NANOPOROUS NICKEL FOR ELECTROCHEMICAL ENERGY CONVERSION

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ABSTRACT
Biodegradable products such as fruits, vegetables and milk have recently been studied as sustainable energy sources. In this work, preparation and electrocatalytic reactions of nanoporous materials in biodegradable fluids made from agricultural products were studied. In order to obtain high efficiency catalysts, 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 catalysts were performed. It is found that nanoporous structures with high electroactive surface areas can be obtained through controlled electrochemical etching in diluted acids. The current density at the nanoporous electrode is three times higher than that of the bulk electrode with the same chemical compositions. A microfuel cell consisting of nanoporous nickel and platinum electrodes is made and tested.

Keywords:
Microfuel cell, Electrochemical energy conversion, Nanoporous metal, Catalysis; Electrochemical dealloying, Biomass, Sustainable energy.

1 INTRODUCTION
Nanoporous materials have been studied for a variety of applications, for example gas sensors [1], self-assembling templates [2, 3], hydrogen adsorbents [4, 5]. Nanoporous materials have played an important role in energy-related applications such as catalysts, and semiconductors in dye-sensitized solar cells [6]. There are increasing interest in using nanoporous materials for catalysis. For example, the photocatalytic activity of alkaline earth metal doped nanoporous TiO₂ was investigated for the degradation of bisphenol-A [7]. The alkaline earth metals used are magnesium and barium. The sol-gel technique was used to dope Mg²⁺ and Ba²⁺ into the parent nanoscale TiO₂. X-ray diffraction and FTIR analysis confirmed that Ba²⁺ was retained only on the surface of the TiO₂ as BaCO₃, while Mg²⁺ was kept in the substitutional sites.

There are several kinds of nanoporous catalysts according to the functionalities. Photocatalyst and electrocatalyst are two commonly used types. Titanium dioxide nanoporous electrodes for photocatalysis were produced by the re-anodization method [8]. Manganese, chromium and cobalt were doped into nanoporous anatase titanium dioxide. It is found that the photocatalytic efficiency is significantly enhanced due to the presence of Mn²⁺ and Cr³⁺ in the nanoporous TiO₂ scaffold. Mn²⁺ is the most efficient dopant, while the incorporation of Co²⁺ shows the least efficiency. TiO₂ supported bi-metallic catalysts (PtRu, PtFe) were used for methanol oxidation [9]. Yang and Xu [10] prepared nanoporous amorphous manganese oxide as an electrocatalyst for oxygen reduction in alkaline solutions. The amorphous manganese oxide catalyst is expected to have potential applications in metal-air batteries and low-power fuel cells. It is found that the amorphous manganese oxide catalyzes a two-electron reduction, converting molecular oxygen into HO₂⁻. High concentration of lattice defects and active sites of the amorphous material are considered as the reasons for significant catalytic activity. Besides metal oxides, gold nanoparticles with a tubular structure are also used as catalysts towards the oxidation and the reduction of hydrogen peroxide (H₂O₂) [11]. As compared with a bulk gold electrode, the gold nanoelectrode has much higher sensitivity.

Nanoporous carbon were prepared using silica particle as the template [12, 13]. Such nanoporous carbon was used as electrochemical catalyst support for direct methanol fuel cell (DMFC) applications. For example, a PtRu (1:1) alloy was supported on the nanoporous carbon [13]. The structural properties of the carbon support played an important role in the metal disper-

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sion and the performance of the DMFC. The support with large pore size and high surface area was favorable for high dispersion of PtRu catalyst and easy formation of the triple-phase boundary. The catalysts with higher metal dispersion and structural integrity showed higher catalytic activities in the methanol electro-oxidation and the DMFC performance test. Heterogeneous catalysts for electrochemical reduction of CO\(_2\) were developed from rhenium complexes. Such complexes were deposited onto a solid support consisting of nanocrystalline TiO\(_2\) film on glass [14]. It was revealed that the nanoporous nature of the TiO\(_2\) substrate increased the number of redox sites per unit surface area.

Noble metals such as palladium and gold as nanoclusters can be incorporated into the nanoporous domains of gel-type functional resins for oxidation catalysis in liquid phases [15, 16]. The surface properties of platinum catalysts based on various nanoporous matrices such as zeolite, silicate and niobiosilicate were investigated [17]. The locations of Pt in the nanopores and the interactions of metal-support were found dependent on the chemical composition and structure of the matrices. Pt may be electroplated onto nanoporous metals such as gold to obtained low Pt loading electrocatalysts for proton exchange membrane (PEM) fuel cells [18].

Nanoporous materials may be made via various methods. Chemical etching is a easy way to make nanoporous metals [19-21], while co-evaporation may be used for preparation of nanoporous metal oxides [22]. Nanoporous Au specimens with ligament-like structures were fabricated by dealloying [19]. Smith, Maaroof and Gentle [20] prepared nanoporous gold films through de-alloying AuAl\(_2\). The nanoporous gold has void densities between 45% and 65%. Zhou, Jin and Xu [21] 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 [23]. Another drawback of chemical dealloying is the environmental pollution due to the frequent use of high concentration, volatile enchatns 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 property of the nanoporous Ni in agricultural products for sustainable energy applications will be evaluated.

2 MATERIALS AND EXPERIMENTAL METHODS

In this part, the materials used in the work will be described first. Experimental setup will be introduced second. Th procedures for electrochemical dealloying will be given. Finally, characterization of the electrocatalytic property will be presented.

2.1 Materials

Copper-nickel wire with the diameter of 0.5 mm was purchased from Alfa Aesar. 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 also purchased from the same supplier. Other chemicals such as hydrochloride acid, sulfuric acid, acetone with ACS purities were ordered from Alfa Aesar. Biodegradable materials such as tomato, milk, chocolate drink and grape fruit juice were used in characterizing the electrocatalytic behavior of the nanoporous Ni.

2.2 Experimental Setup

In this work, a three electrode system was set up for both electrochemical dealloying and electrocatalytic property characterization. The three electrodes are the Ag/AgCl reference electrode, the work electrode, and the platinum counter electrode.

2.3 Electrochemical Dealloying

Electrochemical etching is widely used for metallurgical specimen preparation, surface polishing and machining. Recently, this technique has been studied for selective removal of alloy elements from metallic alloys. In this work, removal of Cu from Cu-Ni alloy by electrochemical etching in diluted HCl and H\(_2\)SO\(_4\) was conducted following the steps as described below.

First, HCl aqueous solution with the concentration of 9 wt% was made. The H\(_2\)SO\(_4\) used has the concentration of 25 wt%. Second, the Cu-Ni was made into a work electrode. The electrode was assembled with the Ag/AgCl reference electrode, and the platinum counter electrode in the cell containing HCl or H\(_2\)SO\(_4\) solution. Under controlled potentials generated by positive cyclic voltammetrical (CV) scan, selective dissolving of metal elements was achieved. As a result, nanoporous Ni was obtained. During the CV scan, changes in anodic current at the work electrodes were recorded. Such information will be used to explain the electrochemical dealloying mechanisms.

2.4 Electrocatalytic Property Characterization

The electrocatalytic activity of the nanoporous Ni in the biodegradable substances of fresh tomato, milk, chocolate drink, and grape fruit juice, respectively, was characterized by cyclic voltammetry (CV). First, we tested the electrochemical behavior of the nanoporous nickel electrode and a bulk Ni electrode in grape fruit juice. The electroactive surface area effect of the nanoporous Ni is revealed. Tomato was also used to form a
cell to examine the effect of surface area on the catalytic oxidation behavior of the nanoporous Ni electrode. Subsequently, the electrocatalytic behaviors of the nanoporous Ni in the milk and chocolate drink (milk) were characterized. During electrocatalytic property test, the same three-electrode cell was used. The nanoporous nickel electrode was used as the catalyst support electrode (work electrode or anode). The platinum wire was used as the counter electrode, and the Ag/AgCl electrode was used as the reference electrode. The initial concentration of KCl filled in the reference electrode is 3M. The potential of the Ag/AgCl electrode versus the standard hydrogen electrode was calculated to be equal to 0.199 V. The Electrochemical Analyzer was used to provide the CV scan functions. The CV scanning range was controlled over a wide potential range of 0.0 V ~ 1.5 V. The initial potential was 0.0 V. The polarity was set as positive. The scan rate was 0.1 V/s. The data acquisition interval was 0.001 V. The quiet time was 2 s, and the sensitivity was 10⁻³ (A/V).

3 RESULTS AND DISCUSSION

3.1 Cyclic Voltammograms of Dealloying

The current density-potential (I-V) response associated with the electrochemical dealloying of copper from the Cu-Ni alloy was obtained. Fig. 1(a) is the cyclic voltammogram showing the current density change at the Cu-Ni alloy electrode in the 25% H₂SO₄ solution, while Fig. 1(b) is the relationship between the specific current and the potential. The results in Fig. 1(a) reveals that in the potential region of less than 0.3 V, the main reaction is the dissolution of Ni into the electrolyte. With the increase of potential, Ni is passivated, and the dissolving of copper becomes the main reaction.

It is noted that which element will be removed for the CuNi alloy through electrochemical dealloying depends on the potential level. Since Ni is less noble than Cu, in the low potential range from 0 to 0.3 V, Ni will dissolve first. Nanoporous copper scaffold is obtained. At higher potential levels, the newly formed surface oxide layer of NiO (passive film) protects the Ni from dissolution, the more noble metal, copper, is the element being removed from the alloy. Therefore, nanoporous Ni is obtained in the potential range from 0.3 to 1.5 V.

In the HCl electrolyte, the reaction of Ni dissolution occurs in a wide potential range up to 0.52 V because NiO passive film is more difficult to form in the presence of Cl⁻. This can be seen from the results shown in Fig. 2(a), the cyclic voltammogram showing the current density change at the Cu-Ni alloy electrode in the 9% HCl. At the higher potential level greater than 0.52 V, copper dissolution becomes the main reaction. Fig. 2(b) is the relationship between the specific current and the potential, showing the same trend of transition from Ni dissolution to Cu dissolution at 0.52 V.

3.2 Effect of Nanopores on Oxidation Behaviors

In order to examine the effect of nanopore on the electrocatalytic behaviors of electrodes in biodegradable fluids, comparative studies on nanoporous nickel and bulk nickel were conducted. The nanoporous electrode was prepared by electrochemical dealloying of the CuNi alloy wire with the diameter of 0.5 mm in the HCl electrolyte as described in Section 3.1. The bulk nickel electrode is made of a pure nickel wire with the diameter of 1.0 mm. Electrochemical catalysis behaviors of both bulk Ni and nanoporous Ni in the grape fruit juice were studied by cyclic voltammetry and the results are shown in Figs. 3(a) and (b). It is noted that the current density at the nanoporous electrode, as shown in Fig. 3(b), is calculated based on the initial area of the alloy before dealloying. The cyclic voltammogram of the bulk Ni as shown in Fig. 3(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 the nanoporous electrode is more effec-

![Figure 1. Cyclic Voltammograms Associated with Electrochemical Dealloying of Cu-Ni in 25% H₂SO₄ Solution: (a) I-V Response; (b) Specific Current Change.](image)

![Figure 2. Cyclic Voltammograms Associated with Electrochemical Dealloying of Cu-Ni in 9% HCl Solution: (a) I-V Response; (b) Specific Current Change.](image)
tive than the bulk Ni in electrochemical catalytic oxidation of the grape fruit juice.

The electrocatalytic behaviors of the above used Ni electrodes without nanopores and with nanopores in fresh tomato were studied. At the same potential, the current density at the bulk nickel electrode shown in Fig. 4(a) is lower than that at the nanoporous nickel electrode shown in Fig. 4(b). This trend is the same as found in the grape fruit juice case. The oxidation of tomato on the bulk electrode has three distinct stages as marked by “A”, “B”, and “C” on the cyclic voltammogram of Fig. 4(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 Fig. 4(b).

3.3 Oxidation Behaviors during the Reversed Scan

Reversed cyclic voltammetry scans were performed to show the reversibility of the nanoporous Ni for electrochemical catalytic oxidation in biodegradable fluids. Figs. 5(a) and (b) are the cyclic voltammograms of nanoporous Ni in the chocolate drink. The solid blue line in Fig. 5(a) reveals the electrochemical oxidation features of the chocolate drink at the nanoporous Ni electrode in the forward scan. The dotted red line in Fig. 5(a) shows the electrochemical oxidation behaviors of the chocolate drink at the nanoporous Ni electrode in the reversed scan. The oxidation reaction controlled features as revealed in both forward scan and backward scan are the same, which means that the reversibility is well kept. Peak “A” as shown in Fig. 5(b) represents the start of electrochemical oxidation of the chocolate drink on the nanoporous Ni at the potential around 0.3 V.

3.4 Effect of Fermentation

The grape fruit juice was sealed in a glass bottle and kept at the room temperature for ten days. Fermentation was observed as revealed by the following signs. The original red color is faded and some white precipitates were found at the bottom of the bottle. Typically, fermentation also results in the formation of alcoholic products, which may cause change in electrochemical oxidation behaviors of the fluid. To verify this, the cyclic voltammogram of nanoporous Ni in the fermented grape fruit juice is shown in Fig. 6. As compared with the catalytic behavior of nanoporous Ni in unfermented grape fruit juice shown in Fig. 3(b), the current density in fermented fluid is about one third higher. This indicates that fermentation facilitates the electrochemical catalytic oxidation of the fluid on the porous Ni electrode. Such results are helpful in recycling stale juices and drinks for green fuel applications. To recycle these discarded fruits and
drinks and convert them into useful energy are meaningful to save energy and clean the environment.

![Figure 6. CYCLIC VOLTAMMOGRAM OF THE NANOPOROUS Ni ELECTRODE IN FERMENTED GRAPE FRUIT JUICE.](image)

3.5 Voltage Generated by the Porous Ni

Finally, we made a microfuel cell consisting of a nanoporous nickel anode, white milk solution and a platinum cathode. The plot of voltage v.s. time is given in Figure 7. The stable output of voltage is about 0.135 V. Obviously, in order to build a practical power generation device, many of such cells are needed.

![Figure 7. VOLTAGE OF NANOPOROUS Ni/WHITE MILK/Pt CELL.](image)

4 CONCLUSIONS

Electrochemical dealloying and electrocatalytic behavior of nanoporous nickel in biodegradable fluids for green fuel applications were performed. High electroactive surface areas in nanoporous nickel were obtained. Based on the preliminary research, the following concluding remarks can be made.

Studies on electrochemical dealloying of the Cu55Ni45 alloy in the 25% sulphuric acid reveal that in the potential region of less than 0.3 V, the main reaction is the dissolution of Ni into the electrolyte. With the increase of potential, Ni is passivated, and the dissolving of copper becomes the main reaction. Therefore, which element is removed for the CuNi alloy through electrochemical dealloying is dependent on the level of the potential used. Since Ni is less noble than Cu, in the low potential range from 0 to 0.3 V, Ni dissolves first. Nanoporous copper scaffold is obtained. At higher potential levels, the newly formed surface oxide layer of NiO (passive film) protects the Ni from dissolution. The more noble metal, copper, is the element being removed from the alloy. Nanoporous Ni is obtained in the potential range from 0.3 to 1.5 V.

In the 9% HCl electrolyte, the reaction of Ni dissolution from the Cu-Ni alloy occurs in a wide potential range up to 0.52 V because NiO passive film is more difficult to form in the presence of Cl\(^-\). At the higher potential level greater than 0.52 V, copper dissolution becomes the main reaction. The transition from Ni dissolution to Cu dissolution at 0.52 V is revealed by cyclic voltammetry.

Comparative studies on nanoporous and bulk specimens show that a nanoporous electrode is more effective than a bulk electrode in electrochemical catalytic oxidation of biodegradable fluids. The cyclic voltammogram of the bulk Ni has the reaction controlled feature. The current density at the nanoporous Ni is as 4 times high as that at the bulk nickel electrode.

Fermentation changes the electrochemical oxidation behaviors of biodegradable fluids, facilitating the electrochemical catalytic oxidation of the fluids on the nanoporous nickel electrode. The cyclic voltammogram of the nanoporous Ni in the fermented grape fruit juice shows that the current density in fermented fluid is about one third higher than that in the unfermented fluid, which indicates that the fermentation makes the oxidation of the fluid on the nanoporous Ni electrode even easier. Such preliminary results may be helpful in recycling stale fruits or drinks for green fuel applications.

ACKNOWLEDGMENT

This work was supported by the research start-up fund and the Summer Faculty Research Fellowship from The University of Toledo.
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