

Screen Printed Catalyst Coated CCMs for Fuel Cells

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Fraunhofer Institute for Solar Energy Systems
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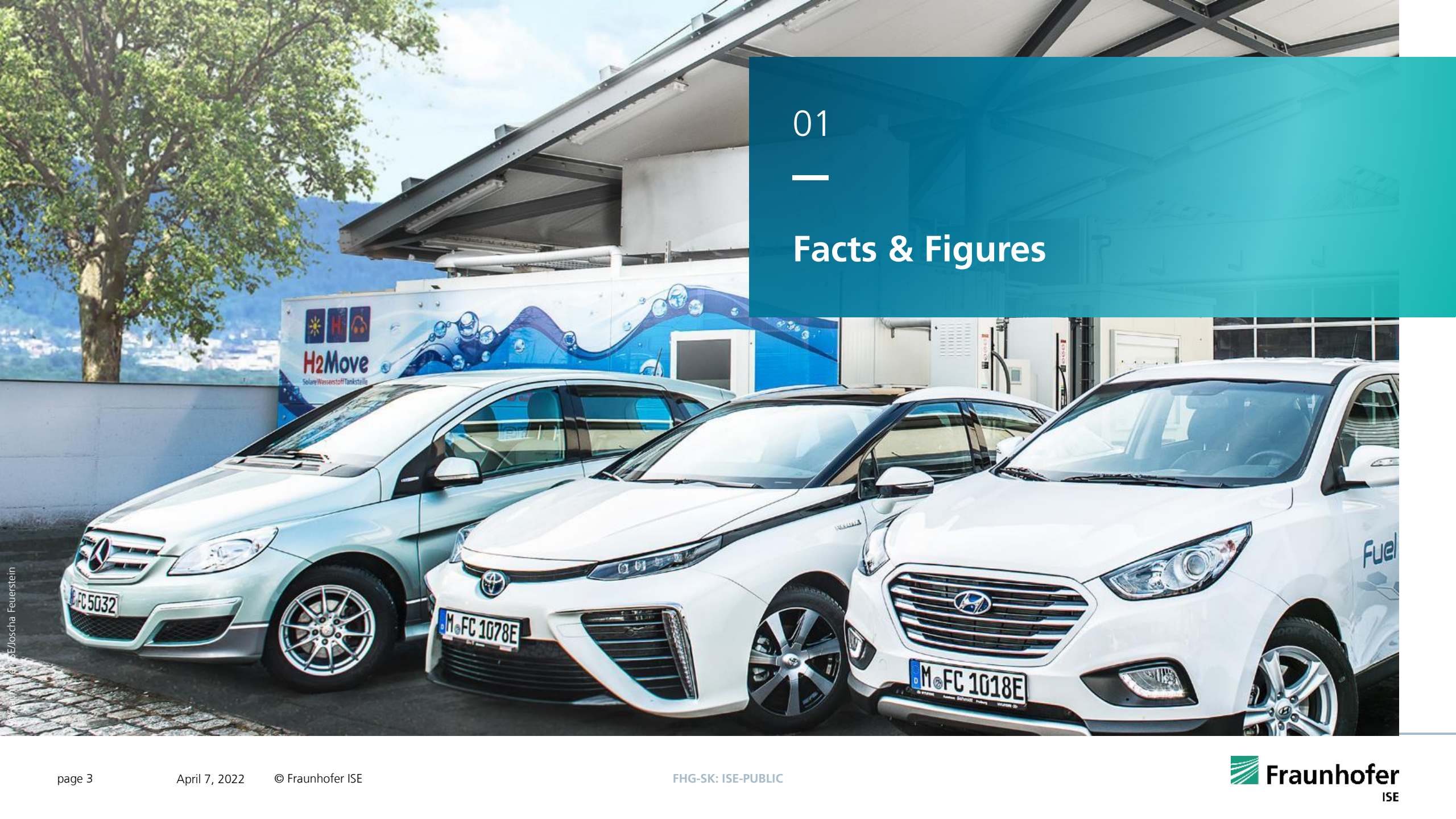
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Screen Printed CCMs

From Lab to Fab

1. Fuel Cells @ Fraunhofer ISE
2. Membrane Electrode Assembly
3. Designing CCMs
4. Process Control
5. Screen Printing of CCMs
6. Summary





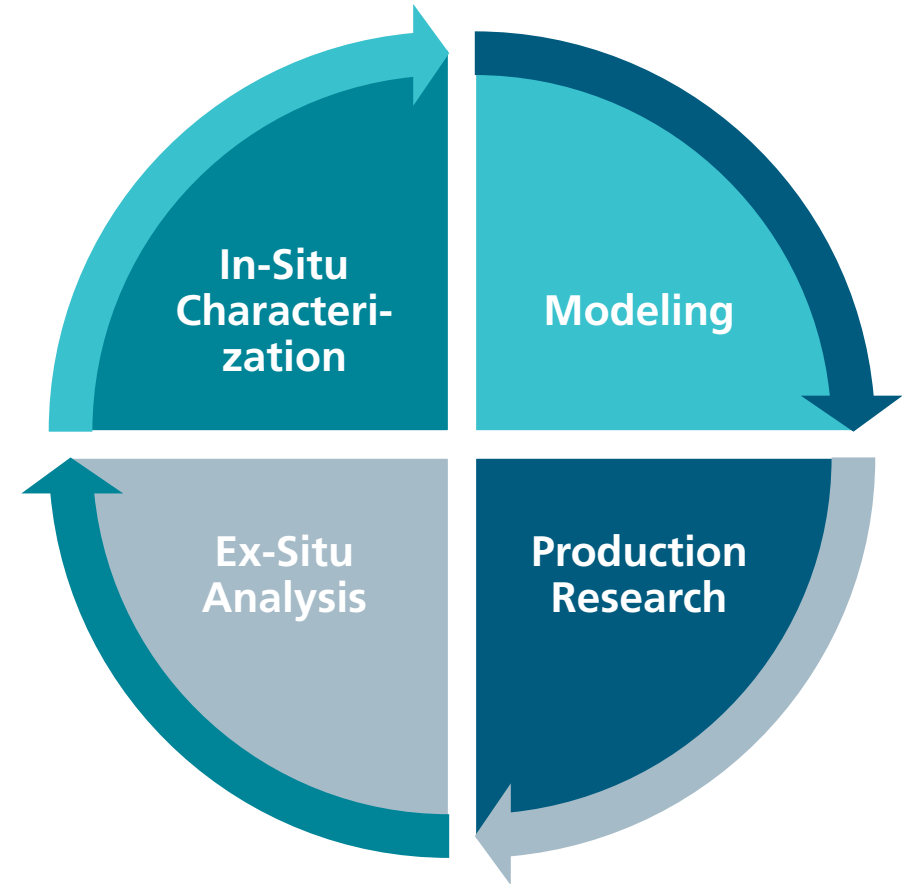
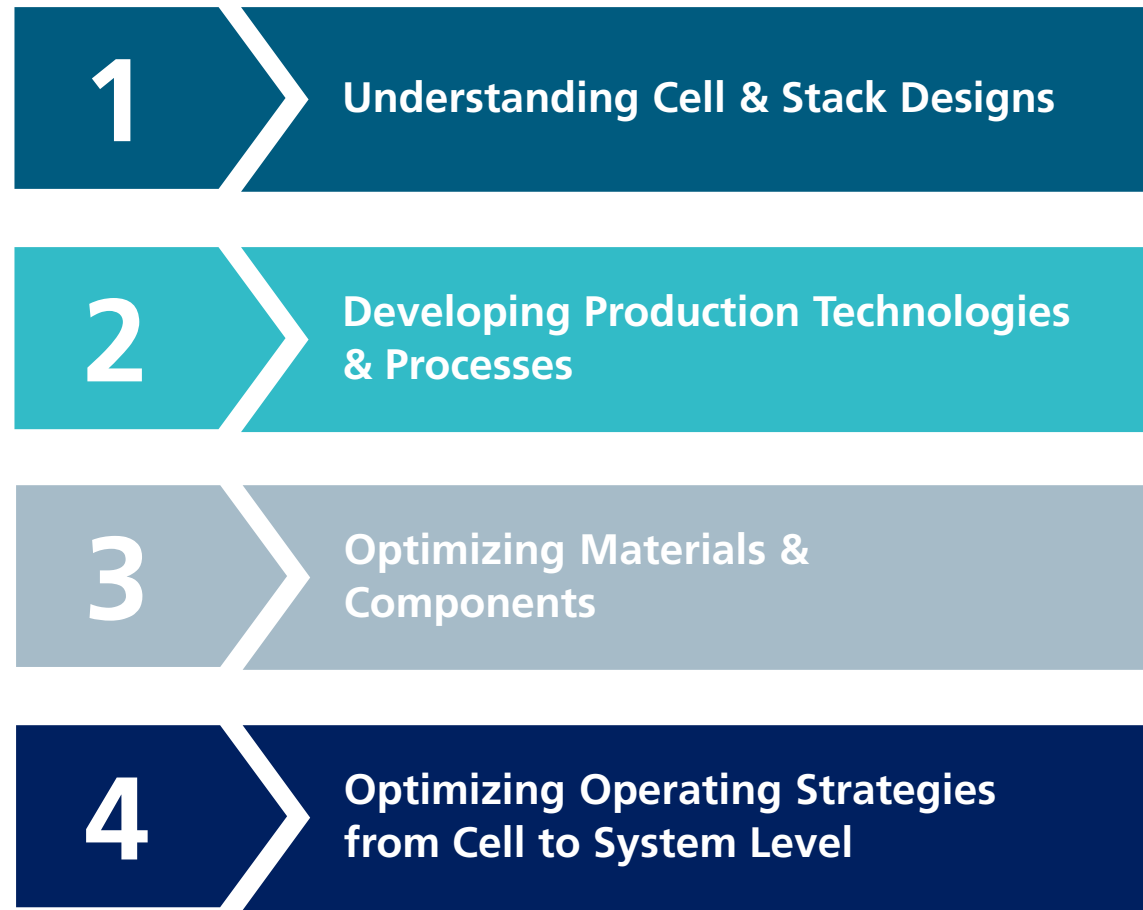
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Facts & Figures

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Value Proposition to Our Customers

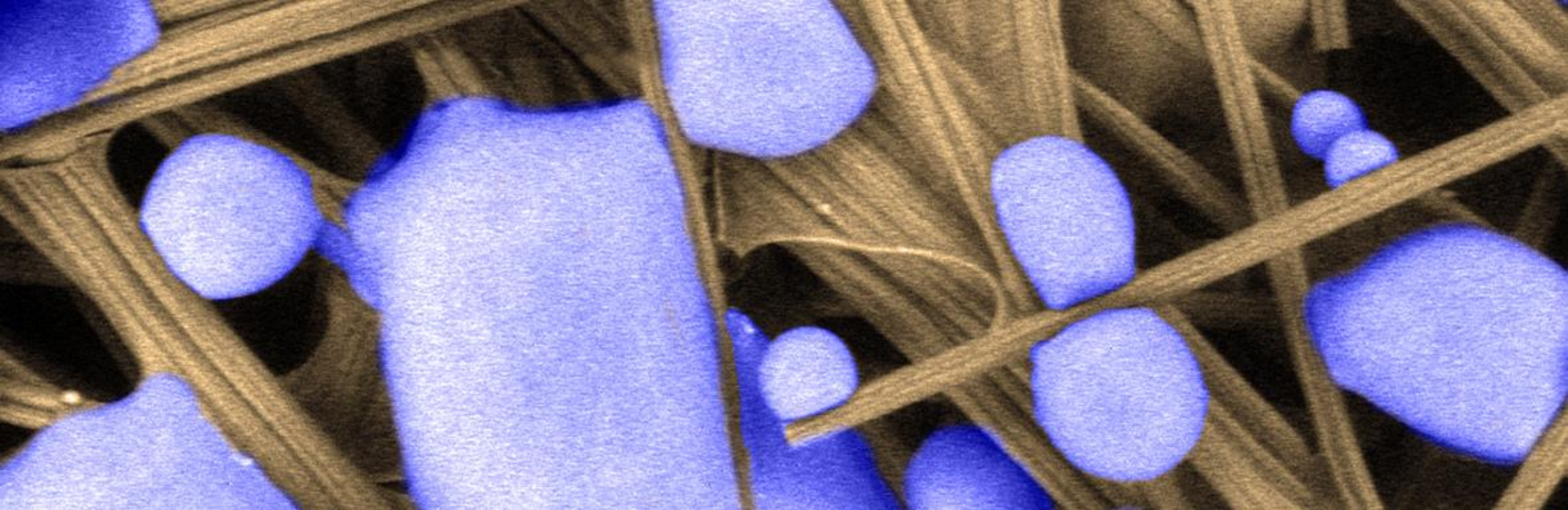
Concentrating on Low Temperature PEM Fuel Cell Membrane Electrode Assemblies



Proofing our results by the international scientific community

YEAR	TITLE/AUTHOR
2021	Activation mechanisms in the catalyst coated membrane of PEM fuel cells [?] Christmann, K.; Friedrich, K.A.; Zamel, N.
2021	Application of Artificial Intelligence in the Context of Fuel Cells: Presentation held at Hydrogen Lunch Online Edition, 18.03.2021, Freiburg, Germany [?] Scherzer, A.-C.; Schneider, P.; Zamel, N.
2021	Application of Artificial Intelligence in the Context of Fuel Cells. An overview of surveyed literature: Presentation held at f-cell, Stuttgart, Germany, Virtual, 14.09.-15.09.2021 [?] Scherzer, A.-C.; Schneider, P.; Zamel, N.
2021	Catalyst Coated Membranes - their Structure, their Performance and their Durability: Presentation held at World Fuel Cell Conference (WFCC), Virtual, Canada, 16.08.2021-20.08.2021 [?] Zamel, N.
2021	Characterizing Automotive PEMFC Membrane Electrode Assemblies: Presentation held at KOITA Fraunhofer Webinar, South Korea, June 7th, 2021 [?] Groos, U.; Georg, A.; Gerteisen, G.; Hebling, C.; Klingele, M.; Sadeler, C.; Scherzer, A.; Schneider, P.
2021	A Decade of German-Canadian Cooperation in Fuel Cells. Looking back at our story so far.: Presentation held at Digitale Informationsreise nach Deutschland für kanadische Akteure: "Elektromobilität: Batterie- und Flexible Produktion", online, Germany, 28.09.2021-30.09.2021 [?] Zamel, N.; Gerteisen, D.; Groos, U.; Hebling, C.
2021	From Catalyst Powder to Membrane Electrode Assembly: Presentation held at Hydrogen Summit, Stuttgart, Germany, September 15th, 2021 [?] Clement, F.; Keding, R.; Klingele, M.
2021	Hydrogen Storage and Electrical Energy Storage: Presentation held at Schweizer H2-Forum, Konstanz, 2021 [?] Zamel, N.; Gerteisen, D.; Groos, U.; Hebling, C.
2021	Representation of Women in STEM: AI-enabled Solutions and More [?] Zamel, N.; Al-Othman, A.
2021	Modeling the Flow Behavior of Catalyst Inks for PEM Fuel Cells by an Evolutionary Algorithm [?] Ney, L.; Singh, R.; Göttlicher, N.; Le, H.-P.; Tepner, S.; Klingele, M.; Keding, R.; Clement, F.

Download our publication from our website:
<https://www.ise.fraunhofer.de/en/business-areas/hydrogen-technologies-and-electrical-energy-storage/fuel-cell-systems.html>



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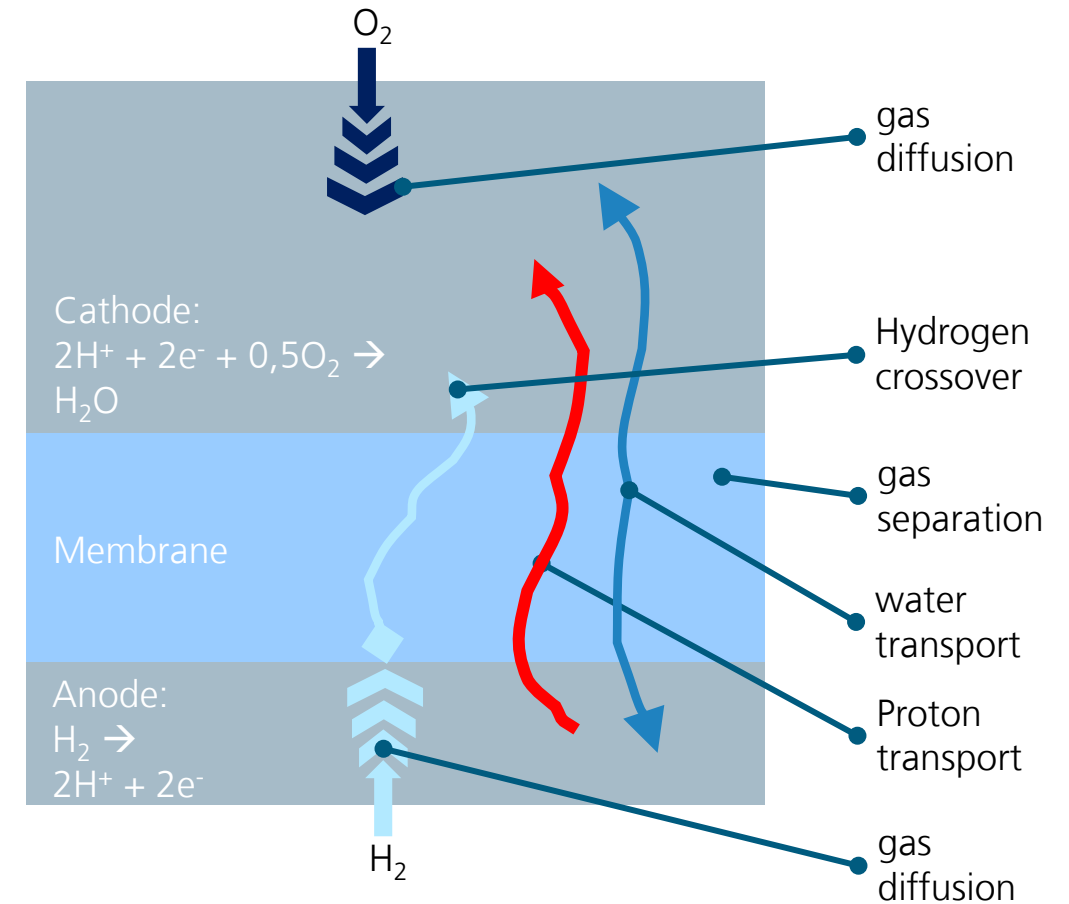
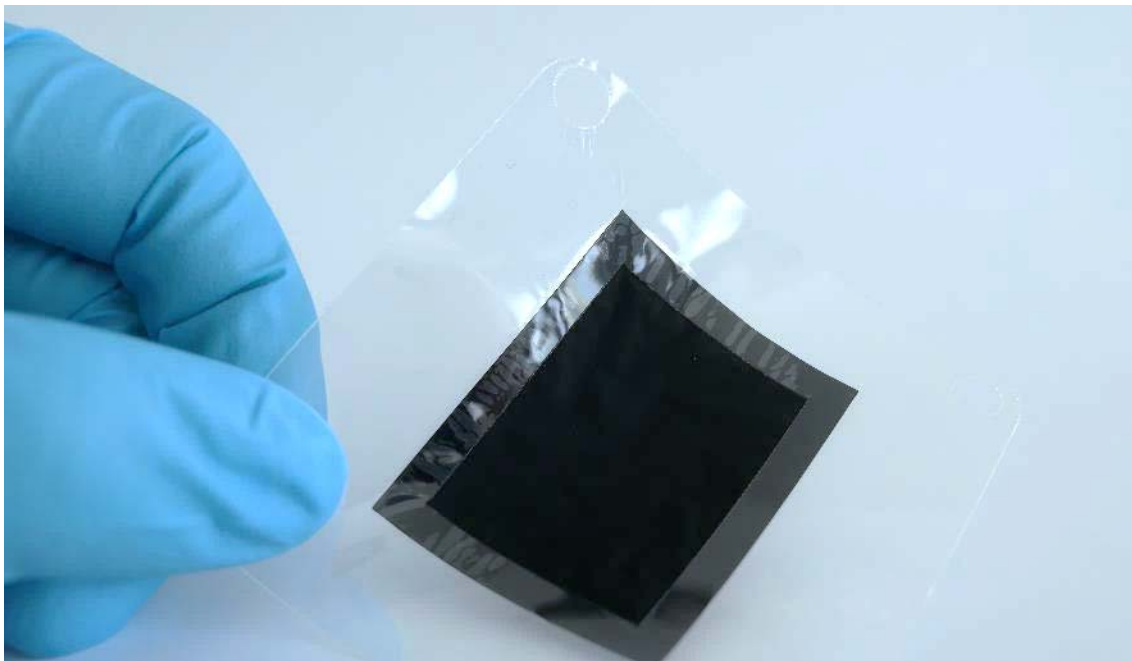
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Membrane Electrode Assembly

Membrane Electrode Assembly (MEA)

The electro-chemical heart of a fuel cell

- CCM: catalyst coated membrane
- MEA: often described as CCM with gas diffusion layer (GDL) attached to both anode and cathode, PEN frames on both sides for stabilization, and gaskets



Motivation: The Membrane Electrode Assembly (MEA)

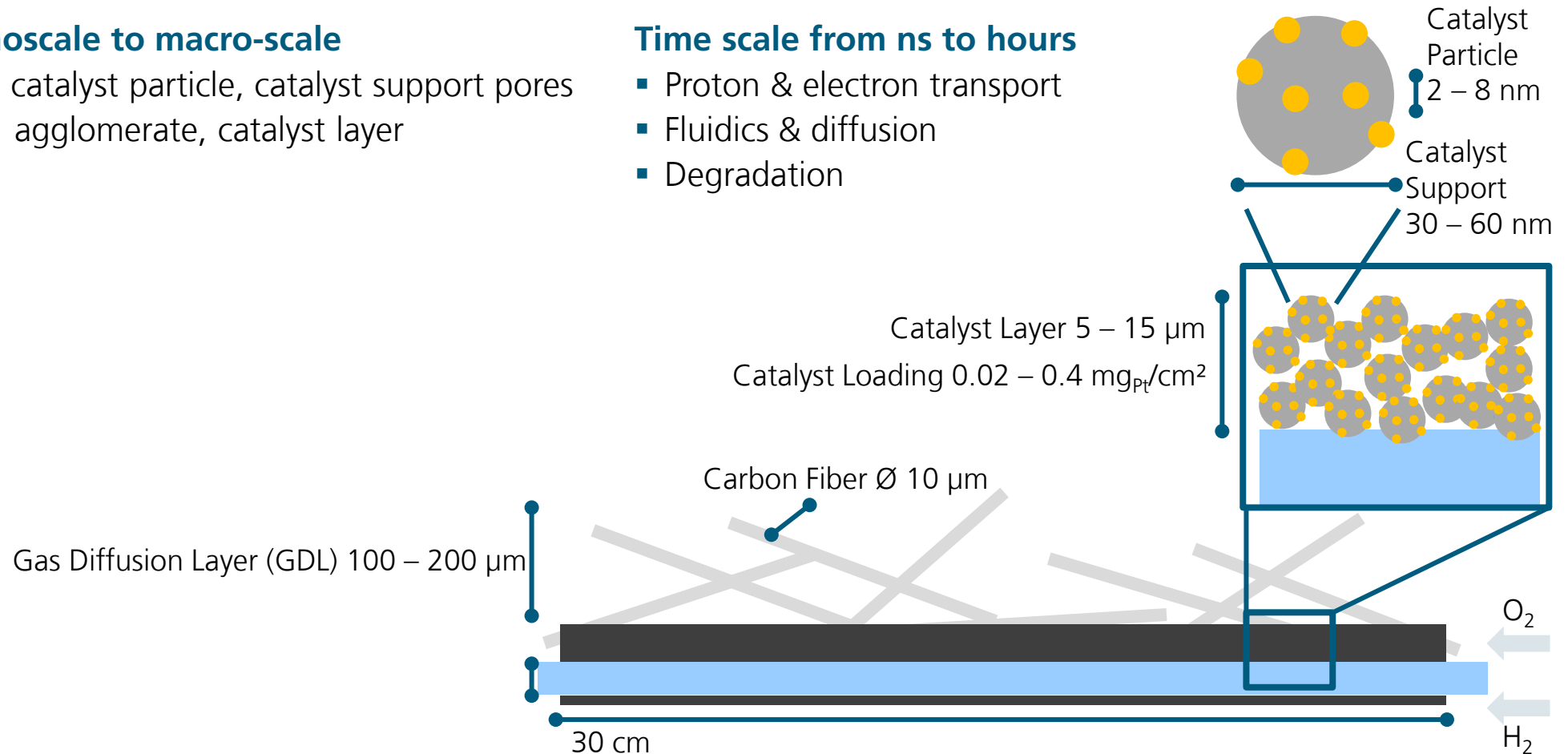
A multi-scale problem with respect to dimension and time

Dimensions from nanoscale to macro-scale

- Nano-scale transport, catalyst particle, catalyst support pores
- ionomer distribution, agglomerate, catalyst layer morphology
- Flow field

Time scale from ns to hours

- Proton & electron transport
- Fluidics & diffusion
- Degradation

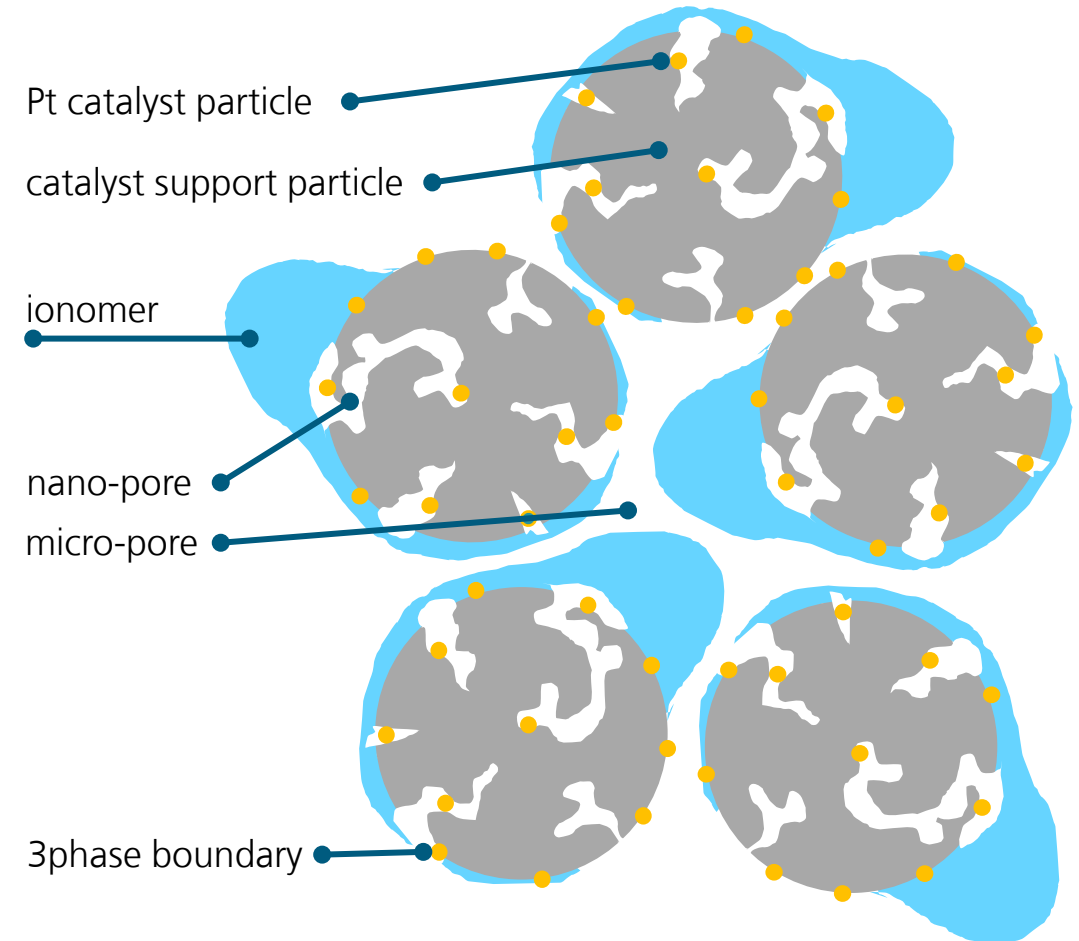


The Catalyst Layer Functions

Enabling the electro-chemical reaction and gas diffusion processes

Phenomena

- Gas diffusion in open (micro) pores, nano-pores, and through ionomer and water films
 - Proton transport through ionomer and water films
 - Proton transport from membrane to catalyst layer interface
 - Electron transport through carbon support particle
 - Electro-chemical reaction at Pt particle (influenced by electro-chemical surface area (ECSA), Pt oxidation, Pt contamination)
- **In-situ characterization** to evaluate all these processes and to assess the different loss mechanisms
- **Ex-situ analysis** to understand the microstructure and element distribution
- **Modelling** to explain the physics
- **Production research** to develop manufacturing processes



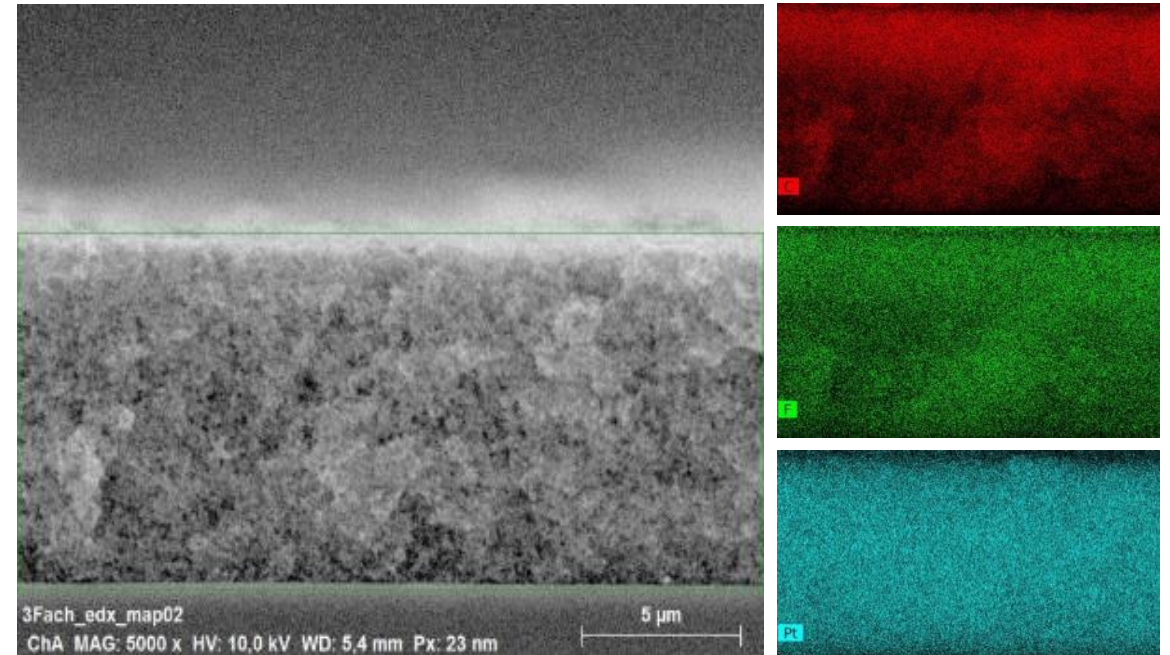
Investigating BoL and EoL Microstructures of Fuel Cell Components

Understanding material composition and structure

Our Analytical Equipment

1. Laserscanning microscope and profilometer for surface microscopy
2. SEM / EDX for element analysis of surfaces
3. XRF for catalyst distribution on surfaces
4. XPS for catalyst analysis
5. FIB-SEM and μ CT for analysis of morphology
6. ICP-MS for element analysis in liquids

Find out more regarding our ex-situ analytics equipment:
<https://www.ise.fraunhofer.de/content/dam/ise/de/downloads/pdf/H2T-Ex-Situ-Analytics.pdf>



Left: scanning electron microscopy (SEM) of 3 screen printed catalyst layers on top of each other. Ionomer content is 30 %, Pt loading 0.271 mg/cm² (for all three layers in total).

Right: Energy dispersive x-ray (EDX) microscopy showing the element distribution (above: carbon; middle: fluorine; below: Pt)

Fraunhofer ISE Single Cell Test Stations

High quality material characterization

Technical Highlights

- 3rd generation of in-house developed test stations
- Fully automated for 24/7 operation
- Operation with air, oxygen, hydrogen, nitrogen, or contaminants
- Dynamic humidification
- State-of-the-art electro-chemical characterization:
 - polarization curve
 - electro-chemical impedance spectroscopy (air/H₂ and N₂/H₂)
 - Cyclovoltammetry & linear sweep voltammetry
 - limiting current measurement
 - CO stripping & CO displacement

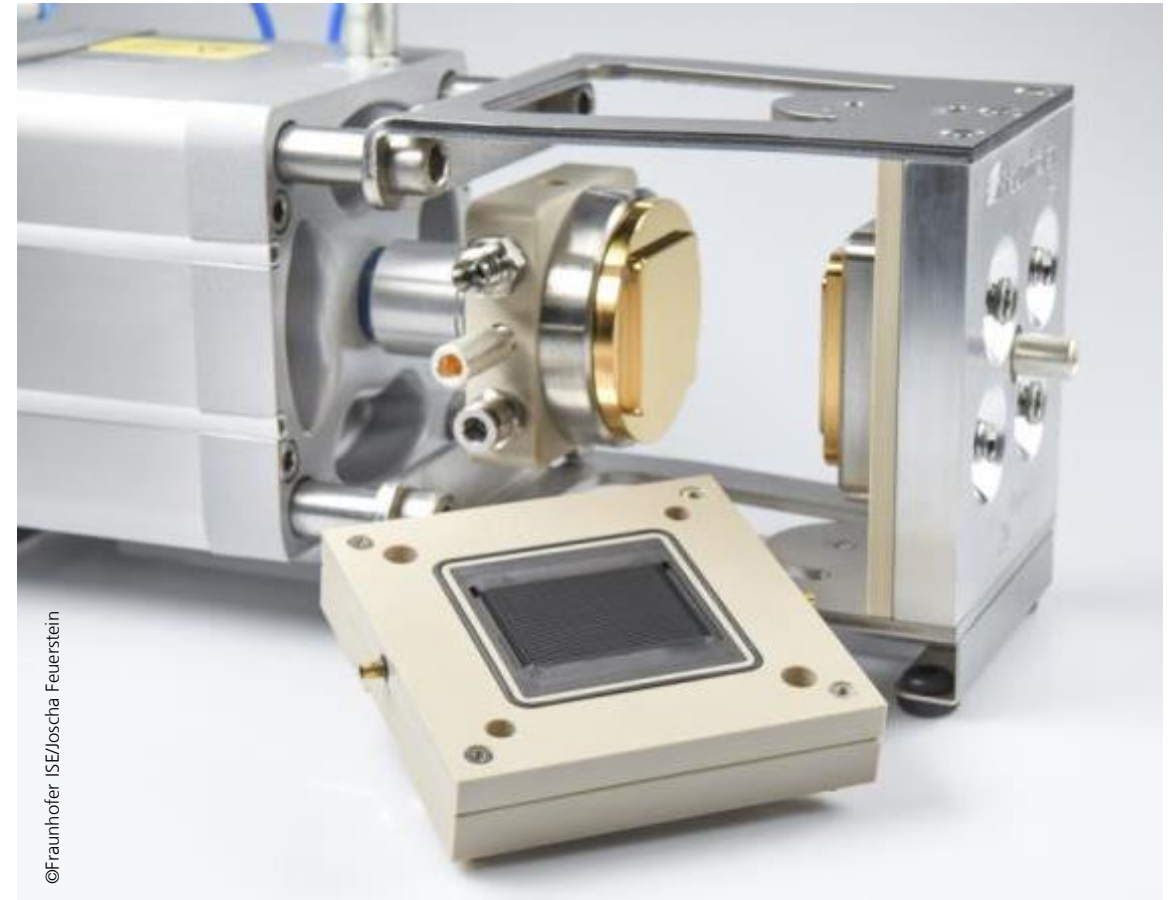


Fraunhofer ISE Baltic Differential Test Cell

High quality material characterization

Technical Highlights

- Differential test cell (zero-gradient) for very homogeneous operating conditions
- Effective liquid cooling
- Controllable (pneumatic) clamping pressure directly on the active area (GDL thickness variable & no gasket compression set-off)
- Graphitic plates guarantee corrosion free long-term operation & customer specific flowfield designs
- Easy handling for fast component exchange and low down-time
- NEWS: also available for metallic plates and in-operando testing of bipolar coatings





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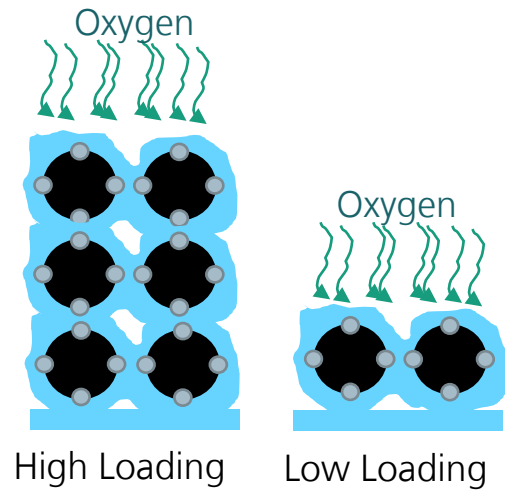
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Designing CCMs

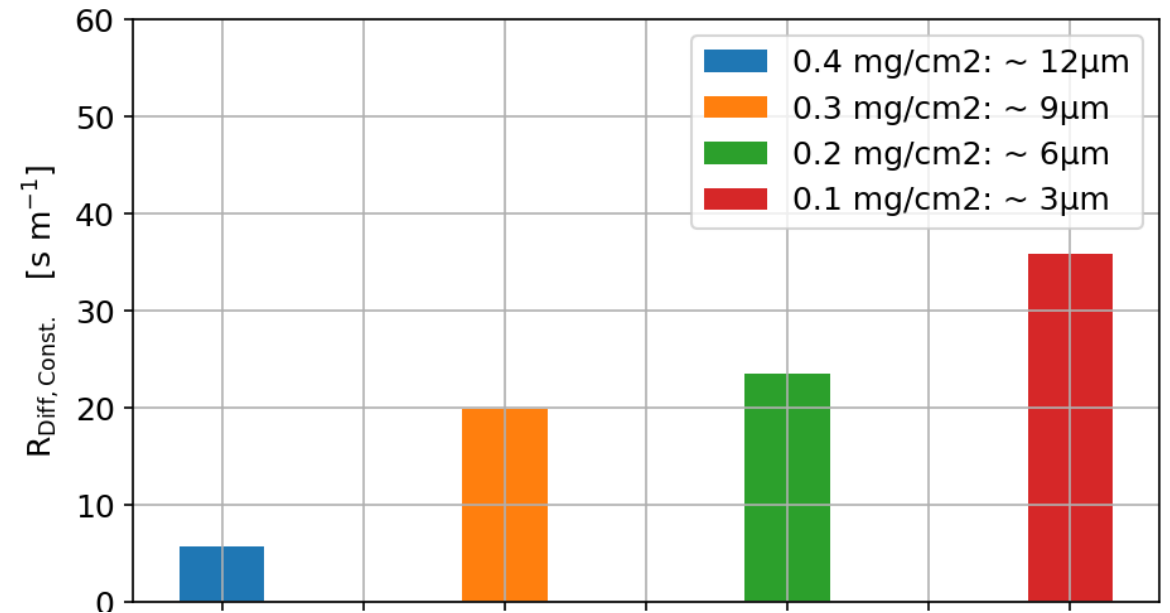
Mass Transport Resistance of Different Catalyst Layers

Limiting Current Measurements

Physical model



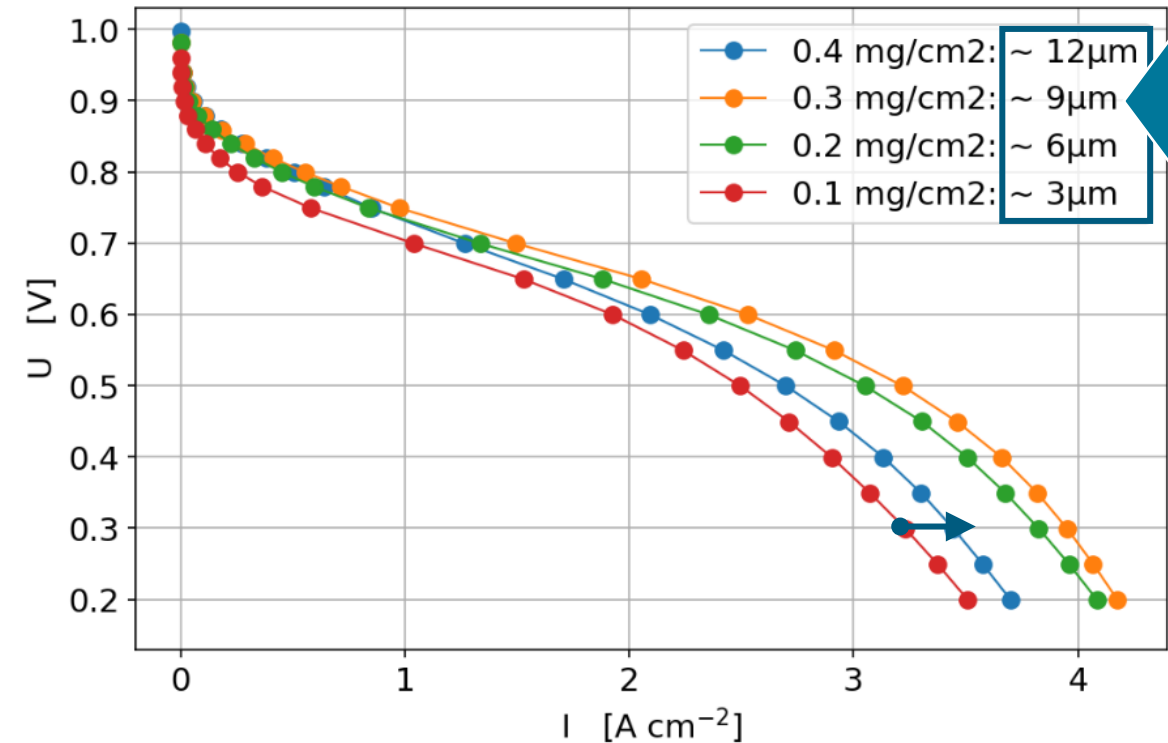
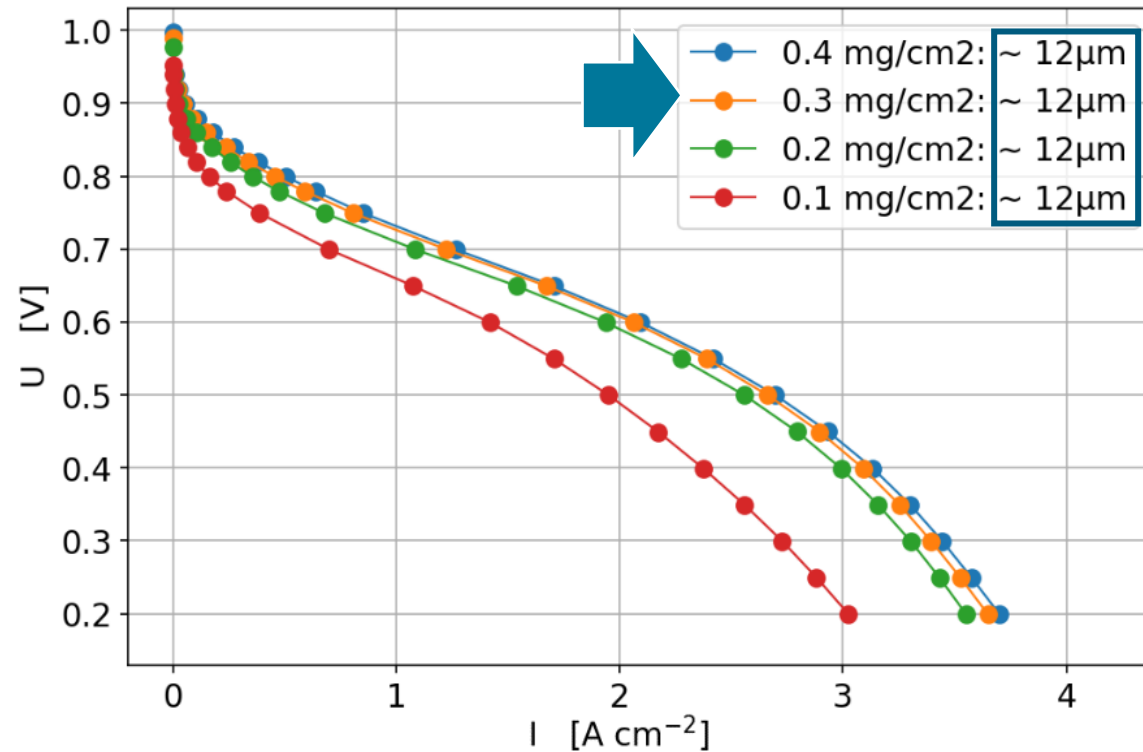
- **Knudsen diffusion resistance grows with shrinking Pt loading as O_2 molecules compete for catalyst sites**



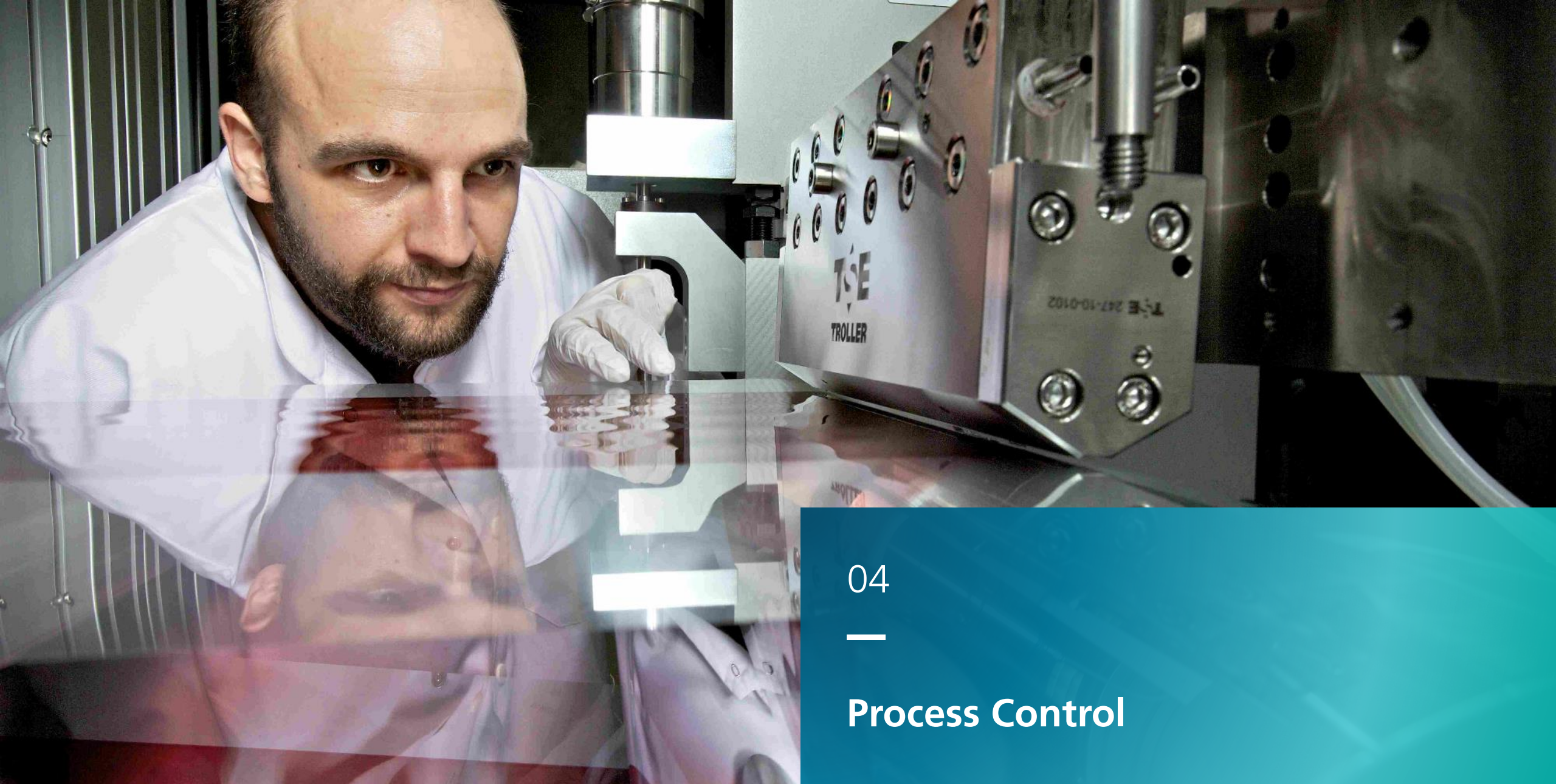
Measured Knudsen diffusion resistance (pressure independent) in catalyst layers with different Pt loadings and thicknesses

Impact of Catalyst Layer Thickness and Pt Loading on Performance

Optimizing the electrodes



➤ Thinner layers with same loadings perform better due to better oxygen diffusion in macro pores



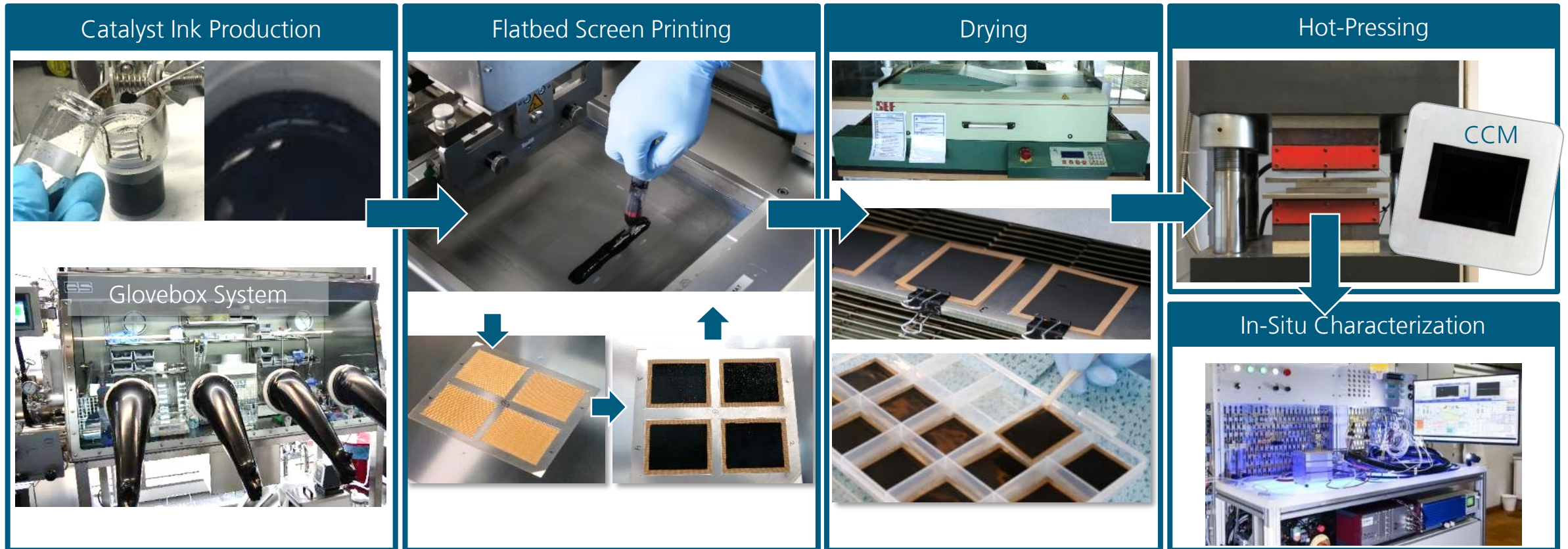
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Process Control

MEA Production Research

Finding best process technologies and parameters – from catalyst powder to complete MEAs



Ney et al., European Coating Symposium ECS 2021, Challenges of Fabricating Catalyst Layers for PEM Fuel Cells using Flatbed Screen Printing, 2021

Printing Process Parameters Influence Catalyst Layer Quality

Ink

- Composition
- Particle size distribution
- Wetting behavior (screen & substrate)
- Rheology
- Chemical stability

Printing Process

- Squeegee pressure, angle, velocity
- Printing & flooding direction
- Snap-off distance
- Amount of ink

Ney et al. "Challenges of Fabricating Catalyst Layers for PEM Fuel Cells using Flatbed Screen Printing", to be published in Journal of Coatings Technology and Research, 2022

Squeegee

- Hardness
- Material
- Geometry (width, form)



Substrate

- Chemical composition/material
- Cleanliness
- Surface roughness & energy
- Tensile strength

Screen

- Mesh count
- Wire thickness, layout, screen angle
- Weave, thickness, wire material, wire roughness
- Emulsion material, thickness, roughness
- Screen tension

Machining

- Alignment of screen & substrate
- Adjustability of printing parameters
- Throughput
- Visual evaluation of printed layer

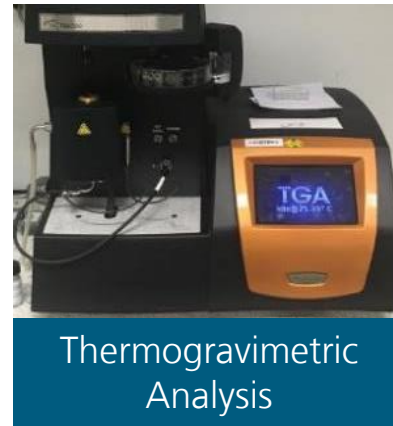
Hot Pressing & Drying

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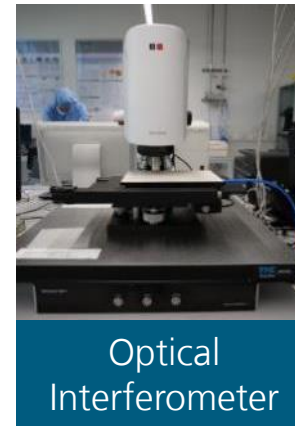
Ex-situ Quality Assurance for Ink & Coating Processes



Laser Diffraction Particle Size Analyzer



Thermogravimetric Analysis



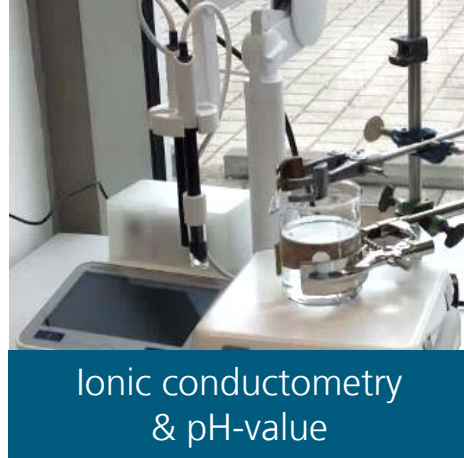
Optical Interferometer



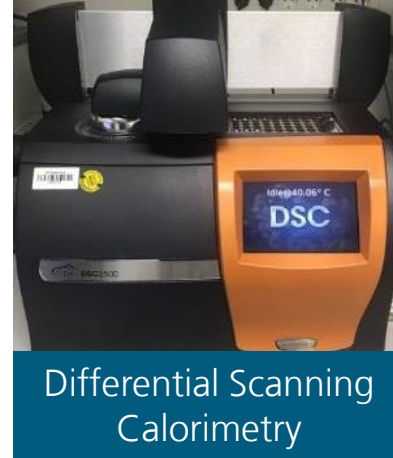
Confocal Laser Scanning Microscope



N₂-Adsorption



Ionic conductometry & pH-value



Differential Scanning Calorimetry



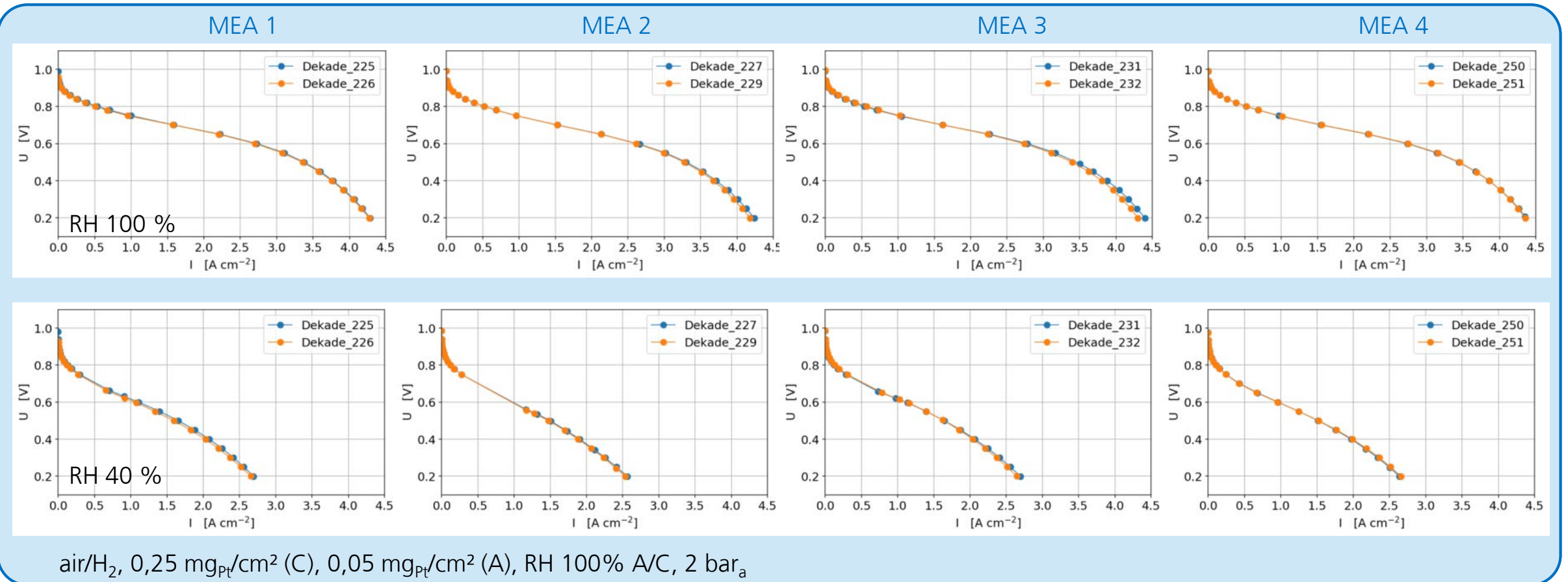
contact angle

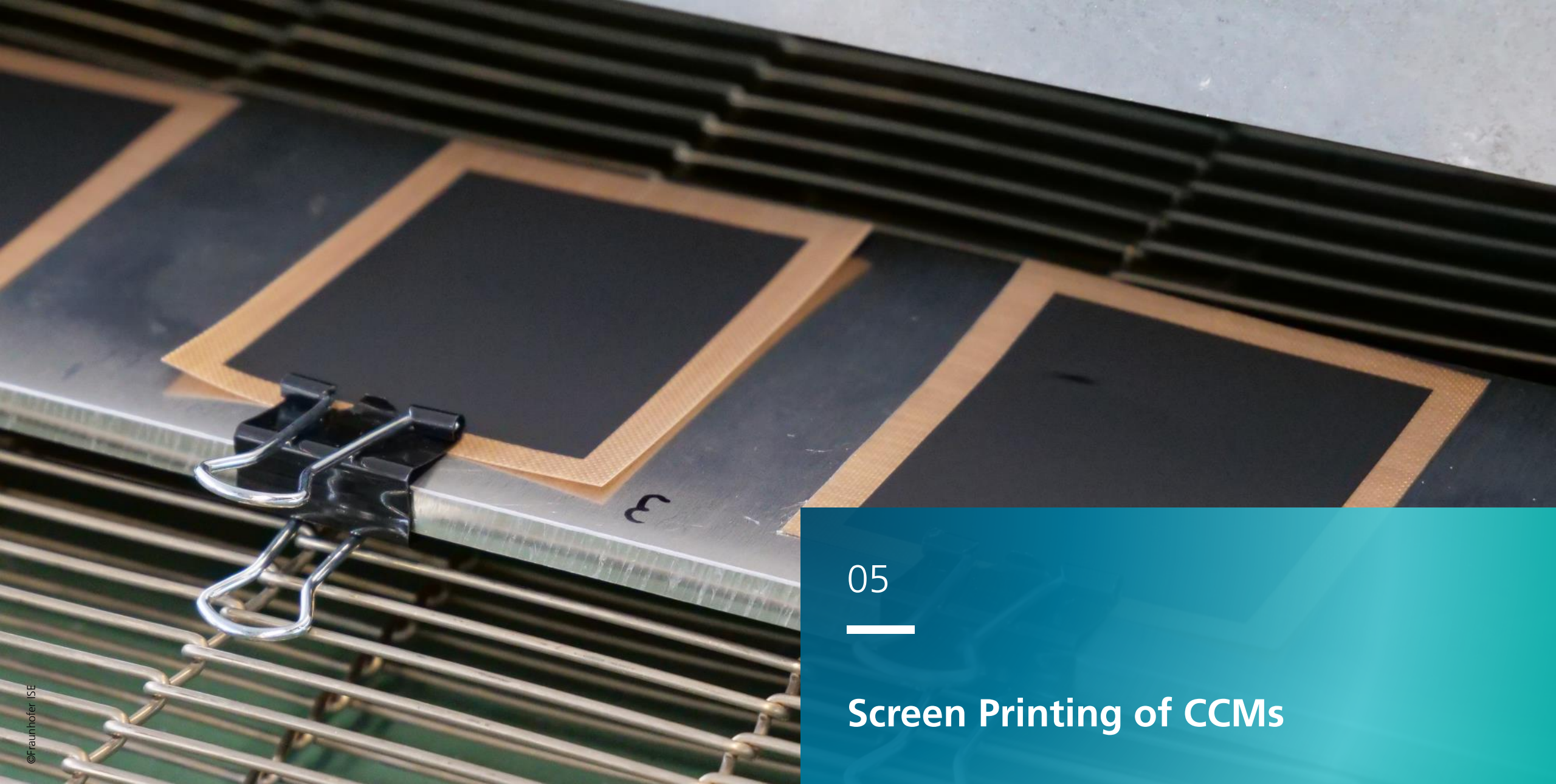


Rotational rheometer

High Reproducibility of Production Process and In-Situ Characterization

Polarization Curves @ wet & dry conditions





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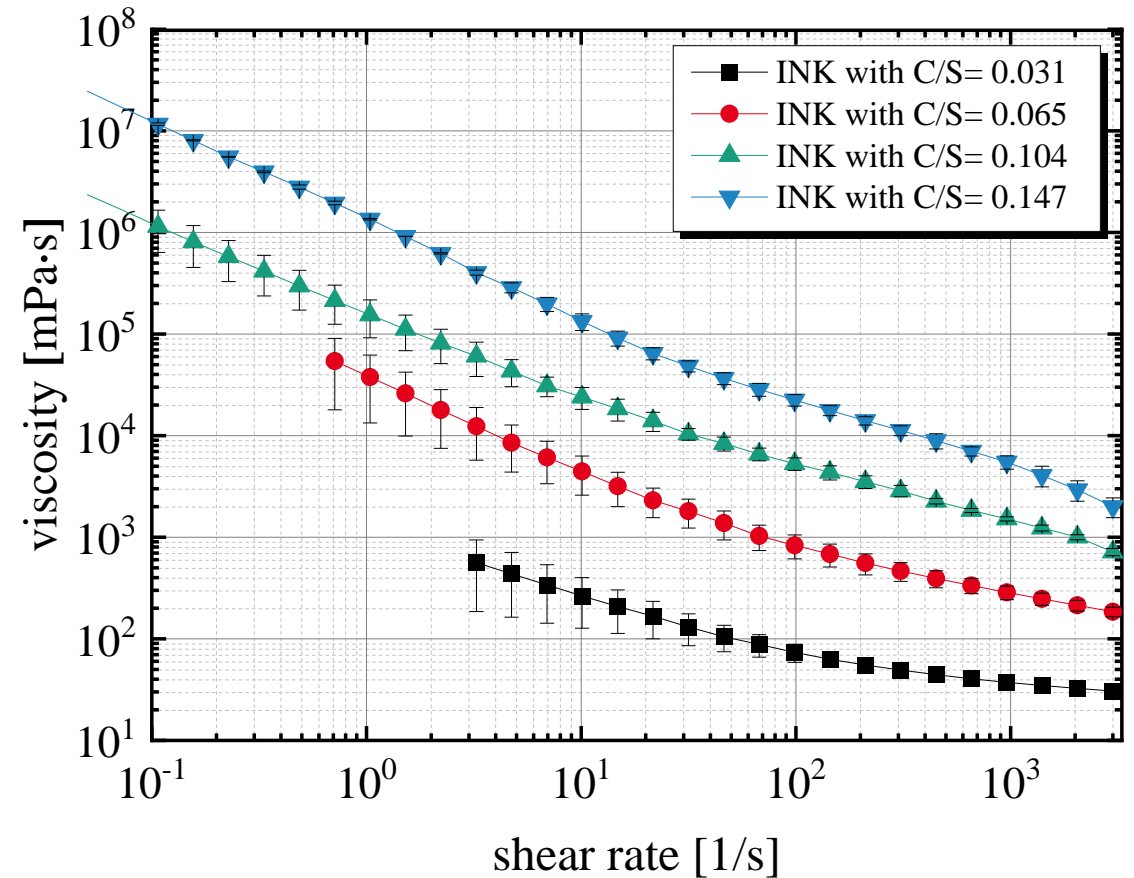
Screen Printing of CCMs

Ink Development

Adjusting the catalyst ink rheology to screen printing

Ink rheology for screen printing

- I/C ratio constant (ionomer to carbon) with Ketjenblack carbon powder and Aquivion® ionomer
 - C/S ratio variation (carbon to solvent)
-
- Strong shear thinning behavior: breaking up of the internal microstructure
 - Higher viscosity with increasing C/S



Ney et al. QC4FC Workshop,
Fraunhofer ISE, 2021

Ink Development

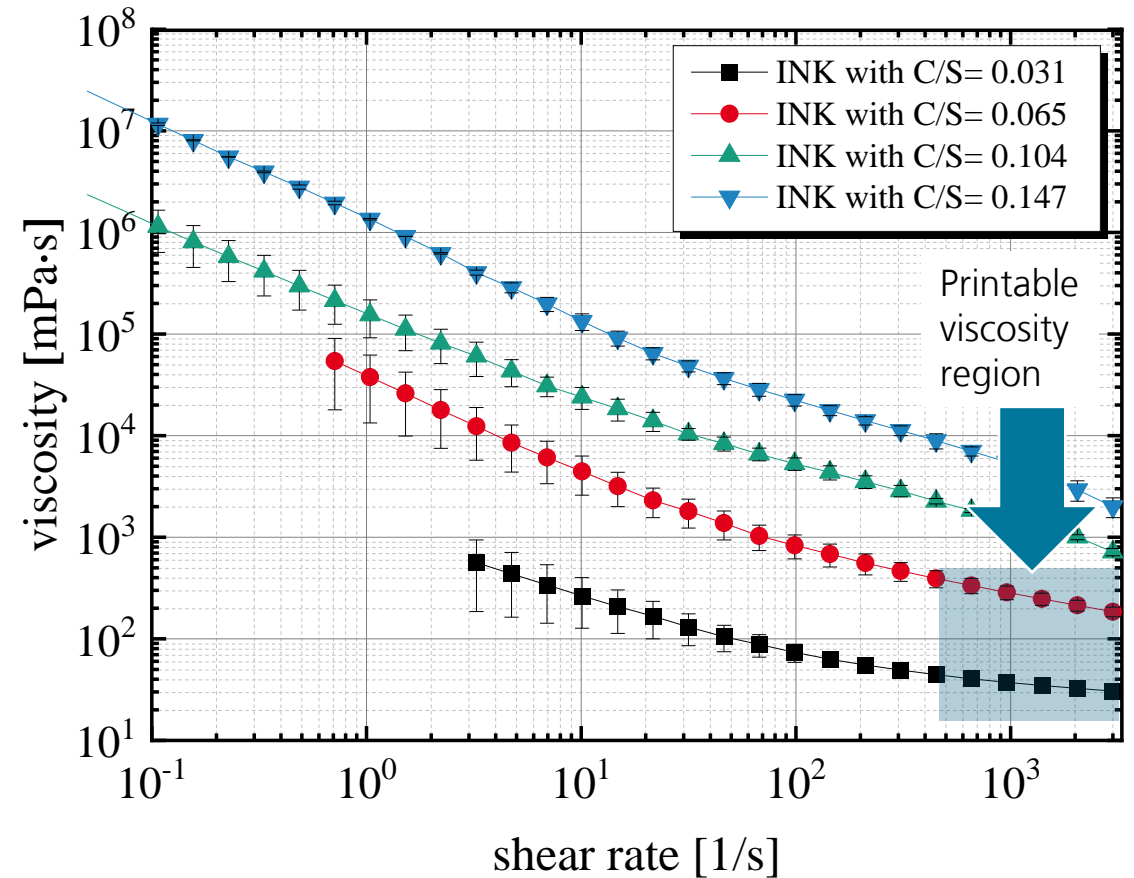
Adjusting the catalyst ink rheology to screen printing

Ink rheology for screen printing

- Apparent shear rate during printing process can be estimated as 600 - 6000 s⁻¹ by

$$\text{shear rate } \dot{\gamma} \approx \frac{\text{squeegee velocity } v}{\text{screen opening } d_0}$$

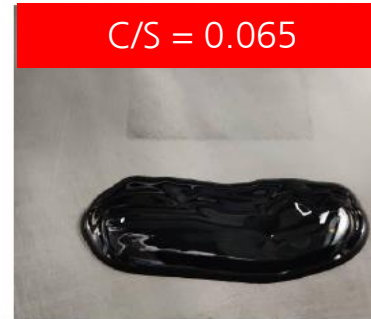
Ney et al. QC4FC Workshop, Fraunhofer ISE, 2021
Ney et al. "Optimization of Fine Line Screen Printing Using in-depth Screen Mesh Analysis." AIP Conference Proceedings, 20006 (2019)
Tepner et al. "The Link between Ag-Paste Rheology and Screen-Printed Solar Cell Metallization." Adv. Mater. Technol., 2000654 (2020)



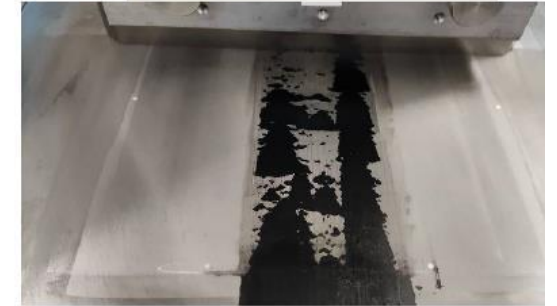
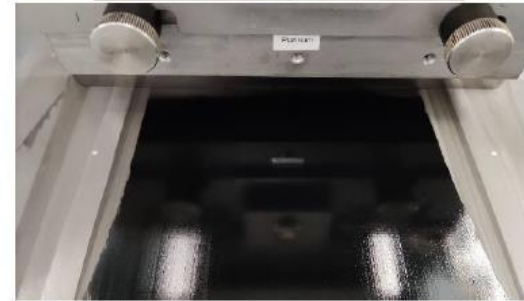
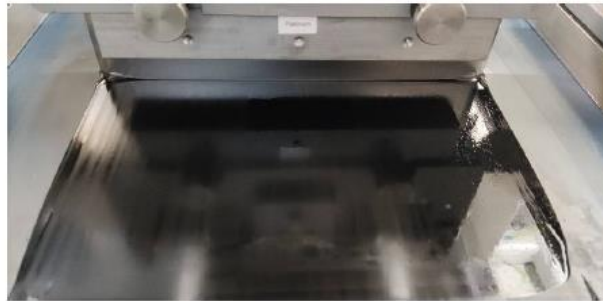
Ink Development

Adjusting the catalyst ink rheology to screen printing

Ink on the screen
before printing

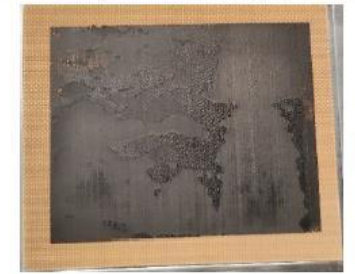
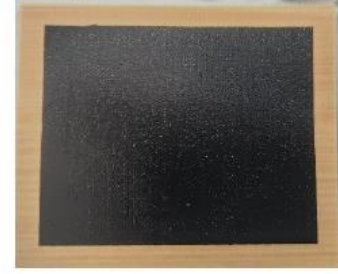


Ink on the screen
after flooding
process



Printed CL

Ney et al. QC4FC Workshop,
Fraunhofer ISE, 2021



Ink Development

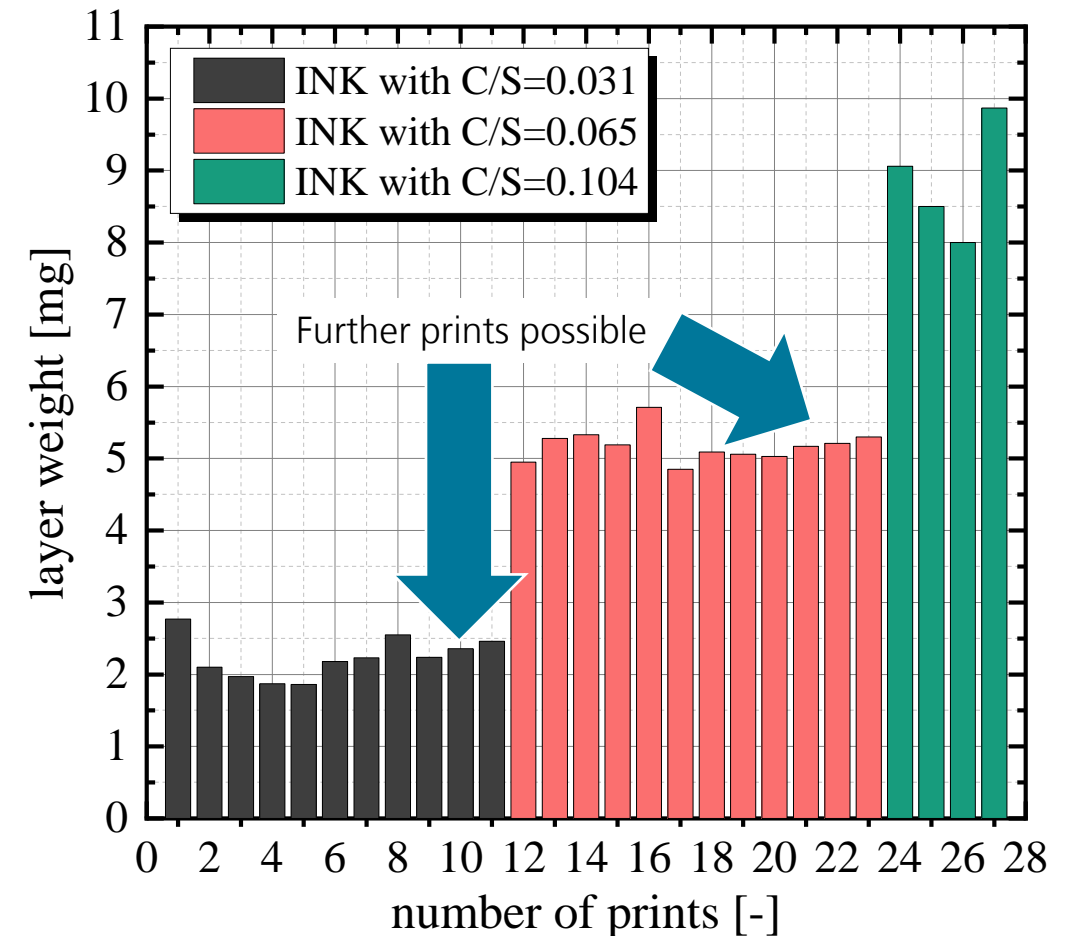
Catalyst layer weight with respect to number of prints and ink

Ink rheology for screen printing

- Solid content (C/S) correlates with applied layer weight and viscosity
- Printable C/S ratio should be in the range of 0.031-0.065 (with I/C=0.7 and Ketjenblack)



Ney et al. QC4FC Workshop,
Fraunhofer ISE, 2021



Ink Composition and Process Stability

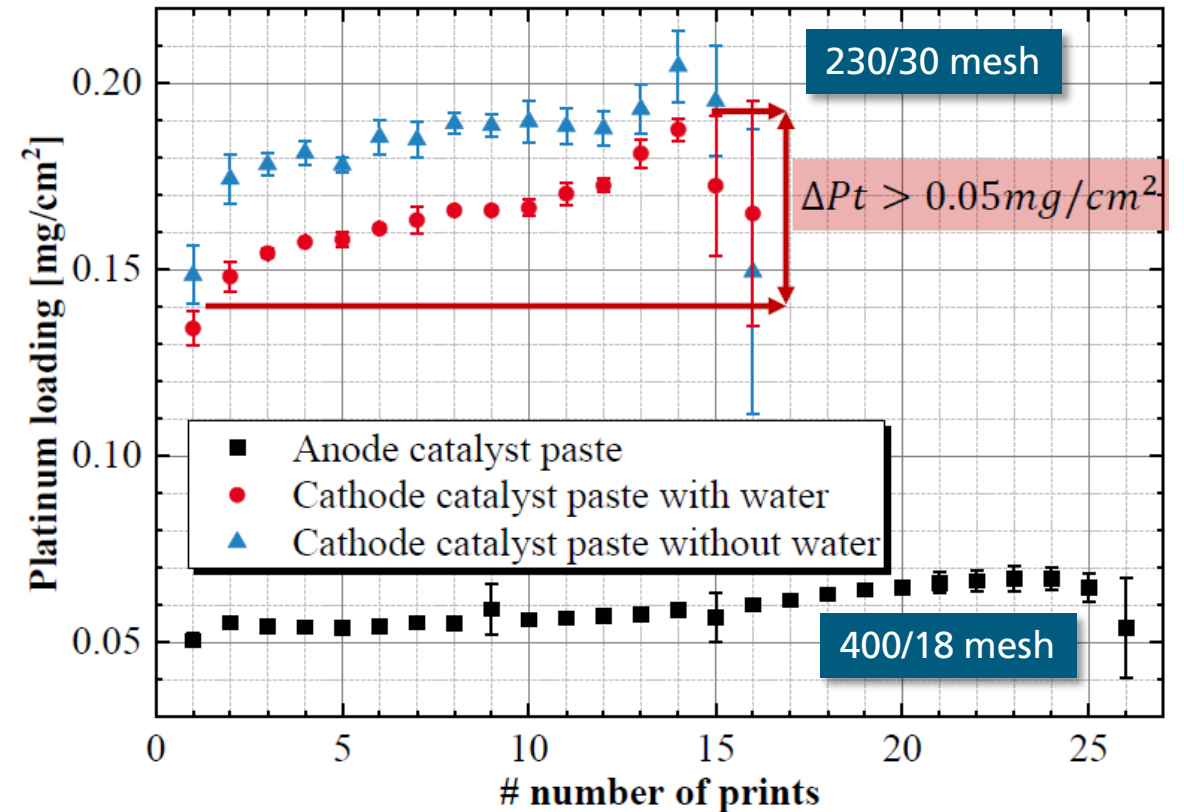
Stability of the Printing Process

Goal

- Anode Pt loading of 0.05 mg/cm²
- Cathode Pt loading of 0.2 mg/cm²

Problem

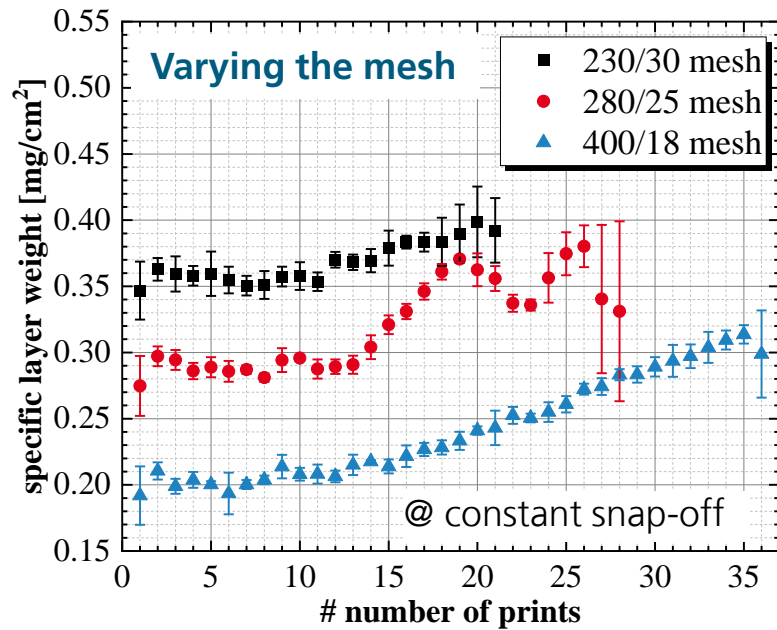
- insufficient process stability: growing layer weights and Pt loadings during printing process
- Evaporation of highly volatile solvents (water) increases the solid content of the paste
- Does water content within the catalyst paste affect MEA performance?



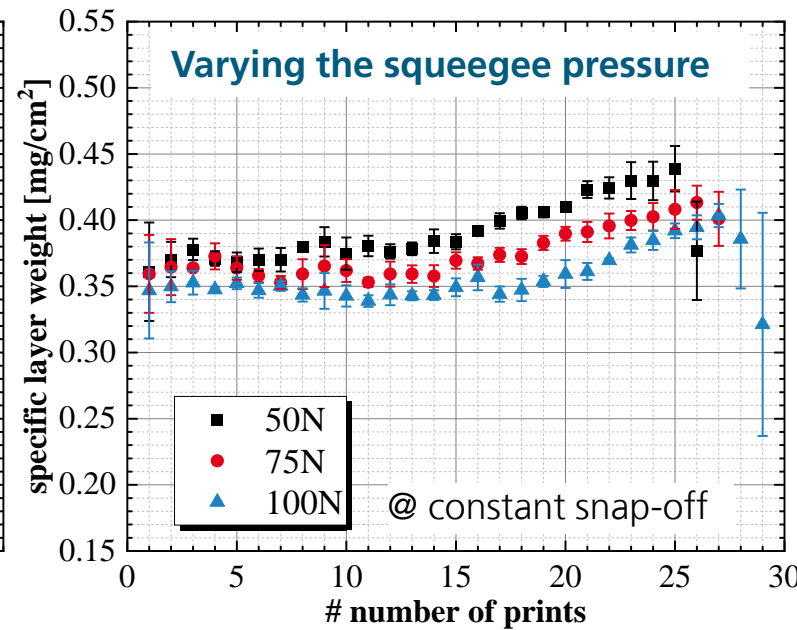
Ney et al., European Coating Symposium ECS 2021, Challenges of Fabricating Catalyst Layers for PEM Fuel Cells using Flatbed Screen Printing, presentation, 2021; to be published in Journal of Coatings Technology and Research, 2022

Catalyst Layer Manufacturing by Screen Printing

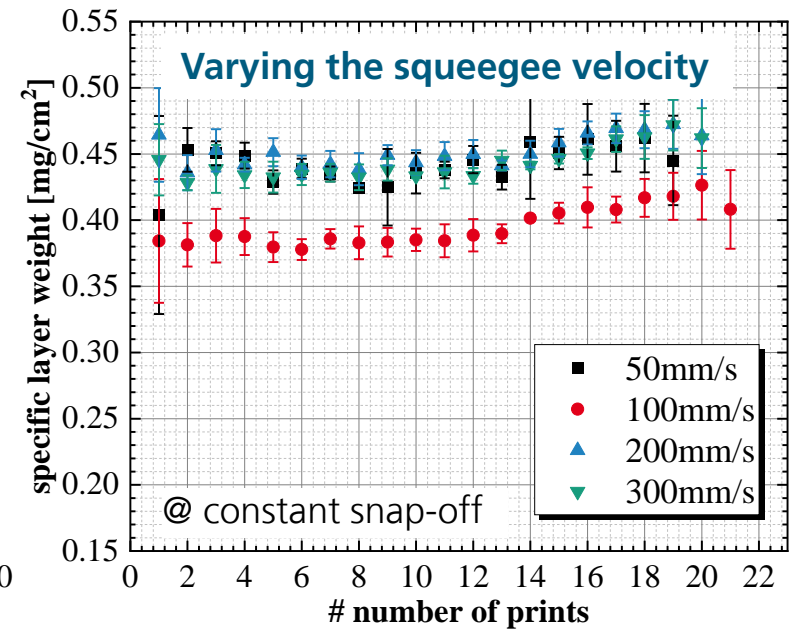
Linking process parameters and layer weight



Increased layer weight by coarser mesh



No significant effect of squeegee pressure



No significant trend in velocity variation

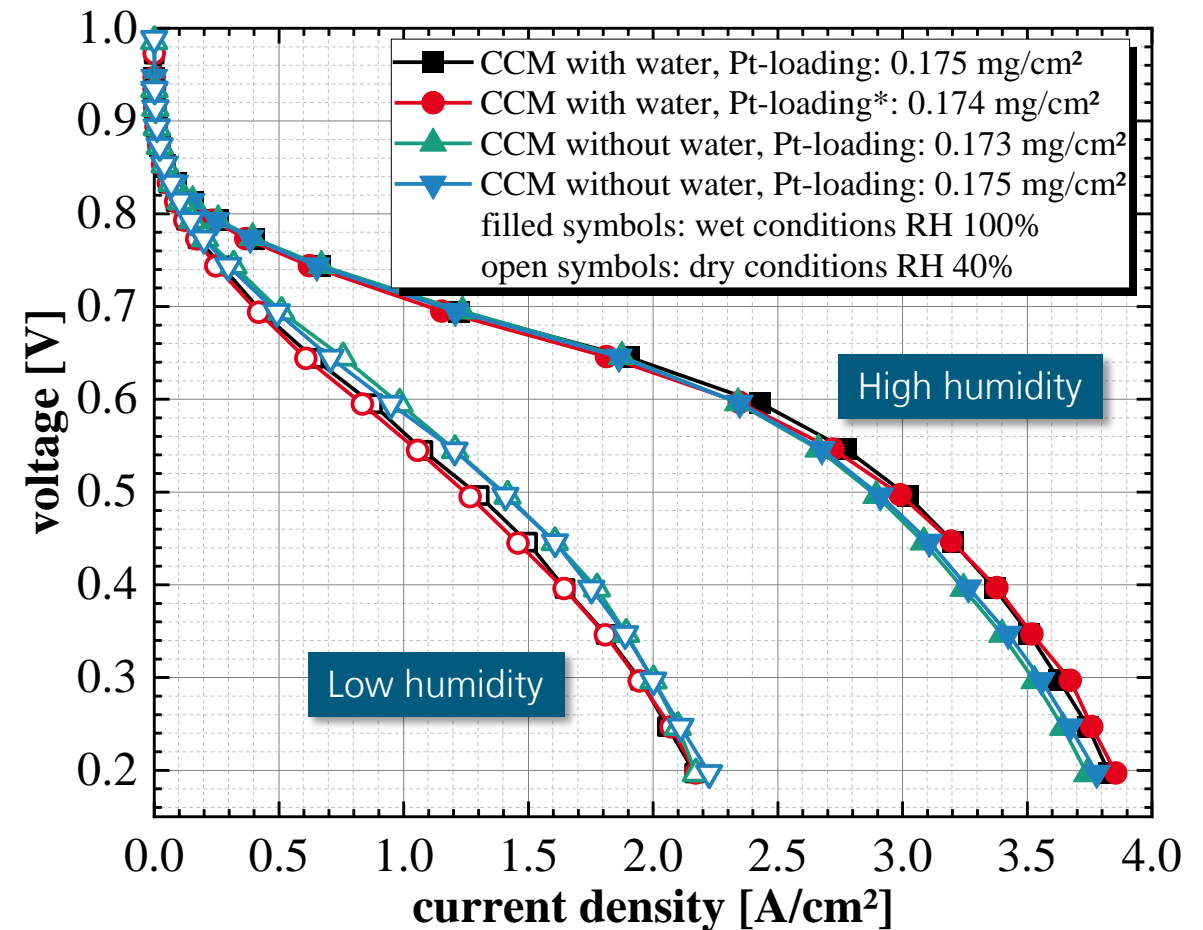
Ney et al., European Coating Symposium ECS 2021, Challenges of Fabricating Catalyst Layers for PEM Fuel Cells using Flatbed Screen Printing, presentation, 2021; to be published in Journal of Coatings Technology and Research, 2022

Effects of Solvents on CCM Performance

Stability of the Printing Process

- Electrochemical Characterization during fuel cell operation of CCMs produced with and without water
- Similar Pt-loadings show very high reproducibility along the process chain
- Water content significantly affects the BoT performance in dependence on relative humidity test conditions
- Choice of solvent is important for printing process stability

Ney et al., European Coating Symposium ECS 2021, Challenges of Fabricating Catalyst Layers for PEM Fuel Cells using Flatbed Screen Printing, presentation, 2021; to be published in Journal of Coatings Technology and Research, 2022



Summary

Screen Printing of Fuel Cell Catalyst Coated Membranes Shows Good Opportunities

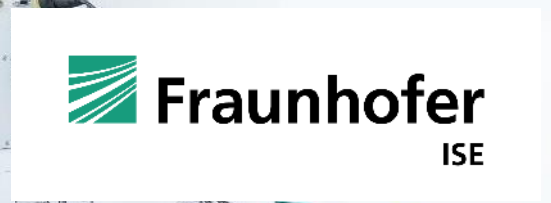
- Ink development is key
- Process control is essential
- Screen printing gives a lot of process flexibility
- CCMs of Fraunhofer ISE show excellent performance

We Offer Our Competences for Your Process Development

- Know-how on ink and process development
- Investigating your components by our analytical equipment
- Characterizing your components with our in-situ test stations

Acknowledgment

To the Ministry of the Environment, Climate, Protection and the Energy Sector Baden-Württemberg for the financial support of our project HyFab-Baden-Württemberg, contract no. L75 20113, and the Project Agency Karlsruhe, Baden-Württemberg Programs (PTKA-BWP) for the administration as well as both for the good cooperation



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Our latest report (German):
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