A3PS

Rethinking Propulsion.

Developments in Hydrogen Production and Storage Technologies

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Hydrogen production

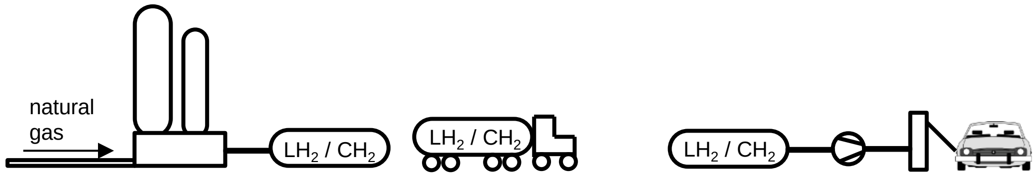
Hydrogen Production Technologies

- **State-of-the-art for large centralized production**
  - **Steam Methane Reforming**
  - **Partial Oxidation**
  - **Authothermal Reforming**

- **Applications for centralized and decentralized production – experimental status**
  - **Methanol Steam Reforming**
  - **Ammonia Cracking**
  - **Chemical Looping Reforming**
  - **Catalytic Cracking of hydrocarbons**
  - **Plasma Reformer**

Hydrogen supply options for fuel cell cars

- **State-of-the-art supply**
  - **Centralized production, truck delivery**



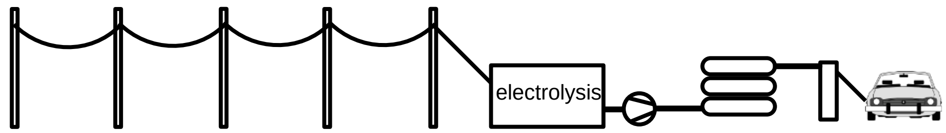
  - **Pipline delivery**

- **Future supply options**
  - **Onsite reforming**

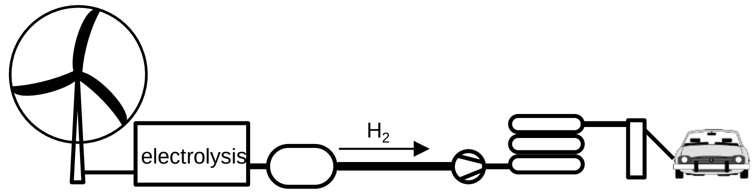
IEA/H2/TR-02/002

Hydrogen supply options for fuel cell cars

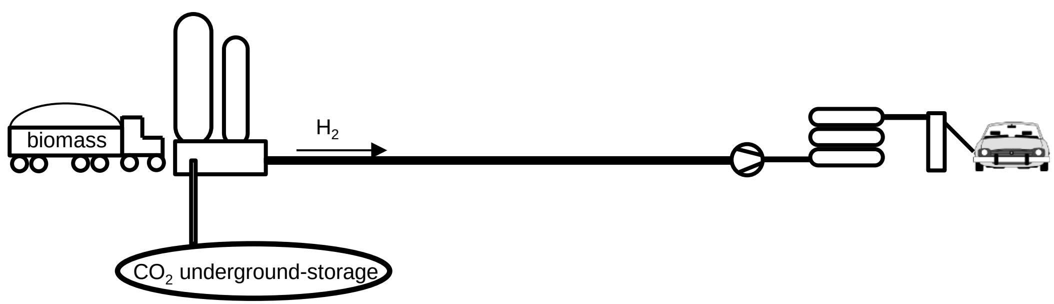
- **Future supply options**
  - **Onsite elctrolysis**



  - **Solar or wind electrolysis system**

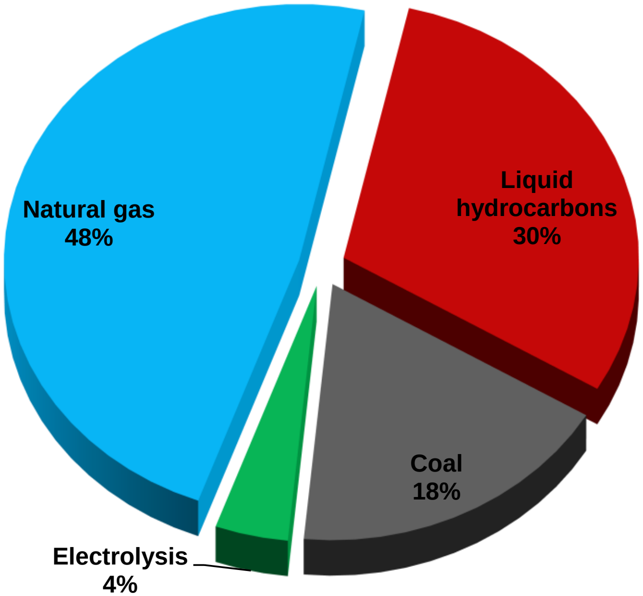


  - **Biomass conversion to hydrogen (including CO_2 sequestration)**



IEA/H2/TR-02/002

Current status of hydrogen production



ChemSusChem 2011, 4, 21–36; Wiley

Zech K, et al. DBFZ Report Nr.19, Hy-NOW, Evaluierung der Verfahren und Technologien für die Bereitstellung von Wasserstoff auf Basis von Biomasse. [last accessed 06.11.14].

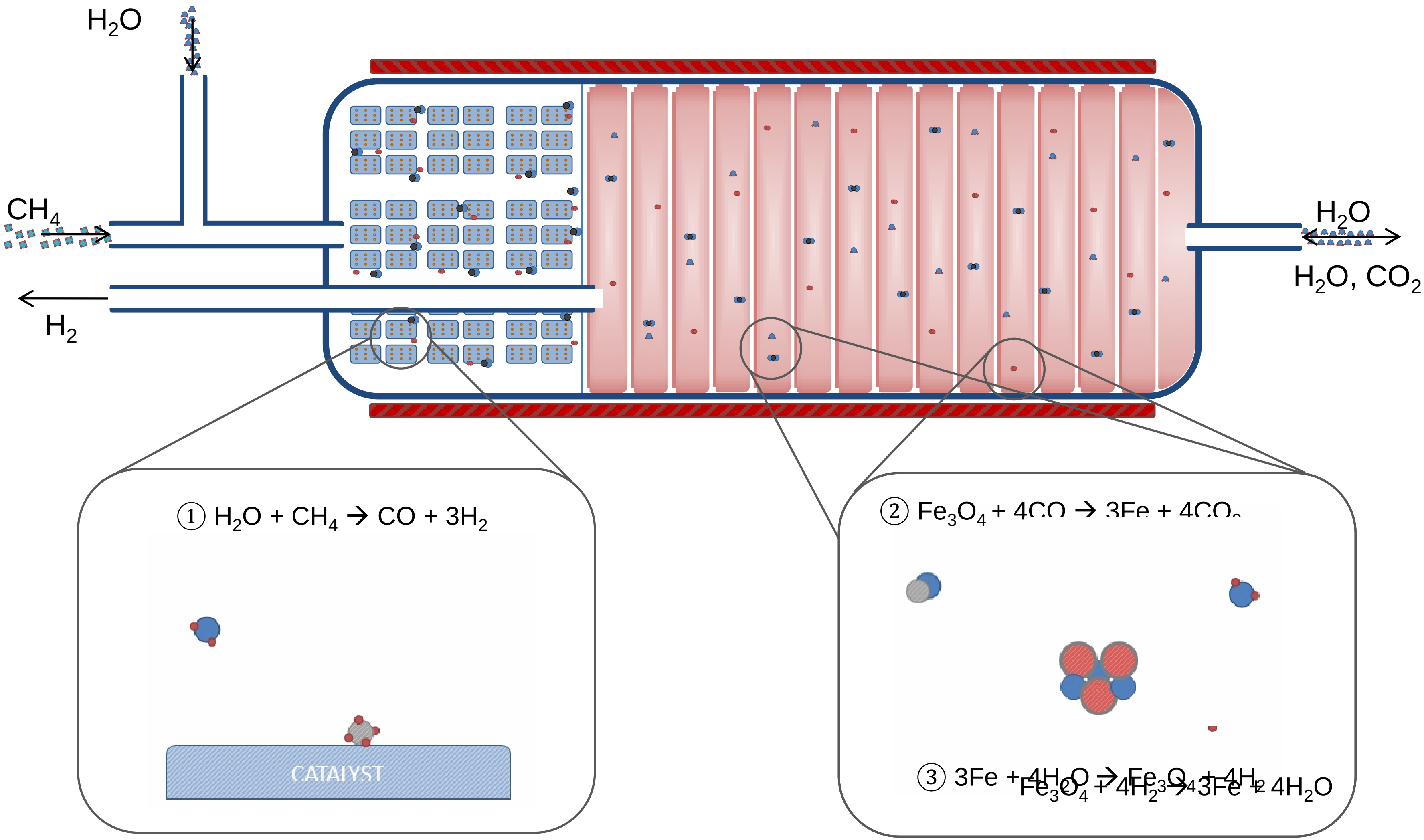
Spath P: et al. Biomass to Hydrogen Porduction Detailed Design and Economics Utilizing the Batelle Columbus Laboratory Indirectly Heated Gasifier. [last accessed 06.11.14].

- Current hydrogen production is based on fossil fuels.
- Hydrogen storage and transportation logistics are significant cost aspects

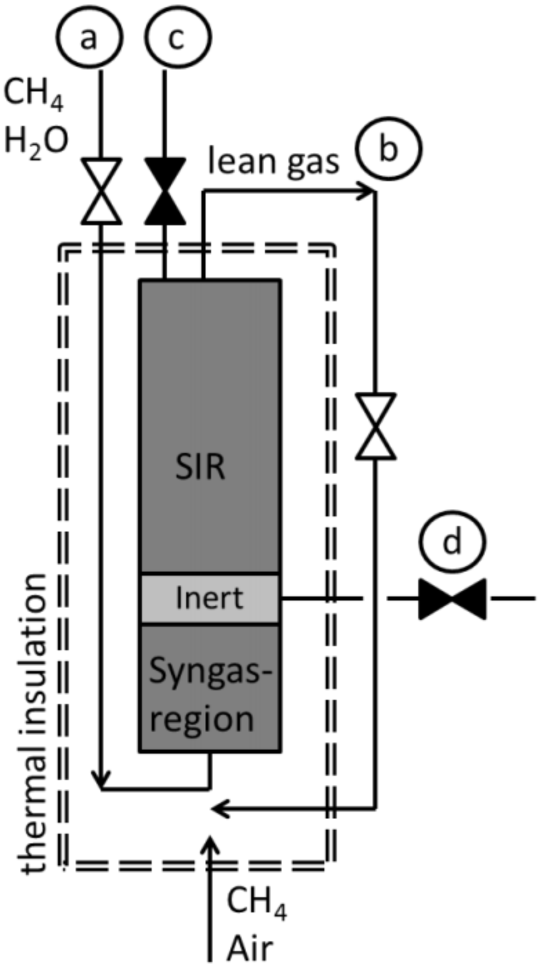
	Centralized production of hydrogen	**Decentralized production of hydrogen**
	Costs of production incl. purification	
[cent/kWh]	4.2 – 6.0	
[€/kg]	1.4 – 2.0	
	Transportation costs	
[€/kg/100km]	0.6	
Transport distance [km]	200	
[€/kg/200km]	1.1	
	Costs of gas compression 500 bar	
[€/kg]	0.5	
	Storage	
[€/kg]	0,2	
Total [€/kg]	**3.2 - 3.8**	

Decentralized hydrogen production

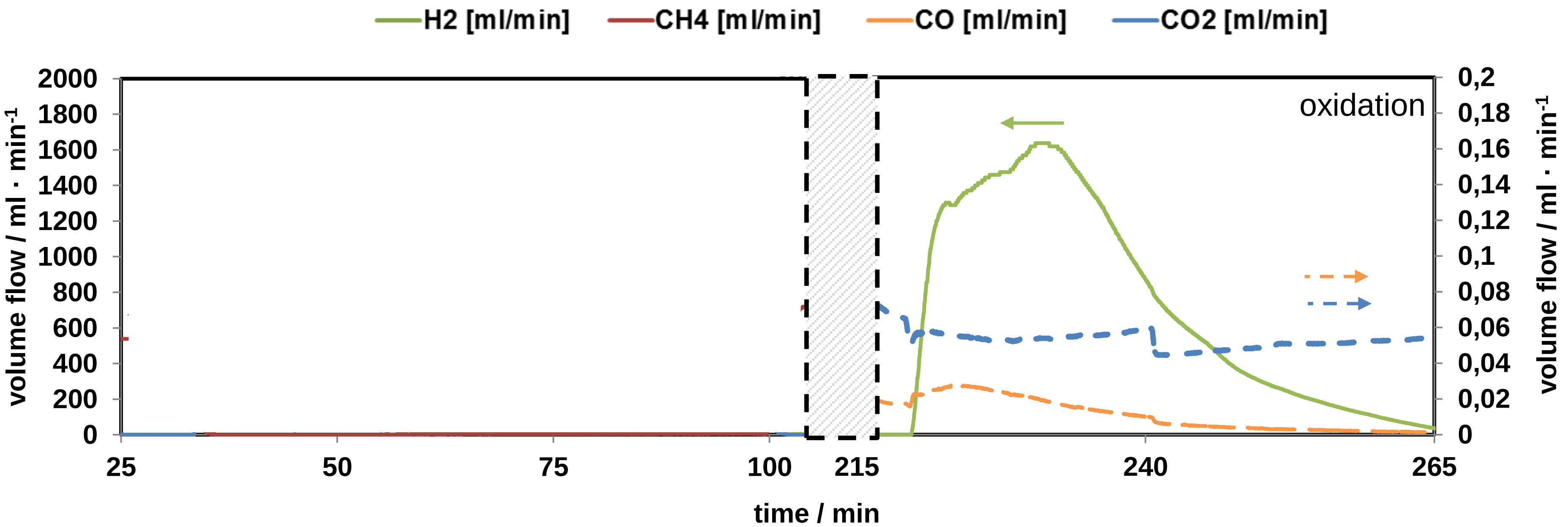
The Reformer Steam Iron Process



The Flex Fuel Reformer - prototype



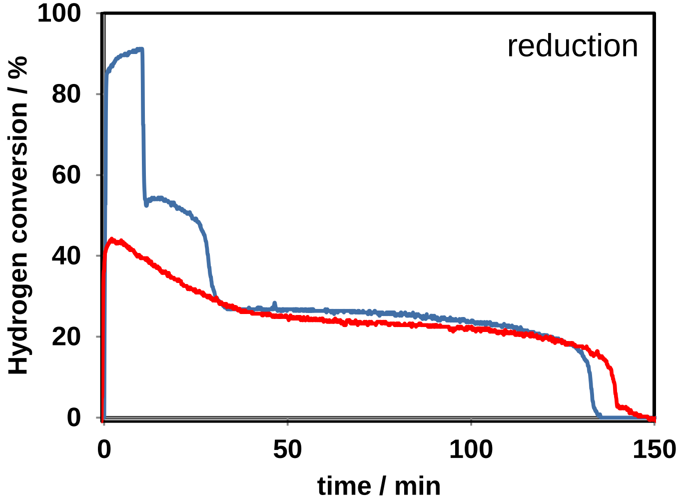
The Flex Fuel Reformer - prototype

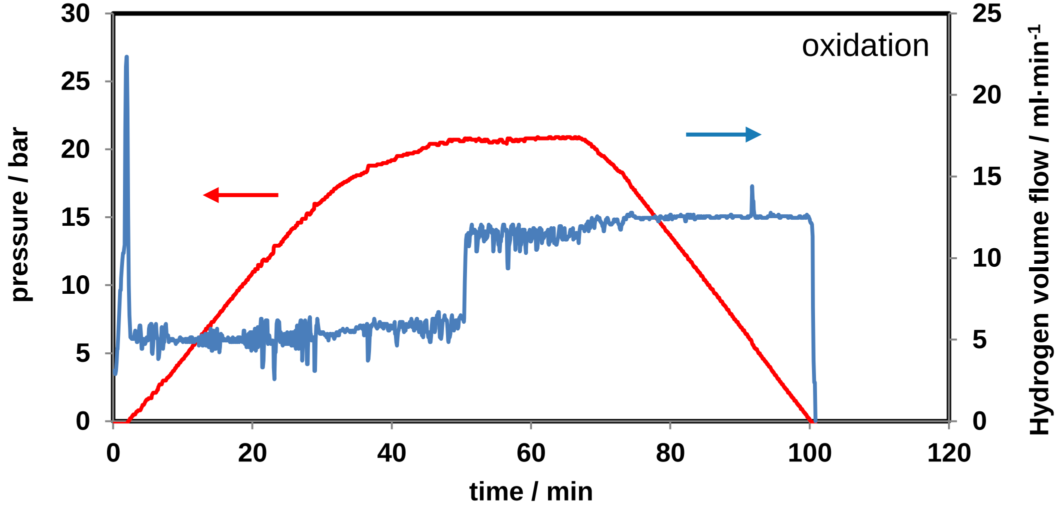


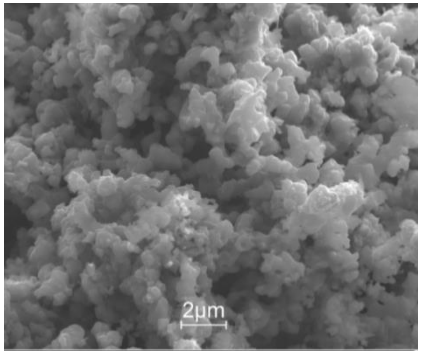
Process conditions:

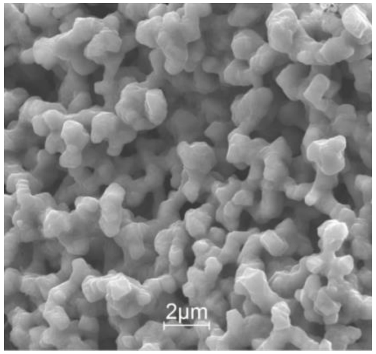
- main impurity: CO_2
- hydrogen purity of 99.99%
- CO content <15 ppm

Steam Iron Process – pressure experiments









Voitic G., et al., Appl. energy, doi:10.1016/j.apenergy.2015.03.095

Summary

The **Reformer Steam Iron Process** enables hydrogen production, purification and storage in one unit

- **Pure hydrogen** was produced from **biogas** using fixed bed reactor systems
- The **production of** pure **pressurized hydrogen** is possible **without additional gas compression** by steam oxidation of iron
- The Reformer Steam Iron Process is suitable for **decentralized hydrogen production**

Hydrogen storage

Chemical Hydrogen Storage

- Many different technologies
  - Metal hydrides, LOHCs, NH_3, NH_3BH_3, MeOH, EtOH…
  - Examples for liquid H_2 carriers
    - LOHCs
    - Aqueous solutions of hydrides ($NaBH_4$, other borohydrides)
    - Slurries of NH_3BH_3
    - MeOH, EtOH

- Why Chemical carriers?
  - For some applications advantageous compared to gaseous H_2 storage
  - Liquid carrier: easy handling, distribution and storage, inexpensive infrastructure
- Differentiation
    - Hydrogen carrier for PEMFC or SOFC
    - Fuels for Direct Fuel Cells (MeOH, EtOH)

Liquid carrier versus conventional storage

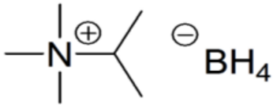
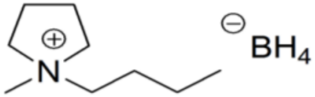
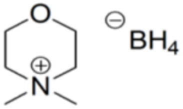
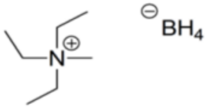
	700 bar storage	LOHC	$NaBH_4$ $IL\text{-}BH_4$	Ammonia borane slurry
Description	Gaseous	Liquid at RT	Aqueous solution liquid at RT	Solid dispersed in liquid carrier fluid
Infrastructure costs	Very high	Conventional infrastructure for liquid fuels		
System cost	High (tank manufacturing)	Cheaper compared to high pressure tank costs		
On-board efficiency	high (>90%)	Below DOE target	high (>90%)	
Off-board efficiency	DOE target in range (60%)	DOE target reached (exothermic regeneration)	Below DOE target	
H_2 price	DOE target ($ 2-4/kg) achievable		Above target, ongoing R&D	
Applications	portable, stationary	stationary H_2 distribution	portable and stationary	

Ionic Liquid for H_2 Storage

Hydrogen Storage in Ionic Liquids

- Borohydride based Ionic Liquids
- Why organic cations instead of sodium?
  - Advantages compared to NaBH4
    - Improved solubility for reaction byproduct (borate)
    - No hydrogen loss
- Research areas
  - Storage medium (proionic)
  - Hydrogen release (TU, VTU)
  - DBFC (TU)
  - System design (TU, VTU)
  - Recycling (proionic, TU, VTU)

Ionic Liquid examples

Name	Structure	H2 capacity (theor.)
TMPA - BH_4		6.9 wt%
BMPyr - BH_4		5.1 wt%
DMMor - BH_4		6.1 wt%
TEMA - BH_4		5.5 wt%

Borohydride H2 release

proionic

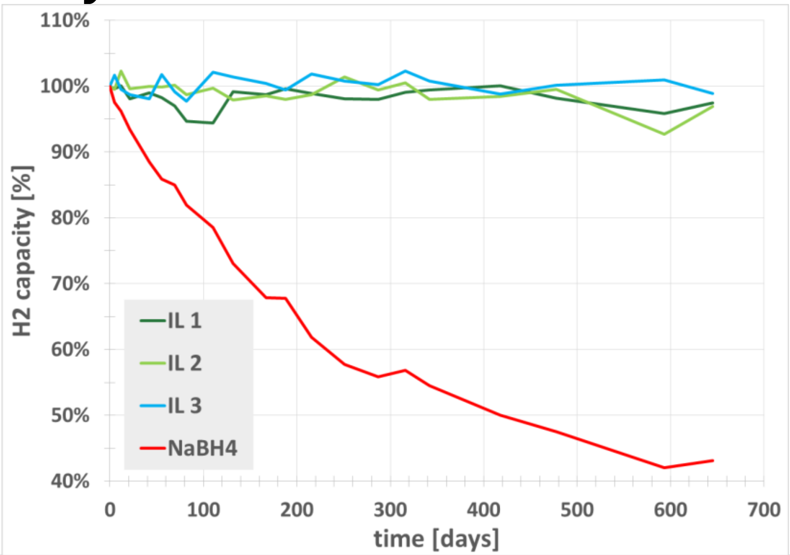
- Storage medium conditions
  - Aqueous solutions
  - Solid carrier with water/steam supply to reactor
- Hydrogen release
  - $IL\text{-}BH_4 + 4H_2O \rightarrow IL\text{-}B(OH)_4 + 4H_2$
  - Catalytic
    - Acids
    - Heterogeneous metal catalysts
  - Thermal

- Properties
  - Pressureless at ambient temperatures
  - No hydrogen release without catalyst
  - Simple handling

Characteristics & Advantages

proionic
VTU engineering

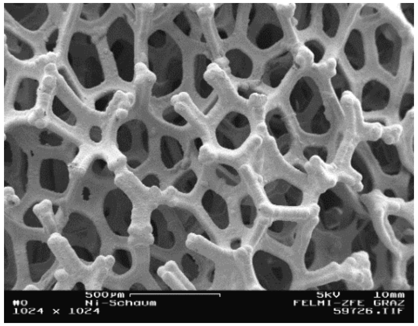
- Liquid storage medium at ambient temperature and pressure
- Non-flammable storage solution
- Simple handling and fuel-filling
- Catalytic H2 release already at ambient temperatures
- No hydrogen release without catalyst
- Long term stable

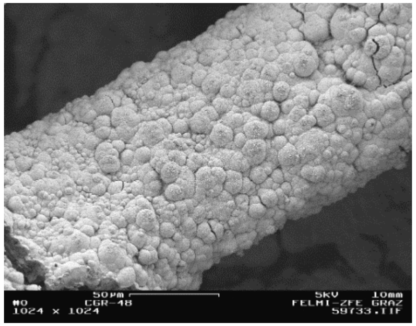


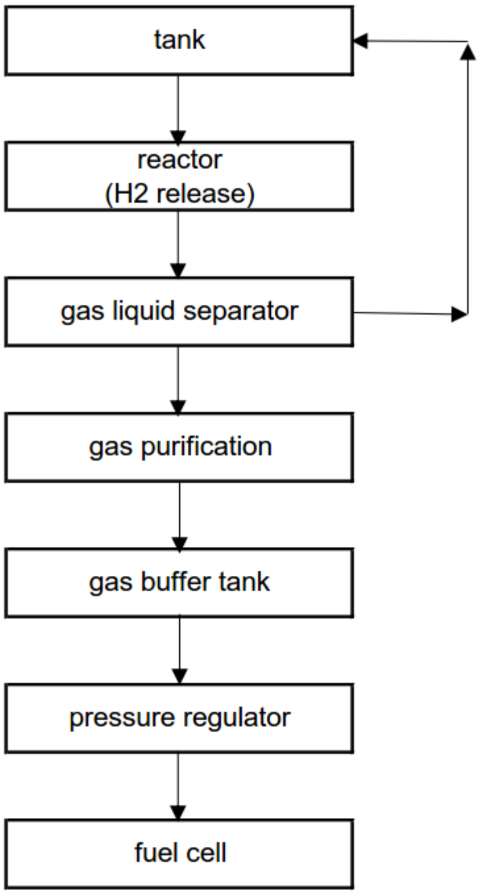
Long term stability of Ionic Liquids compared to $NaBH_4$, same H_2 content and initial conditions, aqu. solutions in 1M NaOH

H2 release and PEMFC system

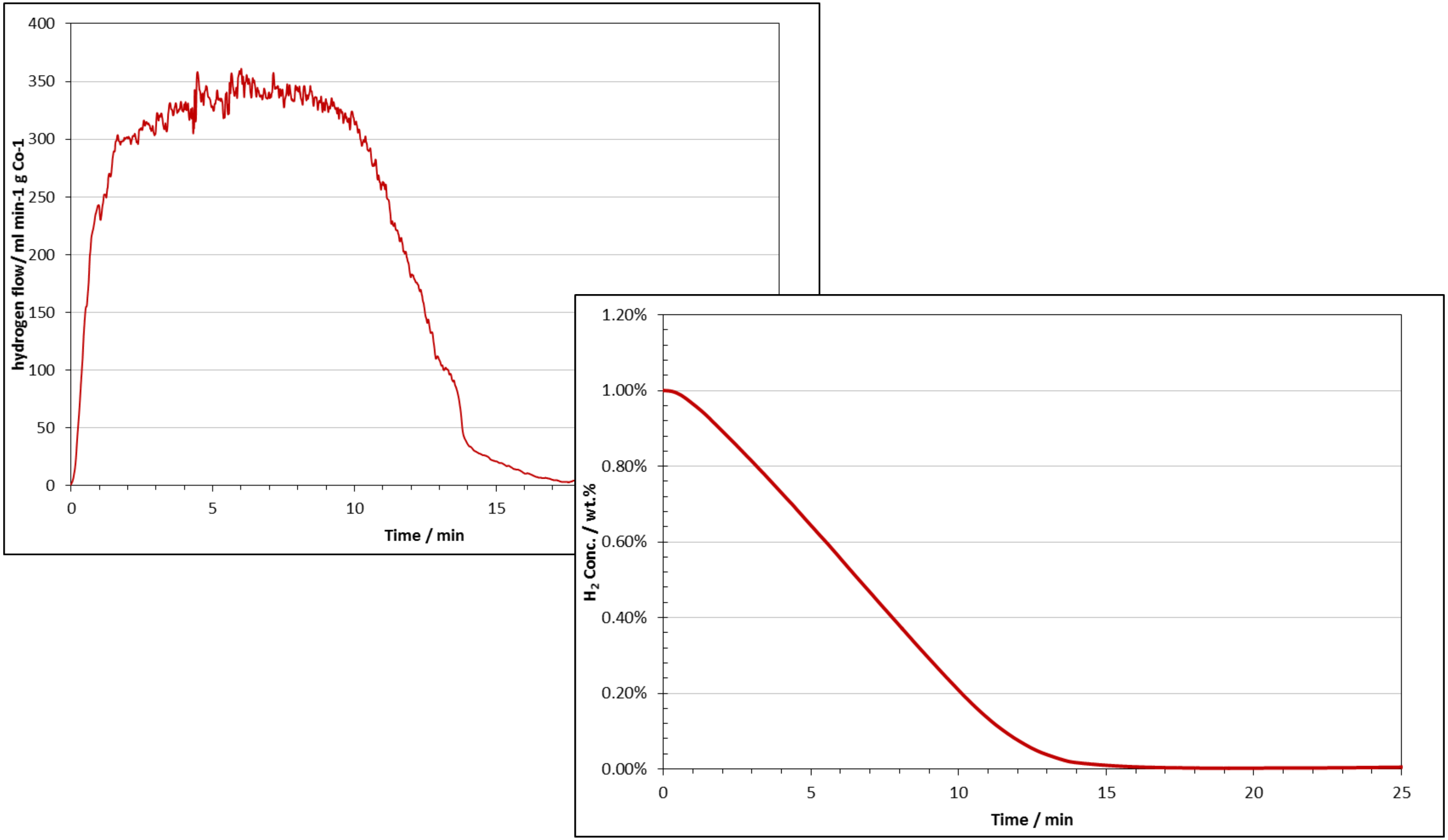
- Exothermic hydrolysis reaction
- Metal catalysts
  - Carrier: Nickel foam / Nickel grid
  - Catalyst: Cobalt, other non noble metals
- Release in cont. flow-through reactor
  - Gas-liquid separation
  - Hydrogen purification
  - PEMFC







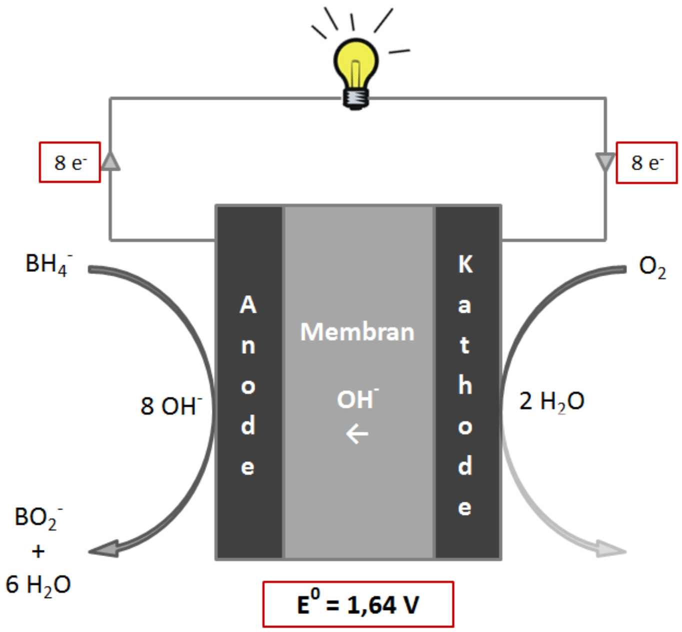
Catalytic hydrogen release - batch



DBFC

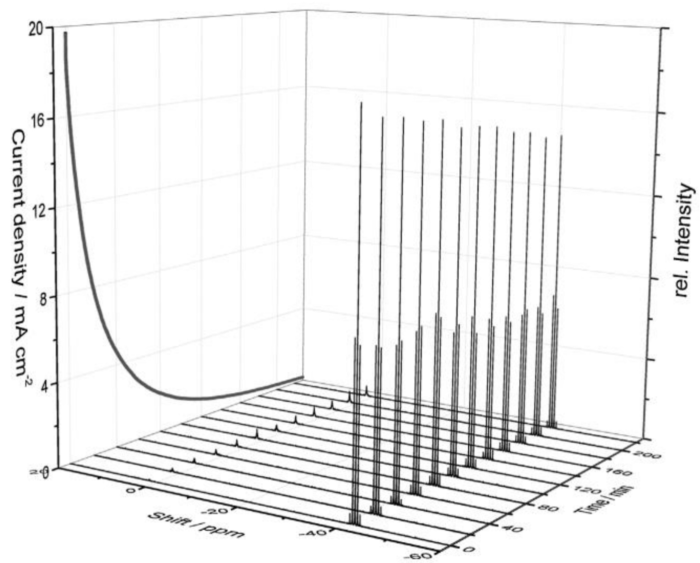
- Research areas
  - Catalyst research
    - Better understanding of reaction mechanism
    - Anode: basic research on Pd/C catalyst
    - Control of side reactions
  - Electrode characterization
  - MEA and cell

- Application field
  - Comparable to DMFC
    - Advantage: Non-flammable storage medium

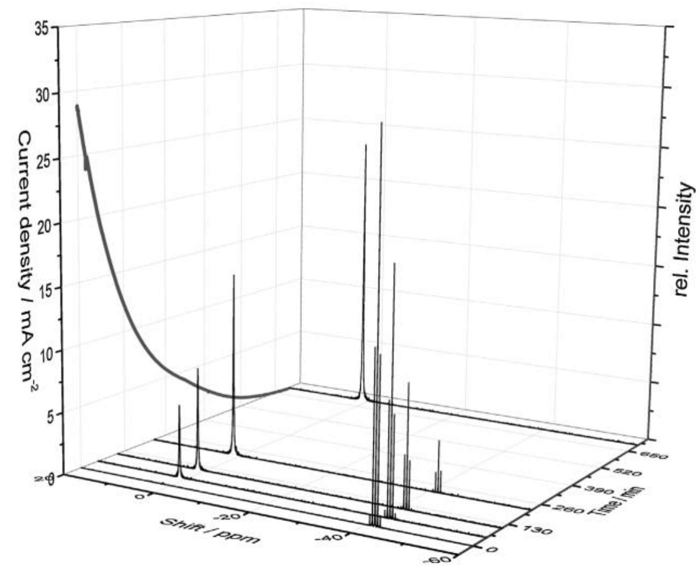


DBFC – reaction mechanism

For high efficiency and long term operation - complete oxidation without intermediate reaction product formation required



Low potential (0.4V vs. RHE):
incomplete conversion, surface blocked



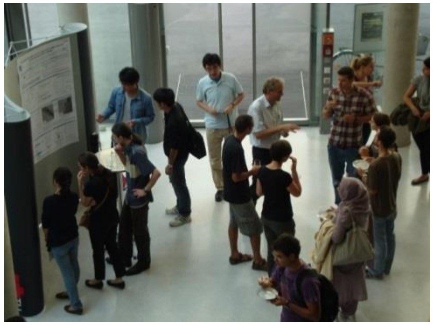
High potential (0.8V vs. RHE):
complete BH4 conversion

Grimmer et al., Applied Cat. B: Environm. 180 (2016) 614-621

Summary

- Development of new H_2 Storage System
  - Ionic Liquids with borohydride as hydrogen carrier
  - Ongoing development of new ionic liquids
- Hydrogen release
  - Basic catalyst research completed
  - Basic reactor design developed
  - Goal: Complete system with PEMFC
- DBFC
  - Research on catalysts and reaction mechanisms
  - Goal: Cell development
- Ongoing research project

Events - Dissemination

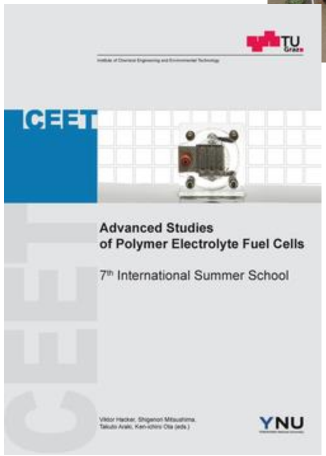


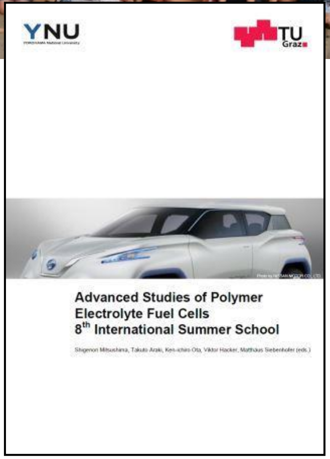
9th FC Summer School 2016

Graz University of Technology in co-operation with Yokohama National University, Japan.
August 29th – September 3rd, 2016

2nd International Workshop on Hydrogen and Fuel Cells

Graz University of Technology
August 31st, 2016





www.tugraz.at/fcsummerschool

Acknowledgements

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