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Recent Advances in Ammonia as a Hydrogen Energy Carrier: From Green Synthesis to End-Use Applications

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Abstract. Ammonia, as a carbon-free and hydrogen-rich compound, with its high volumetric hydrogen density, mild liquefaction and storage transportation conditions, as well as a mature global supply chain, is gradually becoming an ideal hydrogen carrier. This article systematically reviews the research progress of the entire "ammonia-hydrogen" industrial chain. Firstly, this paper analyzes the high carbon emissions and low flexibility challenges faced by the traditional Haber-Bosch process in the energy transition, and discusses the design principles and performance bottlenecks of emerging green ammonia synthesis technologies such as the green Haber process, electrochemical nitrogen reduction, photocatalysis, and plasma catalysis. Secondly, the focus is placed on the diversified utilization of ammonia in the downstream conversion field. The technical paths, electrochemical performances and commercialization obstacles of direct ammonia solid oxide fuel cells, direct ammonia anion exchange membrane fuel cells and proton-conducting ceramic fuel cells are compared. Subsequently, based on this, an analysis from the perspectives of economy and environmental impact is conducted. Finally, the economic advantages of ammonia in the storage and transportation process, as well as its compatibility with existing infrastructure, give it the potential to replace traditional fuels in high-emission sectors such as shipping and power generation.

Keywords: ammonia energy, hydrogen energy carrier, green ammonia synthesis, ammonia fuel cells, carbon neutrality

1. Introduction

Carbon neutrality targets are accelerating the shift toward power systems dominated by wind and solar electricity [1]. The resulting problem is not generation in isolation, but the mismatch between when and where electricity is produced and when and where it is needed. Batteries can smooth short-term fluctuations, yet they are less attractive for multi-week storage or interregional transport at very large scales. For those roles, energy is often better moved and stored in chemical form [2]. Hydrogen is frequently discussed in this context, but the logistics are still burdensome. Liquid hydrogen, for instance, requires cryogenic storage at −253 °C, which raises insulation requirements and adds substantial energy penalties across storage and shipping [3].

Ammonia offers a different trade-off. It contains no carbon, carries a high amount of hydrogen per unit volume (up to 120 kg H_2/m^3), and can be liquefied under comparatively mild conditions, which simplifies handling relative to cryogenic hydrogen [4]. Equally important, ammonia is already produced, traded, and transported globally at scale; the supply chain is established and does not need to be built from scratch. Turning "industrial ammonia" into "energy ammonia", however, is not automatic. The carbon footprint of today's Haber–Bosch production, the limited efficiency and flexibility of renewable-powered synthesis routes, and the constraints in downstream conversion technologies remain practical barriers [5].

This paper surveys the ammonia-to-hydrogen value chain from three angles: low-carbon synthesis, end-use conversion (with a focus on direct ammonia fuel cells), and system-level economic and environmental implications. The organization of the review is summarized in Figure 1.

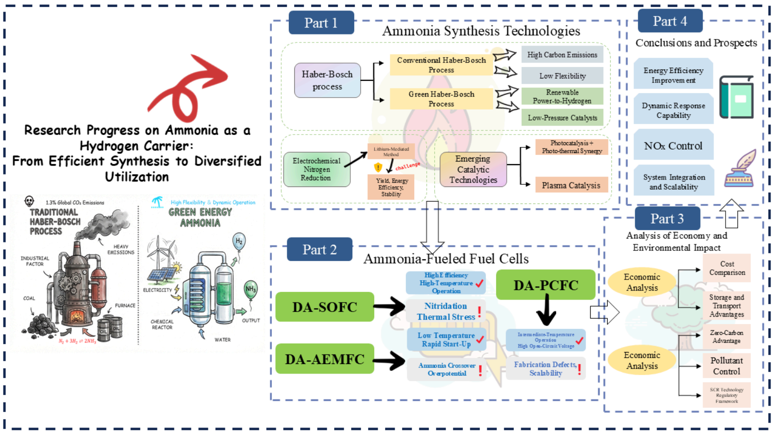

Figure 1. Overall framework of this review

2. Ammonia synthesis technology

2.1. Haber-Bosch process

2.1.1. Conventional Haber–Bosch process

At present, more than 90% of global ammonia production still relies on the Haber–Bosch process, which remains the dominant industrial route for ammonia synthesis [6]. Although this process is technologically mature, it faces two major limitations in the context of the low-carbon energy transition: high carbon emissions due to fossil-based hydrogen production and poor operational flexibility caused by large thermal inertia and long start-up and shutdown cycles [5,7].

Therefore, achieving carbon reduction in ammonia production and enhancing its compatibility with intermittent power sources is the core objective of the "energy ammonia" development. The vision is depicted in Figure 2a, which is a shift from reliance on fossil fuels to an ammonia production and utilization model driven by renewable energy.

2.1.2. Green Haber–Bosch process

The core of the Green Haber-Bosch process lies in using renewable electricity to drive the electrolysis of water for hydrogen production, thereby achieving decarbonization at the source [8]. However, transitioning the traditional process to a green model faces two core challenges: Firstly, there is the issue of system energy efficiency. The hydrogen production pressure of mainstream electrolyzers is usually much lower than the pressure required by the synthesis loop. Recompressing the hydrogen to a traditional high-pressure environment will result in significant energy loss (accounting for approximately 6.6% of the total system energy input) [9]. Developing new catalysts that can maintain a high single-pass conversion rate under low-pressure conditions is crucial for reducing the energy consumption of the system. However, as shown in Figure 2c, the theoretical equilibrium conversion rate of ammonia synthesis is limited by thermodynamics. At low pressure, a lower temperature is required to maintain a high yield, which imposes strict requirements on the low-temperature activity of the catalyst. In addition, Figure 2d highlights the long-term potential of direct electrochemical nitrogen fixation compared with conventional nitrogen-conversion pathways.

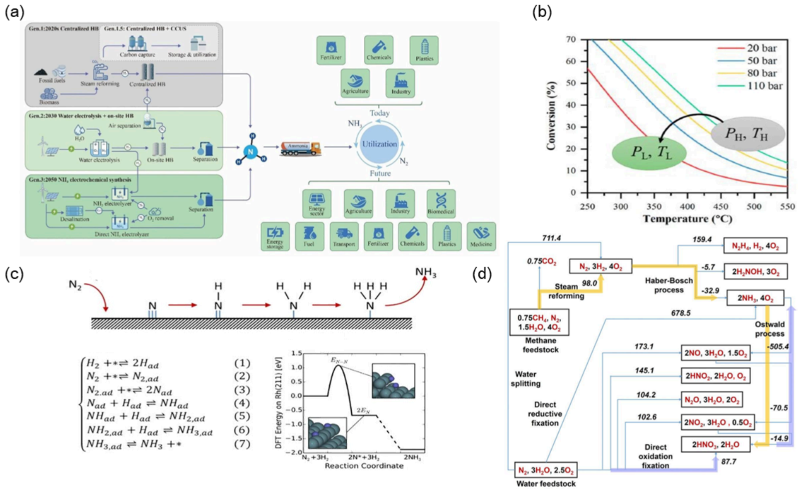

Figure 2. (a) Vision for renewable ammonia production and utilization; (b) representative Haber–Bosch catalytic cycle and key elementary reaction steps, including typical energy barrier calculations; (c) theoretical equilibrium conversion of ammonia synthesis as a function of temperature under different pressures (adapted from Ref [7].); (d) comparison of the atomic and energy economy of different nitrogen fixation pathways (adapted from Ref [6].)

2.2. Electrochemical nitrogen reduction for ammonia synthesis

Electrochemical nitrogen reduction offers a promising route for distributed ammonia synthesis under ambient conditions because it directly uses protons and electrons derived from water [11]. However, its practical application is still constrained by low ammonia production rates, limited energy efficiency, and insufficient experimental reliability. Owing to the low solubility of N_2 in electrolytes, most aqueous NRR systems remain far below industrially relevant production levels. The lithium-mediated pathway is currently the most promising low-temperature route, and its representative catalytic cycle and cell configuration are shown in Figure 3a [12]. At the same time, the effects of lithium salt type and concentration on NH_3 yield and Faradaic efficiency are summarized in Figure 3b, while the possible reaction pathways and interfacial phenomena are illustrated in Figure 3c [12,13]. Despite this progress, competitive hydrogen evolution, low energy efficiency, contamination-induced false positives, and long-term stability issues still prevent large-scale implementation [13,14].

2.3. Emerging catalytic technologies

2.3.1. Photocatalysis

Photocatalytic nitrogen fixation directly uses solar energy to activate semiconductor catalysts and reduce N_2 under ambient conditions. This route is attractive because of its mild operating conditions and low theoretical energy demand, but its practical efficiency remains very low, mainly because of the high stability of N_2 and the rapid recombination of photogenerated charge carriers [15]. To overcome these limitations, photothermal catalysis has attracted increasing attention. As shown in Figure 3d, a dual-temperature-zone catalyst design can improve ammonia production beyond the conventional thermodynamic equilibrium limit, indicating that photothermal synergy is more promising than purely photocatalytic routes for enhancing energy utilization efficiency.

2.3.2. Plasma catalysis

Plasma catalysis combines non-equilibrium plasma with catalytic surfaces to create a highly reactive environment for ammonia synthesis. Its main advantages are rapid start-up and shutdown, mild operating conditions, and strong compatibility with intermittent renewable power [16]. Current studies mainly focus on the synergy between plasma and non-precious-metal catalysts such as Ni/Al_2O_3 and Fe/Al_2O_3. As shown in Figure 3e, under plasma conditions the Eley–Rideal pathway contributes more significantly to ammonia formation than the conventional Langmuir–Hinshelwood pathway, and reactor optimization has further improved system performance [17]. Although its energy consumption is still higher than that of highly optimized Haber–Bosch systems, plasma catalysis remains a promising direction for flexible green ammonia synthesis.

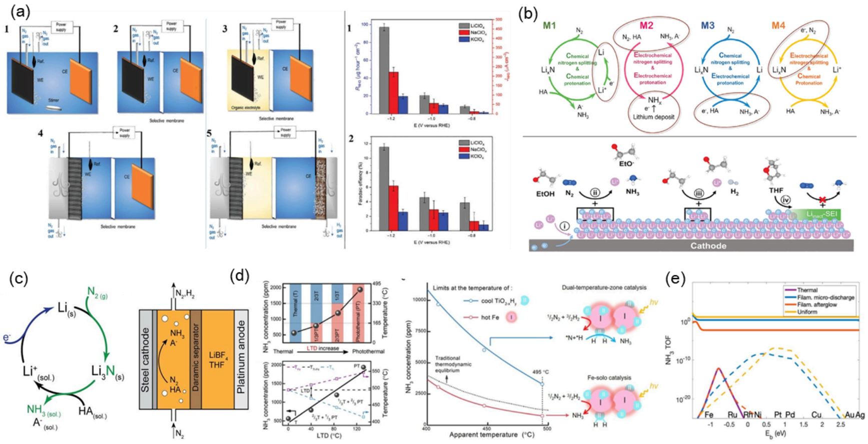

Figure 3. (a) Catalytic cycle and electrochemical cell configuration for lithium-mediated nitrogen reduction to ammonia; (b) effects of lithium salt type and concentration on NH_3 yield and Faradaic efficiency (adapted from Ref [12].); (c) schematic illustration of possible reaction pathways and interfacial phenomena in lithium-mediated nitrogen reduction (adapted from Ref [13].); (d) dual-temperature-zone catalyst design for photothermal ammonia synthesis beyond the thermodynamic equilibrium limit (adapted from Ref [15].); (e) relationship between turnover frequency and N binding energy in plasma-catalytic ammonia synthesis, together with reaction-pathway diagrams over noble-metal and non-precious-metal catalysts (adapted from Ref [16].)

3. Ammonia fuel cells

Fuel cells provide a direct electrochemical route to convert ammonia into electricity. Compared with combustion, this approach can deliver higher conversion efficiency and offers better control over pollutant formation, while avoiding an external cracker and the associated purification steps. In practice, direct ammonia fuel cells are commonly grouped by electrolyte and operating temperature into three families: DA-SOFCs, DA-AEMFCs, and DA-PCFCs. Each family comes with a distinct balance among kinetics (especially ammonia decomposition and ammonia oxidation), materials durability, and system complexity.

3.1. Direct Ammonia Solid Oxide Fuel Cells (DA-SOFCs)

DA-SOFCs operate at high temperature, where ammonia can be decomposed in situ and electrochemical kinetics are fast. As shown in Figure 4a, both oxide-ion-conducting and proton-conducting electrolyte configurations have been explored. With conventional Ni-YSZ cermet anodes, laboratory DA-SOFCs can approach hydrogen-fed performance, and peak power densities around 900 mW cm^{-2} have been reported, together with high overall conversion efficiency.

Current efforts increasingly target lower-temperature operation, because it relaxes materials constraints and improves practical operability.

The current research focuses on enhancing the system's activity at lower temperatures. By incorporating an anode functional layer with high catalytic activity (such as impregnating Ru or loading BaO as a promoter), the decrease in ammonia decomposition rate at low temperatures can be effectively compensated. Furthermore, proton-conducting SOFC, as an emerging technological route, does not produce water vapor at the anode, thus avoiding fuel dilution. While maintaining high current density, its stability is superior to that of traditional oxygen-ion conducting SOFC [18].

Its commercialization faces two major challenges: Firstly, during long-term operation, nickel-based catalysts are prone to undergo nitrogenation reactions in an ammonia atmosphere, causing the volume expansion of the anode material and the generation of microcracks, resulting in performance degradation, as shown in Figure 4b. Secondly, the thermal stress generated by frequent start-stop operations places extremely high demands on the mechanical strength of the ceramic electrolyte film.

3.2. Direct Ammonia Anion Exchange Membrane Fuel Cells (DA-AEMFCs)

The direct ammonia anion exchange membrane fuel cell, by using an alkaline electrolyte membrane, overcomes the problem that the traditional proton exchange membrane is highly susceptible to ammonia poisoning. It is one of the most promising methods for achieving low-temperature conversion of ammonia energy. When using advanced precious metal catalysts (such as Pt and Ir-based) and optimizing the membrane electrode assembly, the peak power density value is usually within the range of 200 - 450 mW/cm^2. Additionally, as shown in Figure 4c, in terms of stack integration, a 75 W DAFC stack composed of 5 50 cm^2 individual cells has successfully been operated. Its average peak power density is comparable to that of a single cell and demonstrates short-term stability [19].

Recent research has focused on developing non-precious metal anode catalysts, such as nickel-based alloys, in an effort to reduce the cost of fuel cells. Meanwhile, by optimizing the performance of the anion exchange membrane, the conductivity of hydroxide ions is enhanced while the fuel penetration problem is alleviated. Additionally, the optimization of mass transfer at the tri-phase interface of the electrode further improves the voltage stability of the cell under high current density [20].

The commercialization of DA-AEMFC is mainly constrained by two major bottlenecks: one is that the anode ammonia oxidation reaction leads to a high overpotential; the other is the ammonia permeation phenomenon, which not only causes fuel waste but also leads to the deterioration of the cathode catalyst performance and a decrease in open-circuit voltage [19].

3.3. Direct Ammonia Protonic Ceramic Fuel Cells (DA-PCFCs)

DA-PCFCs are an emerging approach that has attracted much attention in the field of ammonia energy conversion in recent years. By using proton-conducting ceramic electrolytes, the operating temperature is successfully reduced to the medium-temperature range, combining the high efficiency of high-temperature SOFCs with the material stability of low-temperature fuel cells. Its working principle is shown in Figure 4d. Compared with the traditional oxygen-ion conducting SOFC, DA-PCFC does not generate water vapor on the anode side, avoiding the dilution of the fuel by reaction products. As a result, it can maintain extremely high fuel utilization rate and open-circuit voltage.

With optimized materials and interfaces, peak power densities up to 724 mW cm^{-2} have been reported [21]. Current work focuses on electrolyte transport and interfacial contact, while adding ammonia-decomposition catalytic layers at the anode to reduce activation losses at intermediate temperatures. On the cathode side, triple-conducting materials (electrons/protons/oxide ions) are being explored to expand the active reaction zone and improve current output.

From a system perspective, intermediate-to-low operating temperatures can lower balance-of-plant cost by enabling cheaper interconnects and seals, and they can also improve thermal-cycling tolerance. However, two practical issues are still limiting: incomplete ammonia decomposition can still trigger nitridation in nickel-containing anodes, and kW-scale stack integration (including thermal management and compatibility among components) remains immature. Addressing these engineering constraints is as important as improving intrinsic cell performance for real deployment [21].

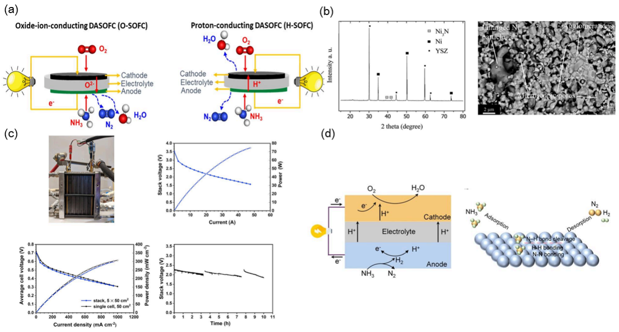

Figure 4. (a) Schematic illustrations of the operating principles of direct ammonia solid oxide fuel cells based on oxide-ion-conducting and proton-conducting electrolytes; (b) XRD patterns of Ni_3N formed after exposing a Ni-YSZ anode to ammonia, together with scanning electron microscopy images of the anode surface (adapted from Ref [18].); (c) photograph of a 75 W DA-AEMFC stack assembled from five 50 cm² single cells, together with its polarization and power-density curves (adapted from Ref [19].); (d) schematic illustration of the operating principle of a direct ammonia protonic ceramic fuel cell (adapted from Ref [21].)

4. Economic and environmental impact analysis

Whether ammonia can serve as an energy carrier at scale is ultimately decided by systems-level constraints, not a single technical metric. In addition to technical feasibility, two questions repeatedly appear in deployment discussions: cost competitiveness and environmental performance across the full value chain. The following section summarizes the major economic drivers (production cost, logistics, and infrastructure leverage) and the main environmental considerations (CO_2 reduction potential, NO_x control, and safety).

4.1. Economic analysis

Ammonia already benefits from an industrial ecosystem that is difficult to replicate quickly for alternative carriers. Storage and shipping are well established, and the required conditions (−33.3 °C or 0.8 MPa for liquefaction) are far less stringent than those for liquid hydrogen (−253 °C). The main economic penalty today is upstream: green ammonia remains more expensive than grey ammonia. Current estimates place green ammonia at roughly USD 720–1400 per ton, compared with USD 110–340 per ton for grey ammonia. The gap is largely tied to electricity price and electrolyzer performance, so continued improvements in electrolysis efficiency and renewable electricity cost are expected to narrow the difference. Figure 5a summarizes this trend and suggests a potential cost crossover around 2030, with renewable ammonia projected to decline to roughly USD 310–610 per ton by 2050 [22].

Logistics favor ammonia in long-distance transport. Global production in 2020 reached 182.6 million tons per year, against a capacity of 224.6 million tons per year, implying about 42 million tons per year of idle capacity that could, in principle, support early-stage energy applications. Ammonia also carries higher volumetric energy density than liquid hydrogen (12.7 MJ L^{-1} vs 8.5 MJ L^{-1}) and avoids cryogenic superinsulation requirements, which can translate into lower transport cost. A fuel cost comparison on an energy basis is provided in Figure 5b.

Infrastructure reuse is another tangible advantage. Roughly 18–20 million tons of ammonia are already traded internationally by sea each year, supported by more than 170 dedicated vessels. Established shipping routes (Figure 5c) and existing storage terminals (Figure 5d) can reduce the capital intensity of early deployment, especially when compared with building a new hydrogen supply chain from the ground up [23].

4.2. Environmental impact analysis

Ammonia is carbon-free at the point of use, so its primary climate benefit comes from replacing carbon-based fuels in hard-to-abate sectors. Shipping is a prominent example: it contributes about 2.6% of global CO_2 emissions, and green ammonia is therefore frequently considered in decarbonization roadmaps. Another pathway is co-firing in power generation. The roadmap cited here proposes demonstration stages that begin at ~20% co-firing, move toward 50–60% in the 2030s, and explore full ammonia firing in the 2040s [23].

The environmental picture is not limited to CO_2, however. Ammonia combustion can produce NO_x, and ammonia slip and N_2O formation must also be managed. In existing engineering practice, selective catalytic reduction is an effective route for NO_x control, but the net environmental benefit depends on achieving both low-carbon operation and low nitrogen-pollutant emissions [22,23]. Safety is another practical constraint. Ammonia is toxic, yet it has been handled at industrial scale for decades under established regulations and operating procedures. With appropriate engineering controls, leakage risk is generally manageable, and the existing infrastructure provides a practical base for scaling ammonia-based energy systems.

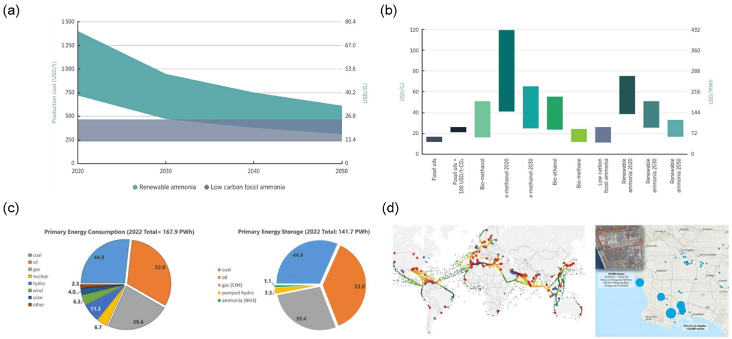

Figure 5. (a) Comparison of the production costs of green ammonia and fossil-based ammonia, together with future cost projections; (b) cost comparison of different fuels on an energy basis (USD/GJ) (adapted from Ref [23].); (c) global seaborne ammonia trade routes in 2020; (d) distribution of ammonia storage tanks in the Los Angeles area, United States, in 2012 (adapted from Ref [22].)

5. Conclusions and outlook

Ammonia offers a realistic pathway to store and move renewable energy in chemical form, largely because it is already produced, transported, and handled at industrial scale. From a synthesis perspective, the conventional Haber–Bosch process remains dominant. However, its decarbonization poses significant challenges. Renewable-powered Haber–Bosch processes, along with alternative nitrogen fixation pathways—including electrochemical, photothermal, and plasma-assisted approaches—are progressing steadily; however, they continue to confront significant challenges related to energy efficiency, operational flexibility under dynamic conditions, and technological scalability.

On the utilization side, direct ammonia fuel cells have exhibited promising performance across multiple platforms; however, their practical deployment remains constrained by challenges related to material durability and system-level engineering. The nitriding of nickel-containing components, the ammonia crossover phenomenon (especially in low-temperature equipment), as well as the complexity of stacking integration and thermal management remain recurring issues.

In terms of the economy and the environment, although the current cost of green ammonia is still higher than that of grey ammonia, with the decline in the cost of renewable energy electricity and the advancement of electrolysis technology, the cost of green ammonia is expected to intersect with that of grey ammonia around 2030 and further decrease. In addition, ammonia has significant advantages in storage and transportation: the liquefaction process is relatively mild, its volume energy density is higher than that of liquid hydrogen, and it can rely on the existing global maritime transportation infrastructure. However, the control of nitrogen oxide emissions and the risk of ammonia leakage remain core challenges.

Looking to the future, the key breakthroughs should focus on three main directions: Firstly, developing precious-metal-free catalytic materials that are resistant to nitrogenation and have high activity; Secondly, establishing flexible synthesis processes and fuel cell systems that can dynamically respond to fluctuations in renewable energy; Thirdly, establishing a comprehensive technical economic and life cycle assessment system covering the entire chain, to promote the transition of "energy ammonia" from concept to engineering practice.

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