Notice

DESCRIPTION CN120041867A

A method for preparing NiCu alloy electrodes based on the synergistic regulation of electrochemical micromachining and electrocrystallization

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[0001]

Technical Field

[n0001]

This invention relates to the field of electrochemical catalytic materials technology, and in particular to a method for preparing NiCu alloy electrodes based on the synergistic regulation of electrochemical microfabrication and electrocrystallization.

[0003]

Background Technology

[n0002]

Hydrogen energy, as a clean energy source, is characterized by high efficiency and zero pollution. Due to its unique characteristics, high efficiency, and ability to produce high-purity hydrogen gas with almost no pollution, it has aroused great research interest.

There are different methods for producing hydrogen, among which electrochemical water splitting is an important and common clean hydrogen production method. This method involves the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. The hydrogen evolution reaction (HER) is one of the key steps in water splitting.

[n0003]

Appropriate electrocatalytic activity and active surface area are the main parameters for achieving electrocatalytic HER activity. Currently, platinum group metals (such as Pt, Ru, Ir and Rh) are recognized as highly efficient HER catalysts, but their large-scale application is limited by their limited uses, high cost and weak stability.

Therefore, replacing this group of noble metal-based catalysts with suitable, low-cost, and high-efficiency metals is the focus of current research.

[n0004]

Nickel-copper alloy (NiCu) is considered a potential alternative material due to its good catalytic properties and stability.

However, the catalytic performance of existing NiCu alloys is still inferior to that of platinum catalysts.

Therefore, how to improve the electrochemical performance of NiCu alloys by optimizing the preparation process has become the focus of current research.

[0007]

Summary of the Invention

[n0005]

To address the shortcomings of existing technologies, the present invention aims to provide a method for preparing NiCu alloy electrodes based on the synergistic regulation of electrochemical micromachining and electrocrystallization. By combining electrochemical micromachining and electrocrystallization, precise control of the surface microstructure is achieved through the synergistic two-step process of micromachining and crystallization. This not only enables precise design of the surface morphology but also significantly improves the catalytic performance of the electrode through the coupling effect of multi-level structures, narrowing the gap with platinum catalysts.

[n0006]

To achieve the above objectives, the technical solution adopted by this invention is as follows: a method for preparing NiCu alloy electrodes based on the synergistic regulation of electrochemical micromachining and electrocrystallization, comprising the following steps:

[n0007]

(1) Electrochemical micromachining: Cut the nickel mesh, use an electrode clip with a

platinum sheet to clamp the longer end to ensure the effective area of the electrode immersed in the electrolyte, pass the current through the nickel mesh in an acidic solution, clean it and dry it for later use.

[n0008]

(2) Ni-Cu gradient crystallization: Nickel crystallization is carried out first, followed by copper crystallization. In the early stage of crystallization, a dense Ni-rich bottom layer is formed, in the middle stage, a Ni-Cu mixed columnar crystal transition layer is formed, and in the later stage, a Cu-rich nano-dendritic surface layer is formed.

[n0009]

As a preferred embodiment, in step (1), the nickel mesh is cut to a size of 1×1.2cm², and the effective area of the electrode immersed in the electrolyte during testing is 1cm². The nickel mesh is energized in a 0.5mol/L H₂SO₄ solution for 30min with a current of 0.05A.

[n0010]

As a preferred embodiment, the Ni-Cu gradient crystallization in step (2) specifically consists of a first-step electrocrystallization and a second-step electrocrystallization. In the first-step electrocrystallization, a nickel mesh is used as the working electrode, and platinum is used as the counter electrode and reference electrode. A layer of Ni is crystallized on the nickel mesh using a three-electrode method. In the second-step electrocrystallization, the nickel mesh that has undergone the first-step electrocrystallization is used as the working electrode, a graphite rod is used as the counter electrode, and Ag/AgCl is used as the reference electrode to crystallize Cu.

[n0011]

As a preferred embodiment, the experimental conditions for the first step of electrocrystallization are as follows: the electrolyte consists of 0.5–1.5 mol/L NiCl・6HO, 0.5 mol/L HO, BOO, and 1.5 mol/L ethylenediamine hydrochloride; the experimental current is 0.01–0.1 A; the temperature is 10–70 °C; the pH of the electrolyte is maintained at 4.2 ± 0.1; and the time is 15 min.

[n0012]

As a preferred embodiment, the experimental conditions for the first step of electrocrystallization are: Ni_NER9 concentration of 1.0 mol/L, temperature of 50°C, current of 0.1A, and time of 15 min.

[n0013]

As a preferred embodiment, in the first step of electrocrystallization, the effects of experimental conditions such as Ni²⁺ concentration, temperature, and current on the hydrogen evolution reaction (HER) are evaluated using the double-layer capacitance (Cdl) and Tafel slope, where the double-layer capacitance is 18.2–36.4 mF*cm⁻² and the Tafel slope is 98.3–123.8 mV*dec⁻¹.

[n0014]

As a preferred embodiment, the experimental conditions for the second step of electrocrystallization are as follows: the electrolyte consists of 0.1–0.2 mol/L CuSO・5HO and 0.5 mol/L NaCHO (sodium citrate); the experimental current is 0.01–0.1 A; the temperature is 10–50 °C; the pH of the electrolyte is maintained at 4.2 ± 0.1; and the time is 15 min.

[n0015]

As a preferred option, the experimental conditions for the second step of electrocrystallization are: Cu_NER19 concentration of 0.15mol/L, temperature of 50°C, current of 0.1A, and time of 15min.

[n0016]

As a preferred approach, in the second step of electrocrystallization, the effects of experimental conditions such as Cu²⁺ concentration, temperature, and current on the hydrogen evolution reaction (HER) were evaluated using the double-layer capacitance (Cdl) and Tafel slope, where the double-layer capacitance was 23.5–38.5 mF*cm⁻² and the Tafel slope was 82.1–124.2 mV*dec⁻¹.

[n0017]

As a preferred method, after electrochemical micromachining of the nickel mesh in a 0.5 mol/L HO・SO solution at a current of 0.05 A for 30 min, the first step of electrocrystallization is performed. The conditions for the first step of crystallization are: the electrolyte includes 1.0 mol/L NiCl・6HO and 0.5 mol/L HO・SO solution. The experimental conditions were: H₃BO₃ and 1.5mol/L ethylenediamine hydrochloride, experimental current 0.1A, temperature 50°C, time 15min; after obtaining the sample, a second step of electrocrystallization was performed, the second step of crystallization conditions were: electrolyte including 0.15mol/L CuSO₄・5H₂O, 0.5mol/L Na₃C₆H₅O₇ (sodium citrate), experimental current 0.1A, temperature 50°C, time 15min; the double layer capacitance of the NiCu alloy after electrochemical testing was 38.5mF*cm⁻², and the Tafel slope was 82.1 mV*dec⁻¹.

[n0018]

Compared with existing technologies, the beneficial effects of this invention are as follows: The NiCu alloy prepared by the experimental method of this invention has a double-layer capacitance (Cdl) of 38.5 mF*cm⁻², which is nearly 8 times that of the original nickel mesh, and a Tafel slope of 82.1 mV*dec⁻¹, which is nearly 40% lower than that of the original nickel mesh. This is significantly better than traditional NiCu alloys and approaches the performance of platinum catalysts (Tafel slope of 43 mV*dec⁻¹), greatly narrowing the gap with platinum catalytic performance. This invention significantly improves the electrocatalytic performance of NiCu alloys while reducing costs by combining electrochemical microfabrication and electrocrystallization techniques.

[0022]

Detailed Implementation

[n0019]

The present invention will be further described below with reference to specific embodiments.

The following embodiments are only used to illustrate the technical solutions of the present invention more clearly, and should not be used to limit the scope of protection of the present invention.

[n0020]

Example 1:

[n0021]

A method for preparing NiCu alloy electrodes based on the synergistic regulation of electrochemical micromachining and electrocrystallization includes the following steps:

[n0022]

(1) Electrochemical micromachining: Cut the nickel mesh into 1×1.2cm NER40 size, use an electrode clamp with a platinum sheet to clamp the longer end, and ensure that the effective area of the electrode immersed in the electrolyte is 1cm NER41. The nickel mesh is energized in 0.5mol/L H NER42 SO NER43 solution for 30min with a current of 0.05A, and then cleaned with an ultrasonic cleaner and dried for later use.

[n0023]

(2) First step of electrocrystallization: Using a nickel mesh as the working electrode and platinum as the counter electrode and reference electrode, a layer of Ni was crystallized on the nickel mesh using a three-electrode method; the electrolyte consisted of 1.0 mol/L NiCl44・6H2O, 0.5 mol/L H2O, BO2O and 1.5 mol/L ethylenediamine hydrochloride, the experimental current was 0.01 A, the temperature was 10 °C, the pH of the electrolyte was maintained at 4.2 ± 0.1, and the time was 15 min;

[n0024]

(3) Second step electrocrystallization: Using the nickel mesh that has undergone the first step electrocrystallization as the working electrode, the graphite rod as the counter electrode, and Ag/AgCl as the reference electrode, Cu was crystallized; the electrolyte included 0.15 mol/L CuSO48・5H2O and 0.5 mol/L Na2C1H2O (sodium citrate), the experimental current was 0.01

A, the temperature was 10 °C, the pH of the electrolyte was maintained at 4.2 ± 0.1, and the time was 15 min.

[n0025]

Furthermore, the experimental conditions for the first step of electrocrystallization in step (2) are changed:

[n0026]

(a) Effect of Ni²⁺ concentration on HER: To compare the hydrogen evolution activity of samples at different Ni⁺ concentrations, three-electrode alkaline electrolysis tests were performed on nickel electrodes at three different concentrations. Table 1 shows the double layer capacitance (Cdl) and Tafel slope of samples at different Ni² concentrations.

[n0027]

Table 1

[n0029]

(b) Effect of temperature on HER: Under the conditions in (a), other conditions were kept constant, and the hydrogen evolution activity of the samples at different temperatures was compared. The results are shown in Table 2.

[n0030]

Table 2

[n0032]

(c) Effect of current on HER: Under the conditions in (b), other conditions were kept constant, and the hydrogen evolution activity of the samples under different currents was compared. The results are shown in Table 3.

[n0033]

Table 3

[n0036]

Furthermore, the experimental conditions for the second step of electrocrystallization in step (3) are changed:

[n0037]

(d) Effect of Cu²⁺ concentration on HER: Changes in the Cu²⁺ concentration in the deposition solution can affect the composition of nickel and copper in the NiCu alloy electrode to a certain extent. To compare the hydrogen evolution activity of samples with different Cu²⁺ concentrations, under the conditions of 0.01A current, 10°C temperature, and 15min time, the concentrations were set to 0.1mol/L, 0.15mol /L, and 0.2mol/L, respectively. The effect of Cu²⁺ concentration on the catalytic performance of the NiCu alloy electrode was studied by testing the hydrogen evolution performance of the alkaline electrolyzer. The results are shown in Table 4.

[n0038]

Table 4

[n0040]

(e) Effect of temperature on HER: Increased temperature can accelerate ion diffusion in the deposition solution, reduce concentration polarization, improve the conductivity of the solution, reduce pinholes, and improve the quality of NiCu alloy coating. Therefore, under the condition of optimal Cu²⁺ concentration, while keeping other experimental parameters constant, the experimental temperature was changed to 10°C (ice-water bath), 30°C (room temperature), and 50°C (water bath heating), and the hydrogen evolution performance of alkaline electrolytic cell was tested. The results are shown in Table 5.

[n0041]

Table 5

[n0044]

(f) Effect of current on HER: Current density has a greater impact on the coarseness of the coating crystals. Therefore, under the conditions of (e), the hydrogen evolution activity of samples under different currents was compared, and the results are shown in Table 6.

[n0045]

Table 6

[n0046]

Sample 1 2 <![CDATA[Cu²⁺concentration/mol*L⁻¹]]> 0.15 0.15

Temperature/°C 50 50 Current/A 0.01 0.1 <!

[CDATA[Double-layer capacitance (Cdl)/mF*cm⁻²]]> 33.4 38.5 <!

[CDATA[Tafel slope/mV*dec⁻¹]]> 100.6 82.

1

[n0047]

Preferably, the platinum electrode was placed in a 30wt% KOH electrolyte environment for HER testing, and the results were compared with those of the sample in this study. The results are shown in Table 7.

[n0048]

Table 7

[n0050]

In summary, after electrochemical micromachining of a nickel mesh in a 0.5 mol/L HO/SO solution at a current of 0.05 A for 30 min, the first step of electrocrystallization was performed. The conditions for the first step were: the electrolyte consisted of 1.0 mol/L NiCl・6HO, 0.5 mol /L HO/BO, and 1.5 mol/L ethylenediamine hydrochloride; the experimental current was 0.1 A; the temperature was 50 °C; and the time was 15 min. After obtaining the sample, the second step of electrocrystallization was performed. The conditions for the second step were: the electrolyte consisted of 0.15 mol/L... The experimental setup consisted of CuSO・5HO and 0.5 mol/L NaCHO (sodium citrate). The experimental current was 0.1 A, the temperature was 50 ° C, and the time was 15 min. Electrochemical testing revealed that the double-layer capacitance of the NiCu alloy was 38.5 mF*cm, nearly eight times that of the original nickel mesh. The Tafel slope was 82.1 mV*dec, almost 40% lower than that of the original nickel mesh, significantly narrowing the gap with platinum catalytic performance.

[n0051]

Therefore, the experimental method of this invention differs from the conventional electrodeposition method for electrode preparation. This invention employs a combination of electrochemical micromachining and electrocrystallization to prepare NiCu alloy electrodes. Electrochemical micromachining refers to the process of creating different microstructure patterns on the surface of a nickel mesh by applying an electric current. Electrocrystallization refers to the process of passing an electric current through an electrolyte, causing the metal cations in the electrolyte to be reduced and grown on the surface of the nickel mesh. The introduction of electrochemical micromachining constructs a micro-nano composite structure on the surface of the nickel electrode, thereby increasing the specific surface area of the nickel electrode and providing more electrochemical active sites for the next step of electrocrystallization, thus improving the electrochemical performance of the NiCu alloy.

Furthermore, by precisely controlling the electrocrystallization process and using a Ni-Cu gradient crystallization method, the submicron-level fine modification of the micromachined nickel substrate is achieved, realizing a synergistic effect between the micromachining and crystallization steps. The microstructure is precisely controlled by first microfabrication to construct a micron-scale framework structure on the electrode surface, and then electrocrystallization, using these structures as a base, induces the growth of dendritic nanostructures to form a composite structure of micron-scale framework and nanodendritic structures. The gradient deposition sequence of Ni-Cu (Ni first, then Cu) and precise pH control (maintained at 4.2±0.1) and temperature control (50°C±0.5°C) are crucial for forming the ideal crystal orientation. In particular, the use of a high current of 0.1A for short-time secondary electrocrystallization induces the in-situ growth of unique dendritic nanostructures. These structures fill the submicron-scale voids generated by microfabrication. This experimental method of synergistic construction of multi-level structures not only optimizes the interfacial properties of NiCu alloys, but also significantly improves their electrocatalytic performance, greatly narrowing the performance gap with noble metal platinum catalysts.

[n0052]

The above description is only a preferred embodiment of the present invention. It should be noted that for those skilled in the art, several improvements and modifications can be made without departing from the technical principles of the present invention, and these improvements and modifications should also be considered within the scope of protection of the present invention.
