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Review

Review of Hydrogen-Driven Power-to-X Technology and Application Status in China

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Abstract: Given China's ambition to realize carbon peak by 2030 and carbon neutralization by 2060, hydrogen is gradually becoming the pivotal energy source for the needs of energy structure optimization and energy system transformation. Thus, hydrogen combined with renewable energy has received more and more attention. Nowadays, power-to-hydrogen, power-to-methanol, and power-to-ammonia are regarded as the most promising three hydrogen-driven power-to-X technologies due to the many commercial or demonstration projects in China. In this paper, these three hydrogen-driven power-to-X technologies and their application status in China are introduced and discussed. First, a general introduction of hydrogen energy policies in China is summarized, and then the basic principles, technical characteristics, trends, and challenges of the three hydrogen-driven power-to-X technologies are reviewed. Finally, several typical commercial or demonstration projects are selected and discussed in detail to illustrate the development of the power-to-X technologies in China.

Keywords: power-to-X; power-to-hydrogen; power-to-methanol; power-to-ammonia; application

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1. Introduction

In recent years, communities have been focused on the importance of energy system transformation and decarbonization [1,2]. In order to tackle climate change and enhance energy security, renewable energy sources have received sustained and widespread attention, especially for solar and wind energy, which have the highest potential as substitutes for fossil fuels for electricity production [3,4]. The European Union (EU) has taken steps to increase the share of renewable energy sources in its energy consumption. In October 2023, the new Renewables Energy Directive ("RED III") was approved, which aims to raise the share from the previous 32% to 42.5% by 2030, with an additional 2.5% indicative supplement to meet the 45% target. As for China, the wind power [5] and photovoltaic (PV) power installations and generations increased rapidly, ranking at the top in the world. By the end of 2023, China's installed capacity of renewable energy had reached 14.5 billion kilowatt, accounting for over 50% of the country's total installed capacity. Moreover, the installed capacity of renewable energy surpassed that of thermal power for the first time in history [6]. The energy structure has been greatly changed. Furthermore, in the 14th Five-Year Plan for renewable energy development [7], China set a clear target that the cumulative installed capacity of wind power and solar power would exceed 120 GW by 2030.

However, the core problem of utilizing renewable energy sources, especially for solar and wind energy, is their inherent unpredictability and intermittency, which makes it difficult to integrate them into the existing power grid and guarantee the power balance [8]. In addition, the distribution of renewable energy resources often varies significantly between regions. In China, the great northwest sand desert is rich in renewable energy sources [9], while the electricity demand is relatively lower. And the existing transmission and distribution of infrastructure in these regions cannot meet the requirements for such a large amount of power output. The southeast of China has fewer renewable energy resources but greater capacity to consume electricity [10]. To address these challenges, hydrogen has the potential to be an ideal carrier for the storage of renewable energy [11].

Hydrogen energy is a kind of secondary energy with high gravimetric energy density. It has nearly four times the energy content of standard coal and three times the energy content of gasoline for the same mass. The gravimetric energy density and volumetric energy density (based on lower heating values) of typical fuels are shown in Table 1 [12]. Moreover, hydrogen is clean and low-carbon [13–15], and its application process only produces water. Whether hydrogen is used for combustion or in fuel cell electrochemical reactions, it does not generate carbon emissions [16,17]. In addition, hydrogen could be applied in multiple fields, including the chemical industry [18], transportation [19,20], electricity, and construction [21].

Table 1. Gravimetric energy density and volumetric energy density (based on lower heating values) of fuels [12].

	Gravimetric Energy Density (MJ/kg)	Gravimetric Energy Density (kWh/kg)	Volumetric Energy Density (MJ/L)	Volumetric Energy Density (kWh/L)
H_2 (35 Mpa)	120.0	33.3	2.8	0.8
H_2 (70 Mpa)	120.0	33.3	4.8	1.3
H_2 (liquid)	120.0	33.3	8.5	2.2
CH_4 (25 Mpa)	50.1	13.9	9.5	2.6
Standard coal	29.3	8.1		
Gasoline	43.1	12.2	32.0	8.9
Diesel	46.0	12.8	38.6	10.7

According to hydrogen production technologies and energy sources, the clean energy industry often classifies by color [22,23]. The main classifications of hydrogen energy in colors are grey hydrogen, blue hydrogen, and green hydrogen [24,25]. The grey hydrogens refer to hydrogen produced by gasification [26], reforming [27] or pyrolysis of fossil fuels, causing carbon emission during the production process. The blue hydrogen combines grey hydrogen with carbon capture and a storage process, reducing the emission of carbon. Green hydrogen is produced by electrolysis (supplied by renewable electricity) [28], photolysis [29], or biomass [30] methods, which are carbon-free in the process. The main classifications of hydrogen energy and their corresponding production technologies as shown in Figure 1. In addition, hydrogen is classified by the industry based on lifecycle greenhouse gas emissions [31]. In 2020, the group standard "Standard and evaluation of low-carbon hydrogen, clean hydrogen and renewable hydrogen" was issued in China, classifying hydrogen into low-carbon hydrogen, clean hydrogen, and renewable hydrogen. In terms of carbon emissions of hydrogen, the carbon emissions of low-carbon hydrogen are no more than 14.51 $kgCO_2e/kgH_2$, while the carbon emissions of clean hydrogen and renewable hydrogen are no more than 4.9 $kgCO_2e/kgH_2$. Renewable hydrogen also requires that energy source of hydrogen production must be renewable energy.

At present, although the majority of hydrogen is grey hydrogen, the proportion of green hydrogen would be significantly increased with the goal of reducing carbon emissions and the rapid development of renewable energy. As for green hydrogen production technologies, there are still many difficult problems to overcome. For example, photolysis suffers from poor stability and efficiency of catalysts [32]. Biomass method is limited by the rate of reaction and scale of technology [30]. Water electrolysis is a promising technology combined with the power produced by renewable energy for large-scale application. The process that uses the excess and underutilized renewable sources [33] to generate electricity and produce green hydrogen via water electrolysis is also called power-to-hydrogen.

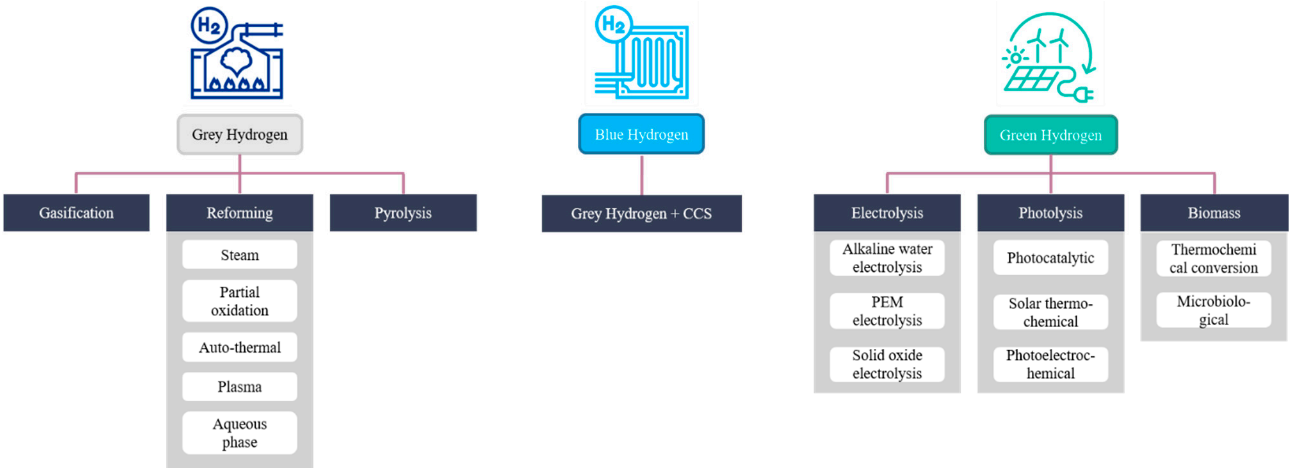


Figure 1. The main classifications of hydrogen energy and their corresponding production technologies.

Considering the drop of the hydrogen chain in diverse applications, the total value chain from power generation by renewable sources to the utilization of hydrogen is commonly termed power-to-X [34–38]. This concept was first summarized in 2013/14 in Germany [39]. In China, in addition to power-to-hydrogen, power-to-methanol and power-to-ammonia are the other two main power-to-X technical routes, which have large development perspective on a commercial scale [40]. Methanol is one of the most important raw materials in the chemical and pharmaceutical industry and for hydrocarbons synthesis [41,42]. It is directly used as a fuel for transportation as an energy carrier. Ammonia is a crucial component for chemical materials synthesis, with over 76% of all nitrogen-based products utilizing it [43]. And it could be used as a carbon-free fuel applied to transportation and power generation. Traditional synthesis methods for these two chemicals involve high carbon emission, while power-to-methanol and power-to-ammonia processes enable a net-neutral decarbonization. Moreover, by extending the use of these two chemicals in the energy field, the demand could be significantly increased, and, thus, offers a major opportunity to implement a green and low-carbon energy system. However, to the best of our knowledge, a clear and exhaustive review on these three hydrogen-driven power-to-X technologies and their application status in China is lacking.

This paper makes contributions for better understanding of the status quo and promoting the sustainable development of China's power-to-X technologies based on hydrogen. The focus of this study is to review the hydrogen energy policies of China, status and development of hydrogen driven power-to-X technologies, including power-to-hydrogen technologies (e.g., alkaline water electrolysis, proton electrolyte membrane water electrolysis, and solid oxide water electrolysis), power-to-methanol technology, and power-to-ammonia technology, in China. According to the general situation of green hydrogen in China, current challenges and future perspectives of hydrogen-driven power-to-X techniques are discussed in detail. Several typical commercial or demonstration projects are also introduced for a better understanding of the application status in China.

2. Hydrogen Energy Policies in China

Many countries, including Japan, France, South Korea, Germany, etc., have launched their national hydrogen strategies, plans, or roadmaps. The Chinese government has also issued a series of hydrogen-energy-related policies to actively promote transformation and decarbonizing of energy systems, such as proposing overall development strategy and promoting crucial technologies progress. The summary of China hydrogen energy policies is shown in Table 2.

Table 2. Summary of China hydrogen energy policies.

Year	Main Policy	Key Points
2006	Outline of the National Medium- and Long-term Planning for Development of Science and Technology (From 2006 to 2020)	Hydrogen energy and fuel cell technologies were incorporated into the advanced energy technologies.
2012	Plan for Development of the Energy Efficient and New Energy Automobile Industry (2012–2020)	The government proposed to drive the development of hydrogen production, storage, transportation, and refueling technology by means of fuel cell application demonstration.
2014	Energy Development Strategy Action Plan (2014–2020)	Hydrogen energy and fuel cell were determined as strategic directions for energy technology innovation
2016	China Energy Technology Innovation Action Plan 2016–2030	The section on hydrogen energy has significantly expanded, covering hydrogen production from renewable energy and nuclear energy, fuel cell distributed power generation, etc.
2019	Government Work Report	For the first time, hydrogen was included in the government work report, which emphasized the need to promote the implementation of charging and hydrogen refueling facilities.
2020	The energy law of the people's republic of China (Exposure Draft)	At the level of national law, hydrogen energy was incorporated in the energy management.
2021	Action Plan for Carbon Dioxide Peaking Before 2030	The plan proposed to explore the large-scale application of hydrogen energy in industry, transportation, construction, and other fields.
2022	New Energy Storage Development Implementation during the 14th Five-year Plan	It clarified the position of hydrogen energy and ammonia energy as a new type of energy storage.
2022	14th Five-year plan for renewable energy development	It was emphasized that large-scale hydrogen production from renewable energy sources was promoted.
2022	China maps 2021–2035 plan on hydrogen energy development	The plan defined the energy properties of hydrogen, and proposed that hydrogen energy would play an important supporting role in the country's green energy transformation.
2023	Guidelines on Hydrogen Energy Industry Standard System Construction (2023)	The guidelines systematically established a standard system for the entire industrial chain of hydrogen energy, including hydrogen production, storage, transportation, and utilization.

As early as the 1980s, the hydrogen energy industry in China began scientific research programs, such as the National High-tech R&D Program (863 Program) and National Basic Research Program of China (973 Program), which included several studies aimed at developing hydrogen fuel cells. Subsequently, policies began to focus on hydrogen energy and hydrogen fuel cells. In 2006, hydrogen energy and fuel cell technologies were incorporated into advanced energy technologies in the outline of the national medium- and long-term planning for development of science and technology (from 2006 to 2020). In recent years, especially since 2019, with the increase in research [44–46], the number of hydrogen energy policies issued by the Chinese government has steadily increased over time [47]. In 2019, for the first time, hydrogen was included in the government work report. In 2022, the China maps 2021–2035 plan on hydrogen energy development was issued, which defined the energy properties and strategic positioning of hydrogen. Particularly, this plan proposed to actively guide the transformation of industries such as synthetic ammonia and methanol from high-carbon processes to low-carbon processes, promoting the green and low-carbon development of high-energy-consuming industries.

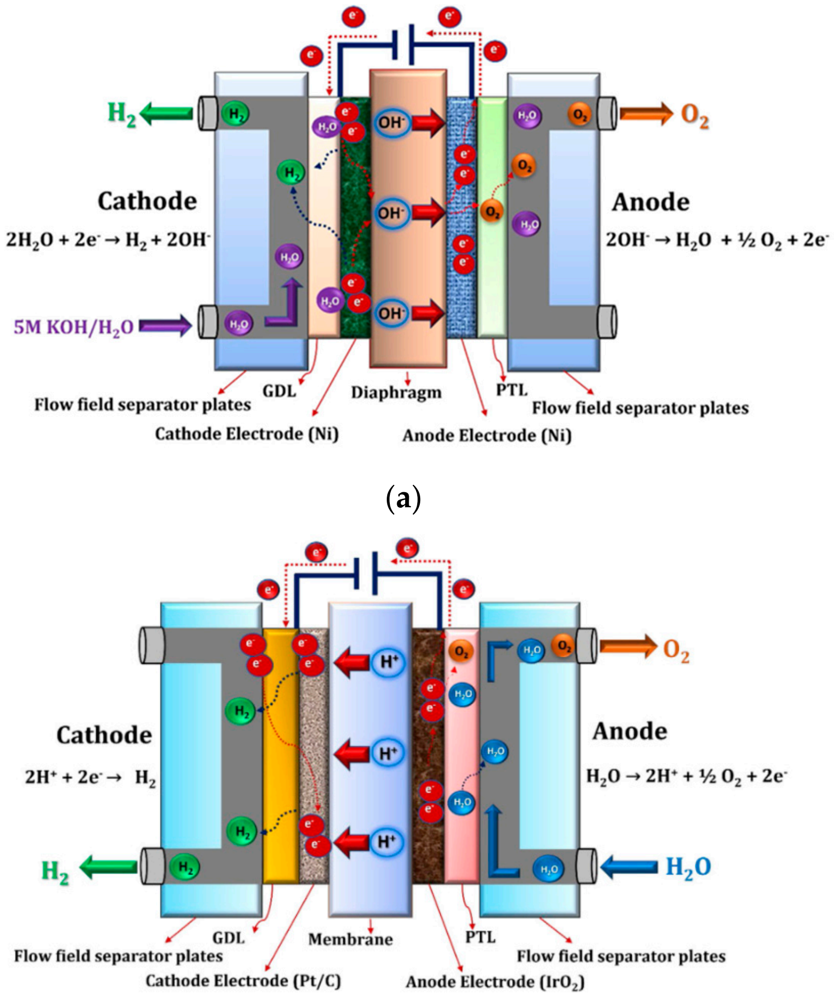
3. Power-to-Hydrogen

China is currently the world's largest producer of hydrogen, producing 37.81 million tons of hydrogen in 2022 [48]. However, most hydrogen is derived from fossil fuels [49], namely, grey hydrogen, with a relatively low proportion of green hydrogen. The percentage of hydrogen production from coal is 57.06%, natural gas is 21.90%, industrial byproduct is 18.15%, water electrolysis is 1.42%, and other sources is 1.47% [50]. According to IEA forecasts, the global production of green hydrogen in 2050 will be much higher than blue hydrogen. By 2060, the vast majority of hydrogen production capacity will be supplied by green hydrogen, of which nearly 80% will come from electrolysis of water. It is clear that water electrolysis powered by renewable sources, i.e., power-to-hydrogen, is an important hydrogen production method for the future.

3.1. Typical Water Electrolysis Techniques

Water electrolysis is the most common electrochemical hydrogen production method [51]. Its basic principle is passing an electric current through water to split it into hydrogen and oxygen. Electrochemical processes involve two half-cell reactions, i.e., hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), occurring at the cathode and anode, respectively [52]. The overall reaction is shown in Equation (1). The reaction takes place in an electrolyzer, which mainly consists of two electrodes (cathode and anode), a diaphragm, and a bipolar plate. Water electrolysis [53–55] is mainly classified into three types: alkaline (ALK) electrolysis, proton exchange membrane (PEM) electrolysis, and solid oxide cell (SOEC) electrolysis [56,57]. Figure 2 presents the schematic diagrams of the three electrolyzer structures. The characteristics of the three typical electrolytic water production technologies are shown in Table 3.

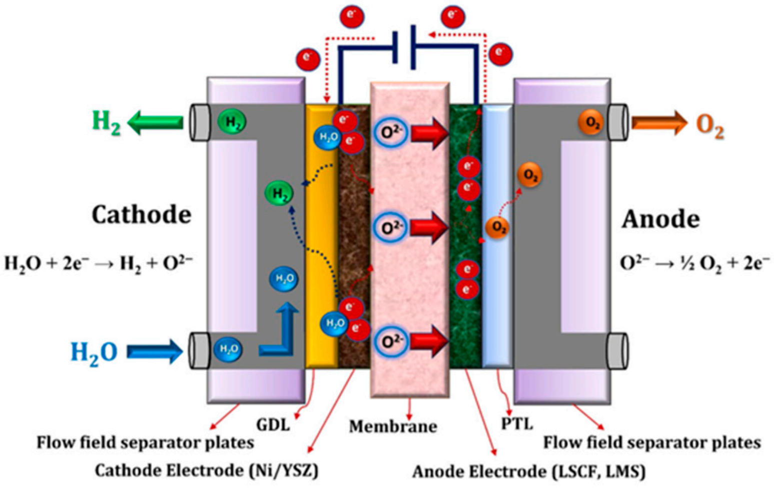
$$2H_2O \rightarrow 2H_2 + O_2 \quad (1)$$



(**a**)

(**b**)

Figure 2. *Cont.*



(c)

Figure 2. The schematic diagrams of the three electrolyzer structures [28]. (**a**) ALK electrolysis. (**b**) PEM electrolysis. (**c**) SOEC electrolysis.

Table 3. Technical characteristics of typical water electrolysis technologies [58].

Type	ALK	PEM	SOEC
Current density (A/cm^2)	0.2~0.7	0.1~2.2	1.0~2.0
Temperature (°C)	50~80	40~80	700~900
H_2 Purity (%)	99.5~99.9	99.99	99.90
Pressure (MPa)	1.0~3.0	2.0~5.0	0.1~1.5
Energy consumption (kWh/Nm^3)	4.5~5.5	3.4~4.4	2.23~2.27
Efficiency (%)	56~80	76~85	90~100
Load range (%)	15~100	0~150	0~120
Respond speed	Dozens of seconds	Several seconds	Several minutes
Lifetime (h)	90,000	20,000~50,000	~7000

The most conventional and mature method for water electrolysis is ALK electrolysis, proposed by Troostwijk and Diemann in 1789 [59,60]. When the current passes, the water obtains electrons via reduction reaction at the cathode, producing H_2 and hydroxide ions (OH^-). To maintain charge balance, the OH^- penetrates the diaphragm, which loses electrons at the anode, producing O_2. The electrode reaction equations of ALK electrolysis are shown in Equations (2) and (3). Although there have been many studies on novel catalysts such as platinum-based catalysts [61] and crystalline catalysts [62], nickel-based catalysts remain the widely used catalysts for commercial ALK electrolyzers due to their relatively high electrocatalytic activity and low cost. In the past, thick asbestos diaphragms were generally used in AKL cells to separate the anolyte and catholyte compartments [63]. Recently, new materials such as nickel oxide, PTFE, and different types of polysulfone have been used to replace thick asbestos materials [64]. The electrolyte could help ionic transport and conduction; the most commonly used electrolyte in ALK electrolyzers is KOH solution with mass fraction of 20–30% [65]. Most ALK electrolyzers adapt tiny-gap or zero-gap structures to reduce ohmic loss [66]. In these structures, the electrode and diaphragm are very close, even in connection.

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \text{ (OER at Anode)} \quad (2)$$

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \text{ (HER at Cathode)} \quad (3)$$

PEM electrolysis is another relatively mature technology for water electrolysis, first introduced in the 1960s [67]. Different from ALK electrolysis, it is a proton that is transported in the PEM electrolyte [68,69]. Protons are generated at the anode and penetrate the diaphragm, obtaining electrons at the cathode, producing H_2. The electrode reaction equations of PEM electrolysis are shown in Equations (4) and (5). The precious metal iridium and its oxides [70] are still the most advanced water anode catalysts for PEM electrolysis because of their best balance of activity and stability for the OER [71]. Generally, HERs require platinum-based catalysts. The most widely used diaphragm for PEM electrolyzers is solid perfluoro sulfonic acid (PFSA). Both precious metal catalysts and PFSA diaphragm cause the costs of PEM electrolyzers to be significantly higher than the costs of ALK electrolyzers. Nevertheless, PEM electrolysis could enhance the purity of hydrogen, with fast dynamic response speed and compact structure. It is still one of the most promising technologies for water electrolysis hydrogen production.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (OER at Anode)} \tag{4}$$

$$4H^+ + 4e^- \rightarrow 2H_2 \text{ (HER at Cathode)} \tag{5}$$

SOEC electrolysis has developed rapidly in recent years, but it still in the laboratory stage and is less mature commercially. The electrode reaction equations of SOEC electrolysis are shown in Equations (6) and (7). At present, oxygen ion (O^{2-}) is the most common SOEC electrolysis carrier. In SOEC electrolyzers, water obtains electrons at the cathode, producing H_2 and O^{2-}, and then O^{2-} penetrates the diaphragm and loses electrons at the anode, producing O_2 [72]. SOEC electrolysis operates at high temperatures compared to other electrolysis technologies. The higher temperatures enable higher efficiencies of SOEC electrolysis [73]. However, that leads to attach the limiting condition to the choice of materials, demanding that electrodes and electrolyte materials retain stability under high-temperature conditions. Currently, anodes commonly use perovskite and cathodes use ceramic–metal composites or perovskite. Materials with high ionic conductivity, such as yttria-stabilized zirconia (YSZ) and doped ceria (CeO_2), are typically used as electrode materials in SOEC electrolysis [74].

$$2O^{2-} \rightarrow O_2 + 4e^- \text{ (OER at Anode)} \tag{6}$$

$$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-} \text{ (HER at Cathode)} \tag{7}$$

3.2. Chinese Electrolyzer Manufacturers

As mentioned before, ALK water electrolysis and PEM water electrolysis technologies are relatively mature; thus, these two types of electrolyzers are more widely used in industry and business, especially for ALK electrolyzers. The majority of Chinese electrolyzer manufacturers focus on producing ALK electrolyzers, and some manufacturers choose to produce PEM electrolyzers. In addition, the application of SOEC water electrolysis technology is not wide enough, but there are a few Chinese electrolyzer manufacturers starting to produce SOEC electrolyzers. Based on preliminary statistics, there have been more than 100 electrolyzer manufacturers in China, distributed mainly in the east of China. Table 4 lists the specific parameters for several Chinese typical electrolyzer manufacturers, such as Peric Hydrogen from Hebei, Longi from Shanxi, Tianjin Mainland Hydrogen Equipment from Tianjin, Shandong Saikesaisi Hydrogen Energy from Shandong, and H_2-Bank Hydrogen from Zhejiang.

Peric Hydrogen is a manufacturer for both ALK and PEM electrolyzers, with an annual output reaching 1.5 GW. The hydrogen production rate for ALK electrolyzer products ranges from 20 Nm^3/h to 2000 Nm^3/h. For ALK electrolyzers, both one-piece equipment and modular equipment are provided. The purity of hydrogen before purification can reach 99.8%, the purity of oxygen can reach 99.2%, and the purity of hydrogen after purification can reach 99.999%. The ALK electrolyzers adopt a bipolar press filter structure, with good seal performance of the insulating gasket. The hydrogen production rate for PEM electrolyzer products ranges from 0.01 Nm^3/h to 300 Nm^3/h. Compared to ALK electrolyzer products, PEM electrolyzer products are smaller in size and lighter in weight, with higher current density and efficiency.

Table 4. Several Chinese typical electrolyzer manufacturers.

Brand	Province	Technology	Hydrogen Production Rate (Nm^3/h)	Hydrogen Pressure (MPa)	Power Consumption (kWh/Nm^3)
Peric Hydrogen	Hebei	ALK	20–2000	1.5–2.5	≤4.3–4.5
		PEM	0.01–200	0.1–3.2	≤5.4
Longi Hydrogen	Shannxi	ALK	1–3000	1.6	4.1–4.3 (ALK Hi1) 4.3–4.5 (ALK G)
Sungrow	Anhui	ALK	≤1000	1.8	-
		PEM	≤250	3	-
Tianjin Mainland Hydrogen Equipment	Tianjin	ALK	0.1–1000	5	≤4.4–4.9
		PEM	0.4–10	7	-
Sany	Hunan	ALK	500–2000	1.8	4.3–4.7
		PEM	≤200	3	4.3
Guofuhee	Jiangsu	ALK	50–1000	-	-
		PEM	4–200	-	-
Kohodo Hydrogen Energy	Guangdong	ALK	0.5–1000	1.6	4.0
Changchun lvdong	Jilin	PEM	≤200	-	-
Shandong Saikesaisi Hydrogen Energy	Shandong	PEM	0.5–200	3	-
BPEG	Beijing	ALK	2–2000	-	4.3
C hySA	Guangdong	PEM	0.2–300	3.5	-
H_2-Bank	Zhejiang	SOEC	2	-	3.5

Longi Hydrogen is a manufacturer for ALK electrolyzers; its output reached 1.5 GW in 2022. It is expected that by 2025, the production capacity of Longi Hydrogen will reach 5–10 GW. According to different products' characteristics, ALK electrolyzers could be divided into two series. The Longi ALK Hi1 series with the maximum hydrogen production is rated to 1000 Nm^3/h, with a power consumption of just 4.1–4.3 kWh/Nm^3. In September 2023, LONGi ALK G series were launched; the biggest draw to this series is that the maximum hydrogen production rate can reach 3000 Nm^3/h. In addition, each model has a service life of around 200,000 h.

Tianjin Mainland Hydrogen Equipment produces ALK electrolyzers, gas purification equipment, and small PEM electrolyzers as main products. The hydrogen production rate for ALK electrolyzer products ranges from 0.1 Nm^3/h to 1000 Nm^3/h, while for PEM electrolyzer products, it ranges from 0.4 Nm^3/h to 10 Nm^3/h. Specifically, the hydrogen production pressure of ALK electrolyzers could reach 5.0 MPa; this is the highest operating pressure of ALK electrolyzers produced in China.

Shandong Saikesaisi Hydrogen Energy is one of the earliest manufacturers engaged in PEM water electrolysis equipment production. It includes 13 series with hydrogen production rates range from 0.5 Nm^3/h to 200 Nm^3/h. At present, PEM electrolyzer products produced by Shandong Saikesaisi hydrogen energy have been exported to more than 30 countries and regions.

H_2-Bank is an electrolyzers manufacturer for SOEC electrolyzers. The operating temperature of SOEC electrolyzers is 750 °C. Moreover, the hydrogen production rate is 2 Nm^3/h and the power consumption is 3.5 kWh/Nm^3.

3.3. Trends and Challenges

The current level of advancement and features of each electrolysis technology are quite different. ALK electrolysis technology is more advanced and cheaper than other electrolysis technologies, and China has a relatively mature alkaline-electrolyzer industry. However, some improvements are still needed, including increasing the current density [75], preventing the crossover of the gases, and widening the operating range. The PEM electrolysis technology is well adapted for integration with variable renewable energy sources. There have been some studies on the flexibility of PEM electrolysis technology via dynamic models or experimental methods [76,77]. Still, the cost-effective cell components need to be developed. It is necessary to address existing challenges by finding transition metals to replace precious metal as catalysts, developing proton exchange membrane materials with high conductivity and low cost, exploiting new preparation methods of membrane electrode assembly, etc. The SOEC electrolysis technology is still in its early stages of development. While it could be more favorably considered for integration with exothermic reactions in synthesis process of methanol or ammonia, the biggest challenge of SOEC electrolysis technology is to maintain structural stability and withstand the thermal stresses generated at long-term high temperatures, which lead to material creep.

In China, with the continuous increase in the installed capacity of renewable energy, the scale of power-to-X systems is increasing. At present, Chinese electrolyzer manufacturers could produce ALK electrolyzers with the maximum hydrogen production rate to 3000 Nm^3/h; these stacks and their balance of plant (BOP) systems still need to be verified by the commercial or demonstration project. Moreover, China boasts a vast landmass, and most renewable energy is located in the less developed regions. Since there are multiple conversion steps from renewable energy to power and power-to-hydrogen, it makes economic sense in regions with favorable renewable energy resources and corresponding land availability [78]. That raises a spatial mismatch between hydrogen energy consumption and supply. The high cost of hydrogen storage and transportation is a barrier; thus, additional research and development is needed.

4. Power-to-Methanol

Methanol is widely used as a basic chemical and in the production of formaldehyde, acetic acid, dimethyl ether, methyl tertbutyl ether, and many other chemicals [79]. The boiling and melting point of methanol at standard atmospheric pressure are 64.7 °C and −97.8 °C, respectively, making it easy to store and transport in liquid form [80]. Due to its much higher volumetric energy density than hydrogen and ease of transport, it can serve as a hydrogen carrier. Methanol can be directly used as a transportation fuel and is also considered as energy. Generally, in industrial applications, syngas is produced from coal gasification or natural gas reforming first, and then methanol is produced from syngas at 5–10 MPa and 250–300 °C using copper (Cu)-based catalysts [81]. Nevertheless, the process in which methanol is produced from captured carbon dioxide and green hydrogen from renewable energy sources has received a lot of attention and research in recent years [82]. The methanol synthesis process of power-to-methanol in this paper refers to this process as well.

4.1. Methanol Synthetic Reaction

The main reaction equations involved in methanol synthesis from H_2 and CO_2 are shown in Equations (8) and (10) [83]. In addition to the methanol formation reaction from CO_2 hydrogenation, the reverse water gas shift (RWGS) reaction as well as the CO hydrogenation to methanol reaction can occur. The whole process of methanol synthesis is thermodynamically exothermic, and lower temperatures promote the CO_2 hydrogenation reaction. However, the average kinetic energy of the reactants increases with the increase in temperature, leading to faster motion and higher collision frequency of the molecules, and, consequently, facilitates the reaction. In general, the temperature range of methanol synthesis process is 250–300 °C. Furthermore, the methanol synthesis process has to occur under elevated pressure normally at the range of 3–5 MPa.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \ \Delta H_{298K} = -49.1 \text{ kJ/mol} \tag{8}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \ \Delta H_{298K} = +41.2 \text{ kJ/mol} \tag{9}$$

$$CO + 2H_2 \rightarrow CH_3OH \ \Delta H_{298K} = -90.8 \text{ kJ/mol} \tag{10}$$

One of the crucial challenges of the CO_2 hydrogenation reaction for researchers is to seek catalysts with efficient methanol production as well as high methanol selectivity. As catalysts are the key factors that determine the cost and efficiency of methanol synthesis from H_2 and CO_2, great attempts have been made in recent years [84–87]. The catalysts used for methanol synthesis from H_2 and CO_2 are mainly various heterogeneous catalysts, including copper-based catalysts [88–90], indium oxide (In_2O_3)-based catalysts [91,92], and noble metal catalysts [93,94]. The catalytic performance of several different catalysts in references is shown in Table 5. Cu-based catalysts are reported in many studies due to their relatively high activity and methanol selectivity. The majority of Cu-based catalysts consist of Cu, ZnO as support, along with different promoters such as aluminum, cerium, zirconium, silicon, boron, gallium, etc. Among them, $Cu/ZnO/Al_2O_3$ catalysts are the most promising for large-scale industrial applications because of their economic benefits, where ZnO as support alters the structure of the Cu phase by adding more active sites to the Cu surface and improving the dispersion of active species, and Al_2O_3 as promoter increases the overall catalytic activity [95]. In addition, $Cu/ZnO/ZrO_2$ catalysts have also received a lot of research attention as they generally show significant catalytic efficiency [96]. In_2O_3-based catalysts exhibit high methanol selectivity and outstanding stability [97]. It has been reported that In_2O_3/ZrO_2 catalysts, i.e., In_2O_3-based catalysts with ZrO_2 as support, demonstrate excellent activity, nearly 100% methanol selectivity and remarkable stability for 1000 h under industrially relevant conditions [98]. Concerns have been raised for noble metal catalysts mainly because of their catalytic and anti-sintering activity. However, noble metal catalysts are currently expensive and economically unfeasible.

Table 5. Catalytic performance of different methanol synthesis catalysts in different references.

Reference	**Catalysts**	**H_2:CO_2**	**Temperature (°C)**	**Pressure (MPa)**	**GHSV (h^{-1})**	**CO_2 Conversion (%)**	**Methanol Selectivity (%)**
Florian et al. [99]	Standard commercial catalyst (Süd-Chemie)	3.1:1	250	8	10,500		
Toyir et al. [100]	$Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$	3.7:1	250	7	10,000		
Doss et al. [101]	commercial catalyst (Johnson Matthey) $Cu/ZnO/Al_2O_3$	3:1	240	6.9	3300	5.81	
Choi et al. [102]	$Cu\text{-}Pd/CeO_2$	3:1	270	3		16.1	26.7
Tan et al. [103]	$Cu/ZnO/Al_2O_3$	3:1	260	3	6000	23.1	31.2
Tan et al. [103]	$CuNi_2/CeO_2{-}NT$	3:1	260	3	6000	17.8	78.8
Zabilskiy et al. [104]	Standard $Cu/ZnO/Al_2O_3$ catalyst (Alfa Aesar)	3:1	260	1.5		2	43
Liang et al. [105]	Cn-Zn/Al foam	3:1	250	3		13.6	64.5
Wang et al. [96]	$Cu/ZnO/ZrO_2$	3:1	220	3		18.9	80.2
Zhang et al. [106]	CuZn/CeO		260	3			68.5
Wang et al. [107]	Cu-Mn-Zn/ZrO	3:1	250	5	4000	6.5	73.7
Martin et al. [98]	In_2O_3/ZrO_2	4:1	300	5	20,000	5.2	99.8
Rui et al. [108]	In_2O_3	4:1	300	5	21,000	8.2	71
Chou et al. [109]	In_2O_3/ZrO_2	4:1	300	4	52,000	10.5	53
Chou et al. [109]	$1.5YIn_2O_3/ZrO_2$	4:1	300	4	52,000	7.6	69
Wang et al. [110]	M_aZrO_x (M_a = Cd, Ga) solid-solution catalysts	3:1	300	5	24,000	4.3–12.4	80
Li et al. [111]	Pd/ZnO-ZIF-8	3:1	270	4.5		9.3	74

4.2. Methanol Synthesis Process System

The methanol synthesis process system from H_2 and CO_2 consists of a compression unit, a reaction unit, a separation and purification unit, and a storage unit. Altogether, it can be divided into four subsections, as shown in Figure 3. In the compression unit, both H_2 and CO_2 as fresh gas are compressed to relatively high pressure, normally between 3 and 5 MPa, by multistage compressors. In the reaction unit, the compressed gas is mixed together and is heated in the heat exchanger first. Then the heated gas is fed to the synthesis reactor, where the catalyst is immersed inside. The synthesis reaction in the reactor has a low single-pass conversion efficiency; hence, gas from the reactor outlet comprises the produced methanol, together with the unreacted H_2, CO_2, CO, and other byproducts such as H_2O. In the separation and purification unit, gas from the reactor outlet is cooled down before entering the flash evaporators. In the first flash evaporator, some vapor is condensed into a liquid form and separated. In the second flash evaporator, crude methanol vapor is condensed into a liquid form and separated with the unreacted H_2, CO_2, and CO. Next, the unreacted H_2, CO_2, and CO are recycled back and mixed together with the compressed fresh gas, and then the reaction process is recycled. The crude methanol, mainly composed of methanol and water, is sent further for distillation forming and is stored in tanks.

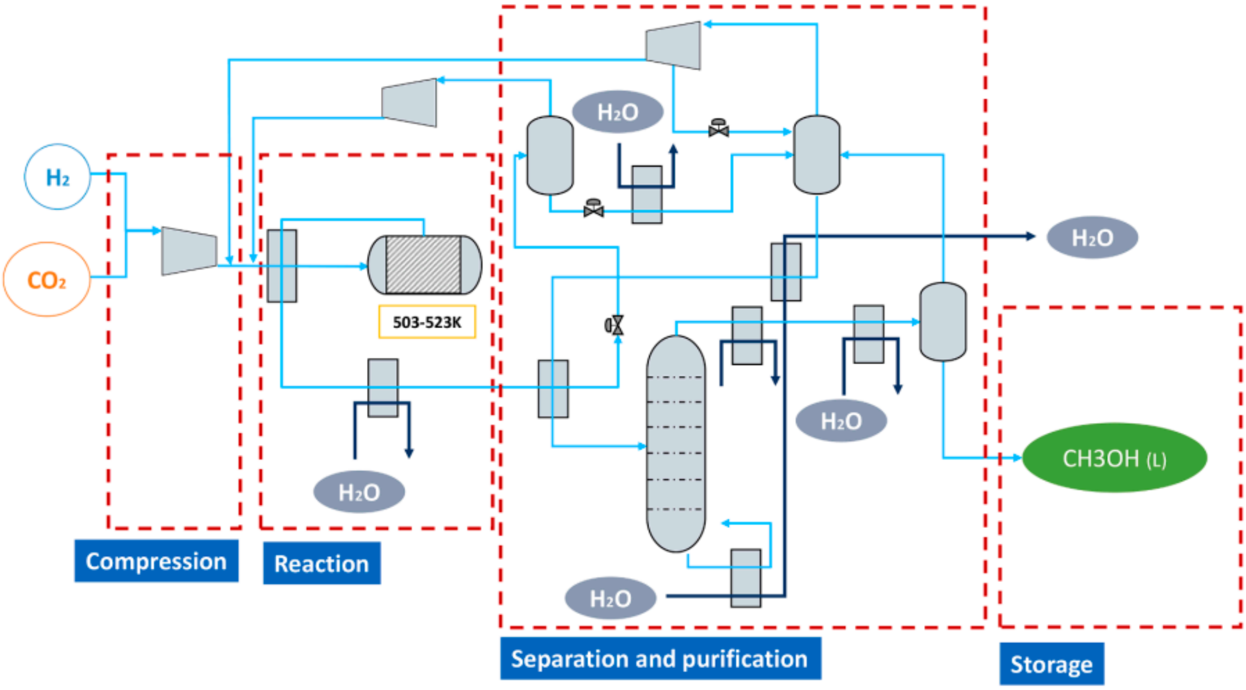


Figure 3. Methanol synthesis process system [112].

4.3. Trends and Challenges

The reactor is one of the core pieces of equipment in a methanol synthesis process system [113]. The primary reactor design considerations are effective heat removal and low pressure drop, as well as flexibility and economics [114]. Nowadays, the dominant and technically well-established reactor is a quasi-isothermal fixed-bed reactor via cooling through vaporizing water [40]. In China, it is also the most used type of reactor for industrial application. The improvement of the reactor should be considered to adapt the newly developed catalysts. In addition, recently, researchers have attempted to develop novel reactors, include membrane reactors, micro (channel and monolith-structured) reactors, and nonthermal dielectric plasma reactors, to improve the efficiency of conversion [115,116].

The integration and optimization of hydrogen production from new energy sources coupled with the methanol synthesis system is the key to the power-to-methanol system. It is necessary to overcome the fluctuation of fresh H_2 and enhance variable load capacity. For these purposes, there have been some studies on capacity planning, dispatch, and the flowsheet optimization model [117–123]. However, because of the complex dynamics of methanol synthesis and distillation-based separation, the capacity planning and integration for the power-to-methanol system needs further study.

Currently, there are many planned or under-construction power-to-methanol projects in China. The market for methanol production is mature and large. However, due to the lack of domestic standards and policies for power-to-methanol products, the products have not received premium attention, and they compete with traditional synthetic methanol products in the same market. This is also a challenge faced by the current development of power-to-methanol in China.

5. Power-to-Ammonia

Ammonia is an important chemical raw material in modern industry and is widely used in the production of fertilizers in agriculture. It is a chemical precursor used in the production of polyimides, nitric acid, nylon, pharmaceuticals, refrigerants, and other industrial materials [124]. As a carbon-free chemical, ammonia has recently been considered as a promising hydrogen carrier, and it is easier to store and transport as a liquid than hydrogen [125]. It can be transported in liquid form at environmental pressure and a temperature of −33 °C, or environmental temperature and a pressure of 0.8 MPa. Furthermore, ammonia can be converted back to hydrogen with low energy consumption, or directly used as a fuel with low carbon emission or a chemical commodity [126]. In modern industry, the ammonia is commonly synthesized through the Haber–Bosch process [127,128], where hydrogen and nitrogen react over iron-based catalysts at 10–30 MPa and 350–550 °C. For power-to-ammonia in this paper, we refer to the process in which the green hydrogen from renewable energy sources reacts with nitrogen obtained by air separation through the thermochemical reaction method.

5.1. Ammonia Synthetic Reaction

The ammonia synthesis from H_2 and N_2 is also thermodynamically exothermic, and the reaction equation is shown in Equation (11). The reaction process in the presence of catalyst mainly includes the following steps [129]: (1) adsorption of hydrogen and nitrogen on the catalyst surface; (2) dissociation of hydrogen and nitrogen molecules to hydrogen and nitrogen atoms, respectively; (3) combination of activated hydrogen atoms with activated nitrogen atoms to form surface-bound ammonia; (4) desorption of ammonia molecules from the catalysts. Because the nitrogen molecule is very stable and is difficult to activate with the strong nitrogen–nitrogen triple bond, the ammonia synthesis reactions from H_2 and N_2 have to occur at high temperature and pressure [130]. The dissociation of nitrogen molecules to nitrogen atoms is the rate-determining step under high-temperature and high-pressure conditions [124].

$$N_2 + 3H_2 \rightarrow 2NH_3 \ \Delta H_{298K} = -45.9 \text{ kJ/mol} \tag{11}$$

Nowadays, significant efforts have been made to improve the conventional thermo-catalytic ammonia synthesis reaction by finding new catalysts that can decrease reaction temperature and pressure. The types of catalysts include iron-based catalysts, ruthenium-based catalysts, cobalt-based catalysts, nickel-based catalysts, and metal-nitride-based catalysts. The catalytic performances of several different catalysts in the references are shown in Table 6. As early as the beginning of last century, many efforts have been made to focus on Fe-based catalysts, which are still the most widely used in the industrial ammonia synthesis today due to their low cost and good catalytic performance [131]. The two typical oxide precursors for Fe-based ammonia synthesis catalysts are magnetite (Fe_3O_4), with an inverse spinal crystal lattice structure, and wustite ($Fe_{1-x}O$), with a cubic lattice structure [132]. Among them, the wustite catalysts show much higher activity and lower reduction temperature than the magnetite catalysts [133]. Generally, small addition of promoters, such as Al_2O_3, K_2O, CaO, and SiO_2, could promote the performance of Fe-based catalysts. The most common structural and electronic promotors for Fe-based ammonia synthesis catalysts are Al_2O_3 and K_2O, respectively [130]. In addition to Fe-based catalysts, Ru-based catalysts are the only other catalysts that can be used in industrial ammonia synthesis. In particular, Ru-based catalysts exhibit high activity at reduced temperature and pressure, which leads to ammonia synthesis under relatively mild conditions. Generally, the synthesis of ammonia from hydrogen and nitrogen using Fe-based catalysts occurs under 350–550 °C and 10–30 MPa. For Ru-based catalysts, the range of reaction temperature is 300–450 °C and the pressure is 4–15 MPa [134]. The other focuses of Ru-based catalysts include the precursor form [135], different support materials [136], and promotors [137]. However, Ru-based catalysts are limited by Ru's insufficient resources and high price.

Table 6. Catalytic performance of different ammonia synthesis catalysts in different references.

Reference	Catalysts	Compositions (wt.%)	H_2:N_3	Temperature (°C)	Pressure (MPa)	GHSV (h^{-1})	NH_3 Concentration (%)
Han et al. [138]	WBC	80.46FeO + 12.66Fe_2O_3 + 1.8Al_2O_3 + 0.6K_2O + 1.8CaO + 2.68others	3:1	350–475	5	30,000	10.4–18.5
Han et al. [138]	Nb-WBC	80FeO + 12.52Fe_2O_3 + 1.8Al_2O_3 + 0.6K_2O + 1.8CaO + 0.6Nb_2O_5 + 2.08others	3:1	350–475	5	30,000	9.6–17.9
Yu et al. [139]	A110-3	68Fe(total) + 2.2Al_2O_3 + 0.59K_2O + 1.2CaO + 0.36SiO_2	3:1	425	15	10,000	19.5
Yu et al. [139]	FA401	68Fe(total) + 2.3Al_2O_3 + 0.58K_2O + 1.1CaO + 0.33SiO_2 + 0.3MgO + 0.38others	3:1	425	15	10,000	20.8
Czekajło et al. [140]	ZBRW-10	2.18Al_2O_3 + 0.44K_2O + 1.3CaO + 2.01CoO_2	3:1	475	10	20,000	10.8
Jafari et al. [141]	Wustite	65.7O + 30.62Fe + 2.4Al + 0.31K + 1Ca	3:1	350–530	3		
Jafari et al. [141]	Magnetite	65.7O + 30.24Fe + 3.3Al + 0.23K + 0.54Ca	3:1	350–530	3		
Kobayashi et al. [142]	Ru/$BaTiO_{2.5}H_{0.5}$	0.9Ru	3:1	400	5		0.17
Han et al. [143]	Ru/$La_2Ce_2O_7$	4Ru	3:1	425	10	10,000	12.94
Lin et al. [144]	Ba-Ru/AC-G	9Ba	3:1	400	10		
Karolewska et al. [145]	(Co-Ce)-Ba/C	9.34Co	3:1	400	9		
Zybert et al. [146]	Co/Ba(CP)		3:1	400	6.3	70,000	
Ye et al. [147]	Ni/CeN NPs	10Ni	3:1	400	0.1	36,000	

5.2. Ammonia Synthesis Process System

The ammonia synthesis process system from H_2 and N_2 consists of four parts: a compression unit, a reaction unit, a refrigeration and separation unit, and a storage unit. The system diagram is shown in Figure 4. First, the fresh H_2 and N_2 are mixed together, where N_2 is extracted from the air via different methods including cryogenic distillation, pressure swing adsorption, and membrane separation [148]. Then, the mixed fresh gas is compressed to the required pressure by multistage compressors. At the heat exchanger, the compressed gas is heated up before entering the synthesis reactor. Similar to methanol synthesis, the ammonia synthesis reaction has a low single-pass conversion efficiency in the reactor [149]. In the refrigeration and separation unit, unreacted H_2 and N_2 are separated with the produced NH_3 and are returned for recycling reactions. The produced NH_3 is stored in tanks in a liquid form.

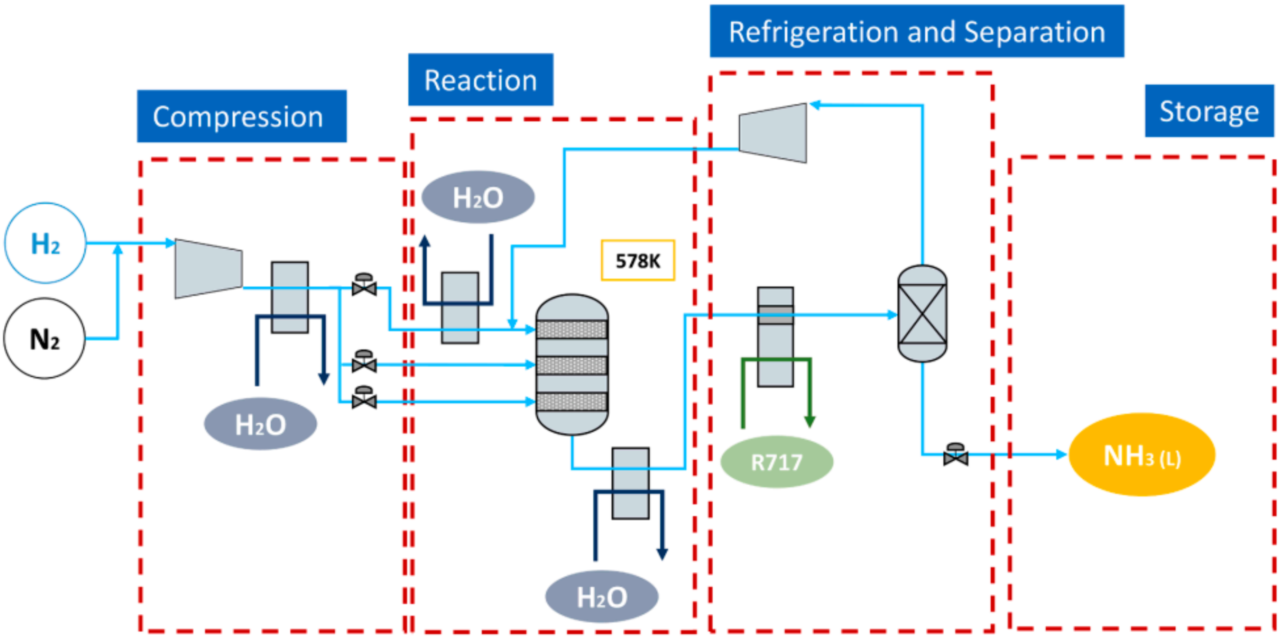


Figure 4. Ammonia synthesis process system [112].

5.3. Trends and Challenges

The presence of oxygen in the fresh gas would reduce the activity of ammonia synthesis catalysts and lead to catalyst poisoning. Recent research has shown that even oxygen impurities below 1 ppm can lead to the obvious deactivation of iron-based ammonia synthesis catalysts [150]. Oxygen is the byproduct of hydrogen production by water electrolysis and it inevitably exists in hydrogen products. Hence, extensive purification processes must be adopted to obtain pure hydrogen to avoid poisoning of the ammonia synthesis catalysts. These purification processes not only increase the initial and operating costs of large-scale ammonia synthesis plants, but also reduce the overall efficiency. Therefore, it is necessary to improve the oxygenate tolerance of catalysts and continue develop new catalysts in the future. In addition, the development of ammonia synthesis catalysts should take into account the intermittency of renewables, making it work efficiently at different loads.

In the traditional chemical industry, most ammonia synthesis process is operated under relatively stable conditions. In China, multiple-bed adiabatic reactors with intercooling stages are generally used as types of ammonia synthesis reactors [151]. For the hydrogen-to ammonia process, rapid and frequent start–stop, and change of reaction temperature and pressure for the reactors are common because of the fluctuations of the fresh hydrogen. This may have adverse effects on materials, instruments, and operation of the ammonia synthesis reactor. The research on integration and flexibility of power-to-ammonia system is not mature enough, either. Overall, substantial efforts need to be devoted to improving the flexibility of ammonia synthesis reactors and power-to-ammonia systems.

Similar to power-to-methanol, ammonia products produced by power-to-ammonia have not received premium attention and do not have enough competitiveness due to the lack of supporting and subsidized policies. There are dozens of power-to-ammonia projects in planning or approval stages in China. It is also an important path for many enterprises to lay out in the hydrogen energy industry. However, sustainable and healthy development of power-to-ammonia in China needs improvements in technology, market, policy, and standards.

6. Typical Commercial or Demonstration Projects

In recent years, following several power-to-X demonstration projects, such as the Lanzhou Liquid Solar Fuel Production Demonstration Project and Kuqa Green Hydrogen Pilot Project, the power-to-X projects have continued to heat up in China. Due to the differences in wind and solar resources, project scales, technical routes, etc., the costs vary significantly among different projects. The approximate costs [40,112,152] for difference power-to-X technologies are shown in Table 7. Dozens of power-to-X projects are currently in progress, and some of the commercial or demonstration projects in China are listed in Table 8. These projects are concentrated in the northwest and northeast regions of China, which are abundant in wind and solar resources. Great breakthroughs have been made in terms of renewable power scale, output of hydrogen, methanol, and ammonia. However, only a few projects have signed product purchase agreements, and the business models still need to be further explored.

China's largest green hydrogen production project has commenced operation in Kuqa city of Aksu prefecture, Xinjiang Uygur autonomous region. The project is also China's first 10,000-ton level solar-generated green hydrogen demonstration project. It mainly comprises three parts: a 200 MW capacity photovoltaic power generation system, a power transmission and transformation system, and a 20,000 tons per annum water electrolysis hydrogen production system. As a demonstration project, it is expected to reduce 485,000 tons of carbon dioxide emissions annually. It is of great significance to promote the development of the green hydrogen industry chain, and promote the transformation and upgrading of the energy industry.

Table 7. The cost for different power-to-X technologies.

	Power-to-Hydrogen			**Power-to-Methanol**	**Power-to-Ammonia**
	ALK	**PEM**	**SOEC**		
Cost	CNY 5437~9425/kW	CNY 14,500/kW	CNY 25,375/kW	CNY 7.91~15.81/kgCH_3OH	CNY 7.12/kgNH_3

Table 8. Some of the commercial or demonstration projects in China.

Project Name	Location	Scale	Status
Guyuan Wind Energy Hydrogen Production Industrial Application Project	Guyuan, Hebei	200 MW wind 10 MW H_2	2022 start operation
Kuqa Green Hydrogen Pilot Project	Kuqa, Xinjiang	200 MW solar 20,000 t/a H_2	2023.06 the first phase start operation
Ordos Green Hydrogen Pilot Project	Ordos, Inner Mongolia	450 MW wind 250 MW solar 30,000 t/a H_2	Under construction
Lanzhou Liquid Solar Fuel Production Demonstration Project	Lanzhou, Gansu	10 MW solar 1000 t/a CH_3OH	2020.01 start operation
The Da'an Wind and Solar Green Hydrogen Synthesis Ammonia Integration Demonstration Project	Da'an, Jilin	700 MW wind power 100 MW solar 32,000 t/a H_2 180,000 t/a NH_3	Under construction
Songwon Hydrogen Energy Industrial Park Project	Songyuan, Jilin	800 MW wind power 100 MW solar 45,000 t/a H_2 200,000 t/a NH_3 20,000 t/a CH_3OH	Under construction
Liaoyuan Power-to-X Project	Liaoyuan, Jilin	1.4 GW wind power 0.4 GW solar 100,000 t/a H_2 38,000 t/a NH_3 620,000 t/a CH_3OH	Under construction
Qianguo Power-to-X Project	Songyuan, Jilin	1.3 GW wind power 20,000 t/a NH_3 400,000 t/a CH_3OH	Planning
Xingan League Energy Carbon-zero Hydrogen Production Project	Ulanhot, Inner Mongolia	1.25 GW wind power 56,200 t/a H_2 300,000 t/a NH_3	Planning

The Lanzhou Liquid Solar Fuel Production Demonstration Project was successfully tested in January 2020, which is China's first 1000-ton level project in converting solar energy into methanol. This project constructed a 10 MW solar photovoltaic power generation system for hydrogen production by water electrolysis, and then hydrogen was used for methanol synthesis combined with carbon dioxide. When the project operates at the design capacity, it could consume 2000 tons of CO_2 and produce 1500 tons of methanol annually. Specifically, the methanol synthesis unit adopts a solid solution bimetallic oxide catalyst (ZnO-ZrO_2) with high methanol selectivity and good stability. The methanol selectivity is greater than 90%, and the catalyst performance degradation after 3000 h of operation is less than 2%.

Construction of the Da'an Wind and Solar Green Hydrogen Synthesis Ammonia Integration Demonstration Project has now commenced, which is also the world's largest green synthetic ammonia project that was launched in 2022. The project is located in an industrial park in the city of Da'an, Jilin province, and it will build a total installed capacity of 800 MW of wind and solar, providing 32,000 tons of hydrogen production and 180,000 tons of synthetic ammonia annually. Among the hydrogen production system, 50 sets of PEM hydrogen production systems and 39 sets of alkaline hydrogen production systems are included. The first phase of this project is expected to start operation in 2024.

7. Conclusions

In China, hydrogen has become an important strategic choice to accelerate energy transformation and upgrading. Hydrogen can be produced from renewable energy by electrolysis as the final energy carrier or converted into X. Collectively, power-to-X provides a cost-effective way to balance the intermittent renewable energy power generation and demands. This paper provides a review of three hydrogen-driven power-to-X technologies and their applications in China, which are power-to-hydrogen, power-to-methanol, and power-to-ammonia. These three hydrogen-driven power-to-X technologies are also the most promoted technical routes in China.

Currently, China has already become the world's largest producer and consumer of hydrogen. Especially for the recent five years, a large number of policies has been issued intensively. In 2022, China issued a hydrogen national strategy for the first time. It states that hydrogen shall play a key role in the development of China's energy sector. Moreover, it explicitly mentions the exploration and promotion of using hydrogen from renewable energy for replacing fossil fuels in industries such as synthetic ammonia and methanol. In conclusion, China attaches importance to the development and application of hydrogen-driven power-to-X technology.

Among the different methods for power-to-hydrogen, ALK water electrolysis, PEM water electrolysis, and SOEC water electrolysis are the three mainstream water electrolysis methods under research. ALK electrolysis is the most mature method; the maximum hydrogen production rate produced by Chinese electrolyzer manufacturers could reach 3000 Nm^3/h. The capacity to integrate with variable renewable energy sources needs improve due to its low load range and long response time. PEM electrolysis has advantages in terms of short time response and widened load range between 0 and 150%. Reducing the cost of cell components could be very challenging. SOEC electrolysis is still less mature commercially, and the stability at high temperatures needs to be studied. Chinese electrolyzer manufacturers are capable of producing the above three types of electrolyzers.

Cu-based catalysts and Fe-based catalysts are the most widely used catalysts in industrial methanol and ammonia synthesis, respectively. For power-to-methanol and power-to-ammonia, it is vitally important for research to proceed on synthetic reaction catalysts with excellent catalytic performance and high selectivity at different loads, with the ability to withstand the harsh reaction conditions, and cost-effectiveness. In addition, in order for both technologies to be applied on larger scales, considerable advances in equipment and systems have to be achieved.

In China, most commercial or demonstration projects of power-to-hydrogen, power-to-methanol, and power-to-ammonia are in planning, approval or construction stages. These projects are located in the regions abundant in wind and solar resources. A few demonstration projects have already been put into operation, whereas demonstrations are a key step for technologies towards reaching the market. All these three hydrogen-driven power-to-X technical routes have very wide popularization and application prospects in China.

In addition, power-to-X are not limited to the as-mentioned three power-to-X technical routes. There are other power-to-X pathways, including power-to-methane, power-to-formic acid, power-to-formaldehyde, and power-to-alkanes, which are rapidly developing and have great prospects. With the development of these technologies and the increase in decarbonization demand, other power-to-X technologies will gain more attention in China.

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