Notice

DESCRIPTION CN115261881A

A method for preparing nickel-copper bimetallic array nanosheet electrodes for urea electrolysis

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[0001]

Technical Field

[n0001]

This invention belongs to the field of urea hydrogen production and energy storage technology, and particularly relates to a method for preparing a nickel-copper bimetallic array nanosheet electrode for urea electrolysis.

[0003]

Background Technology

[n0002]

Environmental pollution and the energy crisis have hindered the development of modern society and are major challenges facing all mankind. Therefore, developing advanced clean energy production technologies is the key to achieving sustainable development.

Hydrogen fuel is considered a new energy carrier with great potential for development due to its high energy density and ability to achieve zero carbon emissions.

Against this backdrop, water electrolysis for hydrogen production has emerged and is widely regarded as an efficient, low-cost, and sustainable green hydrogen production technology.

The hydrogen evolution reaction (HER) occurring at the cathode and the oxygen evolution reaction (OER) occurring at the anode are two important electrochemical processes in a water electrolysis system. However, the OER has a theoretical thermodynamic potential higher than 1.23V because the reaction is controlled by several complex and slow proton coupling and electron transfer processes. Therefore, finding alternative anode reactions to OER is key to achieving energy-efficient hydrogen production. In recent years, electrolytic urea technology has gradually come into people's view. The theoretical operating voltage of the urea oxidation reaction (UOR) is only 0.37V, which gives the electrolysis of urea to produce hydrogen a low energy consumption advantage compared to water electrolysis. In addition, electrolytic urea technology can also treat urea molecules in wastewater, achieving environmental purification while producing hydrogen. Although UOR has a low onset potential, its six-electron transfer process results in a large overpotential. Therefore, preparing highly active catalyst electrodes is a crucial step in achieving efficient urea electrolysis.

[n0003]

Some precious metal materials have been proven to be the most advanced catalysts available today; however, their high cost and scarcity limit their actual industrial production.

Some transition metal elements, represented by Ni, are considered as substitutes for precious metal elements due to their unique electron configuration and high abundance in the Earth's crust. Furthermore, recent studies have confirmed that Ni³⁺ is the actual active site in the UOR process. However, the high oxidation energy barrier required for the oxidation of Ni²⁺ to Ni³⁺ severely slows down the catalytic kinetics. In addition, carbon oxides, as one of the main products of UOR, cause many catalysts to be poisoned and deactivated during continuous operation, resulting in a shortened service life of the electrode.

[0006]

Summary of the Invention

[n0004]

This invention provides a method for preparing a nickel-copper bimetallic array nanosheet electrode for urea electrolysis. The preparation process is a simple "one-pot method". Cu ions are introduced during the acid etching process of nickel foam, thereby growing Ni-Cu bimetallic hydroxide nanosheets in situ on the substrate surface. Relying on the high conductivity of Cu and its regulatory effect on the external electronic structure of Ni, the electron transfer process of the material is accelerated, thereby reducing the oxidation potential of Ni²⁺. In addition, Cu has a strong resistance to CO poisoning. The introduction of Cu improves the stability of the electrode during long-term operation, thus solving the problems of low activity and poor durability that are common in traditional electrode materials used for urea electrolysis.

[n0005]

To achieve the above objectives, the present invention provides a method for preparing a nickel-copper bimetallic array nanosheet electrode for urea electrolysis, comprising the following steps:

[n0006]

S1. Place the nickel foam in an HCl solution and sonicate for 5-15 minutes. After sonication, purify the nickel foam and then dry it in a vacuum drying oven.

[n0007]

S2. Pour dilute hydrochloric acid solution into a polytetrafluoroethylene (PTFE) high-pressure reactor, add Cu salt to the solution, and stir with a magnetic stirrer. When the solution is completely mixed, stop stirring, remove the magnetic stirrer, and place the dried nickel foam into the PTFE high-pressure reactor, ensuring that the nickel foam is completely immersed in the solution. Seal the PTFE high-pressure reactor and move it into a forced-air drying oven to react at 80-150°C. After washing and drying, obtain the NiCu-OH/nickel foam electrode.

[n0008]

As a further description of the above technical solution:

[n0009]

In step S1, the concentration of the HCl solution is 3M; after ultrasonication, the nickel foam needs to be ultrasonicated in ultrapure water for 15 minutes, and then ultrasonicated again in anhydrous ethanol for 10 minutes.

[n0010]

As a further description of the above technical solution:

[n0011]

The Cu salt added in step S2 is Cu(NO₃)₂・6H₂O.

The added Cu salt is Cu(NO₃)₂・6H₂O.

It is worth noting that Cu²⁺ has the property of easy reduction. When

Cu²⁺ in the system comes into contact with Ni element, a displacement reaction occurs, and Cu cubes are formed on the surface of the nickel foam.

Cu cubes can reach sizes of several micrometers, thus providing more space for the growth of nanosheets.

[n0012]

As a further description of the above technical solution:

[n0013]

The stirring time in step S2 is 5 minutes.

[n0014]

As a further description of the above technical solution:

[n0015]

In step S2, the concentration of the dilute hydrochloric acid solution is 1.2×10^{13} M, which stabilizes the initial pH of the reaction system between 2.8 and 3.2.

Within this pH range, elemental Ni is etched by H⁺ in a weakly acidic atmosphere to form Ni²⁺.

Similarly, the substitution reaction of Cu²⁺ can also provide Ni²⁺ to the system.

When [Ni²⁺]・[OH⁻]⩾Ksp, Ni²⁺ will undergo a hydrolysis reaction to generate Ni(OH)₂ nanosheets.

Because the reaction takes place in an acidic environment, the thickness of the Ni(OH)₂ nanosheets is limited, resulting in an ultrathin three-dimensional interconnected nanosheet structure.

Similarly, Cu²⁺ which did not participate in the substitution reaction in the system will also undergo the same process, eventually forming bimetallic hydroxide nanosheets together with Ni²⁺ on the surface of nickel foam and Cu cube.

[n0016]

As a further description of the above technical solution:

[n0017]

Preferably, the reaction temperature in step S2 is 100°C.

[n0018]

As a further description of the above technical solution:

[n0019]

The reaction time in step S2 is 10-30 hours.

[n0020]

As a further description of the above technical solution:

[n0021]

Preferably, the reaction time is 20 hours.

[n0022]

In summary, due to the adoption of the above technical solution, the beneficial effects of the present invention are:

[n0023]

(1) NiCu bimetallic nanosheets were grown in situ on the substrate by acid etching. The excellent electronic control ability of Cu element accelerated the electron transfer process on the material surface.

[n0024]

(2) The resistance of Cu to CO poisoning was utilized to improve the long-term working ability of the catalyst.

[n0025]

(3) Micron-sized Cu cubes were constructed on the surface of nickel foam, providing a larger growth space for catalytically active nanosheets, thereby increasing the nanosheet density on the substrate.

[n0026]

(4) The electrode preparation in this invention uses a "one-pot method", which is simple, easy to scale up, and involves very few reaction raw materials, which greatly reduces production costs.

[0030]

Attached Figure Description

[n0027]

To more clearly illustrate the technical solutions of the embodiments of the present invention, the accompanying drawings used in the embodiments will be briefly introduced below. It should be understood that the following drawings only show some embodiments of the present invention and should not be regarded as a limitation on the scope. For those skilled in the art, other related drawings can be obtained based on these drawings without creative effort.

[n0028]

Figure 1 is a flowchart of the preparation method of the nickel-based high-density nanosheet electrode for urea electrolysis according to the present invention.

[n0029]

Figure 2 is a SEM image of the NiCu-OH/nickel foam involved in Example 1.

[n0030]

Figure 3 is a SEM image of the Ni(OH)₂/nickel foam electrode involved in Comparative Example 1.

[n0031]

Figure 4 shows the linear voltammetry (LSV) test curves of different electrode materials applied to the hydrogen evolution process and urea oxidation process in Comparative Example 1.

[n0032]

Figure 5 shows the Nyquist curves of the different electrodes involved in Comparative Example 1.

[n0033]

Figure 6 shows the chronopotential curves of the different electrodes involved in Comparative Example 1.

[n0034]

Figure 7 shows SEM images of electrode materials with different Cu doping amounts involved in Comparative Example 2.

[n0035]

Figure 8 shows the LSV test curves of electrode materials with different Cu doping amounts involved in Comparative Example 2 applied to the hydrogen evolution process and urea oxidation process.

[0040]

Detailed Implementation

[n0036]

The preferred embodiments of the present invention will now be described in detail.

[n0037]

This invention provides a method for preparing a nickel-copper bimetallic array nanosheet electrode for urea electrolysis, comprising the following steps:

[n0038]

S1. Place the nickel foam in an HCl solution and sonicate for 5-15 minutes. After sonication, purify the nickel foam and then dry it in a vacuum drying oven.

[n0039]

S2. Pour dilute hydrochloric acid solution into a polytetrafluoroethylene (PTFE) high-pressure reactor, add Cu salt to the solution, and stir with a magnetic stirrer. When the solution is completely mixed, stop stirring, remove the magnetic stirrer, and place the dried nickel foam into the PTFE high-pressure reactor, ensuring that the nickel foam is completely immersed in the solution. Seal the PTFE high-pressure reactor and move it into a forced-air drying oven to react at 80-150°C. After washing and drying, obtain the NiCu-OH/nickel foam electrode.

[n0040]

In step S1, the concentration of the HCl solution is 3M; after ultrasonication, the nickel foam needs to be ultrasonicated in ultrapure water for 15 minutes, and then ultrasonicated again in anhydrous ethanol for 10 minutes.

[n0041]

The Cu salt added in step S2 is Cu(NO₃)₂・6H₂O.

The added Cu salt is Cu(NO₃)₂・6H₂O.

It is worth noting that Cu²⁺ has the property of easy reduction. When Cu²⁺ in the system comes into contact with Ni element, a displacement reaction occurs, and Cu cubes are formed on the surface of the nickel foam.

Cu cubes can reach sizes of several micrometers, thus providing more space for the growth of nanosheets.

[n0042]

The stirring time in step S2 is 5 minutes.

[n0043]

In step S2, the concentration of the dilute hydrochloric acid solution is 1.2×10^{34} M, which stabilizes the initial pH of the reaction system between 2.8 and 3.2.

Within this pH range, elemental Ni is etched by H⁺ in a weakly acidic atmosphere to form Ni²⁺.

Similarly, the substitution reaction of Cu²⁺ can also provide Ni²⁺ to the system.

When [Ni²⁺]・[OH⁻]⩾Ksp, Ni²⁺ will undergo a hydrolysis reaction to generate Ni(OH)₂ nanosheets.

Because the reaction takes place in an acidic environment, the thickness of the Ni(OH)₂ nanosheets is limited, resulting in an ultrathin three-dimensional interconnected nanosheet structure.

Similarly, Cu²⁺, which did not participate in the substitution reaction, will undergo the same process and eventually form bimetallic hydroxide nanosheets together with Ni²⁺ on the nickel foam surface and the Cu cubic surface.

[n0044]

Preferably, the reaction temperature in step S2 is 100°C.

[n0045]

The reaction time in step S2 is 10-30 hours.

Preferably, the reaction time is 20 hours.

[n0046]

In summary, due to the adoption of the above technical solution, the beneficial effects of the present invention are:

[n0047]

(1) NiCu bimetallic nanosheets were grown in situ on the substrate by acid etching. The excellent electronic control ability of Cu element accelerated the electron transfer process on the material surface.

[n0048]

(2) The resistance of Cu to CO poisoning was utilized to improve the long-term working ability of the catalyst.

[n0049]

(3) Micron-sized Cu cubes were constructed on the surface of nickel foam, providing a larger growth space for catalytically active nanosheets, thereby increasing the nanosheet density on the substrate.

[n0050]

(4) The electrode preparation in this invention uses a "one-pot method", which is simple, easy to scale up, and involves very few reaction raw materials, which greatly reduces production costs.

[n0051]

Example 1

[n0052]

Example 1 provides a method for preparing a nickel-copper bimetallic array nanosheet electrode for urea electrolysis, comprising the following steps:

[n0053]

Pretreatment of nickel foam substrate:

[n0054]

A 2×3cm piece of commercial nickel foam was placed in a 3M HCl solution and sonicated for 10 minutes.

After ultrasonic treatment, the nickel foam was placed in ultrapure water and ultrasonicated for 15 minutes.

Finally, the nickel foam was placed in anhydrous ethanol and subjected to sonication for another 10 minutes.

The pretreated nickel foam was dried in a vacuum drying oven at 60°C for 2 hours.

[n0055]

Preparation of NiCu bimetallic nanosheet electrodes (NiCu-OH/nickel foam):

[n0056]

Pour 20 mL of 1.2 × 10 NER46 M dilute hydrochloric acid solution into a 100 mL polytetrafluoroethylene high-pressure reactor, and add 0.3 mmol Cu(NO₃)₂・6H₂O to the solution. Stir with a magnetic stirrer for 5 min.

Once the solution is completely mixed, stop the stirring equipment and remove the magnetic spool.

The dried nickel foam is placed inside the reactor to completely immerse it in the solution, and then the reactor is sealed.

The polytetrafluoroethylene high-pressure reactor was transferred into a forced-air drying oven and reacted at 100°C for 20 hours.

After the reaction is complete, allow the reactor to cool naturally to room temperature and remove the internal materials.

Finally, the material was repeatedly rinsed with ultrapure water and dried in a 60°C vacuum drying oven for 2 hours to obtain the NiCu-OH/nickel foam electrode.

[n0057]

Figure 2 shows the SEM image of NiCu-OH/nickel foam. It can be seen from the figure that the surface of the nickel foam substrate is loaded with cubes with a side length of several micrometers. In essence, it is Cu elemental obtained by Cu²⁺ reduction.

NiCu bimetallic hydroxide nanosheets grow in a three-dimensional interconnected manner on the surface of nickel foam and Cu cubes, and nanosheets can be loaded on planes in all directions of the Cu cubes, with the thickness of the nanosheets maintained at 10nm-20nm.

[n0058]

Comparative Example 1:

[n0059]

Pretreatment of nickel foam substrate:

[n0060]

A 2×3cm piece of commercial nickel foam was placed in a 3M HCl solution and sonicated for 10 minutes.

After ultrasonic treatment, the nickel foam was placed in ultrapure water and ultrasonicated for 15 minutes.

Finally, the nickel foam was placed in anhydrous ethanol and subjected to sonication for another 10 minutes.

The pretreated nickel foam was dried in a vacuum drying oven at 60°C for 2 hours.

[n0061]

Preparation of Ni(OH)₂ nanosheet electrodes (Ni(OH)₂/nickel foam):

[n0062]

Pour 20 mL of 3.6 × 10 NER53 M dilute hydrochloric acid solution into a 100 mL polytetrafluoroethylene high-pressure reactor, and place the dried nickel foam inside the reactor to completely immerse it in the solution. Seal the reactor.

The polytetrafluoroethylene high-pressure reactor was transferred into a forced-air drying oven and reacted at 100°C for 20 hours.

After the reaction is complete, allow the reactor to cool naturally to room temperature and remove the internal materials.

Finally, the material was repeatedly rinsed with ultrapure water and dried in a 60°C vacuum drying oven for 2 hours to obtain Ni(OH)₂/nickel foam electrode.

[n0063]

Because the Ksp of Cu²⁺ is tens of orders of magnitude smaller than that of Ni²⁺, it is more likely to undergo hydrolysis and produce H⁺.

Therefore, after removing Cu²⁺ from the reaction system, to maintain a consistent pH atmosphere, the concentration of the dilute hydrochloric acid solution needs to be appropriately increased.

[n0064]

Because the NiCu-OH/nickel foam electrode contains elemental Cu, it exhibits a purplish-red color, while the Ni(OH)2/nickel foam electrode surface only has Ni(OH)₂ nanosheets, and its actual color is dark gray.

[n0065]

Figure 3 shows the SEM image of Ni(OH)₂/foamed nickel.

As can be seen from the figure, a large number of nanosheets are loaded on the surface of the nickel foam, and the thickness of the nanosheets and their three-dimensional interconnection structure are consistent with those of the NiCu-OH/nickel foam electrode.

The difference is that, since Cu²⁺ is not introduced, the surface of this material does not have a cubic structure, and the nanosheets grow flat on the same plane.

[n0066]

Figure 4 shows a comparison of the LSV performance of each electrode in Comparative Example 1 for the hydrogen evolution process and the urea oxidation process.

The NiCu-OH/nickel foam electrode exhibits superior performance and higher hydrogen production efficiency.

The main reason is that Cu modulates the electronic structure of Ni and increases the conductivity of the material, thereby significantly accelerating the charge transfer process on the electrode surface and making Ni²⁺ easier to transform into Ni³⁺.

Furthermore, since the nickel foam surface has Cu cubes, and nanosheets with active materials can grow on each plane of the cube, the electrode has a higher density of nanosheet structure, thus carrying more catalytic sites.

[n0067]

Figure 5 shows the Nyquist curves of each electrode in Comparative Example 1.

Among them, the test curve of NiCu-OH/foamed nickel has the smallest radius, indicating that the material has a smaller charge transfer resistance, which confirms that it has a faster electron transfer process.

[n0068]

Figure 6 shows the chronopotential curves of each electrode in Comparative Example 1, which are used to evaluate the long-term working capability of the electrodes.

At a current density of 50 mA cm⁻², the test curve of NiCu-OH/nickel foam fluctuated within 48 hours, but its potential remained at a relatively stable level.

In contrast, the driving potential of the Ni(OH)₂/foam nickel electrode increases with the extension of working time.

Moreover, this phenomenon does not occur in the HER process, but only in the UOR process.

It can be assumed that the carbon oxides adsorbed on the electrode surface reduce the activity of the electrode.

This also confirms that the excellent stability of NiCu-OH/foamed nickel is related to the introduction of Cu.

[n0069]

Comparative Example 2:

[n0070]

Pretreatment of nickel foam substrate:

[n0071]

A 2×3cm piece of commercial nickel foam was placed in a 3M HCl solution and sonicated for 10 minutes.

After ultrasonic treatment, the foamed nickel was placed in ultrapure water and ultrasonically treated for 15 minutes.

Finally, the nickel foam was placed in anhydrous ethanol and subjected to sonication for another 10 minutes.

The pretreated nickel foam was dried in a vacuum drying oven at 60°C for 2 hours.

[n0072]

Preparation of NiCu bimetallic high-density nanosheet electrodes with different Cu loadings (Ni(OH)₂/nickel foam):

[n0073]

Pour 20 mL of 3.6 × 10 NER67 M dilute hydrochloric acid solution into a 100 mL polytetrafluoroethylene high-pressure reactor, and add 0.1 mmol and 0.5 mmol Cu (NO₃)₂・6H₂O to the solution. Stir with a magnetic stirrer for 5 min.

Once the solution is completely mixed, stop the stirring equipment and remove the magnetic spool.

The dried nickel foam is placed inside the reactor to completely immerse it in the solution, and then the reactor is sealed.

The polytetrafluoroethylene high-pressure reactor was transferred into a forced-air drying oven and reacted at 100°C for 20 hours.

After the reaction is complete, allow the reactor to cool naturally to room temperature and remove the internal materials.

Finally, the material was repeatedly rinsed with ultrapure water and dried in a 60°C vacuum drying oven for 2 hours to obtain NiCu-OH/nickel foam electrodes with different Cu loadings.

[n0074]

Figure 7 shows SEM images of NiCu-OH/nickel foam electrodes with different Cu loadings involved in Comparative Example 2.

When the amount of Cu(NO₃)₂・6H₂O added is 0.1 mmol, there are no obvious Cu cubes on the surface of the nickel foam, and its basic morphology is similar to that of Ni(OH)₂/nickel foam.

When the amount of Cu(NO₃)₂・6H₂O added was increased to 0.5 mmol, a thick layer of elemental Cu was formed on the surface of the nickel foam, and no nanosheets were generated.

[n0075]

Figure 8 shows a comparison of the LSV performance of NiCu-OH/nickel foam electrodes with different Cu loadings for the hydrogen evolution process and the urea oxidation process.

The optimal addition amount is 0.3 mmol Cu(NO₃)₂・6H₂O. Electrodes prepared under this condition exhibit the best hydrogen evolution and urea oxidation performance.

In contrast, the electrode prepared with 0.1 mmol Cu(NO₃)₂・6H₂O has a low Cu doping amount, so its regulatory effect on Ni is not obvious; and because there is no Cu cube, the nanosheets can only grow on a plane, resulting in a low growth density and insufficient catalytic active material in the electrode.

In the electrode prepared with an addition of 0.5 mmol Cu(NO₃)₂・6H₂O, the thick Cu elemental layer on the surface hindered the formation of nanosheets.

[n0076]

The above description is only a preferred embodiment of the present invention, but the scope of protection of the present invention is not limited thereto. Any equivalent substitutions or modifications made by those skilled in the art within the scope of the technology disclosed in the present invention, based on the technical solution and inventive concept of the present invention, should be covered within the scope of protection of the present invention.
