Publishable Summary for 19ENG03 MefHySto
Metrology for Advanced Hydrogen Storage Solutions

Overview

This European project addresses the need of large-scale energy storage, which is required for a shift to renewable energy supply. Such storage is required to supply energy at peak times when renewable sources fluctuate. A possible solution for energy storage is large-scale use of hydrogen. Metrological traceability in the energy infrastructure for hydrogen storage is crucial. Thus, improved knowledge of chemical and physical properties of hydrogen as well as traceable measurements and validated techniques are imperative.

Need

Renewable energy sources fluctuate significantly, and chemical storage of hydrogen is the most promising solution to avoid disruptive effects in energy supply. Depending on the amount, the availability to convert to energy and the required purity, three different storage types are used at present for hydrogen i) medium-sized, safe, reversible storage in solids by hydrides or adsorption in porous media, ii) Insertion in the natural gas grid, and iii) underground storage (UGS) in geological cavities. However reliable standards, reference methods and materials are required for these three storage types as:

- the risks of non-compliance for the energy meters in Power-to-Gas technology needs to be reduced by the assessment of specific thermodynamic data for hydrogen–natural gas mixtures.
- in reversible storage systems important key parameters, e.g. storage capacity or dynamics, need to be made comparable, by developing unified measurement set-ups and procedures based on appropriate reference materials.
- the metrological peculiarities of UGS are largely unknown. Dynamic effects occur during the conversion from natural gas to hydrogen, which over the years leads to drastically altered properties. The potential effects of microbial breakdown of organic materials producing Hydrogen Sulphide (H_2S), need to be addressed in order to meet the very strict requirements of application technology.

Advanced storage solutions are needed in parallel with hydrogen. Therefore, further investigation of new techniques, such as Power-to-Hydrogen, Power-to-Gas, or Gas-to-Power, is needed because of:

- the intermittent operation of a water electrolysis cell for conversion of electrical power to hydrogen induces frequent start-stop transient periods with inherent, unstable, predefined idle conditions. The quality of the hydrogen produced during periods lacking excess electrical energy in the grid is also significantly affected.
- Impurities can provoke major performance losses in fuel cells during the conversion of hydrogen back to electrical power. As such, a detailed and systematic study of compounds/impurities on the performance of fuel cells under load cycling is needed to improve their durability.

Objectives

The overall goal of this project is to provide traceable solutions for advanced hydrogen storage technologies which are required in order to achieve the ambitious new EU energy target for renewable energy by 2030, as per the Renewable Energy European Directive 2018/2001.

The specific objectives of this project are:

1. To assess the quality of hydrogen produced from proton-exchange membrane (PEM) water electrolysis during rapidly imposed transient use periods (0–100 %, 200 % peak) with online gas analysers for measuring key impurities (including water vapour and oxygen).
2. To improve the reference equations of state (EoS) used for modelling hydrogen injection up to 20 % vol. for energy metering by providing traceable density measurements with a target uncertainty of between 0.03 % to 0.5 % as the basis for accurate determination of calorific values of energy gases.

3. To investigate sustainability and reliability of fuel cells (FC), whose performance is affected by impurities in hydrogen and air, by conducting loss-of-performance tests on single-cell and short-stack FCs and to give specification and recommendations for air quality sensors needed for monitoring FC systems.
4. To provide a validated method for measuring and calculating heat conductivity of hydrogen ab/adsorbed in an intermetallic material or porous materials as a function of temperature, pressure, hydrogen absorption capacity and rate, considering dynamic heat flux impact and to develop a harmonised method (< 1 % uncertainty) for stored hydrogen.
5. To tackle metrological and thermodynamic issues in the large-scale storage of hydrogen in underground gas storages (UGS) and the conversion of existing UGS from natural gas to hydrogen.
6. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain (water electrolyser manufacturers, metal hydride tanks manufacturers), organisations engaged in developing standards, end users and energy research.

Progress beyond the state of the art

In general, electrolysis is currently well understood. However, detailed investigations on energy processes and load conditions are still lacking. This includes short-term peak energy loads of up to 200 %, which must be handled safely in order to prevent quality problems or damage to fuel cells (FC) and peripheral equipment. The project will go beyond this state of the art by investigating the quality of hydrogen produced from proton exchange membrane water electrolysis during rapidly imposed transient use periods. This will be done with online gas analysers used for measuring key impurities such as water vapour and oxygen.

In the past, several new energy gas composition standards as well as analytical procedures have been evaluated, such as pure hydrogen, coal mine methane, biomethane, or hydrogen-enriched natural gases with lower percentage ranges of hydrogen. This project will develop new metrology for the measurement of key impurities, new facilities and tests of instrument response time under transient demand, and in conditions relevant to different modes of storage. The extended measurement range, the mixed-gas matrix, and especially the transient conditions are challenges representing significant advances beyond the current state of the art.

The conversion of hydrogen back into electrical energy by a FC is considered as a potential solution to produce carbon-free energy for both stationary and mobile applications. This project will deliver valuable information on FC performance and durability under realistic operating conditions at single cell and stack levels in order to quantify the impact of contaminants in hydrogen and air (as based on existing standards). A special focus will be made on new impurities, such as $C_4Cl_4F_6$ and key-halogenated compounds, as well as on the impact of impurity combination effects (successively or simultaneously) on the FC response using a differential cell up to in-situ characterisations by current density mapping on stacks. Such coupling effects have been rarely studied so far, and this project will go beyond the state of the art in terms of single or coupled contamination threshold definition.

Research in the last few years has provided a large number of suitable materials for H_2 storage, such as metal hydrides for absorption or cryogenic adsorption at temperatures down to liquefied nitrogen, in which almost liquid H_2 storage densities are achieved. Methods for reversible storage, which make H_2 available again in its pure form, are enormously important building blocks in a circular hydrogen economy, especially for the use of FCs. This project will provide the (so far missing) unified methods and protocols for a reliable characterisation of metal hydrides and porous materials (cryo storage). The project will go beyond the current state of the art and do this for the key performance indicators for metal hydrides and porous materials, like volumetric and gravimetric storage capacity, and thermodynamics of ad/absorption and desorption.

Knowledge of the physical and chemical properties of hydrogen and hydrogen-enriched natural gas is relevant for UGS, as temperature and pressure in such circumstances cover a wide range, and several contaminants can originate from the geological reservoirs. This project will go beyond the current state of the art by developing robust analytical methods for hydrogen gas quality measurements for underground gas storage.

Results

To assess the quality of hydrogen produced from proton-exchange membrane (PEM) water electrolysis during rapidly imposed transient use periods with online gas analysers for measuring key impurities.

The project was able to work on the Cavity Ring-Down Spectroscopy (CRDS) for trace humidity and it was tested with nitrogen background gas. Tests in hydrogen on reference gas mixtures (validated against gravimetric standards and a primary standard humidity standard) are shortly to begin. Loan hygrometers from manufacturers with five different measurement principles (SAW, metal oxide dew-point probe, fibre optic, high-pressure chilled mirror, electrolytic) were received and testing commenced in December 2021. PTB has meanwhile successfully performed validation measurements with the selected laser spectrometer for rapid measurement of H_2O impurities in H_2 using the mixtures provided by NPL. A final set of measurements with a dynamic generation system is currently in progress.

Also, a system with a 4-way valve was tested using a fast-responding sensor (0.3 second sampling interval) for fast step changes in water vapour content in conjunction with a primary standard humidity generator. The response time observed, with a rising series reaching a plateau within 30 seconds are encouraging for the system to meet the intended step change interval. The software to analyse the rising and falling measured values from the test instruments and calculate response time values (e.g., t_{90}) with associated uncertainties has also been developed. Moreover, two experimental electrolyser set-ups were prepared equipped with a condenser, µGC and GC-methaniser-FID for assessing various impurities in the hydrogen produced.

In the meantime, the influence of pressure and hydrogen as background gas on the measurement error of the six hygrometer types borrowed from manufacturers was successfully carried out at the NPL in comparison with the NPL reference instrument. The software – custom written in MatLab – makes adjustments for rising and falling data and estimates response times with associated uncertainty. Two manufacturers have provided oxygen concentration analysers for testing, which is currently underway (after successful calibration of the reference oxygen analysers).

To improve the reference equations of state (EoS) used for modelling hydrogen injection up to 20 % vol. for energy metering.

In the project a reference humidity generator and reference hygrometer were set up with the purpose of validating a new spherical microwave resonator. The new spherical resonator was connected to UVa's humidity generator and the reference hygrometer borrowed from INTA. The resonance peaks have been tuned. The setup could be validated with first measurements in air.

NPL have begun to experimentally evaluate the water vapour enhancement factor in H_2 using dynamic generation of humid gas with NPL’s existing primary standard humidity generator.

In the project, a series of high-precision reference gas mixtures will be produced and investigated, with which highly accurate thermophysical measurements will be carried out in order to close gaps in the literature for hydrogen and its mixtures. Six of those reference gas cylinders were already investigated so far consisting of a well-known 11-component natural gas and 0, 10, and 20 % hydrogen. The experimental (p, ρ, T) data of the NG mixtures enriched with H_2 were precisely measured at five different isotherms from 250 K to 375 K and at pressures up to 20 MPa and the results are available as a publication to improve the GERG-2008 Equation of State. A set of three binary mixtures (propane + hydrogen) have also already been prepared with a propane content of 5, 10, and 17 %.Density measurements on these H_2—propane mixtures were performed and also published.

To investigate sustainability and reliability of fuel cells (FC), whose performance is affected by impurities in hydrogen and air and to give specification and recommendations for air quality sensors for monitoring FC systems.

So far, a first document has been produced that reviews current work on hydrogen impurities and specifies possible impurities to be tested in the project (initial definition of pollutants). This was done by building on the preparatory work of previous projects and discussing very closely with ongoing projects. Based on literature data, it has been decided to focus on low “realistic” contaminant levels to better assess the impact on PEMFC for both H_2 and Air. Indeed, synergy effects between NO_x and SO_x species has been highlighted in literature and were further studied. The list of pollutants and possible air components was updated to include NO, NO+NO2, NH3, toluene and SO2.

Fuel cell stack technology was set up and is now available for the project and first reference tests under reference “pure” H_2 as well as H_2 and Air were conducted. To reproduce all measurements, a reference single-cell hardware was defined between CEA and NPL and commercial components for MEA and a complete and identical set of single cells (25 cm²) and MEA components were sent to NPL. This was validated in a small comparison study between CEA and NPL.

The preparation of gas mixtures for fuel cell testing according to the current ISO 14687-2 and the development of analytical methods for VOC compounds analysis in air and sorbents qualification is complete. The mixtures are currently being validated internally.

The fouling/defouling mechanisms and experimental protocols for H_2 fouling will be tested at the NPL in H_2 pumping mode. Performance and durability tests were performed under reference H_2 (4.5 and 6.0 quality) consisting of 500 hours of FC-DLC cycling. Characterisations of the cell were performed every 100 hours to monitor the various degradations of the components. Performance and durability tests were also conducted with both technical (compressed in CEA) and synthetic air (79 % N_2 6.0 + 21 % O_2 5.8), consisting of 500 hours of FC-DLC cycles (cell characterisation every 100 hours). This allows first preliminary specifications for air quality sensors (ambient pollutants and their respective values) to be evaluated.

CEA, with the support of NPL and UDC, has further concretised the CEA demonstration platform H_2 "SENEPY" based on the current experience in this work package. UDC has already started evaluating online analytics to measure pollutants in both the output stream of the PEM electrolyser and the H_2 supply stream of the PEM FC.

To provide a validated method for measuring and calculating heat conductivity of hydrogen ab/adsorbed in an intermetallic material or porous materials for stored hydrogen.

After the start of the project a technology survey on metal hydride storage has been done based on a survey sent to about forty professionals linked to metal hydride research. Also, a technology survey on materials as adsorbents at cryogenic temperatures was performed with similar success. Based on these surveys and expert knowledge, a report on the similarities between used technology for measurements of hydrogen uptakes and thermal conductivity and capacity in metal hydrides and cryo-adsorbents was filed. For both kinds of materials, the hydrogen uptake is measured as pressure-composition-temperature (PCT) curves by either volumetric or gravimetric analysers. The heat of adsorption is calculated from PCT curves at different temperatures. The thermal conductivities are measured by the transient hot wire method. It was planned that MAHYTEC, FHA, BAM and MPG would review the commonalities in measuring the thermal conductivity and dynamic behaviour of metal hydrides and cryoadsorption materials. Since the two technologies run under very different system conditions, the originally planned derivation of a universal method no longer makes sense. It is planned to define the best system conditions for each of the two methods.

Several samples from the same metal hydride blocks were tested by MAHYTEC cyclically and with PCT with 50 cycles per pollutant. PCT measurements were also performed by BAM with the reference material to check the cumulative effect of the pollutants (most blatantly N_2, here tested at 500 ppm) on the adsorption capacity after several adsorption-desorption steps. This is negligible and below the detection limit of the method. The hydrogen uptake of the reference material was also measured before and after the cycle experiment under the same conditions, confirming both the reproducibility of the uptake and the stability of the material during the cycle experiment.

Also reference materials were selected for the planned interlaboratory comparisons. An AB5 alloy metal hydride was selected for the metal hydride storage comparison while a cryoadsorbent (ZIF-8) was selected for the cryogenic storage comparison and already produced in gram scale. Reference material (2 g each) were sent to 10 participants in the round-robin characterisation. Some participants have already sent back the results. All results should be available for evaluation by the end of March.

To tackle metrological and thermodynamic issues in the large-scale storage of hydrogen in underground gas storages (UGS) and the conversion of existing UGS from natural gas to hydrogen.

The course of the changeover of UGS from natural gas to hydrogen varies depending on the type of the underground storage (UGS). In caverns a changeover to high H_2-contents can be achieved quickly, while pore storage tanks must be converted over long periods of time. The analytical requirements are correspondingly different. This information has been compiled through expert statement by underground storage operators.

A significant number of new UGS is currently not expected. Public funds (project funding) are currently being raised for the conversion of caverns to hydrogen. In addition, investigations and evaluations of the material are currently being carried out at various storage facilities in order to determine the possibilities and costs of a conversion. H_2 admixtures to natural gas, but also pure H_2 caverns are considered. The bottleneck seems to be the availability of large volumes of hydrogen. The analytical requirements along with four different hydrogen qualities, which are currently discussed were compiled through expert discussions with underground storage operators and are at hand as early impact results.

The water content of H_2 as a function of pressure and temperature was calculated for the relevant storage conditions between 40–140 bar and at 25, 50 57 and 100 °C by DBI. A document defining the target components for hydrogen storage and the detection limits were also updated. For the components THC (total hydrocarbons) and ammonia, a GC-BID and a GC-MS incl. enrichment were successfully procured and validated. The limits of determination were 2 µmol/mol THC, 1 µmol/mol H_2, CH_4, and CO. The measurements of NH_3 resulted in 0.1 µmol/mol.

Based on information from the project and the project stakeholders the ultrasonic flow measurement principle was identified as the most used principle for UGSs also for the future perspective of NG+H_2 mixtures. Flow stratification of NG and H_2 and inhomogeneities in the mixtures of the two gases where the speed of sound in H_2 is more than triple of that of NG was identified as one of the challenges which can be addressed by means of CFD modelling. The model development of a CFD model consisted of two steps: a) preparation of all software requirements for performing the planned simulations, b) definition of the model parameters such as pipe geometry, flow rate, pressure, temperature, fluid viscosity, etc.

For the flow modelling part a), CMI uses the OpenFOAM software with the built-in solver two LiquidMixingFoam, which is suitable for solving two-component mixtures. For the liquid properties part, CMI has acquired NIST's REFPROP software to calculate the properties of gas mixtures. This provides the necessary inputs for the H_2-NG mixtures such as viscosity, density and sound velocity for different temperatures and pressures. Regarding b), a straight pipe geometry with different inlet conditions is modelled. The interest is on the possible flow stratification and inhomogeneity of H_2-NG mixtures and their effects on the ultrasonic flow measurement of the mixtures. Typical flow rates, temperatures and pressures were obtained from a UGS owner (RAG Austria AG). The CFD simulations are currently underway. The changing parameters of the medium corresponding to the changing H_2-NG ratios (20/80, 50/50, 80/20) are considered.

Impact

The project has promoted the work done through the establishment and update of the project web page http://www.mefhysto.eu. The project has also presented their objectives and work plan in four international and national conferences and in 19 other dissemination activities such as The Hannover Fair and The European Green Week event (Hydrogen Handling and Metrology Day of the "Gat | Wat 2021" online fair and conference). Currently three peer reviewed papers have been published in C Journal of Carbon Research, International Journal of Hydrogen Energy and ACS Applied Energy Materials.

Impact on industrial and other user communities

The gas industry and energy storage operators require reliable measurements of quantities, quality and energy content at the transfer points/hubs in the energy network. The project will allow operators of gas networks and gas storage facilities to select suitable measurement technologies for the traceability of national standards.

The project's results will be used directly by stakeholders involved in the hydrogen cycle, in particular gas and energy customers, developers of analytical equipment, software (e.g., Gas Chromatography (GC) and laser spectroscopy), and providers of analytical service (simple handling of new operating procedures, simplification and standardisation of procedures, conversion to hydrogen technology). The benefits of consolidated physical properties for hydrogen can be exploited, for example, to improve flow measurement and to increase the performance of gas networks.

Accurate measurement of hydrogen purity has economic implications for its downstream use, as significantly higher purity levels are required for FC use than for combustion. The project will provide accurate measurement of impurities, which will feed into business models used by the gas networks, and as a result will support accurate distribution, storage and purification of hydrogen at various points in the energy network.

Hydrogen purity standards currently require monitoring of many trace contaminants at very small concentrations. To cope with this today, investments between 400 k€ and one million € are necessary, whereby the measurement uncertainties are still unsatisfactory. MefHySto – together with the other EMPIR initiatives – is promoting risk-based measurements that meet the requirements and is in dialogue with the analytical manufacturers.

Impact on the metrology and scientific communities

The project will impact the current methods and standards, such as ISO 14687 (Grade A), EN 16723-1 or ISO/TR 27921. Work instructions developed in the project will be used as input for standards used by specialty gas manufacturers and analytical laboratories working according ISO 17025 and 17034 (RM production).

Outputs from the project will provide insight into hydrogen adsorption measurements and can be used by research groups for comparison with reference materials for research into new technologies and materials. In addition, this project will bring together expertise and facilities from a range of technical areas to establish critical mass in Hydrogen research, which is a key area of European metrology. In September 2021 the Fuel Cells and Hydrogen 2 Joint Undertaking and European Union's Horizon 2020 HYDRAITE project (Hydrogen Delivery Risk Assessment and Impurity Tolerance Evaluation) was successfully completed, which was linked to the present project through CEA and NPL experts.

Energy gases are strategically positioned very high within BIPM's Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM). The current document states: "Energy: diversification in the supply of energy gases (...); emerging hydrogen economy (e.g., measurements of impurities in hydrogen); (...); injection of non-conventional gases into existing gas grids". The project, through its NMI/DI partners, will provide valuable input to CCQM.

Impact on relevant standards

The project will improve methods on measuring hydrogen physico-chemical properties for energy gases with varying hydrogen content. The work will improve current analytical methods for gas composition and purity analysis in a number of standards committees including ISO/TC 197 Hydrogen technologies WG27 Hydrogen fuel quality and WG28 Hydrogen quality control, IEC/TC 105 Fuel cell technologies, ISO/TC 158 Analysis of gases JWG7 (Joint ISO/TC 158 - ISO/TC 197 WG: Hydrogen fuel analytical methods), ISO/TC 197 Hydrogen technologies, CEN/TC 234 Gas infrastructure, CEN/CENELEC/JTC 6 Hydrogen in energy systems, ISO/TC 158 Analysis of Gases, ISO/TC 193 Natural gas, CEN/CENELEC Sector Forum Energy Management/WG Hydrogen, CEN/TC 268 Cryogenic vessels and specific hydrogen technologies applications WG5 Specific hydrogen technologies applications, EURAMET Technical Committee for Thermometry (TC-T), and Technical Committee of Metrology in Chemistry (TC-MC) and BIPM CCQM and Consultative Committee for Thermometry (CCT). Our experts are continuously contributing the results to the above-mentioned committees and have planned contributions for the upcoming meetings.

Longer-term economic, social and environmental impacts

As a result of the project, there will be a consolidated and robust method of measuring trace components in hydrogen which will enable the safe operation of mobile and stationary FCs. This will support sustainable and efficient mobility and power supply and help to improve models for purification of hydrogen at various points in the gas network.

The storage of hydrogen enables the storage of volatile renewable energies (wind, sun) on an industrial scale. The project's improved knowledge of thermodynamic issues and the provision of a reliable measurement technique for storage will also help to overcome existing reservations in implementing a new technique.

In general, the project will support a more sustainable economy and a reduction in the use of fossil energy resources. The establishment of metrology for hydrogen storage by the project will help to provide greater confidence for national and EU funding bodies, industry and private investors to roll out the infrastructure required to deliver the transition to large-scale use of hydrogen as an energy vector.

Our experts are also involved in introducing open research questions into new Proposed Research Topics and have been able to contribute successfully to some of the current calls. It is evident that the energy industry continues to be a lively research and development landscape due to its high economic importance and the necessary climate activities.

List of publications

1. Villajos, J. A. Experimental Volumetric Hydrogen Uptake Determination at 77 K of Commercially Available Metal-Organic Framework Materials. C 2022, **8**, *5*. https://doi.org/10.3390/c8010005
2. Lozano-Martín, D., et al., Thermodynamic characterisation of the (H2 + C3H8) system significant for the hydrogen economy: Experimental (p, r, T) determination and equation-of-state modelling, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2022.11.170
3. Balderas-Xicohtencatl R., et al., ZIF-8 Pellets as a Robust Material for Hydrogen Cryo-Adsorption Tanks. ACS Applied Energy Materials. https://doi.org/10.1021/acsaem.2c03719

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	01 September 2020, 36 Months	
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Internal Funded Partners: 1. BAM, Germany 2. CMI, Czech Republic 3. NPL, United Kingdom 4. PTB, Germany	External Funded Partners: 5. CEA, France 6. DBI, Germany 7. DVGW, Germany 8. ERIG, Belgium 9. FHA, Spain 10. MAHYTEC, France 11. MPG, Germany 12. Reganosa, Spain 13. UDC, Spain 14. UVa, Spain	Unfunded Partners: –
RMG: -		