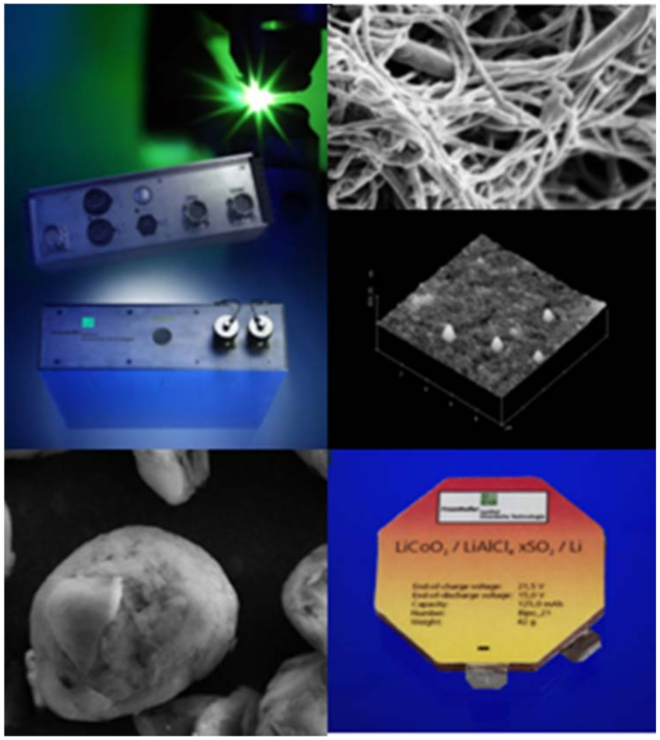
Direct Ethanol Fuel Cells



Fuel Cell Seminar & Exhibition 2008
Phoenix, AZ (USA)

30th October 2008

Carsten Cremers,
Florina Jung, Birgit Kintzel, Domnik Bayer,
Martin Joos, Jens Tübke, Michael Krausa

Applied Electrochemistry
Fraunhofer-Institute for Chemical Technology

Fraunhofer Institut Chemische Technologie

Outline

- Ethanol as fuel for fuel cells
- The Fraunhofer Team DEFC
    - **DEFC electrocatalysts**
    - DEFC membranes
    - DEFC cells and stacks
    - DEFC BoP-components and systems
- **Conversion of ethanol in anion exchange membrane fuel cells**
- **Denaturing additives compatible with fuel cells**
- Conclusions and outlook

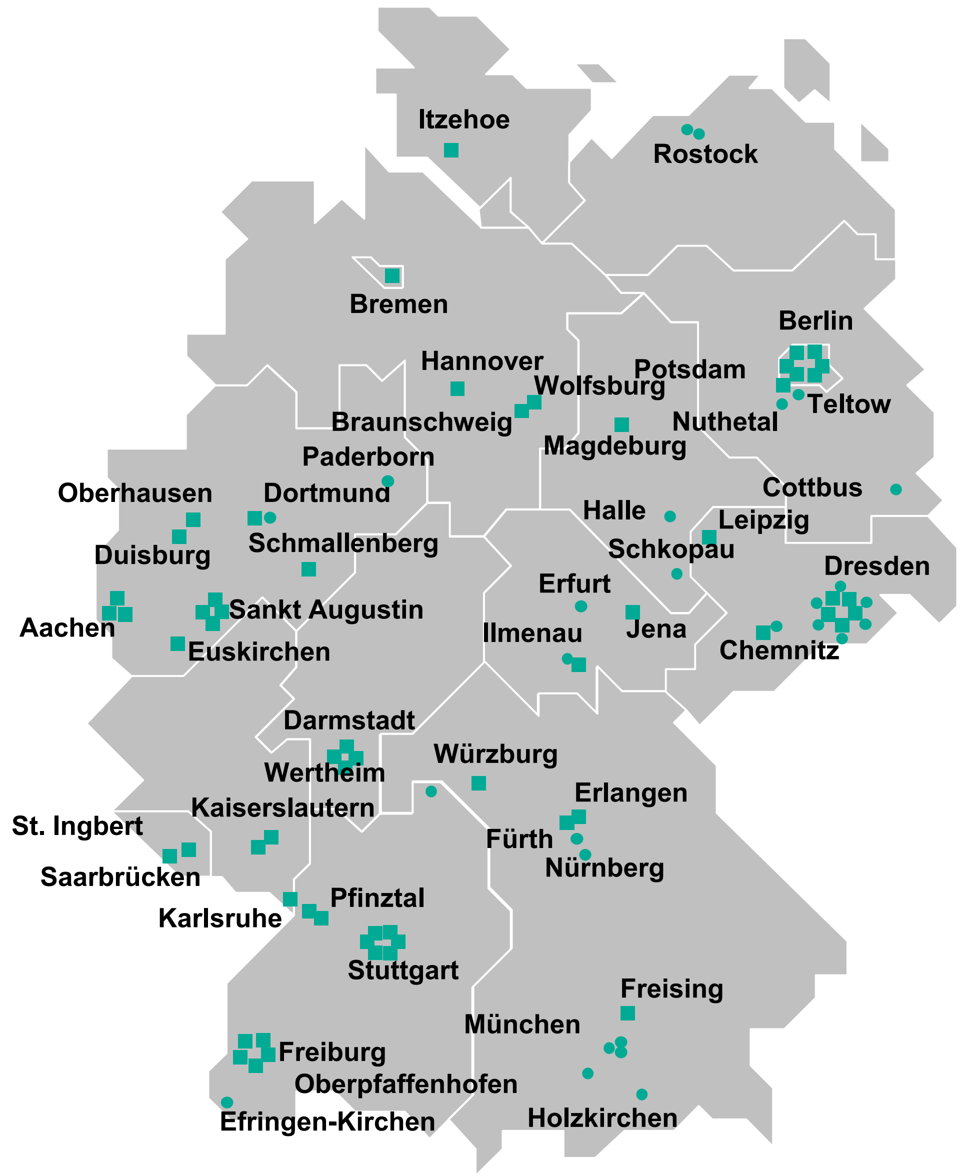
The Fraunhofer Institute for Chemical Technology ICT

and its Department for Applied Electrochemistry AE

The Fraunhofer-Gesellschaft

Locations in Germany

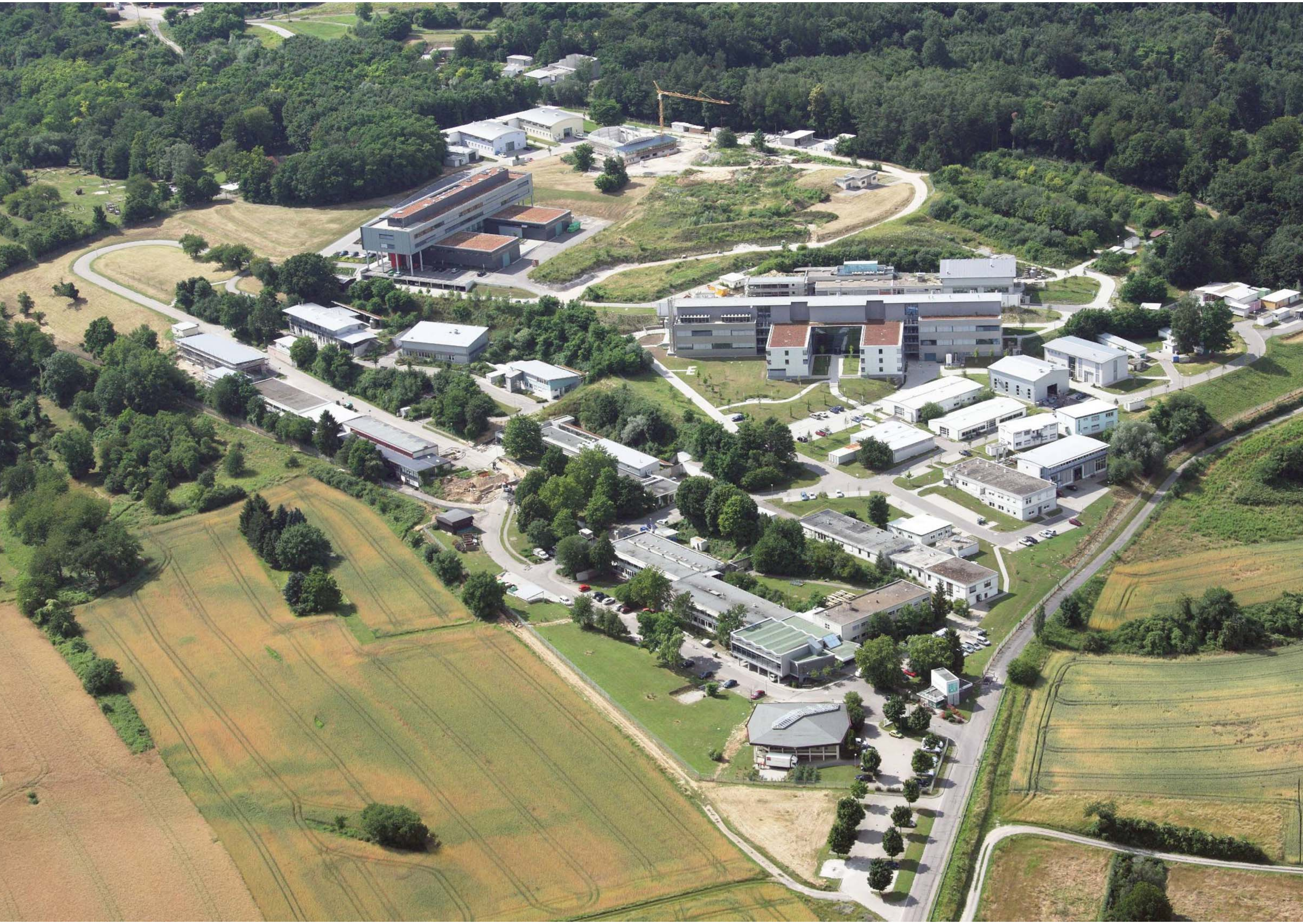
- 56 Institutes
  in 40 locations
- 13,000 employees
- Approx. 1.2 billion Euros
  annual research budget



Fraunhofer Institut Chemische Technologie

ICT – Fraunhofer Institute for Chemical Technology

■ Established	1959
■ Location	Pfinztal Berghausen
Branch	Wolfsburg
■ Staff (full-time equivalent)	410 (approx. 315)
Established positions	282
Scientists, PhD Candidates	102
Graduates, laboratory technicians	89
Workshops, laboratory assistants	69
Administration	39
Trainees	11
Scientific assistants, work experience placements	approx. 100
■ Budget 2007	26.6 Mio €
■ Total site area	200.000 m^2
Laboratories, offices, Pilot plants, workshops	ca. 12.000 m^2
Test sites, infrastructure	ca. 12.000 m^2



ICT Organisation Chart

Institute Director
Prof. Dr. P. Elsner

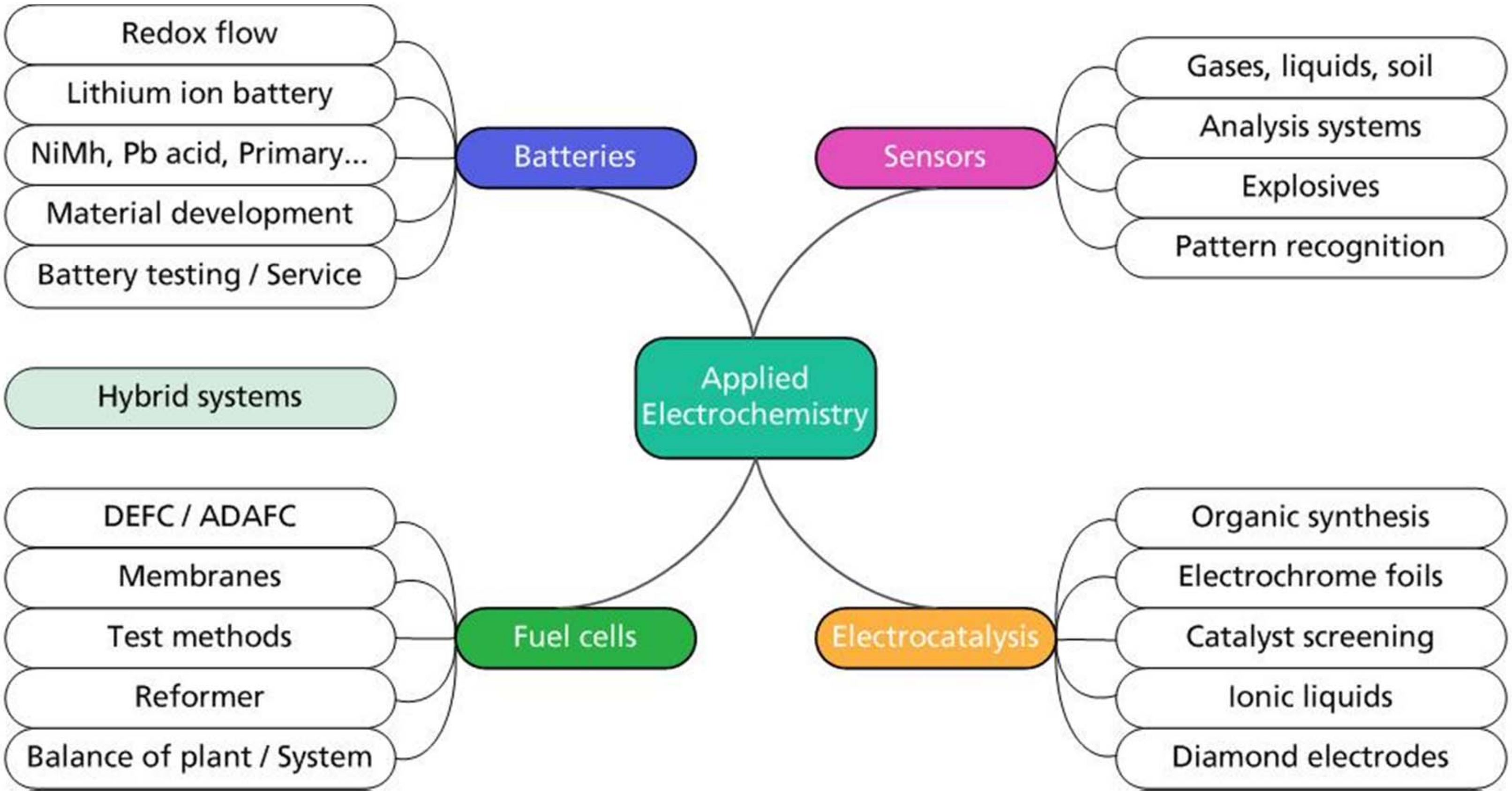
Controlling
C. Steuerwald

General Administration
Dr. B. Hefer, C. Steuerwald
66 employees

General Management
Dr. S. Tröster
12 employees

Energetic Materials	Energetic Systems	Applied Electrochemistry	Environmental Engineering	Polymer Engineering
Dr. H. Krause Dr. T. Keicher Dr. S. Löbbecke	W. Eckl, G. Langer Dr. N. Eisenreich	Dr. J. Tübke Dr. K. Pinkwart	R. Schweppe Dr. J. Woidasky	Dr. F. Henning Dr. J. Diemert R. Bräuning
76 employees	57 employees	30 employees	58 employees	85 employees

Overview Department Applied Electrochemistry



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Ethanol as fuel for fuel cells

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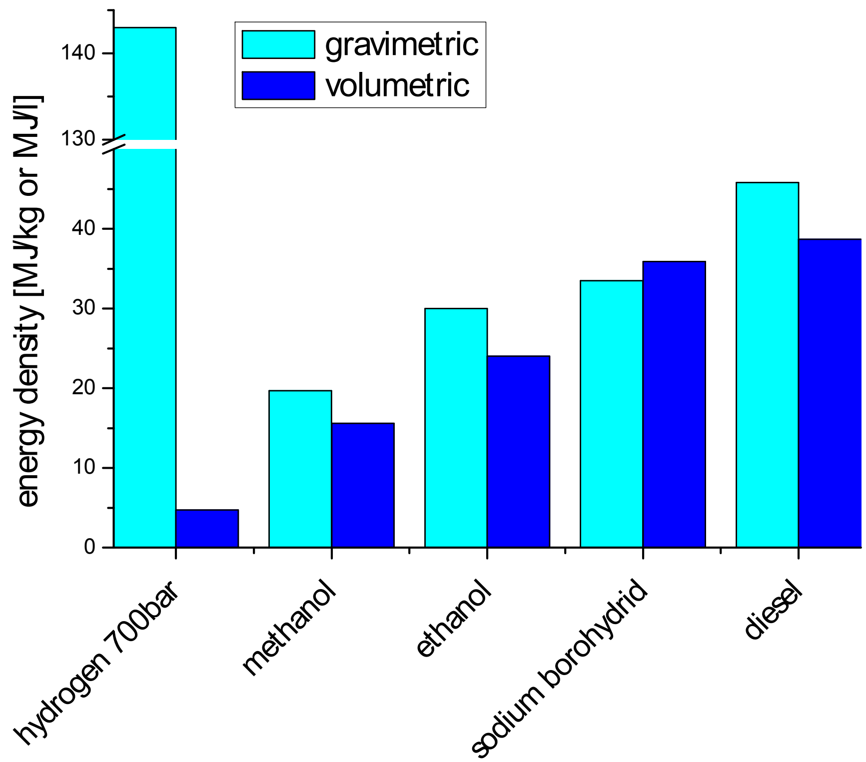
Ethanol as fuel for fuel cells

Fuel requirements for small, (military) fuel cells :

- high energy storage density
- high availability worldwide
  - existing distribution infrastructure
  - low demands to purity
- low risks
  - toxicity
  - reaction to bullet impact
- simple handling



Theoretical energy storage densities for fuels considered for use in small fuel cells.

Ethanol as fuel for fuel cells

Properties of fuels currently considered for use in small fuel cells

Property	Hydrogen 700bar	Sodium borohydride	Methanol	Ethanol	Diesel
Energy storage density	--*	+	O	+	++
Mass of storage reduces with fuel consumption	(*no*)*	no	yes	yes	yes
Gaseous products	no	no	yes	yes	Yes
Availability	-	--	O	++	++
Simplicity of handling	O	O	O (++)	++	++
Potential risks					
toxic	no	no	yes	no	low
explosive	yes(*)	no	no	no	no
flammable	highly	highly	highly	highly	yes
Use in direct converting fuel cells	commercial	under development	commercial	under development	under development
Use as hydrogen source		commercial	commercial	under development	under development

* Because of tank

Ethanol as fuel for fuel cells

Comparison Methanol and Ethanol

	Methanol	Ethanol
Physical properties		
energy density [MJ/kg]	19,7	30,0
boiling point [°C]	64,7	78,0
vapour pressure at 20°C [mbar]	129	58
Other properties		
permitted form of distribution	packaged only	bulk
availability	special supply chain	super market
standard grade	technical without additives	denatured

The logistic footprint of an ethanol-based power supply solution could be much smaller than that of a methanol-based solution, due to better availability and bulk distribution.

Only a suitable denaturing additive needs to be found.

The Fraunhofer Team DEFC

Fraunhofer Institut Chemische Technologie

Competences of the Fraunhofer-Team DEFC

Fraunhofer Institute for	Competences
■ Chemical Technology ICT	■ catalysts
■ Reliabilty and Micro Integration IZM	■ cell design, micro fluidics, micro pumps & valves
■ Interfacial Energeering and Biotechnology IGB	■ membranes
■ Solar Energy Systems ISE	■ fuel cell systems, passive air & fuel suppy
■ Integrated Circuits IIS	■ electronics, battery management
■ Systems and Innovation Research ISI	■ market analysis and standards

Electro-catalytic oxidation of ethanol

Supposed mechanism of the ethanol oxidation on platinum in acidic media

Bold lines: reaction steps leading to the known products (coloured) and corresponding achievable energy densities at 100% yield of the respective product.

$CH_3CH_2OH + Pt \rightarrow Pt(OCH_2\text{-}CH_3) + H^+ + e^-$

$CH_3CH_2OH + Pt \rightarrow Pt(CHOH\text{-}CH_3) + H^+ + e^-$

$Pt(OCH_2\text{-}CH_3) + Pt \rightarrow 2\,Pt + CHO\text{-}CH_3 + H^+ + e^-$ ***4.3 MJ/kg***

$Pt + CHO\text{-}CH_3 \rightarrow Pt(CO\text{-}CH_3) + H^+ + e^-$

$Pt\,(CO\text{-}CH_3) + Pt \rightarrow Pt\text{-}CO + Pt\text{-}CH_3$

$H_2O + Pt \rightarrow PtOH + H^+ + e^-$

$Pt_x(CO) + PtOH \rightarrow (x+1)Pt + CO_2 + H^+ + e^-$ ***28.8 MJ/kg***

$Pt\text{-}CH_3 + Pt\text{-}H \rightarrow 2\,Pt + CH_4$

$CHO\text{-}CH_3 + Pt\text{-}OH \rightarrow Pt + CH_3COOH + H^+ + e^-$ ***10.1 MJ/kg***

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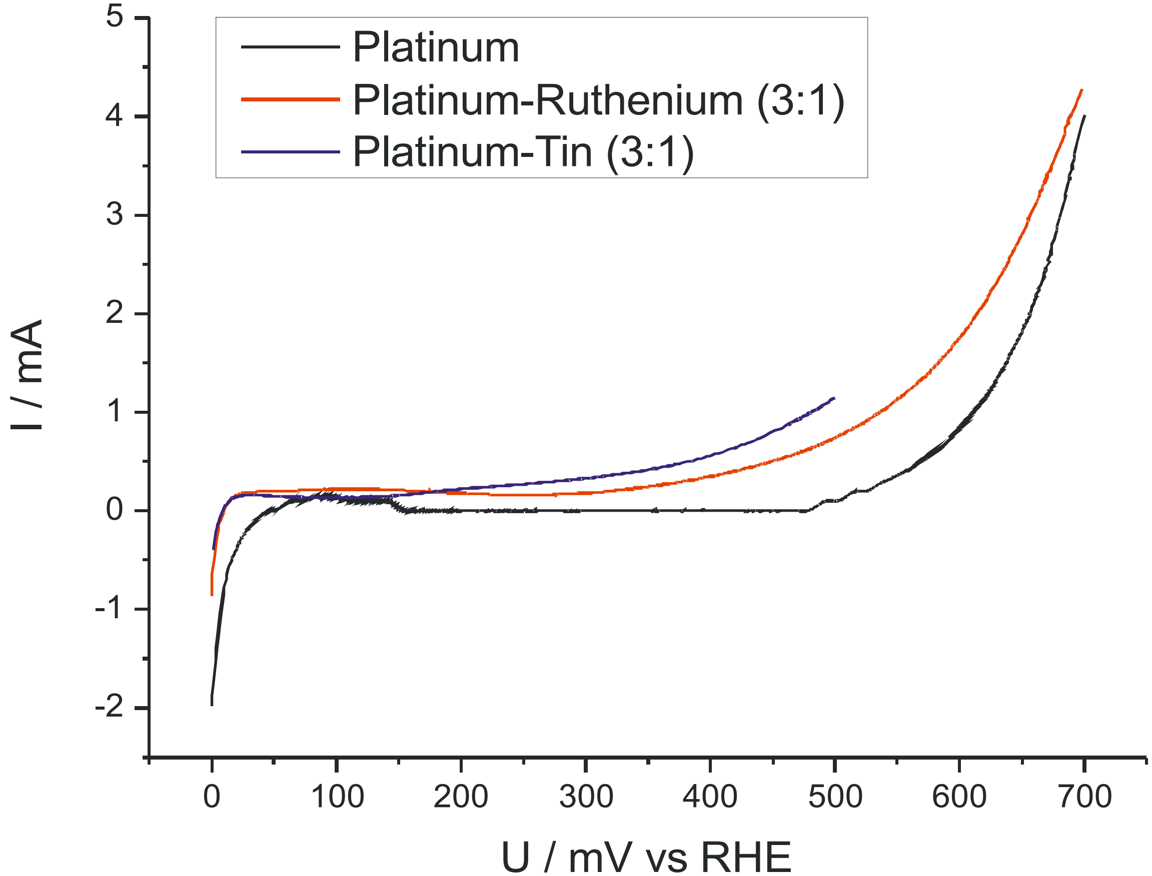
Electro-catalytic oxidation of ethanol in acidic media

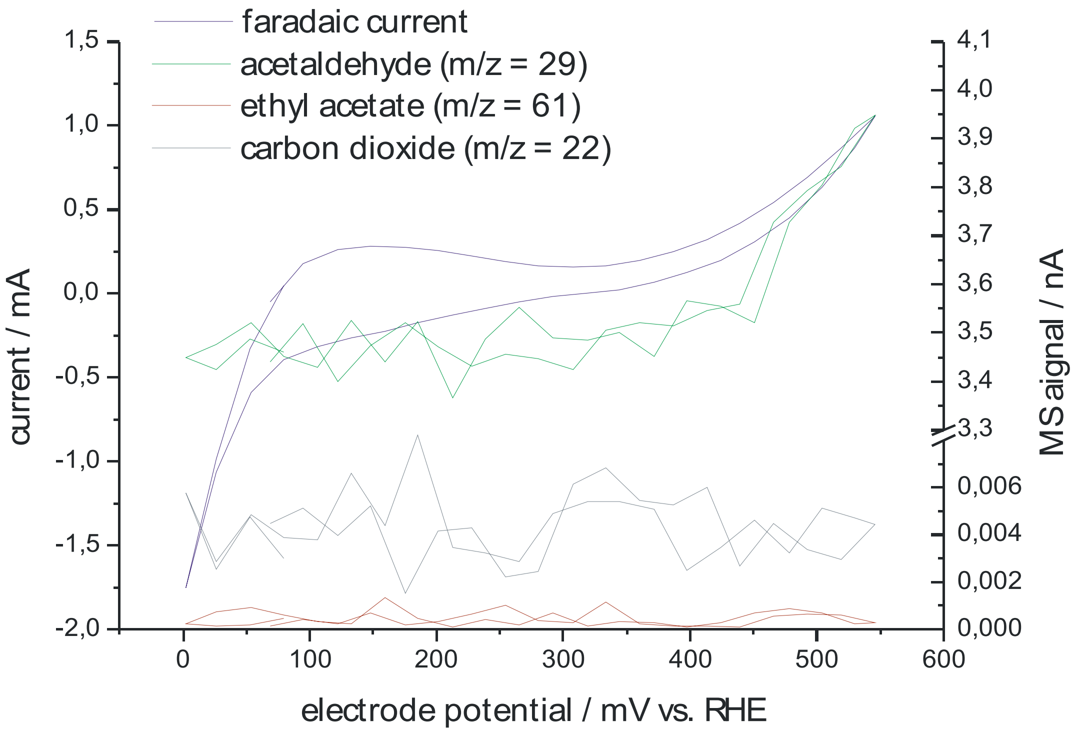


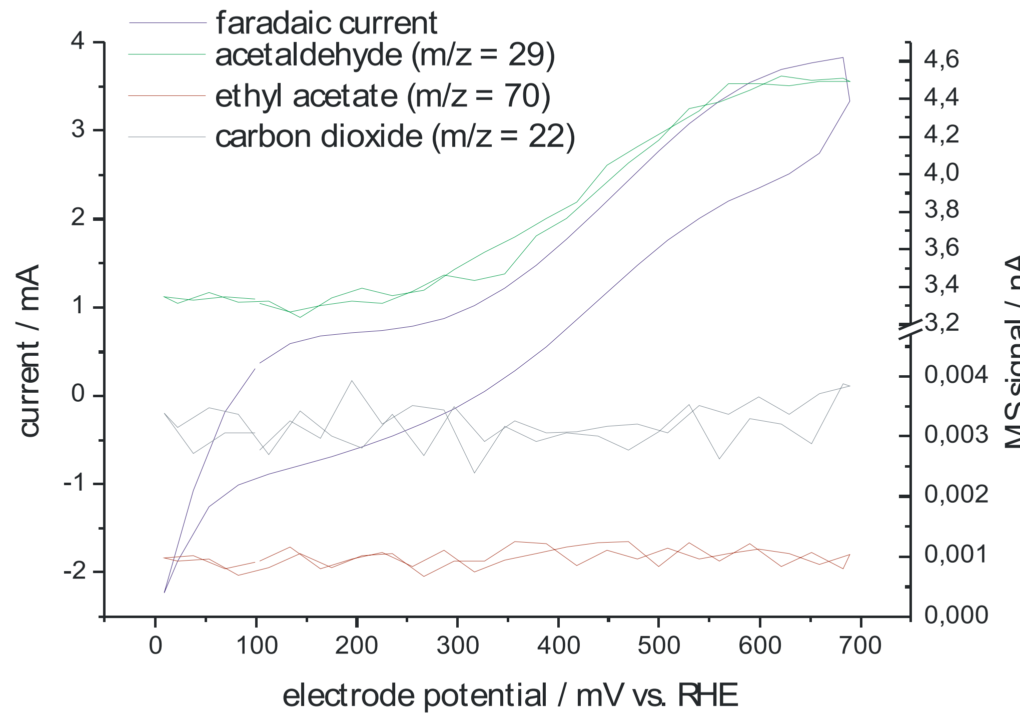
Linear sweep voltammograms of the ethanol oxidation at different electrodes measured in a 1M ethanol, 0.5M sulphuric acid solution at ambient temperature, sweep rate 20 mV/s

In accordance with literature it was found that:

- PtSn exhibits the highest activity
- Pt and PtRu exhibit lower activities

Electro-catalytic oxidation of ethanol in acidic media





MSCVs of the ethanol oxidation at a Pt (left) and a PtSn electrode (right), recorded in a 1M ethanol, 0.5M sulphuric acid solution at ambient temperature, sweep rate 20 mV/s.

In both cases no CO_2 evolution is observed, main product is acetaldehyde.

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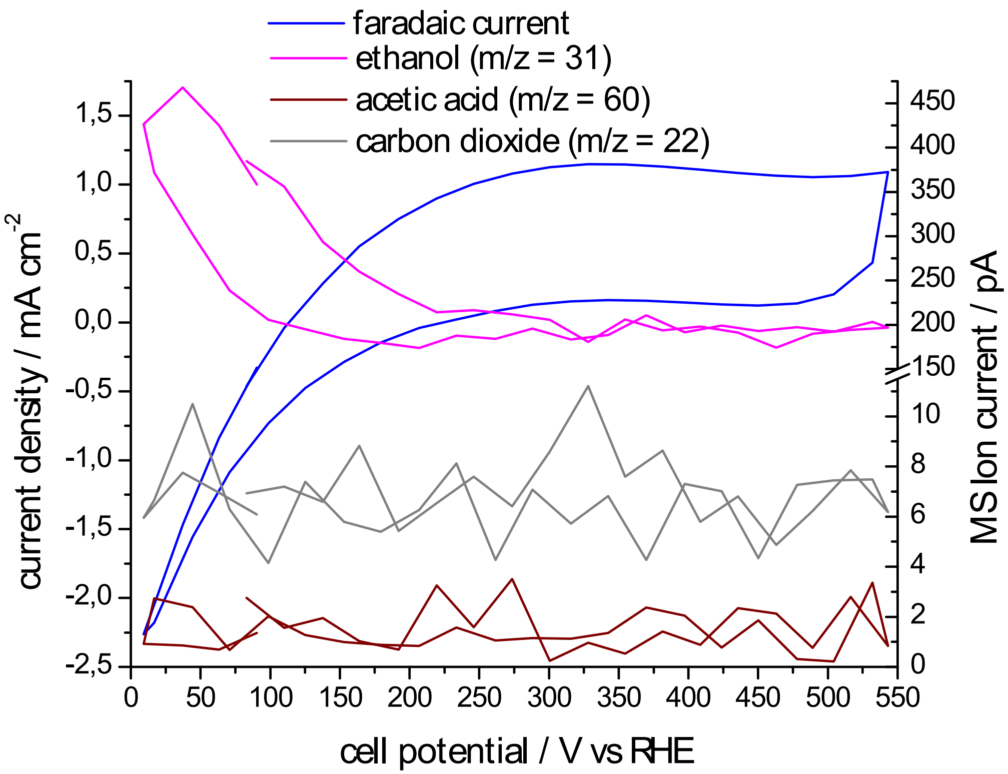
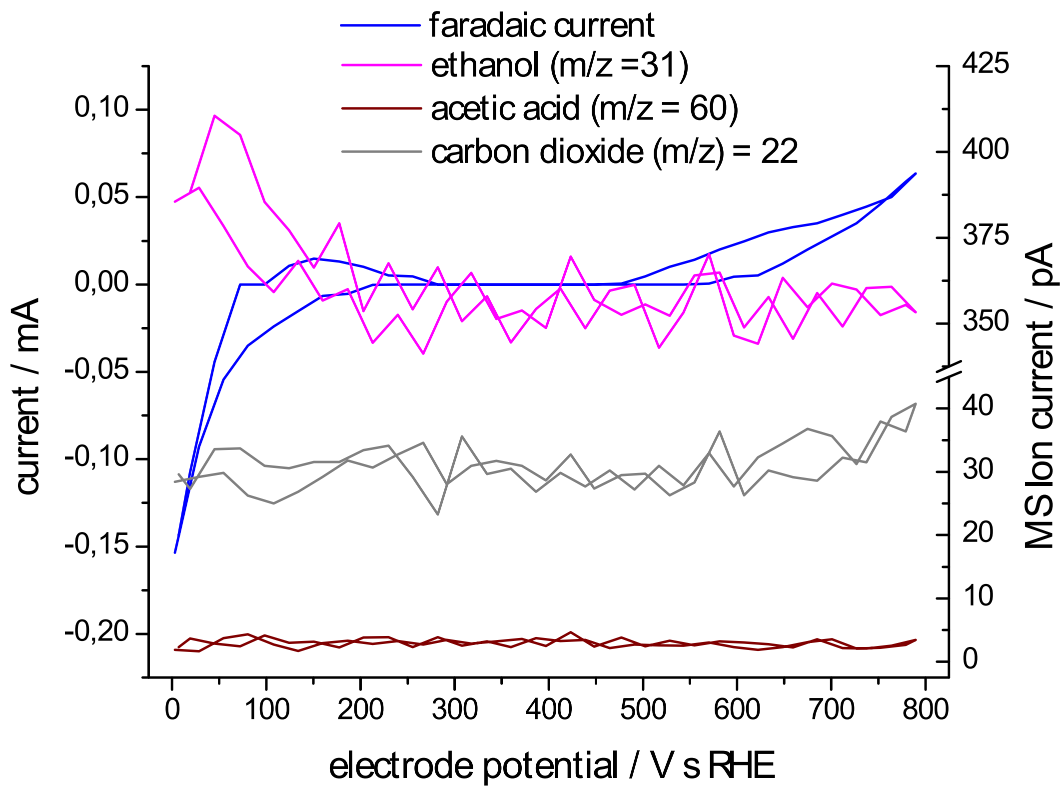
Electro-catalytic oxidation of acetaldehyde in acidic media





MSCV of the acetaldehyde oxidation in sulphuric acid, left at Pt_3Sn right at Pt_3Ru

In both cases the formation of ethanol is observed at low potentials together with a strong cathodic current.

Only at Pt_3Ru an anodic current and CO_2 formation is observed

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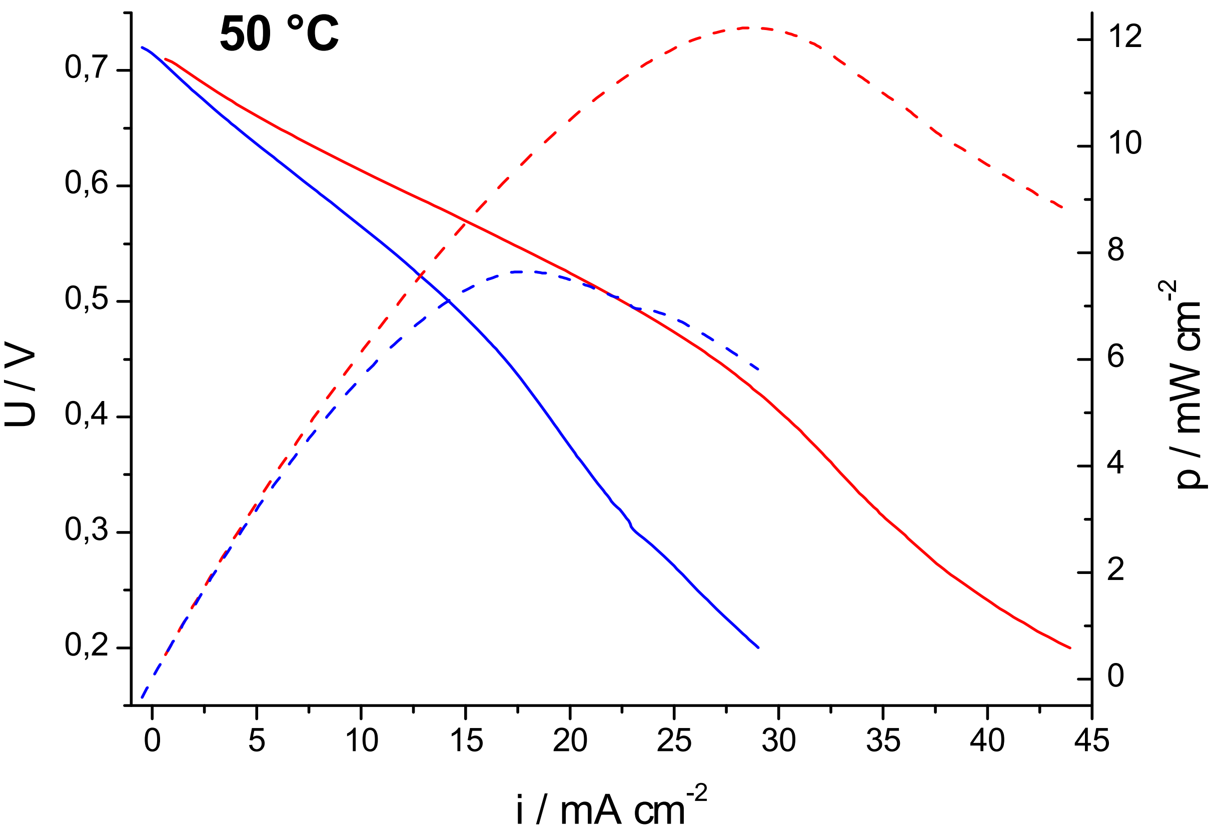
Proton-exchange-membrane-based direct ethanol fuel cell



Tests with MEAs containing both PtSn/C and PtRu/C in the anode layer showed a significantly improved performance compared to MEAs containing only PtSn/C in the anode layer.

I-V and I-P curves of DEFC single cells with a PtSn/C (blue) and a PtSn/C + PtRu/C anode measured at 50 °C, with 1M ethanol and air as the oxidant.

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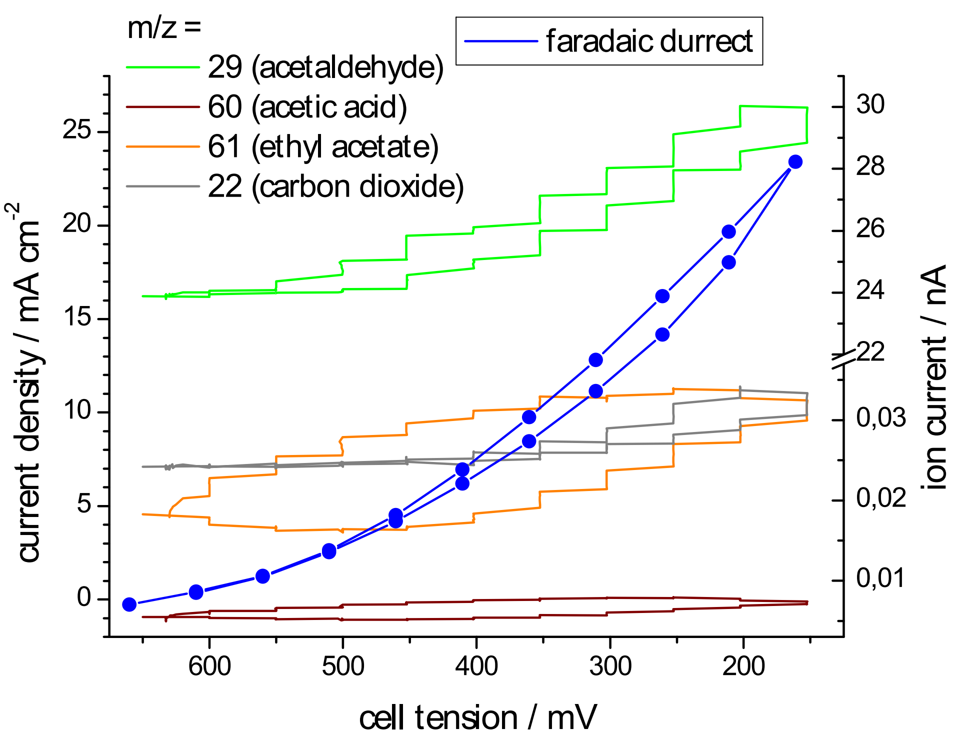
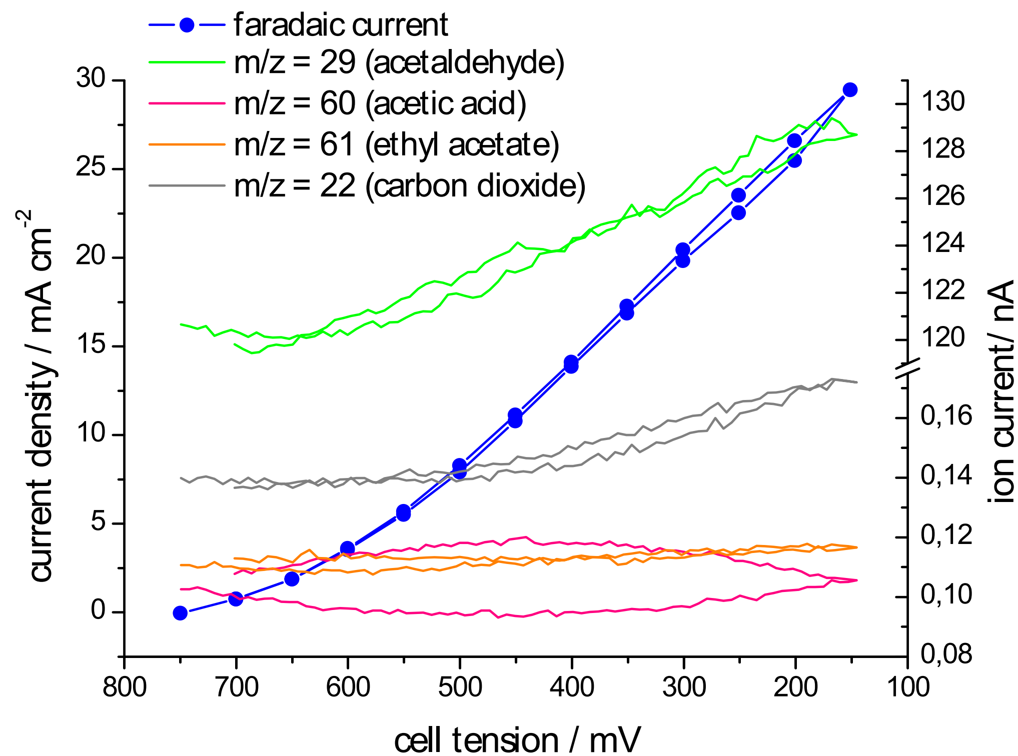
Proton-exchange-membrane-based direct ethanol fuel cell

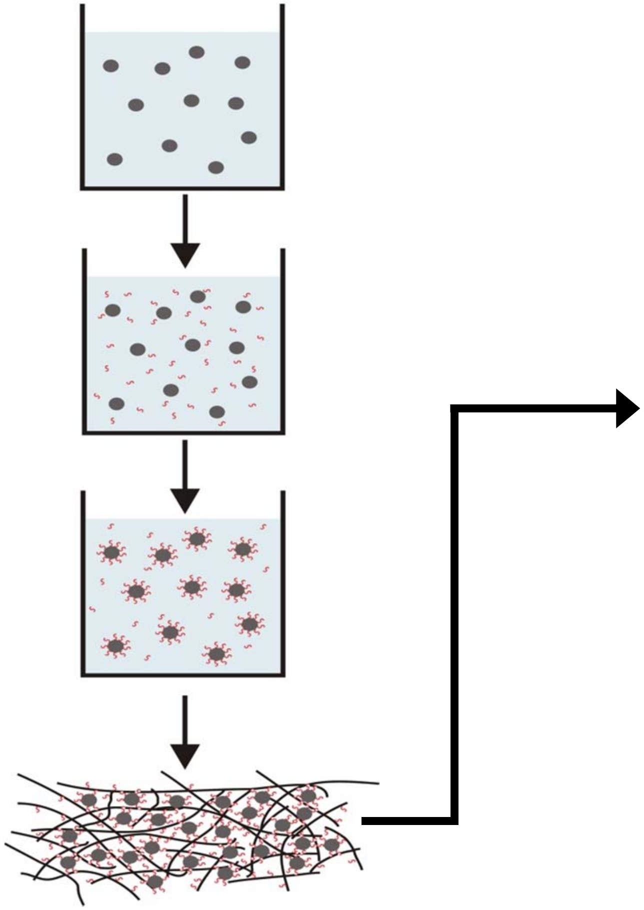


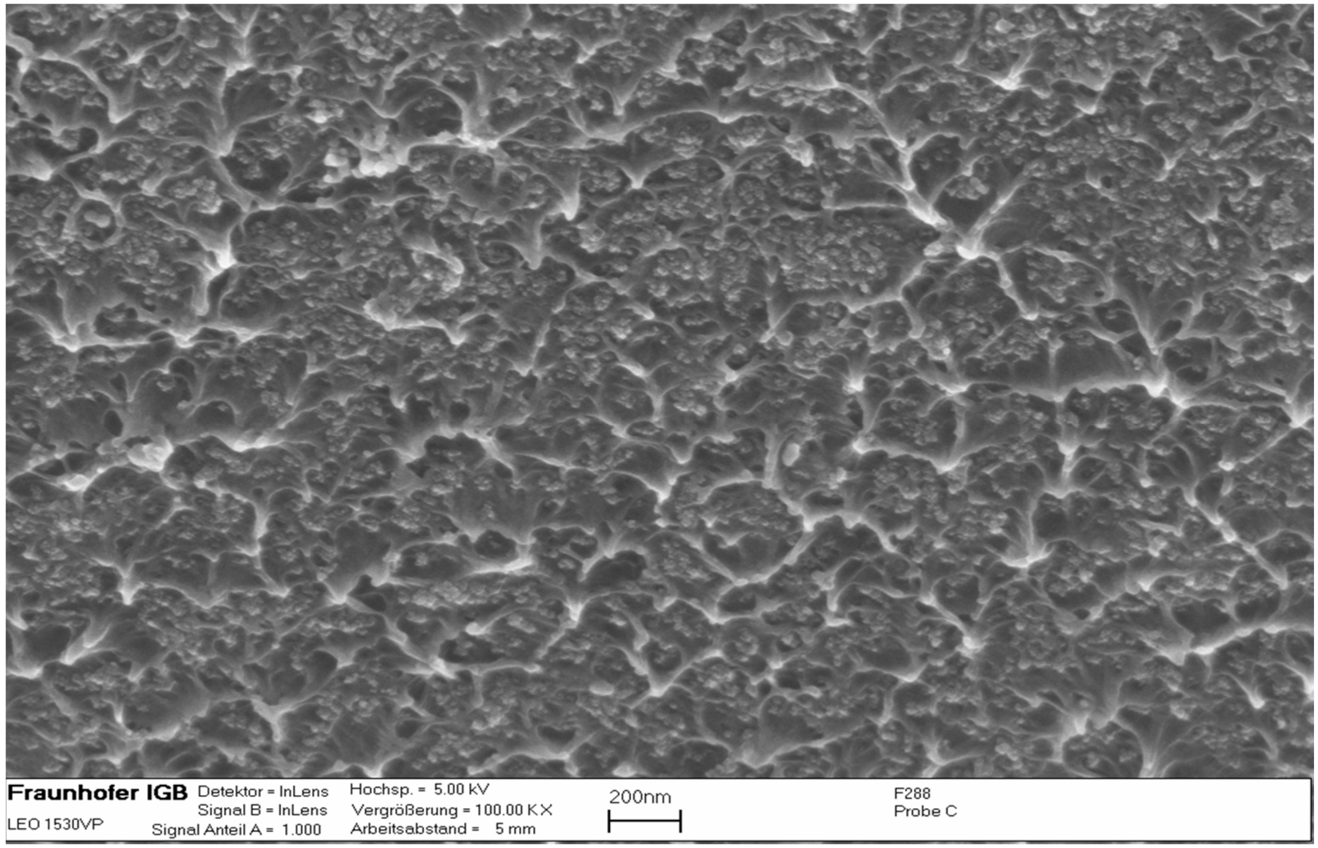


Single cell tests with online MS analytics of the anolyte for single cells with a PtSn/C anode with 3.4 mg/cm^2 (left) and PtSn/C + PtRu/C anode with a total of 1.8 mg/cm^2 (right); measured at 40 °C with 1M ethanol and oxygen as the oxidant.

The mixed anode produces more CO_2 than the PtSn/C anode

Fraunhofer IGB Membrane Development: Preparation Route

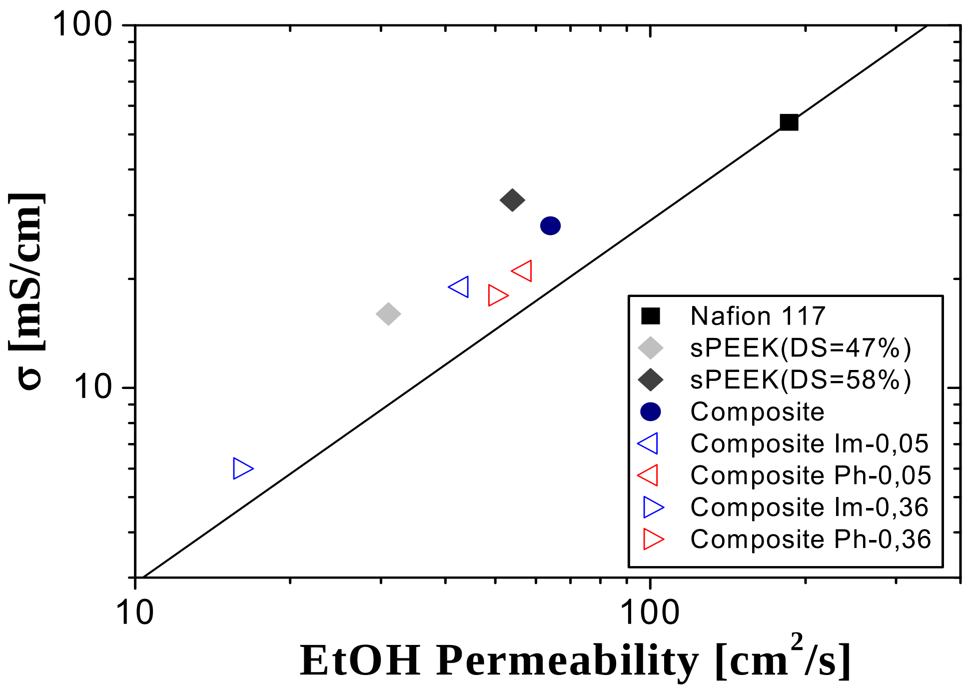


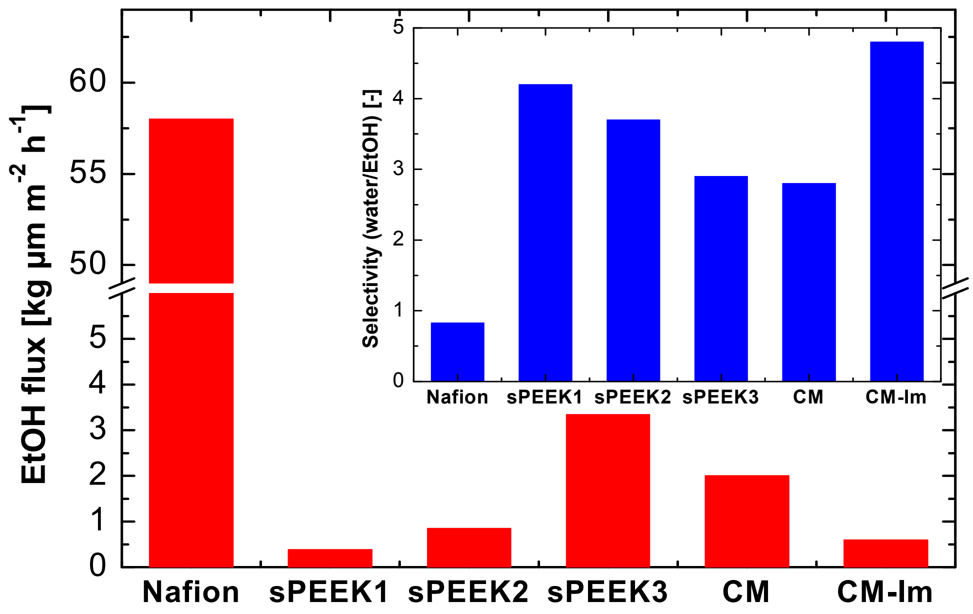


sPEEK (DS=58%); Silica Loading 27,3%

Source K. Roelofs, T. Schiestel Fraunhofer IGB

Fraunhofer IGB DEFC-membranes

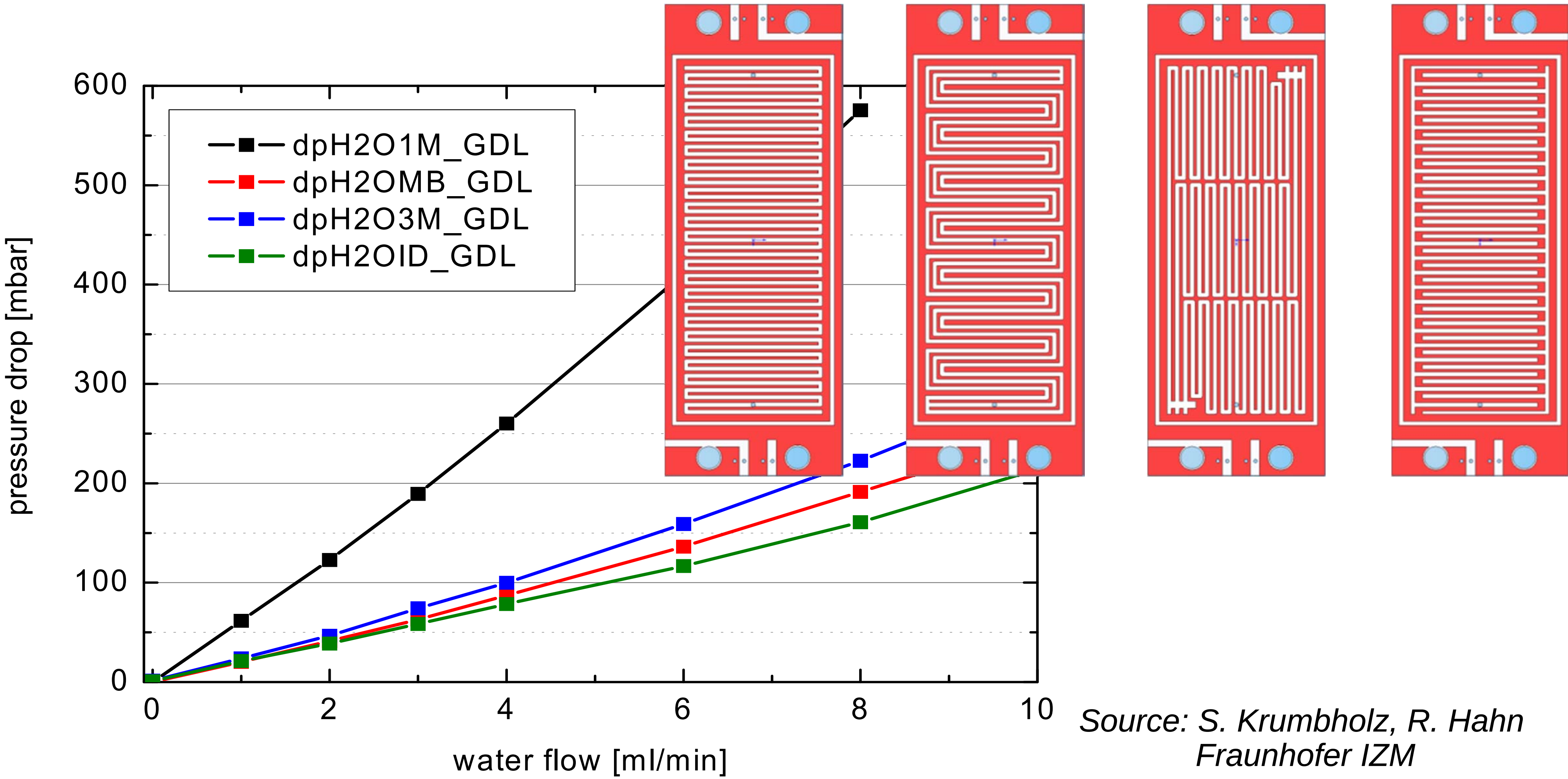




Nafion	: Nafion 117
sPEEK1	: IEC = 1.10 mmol g^{-1}
sPEEK2	: IEC = 1.34 mmol g^{-1}
sPEEK3	: IEC = 1.63 mmol g^{-1}
CM	: Matrix: IEC = 1.34 mmol g^{-1}; Loading: 20%; unmodified
CM-Im	: Matrix: IEC = 1.34 mmol g^{-1}; Loading: 20%; Im-modified

Source: K. Roelofs, T. Schiestel, Fraunhofer IGB

Fraunhofer IZM Flow Field Design for Low Pressure Drop

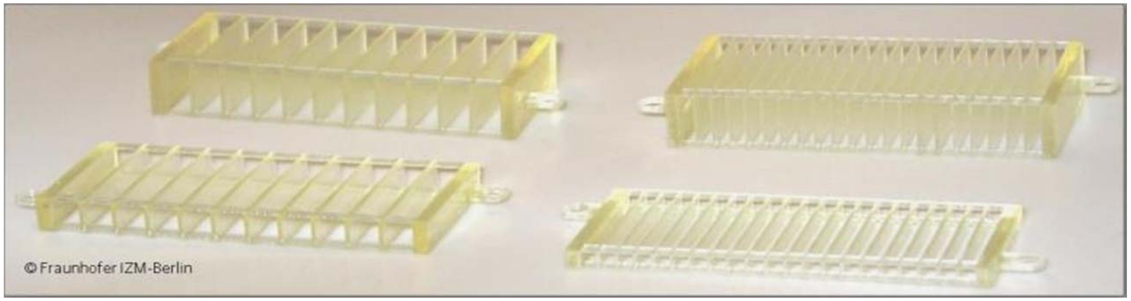


Source: S. Krumbholz, R. Hahn
Fraunhofer IZM

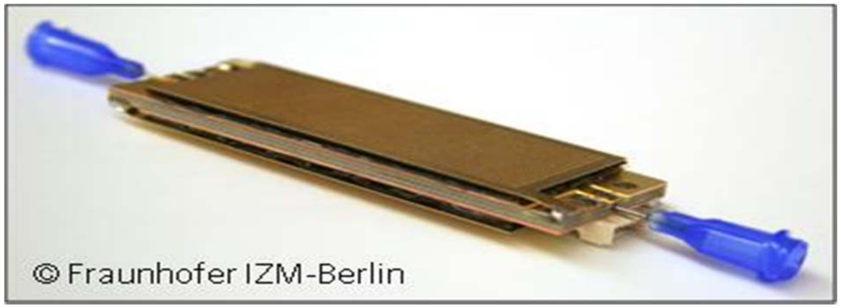
Steffen Krumbhol
krumbholz@izm.fhg.d

Fraunhofer IZM Single Cell and Stack Assembly

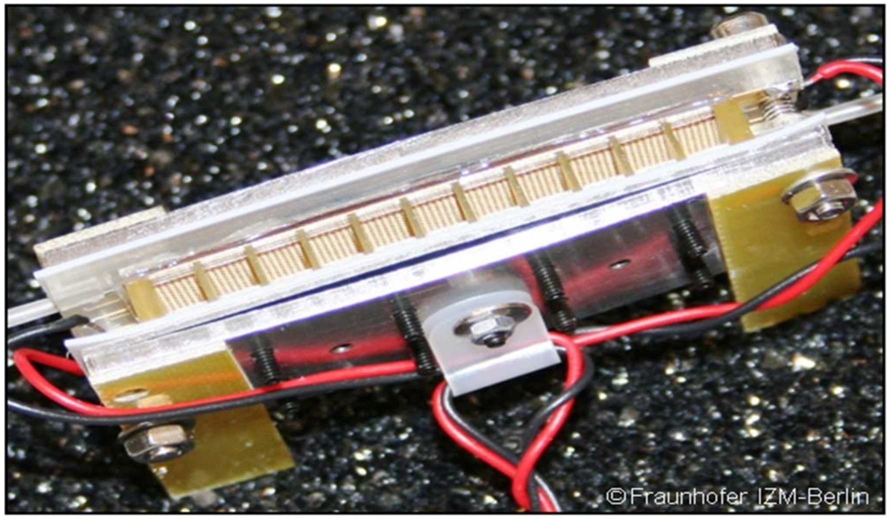
Improved passive air breathing structures made by rapid prototyping



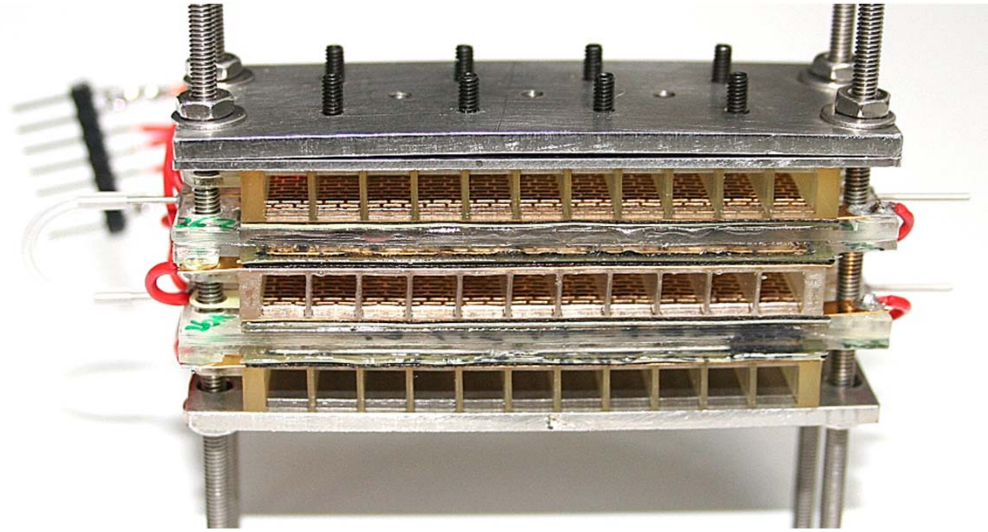
Bi-cell based on PCB-materials



Novel polymer based single cell



4-cell-stack with two bi-cells



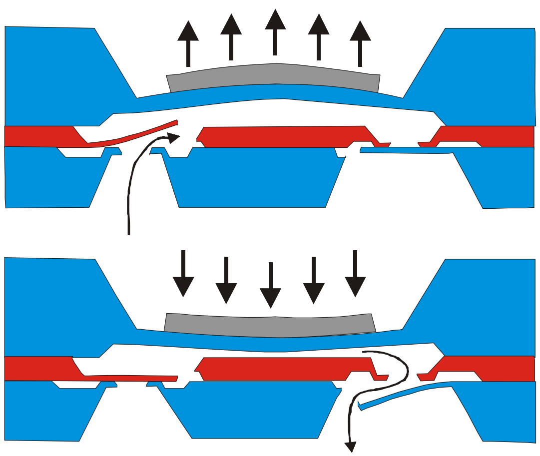
Source: S. Krumbholz, R. Hahn
Fraunhofer IZM

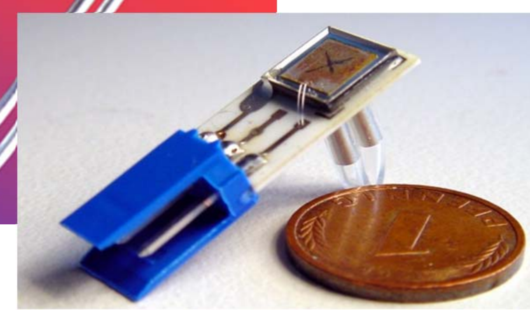
Fraunhofer Institut Chemische Technologie

Steffen Krumbhol
krumbholz@izm.fhg.d

Fraunhofer IZM Micropump for Fuel Cells

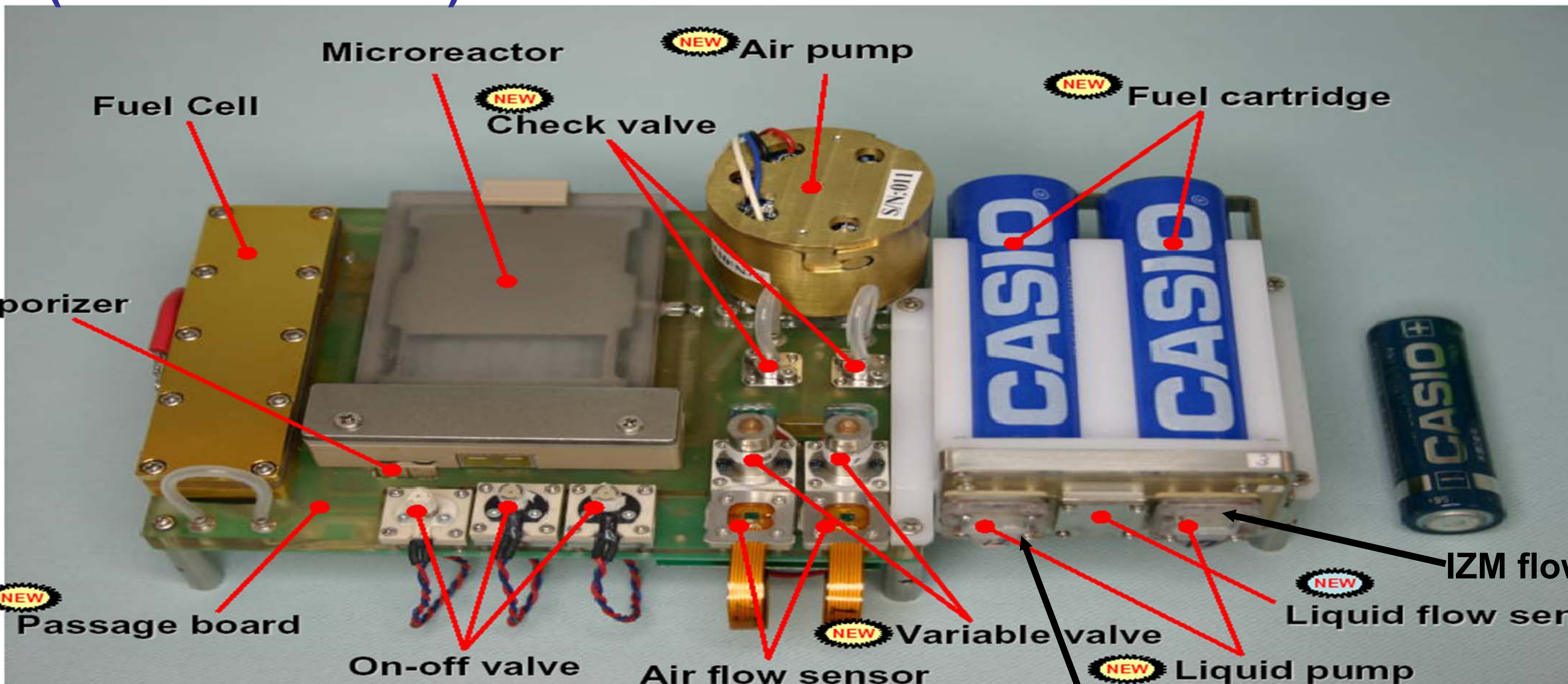
- Fuel dosing pump
- Recirculating pump
- Air pump for cathode
- Normally closed valve





Source: K. Heinrich, M. Richter
Fraunhofer IZM (Munich branch)

Fraunhofer IZM Micropump in Industrial Prototype (Casio Fuel Cell)

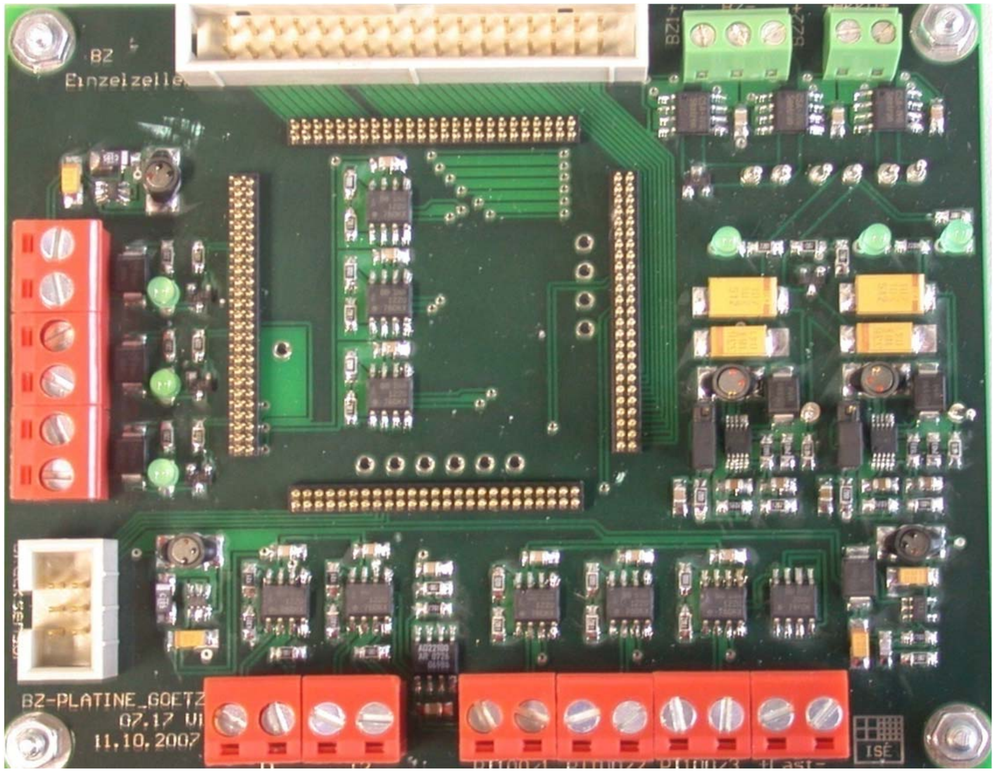


Source: K. Heinrich, M. Richter
Fraunhofer IZM (Munich branch)

IZM micropumps

Fraunhofer ISE / IIS – system control design

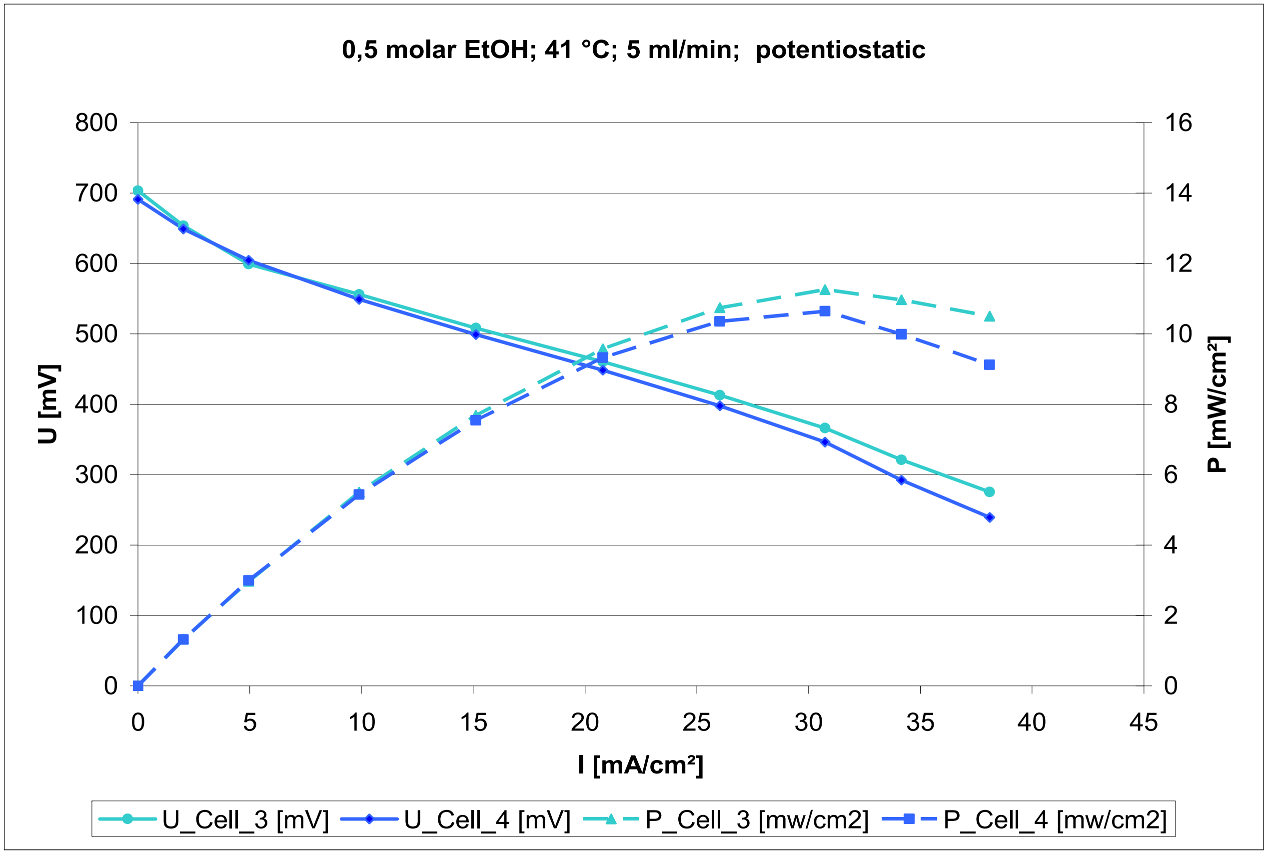
- Microcontroller-based electronic system
- Processing of input data: voltage, current, temperature
- Hybrid system with lithium-polymer battery
- Only one actuator (fuel pump) necessary



Source: S. Keller, J. Melke Fraunhofer ISE
F. Förster, P. Spies Fraunhofer IIS

Fraunhofer ISE – performance tests

- Stack design with 4 cells
- OCV at 700 mV
- Power density > 10 mW/cm²
- Performance under system environment, e.g. ambient temperature, still challenging
- Degradation could be seen within a matter of days

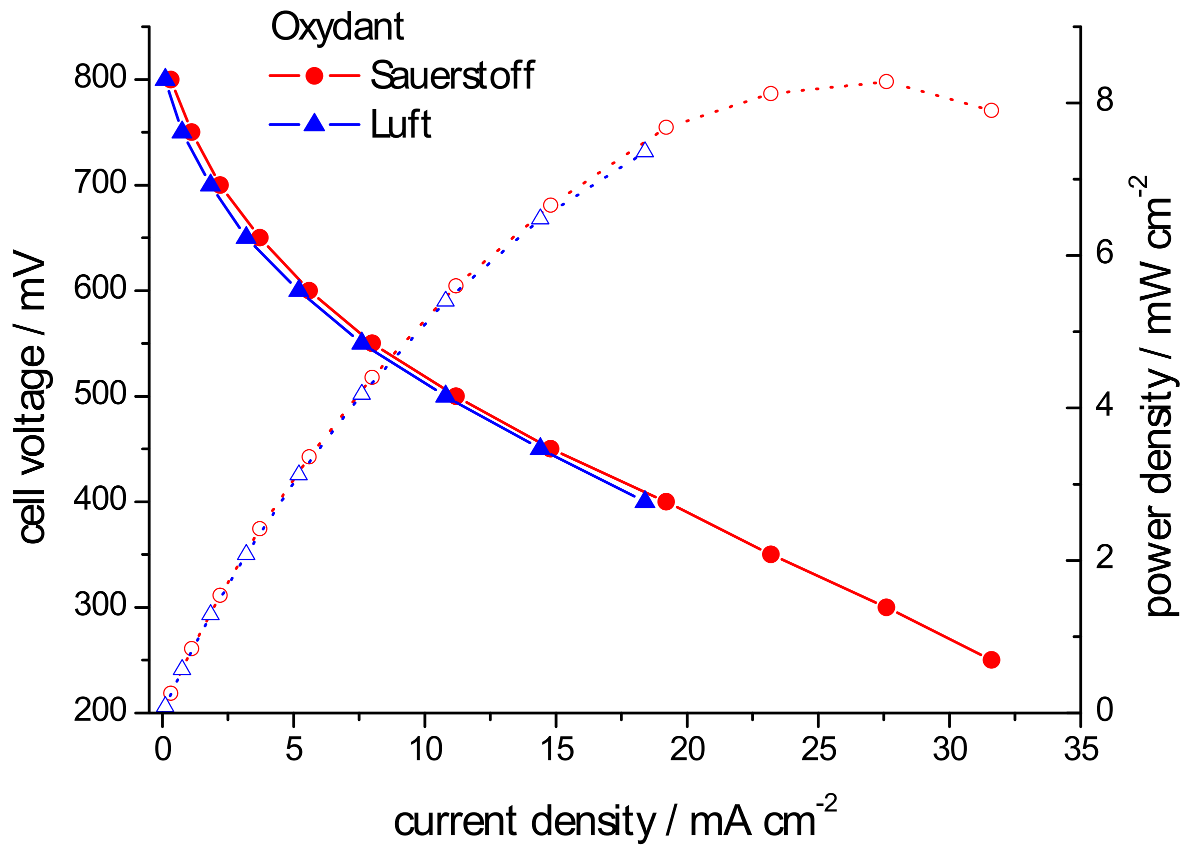


Source: J. Melke, S. Keller
Fraunhofer ISE

Test results for a 4-cell stack designed by Fraunhofer IZM, with mixed bed anode MEAs by Fraunhofer ICT, tested at Fraunhofer ISE

Fraunhofer ISE – performance tests

- Compared to the first generation the performance of the DEFC was increased significantly
- Using sPEEK composite membranes the open circuit voltage and the performance at low temperatures was improved due to reduced cross-over of water and ethanol
- Avoiding PCB materials containing copper the cell degradation in the stacks was significantly increased.



Performance of a DEFC single cell with Fraunhofer IGB sPEEK composite membrane and Fraunhofer ICT electrodes Tested at the Fraunhofer ISE at ambient temperature and pressure using 3M ethanol solution as fuel.

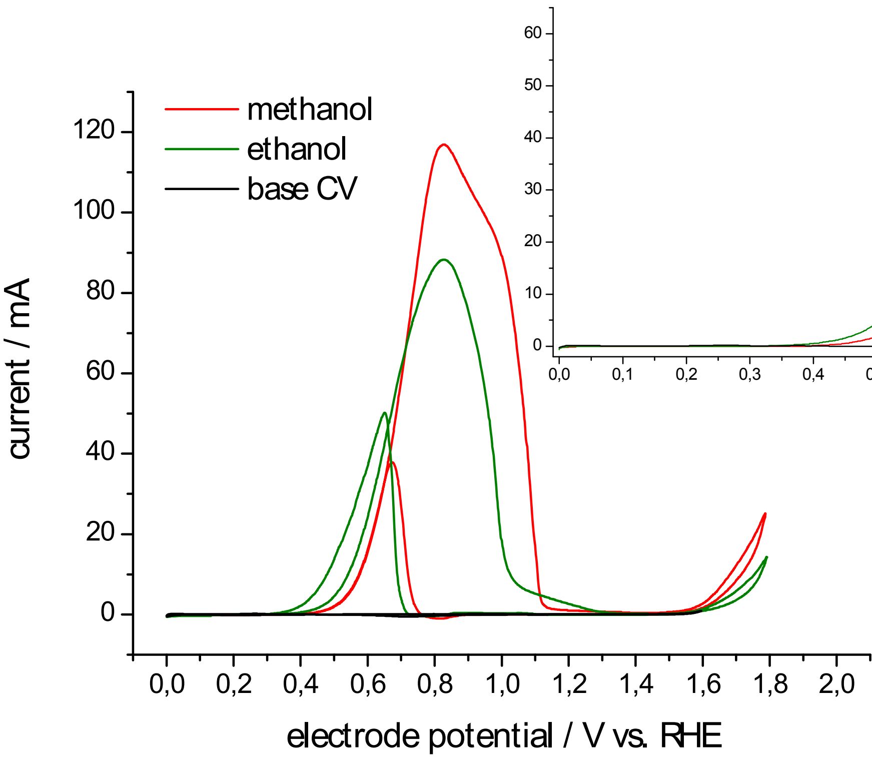
Source: J. Melke, S. Keller
Fraunhofer ISE

Conversion of ethanol in anion exchange membrane fuel cells

Fraunhofer Institut Chemische Technologie

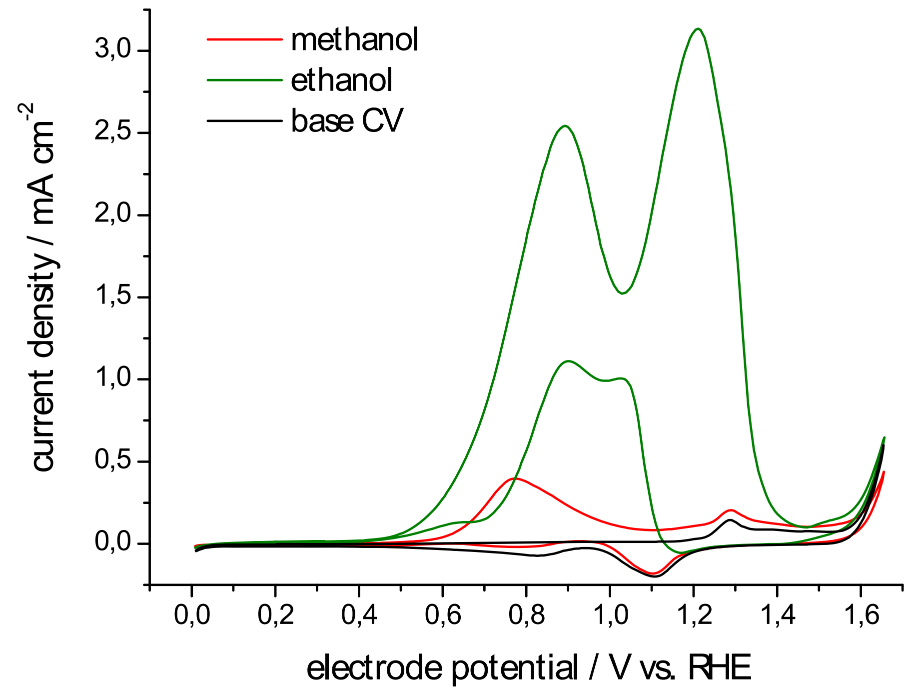
Electrocatalysis of alcohol oxidation in bases

In the alkaline environment platinum becomes more active for the ethanol than the methanol oxidation



CV of the methanol and ethanol oxidation in 0.5 M KOH at platinum at ambient temperature

Even a planar gold electrode becomes active for the ethanol oxidation in this environment



CV of the methanol and ethanol oxidation in 0.5 M KOH at gold at ambient temperature

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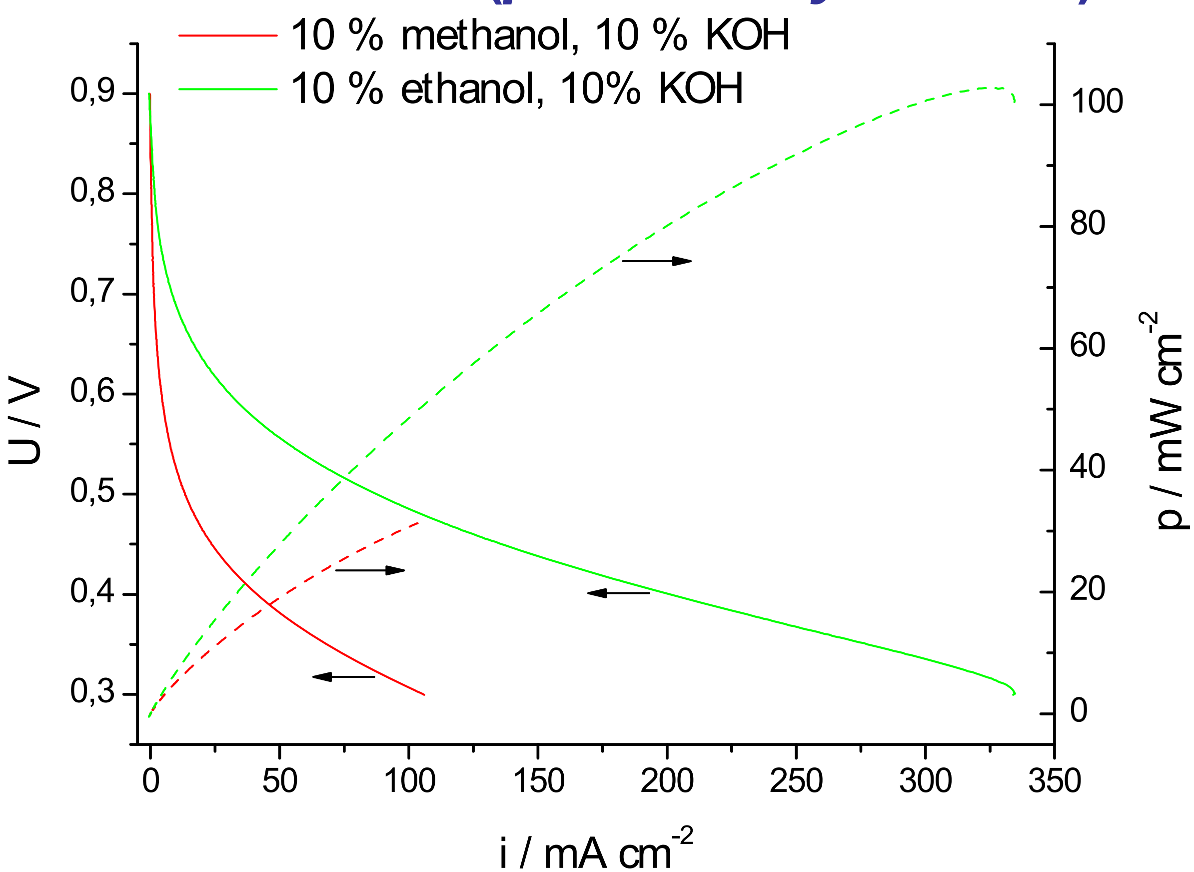
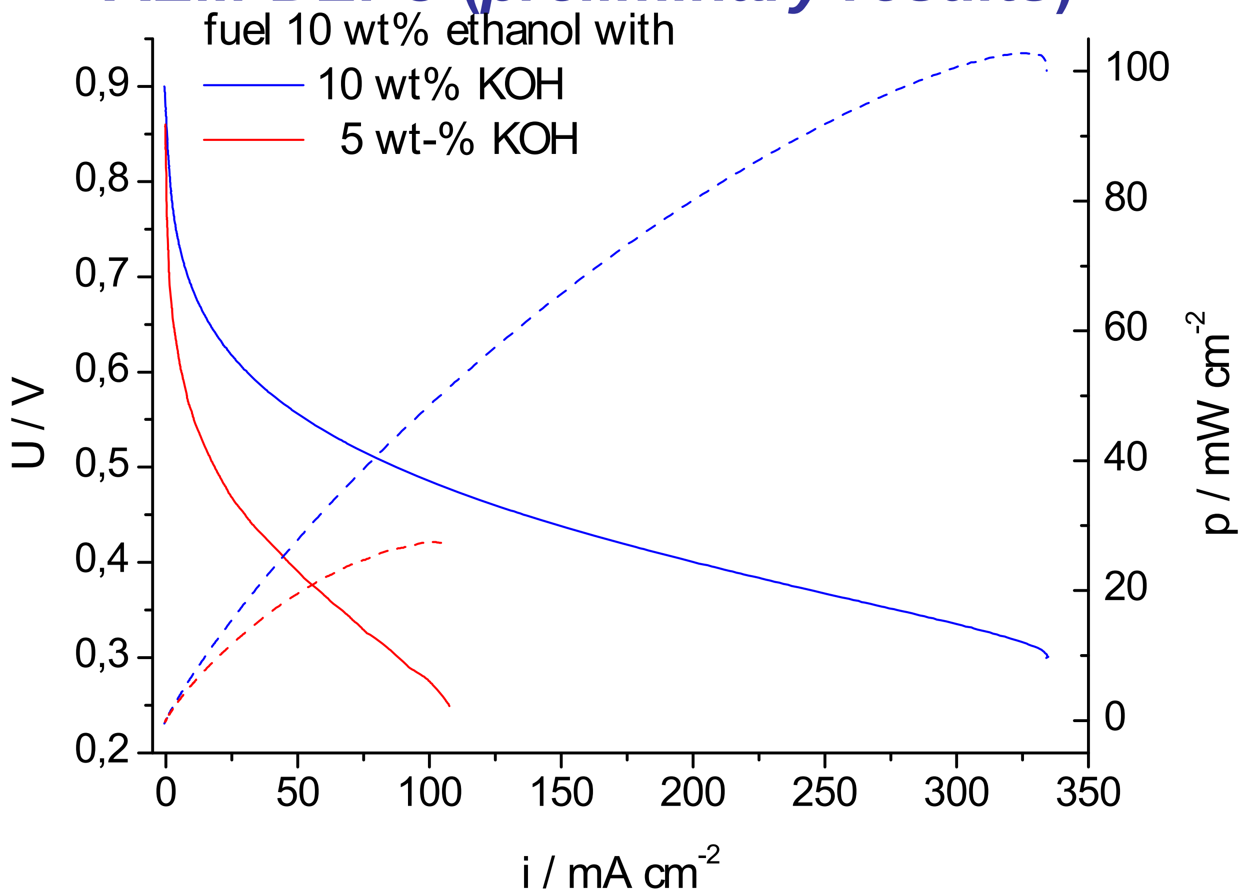
AEM-DAFC (*preliminary results*)



In accordance with the findings at thin film metal electrodes, the AEM-based DAFC delivers a better performance when ethanol instead of methanol is used as fuel.

I-V (straight) and I-P (dashed) curves of an AEM based DAFC using Acta S.p.A. Hypermec GDEs and a Fumatech Fumasep FAA membrane operated with methanol or ethanol, 50°C, air.

AEM-DEFC (*preliminary results*)



The current anode structure requires that a highly concentrated base is provided with the fuel.

A decrease in base concentration causes a severe performance loss.

I-V (straight) and I-P (dashed) curves of an AEM based DEFC using Acta S.p.A. Hypermec GDEs and a Fumatech Fumasep FAA membrane fuelled with ethanol in 10% and 5% KOH, 50°C, air.

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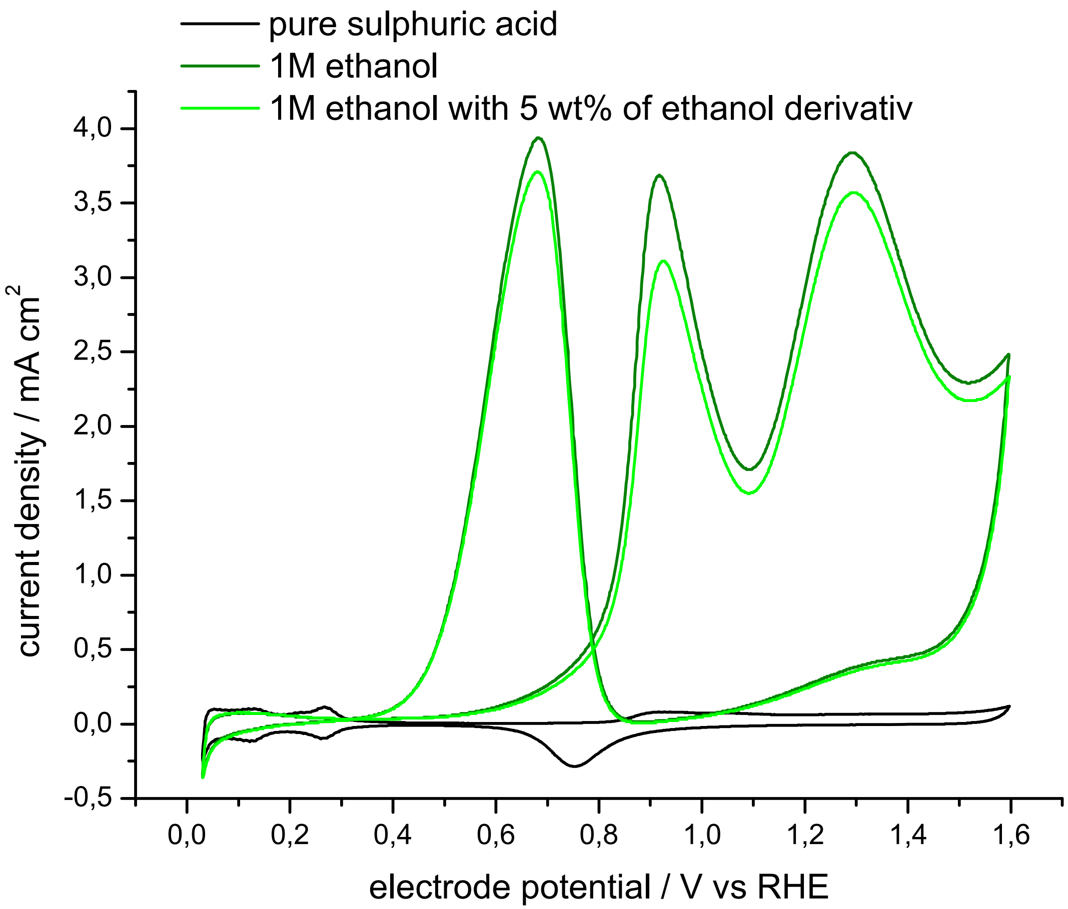
Denaturing additives compatible with fuel cells

Fraunhofer Institut Chemische Technologie

Denaturing additives compatible with fuel cells

- For tax reasons ethanol for use in fuel cells needs to be denatured.
- As DEFCs are still under development, no data concerning the electrochemistry of denaturing additives is currently available.
- In a project funded by the German Federal Ministry for Food, Agriculture and Consumer Protection (BMVEL) Fraunhofer ICT and Süd-Zucker AG are investigating this issue.
- An ethanol derivative showed already very promising first results



CVs of a platinum electrode in sulphuric acid, ethanol in sulphuric acid and ethanol with 5 wt% of an ethanol derivative in sulphuric acid.

Conclusions and Outlook

Fraunhofer Institut Chemische Technologie

Conclusions and Outlook

- Ethanol offers a number of advantages compared to other fuels which are considered for the use in fuel cells;
- In particular the better availability and the possibility to ship ethanol in larger tanks could reduce the logistic footprint for military applications;
- Strategies to achieve the efficient oxidation of ethanol have been determined:
  - Multi-stage catalysis in the acidic environment;
  - Oxidation in the alkaline environment;
- The development of a DEFC prototype by the Fraunhofer Team DEFC has advanced and a prototype will be presented this year;
- Further issues, such as the necessity to use denatured ethanol have been detected and are currently being addressed.

Acknowledgements

- Partial financial support of this work by the following organisations is gratefully acknowledged:
  - Fraunhofer-Gesellschaft
    contract MaVo-DEFC
  - German Federal Ministry for Food, Agriculture and Consumer Protection
    Contract 22003507
  - German Federal Ministry of Defence,
    Federal Office of Defence Technology and Procurement
    Contract E/E411/5C048/2F038

- We would like to thank the organisers for their kind invitation.

- <u>Last but not least we would like to thank you for your attention!</u>