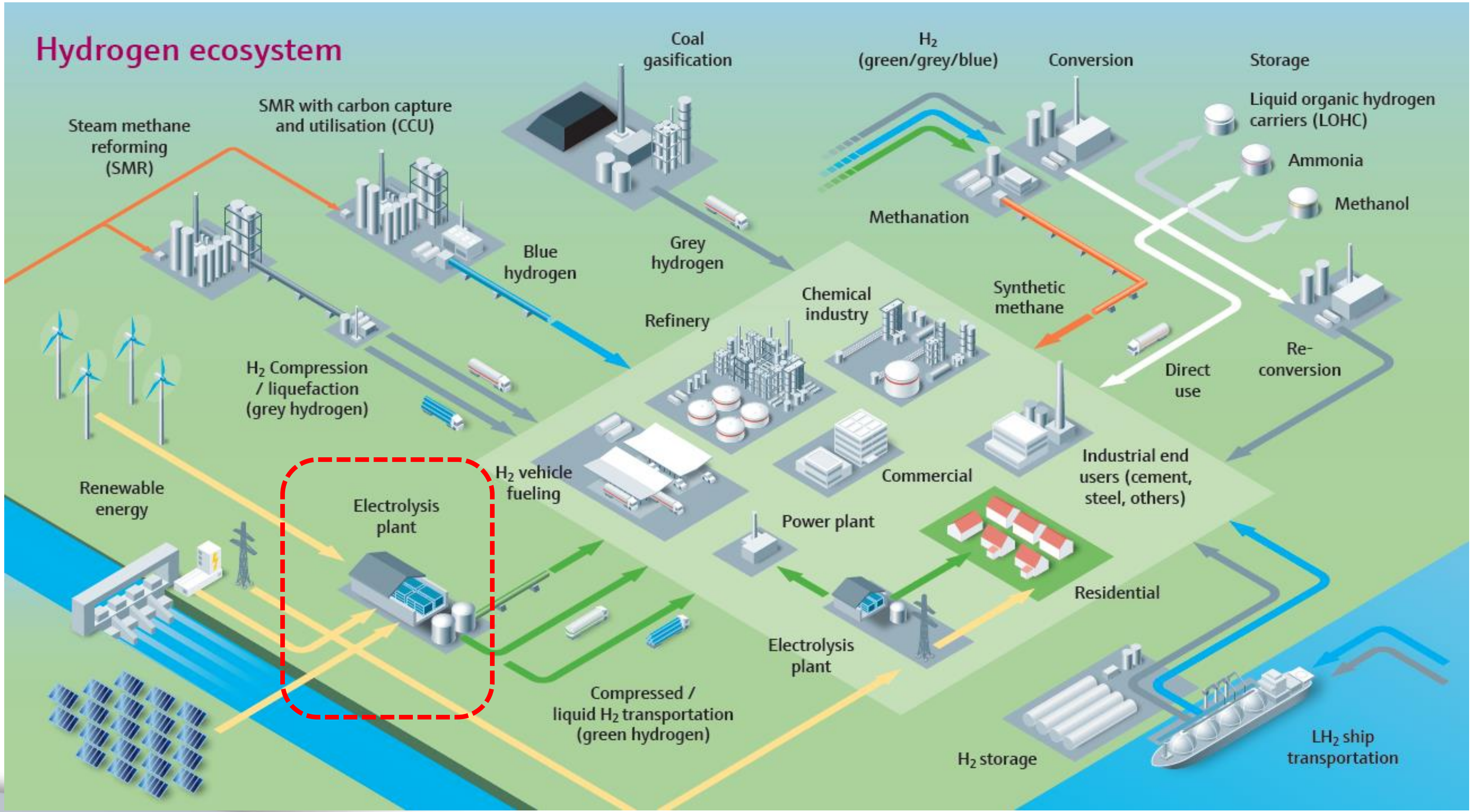
GISI
ASSOCIAZIONE IMPRESE ITALIANE
DI STRUMENTAZIONE

La Misura della Qualità *dell'Idrogeno* per la Garanzia della Sicurezza dei Processi

12.09.2024

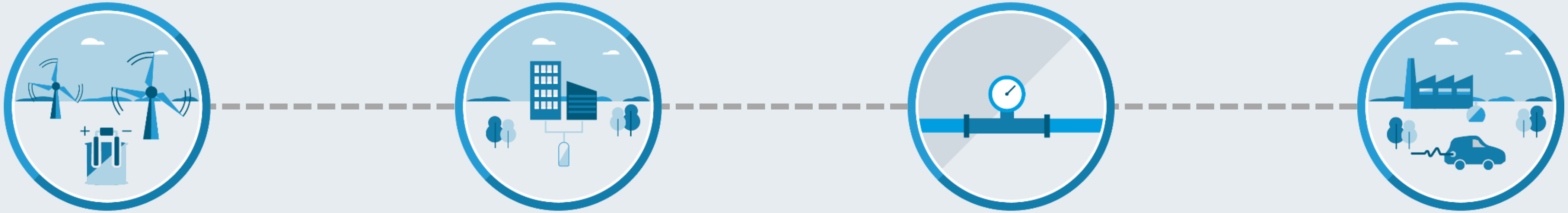
D. Vracevic (Endress+Hauser) - Hydrogen Expo

L'ecosistema dell'idrogeno



H2: Le misure di quantità, qualità e composizione

Produzione | Stoccaggio | Trasporto | Utilizzo



Misure di quantità | Misure di qualità | Misure di composizione

Misura della qualità di H2: ISO 19880-8

D.2.3 Alkaline electrolysis

Alkaline electrolysis has been used for more than a century to produce H_2 from H_2O using electricity. The hydrogen produced at the anode is usually purified from the remaining O_2 through a catalytic reactor and then dried through a temperature swing adsorption (TSA). Table D.2 investigates the potential sources of contaminations. Such contaminants are mainly coming from the H_2O and the air.

Table D.2 — Impurities potentially present in H_2 produced by alkaline electrolysis

Possibility of impurity over threshold	Gaseous impurities
Possible	O_2, H_2O
Improbable	CO_2, CO, CH_4, He, N_2, Ar, TS, NH_3, THC, HCHO, HCOOH, Halogens

NOTE As per the rationale in ISO 14687-2 (see B.2), the presence of water soluble contaminants such as K+ and Na+, which could be present as an aerosol, can be controlled by process control of the level of water contamination precluding the presence of water in liquid form.

D.2.4 Proton exchange membrane electrolysis

PEM electrolysis is the electrolysis of H_2O in a cell equipped with a solid polymer electrolyte that is responsible for the conduction of protons, separation of product gases, and electrical insulation of the electrodes. Table D.3 investigates the potential sources of contaminants. Such contaminations are mainly coming from the H_2O and the air.

Table D.3 — Impurities potentially present in H_2 produced by PEM electrolysis

Possibility of impurity over threshold	Gaseous impurities
Possible	O_2, H_2O,
Improbable	CO_2, CO, CH_4, Ar, TS, N_2, NH_3, THC, HCHO, HCOOH, Halogens

Misura della qualità di H2: ISO 19880-8

ISO 19880-8:2019(E)

Table 4 — Impact of impurities on fuel cell powertrain

Impurity		ISO 14687-2 threshold value[a] [µmol/mol]	Severity class (from ISO 14687-2 to Level 1)	Level 1 value [µmol/mol]	Severity class (greater than Level 1 threshold)
Total non-H_2 gases		300	1	UD	UD
Total nitrogen and argon	N_2, Ar	100	1[b]	300[a]	4
Oxygen	O_2	5	UD	UD	4[c]
Carbon dioxide	CO_2	2	1	3	4
Carbon monoxide	CO	0,2	2-3[d]	1	4
Methane	CH_4	100	1	300	4
Water	H_2O	5	4	5	4
Total sulphur compounds	H_2S basis	0,004	4	>0,004	4
Ammonia	NH_3	0,1	4	>0,1	4
Total hydrocarbons	CH_4 basis	2	1-4[d]	>2	4
Formaldehyde	CH_2O	0,01	2-3[d]	1	4
Formic acid	HCOOH	0,2	2-3[d]	1	4
Halogens		0,05	4	>0,05	4
Helium	He	300	1	300	4
Maximum particulate concentration (liquid and solid)[e]		1 mg/kg	4	>1 mg/kg	4

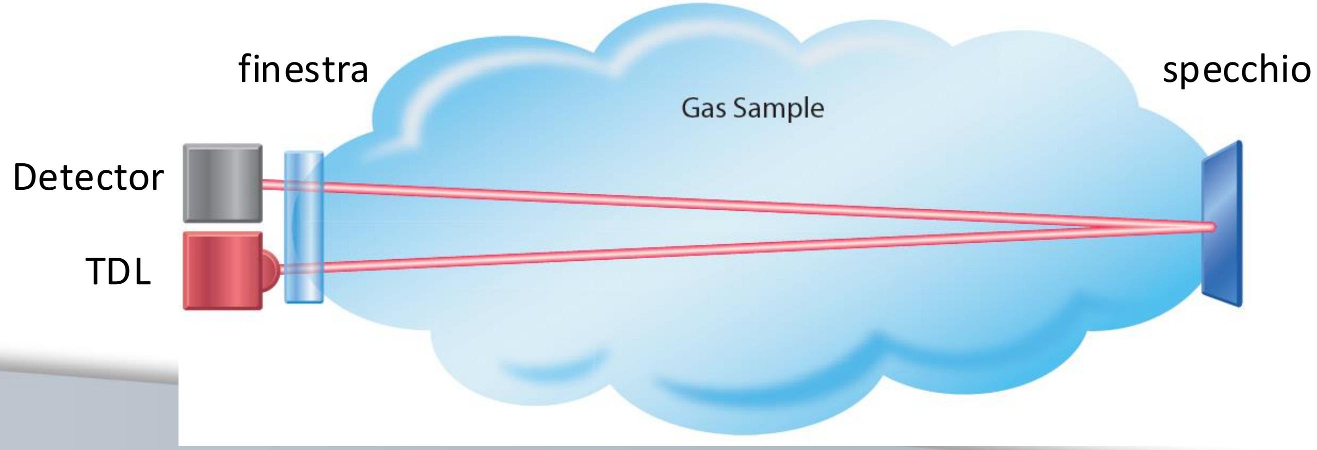
Misura della qualità di H2: la soluzione di E+H

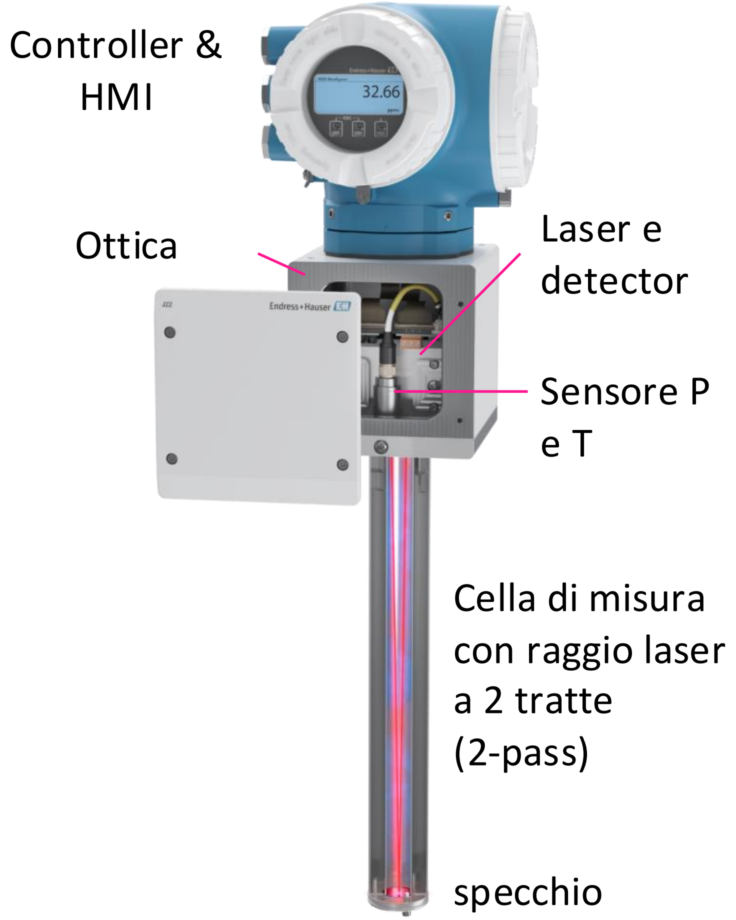
Soluzione per misurare e controllare la presenza di impurità nell'Idrogeno

- H_2O: range 0…10/200/500 ppm con l'analizzatore TDLAS J22
- Ossigeno: range 0…10 ppm con l'analizzatore Quenched Fluorescence (QF) OXY5500

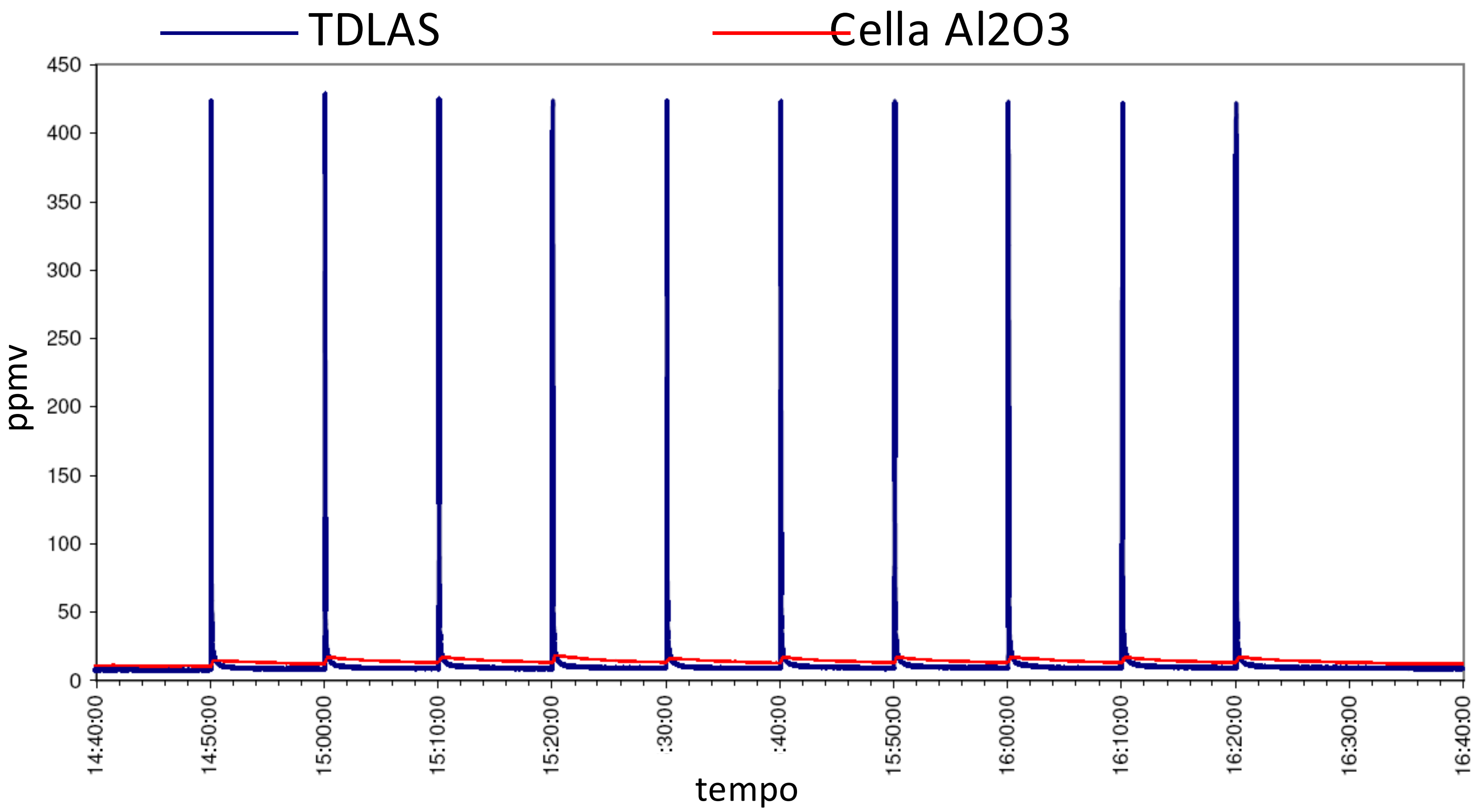
Misura di H_2O con l'analizzatore TDLAS

- L'analizzatore J22 TDLAS utilizza un laser modulabile in frequenza per trasmettere un raggio attraverso il campione da analizzare
- Il detector riceve un raggio di intensità ridotta dall'assorbimento dell'umidità
- La concentrazione dell'umidità è correlata alla quantità di energia assorbita
- La pressione e la temperatura del campione sono misurate e compensate





Misura di H_2O con l'analizzatore TDLAS



Vantaggi di un analizzatore TDLAS:

- Velocità di risposta
- Wet to dry inesistente
- Possibilità di usare un unico sistema in scansione su diversi punti di analisi
- No necessità di calibrazione
- No necessità di bombole

Non solo misure di qualità…portfolio prodotti per elettrolizzatori

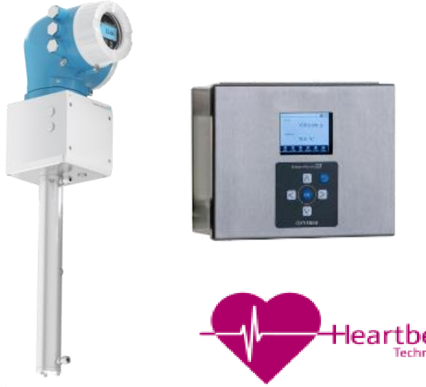
- Portata (elettrolita + idrogeno)

- Trasmettitori di pressione e temperatura

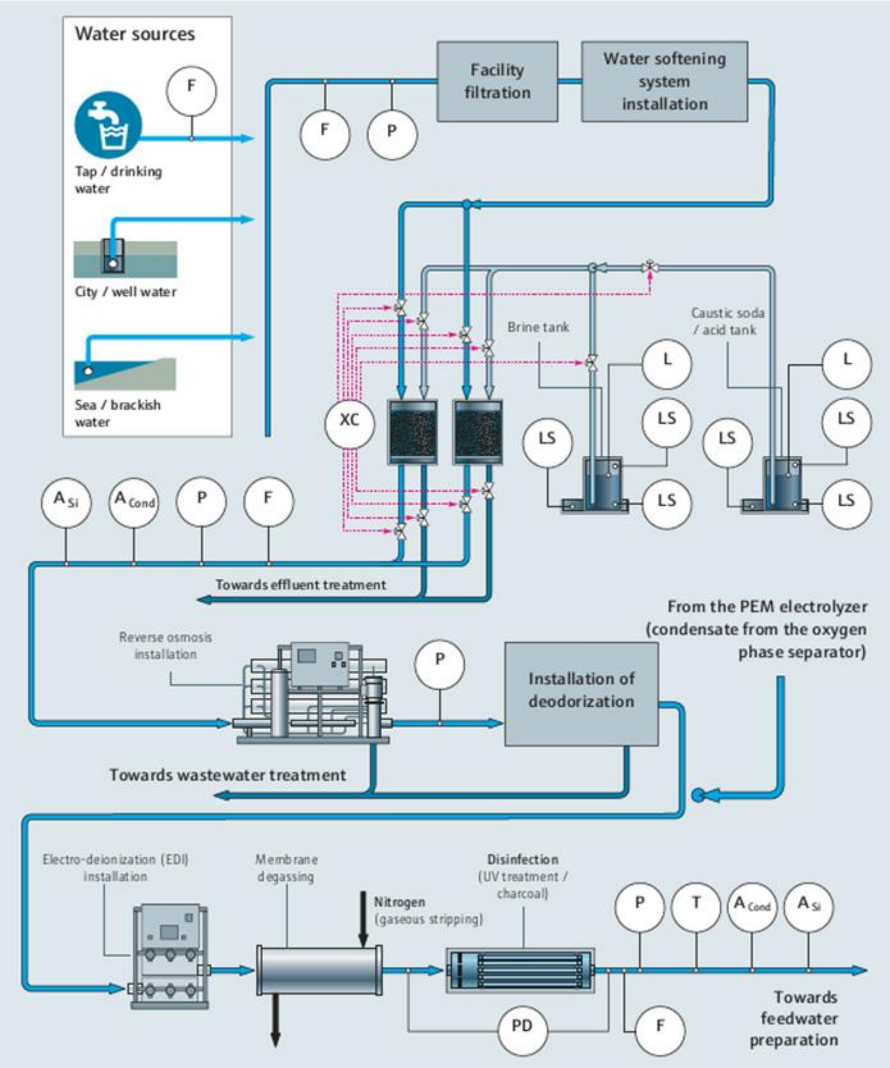
- Trasmettitori di livello

- Analisi liquidi

- Analisi gas



Preparazione acqua di alimento



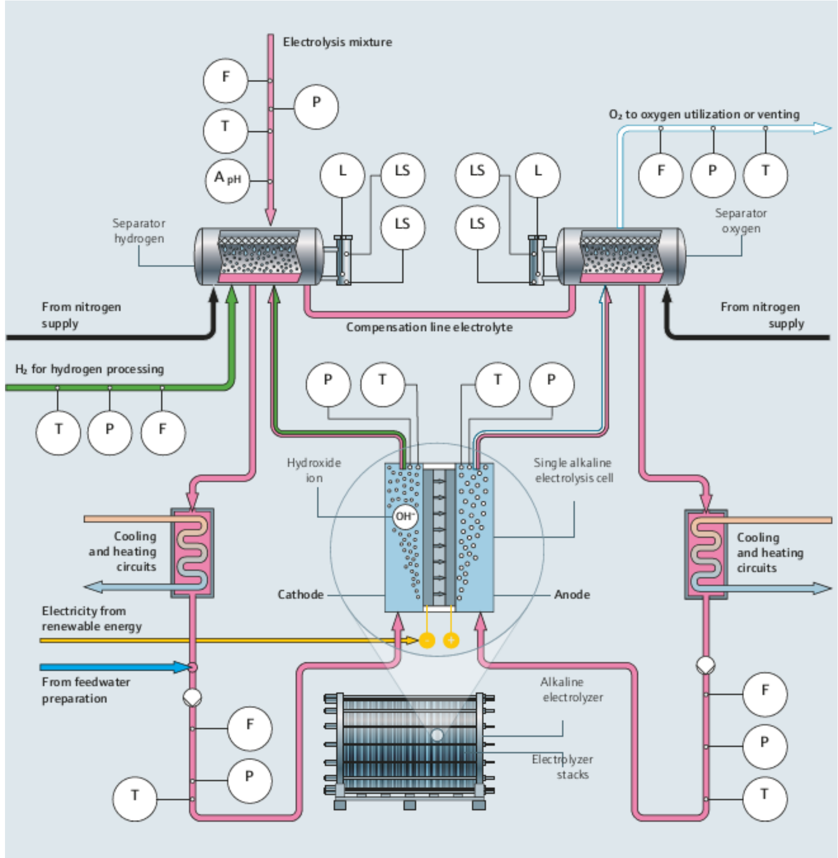
- Misura di portata

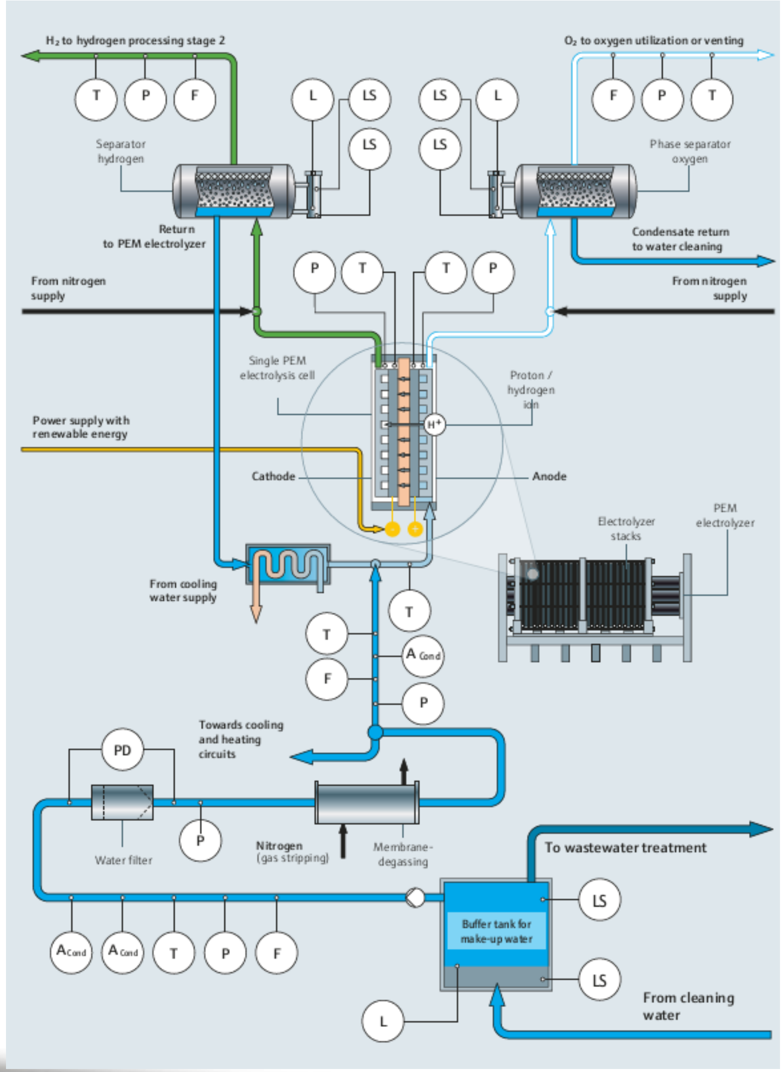
- Misura di pressione

- Misura di conducibilità

- Misura di pressione differenziale
- Misura di livello (controllo di soglia e in continuo)

Elettrolizzatore alcalino e PEM





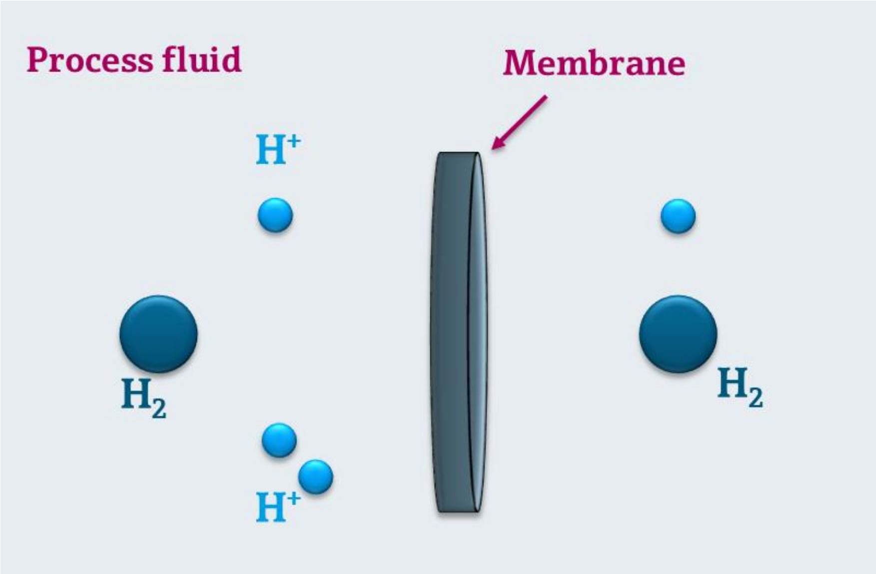
- Misura di portata

- Misura di pressione

- Misura di temperatura
- Misura di livello

- Misura di qualità di H_2

Una sfida nella misura: Permeazione di H2 nelle membrane



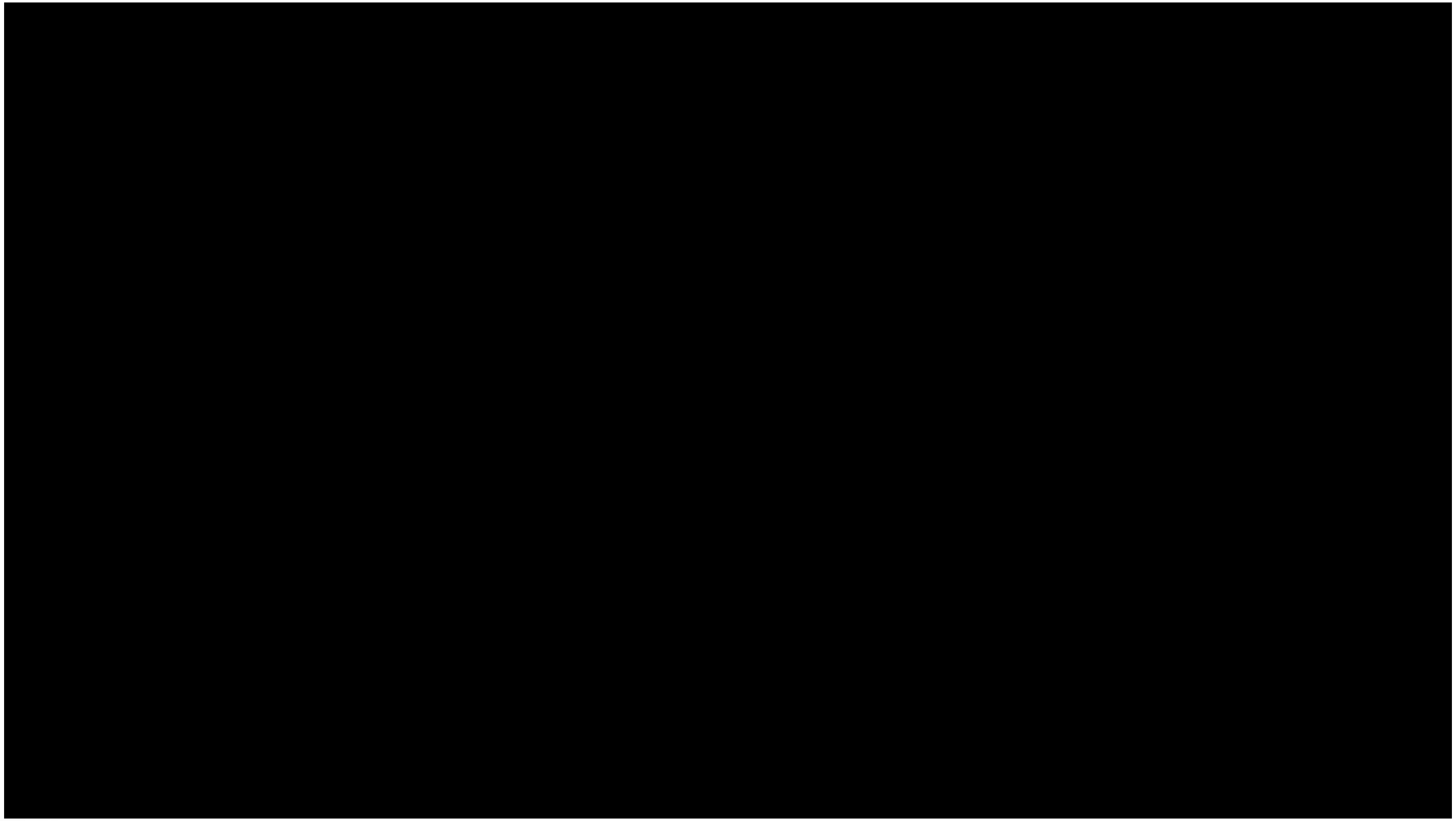
Al fine di ottimizzare il tempo di vita del trasmettitore in applicazioni con idrogeno è importante prestare attenzione ad alcuni fattori:

- Diametro della membrana
- Materiale della membrana

Per risolvere il problema della diffusione di idrogeno, si possono usare due soluzioni per i trasmettitori di pressione:

- membrana con protezioni gold-plating (rivestimento in oro) oppure "combinate" come gold-rhodium (rivestimento in oro-rodio).
- membrana ceramica Ceraphire® fatta di Al2O3 puro al 99,9%.

All'interno di un elettrolizzatore Enapter



Documentazione

Products | Solutions | Services

H_2O and O_2 measurements for green hydrogen production

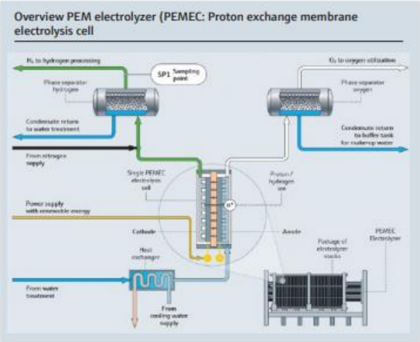


Figure 1: The electrolyzer converts water into hydrogen and oxygen. Trace moisture and oxygen are considered contaminants and must be measured prior to hydrogen processing.

Benefits at a glance

- Reliable H_2O and O_2 measurement in green hydrogen production using TDLAS and QF optical analysis technologies
- Improved safety, process control, and hydrogen quality validation during purification stages
- Accurate, real-time measurements without interferences
- Very fast response times for instant protection of downstream equipment
- No moving parts, no electrolytes, and long-lasting optics to enable extremely low maintenance
- Very reliable construction using solid state sensing elements means extremely high uptime
- Easy to install and commission with health monitoring that provides hands-off operation for years
- Simple in-field component servicing for minimal downtime
- NIST-traceable calibration
- ASTM standard test method compliance and global hazardous area certifications

Green hydrogen is becoming a viable clean energy source to support global efforts to reduce carbon emissions to net zero by 2050. To meet this ambitious target, rapid, reliable measurement of moisture (H_2O) and oxygen (O_2) in hydrogen (H_2) streams is critical to ensure product quality and process safety.

Hydrogen measurement challenges

Hydrogen can be produced from a variety of processes including fossil fuels, nuclear energy, biomass and renewable energy sources. Because it is derived from clean renewable energy sources like solar or wind, green hydrogen will play a key role in the transitioning energy ecosystem. Green hydrogen is produced through a process called electrolysis which divides water into two hydrogen atoms and one oxygen atom. The resulting "pure" hydrogen is then compressed for efficient storage and distribution.

Endress+Hauser
People for Process Automation

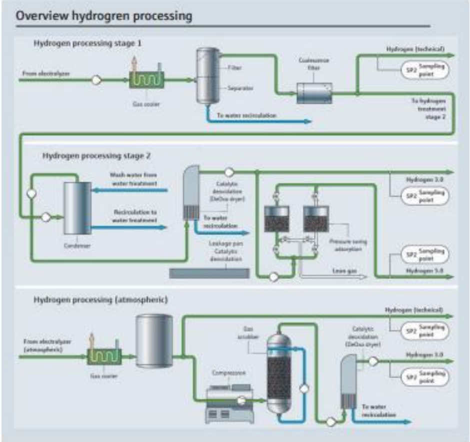


Figure 2: Key measurement points in green hydrogen processing

Accurate, rapid H_2O and O_2 measurement is vital at several key measurement points in this process chain to meet quality compliance regulations and safeguard process equipment and personnel.

Many traditional measurement technologies have sensors that come in direct contact with H_2 streams and are adversely affected by large changes in concentration, pressure, and temperature. Ultimately, these analyzers often deliver unreliable measurements, cause lengthy downtime, and are costly to operate.

After exiting the electrolyzer, hydrogen can contain water vapor and oxygen. Accurate, reliable measurement of these contaminants in real time is essential to maximize process efficiency, safety, and quality compliance. There are several key measurement points in green hydrogen production (Figure 2):

- O_2 and H_2O measurements at the outlet of the electrolyzer
- Trace O_2 and H_2O measurements through the hydrogen processing stages

Hydrogen quality compliance at the outlet of the electrolyzer

Hydrogen is produced by electrolysis plants powered by solar or wind farms, and it is an efficient way to store significant amounts of renewable energy. Hydrogen must meet strict purity requirements to ensure the proper function of hydrogen fuel cells. Optical technologies for H_2O and O_2 measurements offer maintenance-free operation due to their inherent robustness and reliability. Sample point 1 (SP1 in Figure 1) is found directly after the phase separator. This is the first step in removing any moisture carry-over from the electrolysis cell. Excess moisture in the hydrogen stream could indicate issues with the separation process. Meanwhile, excess oxygen in the hydrogen stream is a predictor of membrane degradation within the cell.

Final measurements during hydrogen processing

After phase separation, hydrogen must go through additional processing to achieve high purity. The processing stages may vary depending on the type of electrolyzer and size of the facility. Each stage normally involves additional steps to further remove moisture and oxygen from the stream. Final analytical measurements (shown as SP2) are done after each processing step to ensure that these contaminants are removed to a point where the gas can be compressed for sales. Green hydrogen may be classed based on its purity. Hydrogen 3.0 equates to 99.9% pure, while hydrogen 5.0 is 99.999% pure. The additional processing ensures that oxygen and moisture levels are < 10 ppmv.

A look inside a combined J22 / OXY5500 analyzer system

Endress+Hauser's solution

Endress+Hauser tunable diode laser absorption spectroscopy (TDLAS) and quenched fluorescence (QF) analyzers provide the reassurance that your electrolyzer process has removed H_2O and O_2 contaminants sufficiently to allow you to deliver a quality product to end users. Our analyzers have proven reliability in H_2 green production applications at installations worldwide. Laser-based TDLAS technology provides real-time, non-contact measurements using a near infrared solid-state laser to isolate the distinct peaks in the wavelength absorption spectrum, indicating H_2O with high accuracy.

TDLAS analyzers are able to perform continuously analysis in real-time, while Endress+Hauser's QF analyzers help to further avoid O_2 carry over into pure O_2. Endress+Hauser TDLAS and QF analyzers are demonstrably faster, more accurate, and more stable than other H_2 green production process measurement alternatives, with no contaminant interferences and nearly zero maintenance.

TDLAS and QF analyzers help to future-proof power and energy systems by providing reliable, real-time concentration analysis of hydrogen streams at critical points of transfer. Moisture and oxygen can be detected at the outset of the electrolyzer down to trace ppm levels. TDLAS analyzers are easy to install and commission, have no moving parts or consumables, and feature 24/7 online health monitoring. These capabilities provide hands-off operation for years with nearly no required maintenance.

Conclusion

As energy sources and gas mixtures continue to shift, the infrastructure to produce green hydrogen on an industrial scale will be critically important. TDLAS and QF-based measurement systems should play prominent roles in the processes involved to support this new emerging energy ecosystem. A changing mix of molecules and pipeline infrastructure, coupled with advancements in process automation, will further drive the need for on-line gas analysis in hydrogen processes for enhanced safety, asset integrity, and quality control for decades to come.

Grazie per la Vostra partecipazione e attenzione

ASSOCIAZIONE **IMPRESE ITALIANE**
DI **STRUMENTAZIONE**