Application Note #24

Purity Analysis of Fuel-Cell Hydrogen

Spark™ • HALO 3 • HALO OK • Prismatic 2

GASES & CHEMICALS | CEMS | ENERGY | SEMI & HB LED | ATMOSPHERIC | LAB & LIFE SCIENCE

Hydrogen-Powered Fuel Cell Electric Vehicles

Fuel Cell Electric Vehicles (FCEVs) are considered one of the most promising eco-friendly alternatives to conventional automobiles. They combine advantages of both battery-electric vehicles and vehicles powered by combustion engines:

- Zero emissions—only H_2O is produced as exhaust
- High efficiency (more than 50% better than combustion engines)
- Range similar to conventional vehicles (>400 miles)
- Short refuelling time

An FCEVs high efficiency is a result of converting the hydrogen fuel chemically in combination with an electric drive train rather than burning hydrogen in a combustion engine, which is always subject to thermodynamic limitations.

Principle of a Proton Exchange Membrane Fuel Cell

Most fuel cells used in FCEVs are hydrogen-powered proton exchange membrane (PEM) fuel cells. Figure 1 highlights the principle of operation of a PEM fuel cell: H_2 fuel is injected into the anode side, while O_2 (usually taken simply from the air) is added on the cathode side. A platinum catalyst separates the H_2 molecule's electrons from the protons. While the protons are transferred to the cathode via the membrane, the electrons are directed through the load and produce an electrical current, which powers the vehicle's electric motor. This elegant principle, however, relies mainly on two delicate components: the platinum catalyst and the PEM, both of which are highly sensitive to the quality of the hydrogen fuel. This application note presents an overview of some of the most critical impurities present in hydrogen and how Continuous-Wave Cavity Ring-Down Spectroscopy (CW-CRDS) analyzers can be effective tools to ensure the required hydrogen purity.

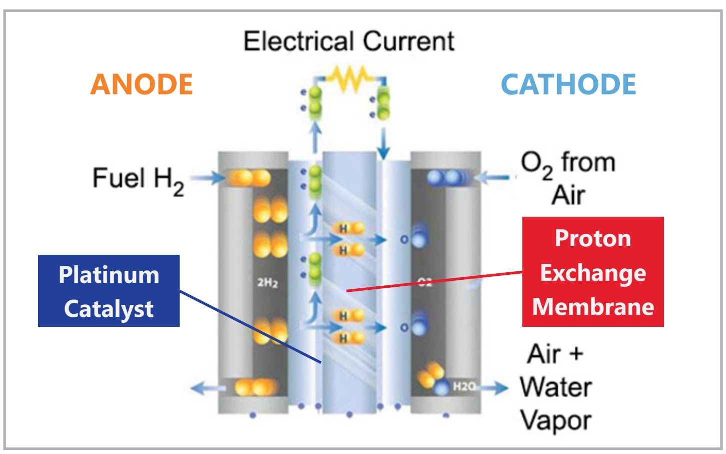

Fig. 1 Schematic and principle of operation of a PEM fuel cell

Critical Contaminants in Fuel-Cell Hydrogen

There is a variety of contaminants that can cause issues for the fuel cell. Some mainly cause a reduction in fuel cell efficiency. This would lead to an FCEV losing power, an effect that is ultimately benign, but extremely annoying to the driver. Other contaminants, however, can cause severe damage to the fuel cell and would outright disable the vehicle. Widespread occurrences of this kind could quickly destroy acceptance of FCEVs by consumers. Thus, hydrogen purity is extremely critical for the long-term success of FCEVs in the automobile market. The allowable limits for different components vary therefore depending on the severity of the effect the molecule has on the fuel cell. The allowable limits are listed in hydrogen fuel purity standards, such as SAE J2719 (Society of Automotive Engineers) or ISO 14687-2 (International Standards Organization). Table 1 lists some of these contaminants in order of the allowable limit.

Tab. 1 Allowable limits for some critical contaminants in H_2 fuel

Contaminant	Allowable Limit
Helium (He)	300 ppm_V
Nitrogen (N_2) & Argon (Ar)	100 ppm_V
Water (H_2O)	5 ppm_V
Oxygen (O_2)	5 ppm_V
Total Hydrocarbons (C_1 basis)	2 ppm_V
Carbon Dioxide (CO_2)	2 ppm_V
Carbon Monoxide (CO)	0.2 ppm_V
Formic Acid (CH_2O_2)	0.2 ppm_V
Ammonia (NH_3)	0.1 ppm_V
Formaldehyde (CH_2O)	0.01 ppm_V
Total Sulfur (incl. H_2S)	0.004 ppm_V

The limits shown in the table are a consensus based on extensive yet ongoing research on the impact of each contaminant on the fuel cell's ability to function properly. As an example, CO and CO_2 are common contaminants that block sites on the catalyst, which leads to a significant impediment of fuel cell efficiency that is

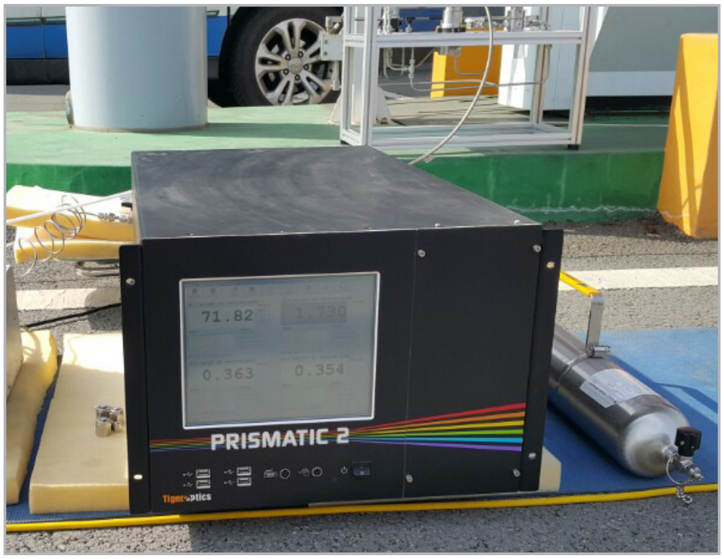

Fig. 2 Prismatic 2 at a hydrogen fueling station in South Korea (picture courtesy of Sunwoo Engineering)

difficult to restore. NH_3 is known to affect membrane conductivity, hindering proton transport and, hence, affect fuel cell efficiency. Sulfur compounds, such as H_2S or SO_2, are considered to be the most harmful contaminants, causing permanent damage to the fuel cell membrane. H_2O is also a critical contaminant, whose measurement is vital for ensuring hydrogen quality. It is a very common contaminant because it finds its way easily into the gas due to its high abundance in air. While not harmful to the fuel cell by itself, H_2O can create a pathway for excess amounts of other, more harmful contaminants to be transported into the hydrogen that have an affinity to water, e.g., NH_3 or CH_2O. In general, the more harmful a contaminant is, the lower its allowable limit. Consequently, some of the limits are extremely low, with sulfur compounds or formaldehyde at low ppb_V levels*. Such low limits pose challenges to many conventional detection methods. CW-CRDS can address this challenge due to its excellent sensitivity with detection capabilities into the parts-per-trillion (molecule dependent). While CW-CRDS is therefore particularly interesting for the contaminants with strictest limits, such as NH_3 or CH_2O, its wide dynamic range and ease-of-use makes it also useful as a real-time monitor for some of the other components, especially H_2O, CO_2, and CO, whose analysis is much more cumbersome with the use of conventional methods, such as GC and FID. With the addition of methane (CH_4), which is commonly used as an indicator for the presence of hydrocarbons, and oxygen (O_2) Tiger's CW-CRDS technology can cover seven critical contaminants in hydrogen fuel.

Origin of Contaminants and Monitoring Requirements

A key source of contaminants is the hydrogen generation process. Most fuel cell experts see electrolysis as the most promising method to generate H_2 sustainably in the future. Electrolysis uses electricity to split H_2O molecules into H_2 and O_2. While energy-intensive, the process can be completely carbon-free by using renewable energy from wind or solar. It can also be generated on-site at a fueling station, thus eliminating the cost and carbon-footprint of transportation. Electrolysis also produces very little contaminants because it uses pure water as source. In reality, however, only a fraction of hydrogen is produced this way.
Most hydrogen today is extracted from natural gas. The most frequently used process is called steam methane reforming (SMR) and allows H_2 production with excellent efficiency, but with the drawback of requiring fossil fuels and emitting greenhouse gases. SMR also allows contaminants present in natural gas to remain in the produced hydrogen; therefore, H_2 can contain all of the compounds listed in the purity standards, including NH_3, CH_2O, CO/CO_2, and sulfur compounds (e.g., H_2S).

Although many contaminants originate from the SMR process, monitoring only directly after production is not sufficient to completely prevent fuel contamination. Additional contaminants, in particular atmospheric components (N_2, O_2, H_2O, etc.) can be added along the distribution chain through leaks in transfer lines, tanks, and valves or through improper operation of equipment. Ultimately, hydrogen has to be monitored at the fueling station to ensure that the dispensed fuel is safe to use in FCEVs. Currently, the most common way is to take samples at each fueling station and analyze the hydrogen in a lab that is outfitted with a battery of analytic equipment; this includes CW-CRDS analyzers, but also large gas chromatographs. With hydrogen infrastructure expected to grow dramatically, this approach will become more and more impractical, increasing demand for on-line fuel analyzers that can continuously monitor hydrogen at a fueling station. CW-CRDS is a promising candidate for this case, as it can be used both in the lab and as a continuous analyzer in the field. Figure 2 shows a picture of a Tiger Optics Prismatic 2 at a fueling station in South Korea. This system is used to verify fuel quality on-site and delivers fast and reliable results. In addition, hydrogen consumption is kept at a minimum: With a flow requirement of <0.1 slpm, the capability of measuring four molecules simultaneously (here, H_2O, CO, CO_2, and

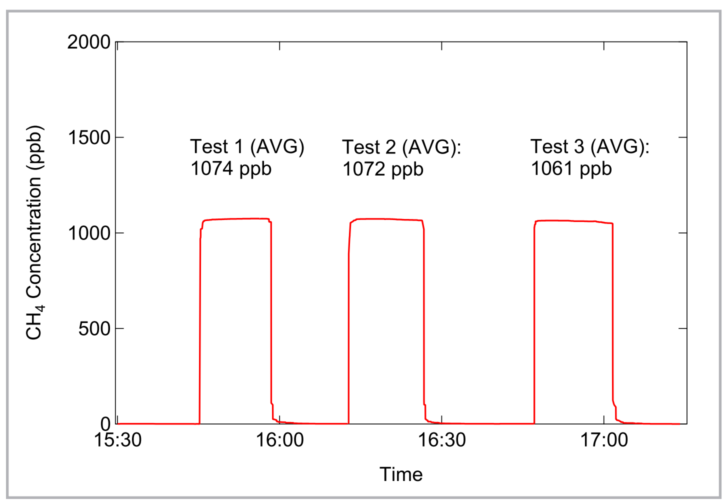

Fig. 3 Repeatability test with a ~1 ppm CH_4 in H_2 sample using a Prismatic 2 CRDS analyzer

*According to the latest updates to ISO 14687, the allowable limit for CH_2O is poised to increase from 0.01 to 0.2 ppm_V.

NH_3), and fast speed of response requiring only minutes to obtain sufficient data, the Prismatic 2 typically consumes less than 0.1 liters per analyte per analysis.

CW-CRDS Analysis of Impurities in Hydrogen

To show the repeatability of CW-CRDS, we used a Prismatic 2 analyzer to measure a hydrogen sample containing approximately 1 ppm_V of CH_4. The sample was introduced three times; each time, the cavity was flushed with dry nitrogen between the measurements. The measurements (see Figure 3) show the fast speed of the CRDS analyzer, with almost immediate up and down response after each sample swap. After allowing a few minutes of stabilization time, the average of each measurement was determined. The three results agree within 0.65% (standard deviation), demonstrating the excellent repeatability of independent measurements using a CW-CRDS analyzer.

In addition to the versatile, multi-species Prismatic 2, Tiger Optics also offers a variety of single-species analyzers, such as the Spark, which is ideal as dedicated analyzer for H_2O, for instance. For detections like CH_2O and NH_3, which demand more sensitivity, the HALO 3 offers an excellent solution. Table 2 shows an overview of Tiger's portfolio of analyzers for fuel-cell hydrogen analysis.

Tab. 2 Tiger Optics' portfolio of analyzers for fuel-cell H_2 analysis

Contaminant	Designated Analyzer Model	
H_2O	Spark H_2O	
CO_2	Spark CO_2	
CO	—	Prismatic 2
CH_4	Spark CH_4	
NH_3	HALO 3 NH_3	
CH_2O	HALO 3 CH_2O	
O_2	HALO OK	

International Measurement Standards

Obtaining repeatable measurements is important to ensure the safety of the fuel for FCEVs. Therefore, international measurement standards have been developed that outline procedures to measure contaminants in hydrogen fuel. Cavity Ring-Down is one of the methods included in these standards. Consequently, CW-CRDS users can refer to these standards for designing sampling systems and conducting sample measurements. ASTM Standard Test Method D7941/D7941M-14 and ISO Standard 21087 both support CW-CRDS for the contaminants mentioned in this application note.

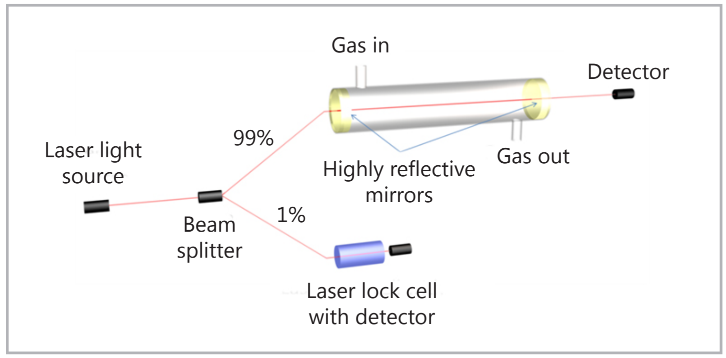

Fig. 4 Principle of CW-CRDS

Continuous-Wave Cavity Ring-Down Spectroscopy

All Tiger Optics instruments are based on CW-CRDS. The key components of the CW-CRDS system are shown in Figure 4.

CW-CRDS works by tuning laser light to a unique molecular fingerprint of the sample species. By measuring the time it takes the light to decay or "ring-down", you receive an accurate molecular count in milliseconds. The time of light decay, in essence, provides an exact, non-invasive, and rapid means to detect contaminants.

Tiger Optics Overview

Tiger Optics introduced the world's first commercial CW-CRDS analyzer in 2001. Today, our instruments monitor thousands of critical points for industrial and scientific applications. They also serve the world's national metrology institutes, where they function as transfer standards for the qualification of calibration and zero gases.

First ISO-Certified CRDS Company

Tiger Optics is the first CRDS Company certified to the ISO 9001:2008 standard of process consistency and continuous quality improvement.

CERTIFIED ISO 9001 TIGER OPTICS

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Tiger Optics
High-Performance Gas Analyzers