Publishable Summary for 15NRM03 HYDROGEN
Metrology for sustainable hydrogen energy applications

Overview

In order to reduce the green-house gases effect, the EU Energy Strategy for transport and the dedicated European policy objectives encourage the wide use of hydrogen for the transport sector. The fast evolution of the hydrogen sector pushes to reconsider the international normative documents. This project is addressing the standardisation needs in the hydrogen-energy sector by supplementing and feeding four ISO standards through metrology research studies: ISO 14687-2, ISO 16111, ISO 19880-8 and ISO 21087. This metrology project provides to the standardisation bodies the guarantee of validated techniques and traceable analysis measurements at the highest accuracy levels.

Need

The use of hydrogen is a promising solution to solve the conflict between the growing need for energy, the depletion of fossil fuels, the greenhouse effect and the climate change challenge. The technical and scientific developments in hydrogen quality control, hydrogen transportation application, distribution, production and storage of hydrogen lead to reassess regulatory documents.

The European Directive on the deployment of alternative fuels infrastructure 2014/94/EU states that the hydrogen purity dispensed at hydrogen refuelling stations should comply with the technical specifications included in ISO 14687-2. The rapid progress of the fuel cell electric vehicles requires revising this standard towards less constraining detection limits and simultaneously ensuring a low impact risk of impurities on fuel cells (ISO 19880-8). A list of established analytical techniques used to measure each impurity in hydrogen according to these specifications is provided in the upcoming ISO 21087 "Hydrogen fuel – Analytical methods – Proton exchange membrane (PEM) fuel cell applications for road vehicles". It specifies also the validation protocol of analytical methods used for ensuring hydrogen quality for transportation. Thus, there is a need now to comply both with accurate analytical measurements at low levels of concentration respecting ISO 14687 specifications with validated techniques. In addition, for cost purpose, the number of required analyses has to be reduced by the use of a multi-component analyser.

The normative framework related to ISO 16111 dedicated to "Hydrogen absorbed in reversible metal hydride" is being improving by the working group 25 within ISO/TC 197 objectives by broadening the scope of the current standard to larger hydrogen volumes through traceable methods for the measurement of the amount of hydrogen absorbed in the metal hydrides. Currently, the different methods available (mass methods or flowmeters) do not provide accurate results. One objective of the project is contributing to improve this hydrogen mass measurement method.

Objectives

This project outputs aim at feeding the revisions and development of four ISO standards dealing with hydrogen characteristics used for transportation and storage.
The specific technical objectives of the project are to:

1. Develop hydrogen quality specifications for fuel cell vehicles, including tolerance levels for impurities in hydrogen and limits for the degradation of fuel cell performance as per ISO 14687-2 'Hydrogen fuel - Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles 2012'. This will include recommendations on maximum concentration of individual compounds based on the new fuel cell degradation studies and on the probability of presence.

2. Propose optimised analytical protocols (including fit-for-purpose analytical methods) and assess an analyser that enables the implementation of ISO 14687-2. The multicomponent analyser should have optimised sampling analysis and meet the required detection limits as per business plans ISO/TC 197 “Hydrogen technologies” 2005-11-07 and CEN/TC 268 “Cryogenic vessels and specific hydrogen technologies applications” 2014-04-04.
3. Develop and validate traceable methods for measuring the hydrogen mass absorbed in storage tanks (hydrides AB, AB2 and AB5), with reference to ISO 16111 “Developing transportable gas storage devices - Hydrogen absorbed in reversible metal hydride”.
4. Contribute to the standards development work of key European and International Standards Developing Organisations ensuring that the outputs of the project are aligned with their needs, communicated quickly to those developing the standards and to those who will use them, and in a form that can be incorporated into the standards at the earliest opportunity.

Progress beyond the state of the art

Development of hydrogen quality specifications for fuel cell vehicles and input proposal for ISO 14687-2 and 19880-8 standards

The current analysis techniques listed in ISO 14687-2 and now recommended in the upcoming ISO 21087 standard to measure hydrogen impurities are costly and time consuming for the actual increased end-use applications of hydrogen and the ongoing improvement of fuel cells for mobile applications. The project will draw up a risk assessment matrix of impurities taking into consideration the probability of presence of hydrogen impurities regarding the hydrogen production process through traceable measurements and their influence and impact in terms of toxicity on the lifetime of new generation of fuel cells. Outputs will be reported to standardisation working groups validating ISO 14687 and ISO 19880-8 standards dealing with hydrogen quality control at fuelling stations.

Development of optimised analytical methods for hydrogen impurity analysis

Multi-component analyzers are a promising way to reduce the number of analyses for hydrogen quality. The proper validation of these instruments is missing. External laboratories as NMIs can validate instruments using well established procedures and certified reference materials. Considering the analytical methods proposed in the upcoming ISO 21087 standard, there is a need to compare and to establish a roadmap for validation of the proposed methods. For that, performance characteristics as working range or LoD will be studied and speciation methods for multispecies families will be developed as total species determination is a real analytical challenge for metrology consideration.

Development of traceable methods for hydrogen mass measurements absorbed in metal hydrides: proposal for a revised ISO 16111 standard

There is a lack of standardised and traceable methods for the measurement of the amount of hydrogen absorbed in metal hydrides, particularly for the increasing absorption capabilities of metal hydrides. A consistent method will be developed for traceable mass measurements of hydrogen absorbed in hydride tanks.

Results

When the project started, standardization activities supported the revision of standards in hydrogen fuel applications: merging of the ISO 14687 standards family (and jointly to revise ISO 14687-2 for hydrogen specifications) and revision of ISO 16111 to widen its application. ISO 14687 standard is in advanced stage of the revision process at ISO/TC 197 (DIS stage stands for Draft International Standard is the antepenultimate step before publication) and ISO 16111 is now published since August 2018. During the timeframe of the project, the analytical methods enabling the assessment of the molar concentrations of impurities in hydrogen and previously suggested in an informative annex of ISO 14687-2 were removed during revision of ISO 14687-2 and development of ISO 14687 in order to be treated in a new standard ISO 21087 “Hydrogen fuel – Analytical methods – Proton exchange membrane (PEM) fuel cell applications for road vehicles” that is currently at DIS stage. The project aims at evaluating the performance of analytical methods, existing and under development, to perform hydrogen purity testing (number of parameters covered, uncertainties, risk for interferences, robustness…) with a high level of confidence. Additionally and during the same time, ISO 19880-8 “Gaseous Hydrogen—Fueling stations—Part 8: Fuel Quality Control” has been developed and it will specify the protocol for ensuring the quality of the gaseous hydrogen quality at fueling stations for PEM fuel cells vehicles.

The four standards are under the responsibility of ISO/TC 197 “Hydrogen Technologies” (jointly with ISO/TC 158 for ISO 21087. Besides the ongoing standardization activities supporting the development of these four ISO standards, the scientific, technical and metrological work performed in the project is highly relevant at the standardization levels. A consideration of the project’s results at standardization levels is still possible.

Development of hydrogen quality specifications for fuel cell vehicles and risk analysis of impurities to manage and limit the degradation of fuel cell performance

The probability of impurities (ammonia, Ar, CO, CO_2, formaldehyde, formic acid, H_2O, He, N_2, O_2, total halogenated compounds, total hydrocarbons compounds, total sulphur compounds) presence in hydrogen for fuel cells was investigated by process experts for steam methane reforming (SMR), PEM water electrolysis and chlor-alkali membrane electrolysis processes. All the hydrogen samples planned to be analyzed have been sampled at SMR and PEM water electrolysis plants and at an HRS for the chlor-alkali membrane electrolysis sample. The three last analyses from SMR will be performed by NMIs in following weeks after the end of the reporting period.

The assessment of impact of three impurities on PEM fuel cell performance under automotive load cycling is now completed. It was previously considered from the literature that their impact was poorly investigated especially over long term and under driving cycling conditions. Ammonia NH_3 is a potential poisoning of ionomer at a fuel cell stack and only a few data concerning low concentrations below 5 μmol/mol are available. The second one is hydrogen chloride HCl that could be absorbed on Pt and enhances its dissolution. Production of chloride ions issued from the presence of HCl is responsible for inhibiting the oxygen reduction reaction. The last one, $C_4Cl_4F_6$ is a compound that has been found in several hydrogen samples and no literature data on its impact was found. It indeed can also be adsorbed on Pt surface and partially decomposed with the formation of HCl and HF in fuel cell test conditions. NH_3 at 2 μmol/mol, HCl at 0.2 μmol/mol and $C_4Cl_4F_6$ at 0.2 μmol/mol have been prepared by NMIs partners of the project. The three impurities have irreversible impacts on the membrane after 900h test and $C_4Cl_4F_6$ degrades sustainably the anode that induces performance losses. Nevertheless, the largest part of losses is recoverable. The actual threshold for ammonia can be relaxed to 0.5 μmol/mol and the announced total halogenated compounds specification of 0.05 μmol/mol is reasonable.

A risk assessment has been proposed taking into consideration the severity level of impurity from literature and the results of the project. It has been integrated to the definition of occurrence declared in the draft ISO 19880-8 standard. Question was raised to add both severity classes in the risk assessment matrix as well as mid-specification higher than ISO thresholds with lowest severity classes. It will be noticed in the final version of risk assessment that the limit of detection of analysers do not fit for all the new ISO specifications.

Development of optimised analytical methods for hydrogen impurity analysis

While ensuring the hydrogen specifications, analytical and sampling methods are detailed in ISO 21087 standard “Hydrogen fuel – Analytical methods – Proton exchange membrane (PEM) fuel cell applications for road vehicles” currently under development. This new standard is under the responsibility of the Joint ISO/TC 158 – ISO/TC 197 working group 7 “Hydrogen fuel analytical standard”. Proposal of optimised validated analytical methods will enable a reduction in the number of required analyses for the hydrogen industry, from well to wheel. New speciation methods for sulphur, halogenated and hydrocarbon species have been developed performed and can be proposed by three NMIs, partners of the project.

The cross-checking control of the analytical methods for measuring all the 13 hydrogen impurities of the ISO 14687-2 standard with regards to the performance characteristics of the methods is completed. The performance characteristics are the working range, detection limit, selectivity, repeatability, linearity, robustness, accuracy, precision, measurement uncertainties, volume needed, pressure required, sampling vessels, other impurities analysable with the method in question, response time, the related standard(s) and the cost estimation of the instrument.

The actual analytical methods for the full implementation if the ISO 14687-2 standard was referenced thanks to contacts made with off-line analyzer manufacturers. Thus, four multi-component analyzers and their specifications have been considered: CRDS (cavity ring-down spectroscopy), FTIR (Fourier Transform InfraRed spectroscopy), OFCEAS (Optical Feedback Cavity Enhanced Absorption Spectroscopy). and BTL

(Broadly Tunable Laser) methods. The design and purpose of multi-component analyzers still need to be based on the clients´ specifications.

Information has been cross-checked after discussion with manufacturers, available data in the literature and feedback from users at laboratories. It has been pointed out the lack of a proper validation of these instruments and the importance to consider now a complete validation of the instruments by external laboratories as NMIs.

Traceable methods for hydrogen mass measurements absorbed in metal hydrides

For the determination of the best fitting system for hydrogen mass measurements, two hydride tanks have been made, filled with AB5 hydride type and AB hydride type and sent to research laboratories for testing.

Charge/discharge cycles have been performed with the metal hydride tanks AB5 received. It was highlighted that the input parameters and experimental conditions as temperature, pressure, flows considering the mass and nature of metal hydride were of prime importance for optimized charging and discharging hydrogen in metal hydride as several unexpected findings have been discovered during the measurements (e.g. over-flow on mass flow meter in case a system with non-regulating valves used, deviation of mass flow meter measurement depending on the line pressure and pressure difference). A good fitting curve on mass flow calibration error is needed to fix biases observed for mass flow meters used. It is recommended also that at lower hydrogen purity level than 4.5 (99.995%), hydrogen degrades the hydride.

Validation of the method is being performed with an AB hydride type replacing the AB5 hydride type previously installed in the tanks. The behaviour of this new hydride is similar to the AB5 hydride but it can be loaded with a higher maximal pressure. The properties differ regarding flow kinetic that is lower for AB-type and a degradation of the AB-hydride during the 20 first cycles can be expected. The measurements with the AB-type hydride have been partially completed.

Work performed in this task led to conclusions about the best-practise test facility design (use of pressure controllers, well-placed as regard to needle-valves and use of one or several flow meters).

Impact

Continuous activities have been undertaken to support the uptake and use of the project's outputs to the stakeholder hydrogen community (industrial and regulatory organisations). The consortium has given a substantial number of technical and general presentations of the project's outputs at international events.

Impact on industrial and other user communities

The industrial and user communities of hydrogen are the targeted beneficiaries of the project outputs. The uptake of the expected knowledge and methods from the project will have a direct effect on the hydrogen industrial community: producers, consumers, distributors and manufacturers of analytical gas analysers and storage tanks. Follow-on collaborations with companies or laboratories not involved in the project as Shell, ITM power, SINTEF, LINDE and CNH2 enabled the achievement of objectives in terms of impurities measurements. AP2E Company, a collaborator of the project, promoted a project output for commercial use towards prospective customers. Moreover, AP2E organized a round-table debate at the Industrial Analysis Exhibition in February 2018 with project's partners questioning the adequate gas analysis methods to control the purity of the hydrogen in order to support the market development of fuel cells. Two articles were published in professional journals in 2018 promoting the project dealing with hydrogen quality.

Industrial stakeholders as fuel cells manufacturers, gas analyser manufacturer or hydrogen producers reiterated their interest to be member of the stakeholder advisory board and to be informed of the expected outputs of the project. A wide variety of European industries are keen to attend the upcoming international workshop of the *Hydrogen* project to be held at the Air Liquide R&D Centre as gas analysers manufacturers, automotive and spatial industries, hydrogen producers or hydrogen storage and distribution companies.

Impact on the metrology and scientific communities

This project is the first metrology European project related to hydrogen within the EMPIR programme and consequently, metrology aspects are now considered in hydrogen scientific programs in Europe as in FCH-JU partnership projects or other H2020 programmes. In a wider way, metrology for hydrogen purposes for industry, standardization or other user communities becomes the guarantee for validated techniques and traceable measurements in any hydrogen topic.

Progressing works have been presented at 16 international conferences and four papers have been published to dedicated scientific journals: one paper has been published in *Measurement Science and Technology* following the International Congress of Metrology, another one was an Open Access publication in the *International Journal of Hydrogen Energy* and two papers are included in proceedings books of conferences (Iberconappice and ISFFM).

The website of the project is regularly updated at http://projects.lne.eu/jrp-hydrogen/ with news items or information regarding events or conference attendance.

Impact on relevant standards

Through the dissemination of the project outputs at the CEN and ISO level, answering cross-cutting issues through metrology studies here provides new knowledge for the improvement of standards. The exploitation of results will directly impact on the standardization works following the close interactions between partners of the project and their commitment in the working groups of ISO/TC 197. Outputs of the project impact the standardisation works in the relevant working groups of the International and European regulatory bodies. The results of the project are now including in agendas of working groups meetings at ISO/TC 197 (WG 28 for hydrogen quality control, WG 27 for hydrogen fuel quality and JWG7 for hydrogen fuel analytical methods). All deliverables of the project will consist in sending to decision makers at working groups of ISO/TC 197 informative and recommendations reports following scientific and experimental project outputs.

Longer-term economic, social and environmental impacts

As a non-toxic gas with a high mass energy density, hydrogen contributes to a reduction of green-house gas emissions. Zero-emission vehicles with hydrogen significantly reduce the pollution levels in urban areas. Therefore, hydrogen produced from renewable energy sources is the energy solution to mitigate the impacts of global climate change. With the ongoing improvement of hydrogen fuel cells for mobile applications, hydrogen is the alternative renewable energy to fossil fuels leading to a potential effect on developing countries' populations that are encouraged to support international and European standards to promote hydrogen use as an energy fuel, to participate to the H2020 programme and decrease their dependency of fossil fuels.

Moreover, achieving durable cost reduction of hydrogen technologies associated with its production, transport and utilization is a matter somehow of defining hydrogen characteristics to ensure access to a product of quality. The revision of the ISO 14687 standard family will contribute to answer to the hydrogen actors and user needs such as automotive industries, gas grids administrators or transportation and storage tanks manufacturers that now expect a specific regulatory framework. The ability to easily control hydrogen purity is an important issue not only for fuel cells manufacturers that will ensure the reliability and lifespan of their products by ISO 19880-8 application, but also for users who will have the guarantee of the performance effectiveness of fuel cells. Development of new generations of gas analyzers will allow them to be competitive in terms of sensitivity, measuring ranges and uncertainty (ISO 21087).

The demand for green technologies is growing and the increasing use of hydrogen leads the hydrogen-related technologies to be developed and improved. At the same time, hydrogen use as a safe energy has to be accepted by the public and education is continuously needed to overcome the feeling of fear that remains mainly when thinking of any hydrogen application. The safe storage of hydrogen in metal hydrides is one of the ways to change mindsets.

List of publications

- Probability of occurrence of ISO 14687-2 impurities in hydrogen: principles and examples from steam methane reforming and electrolysis (water and chlor-alkali) production processes model, T. Bacquart, A. Murugan, M. Carré, B. Gozlan, F. Auprêtre, F. Haloua, T.A. Aarhaug, *International Journal of Hydrogen Energy*, Vol. 43 (2018) pp. 11872-11883, https://doi.org/10.1016/j.ijhydene.2018.03.084

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