Indirect electrosynthesis of ammonia from nitrogen and water by a magnesium chloride cycle at atmospheric pressure

Efficient N₂ fixation is essential for achieving sustainable NH₃ synthesis. Hu et al. propose using Mg, an industrial product of MgCl₂ electrolysis, to fix N₂, and the suggested MgCl₂ cycle facilitates a scalable, low-energy, and C-free synthesis of NH₃ from N₂ and H₂O at atmospheric pressure.

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**Highlights**

- A cycle based on electrolysis of molten MgCl₂ for nitrogen fixation
- Low energy and scalable indirect electrosynthesis of NH₃ at air pressure
- Preparation of pure NH₃ through a solid/solid reaction between Mg₃N₂ and NH₄Cl
Indirect electrosynthesis of ammonia from nitrogen and water by a magnesium chloride cycle at atmospheric pressure

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SUMMARY
Artificial N₂ fixation is one of the most important industrial processes for human beings. However, the current Haber-Bosch process based on fossil fuel suffers from unsustainability and a low N₂ to NH₃ conversion. Here, we report a magnesium chloride cycle for the synthesis of NH₃ from N₂ and H₂O at atmospheric pressure. In this cycle, N₂ reacts with Mg to form Mg₃N₂. Mg and Cl₂ are produced by the electrolysis of molten MgCl₂. NH₄Cl is used to hydrogenolyze Mg₃N₂ to produce NH₃, with anhydrous MgCl₂ being regenerated. The cycle is closed via the reverse Deacon reaction to convert Cl₂ to HCl, which is captured as NH₄Cl with the recyclable NH₃. This indirect electrosynthesis produces NH₃ at an industry-acceptable rate with zero CO₂ emission, a coulombic efficiency >92%, and an energy consumption of 14.1 kWh/kg-NH₃.

INTRODUCTION
In the early 1900s, Haber and Bosch succeeded in synthesizing ammonia (NH₃) through a high-temperature (~500°C) and high-pressure (~170 bar) catalytic reaction between N₂ and H₂; this has revolutionized the industrial manufacture of fertilizer. Its impact is underscored by the fact that ~50% of the N₂ atoms in humans today originate from this synthesis. However, the Haber-Bosch (HB) process consumes ~2% of the world’s power production from fossil fuels and led to the release of >450 million metric tons of CO₂ in 2016. Moreover, with the population increase and growth of the economy, it has been estimated that the global production of NH₃ will increase ~80% to 236 million metric tons by 2050. Therefore, the HB process for NH₃ synthesis could cause serious energy and environmental problems if significant scientific advances are not achieved.

There have been attempts to replace the HB process by an electrolytic approach for more sustainable NH₃ synthesis, which recently became increasingly attractive in the context of energy storage for renewables, considering NH₃ is a good H₂ carrier for the future H₂ economy. Unfortunately, past efforts to directly reduce N₂ on an electrode under ambient conditions encountered industrially unacceptable low NH₃ synthesis rates (<10⁻¹⁰ mol • cm⁻² • s⁻¹), while the target rate is 0.4–1 × 10⁻⁷ mol • cm⁻² • s⁻¹ (or an electrolysis current of 0.25–0.5 A cm⁻², with a current efficiency >50%). It was reported that the electrosynthesis of NH₃ from N₂ and H₂ using molten chloride electrolytes at elevated temperatures could be faster (~10⁻⁸ mol • cm⁻² • s⁻¹), but the result may be flawed, according to a recent investigation. The claim of NH₃ synthesis from N₂ of only a very small amount should be carefully verified by ¹⁵N tracing to avoid false positives.
Recently, it was reported that an indirect electrochemical \(\text{NH}_3\) synthesis, based on electrolyzing molten LiOH into Li, \(\text{O}_2\), and \(\text{H}_2\text{O}\), and using Li to fix \(\text{N}_2\) into \(\text{Li}_3\text{N}\), shows potential advantages of both high speed (\(\sim 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}\)) and coulombic efficiency (88.5%). However, because of the highly corrosive nature of strong bases, the unwanted cathodic reduction of \(\text{OH}^-\) and the inevitable dissolution of the anodic \(\text{H}_2\text{O}\) into the melt (which deteriorates the electrolyte quickly due to its high reactivity with Li), the electrolysis of molten hydroxides has been replaced by that of molten chlorides for the industrial production of alkali metals.

Thus far, the reported direct and indirect electrolytic processes for \(\text{NH}_3\) synthesis have not met the requirements for practical applications because of low productivity, low coulombic efficiency, and/or high energy consumption. Here, we propose a \(\text{MgCl}_2\) cycle (MCC) for the fast, unpressured synthesis of \(\text{NH}_3\) from \(\text{N}_2\) and \(\text{H}_2\text{O}\), as schematically shown in Figure 1A. The MCC process produces \(\text{NH}_3\) with a coulombic efficiency of 96% and an electrolysis energy consumption of...
RESULTS AND DISCUSSION

The MCC process

The main stress of the HB process is the simultaneous catalytic dissociation of $\text{N}_2$ triple bond and hydrogenation. 28,29 The HB process requires a relatively high temperature to facilitate the dissociative adsorption of $\text{N}_2$, which has led to the net decomposition of $\text{NH}_3$ product on the catalyst surface; therefore, an ultra-high pressure is required to push forward the reaction. 29 We are engaged in relieving this stress by distributing the tasks into separated $\text{N}_2$ fixation and hydrogenation, and Figure 1B displays the thermodynamic analysis of each step in the MCC process, including Reactions 1, 2, 3, 4, and 5, where the thermodynamic data were calculated using HSC version 6.0.

\[
\text{MgCl}_2(\ell) = \text{Mg}(\ell) + \text{Cl}_2(g) \quad (\text{DG}^\circ = 512.2 \text{ kJ/mol at 973K})
\] (Reaction 1)

\[
3\text{Mg}(\ell) + 2\text{N}_2(g) = \text{Mg}_3\text{N}_2(\text{DG}^\circ = -263.6 \text{ kJ/mol at 973K})
\] (Reaction 2)

\[
3\text{Cl}_2(g) + 3\text{H}_2\text{O}(g) = 6\text{HCl}(g) + 1.5\text{O}_2(g) \quad (\text{DG}^\circ = -21.5 \text{ kJ/mol at 973K})
\] (Reaction 3)

\[
\text{HCl}(g) + \text{NH}_3(g) = \text{NH}_4\text{Cl}(\text{DG}^\circ = -17.0 \text{kJ/mol at 573K})
\] (Reaction 4)

\[
\text{Mg}_3\text{N}_2 + 6\text{NH}_4\text{Cl} \xrightarrow{\text{3MgCl}_2 + 8\text{NH}_3(g)} (\text{DG}^\circ = -789.5 \text{kJ/mol at 773K})
\] (Reaction 5)

It can be seen that among all of these steps, only Reaction 1 is nonspontaneous, which can be achieved by the mature industrial process—in other words, electrolysis of $\text{MgCl}_2$ in molten chlorides. 30,31 The cathodic Mg is then used to fixate $\text{N}_2$ into $\text{Mg}_3\text{N}_2$ (Reaction 2), which is known to be kinetically feasible. Reaction 3 is the reverse Deacon reaction. It has been developed to convert $\text{Cl}_2$ to $\text{HCl}$, noting here that $\text{Cl}_2$ is the anodic product of the electrolysis (Reaction 1), and $\text{HCl}$ can provide protons for the hydrogenolysis of $\text{Mg}_3\text{N}_2$ and $\text{Cl}^-$ ion for the regeneration of $\text{MgCl}_2$. However, as discussed in detail later, the key point is to reveal an efficient route for the production of pure $\text{NH}_3$ and regeneration of anhydrous $\text{MgCl}_2$, for which we conceived an $\text{NH}_4\text{Cl}$ intermediated reaction between $\text{Mg}_3\text{N}_2$ and $\text{HCl}$ (Reaction 5). The $\text{NH}_4\text{Cl}$ can be prepared by depositing $\text{HCl}$ from Reaction 3 using $\text{NH}_3$ (Reaction 4). In principle, the process shown in Figure 1 can be feasible by replacing $\text{MgCl}_2$ with some other alkali or alkaline earth metal chlorides, such as $\text{LiCl}$ and $\text{CaCl}_2$. However, $\text{MgCl}_2$ is more abundant and cheaper, and has a lower decomposition voltage (Table S1), and therefore is beneficial to energy and cost savings. In addition, Mg is much safer than Li and Ca. Although $\text{Cl}_2$ is a widely used industrial chemical, it has corrosive and toxic properties, and care should be taken to avoid leakage during handling in the laboratory.

$\text{MgCl}_2$ electrolysis

In this work, we tested the electrolysis of $\text{MgCl}_2$ at a rate that is suitable for the scalable synthesis of $\text{NH}_3$. A reference is in the present chlorine alkali industry, 33 which typically proceeds at a rate of 0.2–0.4 A/cm\(^2\). The electrolyte studied here was a molten mixture of $\text{MgCl}_2$-$\text{NaCl-KCl}$ (5:3:2 molar ratio) at 973 K. The decomposition voltage was determined to be ~2.6 V, according to voltammograms recorded on a Mo wire cathode and graphite rod anode, as shown in Figure S1. It is slightly higher than the thermodynamic expectation for pure $\text{MgCl}_2$ because of the lower activity of $\text{MgCl}_2$ in the mixture melt.
The electrolysis was carried out with a Mo sheet cathode at current densities ranging from 0.2 to 1.0 A/cm² (see Figure 2A), and the cell voltage changed from 2.75 to 3.46 V, which is expected from polarizations in the cell, including those from ohmic resistance and electrode kinetics. Furthermore, as can be seen in Figure 2A, the measured cell voltage fluctuated more significantly with increases in the current density. This phenomenon is indicative of gas bubbling due to the increasing evolution of Cl₂ on the anode.

With the electrolysis proceeding, the cell voltage slightly declines. This can be explained by the formation of Mg beads (Figure S2A) on the electrode, leading to an increase of the electrochemical reaction interface. Upon formation and growth, these liquid Mg beads will float on the melt, which is collected by pumping in industry.

In this work, the product, a merged Mg ball (Figure S2B), was taken out after cooling down, which was immersed into a dilute HCl solution to produce H₂ for a determination of the electrolysis efficiency. The electrolysis shows a high coulombic efficiency of 92% and 95% at the current density of 0.2 and 1.0 A/cm², respectively (Figure 2B), which is in line with that reported in industrial electrolysis. 34

N₂ fixation with Mg

N₂ can be easily fixated by Mg. For example, the combustion of Mg in N₂ can be achieved after the ignition of Mg in air (Figure S3). However, the combustion is somewhat uncontrollable for practical production. For a mild reaction, the condition required for a complete reaction between Mg and N₂ was investigated. It was found that at temperatures >973 K, Reaction 2 proceeded very quickly. According to X-ray powder diffraction (XRD) analysis (Figure 3A), it took only ~1 h for a 0.5-mm-thick Mg sheet (~1 g) to be fully nitrided, generating yellow Mg₃N₂ product (inset in Figure 3B). The conversion of Mg to Mg₃N₂ was then quantitatively determined by reacting the product with water (Reaction 6) followed by titration (Figure S4) and spectrophotometric Nessler (SN) analysis (Figure S5) of the dissolved NH₃ after removal of the Mg(OH)₂ precipitate. It was confirmed that the 1-h reaction at 973 K could lead to ~100% conversion of Mg to Mg₃N₂, according to Reaction 2 (Figure 3B).

\[
\text{Mg₃N₂ + 6H₂O = 3Mg(OH)₂ + 2NH}_3 \quad (\text{DG}^0 = -709.5 \text{ kJ/mol at 298 K})
\]  
(Reaction 6)

At temperatures <873 K, the Mg sheet retained its metallic color even after several hours of heating, and the NH₃ detection indicated that only a very small fraction of
Mg has been nitrided. It is thought that at lower temperatures, when Mg is a solid, Mg$_3$N$_2$ formed on the surface could effectively retard further N$_2$ access to the metal underneath. However, at higher temperatures, Mg becomes a liquid and easily deforms to allow further reaction; in fact, the generated Mg$_3$N$_2$ at 973 K was not a compact film but took the form of a powder (Figure S6).

These results indicate that a reaction temperature above the melting point of Mg is essential for the rapid and complete nitridation of Mg. However, the MCC process may not need very much external heat for this step because the electrolysis produces molten Mg, which can be directly fed for the nitridation. An initial heating of the N$_2$ gas to ~973 K may be necessary, but the required heat (20.6 kJ/mol) only accounts for 4.2% of that released by Reaction 2 (487.5 kJ/mol). Therefore, once initiated, the reaction would proceed in a self-propagating manner. For industry-scale production, the reactor should be well designed to avoid violent combustion.

**NH$_3$ synthesis from Mg$_3$N$_2$**

If hydrolysis (Reaction 6) is used for NH$_3$ synthesis, the produced Mg(OH)$_2$ should be converted to MgCl$_2$ for a closed loop, which requires, for example, HCl. Alternatively, the hydrogenolysis of Mg$_3$N$_2$ directly in a HCl solution was tested, which was faster than the hydrolysis in water. HCl is a cheap industrial product, but interestingly, as the MgCl$_2$ electrolysis generates Cl$_2$ at the anode, the reverse Deacon reaction can realize an on-the-spot synthesis of HCl from the Cl$_2$ gas and water vapor. It is worth pointing out that Reaction 3 is a rapid and reversible reaction, and the Deacon reaction has many important applications in current industries. The study of the reverse Deacon reaction has a long history, aiming at a thermochemical cycle for economic H$_2$ production from water. According to previous studies, the reverse Deacon reaction could convert Cl$_2$ to HCl with a conversion ratio of ~95% at elevated temperatures (Table S2), and the synthesis can continually proceed at a HCl production rate of 10$^{-6}$ mol • cm$^{-2}$ s$^{-1}$. However, two difficulties arise from the above wet NH$_3$ generation: one is the separation of NH$_3$ from water and the other is the dehydration of MgCl$_2$. In particular, the latter has long remained an issue in industrial MgCl$_2$ electrolysis. The electrolysis requires anhydrous MgCl$_2$, but the natural MgCl$_2$ comes from seawater, whose dehydration is rather difficult and accounts for ~50% of the total energy.
A huge amount of energy will be saved if anhydrous MgCl₂ can be directly regenerated. Therefore, the goal is to find a dry process, a n d t o d o s o , w e c h e c k t h e g a s - s o l i d r e a c t i o n b e t w e e n HCl and Mg₅N₂ (Reaction 7).

$$\text{Mg}_5\text{N}_2 + 6\text{HCl} (g) = 3\text{MgCl}_2 + 2\text{NH}_3 (g) \quad \Delta G^\circ = -844.0 \text{ kJ/mol at 298 K}$$

(Reaction 7)

Reaction 7 has a high thermodynamic expectation, but according to our observations, there are two main obstacles for this reaction to take place. One is the kinetic difficulty. This gas-solid reaction has difficulty reaching completion at relatively low
temperatures. For example, at 473 K, no visible reaction between the HCl gas and Mg₃N₂ powders was observed (inset in Figure 4A, left). By increasing the temperature to 973 K, the yellow Mg₃N₂ powder changed to white immediately (inset in Figure 4A, right), indicating the conversion of Mg₃N₂ to MgCl₂. Even after reaction for 5 h, there was still much unreacted Mg₃N₂ according to the XRD analysis (Figure 4A), and the maximum conversion of Mg₃N₂ to MgCl₂ was determined to be 90% (Figure 4B). It was found that the generated MgCl₂ sintered seriously as well (Figure S7), likely due to the intense reaction heat released (for example, ΔH° = −998.4 kJ/mol at 673 K). The sintered MgCl₂ encloses unreacted Mg₃N₂ and prevents it from the access of the HCl gas. Another obstacle of the gas-solid reaction comes from the combination reaction between the NH₃ product and the HCl feed, which deposited NH₄Cl at any cooler part of the reactor (Figure S8), making the process difficult to control and the NH₃ product difficult to separate.

To bypass the above difficulties arising from the aqueous-solid and gas-solid processes, we propose an NH₄Cl intermediate reaction between Mg₃N₂ and HCl, noting that NH₄Cl in industry can be produced by the reaction between NH₃ and HCl (Reaction 4). In the present work, the deposition of NH₄Cl may also assist in the separation of HCl from Reaction 3, conducive to a positive equilibrium shift of the reverse Deacon reaction. In principle, this solid-solid reaction has many desirable advantages compared to the aqueous-solid and gas-solid reactions, as listed in Table 1. Its heat effect is significantly lower (ΔH° = −44.0 kJ/mol) than that of the gas-solid reaction, so the sintering of MgCl₂ can be avoided. It generates NH₃ as the only gas in the process; therefore, it is easy to separate. Interestingly, to our knowledge, Reaction 5 is the first reaction reported that could effectively generate pure NH₃. In contrast, the aqueous process requires separation of NH₃ from water, which is difficult considering the huge solubility and large heat of dissolution of NH₃ in water. In the traditional HB process, the conversion from N₂ + H₂ to NH₃ is only ~15%; thus, the separation of NH₃ is also difficult and energy intensive. Moreover, the NH₄Cl·Mg₃N₂ reaction generates anhydrous MgCl₂ as the only solid product, which can be directly fed back into the electrolyzer, distinguishing this solid-solid process from any wet processes.

The feasibility of Reaction 5 was experimentally checked. The stoichiometric mixture of Mg₃N₂ and NH₄Cl powders was heated to different temperatures, and the gaseous product was absorbed by water. Then, the NH₃ yield was determined by acid titration, which was also checked by spectrophotometric analysis. At 473 K, it was found that after 90 min, the original khaki-colored mixture changed to light yellow, as shown in Figure 4C. The reaction nearly ran out of Mg₃N₂ and NH₄Cl, according to the XRD analysis. However, the main solid product was complexes of MgCl₂ and NH₃ (Figure 4D), namely, MgCl₂(NH₃)_x, and the generated NH₃ was only ~20% of that expected. This is because some MgCl₂(NH₃)_x are stable at relatively
low temperatures, which require a temperature of \( \sim 773 \, \text{K} \) to fully decompose.\(^{42}\) It was found that after 50 min of heating at 773 K, the solid product became pure anhydrous MgCl\(_2\), and the NH\(_3\) yield reached at \( \sim 100\% \) (Figure 4E).

This study indicates that the combination of Mg\(_3\)N\(_2\) and NH\(_4\)Cl is quite easy, but it should be pointed out that NH\(_4\)Cl is unstable at 773 K or higher temperatures. Therefore, to prevent the self-decomposition of NH\(_4\)Cl during a large-scale reaction, it is suggested that the reactants be mixed well to facilitate the combination reaction, or to operate the reaction in two stages: at a relatively low temperature for the combination, followed by a high-temperature decomposition to release NH\(_3\).

Since the decomposition of NH\(_3\) to N\(_2\) and H\(_2\) at 773 K is thermodynamically spontaneous, the near-100\% yield of NH\(_3\) through Reaction 5 indicated that this thermal decomposition may be difficult kinetically. For further evidence, the H\(_2\) concentration in the synthesized NH\(_3\) was determined by gas chromatography (GC), which revealed a decomposition percentage of merely \( \sim 0.003\% \) (Figure S9). Zhang et al.\(^{43}\) also revealed that NH\(_3\) was difficult to decompose without a catalyst. A decomposition percentage of 0.7\% at 973 K was reported, which is higher than what we observed because of the higher decomposition temperature. In this regard, the relatively low heat effect of Reaction 5 is another advantage, which helps maintain the temperature but would not lead to thermal runaway during large scalable synthesis.

Isotope-labeled proton nuclear magnetic resonance (\(^1\)H NMR) studies were also performed to confirm the conversion of N\(_2\) to NH\(_3\) via Mg\(_3\)N\(_2\). Single-pulse \(^1\)H NMR spectra of 3 NH\(_3\) samples collected from reactions of Mg\(_3\)\(^{15}\)N\(_2\) + \(^{14}\)NH\(_4\)Cl (S1), Mg\(_3\)\(^{15}\)N\(_2\) + \(^{15}\)NH\(_4\)Cl (S2), and Mg\(_3\)\(^{14}\)N\(_2\) + \(^{14}\)NH\(_4\)Cl (S3) are compared in Figure 4F. Mg\(_3\)N\(_2\) was synthesized by the reaction between Mg and specific N\(_2\) (Reaction 2), and NH\(_4\)Cl was used as received. The NH\(_3\) (in the form of NH\(_4^+\)) solution from Mg\(_3\)\(^{14}\)N\(_2\) + \(^{15}\)NH\(_4\)Cl displayed the typical three symmetric signals of \(^{14}\)NH\(_4^+\) in the chemical shift range between 7 and 7.4 ppm,\(^{44}\) indicating negligible \(^{15}\)N in commercial N\(_2\) and NH\(_4\)Cl. In the case of Mg\(_3\)\(^{15}\)N\(_2\) + \(^{15}\)NH\(_4\)Cl, dominant peaks were the two symmetric signals of \(^{15}\)NH\(_4^+\), but three small signals of \(^{14}\)NH\(_4^+\) were also distinct, similar to that reported by Andersen et al.,\(^{23}\) which can be ascribed to the 2\% \(^{14}\)N impurity in total N of the \(^{15}\)N reagents. By replacing \(^{15}\)NH\(_4\)Cl with \(^{14}\)NH\(_4\)Cl to react with Mg\(_3\)\(^{15}\)N\(_2\), the relative signal intensity of \(^{14}\)NH\(_4^+\) became stronger, but those of \(^{15}\)NH\(_4^+\) were still strong. The NMR of the reaction-generated sample S1 (NH\(_3\) + H\(_2\)SO\(_4\) in d\(_6\)-DMSO) had an average \(^{14}\)NH\(_4^+\)/\(^{15}\)NH\(_4^+\) peak area ratio of 3.8, which is comparable to the value 3 of the standard sample (NH\(_4\)Cl + H\(_2\)SO\(_4\) in d\(_6\)-DMSO) with a \(^{14}\)NH\(_4^+\)/\(^{15}\)NH\(_4^+\) concentration ratio of 3:1 (Figure S10). This roughly confirms the hydrogenolysis of Mg\(_3\)N\(_2\) by NH\(_4\)Cl according to Reaction 5.

It should be pointed out that when these isotope tracing experiments confirmed that the N of the Mg\(_3\)N\(_2\) can be converted to NH\(_3\) by reaction with NH\(_4\)Cl, it would be difficult for these data to make a precise quantification. It has proven that the precise quantification of ammonium can be achieved only when series conditions, such as internal standard, relaxation delay time, signal acquisition time, acid concentration, pulse program, and instrumental settings, are strictly controlled and match each other, rendering conventional NMR not suitable for the NH\(_4^+\) quantification.\(^{23}\) Fortunately, the reactions in the present work generated large amounts of NH\(_3\), with the concentration of NH\(_3\) water reaching as high as 28 mM, far beyond the parts per million range that has been reported in many works of direct electrochemical NH\(_3\) synthesis. Therefore, high precise quantification can be readily achieved by conventional methods such as titrimetric and colorimetric analysis.\(^{23}\) By combining all of the
above analysis results, namely the $^1$H NMR analysis revealing a N$_2$ track from Mg$_3$N$_2$ to NH$_3$, the XRD analysis suggesting the complete extraction of N$_2$ from Mg$_3$N$_2$ by NH$_4$Cl, the titrimetric and colorimetric tests indicating a NH$_3$ yield of ~100%, and the GC analysis clarifying negligible NH$_3$ decomposition, it can be concluded that Reaction 5 is highly feasible for the synthesis of NH$_3$ from Mg$_3$N$_2$.

**Productivity and energy consumption analysis**

The above results indicate that it is possible to harness the industrial Mg electrolysis for an indirect electrosynthesis of NH$_3$. The electrolysis speed of 0.2 A/cm$^2$ corresponds to a rate of $1 \times 10^{-6}$ mol $\cdot$ cm$^{-2}$ $\cdot$ s$^{-1}$ for the generation of Mg, which can be translated into a NH$_3$ synthesis rate of $0.68 \times 10^{-6}$ mol $\cdot$ cm$^{-2}$ $\cdot$ s$^{-1}$ if other reaction steps can proceed at comparable or higher rates. However, the final productivity depends on the step of lowest space time yield. It is worth mentioning that the speed of 0.2 A/cm$^2$ is a typical production speed of the contemporary chlorine alkali industry, which is >100 times faster than most previous electrolytic processes for NH$_3$ synthesis, while the coulombic efficiency is the highest reported to date (Table S3).

According to Figures 3B and 4E, both the nitridation of 1 g Mg and the following NH$_3$ synthesis from Mg$_3$N$_2$ can be completed in ~1 h, equivalent to an NH$_3$ generation rate of ~$10^{-5}$ mol/s. However, these solid-gas and solid-solid processes could be run on a significant scale, making the apparent rate much higher than that of other stages of the process. According to Gupta et al., the conversion of Cl$_2$ to HCl by the reverse Deacon reaction could continually proceed at a rate of $0.61 \times 10^{-6}$ mol $\cdot$ cm$^{-2}$ $\cdot$ s$^{-1}$ at 973 K, allowing a NH$_3$ generation rate of ~$0.41 \times 10^{-6}$ mol $\cdot$ cm$^{-2}$ $\cdot$ s$^{-1}$ by Reaction 5, which can match the electrolysis speed of 0.2 A/cm$^2$. Therefore, it would be easy to coordinate all of these processes for high-speed NH$_3$ synthesis, and finally the NH$_3$ output would be determined by the amount of electrolytically produced Mg.

The energy consumption of the MCC process is also estimated. At the current density of 0.2 A/cm$^2$, electrolysis consumes energy of ~14.1 kWh/kg-NH$_3$. Higher electrolysis speed is possible according to Figure 2A, but the energy consumption will increase, for example, to 16.2 kWh/kg-NH$_3$ at 1 A/cm$^2$. Such an electrolysis energy consumption level represents the lowest level compared to those reported in the literature (Figure S11). All of the other thermochemical steps may require no or very little external energy, because their overall reaction (Reaction 8) is highly exothermic, with an overall enthalpy change of ~$-2,964.52$ kJ/kg-reactants, indicating that these thermal reactions will release huge amounts of heat in practice. Moreover, compared to traditional MgCl$_2$ electrolysis and the HB process, energy savings from the dehydration of MgCl$_2$ and separation of NH$_3$ from N$_2$ and H$_2$ could be achieved by the MCC process.

$$3\text{Mg} \ (973\text{K}) \ + \ 3\text{Cl}_2 \ (g, \ 973\text{K}) \ + \ 3\text{H}_2\text{O} \ (l, \ 298\text{K}) \ + \ \text{N}_2 \ (g, \ 298\text{K}) = 3\text{MgCl}_2(973 \text{K}) \ + \ 2\text{NH}_3(773\text{K}) \ + \ 1.5\text{O}_2(973\text{K}) \quad \Delta H^\circ = \ -1087.98 \text{ kJ/mol} \quad (\text{Reaction 8})$$

Therefore, the overall energy consumption of this MCC process could be lower than that of the coal-based HB process operating in China (54 GJ/ton-NH$_3$, or 15.0 kWh/kg-NH$_3$). Solar and/or wind power have low prices, ranging from $0.01$ to $0.04$/kWh, and these technical data can be translated into a price of $130$–$520$/ton-NH$_3$, which is again highly competitive with the price of NH$_3$ produced by the HB process, especially when carbon tax is considered (Figure 5).

In summary, unpressured synthesis of NH$_3$ from N$_2$ and H$_2$O with an MCC assisted by molten salt electrolysis is proposed and has passed several chemical and electrochemical
The MCC process offers a coulombic efficiency >92%, an unprecedented NH₃ synthesis rate at the level of 10⁻⁶ mol cm⁻² s⁻¹, and an energy consumption of 14.1 kWh/kg-NH₃, which is competitive with the current HB process. A key effort in this study has proven the feasibility and effectiveness of reacting Mg₃N₂ with NH₄Cl for the simultaneous production of pure NH₃ gas and anhydrous MgCl₂. Because the electrolysis of MgCl₂ is the only non-spontaneous step, and all of the other steps indicate overall a highly exothermic process in thermodynamics, it can be anticipated that the MCC process will be of high energy efficiency after proper engineering designs. Thus, we hope that the present work may contribute to the further development of sustainable NH₃ synthesis routes with the potential of scalability.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact
Further information and requests for resources should be directed to and fulfilled by the lead contact, Xianbo Jin (xbjin@whu.edu.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
The authors declare that the data supporting the findings of this study are available in the article and the supplemental information. All other data and codes are available from the lead contact upon reasonable request.

Electrolytic preparation of Mg
The eutectic mixture of anhydrous MgCl₂ (Tianjin Guangfu), NaCl, and KCl (Sinopharm Chemical Reagent) (5:3:2 in molar ratio, 0.34 mol in total) was loaded into a Ni crucible (inner diameter: 40 mm; height: 60 mm), which was then placed in the quartz tube of a
programmable vertical furnace (Wuhan Experimental Furnace Plant). The furnace temperature was raised to and maintained at 200°C/14 for >24 h, and then slowly increased to 973 K until the salt mixture was fully molten. Pre-electrolysis was carried out by applying a voltage of 1.6 V between a graphite rod (10 mm in diameter) anode and a Ni sheet (15 x 15 mm²) cathode to remove moisture and other redox-active impurities. Pre-electrolysis lasted ~10 h until the current reached a low and stable background level.

A Mo rod (2 mm in diameter) and a graphite rod (3 mm in diameter) were used as the working electrode to record cyclic voltammograms in the cathodic and anodic potential ranges, respectively. All of the potential values are reported versus a homemade alumina sealed Ag/AgCl reference electrode whose potential was calibrated against the potential of a Mg/Mg²⁺ electrode in the melt. Constant current electrolysis was implemented to prepare the Mg on a Mo sheet cathode (1 x 1 cm), and a graphite rod sheathed in an alumina tube (with holes on the end wall to allow ion transfer) as the anode. The anodic Cl₂ was led out into the drying column of CaCl₂ and then absorbed with the KOH solution. An Ivium Potentiostat (Ivium Technologies) was used to record cyclic voltammograms and to control the electrolysis at different current densities.

To estimate the current efficiency of Mg generation, the electrolytic Mg was taken out with the Mo electrode after solidification by cooling the temperature down to ~873 K. The Mg was allowed to react in a dilute HCl solution (1 M), and H₂ bubbles were collected to measure the volume \( V_{H_2,m} \), which was used to calculate the current efficiency of electrolysis \( (\eta_h) \) by Equation 1:

\[
\eta_h = \frac{n_{Mg,m}}{n_{Mg,c}} = \frac{n_{H_2,m}}{Q/2F} = \frac{P V_{H_2,m}}{2F} \frac{RT}{Q/2F} \quad \text{(Equation 1)}
\]

where \( n_{Mg,m} \) and \( n_{H_2,m} \) are the calculated mole numbers of Mg and H₂ from \( V_{H_2,m} \), Q is the charge passed during the electrolysis at a current \( I \), \( n_{Mg,c} \) is the mole number of Mg calculated from \( Q \), \( F \) is the Faraday constant, and \( P \) and \( T \) are ambient pressure and temperature, respectively.

Considering that during the electrolysis, the voltage was varying, the electrolysis energy consumption \( W \) was calculated by

\[
W = \eta_h \int_0^I UdI = \eta_h \sum_{k=0}^{n} U_k \Delta t_k \quad \text{(Equation 2)}
\]

where \( U \) represents cell voltage, \( U_k \) is the cell voltage recorded at time \( t_k \), and \( \Delta t \) is the sample interval.

**NH₃ detection through sulfuric acid titration**

A range of 50–200 mL of the as-obtained NH₃ water was taken into a 250–500 mL conical flask, with 2–3 drops of methyl orange solution (0.1%) being added as the indicator. The NH₃ water was then titrated by a H₂SO₄ solution (0.01 M) during shaking. The titration was stopped once a sharp color change from yellow to orange was observed (Figure S4). The consumed H₂SO₄ solution was typically 30–50 mL, with the error within ~0.2 mL (1 drop).

The titration reaction is

\[
2NH_3 + H_2SO_4 = (NH_4)_2SO_4 \quad \text{(Reaction 9)}
\]

The generated amount of NH₃ was than calculated by the consumed H₂SO₄ according to Reaction 9.
**Synthesis of Mg₃N₂ from Mg and N₂**

In a glovebox filled with Ar (VAC OMNI-LAB), a 0.5-mm-thick Mg sheet (~1 g) was loaded into an alumina crucible, which was then placed in a quartz tube with gas vents. The loaded quartz tube was taken out of the glovebox, and the Ar in it was purged by N₂ (99.999%) for ~15 min, followed by placing the tube in a vertical furnace to react at a designated temperature. The N₂ supply (20 mL/min) was continuous. After cooling, the tube was put back into the glovebox, and the reaction product was transferred into a sealable test tube for further analysis.

To estimate the conversion \( \rho(Mg + N₂) \) from Mg to Mg₃N₂ after the Mg + N₂ reaction (Reaction 2), the reaction product was allowed to react with sufficient deionized water (18 mΩ) in a sealed reactor so that the generated NH₃ dissolved in the water. After completion of the reaction, the yellowish Mg₃N₂ turned to white Mg(OH)₂, which was removed from the solution by filtration, and then the NH₃ was titrated by a H₂SO₄ solution.

According to Reactions 6 and 8, 1 mol Mg₃N₂ generates 2 mol NH₃, which consumes 1 mol H₂SO₄ during the titration. Therefore, the generated amount of Mg₃N₂ \( (n_{Mg₃N₂}) \) from Reaction 2 can be calculated by the consumed volume of the H₂SO₄ solution according to Reaction 9:

\[
\rho(Mg + N₂) = \frac{n_{Mg₃N₂,m}}{n_{Mg₃N₂,c}} \times \frac{V_{H₂SO₄,m} \times C_{H₂SO₄}}{n_{Mg₃N₂,c}} \times 100\% \quad \text{(Equation 3)}
\]

where \( n_{Mg₃N₂,c} \) is the molar number of Mg₃N₂ that can be generated in theory according to Reaction 2.

**Synthesis of NH₃ from Mg₃N₂ and HCl**

The synthesized Mg₃N₂ (~1 g) was loaded into an alumina crucible, which was then placed in a quartz tube with Ar protection. After heating to a scheduled temperature, the anhydrous HCl gas was introduced (5 mL/min) into the tube for reaction. The reaction changed the yellowish Mg₃N₂ to white MgCl₂. At the same time, some white crystalline deposit, which was NH₄Cl as expected, formed on the wall of the quartz tube, where the temperature was relatively low.

To estimate the conversion from Mg₃N₂ to NH₃ after the reaction between solid Mg₃N₂ and gaseous HCl (Reaction 7), the solid product was allowed to react with sufficient deionized water to convert any unreacted Mg₃N₂ to NH₃ (aqueous solution). After filtration, the solution was titrated by a H₂SO₄ solution.

Again, the unreacted Mg₃N₂ (mass, \( m_{Mg₃N₂,m} \)) can be determined by the consumed volume of H₂SO₄ and titration and spectrophotometric analysis. Then, the conversion level was calculated by

\[
\rho(Mg₃N₂ + HCl) = 1 - \frac{m_{Mg₃N₂,m}}{m_{Mg₃N₂}} \times \left(1 - \frac{V_{H₂SO₄,m} \times C_{H₂SO₄} \times M_{Mg₃N₂}}{m_{Mg₃N₂}}\right) \times 100\% \quad \text{(Equation 4)}
\]

where \( m_{Mg₃N₂} \) is the mass of the fed Mg₃N₂ and \( M_{Mg₃N₂} \) is the molar mass of Mg₃N₂.

**Synthesis of NH₃ from Mg₃N₂ and NH₄Cl**

In a glovebox (VAC OMNI-LAB) being filled with Ar, 1–4 g of mixed Mg₃N₂ and NH₄Cl (Aladdin Company, dried before using) powders (1:6 in molar ratio) were loaded into an alumina crucible, which was then placed in a quartz tube reactor with gas vents. This reactor was then taken out of the glovebox and heated to a scheduled temperature. During reaction, an Ar flow was used to carry the produced
gaseous NH$_3$ out into deionized water, and the total amount of the generated NH$_3$ was measured by H$_2$SO$_4$ titration.

According to Reactions 5 and 8, the titration will determine the total amount of NH$_3$, but only 2 of 8 units of NH$_3$ generated from Mg$_3$N$_2$. Therefore, only 25% of the consumed H$_2$SO$_4$ should be linked to the reacted Mg$_3$N$_2$, and the conversion from Mg$_3$N$_2$ to NH$_3$ by the reaction between solid Mg$_3$N$_2$ and NH$_4$Cl (Reaction 5) was estimated according to Equation 5:

$$p_{(Mg_3N_2+NH_4Cl)} = \frac{n_{Mg_3N_2,m}}{n_{Mg_3N_2}} = \frac{V_{H_2SO_4,m}}{4} \times C_{H_2SO_4} \times 100\%$$  

(Equation 5)

where $n_{Mg_3N_2,m}$ is the molar number of Mg$_3$N$_2$ calculated from the consumed H$_2$SO$_4$ during titration according to 1 mol Mg$_3$N$_2 \leftrightarrow$ 2 mol NH$_3 \leftrightarrow$ 1 mol H$_2$SO$_4$, and $n_{Mg_3N_2}$ is the amount of the fed Mg$_3$N$_2$.

**NH$_3$ detection by SN method**

Typically, the as-obtained NH$_3$ water was diluted 50–100 times, and ~5 mL was taken out with 100 μL Nessler’s reagent (Macklin Company) being added. The mixture solution was incubated for 20 min at room temperature in the dark and then measured as the absorbance at 420 nm by UV-visible spectroscopy (UV-vis, UV-3600, Shimadzu). A calibration curve was plotted by a series of reference solutions of NH$_4$Cl. The concentration of NH$_3$ was read from the calibration curve.

**NH$_3$ detection by $^1$H NMR**

Common N$_2$ (>99.999%) and NH$_4$Cl (Aladdin Company, dried before using) were used as the $^{14}$N reagents, while the $^{15}$N$_2$ (containing 2% $^{14}$N$_2$) was purchased from Wuhan Newradar Special Gas, and $^{15}$NH$_4$Cl (containing 2% $^{14}$NH$_4$Cl, analytical reagent [AR]) from Aladdin Company. Mg$_3^{14}$N$_2$ and Mg$_3^{15}$N$_2$ were synthesized by reacting the Mg sheet with $^{14}$N$_2$ and $^{15}$N$_2$, respectively. The isotope-labeled NH$_3$ sample was synthesized by the reaction between the isotope-labeled Mg$_3$N$_2$ and NH$_4$Cl, which was dissolved in water with an NH$_3$ concentration of ~28 mM. For NMR analysis, the testing sample was prepared by adding 10 μL NH$_3$ water and 5 μL H$_2$SO$_4$ (98% by weight) in turn into 0.5 mL d$_6$-DMSO. Standard samples were prepared similarly but with the NH$_3$ water being replaced by aqueous solutions of the $^{14}$NH$_4$Cl + $^{15}$NH$_4$Cl mixture, with the $^{15}$NH$_4$Cl concentration in d$_6$-DMSO being fixed at ~0.4 mM. The sample solution was then migrated into a NMR tube. A 400M NMR (Bruker AVANCE III HD equipped with CPP BBO 400S1 BB-H&F-05 Z) was used to record the $^1$H NMR spectra. During the test, both the analysis relaxation time and the corresponding relaxation delay time were 1 s.

**H$_2$ detection in the prepared NH$_3$**

Approximately 400 mL NH$_3$ gas generated at 773 K was absorbed by a 1 M H$_2$SO$_4$ solution, during which the NH$_3$ was replaced by 500 mL Ar. The H$_2$ gas, if any, should remain in the Ar, which was then purged into the sampling loop of a gas chromatograph (FULI 9790II, with a thermal conductivity detector and Ar serving as a carrier gas) for measurement. The calibration curve was made by pre-measurement of several standard gas samples of H$_2$ in Ar. The measurement error was ~±3%.

**Materials characterization**

An XRD pattern was obtained by using a Miniflex 600 X-ray diffractometer with Cu K$_{α}$ irradiation ($λ = 0.154$ nm) at 40 kV and 15 mA. A scan rate of 5° min$^{-1}$ was applied to record the XRD pattern in the range of 2θ = 10°–80° with a step of 0.02°. The powder
sample was pressed onto a Si sample holder in the glovebox, which was then transferred to XRD analysis using a sealable sample box.

The microstructures and morphologies were characterized by scanning electron microscopy (SEM) (FEI Quanta 200). The powder sample was mounted on an Al stub through conducting C adhesive in the glovebox, and a sealable sample box was used to transfer the stub into the SEM chamber for observation.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.xcrp.2021.100425.

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AUTHOR CONTRIBUTIONS

DECLARATION OF INTERESTS
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