

Renewable Power to X module based on ozonation assisted electrochemical energy conversion reaction

Background to the invention

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The invention relates to methods and apparatus for the conversion of air into ammonia and ammonium salts, with ozone produced as a by-product and with minimal levels of waste products.

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Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

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The transformation of atmospheric nitrogen (N_2) to ammonia (NH_3) is essential for many eco-systems and industrial processes. Currently, only bacteria and some plants can synthesize ammonia from air and water at ambient conditions via nitrogen fixation processes. Ammonia is an extremely valuable global commodity at present and appears likely to play a significant role not only in manufacturing but also in energy production, storage and transport as energy carrier in the near future.

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Globally, approximately \$60 billion worth of ammonia is produced every year for utilisation, mostly in the form of fertilizers. Recently, ammonia has been gaining increasing attention as a hydrogen carrier for the hydrogen economy. Ammonia stores almost twice as much energy as liquid hydrogen (by volume) and is easier to ship and distribute for export purposes. Thus, the global ammonia market has significant potential for expansion in upcoming years.

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Ammonia used as fertiliser is currently produced via the large-scale capital-intensive and centralised Haber-Bosch (HB) process, which was developed in the early 20th Century and has changed little in that time. In the HB process, hydrogen (generated from fossil fuel) and nitrogen (extracted from air) are converted to ammonia at a high pressure and temperature. As this process generates up to 2.4 Mt of CO_2 per tonne of NH_3 , there is a clear market pressure to decarbonise this process as countries are increasingly committing to net-zero targets.

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Decarbonization of agriculture and regional economy is dependent on the uptake of renewable electrification as well as “Power to X” (the conversion of electricity into power fuels or clean chemicals) pathways. Amongst these pathways, power to ammonia conversion, particularly in the form of decentralised modules, is projected to play a big role in attaining net-zero emissions as it will enable the reach of renewable electrons to substitute diesel consumption for mobility in mining and farming applications as well as providing zero-carbon fertilizer for agriculture. This potential of renewable ammonia is increasingly being recognized by industry and government, with a number of renewable hydrogen project developers in Australia and beyond substituting fossil-fuel sourced hydrogen with renewable hydrogen that is then used in energy-intensive Haber-Bosch (HB) process to generate renewable ammonia.

While such an approach allows operation of existing HB plants with modification (avoiding assets being stranded), this pathway requires high temperature and pressure - the HB process typically requires high pressures (150 – 250 atmospheres), high temperatures (400 – 500°C), a relatively high purity hydrogen (from steam reforming of methane) feed and a relatively high purity nitrogen (from air separation) feed. Because of this, the HB process consumes a significant amount of energy and is fundamentally incompatible with small scale, delocalised ammonia production as well as making it unfeasible to accommodate intermittent and diffusive renewable energy, as the Haber-Bosch process operates in a dynamic manner and requires long-start up and shut down time. These challenges, coupled with the capital-intensive nature of the HB process, limit its use for decentralized on-demand production.

In recent times, there have been renewed research efforts into power-to-X pathways, including power-to-ammonia pathways, such as electrochemical N_2 reduction to NH_3 (NRR), waste NO_x reduction to NH_3 (NO_xRR) and plasma driven conversion of N_2 and H_2 to NH_3 . However, these routes suffer from low product selectivity and yield, the requirement of suitable waste NO_x feedstocks and high production costs. For instance, the highest yield arising from NRR and plasma conversion is 0.05 and $0.15 \text{ mmol h}^{-1} \text{ cm}^{-2}$, respectively, whereas NO_xRR yield is dependent on the concentration of NO_3^- and NO_2^- sources (highest yield of $1.2 \text{ mmol h}^{-1} \text{ cm}^{-2}$). However, sources of NO_3^- and NO_2^- sources are intermittent in agricultural water or rely on industrial point-source flue gas. With the transition of fossil fuel-based power generation, the available supply of industrial point source flue gas may be questionable in the long-term. The use of standalone plasma-electrolyser hybrids and Li-ion mediated NRR have exhibited promising increases in yield, however, questions on energy requirement and stability of electrodes for continuous cycling remain. There are also concerns on sourcing Li, a critical mineral, which will inevitably impede commercialisation of Li-ion mediated NRR pathway.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Summary of the invention

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According to a first aspect the invention provides a method of producing ammonia and/or ammonium comprising:

- i) ozonation of air to produce a product gas stream comprising ozone and gaseous NO_x species; and
 - 10 ii) electrolytically reducing the gaseous NO_x species by passage from a gas side of a gas diffusion electrode to a catholyte thereby to produce NH_4^+ or NH_3 ; and
- wherein the gas diffusion electrode comprises a metal/metal oxide single atom or dual atom catalyst electrode.

- 15 The gaseous NO_x species may pass through the gas diffusion electrode to and into a catholyte to produce dissolved NO_x^- species which are reduced to provide NH_4^+ and dissolved NH_3 .

- 20 Partial dissolution of NO_x species may take place prior to passage through the gas diffusion electrode, in which case it is introduced to the electrolyser as aqueous catholyte. Any remaining undissolved NO_x is involved in the reaction as gas phase input and undissolved NO_x species are present in contact with the catholyte.

- 25 Dissolved NH_3 may pass from the catholyte through the gas diffusion electrode as gaseous ammonia. Similarly, NH_4^+ in solution may also pass through the gas diffusion electrode. The dissolved NH_4^+ or gaseous ammonia may be collected for use.

- 30 The NO_x species may be in the gas phase and can comprise one or more of NO , N_2O and NO_2 .

The dissolved NO_x^- may comprise both nitrate (NO_3^-) and nitrite (NO_2^-) ions.

- 35 Ideally, the electrolysis is commenced when the concentrations of NO_3^- and NO_2^- are at a predetermined level and preferably the NO_3^- and NO_2^- are in a steady state equilibrium.

In one embodiment, NO_3^- is present in a concentration of 1.7mM and NO_2^- is present in a concentration of 10.0mM when electrolysis is commenced, and thereafter for the duration of electrolysis.

5 The NO_x species may be in both a gas phase and an aqueous phase, and wherein the gas phase comprises one or more of NO , N_2O and NO_2 and the aqueous phase comprises one or more of nitrate and nitrite ions, and wherein the electrolyser is a flow electrolyser which receives the aqueous phase and the gas phase passed through a gas diffusion electrode.

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The gaseous NO_x may be reduced to NH_4^+ the by contact with gas-diffusion-electrode (GDE), for example a Cu-based gas diffusion electrode.

The catholyte may be under an atmosphere comprising NO_x .

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The ozone may be diverted for further use, for instance as a sterilizing agent for waste or contaminated water.

20 In another embodiment, the method of the present invention further includes introducing CO_2 to react with the produced ammonia. In this way, it is possible to form compounds having C-N bonds, for example, formamide and potentially urea.

According to a second aspect, the invention provides a method of producing ammonia and/or ammonium comprising:

25 i) obtaining a gaseous waste stream comprising gaseous NO_x species; and
ii) electrolytically reducing the gaseous NO_x species by passage from a gas side of a gas diffusion electrode to a catholyte thereby to produce NH_4^+ or NH_3 ; and wherein the gas diffusion electrode comprises a metal/metal oxide single atom or dual atom catalyst electrode.

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The gaseous NO_x species may pass through the gas diffusion electrode to and into a catholyte to produce dissolved NO_x^- species which are reduced to provide NH_4^+ and dissolved NH_3 .

35 The NO_x species may comprise one or more of NO , N_2O and NO_2 and the dissolved NO_x^- may comprise both nitrate (NO_3^-) and nitrite (NO_2^-) ions. Ideally, the electrolysis is

commenced when the concentrations of NO_3^- and NO_2^- are at a predetermined level and preferably the NO_3^- and NO_2^- are in a steady state equilibrium.

5 According to a third aspect the invention provides an apparatus for ammonia production comprising:
an ozone generator; and
an electrolyser comprising a gas diffusion electrode according to the second aspect (or prepared by the third aspect); and wherein the output of the ozone generator is fed to a catholyte via the gas diffusion electrode.

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In some embodiments, the output of the ozone generator is fed to the catholyte of the electrolyser directly as gas phase and aqueous phase.

The ozone generator is for preference a dielectric barrier discharge (DBD) ozone generator.

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The apparatus may further include a feed unit, such as a fan or pump, to supply air to the module, said air being a feed gas for the ozone generator.

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The gas diffusion electrode used in the present method (and apparatus) may comprise:

- a support;
- a conductive layer coated on the support;
- a gas permeable membrane coated on the support, wherein the gas permeable membrane is impregnated with a metal/metal oxide single atom or dual atom catalyst.

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The support may be for example graphite felt.

The conductive layer may be for example gold, and for example 100 nm thick.

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The gas permeable membrane may be a cation conducting membrane, for example Nafion, or an Anion Exchange Membrane.

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The gas permeable membrane supports a mixture of the flame sprayed single metal/metal oxide catalyst, such as pyrolyzed copper, and carbon black. The flame spray pyrolyzed copper may for example have a loading on the electrode of 0.1 mg/cm^2 . Alternatively, the gas permeable membrane may support flame sprayed dual metal/metaloxide catalyst.

Any conventional support which has adequate chemical resistance to the conditions may be used, for example, the support may be graphite felt or PTFE.

The conductive layer may be for example gold, and for example 100 nm thick.

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The gas permeable membrane may be Nafion.

The gas permeable membrane may be impregnated with a mixture of flame spray pyrolyzed copper and carbon black. The flame spray pyrolyzed copper may for example have a loading on the electrode of 0.01 to 1 mg cm⁻², for example 0.05 to 0.5 mg cm⁻² or 0.1 mg cm⁻².

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Definitions

In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments of the invention only and is not intended to be limiting. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one having ordinary skill in the art to which the invention pertains.

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Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

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As used herein, the phrase "consisting of" excludes any element, step, or ingredient not specified in the claim. When the phrase "consists of" (or variations thereof) appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole. As used herein, the phrase "consisting essentially of" limits the scope of a claim to the specified elements or method steps, plus those that do not materially affect the basis and novel characteristic(s) of the claimed subject matter.

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With respect to the terms "comprising", "consisting of", and "consisting essentially of", where one of these three terms is used herein, the presently disclosed and claimed subject matter may include the use of either of the other two terms. Thus, in some embodiments not otherwise explicitly recited, any instance of "comprising" may be replaced by "consisting of" or, alternatively, by "consisting essentially of".

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Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term “about”. The examples are not intended to limit the scope of the invention. In what follows, or where otherwise indicated, “%” will mean “volume %”, “ratio” will mean “volume ratio” and “parts” will mean “volume parts”.

The term ‘substantially’ as used herein shall mean comprising more than 50% by volume, mass or weight, according to the context in which it is used, unless otherwise indicated. Preferably, it is meant to mean more than 75%. Even more preferably, it is meant to mean more than 90%. Most preferably, it is meant to mean 100% or close to 100%.

The recitation of a numerical range using endpoints includes all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5 etc.).

The terms “preferred” and “preferably” refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the invention.

It must also be noted that, as used in the specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise.

The prior art referred to herein is fully incorporated herein by reference.

Although exemplary embodiments of the disclosed technology are explained in detail herein, it is to be understood that other embodiments are contemplated. Accordingly, it is not intended that the disclosed technology be limited in its scope to the details of construction and arrangement of components set forth in the following description or illustrated in the drawings. The disclosed technology is capable of other embodiments and of being practiced or carried out in various ways.

Brief description of the drawings

The invention will now be described, by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic of the ozonation-electrolysis process and apparatus of the present invention.

Figure 2 shows NO_x/O_3 production capability of a dielectric barrier discharge (DBD) ozonation system. **(a)** Gaseous NO_x production rate ($\mu\text{mol min}^{-1}$) of the DBD ozonation reactor with different air flow rate. **(b)** Water-dissolved NO_x (NO_3^-) production rate under air flow rate of 4000 mL min^{-1} . **(c)** Comparing energy consumption of the current DBD system with various plasma reactor systems in producing NO_x , such as single reactor glow discharge (SRGD); single reactor spark discharge (SRSD); single reactor glow and spark discharge (SRGSD); double reactor glow and spark discharge (DRGSD); and the current DBD system. **(d)** The DRIFTS spectra of gaseous O_3 under different air flow rate and **(e)** the quantified O_3 production rate ($\mu\text{mol min}^{-1}$).

Figure 3 shows performance of integrated system for ammonium production. *I-t* curves are shown of Cu-based GDE tested using a flow-cell electrolyser with catholyte containing $10.0 \text{ mM NO}_2^-/1.7 \text{ mM NO}_3^-$ (defined as the standard aqueous NO_x^- equilibrium concentration) in $0.5 \text{ M K}_2\text{SO}_4$ aqueous solution with **(a)** gaseous NO_x input, **(b)** no gas input, and **(c)** air input under different applied potentials (V). Dependence of **(d)** FE, **(e)** $j_{\text{NH}_4^+}$, and **(f)** NH_4^+ production yield under different applied potentials. **(g)** *I-t* curves of Cu-based GDE tested using a flow-cell electrolyser under applied potential of -2.5 V with catholyte containing 0 to 3 times of standard aqueous NO_x^- equilibrium concentration with gaseous NO_x input. **(h)** The dependence of FE, $j_{\text{NH}_4^+}$, and NH_4^+ production yield on the aqueous NO_x^- concentration under applied potential of -2.5 V . **(i)** The energy efficiency of the integrated ammonium production system under different applied potentials. **(j)** Ammonia production rate and energy consumption for our system and other NRR and NO_xRR systems in the literatures, i.e., conventional eNRR; Li-intermediary NRR; plasma-assisted NRR; NO_3RR ; and NORR. **(k)** Operation mechanism of the present invention.

Figure 4 shows the physicochemical characterizations and theoretical study. **(a)** SEM images of Cu-based gas-diffusion-electrode. **(b-c)** HR-TEM of Cu particles on as-prepared GDE. **(d-g)** MADDF-STEM image and EDX mappings of the catalysts. **(h-i)** *In-situ* PD measurements with Cu-based GDE under reaction conditions.

Figure 5 shows the effect of the NO_x atmosphere on the rate of ammonia production.

Figure 6 shows the performance of the present invention when operated by a solar cell.

Detailed description of the invention

The skilled addressee will understand that the invention comprises the embodiments and features disclosed herein as well as all combinations and/or permutations of the disclosed embodiments and features.

5 To the best of the present inventors' knowledge, the present invention represents the first time that an ozonation apparatus and electrolytic reduction apparatus have been used in the production of ammonia. The use of such a combination allows for a high rate of production of ammonia from air in the presence of water with the only other requirement being renewable energy.

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The apparatus itself is simple, scalable, and capable of continuous operation and shown in Figure 1. The basic elements are a commercial dielectric barrier discharge (DBD) ozone generator coupled to an electrolyser, which receives the output from the ozone generator.

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Air is taken in by the ozone generator, which converts air into gaseous O_3 and NO_x , which can be directly introduced into a flow electrolyzer equipped with a Cu-based gas-diffusion-electrode (GDE) to transform the gaseous NO_x into NH_4^+ .

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Without wishing to be bound by theory, it is believed to be advantageous to use a DBD ozone generator because the mechanism of action of ozone formation and the presence of ozone is believed to assist in the oxidation of nitrogen to NO_x species.

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Further, it is believed that it is beneficial to include ozone in the electrolyser since this can assist in the suppression of potential undesired side reactions during generation of ammonia from NO_x .

Further, the O_3 (which is unaffected by the electrolyser) and unreacted NO_x can, if desired, be reused, for example, by being directed into irrigation water to reduce bacterial loads or providing a stream of dissolved nitrate in water for agricultural purposes.

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Alternatively, if desired, the ozone treated wastewater solution can be pumped back into the electrolyzer as catholyte where it participates in the NH_4^+ production reaction on the Cu active sites from liquid side of Cu-based GDE. This can be repeated until the dissolved NO_x species are, practically speaking, exhausted.

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As such, the coupled ozonation electrocatalytic system of the present invention is capable for converting of air (N_2 and O_2) into reactive NO_x species (both in the forms of

gaseous NO_x and ionic NO_x^-), which are further converted to ammonia at an efficient production rate.

5 Compared with the conventional electrochemical reduction of N_2 , the present invention addresses both the low inherent solubility of N_2 in electrolyte solution and the high activation energy barrier for directly converting N_2 to NH_4^+ .

10 Compared to conventional ammonia synthesis techniques, the system of the present invention creates an NO_x abundant environment around the catalyst, i.e., combined gaseous NO_x and ionic NO_x^- reactants of equilibrium concentration under stable NO_x input from ozone generator and NO_x consumption by ammonium production at a metal-based GDE. This arrangement enables a high ammonia yield with high energy efficiency.

15 Overall, it can be seen that the present invention takes in air and renewable power, producing commercially useful products, namely NH_4^+ (which can be used as a fertiliser, and ozone, a useful sterilising agent).

20 The apparatus and method can be operated in a continuous or intermittent manner without detriment.

Further, by adjusting the operation conditions, the balance between NH_4^+ production and ozone production can be adjusted.

25 The device is thus particularly suited for a role in attaining net-zero emissions in agriculture and participating in independent regional economies as it enables the utilisation of renewable electrons to substitute fossil fuel consumption for mobility in mining and farming applications as well as provide net zero-carbon fertilizer for agriculture. Further, the scalable nature of this invention means this can potentially be used either as a standalone household module or as a large-scale facility to generate ammonium as hydrogen carrier for export.

30 In use, the apparatus successively converts air to nitrogen oxide intermediaries (NO_x) and then to NH_4^+ at ambient conditions with an energy efficiency of 90 kWh/kg of ammonia.

35 Through modulation of system parameters, the present inventors have been able to achieve a maximum NO_x production rate of $166.5 \text{ mmol h}^{-1}$ (8.1 mmol h^{-1} in $0.5 \text{ M K}_2\text{SO}_4$ electrolyte and $158.4 \text{ mmol h}^{-1}$ in gas phase) and O_3 production rate of 2.9 mmol h^{-1} using a

240 L h⁻¹ air flow rate. When adapted with an electrolyser with 1.2 L h⁻¹ flow rate, a high NH₄⁺ yield of ~1.3 mmol h⁻¹ cm⁻² at a cell voltage of 2.5 V was achieved.

5 The flexibility of this coupled system for both wastewater treatment and ammonia production presents a pathway for decarbonisation of remote and regional applications.

10 The combination of a commercially available ozone generator with an electrolyser system to generate renewable ammonia requires significantly less energy input compared to hybrid plasma-electrolyser pathway and do not require critical minerals which will hinder scale-up, for example alternative approaches which rely heavily in the use of Li intermediary NRR solutions. By converting both NO_x intermediaries in gas phase and liquid phase, this invention allows attaining of high production rates with good efficiency.

15 An important first step in the process of the present invention is the generation of O₃ and NO_x species. In this case, a commercial DBD ozone generator (BMT 803N) was used. Similar DBD ozone generators from other manufacturers can also work well for this system, such as 3S-710 (Beijing Tonglin), POZN-10 (Qingdao Pioneer), BF-XD-35 (Suzhuo Jingtuo), CBR2-25G-B1 (Jindawanxiang), MAT Cold plasma ozone generator (MAT Ozone Technology). The effect of inlet air flow rate supplied to the ozone generator upon the
20 production rate of NO_x and O₃ species was determined using combined gas chromatography-mass spectrometry (GC-MS) and ultraviolet-visible (UV-vis) spectroscopy techniques.

The ozone generator-produced gaseous NO_x is composed primarily of N₂O, NO, and NO₂. The exact composition and production rate of which are dependent on the input air flow
25 rate as indicated in **Figure 2a**. Specifically, the gaseous NO₂ production rate increased from 94.4 μmol min⁻¹ to 2034.2 μmol min⁻¹ when the air flow rate increases from 200 mL min⁻¹ to 4000 mL min⁻¹. For gaseous NO production, the production rate increases linearly from 19.9 μmol min⁻¹ to 87.5 μmol min⁻¹ with the air flow rate ranging from 200 mL min⁻¹ to 1000 mL min⁻¹, however, the NO production rate dramatically drops to 2.1 μmol min⁻¹ when the air flow rate
30 reaches 2000 mL min⁻¹. Further increase in air flow rate to 3000 mL min⁻¹ and 4000 mL min⁻¹ does not significantly change the NO production rate. As for the N₂O production rate, that is 5.1 μmol min⁻¹ at air flow rate of 200 mL min⁻¹, which increases to 13.1 μmol min⁻¹ to 17.4 μmol min⁻¹ with air flow rate ranging from 600 mL min⁻¹ to 4000 mL min⁻¹. In addition, it is noted that the gaseous NO_x production rate in the off gas from an absorption tank filled with 1 L 1.0 M
35 K₂SO₄ aqueous solution decreases compared with the off gas directly collected from the ozone generator, indicating that the gaseous NO_x is being partly absorbed in the aqueous solution. Hence, the amount of ionic NO_x species from NO_x absorption were analyzed and quantified

using UV-vis measurement, which confirmed that only nitrate (NO_3^-) was produced without nitrite (NO_2^-) formation.

5 The kinetic investigation of the nitrate production with 4000 mL min^{-1} air input is shown in **Figure 2b**, the NO_x production rate can be observed to increase linearly with a production rate of $134.6 \text{ } \mu\text{mol/min}$. These results validate the practicality of using an DBD ozone generator to produce both gaseous and ionic NO_x from air. The commercial DBD ozonation system outperformed the single reactor glow discharge (SRGD), single reactor spark discharge (SRSD), single reactor glow and spark discharge (SRGSD), and double
10 reactor glow and spark discharge (DRGSD) regarding its energy consumption required for 1 mol NO_x production, i.e., 0.8 kWh/mol NO_x . Therefore, the DBD ozonation system with efficient NO_x production capability builds a platform for subsequent production of NH_4^+ through electrolysis.

15 In addition to NO_x production from air, the DBD system simultaneously produces ozone. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to detect and quantify the ozone produced from the DBD ozonation system. See **Figure 2c** for comparison.

20 The off gas from the ozone generator with varied air input flow rate ranging from 200 mL min^{-1} to 4000 mL min^{-1} was led into the in-situ DRIFTS cell, which is connected to the FTIR spectrometer (Bruker VERTEX 70v) for the collection of spectra. As shown in **Figure 2d**, two features at $\sim 1020 \text{ cm}^{-1}$ and 1055 cm^{-1} were attributed to the O_3 species, the signal of which was significantly enhanced when the air input flow rate increased from 200 mL/min to 4000
25 mL/min , indicating higher O_3 production rate with increased air input. The O_3 production rate under different air flow rate was further quantified based on the obtained in-situ FTIR spectra, which was plotted in **Figure 2e**. It is noted that the O_3 production rate could be enhanced from $0.7 \text{ } \mu\text{mol min}^{-1}$ to $48.0 \text{ } \mu\text{mol min}^{-1}$ by improving the air input flow rate. The O_3 production enhancement was more significant when air flow rate reaches $>1000 \text{ mL min}^{-1}$, which is
30 consistent with the improvement in gaseous NO_2 production rate. This suggests that amount of O_3 in the ozonation system is important to promote NO_x production toward NO_2 . Additionally, the capability of O_3 production at the level of $48.0 \text{ } \mu\text{mol min}^{-1}$ makes the ozonation system an efficient tool in killing bacteria when utilized in treating the irrigation water for agricultural production.

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The DBD ozone generator treated water with aqueous phase NO_x was then mixed with $0.5 \text{ M K}_2\text{SO}_4$ and fed as catholyte into the electrolyzer alongside gas phase NO_x

generated from the ozone generator. The choice of SO_4^- containing electrolyte solution also ensures that the end NH_4^+ as ammonium sulphate, a common fertilizer with a market value of USD \$1.08 billion in 2021.

5 Within the electrolyzer, a gas-diffusion-electrode (GDE) is located. This gas diffusion electrode is prepared with Au sputtered polytetrafluoroethylene (PTFE) coated graphite felt as substrate and Cu deposited nanoparticles prepared using a flame spray pyrolysis (FSP) method as catalyst (details below), which is used as the cathode whereas a commercial Ni foam is used as the anode. The anode and cathode were separated by an anion exchange
10 membrane (Sustainion®, Dioxide Materials).

 The anode was separated from the anion exchange membrane by KOH anolyte (1.0M) whereas the cathode was separated by 0.5 M K_2SO_4 as catholyte as described above.

15 The present inventors have found that in order to achieve good selectivity and yield of NH_3 from the present invention, it is important to have the dissolved NO_x species (particularly NO_2^- and NO_3^-) present in an equilibrium concentration.

 Equilibrium can be reached by pre-purging the catholyte with ozonation output until
20 the desire equilibrium is achieved. This is the preferred approach as no additional chemical dosing is required, the ozonation apparatus is simply run for a time prior to commencing reduction.

 Alternatively, the reaction can be forced to equilibrium more quickly by the addition
25 of a suitable NO_3^- source.

 Once equilibrium is reached, it can be maintained by balancing the rate of NO_x production from the ozonation apparatus with the rate of aqueous NO_x conversion in the electrolytic reduction cell. In this manner, the apparatus can be operated to achieve maximum
30 NH_4^+ production.

 In addition, the present inventors have found that it is important to have a high gaseous NO_x atmosphere in contact with the aqueous NO_x solution in order to maximise NH_4^+ yield.
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Without wishing to be bound by theory, the high gaseous NO_x production is believed to assist in maintaining the desired aqueous equilibrium which maximises NH_4^+ yield. This is illustrated in figure 5.

- 5 The catalysts that can catalyse this reaction include Copper, Bismuth, Tin, Iron and Zinc and their oxides, Copper-Bismuth oxides, Copper-Tin oxides, Copper-zinc oxides, copper-iron oxide, Copper-Bismuth-Tin oxides, Cu single atom catalysts, Bi single atom catalysts, Tin single atom catalysts, Zn single atom, Iron single atom, or combinations of these single atoms (dual atom catalysts). The catalysts can be plasma-treated to induce defects.
- 10 The single atom catalysts may have atoms that are clustered together and may be present as atomic cluster catalysts.

- The catalyst loading can range from 0.1 mg cm^{-2} to 5 mg cm^{-2} with the electrodes can be drop-casted or directly prepared on the substrates using FSP for the case of metal oxide catalysts.
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- The mixed oxide metals can be prepared using wet-chemistry method, flame spray pyrolysis and thermal spraying techniques. Single atom catalysts/atomic cluster catalysts/dual atom catalysts can be prepared using wet chemistry techniques. The substrates can be carbon fiber paper, graphite felt, PTFE, Titanium mesh, platinized titanium mesh, Copper foam, Nickel foam, etc.
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The conductive layer can be gold, silver, etc. or any other suitably inert conductor.

- 25 The linear sweep voltammetry (LSV) curve over the Cu-based GDE in the electrolyzer with NO_x supplied by the DBD ozone generator is shown in **Figure 3a**, displaying a current density (j) of $\sim 400 \text{ mA cm}^{-2}$ at an applied potential of -2.5 V , while j of $\sim 1000 \text{ mA cm}^{-2}$ at an applied potential of -3.2 V . Constant electrolysis at fixed potentials ranging from -2.1 V to -3.1 V , was then carried out, with the respective current density displayed in **Figure 3b**,
- 30 showing that more negative applied potential resulted in improved current density. Additionally, the stable current density during the measurement indicated the good stability of the catalyst and coupled ozonation-electrolyzer system. Moreover, it is noted that increasing cathodic potential from -2.1 V to -2.5 V leads to an increase in Faradaic efficiency of NH_4^+ ($\text{FE}_{\text{NH}_4^+}$) from 46.6% to 67.6% (**Figure 3c**). Nevertheless, the $\text{FE}_{\text{NH}_4^+}$ decreases with
- 35 more negative applied potential from -2.7 V to -3.1 V , i.e., 41.9% and 21.3%, respectively. Additionally, the highest current density toward NH_4^+ ($j_{\text{NH}_4^+}$) reached 283 mA cm^{-2} at -2.5 V , which corresponds to the highest NH_4^+ production rate of $1320 \text{ } \mu\text{mol cm}^{-2} \text{ h}^{-1}$ (**Figure 3d**). By

adding up the energy consumption for NO_x production and electrochemical NH_4^+ production, the total energy consumption (kWh) for producing 1 kg NH_4^+ is plotted according to the applied potentials (from -2.1 V to -3.1 V). Specifically, the coupled ozonation-electrolysis system operated the most efficiently under applied potentials at -2.3 V and -2.5 V, achieving energy consumption of 91.7 and 94.2 kWh for producing 1 kg NH_4^+ , respectively.

The high NH_4^+ production rate and low energy consumption of the coupled ozonation-electrolysis system make it attractive among the reported electrolysis-based ammonia production techniques, such as the nitrate reduction reaction (NO_3RR), direct electrochemical nitrogen reduction reaction (eNRR),⁸ plasma-assisted NO_x reduction reaction (plasma-assisted NO_xRR) and Li-mediated nitrogen reduction reaction (Li-mediated NRR). (Figure 3e). In addition to the relatively low energy consumption of the DBD ozone generator for producing NO_x , it is postulated that the co-feed of gaseous NO_x (NO , N_2O , and NO_2) together with the ionic NO_x (NO_3^- and NO_2^-) to the Cu catalysts in the electrolyzer set-up also plays an important role in promoting the NH_4^+ production while contributed to the energy efficiency of the coupled system. (Figure 3f).

I-t curves of Cu-based GDE were tested using a flow-cell electrolyser under applied potential of -2.5 V with catholyte containing 0 to 3 times of standard aqueous NO_x^- equilibrium concentration with gaseous NO_x input (Figure 3g).

As indicated in Figure 3h, when the NO_x equilibrium concentration is low, current density and efficiency are low. Increasing the NO_x equilibrium to a certain level maximizes the NH_4^+ production rate, however, exceeding that ratio, not only is not further benefit achieved, but in fact a decrease in ammonia production is observed. The optimal initial aqueous NO_x concentration for maximum NH_4^+ rate was found to be 10.0mM NO_2^- /1.7mM NO_3^- . It can be seen that at 0.5 times this concentration, the production rate is sufficiently less, whereas doubling or even tripling the concentration leads to a diminished NH_4^+ production rate.

Figure 3(i) The energy efficiency of the integrated ammonium production system under different applied potentials.

Figure 3 (j) shows the Ammonia production rate and energy consumption for the present system compared to other NRR and NO_xRR systems described in the literature i.e., conventional eNRR; Li-intermediary NRR; plasma-assisted NRR; NO_3RR ; and NORR.

It is to be noted that in the prior art, a carrier gas is typically required in order to assist in the dissolution of NO_x species prior to reduction. However, the present invention uses ozone to generate suitable gas species which can directly dissolve in aqueous solutions. The present invention requires no additional gas source other than the air that is consumed by the ozone generating apparatus.

Without wishing to be bound by theory, the movement of species across the membrane, between the gaseous feed side and the catholyte, when the device is in operation is shown in figure 3k(i). Again, without wishing to be bound by theory, figure 3k(ii) shows the mechanistic steps at the catalyst surface during the electrolytic reduction of NO_x species.

The Cu based GDE was characterized by a combination of ex-situ and in-situ characterization techniques. The SEM images of the Cu-based GDE is shown in **Figure 4a**, indicating that the Cu particles are deposited on the carbon fiber structures.

The high-resolution TEM (HR-TEM) images (**Figures 4b-c**) shows the Cu catalyst is present as CuO particles (with lattice distance of 0.23 nm attributed to CuO(111) facet) with diameter of 10 to 20 nm and the HAADF-STEM images (**Figure 4d**) and STEM-EDS maps (**Figures 4f-g**) further confirms the Cu catalysts are in the form of CuO (well dispersed Cu and O elements) and surrounded by the carbon black.

To further study the Cu catalyst properties under reaction conditions, the synchrotron-based *in-situ* powder diffraction (PD) experiments were conducted in a custom-built *in-situ* cell equipped with the as-prepared Cu-based GDE as working electrode for electrochemical ammonia production. The cell is filled with aqueous electrolyte containing 0.1 M KNO₃ and 0.5 M K₂SO₄ and operated at -200 mA/cm² for 30 min, while the PD spectra was collected per 5 min. The spectra collected at 0 min, 15 min, and 30 min are shown in **Figure 4h**. Specifically, all spectra exhibited the characteristic peaks of Au (111), Au (002), and Au (022) (COD code: 96-901-2431), which are attributed to the sputtered Au in the substrate.

For the catalysts prior to reaction (0 min), the catalysts exhibited a series CuO characteristic peaks, i.e., CuO (002), CuO (111), CuO (20-2), CuO (202), CuO (11-3), CuO (02-2), and CuO (113) (COD code: 96-101-1149). For the spectrum collected after 15 min reaction, the characteristic peaks of Cu₂O (111), Cu₂O (002), Cu (111), and Cu (002) (COD code: 96-900-7498 and 96-710-1265, respectively) appear with intensity decrease of aforementioned CuO characteristic peaks. This suggests the partial reduction of the original CuO

phase to Cu_2O and Cu species during the reaction. Interestingly, the PD spectrum of the catalyst after 30 min only exhibited Cu species attributed to metallic Cu while no Cu_2O and CuO were detected. This proves that the catalysts would be stable in metallic Cu phase during the reaction.

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Materials

All chemical reagents and solvents utilized in this work were used as received and without any further purification. Deionized water (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used in all experiments.

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Catalyst Synthesis

The Cu-based catalyst was synthesized using a flame spray pyrolysis (FSP) method.

A copper precursor solution comprised of copper 2-ethylhexanoate (Sigma-Aldrich, 92.5–100%) in xylenes (Sigma-Aldrich, reagent grade) was prepared in a manner that the Cu concentration in solution was 0.5 M. This precursor solution was fed to the FSP system with a flow rate of 5 mL min^{-1} using a syringe pump and was atomized using an oxygen flow of 5 mL min^{-1} (Coregas, 99.9%). The flame was ignited and maintained with a supporting flame mixture which consisted of 3.2 L min^{-1} oxygen and 1.5 L min^{-1} methane (Coregas, 499.95%). The flame was directed with the aid of a 5 L min^{-1} flow of oxygen and a vacuum pump toward a glass fiber filter, where the CuO nanomaterials were deposited and collected.

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Then, the synthesized Cu catalyst powder was mixed with carbon black with a weight ratio of 1:1 in ethanol aqueous solution (volume ratio of ethanol and water was 1:1), where the Nafion solution (5 %wt.) was added in to achieve Cu catalyst and Nafion weight ratio of 10:1. The as-prepared Cu/carbon/Nafion ink was sprayed onto an Au-coated graphite felt (graphite thickness of 4.7 mm with 100 nm gold layer) to construct the gas diffusion electrode. The loading Cu catalysts is controlled to be 0.1 mg cm^{-2} .

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NO_x production experiments

The NO_x production experiment was conducted using ozone generator (BMT 803N) under operating power of 135 W. The feed gases for NO_x production are air and O₂, the flowrates of which are controlled by gas flowmeters in a range of 0.2 to 4.0 L min^{-1} .

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Electrochemical experiments

All electrochemical measurements were carried out using an Autolab potentiostat PGSTAT204 (Methrohm) equipped with a current/voltage booster (Booster10A). The Cu-

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based GDE was applied as the working electrode for a customized two-electrode flow-cell electrolyzer, while the Ni foam was used as the counter electrode. The counter electrode and working electrode was separated using an anion-exchange-membrane (AEM, Dioxide Materials). The electrolyzer used 1.0 M KOH as anolyte while used 0.5 M K₂SO₄ as catholyte, respectively at a flow rate of 9.5 mL min⁻¹. Note all *j* reported herein is normalized to the geometric surface area without any *i*R compensation.

Product Analysis

Post-reaction, 0.5 mL of catholyte was collected for analysis using indophenol-blue test to determine NH₄⁺ concentration. The catholyte was pipetted into a 1.5 mL sample tube followed by the addition of (i) 0.4 mL of 1M sodium hydroxide solution (Sigma Aldrich, 99.99%) that consists of 5 wt.% salicylic acid (Sigma Aldrich, 99.99%), 5 wt.% sodium citrate (Sigma Aldrich, 99.99%), (ii) 0.1 mL of 0.05M sodium hypochlorite solution (Sigma Aldrich, 99.99%) and (iii) 30 µL of 1 wt.% sodium nitroferricyanide solution ((Sigma Aldrich, 99.99%), sonicated thoroughly and incubated in the dark at room temperature for a duration of two hours. Dilution of the electrolyte was required as ammonia concentration was high. Afterwards, a Shimadzu UV-3600 UV-vis-NIR spectrophotometer was employed to quantify the amount of ammonia being produced from the electrocatalysis process. The absorbance readings between 550 to 850 nm wavelengths were measured. By using the peak absorbance reading, the performances of all catalysts in generating ammonia were assessed in terms of Faradaic efficiency, and ammonia yield.

Physical characterization

The morphology of CuO was investigated using a scanning electron microscope (FEI Nova NanoSEM 450 FE-SEM) and a high-resolution transmission electron microscope (HR-TEM) JEOL 2100F operating at 200 kV. XRD was carried out using PANalytical X'Pert instrument using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) with a scan range from 10° to 90°. Surface chemical composition was evaluated using XPS with a Thermo ESCALAB250i X-ray photoelectron spectrometer. To prepare the working electrode, a catalyst ink was prepared by dissolving 1.25 mg of CuO in 0.5 mL of deionized water, 0.5 mL of ethanol and 50 µl Nafion® 117 solution (~5% Nafion) by sonication. The catalyst ink was drop-casted on the working area on the = and dried overnight (catalyst loading: ~0.1 mg cm⁻²).

Energy requirements

The relatively low energy consumption of this coupled ozonation-electrolysis system enables effective operation to be carried out under solar power alone. Experiments have

shown an encouraging ammonia production of $136.1 \mu\text{mol cm}^{-2} \text{h}^{-1}$ was achieved when the apparatus was powered by a photovoltaic panel under 1 Sun irradiance. Figure 6 shows the ammonia production performance of the Cu GDE in coupled ozonation-electrolysis system powered by a photovoltaic panel under 1 Sun irradiance.

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Claims:

1. A method of producing ammonia and/or ammonium comprising:
 - i) ozonation of air to produce a product gas stream comprising ozone and gaseous NO_x species; and
 - ii) electrolytically reducing the gaseous NO_x species by passage from a gas side of a gas diffusion electrode to a catholyte thereby to produce NH_4^+ or NH_3 ; andwherein the gas diffusion electrode comprises a metal/metal oxide single atom or dual atom catalyst electrode.
2. A method of producing ammonia and/or ammonium comprising:
 - i) obtaining a gaseous waste stream comprising gaseous NO_x species; and
 - ii) electrolytically reducing the gaseous NO_x species by passage from a gas side of a gas diffusion electrode to a catholyte thereby to produce NH_4^+ or NH_3 ; andwherein the gas diffusion electrode comprises a metal/metal oxide single atom or dual atom catalyst electrode.
3. A method according to claim 1 or claim 2 wherein the gaseous NO_x pass through the gas diffusion electrode to and into a catholyte to produce dissolved NO_x^- species which are reduced to provide NH_4^+ and dissolved NH_3 .
4. A method according to any one of the preceding claims wherein undissolved NO_x species are present in contact with the catholyte.
5. A method according to any one of the preceding claims wherein the gaseous NO_x species comprise one or more of NO , N_2O and NO_2 .
6. A method according to claim 3 wherein the dissolved NO_x^- comprises nitrate (NO_3^-) and nitrite (NO_2^-) ions.
7. A method according to claim 6 wherein the NO_3^- and NO_2^- are in a steady state equilibrium.
8. A method according to any one of the preceding claims wherein electrolysis is commenced when the concentrations of NO_3^- and/or NO_2^- are at a predetermined level.

9. A method according to claim 7 or claim 8 wherein NO_3^- is present in a concentration of 1.7mM and/or NO_2^- is present in a concentration of 10.0mM when electrolysis is commenced.
10. A method according to any one of claims 7 to 9 wherein NO_3^- is present in a concentration of 1.7mM and NO_2^- is present in a concentration of 10.0mM thereafter for the duration of electrolysis.
11. A method according to any one of the preceding claims when the catholyte is under an atmosphere comprising NO_x .
12. A method according to claim 1 wherein the ozone is diverted for use e.g., as a sterilizing agent, e.g., for wastewater.
13. A method according to claim 1 wherein the ozonation of air is by dielectric barrier discharge.
14. A method according to any one of the preceding claims further including introducing CO_2 to react with the produced ammonia.
15. A method according to any one of the preceding claims wherein the metal/metal oxide single atom or dual atom catalyst electrode is selected from one or more of Cu single atom catalysts, Bi single atom catalysts, Tin single atom catalysts, Zn single atom, Iron single atom, CuBi, CuSn, CuZn, CuFe, BiSn, BiZn, BiFe, SnZn, SnFe, ZnFe dual atom and/or oxides thereof.
16. An apparatus for ammonia production comprising:
an ozone generator; and
an electrolyser and wherein the output of the ozone generator is fed to a catholyte of the electrolyser via a gas diffusion electrode.
17. An apparatus according to claim 16 wherein the output of the ozone generator is fed to the catholyte of the electrolyser directly as gas phase and aqueous phase.
18. An apparatus according to claim 16 or 17 wherein the ozone generator is a dielectric barrier discharge (DBD) ozone generator.

19. An apparatus according to any one of claims 16 to 18 further including a feed unit, such as a fan or pump, to supply air to the module, said air being a feed gas for the ozone generator.

20. A method according to any one of claims 1-5 or an apparatus according to any one of claims 16-19 wherein the gas diffusion electrode comprises:

- a support;

- a conductive layer coated on the support;

- a gas permeable membrane coated on the support, wherein the gas permeable membrane is impregnated with a single metal catalyst.