

Openbaar eindrapport HYPSENS

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Aan TKI Nieuw Gas
 Van Huib Blokland
 Onderwerp TKI2021-H2-02

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1. Project information

Projecttitel	Kosten-effectieve on-line sensor voor het meten van verontreinigingen in waterstof.
Acroniem	HYPSENS
Projectnummer	TKI2021-H2-02
Penvoerder	TNO
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Partners	Hobré Instruments, Hygro
Projectperiode	1 januari 2021 to 31 december 2023

Het project is uitgevoerd met subsidie van het Ministerie van Economische Zaken en Klimaat en het Ministerie van Landbouw, Natuur en Voedselkwaliteit, Nationale regelingen EZK- en LNV-subsidies, Topsector Energie uitgevoerd door Rijksdienst voor Ondernemend Nederland.

2. Introduction

Hydrogen fuel cell technology holds great promise for a more sustainable future in the transportation industry. As a clean burning gas, hydrogen does not generate the toxic emissions associated with conventional fossil fuels. Furthermore, hydrogen can be produced from a variety of renewable sources, which makes it a green option for mobility applications.

Table 1 – Allowable impurities (ISO 14687:2019)

Impurity	Threshold (μmol/mol)
Water	5,0
Oxygen	5,0
Helium	300,0
Nitrogen	100,0
Argon	10,0
Carbon Dioxide	2,0
Carbon Monoxide	0,2
Ammonia	0,1
Formic Acid	0,2
Formaldehyde	0,01
Other Hydrocarbons	2,0
Total sulfur compounds	0,004

Hydrogen must maintain an extremely high level of purity during its production, storage, and distribution so it can be effectively used as a fuel. This is the case because even small levels of contamination can damage or destroy fuel cells. As a result, a standard was established (ISO 14687:2019) that specifies the minimum quality characteristics of hydrogen fuel for vehicle and stationary applications. Summarized requirements are shown below.

The way that hydrogen is produced often determines the most likely contaminants. For example, hydrogen sulfide (H₂S) and carbon monoxide (CO) tend to be most problematic for steam methane reforming (SMR) processes, while water (H₂O), oxygen (O₂), and nitrogen (N₂) contaminants can be more frequently observed with

electrolytic systems. Currently, there are no cost effective and rapid analysis systems that can detect these contaminants. Relatively sophisticated laboratory equipment (such as gas chromatography – mass spectrometry) is available, but these tend to be too expensive (50 – 100k€) and complex for the market.

Objectives

The primary goal of the HYPSENS project is to develop cost-effective technologies to measure and analyze impurities in hydrogen gas streams. In particular, applications such as hydrogen filling stations are targeted because the storage capacity is low (and therefore, the cost-tolerance is relatively low) as well as local production sites utilizing electrolysis. An effective sensor would allow a producer to monitor the hydrogen quality and intervene immediately if contaminants are present.

Because the ISO standards for purity are extremely high, the associated detection systems must have complimentary performance, while remaining affordable and able to operate continuously. This type of equipment is needed to successfully establish hydrogen infrastructure chains through the lowering of CAPEX/OPEX, which reduces maintenance requirements and improves reliability.

To meet these demands, we investigated analysis techniques suitable for impurity detection and quantification, including rapid and inexpensive systems capable of high-pressure operation. Our goal was to achieve a technology readiness level (TRL) of 4, which would demonstrate that the concept was suitable for the target contaminants at relevant concentrations.

Consortium

Netherlands Organization for Applied Scientific Research (TNO) - Coordinator

TNO's ambition is to work with knowledge institutions, companies and the government to accelerate the energy transition so that the Netherlands has an energy system without CO₂ emissions by 2050. This also gives the Dutch business community the opportunity to take the lead and export their innovative products and thus contribute globally to the energy transition.

Within the Energy & Materials Transition unit, technology development is underway to accelerate the application of hydrogen. One of the technology areas involves measuring the composition of natural gas/hydrogen mixtures and assessing hydrogen purity. TNO has experts, lab facilities, and an external network to give shape to these developments, and, together with partners, to develop concrete products to enable the energy transition.

Hobré Instruments (Hobré)

Hobré is a manufacturer of analyzers in the energy sector and could potentially manufacture a commercial device for the hydrogen application. Hobré has collaborated with TNO previously in the field of Raman Analyzers as the result of a SBIR project, and it has the ambition to support industry as it transitions to green and efficient processes. In this project, Hobré provided input on general market requirements, facilitated test work, and considered implementation scenarios relevant to gas analysis.

HYGRO

HYGRO develops, designs, and operates projects that range from wind energy production to end user support. A characteristic of the HYGRO approach is effective integration of the different parts of the value chain. An important optimization parameter is establishing the lowest integral cost for the end user. In this project, HYGRO provided input on specific requirements based on a consideration of the entire value chain. HYGRO also identified potential points to incorporate sensor technologies, including where it concerned the control of installations/components, and they contributed to the technology roadmap.

3. Results

In this project, we investigated cost-effective technologies to measure and analyze impurities in hydrogen gas streams. The primary objectives involved selecting meaningful requirements, investigate the feasibility of optical systems, testing coatings that produced the desired sensor response characteristics, and identifying promising approaches for future development. The main results are given below.

A memo with the most critical requirements and use conditions for sensors including an overview of the optical hardware has been made, in close cooperation of HYGRO, Hobr , and TNO. As most interesting use case was chosen for measuring direct after the electrolyzer. Measuring the impurities in the hydrogen stream just after the electrolyzer allows a producer to benchmark its efficiency and track the ageing and degradation of the electrolyzer stacks. It will also facilitate quality monitoring of the hydrogen fuel after maintenance operations that involve purging the equipment with nitrogen. Another element to monitor is residual water vapor, which hastens corrosion and harms downstream equipment such as compressors. These adverse processes shortens equipment lifetime and increases maintenance costs. The main requirements for an hydrogen purity analyzer at the chosen use case:

- Main contaminants: water, oxygen and nitrogen. Nice to have: Carbon monoxide.
- Pressure up to 40 bar
- Hydrogen Flow up to 50 kg/h
- Pipe diameter 4 inch
- ATEX zone 2

Using literature reports and TNO's past experience, we identified promising materials that could preconcentrate contaminants into a thin coating. In general, coatings were made from inorganic compounds as they tend to have fewer absorbances in the mid-infrared compared with organic compounds and have better mechanical stability. At the end, we had selected compounds from a diverse range of materials including metal oxides, metal-organic frameworks, metallic complexes, zeolites, and other microporous/mesoporous materials.

Coatings were then successfully tested in the presence of nitrogen, oxygen, carbon monoxide, and water vapor and their performance was characterized with infrared spectroscopy. Carbon monoxide and water both produced significant responses using a variety of materials. Parameters such as sensitivity, response, and recovery times were identified for the most promising coatings, and various preconditioning methods were explored to minimize drift.

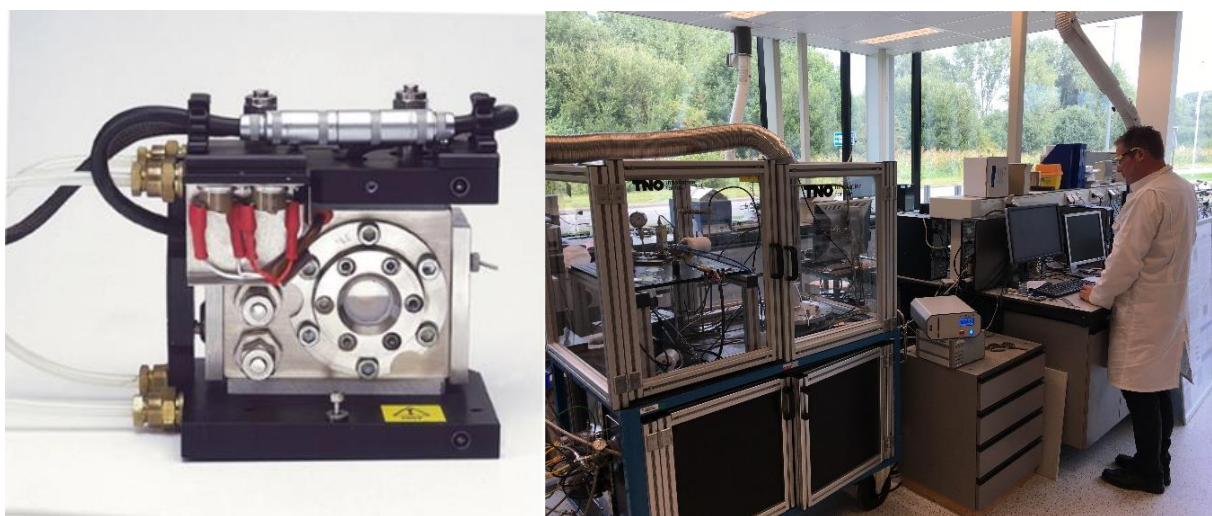


Figure 1 – Lab instrument for testing the coatings with Infrared Spectroscopy (left) and overview of lab setup (right)

Preliminary tests conducted by Hobr  using enhanced optical strategies showed significant improvements for oxygen and water vapor detection with Raman spectroscopy. Coatings developed for infrared analysis could also be incorporated into these devices to further improve sensitivity. Based on the screening results, a Raman system using either modified optics or coatings would be most suitable for future commercial implementation.

We pursued two approaches in parallel to construct a portable system utilizing infrared spectroscopy. In the first, we conducted a market survey to determine if there were commercial spectrometers and gas cells that could be directly combined into a compact demonstrator. In the second approach, we evaluated designs for a custom optical system. At the conclusion of these assessments, we determined that the combination of a commercial spectrometer and gas cell was the most suitable option for the HYPSENS project. The components identified for the custom optical system were relatively low-cost, and these types of parts would be suitable for use in a future, commercial device. Contaminants were tested at high pressure (up to 40 bar), and it was shown that detection was possible at levels relevant to ISO 14687:2019.

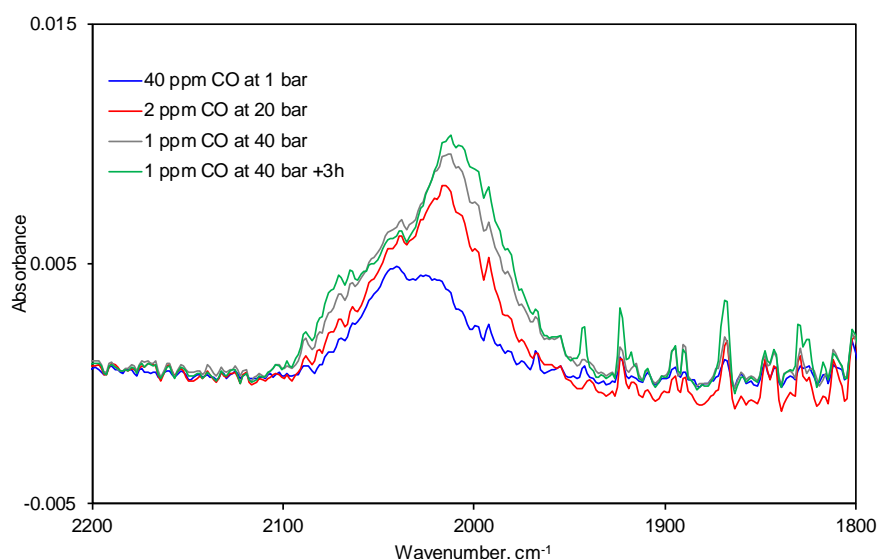


Figure 2 – IR test results for Carbon Monoxide.

Hobr  evaluated several coatings using Raman spectroscopy based on the literature survey and the infrared screening results of TNO. Materials were first tested by illuminating each sample with the Raman laser and looking for signs of fluorescence. Coatings that showed minimal levels of fluorescence were exposed to contaminant gases in hydrogen and the response was recorded. These results were then compared with the coating performance in infrared systems.

HYGRO provided an outline for typical field test conditions, and an outlook for future infrared system development was constructed based on this input. The final report contains information that summarizes the HYPSENS project results.

4. Dissemination and follow-up

Main dissemination was achieved through posters and a presentation during the TKI Nieuw Gas events in April 2022 and May 2023, and the project website of Topsector Energie [Hydrogen Purity Sensor - Topsector Energie](#).

A public report with the main achievements will be published in 2024.

Because of the need for a growing hydrogen sector, including a strong increase in mobility applications, we foresee that the HYPSENS technology development will lead to follow-up activities at both industrial level and R&D level. Hobre will proceed the development of Raman (potentially combined with coatings) for hydrogen purity monitoring. TNO will take part in the Groenvermogen WP2 project 'HyTROS', where research will be done on purity measurements of hydrogen in the gas grid.