A3PS

Rethinking Propulsion.

Low temperature fuel cells and hydrogen production: efficiency improvement by component development

Viktor HACKER

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Technologies, Strategies and R&D-funding programmes
for the Market Introduction of
Alternative Propulsion Systems and Fuels

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in cooperation with

bmvit

Content

- Introduction to R&D at CEET
  - Degradation PEFC
  - Pinhole detection
  - Advanced fuel cell analysis
  - Catalyst development
  - Hydrogen storage
  - Hydrogen production
  - International Energy Agency
  - Yearly Summer School

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  - **Degradation PEFC**
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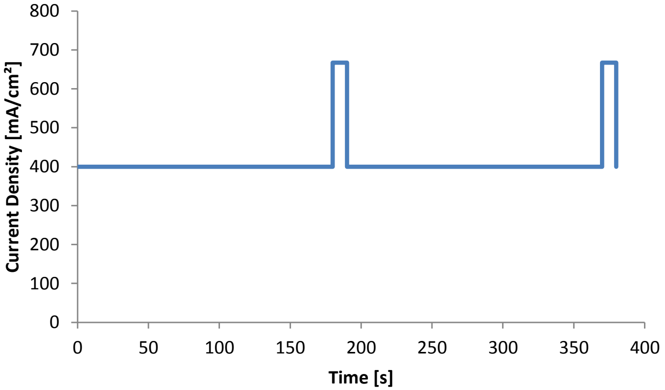
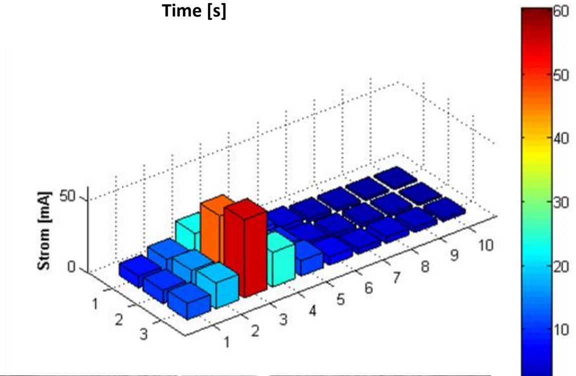
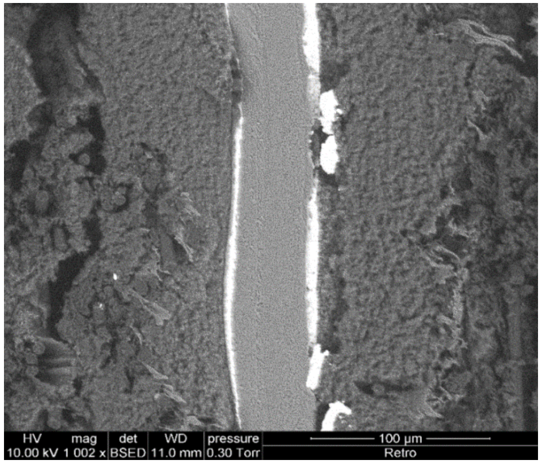
Degradation Phenomena

- **CATALYST DEGRADATION**
    - **Ostwald ripening**: Platinum particles usually are about 4-6 nm, Ostwald ripening causes them to grow, resulting in loss of active surface area.
    - Reduction of Pt^{2+}: Dissolved Pt^{2+} can **diffuse into the membrane**, where it is reduced by H_2. This also reduces the active catalyst surface.
    - **Catalyst poisoning**: Pt adsorbs CO and CO_2 strongly, poisoning of the catalyst.
- **MEMBRANE DEGRADATION**
    - **Thinning:** mechanical or chemical degradation can cause thinning of the membrane. Thereby, gas crossover is favoured and the electric isolation is reduced.
    - **Pinhole Formation**: often preceded by membrane thinning. Holes or cracks are formed.
    - Loss of **ionic species**
- **DEGRADATION OF THE SUPPORT MATERIAL**
    - **Carbon Corrosion**: During fuel starvation, the catalyst carbon support, but also the backing layer can be oxidised instead of hydrogen. CO and CO_2 can then be detected in the anode exhaust gas.
    - **Corrosion of the GDL:** besides the carbon support, PTFE can also be degraded. This causes a loss of hydrophobicity.

Causes of Degradation







- **HYDROGEN STARVATION**

The current density is periodically increased whilst the gas flow is constant, causing a lack of hydrogen. Thereby, degradation mechanisms are accelerated.

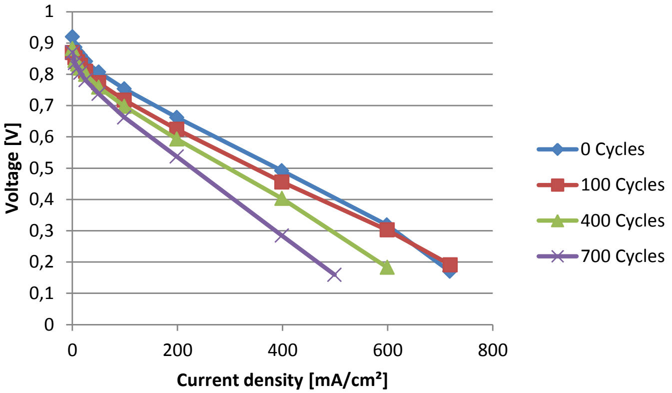
- **LOW HUMIDITY**

A gas humidity below 40% RH, especially at increased temperatures, accelerates **membrane degradation mechanisms**. Mechanical degradation is favoured, resulting in membrane thinning and the formation of pinholes.

- **HIGH HUMIDITY AND HIGH TEMPERATURES**

Especially high temperatures and humidity **favour carbon corrosion**. This causes loss of **electric conductivity, hydrophobicity** and the formation **of carbon monoxide and carbon dioxide**, both being catalyst poison. Furthermore, increased temperatures lead to the degradation of the gas diffusion layers additives, further lowering the hydrophobicity.

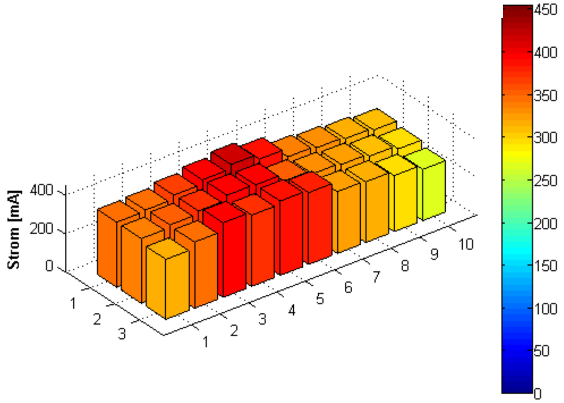
Methods of Detection



- **IN-SITU CHARACTERISATION**

Each cell is characterised by polarisation measurements, electrochemical impedance spectroscopy, cyclic voltammetry and hydrogen diffusion measurements. Furthermore, carbon monoxide and carbon dioxide, both being products of carbon corrosion, can be detected in the exhaust gas.

- **SEGMENTED CELL**

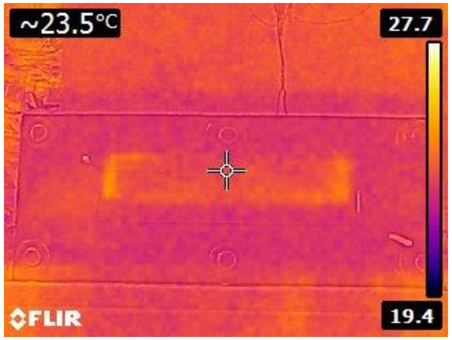


By using a segmented cell, a spatial resolution of the current density during characterisation and during the measurements is possible. Thereby, local defects can be detected.

- **EX-SITU CHARACTERISATION**

EDX measurements and infrared thermography are ex-situ methods. Both require the disassembly of the fuel cell and are considered destructive.

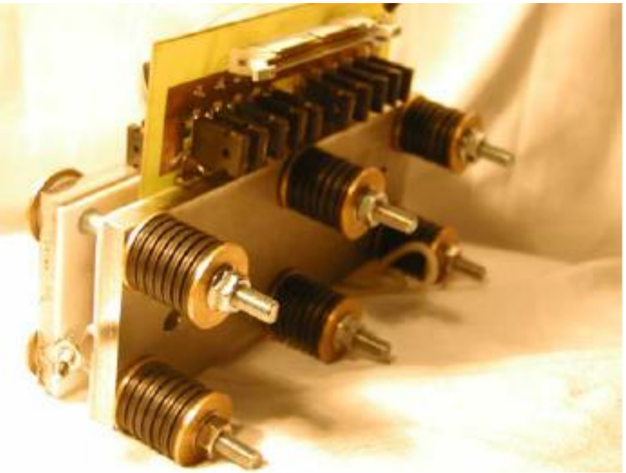
- **INFRARED THERMOGRAPHY**

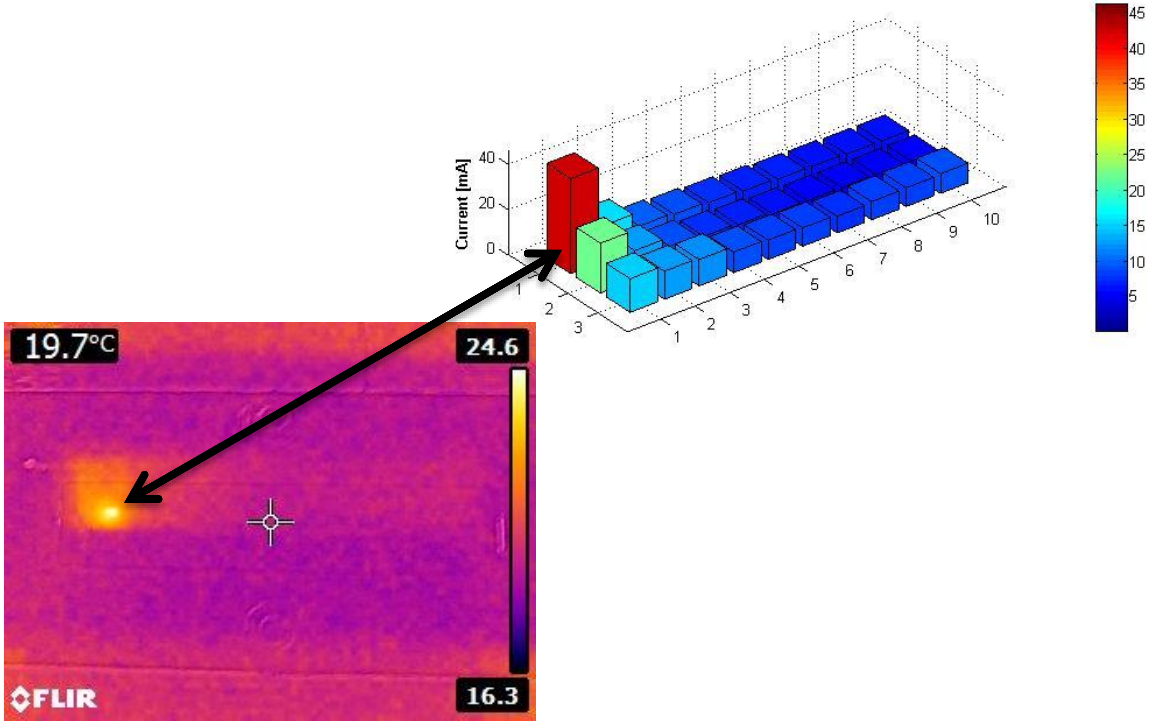


Infrared thermography is a very accurate method to detect membrane thinning and pinholes. In this setup, the anode is in contact with hydrogen, whilst the cathode is in direct contact with the ambient air. When hydrogen diffuses through the membrane, it is directly oxidised at the cathode catalyst. The produced heat can then be detected with an infrared camera.

Defect Localisation in segmented PEM Fuel Cells

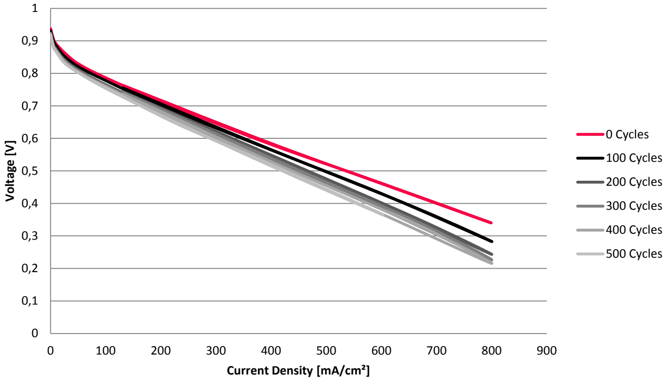
- The formation of pinholes in a polymer electrolyte membrane fuel cell is provoked via accelerated stress tests
- A deeper understanding of the degradation mechanisms can be obtained by using a segmented single PEM fuel cell for defect localisation

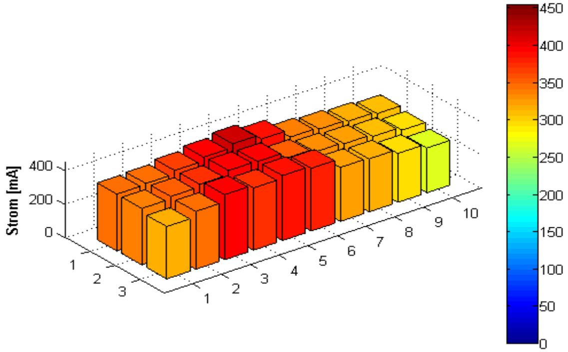




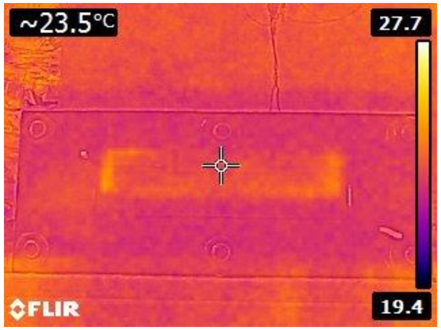
Defect Localisation in segmented PEM Fuel Cells

- In-situ Characterisation
  - Polarisation Measurements
  - Electrochemical Impedance Spectroscopy
  - Cyclic Voltammetry and Hydrogen Diffusion Measurements
  - Carbon Monoxide and Carbon Dioxide Detection in the Off-Gas
  - Segmented Cell: Local defects can be detected by spatial resolution of the current density during characterisation



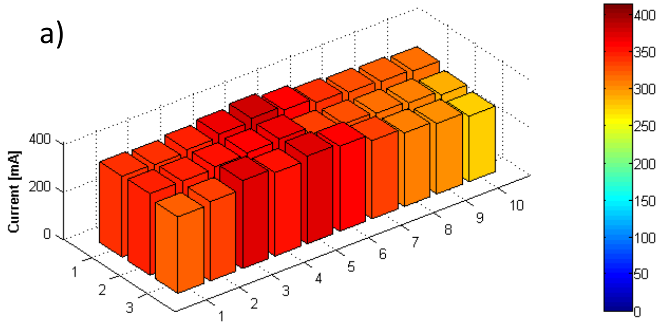


- Ex-situ Characterisation
  - Detection of Membrane Thinning and Pinholes by Infrared Thermography

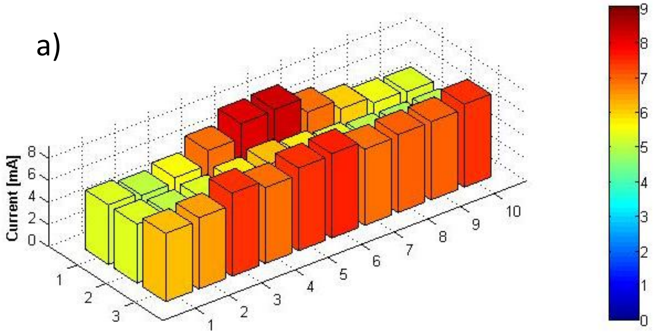


Electrochemical Pinhole Detection

- No vast current decay at the affected segment



- Clearly increased current cross over in the perforated area



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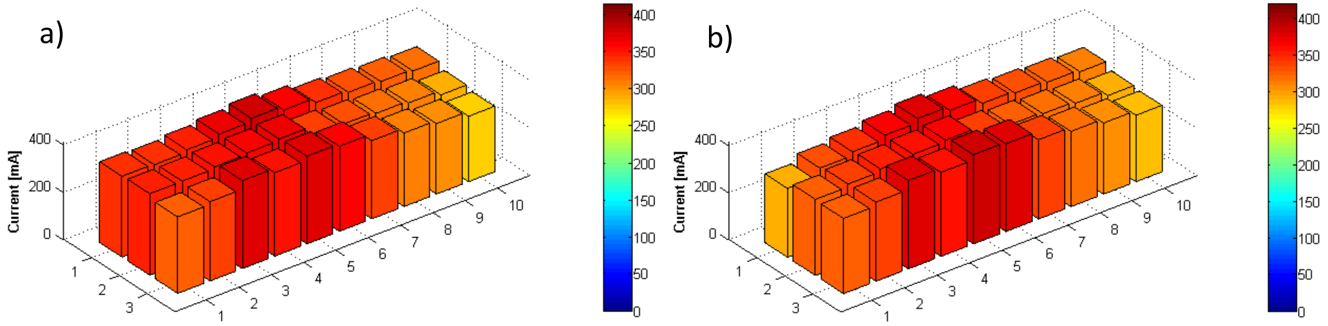

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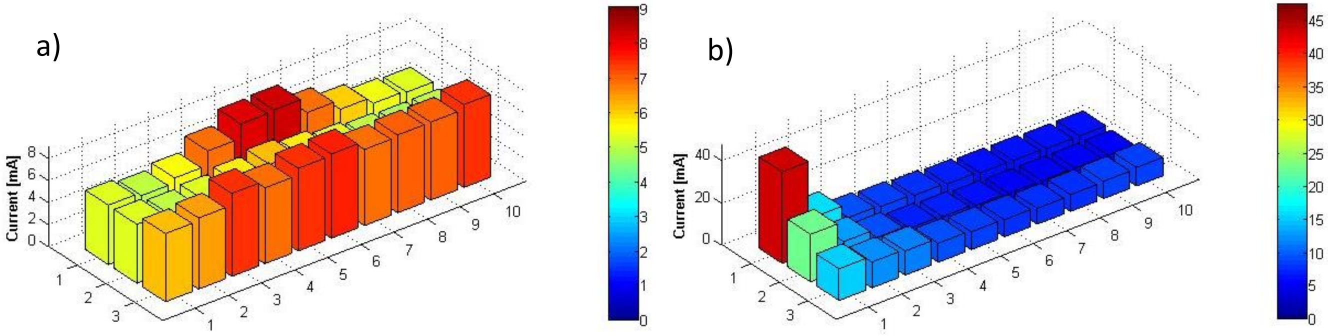
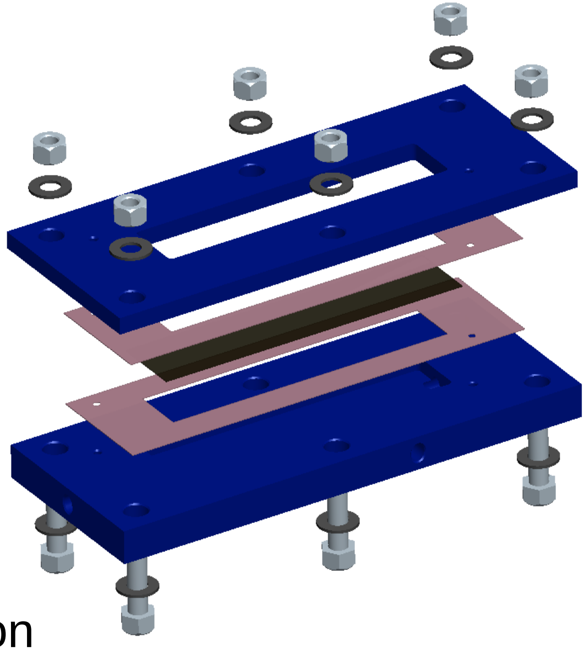
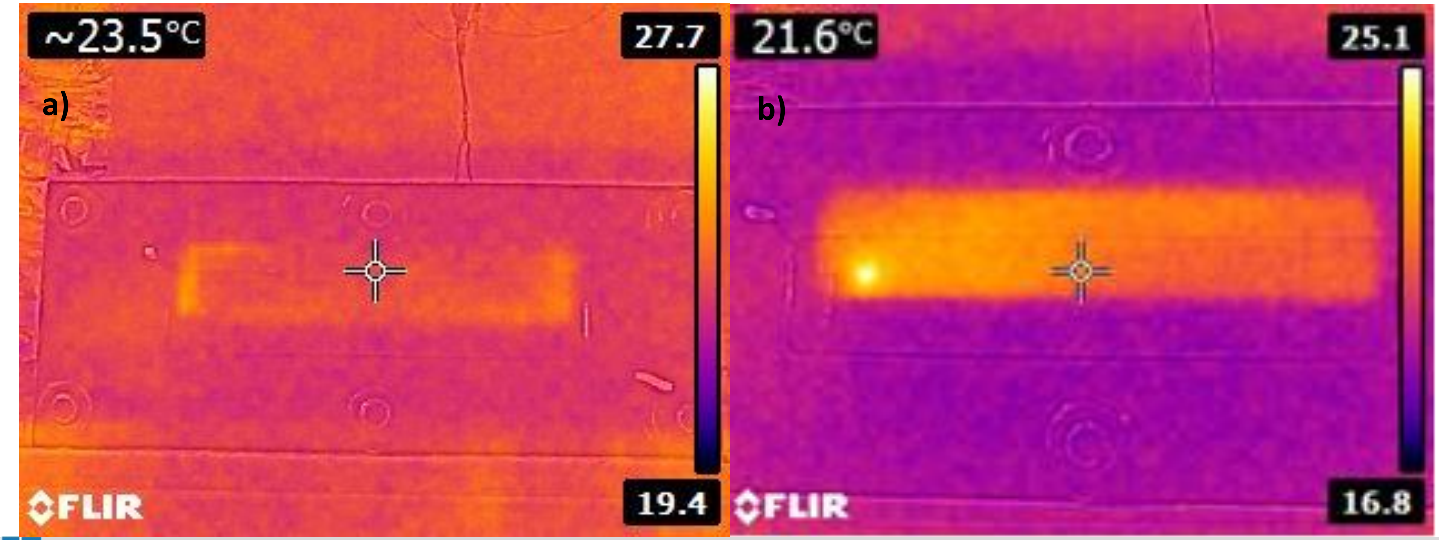


Infrared Thermography

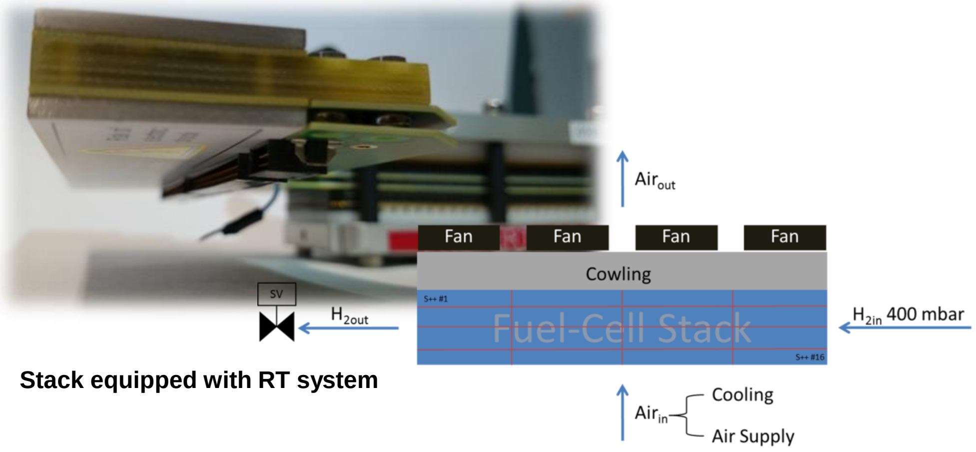


- One side is purged with a hydrogen in nitrogen solution
- One side is open to the ambient air
- Locally increased temperature can be detected by infrared thermography

- Reference without pinhole
- Perforated area clearly visible, better localisation

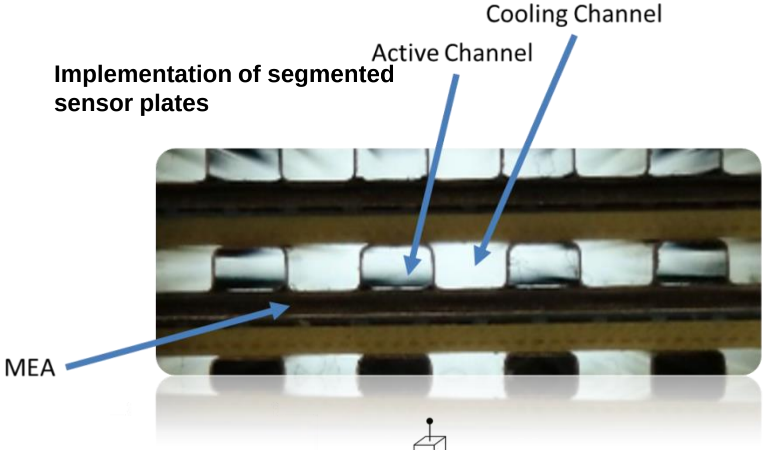


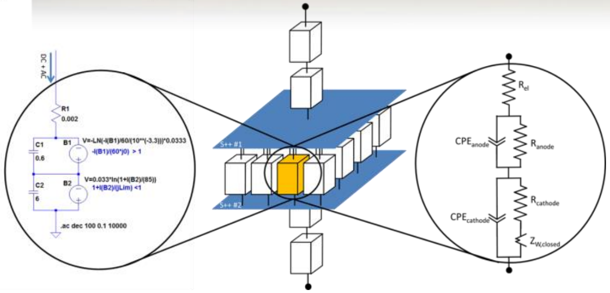
Advanced Fuel Cell Analysis and Diagnostics



Stack equipped with RT system

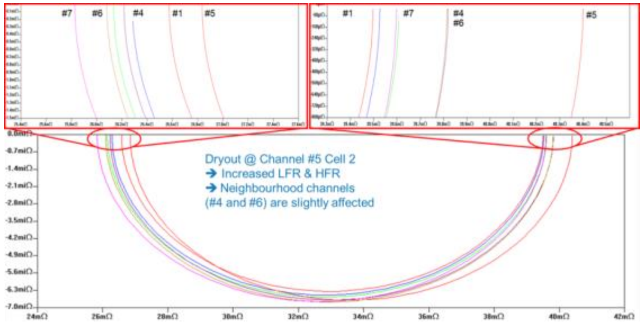
Implementation of segmented sensor plates





Equivalent circuit analysis

- 3 dimensional fuel cell stack diagnosis
- Real time data analysis
- Optimized efficiency due to higher fuel utilization
- Higher lifetime by avoiding critical states

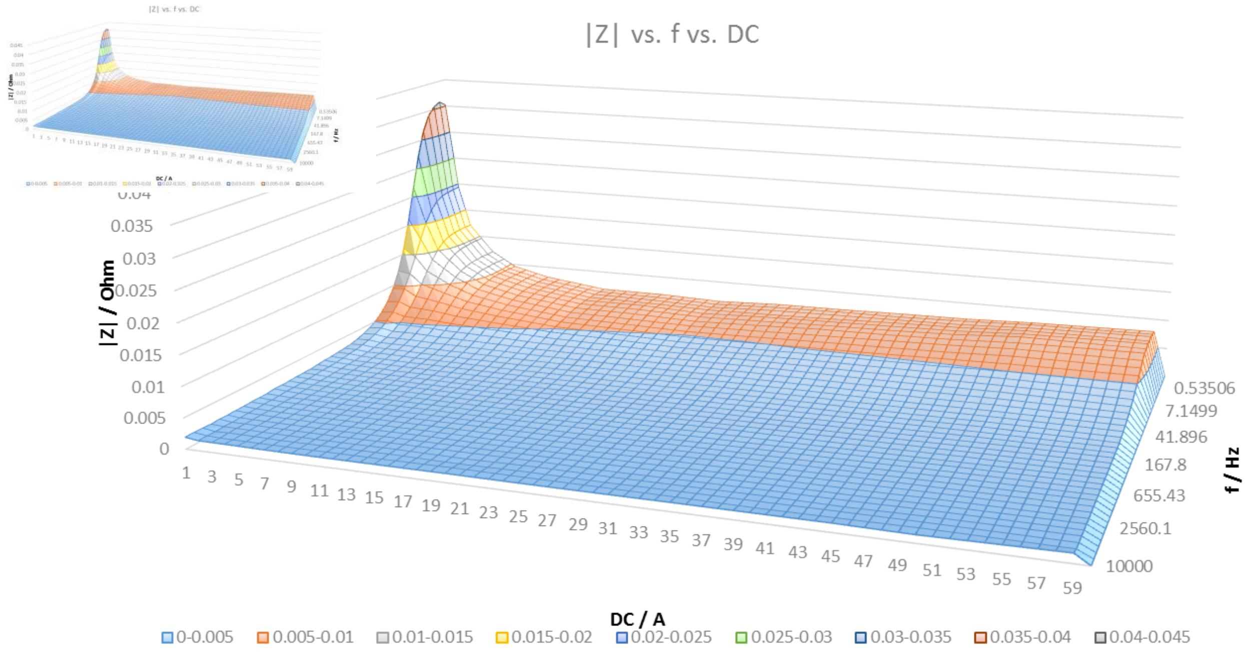


Dryout @ Channel #5 Cell 2
→ Increased LFR & HFR
→ Neighbourhood channels (#4 and #6) are slightly affected

Identifying Nonlinear Areas – Impedance Mapping

Identifying distinctive frequencies for THDA by means of electrochemical impedance spectroscopy at several operating points.

➔The relative change of the impedance with the operating point has to be high to observe harmonics.



An AC64-5 from IE is investigated to create the impedance map:

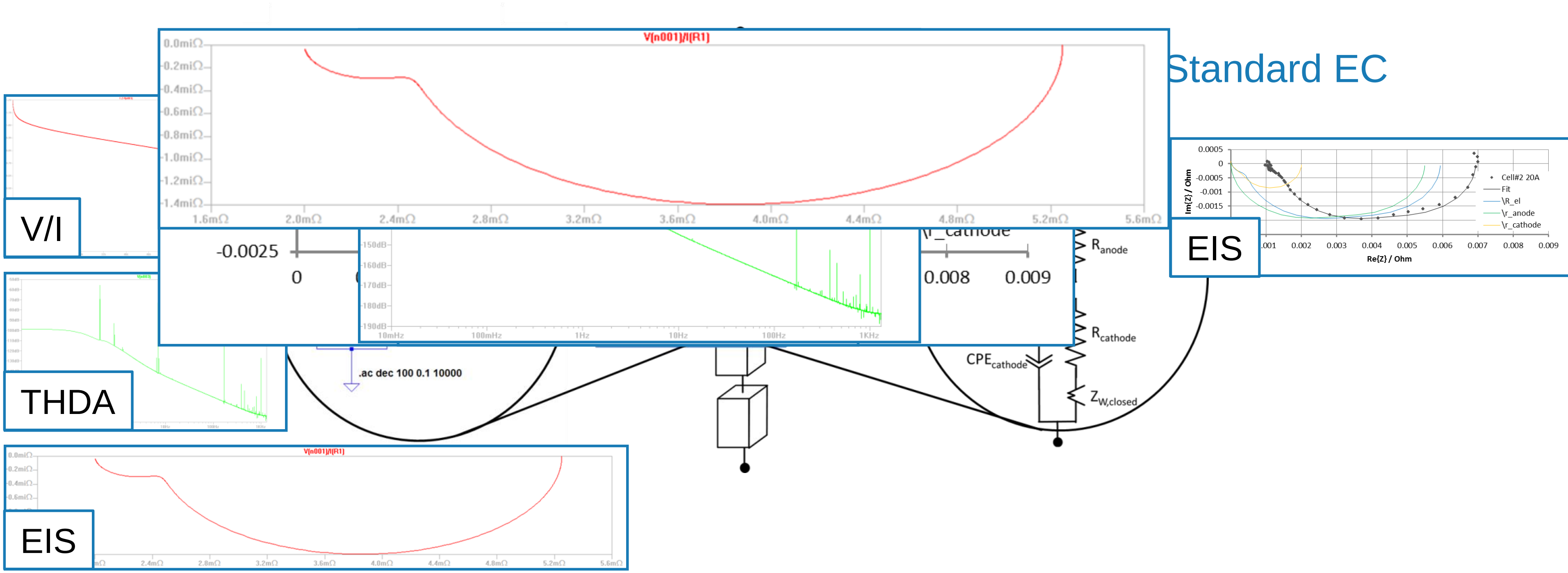
- at optimal conditions
- at harsh conditions

Spatial Large Signal Equivalent Circuits

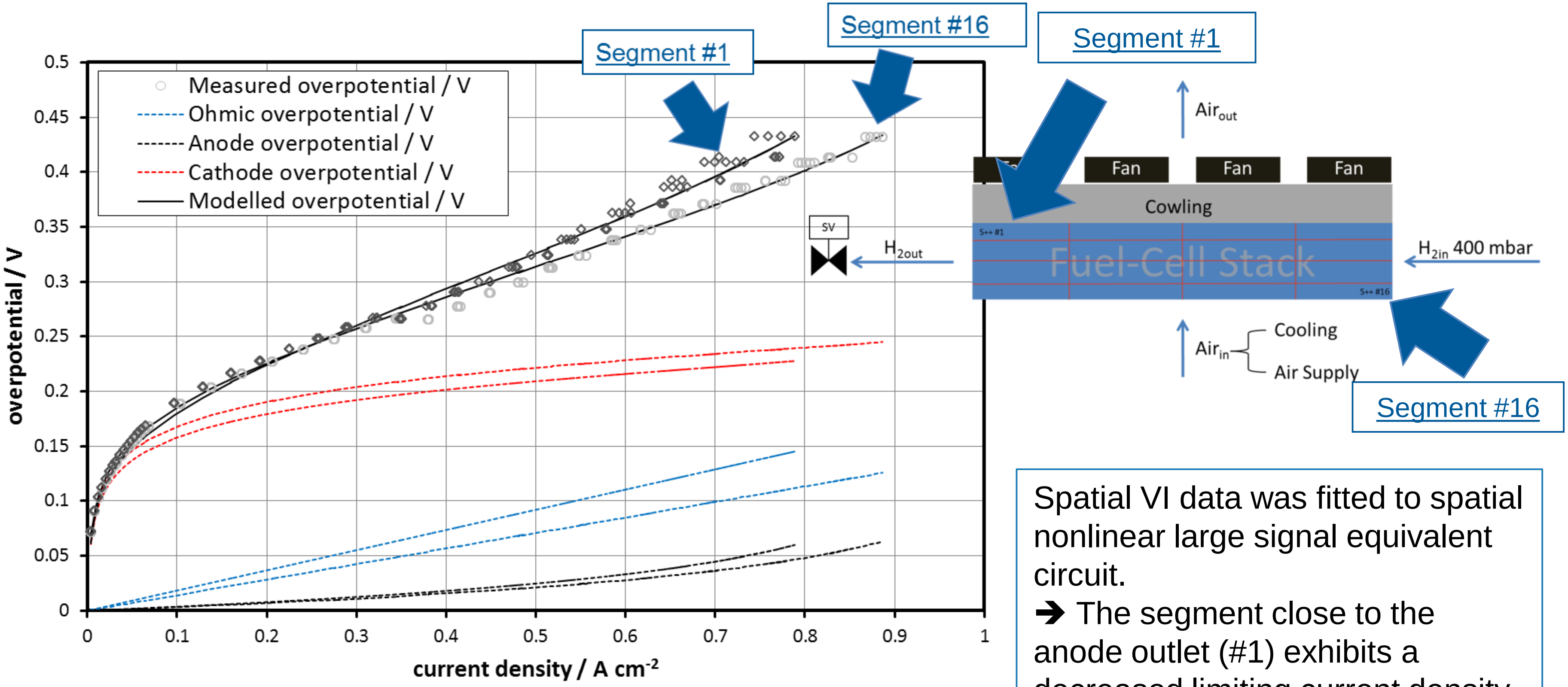
Large Signal Equivalent Circuits (EC) are developed. These enable the simulation of

- Polarisation Curves (V/I)
- Electrochemical Impedance Spectra (EIS)
- Harmonic Distortions (THDA)

of the whole stack, a single cell or a segment within a single cell.



Spatial VI curves and Data Fitting



Spatial VI data was fitted to spatial nonlinear large signal equivalent circuit.

➔ The segment close to the anode outlet (#1) exhibits a decreased limiting current density due to higher concentration polarisation compared to anode inlet segments (e.g. #16)

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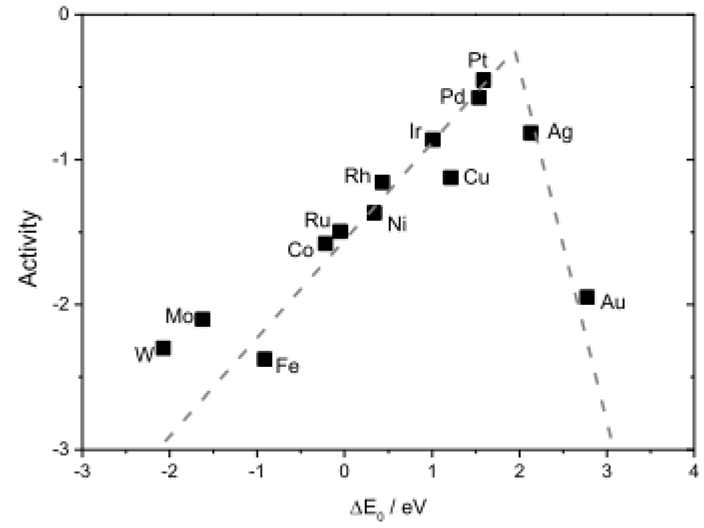
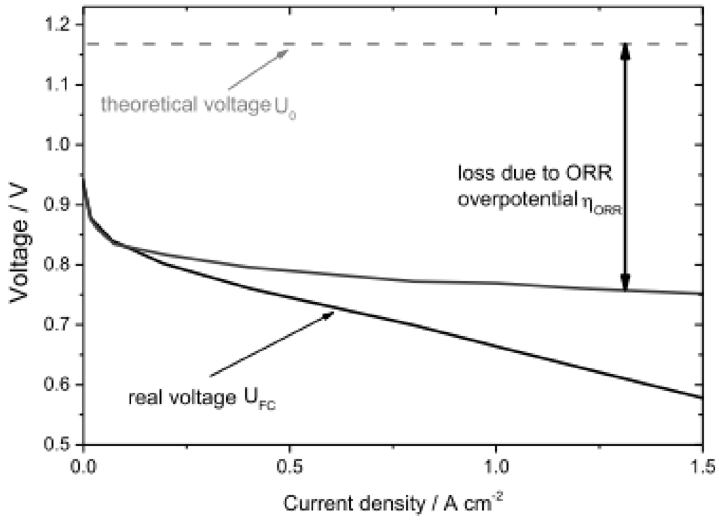
Resource saving catalysts

- Among all pure metals platinum offers the highest activity for reducing oxygen into water
- The slow reaction kinetics of the oxygen reduction reaction (ORR) of platinum is mainly responsible for the cell voltage drop during PEMFC operation
- Approx. 75% of the efficiency loss in PEM fuel cells are assigned to the generation of heat due to the ORR overpotential
- High loadings of platinum are used to compensate the slow reaction kinetics of the ORR

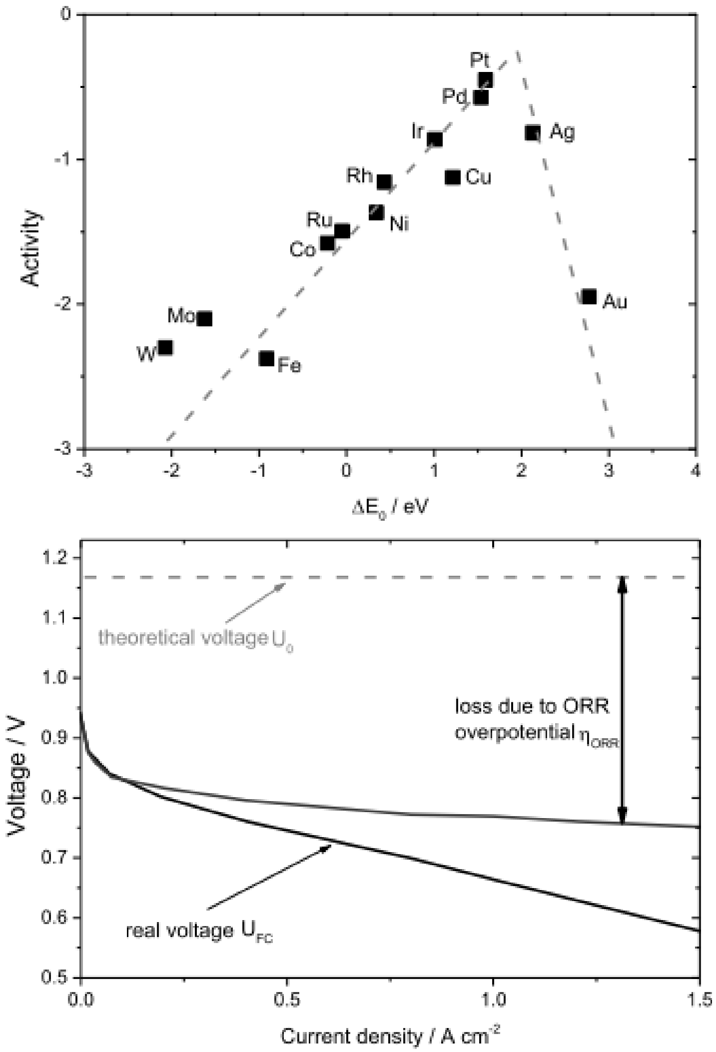




J.K. Nørskov,et al. J. Phys. Chem. B 108 (2004) 17886
H.A. Gasteiger et al. Appl. Catal. B Environ. 56 (2005) 9

Resource saving catalysts

- To achieve this challenging task, new catalysts having a higher activity than pure Pt need to be developed
- The operating conditions in a PEM fuel cell require a certain stability to concentrated acid and simultaneous electrochemical potential load
- one approach to this challenge is to increase the activity of platinum itself
- A strategy for increasing the activity of the platinum and at the same time reducing the precious metal loading is alloying platinum with other transition metals



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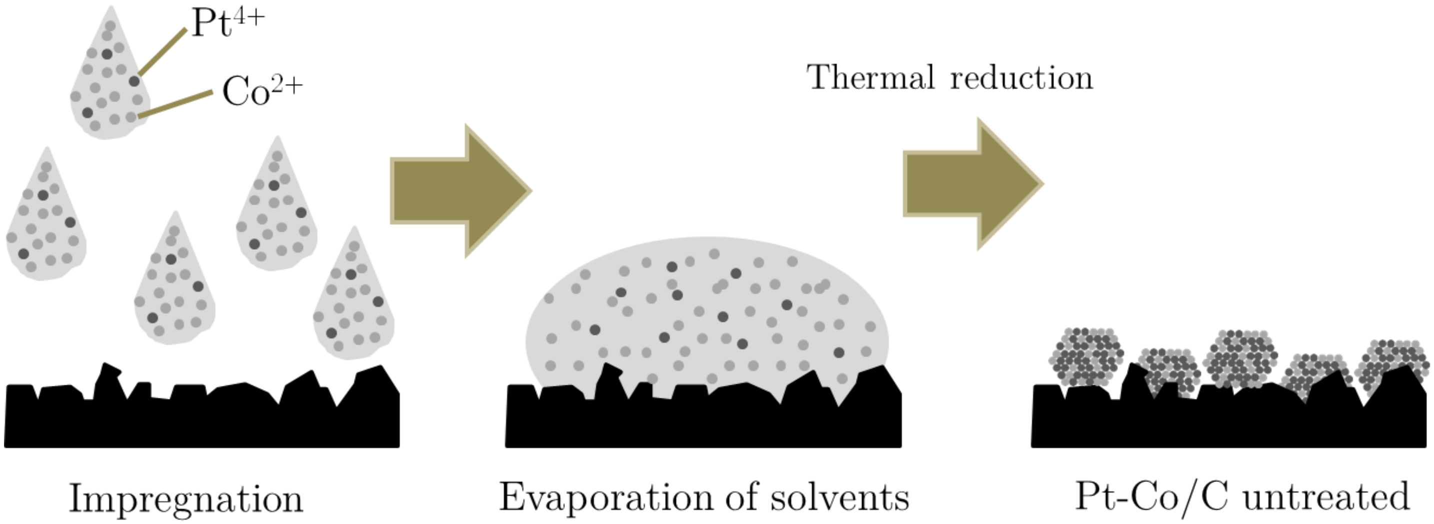
Resource saving catalysts



Pt^{4+}

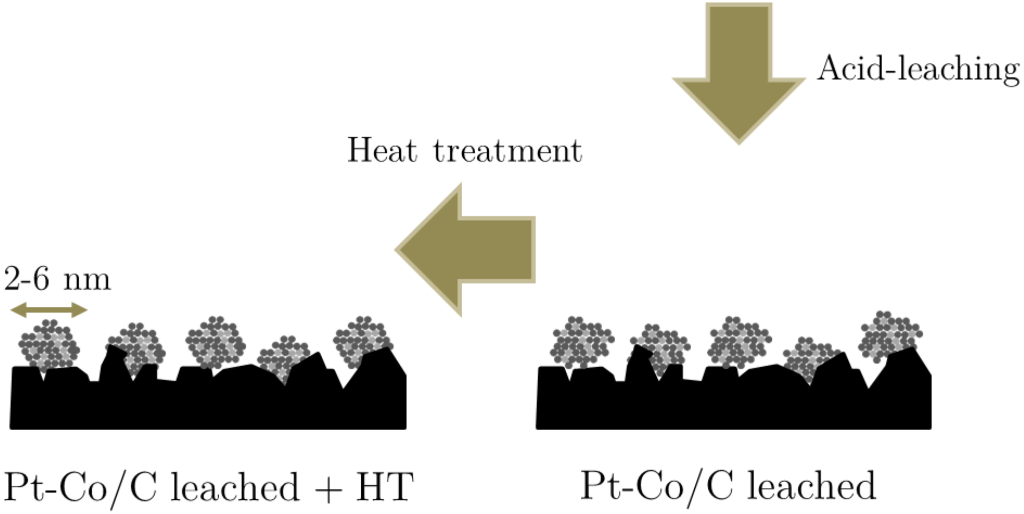
Co^{2+}

Thermal reduction

Impregnation

Evaporation of solvents

Pt-Co/C untreated



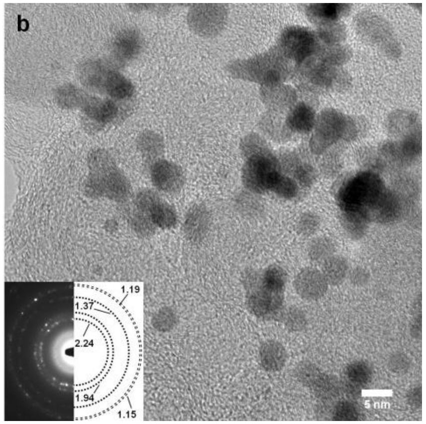
Acid-leaching

Heat treatment

2-6 nm

Pt-Co/C leached + HT

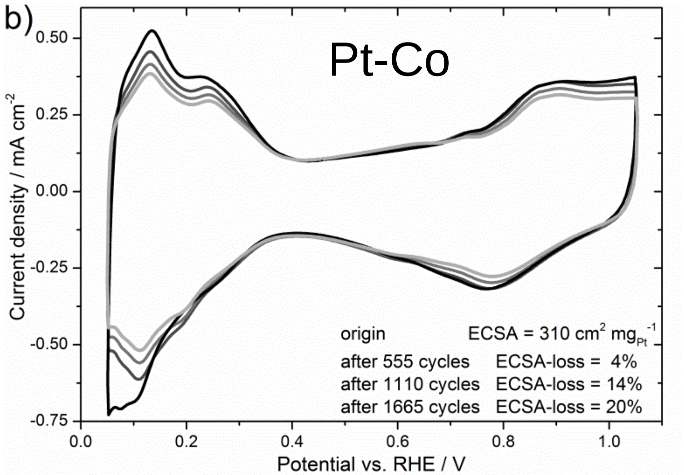
Pt-Co/C leached

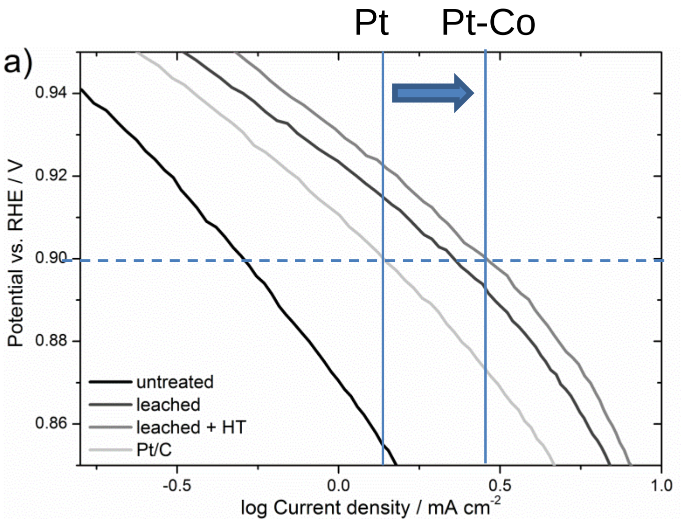


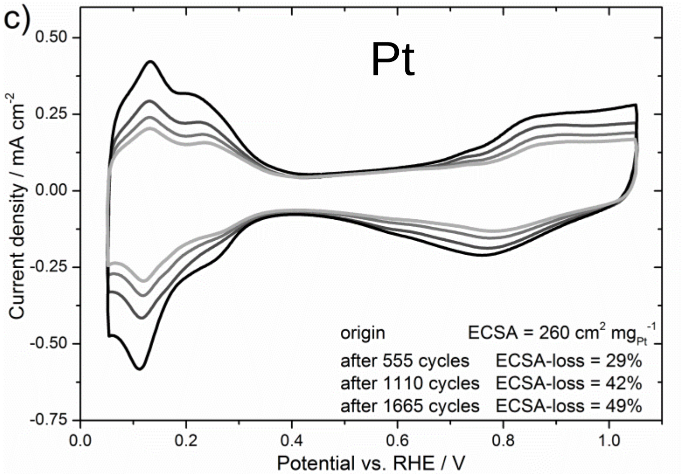
A.Schenk et al. J. Power Sources 266 (2014) 313

Resource saving catalysts

- In comparison to state-of-the-art pure Pt the prepared platinum-cobalt catalysts showed :
  - a higher electrochemical active surface area
  - 2.5 times higher stability in AST degradation
  - 2-fold higher mass activity towards ORR







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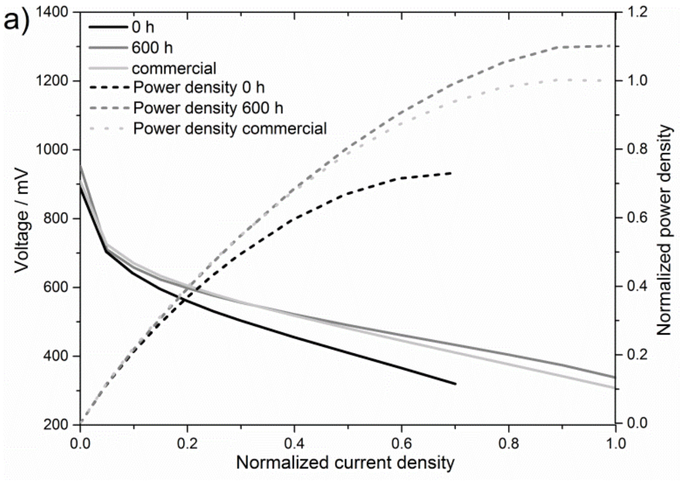
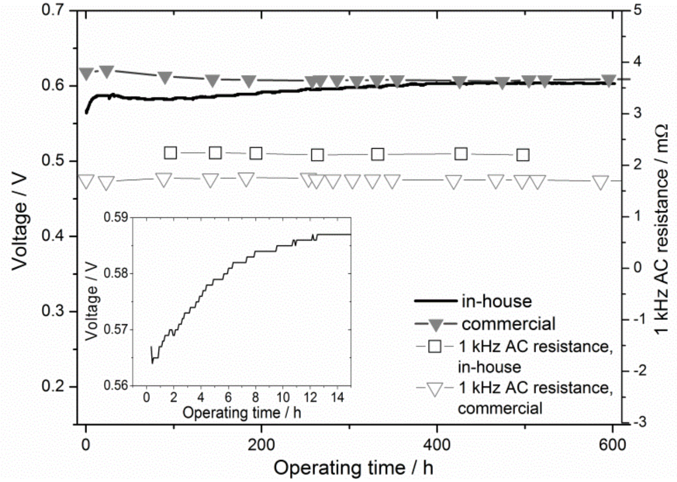
Resource saving catalysts

- Platinum-cobalt catalysts enabled a reduction of the platinum loading by 20% while maintaining the performance of the PEM fuel cell
- Even though the platinum loading was reduced a higher power density was reached by using Pt-Co instead of Pt
- The long term stability and performance of the fuel cell were not compromised by using the Pt-Co catalysts with the reduced platinum loading





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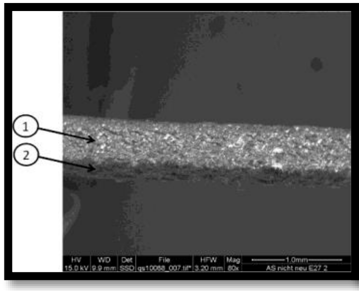
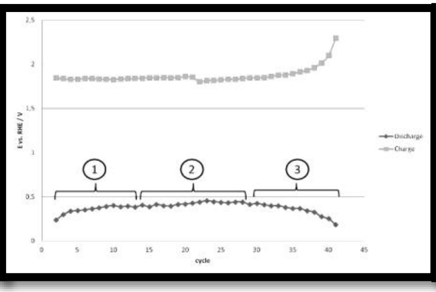
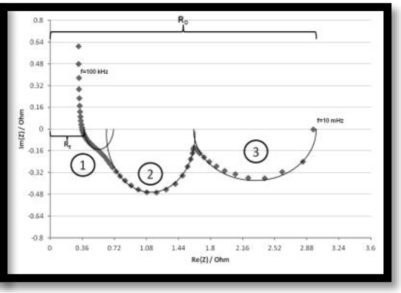
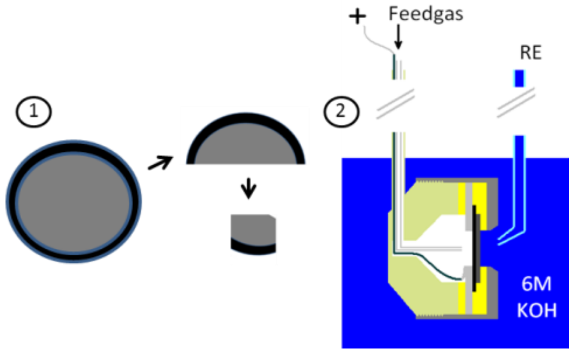
Zinc Air Battery: New Materials for the rechargeable Zinc Air Battery

funded by the Austrian Federal Ministry of Transport, Innovation and Technology (BMVIT) and The Austrian Research Promotion Agency (FFG) through the program a3plus (01/2012-06/2012)









Results

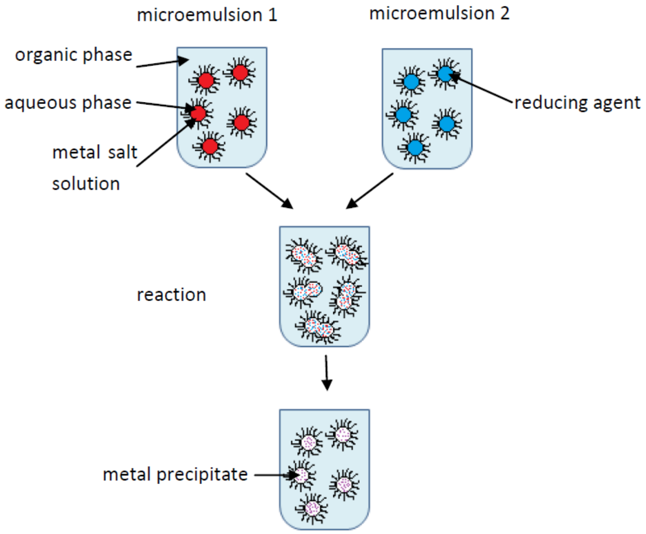
- Equivalent circuit which describes aging effects
- Prototype was developed and operated

Methods

- Accelerated stress tests (AST)
- Continuous State of health monitoring by Electrochemical Impedance Spectroscopy (EIS)

Pt-free catalysts for ethanol oxidation reaction

- Development of Pt-free anode catalysts
  - Bi- or polymetallic
  - Ni-polymer-complexes
- Focus on nickel-based catalysts
- Catalyst synthesis
  - Electroless precipitation
    - water in oil (w/o) microemulsion
    - Reduction with $NaBH_4$



A. Hofer, Development of Pt-free anode catalysts for alkaline direct ethanol fuel cells, Graz University of Technology, 2013.

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Chemical Hydrogen Storage System

Organic Borohydride based H_2 storage system

Liquid storage medium

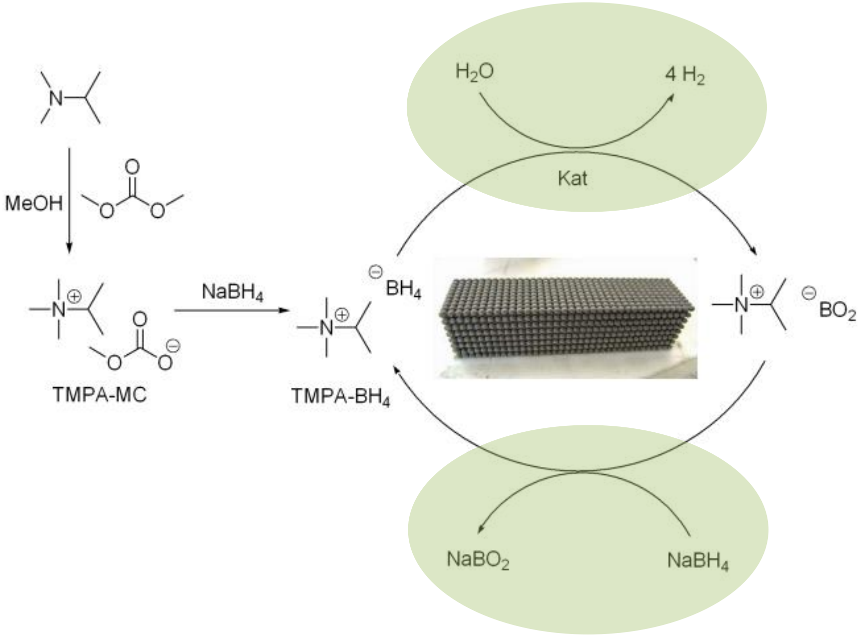
- Properties of ionic liquids
- Aqueous solution
- Pumpable

Catalytic hydrogen release

- Ambient temperature
- Ambient or elevated pressure

Characteristics:

- High long-term stability
- Not flammable
- H_2 storage density of 4.5 wt.%
- Various organic cations



Chemical Hydrogen Storage System

Hydrogen release

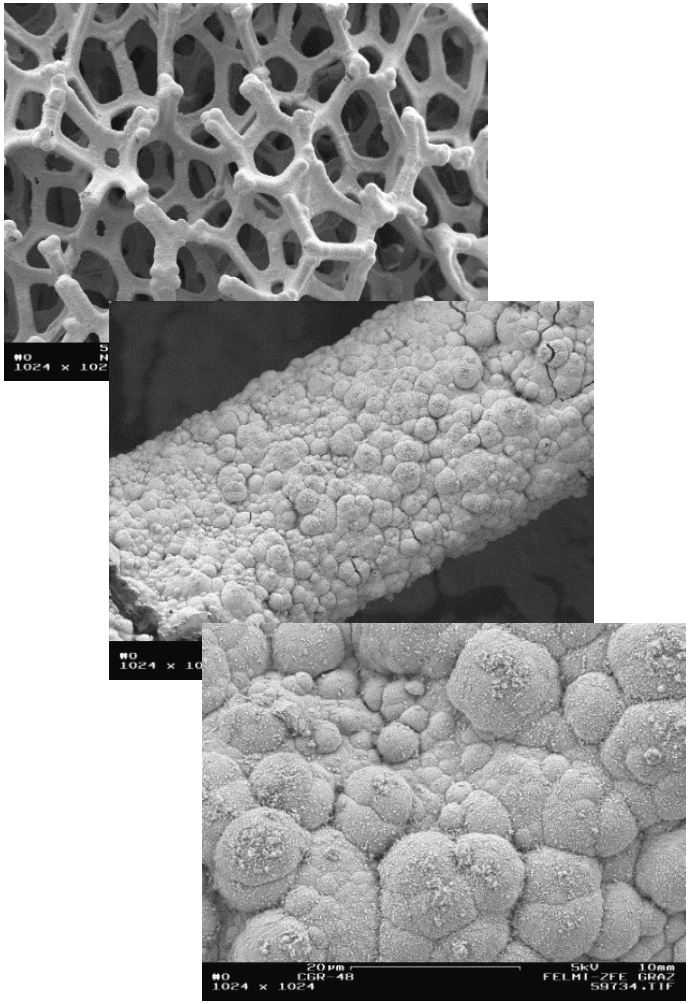
- Catalytic hydrolysis
  - Foam based catalysts
  - Non-noble metals only

- Release reaction:

$$IL\text{-}BH_4 + 2H_2O \rightarrow IL\text{-}BO_2 + 4H_2$$

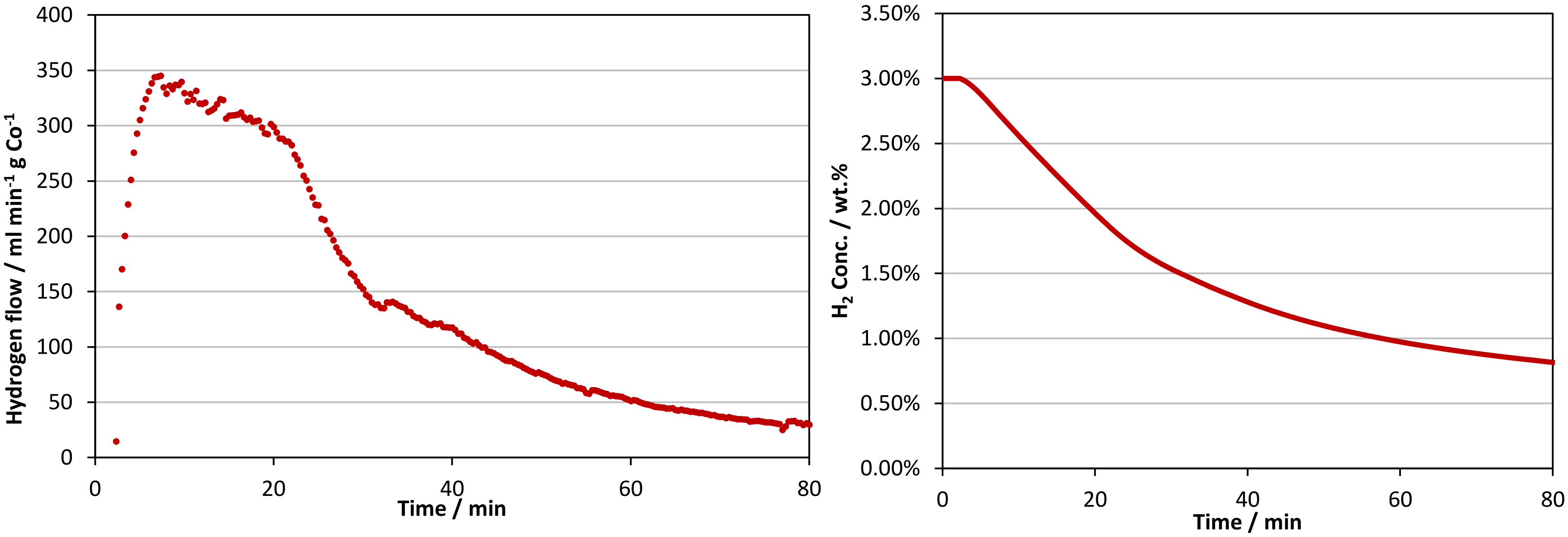
- PEM grade hydrogen

- Research tasks
  - Recycling process of storage medium
  - Catalyst development
  - Reactor and system design



Chemical Hydrogen Storage System

- Catalytic hydrogen release



Conditions: **60°C, unstirred**

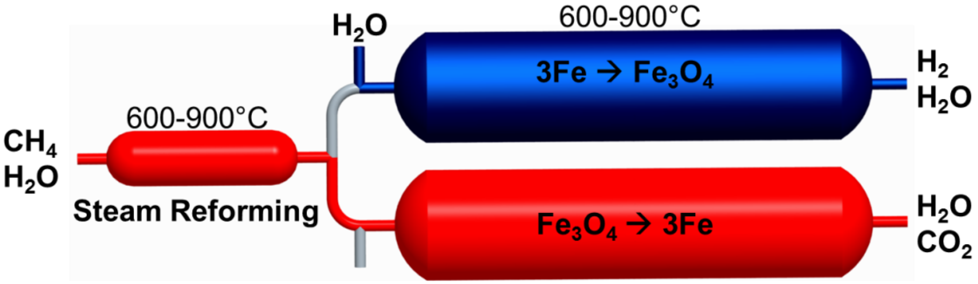
Catalyst: **0.25 cm², 22.9 mg Co**

Hydrogen release is complete in reactor system

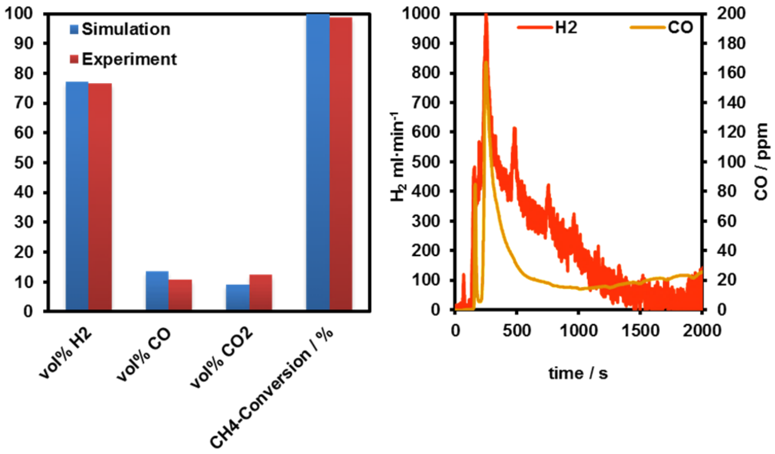
The reformer-steam iron process

The reformer-steam iron process

The **steam iron** enables **decentralised production of pure and compressed hydrogen** in one simple and compact unit.

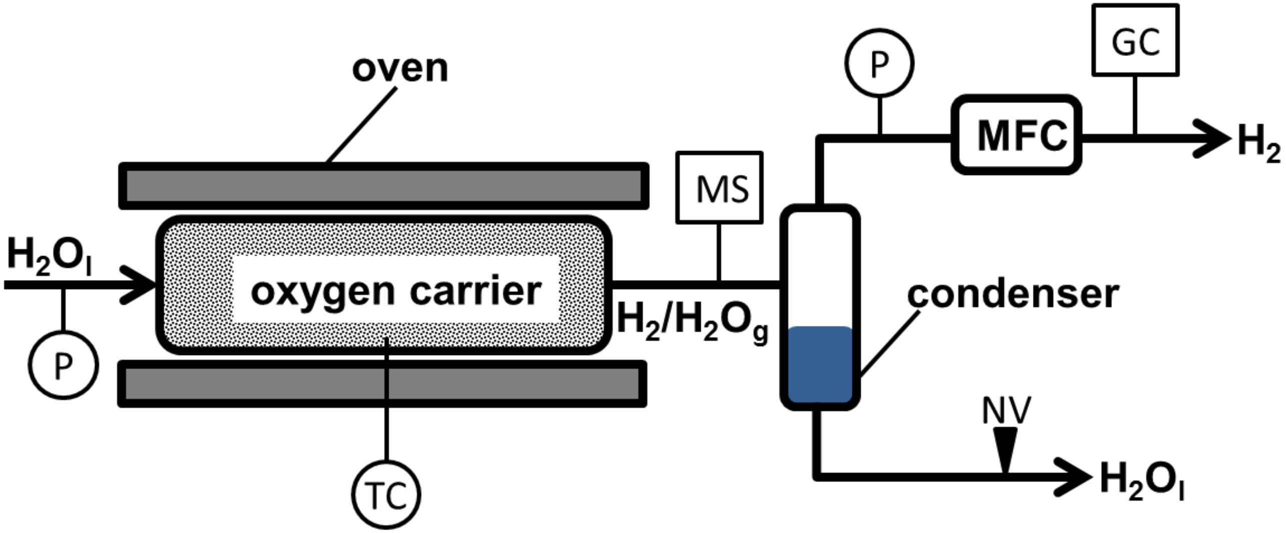


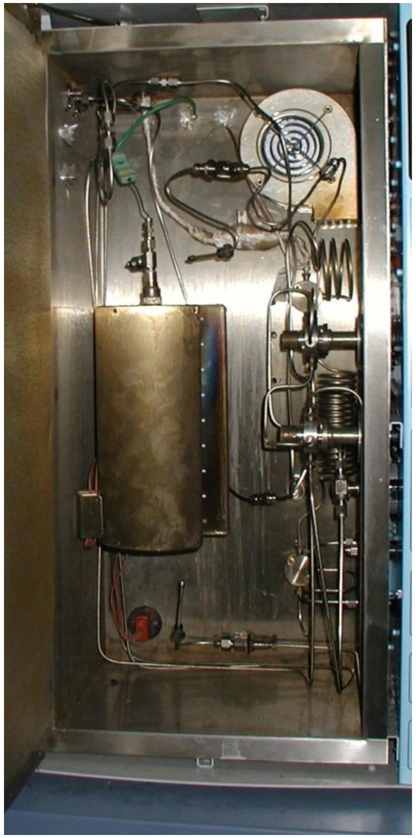
- High overall efficiency eliminating the transportation of hydrogen
- No additional purification systems required
- Safe and stable hydrogen storage technology
- Very high efficiency by directly producing hydrogen at elevated pressure



Prototype development

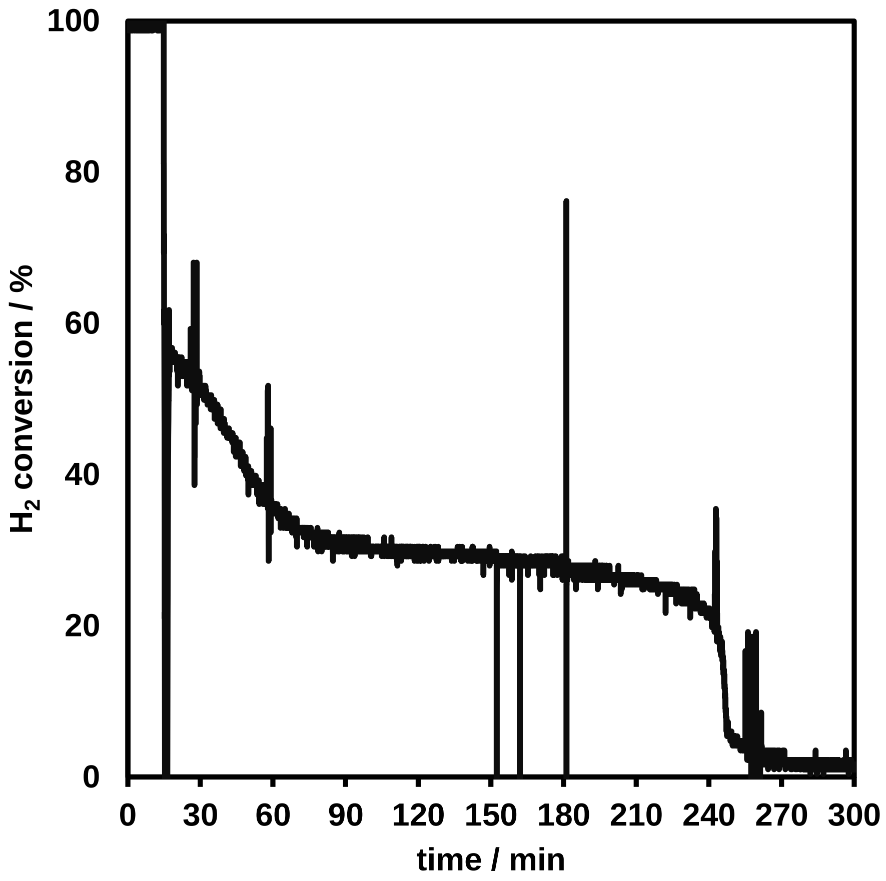
High pressure hydrogen production

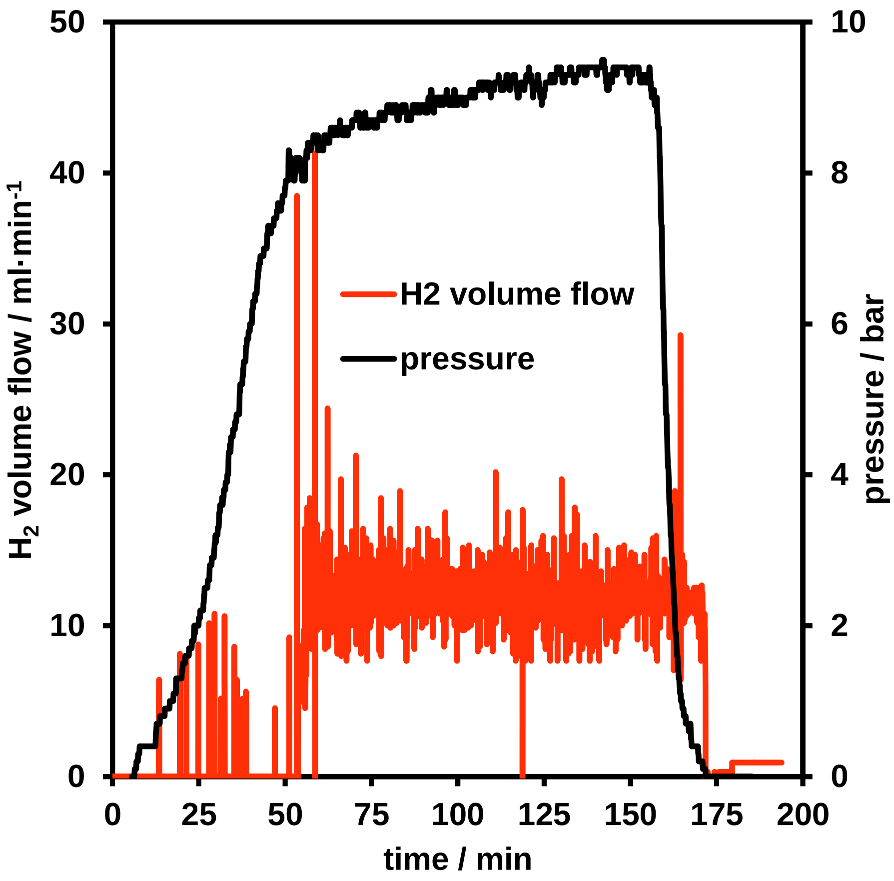




P, TC…	pressure and temperature measurement
NV…	needle valve
MFC…	mass flow controller
GC/MS…	gas analysis

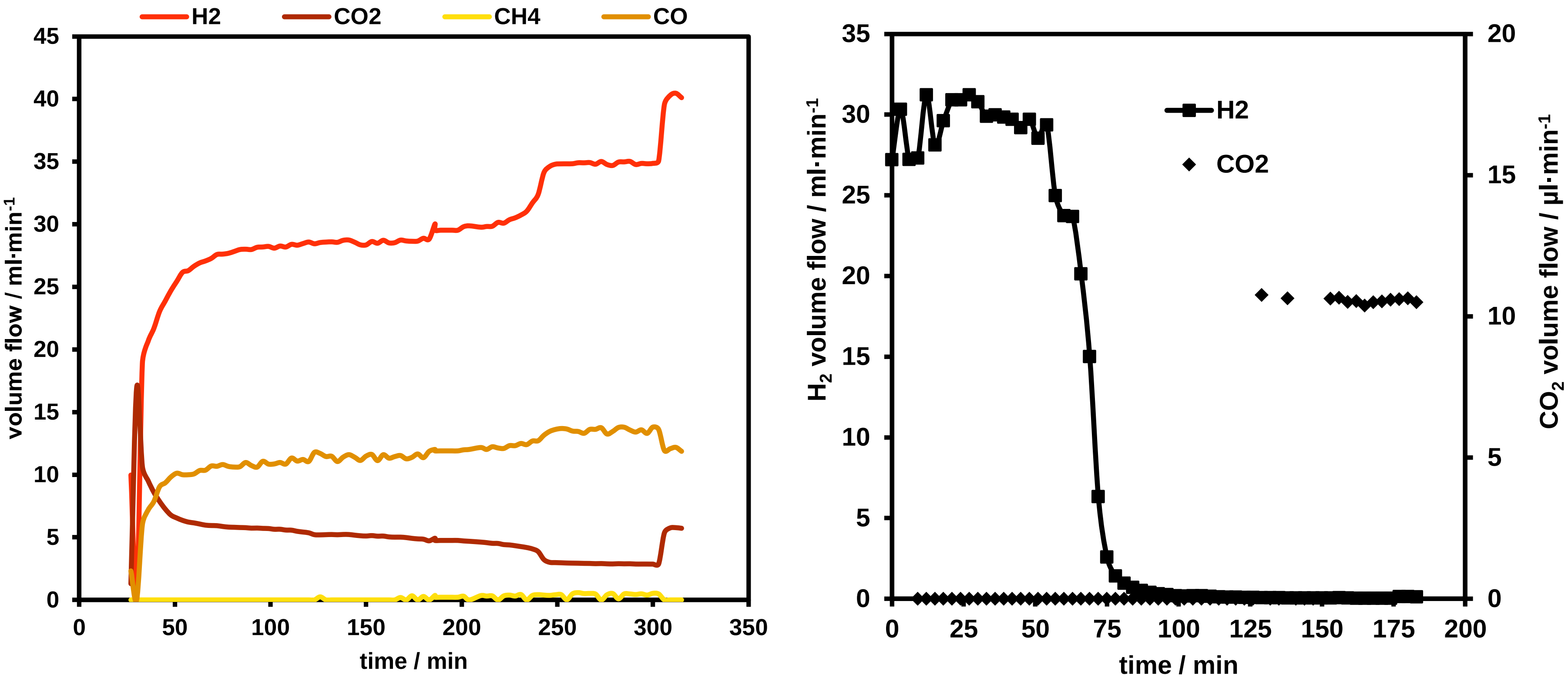
High pressure hydrogen production





- Left: reduction reaction with hydrogen at ambient pressure
- Right: the consecutive pressurised oxidation

High pressure hydrogen production



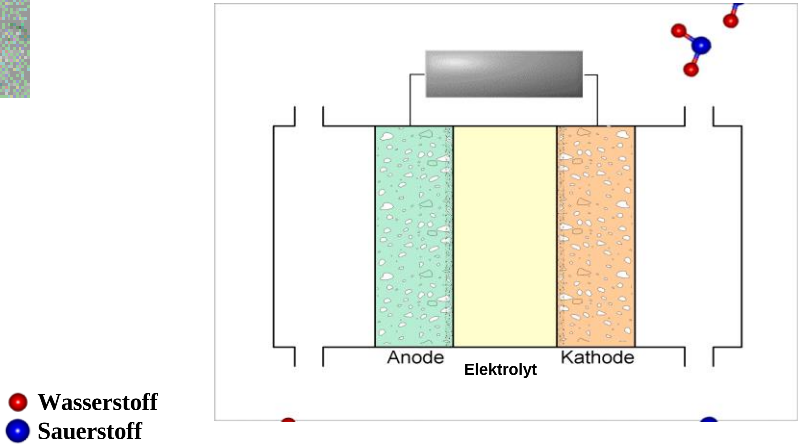
The reduction of a Fe-based oxygen carrier with syngas (left) and its steam-oxidation at a pressure of 8 bar (right).

A small amount a CO2 was detected, with an overall concentration of 700 ppm during the oxidations

CO was not detected

Types of Fuel Cells

Prof. Karl Kordesch‘s Austin A40 (1970)



Content

- Introduction to R&D at CEET
  - Degradation PEFC
  - Pinhole detection
  - Advanced fuel cell analysis
  - Catalyst development
  - Hydrogen storage
  - Hydrogen production
  - **International Energy Agency**
  - **Yearly Summer School**

International Energy Agency - Implementing Agreement on Advanced Fuel Cells

Working Party on Fossil Fuels

Implementing Agreements:

- ☐ Clean Coal Science
- ☐ Enhanced Oil Recovery
- ☐ Fluidized Bed Conversion
- ☐ Greenhouse Gas R&D Programme
- ☐ IEA Clean Coal Centre
- ☐ Multiphase Flow Sciences

Intersectoral:

- ☐ Climate Technology Initiative (CTI)
- ☐ Energy Technology Systems Analysis Programme (ETSAP)
- ☐ Energy Technology Data Exchange (ETDE)

Working Party on Renewable Energy

Implementing Agreements:

- ☐ Bioenergy
- ☐ Geothermal
- ☐ Hydrogen
- ☐ Hydropower
- ☐ Ocean Energy Systems
- ☐ Photovoltaic Power Systems
- ☐ Renewable Energy Technology Deployment
- ☐ Solar Heating and Cooling
- ☐ Solar Paces
- ☐ Wind Energy Systems

Working Party on Energy End Use Technologies

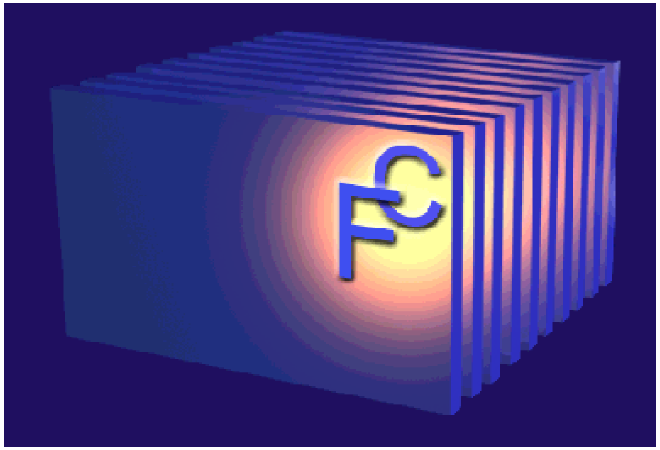
Implementing Agreements:

- ☐ Advanced Fuel Cells
- ☐ Advanced Motor Fuels
- ☐ Advanced Materials for Transportation
- ☐ High-Temperature Superconductivity
- ☐ Demand-Side Management
- ☐ District Heating and Cooling
- ☐ Emissions Reduction in Combustion
- ☐ Industrial Energy Related Technologies
- ☐ Buildings and Communities (ECBCS)
- ☐ Energy Storage
- ☐ Heat Pumping Technologies
- ☐ Hybrid and Electric Vehicles
- ☐ Electricity Networks Analysis
- ☐ Efficient Electrical End Use Equipment R&D (ENARD)
- ☐ International Smart Grid Action Network (ISGAN)

Fusion Power Co-ordinating Committee

Implementing Agreements:

- ☐ Environmental, Safety and Economic Aspects of Fusion Power
- ☐ Fusion Materials
- ☐ Cooperation on Tokamak programmes
- ☐ Nuclear Technology of Fusion Reactors
- ☐ Plasma Wall Interaction in TEXTOR
- ☐ Reversed Field Pinches
- ☐ Stellarator Heliotron Concept
- ☐ Spherical Tori

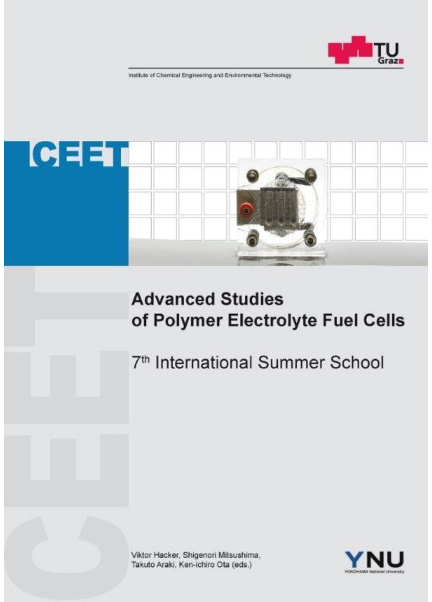


- Representative in Annex PEFC
- Representative in Annex Portable Fuel Fells

http://www.ieafuelcell.com/

International Summer School on Advanced Studies of Polymer Electrolyte Fuel Cells

- organized in co-operation between the **Yokohama National University (YNU)**, Japan and **Graz University of Technology (TUG)**
- internationally recognized experts as lecturers in the field of fuel cell research
- lectures include fundamental studies and advanced aspects of PEFCs.



Institute of Chemical Engineering and Environmental Technology

CEET

Advanced Studies
of Polymer Electrolyte Fuel Cells

7th International Summer School

Viktor Hacker, Shigenori Mitsushima,
Takuto Araki, Ken-ichiro Ota (eds.)

YNU

Thank you!

IEA RESEARCH COOPERATION

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