Application of Proton Exchange Membrane Electrolysis of Water Hydrogen Production Technology in Power Plant

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Abstract. Proton exchange membrane (PEM) electrolyzed water hydrogen production technology has the advantages of high working current density, high electrolysis efficiency, non-polluting reaction, light weight, compact structure, etc. The small-scale electrolyzed water hydrogen production equipment of this technology is used for hydrogen cooling in power plants. The unit field has a wide range of application prospects. This article first introduces the working principle and technical advantages of PEM water electrolysis hydrogen production technology. By comparing with the quantitative results of alkaline water electrolysis hydrogen production technical solutions, it analyzes the technical solutions of PEM electrolysis technology in the hydrogen-cooled generator set of power plants. The equipment composition and economic feasibility further look forward to the development prospects of PEM electrolyzed water technology in power plants and other civilian fields.

1. Introduction
Generator sets are an important part of large thermal power plants. In the actual operation of the generator set, the motor windings and iron core generate a lot of heat due to power loss. In order to avoid the motor burning accident caused by the high temperature of the motor, it is necessary to use a coolant to cool the generator set. The commonly used coolants include air, water, hydrogen, and oil. Among them, hydrogen has high thermal conductivity (thermal conductivity at 25°C). It is 0.182W/(m·K), which is 8.4 times the thermal conductivity of air), small specific gravity, fast diffusion, easy to transport and can be recycled. It is a very effective gas cooling medium. For this reason, the current 330-660 MW thermal power units all use hydrogen as the cooling medium of the generator units. In order to guarantee the hydrogen required by the hydrogen-cooled generator set, a hydrogen supply station must be set up in the power plant to supplement the hydrogen medium in the generator set. The layout of hydrogen supply stations in thermal power plants can be divided into three types: (1) Install a water electrolysis hydrogen production device in the power plant, and prepare hydrogen according to actual needs; (2) Purchase bottled compressed hydrogen; (3) Directly through pipelines Hydrogen is supplied in the power plant. The latter two schemes both rely on local hydrogen sources, and due to the large amount of hydrogen, transportation, storage and pipeline transportation are dangerous. Therefore, many large thermal power plants choose to install hydrogen production stations to produce hydrogen through electrolysis of water and store it in a dedicated storage tank, and provide hydrogen cooling medium to the generator set as needed [1-3].
Water electrolysis hydrogen production technology can be divided into three technologies: alkaline water electrolysis hydrogen production, proton exchange membrane (PEM) water electrolysis hydrogen production, and solid oxide water electrolysis hydrogen production technology. Alkaline electrolysis using lye as the electrolyte is the earliest development, the most mature technology and the lowest-cost hydrogen production technology from electrolysis of water. For this reason, it is widely used in hydrogen production stations in power plants. However, due to the low conductivity of alkaline electrolytes, the efficiency of the alkaline electrolytic cell is low and the working current density is low, generally not higher than 0.6 A/cm². The working current density of PEM water electrolysis technology with polymer as electrolyte can be as high as 1-3A/cm², the electrolysis efficiency is high, the volume is smaller under the same power, and the purity of the hydrogen produced can reach 99.999%. Considered to be the most promising water electrolysis technology. This article discusses the feasibility of applying this technology in hydrogen production stations of large power plants from the principle and economic aspects of PEM water electrolysis technology. The gas volume involved in the article has been converted to standard conditions [4-5].

2. The principle of hydrogen production by PEM water electrolysis

The principle of PEM water electrolysis hydrogen production is the reverse process of PEM fuel cell power generation. The main difference between PEM electrolyzed water hydrogen technology and alkaline electrolyzed water hydrogen technology is that PEM electrolyzed water hydrogen technology uses a polymer cation exchange membrane to replace the diaphragm and liquid electrolyte in alkaline water electrolysis. Isolate the role of gas and ion conduction. When the PEM electrolytic cell is working, water passes through the anode chamber and undergoes an electrochemical reaction at the anode catalytic reaction interface to be decomposed into oxygen, hydrogen ions and electrons. The hydrogen ions generated by the anode pass through the electrolyte diaphragm in the form of hydronium ions, and electrochemically react with the electrons transported through the external circuit at the reaction interface of the cathode chamber to generate hydrogen [6-7].

The electrolyzer of PEM water electrolysis hydrogen production technology is composed of PEM membrane electrodes, bipolar plates and other components. Among them, the membrane electrode is the core component of the electrochemical reaction, which determines the performance of the electrolytic cell. The membrane electrode consists of a proton exchange membrane and an anode and cathode catalyst glued on the proton exchange membrane, and is the place for the water electrolysis reaction. The bipolar plate can connect multiple membrane electrodes in series and separate the membrane electrodes from each other. On both sides of the bipolar plate, there are anode flow channels and cathode flow channels, which play a role in material transport, and at the same time in the electrolysis of water Play the role of conducting electrons in the process. Compared with alkaline electrolysis technology, PEM electrolysis technology has the following advantages:

(1) PEM is a solid polymer electrolyte membrane. The two sides of the membrane can withstand a large pressure difference, and only have a unidirectional conduction effect on hydrogen ions. It can directly separate the reactant hydrogen and oxygen to avoid cross-gassing, and has good safety. The product gas has high purity. For alkaline electrolysis, a liquid electrolytic cell is used, and the porous asbestos cloth becomes a diaphragm by impregnation. Therefore, a strict pressure difference control system must be installed to ensure that no air leakage occurs in the anode and cathode reaction chambers and avoid safety accidents.

(2) The PEM electrolyte membrane can be less than 200 μm, the electrode spacing is small, it can reduce the working voltage and energy consumption, and make the structure of the electrolytic cell more compact.

(3) Water is both a reactant and a cooling medium, eliminating the need for a cooling system and reducing the volume and weight of the device. Because the PEM electrolytic cell uses pure water as the electrolyte, the corrosion of the electrolyte to the tank body is avoided, the reaction product does not contain alkali mist, and the gas purity is higher.
PEM water electrolysis technology has the advantages of high current density, no electrolyte corrosion, work safety and simple control. It is more and more widely used in actual production. It has shown broad application prospects not only in the military but also in the civilian field.

3. Application analysis of PEM electrolysis technology in power plants
Generator sets that use hydrogen as the cooling medium have strict requirements on the pressure, purity and humidity of the supplied hydrogen. For hydrogen pressure, when the oil-hydrogen differential pressure is higher than the specified value, it will cause hydrogen leakage, reduce the purity of the hydrogen in the generator, and reduce the cooling effect; when the hydrogen pressure is lower than the specified value, it is difficult to ensure the flow of hydrogen, the cooling effect will also decrease. Regarding the purity of hydrogen, when the purity of hydrogen in the generator decreases, the insulation of the generator windings will decrease, which will further cause hydrogen cracking of the generator guard ring, which will seriously threaten the safety of the generator; and the reduction of the hydrogen purity of the generator will reduce the cooling effect, which directly affects the efficiency of the generator. Experimental data shows that for every 1% decrease in the purity of hydrogen, the ventilation loss and rotor friction loss increase by 11%. Therefore, the hydrogen purity is required to be greater than 95% during normal operation of the generator. For the humidity of hydrogen, it should be ensured that the dew point of hydrogen in the generator is -5-25℃ under the rated hydrogen pressure. When the hydrogen humidity in the generator is too low, the too dry hydrogen will cause the insulation material to shrink, which will loosen the fixed structure, and even cause cracks in the insulation pad, which will form a safety hazard; when the hydrogen humidity is too high, it will reduce the hydrogen purity on the one hand. And will increase the ventilation friction loss, reduce the cooling effect and generator efficiency; on the other hand, there may be local condensation, which will not only reduce the electrical strength of the winding, but also accelerate the stress corrosion of the rotor guard ring, especially at higher At high working temperature, stress corrosion will cause cracks in the rotor guard ring, threatening the safe operation of the generator.

3.1. Comparison of hydrogen supply schemes

3.1.1. Output of hydrogen production equipment. According to the "Technical Regulations for Chemical Design of Thermal Power Plants", the total capacity of the hydrogen production equipment used must meet the normal consumption of the hydrogen-cooled generator set and the sum of the hydrogen charging capacity that can be produced for the maximum 1 generator within 7 days. Therefore, the output of the hydrogen production equipment is 10m3/h.

3.1.2. Hydrogen storage tank volume. According to the sum of the amount of hydrogen reserved for the hydrogen-cooled generator for 10 days during the overhaul of the hydrogen production equipment and the hydrogen charging amount of the largest hydrogen-cooled generator at a time, the volume of the hydrogen storage tank is 1740 m3. Based on a single hydrogen storage tank of 14 m3 and a storage pressure of 32 MPa, the number of hydrogen storage tanks required is 6 units.

3.1.3. Selection of hydrogen production equipment. According to the above calculations, the hydrogen supply equipment for the two 660 MW generator sets can be selected from the water electrolysis hydrogen production equipment with a hydrogen production capacity of 10m3, and is equipped with 6 hydrogen storage tanks of 14m3. Hydrogen production equipment that meets the above conditions includes 10m3/h PEM electrolyzed water hydrogen production equipment and 10m3/h alkaline electrolyzed water hydrogen production equipment.
3.2. **Comparison of two technologies for hydrogen production by electrolysis of water**

Alkaline water electrolysis hydrogen production equipment system is relatively complicated, mainly including electrolyzer, pressure regulating valve, lye filter, lye circulation pump, lye preparation and storage device, hydrogen purification device and gas detection device and other modules.

Since PEM water electrolysis technology does not require alkaline aqueous solution as electrolyte, PEM can directly block hydrogen and oxygen on both sides of the cathode and anode, greatly simplifying the system structure.

3.3. **Technical and economic analysis of hydrogen production by PEM water electrolysis**

The purity of hydrogen used in hydrogen-cooled generators directly affects the cooling efficiency, wind wiping loss, power generation efficiency and generator life of the generator. The thermal conductivity of hydrogen is 7 times that of air. The higher the purity of hydrogen, the better the cooling efficiency. The density of hydrogen is 1/14 of that of air. The higher the purity of hydrogen, the lower the wind wiping loss of high-speed generators. A study by GE Power Company shows that for a 1000MW generator set, if the hydrogen pressure is set to 517kPa and the hydrogen purity is increased from 95% to 98% when the load is 907MW, the wind wiping loss will be reduced by 685kW, equivalent to Every 1% increase in hydrogen purity can save 228kW of energy.

For every 1% increase in hydrogen purity, the 660MW generator set is equivalent to reducing wind wiping loss by 166 kW. Calculated based on the annual power generation of 8000h, the total energy saving is 166kW×8000h=1328000kW·h. According to the calculation of 0.3 yuan/(kW·h), each unit can save 398 thousand yuan per year. According to the 2×660MW hydrogen production system configuration, each increase of 1% of the hydrogen purity of the 2 units can save energy of 796 thousand yuan.

3.4. **Technical advantages of PEM water electrolysis hydrogen production**

Nowadays, interval hydrogen supplementation is widely adopted at home and abroad. After the hydrogen drops a certain pressure, the hydrogen supplement is performed to the rated pressure. This method of supplementing hydrogen will cause unstable and fluctuating hydrogen pressure, resulting in unstable heat transfer and fluctuations in hydrogen sealing pressure. This fluctuation of winding temperature and wind resistance will affect the energy saving of the generator, winding life, and oil leakage of the oil seal. Therefore, the generator maintains a constant rated hydrogen pressure, which can ensure the stable operation of the generator set, is conducive to hydrogen sealing, and can greatly improve the safety of the system. The hydrogen production capacity of PEM water electrolysis hydrogen production equipment can be intelligently controlled continuously from 0 to 100%, and it can be directly connected to a generator to realize automatic hydrogen supplementation.

The PEM water electrolysis hydrogen production system adopts the direct-connected hydrogen supplement method to maintain the purity of hydrogen and maintain the design requirements of stable hydrogen pressure, realize the optimization of hydrogen pressure and purity, and contribute to the energy saving of generators and the maximum power generation load. contribution. The continuous hydrogen supplement mode implements real-time tracking and recording of the hydrogen supplement amount, so that it can alarm in time to avoid the failure of huge hydrogen leakage and buy time for arranging maintenance. Through online data recording, water, oxygen and other gas pollution leakage can be avoided. The accumulation of faults in the manual hydrogen supplement interval can be used to record the hydrogen supplement rate to determine the real-time leakage, which is helpful for leakage fault calibration and detection.

Because of the technical advantages of PEM water electrolysis hydrogen production, this advanced hydrogen production technology has been widely used. 35 power plants in the United States, 6 power plants in Spain and 6 power plants in Romania have adopted this kind of hydrogen production. technology. The domestic Huaneng Beijing Thermal Power Plant uses a 6m³/h PEM electrolytic hydrogen production device, and Zhejiang Taizhou Power Plant uses a 2m³/h PEM electrolytic water hydrogen production device.
4. Conclusion

PEM water electrolysis hydrogen production technology has high working current density, high electrolysis efficiency (up to 85% or more), and has the advantages of no pollution, light weight and compact structure, which avoids the corrosion of the electrolyte and the anode and cathode of the alkaline electrolytic cell. The safety and other problems caused by the large pressure difference also avoid the requirement of the solid oxide electrolyzer for high temperature conditions, and the device starts fast, so that the small-scale electrolyzed water hydrogen production equipment of this technology has been used in the field of hydrogen-cooled generator sets in power plants. Application, in the civil and aerospace fields, has attracted more and more attention from countries all over the world. In order to improve grid efficiency, safety and stability, in recent years, a regenerative hydrogen-oxygen fuel cell composed of a PEM electrolytic cell with hydrogen production function and a fuel cell with power generation function has been introduced into the power grid as an energy storage device, in order to solve the problem of renewable energy. Large-scale energy storage provides a feasible technical route.

PEM electrolyzed water hydrogen production technology is a safe, clean and efficient hydrogen production technology, but most of the proton exchange membranes currently used are perfluorosulfonic acid type proton exchange membranes, which are more acidic when infiltrated by water, and due to theory, The oxygen evolution potential is high (1.229V), and most metals will corrode at this potential. Therefore, platinum-based noble metals are mostly used in the anode and cathode catalysts, which leads to the high cost of PEM electrolytic cells, which hinders the progress and popularization of this technology. For this reason, the development of new non-precious metal catalysts and new PEMs is the key to reducing costs.

As an emerging energy storage technology, PEM water electrolysis hydrogen production technology is advocating the development of green energy. Nuclear power, hydropower, wind power and other renewable energy sources can be used to produce hydrogen on a large scale. Hydrogen energy can be developed and utilized, so that water electrolysis technology can be applied Power grid peak shaving has become an ideal energy storage conversion device. With the continuous development and improvement of PEM water electrolysis technology, it is foreseeable that PEM water electrolysis technology will have great development prospects in the field of hydrogen energy.

References

[1] D’Arc D F P D, Martins Vieira L G, Ribeiro Damasceno J J. Hydrogen production by a low-cost electrolyzer developed through the combination of alkaline water electrolysis and solar energy use [J]. International Journal of Hydrogen Energy, 2018, 43(9): 4265-4275.

[2] Kovačć, Ankica, Marciuš, Doria, Budin L. Solar hydrogen production via alkaline water electrolysis [J]. International Journal of Hydrogen Energy, 2018.

[3] Koj M, Gimpel T, Schade W, et al. Laser structured nickel-iron electrodes for oxygen evolution in alkaline water electrolysis [J]. International Journal of Hydrogen Energy, 2019, 44 (25): 12671-12684.

[4] Delvaux A, Lumbeeck G, Idrissi H, et al. Effect of microstructure and internal stress on hydrogen absorption into Ni thin film electrodes during alkaline water electrolysis [J]. Electrochimica Acta, 2020, 340: 135970-.

[5] Todoroki N, Wadayama T. Hetero-Layered Ni-Fe Hydroxide/Oxide Nanostructures Generated on Stainless-Steel Substrate for Efficient Alkaline Water Splitting [J]. ACS Applied Materials & Interfaces, 2019, 11(47): 44161-44169.

[6] Schiller G, Lang M, Szabo P, et al. Solar heat integrated solid oxide steam electrolysis for highly efficient hydrogen production [J]. Journal of Power Sources, 2019, 416 (MAR.15): 72-78.

[7] Ketian Z, Mcdonald M B, Genina I E A, et al. A Highly Conductive and Mechanically Robust OH- Conducting Membrane for Alkaline Water Electrolysis [J]. Chemistry of Materials, 2018, 30:acs.chemmater.8b02709-.