

(19) **DANMARK**

(10) **DK/EP 2553229 T3**



(12) **Oversættelse af
europæisk patentskrift**

Patent- og
Varemærkestyrelsen

-
- (51) Int.Cl.: **F 01 N 3/20 (2006.01)** **C 25 B 1/00 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2015-02-16**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2014-12-17**
- (86) Europæisk ansøgning nr.: **11714464.2**
- (86) Europæisk indleveringsdag: **2011-03-31**
- (87) Den europæiske ansøgnings publiceringsdag: **2013-02-06**
- (86) International ansøgning nr.: **US2011030694**
- (87) Internationalt publikationsnr.: **WO2011123620**
- (30) Prioritet: **2010-04-02 US 320447 P**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
- (73) Patenthaver: **Ohio University, 340 West State Street , Unit 14, Athens, OH 45701-2979, USA**
- (72) Opfinder: **BOTTE, Gerardine, G., 7519 Longmeadow Lane, Athens, OH 45701, USA**
- (74) Fuldmægtig i Danmark: **JESPER LEVIN A/S, Vedbæk Strandvej 341, 2950 Vedbæk, Danmark**
- (54) Benævnelse: **Selektiv katalytisk reduktion ved elektrolyse af urinstof**
- (56) Fremdragne publikationer:
US-A1- 2004 057 887
US-A1- 2009 095 636

Description

[0001]

5 FIELD OF INVENTION

[0002] The present invention relates to methods and devices for treating exhaust gases.

BACKGROUND

10

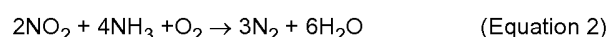
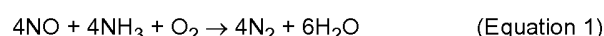
[0003] There is concern over the environmental impact of emissions from power plants and other fossil fuel combustion sources. For example, the exhaust gas of coal-fired power plants contains chemical pollutants such as nitrogen oxides ("NO_x") and sulfur oxides ("SO_x"), as well as particulates, which are also known as "fly ash". Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are means for converting nitrogen oxides (NO_x) into diatomic nitrogen, N₂, and water, H₂O. In SCR, a catalyst is used in combination With a gaseous reductant, which is added to a stream of flue or exhaust gas and is absorbed onto the catalyst. In SCNR, the reductant is injected into the flue gas in a furnace within an appropriate temperature window. Additionally, flue gas conditioning with a gaseous reductant can also enhance electrostatic precipitator performance for removing fly ash. In SCR, SNCR, and fly ash removal systems, the reductant is typically ammonia or urea.

20

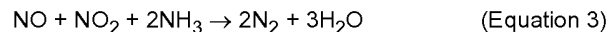
[0004] For example, commercial SCR systems are typically found on large utility boilers, industrial boilers, and municipal solid waste boilers and have been shown to reduce NO_x by 70-95%. More recent applications include diesel engines, such as those found on large ships, diesel locomotives, gas turbines, and even automobiles.

25

[0005] The NO_x reduction reaction takes place as the gases pass through the catalyst chamber. Before entering the catalyst chamber the ammonia, or other reductant, such as urea, is injected and mixed with the gases. The chemical equations for using either anhydrous or aqueous ammonia for a selective catalytic reduction process are:

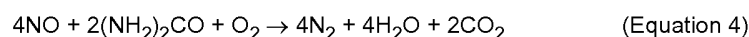


30



The reaction for urea as a reductant instead of ammonia is:

35



[0006] The reaction has an optimal temperature range between 350°C and 450°C, but can operate from 225°C to 450°C with longer residence times. The minimum effective temperature depends on the various fuels, gas constituents and catalyst geometry.

40

[0007] In SNCR systems, the absence of a catalyst increases the temperature for the reduction reaction. For example, the temperature window for efficient operation of an SNCR system is typically between 900°C and 1,100°C depending on the reagent and conditions of the SNCR operation.

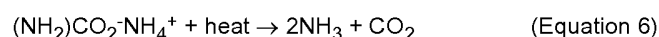
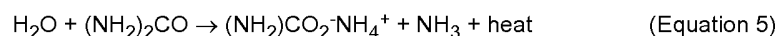
45

[0008] Compared to urea, ammonia is more reactive, is more easily dispersed uniformly into the flue gas stream and is active over a broader temperature range, as well as being more efficient. Urea, as such, while also an effective reductant, forms unwanted byproducts, such as carbon monoxide (CO) and nitrous oxide (N₂O), both of which are now under critical scrutiny by environmental authorities.

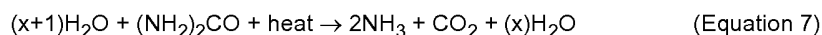
50

[0009] Commonly urea is thermally hydrolyzed to form ammonia for exhaust gas treatment applications. The hydrolysis of urea to form ammonia can be broken down into two distinct reactions. The first reaction is a mildly exothermic reaction, wherein heat is given off as urea hydrolyzes to form ammonium carbamate. The second reaction, in which the ammonium carbamate is converted to ammonia and carbon dioxide, is strongly endothermic, which overall dominates the thermodynamics of the conversion of urea to ammonia and carbon dioxide, *i.e.*, the overall reaction is endothermic. Therefore, the hydrolysis of urea requires a substantial amount of heat and quickly stops when the supply of heat is withdrawn. For example, the liberation of ammonia commences at around 110°C and becomes rapid at around 150°C to 160°C, with or without catalytic assistance.

55



Excess water promotes the hydrolysis reaction, the overall reaction for which is as follows:



[0010] However, under the reaction conditions necessary to affect useful throughput, the water quality is important. For example, in a conventional thermal hydrolysis of urea to ammonia for an SCR system, an aqueous solution of urea is atomized through a spray nozzle into a heated vaporization chamber. As such, the excess water is also vaporized during the hydrolysis of urea to ammonia, thereby leaving behind any non-volatile substances such as minerals. Minerals and other non-volatile substances can adhere to equipment surfaces, such as spray nozzles and the vaporization chamber walls, and build up over time, which may lead to blockage of the spray nozzle or reduced heat transfer efficiency to the vaporization chamber. Thus, the water used in thermal hydrolysis systems needs to be demineralized.

[0011] Further, the thermal hydrolysis of urea method is also sensitive to the quality of the urea. For example, formaldehyde present in urea can negatively affect the performance of an SCR system in a way similar to that of using demineralized water.

[0012] In view of the foregoing, the hydrolysis of urea requires an external heat source to initiate the reaction, even when coupled with combustion engines, and also is sensitive to the extent of demineralization of the water and the quality of urea used in the hydrolysis. Therefore, more efficient methods for generating ammonia for exhaust gas treatment applications are needed.

[0013] US 2009/095636 discloses a method using an electrolytic cell to electrolyze urea to produce at least one of H₂ and NH₃. An electrolytic cell having a cathode with a first conducting component, an anode with a second conducting component, urea and an alkaline electrolyte composition in electrical communication with the anode and the cathode is used to electrolyze urea. The alkaline electrolyte composition has a hydroxide concentration of at least 0.01 M.

SUMMARY OF THE INVENTION

[0014] The invention is defined by the claims.

[0015] The present invention is premised on the realization that ammonia can be produced from the electrolysis of urea to supply exhaust gas treatment applications, such as selective catalytic reduction (SCR) systems, selective non-catalytic reduction (SNCR) systems, and/or flue gas conditioning systems.

[0016] According to one embodiment of the present invention, a method for supplying NH₃ to an exhaust gas treatment system is provided. The method includes producing ammonia by an electrolytic hydrolysis of urea effected by applying a voltage difference to an electrolytic cell, recovering at least a portion of the NH₃, and transferring the at least a portion of the NH₃ to the exhaust gas treatment system. The electrolytic cell includes a cathode having a first conducting component, an anode having a second conducting component, urea, and an alkaline electrolyte composition in electrical communication with the anode and the cathode, where the alkaline electrolyte composition has a hydroxide concentration of at least 0.01 M or a pH of at least 8. The voltage difference is applied across the cathode and the anode, and the voltage difference is sufficient to effect the electrolytic hydrolysis of urea to produce at least NH₃.

[0017] According to another embodiment of the present invention, there is provided a method for reducing nitrogen oxide (NO_x) emissions and/or particulate matter in a combustion exhaust gas during ongoing operation. The method comprises injecting ammonia into the combustion exhaust gas upstream of at least one of a selective catalytic reduction (SCR) device, a selective non-catalytic reduction (SNCR) device, or an electrostatic precipitator device. The ammonia is supplied by applying a voltage difference to an electrolytic cell, which includes a cathode having a first conducting component, an anode having a second conducting component, urea, and an alkaline electrolyte composition in electrical communication with the anode and the cathode, where the alkaline electrolyte composition has a hydroxide concentration of at least 0.01 M or a pH of at least 8. The voltage difference is applied across the cathode and the anode, and the voltage difference is sufficient to effect the electrolytic hydrolysis of urea to produce at least NH₃.

[0018] According to yet another embodiment of the present invention, an exhaust gas treatment system is provided. The exhaust gas treatment system comprises at least one of a selective catalytic reduction system, a selective non-catalytic reduction system, or a flue gas conditioning system and an ammonia generator. The ammonia generator comprises an electrolytic cell including a cathode having a first conducting component, an anode having a second conducting component, urea, a voltage source, an alkaline electrolyte composition in electrical communication with the anode and the cathode, and an ammonia outlet from the ammonia generator in communication with the at least one of the selective catalytic reduction system, the selective non-catalytic reduction system, or the flue gas conditioning system. The alkaline electrolyte composition has a hydroxide concentration of at least 0.01 M or a pH of at least 8.

[0019] The invention will be further appreciated in light of the following detailed description and drawings in which:

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the general description of the invention given above, and the detailed description given below, serve to describe the invention.

FIG. 1 is a schematic representation of a method to produce ammonia from urea;

FIG 2 is a diagrammatical view of a simplified electrolytic cell coupled to exhausted combustion gases;

FIG. 3 is a diagrammatical view of a method to purify exhaust gases from a combustion engine;

FIG. 4 is a plot of current density at a constant voltage (1.4 V) in the electrochemical cell over time;

FIG. 5 is a plot of current density at a constant voltage (1.33 V) in the electrochemical cell over time;

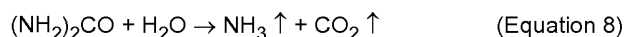
FIG. 6 is a diagrammatic depiction of an electrolytic ammonia generator system according to an embodiment of the present invention; and

FIG. 7 is expanded assembly of an electrolytic flow cell according to an embodiment of the present invention.

DETAILED DESCRIPTION

[0021] The SCR or SNCR of nitrogen oxides (NO_x) and/or the reduction of fly ash is facilitated by the electrolysis-induced hydrolysis of urea and is described herein. Advantageously, the electrolytic cell conditions may be modified to additionally generate hydrogen, which may be injected to increase fuel efficiency, to provide heat into the electrolytic cell, or to provide electricity into the electrolytic cell.

[0022] Referring now to FIG. 1, urea may be subjected to electrolysis-induced hydrolysis in an electrolytic device. The electrolytic device may comprise a cell or multiple cells that each contains an anode and a cathode. The electrolytic cell can operate in batch mode, continuous mode, semi-continuous, and with recirculation, as needed to provide on demand and controlled injection of ammonia into a process gas stream such as a combustion gas exhaust. At the anode, the working electrode of the cell, urea may be hydrolyzed to ammonia. The overall hydrolysis reaction is provided in Equation 8 below.



[0023] Referring more particularly to FIG. 2, a simplified electrolytic cell 1 representing a single batch-type arrangement comprises a tank 2, which may be made of light gauge iron, steel, TEFLON®, or other material not attacked by an alkaline electrolyte composition. An electrode assembly comprising two electrodes, an anode 3 and a cathode 4, is suspended within an alkaline electrolyte composition 6 contained in tank 2. Optionally, a separator 5 may be positioned between the anode and cathode. In this single batch-type arrangement, the alkaline electrolyte composition 6 includes an effective amount of urea as described below. The anode 3 and cathode 4 are electrically connected to a voltage source 7, which provides the electrical energy for the electrolysis of urea contained in the alkaline electrolyte composition 6. In a batch-type arrangement, the alkaline electrolyte composition may be stirred to facilitate mass transfer. It will be readily apparent to one of ordinary skill in the art that the above cell is readily adaptable to a continuous flow cell configuration, semi-continuous, and with recirculation of the alkaline electrolyte composition.

[0024] The electrodes comprise a conductor or a support which can be coated with one or more active conducting components. Exemplary conductors include, but are not limited to, metals such as nickel and platinum, alloys such as carbon steel or stainless steel, or other materials capable of conducting electricity such as carbon or graphite. Exemplary electrode support materials may be chosen from many known supports, such as foils, meshes, sponges, and beads, for example. The support materials may include, but are not limited to, Ni foils, Ti foils, graphite, carbon fibers, carbon paper, glassy carbon, carbon nanofibers, and carbon nanotubes. Aside from these specific support materials listed, other suitable supports will be recognized by those of ordinary skill in the art.

[0025] Accordingly, the cathode may comprise a conductor that is inert to an alkaline electrolyte composition. Additionally, the cathode may further include a support material that is inert to the alkaline electrolyte compositions and coated with one or more active conducting components. For example, the conducting component of the cathode may include carbon, cobalt, copper, iridium, iron, nickel, palladium, platinum, rhodium, ruthenium, or mixtures or alloys thereof. Exemplary conducting components include carbon steel and stainless steel.

[0026] The anode may comprise a conductor that is inert to the alkaline electrolyte composition. Additionally, the anode may further include a support material that is inert to the alkaline electrolyte compositions and coated with one or more active conducting components. According to embodiments of the present invention, the reaction of urea hydrolysis occurs at the conducting component of the anode. Therefore, the conductor and/or the conducting component at the anode is one or more metals active toward electrolytic hydrolysis of urea. Active metals may include cobalt, copper, iridium, iron, platinum, nickel, rhodium, ruthenium, or mixtures or alloys thereof, for example, and in particular, nickel. The active metals may be in an oxidized form, such as nickel oxyhydroxide.

[0027] The structure of the anode is not limited to any specific shape or form. For example, the active metal may be formed as foil, wire, gauze, bead, or coated onto a support.

[0028] Exemplary working electrodes include, nickel electrodeposited on a carbon support, such as carbon fibers, carbon paper, glassy carbon, carbon nanofibers, or carbon nanotubes, and nickel formed into beads and suspended in a nickel gauze.

[0029] One electrode found to be favorable to the electrolysis-induced hydrolysis of urea is an activated nickel oxyhydroxide modified nickel electrode (NOMN) on different 4 cm²-metallic substrates (Ni foil, Ni gauze, Ti foil and Ti gauze) that have been electroplated with 10±0.1 mg of Ni using a Watts bath. Specifically, the plated nickel electrode is activated by immersed in a solution containing nickel sulfate, sodium acetate, and sodium hydroxide at 33°C. Stainless steel is used as counter electrode. The plated nickel electrode may be used as the anode and cathode by manual polarity switching at 6.25 A/m² for four 1-minute cycles and two 2-minute cycles. Finally, the electrode is kept as the anode at the same current and maintained thereat for two hours. The activated electrode yields higher current densities than those of M/Ni, where M represents a metallic substrate.

[0030] The separator compartmentalizes the anode and cathode. Separators should be constructed from materials chemically resistant to the alkaline electrolyte composition. Many polymers are suitable for constructing separators, such as Teflon® and polypropylene. Separators are not required for simple batch-type arrangements, but may be advantageous for continuous flow electrochemical cells or fuel cells. Separators may include ion exchange membranes, solid electrolytes or electrolytic gels, for example. Separators may be permeable, semi-permeable or impermeable to gases or liquids.

[0031] According to the present invention, the electrolyte composition is alkaline and has a hydroxide ion concentration of at least 0.01 M or a pH of at least 8. According to one example, the alkaline electrolyte composition has a hydroxide concentration of at least 0.01 M and a pH of at least 8. As such, the alkaline electrolyte composition may include a sufficient quantity of any suitable hydroxide salt, carbonate salt or bicarbonate salt to provide an electrolyte composition with a hydroxide ion concentration of at least 0.01 M and/or a pH of at least 8. An alkali metal hydroxide or alkaline earth metal hydroxide salt, such as lithium hydroxide, rubidium hydroxide, cesium hydroxide, barium hydroxide, strontium hydroxide, potassium hydroxide, sodium hydroxide, magnesium hydroxide, calcium hydroxide, and mixtures thereof may be used. In particular, the alkaline electrolyte composition includes potassium hydroxide. Advantageously, the sequestration of CO₂ gas, shown in Equation 1, may be realized by the reaction of CO₂ with hydroxide to form carbonate, which may be retained in the alkaline electrolyte composition. Similarly, alkali metal carbonates or bicarbonate salts or alkaline earth metal carbonates or bicarbonate salts are also suitable electrolytes.

[0032] The concentration of the hydroxide, carbonate, or bicarbonate salts may vary according to embodiments of the invention. For example, according to one embodiment, the concentration of the hydroxide, carbonate, or bicarbonate salts may be from about 0.01 M to about 8 M. In another example, the concentrations of potassium hydroxide, potassium carbonate, potassium bicarbonate, sodium hydroxide, sodium carbonate, or sodium bicarbonate from about 2 M to about 8 M and from about 4 M to about 8 M, are particularly effective.

[0033] The alkaline electrolyte composition may comprise a gel, such as a solid polymer electrolyte. Suitable gels include, but are not limited to, those containing polyacrylic acid, polyacrylates, polymethacrylates, polyacrylamides and similar polymers and copolymers.

[0034] The electrolytic gel may be prepared using any suitable method. One method includes forming a polymer and then injecting a hydroxide, a carbonate or a bicarbonate salt electrolyte into the polymer to form a polymeric mixture. In another method, the monomer may be polymerized in the presence of a hydroxide, a carbonate, or bicarbonate salt electrolyte.

[0035] According to one embodiment, the electrodes are separated by the electrolyte gel which contains an effective hydroxide, carbonate, or bicarbonate ion concentration. The anode is contacted with a urea solution as the feed stock. The cathode is then contacted with a suitable aqueous solution, such as water or a hydroxide, carbonate, or bicarbonate solution, for example.

[0036] Alternatively, the gel electrolyte is not fixed and can flow through an electrolytic cell. According to another embodiment, urea may be contained within the gel or an aqueous solution comprising urea may flow within the gel electrolyte.

[0037] In the cell shown in FIG. 2, the electrolyte composition 6 includes urea, which may vary from trace amounts up to about a saturated solution, which is approximately 12 M at standard temperature and pressure. Advantageously,

the specific source and purity of the urea is not particularly limited.

[0038] Moreover, for the formation of aqueous solutions of urea, the specific source and purity of the water used in making the aqueous solution is not particularly limited or critical. One reason for this advantage is that, according to embodiments of the present invention, the entire aqueous solution comprising urea is not volatilized to thereby leave behind trace minerals and other non-volatile materials. Instead, the majority of the water remains in the liquid form, which substantially maintains the trace minerals in solution. Additionally, after the electrolytic hydrolysis of at least a portion of the urea within the electrolytic cell, the aqueous solution or the alkaline electrolyte solution being discharged from the electrochemical cell may be recirculated.

[0039] Voltage source 7 may be any available source, such as batteries, fuel cells, power from the grid, and renewable energy sources, such as a solar cell or a wind-turbine generator, for example. When the electrolytic cell is coupled with an SCR system on a motor vehicle, the electric source may be from an alternator. In order to attain desired efficiencies, a voltage sufficient to initiate the electrolytic hydrolysis of urea is required. But it is preferable that the voltage not be so high as to significantly electrolyze water. Generally, the minimum voltage required to electrolyze or electrolytically-hydrolyze urea is about 0.85 volts. The voltage required to electrolyze water is greater than 1.7 volts with a platinum electrode at standard conditions, but the rate of electrolysis and/or electrolysis-induced hydrolysis depends on other factors, such as temperature and ionic strength/conductivity. Based on the foregoing, the voltage range applied to the electrolytic cell to electrolytically-hydrolyze urea may be from about 0.85 volts to less than about 1.7 volts. The voltage range may be from about 1.2 volts to about 1.6 volts. Typically, the electrolytic cell will be operated at a constant voltage within these ranges.

[0040] Additionally, the rate of producing ammonia and/or hydrogen from urea may be controlled by varying the voltage within different regions of the electrolytic cell. For example, in a packed-bed type electrolytic cell, the voltage within the packed-bed of an anodic catalyst material can be adjusted along the catalyst bed to control the rate of ammonia production and/or injection into an SCR or SNCR device. As such, different regions in the catalyst bed may have different potentials to control the rate of ammonia production. For example, a packed bed column configuration may include a plurality of anodes with each being electrically insulated from the other anodes and capable of having voltage controlled separately thereto, such as that represented in FIG. 6. For a given maximum production of ammonia, the totality of the anodes may be polarized. However, when a lower amount of ammonia is desired, then less than all of the anodes are polarized.

[0041] Amperage or current density may affect the performance of an electrolytic cell, as well. Pure water has poor electrical conductivity and, as such, electrolysis in pure water is very slow and essentially occurs due to the self-ionization of water. Generally, the rate of electrolysis increases by adding an electrolyte, such as a salt, an acid or a base. Therefore, the presence of an added hydroxide ion, a carbonate ion or a bicarbonate ion and its respective counter ion, in the alkaline electrolyte composition enables the conduction of electrical current. The current density of the electrolytic cell described herein ranges from about 1 mA/cm² to about 500 mA/cm². In some embodiments, the current density range may be from about 50 mA/cm² to about 400 mA/cm². The current density range may be from about 200 mA/cm² to about 300 mA/cm². Overall, it is only necessary to provide a sufficient amount of current to induce the active form of the active metal, which comprises the anode, to cause the hydrolysis of urea. Typically, the electrolytic cell will be operated at a constant current or current density within these ranges.

[0042] The electrical current may also be used to control the production of ammonia from the electrolytic hydrolysis of urea and therefore control the rate of injecting ammonia into an exhausted gas treatment system. For example, a given electrical current may be required to induce the active form of the active metal in all the regions of the anode to maximize the production of ammonia. The applied current may be lowered when the need for ammonia decreases.

[0043] Electrolytic cells may operate over varying ranges of pressure and temperature. The operating pressure may be about atmospheric pressure or ambient pressure with no upper pressure limit other than the physical limits of the reaction vessel. If desired, the operating pressure of the electrolytic cell may be varied to control the rate of ammonia that is injected into an exhaust gas. The operating temperature range may be from about 0°C to about 100°C. An acceptable operating temperature range may be from about 40°C to about 80°C. More specifically, an operating temperature range from about 60°C to about 70°C is particularly useful.

[0044] The temperature in the electrolytic cell may be controlled with any available source. For example, the electrolytic cell may further include a heater apparatus operatively coupled to electrolytic cell, and/or a recirculation system operatively coupled to the electrolytic cell, wherein the recirculation system contains at least a portion of the alkaline electrolyte composition. Exemplary heating apparatus include heating jackets that surround the electrolytic cell, from which heat may be supplied by external sources, such as steam, heated water, or other heated fluids. Other possible heating sources can include, but are not limited to, electric heaters or combustion gases. Alternatively, or in addition, the recirculation system may also include a heating apparatus for increasing the temperature of the alkaline electrolyte composition at a point external to the electrolytic cell. The desired heating source may depend on the availability and/or compatibility with the system. For example, electric heat may be the most convenient way to provide the heat to achieve a desired operating temperature for the use of the electrolytic cell in an automobile SCR system, especially during cold start and during extreme weather conditions. Accordingly, the electrolytic cell may have temperature control that is independent

of the temperature of the engine.

[0045] It will be readily apparent to one of ordinary skill in the art that the above-described electrolytic cell is readily adaptable to a continuous flow cell configuration, semi-continuous, and with recirculation of the alkaline electrolyte composition. For example, an exemplary system for the continuous generation of sufficient quantities of ammonia to adequately supply the needs of a coal fired power plant on a continuous basis is shown in FIG. 6. From a urea storage container 10, urea prill is supplied via a rotary feed valve 12 to a mix tank 14 where the urea prill is mixed with water from a water supply 16 to form a urea solution. The mix tank 14 includes a discharge line 18, which supplies the urea solution to a urea solution feed pump 20 to transfer the urea solution to a urea electrolyte tank 24 through the urea electrolyte tank inlet 22. A urea solution recirculation line 26 permits continuous operation of the urea solution feed pump 20. According to this embodiment, the urea electrolyte composition is formed by mixing the urea solution from the mix tank 14 with an alkaline electrolyte composition including hydroxide, carbonate, or bicarbonate salts of alkali metals or alkaline earth metal, or combinations thereof. The urea electrolyte tank 24 includes a discharge line 28, which supplies the urea electrolyte solution to a urea electrolyte solution feed pump 30 to transfer the urea electrolyte solution through an electrolytic cell inlet 32 to an electrolytic cell 34. A urea electrolyte solution recirculation line 36 permits continuous operation of the urea electrolyte solution feed pump 30, and may also participate in control of the volume or level of urea electrolyte solution within the electrolytic cell 34. The electrolytic cell 34 includes a heating jacket 38 having an inlet line 40 and an outlet line 42 for recirculating heating fluids therethrough.

[0046] One typical flow cell design is that of a packed-bed type of electrolytic flow cell, which enables the voltage and/or the current within the packed bed of anodic catalyst material to be varied along the catalyst bed and thereby control the rate of ammonia evolution. A packed-bed type flow cell is depicted in FIG. 6 with V1-V6 representing the variable voltage capability of the electrolytic cell 34, where the insulating materials between the electrically insulated regions of the packed anodic catalyst bed are not shown. This configuration is also adaptable for controlling the amount of urea being hydrolyzed based on the level or volume of urea electrolyte solution covering the catalyst bed. In other words, varying an area percentage of a total area of the anodic catalyst bed in contact with a urea solution will vary the rate of ammonia production. As such, increasing the amount of urea electrolyte solution covering the available catalyst bed will increase the rate of ammonia production.

[0047] During operation, the urea electrolyte solution flows through the electrolytic cell 34 and thereby contacting the electrodes. Accordingly, the generated ammonia from the electrolytic hydrolysis of urea is supplied to an exhaust gas treatment system through an ammonia discharge line 44. Depending on the electrolytic cell operating conditions, hydrogen may also be produced and supplied to auxiliary systems through a hydrogen gas discharge line 46. The urea electrolyte solution, after having been depleted of at least a portion of its urea, is returned to the urea electrolyte tank 24 through urea electrolyte return line 48.

[0048] Other flow cell designs are also amenable to the instant embodiment. As shown in FIG. 7, a flow cell 60 may include a jacketed containment vessel 62 having a tubular cathode 64, a tubular anode 66 and a vessel lid 68. The jacketed containment vessel 62 may be thermally controlled by any suitable method. The jacketed vessel 62 further includes inlet 70. When present, a tubular separator 72 compartmentalizes the tubular cathode 64 and the tubular anode 66, which permits separation of the effluents therefrom. Accordingly, each electrode chamber may have its own discharge port, whereby the vessel lid 68 is configured to accommodate a cathode connector tubing 74 and an anode connector tubing 76. For example, the cathode connector tubing 74 may be hollow and include a conductor to thereby provide both a discharge flow path from the proximity of the tubular cathode 64 and an electrical connection. Similarly, the anode connector tubing 76 may be hollow and include a conductor to thereby provide both a discharge flow path from the proximity of the tubular anode 66 and an electrical connection.

[0049] The present invention will be further appreciated in view of the following examples.

EXAMPLE 1

[0050] Two closed cells (1000 mL) were assembled. Each cell was filled with 200 mL of 7 M KOH and 0.33 M urea solution, and stirred at 120 rpm. Voltage (1.4 V) was applied to cell B (supplied with Arbin Industries MSTAT) using a Rh-Ni anode (0.15 mg/cm² Rh on Ni foil, 10 cm²) and platinum foil (10 cm²) as the cathode. Samples were taken via liquid sampling ports and analyzed for ammonia concentration periodically by extracting 10 mL and diluting 1:100 with distilled water. A 50 mL aliquot of this analyte was added to a flask, 1 mL of pH adjusting solution was added with stirring, and the solution was analyzed using an ion selective electrode. After two hours of constant voltage operation, Cell A and B contained aqueous ammonia concentrations of 3600 and 4700 ppm, respectively (Table 1). After 3 hours of operation, cell A increased to 3800 ppm while cell B increased to 6450 ppm, which provided that the cell with applied potential had 41% higher conversion of urea to ammonia. Cell B averaged about 25 mA/cm² during the first two hours, which decreased to near 8 mA/cm² for the third hour (Figure 4). These results show that the lower current density was more effective in converting the urea to ammonia.

[0051]

Table 1. Urea hydrolysis via electrolysis samples.

Test Time (total hrs)	Cell	ppm NH ₃ (liquid Phase)	Avg. Current (mA)	% increase w/ electrolysis
2	A	3637	98	23
	B	4715		
3	A	3800	30	41
	B	6450		

[0052] Application of 1.4 V to cell B resulted in a 41% higher conversion after 3 hours of operation, indicating that the urea to ammonia reaction is in fact enhanced by electrolysis. Electrolysis at a low voltage contributes to kinetics of the urea to ammonia conversion.

EXAMPLE 2.

[0053] Two closed cells (1000 mL) were assembled with Rh-Ni anodes (8 cm² each; cell A: 0.05 mg/cm², cell B: 0.15 mg/cm²) and platinum foil cathodes (15 cm²), filled with 7 M KOH and 0.33 M urea, and heated to 70°C. Liquid sampling ports were included for monitoring aqueous ammonia concentration ex-situ by ISE throughout the duration of the experiment. Voltage (1.33 V) was applied to both cells A and B (supplied with Arbin Industries MSTAT) with 120 rpm stirring. A lower voltage was chosen as compared to Example 1 above because it was postulated that a lower voltage, which will provide a lower current density, was needed to affect the NiOOH catalyzed reaction to ammonia.

[0054] Samples were taken and analyzed for ammonia-concentration periodically by extracting 10 mL and diluting 1:100 with distilled water. A 50 mL aliquot of this analyte was added to a flask with stirrer and ISE electrode and 1 mL of pH adjusting solution, as described in Experiment 1. After two hours of constant voltage operation, Cell A and B contained aqueous ammonia concentrations of 4890 and 6470 ppm, respectively (Table 2). These concentrations did not increase after the third hour of operation. The average current in each cell for the first two hours was 1.5 and 2.0 mA/cm² for cell A and B, respectively (Figure 5). It is postulated that the apparent stoppage in urea conversion to ammonia after the first sample period is likely the result of the current density dropping to around 1 mA/cm² after 2 hours, which may be below the level necessary to affect the reaction. It was observed that a black precipitate formed on the platinum cathode in both cells. Most of the conversion affected by applied potential probably took place within the first hour where average current was 2-3 mA/cm². Otherwise, leakage from the liquid sampling ports could explain the lack of increase in conversion.

[0055]

Table 2: Urea hydrolysis via electrolysis samples.

Time	Cell A ppm NH ₃	Cell B ppm NH ₃
2 hrs	4890	6470
3 hrs	4580	6400

[0056] Based on these results, the effect of current density on the conversion of urea to ammonia and the effect of catalyst loading Cell B exhibited a higher conversion than cell A, probably because it had an anode with higher loading of rhodium and operated under a slightly higher average current density. Again, these results show that electrolysis at a low voltage can contribute to favorable kinetics of the urea to ammonia conversion.

[0057] For example, for a Diesel truck application, providing 0.5 Kg of ammonia per hour to an SCR unit at a current of 6.25 amps and a cell voltage of 1.33 volts, would correspond to 8.31 watts of power. The thermal energy consumed would be 1,980 kilojoules. Additionally, under these conditions, approximately 0.23 g/hour of hydrogen may be generated, which equates to about 33 kilojoules of thermal energy, and may be injected into the combustion engine of the diesel truck to minimize carbon dioxide emissions and increase fuel efficiency.

[0058] In another example, for a 500 MW coal-fired power plant, providing 200 Kg of ammonia per hour to an SCR unit at a current of 2,500 amps and a cell voltage of 1.33 volts, would correspond to 3.325 kilowatts of power. The thermal energy consumed would be 792,000 kilojoules. Additionally, under these conditions, approximately 93.3 g/hour of hydrogen may be generated, which equates to about 13,228 kilojoules of thermal energy.

EXAMPLE 3

[0059] Electrolytic Hydrolysis of Urea: A cell containing 7 M KOH/0.33 M urea solution at atmospheric pressure was subjected to electrolysis-induced hydrolysis. A cell voltage of 1.4 volts was applied to a 2x2.5 cm² carbon-paper anode deposited with Ni, and a 5x5 cm² Pt foil cathode. Under these conditions, the presence of ammonia was detected from the conversion of urea into ammonia and carbon dioxide. The hydrolysis pathway becomes favorable with increasing hydroxide salt concentration and increasing temperatures. For example, urea samples contained in 0 M, 1 M, 5 M and 7 M KOH at 50°C for 89 hours produced 0.7%, 4.2%, 27.4% and 36.7% hydrolysis, respectively. A 7 M KOH sample of urea at 70°C for 24 hours provided over 95% hydrolysis.

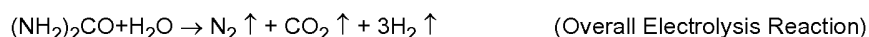
EXAMPLE 4

[0060] Flow Cell Hydrolysis of Urea: In a sandwich-style urea electrolytic cell that compartmentalized the anode and cathode, a polypropylene membrane was used as a separator. The anode was constructed of a 5 cm² carbon-paper support, on which was electrodeposited Ni. The cathode was constructed of a 5 cm² carbon paper support, on which was electrodeposited Pt. The electrodes were immersed in 5M KOH/0.33 M urea at 70°C. A cell voltage of 1.33 volts was applied and ammonia evolved from the anode. It was noted that a small amount of hydrogen was produced from the cathode. The respective gases were analyzed using a MG2 SRI 8610C gas chromatograph with a thermal conductivity detector (TCD), Haysep column, and a molecular sieve column. Pure hydrogen was observed at the cathode, while ammonia, N₂ and small amounts H₂ were observed from the anode in gas phase. The hydrogen on the anode side of the separator is believed to arise from hydrogen passing through the polypropylene membrane. Ammonia was further detected in the liquid phase using an Orion ammonia selective electrode (ISE). No carbon species were detected in gas phase. It is postulated that any CO₂ that may have been generated was quickly transformed into potassium carbonate.

EXAMPLE 5

[0061] Electrolysis of Urea: A cell containing 5 M KOH/0.33 M urea solution at 25°C and atmospheric pressure was subjected to electrolysis. A cell voltage of 1.4 volts was applied to a 2x2.5 cm² carbon-paper anode deposited with Ni, and a 5x5 cm² Pt foil cathode. It was determined by gas chromatography that the electrolysis of urea produced nitrogen at the anode of this electrolytic cell, whereas hydrogen was produced at the cathode. Ammonia, which is presumably derived from the electrolysis-induced hydrolysis of urea, was detected in the electrolyzed solution using an Orion ammonia selective electrode (ISE). No carbon species were detected in the gas phase. It is postulated that the generated CO₂ was quickly transformed into potassium carbonate by reacting with potassium hydroxide in the alkaline electrolyte composition.

[0062] Therefore, at the anode, urea may be oxidized to nitrogen and carbon dioxide. At the cathode, the counter electrode, hydrogen may be produced, as shown in the following reaction:



[0063] Therefore, in addition to the electrolysis-induced hydrolysis of urea to supply the requisite ammonia reductant to an exhaust gas treatment system, under the appropriate conditions, the foregoing electrolysis of urea may provide hydrogen, which may be injected into a combustion chamber that is attached to the exhaust gas treatment system, as shown in FIG. 3. Thus, adding hydrogen to the combustion chamber may facilitate improved fuel combustion efficiency, as well as reducing unwanted emission by-products.

EXAMPLE 6

[0064] The model system in accordance with the embodiment represented in FIG. 6 has been designed with an electrolytic cell having a total volume of 825 liter, with 660 liters of an anodic bed providing 1,247 m² of active metal surface. Extrapolating the experimental data obtained from a batch-type configuration, operation mass transfer parameters were calculated for the foregoing system. Additionally, a comparison was made between the inventive electrolytic hydrolysis method (EU2A) and the commonly-used chemical hydrolysis. As shown in Table 4 below, the electrolytic urea to ammonia (EU2A) hydrolysis method provides an ammonia stream which is predominantly (e.g., 64 molar %) comprised of ammonia. The calculated parameters and comparison data are shown in Tables 3 and 4, respectively.

[0065]

EP 2 553 229 B1

Table 3: Calculated operating parameters.

Stream	Rate (kg/hr)	Composition (%)
1: Prill urea	352.9	100.0
2: Water	119.4	100.0
3: Concentrated urea	472.3	Urea: 74.7 H ₂ O: 25.3
4: Urea electrolyte reactor feed	1138.0	Urea: 31.0 K ₂ CO ₃ : 22.5 H ₂ O: 46.5
5: Electrolyte recycle	665.7	K ₂ CO ₃ : 38.4 H ₂ O: 61.6
6: NH ₃ to SCR (@ 70°C; 30 psig)	472.2	NH ₃ : 42.4 -CO ₂ : 54.7 H ₂ O: 2.9
7: Hydrogen to fuel cell	0.1	100.0
8: Saturated steam (150 psig)	394.8	100.0
9: Exhausted steam (150 psig)	394.8	100.0

[0066]

Table 4: Comparison of methods.

Description	Chemical hydrolysis	EU2A
Volume of reactor (liters)	7,250	825
SCR Ammonia Reagent	200 kg/hr	200 kg/hr
Dry Urea Flow Rate	352	352
Reagent Concentration	50 % wt	40-60 % wt
DI water	375 kg/hr	119 kg/hr
Steam heating (150 psig)	840 kg/hr	395 kg/hr
Power	N/A	1.8 kW **
Gas Molar Composition		
NH ₃ (%)	22.8	64.0
CO ₂ (%)	11.4	32.0
H ₂ O (%)	65.8	4.0

** Reusing the hydrogen in a fuel cell with 50% efficiency.

[0067] One issue commonly encountered in electrolytic cells, is the slow deactivation of the one or both of the electrodes. In some instances, the deactivation may be attributed to the attachment of an oxidized film on the anode and/or the attachment of scale on the surface of the cathode. This deactivation process deteriorates the electrolytic efficiency of the cell. For example, as this deactivation occurs, the current density can, in some instances, decrease for a constant applied voltage, thereby reducing the rate of electro-oxidation. Alternatively, the current density sometimes can be sustained by increasing the applied voltage. In either instance, energy is wasted and the overall efficiency of the cell is diminished.

[0068] From an operational perspective, regeneration of the electrodes by reversing the applied voltage for a period of time can be useful. The reversed voltage may be the same or different as the operating voltage. The reversal voltage may range from about 0.5 volts to about 2.0 volts. Another suitable reversal voltage may range from about 1.4 volts to about 1.6 volts.

[0069] During regeneration, the period of time for applying a reversed voltage may vary from just a few minutes to tens of hours. For example, the first and second conducting components may both include one or more metals active toward electrochemical oxidation of urea, therefore either electrode may function as a cathode and produce hydrogen. As such, reversing the voltage is effectively an uninterrupted process, thereby allowing the reversed voltage to be applied for an indefinite period of time or until deactivation is again encountered. According to the operating conditions of the electrochemical cell described herein, electrodes may be operated for about 5 hours to about 20 hours before losing

activity and requiring activation.

[0070] Conversely, if the anode's conducting component is comprised of a metal inactive toward electrochemical oxidation of urea, the regeneration may be achieved in about 1 minute to about 20 minutes at about 1.4 volts. In some instances, reactivation can be achieved in about 6 minutes at 1.4 volts.

5 **[0071]** For SCR applications, the SCR unit is not particularly limited to any specific configuration or catalyst. For example, plate, honeycomb, pellet, bead, fiber or corrugated configurations are suitable for use. Moreover, the catalyst is not limited to any species or form. For example, traditional catalysts based on vanadium, titanium, or iron or copper-promoted zeolite catalysts are suitable for use. Additionally, newer SCR catalysts, such as those disclosed in U.S. Patent No. 7,527,776 by Golden et al. may be used. Similarly, for SNCR applications and/or gas flue conditioning applications,
10 the SNCR unit and/or the particle precipitator are not particularly limited to any specific design.

[0072] Accordingly, the electrolytic cells according to embodiments of the present invention may be adapted to couple with commercially available SCR or SNCR units or flue gas conditioning systems. For example, the electrolytic cell may be adapted to work with existing ammonia generators that thermally hydrolyze urea, or the electrolytic cell may be designed to be the lone source of ammonia for the exhaust gas treatment systems. Alternatively, the cell and the exhaust
15 gas treatment system, such as an SCR or an SNCR system, may be designed as a combined unit.

[0073] The ammonia may normally be introduced into the exhaust gas prior to an electrostatic precipitator, an SNCR unit, or prior to contacting a catalyst within an SCR unit. The exhaust gas and the ammonia as a reducing agent may be contacted with the catalyst, thereby reducing the nitrogen oxides in the exhaust gas. The optimization of temperatures, pressures, flow rates and the like can readily be achieved by one having ordinary skill in the art of exhaust gas treatment
20 technology.

[0074] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. As well, the terms "a" (or "an"), "one or more" and "at least one" can be used interchangeably herein. It is also to be noted that the terms "comprising", "including", "characterized by" and "having" can be used interchangeably.

25 **[0075]** While the present invention has been illustrated by the description of one or more embodiments thereof, and while the embodiments have been described in considerable detail, additional advantages and modifications will readily appear to those skilled in the art. The various features of exemplary embodiments described herein may be used in any combination.

Patentkrav**1. Fremgangsmåde, der omfatter:**

5 fremstilling af ammoniak ved hjælp af elektrolytisk hydrolyse af urinstof opnået ved at anvende en spændingsforskel på en elektrolytisk celle, hvilken fremgangsmåde omfatter:

en katode, der har en første ledende komponent,

en anode, der har en anden ledende komponent,

urinstof, og

10 en alkalisk elektrolytsammensætning i elektrisk forbindelse med anoden og katoden, hvor den alkaliske elektrolytsammensætning har en hydroxidkoncentration på mindst 0,01 M eller en pH på mindst 8,

hvor spændingsforskellen anvendes over katoden og anoden, hvor spændingsforskellen er tilstrækkelig til at opnå den elektrolytiske hydrolyse af urinstof til at fremstille i det mindste NH_3 ;

15 hvor fremgangsmåden enten er med henblik på tilførsel af NH_3 til et afgasbehandlingssystem, og endvidere omfatter:

genvinding af i det mindste en del af NH_3 'et; og

20 overførsel af den i det mindste en del af NH_3 'et til afgasbehandlingssystemet,

eller, hvor fremgangsmåden er med henblik på reduktion af kvælstofoxid-(NO_x)-udslip og/eller partikelstof i en forbrændingsgas under vedvarende drift, og endvidere omfatter:

25 injektion af ammoniak i forbrændingsgassen opstrøms for i det mindste en af en selektiv, katalytisk reduktions-(SCR)-anordning, en selektiv,

ikke-katalytisk reduktions-(SNCR)-anordning, eller en elektrostatisk udskilleranordning.

- 5 **2.** Fremgangsmåde ifølge krav 1 for tilførsel af NH_3 til et afgangssystem, hvor afgangssystemet omfatter mindst en af et selektivt katalytisk reduktionssystem, et selektivt ikke-katalytisk reduktionssystem, og/eller et røggaskonditioneringssystem.
- 10 **3.** Fremgangsmåde ifølge krav 1, der endvidere omfatter at øge et forbrændingssystemets brændstofeffektivitet, idet fremgangsmåden omfatter:
- tilførsel af H_2 til et brændkammer af forbrændingssystemet, hvor hydrogenet tilføres ved:
- anvendelse af spændingsforskellen på den elektrolytiske celle, hvor den
- 15 spændingsforskel, der anvendes over katoden og anoden, er tilstrækkelig til at fremstille NH_3 og H_2 .
- 4.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den første ledende komponent omfatter kulstof, kobolt, kobber, iridium, jern, nikkel,
- 20 palladium, platin, rhodium, ruthenium eller blandinger eller legeringer deraf.
- 5.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den anden ledende komponent omfatter kobolt, kobber, iridium, jern, platin, nikkel, rhodium, ruthenium eller blandinger eller legeringer deraf.
- 25 **6.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, hvor den anden ledende komponent omfatter en oxideret form af kobolt, kobber, iridium, jern, platin, nikkel, rhodium, ruthenium eller blandinger eller legeringer deraf.

7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, der endvidere omfatter:

at påvirke et NH₃-produktionsniveau ved at variere i det mindste en af

- 5 den elektrolytiske celles temperatur,
 den elektrolytiske celles tryk,
 en på den elektrolytiske celle anvendt elektrisk strøm, eller
 en på den elektrolytiske celle anvendt spænding;

at variere en spænding, der anvendes på en del af anoden, hvor anoden omfatter et katalysatorleje; eller

- 10 at variere en fladeindholdsandel af et totalt fladeindhold af det anodiske katalysatorleje i kontakt med en urinstofløsning.

- 15 **8.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den alkaliske elektrolytsammensætning omfatter et alkalimetal- eller jordalkalimetalsalt af en hydroxid, et karbonat, et bikarbonat eller kombinationer deraf.

- 20 **9.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den elektrolytiske celle endvidere omfatter en varmeanordning, der er driftsmæssigt forbundet med den elektrolytiske celle, og et recirkulationssystem, der er driftsmæssigt forbundet med den elektrolytiske celle, hvor recirkulationssystemet indeholder i det mindste en del af den alkaliske elektrolytsammensætning.

- 25 **10.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor spændingsforskellen anvendes som en konstantspænding.

11. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 10, hvor anvendelse af spændingsforskellen på den elektrolytiske celle videre omfatter

at variere spændingsforskellen for at regulere fremstillingen af NH_3 .

5 **12.** Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor den elektrolytiske celle endvidere omfatter et temperaturreguleringssystem, der indbefatter en varmekilde.

13. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor spændingsforskellen er større end cirka 0,85 volt.

10 **14.** Afgasbehandlingssystem, der omfatter:

mindst en af et selektivt, katalytisk reduktionssystem, et selektivt, ikke-katalytisk reduktionssystem, og/eller et røggaskonditioneringssystem; og

en ammoniakgenerator, der omfatter en elektrolytiske celle, der består af:

15 en katode, der har en første ledende komponent,

en anode, der har en anden ledende komponent,

urinstof,

en spændingskilde, der tilfører en spænding til den elektrolytiske celle,

20 en alkalisk elektrolytsammensætning i elektrisk forbindelse med anoden og katoden, hvor den alkaliske elektrolytsammensætning har en hydroxidkoncentration på mindst 0,01 M eller en pH på mindst 8; og

25 et ammoniakudløb fra ammoniakgeneratoren i forbindelse med den mindst ene af det selektive, katalytiske reduktionssystem, det selektive, ikke-katalytiske reduktionssystem, og/eller røggaskonditioneringssystemet.

5 **15.** System ifølge krav 14, hvor den første ledende komponent omfatter kulstof, kobolt, kobber, iridium, jern, nikkel, palladium, platin, rhodium, ruthenium eller blandinger eller legeringer deraf.

10 **16.** System ifølge enten krav 14 eller krav 15, hvor den anden ledende komponent omfatter kobolt, kobber, iridium, jern, platin, nikkel, rhodium, ruthenium eller blandinger eller legeringer deraf.

15 **17.** System ifølge et hvilket som helst af kravene 14 til 16, hvor spændingskilden tilfører en spænding på mere end 0,85 volt.

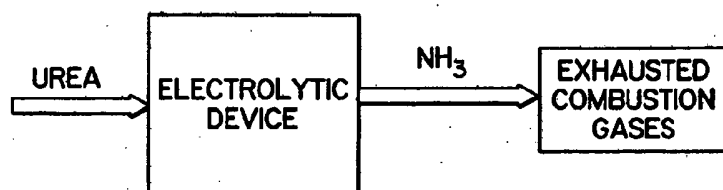


FIG. 1

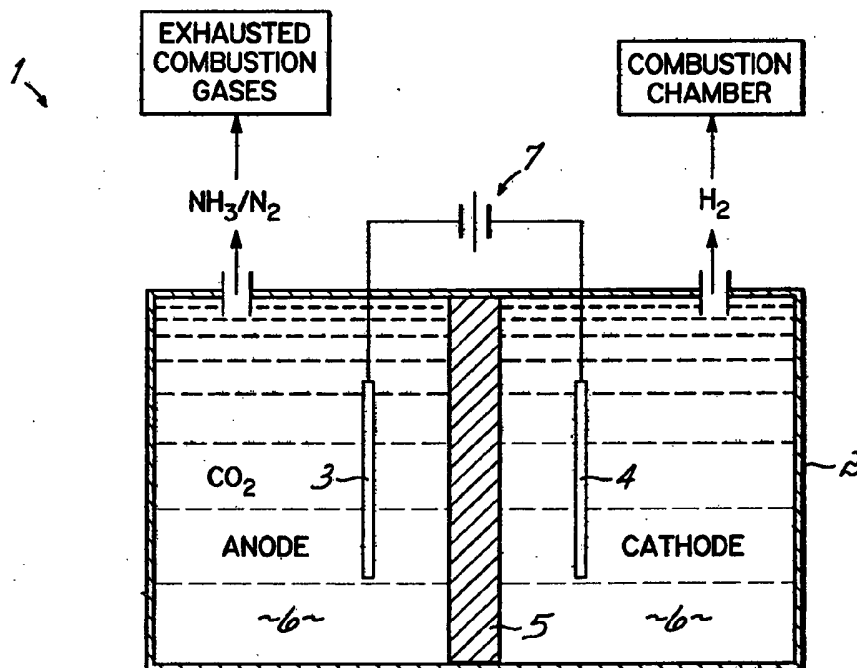


FIG. 2

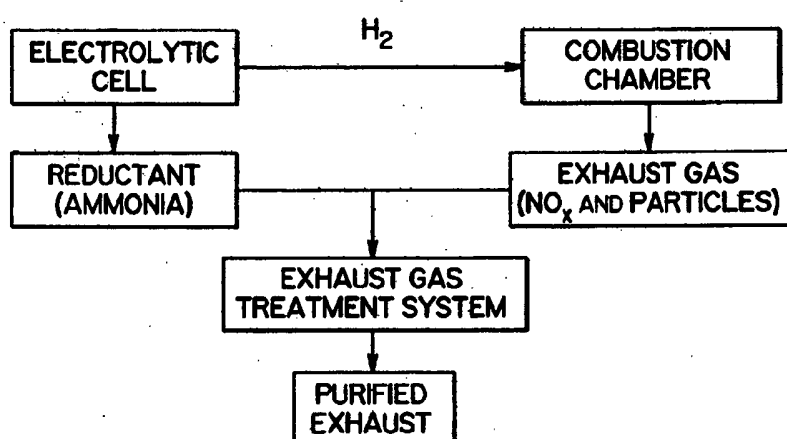


FIG. 3

EP 2 553 229 B1

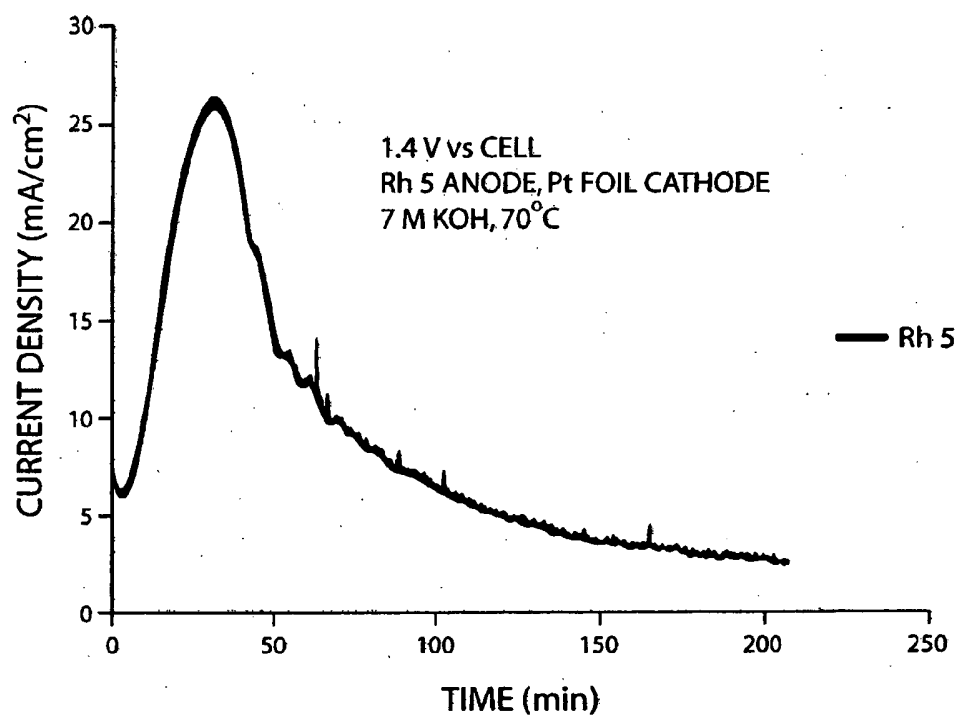


FIG. 4

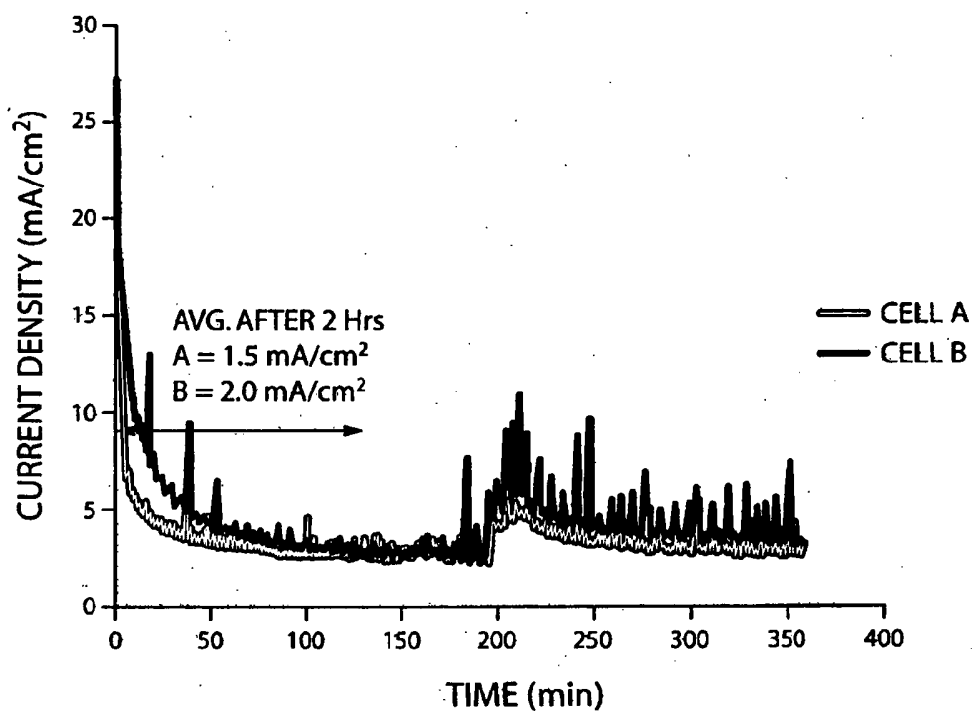


FIG. 5

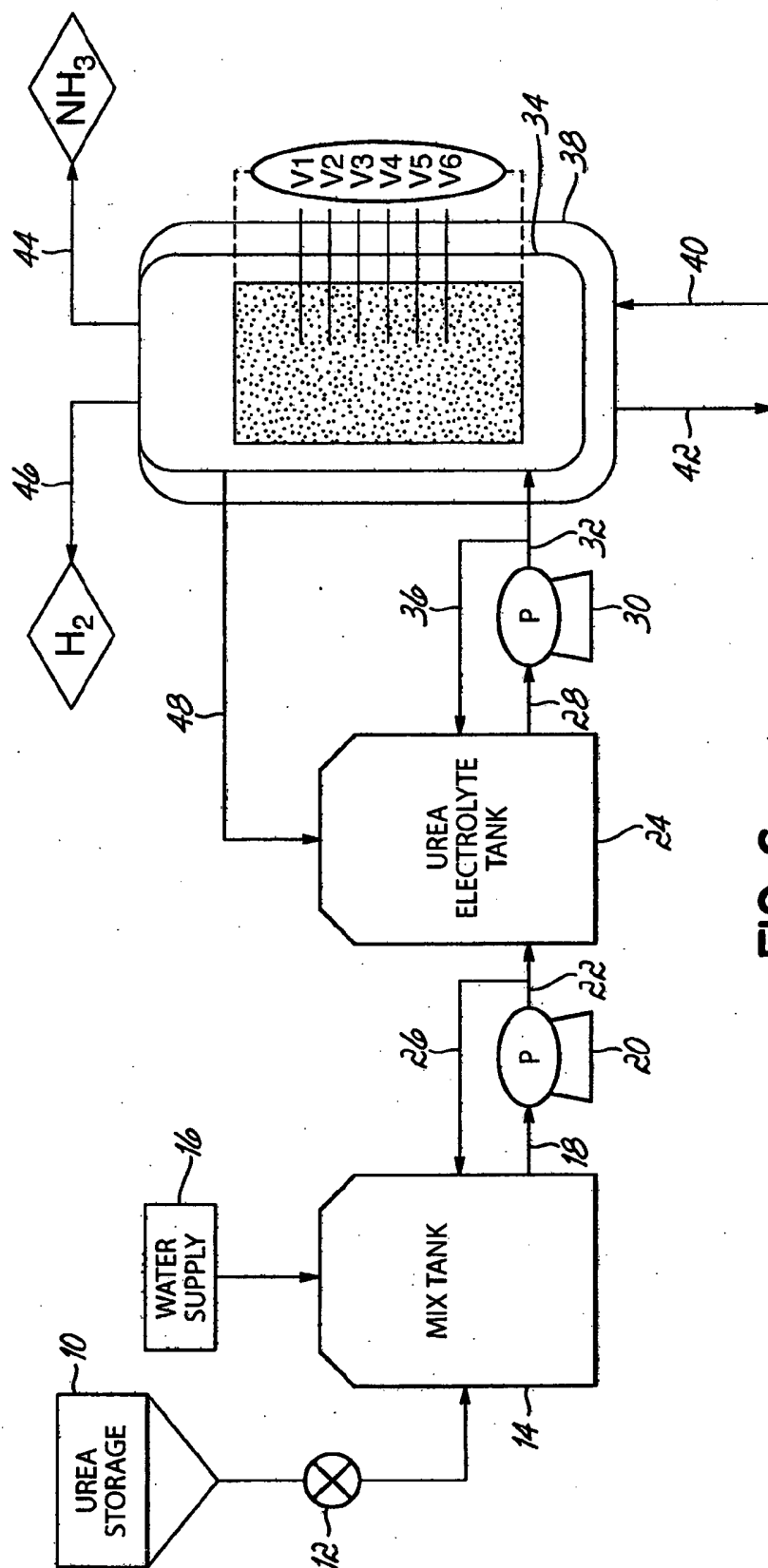


FIG. 6

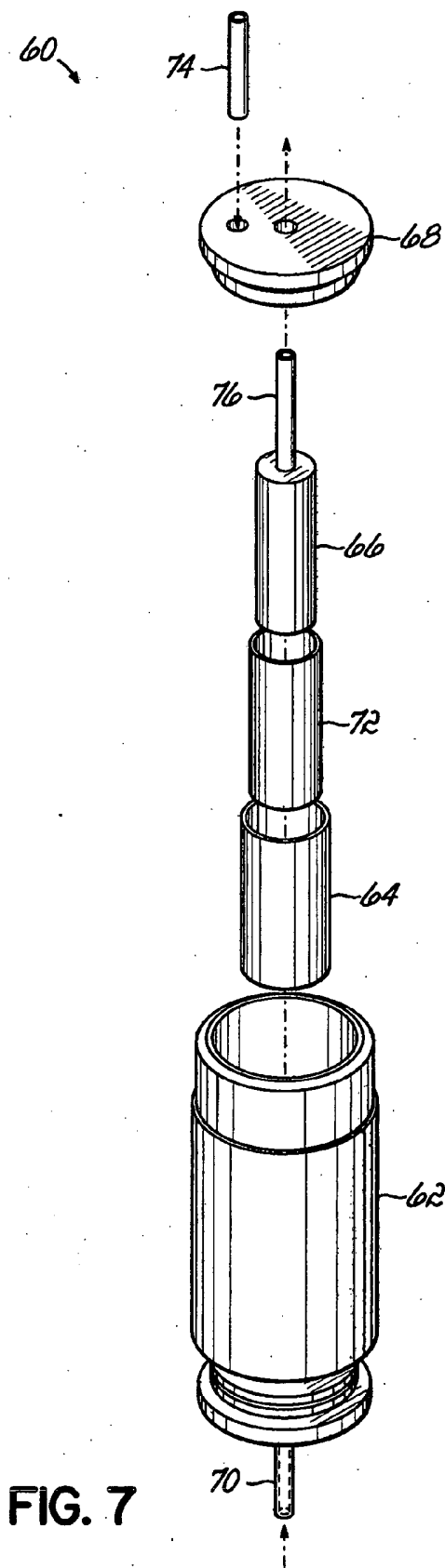


FIG. 7