Future Trends for Electrolysers in Nuclear Industry

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Abstract

The nuclear industry, through the application of electrolysers, can provide a solution to energy shortage with its competitive cost and can be one of the major future sources of hydrogen production with zero carbon emission. In addition, development of complementary, yet critical processes for upgrading or detritiation of the heavy water in the nuclear industry can be advanced with the application of electrolysers. Regardless of the technology, the electrolyser's development and application are facing many technical challenges including radiation and catalysis.

In this paper, three main types of electrolysers are discussed along with their advantages and disadvantages. Proton Exchange Membrane (PEM) electrolysers look promising for hydrogen (or its isotopes) production. For this reason, Atomic Energy of Canada Limited (AECL) in collaboration with Tyne Engineering has started design and fabrication of PEM electrolysers with more than 60 Nm³/hr hydrogen production capacity for the application in nuclear industry. This electrolyser is being designed to withstand high concentrations of tritium.

Keywords: Electrolysers, Proton Exchange Membrane, Alkaline, Nuclear, Hydrogen, Tritium, energy, Tyne Engineering, AECL.

1. Introduction

Fossil fuels could not provide a sustainable solution to the energy requirement of the developed and developing nations as it is expected that global demand will increase by more than 50% by 2030 according to the International Energy Agency (IEA)[1]. These natural resources are limited and they cause greenhouse gas emission that brings the global community to a consensus that an alternative must be found.

There is a growing belief that green and renewable energies such as solar and nuclear could constitute the major sources of the energy in the future. Hydrogen like electricity is an energy carrier and unlike electricity it can provide a good means of energy storage. There are, however, certain barriers to overcome, for example, the total annual global hydrogen generation capacity is over 600 billion Nm³, equivalent to about 55 million tons per year, is equivalent to less than 2% of total global energy consumption[2] and currently derives largely from fossil fuels.

The nuclear industry can provide a solution to this challenge because of its competitive operating cost. It could be the major future source of hydrogen production with zero carbon emission. Energy from nuclear sources in the form of electricity or waste heat can be converted efficiently to hydrogen through the electrolysis of water. In the former case electricity is applied directly to water, and in the latter, waste heat and electricity may be applied to copper chloride salts as a method of producing hydrogen [3-5]. Electrolysers are an important component of these and similar processes. In addition, development of other complementary processes in the nuclear industry would put more emphasis on the application of electrolysers. For instance, in the Combined Electrolysis and Catalytic Exchange (CECE) process which has been developed for detritiation and upgrading of heavy and light water in nuclear reactors, electrolysers are the main components.

Then the question arises as what type of electrolyser? Currently there are three types of electrolysers which include alkaline electrolysers, Proton Exchange Membrane (PEM) electrolysers, and high temperature electrolysers. While these electrolysers are in different stages from marketing point of view, it would be beneficial to learn their working mechanism.

2. Alkaline Electrolysers

Currently most of the commercial water electrolysis technologies use acidic or alkaline electrolyte systems for hydrogen generation. Alkaline electrolysers are the most common large-scale electrolysers in the market. Most commonly, aqueous potassium hydroxide solution is circulated through several cells to complete the electrochemical reactions and produce hydrogen. Process flow diagram of alkaline electrolysers is presented in Figure 1.

Water passes through the water purification system to produce water quality of type 2 ASTM. Then, caustic solution of 20-30% w concentration is made and fed into the electrolyser. Water splits into two separate streams of hydrogen and oxygen. Some caustic droplets become entrained in each gas stream as well as moisture, and must be separated and dried. The finish product has the purity of 99.9%.



Figure 1. Process Flow Diagram for an Alkaline Electrolyser

The following half reactions take place in the electrolyser:

Anode:	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
Cathode:	$4H^+ + 4e^- \rightarrow 2H_2$
Electrolyte:	$4H_2O \rightarrow 4H^+ + 4OH^-$
Total:	$2H_2O \rightarrow O_2 + 2H_2$

Advantages of alkaline electrolysers include mature design with a proven track record and simple design with inexpensive materials. The hydrogen production capacity of this type of electrolyser covers a wide range from $0.1 \text{ Nm}^3/\text{hr}$ up to 600 Nm³/hr hydrogen production. In addition to its reliability, this large capacity can provide more flexibility in any process in which hydrogen production capacity is important. In alkaline electrolysers, operational parameters including temperature and pressure are low with temperatures ranging between 40- 90 °C and pressure up to 25 bar. The main operating cost for these electrolysers is the cost of electricity. For nuclear power plants with large electricity production, the operating cost is low and can be estimated at 0.21 CAD/m^3 (2.66 CAD/kg H₂) based on 0.04 CAD/kWh electricity cost.

Alkaline electrolysers suffer from some significant drawbacks. For instance, their efficiencies are relatively low with efficiencies quoted in the 55-74% range [6]. In addition, the current density of alkaline electrolysers ranges from 0.3-0.5 A/cm² resulting in the large size of the electrolysers. The main concern in the nuclear industry, however, is the use of caustic material. Caustic materials can be corrosive and necessitate extra care to prevent inadvertent entry into process systems.

The major future challenges in research and development for alkaline electrolysers is to develop process components to cut costs and increase efficiency in order to retain their competitive advantage over new types of electrolysers—especially PEMs.

3. High Temperature Electrolysers

High temperature electrolysers are the second major category. It is based on the same technology as high-temperature fuel cells i.e. solid oxide electrolyser cell (SOEC). The temperature range is between 800-1000°C. High temperature is in favor of higher efficiency. Therefore, overall process efficiency (around 85% to 95%) in this class of electrolysers can be relatively high (compared to low temperature electrolysers) as the electrical energy needed to split water is considerably less than electrolysis at 70 °C.

These electrolysers are still in the research and development stage, and so it is yet not clear whether they will live up to their promise, or be more reliable or affordable for application in nuclear industry. In addition, the main attraction for application of these electrolysers is with future reactor designs that may produce heat at 800°C or higher.

4. Proton Exchange Membrane (PEM) Electrolysers

This class of electrolysers uses a proton exchange membrane (PEM) instead of liquid (caustic) electrolyte. As membranes have acidic properties, they transfer protons from anode to cathode to complete the electrical circuit. Their application in PEM electrolysers give the advantage to this type over their rival alkaline electrolysers as it can simplify the system design (including peripherals), reduce the size, and reduce the number of unit operations attached to the electrolyser. Figure 2 represent the basic structure of a PEM electrolyser.



Figure 2. PEM electrolysis components [7]

When water contacts with the positively charged anode, oxidation takes place that produces oxygen, protons, and electrons. Protons that are produced in this reaction pass through the membrane to the cathode where they receive electrons and are reduced to hydrogen gas. Half reactions can be described as the following:

Anode: $H_2O \to 0.5 \ O_2 + 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Total: $H_2O \rightarrow 0.5 O_2 + H_2$

Unlike alkaline electrolysers, in which hydrogen needs purification from caustic materials after production, hydrogen which is produced from a PEM electrolyser is extremely pure. Therefore, there is no need for auxiliary equipments such as gas separator, caustic tank, or possibly the deoxidizer. This reduces the footprint of the system where it is necessary in process. Figure 3 shows the process flow diagram of a PEM electrolyser.



Figure 3. Process Flow Diagram for a PEM electrolyser

PEM electrolysers are getting more attention as they show a competitive advantage by providing higher efficiency, using higher current density, using smaller size compartments, and producing higher purity hydrogen while it is caustic free with good ability to cope with transient variations in electric power input. Producing highly pure hydrogen and oxygen with purity of greater than 99.99% are very important for some applications such as nuclear, submarines and space shuttles. While their flexibility with electrical source has no advantage in nuclear industry, it makes them a suitable choice with renewable energy resources such as wind or solar systems. On the other hand, using no caustic as the electrolyte appeals to nuclear related processes such as the Combined Electrolysis and Catalytic Exchange (CECE) systems where entrainment of caustic materials and its potential dissolution in heavy water along with radioactive contamination could cause extreme corrosion. Figure 4 shows corrosions in an alkaline electrolyser which has been in service in a nuclear industry for less than two years. Corrosion happened as a result of caustic materials entrainment due to minor operational damage of the cell.

PEMs operate at moderate conditions through a wide range of temperatures with the most quoted temperature around 80-90 °C. Nafion which is the most common membrane for PEM electrolysers was developed by DuPont; lose its operational capacity due to the loss of water at higher temperature.



Figure 4. Corrosion in an Alkaline Electrolyser which is caused by caustic entrainment.

There are, however, membranes such as PBI (Polybenzimidazole) with higher operating temperatures. PEM electrolysers can potentially be designed for operating pressures up to several hundred bar, and their stability and small size can make them suitable for both stationary and mobile operation or applications that require high pressure output. Outlet pressure can be modified according to need without utilizing compressors.

There are some drawbacks to PEM electrolysers. PEMs comprise of elements such as membranes, precious metal catalysts, and metallic bipolar plates which are expensive and require cutting edge equipments/ technology. PEM electrolyser capital cost has been reduced due to technology advancement. This trend will continue as illustrated by the Department of Energy (DOE) in the United States whose cost targets for hydrogen production by PEM's lowered substantially over the last few years, and as summarized in Table 1 provides even lower targets for 2017.

	2006	2017 (DOE-US Target)*
Hydrogen Cost (\$/kg-H2)	\$4.8	< \$3.00
Electrolyser Capital Cost (\$/kg- H2)	\$1.2	\$0.3
Electrolyser capital cost (\$/kW)	\$1500	\$125

Table 1. Trends and cost target for hydrogen production by PEM electrolysers.

*Based on 0.04 CAD electricity costs.

Another drawback for PEM electrolysers is short life expectancy of the membranes especially for the nuclear industry where radioactive materials can reduce the life span of the membrane significantly. Many research centers around the world, Atomic Energy of Canada Limited (AECL) and Tyne Engineering included, are applying resources to improving the quality of membranes and increasing their life span. The continuing output of publications in this area demonstrates the important of this topic in both academia and industry [8-12]. It is reasonable to believe that PEM electrolyser performance will continue to significantly improve by continuous research on material development and stack design. Advancement in sciences such as surfaces and interfaces, catalysis, nanomaterials (nano science in general), and membrane will help to improve PEMs even more, and further advance their marketability.

5. Our Approach

Atomic Energy of Canada Limited Chalk River Laboratories (AECL-CRL) in collaboration with Tyne Engineering has started design and fabrication of a large PEM electrolyser with more than 60 Nm³/hr hydrogen production capacity and using a membrane capable of withstanding high beta exposure as will be in the case for processing heavy water in CANDU® reactors. The cell design will include many unique characteristics, including modular design in which hydrogen production can be scaled up or down, large cell diameter, special membrane which resists beta radiation, special design to avoid leakage of tritium/hydrogen, and high current density. The target life span for this PEM electrolyser is between 35000 and 45000 hours, which makes it a competitive rival to alkaline electrolysers in or out of a tritium (beta) environment. Figure 5 represents a special mini CECE test rig that was designed and operated to test membranes in a highly elevated tritium environment.

6. Conclusion

Hydrogen production as a renewable source for clean energy is an important focus for world research and development. Many countries have moved beyond this stage and have already started preparation of infrastructure and facilities in their communities to meet the year 2030 target. Although there are many processes for production of hydrogen, the greenest method involves the application of non-greenhouse gas source electricity to an electrolyser in which water separates into hydrogen and oxygen.

The nuclear industry with the availability of electricity and waste heat is able to make extensive use of the technologies described above. In addition to hydrogen production, there are other processes under development or in the marketing stage, such as CECE processes and systems which depend on tritium and deuterium (other isotopes of hydrogen). Electrolysers are the main components in these processes, too.

Among the three main electrolysers types that were discussed in this paper, we, at Tyne Engineering and AECL strongly believe that PEM electrolysers have excellent potential for further growth and development in nuclear industry. Receipt of two grants from the government

of Canada for development and manufacturing of PEM electrolyser for nuclear applications supports our view and these are being put to good use to make the CECE system with a PEM electrolyser a reality.



Figure 5. a mini CECE process rig for testing membrane in radioactive environment.

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