Analysis of Research Progress in Different Hydrogen Production Methods

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**Abstract.** In an era of energy scarcity, the need to find cleaner and non-polluting energy sources is paramount. Among the most appropriate energy sources is hydrogen. This paper compares and contrasts the main hydrogen production technologies at this stage, such as hydrogen derived from industrial waste, hydrogen from fossil fuels, and hydrogen produced by electrolyzing water. The results indicate that the primary source of hydrogen production at this time is fossil fuels; industrial production of hydrogen and hydrogen from electrolytic water still requires improvement; hydrogen production is not a significant energy source at the moment; and further research and development are required to make hydrogen production technology available for the energy transition. As well as, technologies for producing hydrogen must also figure out how to make the process more affordable and efficient, such as more stable and durable catalysts. A key component of future development is the technology for producing hydrogen.

# Introduction

With the increase in population and economic development, human demand for energy has been rising, while traditional resources are gradually being depleted. Conventional energy sources are also causing increasing problems in terms of environmental pollution. Finding an environmentally friendly, renewable energy resource that can substitute current sources of energy is therefore crucial to supplying future energy demands. Hydrogen, as a clean energy source, reacts chemically with oxygen and produces no harmful chemicals during combustion. Hydrogen has a very high calorific value, with 1kg of hydrogen giving off about 143,000kJ of heat. A large amount of heat is given off in combustion, and hydrogen has more than four times the calorie content of carbon coke and 3 times that of gasoline. So far, to fulfil the "dual-carbon" objective, China has been aiming at a clean energy transition . At this point, the primary development directions are the development of electrolytic water hydrogen production, the optimisation of conventional fossil fuel hydrogen generation technologies, and improving the efficiency of industrial by-product hydrogen extraction. This study's goals are to present an in-depth look of current (novel) methods of producing hydrogen, such as electrolytic water, and to study and predict future trends. In this era of energy constraints, industrialised production and storage of hydrogen energy at a reasonably low cost could alleviate energy shortages and excessive pollution.

# Research on different hydrogen production methods

According to the existing stage in China, the old method of producing hydrogen mainly relies on fossil fuels or industrial by-products, the technology is more mature but with higher carbon emission, and the hydrogen produced is mostly grey hydrogen. Novel hydrogen production technologies, on the other hand, focus on cleanliness, efficiency and sustainability, depending on sustainable energy sources or advanced catalysis. Thermochemical cycles, photolysis of water, biomass, and electrolysis of water are examples of common novel methods for producing hydrogen.

## Hydrogen Production from Coal

China's fossil fuel-based hydrogen generation has two major parts: hydrogen production from coal and hydrogen production from natural gas. At the beginning of the 20th century. In order to address the issues of energy supply and industrial raw material demand, Germany was the pioneer in the application of coal hydrogen production technology, such as in the chemical industry Germany provided hydrogen energy to produce ammonia and methanol products. China is rich in coal. The China Coal Industry Association has surveyed that China has 14 percent of the world's coal reserves, amounting to 1.3 trillion tons [1]. The two steps in the production of hydrogen from coal are coal gasification and gas purification, coal gasification is mainly through the reaction between coal and water vapour to produce carbon monoxide and hydrogen equations are shown below:

C+H2O→CO↑+H2↑ (1)

Carbon dioxide in the air can also react with coal in a redox reaction to form CO making it possible to continue to react with water vapour to produce hydrogen Equation see below:

C+CO2→2CO (2)

CO+H2O→CO2+H2 (3)

Hydrogen can contain by-products such as CO, CO2 and other gases, which need to be purified using gas purification. Common purification methods include scrubbing, adsorption and membrane separation, all of which increase the purity of prepared hydrogen [2].

The advantage of hydrogen production from coal is that the raw material is very abundant and the cost is not high, which is suitable for places with abundant coal resources such as Shanxi, Inner Mongolia and Shaanxi in China. The method for producing hydrogen from coal is currently advanced enough for widespread industrial use. China's reliance on imported energy is lessened by the utilisation of coal resources.

The process's drawback is that the hydrogen generated from coal is grey hydrogen, which pollutes the environment and releases roughly 11 kg of greenhouse gases for every kilogramme of hydrogen generated. Hydrogen generation requires high temperatures and pressures, which makes it less energy-efficient and more energy-intensive. In the coal gasification process, sulphur-containing and nitrogen oxides are produced, and these pollutants need to be separated and collected, which can pollute the environment.

## Natural Gas-based Hydrogen Generation

## As early as the 20th century Germany began to study the technology of hydrogen production from natural gas and made important breakthroughs in this field. The steam reformation of methane (SMR), partial oxidation of methane (POM), autothermal reforming of methane (ARM), and dry reforming of methane (DRM) are the primary processes for producing hydrogen from natural gas. SMR currently leads China's natural gas to hydrogen production market due to its maturity and low costs. The reaction involves natural gas and a catalyst (nickel-based catalyst) and takes place at temperatures between 700 and 1000°C., and the equation for the preparation is given below:

CO+H2O→CO2+H2 (3)

CH4+H2O→CO+3H2 (4)

A mixture of CH4, CO, CO2, H2, and H2O is the end result of the reaction between natural gas and water vapour, which produces CO and H2. The byproducts of this reaction subsequently react to produce CO2 and H2. After separation and purification, H2 is ultimately obtained from the resultant gas [3].

The benefit of using natural gas for hydrogen production is that it is among the least expensive methods available, costing far less than electrolysis of water. The SMR process has been developed and ready for large-scale manufacturing. The production process has a significant benefit over other hydrogen generation techniques due to its high energy conversion rate, which can reach 70–85%. Natural gas offers a rather steady supply of transported materials and a broad distribution of resources in terms of raw materials.

The disadvantages of this technology are that the price of natural gas fluctuates greatly depending on international political and economic influences, and production costs are unstable. Hydrogen production requires multiple processes with high operating costs. Conventional hydrogen production from natural gas has a long process flow and low energy utilisation. Large volumes of carbon dioxide are released during the conventional process of producing hydrogen from natural gas, which is not environmentally beneficial.

## Industrial By-production Of Hydrogen

At the beginning of the 20th century, industrial by-production of hydrogen was first used in the chlor-alkali industry, where salt water was electrolyzed to produce chlorine and sodium hydroxide, and at the same time a certain amount of hydrogen was produced. In the process of hydrogen production from natural gas, as of 2022, China is producing up to 553,400 tonnes of hydrogen by-products on ethylene, which is 64.5 kg of hydrogen for every tonne of ethylene produced[4]. There must be a method to separate and purify such a huge quantity of hydrogen. Pressure swing adsorption (PSA) gas separation technology is currently the primary technique for the extraction and filtration of hydrogen in the industrial by-production process. Selective adsorption of unwanted components by means of a solid adsorbent at a certain pressure. The solid adsorbent chosen needs to have a weak adsorption capacity for the target gas and a strong adsorption capacity for other components of the gas. Separation and purification of gases are achieved by periodically varying the pressure (pressurised adsorption and desorption at reduced pressure), also known as variable pressure adsorption mixing technique [5].

Industrial by-production of hydrogen has the advantage of low feedstock costs and does not require additional energy inputs. Simply converting the by-products of the industrial process into high-value hydrogen separation saves resources and reduces harmful emissions, making it friendlier to the environment. Variable pressure adsorption and membrane separation in industrial by-product hydrogen production are well-established methods to efficiently extract hydrogen from by-products.

The disadvantage of industrial by-production of hydrogen is that it is dependent on the operation of the main process, and if the main supply is shut down, the by-production of hydrogen will not be produced. The process of full purification is extremely complex, and it is challenging to guarantee high purity of separated and purified hydrogen. The cost of producing hydrogen rises as the solid adsorbent gradually loses its effectiveness and needs replacing on a regular basis.

## Hydrogen Production by Electrolysis of Water

The beginning of the electrolysis of water to produce hydrogen technology began in 1800, the British scientists William Nicholson and Anthony Carlisle electrolysis of water, water decomposition into hydrogen and oxygen. This technology is efficient and clean and does not produce polluting gases. Alkaline water electrolysis (AWE), proton exchange membrane water electrolysis (PEM), anion exchange membrane water electrolysis (AEM), and solid oxide electrolysis cell (SOEC) are the four forms of water electrolysis currently used to produce hydrogen. The main reaction equations are as follows:

2H2O→2H2↑+O2↑ (5)

### Alkaline Electrolysis of Water Technology(AWE)

In 1931, the first equipment for alkaline electrolysis of water was manufactured in Japan. The principle is mainly by filling the two electrodes with a certain concentration of electrolyte solution such as KOH and NaOH. To obtain electrons to reduce to hydrogen, the cathode goes through a reduction reaction; to lose electrons to oxidise to oxygen, the anode goes through an oxidation reaction. The equations for each electrode are shown below:

Cathode: 4H2O+4e-→2H2↑+4OH- (6)

Anode: 4OH--4e-→2H2O+O2↑ (7)

The choice of electrode material affects the electrolysis rate, cost and equipment life. The cathode is the process of hydrogen precipitation and requires high catalytic activity and stability. The conventional use of nickel-molybdenum (Ni-Mo) alloys and nickel-iron (Ni-Fe) alloys as cathode materials can both enhance the catalytic performance for efficient hydrogen production. Novel materials are sulphides of transition metals (e.g. MoS₂, WS₂), which provide higher catalytic activity and further cost reductions, but are less stable.

The lower price of producing hydrogen, the technology's maturity, its extended service life, and its suitability for large-scale industrial production are its advantages. The required electrolyte raw materials such as KOH and NaOH are also easily available.

The technology needs to be upgraded because the electrodes are susceptible to corrosion leading to deactivation and the hydrogen production efficiency is low, reaching only 60-75%. The switching of the alkaline electrolyser takes a long time not able to respond quickly. The switching speed of the equipment cannot be well controlled [6]. As the electrolyte is highly corrosive, the sealing of the equipment has high requirements and the material should be corrosion-resistant, which increases the maintenance cost.

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### Water Electrolysis with Proton Exchange Membrane Technology(PEM)

In the mid-20th century, proton exchange membranes were first applied to fuel cells by the research team of General Electric (GE), and later gradually expanded to hydrogen production by water electrolysis. Proton exchange membranes are selectively permeable membranes that allow protons (H+) to pass through. At the anode, water oxidises and loses electrons to produce hydrion and oxygen;At the cathode, hydrogen ions reduce and acquire electrons to produce hydrogen gas. The gases obtained were collected and the reaction equation is given below:

Cathode: 4H++4e−→2H2 (8)

Anode: 2H2O-4e−→4H++O2 (9)

The core components of proton exchange membrane hydrogen production are the proton exchange membrane, catalytic electrode, gas diffusion layer, and bipolar plate. A common material for exchange membranes is perfluorosulfonic acid membranes (e.g. Nafion) used to transfer H+ and isolate hydrogen and oxygen. The cost of the electrode materials used is high and precious metal catalysts are mostly used. In this case, the anode material is generally chosen as iridium dioxide and the cathode material is chosen as platinum and other metals [7]. The gas diffusion layer allows gas and water transport while conducting protons. The bipolar plate then distributes the gas and water drinking current while supporting the membrane electrode assembly.

With 70–90% hydrogen production efficiencies, this technology has the advantage of being more effective at water electrolysis than alkaline water electrolysis. The system can respond quickly, with start-up and stopping times dramatically reduced to less than 3 minutes compared to hydrogen production from alkaline electrolytic water. Filtration through a proton exchange membrane produces very pure hydrogen (99.9%) at the cathode, eliminating the need for additional separation and purification.

Disadvantages exist in that the membrane electrode and bipolar plate are a large part of the cost, and the iridium element in the anode catalyst is expensive, with less than 10t of annual production worldwide, and the price is usually above $1000/g. The anode catalyst could be a major obstacle to hydrogen production technology if large-scale production is carried out [8]. It can be seen that the material cost of using precious metal catalysts (e.g. platinum, iridium) is high. Proton exchange membranes (e.g. Nafion) are also expensive. If cheaper electrode materials and catalysts can be found in future research, PEM technology will be suitable for large-scale production.

### Water Electrolysis with Anion Exchange Membranes Technology(AEM)

Anionite membrane originated from the study of ion exchange resins, where it was found that polymers could selectively permeate anions (OH-), and with the development of science and technology, anion exchange membranes began to be used to produce hydrogen. The bipolar plate, gas diffusion layer, catalytic electrode, and anion exchange membrane are the main parts of the process. The exchange membranes are generally quaternary based (e.g., quaternised polyaryl ethers), which selectively allow hydroxide to pass through while blocking cations, resulting in a purer gas [6]. The cathode in the catalytic electrode uses non-metallic catalysts such as nickel (Ni) and cobalt (Co). The anode uses nickel-iron (Ni-Fe) oxides, cobalt-iron (Co-Fe) oxides, and so on. The gas diffusion layer and the bipolar plate function as components in the proton exchange membrane hydrogen production technology. The anode experiences an oxidation reaction, losing electrons to get oxidised to oxygen, while the cathode experiences a reduction reaction, gaining electrons to be reduced to hydrogen. The reaction equation is shown below:

Cathode: 4H2O+4e−→2H2+4OH− (10)

Anode: 4OH−-4e−→2H2O+O2 (11)

The advantage of this technology is that the electrodes use non-precious metal catalysts, and the cost is significantly lower than PEM electrolysis of water for hydrogen production. The efficiency of hydrogen production is not as high as that of PEM water electrolysis, but it is higher than that of AWE water electrolysis, which can reach 60-80 percent. The start-stop speed is as fast as PEM electrolysis of water, which can be combined with unstable wind and light energy. Pure water or a lower concentration of KOH solution can be used as the electrolyte for the electrolysis tank, which can effectively avoid the problem of excessive corrosiveness caused by too high a concentration, and help to protect the equipment so that it can operate for a longer period of time [9].

The direction to be upgraded is the poor ionic conductivity and durability of anion exchange membranes, which requires continued research and development. The stability of the catalyst is also a problem that exists and cannot be operated for long periods of time. Non-precious metal catalysts degrade and deactivate during use, thus affecting the effectiveness of producing hydrogen. The technology remains in the research, development, and demonstration stages, making it immature at this point. There is a need to find some more durable and stable materials to be used as anion exchange membranes to bring down the cost further [6].

### Solid Oxide Electrolysis technology(SOEC)

The SOEC method breaks down water into H2 and O2 at extreme temperatures (usually 700°C to 1000°C) using a solid oxide electrolyte. The core components of this technology are a solid oxide electrolyte, a cathode material, an anode material, and a linker material. The solid oxide electrolyte is usually yttrium oxide stabilised zirconia (YSZ) or doped cerium oxide (e.g., GDC), which is responsible for conducting oxygen ions (O²-) and isolating hydrogen and oxygen. The cathode material is usually a nickel-yttrium oxide stabilised zirconia (Ni-YSZ) composite. Water vapour undergoes an at-cathode reduction process and gains electrons to generate hydrogen and oxygen ions. Using a solid oxide electrolyte with high ionic conductivity at high temperatures. In the contrary side of the current, the oxygen ions go through the solid oxide electrolyte and congregate close to the anode. The anode material is usually chosen as a calcite oxide, which catalyses the oxidation reaction of oxygen ions to lose electrons and generate oxygen. The linker material is made of chromium-based alloy (e.g., Crofer 22 APU) or ceramic material and is responsible for connecting the single cell and conducting the electrons [10]. The reaction equation is shown below:

Cathode: H2O+2e−→H2+O2− (12)

Anode: O2−-2e−→1/2O2 (13)

Compared to other water electrolysis such as AWE water electrolysis and PEM water electrolysis, SOEC water electrolysis has higher electrolytic efficiency and electrochemical performance, typically in the range of 75 to 100 percent. The technology is a low energy consuming and can utilise waste heat from industry to react and save electricity.

The disadvantage is that the high-temperature environment requires high material heat resistance and equipment sealing. Slow start-up makes it difficult to respond quickly to power fluctuations. High-temperature materials such as ceramic electrolytes are expensive, and the durability of the materials at high temperatures is a challenge, and long-term high-temperature operation may lead to material degradation, affecting the life of the equipment. Currently not widely used, still belongs to the research stage.

# Challenges and developments

The three main techniques of producing hydrogen are electrolysis of water, generation from byproducts of manufacturing and production from fossil fuels. Challenges in fossil energy include the production of large amounts of carbon dioxide during hydrogen production, which is in contradiction with the global ‘dual-carbon’ goal. Large-scale hydrogen production is challenging due to the main process's limitations on hydrogen from industrial by-products, and the secondary process's less pure hydrogen requires separation and purification and this surely raises the difficulty and expense of producing pure hydrogen. The primary challenge in producing hydrogen from electrolytic water is choosing electrode materials; specifically, how to identify more stable and long-lasting materials. The creation of hydrogen is not very efficient and requires additional development. In the future, we must develop towards the road of green hydrogen production, in line with China's ‘dual-carbon’ goal, it must be as far as possible to make use of sustainable energy sources to generate hydrogen (such as wind power, photovoltaic) electrolysis of water to produce hydrogen, to achieve zero carbon emissions. High ionic conductivity, corrosion-resistant exchange membranes must be developed in order to increase the effectiveness in water electrolysis technology, and low-cost, high-efficiency non-precious metal catalysts must be developed in order to lower the cost of water electrolysis technology.

# Conclusion

The existing hydrogen manufacturing processes remain heavily influenced by petroleum-based hydrogen production, which can be more polluting, according to this paper's analysis of the various hydrogen production methods at this point. To achieve carbon compliance and carbon neutrality in line with China's policies, a greener and non-polluting hydrogen production technology is undoubtedly needed. The maturation of pure hydrogen technology will not happen overnight. China should gradually cut back on its use of coke and gas to produce hydrogen, focus more on creating new technologies, like electrolysing water to produce hydrogen, and use cleaner energy to make the transition to clean energy, which will lower CO2 emissions. Enhancing the system process, finding a long-lasting solid catalyst that is difficult to deactivate, and enhancing the separation and purifying effects are all essential in the synthesis of hydrogen from industrial byproducts. There are different methods of hydrogen production in electrolytic water technology, each with its own advantages and disadvantages. For instance, the synthesis of hydrogen from alkaline electrolytic water is inexpensive and feasible on an enormous scale. Finding a suitable material is required to compensate for the limitations of this technology because, although anion exchange membranes produce hydrogen more efficiently than alkaline electrolysis, their lon-conductivity and durability are poor and they cannot be used for a considerable amount of time. In this paper, we introduce the current hydrogen production technology to provide a direction for scientific exploration, promote clean energy transition, and achieve China's ‘dual-carbon’ goal. The technology for producing hydrogen is examined for its benefits and drawbacks in order to serve as a guide for future advancements. Improve the efficiency of energy use and optimise the energy structure with clean energy. In the future, if the technology for producing hydrogen is developed enough to take the place of coke and natural gas as the primary energy source, it can achieve zero pollution of the environment, and the raw materials needed are inexhaustible, the future of hydrogen production technology still has a lot of room for development.

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