Karlsruhe Institute of Technology

Institute for Micro Process Engineering (IMVT)

Ultra-compact micro structured palladium membrane reactors for hydrogen production

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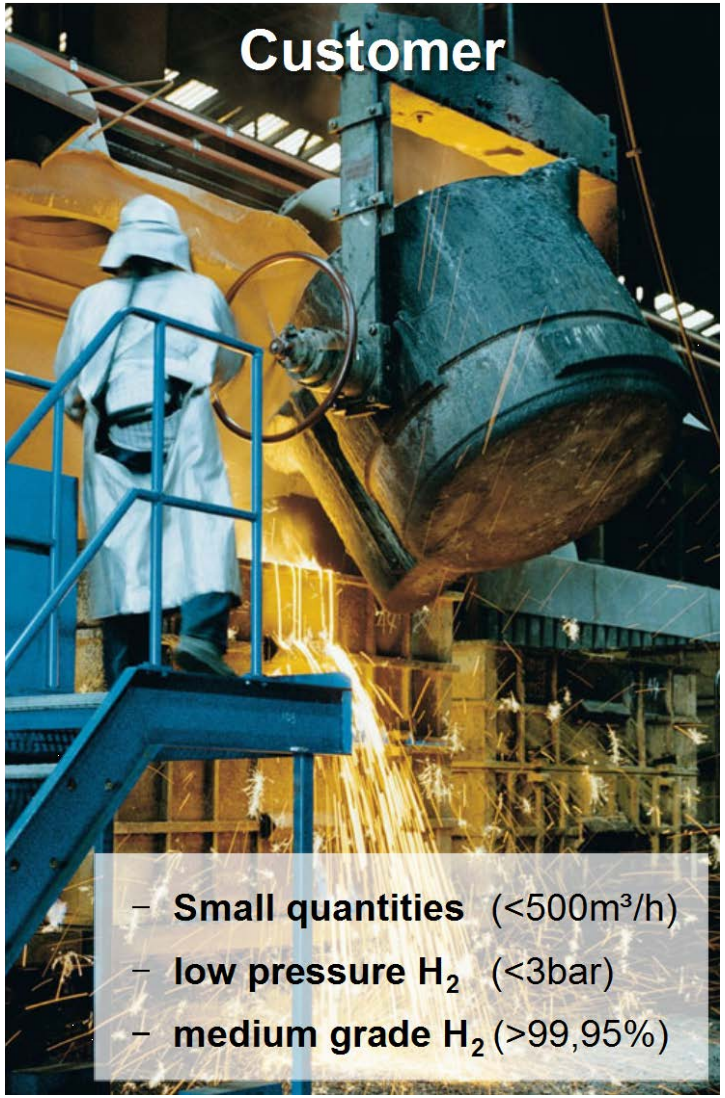
AGENDA

1. Introduction – Micro structured membrane reactors for hydrogen production
2. On-site steam methane reforming – The µ-Enhancer
3. Dehydrogenation of liquid organic hydrogen carriers – The system MCH / TOL
4. Simplified modeling of a micro channel membrane reactor will wall-coated catalyst
    1. Derivation of the governing equations
    2. Flexible solution using Matlab®
5. Some points to remember

SMALL CAPACITY HYDROGEN SUPPLY
AN OPPORTUNITY FOR NEW TECHNOLOGY SUCH AS MEMBRANE REACTORS

Hydrogen supply
< 500 m³/h
on-site



Dittmeyer & Schödel, ICCMR-11, **2013**

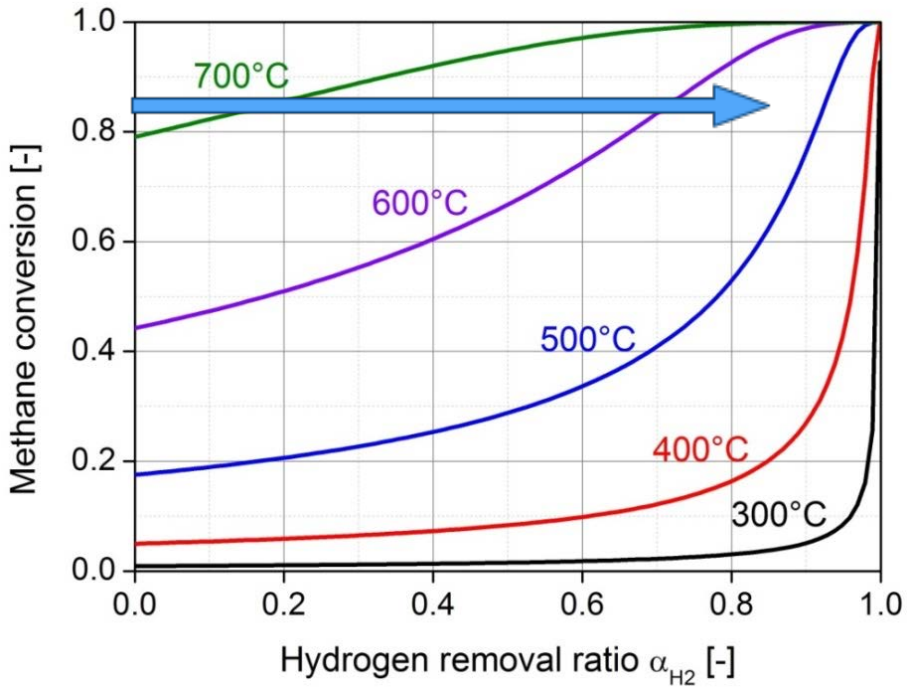
WHY MEMBRANE REACTORS IN HYDROGEN PRODUCTION?

- **Equilibrium shift**
- **Integrated purification**

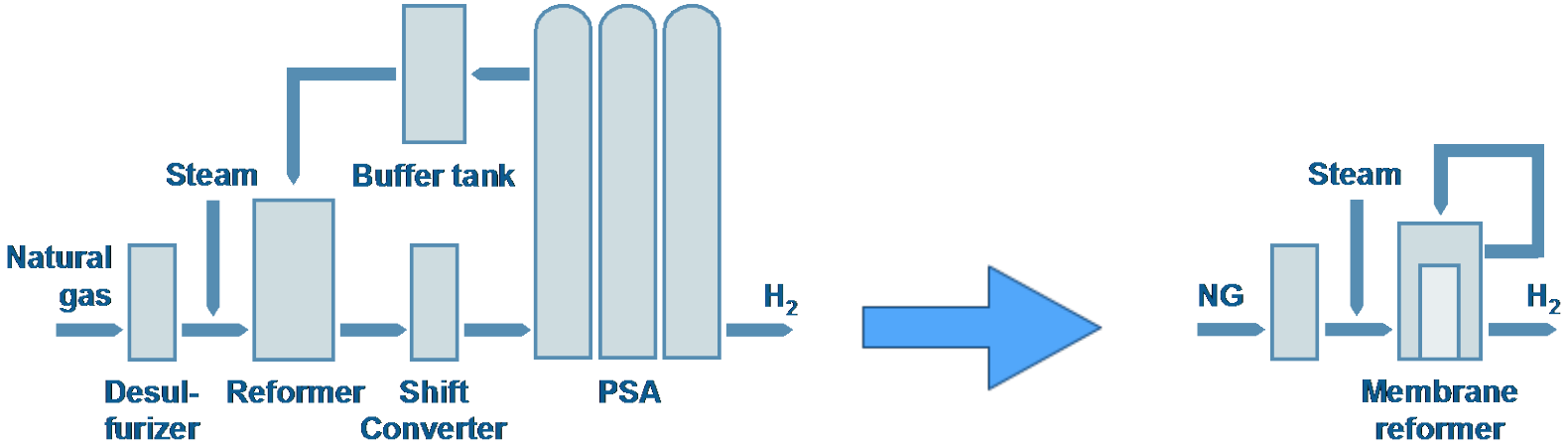
Steam methane reforming

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$



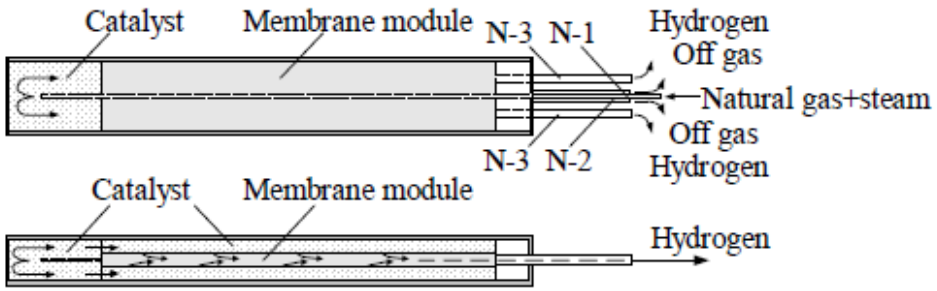
more energy-efficient, lower OPEX



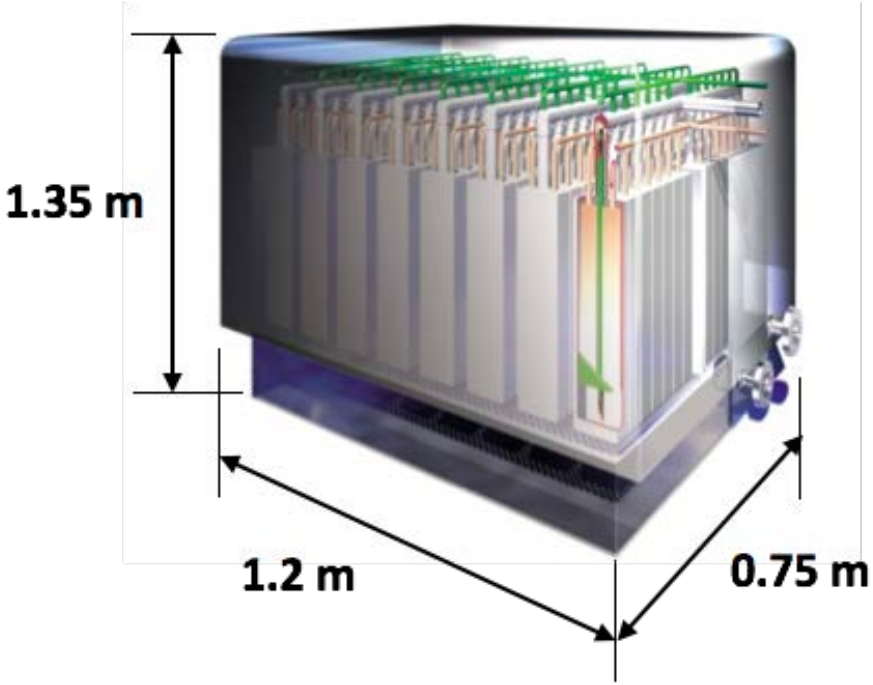
simpler process, reduced CAPEX

Tokyo Gas

Modules:



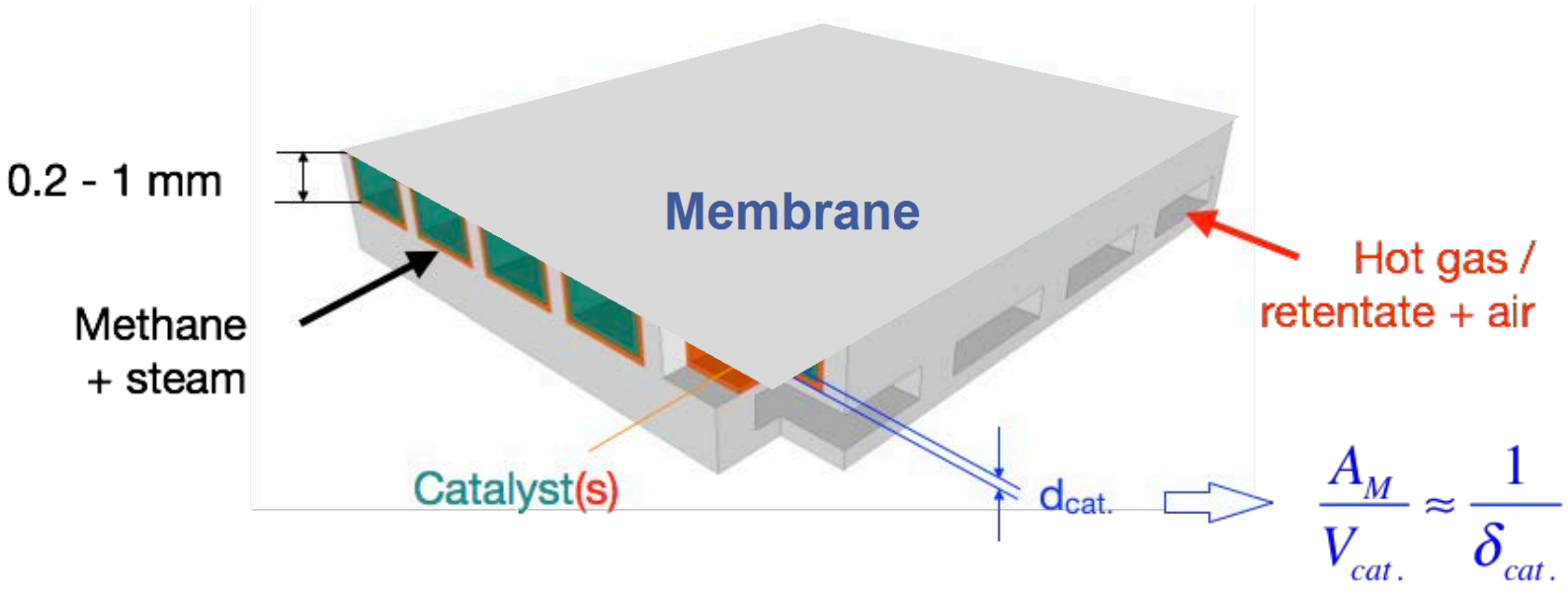
Modular reformer system:
40 m_N^3/h H_2



Yasuda et al., **2005**, ICCMR-7, Cetraro

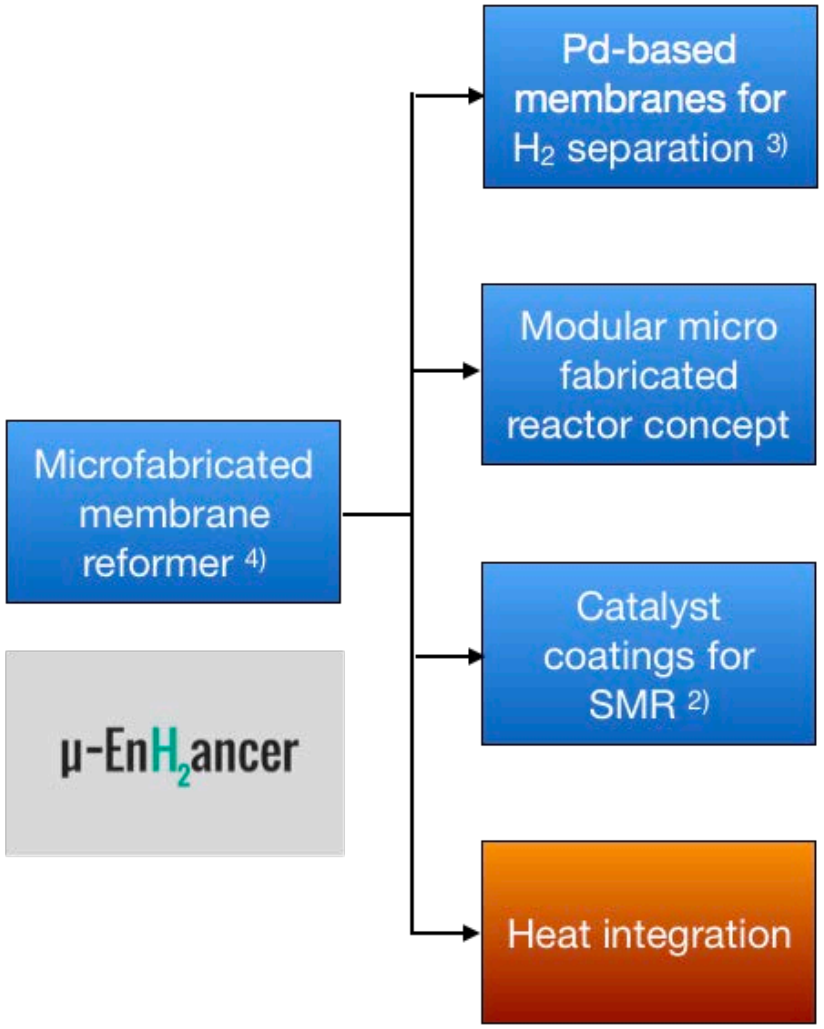
Kurokawa et al., **2010**, Demonstration of Highly-Efficient Distributed Hydrogen Production from Natural Gas with CO_2 Capture, WHEC2010, Essen

WHY MICRO FABRICATION?



Benefits:

- Very large membrane surface area per catalyst volume (ca. 10^3 – 10^6 m^{-1})
- Negligible mass transport resistance towards membrane even for high-flux membranes
- Efficient heating by hot gas or catalytic combustion of retentate with air
- High compactness / low weight / modular plant design



- Preparation of defect-free membranes
- Concepts for thermal and mechanical stability

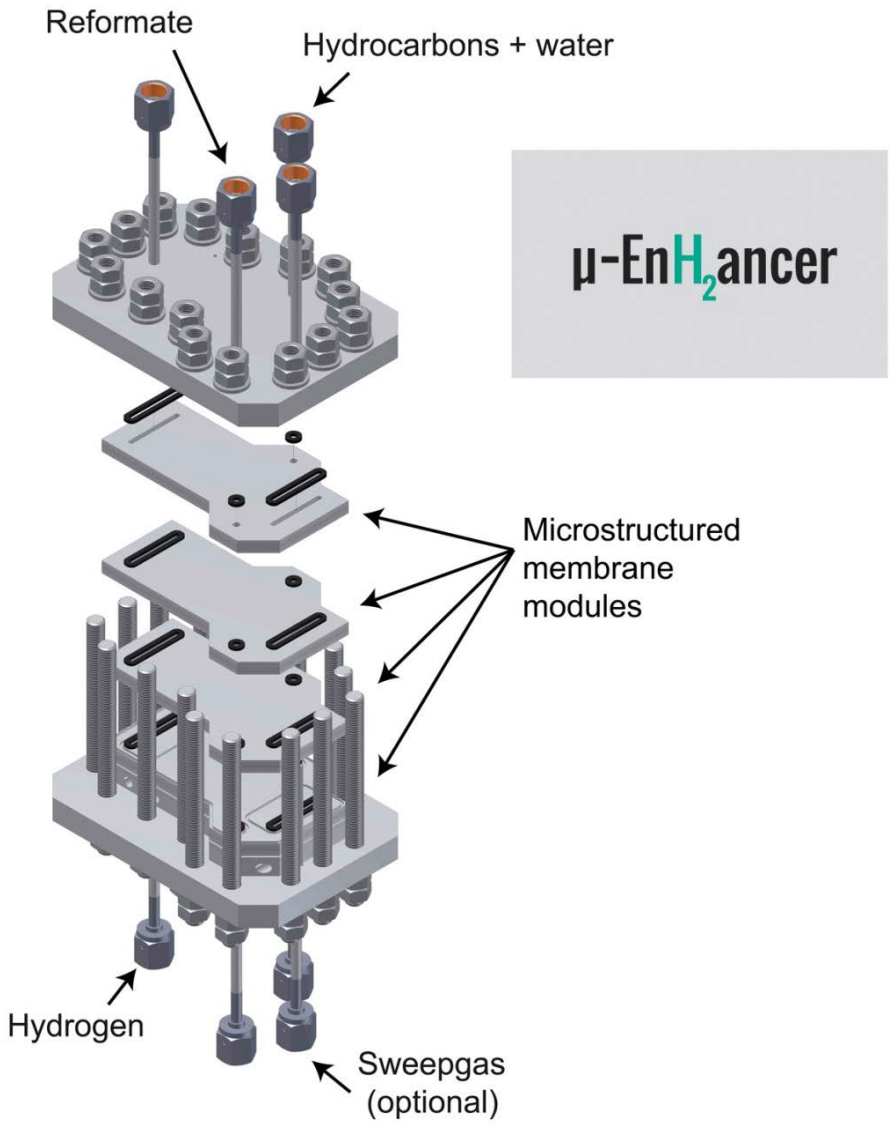
- Membrane integration by laser welding
- H_2 permeation experiments
- Mass transport performance 3)

- Preparation of Rh/Al_2O_3 catalysts
- Activity and stability tests
- Reaction kinetics without membrane

Integration in a technical reactor by laser welding

1) Boeltken et al., CE&P: Process Intensif. 67 (2013) 136-147
2) Lee et al., Appl. Catal. A:Gen. 467 (2013) 69-75
3) Boeltken et al., J. Membr. Sci. 468 (2014) 233-241
4) Boeltken et al., Int. J. Hydr. Energy 41 (2014) 18058-18068

MODULAR MEMBRANE REACTOR DESIGN



Pre-reforming stage

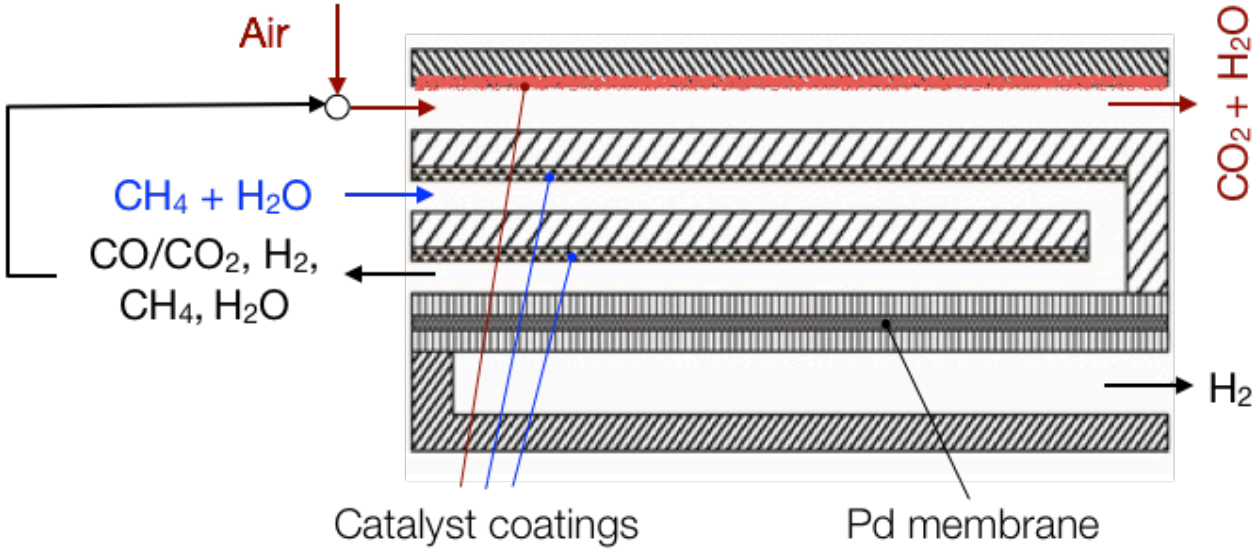
- Cracking of higher hydrocarbons (natural gas)
- Build-up of H_2 partial pressure (by reforming)

Reforming stage

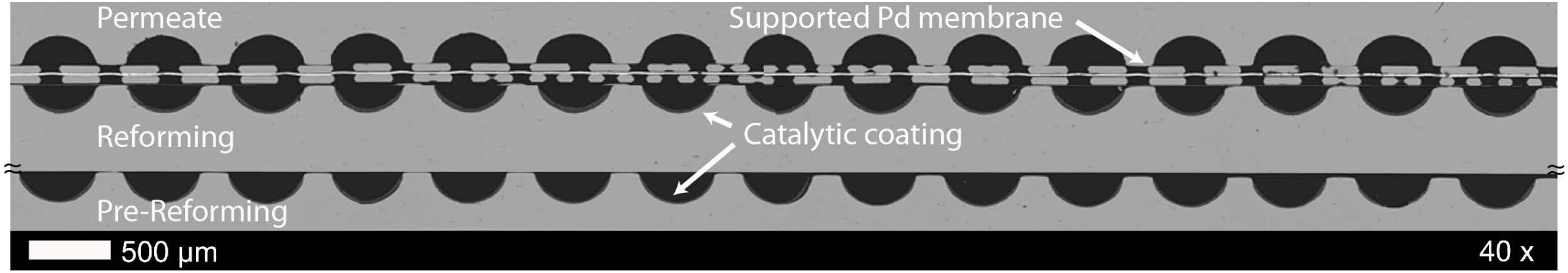
- Reforming
- H_2 separation

Retentate combustion zone

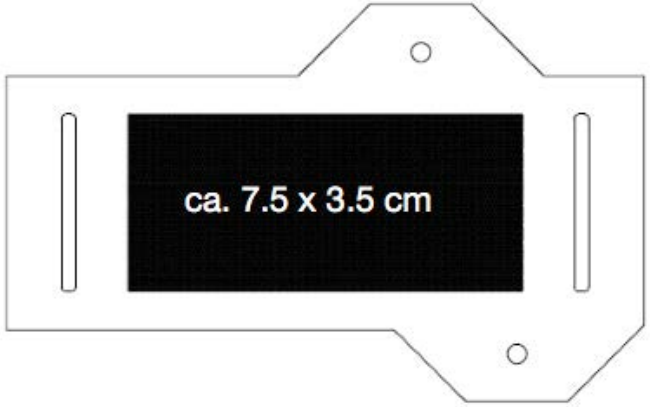
- Heat transfer to the reforming zone

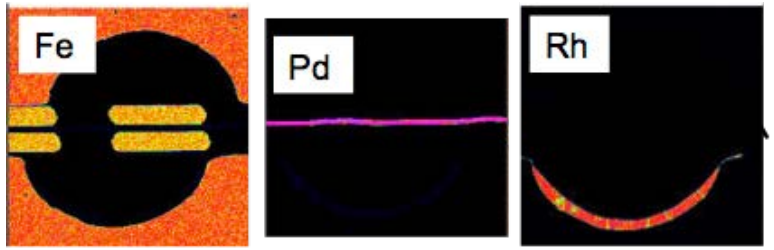


REAL MODULE AND CHANNEL FORMAT



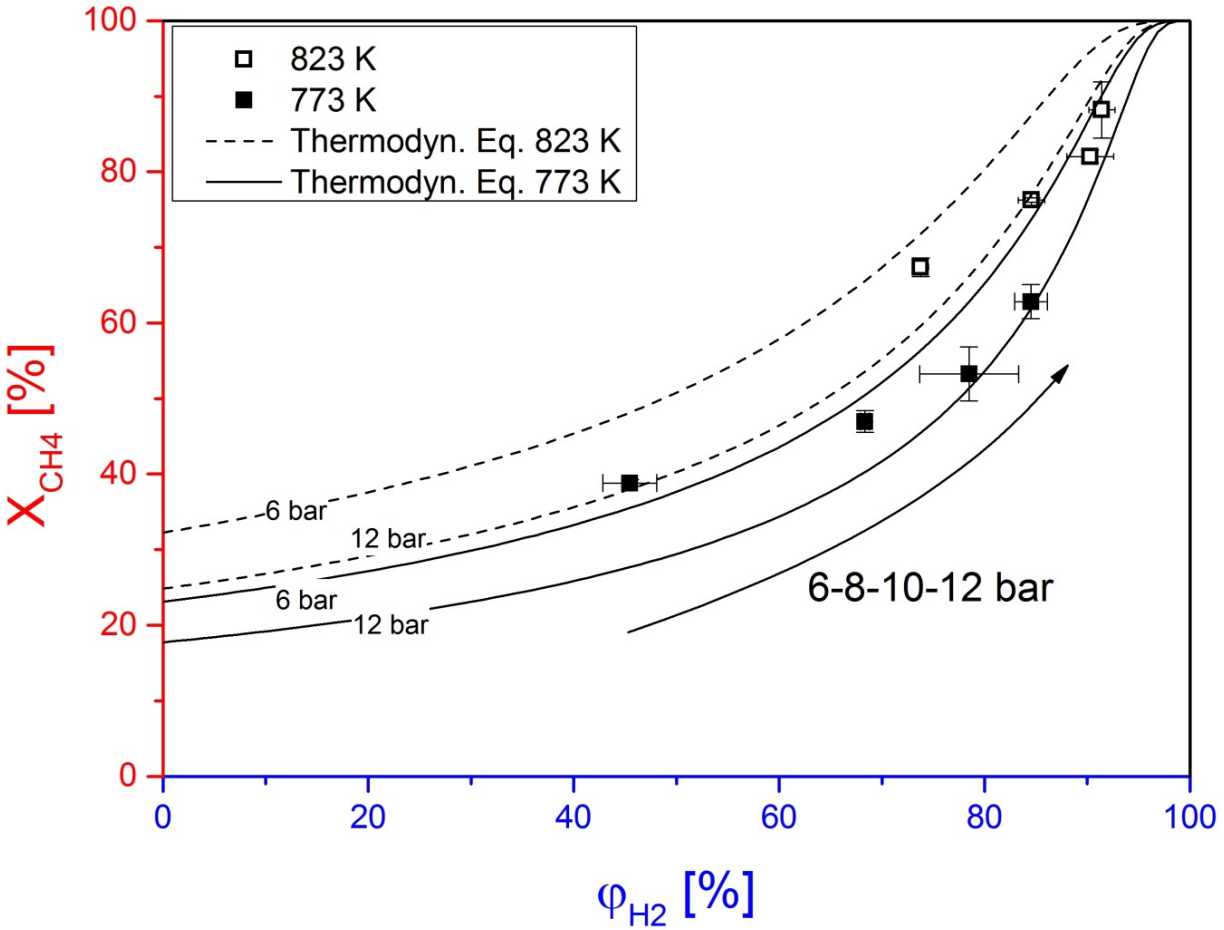
- Modules built from high-temperature corrosion-resistant material (Nicrofer)
- Microchannels by chemical etching (500 x 200 µm)
- Thin palladium foil, i.e., typically 12 µm, sandwiched between two etched microsieves to provide mechanical stability
- Microsieves coated with inorganic diffusion barrier layer to prevent membrane degradation at high temperature
- Catalyst layers by inkjet printing (10-15 µm, 50 mm pre-reforming, 70 mm reforming/membrane)





SELECTED RESULTS - CONVERSION VERSUS HYDROGEN RECOVERY

Variation of retentate pressure; W/F = 0.33 g_{Cat} h / mol CH_4; S/C = 3



Conversion is close to equilibrium considering the fraction of hydrogen removed

Activity of catalyst high enough to respond to H_2 removal

Boeltken et al., Int. J. Hydr. Energy, **2014**, 39, 18058-18068.

COMPARISON TO PREVIOUS / OTHER SYSTEMS

Reference	s_{Pd} [µm]	A_{Pd} [cm^2]	Catalyst	T [K]	Δp [bar]	X_{CH_4} [%]	φ_{H_2} [%]	W/F [$g_{Cat}h/mol_{CH_4}$]	A_{Pd}/V_R [m^2/m^3]	$\dot{V}_{H_2}/V_R$ [Nm^2/(m^{3}h)]	$\dot{V}_{H_2}/A_{Pd}$ [Nm^2/(m^{2}h)]
Uemiya et al. [4] [1]	20	25.1	Ni-based	773	8[a]	90	91	64.75	39.3	230	5.9
Tong et al. [6] [2]	8	20	Ni/Al_2O_3	823	10[b]	72	51	74.71	110.1	1289	11.7
Hwang et al. [14] [3]	6.2	33.2	Ni-based	813	20	79	96	n.a.	6.3	58	9.2
Tokyo Gas [15,35] [4]	20	98918.4	Ni-based	823	8.7[c]	79	n.a.	n.a.	8.1	33	4.1
µ-EnH$_2$ancer [this work]	12.5	26.3[d]	Rh/Al_2O_3	823	11	87	92	0.33	41/66[e]	472/739[e]	12.1
Fernandez [5]	3-5	160	Ni-based	823	1.27	76	20	n.a.	8.0	21	3.0
Mahecho-Botero [6]	25	1800	Ni-based	823	8.97	80	62.5	n.a.	22.5	125	5.5

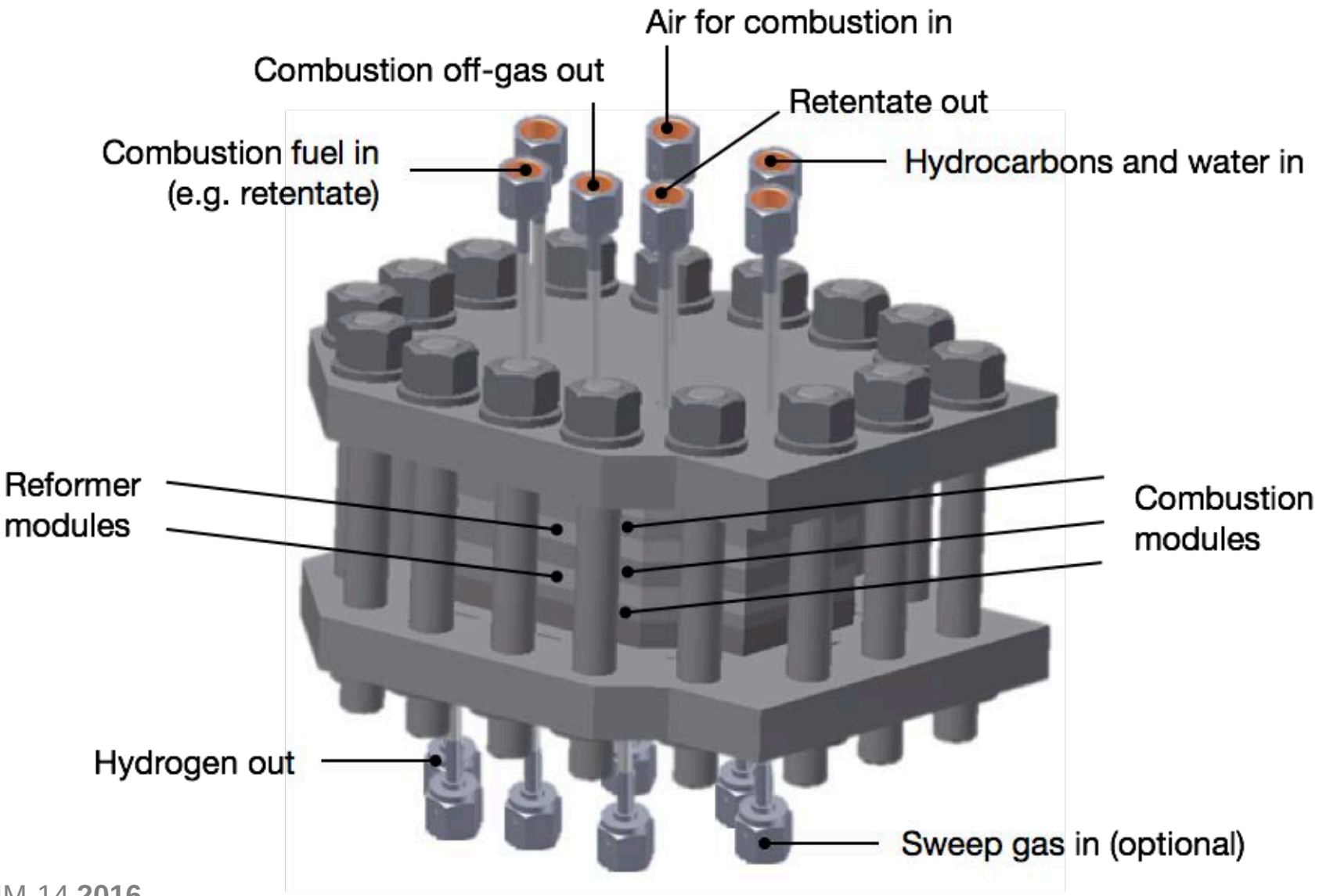
[a] Sweep gas 500 ml/min Ar ($p_{H_2,Perm}$ = 0.38 bar).
[b] Sweep gas 470 ml/min N_2.
[c] Vacuum ($p_{H_2,Perm}$ = 0.4 bar).
[d] Effective membrane area (across the microchannels).
[e] Optimized membrane module with thinner microstructured foils.

- Highest hydrogen production rate per membrane area
- High volumetric hydrogen production rate
- Very compact 41/66 m^{-1}

Boeltken et al., Int. J. Hydr. Energy, **2014**, 39, 18058-18068.

1) Uemiya et al., Appl. Catal. **1991**, 67, 223 - 230.
2) Tong et al., Catal. Today **2006**, 111, 147 - 152.
3) Hwang et al., Int. J. Hydr. Energy **2012**, 37, 6601 - 6607.
4) Shirasaki et al., Int. J.Hydr. Energy **2009**, 34, 4482 - 4487.
5) Fernandez et al., Int. J. Hydr. Energy **2017**, 42, 13763-13776.
6) Mahecha-Botero et al., Chem. Eng. Sci. **2008**, 63, 2752-2762.

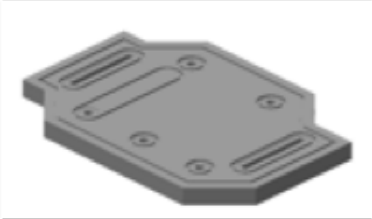
NEW SYSTEM WITH FLUIDIC HEATING ESTABLISHED



Dittmeyer et al., ICIM-14 **2016**

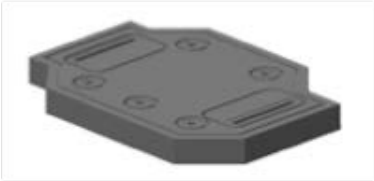
NEW MODULES

Combustion module
5 plates, 7.2 mm height



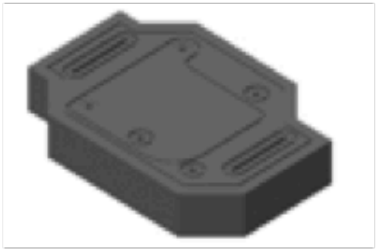
- Gas distribution
- Combustion fuel feeding
- Combustion fuel distribution into plate 4
- Oxidant gas feeding and combustion
- Gas distribution

Reforming module
8 plates; 9.4 mm height



- Gas distribution
- Gas distribution
- Hydrogen removal
- Etched micro sieve support
- Palladium foil
- Etched micro sieve support
- Reforming zone
- Pre-reforming zone
- Gas distribution

Module with integrated reforming and combustion zones
11 plates; 14.4 mm height



- Gas distribution
- Combustion fuel feeding and distribution into plate 3
- Oxidant gas feeding and combustion
- Gas distribution
- Gas distribution
- Permeate gas
- Etched micro sieve support
- Palladium foil
- Etched micro sieve support
- Reforming zone
- Pre-reforming zone
- Gas distribution

- all plates fabricated
- microchannel plates awaiting coating with new catalyst
- new porous metal-supported membranes in preparation

Dittmeyer et al., ICCMR-13 **2017**

GENERAL INFORMATION

EXHIBITION

Are you a technology or solution provider and would like to actively contribute to this conference?

The exhibition is an integral part of the IMRET and offers a unique opportunity to promote your technologies, products and services. Equipment suppliers, engineering companies as well as research institutes are invited to participate in the exhibition.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FIRST ANNOUNCEMENT

21 – 24 October 2018
Karlsruhe · Germany

IMRET 2018
15th International Conference on Micro Reaction Technology

www.dechema.de/IMRET2018


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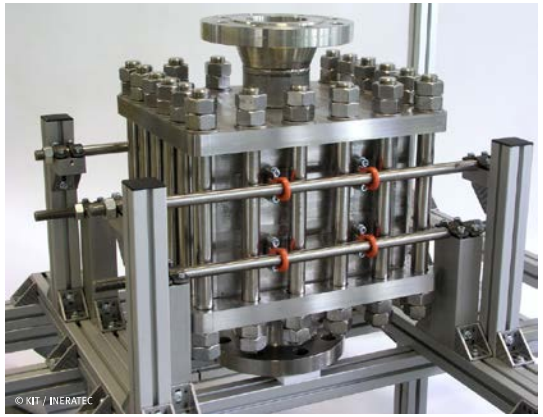
SUPPORTED BY:
ProcessNet Working Group Microreaction Engineering and International Flow Chemistry Society

INVITATION TO IMRET 15

For its 15th edition, the International Conference on Micro Reaction Technology (IMRET) is coming back to where it all began. Since the start of this "place to be" for chemists, chemical engineers and micro systems engineers, the event has demonstrated a variety of new applications in chemical engineering, chemistry, related disciplines like energy supply, and even more different fields such as analytics, life science and medicine. Yet, as each of the involved disciplines has seen amazing progress, the mission of providing an effective platform for exchange is more topical than ever.

IMRET 15 therefore sets out to become once more the place where new developments regarding all facets of micro process engineering and flow chemistry will be jointly discussed for mutual benefit.

IMRET 15 will take place in the city of Karlsruhe from 21 October to 24 October 2018, organised by DECHEMA e.V. with the support of the German ProcessNet Working Group Microreaction Engineering, the IMRET Steering Committee and the International Flow Chemistry Society.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TOPICS / DATES / COMMITTEE

CONFERENCE TOPICS

- **Mixing and heat transfer in micro systems**
- **Reactions and catalysis in flow systems**
- **Downstream processing**
- **Modelling/simulation**
- **Fabrication of micro-structured devices**
- **Process automation, sensors, digitalization**
- **Modular plant concepts**
- **New applications in chemistry, biology, energy etc.**
- **Industrial implementation**

IMPORTANT DATES

October 2017	Submission of abstract is open
February 2018	End of abstract submission
April 2018	Notification of acceptance
May 2018	Final programme
21 - 24 October 2018	IMRET 15 takes place

LOCAL ORGANISING COMMITTEE

Dr. Alexis Bazzanella	DECHEMA e.V.
Prof. Dr. Roland Dittmeyer	KIT, Institute for Micro Process Engineering
Dr. Kerry Gilmore	Max Planck Institute of Colloids and Interfaces
Dr. Christian Holtze	BASF SE
Prof. Dr. Gunther Kolb	Fraunhofer ICT-IMM
Dr. Stefan Loebbecke	Fraunhofer Institute for Chemical Technology ICT

www.dechema.de/IMRET2018

RH/AL_2O_3 CATALYSTS BY FLAME SPRAY PYROLYSIS

Catalyst	Rh loading[a] (%)	H_2 chemisorption results			TEM results	
		Rh active sites (A_{chem})[b] (μmol/g_{cat})	Rh dis-persion[c] (%)	Rh particle size (P_{chem})[d] (nm)	Rh particle size (P_{TEM})[e] (nm)	Rh active sites (A_{TEM})[f] (μmol/g_{cat})
5Rh/FAl	3.85	174	47	2.4	1.6	290
5Rh/SAl	2.75	117	44	2.5	3.5	90
1Rh/FAl	0.94	69	75	1.5	1.0	105
1Rh/SAl	0.84	59	73	1.5	1.7	53
0.2Rh/FAl	0.20	13	69	1.6	–	--
0.2Rh/SAl	0.20	12	61	1.8	–	--

a Rh loading derived from ICP-OES.

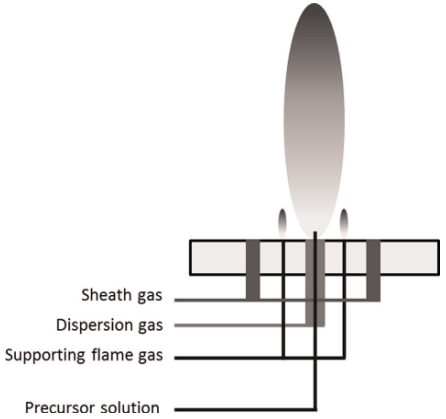
b From H_2 uptake in chemisorption assuming a stoichiometry of H/Rh = 1.

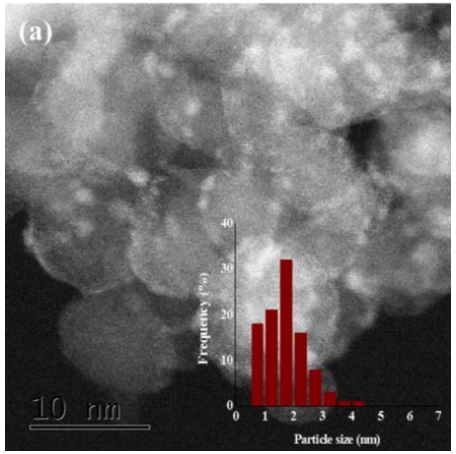
c Ratio of active Rh from H_2 chemisorption and Rh content from ICP-OES.

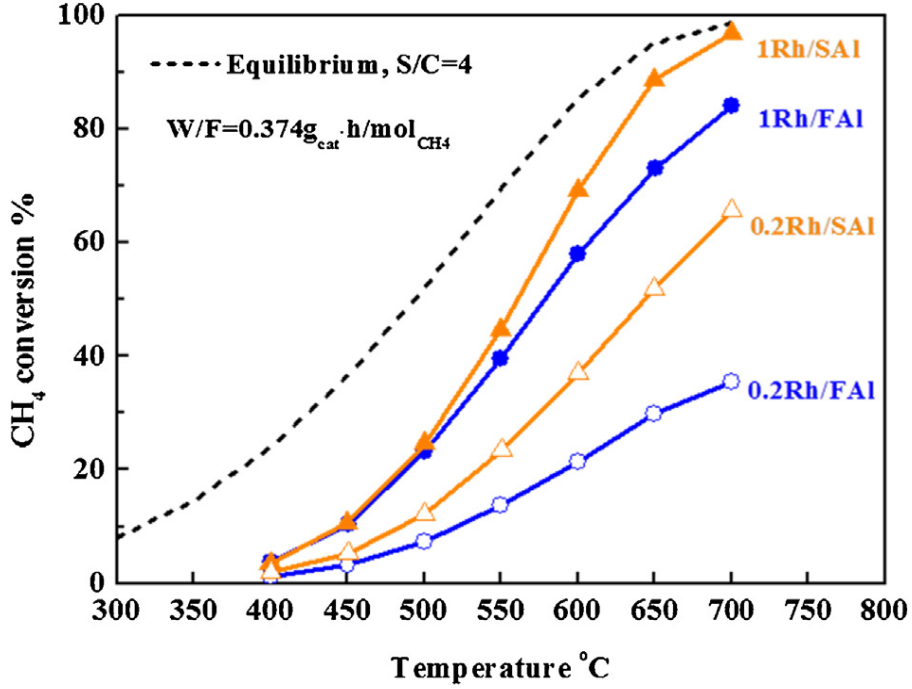
d From metal dispersion by H_2 chemisorption.

e From TEM measurements.

f Derived from TEM results.





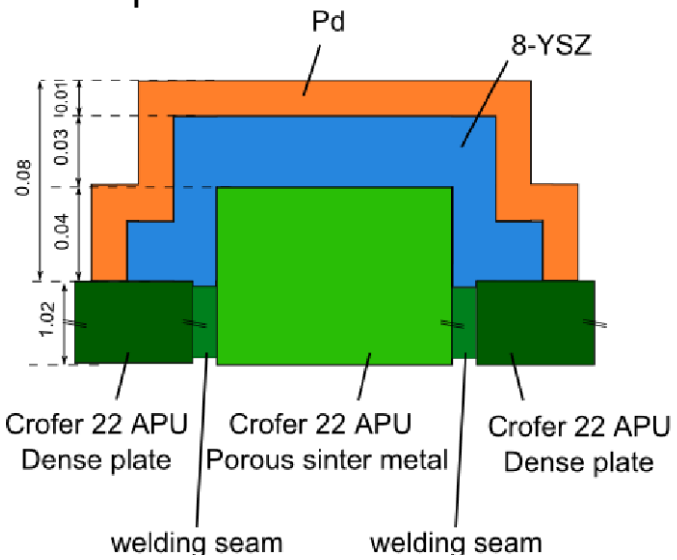


Yu et al., Appl. Catal. B: Environ. **2016**, 198, 171–179.

PLANAR METAL-SUPPORTED PD MEMBRANES

In cooperation with Forschungszentrum Jülich (Martin Bram, IEK-1)

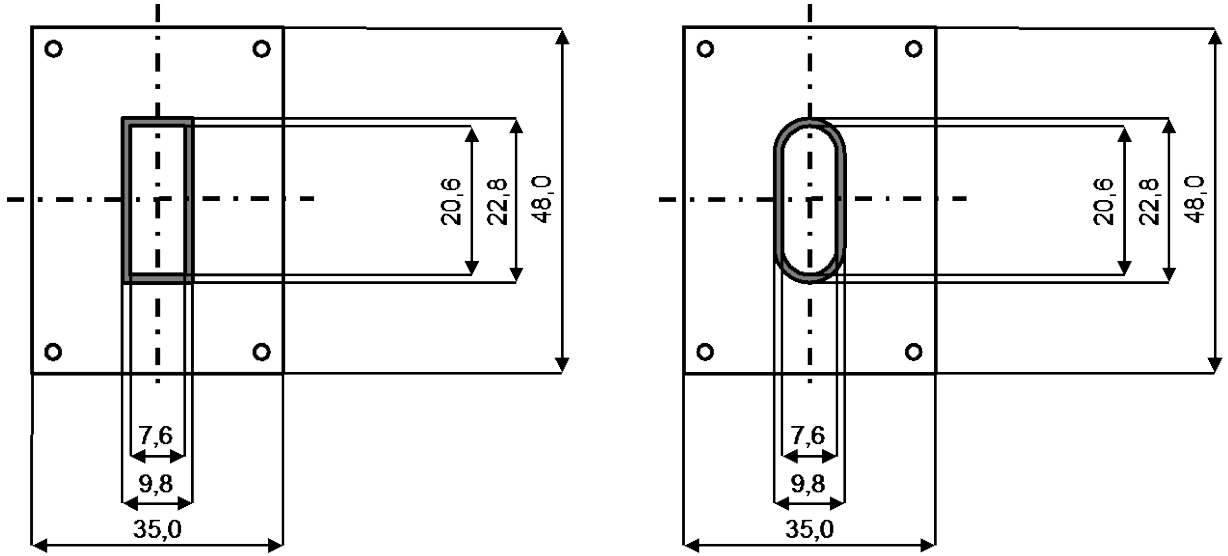
Concept



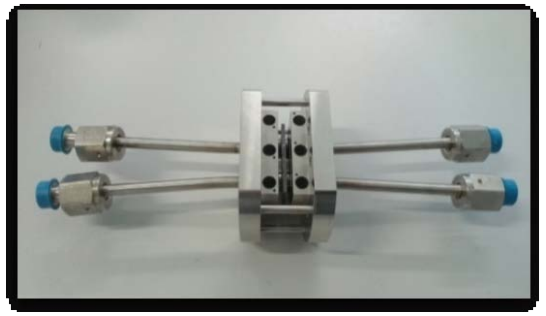
- **Pd:** ca. 4 - 12 µm (foil or SPS coating)
- **8-YSZ:** ca. 20 - 40 µm
- **Sinter metal:** ca. 1 mm

Dittmeyer et al., ICCMR-13 **2017**

Test specimen

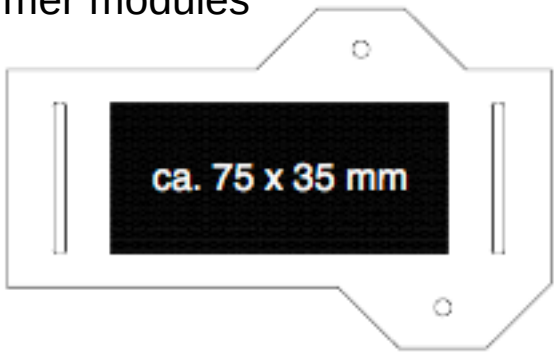


Testing unit



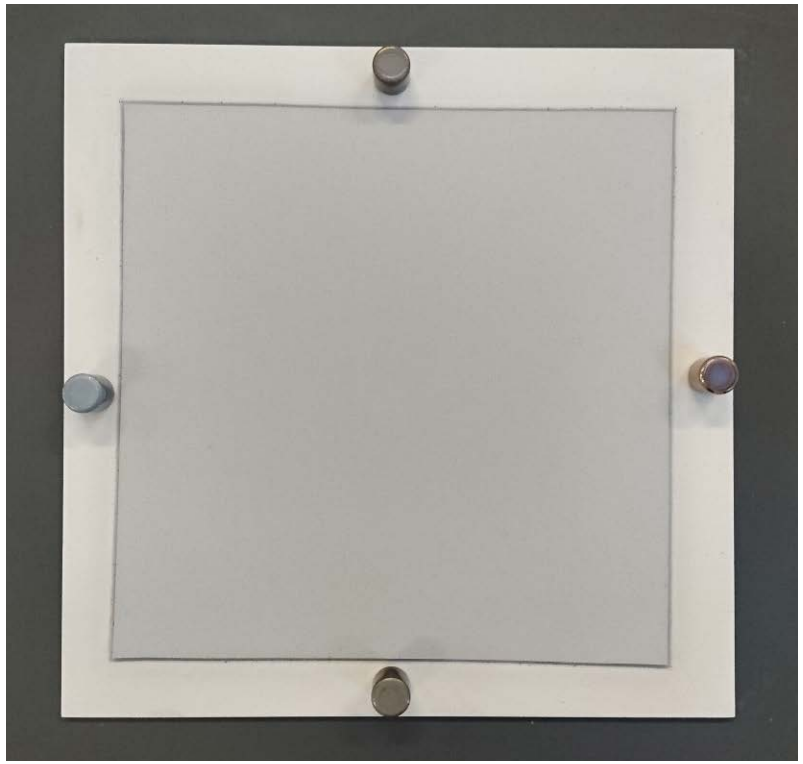
Boeltken et al., CE&P **2013**, 67,136-147

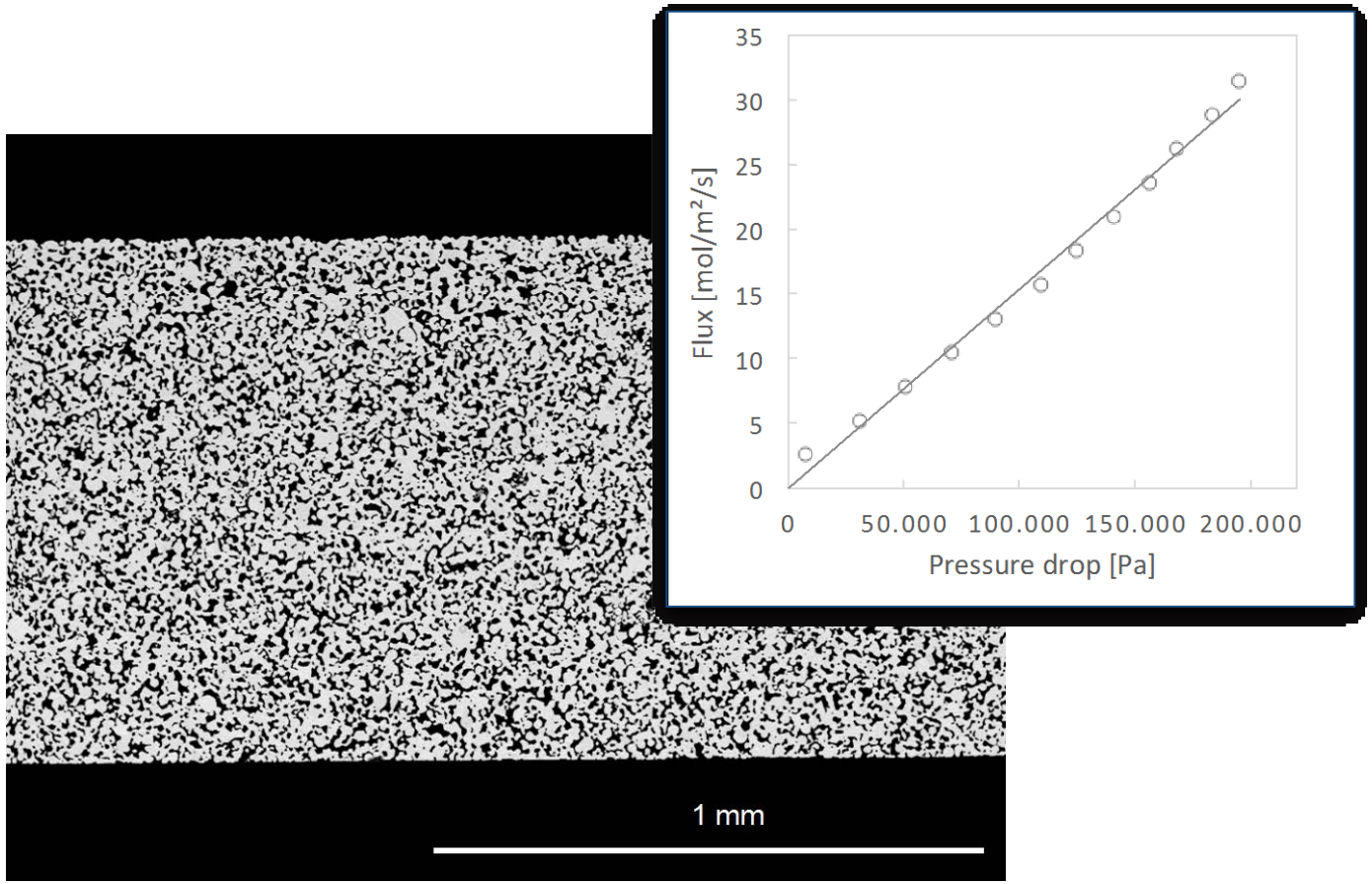
Transfer to membrane reformer modules



POROUS SHEETS FROM CROFER 22 APU BY TAPE CASTING / SINTERING

Forschungszentrum Jülich (Martin Bram, IEK-1)



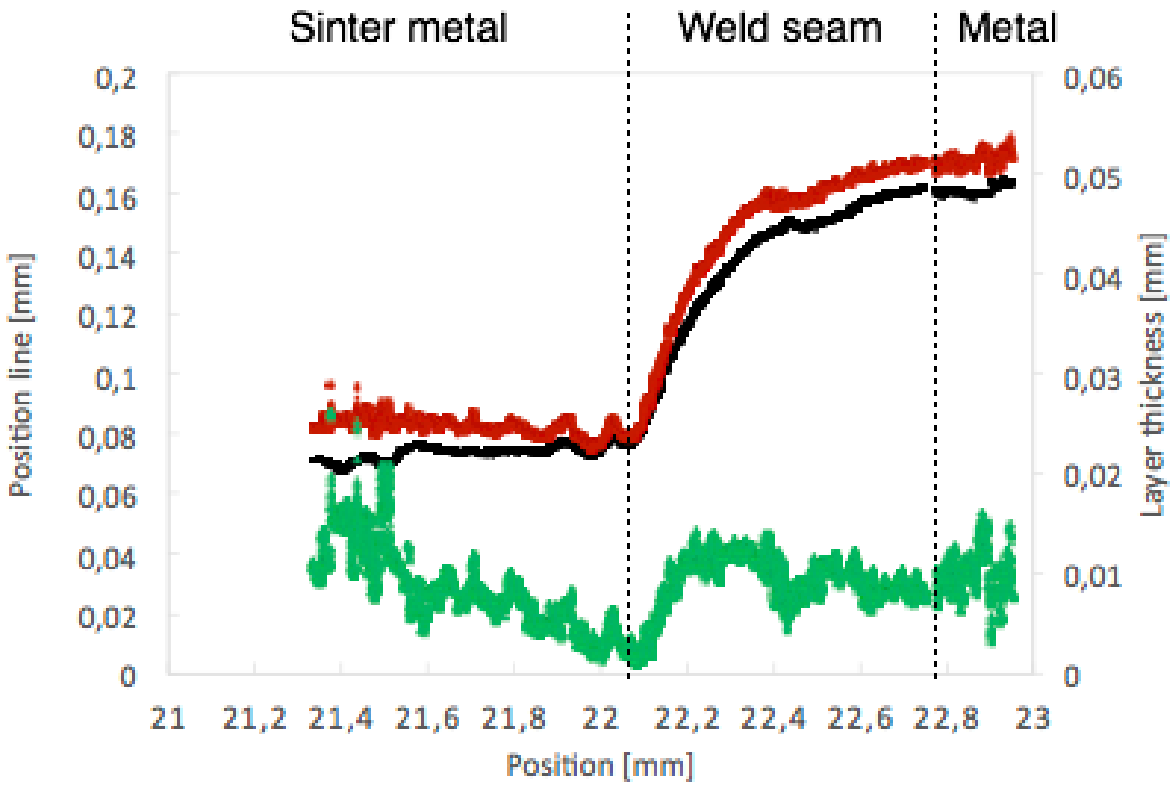


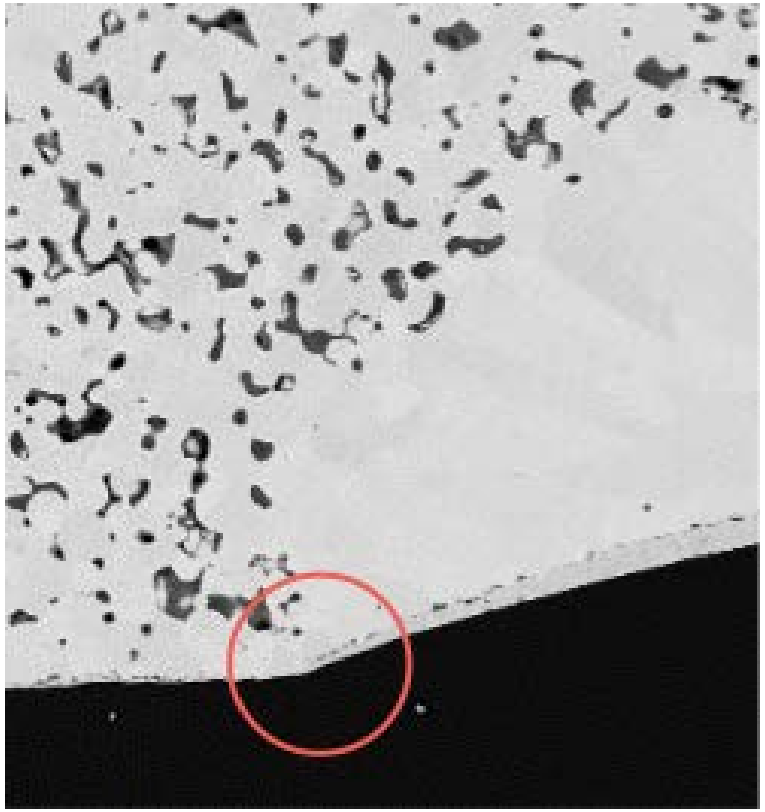
- Porosity: 27 ± 4% (29.5 ± 0.9%)
- Thickness: 1.08 ± 0.05 mm

- N_2 permeability: 0.162 ± 0.003 µmol/m/s/Pa
- N_2 permeance: 1.5×10^{-4} mol/m^2/s/Pa

COATING WITH POROUS 8YSZ

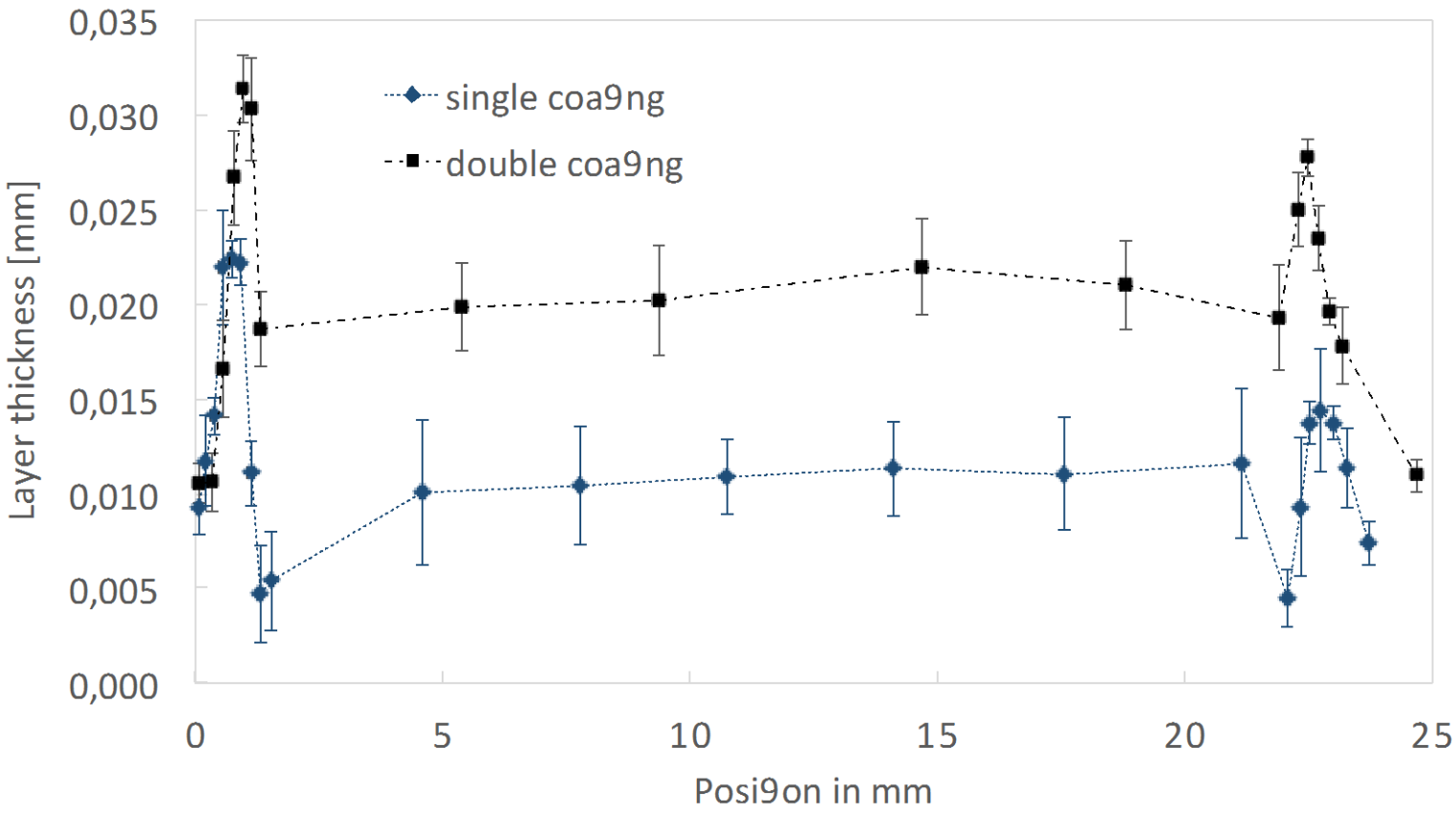
Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)





SINGLE VERSUS DOUBLE LAYER COATING

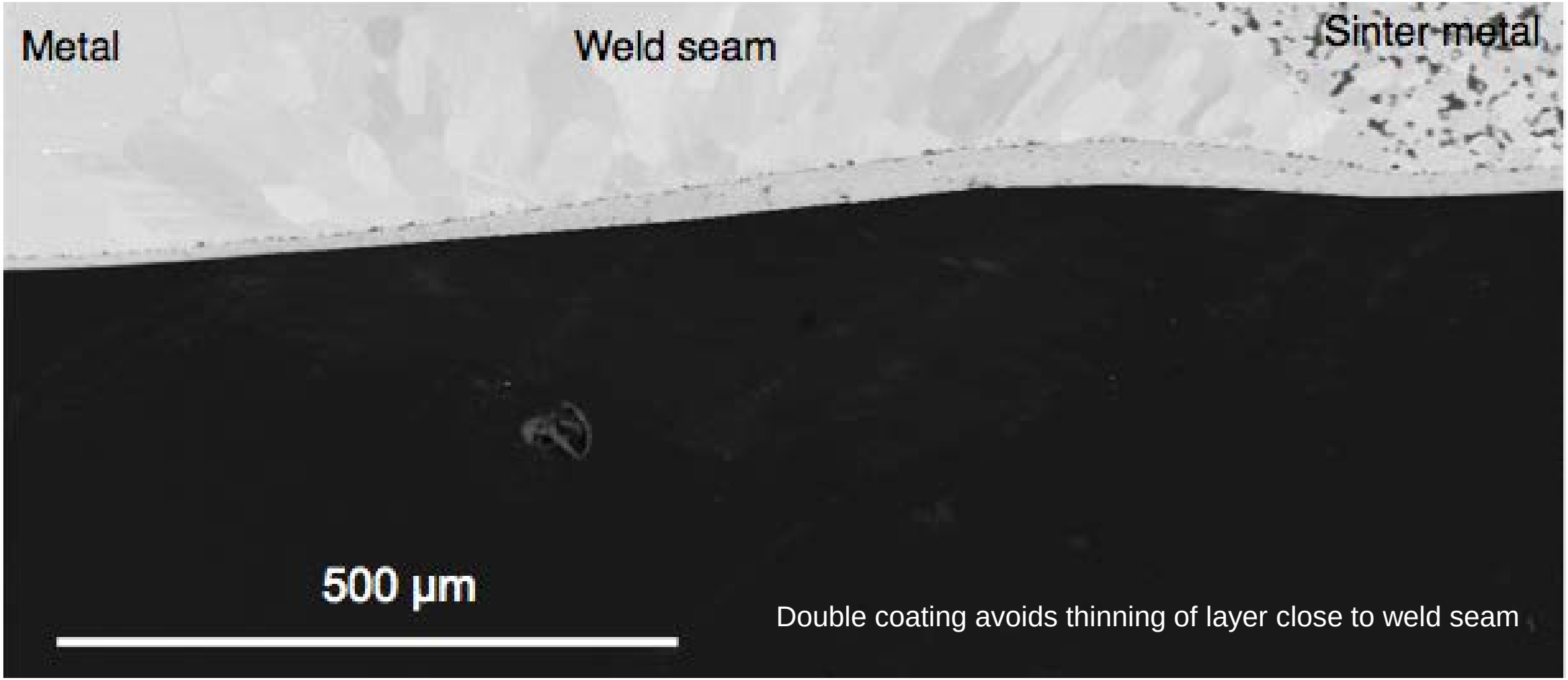
Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)



Layer thickness derived from SEM (Matlab® routine)

DOUBLE LAYER COATING

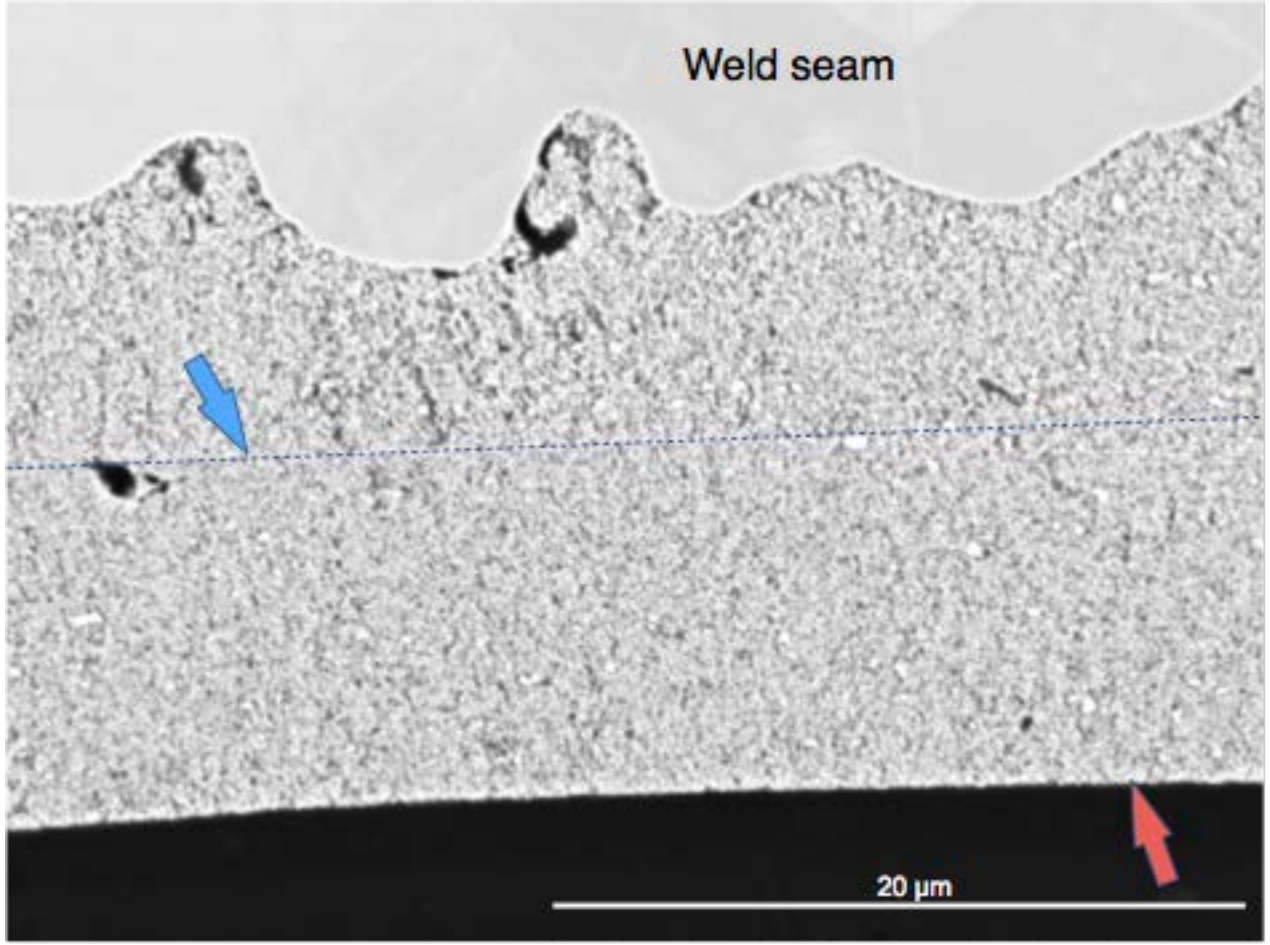
Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)



Double coating avoids thinning of layer close to weld seam

DOUBLE LAYER COATING

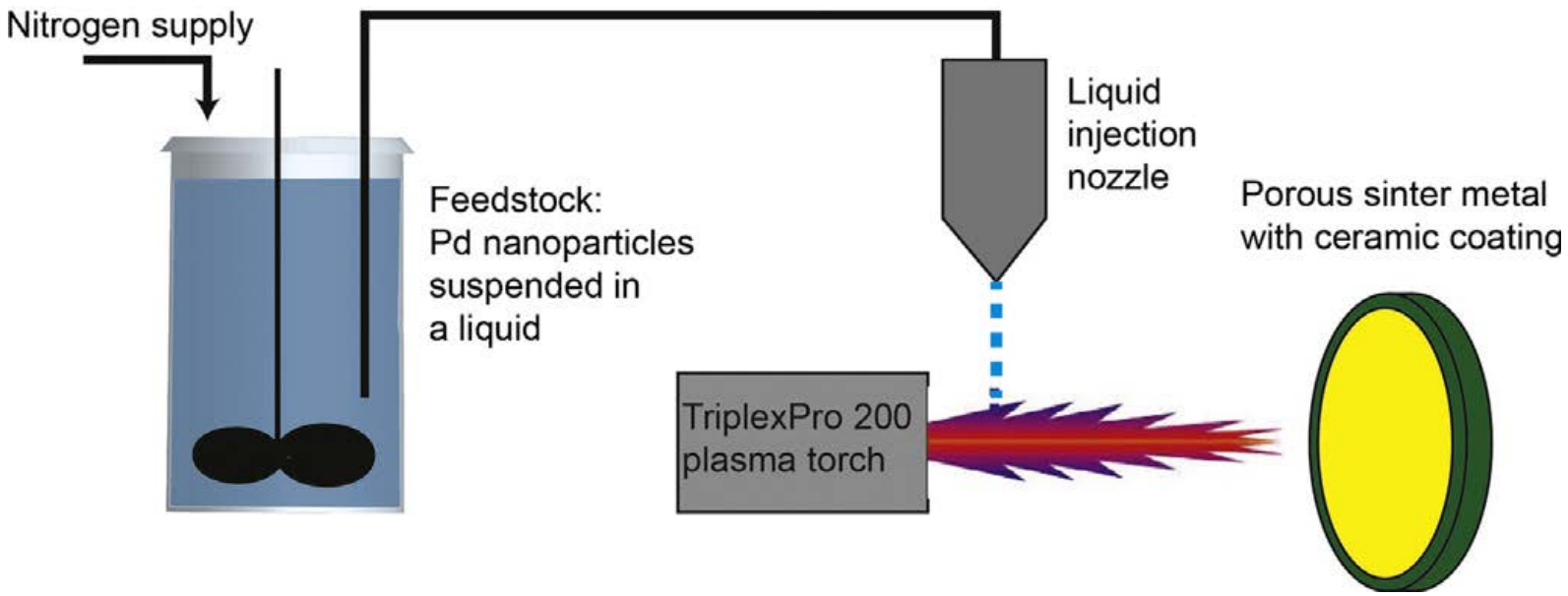
Forschungszentrum Jülich (Martin Bram, IEK-1, Paul Kant, IMVT)



Nice smooth surface for coating with thin Pd or Pd alloy layer

SUSPENSION PLASMA SPRAYING OF PD NANOPARTICLES

In cooperation with the German Aerospace Center (Sayed-Asif Ansar, Dirk Ullmer, TT, Stuttgart)



- Stable suspension of Pd nanoparticles obtained
- Injection system and plasma parameters being optimised
- First coating experiments performed on test specimen (Pd layers are not yet gastight)
- Transfer to membrane reformer modules

Boeltken et al., J. Membr. Sci. **2014**, 468, 233-241.

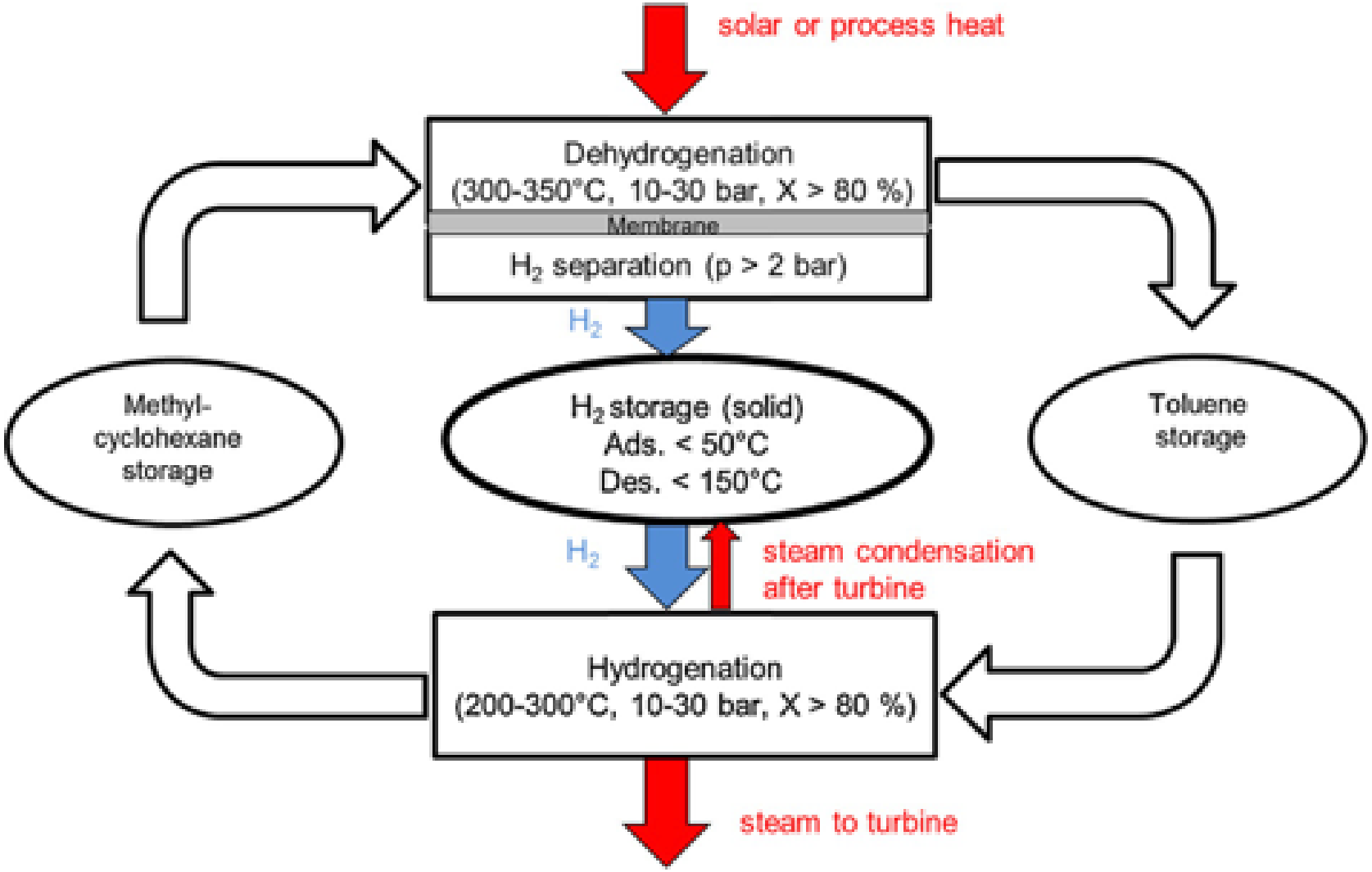
Application background

Liquid organic reaction cycle (LORC) for long-term storage of intermediate temperature heat

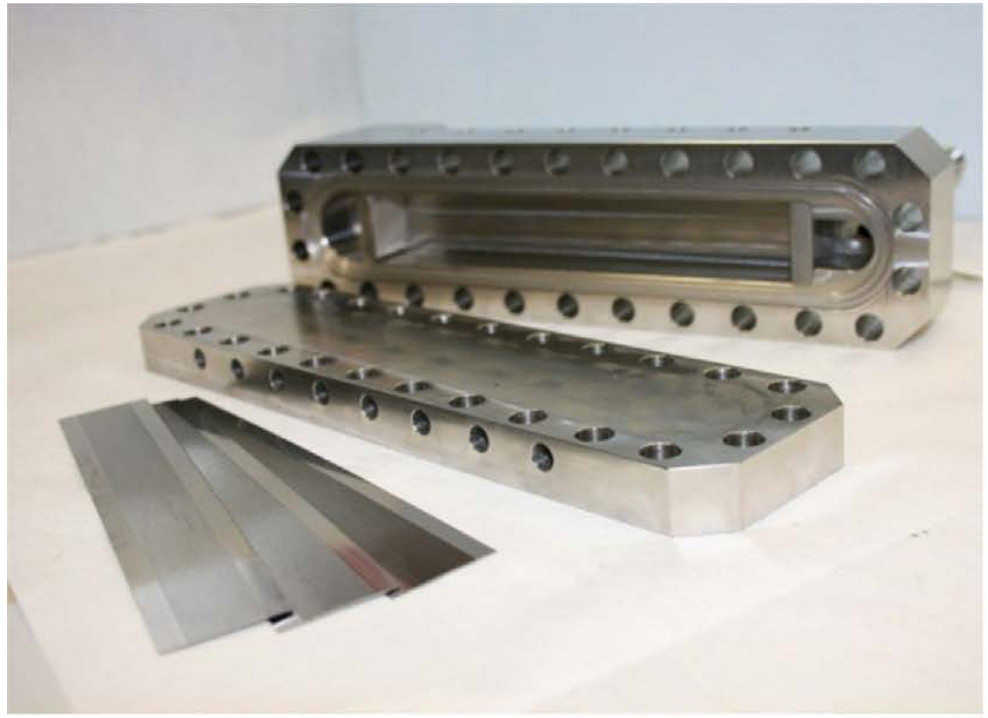
MCH dehydrogenation to toluene:

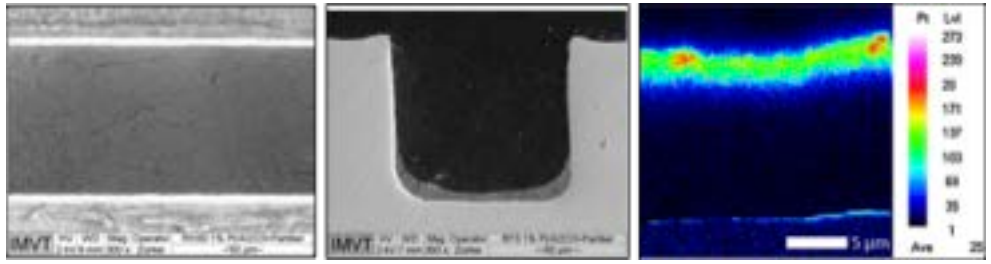
$$C_7H_{16} \rightleftharpoons C_7H_8 + 3H_2$$

Catalyst: 1 wt.-% Pt/γ-Al_2O_3



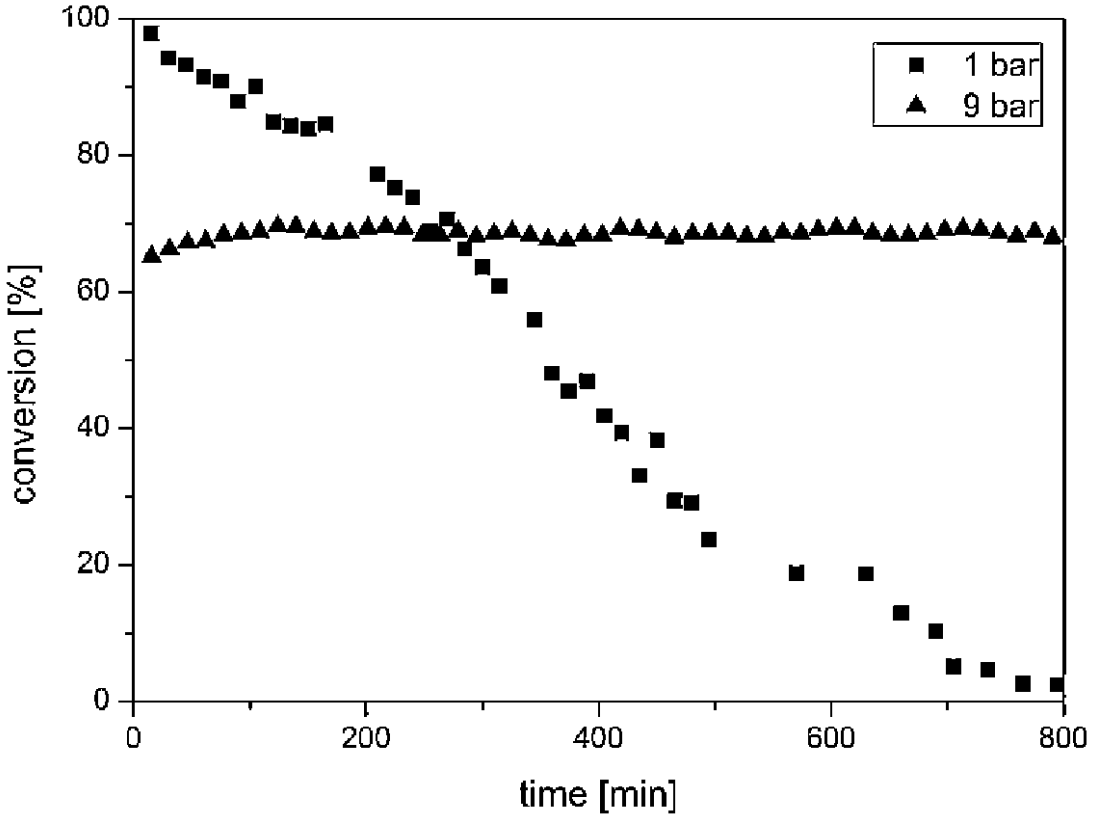
Kreuder et al., Catal. Today, **2015**, 242, 211-220.





Influence of pressure on the deactivation rate.

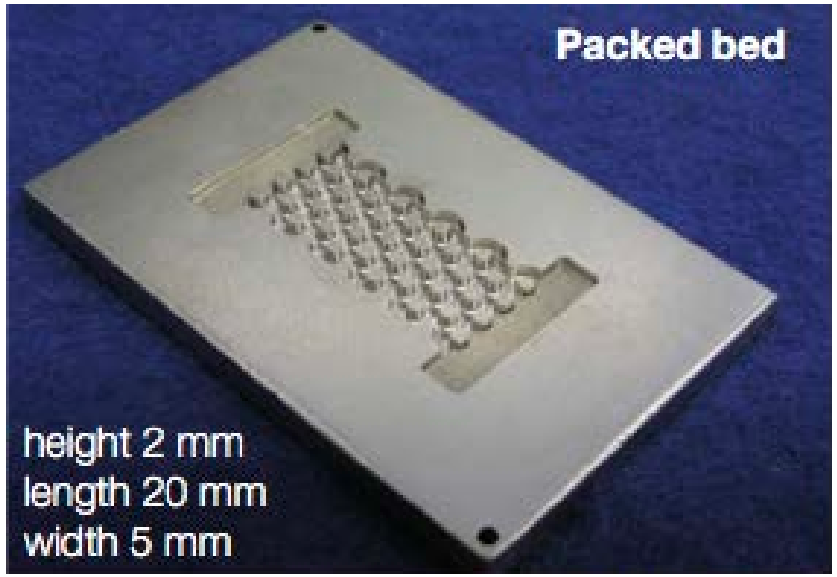
T = 325° C. modified contact time W/F 4000 kg s m^{-3} (1 bar) and 750 kg s m^{-3} (9 bar). MCH/N_2 50/50.

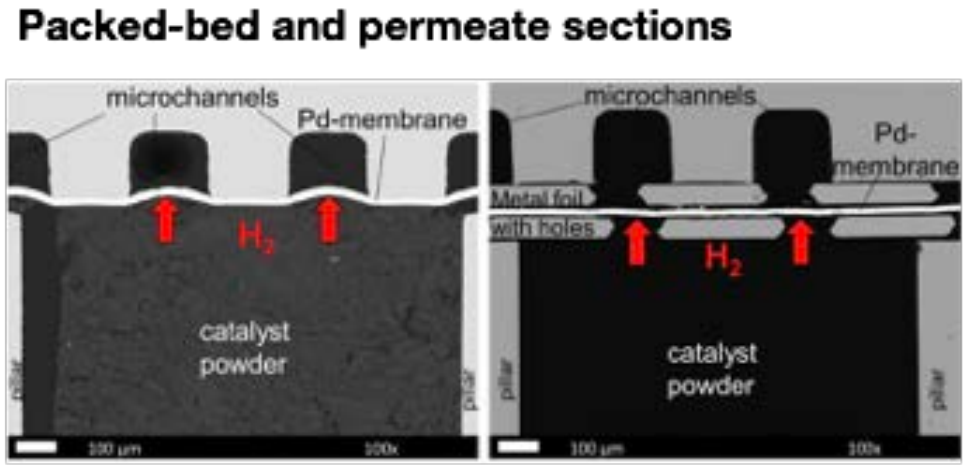


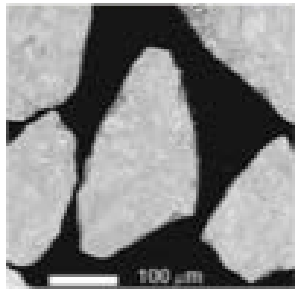
- Kinetic studies in BERTY-type recycle reactor showed much slower deactivation by carbon formation

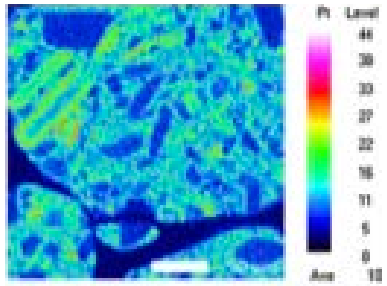
Kreuder et al., Catal. Today, **2015**, 242, 211-220.

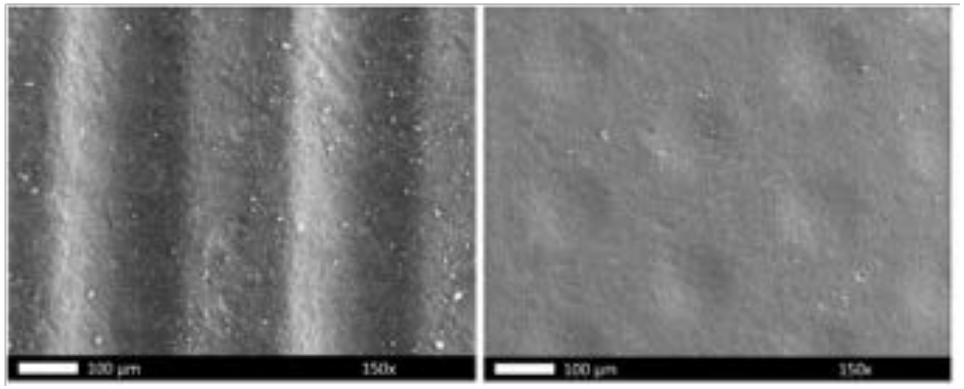
Micro Packed-Bed Membrane Reactor – First Design









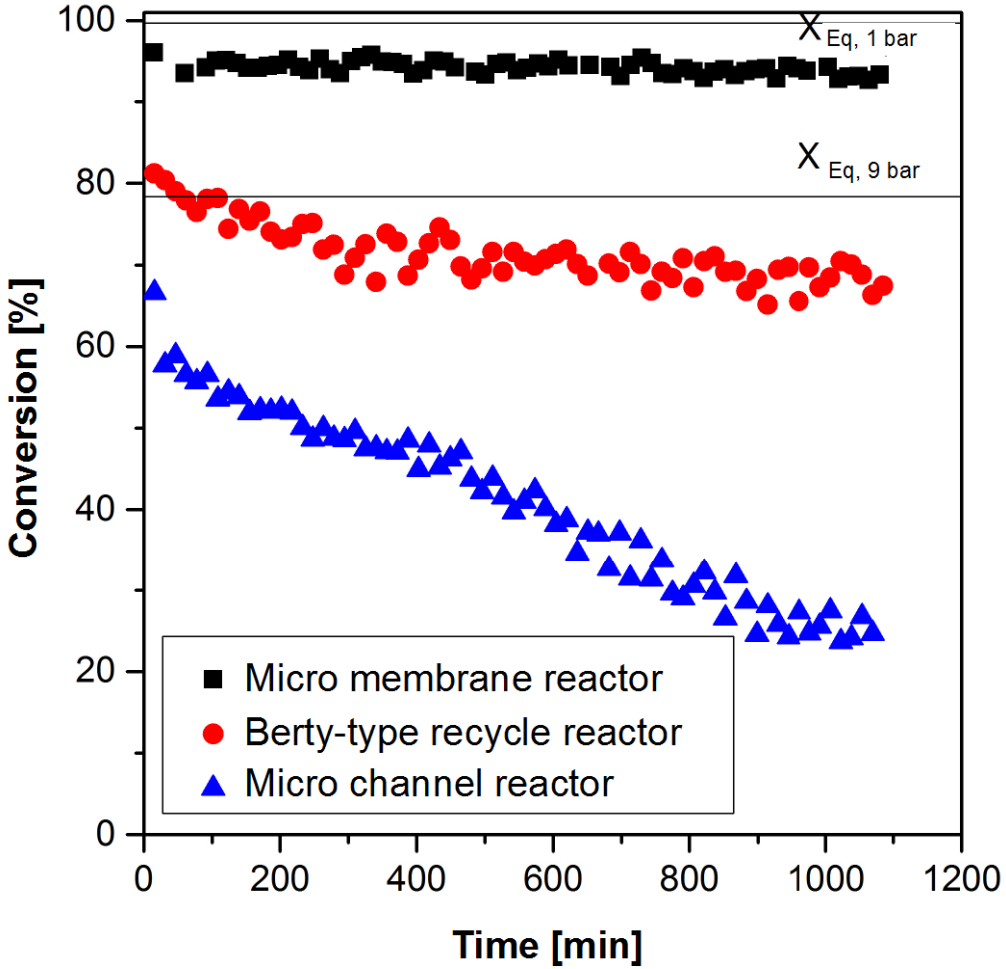


Module	Q_0 mol*m^{-1}*s^{-1}*Pa$^{-0.5}$	E_a kJ*mol^{-1}	Q (350 °C) mol*m^{-1}*s^{-1}*Pa$^{-0.5}$	S-
membrane B	2.8*10^{-7}	14.6	1.7*10^{-8}	>3000
membrane C	2.0*10^{-6}	26.7	1.1*10^{-8}	>25,000
membrane D	3.7*10^{-7}	16.8	1.5*10^{-8}	>85,000
Boeltken et al. [18]	2.6*10^{-7}	14.6	1.6*10^{-8}	>30,000

Kreuder et al., Int. J. Hydr. Energy, **2016**, 41, 12082-12092.

CATALYST DEACTIVATION BY COKING

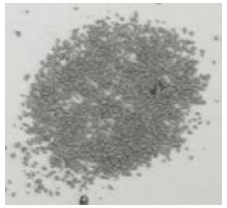
Effect of hydrogen on deactivation. W/F = 250 kg s m^{-3}.



fresh

350° C, 9 bar
back permeation of H_2 in entrance region

348° C, 1 bar
perfect back mixing, i.e., H_2 concentration at reactor effluent level



after use

400° C, 9 bar
no back mixing, i.e., low H_2 partial pressure in entrance region

Carbon content stable around 0.8 wt.-% (TGA, 400° C, BERTY reactor, up to 25 h)

Procedure

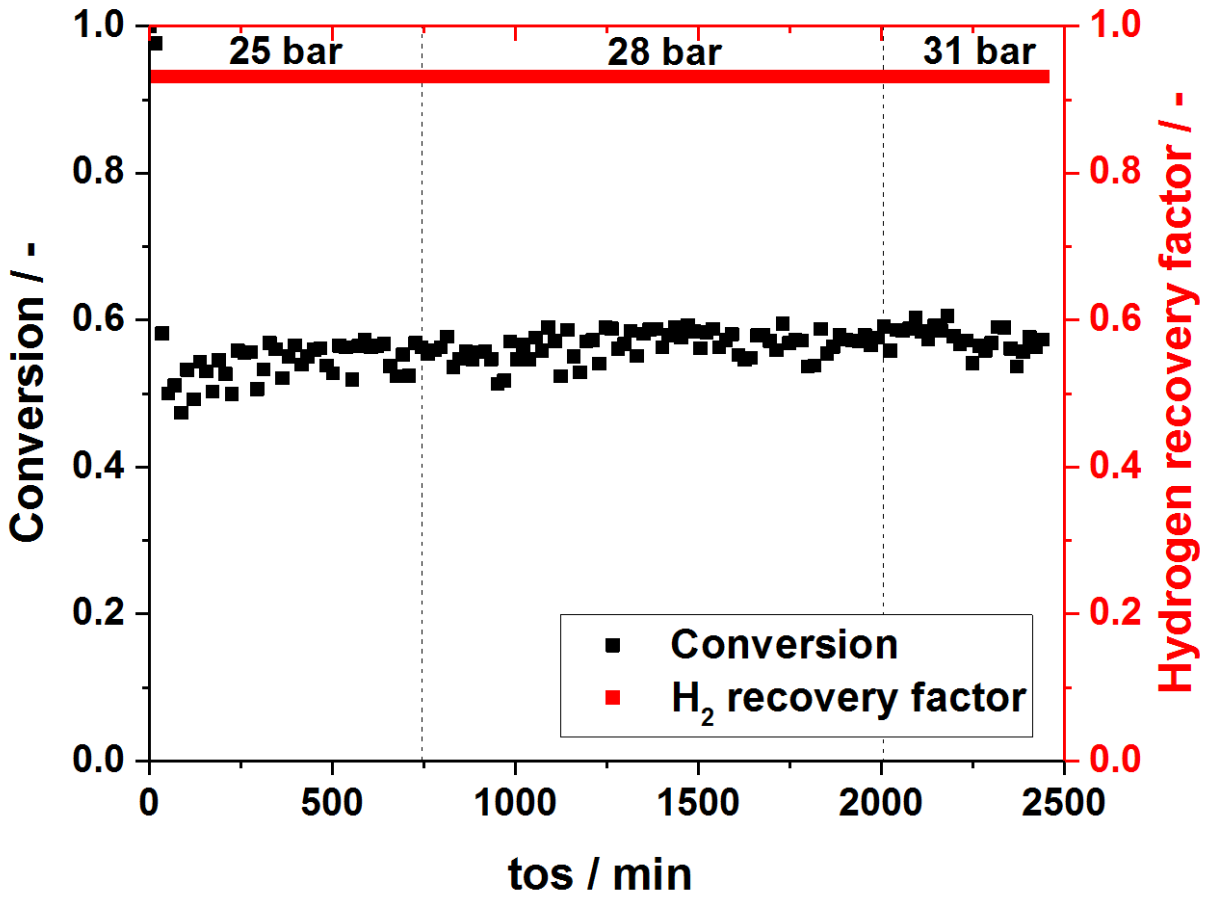
- 1 h treatment in a flow of 5 ml/min air plus 50 ml/min N_2 for during off the deposits
- 1 h treatment in a flow of 50 ml/min H_2 for reduction of the catalyst surface

$T = 400^{\circ}$ C.
$P_{Ret} = 9$ bar.
$W/F = 250\ kg \cdot s \cdot m^{-3}$.
$X_{Eq.} = 99\%$.

Kreuder et al., Int. J. Hydr. Energy, **2016**, 41, 12082-12092.

MODIFIED PACKED-BED DESIGN

Reduced bed height of 0.5 mm / enlarged area



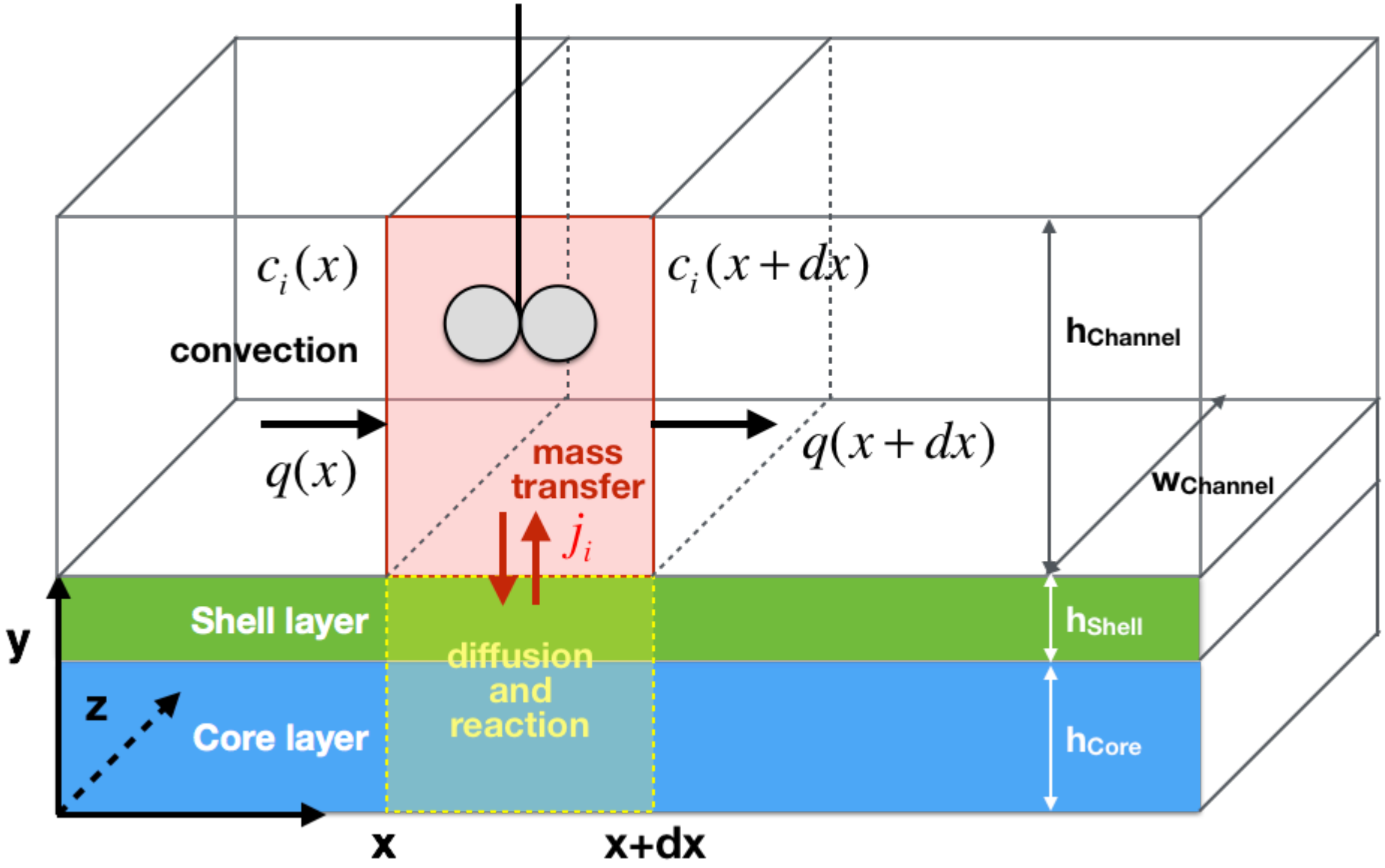
On-going work:

- Further optimisation of reactor geometry based on simulations (optimised bed height, longer packed bed section).
- Catalyst improvement regarding coking.
- Scale-up and test in integrated process.

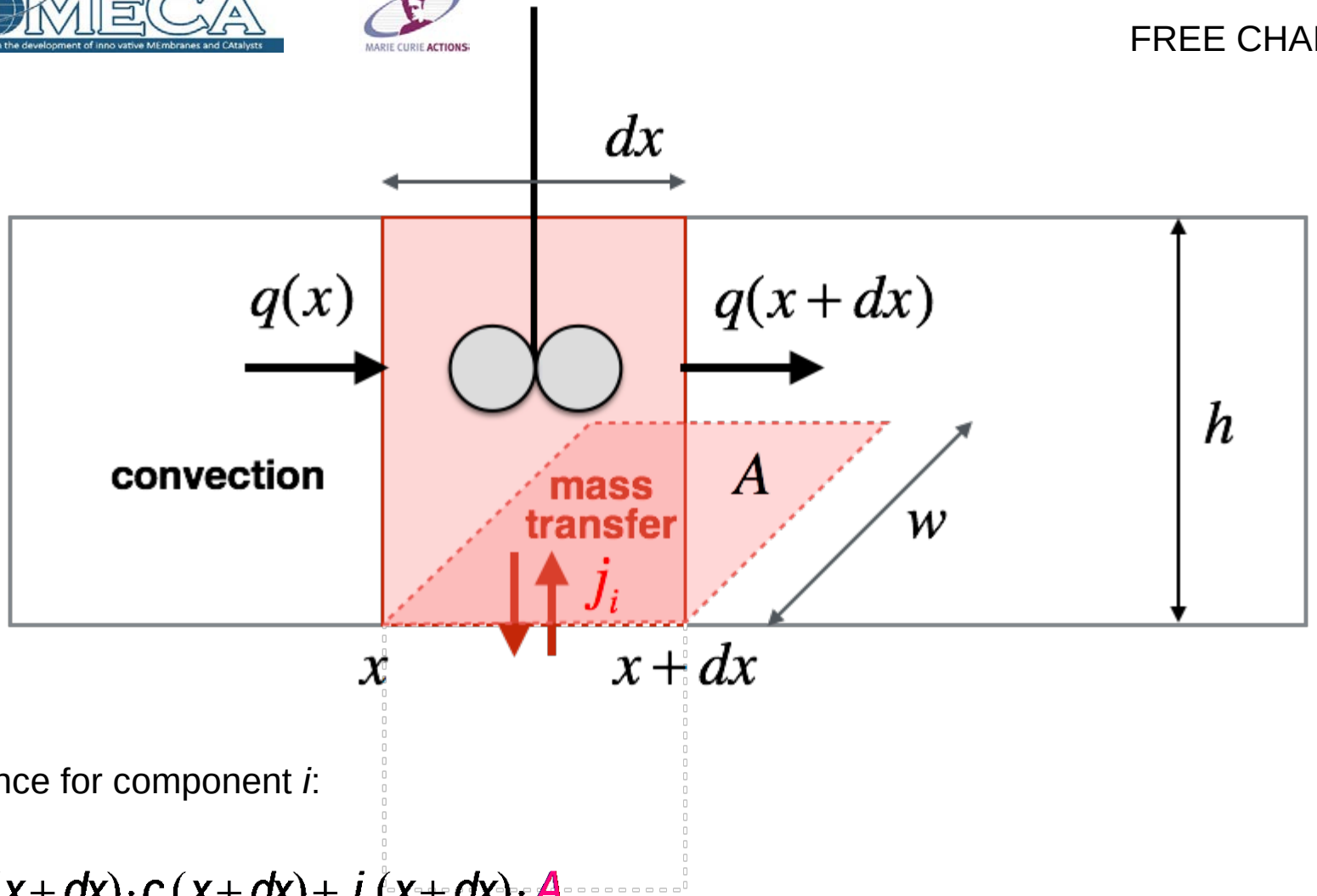
T = 350° C. P_{Ret} = 28-31 bar. W/F = 125 kg·s·m^{-3}.

Kreuder et al., Int. J. Hydr. Energy, **2016**, 41, 12082-12092.

WALL-COATED REACTION CHANNEL - UNIVERSAL APPROACH



FREE CHANNEL VOLUME



CSTR material balance for component *i*:

$$0 = q(x)\cdot c_i(x) - q(x+dx)\cdot c_i(x+dx) + j_i(x+dx)\cdot A$$

$$0 = \left[u(x)\cdot c_i(x) - u(x+dx)\cdot c_i(x+dx)\right]\cdot w\cdot h + k_{ig}\cdot\left(c_i^*(x+dx) - c_i(x+dx)\right)\cdot w\cdot dx$$

new flow velocity u(x+dx) for ideal gas and constant pressure:

total volume flow to/from layer

$$u(x+dx)\cdot w\cdot h = u(x)\cdot w\cdot h + \overbrace{\left[\sum_i k_{ig}\cdot\left(c_i^*(x+dx)-c_i(x+dx)\right)\right]}^{\text{total volume flow to/from layer}}\cdot w\cdot dx\cdot\frac{RT}{p}$$

total molar flux to/from layer

$$u(x+dx) = u(x) + \frac{dx}{h}\cdot\frac{RT}{p}\sum_i k_{ig}\cdot\left(c_i^*(x+dx)-c_i(x+dx)\right)$$

in material balance:

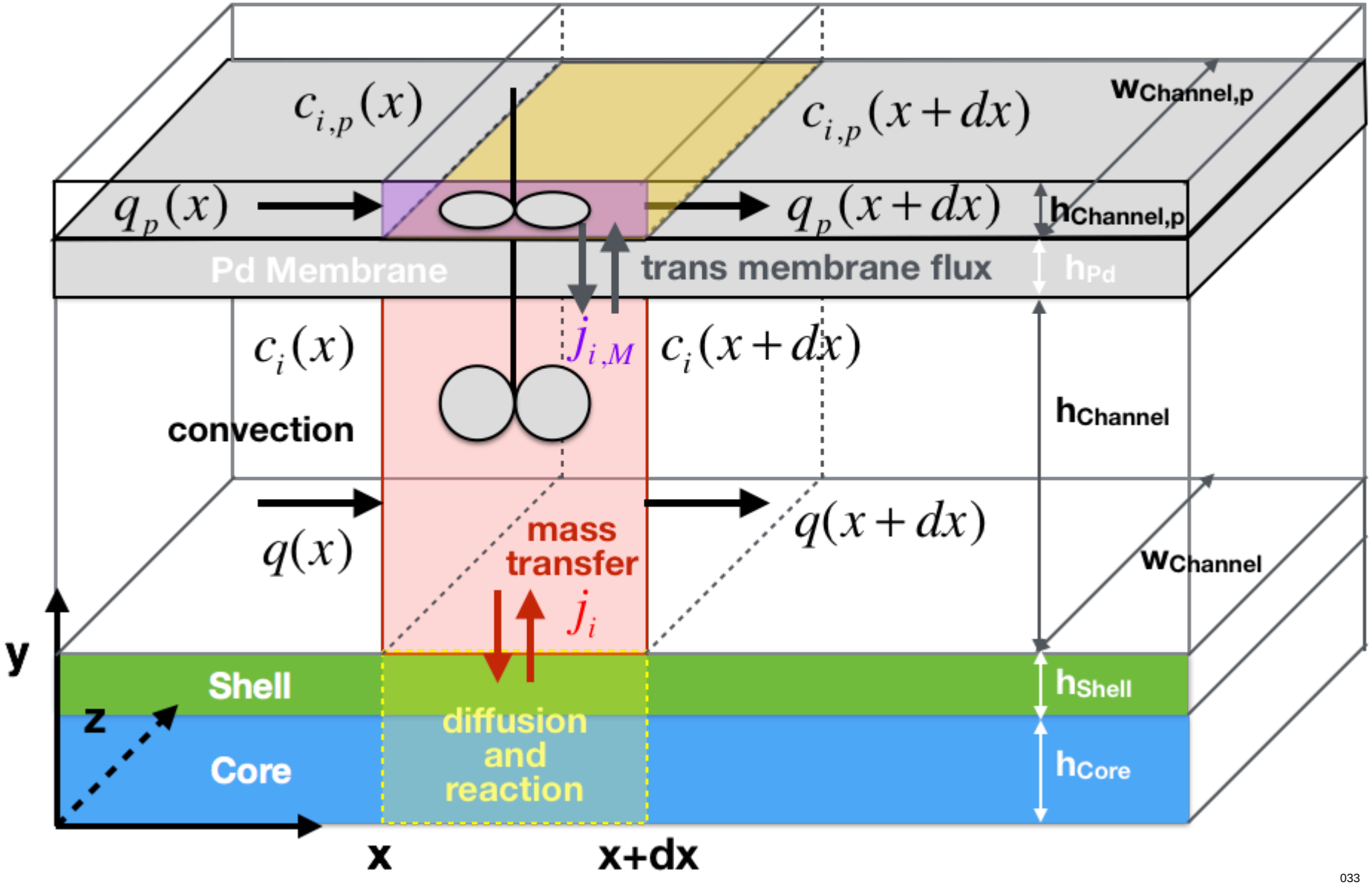
$$0 = u(x)\cdot\left[c_i(x)-c_i(x+dx)\right] - \frac{dx}{h}\cdot\frac{RT}{p}\cdot\left[\sum_i k_{ig}\cdot\left(c_i^*(x+dx)-c_i(x+dx)\right)\right]\cdot c_i(x+dx)+\ldots$$

$$\ldots k_{ig}\cdot\left(c_i^*(x+dx)-c_i(x+dx)\right)\cdot\frac{dx}{h}$$

concentration on the surface is given by reaction/diffusion inside layer

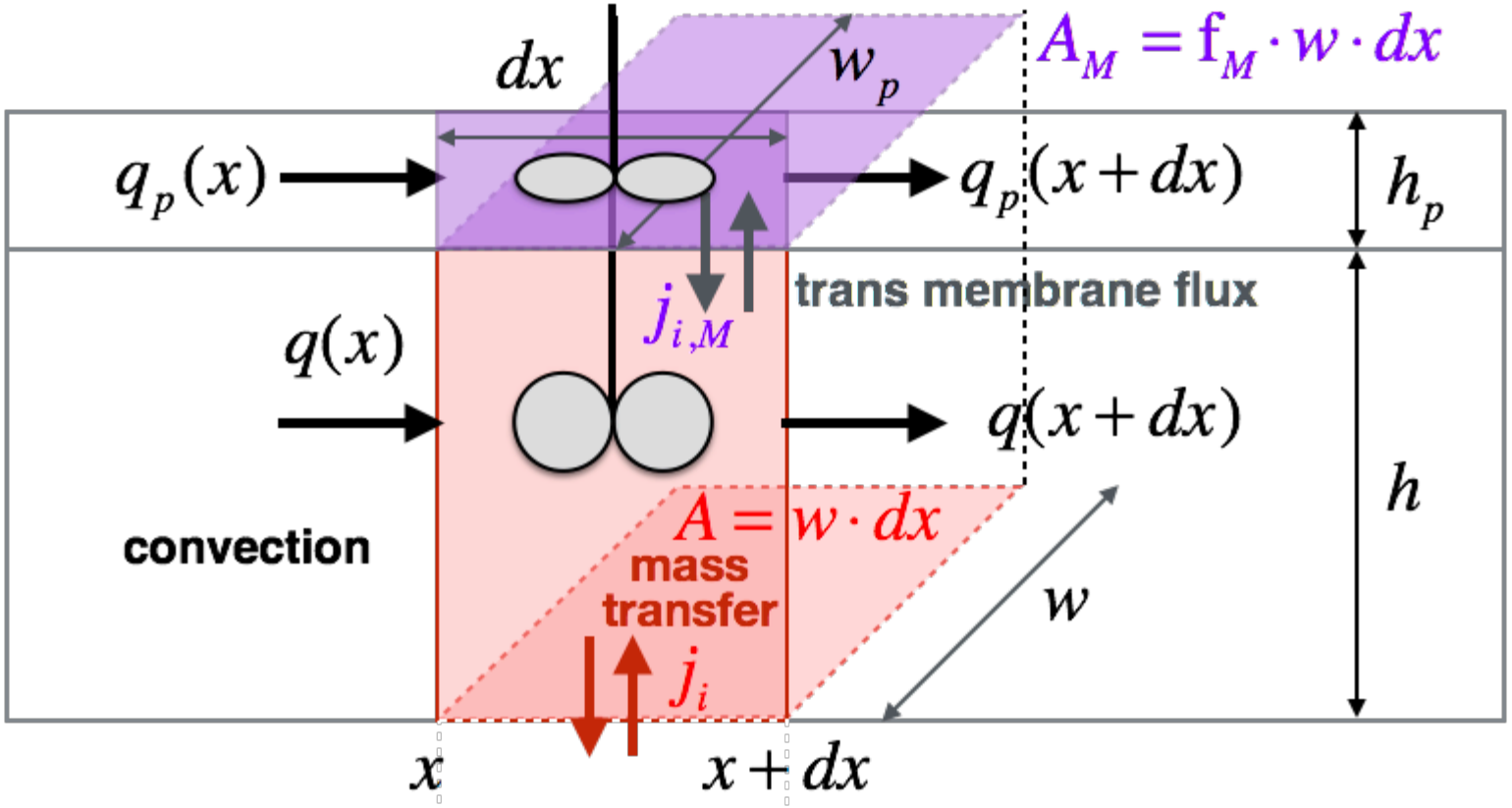
DOUBLE LAYER WITH ADJACENT PD MEMBRANE

now, the situation with Pd membrane:



FREE CHANNEL VOLUME (REACTION SIDE)

same approach:



CSTR material balance component i (reaction side):

$$0 = q(x) \cdot c_i(x) - q(x+dx) \cdot c_i(x+dx) + j_i(x+dx) \cdot A + j_{i,M}(x+dx) \cdot A_M$$

$$0 = \left[u(x) \cdot c_i(x) - u(x+dx) \cdot c_i(x+dx)\right] \cdot w \cdot h + k_{ig} \cdot \left(c_i^*(x+dx) - c_i(x+dx)\right) \cdot w \cdot dx + \ldots$$

$$\ldots j_{i,M}(x+dx) \cdot w \cdot f_M \cdot dx$$

FREE CHANNEL VOLUME (REACTION SIDE)

the membrane flux connects both compartments:

$$j_{i,M}(x+dx) = -\frac{Q_{H_2}}{s_M} \cdot (RT)^{0.5} \cdot \left(c_{H_2}^{0.5}(x+dx) - c_{H_2,p}^{0.5}(x+dx) \right) \quad \text{for } i = H_2$$

$$j_{i,M}(x+dx) = 0 \quad \text{for } i \neq H_2$$

here $j_{i,M}$ is positiv if hydrogen enters the reaction compartment via the membrane

again, new flow velocity u(x+dx) for ideal gas and constant pressure:

$$u(x+dx)\cdot w\cdot h = u(x)\cdot w\cdot h + \overbrace{\left[\sum_i k_{ig}\cdot\left(c_i^*(x+dx)-c_i(x+dx)\right)\right]}^{\text{total volume flow to/from layer}}\cdot w\cdot dx\cdot\frac{RT}{p}+\ldots$$

total molar flux to/from layer

total molar flux to/from permeate

$$\underbrace{\ldots-\frac{Q_{H_2}}{s_M}\cdot(RT)^{0.5}\cdot\left(c_{H_2}^{0.5}(x+dx)-c_{H_2,p}^{0.5}(x+dx)\right)\cdot w\cdot f_M\cdot dx\cdot\frac{RT}{p}}_{\text{total volume flow to/from permeate}}$$

$$u(x+dx)=u(x)+\frac{dx}{h}\cdot\frac{RT}{p}\cdot\left[\sum_i k_{ig}\cdot\left(c_i^*(x+dx)-c_i(x+dx)\right)-\ldots\right.$$

$$\left.\ldots f_M\cdot\frac{Q_{H_2}}{s_M}\cdot(RT)^{0.5}\cdot\left(c_{H_2}^{0.5}(x+dx)-c_{H_2,p}^{0.5}(x+dx)\right)\right]$$

FREE CHANNEL VOLUME (REACTION SIDE)

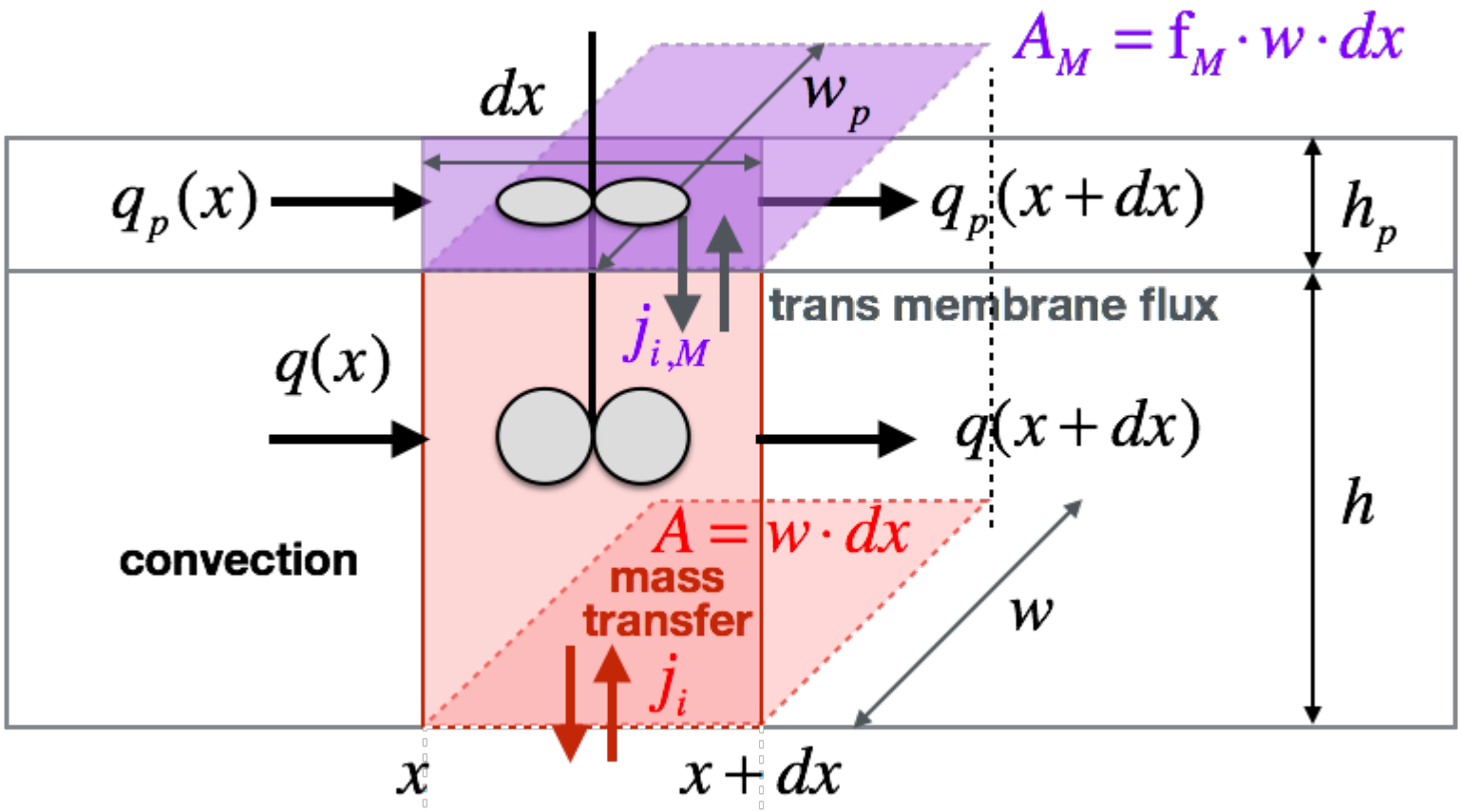
in material balance:

concentration on the surface is given by reaction/diffusion inside layer

concentration in the permeate (has to be determined by permeate side material balance)

FREE CHANNEL VOLUME (PERMEATE SIDE)

so, permeate side:



CSTR material balance component i (permeate side):

$$0 = q_p(x) \cdot c_{i,p}(x) - q_p(x+dx) \cdot c_{i,p}(x+dx) - j_{i,M}(x+dx) \cdot A_M$$

$$0 = \left[u_p(x) \cdot c_{i,p}(x) - u_p(x+dx) \cdot c_{i,p}(x+dx) \right] \cdot w_p \cdot h_p - j_{i,M}(x+dx) \cdot w \cdot f_M \cdot dx$$

FREE CHANNEL VOLUME (PERMEATE SIDE)

here as well, new flow velocity $u_p(x+dx)$ for ideal gas and constant pressure:

$$u_p(x+dx)\cdot w_p\cdot h_p = u_p(x)\cdot w_p\cdot h_p + \ldots$$

$$\underbrace{\ldots \underbrace{\frac{Q_{H_2}}{s_M}\cdot (RT)^{0.5}\cdot\left(c_{H_2}^{0.5}(x+dx)-c_{H_2,p}^{0.5}(x+dx)\right)}_{\text{total molar flux to/from permeate}}\cdot w\cdot \mathrm{f}_M\cdot dx\cdot\frac{RT}{p}}_{\text{total volume flow to/from permeate}}$$

$$u_p(x+dx) = u_p(x) + \frac{dx}{h_p}\cdot \mathrm{f}_M\cdot\frac{w}{w_p}\cdot\frac{(RT)^{1.5}}{p}\cdot\frac{Q_{H_2}}{s_M}\cdot\left[c_{H_2}^{0.5}(x+dx)-c_{H_2,p}^{0.5}(x+dx)\right]$$

note that pressure p here is the permeate pressure, which is in general different from the reaction side pressure

FREE CHANNEL VOLUME (PERMEATE SIDE)

in material balance:

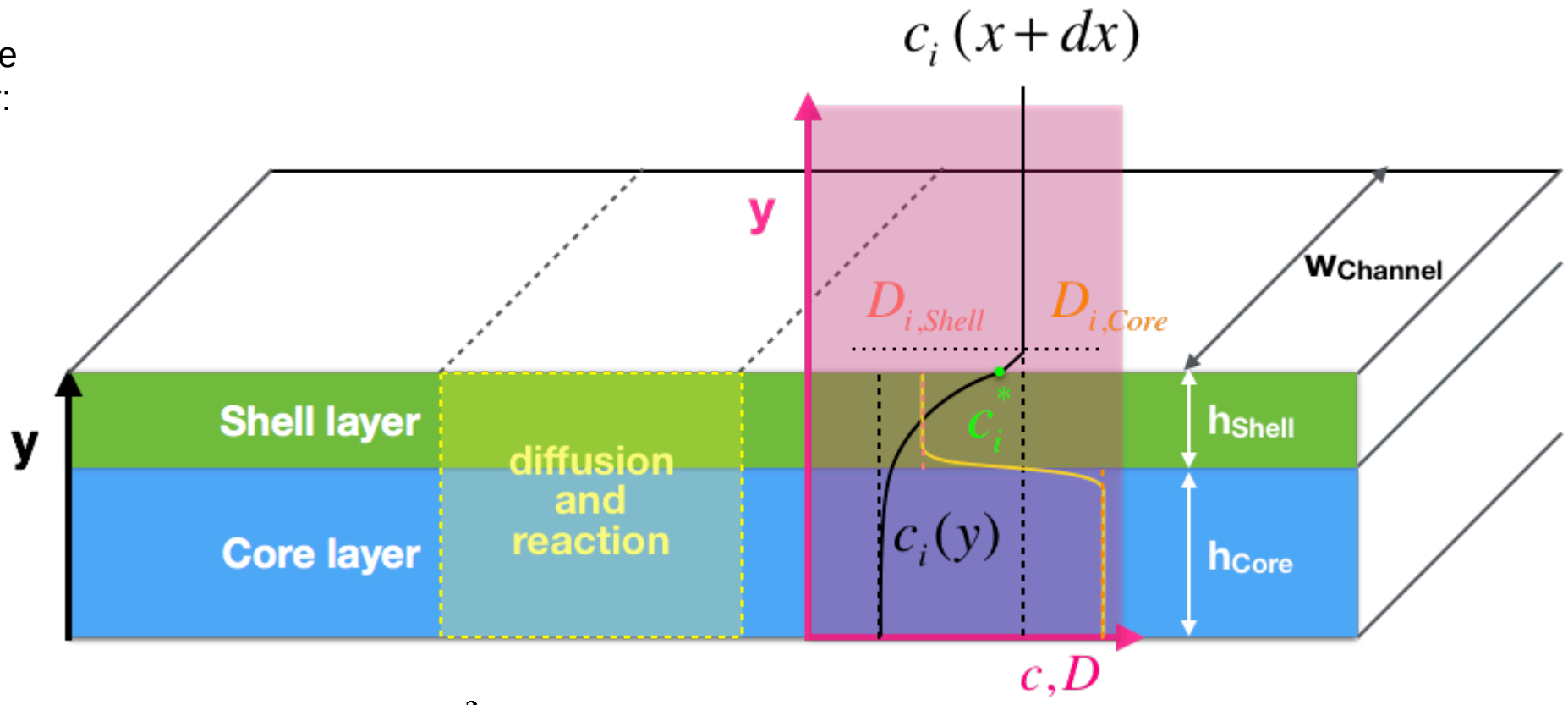
$$0 = u_p(x)\cdot\left[c_{i,p}(x) - c_{i,p}(x+dx)\right] + \ldots$$

$$\ldots\frac{dx}{h_p}\cdot \mathrm{f}_M \cdot \frac{w}{w_p}\cdot\frac{(RT)^{1.5}}{p}\cdot\frac{Q_{H_2}}{s_M}\cdot\left(c_{H_2}^{0.5}(x+dx) - c_{H_2,p}^{0.5}(x+dx)\right)\cdot c_{i,p}(x+dx) - \ldots$$

$$\ldots j_{i,M}\cdot \mathrm{f}_M \cdot \frac{dx}{h_p}$$

again, note that pressure p here is the permeate pressure, which is in general different from the reaction side pressure

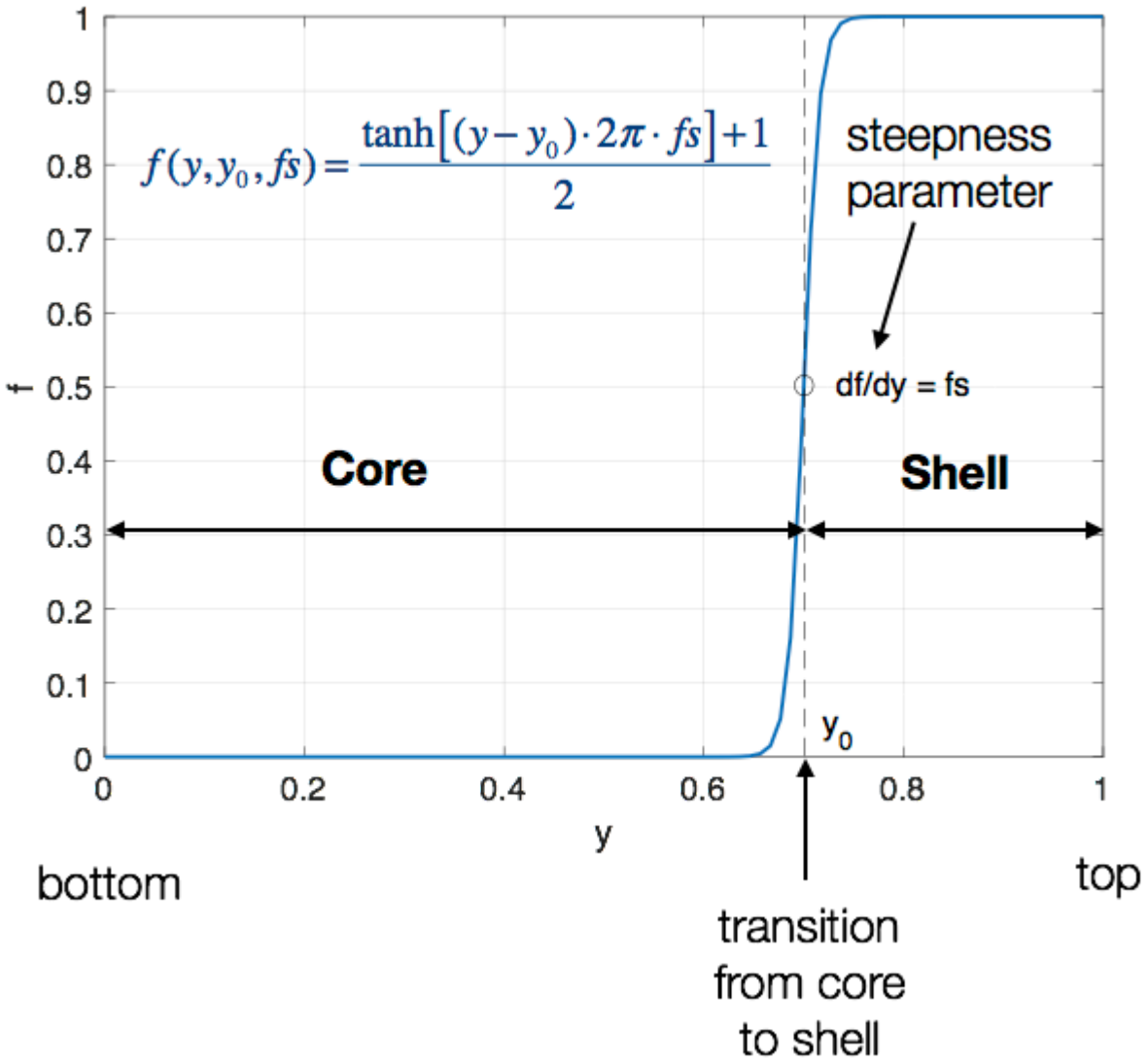
now, we need to solve the ODE for the layer:



Standard ODE (constant diffusivity): $$0 = D_i \cdot \frac{d^2 c_i}{dy^2} + R_i(c_i, T)$$

- different diffusivities D_i in the two layers can be handled via position-dependent effective diffusivity $D_i(y)$
- the presence of different catalysts in the two layers can also be handled via position-dependent catalyst mass concentrations $\rho_{Cat,j}(y)$

NON-DIMENSIONAL FUNCTION F WITH 2 PARAMETERS



Effective diffusivity as step function:

$$D_i = D_{i,Core} + f(y)\cdot\left(D_{i,Shell} - D_{i,Core}\right)$$

Catalyst mass concentrations as step functions:

$$\rho_{Cat,Core}(y) = [1 - f(y)]\cdot \rho_{Core}$$

$$\rho_{Cat,Shell}(y) = f(y)\cdot \rho_{Shell}$$

ODE SYSTEM FOR POSITION-DEPENDENT DIFFUSIVITY $D_I(Y)$

$$0 = -D_i(y)\cdot\frac{dc_i}{dy}(y)\cdot dx\cdot w + D_i(y+\Delta y)\cdot\frac{dc_i}{dy}(y+\Delta y)\cdot dx\cdot w + \left[\frac{R_i(y)+R_i(y+\Delta y)}{2}\right]\cdot\Delta y\cdot dx\cdot w$$

influx outflux source term

$$0 = -D_i\cdot\frac{dc_i}{dy} + \left[D_i + \frac{dD_i}{dy}\cdot\Delta y\right]\cdot\left[\frac{dc_i}{dy} + \frac{d^2c_i}{dy^2}\cdot\Delta y\right] + \left[\frac{R_i + R_i + \frac{dR_i}{dy}\cdot\Delta y}{2}\right]\cdot\Delta y$$

$$0 = \boxed{-D_i\cdot\frac{dc_i}{dy} + \left[D_i\cdot\frac{dc_i}{dy}\right.} + \frac{dD_i}{dy}\cdot\Delta y\cdot\frac{dc_i}{dy} + D_i\cdot\frac{d^2c_i}{dy^2}\cdot\Delta y + \frac{dD_i}{dy}\cdot\cancel{\frac{d^2c_i}{dy^2}\cdot(\Delta y)^2}\Bigg] + \left[R_i\cdot\Delta y + \frac{1}{2}\cdot\cancel{\frac{dR_i}{dy}\cdot(\Delta y)^2}\right]$$

$$0 = \frac{dD_i}{dy}\cdot\frac{dc_i}{dy} + D_i\cdot\frac{d^2c_i}{dy^2} + R_i \quad \Rightarrow \quad \frac{d^2c_i}{dy^2} = -\frac{R_i(y)}{D_i(y)} - \frac{1}{D_i(y)}\cdot\frac{dD_i(y)}{dy}\cdot\frac{dc_i}{dy}$$

extra term

ODE SYSTEM FOR POSITION-DEPENDENT DIFFUSIVITY $D_I(Y)$

$$\frac{d^2c_i}{dy^2} = -\frac{R_i(y)}{D_i(y)} - \frac{1}{D_i(y)} \cdot \frac{dD_i(y)}{dy} \cdot \frac{dc_i}{dy}$$

where: $$\frac{dD_i(y)}{dy} = \left(D_{i,core} - D_{i,shell}\right) \cdot \frac{df}{dy}$$

and: $$\frac{df}{dy} = \frac{df}{dy' \cdot s} = \frac{1}{s} \cdot \left(1 - \tanh^2\left[\left(y' - y'_0\right) \cdot 2\pi \cdot f_s\right]\right) \cdot \pi \cdot f_s$$

due to: $s = h_{core} + h_{shell}$ $\qquad y' = \frac{y}{s}$ $\qquad y'_0 = \frac{h_{core}}{s}$

$$\frac{d^2 c_i}{dy^2} = -\frac{R_i(y)}{D_i(y)} - \frac{1}{D_i(y)} \cdot \frac{dD_i(y)}{dy} \cdot \frac{dc_i}{dy}$$

Boundary conditions:

y=0	$y=h_{Core}+h_{Shell}$	
$\left.\frac{dc_i}{dy}\right\|_{y=0} = 0$	infinite mass transfer rate	$c_i\big\|_{y=h_{Core}+h_{Shell}} = c_i(x+dx)$
	finite mass transfer rate	$D_{i,Shell} \cdot \left.\frac{dc_i}{dy}\right\|_{y=h_{Core}+h_{Shell}} = k_{ig} \cdot \left(c_i(x+dx) - c_i^*(x+dx)\right)$

concentration in bulk phase

concentration on top of double layer

CONNECTING ODE SYSTEM WITH CSTR MATERIAL BALANCE

Case 1: infinite mass transfer rate

$$c_i\Big|_{y=h_{Core}+h_{Shell}} = c_i\,(x+dx)$$

flux from/to layer is expressed with the concentration gradient at top of the double layer

$$0 = u(x)\cdot\left[c_i(x) - c_i(x+dx)\right] - \frac{dx}{h}\cdot\frac{RT}{p}\cdot\left[\sum_i k_{ig}\cdot\left(c_i^*(x+dx) - c_i(x+dx)\right) - \ldots\right.$$

$$\left.\ldots \mathrm{f}_M\cdot\frac{Q_{H_2}}{s_M}\cdot\left(RT\right)^{0.5}\cdot\left(c_{H_2}^{0.5}(x+dx) - c_{H_2,p}^{0.5}(x+dx)\right)\right]\cdot c_i(x+dx) + \ldots$$

$$\ldots k_{ig}\cdot\left(c_i^*(x+dx) - c_i(x+dx)\right)\cdot\frac{dx}{h} + j_{i,M}\cdot\mathrm{f}_M\cdot\frac{dx}{h}$$

where: $$k_{ig}\cdot\left(c_i^*(x+dx) - c_i\,(x+dx)\right) = -D_{i,Shell}\cdot\frac{dc_i}{dy}\Big|_{y=h_{Core}+h_{Shell}}$$

$$0 = u(x)\cdot\left[c_i(x) - c_i(x+dx)\right] - \frac{dx}{h}\cdot\frac{RT}{p}\cdot\left[\sum_i -D_{i,Shell}\cdot\left.\frac{dc_i}{dy}\right|_{y=h_{Core}+h_{Shell}} - \ldots\right.$$

$$\left.\ldots \mathrm{f}_M\cdot\frac{Q_{H_2}}{s_M}\cdot(RT)^{0.5}\cdot\left(c_{H_2}^{0.5}(x+dx) - c_{H_2,p}^{0.5}(x+dx)\right)\right]\cdot c_i(x+dx) - \ldots$$

$$\ldots D_{i,Shell}\cdot\left.\frac{dc_i}{dy}\right|_{y=h_{Core}+h_{Shell}}\cdot\frac{dx}{h} + j_{i,M}\cdot\mathrm{f}_M\cdot\frac{dx}{h}$$

rearranging:

$$\left.c_i\right|_{y=h_{Core}+h_{Shell}} = c_i(x+dx) = \frac{u(x)\cdot c_i(x) - \frac{dx}{h}\cdot\left[D_{i,Shell}\cdot\left.\frac{dc_i}{dy}\right|_{y=h_{Core}+h_{Shell}} - j_{i,M}\cdot\mathrm{f}_M\right]}{u(x) - \frac{dx}{h}\cdot\frac{RT}{p}\cdot\left[\sum_i D_{i,Shell}\cdot\left.\frac{dc_i}{dy}\right|_{y=h_{Core}+h_{Shell}} + \mathrm{f}_M\cdot\frac{Q_{H_2}}{s_M}\cdot(RT)^{0.5}\cdot\left(c_{H_2}^{0.5}(x+dx) - c_{H_2,p}^{0.5}(x+dx)\right)\right]}$$

- $c_{H2,p}(x+dx)$ is found from the hydrogen material balance for permeate side for given sweep gas flow rate, permeate pressure and reaction side hydrogen concentration.
- owing to Sievert's law this requires the solution of a nonlinear equation.

Flexible approach - 1D cascade of cells with the option to limit the concentration change per cell via step size control

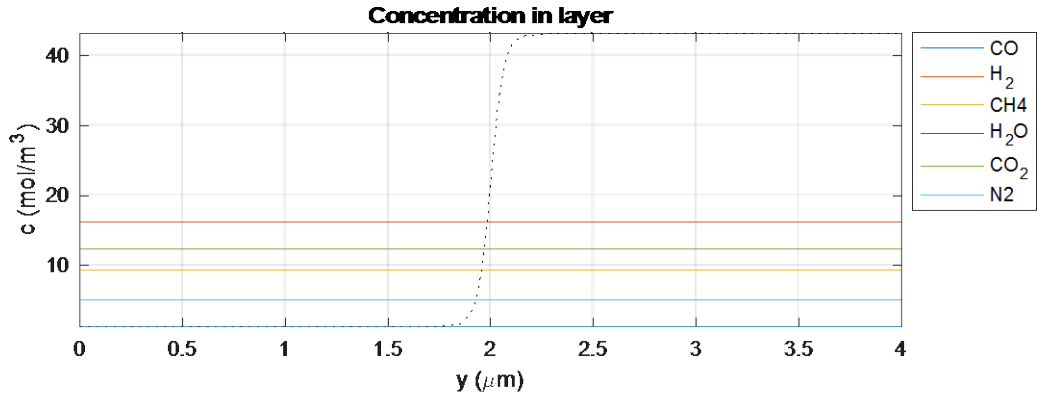
- solved profiles for one cell are used as initial guess for subsequent cell
- mole flows in both compartments are updated based on solved profiles
- graphics for monitoring progress of the calculation
- material balance checks
- heat balance not yet implemented
- pressure drop along channel neglected

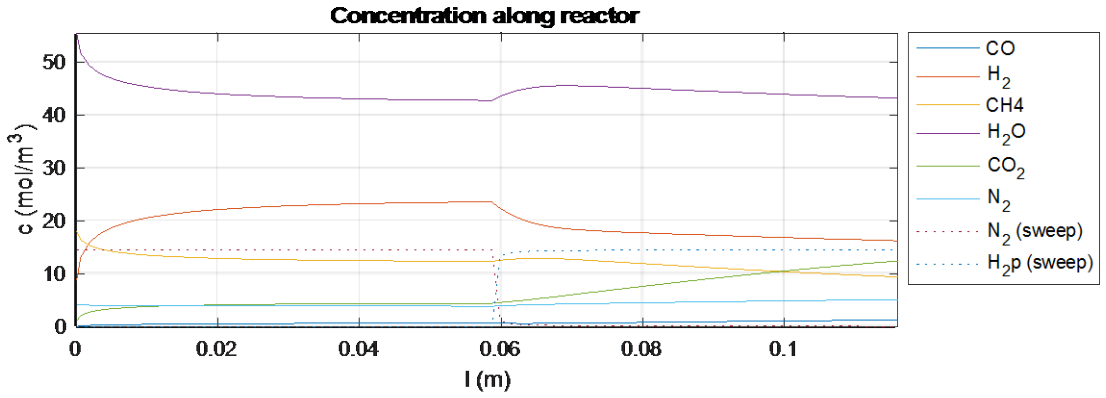
bvp4c - reliable boundary value problem solver with adaptive grid

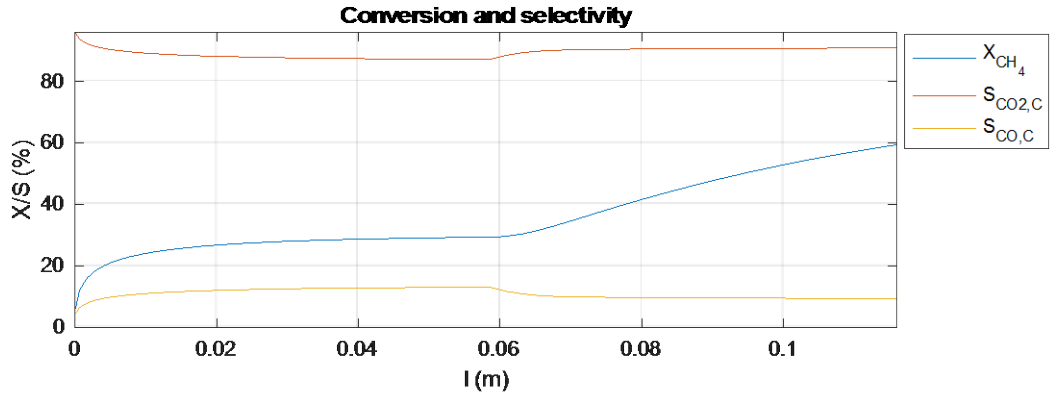
- CSTR material balance and membrane transport integrated in the definition of the boundary conditions
- nonuniform catalyst distribution and effective diffusivity - two distinct layers approximated by S-shaped distribution function

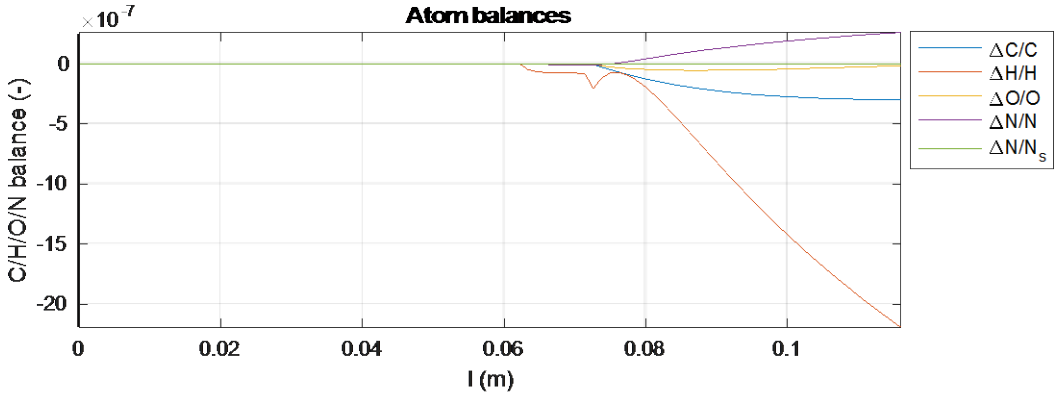
Exchangeable kinetics and permeation

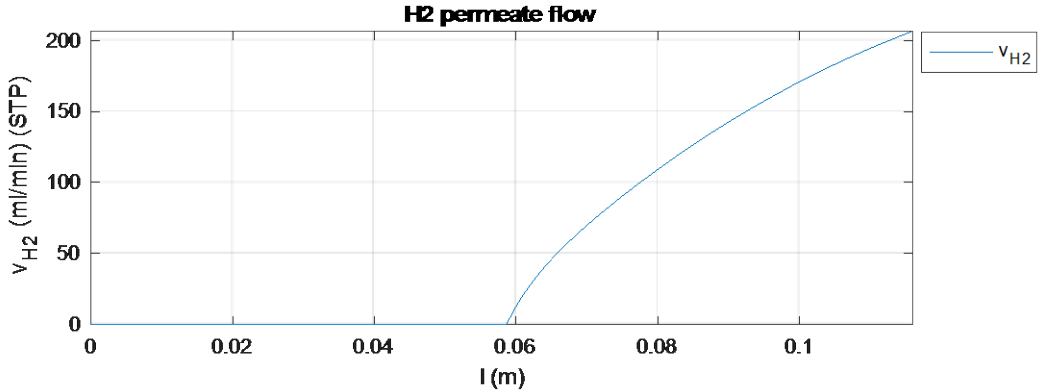
Matlab Program – Graphical Output

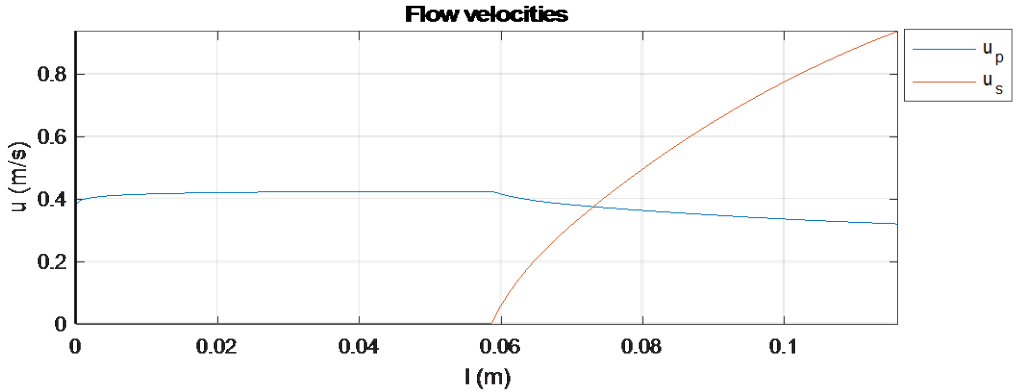












First commercial applications of membrane reactors may appear in

•small-capacity hydrogen production for industrial uses via on site reforming (low pressure, moderate purity),

•hydrogen generation from LOHC in the context of hydrogen logistics,

rather than in large-scale reforming or WGS.

•Transport effects may have a big influence on reactor performance (yield, selectivity, space time yield, etc.); this holds especially for membrane reactors where the reactions kinetics should not only match the usual heat and mass transport rates but also the permeation kinetics.

•Matlab is a flexible platform for building your own customised models for „multiscale“ reactor simulation

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Thank you for your attention

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