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- (73) Patenthaver: **Siemens Aktiengesellschaft, Werner-von-Siemens-Straße 1, 80333 München, Tyskland**
- (72) Opfinder: **HUGHES, Timothy, 16 Denchworth Road, Wantage OX12 7AU, Storbritannien**
- (74) Fuldmægtig i Danmark: **Zacco Denmark A/S, Arne Jacobsens Allé 15, 2300 København S, Danmark**
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US-A1- 2011 120 880
S. GIDDEY ET AL: "Review of electrochemical ammonia production technologies and materials", INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, vol. 38, no. 34, 1 November 2013 (2013-11-01), pages 14576-14594, XP055112095, ISSN: 0360-3199, DOI: 10.1016/j.ijhydene.2013.09.054
RONG LAN ET AL: "Synthesis of ammonia directly from air and water at ambient temperature and pressure", SCIENTIFIC REPORTS, vol. 3, 29 January 2013 (2013-01-29), pages 1145-1152, XP055290600, DOI: 10.1038/srep01145

DESCRIPTION

[0001] The present invention relates to electrochemical cells, particularly hybrid electrochemical cells for synthesis of ammonia NH_3 .

[0002] Known approaches to the requirement for synthesis of ammonia include:

1. (1) Haber Bosch process - pressurization and heating of N_2 and H_2 over an iron catalyst;
2. (2) Electrochemical synthesis with a molten salt electrolyte and gas electrodes [1-3]; and
3. (3) Electrochemical synthesis with a solid electrolyte and electrocatalytic electrodes [4-6].
 1. [1] Murakami T. , T. Nishikiori , T. Nohira , and Y. Ito , "Electrolytic Synthesis of Ammonia in Molten Salts Under Atmospheric Pressure", J. Amer. Chem. Soc. 125 (2) , pp. 334-335 (2003) .
 2. [2] Murakami T. et al., "Electrolytic Ammonia Synthesis from Water and Nitrogen Gas in Molten Salt Under Atmospheric Pressure", Electrochim. Acta 50 (27), pp. 5423-5426 (2005) .
 3. [3] US Patent 6,881,308 B2
 4. [4] Marnellos,G.,Zisekas,S.,and Stoukides,M. (2000). Synthesis of ammonia at atmospheric pressure with the use of solid state proton conductors. J. Catal. 193, 80-88. doi:10.1006/jcat.2000.2877
 5. [5] Lan, R., Irvine, J.T.S., and Tao, S. (2013). Synthesis of ammonia directly from air and water at ambient temperature and pressure. Sci.Rep. 3, 1145. doi:10.1038/srep01145
 6. [6] Skodra, A., and Stoukides, M. (2009). Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure. Solid State Ionics 180, 1332-1336.

[0003] The present invention seeks to provide alternative methods and apparatus for the synthesis of ammonia from water and nitrogen N_2 .

[0004] Accordingly, the invention provides methods and apparatus as defined in the appended claims.

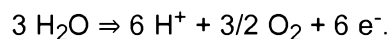
[0005] The above, and further objects, characteristics and advantages of the present invention will become more apparent from the following description of certain embodiments thereof, in conjunction with the appended claims wherein:

- Fig. 1 illustrates an exemplary electrochemical cell as provided by an embodiment of the present invention.

[0006] The embodiment of the invention shown in Fig. 1 comprises an electrochemical cell 10 with four partitioned volumes 1-4. The first volume is a first chamber 1. In use, steam H_2O is introduced into this first chamber. The second volume is a second chamber 2, which comprises a solid-state proton conductor. Possible proton conducting materials for the second chamber 2 include as Y-doped BaZrO_3 (BZY) or yttria-stabilized zirconia (YSZ), but other proton conducting materials may be employed. The third volume comprises a nitride conductor such as a molten salt eutectic, for example $\text{LiCl/KCl/Li}_3\text{N}$. Nitrogen N_2 is introduced into the fourth volume 4.

[0007] The whole electrochemical cell 10 may be operated at an elevated temperature. Three electrodes 5, 6, 7 are provided, and in use are connected to a split power supply 8 such that electrode 5 is an anode at a positive voltage of typically 0.5 - 2V; electrode 6 is an earth or virtual earth at 0V and electrode 7 is a cathode at a negative voltage of typically 0.5 - 2V.

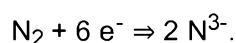
[0008] Operation of the electrochemical cell 10 may proceed as follows. Anode electrode 5 is a porous electrode made from an electrocatalyst which receives steam H_2O introduced into the first volume 1 and promotes the anode reaction:



[0009] The evolved oxygen gas O_2 may be collected as a by-product of the method of the present invention.

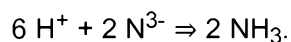
[0010] The protons H^+ are transported through the proton conducting electrolyte in second volume 2 to the ground electrode 6.

[0011] The cathode electrode 7 is a gas electrode made from a porous electrocatalyst which receives nitrogen N_2 introduced into the fourth volume 4 and promotes the cathode reaction:



[0012] The nitride ions N^{3-} are transported through the nitride-conducting electrolyte in volume 3 to the ground electrode 6.

[0013] At the ground electrode 6 the N^{3-} and H^+ ions combine to form ammonia NH_3 product which is given off as a gas and collected:



[0014] The ground electrode 6 is made from a suitable material in order to facilitate this reaction, such as Ru, Rh or similar.

[0015] The structure of the electrochemical cell of the present invention allows steam H_2O to be used as the source of hydrogen in the ammonia product, rather than hydrogen H_2 as is commonly the case in conventional methods and apparatus for synthesising ammonia. This enables the electrochemical synthesis of ammonia NH_3 without requiring a separate electrolysis stage to generate hydrogen H_2 , or the need to buy and store hydrogen H_2 , resulting in a much simpler system design.

[0016] A particular feature of the electrochemical cell of the invention and the attendant method of operation is the integration of the proton-conducting electrolyte and nitride-conducting electrolyte into a single system. The three-electrode electrochemical cell assembly 10 allows the processes of water electrolysis at the anode to generate protons H^+ ; the process of nitrogen gas reduction to nitride ions N^{3-} at the cathode; and ammonia formation at the ground electrode 6 to be separated, allowing optimization of each process individually. Preferably, a split power supply 8 with (virtual) ground is used, to allow the separation of the processes. Alternatively, separate power supplies may be used, one between the anode 5 and ground 6, the other between ground 6 and the cathode 4.

[0017] While the present invention relates to the application of ammonia synthesis from steam and nitrogen gas, the electrochemical cell and the synthesis disclosed herein may be applied to the production of other gaseous products from first and second ionic components (not claimed). In general, means are provided for introducing a first source material (in the claimed invention, steam) into the first volume 1 and means are provided for introducing a second source material (in the claimed invention, nitrogen) into the fourth volume; a first electrolyte is provided between the anode 5 and the ground electrode 6; a second electrolyte is provided between the cathode 7 and the ground electrode 6. Voltages $+V$ and $-V$ are applied respectively to the anode and cathode, with reference to a ground voltage at ground electrode 6. At the anode, a first ionic component (in the claimed invention, H^+) is produced from the first source material. At the cathode, a second ionic component (in the claimed invention, N^{3-}) is produced from the second source material. The first ionic component traverses the first electrolyte under the influence of the voltage gradient between the anode and the ground electrode, to reach the ground electrode. The second ionic component traverses the second electrolyte under the influence of the voltage gradient between the cathode and the ground electrode, to reach the ground electrode. The first ionic component and the second ionic component react at the ground electrode to form a product (in the claimed invention, NH_3). Means should be provided to collect the product. Means may also be provided to collect any

by-products generated at the anode or cathode. Further modifications and variations are possible, within the scope of the invention as defined by the appended claims, as will be apparent to those skilled in the art.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- [US6881308B2](#) [\[0002\]](#)

Non-patent literature cited in the description

- **MURAKAMI T.T. NISHIKIORIT. NOHIRAY. ITO**Electrolytic Synthesis of Ammonia in Molten Salts Under Atmospheric PressureJ. Amer. Chem. Soc., 2003, vol. 125, 2334-335 [\[0002\]](#)
- **MURAKAMI T. et al.**Electrolytic Ammonia Synthesis from Water and Nitrogen Gas in Molten Salt Under Atmospheric PressureElectrochim. Acta, 2005, vol. 50, 275423-5426 [\[0002\]](#)
- **MARNELLOS,G.ZISEKAS,S.STOUKIDES,M.**Synthesis of ammonia at atmospheric pressure with the use of solid state proton conductorsJ. Catal., 2000, vol. 193, 80-88 [\[0002\]](#)
- **LAN, R.IRVINE, J.T.S.TAO, S.**Synthesis of ammonia directly from air and water at ambient temperature and pressureSci.Rep., 2013, vol. 3, 1145- [\[0002\]](#)
- **SKODRA, A.STOUKIDES, M.**Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressureSolid State Ionics, 2009, vol. 180, 1332-1336 [\[0002\]](#)

Patentkrav

1. Indretning til fremstilling af ammoniak ud fra første og andre ioniske bestanddele, omfattende:

5 en elektrokemisk celle (10) omfattende fire voluminer (1, 2, 3, 4), en porøs anode (5) mellem et første volumen (1) og et andet volumen (2), en masse-elektrode (6) mellem det andet volumen (2) og det tredje volumen (3) og en porøs katode (7) mellem det tredje volumen (3) og det fjerde volumen (4);

- midler til indføring af damp H_2O i det første volumen (1);

10 - midler til indføring af nitrogen N_2 i det fjerde volumen (4) ;

- en første elektrolyt tilvejebragt mellem anoden (5) og masseelektroden (6);

- en anden elektrolyt er tilvejebragt mellem katoden (7) og masseelektroden (6),

yderligere omfattende:

15 - mindst en strømforsyning (8), indrettet til at påtrykke en positiv spænding +V på anoden (5), i forhold til masseelektrodens (6) spænding, og for at påtrykke en negativ spænding på katoden (7), i forhold til masseelektrodens spænding.

2. Fremgangsmåde til fremstilling af ammoniak ved anvendelse af en indretning ifølge krav 1, omfattende de følgende trin:

20 - at påtrykke en positiv spænding +V på anoden (5), i forhold til masseelektrodens (6) spænding;

- at påtrykke en negativ spænding -V på katoden (7), i forhold til masseelektrodens (6) spænding;

25 - at indføre damp H_2O i det første volumen (1), hvor dampen H_2O reagerer ved anoden for at tilvejebringe protoner H^+ i første elektrolyt i det andet volumen (2);

- at indføre nitrogen N_2 i det fjerde volumen (4), hvor nitrogenet N_2 reagerer ved katoden for at tilvejebringe nitridioner N^{3-} i anden elektrolyt i det tredje volumen (3);

30 - at generere ammoniak på masseelektroden (6) ved reaktion mellem protonerne H^+ og nitridionerne N^{3-} .

3. Fremgangsmåde ifølge krav 2, yderligere omfattende et trin, hvor ammoniakken fremstillet på masseelektroden (6) opsamles.

5 **4.** Fremgangsmåde ifølge krav 2 eller krav 3, yderligere omfattende et trin, hvor et biprodukt, der genereres på anoden eller katoden, opsamles.

DRAWINGS

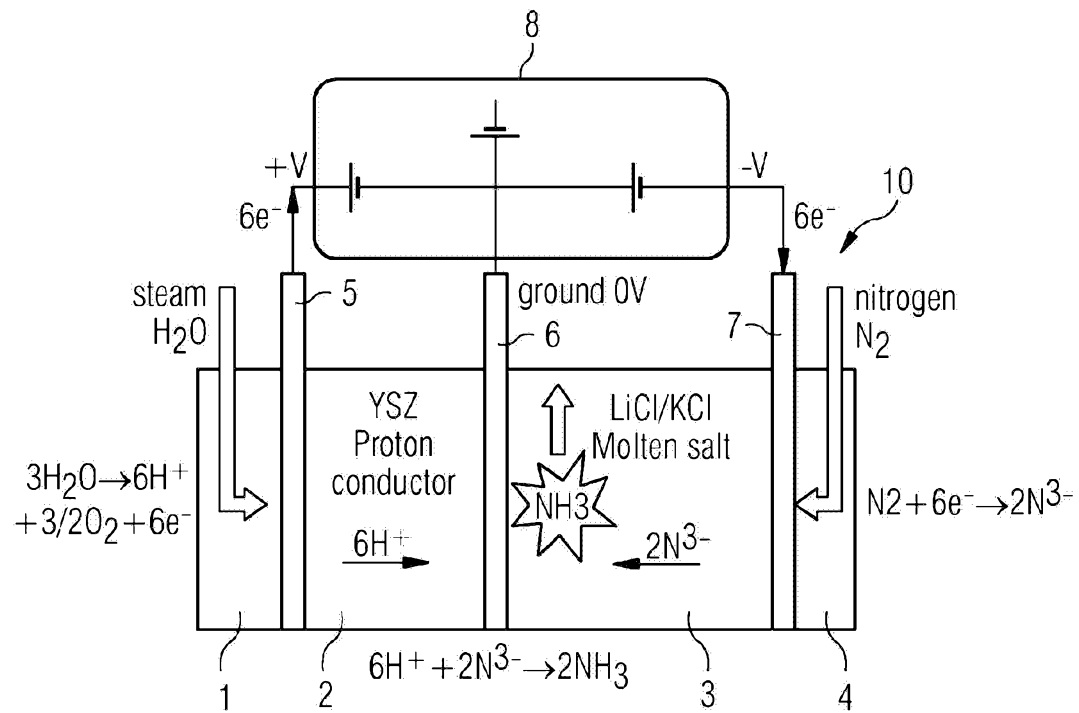


FIG. 1