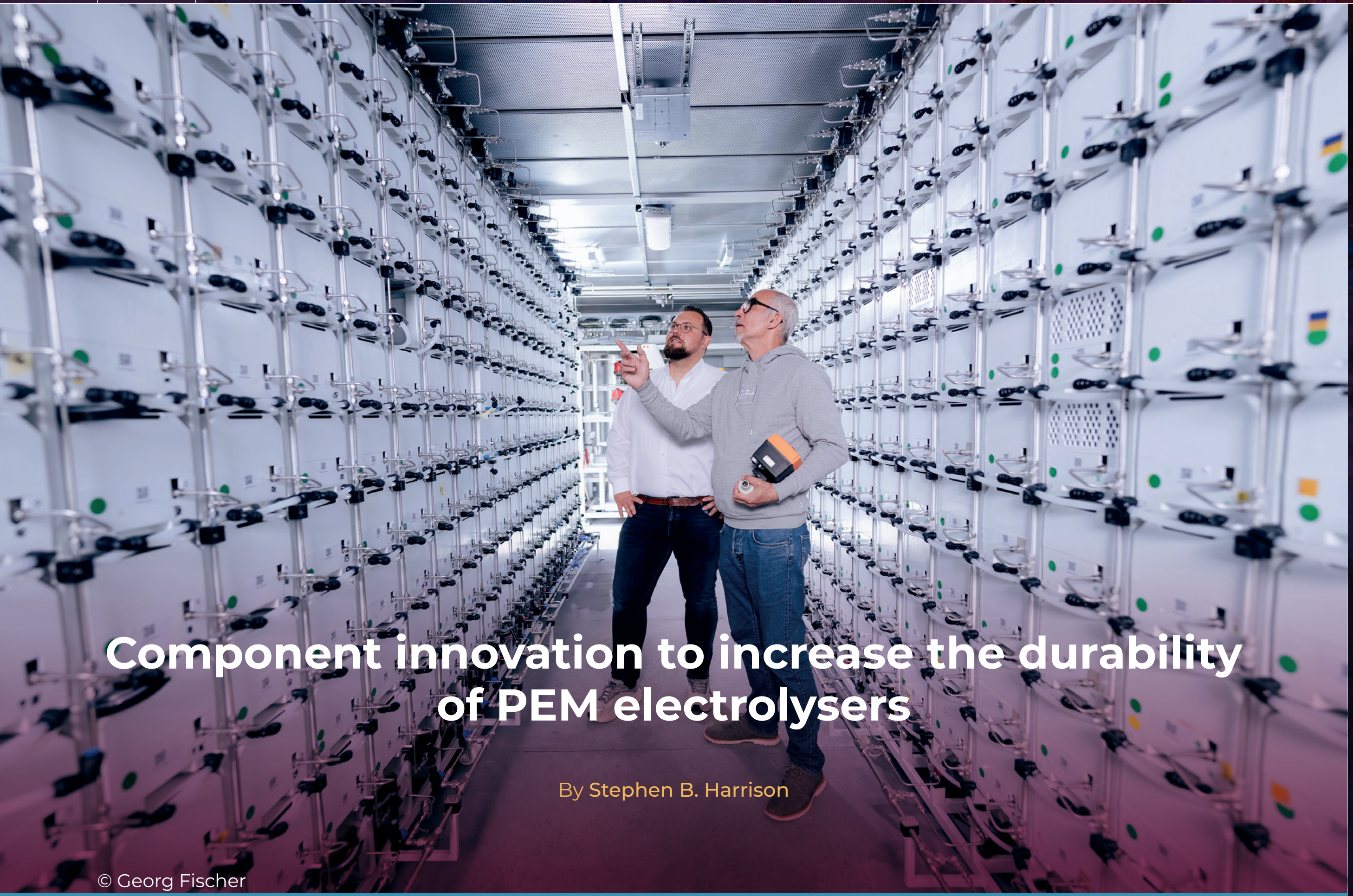

Component innovation to increase the durability of PEM electrolysers

By Stephen B. Harrison

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Building an excellent electrolyser is like cooking a great meal: choose only the absolute best ingredients and cook them to perfection. The components incorporated into the stack and balance of plant are the key ingredients. Good system design and high-quality manufacturing must then follow.

Given the number of components in an electrolyser system, and the multiple options for each component, there are thousands of degrees of freedom that an electrolyser OEM can leverage to optimise their product for cost, efficiency, dynamic response, or durability.

Only the best electrolyser OEMs, using the best components, can outperform their rivals on multiple performance attributes. Component-level choices matter. And on top of that, there must be a cohesive concept which integrates the holistic design, from feed water entering the system to pure, pressurised hydrogen leaving it.

Technology classes

There are four broad categories of electrolyser technology to split water into hydrogen and oxygen.

1. Alkaline water electrolysers (AWE) operate using an electrolyte which contains about 30% by mass of potassium hydroxide (KOH). This is referred to as lye and is an extremely alkaline medium.
2. Anion exchange membrane (AEM) electrolysers also use an alkaline electrolyte. In comparison to the AWE technology, the AEM electrolyte will either have a lower concentration of KOH or use a benign bicarbonate solution.
3. Proton exchange membrane (PEM) electrolysers use pure water as the electrolyte. During electrolysis, an acidic environment is created. This is a key differentiator between PEM electrolysers and the AWE and AEM classifications.
4. Solid oxide electrolyser cells (SOECs) use a solid electrolyte. Their design and operation are vastly different to AWE, AEM and PEM systems, which rely on liquid electrolytes. Furthermore, SOECs generally operate in the temperature range 700–900°C – significantly higher than AWE, AEM and PEM technologies, which operate in the range of 60–120°C.

Acidity is unavoidable in PEM systems

Materials selection for AWE and AEM electrolysers operating in an alkaline liquid is different to the case for PEM. Additionally, the AWE and AEM stacks are more robust than PEM stacks, meaning they are more tolerant of some impurities in the electrolyte.

Hunor Kacso, Team Lead at Hydrogen Training Solutions, who previously worked at ITM Power, said, "The PEM membrane must be manufactured from an extremely resilient polymer to avoid it being damaged by the acidity surrounding it." A fluorinated, sulphonated polymer called perfluorosulfonic acid (PFSA) is the default choice to achieve this goal.

Using a fluorinated polymer is a double-edged sword. On the one side, the fluorine makes the polymer robust. On the other side, the acidity in the PEM stack is so extreme that some fluorine is released from the PFSA membrane as hydrofluoric acid (HF). HF is one of the most aggressive acids known to chemistry.

"Over time, HF attacks the highly sensitive PEM electrolyser's proton exchange membrane, which is intentionally very thin to reduce ohmic losses," Kacso continued.

Durable PEM membranes

Kacso added, "In essence, a PEM stack with a PFSA membrane is designed to destroy itself. The challenge is to balance the design to achieve several years of stable operation at high efficiency before the stack deteriorates to such an extent that the electricity input required to generate hydrogen rises to such an amount that re-investment in new stacks is cost-effective."

Avoidance of HF would be possible if an alternative membrane were to be used. The selection of a membrane that avoids fluoropolymers would also reduce concerns related to 'PFAS': per- and polyfluoroalkyl substances, which are known as 'forever chemicals' and are harmful to the environment and extremely difficult to break down in nature.

Chemicals firm Toray and several other companies are working to develop fluorine-free, PFAS-free PEM membranes. However, at present, the state of the art relies on PFAS due to its resilience.

Feed water purification

The feed water to the electrolyser must be purified to an extremely low level of ionic conductivity. The purification equipment for this can include ultrafiltration, reverse osmosis, electro-deionisation and ion exchange resin beds.

However, even the most robust purifiers allow a few parts per billion of contaminant ions such as calcium, magnesium and iron to be introduced to the electrolyser. The presence of iron oxide particles in the size range of 0.1-5 µm in the electrolyser recirculation water can be observed through 'rouging'. Rouging is caused when pure water at around 60°C comes in contact with stainless steel.

"Some of these metallic ion impurities are very damaging to the membrane," Kacso said. "Big cations such as calcium and magnesium are membrane killers because they block the proton transfer 'pores' in the membrane."

Blockages in the proton exchange membrane lead to a progressive increase in ohmic resistance. In turn, that means a reduction in the stack efficiency and an increase in electricity consumption per kilogramme of hydrogen produced. This is a core reason for PEM stack degradation.

Limitations of stainless steel

Stainless steel is commonly selected for water purification systems and PEM electrolyser pipework because it is strong and releases fewer ions into the water than carbon steel. However, even the highest grades of stainless steel can release metallic ions into the feed water and circulating water.

Specification of drawn stainless steel tubing with internally polished surfaces is essential if this material is used in PEM electrolysers and ultra-pure water treatment systems. This is potentially a limitation to the scale-up of PEM electrolyser stacks because this type of pipework is only available at smaller diameters.

The use of large-diameter stainless steel pipe, fabricated with a welded seam, would be fatal for a PEM electrolyser. At a microscopic level, the weld is rough and porous and may be a catastrophic source of ionic contamination. Similarly, when joining stainless steel piping sections, welds must be avoided. >>

The case for plastic pipework

“An alternative approach to minimise the potential for damage to the membrane is to minimise the use of metallic pipework in contact with the feed water and ultra-pure water in the electrolyser recirculation circuit,” Kacso said. With fewer impurities reaching the membrane and catalysts, the stack degradation rate is reduced, and its usable lifetime is extended.

Similar to the many grades of steel and stainless steel that might be selected, there are many types of plastic that are used to construct pipes. Not all of these are suitable for use in PEM electrolysers. Only appropriate, sophisticated engineering plastics should be used.

Engineering plastics

There are many different plastics that we encounter in our daily lives. Polyethylene (PE) is commonly used to make bags and food packaging. Polypropylene (PP) is denser and is preferred for car parts. Applications of Polyvinylchloride (PVC) range from construction materials for window frames to medical devices.

Cyrus Ardjomandi, Business Development Manager at plastic pipe manufacturer and component Georg Fischer AG explained, “Engineering plastics differ from household plastics due to their enhanced properties of temperature, pressure or chemical resistance.” When designing a PEM electrolyser, superior performance in all three of these attributes is essential.

“Georg Fischer supplies PP and PE for use in ambient temperature applications such as water purification systems and cooling water circuits in electrolysers,” Ardjomandi said.

“For PEM water circulation, where the temperature is around 60°C, we select premium grades, such as PP-H.” PP-H is constructed from a homopolymer material, and the manufacturing process ensures very smooth internal wall surfaces, and virtually no extractable ionic or particulate contamination is present.

“Moving beyond the water treatment system, PVDF and ECTFE are highly stable fluoropolymer materials which are suitable for use in the condensate water return line from the oxygen phase separator,” Ardjomandi added. They are non-corrosive and therefore minimise iron ion release and avoid rouging of the recirculation water and damage to the stack.

“Georg Fischer has supplied PVDF to highly sensitive applications in the pharmaceutical, biotechnology and semiconductor sectors for many years. It is specially cleaned to be oil- and grease-free. At present, we are experiencing a high degree of interest from electrolyser OEMs to use these materials in PEM systems at pressures of up to around 10 bar.”

PVDF-HP fittings are generally manufactured in an ISO Class 5 cleanroom: the same category that is used to manufacture less-critical semiconductor components.

Pressure limitations

Many PEM electrolysers produce hydrogen at an elevated pressure between 20 and 40 bar. A notable exception to this is Siemens Energy’s Elyzer-P, which operates close to atmospheric pressure. The oxygen side of PEM systems can either be at a low pressure in the order of 3 bar or at an elevated pressure similar to the hydrogen side of the system.

There is a trade-off between temperature and pressure when using thermoplastic components: at higher temperatures, the maximum safe working pressure is reduced. PEM electrolysers generally operate at around 60°C, and the maximum pressure rating of PP is reduced by half at this temperature compared to the allowable pressure for operation at 20°C.

Ardjomandi stated, “Similar to PVDF, Ethylene Chlorotrifluoroethylene (ECTFE) is a thermoplastic with excellent chemical resistance. ECTFE has some advantages over PVDF, namely, it is less susceptible to chemical stress and can be used at higher temperatures. These characteristics make it ideal for electrolyser piping circuits in PEM electrolyser systems.”

Gases, liquids and oxygen compatibility

In PEM electrolysers, plastics are generally used to transport liquids, not gases. A primary application is in the feed water purification and conditioning area, where the water is purified to remove particles, dissolved organic compounds, gases and ions.

In addition to selecting appropriate engineering plastics, components must be cleaned to remove any traces of oils or grease that may have been used during manufacturing. For valves, this is especially important since it would not be appropriate for lubricants that might be used on the moving parts of the valve stem to enter the electrolyser feed water.

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The phase separators, which allow the oxygen and hydrogen gases to be removed from the recirculating water, are generally manufactured from stainless steel. They may need to be certified pressure vessels, and the use of plastics in this instance may not be appropriate.

“Downstream of the phase separator, some PEM and AEM electrolysers are being built with Georg Fischer plastic pipes and fittings in the condensate water return lines from the phase separator to the stack,” Ardjomandi said.

Downstream of the phase separators, stainless steel is generally specified for pipework and valves in contact with the oxygen and hydrogen gases. Stainless steel can easily be cleaned to be compatible with oxygen gas. Furthermore, it is non-flammable and can be constructed to tolerate very high pressures.

PEM electrolyser stack architecture and critical components