Comparison between hydrogen production by alkaline water electrolysis and hydrogen production by PEM electrolysis

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Abstract: Hydrogen is an ideal clean energy source that can be used as an energy storage medium for renewable energy sources. The water electrolysis hydrogen production technology, which is one of the mainstream hydrogen production methods, can be used to produce high-purity hydrogen and other energy sources can be converted into hydrogen storage by electrolysis. Hydrogen production by alkaline water electrolysis and hydrogen production by PEM electrolysis are all water electrolysis hydrogen production technologies that have been industrially applied. From the application point of view, the paper compares the working principle of the two kinds of electrolyzers, the process flow of hydrogen production equipment, advantages and disadvantages. This article provides a reference for relevant researchers.

1. Introduction
Due to the limited reserves of fossil fuels and various environmental problems, the development of clean new energy and renewable energy is an inevitable trend of energy development. The intermittent and unstable nature of renewable energy is the main problem that restricts the development of renewable energy. How to store and sustain the steady release of renewable energy is a major problem in the current use of renewable energy.

Hydrogen is an ideal clean energy source. Compared with other energy sources, hydrogen has high calorific value, high energy density, and multiple storage methods\cite{1}. In addition, hydrogen can also be used as an energy storage medium to store energy in renewable energy systems\cite{2}. There are many hydrogen production methods. However, hydrogen production by water electrolysis has a negligible position in the market due to its high purity, simple operation and no pollution, and it is also the most commonly used method for converting renewable energy into hydrogen storage.

At present, common water electrolysis hydrogen production technologies that have been industrialized include alkaline water electrolysis hydrogen production and PEM electrolysis hydrogen production. From the perspective of industrial application, the paper compares the working principle of the electrolyzers corresponding to the two hydrogen production technologies, the process flow, the operating conditions, the advantages and disadvantages of the hydrogen production equipment, and elaborates the characteristics of the two hydrogen production methods. The content of the article provides reference for relevant researchers.

2. The working principle of the electrolyzers
Hydrogen production electrolyzer is the core of electrolysis water hydrogen production technology,
which not only directly affects the hydrogen production efficiency of equipment, but also accounts for a large proportion of equipment manufacturing costs.

2.1. The working principle of alkaline electrolyzer
The alkaline electrolyzer uses 30% wt KOH solution or 25% wt NaOH solution as electrolyte. The DC current density is 2000A/m$^2$~4000A/m$^2$, the working temperature is generally maintained at 80°C~90°C, and the working pressure is within 3.2MPa. It also needs to ensure equal pressure operation. Structurally, the electrolytic cell uses a permeable membrane, such as asbestos, polyphenylene sulfide. The electrode uses a porous nickel-based electrode, and there are also end plate, gasket, plate, fasteners and other components.

The principle of single chamber electrolysis reaction is shown in Figure 1[3]. The alkaline electrolyte enters the anode and cathode regions on both sides of the membrane, and water molecules can permeate through the membrane to the other side. After the electric current, the water molecules in the electrolyte in the cathode region combine with electrons to form hydrogen and hydroxide ions, and in the anode region, the hydroxide ions lose electrons to generate oxygen and water. Due to the hindrance of the permeable membrane, the gas generated by the electrolysis cannot pass through the membrane to the other side in a large amount, and the generated gas and the electrolyte are discharged from the chamber together for treatment.

2.2. The working principle of PEM electrolyzer
The PEM electrolyzer is a kind of solid oxide hydrogen production cell. The electrolyzed raw material is deionized water. The DC current density is 10000A/m$^2$~20000A/m$^2$, which is about 5 times that of the alkaline water hydrogen electrolyzer. The PEM electrolyzer, with its working temperature of 50 °C~80°C, pressure less than 5 MPa and the volume smaller than the alkaline electrolyzer, can be operated under different pressure.

The structure of the PEM electrolyzer is similar to that of the alkaline electrolyzer. The main difference is the use of a thin film-electrode assembly (also known as a membrane electrode) to form a zero-pole spacing[4]. The separator is a Nafion membrane, which is strongly acidic after being soaked in water, and the anode catalyst and the cathode catalyst are attached to both sides of the separator by electroless plating or hot pressing.

Table 1. Comparison of characteristics of alkaline electrolyzer and PEM electrolyzer.

| Name   | Alkaline electrolyzer | PEM electrolyzer |
|--------|------------------------|------------------|
| Electrolyte | 30% wt KOH solution or 25% wt NaOH solution | Solid polymer |
Current density (A/m²) | 2000~4000 | 10000~20000
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Work pressure (MPa) | ≤3.2MPa | ≤5MPa
Operating temperature (°C) | 80-90 | 50-80
Hydrogen purity (%) | ≥99.8 | ≥99.99
Export component | O₂⁺ Lye, H₂⁺ Lye | O₂⁺ Deionized water, H₂⁺ Trace deionized water
Raw material | Deionized water and alkali | Deionized water
Corrosion | Alkaline corrosion | No
Operating characteristics | Isobaric operation | Differential pressure operation
Structural features | End plate, gasket, permeable membrane, plate, fasteners, etc. | Similar structure, but using membrane electrode, zero pole spacing
Volume and weight | Big | Small, about 1/3 of the alkaline electrolyzer
Manufacturing cost | Low | High
Lifetime | 10 years | 3~4 years

The reaction principle of the PEM electrolyzer is shown in Figure 2[4]. Unlike the alkaline electrolyzer, the deionized water only needs to enter the anode side of the electrolyzer. After energization, oxygen and hydrogen ions are generated on the anode side of the membrane electrode, and hydrogen ions reach the cathode side in a hydrated state (H⁺XH₂O) to generate hydrogen gas. The membrane separates hydrogen from oxygen. Because of the separation of the Nafion membrane and the absence of solution voltage drop, this method has a high energy efficiency for hydrogen production[5]. However, since the catalyst uses a noble metal, the manufacturing cost of the electrolyzer is high. The characteristics of the two types of electrolyzers are shown in Table 1.

3. Process flow of electrolytic hydrogen production equipment

3.1. Process for producing hydrogen by alkaline water electrolysis

The alkaline water hydrogen production device mainly comprises three parts: an alkaline water hydrogen production system, a control cabinet and a rectifier cabinet. The alkaline water hydrogen generator includes an alkaline electrolyzer, a hydrogen separator, an oxygen separator, a gas cooler, a lye circulating pump, a lye cooler, a water storage tank, an alkali tank, control valves, and some other components.

Figure 3. Alkaline water electrolysis hydrogen production process flow chart.
The alkaline hydrogen production process is shown in Figure 3[6]. When the equipment is started, the electrolyte is evenly mixed in the alkali tank, and then pressurized into the electrolytic tank through the pump to enter the entire hydrogen production system. After the liquid in the separator reaches the specified liquid level, the lye inlet valve is closed and the power is turned on. After the alkali solution is electrolyzed in the alkaline electrolyzer, the hydrogen separator and the oxygen separator are respectively introduced from the hydrogen side of the electrolyzer and the oxygen side outlet in a gas-liquid mixed state. The gas is cooled from the upper part of the separator and discharged. The liquid merges into the bottom of the separator at the bottom of the separator and circulates.

At the time of electrolysis, since the water is reduced due to electrolysis, it is necessary to periodically replenish water into the hydrogen separator. At the same time, it is necessary to regularly check the specific gravity of the alkali solution and replenish the alkali solution. Since the alkaline electrolyzer can only be operated at the same pressure, the hydrogen generator needs to be gradually pressurized to the set pressure by the regulating valve at the start, which causes the start-up time to be about 1 hour.

3.2. PEM electrolysis hydrogen production process

The PEM hydrogen production unit includes a PEM hydrogen production system, a control system, and a DC power supply. Compared with the alkaline water hydrogen production system, the PEM hydrogen production system is relatively simple: the gas aftertreatment device is relatively small, no special alkali tank is needed, and the water tank can also be used as an oxygen separator.

![Diagram of PEM hydrogen production process](image)

Figure 4. PEM hydrogen production process flow chart.

The PEM hydrogen production process is shown in Figure 4[7]. When the equipment is started, the water in the water tank is replenished to the set liquid level, and the circulation pump is turned on to circulate, and the water level of the hydrogen separator is observed to reach the designated position. After the liquid level in the water tank and the hydrogen separator is stabilized, the DC power source is energized and the PEM electrolytic cell starts to electrolyze. Oxygen and water are separated into the water tank and separated, and the oxygen is filtered through a molecular sieve to be discharged. Hydrogen and a small amount of water enter the hydrogen separator, and the hydrogen gas passes through the molecular sieve for further treatment. After the water in the hydrogen separator reaches a certain liquid level, part of the water flows into the water tank.

During operation, electrolysis causes a decrease in moisture, so it is necessary to control the amount of water replenishment. In addition, the PEM electrolyzer can be operated under differential pressure. It does not need to be gradually regulated like hydrogen by alkaline water when starting up. The pressure of the regulating valve can be directly set to the specified pressure, and the equipment can be stabilized in 15 minutes.
4. Conclusion
From the working principle of the electrolyzer and the process flow of the electrolytic hydrogen production device, the hydrogen production technology of alkaline water electrolysis and the hydrogen production technology of PEM are compared in the paper.

The alkaline water hydrogen production technology is mature and the manufacturing cost is low. At present, the hydrogen production amount of 1000m³/h has been achieved, which is suitable for the current large-scale hydrogen production-hydrogenation station. However, this technology has the disadvantages of slow start-up, corrosion, complicated maintenance, and many components of the device.

PEM hydrogen production technology has the advantages of fast start-up, no corrosion, simple maintenance, and fewer components[8]. At present, the most advanced equipment can produce hydrogen of 400m³/h. High manufacturing costs are the main factors that restrict the development of PEM hydrogen production technology.

Acknowledgement
This research was supported by Beijing University of Chemical Technology and BeiJing CEI Technology Co., LTD.

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