



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

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The N≡N bond (225 kcal mol<sup>-1</sup>) 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 N<sub>2</sub> separation and H<sub>2</sub> production stages. A maximum ammonia production rate of 1.14 × 10<sup>-5</sup> mol m<sup>-2</sup> s<sup>-1</sup> 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 storage<sup>1</sup>.

Globally 131 million tons of ammonia were produced in 2010<sup>2</sup>. 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<sup>3,4</sup>. Natural gas or coal is used as the energy source of the ammonia industry. 1.87 tons of CO<sub>2</sub> is released per ton of ammonia produced<sup>5</sup>. Globally 245 million tons of CO<sub>2</sub> were released by the ammonia industry in 2010 equivalent to about 50% of the UK CO<sub>2</sub> emissions (495.8 million tons) in that year<sup>6</sup>. In the Haber-Bosch process, the presence of ppm level oxygen may poison the commonly used Fe-based catalysts. In industry, extensive purification of N<sub>2</sub> and H<sub>2</sub> is needed and this remarkably increases the overall cost of the process<sup>7,8</sup>. 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 nitrogen<sup>9</sup>. Following this pioneering work, there are several key reports on synthesis of ammonia under mild conditions through complex intermediates<sup>3,10–15</sup>. On the other hand, ammonia can be synthesised at room temperature through electrochemical synthesis<sup>3,10–15</sup>. In 1985, for the first time, Pickett et al. reported the electrochemical synthesis of ammonia at room temperature through protolysis of cis-[W(N<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>]<sup>16</sup>. There were reports on electrochemical synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub> using Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the electrolyte but the current was quite small<sup>17,18</sup>. This could be related to the low proton conductivity of Na<sub>2</sub>SO<sub>4</sub> 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<sup>19,20</sup>. Some perovskite oxides exhibit high proton conductivity and have been used in solid oxide fuel cells<sup>19,21,22</sup>. Stoukides reported the electrochemical synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub> at 570°C based on a solid proton-conducting oxide SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-δ</sub><sup>23</sup>. The authors also further reported the synthesis of ammonia directly from N<sub>2</sub> and H<sub>2</sub>O bypassing the process of H<sub>2</sub> production<sup>24</sup>. There are other reports on electrochemical synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub>O in molten salts at a temperature ~300°C<sup>25,26</sup>. Recently we reported electrochemical synthesis of ammonia at ~500°C based on oxide-carbonate composite electrolytes<sup>4,27</sup>. Ammonia tends to decompose at ~500°C<sup>28</sup> therefore low temperature synthesis is necessary to avoid ammonia decomposition; however, most good low temperature proton conducting materials are based on acidic materials<sup>29</sup>. 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)<sup>29</sup>. In 2000, Kordali et al. reported the synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub>O 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°C<sup>30</sup>. Although ammonia was synthesised from N<sub>2</sub> and H<sub>2</sub>O at room temperature using 2 M KOH solution as electrolyte, N<sub>2</sub> cannot be replaced by air as CO<sub>2</sub> in air may react with KOH to form K<sub>2</sub>CO<sub>3</sub>. It was reported that ammonia has been synthesised from N<sub>2</sub> and H<sub>2</sub> based on acidic H<sup>+</sup>-form Nafion membrane, with Ni-SDC (Sm-doped CeO<sub>2</sub>) as anode, SmBa-CuMO<sub>5+δ</sub> as cathode with maximum formation rate of  $4.1 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$  at 25°C<sup>31</sup>; however, the chemical compatibility of active metal Ni with the strongly acidic Nafion membrane is concerning. The reaction between active Ni and H<sup>+</sup>-form Nafion may form Ni<sup>2+</sup>-form Nafion and thus lose proton conduction therefore the reaction would not be sustainable<sup>32</sup>. In addition, to synthesise ammonia directly from air without the N<sub>2</sub> 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<sup>33,34</sup>. 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 N<sub>2</sub>) and H<sub>2</sub>O (instead of H<sub>2</sub>) under a mild condition (room temperature, one atmosphere) with supplied electricity which can be obtained from renewable resources such as solar, wind or marine.

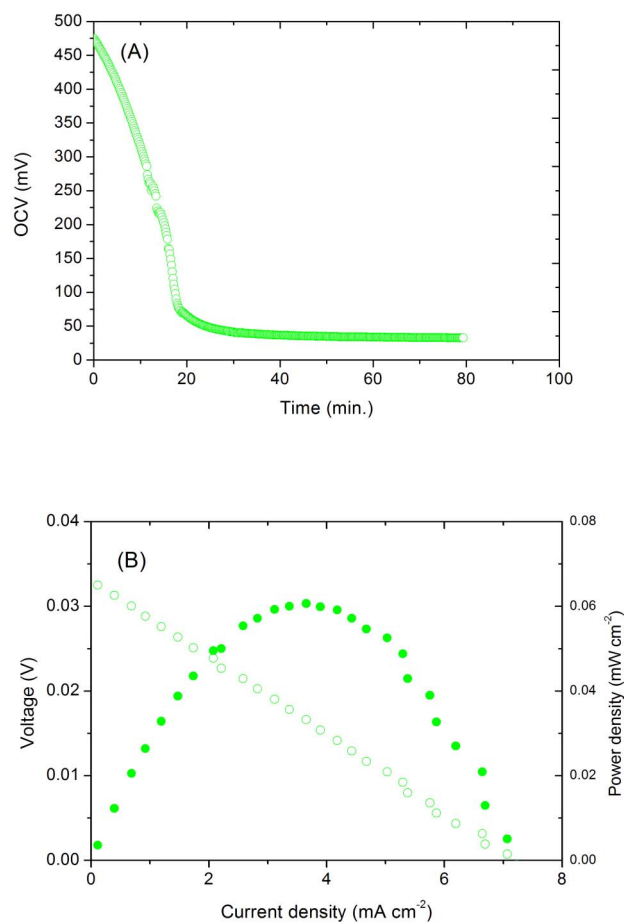
## Results

**Proton conduction of mixed NH<sub>4</sub><sup>+</sup>/H<sup>+</sup> conducting Nafion 211 membrane.** Ammonia is a base, the acidic Nafion membrane readily reacts with ammonia to form NH<sub>4</sub><sup>+</sup>-form Nafion. In our experiments, for the first time, it was demonstrated that NH<sub>4</sub><sup>+</sup>-form Nafion exhibits proton conduction through concentration cell measurements. A mixed NH<sub>4</sub><sup>+</sup>/H<sup>+</sup> conducting Nafion 211 membrane was used as solid electrolyte for electrochemical synthesis of ammonia. Conventional H<sup>+</sup>-form Nafion membrane will be converted to NH<sub>4</sub><sup>+</sup>-form in the presence of ammonia. It is necessary to maintain the stability of the membrane electrolyte under the synthesis conditions<sup>35</sup>. It has been reported that the ionic conductivity of NH<sub>4</sub><sup>+</sup>-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%<sup>35</sup>. The high ionic conductivity is believed due to NH<sub>4</sub><sup>+</sup> ions but proton conduction cannot be ruled out. It has been reported that some inorganic ammonium salts such as (NH<sub>4</sub>)<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> exhibit proton conduction<sup>36,37</sup>. Therefore the NH<sub>4</sub><sup>+</sup>-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<sup>+</sup>-form Nafion 211 membrane was converted into NH<sub>4</sub><sup>+</sup>-form Nafion through the reaction between 35 wt% ammonia aqueous solution and the H<sup>+</sup>-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 H<sub>2</sub> (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<sup>+</sup> or/and O<sup>2-</sup> conduction. When the air was replaced by 5%H<sub>2</sub>/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  $7 \text{ mA cm}^{-2}$  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 H<sub>2</sub>/5%H<sub>2</sub>-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 NH<sub>4</sub><sup>+</sup> ions although NH<sub>4</sub><sup>+</sup> ions are proton carriers too. Therefore, the thus treated membrane is a mixed NH<sub>4</sub><sup>+</sup>/H<sup>+</sup> conductor and can be used for electrochemical synthesis of ammonia because it is chemically compatible with ammonia.

**Thermodynamic evaluation on electrochemical synthesis of NH<sub>3</sub> from H<sub>2</sub>/H<sub>2</sub>O and N<sub>2</sub>.** In order to consider the potential for electrochemical synthesis of ammonia, a thermodynamic evaluation on synthesis of ammonia from H<sub>2</sub> and N<sub>2</sub> was carried-out<sup>38</sup>. In theory, the reaction is spontaneous at a temperature below  $\sim 175^\circ\text{C}$  when the partial pressure of H<sub>2</sub> and N<sub>2</sub> 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 NH<sub>3</sub> from H<sub>2</sub> or H<sub>2</sub>O is

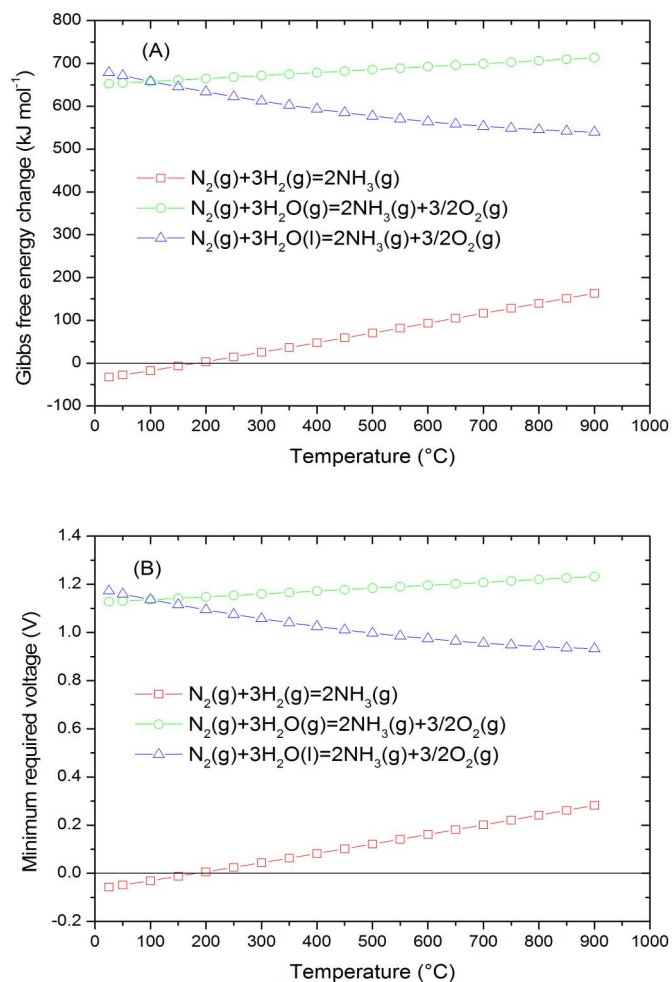


**Figure 1** | (A) The recorded potential change from a H<sub>2</sub>/air cell to a H<sub>2</sub>/5%H<sub>2</sub>-Ar concentration cell; (B) The I-V and power curves of the H<sub>2</sub>/5%H<sub>2</sub>-Ar concentration cell.

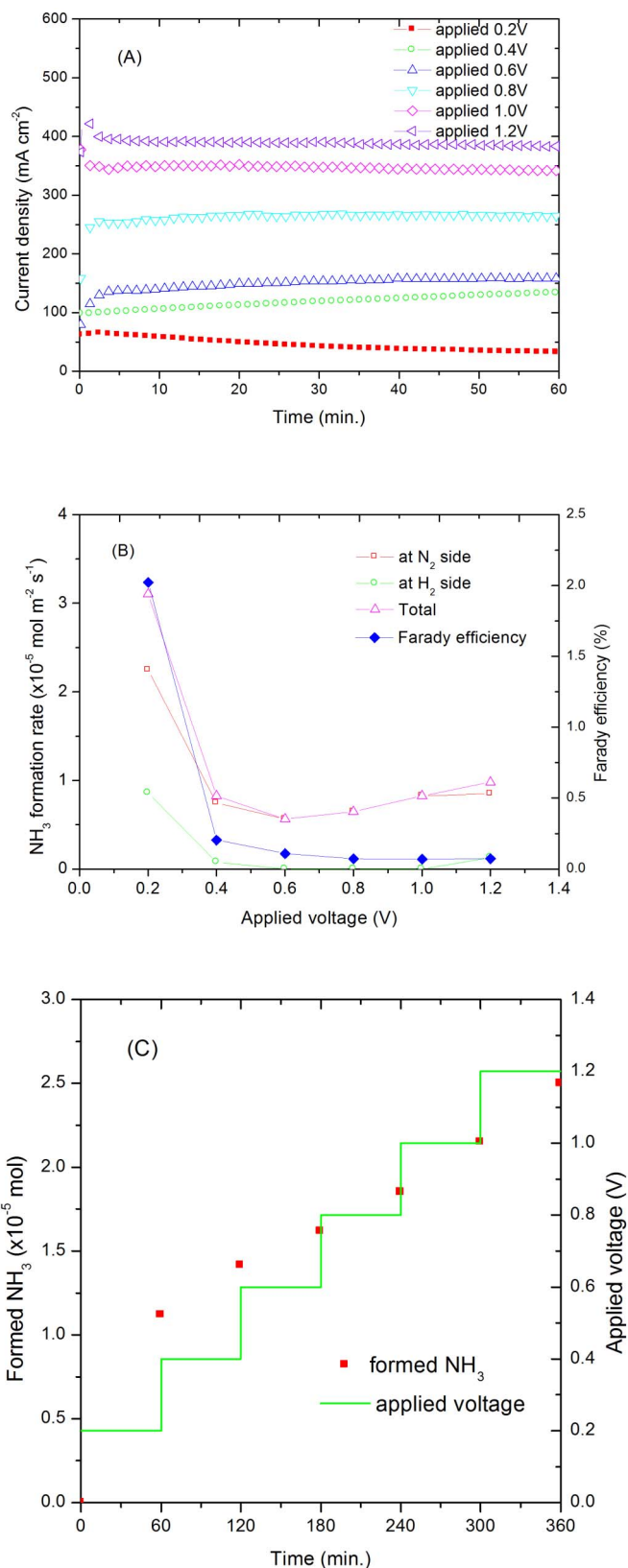


shown in Fig. 2B. At 25°C, a minimum voltage of 1.17 V is required for electrochemical synthesis of ammonia from liquid water and N<sub>2</sub> at partial pressure of 1 bar.

**Synthesis of ammonia from H<sub>2</sub> and N<sub>2</sub>.** Ammonia was first synthesised from conventional precursors, H<sub>2</sub> and N<sub>2</sub> using the electrochemical cell. As shown in Fig. 3A, an initial current of 58 mA cm<sup>-2</sup> 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<sup>-2</sup> 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  $3.1 \times 10^{-5}$  mol m<sup>-2</sup> s<sup>-1</sup> was observed at 0.2 V which is about three orders of magnitude higher than the previously reported value reported by Kordali et al<sup>30</sup> and is comparable to those reported by Liu et al<sup>31</sup>. As shown in Fig. 3C, the formed ammonia increased with time. The amount of generated ammonia was  $1.13 \times 10^{-5}$  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 NH<sub>4</sub>-form of the membrane ( $9.14 \times 10^{-6}$  mol) if all the

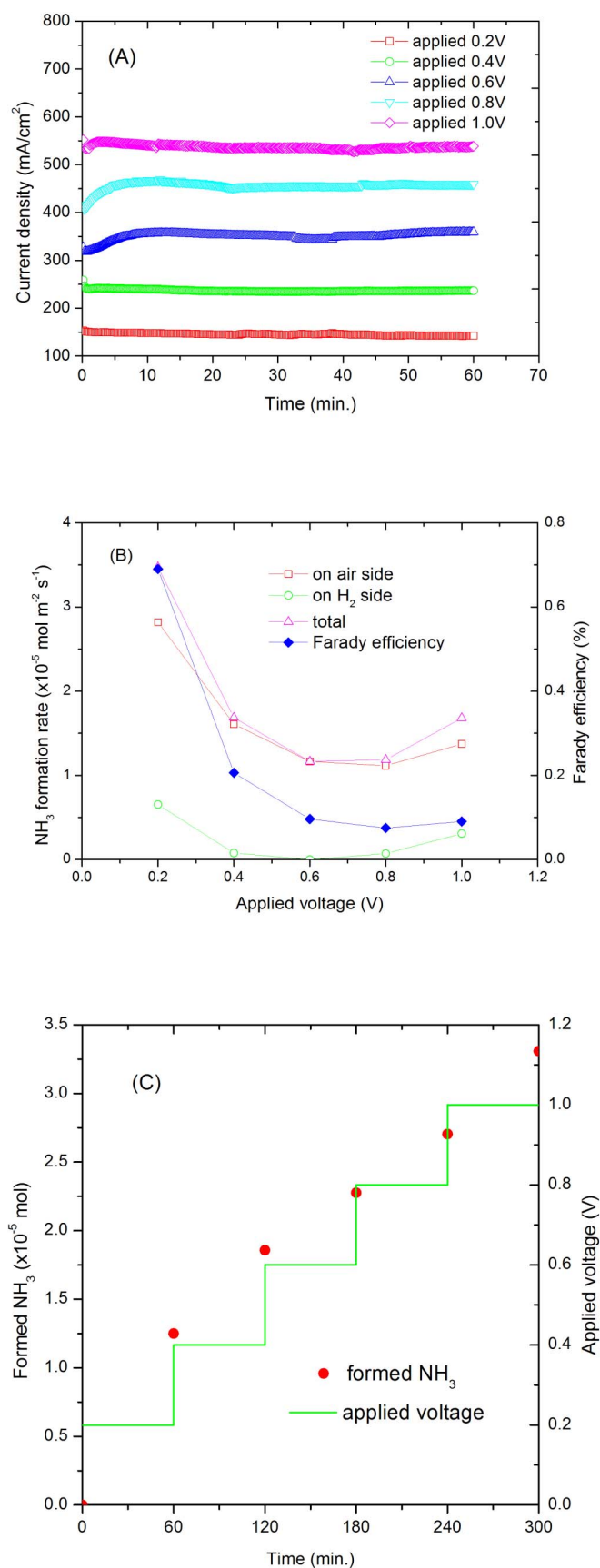


**Figure 2** | (A) The Gibbs free energy change for electrochemical synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O (gaseous or liquid) at pressure of 1 bar; (B) The minimum applied voltage required for electrochemical synthesis of ammonia from N<sub>2</sub>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



**Figure 3** | (A) Current density of a N<sub>2</sub>, Pt | Nafion 211 | Pt, H<sub>2</sub> cell under different applied voltages. Cathode was supplied with N<sub>2</sub>, anode was supplied with H<sub>2</sub>. (B) The ammonia formation rate at N<sub>2</sub> and H<sub>2</sub> sides, total ammonia formation rate and Faraday efficiency. (C) The relationship between formed NH<sub>3</sub> and time of a N<sub>2</sub>, Pt | Nafion 211 | Pt, H<sub>2</sub> cell under different applied voltages. Cathode was supplied with N<sub>2</sub>, anode was supplied with H<sub>2</sub>.





**Figure 4** | (A) Current density of an Air Pt | Nafion 211 | Pt, H<sub>2</sub> cell under different applied voltages. Cathode was supplied with air, anode was supplied with H<sub>2</sub>. (B) The ammonia formation rate at air and H<sub>2</sub> sides,

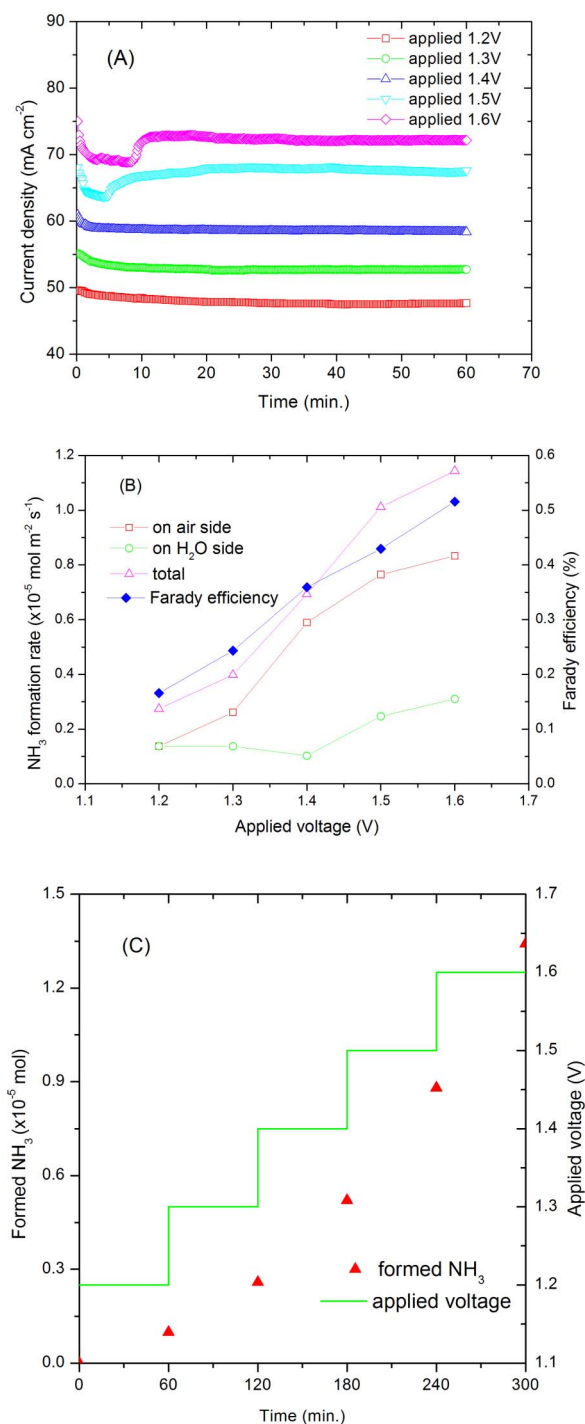
total ammonia formation rate and Faraday efficiency. (C) The relationship between formed NH<sub>3</sub> and time of an Air, Pt | Nafion 211 | Pt, H<sub>2</sub> cell under different applied voltages. Cathode was supplied with air, anode was supplied with H<sub>2</sub>.

current arose from NH<sub>4</sub><sup>+</sup> transport which is unlikely, or estimated dissolved ammonia ( $8.02 \times 10^{-6}$  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 N<sub>2</sub> side, a small amount of ammonia was also observed at the H<sub>2</sub> 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 N<sub>2</sub> side may *in situ* dissolve in water, diffuse to the H<sub>2</sub> side then brought out by the flowing H<sub>2</sub>. 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 H<sub>2</sub> and air.** Air contains 78% N<sub>2</sub> therefore it would be better to synthesise ammonia directly from air without the separation process. When N<sub>2</sub> at the cathode was replaced by air, a stable current density of 142 mA cm<sup>-2</sup> was observed when the cell voltage was 0.2 V (Fig. 4A). At 1.0 V, the current density stabilised at 537 mA cm<sup>-2</sup>. This indicates that the membrane is fairly stable. Comparing to the H<sub>2</sub>/N<sub>2</sub> cell, the current densities are higher for the H<sub>2</sub>/air cell, possibly due to the extra driving force from O<sub>2</sub> in air. Interestingly, ammonia was also produced on the air side with a small amount at the H<sub>2</sub> 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 H<sub>2</sub>/N<sub>2</sub> 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 N<sub>2</sub> 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 O<sub>2</sub> 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 H<sub>2</sub>O 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 H<sub>2</sub> at the anode was replaced by water. At 1.2 V, the current density of the cell was 47 mA cm<sup>-2</sup>, lower than that for the H<sub>2</sub>/N<sub>2</sub> 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 H<sub>2</sub> was fed at the anode. The highest ammonia formation rate was observed at low applied voltage when H<sub>2</sub> 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, H<sub>2</sub>O cell under different applied voltages. Cathode was supplied with air, anode was supplied with H<sub>2</sub>O. (B) The ammonia formation rate at air and H<sub>2</sub>O sides, total ammonia formation rate and Faraday efficiency. (C) The relationship between formed NH<sub>3</sub> and time of an Air, Pt | Nafion 211 | Pt, H<sub>2</sub>O cell under different applied voltages. Cathode was supplied with air, anode was supplied with H<sub>2</sub>O.

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

## Discussion

In most reports, H<sub>2</sub> and N<sub>2</sub> were commonly used as precursors for electrochemical synthesis of ammonia while H<sub>2</sub> production and N<sub>2</sub>

separation are essential<sup>4</sup>. H<sub>2</sub> production can be bypassed if H<sub>2</sub>O was used as a precursor; however, the reaction between H<sub>2</sub>O and N<sub>2</sub> 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 N<sub>2</sub> and H<sub>2</sub>O at 570°C<sup>15</sup> or 300°C<sup>22,23</sup>, the formed ammonia tends to decompose to N<sub>2</sub> and H<sub>2</sub> 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 H<sub>2</sub>O uptake of Nafion 117 membrane was 20.64 vol% at room temperature, investigated by small angle neutron scattering technology<sup>39</sup>. 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  $8.02 \times 10^{-6}$  mol (please see supplement information) which is smaller than the generated ammonia in the first experiment, from H<sub>2</sub> and N<sub>2</sub> while applied at 0.2 V for 1 hour ( $1.13 \times 10^{-5}$  mol, Fig. 3C). This value is also higher than the formed ammonia from possible decomposition of NH<sub>4</sub><sup>+</sup>-form Nafion ( $9.14 \times 10^{-6}$  mol). The total ammonia from decomposition of NH<sub>4</sub><sup>+</sup>-form Nafion and dissolved NH<sub>3</sub> in absorbed water is  $1.72 \times 10^{-5}$  mol which is significantly smaller than the total measured ammonia  $7.15 \times 10^{-5}$  mol (Figs. 3C, 4C and 5C). It should be noted that the NH<sub>4</sub><sup>+</sup>-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 H<sub>2</sub> and N<sub>2</sub> 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<sup>+</sup>/NH<sub>4</sub><sup>+</sup>-form Nafion to the other side to react with N<sub>2</sub> to electrochemically form NH<sub>3</sub>;



The overall reaction is:

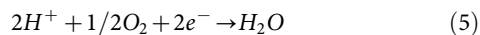


However, the reaction between proton and N<sub>2</sub> depends on both thermodynamics and kinetics. Considering the over-potential on both electrodes, if the 'net' potential difference between the two electrodes is above the value displayed in Fig. 2B, then thermodynamically reaction (3) should happen. 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 N<sub>2</sub>/air side are required. The protons at the reduction electrode not only react with N<sub>2</sub> to form NH<sub>3</sub>, but can receive electrons to form H<sub>2</sub> as well;



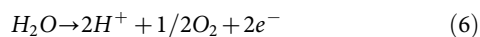
When 0.2 V is applied, only 2% applied electricity was converted to ammonia while the other 98% was converted to H<sub>2</sub>. The H<sub>2</sub> flow rate at the reduction electrode is proportional to the current across the cell. When higher voltage was applied, the current across the cell also increased (Fig. 3A). Most of the protons were converted to H<sub>2</sub> 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 N<sub>2</sub> at the reduction electrode was replaced by air, besides reaction (4), another important reaction is between protons and oxygen in the air;



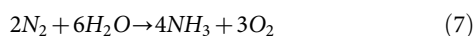
This is also the cathode reaction for a H<sub>2</sub>/O<sub>2</sub> fuel cell. This reaction indicates that, under certain conditions, a small amount of ammonia may be formed when air was used as oxidant in hydrogen fuel cells. It has been reported that ammonia can passivate the oxygen reduction reaction (5) at the cathode of a proton exchange membrane fuel cell<sup>40</sup>. On the other hand, the passivation of ammonia on Pt/C catalysts for reaction (5) may suppress the formation of H<sub>2</sub>O, which may favour the competitive reaction between protons and N<sub>2</sub> in air to form ammonia. From this point of view, if a suitable catalyst is identified to suppress the formation of H<sub>2</sub>O 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 N<sub>2</sub> in air to form ammonia while O<sub>2</sub> is formed at the oxidation electrode.

The overall reaction is:



While ammonia is produced at the air side, O<sub>2</sub> 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 synthesis<sup>32</sup>. In the future, other low cost ammonia synthesis catalysts such as Co<sub>3</sub>Mo<sub>3</sub>N and Ni<sub>2</sub>Mo<sub>3</sub>N<sup>41</sup> can be used to replace Pt for selective ammonia synthesis under mild conditions. The acidity of the H<sup>+</sup>/NH<sub>4</sub><sup>+</sup>-form Nafion membrane would be much weaker than the H<sup>+</sup>-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% H<sub>2</sub>O<sub>2</sub> for 1 hour, rinsed by deionised water, boiled in deionised water for 2 hours then in 0.5 M H<sub>2</sub>SO<sub>4</sub> 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<sup>-2</sup>. 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 cm<sup>2</sup> 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<sup>+</sup>-form Nafion 211 membrane into NH<sub>4</sub><sup>+</sup>-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.** H<sub>2</sub> (or water) and N<sub>2</sub> (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 H<sub>2</sub>SO<sub>4</sub> (0.001 M). The concentration of NH<sub>4</sub><sup>+</sup> 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 [NH<sub>4</sub><sup>+</sup>] is the measured NH<sub>4</sub><sup>+</sup> ion concentration, V is the volume of the dilute H<sub>2</sub>SO<sub>4</sub> for ammonia collection, t is the adsorption time and A is the effective area of the cell.

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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

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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# Supplementary Information

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

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### 1. Estimation of complete decomposition of NH<sub>4</sub>-form Nafion 211 membrane

H-form Nafion formula: C<sub>7</sub>HF<sub>13</sub>O<sub>5</sub>SC<sub>2</sub>F<sub>4</sub>, molecular weight: 544

NH<sub>4</sub>-form Nafion formula: C<sub>7</sub>H<sub>4</sub>NF<sub>13</sub>O<sub>5</sub>SC<sub>2</sub>F<sub>4</sub>, molecular weight: 561

Nafion membrane density: 2.05g/cm<sup>3</sup>

The Nafion membrane we used with area 1cm<sup>2</sup>, thickness 25 μm, volume 2.5×10<sup>-3</sup> cm<sup>3</sup>, weight 5.125×10<sup>-3</sup> g

The molar of NH<sub>4</sub>-form Nafion for this membrane is: 5.125×10<sup>-3</sup>/561 = 9.14 × 10<sup>-6</sup> mol

As 1 mol NH<sub>4</sub>-form Nafion will generate 1 mol NH<sub>3</sub> (if completely decomposed), then should generate 9.14×10<sup>-6</sup> mol ammonia at maximum.

### 2. Estimation of dissolved ammonia in the membrane

The volume of membrane is 2.5×10<sup>-3</sup> cm<sup>3</sup> or, 2.5×10<sup>-3</sup> ml. It has been reported that the maximum H<sub>2</sub>O 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<sup>-3</sup> ml × 20.64vol% = 5×10<sup>-4</sup> ml which is equivalent to 5.0×10<sup>-4</sup> 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](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:

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