl reference electrode, the work electrode, and the platinum counter electrode. Selective removal of Ni for Au-Ni alloy and Cu from Cu-Ni alloy by electrochemical etching in diluted HCl and H₂SO₄ was conducted. First, HCl aqueous solution with the concentration of 9 wt% was made. The H₂SO₄ used has the concentration of 25 wt%. Second, the Au-Ni and Cu-Ni were made into two separate work electrodes. Each work electrode was assembled with the Ag/AgCl reference electrode, and the platinum counter electrode in the cell containing HCl or H₂SO₄ solution. Under controlled potentials generated by positive cyclic voltammetry (CV) scan, selective dissolving of metal elements was achieved. As a result, nanoporous Au and nanoporous Ni were obtained. The electrocatalytic activities of the nanoporous Au and nanoporous Ni in the biodegradable substances of fresh tomato, milk, chocolate drink, and grape fruit juice, respectively, were characterized by cyclic voltammetry (CV). The scanning rate is 0.01 V/s. The tests were done at the same temperature of 25°.

3. Results and Discussion

3.1. Effect of Nanopores on Catalytic Oxidation Behaviors. In order to examine the effect of nanopore on the electrocatalytic behavior of electrodes in biodegradable fluids,

comparative studies on nanoporous nickel and bulk nickel were conducted. Electrochemical catalysis behavior of both bulk Ni and nanoporous Ni in the grape fruit juice was studied by cyclic voltammetry and the results are shown in Figures 1(a) and 1(b). The current density at the nanoporous electrode, as shown in Figure 1(b), is calculated based on the initial area of the alloy before dealloying. The cyclic voltammogram of the bulk Ni as shown in Figure 1(a) has the reaction controlled feature as the porous Ni electrode. However, the current density at the nanoporous Ni is as 4 times high as that at the bulk nickel electrode, which reveals that the nanoporous electrode is more effective than the bulk Ni in electrochemical catalytic oxidation of the grape fruit juice.

Some insights into calculating the area of nanoporous material can be obtained from the results. Typically, the charge associated with the electrochemical catalytic oxidation is proportional to the real surface area of the electrode. Therefore, the magnitude of the current density can be used to calculate the surface area of the electrode. It is shown that the current density for the electrode increased due to the dealloying of copper from the nickel-copper alloy wire. The results in Figure 1 indicates that the real electrochemically active area of the pore electrode is about 3 times higher than the bulk wire material. Similar results were also obtained for gold-nickel material.

The electrocatalytic behavior of the above used Ni electrodes without nanopores and with nanopores in fresh tomato was studied. At the same potential, the current density at the bulk nickel electrode shown in Figure 2(a) is lower than that at the nanoporous nickel electrode shown in Figure 2(b). This trend is the same as found in the grape fruit juice case. The oxidation of tomato on the bulk electrode

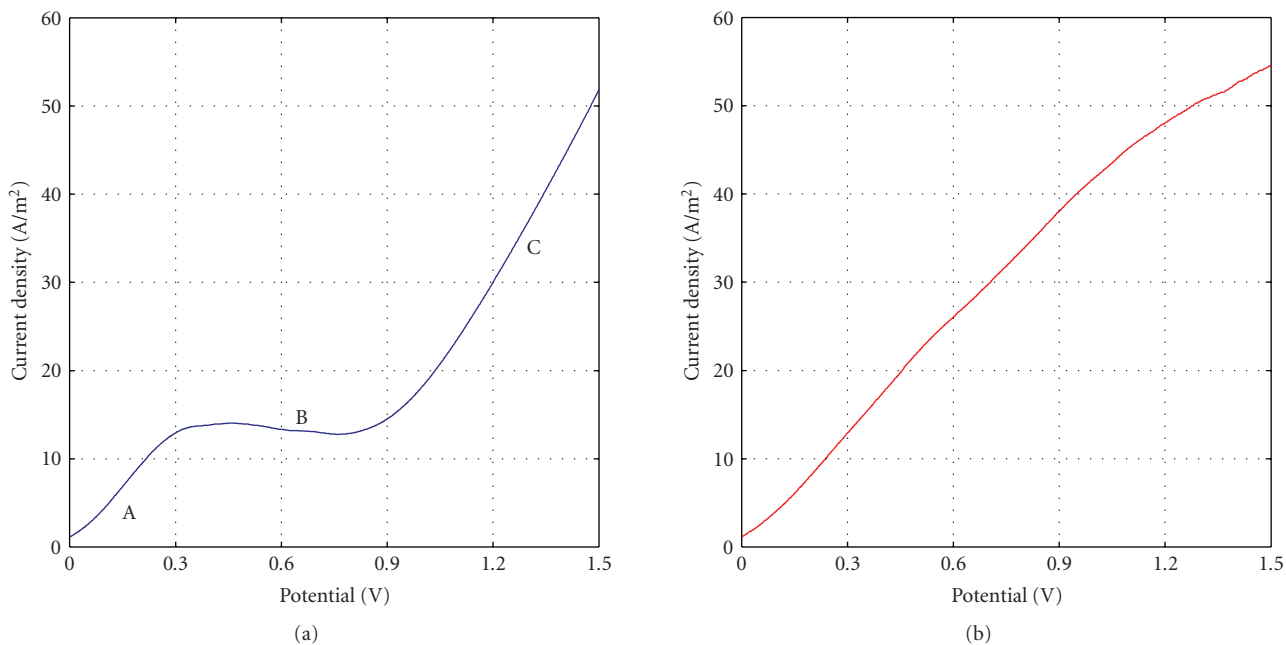


FIGURE 2: Cyclic voltammograms of Ni electrode in tomato : (a) without pore ; (b) with pores.

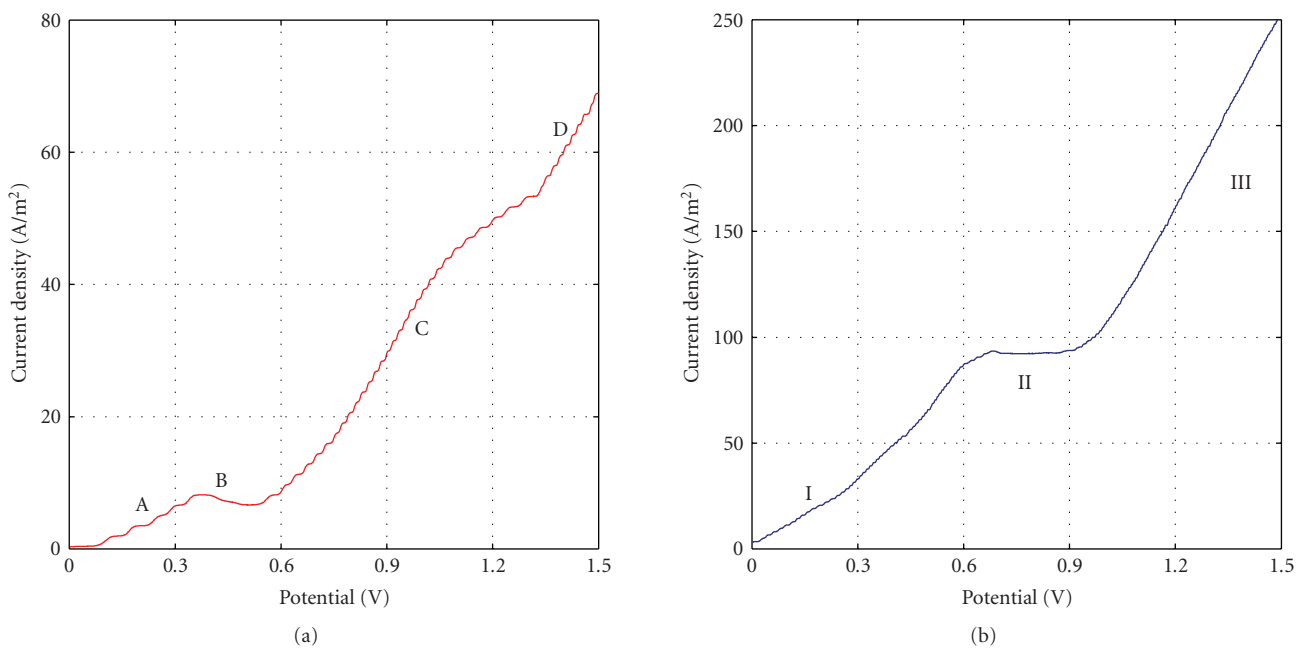


FIGURE 3: Cyclic voltammograms of the nanoporous Au and nanoporous Ni in milk: (a) nanoporous Au; (b) nanoporous Ni.

has three distinct stages as mark by “A”, “B”, and “C” on the cyclic voltammogram of Figure 2(a). In stage “A” and “C”, oxidation reactions are the controlled processes. In stage “B”, the diffusion controlled feature is shown. At the nanoporous Ni electrode, only the reaction controlled behavior in the tomato juice was found, which is revealed by the cyclic voltammetry results in Figure 2(b).

3.2. Effect of Metal Type on Catalytic Oxidation Behaviors. The electrochemical catalytic behavior of both nanoporous nickel and nanoporous gold in biodegradable fluids was studied to examine the effect of metal types. Both the nanoporous Au and nanoporous Ni were prepared by electrochemical dealloying in the 9% HCl electrolyte. Figure 3(a), the cyclic voltammogram of nanoporous Au in

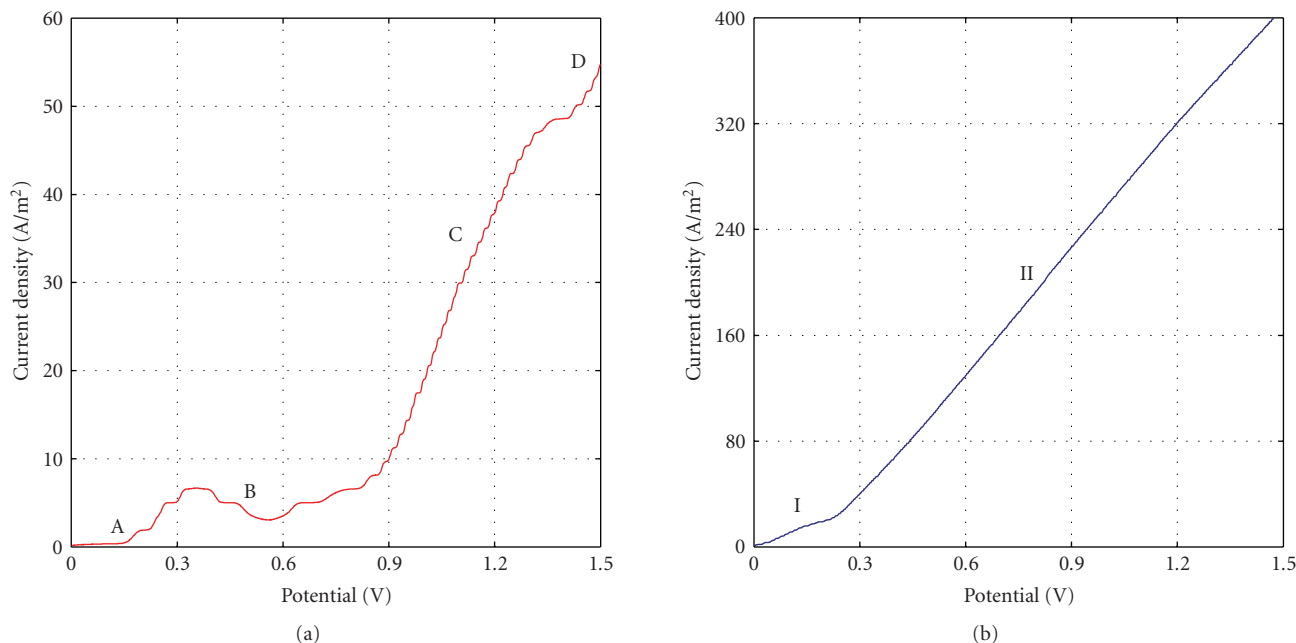


FIGURE 4: Cyclic voltammograms of the nanoporous Au and nanoporous Ni in chocolate dink: (a) nanoporous Au; (b) nanoporous Ni.

the milk, shows four stages of electrochemical oxidation as marked by “A”, “B”, “C”, and “D”. One of the reasons for such a complex cyclic voltammogram is due to the complexity of the composition of the milk. The cyclic voltammogram of nanoporous Ni in the milk, also shows a multi-stage electrochemical oxidation behavior as marked by “I”, “II”, and “III” in Figure 3(b). Stages “I” and “III” are reaction controlled behaviors, while stage “II” is the diffusion-controlled behavior. At any given potential, the current density at the nanoporous Ni electrode is higher than that at the nanoporous Au electrode. This is reasonable because the nominal porosity of the nanoporous Au is about 18%, while this value for the nanoporous Ni is about 55%. The nanoporous Ni has much higher surface area than that of the nanoporous Au. Therefore, the specific current calculated based on the initial surface area for the nanoporous Ni electrode is higher.

The electrochemical catalytic behavior of the nanoporous nickel and nanoporous gold in the chocolate drink was also studied. Figure 4(a), the cyclic voltammogram of nanoporous Au in the chocolate drink, reveals four stages of electrochemical oxidation as marked by “A”, “B”, “C”, and “D”. The cyclic voltammogram obtained from the test in the chocolate drink is very similar to that obtained from the milk. This is because the compositions of the two biodegradable solutions are very close. The cyclic voltammogram of nanoporous Ni in the chocolate drink only shows two distinct stages denoted by “I”, and “II” in Figure 4(b). Both stages “I” and “II” are under reaction control. Similar to the results shown in Figure 3(a) and 3(b), the current density at the nanoporous Ni electrode is higher than that at the nanoporous Au electrode because both the nominal porosity and the active surface area of the nanoporous Ni are higher than those of the nanoporous Au.

It should be pointed out that for electrochemical oxidation of many materials, pH value may have very significant effect on the process. In this paper, we measured the pH value of the fluids. The pH value for fresh tomato is around 6.0. The pH value for chocolate drink is 6.5. The pH value for the grape fruit juice is 6.3. After the electrochemical tests, the pH value for each fluid dropped less than 0.1 unit. Such a little change in the pH value might cause the slightly shift of oxidation peak according to the calculation by Nernst equation, but it should not change the characteristic peaks. Therefore it is concluded that the difference in electrocatalytic properties of different fluids is not related to the minor change of the pH value.

Transmission electron microscopic (TEM) study of the porous materials is helpful in examining the high resolution morphology, showing the dislocation structure around the nanopores, determining the crystallographic orientation of the nanopores. This would be one of our future work on the porous materials.

4. Conclusions

Electrochemical dealloying and electrocatalytic behaviors of nanoporous metals in biodegradable fluids were performed. High electroactive surface areas in nanoporous nickel and nanoporous gold were obtained. Based on the preliminary research, the following concluding remarks can be made.

Comparative studies on nanoporous and bulk metallic catalysts show that nanoporous electrodes are more effective than bulk electrodes in electrochemical catalytic oxidation of biodegradable fluids. The cyclic voltammogram of the bulk Ni has the same reaction controlled feature as the porous Ni electrode. However, the current density at the nanoporous Ni is as 4 times high as that at the bulk nickel electrode.

The electrochemical catalytic properties of the nanoporous nickel and nanoporous gold in biodegradable fluids are different. Although multi-stage catalytic oxidation behaviors are found at both types of electrode, the nanoporous nickel shows a reaction controlled electrochemical catalytic behavior. The nanoporous gold shows both reaction and diffusion controlled mechanisms.

Acknowledgments

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