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Synthesis of ammonia directly from air and water at ambient temperature and pressure

Rong Lan¹, John T. S. Irvine² & Shanwen Tao¹

¹Department of Chemical and Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK, ²School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK.

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Correspondence and requests for materials should be addressed to S.T. (shanwen.tao@strath.ac.uk)

The N≡N bond (225 kcal mol⁻¹) in dinitrogen is one of the strongest bonds in chemistry therefore artificial synthesis of ammonia under mild conditions is a significant challenge. Based on current knowledge, only bacteria and some plants can synthesise ammonia from air and water at ambient temperature and pressure. Here, for the first time, we report artificial ammonia synthesis bypassing N₂ separation and H₂ production stages. A maximum ammonia production rate of 1.14 × 10⁻⁵ mol m⁻² s⁻¹ has been achieved when a voltage of 1.6 V was applied. Potentially this can provide an alternative route for the mass production of the basic chemical ammonia under mild conditions. Considering climate change and the depletion of fossil fuels used for synthesis of ammonia by conventional methods, this is a renewable and sustainable chemical synthesis process for future.

Given the need to feed a growing world population whilst simultaneously reducing global carbon emissions, it is desired to break the link between industrial production of agricultural fertilisers based on ammonia and the use of fossil fuels. On the other hand, energy storage is a big challenge for renewable electricity. To synthesis basic chemicals such as ammonia from renewable electricity through electrochemical processes is a good option to save on carbon emissions and to reduce the pressure on renewable energy storage¹.

Globally 131 million tons of ammonia were produced in 2010². The dominant ammonia production process is the Haber-Bosch process invented in 1904 which requires high temperature (~500°C) and high pressure (150–300 bar), in addition to efficient catalysts^{3,4}. Natural gas or coal is used as the energy source of the ammonia industry. 1.87 tons of CO₂ is released per ton of ammonia produced⁵. Globally 245 million tons of CO₂ were released by the ammonia industry in 2010 equivalent to about 50% of the UK CO₂ emissions (495.8 million tons) in that year⁶. In the Haber-Bosch process, the presence of ppm level oxygen may poison the commonly used Fe-based catalysts. In industry, extensive purification of N₂ and H₂ is needed and this remarkably increases the overall cost of the process^{7,8}. Therefore researchers have been seeking a simpler way for synthesis of ammonia from nitrogen separated from air. To the best of our knowledge, the first report on synthesis of ammonia from nitrogen at room temperature is through the reduction of ligating molecular nitrogen⁹. Following this pioneering work, there are several key reports on synthesis of ammonia under mild conditions through complex intermediates^{3,10–15}. On the other hand, ammonia can be synthesised at room temperature through electrochemical synthesis^{3,10–15}. In 1985, for the first time, Pickett et al. reported the electrochemical synthesis of ammonia at room temperature through protolysis of cis-[W(N₂)₂(PMe₂Ph)₄]¹⁶. There were reports on electrochemical synthesis of ammonia from N₂ and H₂ using Na₂SO₄ aqueous solution as the electrolyte but the current was quite small^{17,18}. This could be related to the low proton conductivity of Na₂SO₄ solution. It is expected that the current density and ammonia production rate would be much higher if a conductive electrolyte is applied.

Proton conductors are important electrolytes for electrochemical devices^{19,20}. Some perovskite oxides exhibit high proton conductivity and have been used in solid oxide fuel cells^{19,21,22}. Stoukides reported the electrochemical synthesis of ammonia from N₂ and H₂ at 570°C based on a solid proton-conducting oxide SrCe_{0.95}Yb_{0.05}O_{3-δ}²³. The authors also further reported the synthesis of ammonia directly from N₂ and H₂O bypassing the process of H₂ production²⁴. There are other reports on electrochemical synthesis of ammonia from N₂ and H₂O in molten salts at a temperature ~300°C^{25,26}. Recently we reported electrochemical synthesis of ammonia at ~500°C based on oxide-carbonate composite electrolytes^{4,27}. Ammonia tends to decompose at ~500°C²⁸ therefore low temperature synthesis is necessary to avoid ammonia decomposition; however, most good low temperature proton conducting materials are based on acidic materials²⁹. Ammonia is a weak base and readily reacts with an acidic membrane



reducing the proton conductivity. Sulfonated Nafion has been demonstrated as the best proton-conducting polymer which has been widely used in proton exchange membrane fuel cells (PEMFCs)²⁹. In 2000, Kordali et al. reported the synthesis of ammonia from N₂ and H₂O based on a Ru/C cathode, Pt anode, 2 M KOH aqueous solution as the electrolyte using Nafion as a separation membrane (not electrolyte) and an ammonia formation rate of $\sim 170 \text{ ng h}^{-1} \text{ cm}^{-2}$ ($2.78 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$) was achieved at 20°C³⁰. Although ammonia was synthesised from N₂ and H₂O at room temperature using 2 M KOH solution as electrolyte, N₂ cannot be replaced by air as CO₂ in air may react with KOH to form K₂CO₃. It was reported that ammonia has been synthesised from N₂ and H₂ based on acidic H⁺-form Nafion membrane, with Ni-SDC (Sm-doped CeO₂) as anode, SmBa-CuMO_{5+ δ} as cathode with maximum formation rate of $4.1 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ at 25°C³¹; however, the chemical compatibility of active metal Ni with the strongly acidic Nafion membrane is concerning. The reaction between active Ni and H⁺-form Nafion may form Ni²⁺-form Nafion and thus lose proton conduction therefore the reaction would not be sustainable³². In addition, to synthesise ammonia directly from air without the N₂ separation stage would be a better choice.

It is well known that some higher plants can synthesise ammonia or its derivatives directly from air and water at room temperature^{33,34}. The ammonia produced by plants is normally directly used as fertiliser by the plants. To the best of our knowledge, there is no report on artificial synthesis of ammonia direct from air and water. It has been a dream for researchers who can imitate this natural process to synthesise ammonia under similar conditions. In this report, for the first time, we demonstrated that ammonia can be synthesised directly from air (instead of N₂) and H₂O (instead of H₂) under a mild condition (room temperature, one atmosphere) with supplied electricity which can be obtained from renewable resources such as solar, wind or marine.

Results

Proton conduction of mixed NH₄⁺/H⁺ conducting Nafion 211 membrane. Ammonia is a base, the acidic Nafion membrane readily reacts with ammonia to form NH₄⁺-form Nafion. In our experiments, for the first time, it was demonstrated that NH₄⁺-form Nafion exhibits proton conduction through concentration cell measurements. A mixed NH₄⁺/H⁺ conducting Nafion 211 membrane was used as solid electrolyte for electrochemical synthesis of ammonia. Conventional H⁺-form Nafion membrane will be converted to NH₄⁺-form in the presence of ammonia. It is necessary to maintain the stability of the membrane electrolyte under the synthesis conditions³⁵. It has been reported that the ionic conductivity of NH₄⁺-form Nafion is very much dependent on the humidity and reached $\sim 0.05 \text{ S/cm}$ at 80°C with a relative humidity 100%³⁵. The high ionic conductivity is believed due to NH₄⁺ ions but proton conduction cannot be ruled out. It has been reported that some inorganic ammonium salts such as (NH₄)₃H(SeO₄)₂ exhibit proton conduction^{36,37}. Therefore the NH₄⁺-form Nafion may exhibit a certain level of proton conduction which can be used for continuous synthesis of ammonia.

The membrane electrode assembly (MEA) for synthesis of ammonia was fabricated by a process described in the experimental part. The H⁺-form Nafion 211 membrane was converted into NH₄⁺-form Nafion through the reaction between 35 wt% ammonia aqueous solution and the H⁺-form membrane in the MEA. The MEA was then washed by de-ionised water for a week by pumping water through both sides of the cell until no ammonia can be detected at the outlets of the cell. A potential of 40 mV was applied to the MEA for 4 hours to activate the cell prior to concentration cell measurements. When wet H₂ (ambient temperature humidification) was introduced to the anode, wet air (also ambient temperature humidification) was used at the cathode, an OCV of $\sim 475 \text{ mV}$ was

obtained, indicating the membrane exhibit H⁺ or/and O²⁻ conduction. When the air was replaced by 5%H₂/Ar to form a hydrogen concentration cell, the OCV of the cell gradually decreased and stabilised at $\sim 32.8 \text{ mV}$ (Fig. 1A). The I-V curve of this hydrogen concentration cell is shown in Fig. 1B. A maximum current density of 7 mA cm^{-2} was observed indicating migration of protons through the membrane. The proton conduction of the thus treated membrane was thus demonstrated by a hydrogen concentration cell. The theoretical OCV of the wet H₂/5%H₂-Ar concentration cell is 38.47 mV estimated from the Nernst Equation. The proton transfer number is therefore $\sim 85\%$ assuming no leakage or crossover of gases. The other 15% ionic conductivity is possibly attributed to the NH₄⁺ ions although NH₄⁺ ions are proton carriers too. Therefore, the thus treated membrane is a mixed NH₄⁺/H⁺ conductor and can be used for electrochemical synthesis of ammonia because it is chemically compatible with ammonia.

Thermodynamic evaluation on electrochemical synthesis of NH₃ from H₂/H₂O and N₂. In order to consider the potential for electrochemical synthesis of ammonia, a thermodynamic evaluation on synthesis of ammonia from H₂ and N₂ was carried-out³⁸. In theory, the reaction is spontaneous at a temperature below $\sim 175^\circ\text{C}$ when the partial pressure of H₂ and N₂ is 1 bar (Fig. 2A). It is expected that ammonia would be produced as long the applied voltage is higher than the electrode over-potential. When water is used for electrochemical synthesis of ammonia, the positive standard Gibbs free energy change indicates the reaction is non-spontaneous and applied potential is required (Fig. 2A). The corresponding required voltage for electrochemical synthesis of NH₃ from H₂ or H₂O is

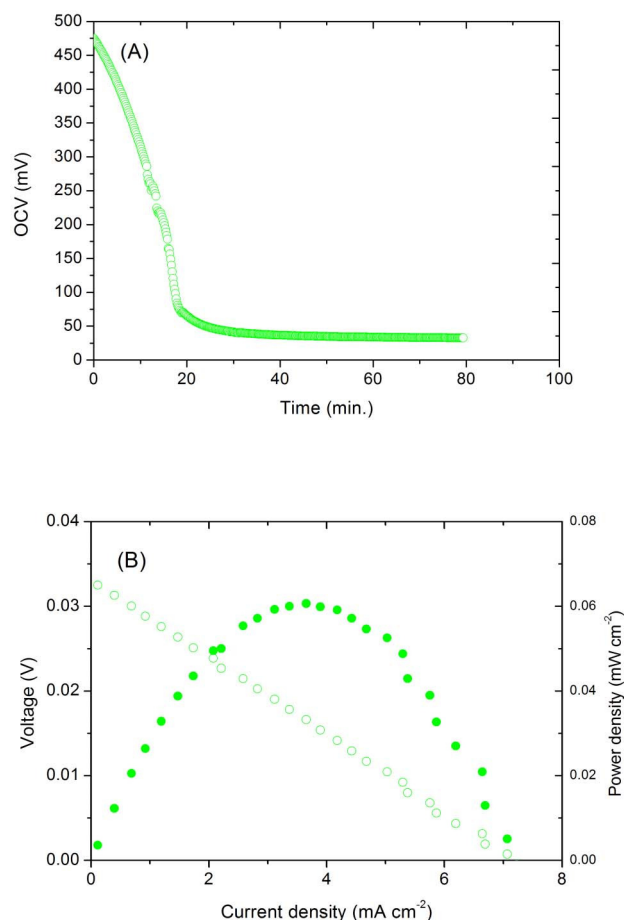


Figure 1 | (A) The recorded potential change from a H₂/air cell to a H₂/5%H₂-Ar concentration cell; (B) The I-V and power curves of the H₂/5%H₂-Ar concentration cell.



shown in Fig. 2B. At 25°C, a minimum voltage of 1.17 V is required for electrochemical synthesis of ammonia from liquid water and N₂ at partial pressure of 1 bar.

Synthesis of ammonia from H₂ and N₂. Ammonia was first synthesised from conventional precursors, H₂ and N₂ using the electrochemical cell. As shown in Fig. 3A, an initial current of 58 mA cm⁻² was observed even at an applied voltage of 0.2 V. The current decreases after 3 minutes, possibly due to the reaction between produced ammonia and the membrane. Instead of decreasing, the current gradually increases when 0.4V is applied indicating the reaction has completed. A current density of 390 mA cm⁻² has been achieved at room temperature when 1.2 V is applied (Fig. 3A). The ammonia formation rates at different applied voltage are shown in Fig. 3B. The highest ammonia formation rate of 3.1×10^{-5} mol m⁻² s⁻¹ was observed at 0.2 V which is about three orders of magnitude higher than the previously reported value reported by Kordali et al³⁰ and is comparable to those reported by Liu et al³¹. As shown in Fig. 3C, the formed ammonia increased with time. The amount of generated ammonia was 1.13×10^{-5} mol after applying 0.2 V for 1 hour (Fig. 3C) which is higher than the estimated maximum amounts of ammonia that could be generated from the decomposition of the NH₄-form of the membrane (9.14×10^{-6} mol) if all the

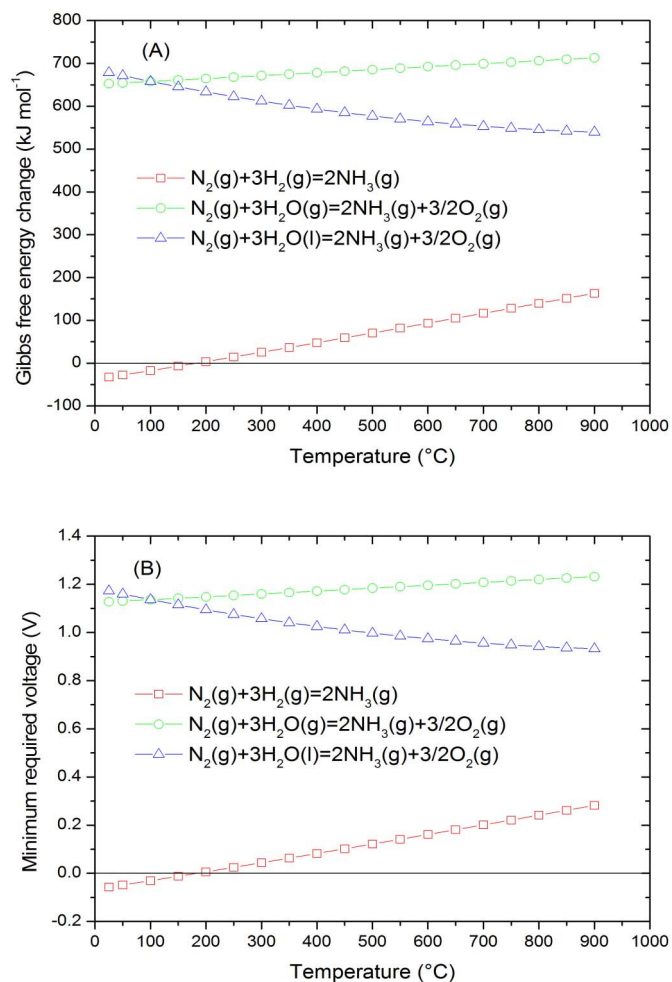


Figure 2 | (A) The Gibbs free energy change for electrochemical synthesis of ammonia from N₂ and H₂, N₂ and H₂O (gaseous or liquid) at pressure of 1 bar; (B) The minimum applied voltage required for electrochemical synthesis of ammonia from N₂ and H₂ at pressure of 1 bar (the negative voltage at a temperature below 200°C means spontaneously generated voltage), N₂ and H₂O (gaseous or liquid).

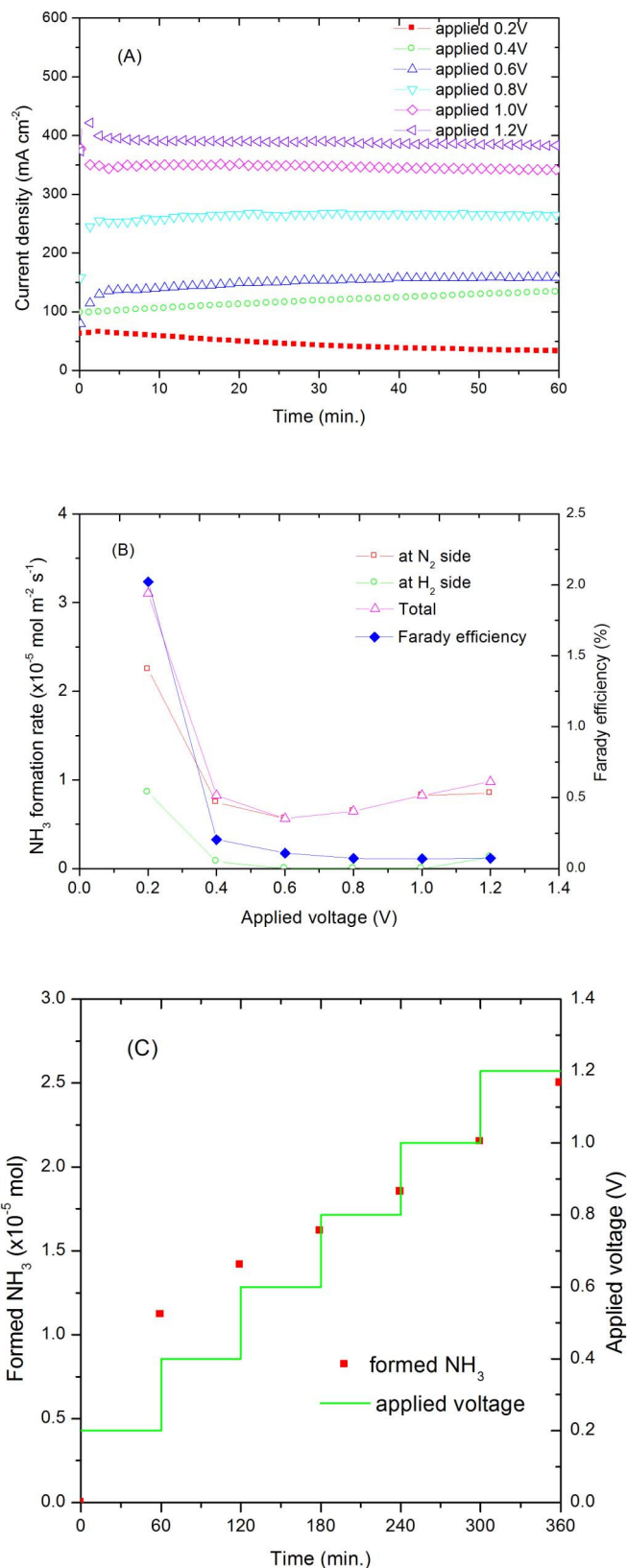


Figure 3 | (A) Current density of a N₂, Pt | Nafion 211 | Pt, H₂ cell under different applied voltages. Cathode was supplied with N₂, anode was supplied with H₂. (B) The ammonia formation rate at N₂ and H₂ sides, total ammonia formation rate and Faraday efficiency. (C) The relationship between formed NH₃ and time of a N₂, Pt | Nafion 211 | Pt, H₂ cell under different applied voltages. Cathode was supplied with N₂, anode was supplied with H₂.

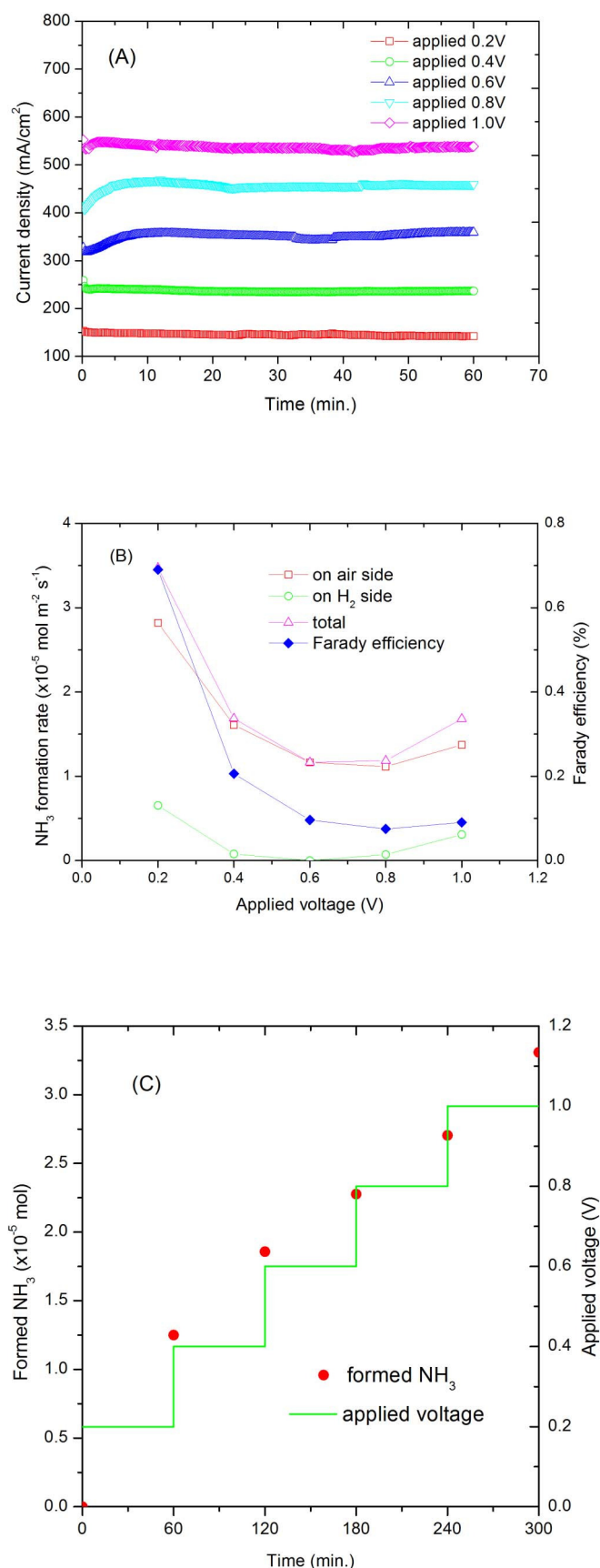


Figure 4 | (A) Current density of an Air Pt | Nafion 211 | Pt, H₂ cell under different applied voltages. Cathode was supplied with air, anode was supplied with H₂. (B) The ammonia formation rate at air and H₂ sides,

total ammonia formation rate and Faraday efficiency. (C) The relationship between formed NH₃ and time of an Air, Pt | Nafion 211 | Pt, H₂ cell under different applied voltages. Cathode was supplied with air, anode was supplied with H₂.

current arose from NH₄⁺ transport which is unlikely, or estimated dissolved ammonia (8.02×10^{-6} mol) (please see supplementary information). This result demonstrates that the generated ammonia is from the electrosynthesis process.

The higher ammonia formation rate at lower voltage may be due to the lower hydrogen ion supply at the cathode which gives more time for formation of ammonia according to reaction (2). Between 0.6 and 1.2 V, the formed ammonia slightly increased at higher voltage (Fig. 3B). Although ammonia was mainly observed at the N₂ side, a small amount of ammonia was also observed at the H₂ side when the formation rate was relatively high. One of the possible reasons is that, ammonia is very soluble in water, at higher formation rate, some of the formed ammonia at N₂ side may *in situ* dissolve in water, diffuse to the H₂ side then brought out by the flowing H₂. On the other hand, there could be some cross-over effects too which is common in electrochemical cells based on polymer electrolytes.

Synthesis of ammonia from H₂ and air. Air contains 78% N₂ therefore it would be better to synthesise ammonia directly from air without the separation process. When N₂ at the cathode was replaced by air, a stable current density of 142 mA cm⁻² was observed when the cell voltage was 0.2 V (Fig. 4A). At 1.0 V, the current density stabilised at 537 mA cm⁻². This indicates that the membrane is fairly stable. Comparing to the H₂/N₂ cell, the current densities are higher for the H₂/air cell, possibly due to the extra driving force from O₂ in air. Interestingly, ammonia was also produced on the air side with a small amount at the H₂ side when the formation rate is relatively high (Fig. 4B). At the same cell voltage, the ammonia formation rates are also higher than those for H₂/N₂ cell. The formed ammonia increased against time (Fig. 4C). This experiment indicates that ammonia can be synthesised directly from air without gas separation. This is consistent with thermodynamic evaluation concluding reaction (3) is spontaneous at a temperature below 175°C when the partial pressure of N₂ is at 1 bar although it is slightly lower in air (Fig. 3A). Another parallel reaction at the cathode is formation of water between proton and O₂ in air; however, if a selective catalyst for ammonia synthesis is used, the reaction can be kinetically in favour of ammonia formation. Comparing to conventional Haber-Bosch process, due to different catalysts used along with various synthesis conditions, the oxygen poisoning on ammonia synthesis catalysts is not an issue.

Synthesis of ammonia directly from H₂O and air. Water is the most abundant source for hydrogen. It would be a better choice if we can directly synthesise ammonia from air and water bypassing the hydrogen production stage. Therefore H₂ at the anode was replaced by water. At 1.2 V, the current density of the cell was 47 mA cm⁻², lower than that for the H₂/N₂ cell, possibly due to the high electrode polarisation at the water side (Fig. 5A). The ammonia formation rates increase at higher cell voltage (Figs. 5B). The ammonia formation rate is slightly lower than that when H₂ was fed at the anode. The highest ammonia formation rate was observed at low applied voltage when H₂ was used at anode (Figs. 3B & 4B); however, when water was supplied at the anode, the ammonia formation rate increased against applied voltage (Fig. 5B). When a dc voltage was applied to the cell, hydrogen was pumped to the cathode through transfer of protons in the electrolyte membrane. At high applied voltage, the high hydrogen flow rate may limit the lifetime of hydrogen species at the electrode/electrolyte/gas interfaces therefore the ammonia formation rate is relatively lower (Fig. 5C). In conclusion, for the first time, this experiment clearly indicates that

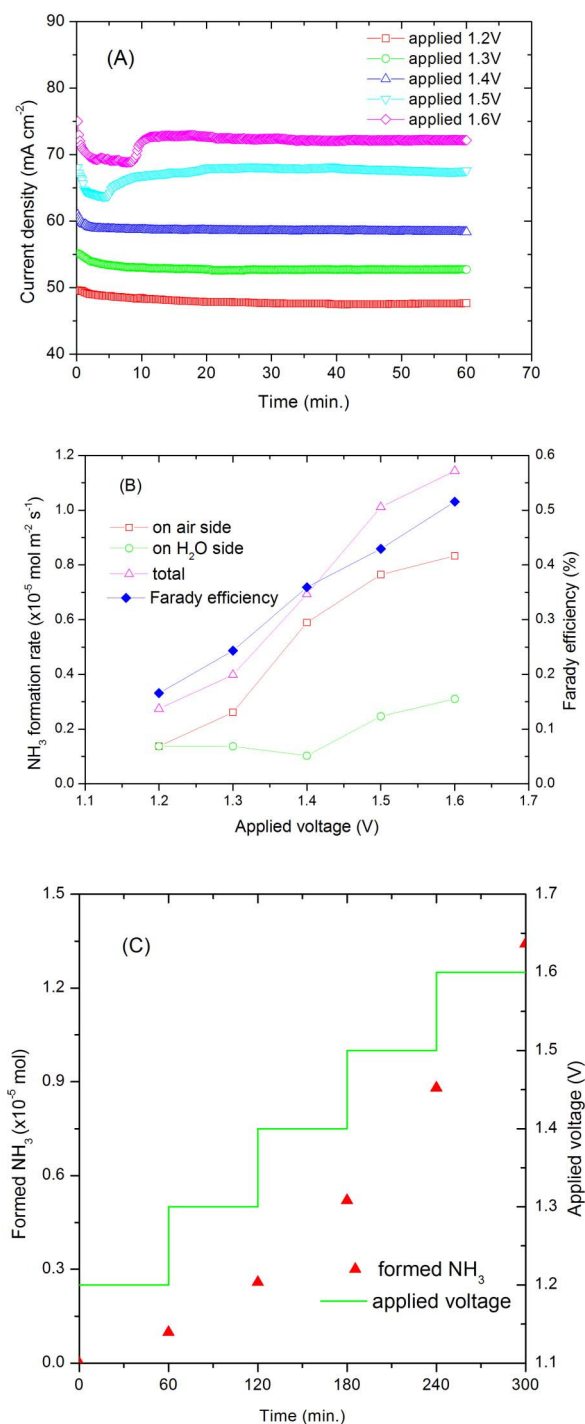


Figure 5 | (A) Current density of an Air, Pt | Nafion 211 | Pt, H₂O cell under different applied voltages. Cathode was supplied with air, anode was supplied with H₂O. (B) The ammonia formation rate at air and H₂O sides, total ammonia formation rate and Faraday efficiency. (C) The relationship between formed NH₃ and time of an Air, Pt | Nafion 211 | Pt, H₂O cell under different applied voltages. Cathode was supplied with air, anode was supplied with H₂O.

ammonia can be directly synthesised from air and water at room temperature and one atmosphere.

Discussion

In most reports, H₂ and N₂ were commonly used as precursors for electrochemical synthesis of ammonia while H₂ production and N₂

separation are essential⁴. H₂ production can be bypassed if H₂O was used as a precursor; however, the reaction between H₂O and N₂ to form ammonia is thermodynamically non-spontaneous under normally pressure (Fig. 2B); however, this can be achieved through electrochemical process because the applied voltage provides extra driving force. Although there are a few reports on electrochemical synthesis of ammonia from N₂ and H₂O at 570°C¹⁵ or 300°C^{22,23}, the formed ammonia tends to decompose to N₂ and H₂ because thermodynamically the decomposition temperature of ammonia is around 175°C (Fig. 2A). Therefore, a synthesis temperature below 175°C is required in order to avoid decomposition of formed ammonia.

In order to demonstrate that the produced ammonia is from the electrochemical process, the maximum amount of dissolved ammonia has been estimated. It has been reported that the maximum H₂O uptake of Nafion 117 membrane was 20.64 vol% at room temperature, investigated by small angle neutron scattering technology³⁹. It is assumed that Nafion 211 membrane would exhibit similar behaviour. The maximum dissolved ammonia in the absorbed water in the used Nafion membrane was estimated to be 8.02×10^{-6} mol (please see supplement information) which is smaller than the generated ammonia in the first experiment, from H₂ and N₂ while applied at 0.2 V for 1 hour (1.13×10^{-5} mol, Fig. 3C). This value is also higher than the formed ammonia from possible decomposition of NH₄⁺-form Nafion (9.14×10^{-6} mol). The total ammonia from decomposition of NH₄⁺-form Nafion and dissolved NH₃ in absorbed water is 1.72×10^{-5} mol which is significantly smaller than the total measured ammonia 7.15×10^{-5} mol (Figs. 3C, 4C and 5C). It should be noted that the NH₄⁺-form Nafion membrane was washed by de-ionised water until no ammonia was detected in outlets of the cell. Considering the amounts of generated ammonia in experiments, it is clear that the collected ammonia cannot be from the dissolved ammonia from absorbed water in or the decomposition of ammonium Nafion membrane.

When H₂ and N₂ were used for electrochemical synthesis of ammonia, at the oxidation electrode, hydrogen loses electrons while protons are formed.



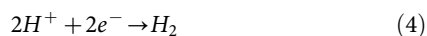
The formed protons will transfer through the H⁺/NH₄⁺-form Nafion to the other side to react with N₂ to electrochemically form NH₃;



The overall reaction is:

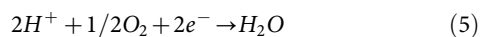


However, the reaction between proton and N₂ depends on both thermodynamics and kinetics. Considering the over-potential on both electrodes, if the 'net' potential difference between the two electrodes is above the value displayed in Fig. 2B, then thermodynamically reaction (3) should happen. However, a lot of reactions are under kinetic control particularly at low temperatures. The Faraday efficiency of reaction (3) is shown in Fig. 3B. It is about 2% when 0.2 V voltage was applied while decreased to less than 1% when higher voltage was applied. When air was used at the oxidation electrode or water at the reduction electrode, the Faraday efficiency for ammonia formation was both less than 1% (Figs. 4B and 5B) which means only a small portion of supplied electricity was converted into ammonia. The Faraday efficiency also increased when the current across the cell is relatively low indicating higher voltage may also facilitate reaction (2) (Fig. 5B) when water instead of hydrogen was flowed at the cathode. More efficient catalysts at the N₂/air side are required. The protons at the reduction electrode not only react with N₂ to form NH₃, but can receive electrons to form H₂ as well;



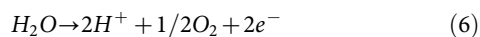
When 0.2 V is applied, only 2% applied electricity was converted to ammonia while the other 98% was converted to H₂. The H₂ flow rate at the reduction electrode is proportional to the current across the cell. When higher voltage was applied, the current across the cell also increased (Fig. 3A). Most of the protons were converted to H₂ again because the dwelling time of protons on the Pt/C electrode will be shorter thus the overall Faraday efficiency for ammonia formation decreased (Fig. 3B).

When N₂ at the reduction electrode was replaced by air, besides reaction (4), another important reaction is between protons and oxygen in the air;



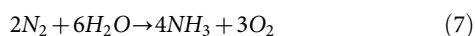
This is also the cathode reaction for a H₂/O₂ fuel cell. This reaction indicates that, under certain conditions, a small amount of ammonia may be formed when air was used as oxidant in hydrogen fuel cells. It has been reported that ammonia can passivate the oxygen reduction reaction (5) at the cathode of a proton exchange membrane fuel cell⁴⁰. On the other hand, the passivation of ammonia on Pt/C catalysts for reaction (5) may suppress the formation of H₂O, which may favour the competitive reaction between protons and N₂ in air to form ammonia. From this point of view, if a suitable catalyst is identified to suppress the formation of H₂O according to reaction (5) while in favour of reaction (3), air can be directly used as nitrogen sources for electrochemical synthesis of ammonia.

Production of hydrogen through electrolysis for electrochemical energy storage has been widely investigated. Water can be used for direct electrochemical synthesis of ammonia. Then the reaction at the oxidation electrode is:



The formed protons will transfer through the proton-conducting membrane, react with N₂ in air to form ammonia while O₂ is formed at the oxidation electrode.

The overall reaction is:



While ammonia is produced at the air side, O₂ is also produced at the water side which can be used for other applications such as oxyfuel combustion.

It should be noted that this is just a starting point to directly synthesis ammonia from air and water at room temperature although theoretically Pt is not among the best catalysts for ammonia synthesis³². In the future, other low cost ammonia synthesis catalysts such as Co₃Mo₃N and Ni₂Mo₃N⁴¹ can be used to replace Pt for selective ammonia synthesis under mild conditions. The acidity of the H⁺/NH₄⁺-form Nafion membrane would be much weaker than the H⁺-form Nafion allowing selection of a large range of catalysts for ammonia synthesis. This is a low temperature, low pressure process with flexibility in scale and location. This technology will break the link between ammonia industry and fossil fuels. Considering climate change and the depletion of fossil fuels used for synthesis of ammonia by conventional method, this is a renewable and sustainable chemical synthesis process for future.

Methods

Fabrication of electrochemical cell for ammonia synthesis. Nafion 211 membrane (DuPont®) was boiled in 3% H₂O₂ for 1 hour, rinsed by deionised water, boiled in deionised water for 2 hours then in 0.5 M H₂SO₄ for 1 hour. After rinsing with deionised water a few times, the membrane was stored in deionised water for cell fabrication.

Pt/C (E-Tek, 30 wt%) on SGL gas diffusion layer (GDL 10 BC) was used as both electrodes with a Pt loading of 1 mg cm⁻². Some 5% Nafion suspension (Aldrich) and isopropanol were mixed with Pt/C catalysts for preparation of the catalytic layer. The membrane electrode assembly (MEA) with a working area of 1 cm² was fabricated by hot pressing.

The MEA was put in electrochemical cell testing jig using graphite as bipolar plates. 35 wt% ammonia aqueous solution (Alfa Aesar) was pumped to both sides of the cell by a parasitic pump (Waterson Marlon 320) for one day to convert H⁺-form Nafion 211 membrane into NH₄⁺-form. De-ionised water was then pumped to the cell for one week to clean up the residual ammonia and no ammonia can be detected from the outlets. A d.c. voltage of 40 mV was applied to the cell for 4 hours to activate the MEA and improve the electrode/electrolyte interfaces then air was flowed through both cathode and anode chambers overnight before ammonia synthesis experiments. All the presented experimental data were collected from the same MEA.

Ammonia synthesis and detection. H₂ (or water) and N₂ (or air) were passed through room temperature water first then filled into the chambers of the cell. The dc potential was applied by a Solartron 1470A electrochemical interface controlled by software Cell Test® for automatic data collection. The order for applied voltage was from low to high. The produced ammonia was collected by dilute H₂SO₄ (0.001 M). The concentration of NH₄⁺ in the absorbed solution was analysed using Nessler's reagent (Aldrich). The produced ammonia was detected using an ammonia meter (Palintest 1000) and the rate of ammonia formation was calculated using the following equation.

$$r_{NH_3} = \frac{[NH_4^+] \times V}{t \times A}$$

Where [NH₄⁺] is the measured NH₄⁺ ion concentration, V is the volume of the dilute H₂SO₄ for ammonia collection, t is the adsorption time and A is the effective area of the cell.

- Lan, R., Irvine, J. T. S. & Tao, S. W. Ammonia and related chemicals as potential indirect hydrogen storage materials. *Inter. J. Hydrogen Energy* **37**, 1482–1494 (2012).
- Bastidas, D. M., Tao, S. W. & Irvine, J. T. S. A symmetrical solid oxide fuel cell demonstrating redox stable perovskite electrodes. *J. Mater. Chem.* **16**, 1603–1605 (2006).
- Pool, J., Lobkovsky, E. & Chirik, P. Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex. *Nature* **427**, 527–530 (2004).
- Amar, I. A., Lan, R., Petit, C. T. G. & Tao, S. W. Solid-state electrochemical synthesis of ammonia: a review. *J. Solid State Electrochem.* **15**, 1845–1860 (2011).
- <http://www.kbr.com/Newsroom/Publications/Articles/Carbon-Dioxide-Capture-and-Storage-in-the-Nitrogen-Syngas-Industries.pdf>. (Access 28th August, 2012).
- <http://www.decc.gov.uk/assets/decc/11/stats/climate-change/4282-statistical-release-2010-uk-greenhouse-gas-emissi.pdf>. (Access 28th August, 2012).
- Waugh, K. C., Butler, D. & Hayden, B. E. The mechanism of the poisoning of ammonia-synthesis catalysts by oxygenates O₂, CO and H₂O - An in-situ method for active surface determination. *Catal. Lett.* **24**, 197–210 (1994).
- Jennings, J. *Catalytic ammonia synthesis: fundamentals and practice*. (Springer, 1991).
- Chatt, J., Pearman, A. & Richards, R. The reduction of mono-coordinated molecular nitrogen to ammonia in a protic environment. *Nature* **253**, 39–40 (1975).
- Yandulov, D. & Schrock, R. Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. *Science* **301**, 76 (2003).
- Avenier, P. *et al.* Dinitrogen dissociation on an isolated surface tantalum atom. *Science* **317**, 1056 (2007).
- Nishibayashi, Y. *et al.* Buckminsterfullerenes: A non-metal system for nitrogen fixation. *Nature* **428**, 279–280 (2004).
- Laplaza, C. & Cummins, C. Dinitrogen cleavage by a three-coordinate molybdenum (III) complex. *Science* **268**, 861 (1995).
- Himmel, H. & Reiher, M. Intrinsic dinitrogen activation at bare metal atoms. *Angew. Chem. Inter. Edition* **45**, 6264–6288 (2006).
- Schrock, R. Catalytic reduction of dinitrogen to ammonia by molybdenum: theory versus experiment. *Angew. Chem. Inter. Edition* **47**, 5512–5522 (2008).
- Pickett, C. & Talarmin, J. Electrosynthesis of ammonia. *Nature* **317**, 652–653 (1985).
- Furuya, N. & Yoshida, H. Electroreduction of nitrogen to ammonia on gas-diffusion electrodes modified by Fe-phthalocyanine. *J. Electroanalytical Chem.* **263**, 171–174 (1989).
- Furuya, N. & Yoshida, H. Electroreduction of nitrogen to ammonia on gas-diffusion electrodes modified by metal-phthalocyanines. *J. Electroanalytical Chem.* **272**, 263–266 (1989).
- Norby, T. Solid-state protonic conductors: principles, properties, progress and prospects. *Solid State Ionics* **125**, 1–11 (1999).
- Kreuer, K. D. Proton conductivity: Materials and applications. *Chem. Mater.* **8**, 610–641 (1996).
- Iwahara, H., Esaka, T., Uchida, H. & Maeda, N. Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production. *Solid State Ionics* **3–4**, 359–363 (1981).



22. Tao, S. W. & Irvine, J. T. S. A stable, easily sintered proton-conducting oxide electrolyte for moderate-temperature fuel cells and electrolyzers. *Adv. Mater.* **18**, 1581–1584 (2006).
23. Marnellos, G. & Stoukides, M. Ammonia synthesis at atmospheric pressure. *Science* **282**, 98–100 (1998).
24. Skodra, A. & Stoukides, M. Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure. *Solid State Ionics* **180**, 1332–1336 (2009).
25. Murakami, T., Nohira, T., Goto, T., Ogata, Y. H. & Ito, Y. Electrolytic ammonia synthesis from water and nitrogen gas in molten salt under atmospheric pressure. *Electrochim. Acta* **50**, 5423–5426 (2005).
26. Murakami, T. *et al.* Electrolytic synthesis of ammonia from water and nitrogen under atmospheric pressure using a boron-doped diamond electrode as a nonconsumable anode. *Electrochem. & Solid State Lett.* **10**, E4–E6 (2007).
27. Amar, I. A., Lan, R., Petit, C. T. G., Arrighi, V. & Tao, S. W. Electrochemical synthesis of ammonia based on a carbonate-oxide composite electrolyte. *Solid State Ionics* **182**, 133–138 (2011).
28. Perman, E. & Atkinson, G. The Decomposition of Ammonia by Heat. *Proceedings of the Royal Society of London* **74**, 110–117 (1904).
29. Kundu, P. P. & Pal, A. Cation exchange polymeric membranes for fuel cells. *Reviews in Chemical Engineering* **22**, 125–153 (2006).
30. Kordali, V., Kyriacou, G. & Lambrou, C. Electrochemical synthesis of ammonia at atmospheric pressure and low temperature in a solid polymer electrolyte cell. *Chem. Comm.* 1673–1674 (2000).
31. Zhang, Z. F., Zhong, Z. P. & Liu, R. Q. Cathode catalysis performance of SmBaCuMO_{5+δ} (M=Fe, Co, Ni) in ammonia synthesis. *J. Rare Earths* **28**, 556–559 (2010).
32. Skulason, E. *et al.* A theoretical evaluation of possible transition metal electrocatalysts for N₂ reduction. *Phys. Chem. Chem. Phys.* **14**, 1235–1245 (2012).
33. Burns, R. & Hardy, R. Nitrogen fixation in bacteria and higher plants. *Molecular Biology, Biochemistry, and Biophysics* **21**, 1–189 (1975).
34. Benemann, J. & Valentine, R. The pathways of nitrogen fixation. *Advances in Microbial Physiology* **8**, 59–104 (1972).
35. Hongsirakarn, K., Goodwin, J. Jr., Greenway, S. & Creager, S. Influence of ammonia on the conductivity of Nafion membranes. *J. Power Sources* **195**, 30–38 (2010).
36. Moskvich, Y. N., Polyakov, A. M. & Sukhovskiy, A. A. The NMR-study of ionic motions and conductivity mechanisms in protonic conductors MHSeO₄ and M₃H(AO₄)₂. *Ferroelectrics* **81**, 1161–1164 (1988).
37. Pawowski, A., Pawlaczyk, C. & Hilczer, B. Electric conductivity in crystal group Me₃H(SeO₄)₂ (Me: NH⁴⁺, Rb⁺, Cs⁺). *Solid State Ionics* **44**, 17–19 (1990).
38. Binnewies, M. & Milke, E. *Thermochemical data of elements and compounds*. (Wiley Online Library, 1999).
39. Young, S. K., Trevino, S. & Beck Tan, N. C. Small-angle neutron scattering investigation of structural changes in nafion membranes induced by swelling with various solvents. *Journal of Polymer Science Part B: Polymer Physics* **40**, 387–400 (2002).
40. Halseid, R., Vie, P. J. S. & Tunold, R. Effect of ammonia on the performance of polymer electrolyte membrane fuel cells. *J. Power Sources* **154**, 343–350 (2006).
41. Hargreaves, J. S. J. & McKay, D. A comparison of the reactivity of lattice nitrogen in Co₃Mo₃N and Ni₂Mo₃N catalysts. *J. Mol. Catal. A-Chem.* **305**, 125–129 (2009).

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Author contributions

S.W.T. and R.L. drafted and J.T.S.I. revised the manuscript. S.W.T. and J.T.S.I. conceptualized the study. R.L. and S.W.T. performed synthesis, characterization and analysis.

Additional information

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Supplementary Information

Synthesis of ammonia directly from air and water at ambient temperature and pressure

Rong Lan^a, John T.S. Irvine^b and Shanwen Tao^{a*}

1. Estimation of complete decomposition of NH₄-form Nafion 211 membrane

H-form Nafion formula: C₇HF₁₃O₅SC₂F₄, molecular weight: 544

NH₄-form Nafion formula: C₇H₄NF₁₃O₅SC₂F₄, molecular weight: 561

Nafion membrane density: 2.05g/cm³

The Nafion membrane we used with area 1cm², thickness 25 μm, volume 2.5×10⁻³ cm³, weight 5.125×10⁻³ g

The molar of NH₄-form Nafion for this membrane is: 5.125×10⁻³/561 = 9.14 × 10⁻⁶ mol

As 1 mol NH₄-form Nafion will generate 1 mol NH₃ (if completely decomposed), then should generate 9.14×10⁻⁶ mol ammonia at maximum.

2. Estimation of dissolved ammonia in the membrane

The volume of membrane is 2.5×10⁻³ cm³ or, 2.5×10⁻³ ml. It has been reported that the maximum H₂O uptake of Nafion 117 membrane was 20.64 vol% at room temperature, investigated by small angle neutron scattering technology (*Young, S. K., Trevino, S. & Beck Tan, N. C. Small - angle neutron scattering investigation of structural changes in nafion membranes induced by swelling with various solvents. Journal of Polymer Science Part B: Polymer Physics* 40, 387-400 (2002)). It is assumed that Nafion 211 membrane would exhibit similar behaviour. Assuming the adsorbed water volume is the same for Nafion 211 membrane, 2.5×10⁻³ ml × 20.64vol% = 5×10⁻⁴ ml which is equivalent to 5.0×10⁻⁴ g. The solubility of ammonia at 25°C is 31% by weight (<http://en.wikipedia.org/wiki/Ammonia>). The density of 32wt% ammonia aqueous solution at is 0.88g/ml at 25°C

(http://en.wikipedia.org/wiki/Ammonium_hydroxide). It is estimated that the density of 31wt% ammonia aqueous solution is 0.88g/ml. The dissolved ammonia is estimated as:

$$5.0 \times 10^{-4} \text{ ml} \times 0.88 \text{ g/ml} \times 31\% = 1.364 \times 10^{-4} \text{ g}$$

Convert to molar:

$$1.364 \times 10^{-4} / 17 = 8.02 \times 10^{-6} \text{ mol.}$$