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M-ERA.NET Call 2021 success stories:
enabling innovation through collaborative projects

IMMENSE.

$H_2 + O_2$ → H_2O

https://www.immense-mera.net

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CCM: Catalyst Coated Membrane
PEM: Polymer Electrolyte Membrane
PEMFC: PEM Fuel Cell

Inkjet manufacturing of CCMs for PEMFC by development of catalytic inks & their deposition

Take home message: Inkjet-printed catalyst layers on PEM employing bio-based ionomers and microwave synthesized catalysts are functional and pave the way for affordable and sustainable energy (SDG 7) and innovative industrial processes (SDG 9)

Objectives of the project

1. Inkjet-ink preparation and inkjet printing process
2. Flexibility in design with new material system
3. Advanced mathematical modelling of stack
4. Short stack fuel cell demonstrator

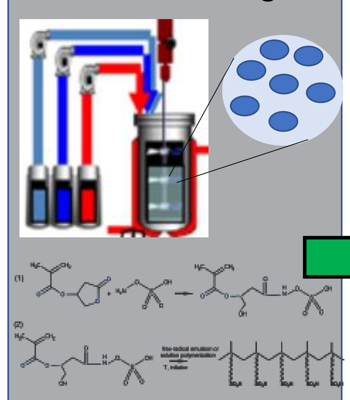
Key findings

- Inkjet-printed CCMs perform better than state-of-the art ultrasonic sprayed ones at significantly lower Pt loading
- Synthesized bio-based ionomers present good and temperature stable ionic conductivity
- Microwave synthesis of Pt/C catalysts are basis for core shell catalyst development
- Newly developed materials show performance comparable to commercial ones
- Simulation of catalyst distribution generates better understanding for processes
- Project results meet industrial target performance parameters

Process workflow

Universidad del País Vasco / Euskal Herriko Unibertsitatea

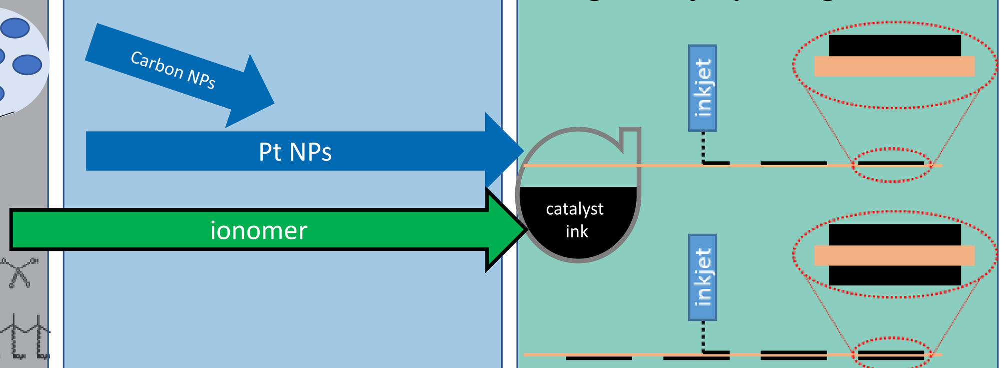
ionomer design



- Synthesis of polymers

TUBAF

catalyst design



- Synthesis of C/Pt NPs
- Synthesis of core/shell NPs

Fraunhofer ENAS

ink formulation & digital inkjet printing

- Inkjet printing process
- Layer properties

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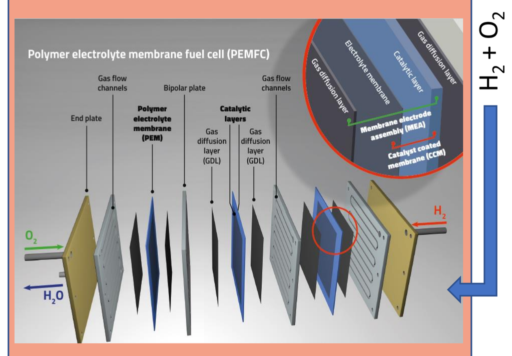
evaluation of PEMFC



- Characterization of CCMs
- Degradation kinetics (long-term stability)
- Post-mortem analysis of the MEA
- Simulation of stack

- target performance parameters
- durability
- cell and short stack testing

ÚJV

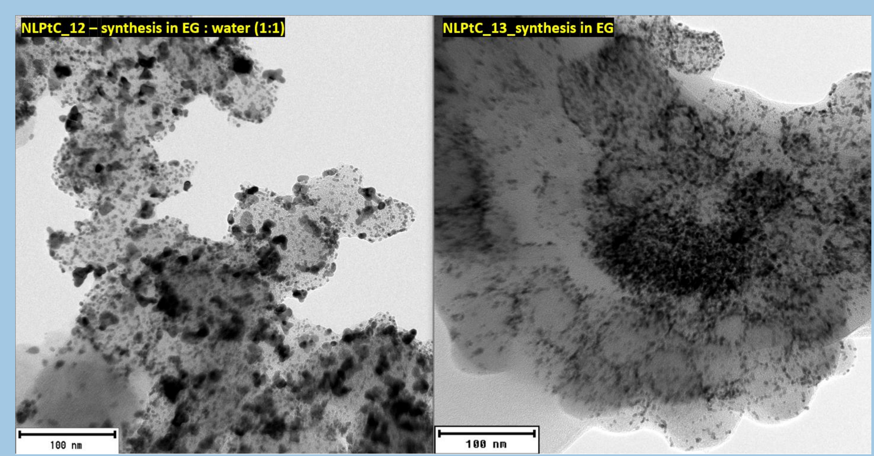
Catalyst design

Technische Universität Bergakademie Freiberg, Germany

TUBAF The University of Resources. Since 1765.

Pure Platinum Catalyst

- Platinum nano particles immobilized on carbon support (approx. 50 nm)
- Platinum Particle size < 10 nm
- Synthesis via polyol process enhanced via microwave reactor
- High efficiency and short reaction times of under one hour

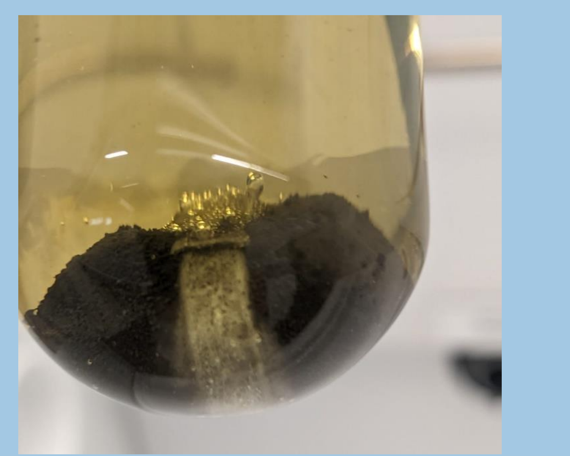


TEM images: right, Pt on Carbon produced with EG to water (v:v) 1:2 and Pt on Carbon with EG to water content (v:v) 2:1

+ Higher amount of reductive agent ethylene glycol speeds up reaction and simultaneously acts as capping agents reducing crystal size and preventing aggregation, homogeneous PDS
– Precursor is significantly less soluble in pure ethylene glycol

Platinum Alloy Catalyst

- Platinum alloys with nickel and cobalt have superior catalysis properties when compared to pure platinum (111)
- Cobalt and nickel are significantly harder to produce via the polyol process as they have a lower reduce potential



Photograph: metallic cobalt particles amassed around poles of magnetic stirring bar

+ Increase in pH necessary to prevent formation of highly stable EG-metal ion complexes and enhance reduction
+ Lower material cost
– Elevated temperature at boiling point of EG
– Increase in reaction time by 200 %

Synthesis of polymers for ionomer

Universidad del País Vasco/Euskal Herriko Unbertsitatea, Spain

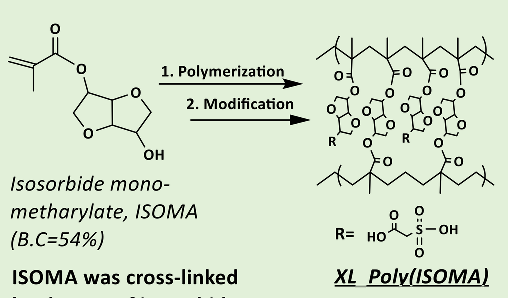
UPV EHU

I. PROTON EXCHANGE MEMBRANE OPTIMIZATION: BIO-BASED PEMS

- A library of bio-based materials is being developed as an alternative for PFSAs and which will provide us with a more sustainable and affordable production of PEMFCs.

II. SYNTHESIS AND RESULTS

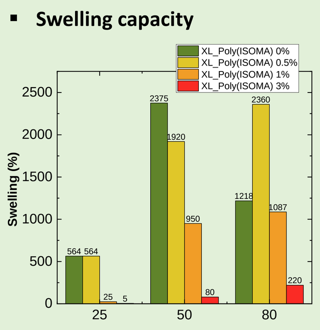
ISOSORBIDE METHACRYLATE



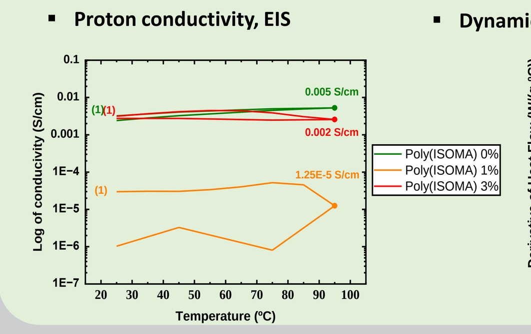
Isosorbide mono-metharylate, ISOMA (B.C=54%)

ISOMA was cross-linked by the use of isosorbide dimethacrylate at different percentages 0-5%.

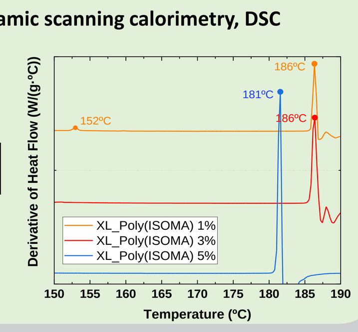
- **Swelling capacity**



- **Proton conductivity, EIS**

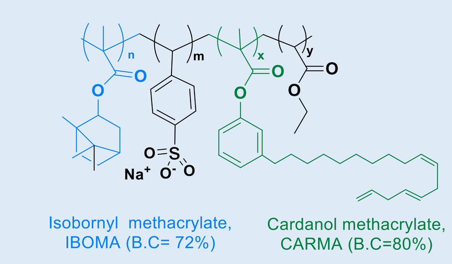


- **Dynamic scanning calorimetry, DSC**



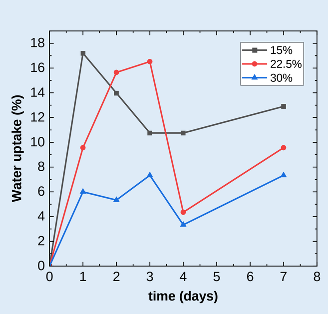
ISOBORNYL AND CARDANOL METHACRYLATE

Poly (IBOMA-co-NaSS-co-CARMA-co-EA)

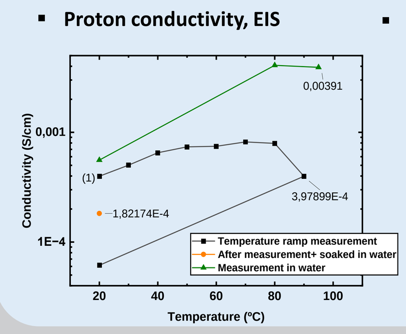


Synthethised in water-dispersed media. CARMA percentage has been varied 15-30%.

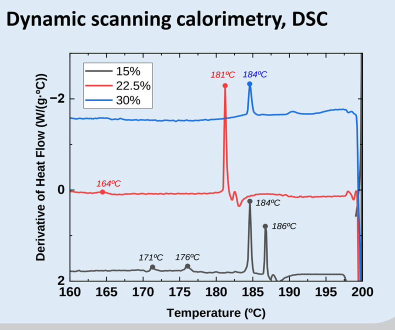
- **Water uptake**



- **Proton conductivity, EIS**



- **Dynamic scanning calorimetry, DSC**



III. CONCLUSIONS

XL_Poly(ISOMA)_3 % ionomer looks as a promising material for PEMFCs:
✓ Reduced swelling.
✓ Thermally stable : Tg~180 °C
✓ Great proton conductive at elevated T: $5 \cdot 10^{-3}$ S/cm.

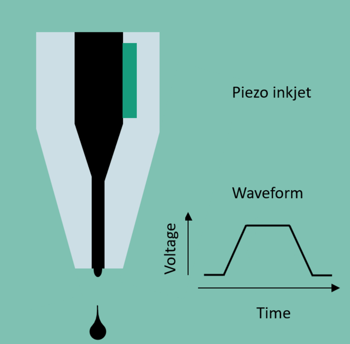
Poly (IBOMA-co-NaSS-co-CARMA-co-EA)_15 % showed:
✓ Biggest water uptake capacity
✓ Thermally stable : Tg~170 °C
✓ Great proton conductive at elevated T: $3 \cdot 10^{-4}$ S/cm.

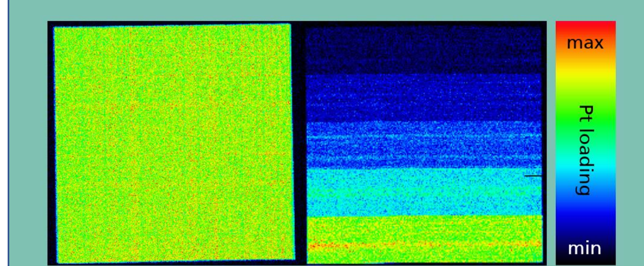
Ink formulation and inkjet printing

Fraunhofer Institute for Electronic Nano Systems ENAS, Chemnitz, Germany

Fraunhofer ENAS

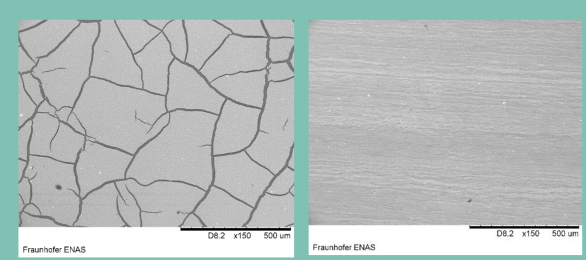
- ➢ Ink design for inkjet process
- ➢ **Direct deposition** of catalyst ink by **industrial inkjet** printhead on variety of commercial membranes (15 µm – 60 µm)
- ➢ Homogenous Pt distribution and crack free catalyst layers at optimized printing and drying conditions



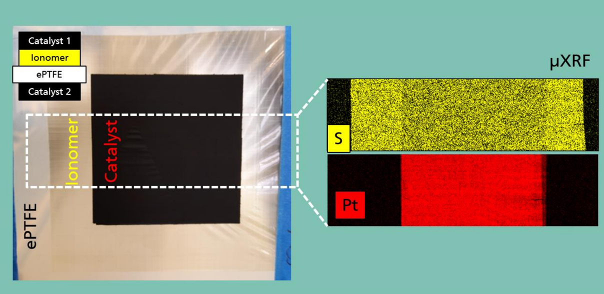


Pt maps for homogenous and in-plane graded catalyst layers (5 cm x 5 cm) printed on membrane

Doble CCMs printed on thick (60 µm) and thin (20 µm) membranes (catalyst area 10 cm x 10 cm)



Images of catalyst layers printed on membrane at initial (left) and optimized (right) printing conditions



Fully inkjet printed CCM with printed membrane

- ➢ Tailored Pt loading (0.1 – 0.3 mg_{Pt}/cm^2)
- ➢ Tailored electrode size (5 cm x 5 cm, 10 cm x 10 cm, extension feasible)
- ➢ Tailored catalyst design (e.g. flowfield, in-plane gradients)
- ➢ Inkjet printed membranes

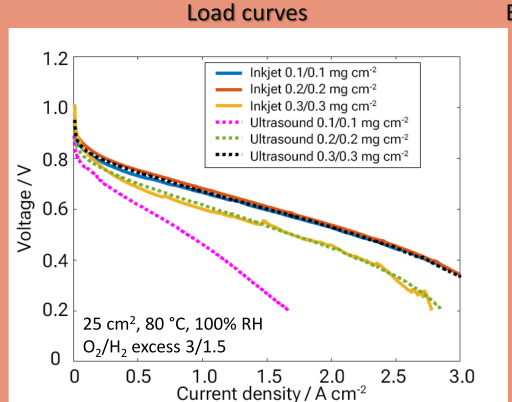
PEMFC evaluation and simulation of stack

University of Chemistry and Technology Prague, Czech Republic

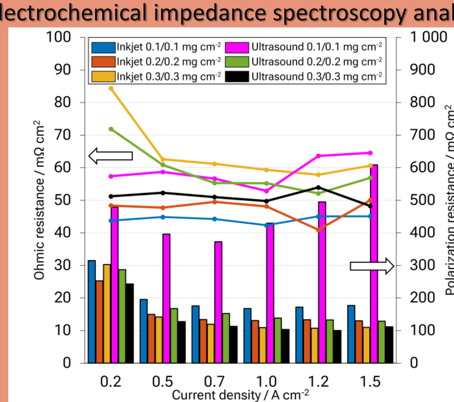
UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

Comparison of inkjet printed and ultrasonically coated catalyst layers

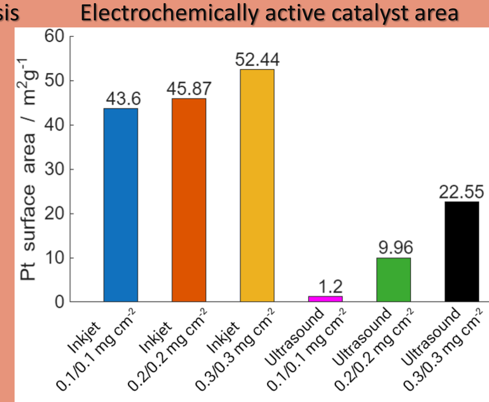
Load curves



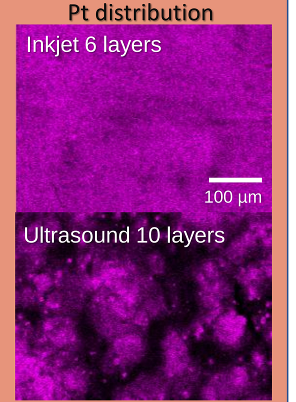
Electrochemical impedance spectroscopy analysis



Electrochemically active catalyst area

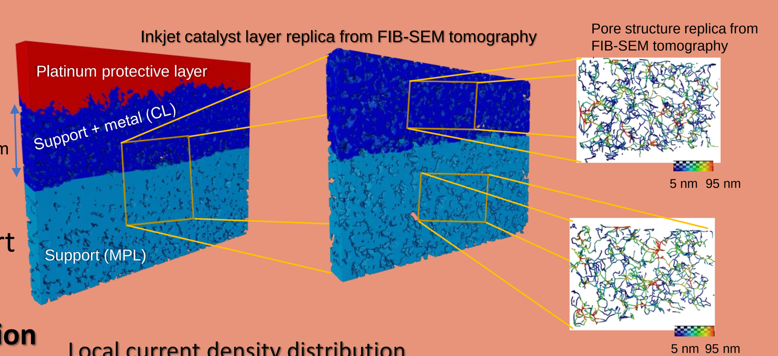


Pt distribution

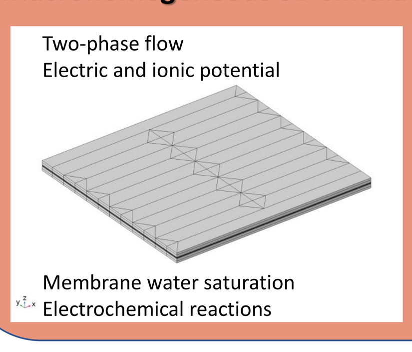


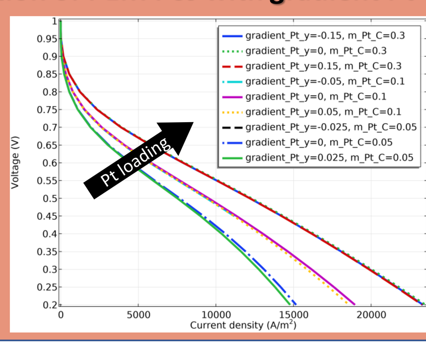
Inkjet-printed layers:

- Better performance at low Pt loadings
- Lower Ohmic and polarization resistance at low Pt loadings
- Higher electrochemically active catalyst area
- Homogeneous Pt distribution at lower Pt loadings
- Homogeneous pore structure and higher porosity – better gas transport

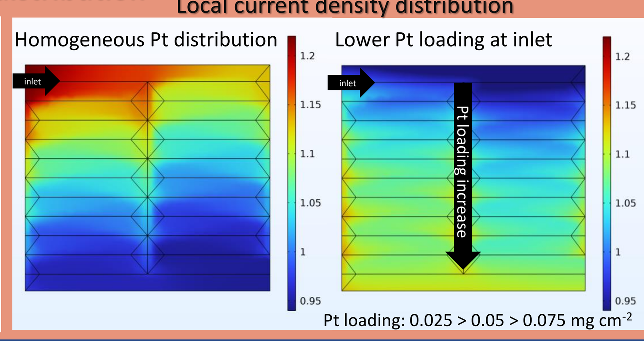


Macrohomogeneous 3D simulation of PEM FCs with gradient Pt distribution





Local current density distribution



- In-plane gradient has bigger effect at low Pt loadings
- Homogenization of local current density – long-term FC stability

Industrial relevance

ÚJV Řež, a.s., Czech Republic

- Cost analysis
- Current market analysis
- Creating a business model
- Comparison of the resulting price from the business model with the commercial competition

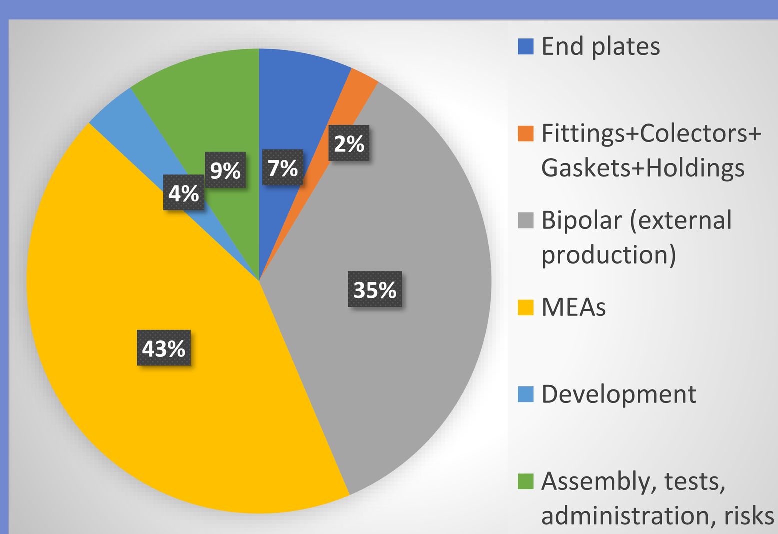


Fig. 1 Costs shares for stack production, © ÚJV Řež a. s., Miroslav Kludský

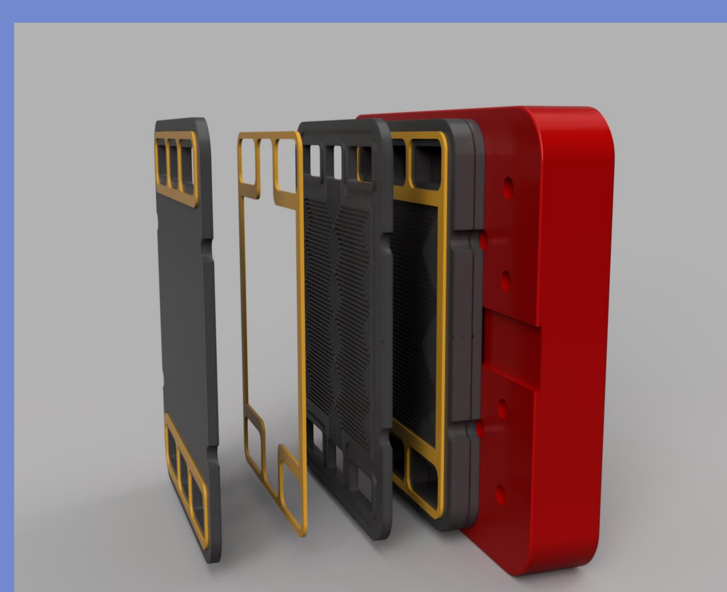


Fig. 2 Fuel cell production model - assembly (gasket, bipolar plates, endplate), © ÚJV Řež a.s., Miroslav Kludský

- Creating a stack prototype for developed MEA
- Stack optimization
- Testing MEA in dimensions common for fuel cells with outputs of approximately 10 kW

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T A Č R

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