Application note

Green hydrogen

Thermo Scientific Prima BT and Prima PRO Process Mass Spectrometers

Improving production of green hydrogen with fast, precise gas analysis MS

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Introduction

As the global climate crisis worsens year on year, and the acceptance that fossil fuels have become progressively more depleted, subject to greater demand and significantly more expensive, there has been an almost global acceptance that a move towards a lower-carbon economy is a necessity. 2020 and 2021 were key years for this as several countries, as well as the European Union,[1] released strategies for a transformation towards a hydrogen economy. These strategies have cemented the drive towards a new way to generate and utilize energy in all parts of heavy industry, power-to-x (taking surplus renewable electricity and converting it into other energy carriers to store the energy for later use), transport, as well as the way we heat and power our homes.

Hydrogen generation can be classified in several different ways, including by the amount of carbon that is released, or by the method of generation. Green hydrogen is seen by many as the only truly carbon neutral way to generate hydrogen and could be a key driver towards a cleaner future. Green hydrogen is produced via electrolysis, with the electrolyzer being powered with renewable energy, namely wind and solar. There are several distinct types of electrolyzers used for the generation of green hydrogen, they all follow the same basic principles. To decompose water into hydrogen and oxygen, a direct current electrical supply is applied to a pair of electrodes that are in contact with a pure water supply and are often separated by a membrane (although there are examples of membrane-free electrolysis). On one side pure oxygen is liberated, and on the other pure hydrogen.

There are three main types of electrolyzers in use:

- Alkaline electrolyte membrane (AEM)
- Polymer electrolyte membrane (PEM)
- Solid oxide electrolyte cell (SOEC)

AEM uses a liquid electrolyte solution, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH), and water. Hydrogen is produced in a 'cell' which consists of an anode, cathode, and membrane. The cells are typically assembled in series in a 'cell stack' that produces more hydrogen and oxygen as the number of cells increases.

When current is applied on the cell stack, the hydroxide ions (OH^-) move through the electrolyte from the cathode to the anode of each cell, with hydrogen gas bubbles generated on the cathode side of the electrolyzer and oxygen gas at the anode, as shown in Figure 1 below.

PEM uses a cell with a solid polymer electrolyte. It offers higher current density and higher-pressure operation than the alkaline electrolyzer. When current is applied on the cell stack, water splits into hydrogen and oxygen and the hydrogen protons pass through the membrane to form H_2 gas on the cathode side.

SOEC uses a solid ceramic material as the electrolyte. Electrons from the external circuit combine with water at the cathode to form hydrogen gas and negatively charge ions. Oxygen then passes through the solid ceramic membrane and reacts at the anode to form oxygen gas and generate electrons for the external circuit. SOECs have the potential to become much more efficient than PEM and alkaline but need to operate at a much higher temperature (above 500°C) than alkaline and PEM electrolyzers (up to 80°C).

A schematic of a typical PEM electrolyzer is shown in Figure 1.

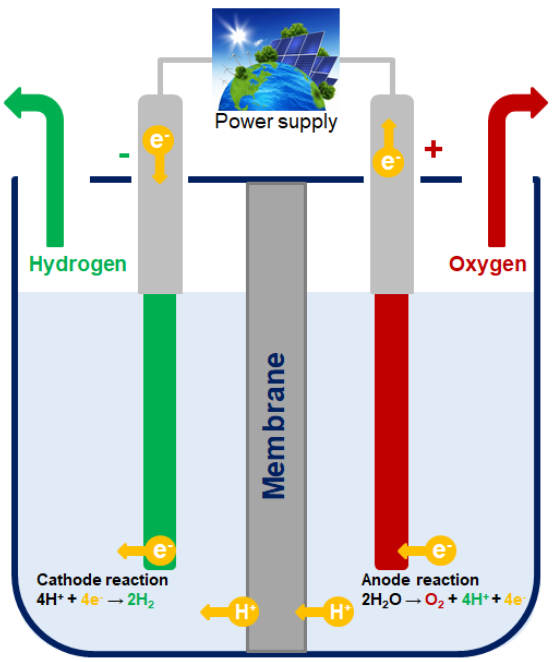

Figure 1: Typical polymer electrolyte membrane cell.

Process analytical requirements

All three types of cells aim to produce 'pure' hydrogen and 'pure' oxygen, so a key analytical requirement is to measure impurities in these two gases. In the case of hydrogen, analysis of oxygen and water levels is important; in that of oxygen, analysis of hydrogen and water levels is equally important.

Table 1 shows a typical performance specification for a Thermo Scientific™ Prima PRO Process Mass Spectrometer analyzing three streams, 'pure' hydrogen, 'pure' oxygen and a mixture of hydrogen (~ 66%) and oxygen (~ 33%). This analysis was prepared for a novel, membrane-free electrolyzer that outputs a mixed stream, this stream is then separated into hydrogen and oxygen via cryogenic separation.

Table 1. Typical Prima PRO performance specification for three green hydrogen process streams.

	Sample gas 1	Prima PRO lower detection limit	Prima PRO standard deviation
Component	Concentration %mol	Concentration %mol	%mol
Hydrogen	>95%		≤0.02%
Water	<5%	≤0.02%	≤0.01%
Oxygen	<5%	≤0.01%	≤0.01%

	Sample gas 2	Prima PRO lower detection limit	Prima PRO standard deviation
Component	Concentration %mol	Concentration %mol	%mol
Hydrogen	<1%	≤0.05%	≤0.01%
Water	<1%	≤0.02%	≤0.01%
Oxygen	>99%		≤0.02%

	Sample gas 3	Prima PRO lower detection limit	Prima PRO standard deviation
Component	Concentration %mol	Concentration %mol	%mol
Hydrogen	>66%		≤0.05%
Water	<1%	≤0.02%	≤0.01%
Oxygen	>33%		≤0.05%

In new applications such as green hydrogen, it is often necessary to develop new analytical methods in the laboratory, which are then transferred to an industrial scale as the process is 'scaled up.' It is therefore vital that the results from the laboratory gas analysis MS correlate directly with those obtained from the process MS. Although the external packaging of the two analyzers may be very different (the process MS should be capable of installation in a hazardous area, for example), the analytical performance should be identical.

Figures 2 and 3 show results from a Thermo Scientific™ Prima BT Process Mass Spectrometer measuring product gas streams directly from an electrolyzer. Prima's analysis speed is significantly faster than technologies such as GC, so it can resolve concentration changes in hydrogen, oxygen, and water in real-time. Its wide dynamic range handles concentrations from 100 % to < 100 ppm in a single measurement, and its ability to measure all three components with a single technology is advantageous over three different gas analyzers. Also, Prima's multipoint capability means that as electrolysis technology scales up, all the individual stacks can be monitored with a single instrument.

Each figure represents a different experimental scenario using cutting-edge electrolysis technology; Prima BT was able to provide insights into the process that were not possible with alternative technologies.

Figure 2 shows results from a 70:30 hydrogen: oxygen mixed gas stream. The operators concluded the liquid oxygen level was too full, thereby preventing separation from occurring.

Figure 3 shows a pure oxygen stream, indicating that oxygen purity increases as water is removed from the stream. Analysis of water vapor proved to be particularly useful in improving process understanding—Prima BT's results were consistent with results from a dew point meter and were used to monitor the effectiveness of the dryer in removing water vapor. It also identified the potential need for the dryer's regeneration cycle to be increased.

Figure 4 shows our Prima BT laboratory magnetic sector MS capable of monitoring 16 gas streams, Figure 5 shows our Prima PRO Ex process magnetic sector MS capable of monitoring 64 gas streams, suitable for installation in an ATEX Zone 1 area.

All current and potential electrolyzer installations are modular, based on stacks. Each stack represents two measurement points (H_2 stream and O_2 stream), so a 5-stack electrolyzer would require 10 measurement points. Other sample points could also require analysis, for example the H_2 and O_2 pipeline and transport points.

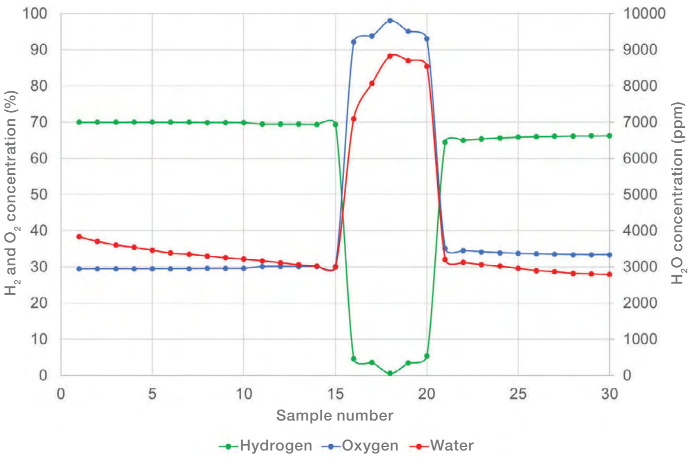

Figure 2: Measurement of mixed gas stream from an R&D scale electrolyzer.

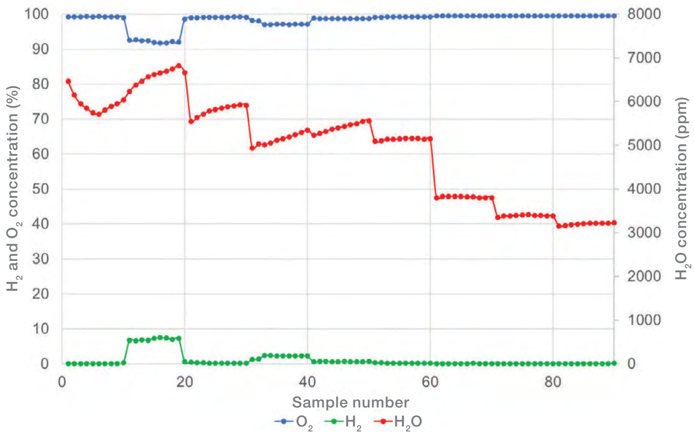

Figure 3: Measurement of pure oxygen stream from megawatt scale electrolyzer.

Figure 4: Prima BT benchtop MS.

Figure 5: Prima PRO Ex Hazardous Area Process MS.

Benefits of magnetic sector mass spectrometry

Two main types of gas analysis mass spectrometers can be used for hydrogen studies, with the magnetic sector MS providing greater stability and better precision than the quadrupole MS. Unlike the flat-topped peak generated by the magnetic sector, the quadrupole produces a Gaussian peak. So, it is 'fault sensitive'—any drift in the mass scale will produce an error in the peak height measurement by measuring intensity on the shoulder of the peak rather than the peak maxima. This must be corrected by more frequent calibration.

Figure 6 shows a schematic of our magnetic sector analyzer, together with the characteristic flat top peak it produces.

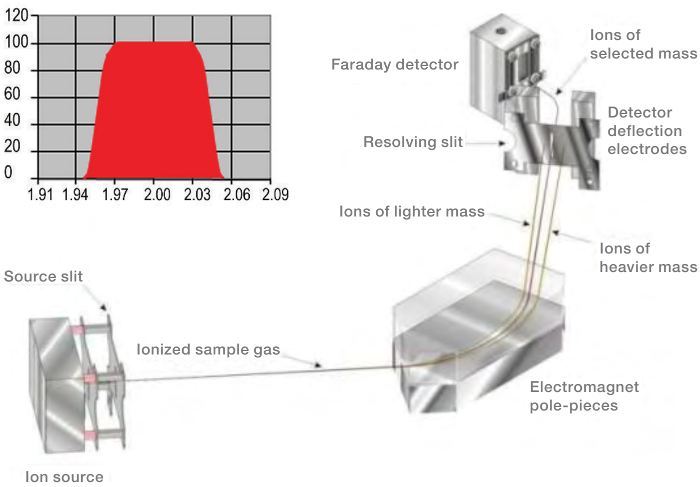

Figure 6: Schematic of Thermo Scientific Magnetic Sector analyzer and flat-topped peak for mass 2 (hydrogen).

Quadrupole MS also suffers from an effect known as 'zero blast,' the RF amplitudes at low masses are too low to stop all ions from reaching the detector leading to a tail effect starting at 0 amu and extending as far as 4 amu. This noise from the zero blast, which is constantly changing, causes detection and resolution of the hydrogen peaks at mass 1 and 2 to be compromised. The magnetic sector MS has a curved flight path for the ions, unlike the quadrupole which is straight. This means that it is impossible for ions to reach the detector when they should not, they must be deflected by the magnet to hit the detector. As a result, hydrogen resolution is superior on a Prima PRO or Prima BT Process Mass Spectrometer than on a quadrupole equivalent.

Competition

Discrete gas analyzers are a ubiquitous alternative to mass spectrometry for this category of measurement. They are relatively low-cost options that usually offer a single component analysis of a gaseous species in a specific gas matrix. For example, hydrogen. In the case of an electrolyzer, at least two analyzers would be required, one for the oxygen outlet and one for the hydrogen outlet. As electrolyzer systems scale up, so will the number of required gas analyzers. The use of a Prima PRO in this scenario offers two key advantages over discrete gas analyzers. The first is the multi-point capability, meaning there is no variability in the measurement between streams, gas analyzers offer some uncertainty in the measurement based on variability from analyzer to analyzer. The second advantage is precision. Prima BT and Prima PRO offer a higher level of precision by at least an order of magnitude when compared with discrete gas analyzers.

Rapid multistream sampling

If the MS is to monitor all process streams, then a fast, reliable means of switching between streams is required. Solenoid valve manifolds have too much dead volume and rotary valves suffer from poor reliability, so we developed the unique RMS Rapid Multistream Sampler. It offers an unmatched combination of sampling speed and reliability and allows sample selection from 1 of 32 or 1 of 64 streams. Stream settling times are application dependent and completely user configurable. The RMS includes digital sample flow recording for every selected stream. This can be used to trigger an alarm if the sample flow drops, for example if a filter in the sample conditioning system becomes blocked.

The Prima PRO RMS can be heated to 120°C and the position of the stream selector is optically encoded for reliable, software-controlled stream selection. Temperature and position control signals are communicated via Prima PRO's internal network.

As the RMS is a selector rather than a valve, all process streams flow continuously through the selector. If the RMS is sampling both hydrogen and oxygen streams, it is therefore important to ensure the resulting mixture is safe. In order to dilute the flammable sample gases in the RMS to a safe level, and to minimize crosstalk between pure hydrogen and pure oxygen sample streams, an inert gas purge (typically nitrogen) is connected to a spare sample port on the RMS. In addition to this, a nitrogen purge is applied to the rotary pump to dilute down the gases passing through the pump to a safe level.

The RMS is shown in schematic form in Figure 7. It has a three-year warranty as standard; no other multistream sampling device offers the same level of guaranteed and proven reliability.

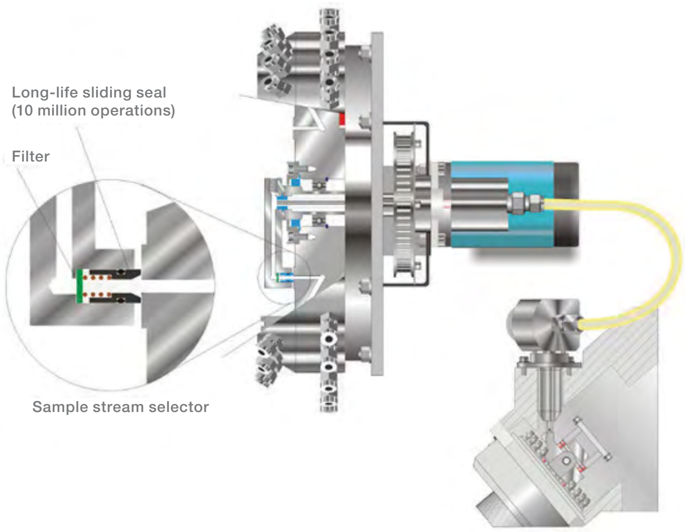

Figure 7: Rapid multistream sampler.

Software

Thermo Scientific™ GasWorks™ Software supports the analysis of an unlimited number of components per stream, and an unlimited number of user-defined calculations (called Derived Values). An unlimited number of analytical methods can be set up, so different analyses can be defined for different process streams. Analog signals, from temperature and pressure sensors for example, can also be logged, displayed, and used in Derived Value calculations. A range of industry-standard protocols are available for communicating with plant process control systems.

Table 2. Example Prima BT performance specification.

Component	Sample gas 1 %mol	Prima BT lower detection limit %mol	Prima BT standard deviation %mol
Hydrogen	90 – 100%		≤0.02%
Nitrogen + Carbon monoxide	0 – 10%	≤0.02%	≤0.01%
Oxygen	0 – 10%	≤0.01%	≤0.01%
Carbon dioxide	0 – 10%	≤0.001%	≤0.01%

Component	Sample gas 2 %mol	Prima BT lower detection limit %mol	Prima BT standard deviation %mol
Hydrogen	0 – 10%	≤0.05%	≤0.01%
Oxygen	90 – 100%		≤0.01%

Analysis time will be approximately 5 seconds. The settling time on changing sample streams will be 55 seconds, so the cycle time to measure both sample streams will be 2 minutes.

Examples of processes adapting to green hydrogen

Examples of industrial processes whose carbon footprint can be significantly reduced by using green hydrogen include:

Ammonia

Ammonia manufacturing is the world's third-largest industrial process emitter of carbon dioxide, creating half a billion tonnes of CO_2 each year, almost 2% of global CO_2 emissions. It is produced by reacting methane with steam to produce hydrogen, then reacting it with nitrogen from air in a 3:1 ratio. However, steam methane reforming also gives off carbon dioxide. In contrast, green ammonia can be produced with hydrogen that has been separated from water using renewable electricity.

Iron and steel

Among heavy industries, the iron and steel sector ranks first when it comes to CO_2 emissions. It directly accounts for 2.6 gigatonnes of carbon dioxide (Gt CO_2) emissions annually, 7% of the global total from the energy system and more than the emissions from all road freight.[2]

The industry aims to be net zero by 2050 and is moving away from blast furnaces to direct reduction ironmaking (DRI) for primary iron production. Electric arc furnaces (EAF) which can recycle scrap metal, are increasingly being used to produce steel. In DRI processes, hydrogen is used to reduce iron oxide to iron, and in EAF processes, hydrogen can be used to power the furnace.

Both industries have successfully been using Thermo Scientific process MS for many years to improve process efficiency, and this success can be replicated with the new green hydrogen-based processes.

Summary

Magnetic sector mass spectrometers have demonstrated the highest levels of precision, stability, and reliability in measuring hydrogen in a wide range of processes over many years. Now, with the ever-increasing focus on replacing fossil fuels with renewables, green hydrogen produced by electrolysis is arguably the only truly carbon neutral way to generate hydrogen and is a leading hydrogen production pathway to achieve the US DOE's Hydrogen Energy Earthshot goal of reducing the cost of clean hydrogen by 80% to $1 per 1 kilogram in 1 decade ('1 1 1').[3] Thermo Scientific Prima BT and Prima PRO Magnetic Sector Mass Spectrometers are already providing fast, precise off-gas analysis through laboratory research, to pilot plants, and to full-scale production for this vitally important new industry. Prima BT provides a bench-top solution for laboratory scale reactors, being configured with 15 samples and 6 calibration ports. Prima PRO is equipped to monitor 60+ reactors and is available for Zone 1 and Class 1 Div 2 hazardous area installation. The highly precise and complete gas composition measurements provided by both models are easily incorporated into a process control system.

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