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Application News

Online TOC Analyzer TOC-1000e

Process Monitoring of PEM H_2 Electrolysis Feed Water Using TOC-1000e

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User Benefits

- The quality of ultrapure water is critical to the reliability and economic viability of green hydrogen production
- Online analysis by TOC-1000e allows monitoring of PEM electrolysis feed water for ionic and organic contamination
- High portability enables both continuous analysis and flexible deployment to key locations throughout the plant

■ The low-carbon hydrogen economy

A key goal in the fight against climate change is the decarbonization of our economy. While this includes the electrification of individual sectors, it is not easy to implement in some areas such as transportation, metal, and chemical production. Here, the use of hydrogen as a secondary energy carrier is seen as one way to reduce carbon emissions. Hydrogen is neither toxic nor radioactive, and it can be used in various applications, such as industry and mobility, without producing pollutants. However, hydrogen gas (H_2) is almost impossible to find in its pure form in nature and must therefore be produced. In the future concept of the "hydrogen economy", H_2 is to be produced directly from water using renewable energies as the primary energy source to achieve a low-emission climate balance. This is referred to as "green hydrogen". Proton Exchange Membrane (PEM) electrolysis is a clean and efficient way to produce hydrogen gas.

■ PEM H_2 electrolysis

In contrast to classical alkaline electrolysis, PEM electrolysis uses solid polymer electrolytes to enable higher current densities achievable at high pressure. In the actual PEM cell, called stack, water is circulated around a semi-permeable membrane that separates anode and cathode electrodes. When an electric current is passed through these electrodes, water molecules are split into hydrogen (protons), which can pass through to the cathode, and oxygen, which remains at the anode. Catalyst layers on the membrane, typically platinum group materials (PGM), catalyze the gas evolution reaction. The output of PEM stacks is relatively easy to control, making them particularly suitable for energy sources with variable production rates, such as wind power or photovoltaics. It also means that no additives (such as liquid electrolytes) other than water and electrical energy are required to produce hydrogen by PEM electrolysis.

■ Water quality for PEM electrolysis

In fact, huge amounts of clean, green hydrogen are needed to realize the "hydrogen economy". This in turn requires large quantities of water, to be precise 9 liters per kilogram of hydrogen produced on a purely stoichiometric basis. In addition, the quality of the water used to operate the electrolyzer is critical. Poor quality feed water is a common cause of stack failure. To maintain the efficiency of the electrochemical process and the durability of the stack, many manufacturers specify maximum concentrations of electrical conductivity and organic matter, expressed as total organic carbon (TOC). Specifications for TOC and conductivity are often based on international guidelines for laboratory grade ultrapure water (UWP), such as ASTM D1193-06 or ISO 3696. UWP that meets ASTM Type 1 / ISO Grade 1 specifications or equivalent is often used, while the "EU harmonized protocols for testing of low temperature water electrolysis" calls for grade 2 water. Generally, manufacturers will define the specific water quality requirements for their PEM electrolyzer (Table 1).

Table 1 Example water specification for a PEM electrolysis stack

Parameter	Limit value	Contaminant group	Possible adverse effects
TOC	<50 ppb	Organic compounds	Membrane fouling, corrosion, biofilm, hydrogen impurity
Conductivity	<0,1 µS/cm	Ions and inorganic impurities	PEM substitution, catalyst damage, H_2 impurity, corrosion, catalyst damage
Resistivity	>10 MΩcm		

Ionic ingredients, such as dissolved salts and minerals, increase the electrical conductivity of water. Both naturally occurring and synthetic organic compounds in water can also have adverse effects. Excessive contaminants, even in small amounts, can irreversibly damage the stack, affecting membrane performance and lifespan through proton replacement, adsorption, deposition, and adverse reactions, with cationic impurities being a contributing factor. Anions can lead to issues like chlorine evolution, impacting hydrogen quality and corroding metallic components, including catalysts. Organic contaminants, expressed as TOC, can hinder electrolyzer performance by adsorption, reducing electrochemical activity, and increasing catalyst dissolution. They may also oxidize into CO_2 and CO, affecting H_2 quality, especially in automotive applications. The source water quality significantly influences required water treatment technology, and monitoring critical quality parameters is crucial for long-term economic green hydrogen production.

■ Water pretreatment and UPW polishing

The cost of producing solar and wind energy is lowest especially in hot, sunny regions, as well as coastal and offshore locations with relatively strong, steady winds. At the same time, however, these are often locations where the available raw water quality must be critically assessed in order to properly design the appropriate water treatment technology (Table 2). In fact, in addition to the use of relatively clean drinking water, the purification of highly saline seawater or wastewater is no problem with the right purification system, as long as the PEM stack is ultimately fed with ultrapure water. This is typically done in a roughly two-part process using different techniques depending on the water quality available. The "pretreatment system" is used to bring the raw water to a quality similar to drinking water. It is then processed in the "UPW polishing system" to the final ultrapure water required for the PEM stack (Fig. 1).

Table 2 Pretreatment and polishing techniques and their purpose

Pretreatment technique	Short name	Contaminant removed
Sand filtration / aeration	Prefiltration	Iron and manganese
Ultrafiltration	UF	Particles, organics, microbiology
Softening / Antiscalant dosing	Softener	Hardness causing ions
Membrane degasser		Dissolved gases (e.g. CO_2)
Reverse osmosis	RO	Salt, particles, microbiology, ionic load, organics
Electrodeionization	EDI	Removal of ions and ionizable contaminants
Ion exchange resin	Polisher	Final contaminants (<0,1 µS/cm)

In particular, the use of seawater appears to be difficult in terms of energy consumption, since its production requires up to 4 times more energy (7-9 kWh/m^3) than the use of groundwater. However, when compared to the energy consumption for electrolysis of ultrapure water, which is approximately 5000 kWh/m^3, it becomes clear that this is only a small part of the total energy consumption of the plant. In the production of ultrapure water, the attractive forces between water molecules and impurities are overcome, whereas in electrolysis the strong covalent bond between the atoms of the water molecule is broken. On the other hand, it is also clear why monitoring the water purification system is so important. Without ultrapure water, no hydrogen can be produced. The cost of each percent of lost energy efficiency due to PEM stack degradation exceeds the energy spent on water purification many times over.

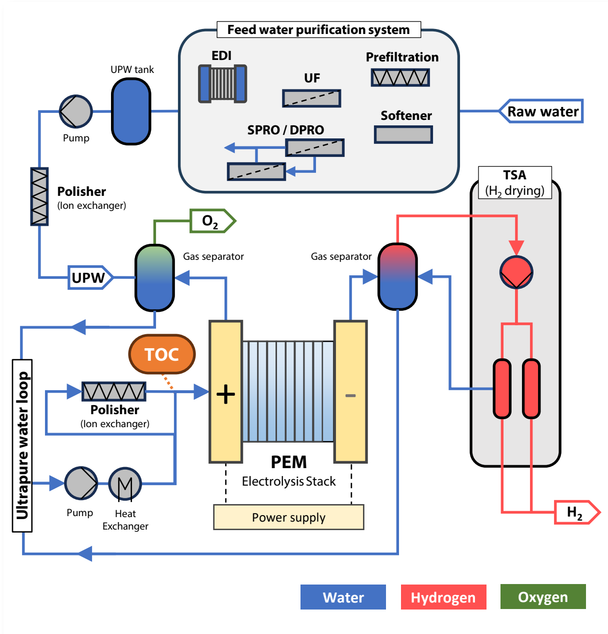


Fig.1 schematic diagram of an electrolysis plant incl. infrastructure

■ Online TOC and conductivity monitoring

Not only is the water pre-treatment system important, but so is the instrumentation to monitor its operation. To ensure long-term operation of the electrolysis plant and avoid additional costs, problems in the water treatment must be detected before they cause issues in the heart of the plant, the PEM stack. Water quality is particularly important within the so-called "ultrapure water loop". This loop is used to supply water for electrolysis from the feedwater treatment system, but also to remove large amounts of heat lost during electrolysis. As the water circulates, impurities are continuously introduced, so that a partial flow of UPW is finally purified again with the aid of an ion exchange resin ("polisher") before it enters the anode. This is the point at which an on-line TOC analyzer can provide final clearance.

There is no direct correlation between the TOC and electrical conductivity parameters and the presence of contamination, so it is advisable to record both. TOC analyzers that use the differential conductivity method, such as the Shimadzu TOC-1000e (Fig. 2), provide readings for TOC, temperature and conductivity at short intervals. Fig. 3 shows continuous measurement of ASTM Type 1 ultrapure water over a period of approximately 2 days with a cycle time of 2,5 minutes. Contaminants can be detected very quickly and with high sensitivity before they cause problems. Detecting contamination or near-contamination events, may facilitate recovery of an electrolyzer.

■ Shimadzu TOC-1000e

The TOC-1000e specializes in online monitoring of ultrapure water applications. With a detection limit of 0,1 ppb and fast oxidation technology, the TOC-1000e accurately measures both the TOC content and electrical conductivity of water. It is the first process analyzer in the eTOC series and complements Shimadzu's portfolio of advanced TOC analyzers for a wide range of applications - from ultrapure water to wastewater, solid samples and swab tests.

Technologies

- Excimer UV lamp

Uses mercury free excimer (short for “excited dimer”) lamp. Ultraviolet light at 172 nm breaks down even hard to oxidize components, so that no contamination remains undetected. The lamp has a long service life because it only needs to be switched on when it is needed and is not constantly lit. Facilitates annual maintenance and calibration.

- Active-Path™

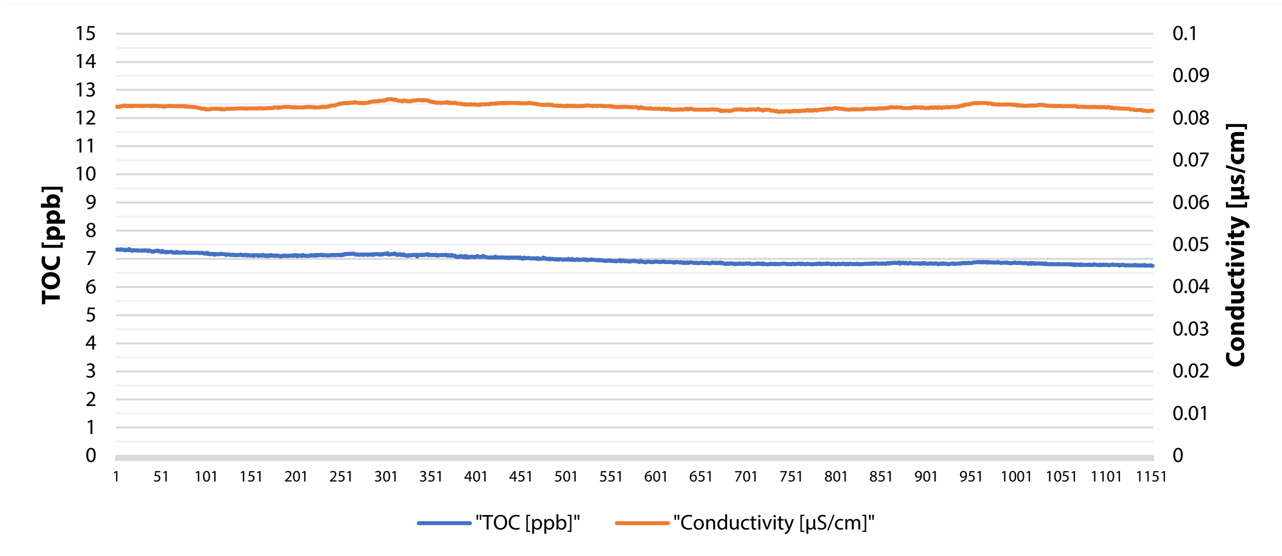
Sample flows directly through the lamp for most efficient irradiation. Avoids air pockets that lead to unwanted ozone generation and minimizes contamination and carryover effects.

Features:

- Vial sampler allows annual calibration at the installation site. There is no need to send the analyzer for factory calibration.
- Exceptional connectivity facilitates bi-directional communication by Modbus TCP. An inbuilt web server allows easy remote diagnosis and detailed data view including history.
- Small and lightweight. Weights less than 3 kg with front plate area the size of an A4 paper sheet. Allows for flexible detail troubleshooting on specific parts of the electrolysis plant.

Fig.2 TOC-1000e Online-TOC/Conductivity analyzer

Fig.3 Online TOC and conductivity monitoring of ASTM Type 1 ultrapure water using TOC-1000e



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