Refuelling of fuel cell vehicles by hydrogen from the LOHC process

by Alexander Seidel

Hydrogen plays a major role in achieving the energy revolution and a zero-emission policy especially in the mobility sector. The LOHC (liquid organic hydrogen carrier) concept is a capable technology for supplying hydrogen refuelling stations due to its high hydrogen storage densities (57 kg\(_{\text{H}_2}\) m\(^3\text{LOHC}\)) and easy handling (liquid, low toxicity, low flammability). ISO and SAE standards strictly regulate hydrogen qualities. The suitability of hydrogen from the LOHC process for fuel cells, was proven by Hydrogenious Technologies in intensive field-tests with a fuel cell system in application as well as analytically with the H\(_2\)-Quality module.

1. HYDROGEN IN THE MOBILITY SECTOR – THE ENERGY SOURCE OF THE FUTURE

In view of the climate goals of 2050 and the reduction of CO\(_2\)-equivalent emissions by 80 % by 2030 many experts predict that hydrogen will be one of the most important future sources of energy. In the mobility sector, in particular, hydrogen will play a key role in achieving the reduction goals. The hydrogen infrastructure in Europe is growing rapidly. According to H\(_2\)Mobility, 44 hydrogen refuelling stations are already in operation in Germany and 48 additional stations are currently under space between construction and [1]. Germany thus has the second largest hydrogen fueling station network in the world after Japan.

The refueling of fuel cell vehicles (FCEV) at the hydrogen refueling stations largely standardized by the ISO and SAE standards. Parameters have been set which allow refueling of light-duty fuel cell vehicles within 3-5 minutes. In addition to the refueling process itself, the hydrogen quality is also defined in order to prevent damage to the fuel cells.

However, neither the hydrogen source nor the hydrogen supply of the refueling stations are being regulated. Consequently, not only the gas suppliers and manufacturers but also the technologies themselves compete for supplying hydrogen refueling stations. While small scale hydrogen refueling stations are typically supplied by pressurized hydrogen (CGH), larger stations are often supplied by liquid hydrogen (LH) or on-site production via steam reforming or electrolysis. The delivery of liquid organic hydrogen carriers (LOHC), in which hydrogen is stored, represents a viable alternative. Liquid organic hydrogen carriers can store up to 630 Nm\(^3\) hydrogen per m\(^3\) LOHC (equivalent to ~ 1 t). Being stored this way, hydrogen is easy to handle. Hydrogenious Technologies has developed the LOHC technology using the carrier material Dibenzyltoluene (market name: Marlotherm\(^\text{®}\) SH). It is hardly toxic, non-explosive, flame-retardant and not classified as dangerous goods. Furthermore Dibenzyltoluene can be transported in the existing fuel infrastructure as well as stored for long periods of time under ambient conditions without losses. In order to use the stored hydrogen, the liquid organic hydrogen carrier is dehydrogenated in a catalytic reaction.

2. THE LOHC-TECHNOLOGY

The LOHC technology is based on the chemical bonding of hydrogen to liquid organic carriers, which are mostly aromatic hydrocarbons or heterocyclic substances. The loading takes place via an exothermic hydrogenation reaction, the discharge via an endothermic dehydrogenation. In contrast to some other chemical hydrogen storage processes, these reactions are reversible. The carrier molecule is cycled between a loaded and unloaded state. The worldwide research and development work in
the field of LOHC is based on different LOHC substances. The most technically advanced concept, which is pursued by Hydrogenious Technologies, is based on the use of the common heat transfer oil dibenzyltoluene, which is available in large quantities and is not classified as a dangerous good. As shown in Figure 1, hydrogen chemically bound to the molecule by saturation of the aromatic rings in the hydrogenation.

Compared to other technologies that store hydrogen at temperatures of -253 °C or at pressures up to 500 bar, using LOHC technology greatly reduces the cost of handling hydrogen. Transport and storage costs account for up to 70% of the total cost of hydrogen supply using traditional high pressure or cryogenic hydrogen storage technologies. Storing hydrogen in LOHC can increase transport capacities by a factor of five, which reduces transport costs by up to 80%. An overview of the storage densities of common hydrogen storage technologies is shown in Figure 2.

Future operation of central LOHC hydrogenation plants are possible at locations where a large amount of by-product hydrogen is produced. The hydrogen-rich or loaded LOHC (LOHC+) can be transported via standard tank trucks to the hydrogen refueling stations, which are equipped with a dehydrogenation system (Release-BOX). There, the hydrogen can be produced as needed and then integrated into the existing hydrogen refueling station technology. The German Climate Action Plan of 2050 acknowledges that LOHC technology has considerable potential for establishing hydrogen as a fuel [2].

3. HYDROGEN FOR FUEL CELL VEHICLES

The purity of the hydrogen at hydrogen refueling stations is specified by the international standard ISO-14687-2. In the year 2004 this new standard was elaborated by the committee 197 and was valid for fuel cells vehicles as well as for vehicles with a combustion engine. This is why in particular CO and sulfur limits were insufficient for FCEVs. The limits were selected very strictly as the major priority was given to the optimization of the lifetime of fuel cells. They were based on an initial list of permissible contaminants, which was created by the Canadian Fuel Cell Partnership in 2003. The work of the Technical Committee 197 finally resulted in 2008 in a technical standard and ended in 2012 in the international standard ISO-14687-2. At a national level, SAE developed the SAE J2719 standard in the USA, which is harmonized most widely with the standard ISO-14687-2. At present, this standard is under revision due to its conservative approach. New research results will be taken into account (for example, that of the DoE (U.S. Department of Energy)) [3]. These research results include for instance explicit degeneration effects

![Figure 1: Concept of the LOHC-cycle for the storage and release of hydrogen](image1)

![Figure 2: Hydrogen densities as a function of pressure and temperature. Marking common areas for common hydrogen storage technologies (LOHC – green, compressed small ‘gaseous’ hydrogen (CGH2) – red, liquid hydrogen (LH2) – blue, compressed cryogenic hydrogen (CcH2) - violett)](image2)

<table>
<thead>
<tr>
<th>Contamination</th>
<th>chem. formular</th>
<th>Maximum concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H2O</td>
<td>5 ppmV</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>C2H6 (CH2-Basis)</td>
<td>2 ppmV</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O2</td>
<td>5 ppmV</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>300 ppmV</td>
</tr>
<tr>
<td>Nitrogen / Argon</td>
<td>N2 /Ar</td>
<td>100 ppmV</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO2</td>
<td>2 ppmV</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>0.2 ppmV</td>
</tr>
<tr>
<td>Sulphurous substances</td>
<td>H2S, COS, CS2, etc.</td>
<td>0.004 ppmV</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>0.01 ppmV</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCOOH</td>
<td>0.2 ppmV</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH3</td>
<td>0.1 ppmV</td>
</tr>
<tr>
<td>Halogenated substances</td>
<td>HCl, HBr, Cl2, etc.</td>
<td>0.05 ppmV</td>
</tr>
<tr>
<td>Particles</td>
<td>–</td>
<td>1 ppmW</td>
</tr>
<tr>
<td>Total Contamination</td>
<td></td>
<td>300 ppmV</td>
</tr>
<tr>
<td>Required H2-purity</td>
<td></td>
<td>99.97 %</td>
</tr>
<tr>
<td>Purity</td>
<td></td>
<td>3.7</td>
</tr>
</tbody>
</table>
of individual impurities or the economic consequences of ultra-high purification.

Regardless of some likely changes of the permitted limits in the near future, the results shown below demonstrate that even today, hydrogen from LOHC dehydrogenation is suitable for the operation of PEM fuel cells. The example of some of the main components demonstrates that the strict limits of ISO-14687-2 are kept.

4. ANALYSIS FOR DETERMINING THE QUALITY OF HYDROGEN

In addition to the actual compliance with the limits set by ISO and SAE for contaminations in hydrogen for use in fuel cell vehicles, even the analysis of these impurities is an extraordinary challenge. The analysis of individual substances requires a variety of different measurement principles. The ASTM (American Society for Testing and Material) has already proposed and standardized methods for analyzing a majority of the substances. Nonetheless, a holistic determination of all impurities is complex. Furthermore, samplings of hydrogen show considerable sources of error.

This is the reason why the National Innovation Program Hydrogen and Fuel Cell Technology funded the Hy-Lab project since 2017 for 2.5 years with € 3.08 million. In the Hy-Lab project, the institutes ZBT (Zentrum für Brennstoffzellentechnik Duisburg) and ZSW (Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg) have committed themselves to the development of an independent laboratory for hydrogen quality measurement according to international standards. The project will be carried out in close cooperation with NOW (Nationale Organisation Wasserstoff- und Brennstoffzellenforschung). This funded project alone shows the importance of a qualified analysis.

Even if there are opportunities in the future for hydrogen to be completely analysed according to ISO in independent laboratories, quality assurance is required within the LOHC process. In order to rule out possible risks of contamination through sampling, Hydrogenious Technologies has established an In-Line-Analysis tailored to the expected impurities. With the H₂-Quality-Module it is possible to quantify the most important impurities from the LOHC process. The H₂-Quality-Module can be coupled as a mobile unit to any existing hydrogen release

![Figure 3: Process Flow Diagram of the H₂-Quality-Module from Hydrogenious Technologies with FTIR, NIR, PID and dew point sensor](image-url)

![Figure 4: FTIR spectrum of the LOHC product hydrogen with the labeled specific bands for detection of the impurities](image-url)
unit to measure contaminants in the hydrogen stream. Figure 3 shows a process flow diagram of the H₂-Quality-Module. The analysis techniques used are briefly presented below.

4.1 Photo-Ionization Detector (PID)

Photo-Ionization detectors are often used as field meters for TOC (Total Organic Carbon) measurement. In the PID sensor typically UV lamps are used, which excite and ionize the gas sample in a sample chamber. The released electrons flow in the process via a collecting electrode. The result is a measurable current that corresponds to a concentration.

The sensor Hydrogenious Technologies uses is a krypton lamp with an ionization energy of 10.6 eV. Molecules with a higher ionization energy are not detected. These include the main air components as well as methane, which has an ionization energy of 13.3 eV. Methane can be proven with other measuring principles (see below).

The detection limit of the PID sensor is 1 ppb. The photoionization detector is excellently suited to quantify the totality of hydrocarbons in the gas, with the exception of methane. However, the composition of the hydrocarbons should be as constant as possible, since the response factors of the individual substances may differ from one another.

4.2 Impedance Dew Point Sensor

To determine the moisture in gases, so-called dew point sensors are often used. Most of them are designed as a mirror dew point sensor. Disadvantage of this measuring principle is the cross sensitivity to all other condensable substances. For this reason, a ceramic impedance dew point sensor is used.

The sensor is based on the measurement of a resistance between two DC electrodes. A hygroscopic but non-conductive layer separates these two electrodes. By adsorption of water, the resistance of the ceramic layer changes, which is translated into a water concentration in the gas. The advantage of this sensor is that it is almost insensitive to other substances and reacts quickly. The moisture sensor used by Hydrogenious has a measuring range of 0.01 - 23,000 ppmV.

4.3 Near-Infrared-Spectroscopy (N-IR)

The Near-Infrared-Spectroscopy is based on the principle of vibrational spectroscopy in which the normal vibrations of the molecules are excited by electromagnetic radiation in the wavenumber range between 4,000 and 13,000 cm⁻¹. By this method, CO, CO₂ and CH₄ can be detected from 0 to 1000 ppmV, at a resolution of 1 ppmV.

4.4 Fourier Transform Spectrometer (FTIR)

A versatile measuring principle for the quality control of hydrogen for fuel cells is the FTIR spectrometry. For many substances that are limited in hydrogen according to ISO-14687-2, ASTM has already standardized FTIR-based test methods.

The operation of the FTIR is based on the Fourier transformation of a recorded interferogram. The interferogram is generated by interferences of a splitted HeNe laser beam, which passed through the sample. The first part of the laser passes a solid mirror and the examined sample to the detector. The other part of the beam is reflected on a moving mirror and then passes the sample. Each wavelength of the radiation spectrum interferes individually, resulting in a characteristic interferogram. From these, Fourier transformation can be used to calculate the spectrum over the entire wavelength range. Since the various components in a gas mixture at different wavelengths absorb radiation, the substances can be clearly assigned.

Hydrogenious Technologies uses a spectrometer equipped with a 5 m gas cell for extra precise measurements. By using the PNNL (Pacific Northwest National Laboratory) library, it is also possible to measure all substances contained in the PNNL without additional calibration. Due to the high number of reference spectra, it is also possible to fit overlays of individual components and thus increase the accuracy. Table 2 lists the detection

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limits ISO FDIS 14687-2 (ppmV)</th>
<th>Detection limit FTIR (ppmV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>CO</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.01</td>
<td>0.08</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>0.20</td>
<td>0.03</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>2.00</td>
<td>0.1 - 1 depending on single compounds</td>
</tr>
<tr>
<td>Methane</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td>Water</td>
<td>5.00</td>
<td>0.22</td>
</tr>
<tr>
<td>Hologenated compounds</td>
<td>0.05</td>
<td>Different, depending on single compounds</td>
</tr>
</tbody>
</table>
limits of selected substances and the maximum allowed concentration of these according to ISO 14687-2.

5. HYDROGEN FROM LOHC DEHYDROGENATION

Crucial for the suitability of the LOHC concept for the supply of filling stations is the hydrogen quality. Whereas in other storage technologies the question of hydrogen quality is usually addressed at the hydrogen source location, in the case of storage in LOHC it becomes relevant at the site of the application. For example, hydrogen produced by steam methane reforming is purified directly at the site of production. Hydrogenious Technologies uses control methods to determine if and to what extent hydrogen needs to be purified from the LOHC process. For this purpose, raw gas, which leaves the dehydrogenation reactor without further purification steps, was examined. On this basis, further process stages are designed to obtain hydrogen in fuel cell quality.

5.1 Composition of the crude gas exiting the dehydrogenation reactor

Because the release of hydrogen from LOHC occurs in a catalyzed chemical reaction at elevated temperature, issues such as selectivity, phase equilibria, and solubility play a key role in hydrogen quality. Since the LOHC is a liquid hydrocarbon, the study mainly focuses on the evaporation of the carrier molecule in the gas phase and their possible chemical conversion into by-products. The influence of impurities in the air as well as those from the technical LOHC production was also investigated. For these reasons, one focused explicitly on TOCs, CO, CO₂ and H₂O for the investigation of gas purity.

The experiments were carried out in a continuous laboratory dehydrogenation reactor, to which the above-described H₂-Quality-module for measuring the quality of hydrogen was connected. The laboratory dehydrogenation unit consists of a heated tube filled with catalyst. After a phase separation of LOHC and hydrogen, only passive cooling to about room temperature takes place. No further purification steps are switched between reactor and H₂-Quality-module. Figure 4 shows an example of the FTIR analysis.

The reaction parameters such as pressure, temperature and residence time of the LOHC in the reactor have to be adjusted correctly in order to achieve an optimum raw gas quality. This is in close interaction with the choice of the dehydrogenation catalyst.

The following considerations initially relate to a LOHC material, which has been previously hydrogenated but has not yet undergone further cycles of dehydrogenation and hydrogenation. As will be seen later, the purity of the released hydrogen improves significantly at higher cycle numbers. This is an indication that the impurities initially found to a considerable extent do not originate from the reaction, but were already solved in the LOHC from the beginning.

Most of the impurities in the hydrogen are hydrocarbon compounds. Since the dehydrogenation takes place at about 300 °C, it can be assumed that the hydrogen at the end of the reactor is saturated with those hydrocarbons, which pass into the gas phase at these temperatures. By cooling the gas stream, this amount is indeed significantly reduced, nevertheless traces remain in the hydrogen. The determined concentration is at a single dehydro-
H2 generation of the loaded LOHCs at about 400 ppmV. Hydrocarbons ultimately act very differently on fuel cells, for example, methane behaves inertly on the anode side, but reduces the stack performance through steady accumulation. On the other hand, aromatics adsorb on the anode side and block the adsorption sites for hydrogen.

In addition to the TOCs, which are mainly found due to evaporation of the LOHC carrier material, water was measured with proportions up to 300 ppmV. Water is soluble in small amounts in LOHC, Aslam et al. [5] found a solubility of 1000 ppm in the hydrogenated LOHC and 9000 ppm in the dehydrogenated LOHC. During long-term storage, the carrier material saturates by air humidity. The dissolved water can ultimately be recovered in hydrogen. A suitable storage and tank concept can minimize this influence. Water behaves inertly in the fuel cell, but the concentrations must be kept low to avoid the formation of ice in the fuel cell system.

Carbon dioxide is largely inert in the fuel cell. CO2 lowers the hydrogen concentration on the anode side just like CH4. After dehydrogenation of LOHC+, a maximum of 5 ppm of CO2 was detected in the hydrogen. Similar to water, carbon dioxide comes mainly from ambient air. It is still unclear whether CO2 forms small amounts of CO in the fuel cell by reverse water gas shift reaction.

Carbon monoxide, unlike CO2, has been shown to be harmful to fuel cells. Carbon monoxide strongly adsorbs to the platinum-based catalytic materials and blocks these hydrogen adsorption sites needed for dissociation. CO was measured only in “virgin” LOHC with a low number of cycles in small amounts in LOHC-hydrogen. The measured carbon monoxide content increased significantly as a function of increasing LOHC feed flow in the reactor, which is shown in Figure 5. This indicates that carbon monoxide originates from the LOHC and does not come from the reaction itself. With a measured maximum of 3.1 ppmV CO for LOHC material which is dehydrogenated for the first time, this value significantly exceeds the limit of 0.2 ppmV by ISO 14687-2.

Formic acid, ammonia formaldehyde and hydrogen sulfide were never detected in the experiments.

Experiments with recycled material have demonstrated the influence of dissolved impurities in LOHC on hydrogen quality. In a closed autoclave, LOHC was hydrogenated and dehydrated in a semi-batch mode for several cycles. The carrier medium at no time had contact with the air atmosphere. During each test, the gas quality was measured. Figure 6 shows the strongly decreasing course of the TOCs in the gas stream over the number of cycles. The proportion of TOCs decreases by more than 60% within 15 cycles, with a reduction of 50% already after the first 4 cycles. The 15-fold recycled material was then fed directly, without storage, to a continuous dehydrogenation as described above. In this experiment, even a reduction of hydrocarbons in the product gas by 72.5%, compared to the reference experiment, was found.

The contamination with carbon monoxide, which is harmful to fuel cells, was reduced completely by 100%. The amount in the gas stream was reduced from 3.1 ppmV to 0.0 ppmV after recycling the material. Thus, a degradation of the catalytic fuel cell membrane by CO in LOHC hydrogen is excluded after only a few cycles.

These experiments support the thesis that most of the contaminants in LOHC-hydrogen come from dissolved substances in the carrier medium. The continuous cycle of hydrogenation and dehydrogenation significantly increases the quality of the raw gas. In combination with a storage and tank concept with moisture and air exclusion, the quality can be increased even further. Since crude hydrogen does not meet the ISO standard...
5.2 Pure LOHC hydrogen in fuel cell quality

To operate fuel cells, the remaining impurities have to be removed from the raw gas. In addition to state-of-the-art techniques such as simple activated carbon filtration or pressure swing adsorption, as used in steam reforming, new concepts such as membrane filtration using the palladium membrane are also being investigated at Hydrogenious Technologies. However, as shown below, hydrogen can already be produced in fuel cell quality with simple activated carbon filtration.

The ReleaseBox HD101 (Figure 7) is Hydrogenious Technologies first demonstration plant on an industrial scale. The system delivers up to 3 kg H₂ h⁻¹ and is integrated into the Smart Grid of the Fraunhofer IOA in Stuttgart. A PEM fuel cell with a nominal power of 25 kWₐₑ produces electricity from the hydrogen stored with LOHC.

To separate the impurities contained in the raw gas, a dry-adsorber-bed is used. A combination of activated carbon and metal oxide adsorber materials separates hydrogen from hydrocarbons, as well as CO and CO₂, to achieve fuel cell quality. After the adsorber bed, 0.1 ppm of hydrocarbons in the hydrogen stream were measured with the PID detector. In addition, no more CO could be detected in the exhaust by means of FTIR. Thus, the gas flow reaches fuel cell quality, as it is required at hydrogen refueling stations. The cleaning according to the adsorption principle is suitable to eliminate hydrocarbons and carbon monoxide almost completely.

Figure 8 shows the operation of the fuel cell of the ReleaseBox HD101 at the Fraunhofer IOA in Stuttgart. Both, a stationary operation at the first operating point and a dynamic load change operation of the fuel cell can be easily operated without loss of performance of the fuel cell.

Hydrogenious Technologies will pursue further work on the evaluation of various purification concepts as well as the establishment of additional analytics at in order to prove the quality requirements of ISO-14687-2 in more detail in the future.

6. CONCLUSION

Due to its good transportability and easy handling, LOHC is ideally suited as a hydrogen mass storage system at hydrogen refueling stations. With LOHC, 57 kg of hydrogen per m³ of LOHC can be stored. Since the release of hydrogen requires a chemically catalytic reaction, the question of hydrogen purity is particularly important. The limit values specified in ISO 14687-2 are already achieved for the main components with simple purification steps. The so-called crude H₂ that is obtained directly after the reactor without further purification contains mainly hydrocarbon impurities. If LOHC undergoes the hydrogenation and dehydrogenation cycle several times, as is the case in the life cycle of the LOHC anyway, these contaminants can be reduced to about 110 ppmV. The traces of CO that vanish after only a few cycles anyway, as well as the remaining hydrocarbons in the crude gas, can be filtered out by means of adsorption in simple activated carbon filters or in pressure swing adsorption plants. Thus, the LOHC technology, with its advantages of high storage density and easy handling, delivers hydrogen for fuel cells reliably.

THANKS

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