

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
29 September 2005 (29.09.2005)

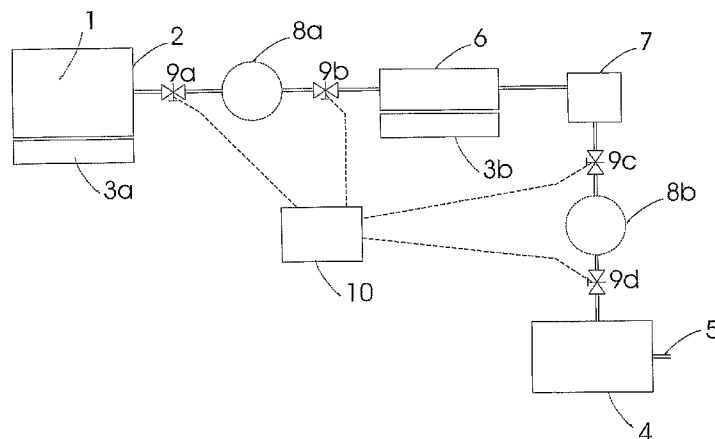
PCT

(10) International Publication Number
WO 2005/091418 A2

- (51) International Patent Classification⁷: **H01M 8/22**, 8/06 (DK). **QUAADE, Ulrich** [DK/DK]; Gammelmosevej 331, DK-2880 Bagsværd (DK).
- (21) International Application Number: PCT/DK2005/000196 (74) Agent: **ZACCO DENMARK A/S**; Hans Bekkevolds Allé 7, DK-2900 Hellerup (DK).
- (22) International Filing Date: 22 March 2005 (22.03.2005) (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: PA 2004 00469 23 March 2004 (23.03.2004) DK (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (for all designated States except US): **AMMINEX A/S** [DK/DK]; Kemitorvet, Bygning 206, DK-2800 Kgs. Lyngby (DK).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **CHRISTENSEN, Claus, Hviid** [DK/DK]; Vildroseparken 39, DK-3540 Lyngby (DK). **JOHANNESSEN, Tue** [DK/DK]; Platanhaven 110, DK-2600 Glostrup (DK). **NØRSKOV, Jens, Kehlet** [DK/DK]; Kong Valdemarsvej 66, DK-2940 Holte

[Continued on next page]

(54) Title: USE OF AN AMMONIA STORAGE DEVICE IN PRODUCTION OF ENERGY



(57) Abstract: An electric power generating unit comprising (i) an ammonia storage device in the form of a container comprising an ammonia absorbing and releasing salt of the general formula: $M_a(NH_3)_nX_z$, wherein M is one or more cations selected from alkali metals, alkaline earth metals, and transition metals such as Li, K, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu or Zn, X is one or more anions selected from fluoride, chloride, bromide, iodide, nitrate, thiocyanate, sulphate, molybdate, phosphate, and chlorate ions, a is the number of cations per salt molecule, Z is the number of anions per salt molecule, and n is the coordination number of 2 to 12. (ii) means for heating said container and ammonia absorbing and releasing salt for releasing ammonia gas and (iii) a fuel cell for converting ammonia directly into electric power; or (iiib1) a reactor for dissociating ammonia into hydrogen and nitrogen and (iiib2) a fuel cell for converting hydrogen into electric power is useful for large stationary energy producing facilities, but also for use for is useful for large stationary energy producing facilities, but also for use for small rechargeable and/or replaceable power supply units for micro-fabricated or miniaturized ammonia decomposition reactors for use in mobile units and portable devices may be used for large energy producing facilities, and by use of small rechargeable and/or replaceable ammonia storage decomposition reactors, it is also possible to provide energy for mobile units and portable devices.

WO 2005/091418 A2



Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE

Use of an Ammonia Storage Device in Production of Energy

BACKGROUND OF THE INVENTION**5 1. Field of the Invention**

This invention relates to the use of an ammonia storage device containing a metal ammine complex for reversible storage of ammonia in solid form. Upon release, ammonia is used either directly as a fuel in fuel cells or decomposed into dihydrogen and dinitrogen, which after an optional purification
10 tion step can be used as a fuel in fuel cells.

2. Description of the Related Art

The potential advantages of using fuel cells have received significant attention. Application of dihydrogen or ammonia as a fuel, e.g., in fuel cells
15 is attractive because it generates no polluting emissions [Hoogers, Thompsett, CatTech 2000, 3, 106]. In large-scale production facilities, dihydrogen or ammonia is produced from coal, naphtha or natural gas [Dybkjær, in Ammonia: Catalysis and Manufacture (Ed. Nielsen), Springer, 1995] and steam and air. This obviously generates CO₂ but by application
20 of appropriate sequestration strategies [Lackner, Annu. Rev. Energy Environ. 2002, 27, 193], ammonia or dihydrogen can, if desired, be produced without any net release of carbon oxides. So far, the main focus has been on using dihydrogen as a fuel. However, this attractive application has
25 been hindered due to problems of storing sufficient amounts of dihydrogen in gaseous and even in liquid forms [Schlapbach & Züttel, Nature 2001, 414, 353]. To overcome this difficulty, various solid hydrogen storage materials have been proposed but the gravimetric hydrogen storage capacity is still low and the reversible storage and release of hydrogen requires relatively high pressure and temperature. Currently, attention is focused at
30 the use of complex chemical hydrides [WO 03/04553 A2] but there are still

no materials that fulfil the specifications defined by The US Department of Energy [www.energy.gov]. Since dihydrogen cannot yet be stored with a sufficient volumetric efficiency, alternatives have been investigated.

Among the most promising sources of dihydrogen, methanol has attracted
5 significant attention both as a possible source of dihydrogen that can be easily transported or for use in the direct methanol fuel cell [Hogart, Prospects of the direct methanol fuel cell, Fuel cell technology handbook (2003)]. However, compared to dihydrogen or ammonia as a fuel this would require both central CO₂ sequestration at the methanol production
10 facility and also decentral sequestration at each operating fuel cell, if all harmful contributions to the ecobalance should be avoided. Similar problems are necessarily encountered with all other carbon-containing fuels for fuel cells, such as e.g., methane, gasoline, diesel and ethanol. Ammonia is already produced in large facilities with daily production capacities that can
15 be in excess of 3000 metric tons. It has been calculated that in terms of overall efficiency, ammonia is an attractive alternative to methanol [Metkemeijer & Achard, Int. J. Hydrogen Energy 1994, 19, 535].

Ammonia or ammine complexes, i.e. coordination compounds in which
20 ammonia is bound to a metal ion have been known since the 19th century and many such compounds are today considered classical inorganic compounds. In the early literature, ammine complexes were often formed by reaction of metal salts with gaseous ammonia. Similarly, in many cases it
25 was shown that new compounds containing less or even no ammonia could be formed by controlled thermal degradation of various ammine complexes.

It is well-known in the art that ammonia can be used directly as a fuel for certain high-temperature fuel cells [Wojcik, Middleton, Damopoulos, van
30 Herle, J.Power Sources, 2003, 118, 342]. Similarly, it is known that am-

monia can be decomposed catalytically to mixtures of dihydrogen, dinitrogen and unreacted ammonia, which can be used directly as a fuel in e.g., alkaline fuel cells (AFC) [Kordesch et al., J.Power Sources 2000, 86, 162], but only after removal of ammonia traces in other types, such as in proton
5 exchange membrane (PEM) fuel cells [Chellappa et al., Appl. Catal. A., 2002, 227, 231]. Currently, an infrastructure that allows transportation of liquid ammonia, primarily for use in agriculture, already exists. Furthermore, ammonia is one of the chemicals of which the largest amount is produced on a worldwide basis. Thus, there are many possible advantages of using ammonia for reversible hydrogen storage. However, one
10 particular disadvantage has prohibited the possibility for developing this technology, and this is the difficulty of convenient and safe transportation of ammonia [Schlögl, Angew. Chem. Int. Ed. 2003, 42, 2004]. The use of ammonia stored as liquid in pressurized containers at room temperature
15 may result in uncontrolled release of large quantities of toxic ammonia in case of physical damage on a container. It is an object of the present invention to overcome this difficulty and to make efficient use of ammonia as a fuel in fuel cells and/or as a source of dihydrogen also for use in fuel cells.

20

It has been suggested that such metal-ammine complexes might be used to increase the efficiency of ammonia production plants by allowing easy separation of ammonia from the equilibrium mixture by pressure swing adsorption [Liu & Aika, Chem. Lett. 2002, 798].

25

Furthermore, ammine complexes have been demonstrated for use in connection with cooling and refrigeration, where absorption desorption cycles are employed for efficient cold production.

The present invention is clearly distinguished from these two applications of the reversible absorption of ammonia in metal salts in that the invention regards the use of said complexes as energy carriers, thereby placing the invention within an entirely different technical field.

5

SUMMARY OF THE INVENTION

In a first aspect the invention relates to an electric power generating unit comprising

(i) an ammonia storage device in the form of a container comprising
10 an ammonia absorbing and releasing salt of the general formula:

$M_a(NH_3)_nX_z$, wherein M is one or more cations selected from alkali metals, alkaline earth metals, and transition metals such as Li, Na, K, Cs, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn or combinations thereof such as NaAl, KAl, K_2Zn , CsCu, or K_2Fe , X is one or more anions selected from fluoride,
15 chloride, bromide, iodide, nitrate, thiocyanate, sulphate, molybdate, phosphate, and chlorate ions, a is the number of cations per salt molecule, z is the number of anions per salt molecule, and n is the coordination number of 2 to 12,

(ii) means for heating said container and ammonia absorbing and
20 releasing salt for releasing ammonia gas and

(iiia) a fuel cell for converting ammonia directly into electric power;
or

(iiib1) a reactor for dissociating ammonia into hydrogen and nitro-
gen and

25 (iiib2) a fuel cell for converting hydrogen into electric power.

In a second aspect the invention relates to the use of an ammonia storage device in the form of a container comprising an ammonia absorbing and releasing salt of the general formula: $M_a(NH_3)_nX_z$, wherein M is one or
30 more cations selected from alkali metals, alkaline earth metals, and transi-

tion metals such as Li, Na, K, Cs, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn or combinations thereof such as NaAl, KAl, K₂Zn, CsCu, or K₂Fe, X is one or more anions selected from fluoride, chloride, bromide, iodide, nitrate, thiocyanate, sulphate, molybdate, phosphate, and chlorate ions, a is the number of cations per salt molecule, z is the number of anions per salt molecule, and n is the coordination number of 2 to 12 as a source of energy in a electric power generating unit comprising

5 (1) means for heating said container and ammonia absorbing and releasing salt for releasing ammonia gas,

10 (2a) a fuel cell for converting ammonia directly into electric power; or comprising

(2b1) a reactor for dissociating ammonia into hydrogen and nitrogen and

(2b2) a fuel cell for converting hydrogen into electric power.

15

Brief Description of the Drawings

The invention is disclosed more in detail with reference to the drawings in which

Fig.1 schematically shows parts of an embodiment of a power generating unit according to the invention,

20 Fig. 2 schematically shows parts of a preferred embodiment of a power generating unit according to the invention, and

Fig. 3 schematically shows parts of another preferred embodiment of a power generating unit according to the invention.

25

Detailed Description of the Present Invention

The present invention is based on the use of an ammonia storage device holding metal-ammine salts as solid storage media for ammonia, which in turn is used, either in its pure form or after decomposition to a gas mixture containing dinitrogen and dihydrogen, as a feedstock for an energy pro-

30

ducing unit such as a fuel cell. The metal-ammine salt is a salt that releases ammonia upon heating, during which it acts as an ammonia releasing salt. After all, or part of, the contained ammonia is released from the metal-ammine, it is possible to adsorb ammonia to the resulting solid, and the salt acts as an ammonia absorbing salt. Thus, the metal-ammine salt constitutes a reversible solid storage medium for ammonia, which represent a safe and practical option for storage and transportation of ammonia. Ammonia is typically released from the preferred metal ammine salt by heating the salt to temperatures in the range of 10-550 °C.

10

The present invention may be used for large energy producing facilities, and by use of small rechargeable and/or replaceable ammonia storage containers combined with micro-fabricated/miniaturized ammonia decomposition reactors, it is also possible to provide energy for mobile units and portable devices such as a laptop computer.

15

Solid ammonia storage media according to the present invention may contain substances that bind ammonia in the form of a chemical complex.

These include ionic salts, particularly chlorides and/or sulphates of one or more alkali metals, alkaline earth metals and/or one or more 3d subgroup

20

elements. The ionic salts include $MgCl_2$, $MgBr_2$, $Mg(ClO_4)_2$, $ZnCl_2$, $Zn(NO_3)_2$, $ZnBr_2$, ZnI_2 , $ZnSO_4$, K_2ZnCl_4 , $(NH_4)_2ZnCl_4$, $(NH_4)_3ZnCl_5$, $Ca(NO_3)_2$, $CaBr_2$, CaI_2 , $CaCl_2$, $Ca(ClO_4)_2$, $BaCl_2$, $BaBr_2$, BaI_2 , $Ba(NO_3)_2$, $BeCl_2$, $FeCl_2$, $Fe(NO_3)_2$, $FeCl_3$, $FeBr_2$, FeI_2 , $FeSO_4$, $Fe(CNS)_2$, K_2FeCl_5 , $SrCl_2$, $SrBr_2$, SrI_2 , $Co(NO_3)_2$, $CoCl_2$, $CoBr_2$, CoI_2 , $CoSO_4$, $Co(CNS)_2$, $CoCl_3$, $NiCl_2$, NiI_2 , $NiSO_4$, $Ni(NO_3)_2$, $Ni(ClO_4)_2$, $MnCl_2$, $MnBr_2$, $Cu(NO_3)_2$, $CuCl_2$, $CuBr_2$, CuI_2 , $CuSO_4$, $CrCl_2$, NH_4AlCl_4 , $KAlCl_4$, NH_4Cl , $NaBr$, $CsCuCl_3$, $TaCl_2$, $SnCl_2$, $PbCl_2$, Li_2SO_4 , Li_3PO_4 and $LiCl_2$.

25

The present invention relates to an electric power generating unit comprising

(i) an ammonia storage device in the form of a container comprising an ammonia absorbing and releasing salt of the general formula:

5 $M_a(NH_3)_nX_z$, wherein M is one or more cations selected from alkali metals, alkaline earth metals, and transition metals such as Li, Na, K, Cs, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn or combinations thereof such as NaAl, KAl, K_2Zn , CsCu, or K_2Fe , X is one or more anions selected from fluoride, chloride, bromide, iodide, nitrate, thiocyanate, sulphate, molybdate, phosphate, and chlorate ions, a is the number of cations per salt molecule, z is
10 the number of anions per salt molecule, and n is the coordination number of 2 to 12,

(ii) means for heating said container and ammonia absorbing and releasing salt for releasing ammonia gas and

15 (iiia) a fuel cell for converting ammonia directly into electric power; or

(iiib1) a reactor for dissociating ammonia into hydrogen and nitrogen and

(iiib2) a fuel cell for converting hydrogen into electric power.

20

The use of ammonia storing materials in connection with energy storage is considered new. The ability of metal ammines to absorb and to desorb ammonia is well known in the literature, but their potential as energy carriers has not been proposed until now. This finding and the demonstration
25 of the use of these salts as viable energy carriers lies far from all existing technology, and the high energy densities of some materials provides a leap as compared to the feasible storage densities for hydrogen. Furthermore, the system is remarkably safe compared to virtually all other energy carriers, and especially the known hydrogen storage media. At the same

time, metal ammine salts can release ammonia/hydrogen at much higher rates than what is possible for comparable solid hydrogen storage media. Summing up, metal amine salts solves a number of problems hampering the use of the existing media for energy storage by providing higher energy density, improved user safety, simpler handling and transport, good compatibility with most or all known types of fuel cells and/or more favorable release kinetics than existing technologies for storing fuel for fuel cells.

10 A power generating unit of the invention may be a disposable unit for use in devices having limited expected time of use and where a high density of energy is desirable as a replacement of traditional battery technology in e.g. laptop computers, or as source of energy for e.g. radio transmitters for use in deserted areas or in space.

15 According to a preferred embodiment of the invention the electric power generating unit comprises means for adding ammonia to saturate the ammonia absorbing and releasing salt with ammonia rendering the unit rechargeable which is preferred for uses in which the consumption of energy is considerable as compared to the ammonia storing capacity of the unit.

25 During release of ammonia the original complex metal-ammine salt of the formula $M_a(NH_3)_nX_z$ is gradually transformed into another complex of the formula $M_a(NH_3)_mX_z$ wherein $m < n$. When all the desired ammonia has been released, the resulting $M_a(NH_3)_mX_z$ may be converted back into $M_a(NH_3)_nX_z$ by an absorption treatment with an ammonia-containing gas stream. Preferably, the adsorption of ammonia is carried at a temperature below 100 °C simply by passing the ammonia containing gas through the ammonia absorbing salt.

30

Typical hydrogen contents of the metal ammine complexes are in the range of 3-14wt%, preferably above 5 wt%. For several metal-ammine salts it is possible to release all ammonia and then transform the resulting material back into the original metal-ammine salt in a large number of cycles. This obviously constitutes preferred embodiments. For mobile units and for small portable devices, it is particularly useful to hold the metal-ammine in a container that can be detached from the fuel cell and recharged with ammonia in a separate recharging unit.

Typical ammonia contents of the metal ammine complexes are typically in the range of 20-60 wt%, preferably above 30 wt%. In a preferred embodiment of the invention the ammonia absorbing and releasing salt is $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, which contains 51.7 wt% ammonia. Thus, the present invention offers ammonia storage at significantly higher densities (both on a volume and a weight basis) than both aqueous ammonia and aqueous urea nearly approaching the ammonia volume density of liquid ammonia.

A solid storage medium containing magnesium chloride is advantageously used. At ambient conditions magnesium chloride stores up to 6 molecules of ammonia per magnesium ion, forming $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$. This storage medium has an approximate density of 1.2 grams/cm³, leading to a stored amount of 620 grams ammonia per litre storage medium. If the hydrogen in this ammonia is released by decomposition, 109 grams hydrogen can be delivered. This hydrogen density is comparable to the theoretical hydrogen density of complex hydrides as NaBH_4 or LiAlH_4 , while the storage media of the current invention are both safer and more convenient from a technological point of view.

Using $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, the ammonia vapour pressure at 25°C will be only 0.002 bar, building up to approximately 8 bar at 200 °C. A device accord-

ing to the present invention can advantageously be operated so that the ammonia pressure is between 1.5 and 10 bar.

5 In another preferred complex of $\text{Li}(\text{NH}_3)_4\text{Cl}$ or $\text{Li}(\text{NH}_3)_5\text{Cl}$ the ammonia contents is as high as 62 wt% and 67 wt%, respectively.

10 In a preferred embodiment of the invention the salt is in the form of a fine powder of micro crystals or located on a porous support material, which facilitates the handling thereof and the keeping in the storage device.

In one embodiment of the invention the means for heating is in the form of an electrical resistive heating device.

15 Heat required to release the ammonia may be generated by electrical resistive heating being simple to control, but may also be generated by an exothermic chemical reaction wherein ammonia or hydrogen is oxidized in a manner known per se and/or by heat exchange with the energy producing unit.

20 Supplying power to microelectronic or micro-electromechanical systems suffers from the paradox that the power-generating unit is often larger than the device itself and for remote and autonomous operation the energy density has to be increased dramatically as compared to even the best lithium-ion battery technology [Holladay, Jones, Phelps and Hu, J. Power
25 Sources 108 (2002) 21-27]. To increase the energy density micro sized fuel cells are developed, but again the main problem is storage of e.g. hydrogen as fuel. The use of hydrocarbons or alcohols such as methanol requires many steps of evaporating, reforming and CO cleanup together with handling of both liquid and gas phases being difficult to integrate and control on a chip. The ammonia storage device combined with an ammonia
30

tolerating fuel cell greatly simplifies the integration and control on a chip and increases the energy density by an order of magnitude compared to battery technology.

- 5 For very small scale applications the entire container and means for heating are micro fabricated using processes such as mechanical grinding, chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron beam lithography, photo lithog-
10 raphy, or laser lithography.

Micro size power generating units according to the invention may be micro fabricated using processes known per se such as mechanical grinding, chemical vapour deposition (CVD), plasma enhanced chemical vapour
15 deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron beam lithography, photo lithog-raphy, or laser lithography.

When dissociating ammonia into hydrogen and nitrogen before use in ac-
20 cordance with an embodiment of the invention, a reactor for dissociating ammonia preferably contains a heterogeneous catalyst for accelerating the processes and reducing the energy input needed.

When dissociating ammonia into hydrogen and nitrogen it is in some
25 cases preferred to purify the gas for remaining ammonia before feeding the gas to the fuel cell. Such gas purification may be performed using either an acidic aqueous solution such as 2M H₂SO₄ or an ammonia absorbing salt of the formula M_aX_z-type such as MgCl₂. By both methods, residual ammonia levels may be decreased to below 10 ppm. According to the
30 present invention, this purification step can also be carried out using solid

acidic media, high surface area compounds such as activated carbon and/or other ammonia absorbing salts of the M_aX_z -type.

5 A heterogeneous catalyst suitably comprises a support carrying an active phase. The support consists of a thermally stable material with a high surface area such as a ceramic, facilitating dispersion of the active phase

10 It is preferred that the active phase comprises dispersed nanoparticles (having a size in the range up to 100 nanometres) of transition metals or compounds thereof such as Co_3Mo_3N , Ru, Co, Ni and Fe or mixtures thereof. The active phase is preferably promoted with alkali metals or alkaline earth metals such as K, Ca, and/or Ba.

15 A power generating unit according to the invention may further comprise a combustion device wherein a part of the hydrogen produced in the reactor, unreacted hydrogen from the fuel cell or a mixture thereof is oxidized for providing heat for heating the ammonia storage device for providing energy required for carrying out the processes in the power generating unit.

20 In cases where ammonia is decomposed into dihydrogen and dinitrogen, the required heat may similarly be generated by electrical resistive heating and/or from an exothermic reaction and/or by heat exchange with the energy producing unit. The preferred method of heating depends on which type of fuel cell is used, and particularly on the operating temperature of
25 the fuel cell. However, in all cases there is a significant advantage of supplying the heat necessary for ammonia desorption and for the possible ammonia decomposition directly from the fuel cell through electrical resistive heating or indirectly through heat exchange either with the fuel cell itself or from heat generated by controlled combustion of the exit gas from
30 the fuel cell. The heat can also be generated by directly using a minor

fraction of the dihydrogen from the decomposition unit in a combustion reaction.

5 The heat can also be generated by directly using a minor fraction of the dihydrogen from the decomposition unit in a combustion reaction. If the invention is used with an alkaline fuel cell operating at elevated temperature (typically up to 260°C), a preferred option is to use an ammonia absorbing and desorbing salt releasing ammonia below the operating temperature of the fuel cell.

10

In a preferred embodiment of the invention the power generating unit further comprises a combustion device wherein a fraction of the hydrogen produced in the reactor, unreacted hydrogen from the fuel cell or a mixture thereof is oxidized for providing heat for heating said reactor for dissociating ammonia.

15

In another preferred embodiment of the invention the power generating unit further comprises a combustion device wherein a fraction of the ammonia released from the ammonia storage, unreacted ammonia from the fuel cell or a mixture thereof is oxidized for providing heat for heating said ammonia storage device.

20

In a further preferred embodiment of the invention the power generating unit further comprises a combustion device wherein a fraction of the ammonia released from the ammonia storage, unreacted ammonia from the fuel cell or a mixture thereof is oxidized for providing heat for heating said reactor for dissociating ammonia.

25

It is especially preferred when the constituents of a power generating unit according to the invention are dimensioned to provide full balancing of the

30

complete unit reducing the volume of and energy loss in the electric power generating unit. Balancing the unit will consist of optimizing tube dimensions, flows, insulation, temperatures etc. to obtain the optimal output of electrical energy from the electric power generating unit.

5

The power generating unit according to the invention is especially suitable for providing a micro-size power source for microelectronic devices or micro-electro-mechanical-systems (MEMS).

10 A reactor for dissociating ammonia is preferably a part of a micro-size electric system being micro fabricated using processes known per se such as mechanical grinding, chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron
15 beam lithography, photo lithography, or laser lithography.

According to the invention it is possible to divide the reactor for dissociating ammonia into two parts, one part being operated at a low temperature that dissociates most ammonia and another part being operated at a high
20 temperature that dissociates the last present fraction of ammonia. Such setup reduces the area to be held at high temperature, thus reducing the amount of heat loss.

In another aspect the invention relates to the use of an ammonia storage
25 device in the form of a container comprising an ammonia absorbing and releasing salt of the general formula: $M_a(NH_3)_nX_z$, wherein M is one or more cations selected from alkali metals, alkaline earth metals, and transition metals such as Li, Na, K, Cs, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn or combinations thereof such as NaAl, KAl, K_2Zn , CsCu, or K_2Fe , X is one
30 or more anions selected from fluoride, chloride, bromide, iodide, nitrate,

thiocyanate, sulphate, molybdate, phosphate, and chlorate ions, a is the number of cations per salt molecule, z is the number of anions per salt molecule, and n is the coordination number of 2 to 12 as a source of energy in a electric power generating unit comprising

5 (1) means for heating said container and ammonia absorbing and releasing salt for releasing ammonia gas,

(2a) a fuel cell for converting ammonia directly into electric power; or comprising

10 (2b1) a reactor for dissociating ammonia into hydrogen and nitrogen and

(2b2) a fuel cell for converting hydrogen into electric power.

In one embodiment of this aspect the electric power generating unit according further comprises means for adding ammonia to saturate the ammonia absorbing and releasing salt with ammonia rendering the unit re-chargeable.

In a preferred use of the invention the ammonia absorbing and releasing salt is $Mg(NH_3)_6Cl_2$ offering very high density of ammonia storage and enabling working the unit at a relatively low pressure.

It is preferred to use the salt is in the form of a fine powder of micro crystals or located on a porous support material.

25 In one embodiment of the invention an electrical resistive heating device is used as the means for heating.

In another embodiment of the invention chemical reactions are used for providing heating.

In a preferred use the container and means for heating are a part of a micro-size electric system being micro fabricated using processes known per se such as mechanical grinding, chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron beam lithography, photo lithography, or laser lithography.

When a reactor for dissociating ammonia is used, it preferably contains a heterogeneous catalyst for accelerating the processes and reducing the energy input needed.

When used, the heterogeneous catalyst preferably comprises a support and an active phase.

It is preferred to use an active phase comprises dispersed nanoparticles of transition metals or compounds thereof such as $\text{Co}_3\text{Mo}_3\text{N}$, Ru, Co, Ni and Fe or mixtures thereof.

In the use of the invention the power generating unit may further comprise a combustion device wherein a part of the hydrogen produced in the reactor, unreacted hydrogen from the fuel cell or a mixture thereof is oxidized for providing heat for heating the ammonia storage device for providing energy required for carrying out the processes in the power generating unit.

In one preferred use according to the invention the power generating unit further comprises a combustion device wherein a fraction of the hydrogen produced in the reactor, unreacted hydrogen from the fuel cell or a mixture thereof is oxidized for providing heat for heating said reactor for dissociating ammonia.

In another preferred use according to the invention the power generating unit further comprises a combustion device wherein a fraction of the ammonia released from the ammonia storage, unreacted ammonia from the fuel cell or a mixture thereof is oxidized for providing heat for heating said ammonia storage device.

In a further preferred use of the invention the power generating unit further comprises a combustion device wherein a fraction of the ammonia released from the ammonia storage, unreacted ammonia from the fuel cell or a mixture thereof is oxidized for providing heat for heating said reactor for dissociating ammonia.

According to a preferred use according to the invention the constituents of the power generating unit are dimensioned to provide full balancing of the complete unit reducing the volume of and energy loss in the electric power generating unit. Balancing the unit will consist of dimensioning tubes, chambers, flows, insulation, temperatures etc. to obtain the optimal output of electrical energy from the electric power generating unit.

In a preferred use according to the invention the power generating unit is in the form of a micro-size power source for microelectronic devices or micro-electro-mechanical-systems (MEMS).

In a preferred embodiment of the invention a reactor for dissociating ammonia being divided into two parts is used, one part operated at a low temperature that dissociates most ammonia and another part operated at a high temperature that dissociates the last present fraction of ammonia.

Description of the Preferred Embodiments

The invention is now explained more in detail with reference to the drawings showing flow charts of preferred embodiments of a plant for working the invention.

5

Reference is made to figure 1 schematically showing parts of a power generating unit according to the invention. The unit has a solid ammonia storage medium 1, placed in a container 2 which can be heated using a heating device 3a. The size of container 2 and accordingly the amount of solid ammonia storage medium may be scaled according to the requirement for energy storage capacity of the specific application of the invention. As systems according to the present invention may have sizes ranging from micro to mega scale, the storage capacity must vary accordingly. Substances that are able to store ammonia at ambient conditions (approximately 20°C and 1 bar) only building up low ammonia pressures (<1 bar) in closed systems are preferred for use as solid ammonia storage media according to the invention.

10

15

In a preferred embodiment of the invention the solid ammonia storage material can be reloaded by adding gaseous or liquid ammonia to the storage container 2 through a filling nozzle, the storage material then absorbing ammonia at ambient temperature.

20

The heating device 3a can use either resistive electric heating or one of several possible chemical processes for heating the solid ammonia storage medium. Preferable chemical reactions for generation of heat could be the combustion of residual hydrogen from the exhaust 5 of the electrochemical power generating unit 4 or of part of the ammonia released from the solid storage medium. Such combustions could advantageously be carried out over a catalyst.

25

30

In one preferred embodiment, the electrochemical power generating unit 4 is a fuel cell running directly on ammonia. This fuel cell could advantageously be of the SOFC or AFC type.

- 5 Figure 2 shows another embodiment of a power generating unit of the invention in which the electrochemical power generating unit could be a fuel cell running on hydrogen. In this application, ammonia from the solid ammonia storage 1 is passed over a heterogeneous ammonia decomposition catalyst 6. The catalyst decomposes ammonia into hydrogen and nitrogen.
- 10 Preferred catalysts for this decomposition could be deposited on a support, and the active phase could contain dispersed nanoparticles of Co₃Mo₃N, Ru, Co, Ni or Fe or mixtures thereof. If a sufficient amount of catalyst is used at 1 bar and 300°C the residual amount of ammonia at equilibrium is only 1.9 %. Heat energy for the decomposition catalyst 6 is
- 15 supplied from heating element 3b using energy obtained in the same ways as described for heating element 3a. In one preferred embodiment, the container 2 and decomposition catalyst 6 are integrated into one unit, allowing heat for both reactors to be provided by the same heating element.
- 20 If the introduction of small amounts of ammonia into the electrochemical power generating device is undesirable (as in the case of the device being a fuel cell of the PEM type), the gas mixture can be cleaned in a separate or integrated unit 7. This unit could consist of an absorbent as an acidic zeolite or an ionic salt of the type also feasible as solid ammonia storage
- 25 materials. In another embodiment, this gas cleaning could be done using a membrane for separation of hydrogen from the other constituents of the gas. In a preferred embodiment, this membrane could be made of Pd.

In figure 3 is shown a further preferred embodiment in which the system is

30 built as described in connection with the embodiment of figure 2 and fur-

ther being provided with optional buffer volumes 8a and/or 8b and one or more magnetically actuated valves 9a-9d. An electronic controller 10 monitors and controls flows and heating adjusting it to the fuel requirement of the electrochemical power generating device.

5

Specific examples of systems according to the present invention

The invention is further elucidated in detail in the below specific examples of working the invention.

10 Example 1: Ammonia desorption from metal ammine halides

Absorption of ammonia is exemplified by $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ and $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$.

Release of ammonia from $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ was accomplished by placing 1.1 grams of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ in a container of 10 millilitres internal volume
15 equipped with a single outgoing tube connected to flow measuring apparatus. The container was sealed, and heated by resistive electric heating at an increase of temperature of $0.2^\circ\text{C}/\text{min}$. The resulting flow of ammonia is shown in figure A, and the integral liberated amount constitutes the entire theoretical amount of 6 moles NH_3 pr. mole NiCl_2 within the measurement
20 error.

Similar tests were performed with $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ to exemplify desorption from alkaline earth metal ammine halides. The resulting flow of ammonia is shown in figure B, and the integral liberated amount again constitutes
25 the entire theoretical amount of 6 moles NH_3 pr. mole MgCl_2 within the measurement error.

Example 2: Uptake of gaseous ammonia in metal salts of the general structure M_aX_z .

Salts of the general formula M_aX_z were exposed to gaseous ammonia and the absorption was investigated using x-ray diffraction. $ZnCl_2$, $CuSO_4$, $CoCl_3$, $MgCl_2$ and $NiCl_2$ were investigated after exposure to gaseous ammonia at 1 bar pressure and room temperature. The results are shown in figures C - G. One further experiment showed that ammonia absorption of $MgCl_2$ was complete in less than 20 min at 8 bar ammonia pressure.

Example 3: Reversibility of the absorption desorption cycle

The reversibility of the absorption cycles were investigated by x-ray diffraction of $MgCl_2$ after absorption and subsequent desorption, figure H, and after a second absorption, figure I. When compared with figure F it is found that the changes in crystal structure during absorption/desorption of ammonia are reversible.

Example 4: Preparation of An electric power generating unit according to the invention.

A unit according to the present invention, delivering hydrogen for a PEM fuel cell was constructed. This unit comprised a container for ammonia storage compound, a buffer chamber for gaseous ammonia (approx. 200 millilitres), a device for flow regulation, a heated catalyst for ammonia decomposition, a scrubber for removal of residual ammonia and a PEM fuel cell delivering power for an electric motor.

In order to demonstrate the feasibility of the invention, $Mg(NH_3)_6Cl_2$ was used as ammonia storage compound in the container. The container was heated by electric resistive heating. Figure J shows characteristics of the pressure development in the buffer volume when ammonia was vented dynamically to the remaining system at an average rate of 70 millilitres/min. As the heating in this embodiment was regulated on/off after a simple pressure criterion, the temperature oscillated as appears from fig-

ure K. This leads to the oscillations in pressure seen in figure J. Apart from the oscillations in temperature, three distinct plateaus are recognised. These correspond to the three stages of ammonia desorption from $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ also recognised in figure B.

5

After leaving the flow controlling device, ammonia was passed through a reactor for decomposing ammonia into nitrogen and hydrogen. This reactor was equipped with 1.0 grams of an iron based catalyst, and heated by electric resistive heating.

10

In this embodiment, the last process before the gas enters the fuel cell was removal of remaining ammonia from the catalytic reactor.

This gas purification has been performed using either an acidic aqueous solution (e.g. 2M H_2SO_4) or an ammonia absorbing salt of the M_aX_z type (for example MgCl_2). By both methods, residual ammonia levels could be decreased below 10 ppm.

Example 5: Dissociation of ammonia in a micro fabricated reactor.

In this example it is demonstrated that ammonia decomposition may be carried out in micro fabricated reactors produced by photo lithography and dry etching on a silicon wafer. The reactors had internal volumes of 4 microlitres each and were sealed using Pyrex glass. In the reactors was placed a catalyst consisting of Ru or Ba promoted Ru supported on alumina. The catalytic activity in terms of hydrogen production per mole Ru per hour in these reactors is shown in FIG. L as function of reactor temperature. As appears from figure L, the fraction of ammonia which is decomposed can be as high as 98% at 400°C.

Claims

1. An electric power generating unit comprising
 - (i) an ammonia storage device in the form of a container comprising
5 an ammonia absorbing and releasing salt of the general formula:
 $M_a(NH_3)_nX_z$, wherein M is one or more cations selected from alkali metals, alkaline earth metals, and transition metals such as Li, Na, K, Cs, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn or combinations thereof such as NaAl, KAl, K_2Zn , CsCu, or K_2Fe , X is one or more anions selected from fluoride,
10 chloride, bromide, iodide, nitrate, thiocyanate, sulphate, molybdate, and phosphate ions, a is the number of cations per salt molecule, z is the number of anions per salt molecule, and n is the coordination number of 2 to 12,
 - (ii) means for heating said container and ammonia absorbing and
15 releasing salt for releasing ammonia gas and
 - (iiia) a fuel cell for converting ammonia directly into electric power;
or
 - (iiib1) a reactor for dissociating ammonia into hydrogen and nitro-
gen and
20 (iiib2) a fuel cell for converting hydrogen into electric power.
 2. The electric power generating unit according to claim 1 further compris-
ing means for adding ammonia to saturate the ammonia absorbing and
releasing salt with ammonia.
25
 3. The electric power generating unit according to claim 1, wherein said
ammonia absorbing and releasing salt is $Mg(NH_3)_6Cl_2$.

4. The electric power generating unit according to any of claims 1-3, where the salt is in the form of a fine powder of micro crystals or located on a porous support material.
- 5 5. The electric power generating unit according to any of claims 1-3, where the means for heating is in the form of an electrical resistive heating device.
6. The electric power generating unit according to any of claims 1-3, where
10 said means for heating is provided by a heat produced by chemical reactions.
7. The electric power generating unit according to claim 1 where the container and means for heating are a part of a micro-size electric system being
15 micro fabricated using processes such as mechanical grinding, chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron beam lithography, photo lithography, or laser lithography.
- 20
8. The power generating unit according to claim 1 where the reactor for dissociating ammonia contains a heterogeneous catalyst.
9. The power generating unit according to claims 8 where said heterogeneous
25 catalyst comprises a support and an active phase.
10. The power generating unit according to claims 9 where said active phase comprises dispersed nanoparticles of transition metals or compounds thereof such as $\text{Co}_3\text{Mo}_3\text{N}$, Ru, Co, Ni and Fe or mixtures thereof.

11. The power generating unit according to any of claims 1-10 further comprising a combustion device wherein a part of the hydrogen produced in the reactor, unreacted hydrogen from the fuel cell or a mixture thereof is oxidized for providing heat for heating the ammonia storage device.

5

12. The power generating unit according to any of claims 1-10 further comprising a combustion device wherein a fraction of the hydrogen produced in the reactor, unreacted hydrogen from the fuel cell or a mixture thereof is oxidized for providing heat for heating said reactor for dissociating ammonia.

10

13. The power generating unit according to any of claims 1-10 further comprising a combustion device wherein a fraction of the ammonia released from the ammonia storage, unreacted ammonia from the fuel cell or a mixture thereof is oxidized for providing heat for heating said ammonia storage device.

15

14. The power generating unit according to any of claims 1-10 further comprising a combustion device wherein a fraction of the ammonia released from the ammonia storage, unreacted ammonia from the fuel cell or a mixture thereof is oxidized for providing heat for heating said reactor for dissociating ammonia.

20

15. The power generating unit according to claims 1-14 where the constituents thereof are dimensioned to provide full balancing of the complete unit.

25

16. The power generating unit according to any of claims 1-14 in the form of a micro-size power source for microelectronic devices or micro-electromechanical-systems (MEMS).

30

17. The power generating unit according to claim 1 where said reactor for dissociating ammonia is a part of a micro-size electric system being micro fabricated using processes such as mechanical grinding, chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition
5 (PECVD), electron cyclotron resonance (ECR), sputtering , etching, lithographic methods such as electron beam lithography, photo lithography, or laser lithography.

18. The power generating unit according to any of claims 1-10 where the
10 reactor for dissociating ammonia is divided into two parts, one part operated at a low temperature that dissociates most ammonia and another part operated at a high temperature that dissociates the last present fraction of ammonia.

15 19. The use of an ammonia storage device in the form of a container comprising an ammonia absorbing and releasing salt of the general formula: $M_a(NH_3)_nX_z$, wherein M is one or more cations selected from alkali metals, alkaline earth metals, and transition metals such as Li, Na, K, Cs, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, or Zn or combinations thereof such as
20 NaAl, KAl, K_2Zn , CsCu, or K_2Fe , X is one or more anions selected from fluoride, chloride, bromide, iodide, nitrate, thiocyanate, sulphate, molybdate, phosphate, and chlorate ions, a is the number of cations per salt molecule, z is the number of anions per salt molecule, and n is the coordination number of 2 to 12 as a source of energy in a electric power generating unit comprising
25

(1) means for heating said container and ammonia absorbing and releasing salt for releasing ammonia gas,

(2a) a fuel cell for converting ammonia directly into electric power; or comprising

(2b1) a reactor for dissociating ammonia into hydrogen and nitrogen and

(2b2) a fuel cell for converting hydrogen into electric power.

- 5 20. The use according to claim 19 wherein the electric power generating unit according further comprises means for adding ammonia to saturate the ammonia absorbing and releasing salt with ammonia.

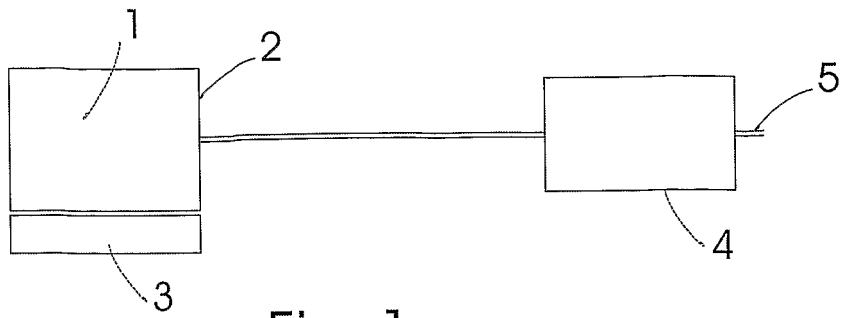


Fig. 1

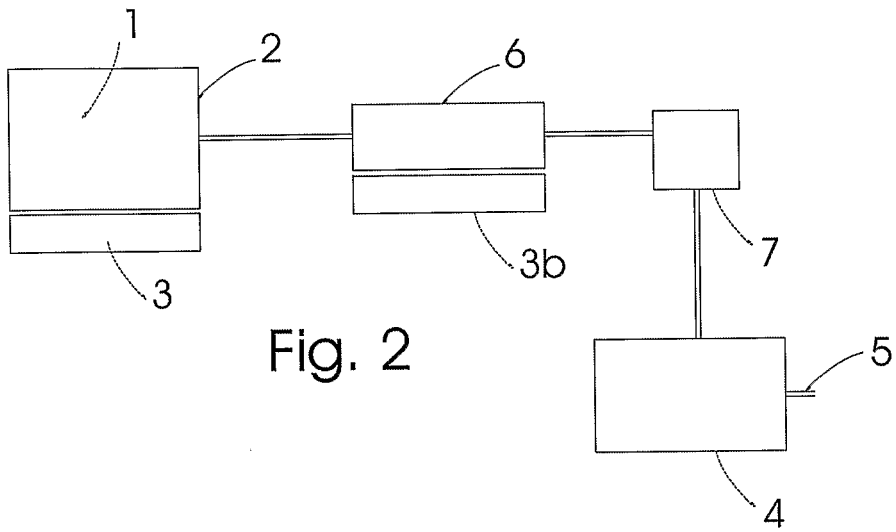


Fig. 2

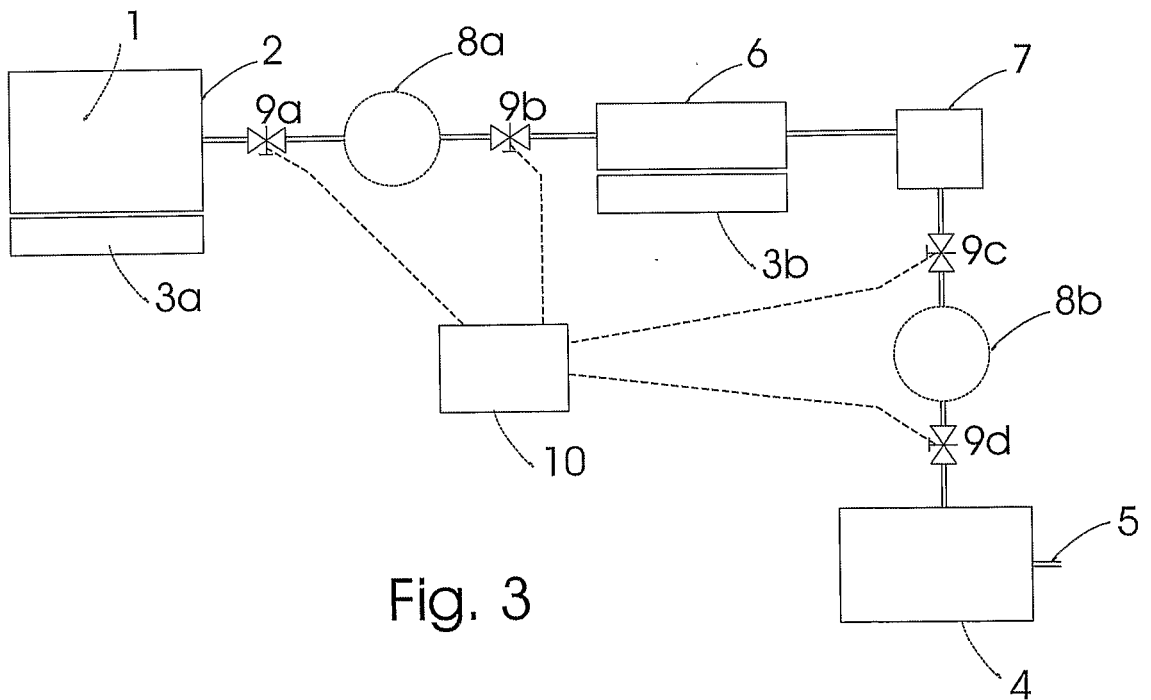


Fig. 3

FIG. A NiCl₂

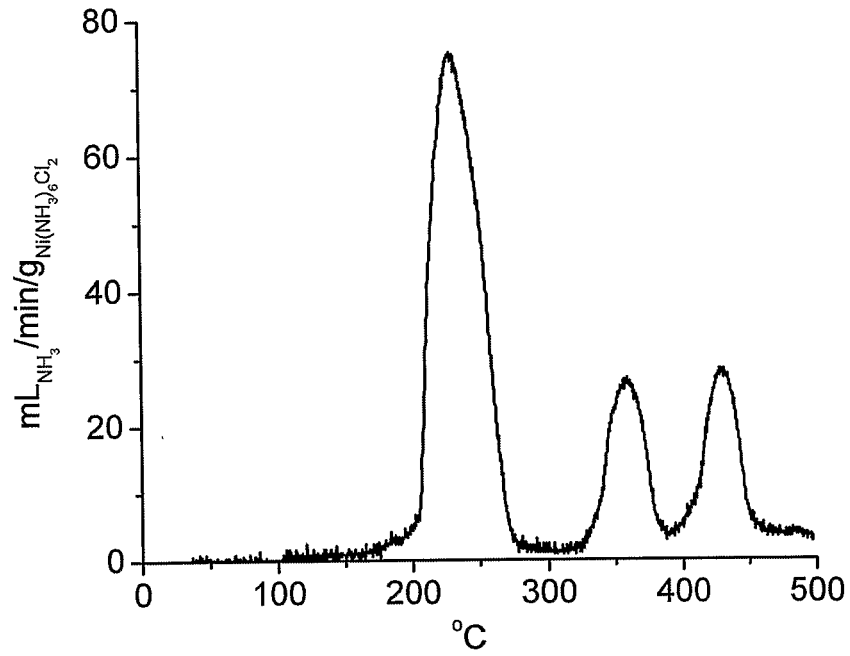


FIG. B MgCl₂

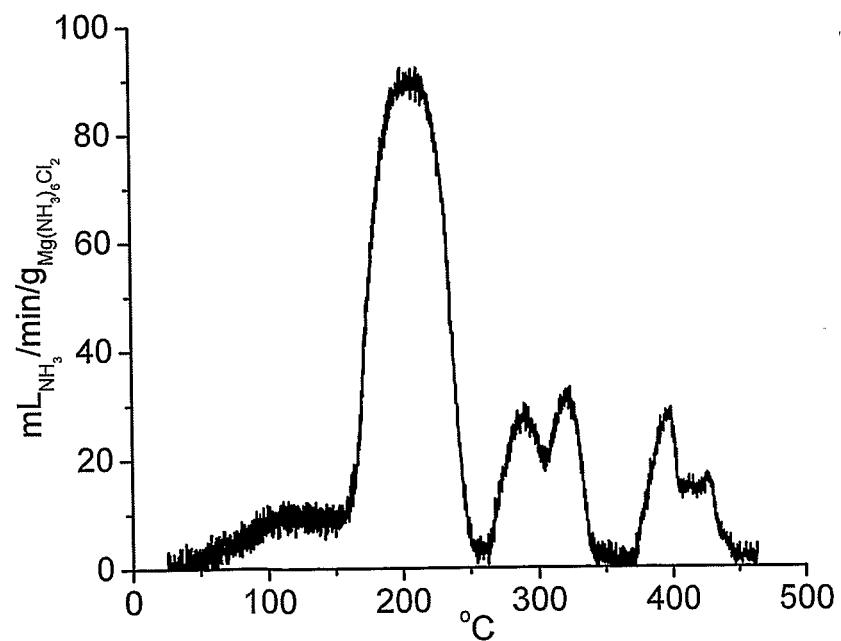


FIG. C ZnCl₂

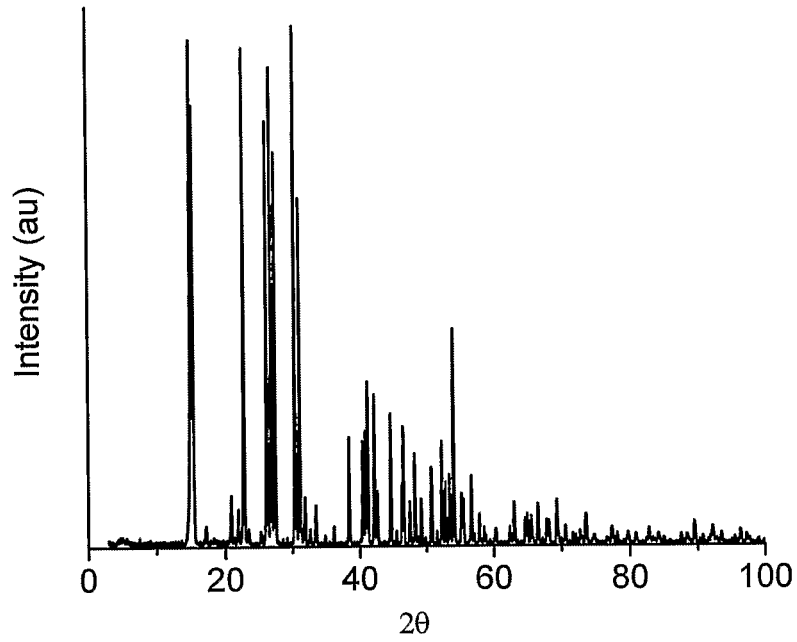
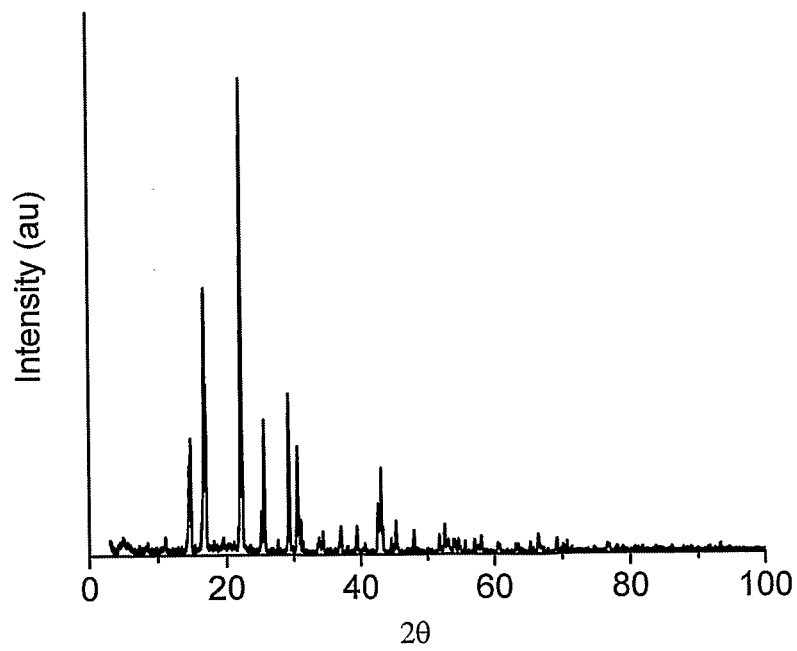


FIG. D CuSO₄



4 / 8

FIG. E CoCl₃

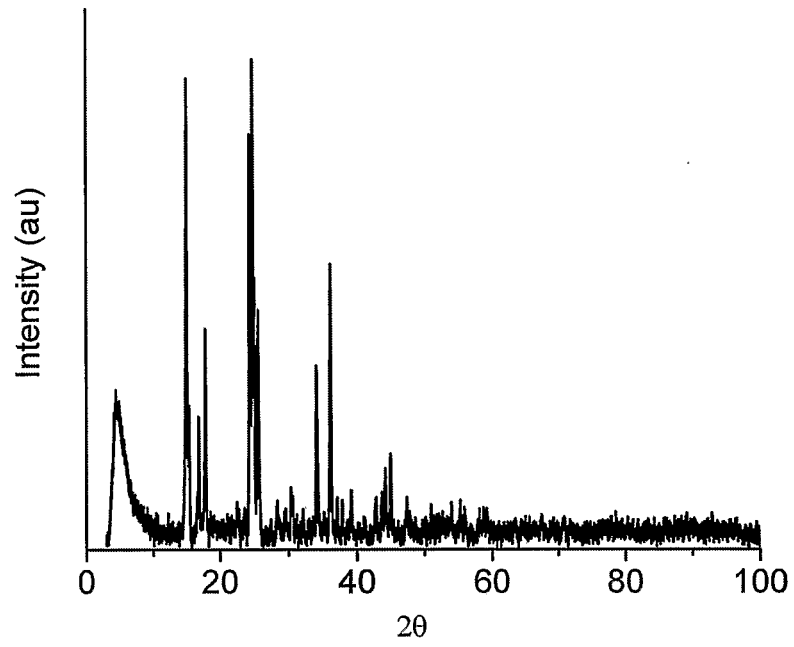


FIG. F MgCl₂ 1 abs

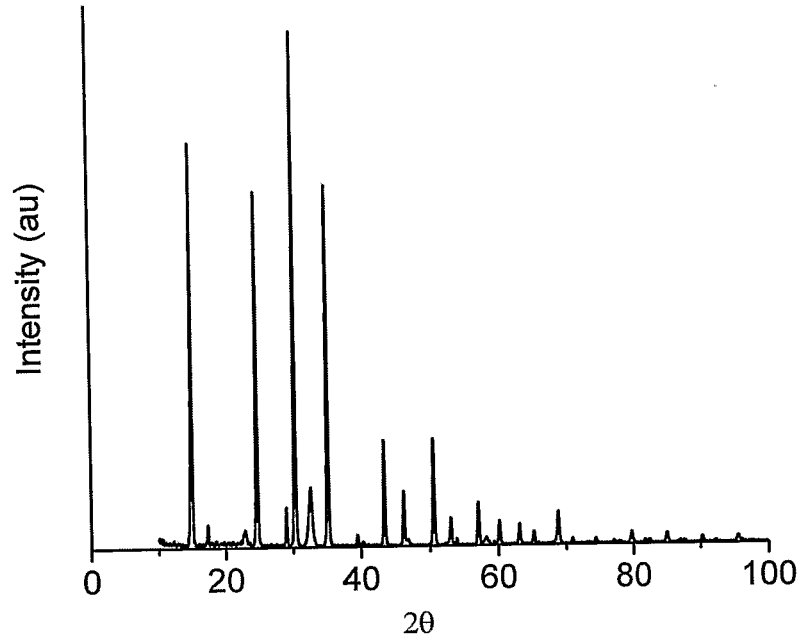


FIG. G NiCl₂ 1 abs

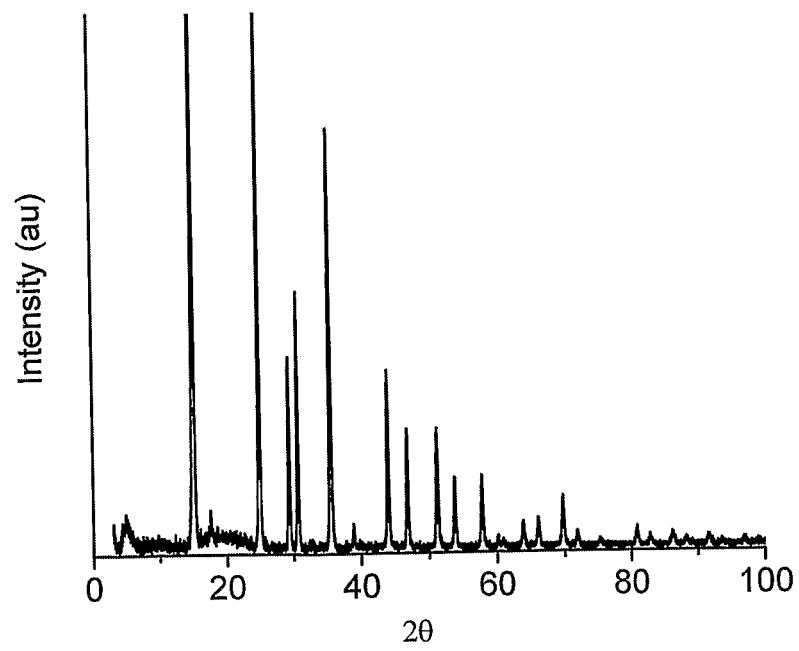


FIG. H MgCl₂ 1 des

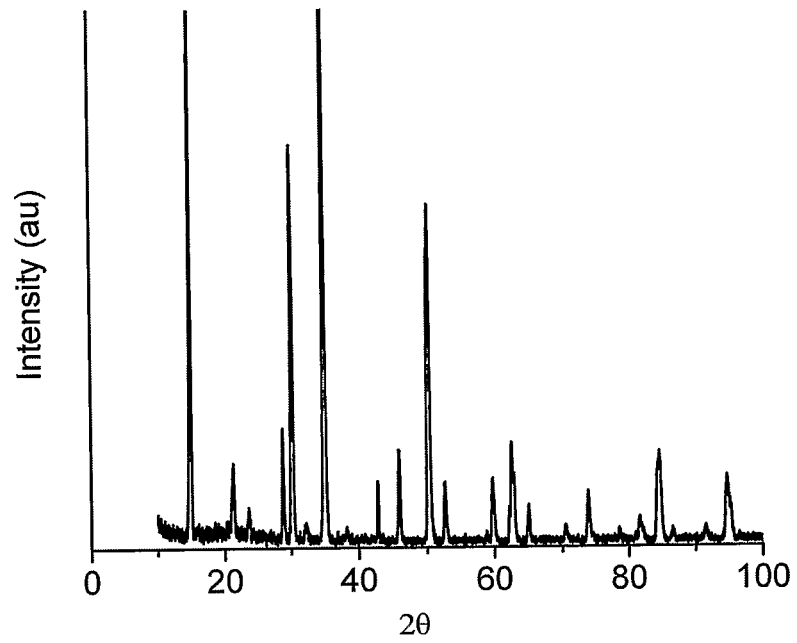
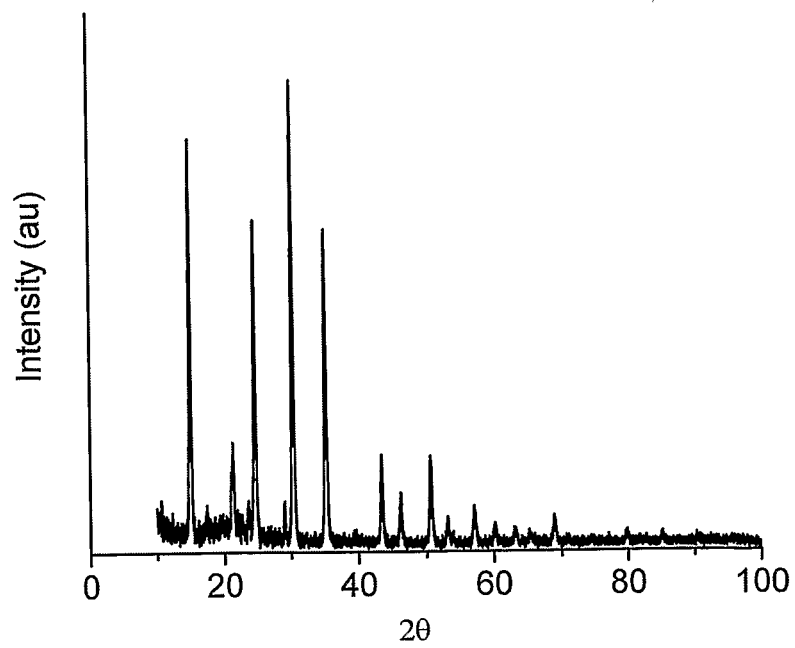


FIG. I MgCl₂ 2 abs



7 / 8

FIG. J

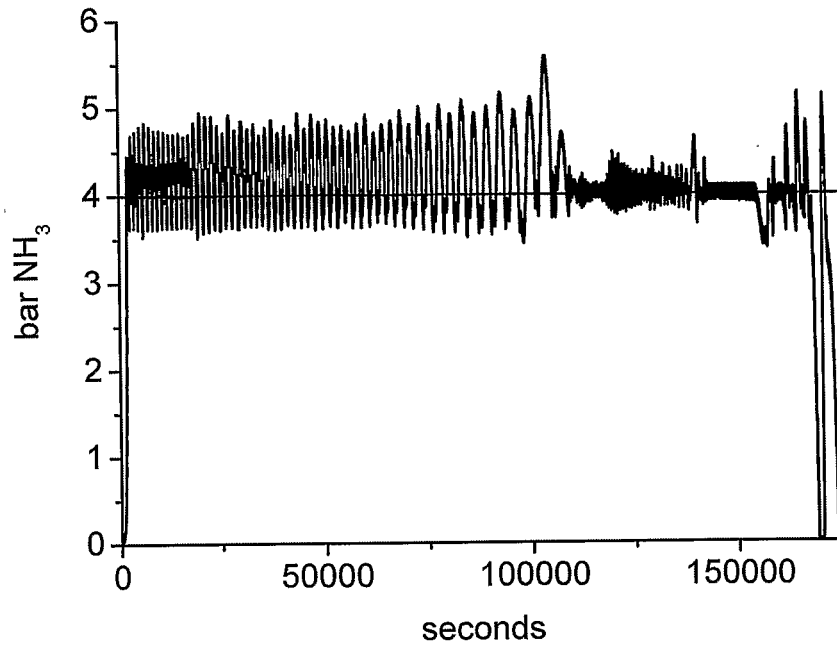


FIG. K

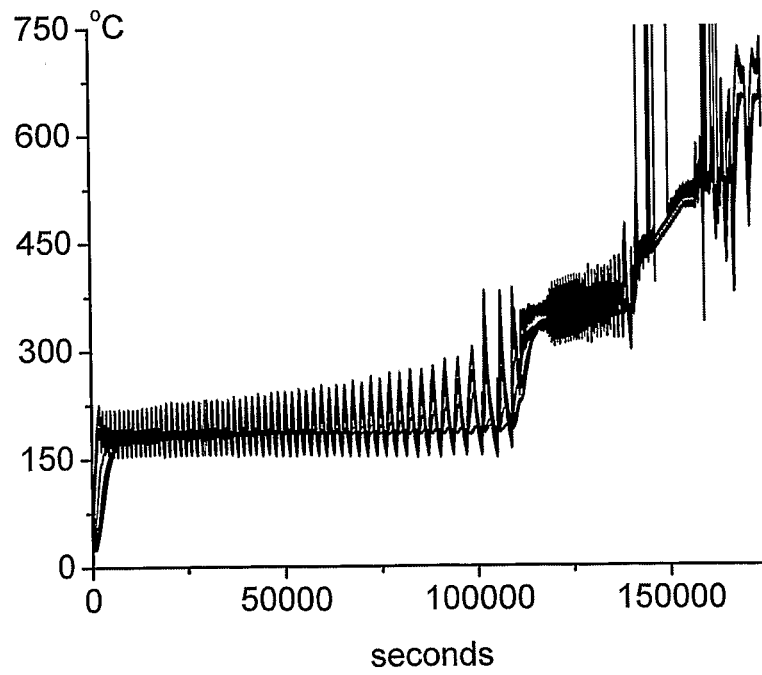


FIG. L

