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(54) **SYSTEM AND METHOD FOR ALTERNATELY PERFORMING UREA ELECTROLYSIS-BASED HYDROGEN PRODUCTION AND CARBON REDUCTION, AND APPLICATION SYSTEM**

(57) Disclosed is a system and method for alternately performing urea electrolysis-based hydrogen production and carbon reduction, and an application system. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction includes a housing, a first electrode chamber, a second electrode chamber and a third electrode chamber. A first electrode, a first separator, a second electrode, a second separator and a third electrode are sequentially arranged in the housing. The first electrode chamber is a closed cavity formed by the first electrode, the first separator and the inner wall of the housing, and is used for producing a hydrogen evolution reaction. The third electrode chamber and the second electrode chamber can alternately produce the oxidation reaction of urea and the reduction reaction of carbon dioxide.

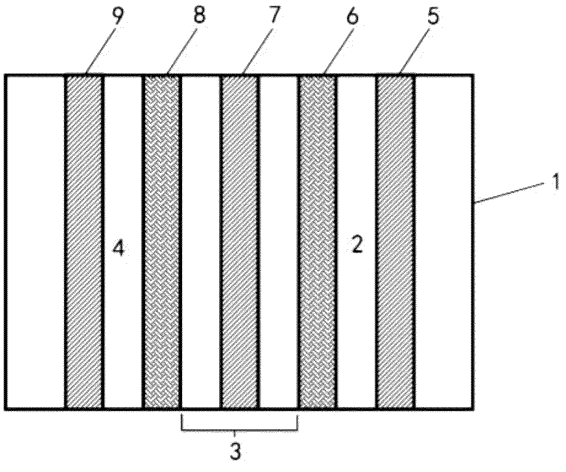

FIG.1

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Description

Technical Field

[0001] This disclosure relates to the technical field of hydrogen production and carbon dioxide utilization, specifically to a system and method for alternately performing urea electrolysis-based hydrogen production and carbon reduction, and an application system.

Background Art

[0002] At present, water electrolysis-based hydrogen production is the only technological approach that can achieve industrial green hydrogen production, which is of great significance for achieving the dual carbon goal. In order to improve the cost competitiveness of green hydrogen produced by water electrolysis-based hydrogen production, it is necessary to further reduce the electricity consumption of water electrolysis-based hydrogen production. Urea, as an electrolyte additive, can theoretically reduce the theoretical energy consumption of electrolysis-based hydrogen production (only 1/5 of direct electrolysis of water). In addition, urea can be obtained from industrial waste or human and animal urine, with the additional effect of purifying wastewater while obtaining hydrogen, making it a good way to reduce hydrogen production costs.

[0003] However, an electrolysis-based hydrogen system adding urea as an electrolyte has the following problems: carbon dioxide generated at the anode is easily converted to carbonate in an alkaline environment, which tends to form carbonate crystals and cause separator clogging, which affects the performance of the electrolysis-based hydrogen production, resulting in higher voltages, lower lifetimes, and so on; and carbon dioxide depletion of alkaline ions results in additional costs. In addition, even if carbon dioxide is not converted into carbonate, its emission may cause pollution; cross-separator mixing of carbon dioxide with hydrogen can result in reduced hydrogen quality, leading to increased subsequent purification costs. Therefore, there is a need to solve the problem of carbon dioxide generated in the process of urea electrolysis-based hydrogen production, avoiding the direct emission of carbon dioxide and pollution of hydrogen, as well as the consumption of alkaline ions and carbonate fouling caused by carbon dioxide.

[0004] It is a good way to convert carbon dioxide into formic acid, methanol, and other liquid organic compounds through reduction reactions, which are further used as industrial raw materials or fuels in chemical production, fuel cell power generation, and other fields. However, the carbon dioxide conversion reaction will cause additional costs. Electrochemical reduction is a mild and efficient production method, but a suitable system needs to be designed to realize the coupling of urea electrolysis and carbon dioxide reduction.

Summary of the Invention

[0005] Thus, it is an objective of the present disclosure to provide a system for alternately performing urea electrolysis-based hydrogen production and carbon reduction, wherein a first electrode chamber can produce a hydrogen evolution reaction of water, and a second electrode chamber and a third electrode chamber can alternately produce the oxidation reaction of urea and reduction reaction of carbon dioxide, so that the carbon dioxide produced from urea electrolysis can be converted in time during the reaction, reducing the mixing pollution of carbon dioxide on the product hydrogen, improving the efficiency of electrolysis-based hydrogen production, and reducing the overall cost of the process. At the same time, through electrochemical reaction, carbon dioxide is reduced to form valuable products, avoiding the release of carbon dioxide, and achieving the purpose of zero carbon emission.

[0006] It is another objective of the present disclosure to provide a method for alternately performing urea electrolysis-based hydrogen production and carbon reduction.

[0007] It is yet another objective of the present disclosure to provide a system for alternately performing urea electrolysis-based hydrogen production and carbon reduction.

[0008] In order to achieve the above objectives, proposed in an embodiment of a first aspect of the present disclosure is a system for alternately performing urea electrolysis-based hydrogen production and carbon reduction, including a housing, a first electrode chamber, a second electrode chamber and a third electrode chamber;

a first electrode, a first separator, a second electrode, a second separator, and a third electrode are successively arranged in the housing, and a space is left between the adjacent two of the first electrode, the first separator, the second electrode, the second separator, and the third electrode;
the first electrode chamber is a closed cavity formed by the first electrode, the first separator, and an inner wall of the housing, and is used for producing a hydrogen evolution reaction; the first electrode chamber is provided with a first gas outlet, a first inlet, and a first outlet;
the second electrode chamber is a closed cavity formed by the first separator, the second separator, and an inner wall

of the housing; the second electrode is provided in the second electrode chamber; the second electrode chamber is provided with a second gas outlet, a second inlet and a second outlet; and
the third electrode chamber is a closed cavity formed by the second separator, the third electrode and the inner wall of the housing; the second electrode chamber is provided with a third gas outlet, a third inlet, and a third outlet; the third electrode chamber and the second electrode chamber can alternately produce the oxidation reaction of urea and the reduction reaction of carbon dioxide.

[0009] In the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction, a first electrode chamber can produce the hydrogen evolution reaction of water, and a second electrode chamber and a third electrode chamber can alternately produce the urea oxidation reaction and reduction reaction of carbon dioxide, so that the carbon dioxide produced from urea electrolysis can be converted in time during the reaction, reducing the mixing pollution of carbon dioxide on the product hydrogen, improving the efficiency of electrolysis-based hydrogen production, and reducing the overall cost of the process. At the same time, through electrochemical reaction, carbon dioxide is reduced to form valuable products, avoiding the release of carbon dioxide, and achieving the purpose of zero carbon emission.

[0010] In some embodiments of the present disclosure, an alkaline aqueous solution is provided in the first electrode chamber; in the second electrode chamber and the third electrode chamber, an alkaline urea solution is provided in the electrode chamber that produces the oxidation reaction of urea, and a CO_2-saturated bicarbonate solution is provided in the electrode chamber that produces the reduction reaction of carbon dioxide.

[0011] In some embodiments of the present disclosure, the second electrode chamber is further provided with a second gas inlet, and the third electrode chamber is further provided with a third gas inlet; and all of the alkaline aqueous solution, the alkaline urea solution and the CO_2-saturated bicarbonate solution are circulated.

[0012] In some embodiments of the present disclosure, the alkaline aqueous solution is a 20-30 wt% potassium hydroxide solution; the alkaline urea solution is a mixed solution of potassium hydroxide, urea, and water, and the contents of potassium hydroxide and urea in the mixed solution are 20-30 wt% and 1-10 wt%, respectively; the pH of the CO_2-saturated bicarbonate solution is 7-11; the concentration of bicarbonate in the CO_2-saturated bicarbonate solution is 0.1-1 M, and the bicarbonate is sodium bicarbonate or potassium bicarbonate.

[0013] In some embodiments of the present disclosure, the first electrode is a conductive substrate having a surface provided with a loading layer; the conductive substrate is a metal plate or a porous plate; the material of the loading layer is one or an alloy of two or more of Pt, Ru, Rh, Ir, Ni, Co, Fe, Zn, and Ti.

[0014] In some embodiments of the present disclosure, the first separator and the second separator are both porous separators or anion exchange membranes with OH^- conductivity; the porous separator is a Zirfon membrane; the anion exchange membrane is a polyarylether membrane, a polyethylene membrane, a polystyrene membrane, a polytetrafluoroethylene membrane, or a polyphenyl membrane modified with a cationic group; the cationic group is a polyalkylammonium, imidazolium, pyridinium, or piperidinium salt.

[0015] In some embodiments of the present disclosure, the second electrode and the third electrode are both reticulated conductive substrates loaded with an active catalytic layer on the surface; the reticulated conductive substrate is a metal material or a carbon material; the material of the active catalytic layer includes a first active component and a second active component; the first active component is a component having electrocatalytic activity for the reduction of carbon dioxide and the second active component is a component having electrocatalytic activity for the oxidation of urea.

[0016] In some embodiments of the present disclosure, the first active component is one or an alloy of two or more of Cu, Pb, Hg, Tl, In, Sn, Cd, and Bi; and the second active component is one or an alloy of two or more of Pt, Ru, Rh, Ir, Ni, Co, Fe, Zn, and Ti. In order to achieve the above objective, an embodiment of a second aspect of the present disclosure proposes a method for alternately performing urea electrolysis-based hydrogen production and carbon reduction, including:

in a first duty cycle, connecting both the first electrode and the third electrode to the negative electrode of the external power supply, and connecting the second electrode to the positive electrode of the external power supply, wherein the first electrode chamber produces a hydrogen evolution reaction, the second electrode chamber produces an oxidation reaction of urea, and the third electrode chamber produces a reduction reaction of carbon dioxide;
in a second duty cycle, connecting both the first electrode and the second electrode to the negative electrode of the external power supply, and connecting the third electrode to the positive electrode of the external power supply, wherein the first electrode chamber produces the hydrogen evolution reaction, the second electrode chamber produces the reduction reaction of carbon dioxide, and the third electrode chamber produces the oxidation reaction of urea;
the first duty cycle and the second duty cycle are performed alternately; there are four sources of carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles:

the first type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is the carbon dioxide produced by urea oxidation;

the second type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is carbon dioxide produced by urea oxidation and carbon dioxide obtained after the separation and purification of the gases after the reduction reaction of carbon dioxide;

the third type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is carbon dioxide produced by urea oxidation and exogenous carbon dioxide; and

the fourth type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is carbon dioxide produced by urea oxidation, obtained after the separation and purification of the gases after the reduction reaction of carbon dioxide, and exogenous carbon dioxide.

[0017] Advantageous effects of the method for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure are substantially the same as those of the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure, and will not be described in detail herein.

[0018] In some embodiments of the present disclosure, switching to the second duty cycle is performed when the pressure in the second electrode chamber is increased by 5-10% during the first duty cycle; and switching to the first duty cycle is performed when the pressure in the third electrode chamber is increased by 5-10% in the second duty cycle.

[0019] In order to achieve the above objective, proposed in an embodiment of a third aspect of the present disclosure is a system for urea electrolysis-based hydrogen production and carbon reduction including the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction as described above, an external power supply, an alkaline aqueous solution reservoir, an alkaline urea solution reservoir, and a product reservoir; wherein the first gas outlet is in communication with a hydrogen storage tank or a hydrogen line; the first inlet is in communication with an outlet of the alkaline aqueous solution reservoir; the first outlet is in communication with an inlet of the alkaline aqueous solution reservoir; the external power supply includes at least one positive electrode and at least two negative electrodes.

[0020] In some embodiments of the present disclosure, based on the oxidation reaction of urea producing in the second electrode chamber, and the reduction reaction of carbon dioxide producing in the third electrode chamber, the first electrode and the third electrode are respectively connected to one negative electrode, and the second electrode is connected to the positive electrode; the second inlet is in communication with an outlet of the alkaline urea solution reservoir, and the second outlet is in communication with an inlet of the alkaline urea solution reservoir; the third inlet is in communication with the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the third outlet is in communication with an inlet of the product reservoir; the third gas outlet is in communication with a nitrogen/carbon dioxide gas separator, and a carbon dioxide outlet of the nitrogen/carbon dioxide gas separator is in communication with the third gas inlet; the third gas inlet is in communication with an exogenous carbon dioxide line.

[0021] In some embodiments of the present disclosure, based on the reduction reaction of carbon dioxide producing in the second electrode chamber, and the oxidation reaction of urea producing in the third electrode chamber, the first electrode and second electrode are respectively connected to one negative electrode, and the third electrode is connected to the positive electrode; the third inlet is in communication with the outlet of the alkaline urea solution reservoir, and the third outlet is in communication with the inlet of the alkaline urea solution reservoir; the second inlet is in communication with the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the second outlet is in communication with the inlet of the product reservoir; the second gas outlet is in communication with the nitrogen/carbon dioxide gas separator, and the carbon dioxide outlet of the nitrogen/carbon dioxide gas separator is in communication with the second gas inlet; and the second gas inlet is in communication with the exogenous carbon dioxide line.

[0022] Advantageous effects of the system for performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure are substantially the same as those of the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure, and will not be described in detail herein.

[0023] In some embodiments of the present disclosure, based on the oxidation reaction of urea producing in the second electrode chamber and the reduction reaction of carbon dioxide producing in the third electrode chamber, circulation pumps are installed on the communication line between the first inlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the first outlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the second inlet and the outlet of the alkaline urea solution reservoir, the communication line between the second outlet and the inlet of the alkaline urea solution reservoir, the communication line between the third inlet and the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the communication line between the third outlet and the inlet of the product reservoir.

[0024] In some embodiments of the present disclosure, based on the reduction reaction of carbon dioxide producing in the second electrode chamber and the oxidation reaction of urea producing in the third electrode chamber, circulation pumps are installed on the communication line between the first inlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the first outlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the third inlet and the outlet of the alkaline urea solution reservoir, the communication line

between the third outlet and the inlet of the alkaline urea solution reservoir, the communication line between the second inlet and the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the communication line between the second outlet and the inlet of the product reservoir.

[0025] Additional aspects and advantages of the present disclosure will be set forth in part in the description which follows and, in part, will be obvious from the description, or may be learned by practice of the present disclosure.

Brief Description of the Drawings

[0026] The foregoing and/or additional aspects and advantages of the present disclosure will become apparent and readily appreciated from the following description of the embodiments, taken in conjunction with the accompanying drawings of which:

FIG. 1 is a simple structural schematic diagram of a system for performing urea electrolysis-based hydrogen production and carbon reduction according to an embodiment of the present disclosure.

FIG. 2 is a simple structural schematic diagram of a system for performing urea electrolysis-based hydrogen production and carbon reduction in a duty state (a second electrode chamber produces an oxidation reaction of urea and a third electrode chamber produces a reduction reaction of carbon dioxide) according to an embodiment of the present disclosure.

FIG. 3 is a simple structural schematic diagram of a system for performing urea electrolysis-based hydrogen production and carbon reduction in a duty state (a second electrode chamber produces a reduction reaction of carbon dioxide and a third electrode chamber produces an oxidation reaction of urea) according to an embodiment of the present disclosure.

Reference signs:

[0027] 1-housing; 2-first electrode chamber; 3-second electrode chamber; 4-third electrode chamber; 5-first electrode; 6-first separator; 7-second electrode; 8-second separator; 9-third electrode; 100-system for alternating urea electrolysis-based hydrogen production and carbon reduction; 200-alkaline aqueous solution reservoir; 300-alkaline urea solution reservoir; 400-product reservoir; 500-hydrogen storage tank; 600-nitrogen/carbon dioxide gas separator; 700-exogenous carbon dioxide line; 800-lye reservoir.

Detailed Description of the Invention

[0028] Reference will now be made in detail to the embodiments of the present disclosure, examples of which are illustrated in the accompanying drawings. The embodiments described below with reference to the figures are exemplary and are intended to be illustrative of the present disclosure and are not to be construed as limiting the present disclosure.

[0029] The materials and equipment referred to in the examples of this disclosure, unless otherwise specified, are commercially available materials and equipment; the methods referred to in the examples of the present disclosure, unless otherwise specified, are conventional experimental methods.

[0030] A system for alternately performing urea electrolysis-based hydrogen production and carbon reduction, a method for alternately performing urea electrolysis-based hydrogen production and carbon reduction, and a system for urea electrolysis-based hydrogen production and carbon reduction according to embodiments of the present disclosure will be described below with reference to the accompanying drawings. FIG. 1 is a simple structural schematic diagram of a system for performing urea electrolysis-based hydrogen production and carbon reduction according to an embodiment of the present disclosure.

[0031] As shown in FIG. 1, the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to an embodiment of the present disclosure includes a housing 1, a first electrode chamber 2, a second electrode chamber 3, and a third electrode chamber 4. A first electrode 5, a first separator 6, a second electrode 7, a second separator 8, and a third electrode 9 are successively arranged in the housing 1. A space is left between the adjacent two of the first electrode 5, the first separator 6, the second electrode 7, the second separator 8, and the third electrode 9. The first electrode chamber 2 is a closed cavity formed by the first electrode 5, the first separator 6, and an inner wall of the housing 1, and is used for producing a hydrogen evolution reaction. The first electrode chamber 2 is provided with a first gas outlet, a first inlet, and a first outlet. The second electrode chamber 3 is a closed cavity formed by the first separator 6, the second separator 8, and an inner wall of the housing 1. The second electrode 7 is provided in the second electrode chamber 3. The second electrode chamber 3 is provided with a second gas outlet, a second inlet and a second outlet. The third electrode chamber 4 is a closed cavity formed by the second separator 8, the third electrode 9, and

the inner wall of the housing 1. The second electrode chamber 3 is provided with a third gas outlet, a third inlet, and a third outlet. The third electrode chamber 4 and the second electrode chamber 2 can alternately produce the oxidation reaction of urea and the reduction reaction of carbon dioxide.

[0032] In the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction, a first electrode chamber can produce a hydrogen evolution reaction of water, and a second electrode chamber and a third electrode chamber can alternately produce an oxidation reaction of urea and a reduction reaction of carbon dioxide, so that the carbon dioxide produced from urea electrolysis can be converted in time during the reaction, reducing the mixing pollution of carbon dioxide on the product hydrogen, improving the efficiency of electrolysis-based hydrogen production, and reducing the overall cost of the process. At the same time, through electrochemical reaction, carbon dioxide is reduced to form valuable products, avoiding the release of carbon dioxide, achieving the purpose of zero carbon emission.

[0033] In some embodiments of the present disclosure, the first electrode and the third electrode may be proximate to an inner wall of the housing proximate thereto. In other embodiments of the present disclosure, the first and third electrodes may also be spaced apart from their immediately adjacent housings (as shown in FIG. 1).

[0034] In some embodiments, the first electrode 5, the first separator 6, the second electrode 7, the second separator 8, and the third electrode 9 can all be welded to the inner wall of the housing 3 or connected to the inner wall of the housing 1 by means of sealing rings, bolts or the like, as long as it is ensured that the first electrode chamber, the second electrode chamber and the third electrode chamber are all closed chambers.

[0035] It should be noted that the shape of the housing 1 is not limited, and the housing 1 may have a cuboid shape, a cube shape, a cylindrical shape, or the like. The material of the housing is also not limited and may be a metal material such as stainless steel or a corrosion-resistant plastic material such as PTEF. The first electrode 5, the first separator 6, the second electrode 7, the second separator 8, and the third electrode 9 may be arranged parallel to each other, or may be inclined at different angles to each other, so long as the first electrode and the first separator and the housing can constitute the first electrode chamber, the first separator and the second separator and the housing can constitute the second electrode chamber, and the second separator and the third electrode and the housing can constitute the third electrode chamber. Preferably, in order to facilitate processing and mounting, the housing has a cuboid shape, a cube shape. All the first electrode 5, the first separator 6, the second electrode 7, the second separator 8, and the third electrode 9 are arranged in parallel and perpendicular to the top and bottom of the housing.

[0036] In some embodiments, the first electrode chamber 2 is provided with an aqueous alkaline solution, preferably a 20-30 wt% potassium hydroxide solution. In the second electrode chamber 3 and the third electrode chamber 4, an alkaline urea solution is provided in the electrode chamber that produces the oxidation reaction of urea, and a CO_2-saturated bicarbonate solution is provided in the electrode chamber that produces the reduction reaction of carbon dioxide. Preferably, the alkaline urea solution is a mixed solution of potassium hydroxide, urea, and water, and the contents of potassium hydroxide and urea in the mixed solution are 20-30 wt% and 1-10 wt%, respectively. The pH of the CO_2-saturated bicarbonate solution is 7-11, preferably 9-10, in order to increase the selectivity of carbon dioxide reduction over HER. The concentration of bicarbonate in the CO_2-saturated bicarbonate solution is 0.1-1 M, and the bicarbonate is sodium bicarbonate or potassium bicarbonate.

[0037] In some embodiments, a second gas inlet is further provided in the second electrode chamber 3 and a third gas inlet is further provided in the third electrode chamber 4 in order to allow the introduction of exogenous carbon dioxide or/and the generated carbon dioxide in the mixed gas after the reduction reaction of carbon dioxide. The alkaline aqueous solution, alkaline urea solution and CO_2-saturated bicarbonate solution all circulate, which can promote gas-liquid mixing and mass transfer within each electrode chamber, and improve the reaction kinetic rate. For the purpose of achieving a homogeneous circulating flow of the alkaline aqueous solution, the alkaline urea solution and the CO_2-saturated bicarbonate solution, one possible way is: in use, the first inlet is in communication with the outlet of the alkaline aqueous solution reservoir 200 via a first line; the first outlet is in communication with the inlet of the alkaline aqueous solution reservoir 200 via a second line; the second inlet is in communication with the outlet of the alkaline urea solution reservoir 300 and the outlet of the alkaline aqueous solution reservoir 200 or the outlet of the lye reservoir 800 via a third line and a fourth line, respectively; the second outlet is in communication with the inlet of the alkaline urea solution reservoir 300 and the inlet of the product reservoir 400 via a fifth line and a sixth line, respectively; the third inlet is communicated with the outlet of the alkaline urea solution reservoir 300 and the outlet of the alkaline aqueous solution reservoir 200 or the outlet of the lye reservoir 800 through a seventh line and an eighth line, respectively; and the third outlet is communicated with the inlet of the alkaline urea solution reservoir 300 and the inlet of the product reservoir 400 through a ninth line and a tenth line, respectively. In addition, a circulation pump and a valve are installed on each line (as shown in FIGs. 2 and 3, in which the circulation pump and the valve are not shown). Thus, whether the first electrode chamber produces the hydrogen evolution reaction, the second electrode chamber produces the oxidation reaction of urea, and the third electrode chamber produces the reduction reaction of carbon dioxide, or the first electrode chamber produces the hydrogen evolution reaction, the second electrode chamber produces the reduction reaction of carbon dioxide, and the third electrode chamber produces the oxidation reaction of urea, the circulation of the alkaline aqueous solution in the first electrode chamber, the circulation of the alkaline urea solution in the second electrode chamber or the third electrode chamber that

produces the oxidation reaction of urea, and the circulation of CO_2-saturated bicarbonate solution in the third chamber or second electrode chamber that produces the reduction reaction of carbon dioxide can be controlled by controlling the on/off of valves on different communication lines. Note that, when the third inlet of the third electrode chamber or the second inlet of the second electrode chamber that produces the reduction reaction of carbon dioxide is in communication with the alkaline aqueous solution reservoir, the alkaline aqueous solution reservoir may be shared with the alkaline aqueous solution reservoir in communication with the first inlet of the first electrode chamber that produces the hydrogen evolution reaction. When the third inlet of the third electrode chamber or the second inlet of the second electrode chamber that produces the reduction reaction of carbon dioxide is in communication with the lye reservoir, the lye reservoir may be another separately provided potassium hydroxide solution reservoir. The alkaline aqueous solution reservoir shall be regularly supplied with water to maintain a certain alkaline concentration. It should also be noted that in order to ensure that there is a sufficient CO_2-saturated bicarbonate solution in the third electrode chamber or the second electrode chamber that produces the reduction reaction of carbon dioxide, it is necessary to mix the alkaline liquid and the carbon dioxide entering the third electrode chamber or the second electrode chamber that produces the reduction reaction of carbon dioxide with each other to reach a saturated state, which requires a non-current pre-reaction for a period of time in the initial stage of the reduction reaction of carbon dioxide in the third electrode chamber or the second electrode chamber that produces the reduction reaction of carbon dioxide. The carbon dioxide generated at the third electrode or the second electrode (or the carbon dioxide generated at the third electrode or the second electrode and the carbon dioxide inputted from an external source) is allowed to react with the circulating alkaline solution entering the third electrode chamber or the second electrode chamber that produces the reduction reaction of carbon dioxide to reach saturation, and then the electrification reaction is started. In addition, it needs to be stated that the preparation of the alkaline urea solution in the alkaline urea solution reservoir can include introducing the potassium hydroxide solution in the potassium hydroxide solution reservoir and the urea solution in the urea solution reservoir respectively into the alkaline urea solution reservoir in a proportion and mixing uniformly. The potassium hydroxide solution reservoir can be shared with the alkaline aqueous solution reservoir of the first electrode chamber that produces the hydrogen evolution reaction. In some embodiments, the first gas outlet, the first inlet and the first outlet are provided on the housing 1 corresponding to the first electrode chamber 2, for example, the first gas outlet and the first inlet are provided on the top of the housing 1 and the first outlet is provided on the bottom of the housing 1. Similarly, the second gas inlet, the second gas outlet, the second inlet, and the second outlet are all provided on the housing 1 corresponding to the second electrode chamber 3. The third gas inlet, the third gas outlet, the third inlet, and the third outlet are all provided on the housing 1 corresponding to the third electrode chamber 4. For example, the second gas inlet, the second gas outlet, the second inlet, the third gas inlet, the third gas outlet, and the third inlet are all provided at the top of the housing 1, and the second outlet and the third outlet are provided at the bottom of the housing 1.

[0038] In some embodiments, the first electrode 5 is a conductive substrate having a surface provided with a loading layer. In some embodiments, the conductive substrate may be a metal plate, such as a copper plate, a stainless-steel plate, etc. In other embodiments, the conductive substrate may be a porous plate, such as a metal foam or a carbon material, wherein the metal foam may be nickel foam, copper foam, iron-nickel foam, nickel-molybdenum foam, etc. and the carbon material may be graphite, activated carbon, etc. In some embodiments, the material of the loading layer is one or an alloy of two or more of P, Ru, Rh, Ir, Ni, Co, Fe, Zn, and Ti. In some embodiments of the present disclosure, the conductive substrate has a thickness of 100-500 micrometers, and the loading layer has a thickness of 5-100 nanometers.

[0039] Note that, in some embodiments of the present disclosure, the method for preparing a conductive substrate having a surface provided with a loading layer includes: providing the material of the loading layer on the conductive substrate by means of electrodeposition, impregnation, etc. and the specific forming method, process conditions, etc. are conventional techniques in the art and are not the focus of the embodiments of the present disclosure.

[0040] The electrochemical reaction of the first electrode surface is as follows:

$$6H_2O+6e^-\rightarrow 3H_2+6OH^-.$$

[0041] In use, the first electrode is connected to an external power supply.

[0042] In some embodiments of the present disclosure, both the first separator 6 and the second separator 8 may be selected to be a porous separator, such as a commercial Zirfon membrane (polysulfone loaded with 85 wt% ZrO_2 nanoparticles) or the like. In other embodiments of the present disclosure, both the first separator 6 and the second separator 8 may be selected as anion exchange membranes having OH^- conductivity. Preferably, the anion exchange membrane may be selected from a polyarylether membrane, a polyethylene membrane, a polystyrene membrane, a polytetrafluoroethylene membrane, or a polyphenyl membrane modified with a cationic group, wherein the cationic group may be selected from a polyalkyl ammonium salt, an imidazolium salt, a pyridinium salt, or a piperidinium salt, for example, the polyalkyl ammonium salt may be selected from a trialkyl quaternary ammonium salt, a trimethyl quaternary ammonium salt, etc.

[0043] In some embodiments of the present disclosure, the method of preparing an anion exchange membrane having

OH^- conductivity includes: monomer polymerization (a monomer modified with a cationic group is directly polymerized with a structural group. For example: quaternary ammonium poly(N-methyl-piperidine-co-p-terphenyl) (QAPPT) can be prepared by:

1) Reaction of p-terphenyl with N-methyl-4-piperidone under the catalysis of trifluoromethanesulfonic acid and trifluoroacetic acid to form a linear polymer catalyzed by trifluoromethanesulfonic acid and trifluoroacetic acid. 2) Conversion of the piperidine group of the polymer to a quaternary ammonium salt: reaction with CH_3I in a mixed NMP/DMSO solvent at 70°C. 3) Final formation of QAPPT with OH^-: treatment with KOH solution for a period of time, or post-modification (the polymer membrane can be directly subjected to cationic group modification. For example, a poly (tetrafluoroethylene) membrane is used as a base material, and chloromethylstyrene is modified thereon through a grafting reaction, followed by quaternization and alkalization using a trimethylamine solution and a KOH solution).

[0044] In some embodiments, the second electrode 7 and the third electrode 9 are both reticulated conductive substrates loaded with an active catalytic layer on the surface.

[0045] The reticulated conductive substrate can be selected from metal materials such as stainless steel and copper, and can also be selected from carbon materials such as graphite and activated carbon; the surface mesh diameter of the reticulated conductive substrate is 0.5-1 mm, and the surface porosity is more than 80%, which facilitates the passage of gas. In some embodiments, the material of the active catalytic layer includes a first active component and a second active component. The first active component is a component having electrocatalytic activity for the reduction of carbon dioxide, such as one or an alloy of two or more of Cu, Pb, Hg, Tl, In, Sn, Cd, and Bi. The second active component is a component having electrocatalytic activity for the oxidation of urea, such as one or an alloy of two or more of Pt, Ru, Rh, Ir, Ni, Co, Fe, Zn, and Ti. The second electrode and the third electrode have the activity of catalyzing the oxidation of urea and catalyzing the reduction of carbon dioxide simultaneously by using the active catalytic layer of multiple active components. In some embodiments, the reticulated conductive substrate has a thickness of 100-500 microns; and the thickness of the active catalytic layer is 5-100 nm.

[0046] In some embodiments of the present disclosure, the method of preparing a reticulated conductive substrate loaded with an active catalytic layer on the surface includes: providing the material of the catalytically active layer on the reticulated conductive substrate by means of electrodeposition, impregnation, etc. and the specific forming method, process conditions, etc. are conventional techniques in the art and are not the focus of the embodiments of the present disclosure.

[0047] In the stage of oxidation reaction of urea, the second/third electrode is connected to the positive electrode of the external power supply.

[0048] The electrochemical reaction at the second/third electrode surface is as follows: $CO(NH_2)_2+6OH^-\rightarrow N_2+5H_2O+CO_2+6e^-$.

[0049] In the stage of reduction of carbon dioxide, the second electrode/third electrode is connected to the negative electrode of the external power supply, and the electrochemical reactions at the surface are as follows:

$$CO_2+H_2O+2e^-\rightarrow HCOOH+OH^-;$$

$$CO_2+3H_2O+4e^-\rightarrow HCHO+4OH^-;$$

and

$$CO_2+3H_2O+6e^-\rightarrow CH_3OH+2OH^-.$$

[0050] By switching the cathode and anode properties of the second electrode and the third electrode, a continuous process of urea electrolysis-based carbon dioxide-carbon dioxide reduction can be achieved to produce valuable products, and exogenous urea and exogenous carbon dioxide can be continuously consumed, with good resource conversion efficiency.

[0051] It should be noted that valves may be installed at each of the gas outlet, the gas inlet, the liquid inlet, and the liquid outlet as needed.

[0052] The working principle of the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure (namely, the method for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure) is as follows:

In use, the first gas outlet is in communication with the hydrogen storage tank 500 or the hydrogen line; the first inlet is in communication with the outlet of the alkaline aqueous solution reservoir 200; the first outlet is in communication with the inlet of the alkaline aqueous solution reservoir 200; a circulation pump is further installed on each communication line

between the first inlet, the first outlet, and the alkaline aqueous solution reservoir 200. The alkaline aqueous solution enters the first electrode chamber 2 and circulates in the first electrode chamber 2.

[0053] As shown in FIG. 2, in the first duty cycle, the first electrode 5 and the third electrode 9 are both connected to the negative electrode of the external power supply. The second electrode 7 is connected to the positive electrode of the external power supply.

[0054] The second gas inlet and the second gas outlet are closed. The second inlet is in communication with the outlet of the alkaline urea solution reservoir 300 and the second outlet is in communication with the inlet of the alkaline urea solution 300. The third gas outlet is in communication with a nitrogen/carbon dioxide gas separator 600, and the third gas inlet may be closed without ventilation or is connected to an exogenous carbon dioxide line 700 from thermal power plants, chemical plants, steelmaking, and other waste gas capture systems, or/and is in communication with a carbon dioxide outlet connected to the nitrogen/carbon dioxide gas separator 600. The third inlet is in communication with the outlet of the alkaline aqueous solution reservoir 200, and the third outlet is in communication with the inlet of the product reservoir 400. A circulation pump is mounted on each communication line between the second inlet, the second outlet, and the alkaline aqueous solution reservoir 200.

[0055] Circulation pumps are mounted on the communication line between the third inlet and the alkaline urea solution reservoir 300, and the communication line between the third outlet and the inlet of the product reservoir 400. The alkaline urea aqueous solution enters the second electrode chamber and circulates in the second electrode chamber 3.

[0056] The alkaline aqueous solution enters the third electrode chamber 4, and circulates in the third electrode chamber 4. The electrolytic alkaline aqueous solution in the first electrode chamber 2 is electrolyzed to produce a hydrogen evolution reaction. The generated hydrogen is collected via a hydrogen storage tank 500 or is used via a hydrogen line. OH^- enters the second electrode chamber 3 via the first separator 6. The second electrode chamber 3 produces the oxidation reaction of urea. The generated carbon dioxide enters the third electrode chamber 4 via the second separator 8. The third electrode 9 is initially unpowered, so that the carbon dioxide generated in the oxidation reaction of urea in the second electrode chamber (or the carbon dioxide generated by the carbon dioxide generated in the oxidation reaction of urea in the second electrode chamber and the carbon dioxide imported from an external source; or carbon dioxide produced by the carbon dioxide produced in the oxidation reaction of urea in the second electrode chamber and carbon dioxide obtained after separation and purification of the gases after the reduction reaction of carbon dioxide in the third electrode chamber; or carbon dioxide produced by the carbon dioxide produced in the oxidation reaction of urea in the second electrode chamber, carbon dioxide obtained after separation and purification of the gas after the reduction reaction of carbon dioxide in the third electrode chamber, and carbon dioxide imported from an external source) reacts with the circulating alkaline liquid entering the third electrode chamber 4 to reach saturation, so as to ensure that there is a CO_2-saturated bicarbonate solution available for the reduction reaction of carbon dioxide in the third electrode chamber 4.

[0057] Then the third electrode 9 is powered for the reaction, and the third electrode chamber 4 produces the reduction reaction of carbon dioxide. The carbon dioxide from the second electrode chamber 3 or the carbon dioxide from the second electrode chamber 3 and the exogenous carbon dioxide entering from the third gas inlet reacts with the CO_2-saturated bicarbonate solution in the third electrode chamber 4 to convert the carbon dioxide into formic acid, methanol and formaldehyde, which are flow out of the third electrode chamber 4 via the third outlet and are collected via the product reservoir 400. A small amount of carbon dioxide which has not reacted completely and the nitrogen generated from the oxidation of urea in the second electrode chamber 3 enter the nitrogen/carbon dioxide gas separator 600 via the third gas outlet for separation. The separated carbon dioxide can be recycled back to the third electrode chamber 4 for reuse. The nitrogen is transported as a product. Preferably, the nitrogen/carbon dioxide gas separator employs a membrane separator.

[0058] During the first duty cycle, the first electrode chamber produces a reaction at the first electrode surface: $2H_2O+2e^- \rightarrow H_2+2OH^-$; the second electrode chamber produces a reaction at the second electrode surface:

$$CO(NH_2)_2+6OH^- \rightarrow N_2+5H_2O+CO_2+6e^-;$$

the third electrode chamber produces reactions at the third electrode surface:

$$CO_2+H_2O+2e^- \rightarrow HCOOH+OH^-;$$

$$CO_2+3H_2O+4e^- \rightarrow HCHO+4OH^-;$$

and

$$CO_2+3H_2O+6e^- \rightarrow CH_3OH+2OH^-.$$

[0059] As shown in FIG. 3, in the second duty cycle, similar to the first cycle, the first electrode 5 and the second electrode

7 are both connected to the negative electrode of the external power supply, and the third electrode 9 is connected to the positive electrode of the external power supply. The first electrode chamber 2 produces a hydrogen evolution reaction, the second electrode chamber 3 produces a reduction reaction of carbon dioxide, and the third electrode chamber 4 produces an oxidation reaction of urea.

[0060] During the second duty cycle, the first electrode chamber produces a reaction at the first electrode surface: $2H_2O+2e^-\rightarrow H_2+2OH^-$; the second electrode chamber produces reactions at the second electrode surface:

$$CO_2+H_2O+2e^-\rightarrow HCOOH+OH^-;$$

$$CO_2+3H_2O+4e^-\rightarrow HCHO+4OH^-;$$

and

$$CO_2+3H_2O+6e^-\rightarrow CH_3OH+2OH;$$

the third electrode chamber produces a reaction at the third electrode surface:

$$CO(NH_2)_2+6OH^-\rightarrow N_2+5H_2O+CO_2+6e^-.$$

[0061] The first duty cycle and the second duty cycle alternate throughout the operation. The criteria for the end of the first duty cycle are: the carbon dioxide generated in the second electrode chamber 3 is absorbed by the lye in the third electrode chamber 4, while the concentration of carbon dioxide in the second electrode chamber 3 is controlled to prevent the first separator 6 and the second separator 8 from being blocked by carbonate. The criteria for determining that the first duty cycle needs to be switched to the second duty cycle is the pressure in the second electrode chamber 3 is increased by 5-10% (monitored by connecting a pressure gauge). The criteria for the end of the second duty cycle are: the carbon dioxide generated in the third electrode chamber 4 is absorbed by the lye in the second electrode chamber 3, while the carbon dioxide concentration in the third electrode chamber 4 is controlled to prevent the second separator 8 from being blocked by carbonate. The criteria for determining that the second duty cycle needs to be switched to the first duty cycle is the pressure in the third electrode chamber 4 is increased by 5-10% (monitored by connecting a pressure gauge).

[0062] In the whole working process of the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure, continuous urea consumption and timely conversion consumption of carbon dioxide in the electrolysis system are realized in time through the switching between the conversion reaction of carbon dioxide and the oxidation reaction of urea, so as to avoid the consumption of carbon dioxide to hydroxyl ions in the alkaline system of the first electrode chamber, reduce the fouling of the electrolysis separator (the first separator), and improve the efficiency of the electrolysis-based hydrogen production reaction. Carbon dioxide is reduced to form a valuable liquid product, which is beneficial for the next cycle to promote the equilibrium of the electrolysis reaction to move forward, reduce the mixing pollution of carbon dioxide to the product hydrogen while improving the overall reaction efficiency, and avoiding the release of carbon dioxide to achieve the goal of zero carbon emission.

[0063] As shown in FIGS. 2 and 3, the system for urea electrolysis-based hydrogen production and carbon reduction according to the embodiment of the present disclosure includes a system 100 for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiment of the present disclosure, an external power supply (not shown), an alkaline aqueous solution reservoir 200, an alkaline urea solution reservoir 300, and a product reservoir 400. The first gas outlet is in communication with a hydrogen storage tank 500 or a hydrogen line. The first inlet is in communication with an outlet of the alkaline aqueous solution reservoir 200. The first outlet is in communication with an inlet of the alkaline aqueous solution reservoir 200. The external power supply includes at least one positive electrode and at least two negative electrodes.

[0064] In some embodiments of the present disclosure, based on the oxidation reaction of urea producing in the second electrode chamber 3, and the reduction reaction of carbon dioxide producing in the third electrode chamber 4, the first electrode 5 and the third electrode 9 are respectively connected to one negative electrode, and the second electrode 7 is connected to the positive electrode; the second inlet is in communication with an outlet of the alkaline urea solution reservoir 300, and the second outlet is in communication with an inlet of the alkaline urea solution reservoir 300; the third inlet is in communication with the outlet of the alkaline aqueous solution reservoir 200 or the outlet of the lye reservoir 800, and the third outlet is in communication with an inlet of the product reservoir 400; the third gas outlet is in communication with a nitrogen/carbon dioxide gas separator 600, and a carbon dioxide outlet of the nitrogen/carbon dioxide gas separator 600 is in communication with the third gas inlet; the third gas inlet is in communication with an exogenous carbon dioxide line 700. based on the reduction reaction of carbon dioxide producing in the second electrode chamber 3, and the oxidation reaction of urea producing in the third electrode chamber 4, the first electrode 5 and second electrode 7 are respectively

connected to one negative electrode, and the third electrode 9 is connected to the positive electrode; the third inlet is in communication with the outlet of the alkaline urea solution reservoir 300, and the third outlet is in communication with the inlet of the alkaline urea solution reservoir 300; the second inlet is in communication with the outlet of the alkaline aqueous solution reservoir 200 or the outlet of the lye reservoir 800, and the second outlet is in communication with the inlet of the product reservoir 400; the second gas outlet is in communication with the nitrogen/carbon dioxide gas separator 600, and the carbon dioxide outlet of the nitrogen/carbon dioxide gas separator 600 is in communication with the second gas inlet; and the second gas inlet is in communication with the exogenous carbon dioxide line 700. Preferably, the nitrogen/carbon dioxide gas separator employs a membrane separator.

[0065] The advantageous effects of the system for urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure are substantially the same as those of the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction described above, and will not be described again.

[0066] In some embodiments, based on the oxidation reaction of urea producing in the second electrode chamber 3 and the reduction reaction of carbon dioxide producing in the third electrode chamber 4, circulation pumps are installed on the communication line between the first inlet and the outlet of the alkaline aqueous solution reservoir 200, the communication line between the first outlet and the outlet of the alkaline aqueous solution reservoir 200, the communication line between the second inlet and the outlet of the alkaline urea solution reservoir 300, the communication line between the second outlet and the inlet of the alkaline urea solution reservoir 300, the communication line between the third inlet and the outlet of the alkaline aqueous solution reservoir 200 or the outlet of the lye reservoir 800, and the communication line between the third outlet and the inlet of the product reservoir 400.

[0067] In some embodiments, based on the reduction reaction of carbon dioxide producing in the second electrode chamber 3 and the oxidation reaction of urea producing in the third electrode chamber 4, circulation pumps are installed on the communication line between the first inlet and the outlet of the alkaline aqueous solution reservoir 200, the communication line between the first outlet and the outlet of the alkaline aqueous solution reservoir 200, the communication line between the third inlet and the outlet of the alkaline urea solution reservoir 300, the communication line between the third outlet and the inlet of the alkaline urea solution reservoir 300, the communication line between the second inlet and the outlet of the alkaline aqueous solution reservoir 200 or the outlet of the lye reservoir 800, and the communication line between the second outlet and the inlet of the product reservoir 400.

[0068] It should be noted that in the urea electrolysis-based hydrogen production and carbon reduction system of the embodiments of the present disclosure, valves can be installed on each line according to needs, which is a conventional technique in the art and does not fall within the protection focus of the present disclosure.

[0069] The operating principle of the system for urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure is substantially the same as the operating principle of the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction according to the embodiments of the present disclosure, and will not be described in detail herein.

[0070] In the description of this specification, references to descriptions of the terms "one embodiment", "some embodiments", "example", "specific examples", or "some examples", etc. mean that a particular feature, structure, material, or characteristic described in connection with the embodiment or example is included in at least one embodiment or example of the present disclosure. In this description, schematic representations of the terms above do not necessarily refer to the same embodiment or example. Furthermore, the particular features, structures, materials, or characteristics described may be combined in any suitable manner in any one or more embodiments or examples. Further, the different embodiments or examples and the features of the different embodiments or examples described in this description can be integrated and combined by a person skilled in the art without contradicting each other.

[0071] While examples of the present disclosure have been shown and described, it will be understood that the above-described embodiments are illustrative and not restrictive and that changes, modifications, substitutions, and alterations may be made by those skilled in the art without departing from the scope of the present disclosure.

Claims

1. A system for alternately performing urea electrolysis-based hydrogen production and carbon reduction, comprising a housing, a first electrode chamber, a second electrode chamber, and a third electrode chamber;

   a first electrode, a first separator, a second electrode, a second separator, and a third electrode are successively arranged in the housing, and a space is left between the adjacent two of the first electrode, the first separator, the second electrode, the second separator, and the third electrode;
   the first electrode chamber is a closed cavity formed by the first electrode, the first separator, and an inner wall of the housing, and is used for producing a hydrogen evolution reaction; the first electrode chamber is provided with

a first gas outlet, a first inlet, and a first outlet;
the second electrode chamber is a closed cavity formed by the first separator, the second separator, and an inner wall of the housing; the second electrode is provided in the second electrode chamber; the second electrode chamber is provided with a second gas outlet, a second inlet and a second outlet; and
the third electrode chamber is a closed cavity formed by the second separator, the third electrode and the inner wall of the housing; the second electrode chamber is provided with a third gas outlet, a third inlet, and a third outlet; the third electrode chamber and the second electrode chamber can alternately produce the oxidation reaction of urea and the reduction reaction of carbon dioxide.

2. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of claim 1, wherein an alkaline aqueous solution is provided in the first electrode chamber; in the second electrode chamber and the third electrode chamber, an alkaline urea solution is provided in the electrode chamber that produces the oxidation reaction of urea, and a CO_2-saturated bicarbonate solution is provided in the electrode chamber that produces the reduction reaction of carbon dioxide.

3. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of claim 1 or 2, wherein the second electrode chamber is further provided with a second gas inlet, and the third electrode chamber is further provided with a third gas inlet; and all of the alkaline aqueous solution, the alkaline urea solution and the CO_2-saturated bicarbonate solution are circulated.

4. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of claim 2 or 3, wherein the alkaline aqueous solution is a 20-30 wt% potassium hydroxide solution; the alkaline urea solution is a mixed solution of potassium hydroxide, urea, and water, and the contents of potassium hydroxide and urea in the mixed solution are 20-30 wt% and 1-10 wt%, respectively; the pH of the CO_2-saturated bicarbonate solution is 7-11; the concentration of bicarbonate in the CO_2-saturated bicarbonate solution is 0.1-1 M, and the bicarbonate is sodium bicarbonate or potassium bicarbonate.

5. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of any one of claims 1 to 4, wherein the first electrode is a conductive substrate having a surface provided with a loading layer; the conductive substrate is a metal plate or a porous plate; the material of the loading layer is one or an alloy of two or more of Pt, Ru, Rh, Ir, Ni, Co, Fe, Zn, and Ti.

6. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of any one of claims 1 to 5, wherein the first separator and the second separator are both porous separators or anion exchange membranes with OH^- conductivity; the porous separator is a Zirfon membrane; the anion exchange membrane is a polyarylether membrane, a polyethylene membrane, a polystyrene membrane, a polytetrafluoroethylene membrane, or a polyphenyl membrane modified with a cationic group; the cationic group is a polyalkylammonium, imidazolium, pyridinium, or piperidinium salt.

7. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of any one of claims 1 to 6, wherein the second electrode and the third electrode are both reticulated conductive substrates loaded with an active catalytic layer on the surface; the reticulated conductive substrate is a metal material or a carbon material; the material of the active catalytic layer comprises a first active component and a second active component; the first active component is a component having electrocatalytic activity for the reduction of carbon dioxide and the second active component is a component having electrocatalytic activity for the oxidation of urea.

8. The system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of claim 7, wherein the first active component is one or an alloy of two or more of Cu, Pb, Hg, Tl, In, Sn, Cd, and Bi; and the second active component is one or an alloy of two or more of Pt, Ru, Rh, Ir, Ni, Co, Fe, Zn, and Ti.

9. A method for alternately performing urea electrolysis-based hydrogen production and carbon reduction of any one of claims 1 to 8, comprising:

in a first duty cycle, connecting both the first electrode and the third electrode to the negative electrode of the external power supply, and connecting the second electrode to the positive electrode of the external power supply, wherein the first electrode chamber produces a hydrogen evolution reaction, the second electrode chamber produces an oxidation reaction of urea, and the third electrode chamber produces a reduction reaction of carbon dioxide;

in a second duty cycle, connecting both the first electrode and the second electrode to the negative electrode of the external power supply, and connecting the third electrode to the positive electrode of the external power supply, wherein the first electrode chamber produces a hydrogen evolution reaction, the second electrode chamber produces a reduction reaction of carbon dioxide, and the third electrode chamber produces an oxidation reaction of urea;
the first duty cycle and the second duty cycle are performed alternately; there are four sources of carbon dioxide that produces a reduction reaction of carbon dioxide during the first and second duty cycles:

the first type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is the carbon dioxide produced by urea oxidation;
the second type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is carbon dioxide produced by urea oxidation and carbon dioxide obtained after the separation and purification of the gases after the reduction reaction of carbon dioxide;
the third type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is carbon dioxide produced by urea oxidation and exogenous carbon dioxide; and
the fourth type, the carbon dioxide that produces the reduction reaction of carbon dioxide during the first and second duty cycles is carbon dioxide produced by urea oxidation, obtained after the separation and purification of the gases after the reduction reaction of carbon dioxide, and exogenous carbon dioxide.

10. The method of claim 9, wherein switching to the second duty cycle is performed when the pressure in the second electrode chamber is increased by 5-10% during the first duty cycle; and switching to the first duty cycle is performed when the pressure in the third electrode chamber is increased by 5-10% in the second duty cycle.

11. A system for urea electrolysis-based hydrogen production and carbon reduction comprising the system for alternately performing urea electrolysis-based hydrogen production and carbon reduction of any one of claims 1 to 8, an external power supply, an alkaline aqueous solution reservoir, an alkaline urea solution reservoir and a product reservoir; wherein the first gas outlet is in communication with a hydrogen storage tank or a hydrogen line; the first inlet is in communication with an outlet of the alkaline aqueous solution reservoir; the first outlet is in communication with an inlet of the alkaline aqueous solution reservoir; the external power supply comprises at least one positive electrode and at least two negative electrodes.

12. The system of claim 11, wherein based on the oxidation reaction of urea producing in the second electrode chamber, and the reduction reaction of carbon dioxide producing in the third electrode chamber, the first electrode and the third electrode are respectively connected to one negative electrode, and the second electrode is connected to the positive electrode; the second inlet is in communication with an outlet of the alkaline urea solution reservoir, and the second outlet is in communication with an inlet of the alkaline urea solution reservoir; the third inlet is in communication with the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the third outlet is in communication with an inlet of the product reservoir; the third gas outlet is in communication with a nitrogen/carbon dioxide gas separator, and a carbon dioxide outlet of the nitrogen/carbon dioxide gas separator is in communication with the third gas inlet; the third gas inlet is in communication with an exogenous carbon dioxide line; and

based on the reduction reaction of carbon dioxide producing in the second electrode chamber, and the oxidation reaction of urea producing in the third electrode chamber, the first electrode and second electrode are respectively connected to one negative electrode, and the third electrode is connected to the positive electrode;
the third inlet is in communication with the outlet of the alkaline urea solution reservoir, and the third outlet is in communication with the inlet of the alkaline urea solution reservoir;
the second inlet is in communication with the outlet of the alkaline aqueous solution reservoir or an outlet of a lye reservoir, and the second outlet is in communication with the inlet of the product reservoir; the second gas outlet is in communication with the nitrogen/carbon dioxide gas separator, and the carbon dioxide outlet of the nitrogen/carbon dioxide gas separator is in communication with the second gas inlet; and the second gas inlet is in communication with the exogenous carbon dioxide line.

13. The system of claim 11, wherein based on the oxidation reaction of urea producing in the second electrode chamber and the reduction reaction of carbon dioxide producing in the third electrode chamber, circulation pumps are installed on the communication line between the first inlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the first outlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the second inlet and the outlet of the alkaline urea solution reservoir, the communication line between the second outlet and the inlet of the alkaline urea solution reservoir, the communication line between the

third inlet and the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the communication line between the third outlet and the inlet of the product reservoir; and

based on the reduction reaction of carbon dioxide producing in the second electrode chamber and the oxidation reaction of urea producing in the third electrode chamber, circulation pumps are installed on the communication line between the first inlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the first outlet and the outlet of the alkaline aqueous solution reservoir, the communication line between the third inlet and the outlet of the alkaline urea solution reservoir, the communication line between the third outlet and the inlet of the alkaline urea solution reservoir, the communication line between the second inlet and the outlet of the alkaline aqueous solution reservoir or the outlet of the lye reservoir, and the communication line between the second outlet and the inlet of the product reservoir.

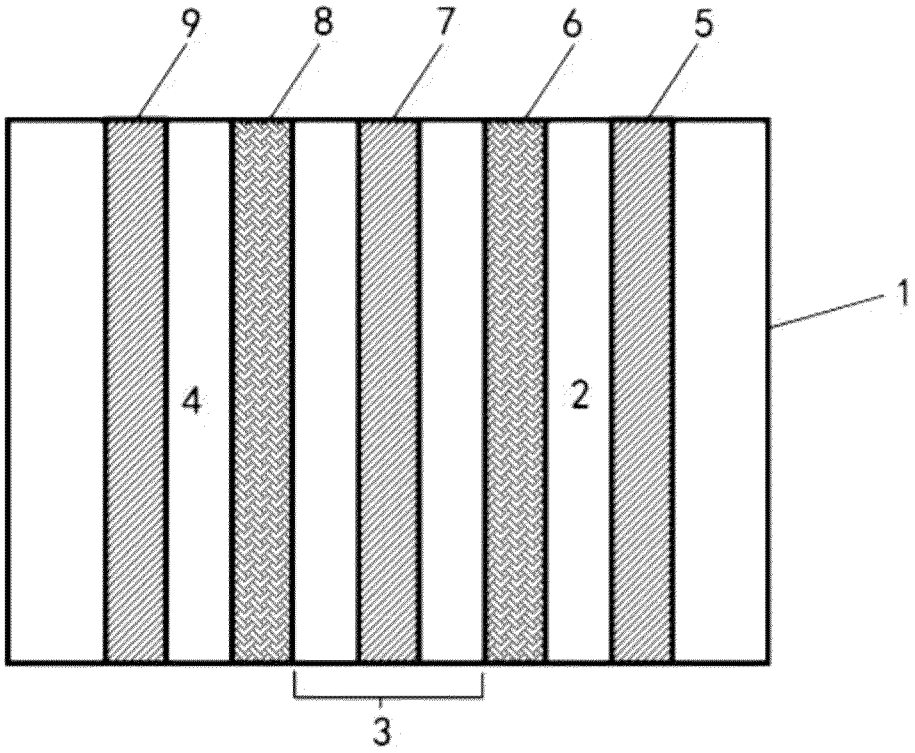

FIG.1

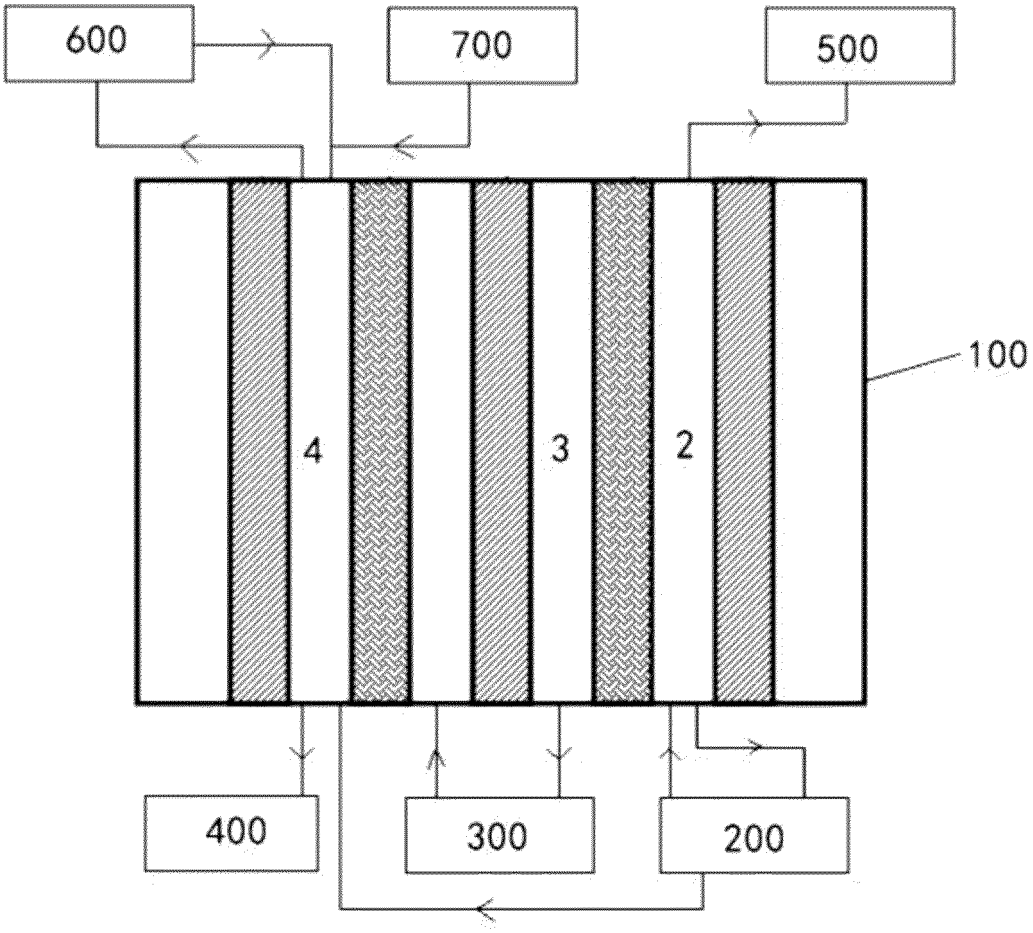

FIG.2

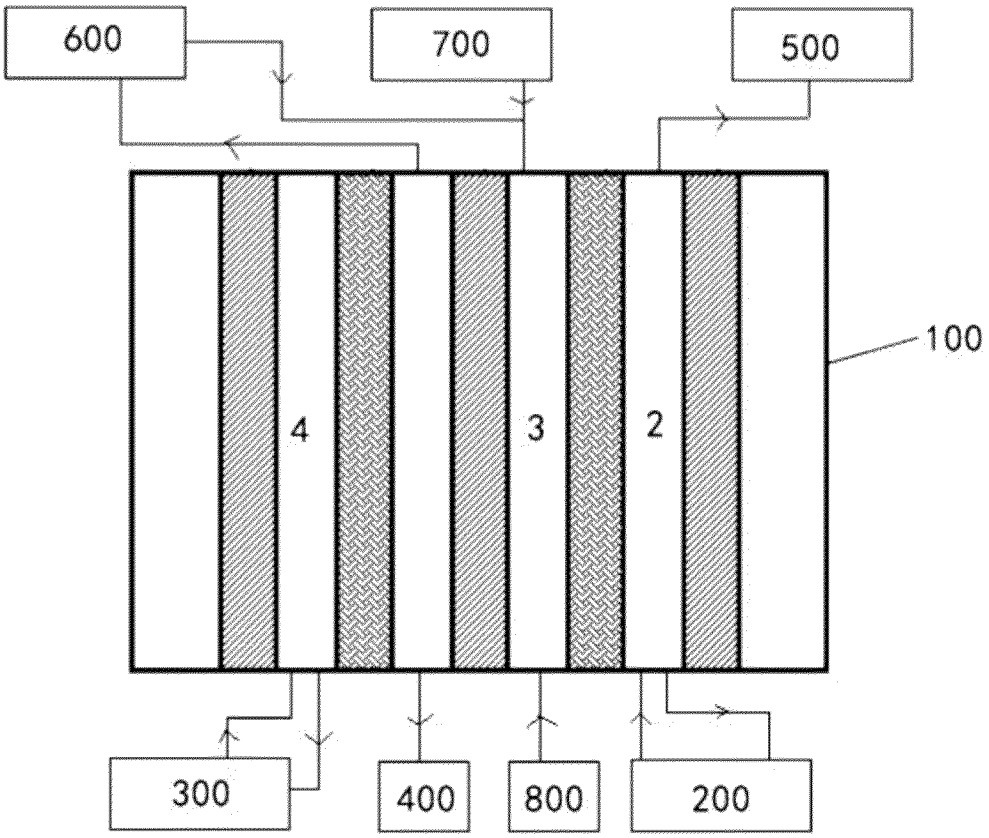

FIG.3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/098978

A. CLASSIFICATION OF SUBJECT MATTER

C25B9/21(2021.01)i; C25B1/04(2021.01)i; C25B1/01(2021.01)i; C25B3/07(2021.01)i; C25B3/26(2021.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25B9/-; C25B1/-; C25B3/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, CNTXT, CNKI, VEN, WPABSC, USTXT, WOTXT, Web of Science: 华能, 张畅, 郭海礁, 徐显明, 王金意, Huaneng, zhang chang, guo haijiao, xu xianming, wang jinyi, 尿素, 二氧化碳, 还原, 氧化, 电解, 交替, 隔膜, urea, CO2, carbon dioxide, reduct+, oxidat+, electroly*, alternat+, membrane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 115305492 A (CHINA HUANENG GROUP CLEANING ENERGY TECHNOLOGY RESEARCH INSTITUTE CO., LTD. et al.) 08 November 2022 (2022-11-08) claims 1-10	1-13
A	CN 110273163 A (YAN WEI) 24 September 2019 (2019-09-24) description, paragraphs 0028-0041	1-13
A	CN 208189712 U (CHINA HUANENG GROUP CLEANING ENERGY TECHNOLOGY RESEARCH INSTITUTE CO., LTD.) 04 December 2018 (2018-12-04) entire document	1-13
A	US 2011302909 A1 (BOTTE GERARDINE G et al.) 15 December 2011 (2011-12-15) entire document	1-13
A	US 2018202056 A1 (KOREA INSTITUTE ENERGY RESEARCH) 19 July 2018 (2018-07-19) entire document	1-13

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 August 2023	**22 August 2023**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/098978

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2022170166 A1 (UNIVERSITY OF TORONTO GOVERNING COUNCIL) 02 June 2022 (2022-06-02) entire document	1-13

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2023/098978

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	115305492	A	08 November 2022	None			
CN	110273163	A	24 September 2019	None			
CN	208189712	U	04 December 2018	None			
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