Analysis of the Purity of Hydrogen at Public Hydrogen Refuelling Stations in Germany

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18th August 2021

World Fuel Cell Conference 2021

DLR

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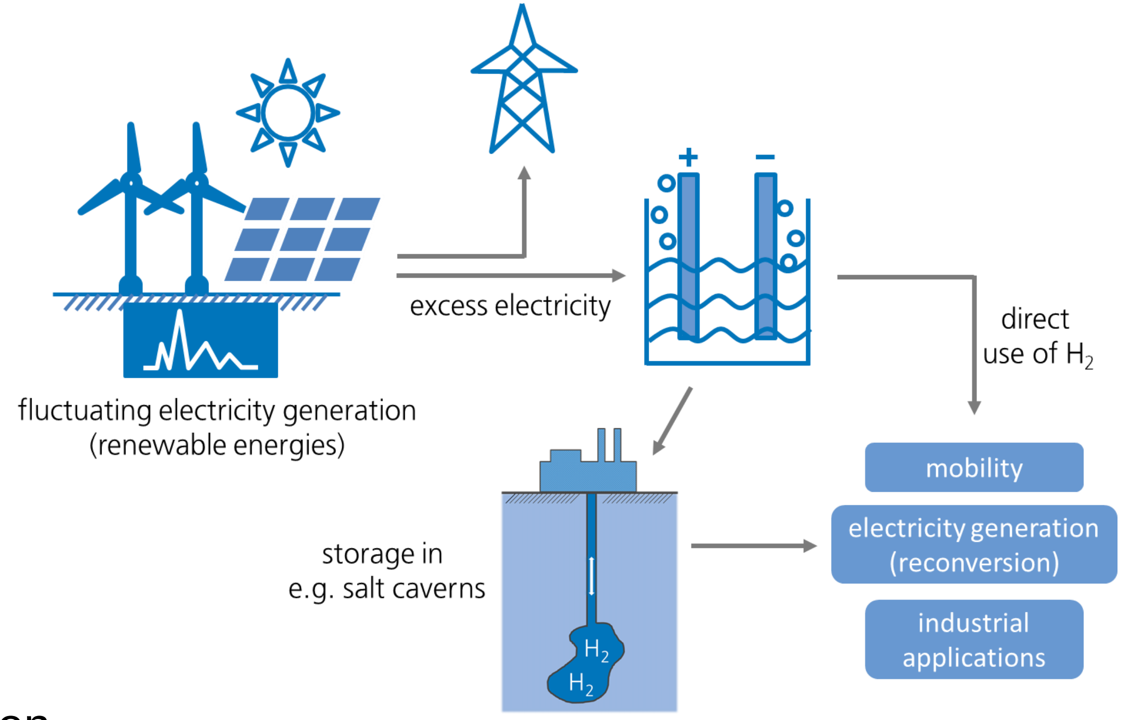
Motivation and Objective

- High purity requirements of hydrogen for fuel cell applications demand precise analytics, reasonable sampling devices and probing procedure

- H_2 as potential storage medium to compensate for volatility (seasonal)



→ Gas analysis according to ISO/DIN standards

→ Investigation of factors influencing the purity of hydrogen
  - Synthesis process (steam reforming, electrolysis, …)
  - Storage of hydrogen in salt caverns
  - Influence of used materials (high-pressure pipelines, sealings, …)

Analysis of Contaminants in Hydrogen with Mass Spectrometry According to DIN 17124 and ISO 14687

- High-performance gas analyser V&F, type AirSense
  - Measurement principle: High-resolution Ion Molecule Reaction Mass Spectrometry
  - Necessary amount: 10-15 L gas volume for values ± 2 % (fast analysis with 5 L possible)

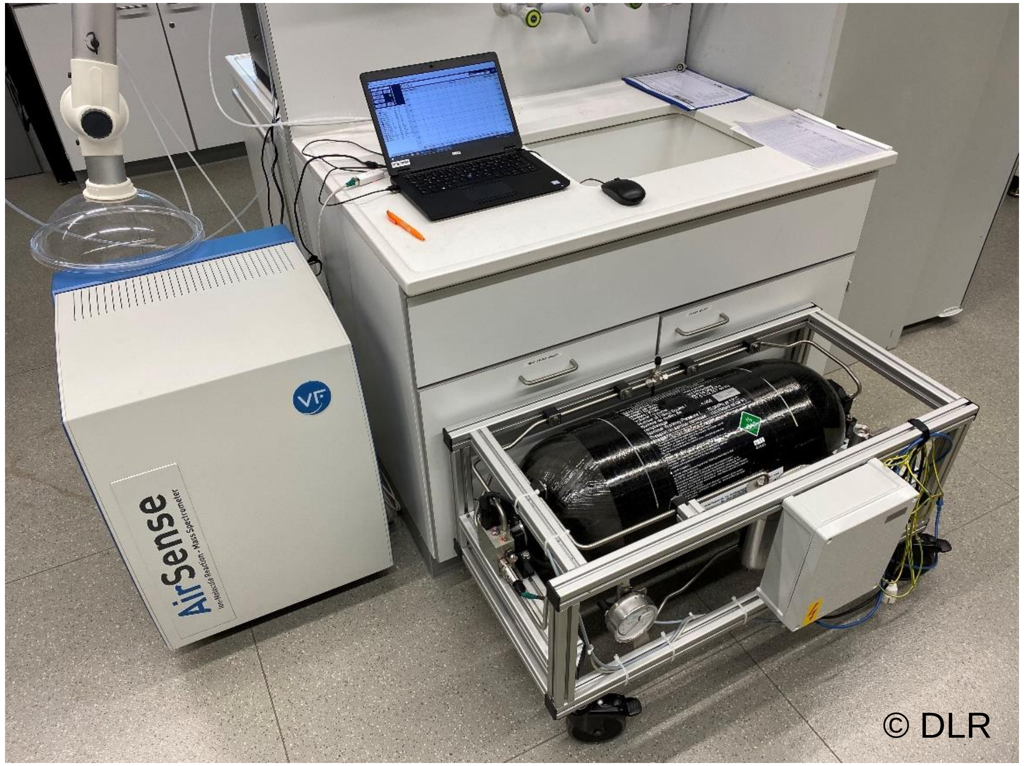
- Detectable gases from DIN 17124: H_2O, total hydrocarbons, O_2, CO_2, CO, total sulphur compounds, HCHO, HCOOH, NH_3, HCl, N_2
  - Measuring range: 0 – 100 ppm
  - Daily calibration with 8 test gases and H_2 6.0

	DIN 17124[1] [ppm]	AirSense [ppm]
H_2O	5	0.58
Total Hydrocarbons	2	(limited)
CH_4	100	0.02
O_2	5	0.14
CO_2	2	0.02
CO	0.2	0.45
Total Sulphur	0.004	0.003
HCHO	0.2	0.007
HCOOH	0.2	0.005
NH_3	0.1	0.002
Halides	0.05	HCl: 0.02
N_2	300	1.65
He, Ar	300	–

[1] DIN EN 17124:2019-07, DIN, **2019**, p. 7.

Sampling Device for Hydrogen to Investigate the Purity at Hydrogen Refuelling Stations

- Composite type IV high-pressure hydrogen tank (37 L)
- Design comparable to tanks in fuel cell vehicles
- Sensors for inner temperature, pressure and flow rate
- Receptacle to use standardised dispenser at HRS for non-communicative refuelling up to 875 bar, electronic controlled outlet valve with safety equipment
- **Specific sampling procedure developed for analysis of contaminants in H_2**



Specific Sampling Procedure Developed for Reliable Analysis of Contaminants in Hydrogen

- Minimum pressure: 1.8 Mpa
- Evacuation of sampling device not possible (possible damage of PTFE inliner)

Sampling procedure according to ASTM D7606

- Emptying of sampling device to 1.8 MPa
- Flowing 1 kg through sampling device
- Emptying of sampling device to 1.8 Mpa
- Filling of sampling device to amount necessary for analysis in the laboratory

- Short line lengths, passivated stainless steels

First Successful Sampling and Analysis of H_2 from a (Non-Public) Research HRS in Groningen

Contaminant	Concentration [ppm]	DIN 17124[1] [ppm]
H_2O	19.3	5
CH_4	Below LOD	100
O_2	2.5	5
CO_2	2.9	2
CO	((1.5))	0.2
Total Sulphur	Below LOD	0.004
HCHO	Below LOD	0.2
HCOOH	0.01	0.2
NH_3	0.014	0.1
Halides	HCl: 0	0.05
N_2	Approx. 700	300

[1] DIN EN 17124:2019-07, DIN, **2019**, p. 7.

Sampling and Analysis of Hydrogen from the HRS in Huntorf

Contaminant	Concentration [ppm]	DIN 17124[1] [ppm]
H_2O	4.6	5
CH_4	Below LOD	100
O_2	2.5	5
CO_2	0.3	2
CO	0.3	0.2
Total Sulphur	0.004	0.004
HCHO	Below LOD	0.2
HCOOH	0	0.2
NH_3	0	0.1
Halides	HCl: 0	0.05
N_2	155	300

[1] DIN EN 17124:2019-07, DIN, **2019**, p. 7.

Second Sampling and Analysis of Hydrogen from the HRS in Huntorf

Contaminant	Concentration [ppm]	DIN 17124[1] [ppm]
H_2O	0.9	5
CH_4	Below LOD	100
O_2	1.1	5
CO_2	0.1	2
CO	0.2	0.2
Total Sulphur	0	0.004
HCHO	Below LOD	0.2
HCOOH	0	0.2
NH_3	0	0.1
Halides	HCl: 0	0.05
N_2	8.4	300

[1] DIN EN 17124:2019-07, DIN, **2019**, p. 7.

Are Synthesis and Processing of Hydrogen at HRS Directly Influencing the Quality of Hydrogen?

- Hydrogen obtained via electrolysis has the potentially **highest purity**, minor contamination: N_2, O_2, H_2O [1, 2]

- HRS sampling in **Groningen, NL** (on-site PEM electrolysis, atm. pressure): contamination in form of N_2 (≈ 700 ppm), H_2O (≈ 19 ppm) and CO_2 (≈ 3 ppm)

- First HRS sampling in **Huntorf** (on-site alkaline electrolysis, high pressure): contamination in form of H_2O (≈ 5 ppm) and sulphur components (≈ 4 ppb)
  - Compression via piston compressor and long-term storage at 500 bar

- Second HRS sampling in **Huntorf** showed very high purity, only minor contamination
  - No compression and storage, H_2 directly sampled from electrolyser (outlet pressure ≈ 100 bar)

- **Compression** (piston compressor) and **processing** (storage) at HRS **influence the purity** of hydrogen

[1] T. Bacquart et al. *J. Power Sources* **2019**, *444*, 227170. [2] T. Bacquart et al., *Int. J. Hydrogen Energ.* **2018**, *43*, 11872-11883.

More Sampling of Hydrogen is Necessary for Further Insights of Influencing Factors

- Sampling at different HRS with **varied synthesis routes** (e.g. SMR) necessary for final conclusions

- Which additional factors beyond the HRS influence the quality of hydrogen?

- Investigation of the influence of the **storage** of hydrogen in **salt caverns**
    - High-pressure experiments with test reactors to **simulate cavern conditions** in the laboratory

- Which **impact** do the **materials** used for conducting and processing hydrogen have on the purity?
    - Investigation of sealings, cements and steels under elevated temperature and pressure

- Which **purification steps** and **sensors** are essentially needed to guarantee high quality at every refuelling of a fuel cell vehicle

Thank you for your kind attention!
Questions and discussion are welcome

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