Analysis of the Purity of Hydrogen at Public Hydrogen Refuelling Stations

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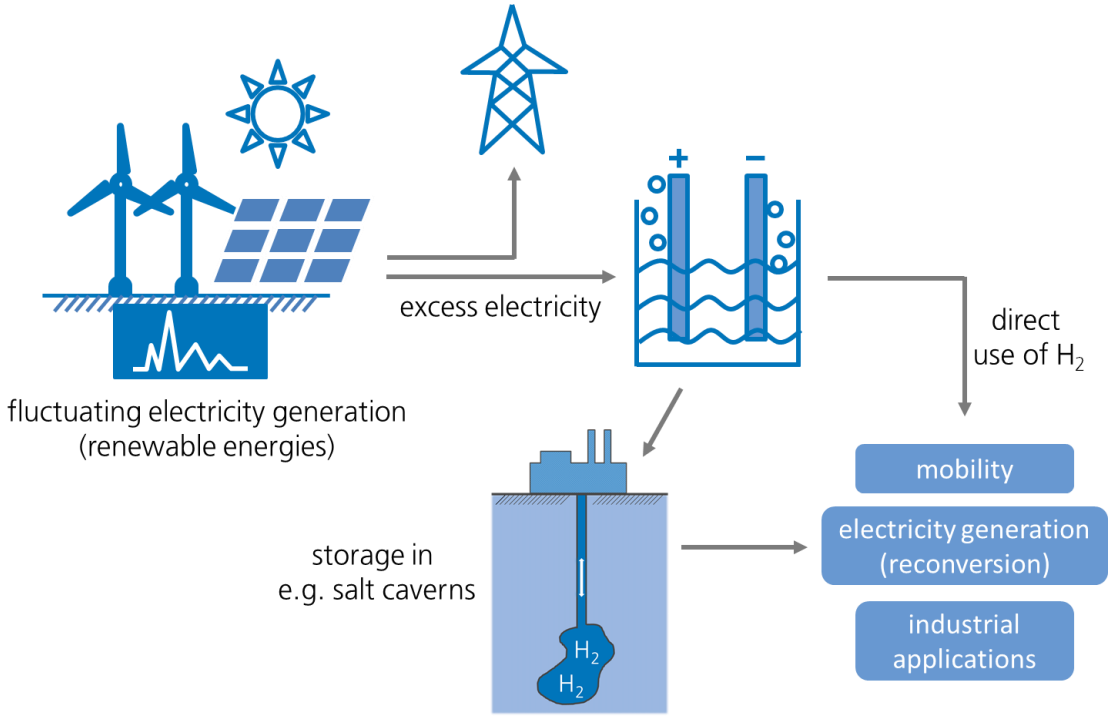
Motivation and Objective

- 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/EN 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 EN 17124 and ISO 14687

- High-performance gas analyser V&F, CombiSense
  - Measurement principle: Combined Ion Molecule Reaction (IMR) and Electron Impact (EI) Mass Spectrometry
  - Necessary amount: 10-15 L gas volume for values ± 2 % (fast analysis with 5 L possible)

- Detectable gases from EN 17124 [1]: H_2O, total hydrocarbons, O_2, CO_2, CO, total sulphur, HCHO, HCOOH, NH_3, HCl, N_2, He, Ar
  - Measuring range: 0 – 100 ppm
  - Daily calibration with 10 test gases and H_2 6.0

	EN 17124[1] [ppm]	CombiSense [ppm]
H_2O	5	0.61
Total Hydrocarbons	2	0.01
CH_4	100	0.02
O_2	5	0.11
CO_2	2	0.05
CO	0.2	0.17
Total Sulphur	0.004	0.003
HCHO	0.2	0.01
HCOOH	0.2	0.01
NH_3	0.1	0.01
Halides	0.05	HCl: 0.04
N_2	300	0.81
He	300	1.38
Ar	300	0.10

[1] DIN EN 17124:2019-07 Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles, **2019**.

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

- Composite **type IV high-pressure** hydrogen tank (37 L)
- Design similar to tanks in fuel cell vehicles
- Sensors for inner temperature, pressure and flow rate
- Receptacle to use standardised dispenser at HRS for **FCEV-independent 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 of tank system: 1.8 MPa
- Evacuation of sampling device and open end purging not possible (potential damage of PE liner)

Sampling procedure according to ASTM D7606 [2]

- 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

[2] ASTM International Committee, ASTM D7606 Practice for Sampling of High Pressure Hydrogen and Related Fuel Cell Feed Gases, **2017**.

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

Contaminant	Concentration [ppm]	EN 17124[1] [ppm]
H_2O	19.23 ± 4.24	5
CH_4	Below LOD	100
Total Hydrocarbons	0.34 ± 0.07	2
O_2	2.86 ± 0.54	5
CO_2	2.90 ± 0.09	2
CO	((1.62 ± 0.11))	0.2
Total Sulphur	0.002	0.004
HCHO	Below LOD	0.2
HCOOH	0.01 ± 0.001	0.2
NH_3	Below LOD	0.1
Halides	HCl: Below LOD	0.05
N_2	761.68 ± 22.72	300

[1] DIN EN 17124:2019-07 Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles, **2019**.

Sampling and Analysis of Hydrogen from the HRS in Huntorf, Germany

Contaminant	Concentration [ppm]	EN 17124[1] [ppm]
H_2O	3.56 ± 0.73	5
CH_4	Below LOD	100
Total Hydrocarbons	0.01 ± 0.003	2
O_2	2.76 ± 0.68	5
CO_2	0.27 ± 0.01	2
CO	0.36 ± 0.09	0.2
Total Sulphur	0.002 ± 0.001	0.004
HCHO	Below LOD	0.2
HCOOH	Below LOD	0.2
NH_3	Below LOD	0.1
Halides	HCl: Below LOD	0.05
N_2	163.60 ± 5.01	300

[1] DIN EN 17124:2019-07 Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles, **2019**.

Second Sampling and Analysis of Hydrogen from the HRS in Huntorf, Germany

Contaminant	Concentration [ppm]	EN 17124[1] [ppm]
H_2O	0.94 ± 0.35	5
CH_4	Below LOD	100
Total Hydrocarbons	Not analysed	2
O_2	1.61 ± 0.44	5
CO_2	0.11 ± 0.01	2
CO	Below LOD	0.2
Total Sulphur	Below LOD	0.004
HCHO	Below LOD	0.2
HCOOH	Below LOD	0.2
NH_3	Below LOD	0.1
Halides	HCl: Below LOD	0.05
N_2	9.20 ± 1.40	300

[1] DIN EN 17124:2019-07 Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles, **2019**.

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 [3, 4]

- HRS sampling in **Groningen, NL** (on-site PEM electrolysis, atm. pressure): contamination in form of N_2 (≈ 761 ppm), H_2O (≈ 19 ppm) and CO_2 (≈ 3 ppm)

- First HRS sampling in **Huntorf, DE** (on-site alkaline electrolysis, high pressure): contamination in form of H_2O (≈ 4 ppm) and CO (≈ 0.36 ppm)
  - Compression via piston compressor and long-term storage at 500 bar

- Second HRS sampling in **Huntorf, DE** showed very high purity!
  - 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

[3] T. Bacquart et al. *J. Power Sources* **2019**, *444*, 227170. [4] 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 [5]
- Performing **round robin tests for validation** of lab equipment in compliance with ISO 21087
- 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 single refuelling of a fuel cell vehicle?

[5] ISO 21087:2019-06 Gas analysis – Analytical methods for hydrogen fuel – Proton exchange membrane (PEM) fuel cell applications for road vehicles, **2019**.

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

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