Scale Up↑ of structured catalysts for ammonia synthesis

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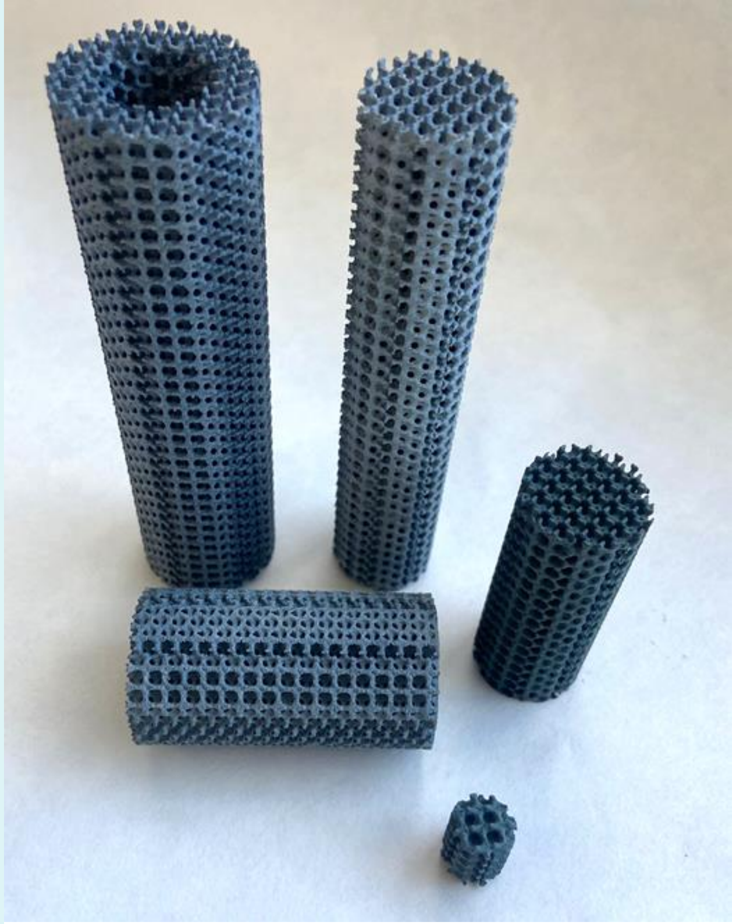


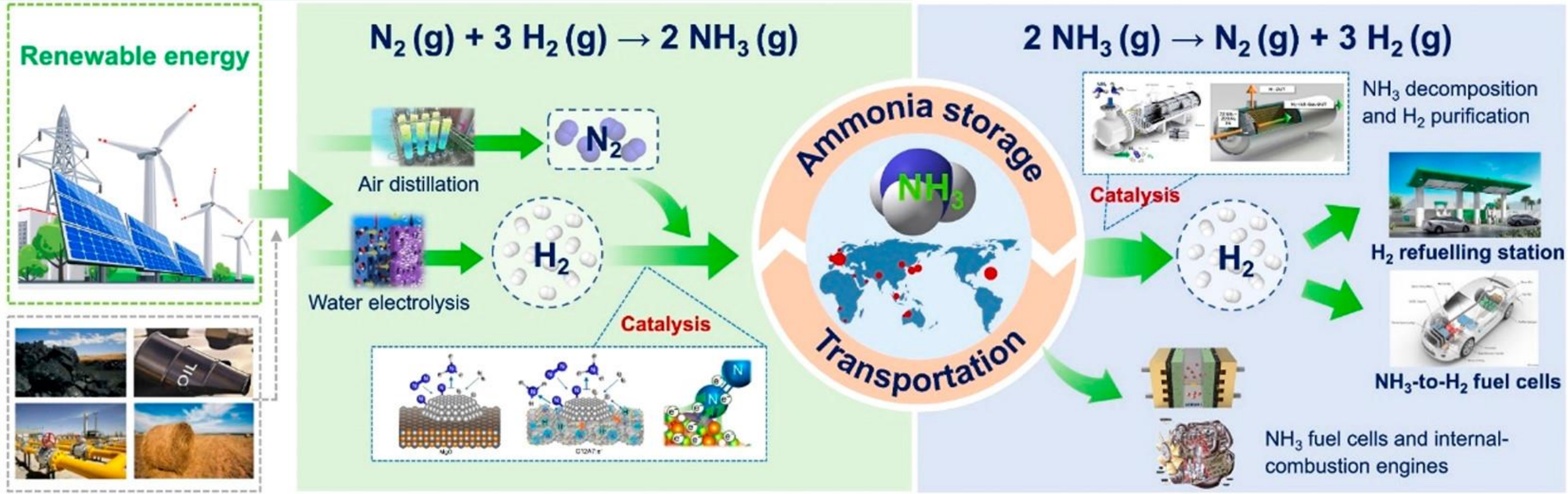
Ammonia as Energy Carrier

Webinar

October 17rd 2024

AMBHER
AndreaH
Funded by the European Union

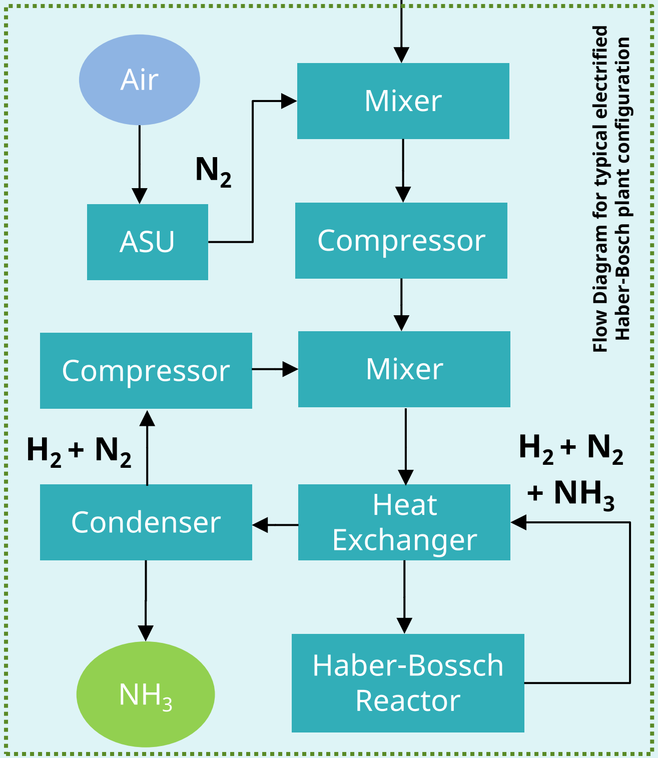
Why Ammonia?



Ammonia as Energy Carrier via Ammonia Synthesis and Decomposition

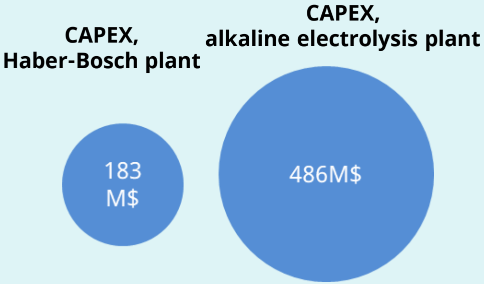
THE DECARBONISATION OF AMMONIA PRODUCTION

Green Ammonia production

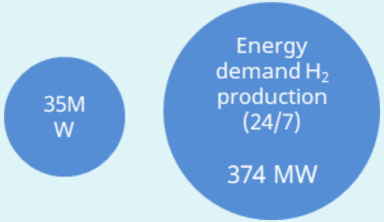


"Drawbacks"

- *The capital expenditure for a green ammonia production plant is dominated by the electrolyzer cost*

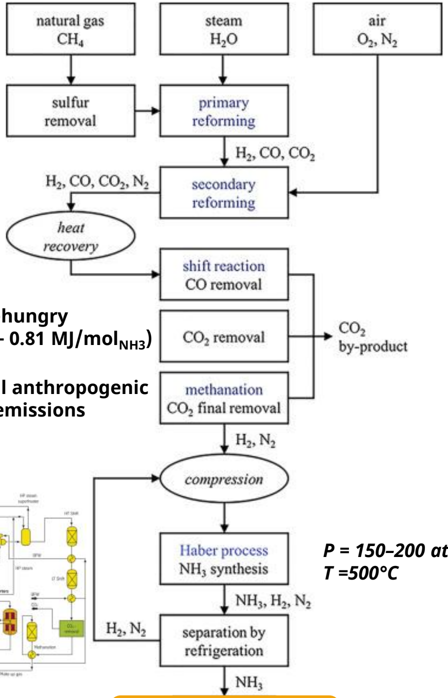


- *The energy supply for green hydrogen feedstock is significantly greater than the electricity demand for the HB process.*



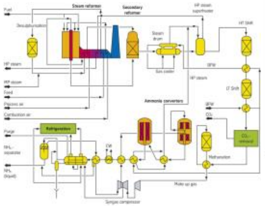
AMMONIA PRODUCTION ON A LARGE SCALE

Flow Diagram for the Multi-step Haber-Bosch Ammonia Production Process



Energy-hungry
(0.58 MJ/mol_{NH3} – 0.81 MJ/mol_{NH3})

1.6% of total anthropogenic CO_2 emissions



P = 150–200 atm
T =500°C

Brown ammonia

$3H_2 + N_2 \rightarrow 2NH_3$, ΔH = -92 Kj/mol

- Daily production capacity: 1000 - 2200t
- Efficiency: 65%
- Gas velocities: 10000–20000 $m^3/m_{cat.}^3 h$
- Typical conversions: 8–15%

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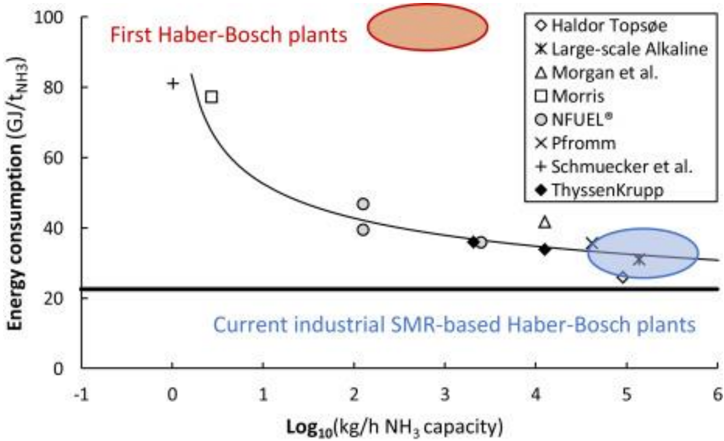
THE DECARBONISATION OF AMMONIA PRODUCTION

- **Scale-Down and Intermittency issues**

"Renewable sources of energy such as biomass, solar, wind or geothermal are characterized by a highly distributed production across regions"

- ***Distributed production corresponds to the production at small scales****, for green ammonia production the step forward is* ***dawn-size of large-scale plant*** *and modularization;*
- *A large-scale ammonia plant (≥1000 t_{NH3}/d) consumes about 2–7 GJ/t_{NH3} for pressurizing, heating, pumping and utilities;*
- *At intermediate scales (3–20 t_{NH3}/d), this energy consumption increases to typically 13–14 GJ/t_{NH3};*
- *At very small scales (<0.1 t_{NH3}/d), heat is even required to keep the ammonia synthesis reactor at the synthesis temperature due to radial heat losses, and hydrogen and nitrogen production also becomes less efficient*
- *Intermittent* ***solar power and wind power cause variations in electricity supply****. Therefore, the synthesis loop should either be able to ramp up and down fast, or batteries should be installed to operate the synthesis loop at constant load*

Energy consumption of various electrolysis-based Haber-Bosch processes (academic and industrial estimates).
The bold line represents the thermodynamic minimum energy consumption (22.5 GJ/t_{NH3})



$$E = (52.58 * \log_{10}(\text{capacity in kg/h}))^{-0.30}$$

Upon scale-down, heat losses increase and the energy consumption increases

Milder operating conditions in the synthesis loop are required for effective scale-down

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AMMONIA AND MOF BASED HYDROGEN STORAGE FOR EUROPE

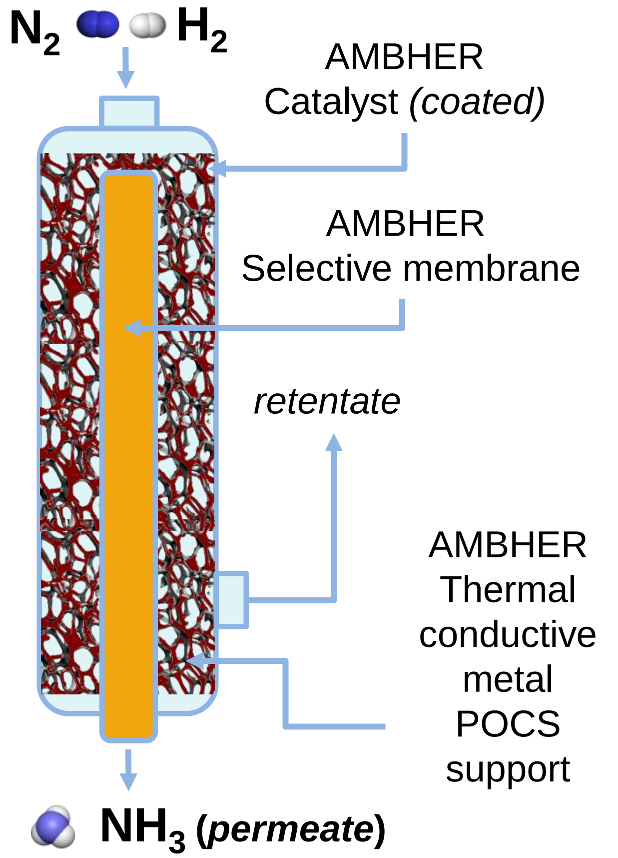
AMBH2ER

WP3
"Key materials and components for long term Hydrogen Storage"

***Task 3.3**: Bench-scale (TRL 4) 3D printed POCS and novel JM catalysts:*

***Subtask 3.3.1:** Design, manufacture and heat transfer performance characterization (under non-reactive conditions) of 3D printed POCS and commercial open cell foam [ENGIE. M1-M24]*
***Subtask 3.3.2**: Catalytic activation, characterization and performances of thermal conductive open-cell foams and POCS with commercial reference catalyst (1st generation) [CNR, ENGIE. M1-M24]*
***Subtask 3.3.3:** Preparation and tests of novel Fe, Ru based catalysts [JM. M1-M24]*
***Subtask 3.3.4**: Preparation of structured catalysts (2nd generation) for single CMR [CNR, ENGIE, TUE. M20-M24]*
***Subtask 3.5.2:** Fabrication of structured catalysts (POCSs activated with novel catalyst) for single membrane reactor (TRL4) and the demonstrator plant (TRL5) [CNR, ENGIE, JM, M30-40]*

Integration POCS catalysts with membranes in a membrane reactor



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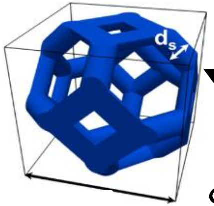
Periodical Open Cellular Structures (POCS) 3D printed

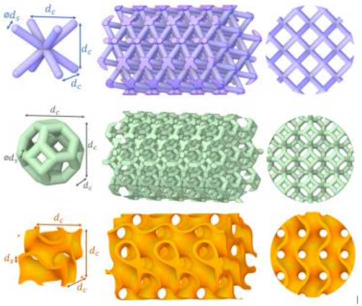
❑ *Schematic sequence of POCSs manufacturing process*

User Input

STL file generation



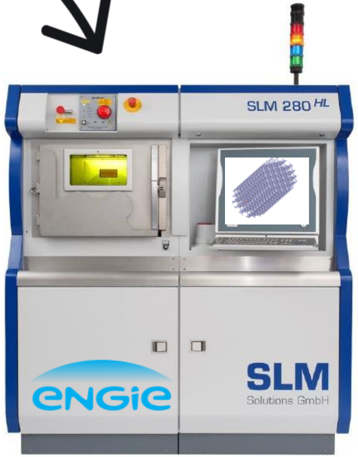
Strut diameter



Detailed design with Netfabb software

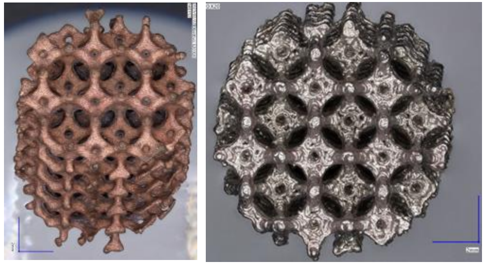
Metal powder

Three-dimensional (3D) printing



Selective Laser Melting (SLM)

Final POCS Supports



Process output

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POCSs Manufacturing

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ENGIE

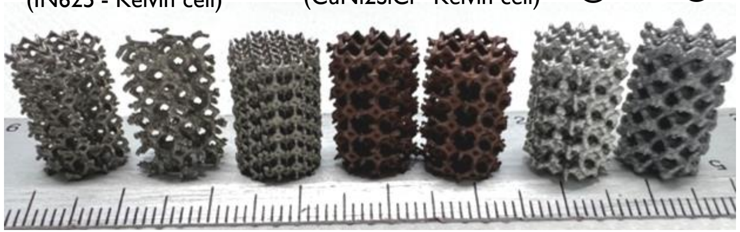
❑ *Periodical Open Cellular Structures (POCS)*

Material	Cell type	Cell size (mm)	Strut diameter (mm)	Volume (cm^3)	Surface (cm^2)	Surface/ Volume ratio	Theor. Relative Density
Al alloy (AlSi10Mg)	BCC	3	0.6	0.220	12.94	58.82	0.17
	Kelvin	3	0.6	0.290	15.23	52.52	0.21
Cu alloy (CuNi2SiCr)	Kelvin	3	0.6	0.290	15.23	52.52	0.21

Material	Cell type	Cell size (mm)	Strut diameter (mm)	Volume (cm^3)	Surface (cm^2)	Surface/ Volume ratio	Theor. Relative Density
Ni alloy (IN625)	Kelvin	3	0.6	0.290	15.23	52.52	0.21
		4	0.6	0.153	9.08	59.37	0.11
		3	0.8	0.518	16.93	32.68	0.36
		3	0.4	0.126	11.21	88.97	0.10
		1.5	0.3	0.292	29.79	102.02	0.23
		4	0.8	0.278	11.39	40.97	0.19
		2	0.4	0.288	22.46	78.00	0.22
		2	0.6	0.631	25.20	39.94	0.45

- Ni Alloy (IN625 - Kelvin cell)
- Cu Alloy (CuNi2SiCr -Kelvin cell)
- Al Alloy AlSi10Mg

(Kelvin c.) (BCC c.)

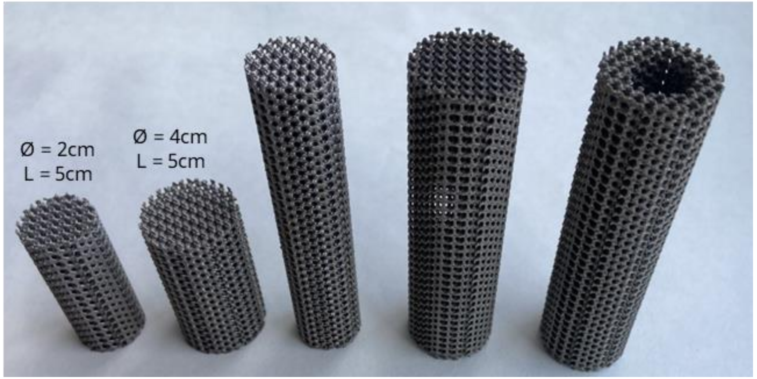


Ø = 1cm, L = 1.5cm

Ø = 2cm L = 10cm

Ø = 4cm L = 10cm

Ø = 2,66cm L = 10cm



FPMaT

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POCSs Manufacturing

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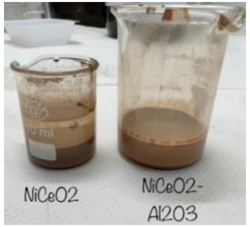
❑ Scale-up strategy

- ***Microscale studies***

Influence of :

1. *Slurry composition;*
2. *Catalyst formulation;*
3. *Powder ball milling rate;*
4. *Slurry ball milling time;*
5. *Support Thermal Treatment;*
6. *Support Anodization;*
7. *Primer (Disperal P2) utilization;*
8. *Support geometry (BCC, Kelvin);*
9. *Calcination temperature and time;*
10. *POCSs sand-blasted pretreatment;*
11. *Mechanical stability*



Slurry composition

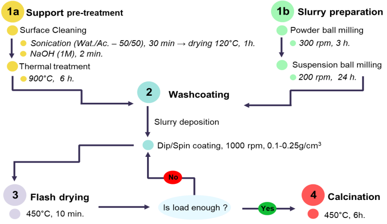
Glycerol	Water	Solid	PVA
42.5 %	33.6 %	22.4 %	1.5 %

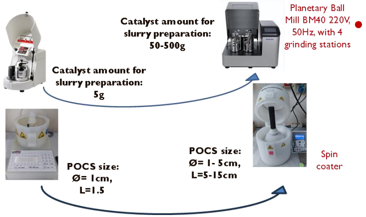
Ø = 1cm, L = 1.5cm

- ***Intermediate scale-up***

Influence of :

1. *Slurry optimisation;*
2. *Coating process optimization;*

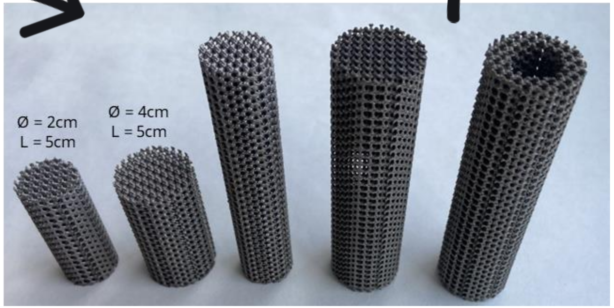




Ø = 2cm L = 10cm

Ø = 4cm L = 10cm

Ø = 2,66cm L = 10cm



- ***Final scale-up for prototype***

Influence of :

1. *Equipment size;*

Ø = 51cm, L = 10 - 20cm

3D PRINTED SUPPORTS CHARACTERIZATION

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❑ *Morphological characterizations and porosity*

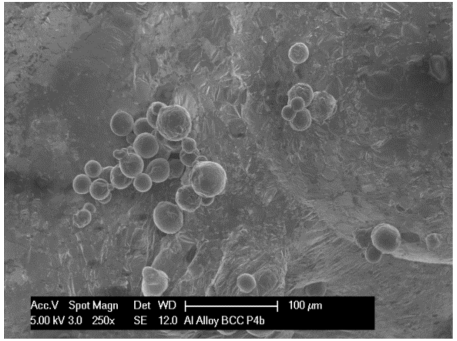
Material	Cell type	Cell size (mm)	Strut diameter (mm)	** Solid Volume (cm³)	** Solid density (g/cm³)	Internal Surface area (cm²)	** Porosity (%)	** Geom. density (g/cm³)	Specific surf. area (cm²/cm³)	Relative density
IN625	BCC	2 (2*)	0.4 (0.41*)	0.219	10.87	9.45	82.9	2.80	87.03	0.17
IN625	BCC	2 (2*)	0.6 (0.6*)	0.489	8.79	24.52	63.9	2.02	48.77	0.36
IN625	BCC	3 (3*)	0.4 (0.4*)	0.099	11.31	19.06	92.1	3.65	95.66	0.08
IN625	BCC	3 (3*)	0.6 (0.59*)	0.220	8.86	23.85	83.3	0.95	58.82	0.17
IN625	BCC	3 (4*)	0.8 (0.75*)	0.395	4.41	9.47	71.5	1.66	39.01	0.29
IN625	BCC	4 (4*)	0.6 (0.62*)	0.116	9.14	12.94	91.2	1.48	64.48	0.09
IN625	BCC	4 (3*)	0.8 (0.75*)	0.206	16.02	15.41	85.2	0.90	45.85	0.15
IN625	BCC	1.5(1.5*)	0.3 (0.3*)	0.212	12.08	7.48	83.3	2.80	115.66	0.17

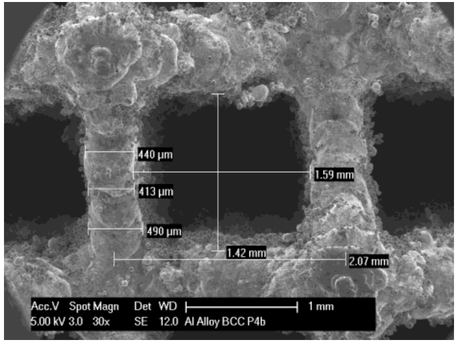
*Measured value: *Calculated from optical images, **Calculated from He pycnometer measurement*

Ø = 1cm, L = 1.5cm

Elium pycnometer (Model 1305 Multivolume, Micromeritics)

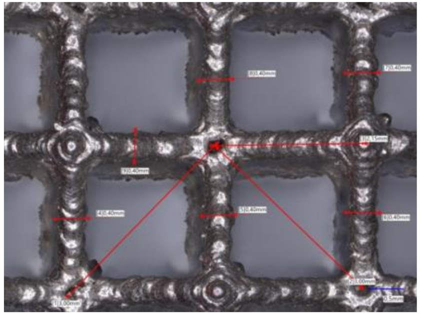
- **SEM micrographs**



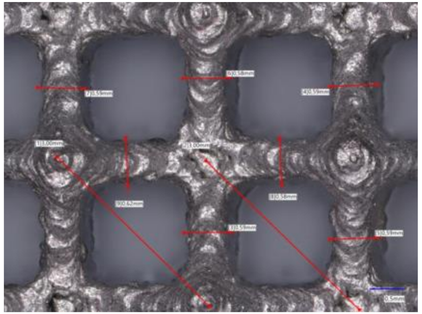


▪ Optical microscope images of as-built BCC Ni-alloy POCS

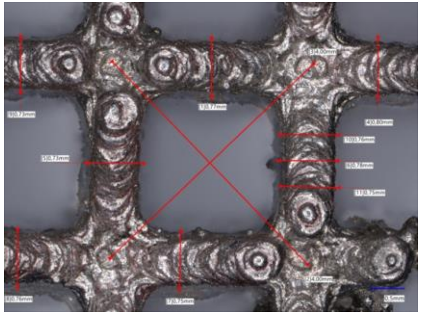
Cell Type = 3, Ø Strut =0.4mm,
SSA = 95.66 cm²/cm³, Porosity = 92%



Cell Type = 3, Ø Strut =0,6 mm,
SSA = 58,82 cm²/cm³, Porosity = 83,3%



Cell Type = 3, Ø Strut =0,8 mm,
SSA = 39,01 cm²/cm³, Porosity = 71,3%



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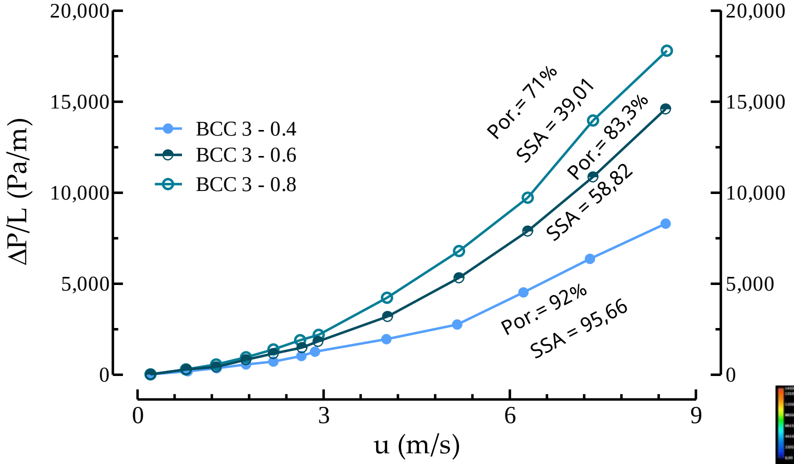
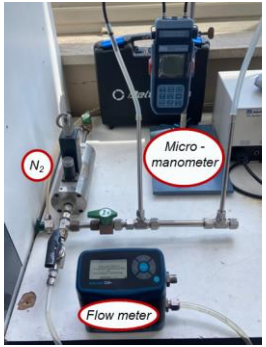
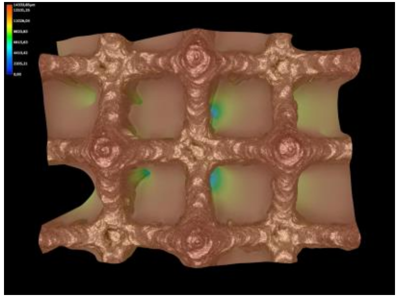
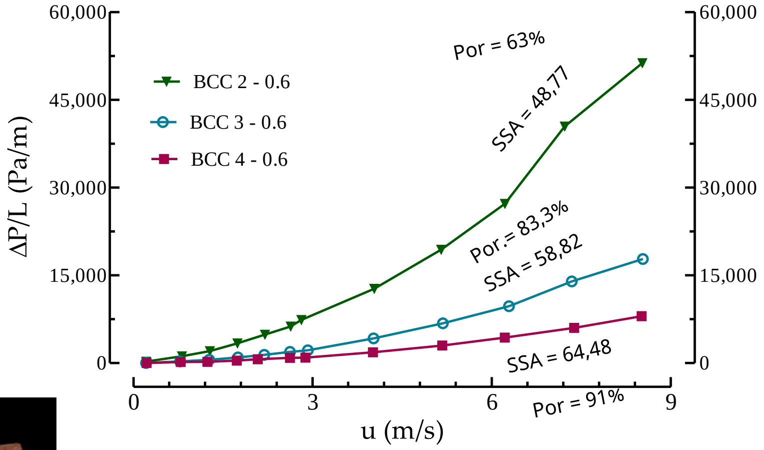
❑ *Pressure drop*









3D PRINTED SUPPORTS CHARACTERIZATION

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❑ *Morphological characterizations and porosity*

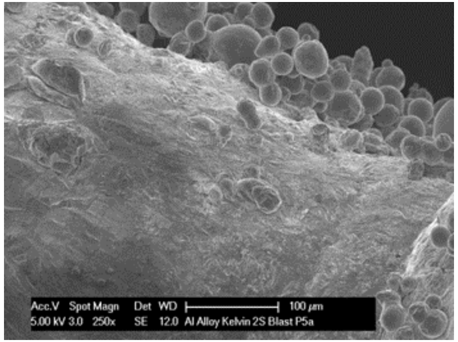
Material	Cell type	Cell size (mm)	Strut diameter (mm)	**Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	** Geom. density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
IN625	KELVIN	2 (2*)	0.6 (0.4*)	0.631	9.30	25.20	54.5	4.99	39.94	54.5
IN625	KELVIN	3 (3.04*)	0.4 (0.44*)	0.126	14.21	11.21	90.4	1.52	88.97	90.4
IN625	KELVIN	3 (3*)	0.6 (0.69*)	0.290	10.14	15.23	78.7	2.50	52.52	78.7
IN625	KELVIN	3 (3*)	0.8 (0.86*)	0.518	9.42	16.93	64.4	4.14	32.68	64.4
IN625	KELVIN	4 (4*)	0.6 (0.61*)	0.153	10.85	9.08	88.6	1.41	59.37	88.6

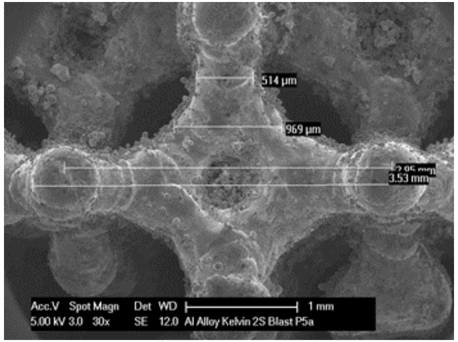
*Measured value: *Calculated from optical images, **Calculated from He pycnometer measurement*

Ø = 1cm, L = 1.5cm

Elium pycnometer (Model 1305 Multivolume, Micromeritics)

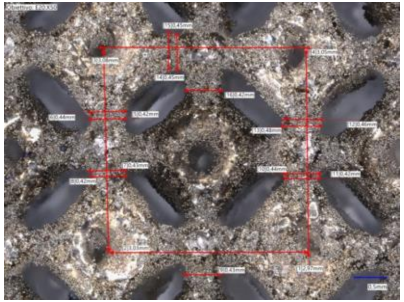
- **SEM micrographs**



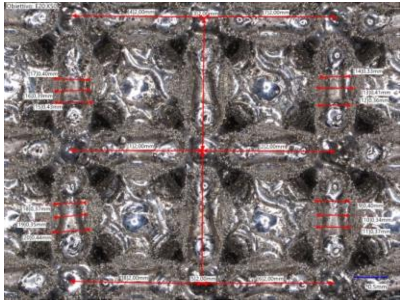


▪ Optical microscope images of as-built kelvin Ni-alloy POCS

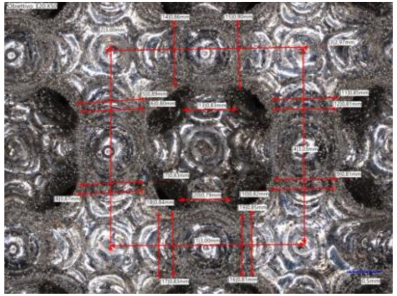
Cell Type = 3, Ø Strut =0.4mm, SSA = 88.9 cm^2/cm^3, Porosity = 90.4%



Cell Type = 3, Ø Strut =0,6 mm, SSA = 52,52 cm^2/cm^3, Porosity = 78,7%



Cell Type = 3, Ø Strut =0,8 mm, SSA = 32,68 cm^2/cm^3, Porosity = 64.4%



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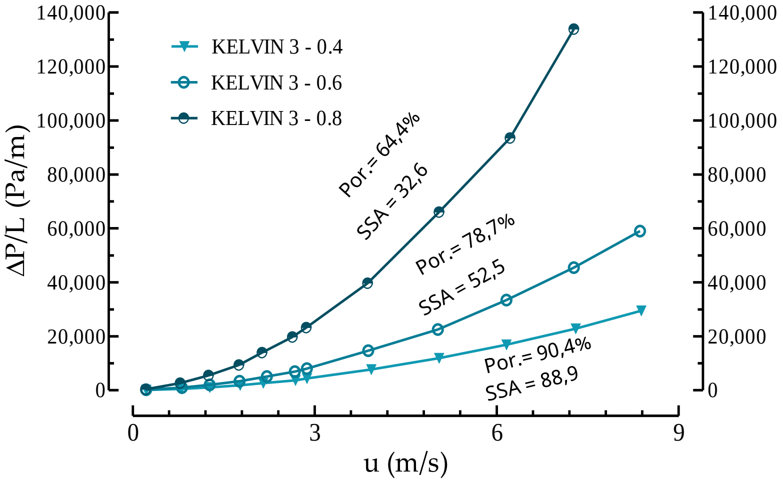
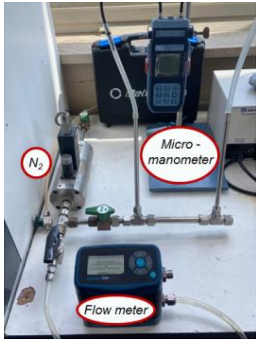
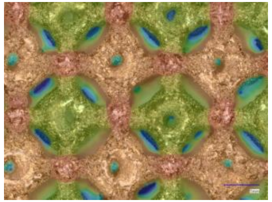
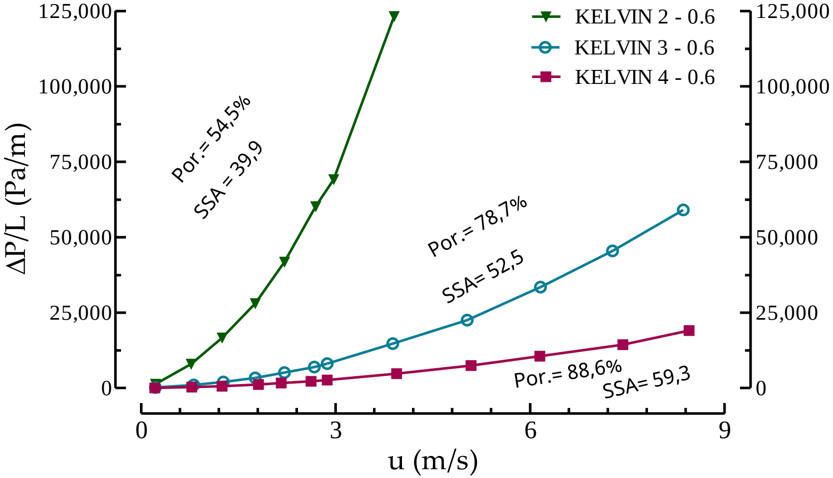
❑ *Pressure drop*









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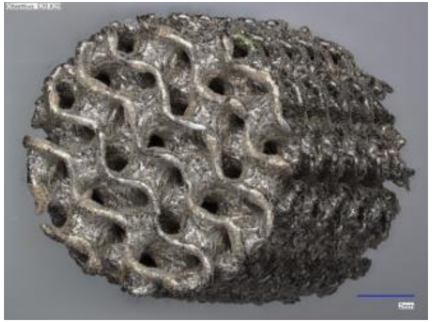
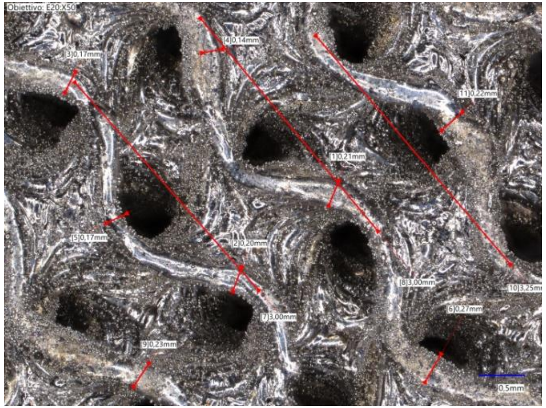
❑ *Morphological characterizations and porosity*

Ø = 1cm, L = 1.5cm

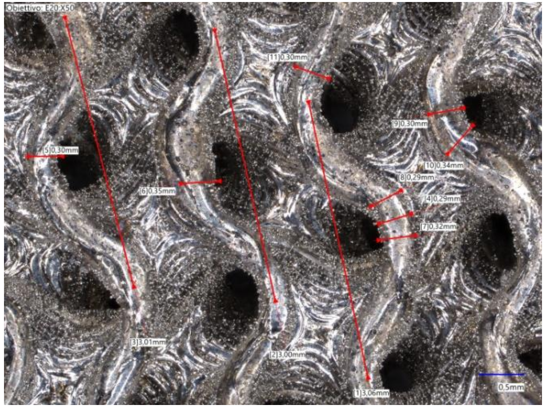


- **Optical microscope images of as-built GIROYD Ni-alloy Triply Periodic Minimal Surface (TPMS) structure**

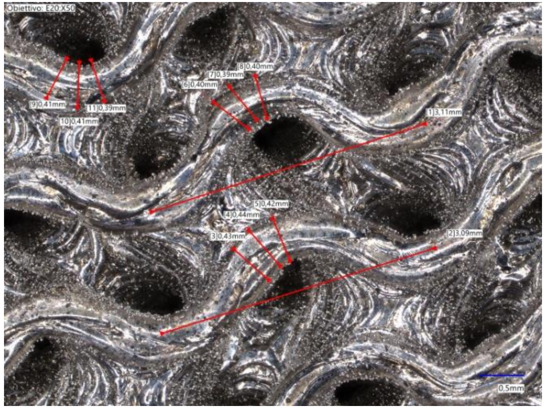
Cell Type = 3, Ø Strut =0.23mm,
SSA = 20.4 cm^2/cm^3 , Porosity = 79%



Cell Type = 3, Ø Strut =0,3 mm,
SSA = 20,1 cm^2/cm^3 , Porosity = 69,4%



Cell Type = 3, Ø Strut =0,4 mm,
SSA = 19.5 cm^2/cm^3 , Porosity = 61%



3D PRINTED SUPPORTS CHARACTERIZATION

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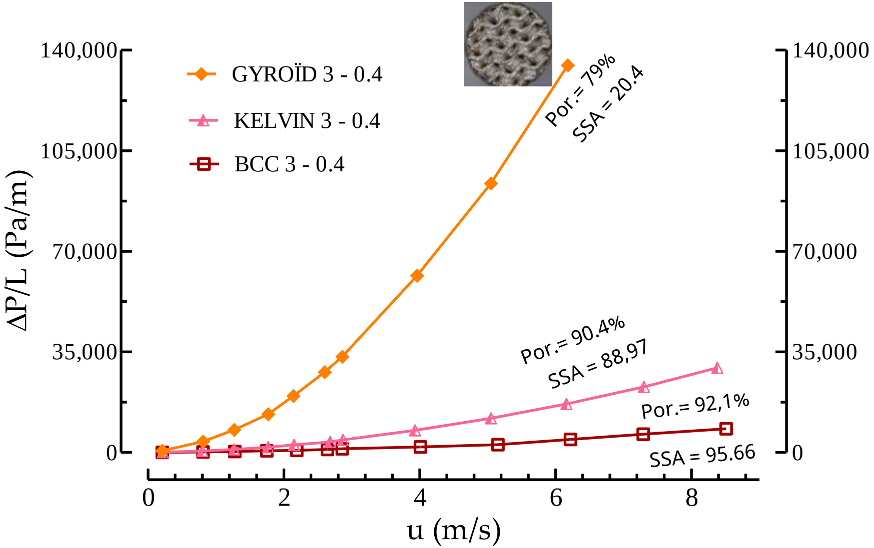
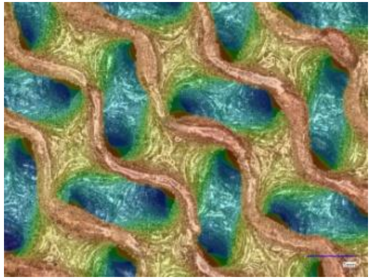
❑ *Pressure drop (comparison Gyroid, Kelvin, BCC)*

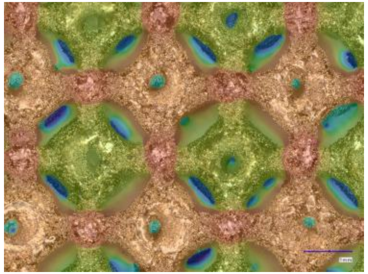


GYROID



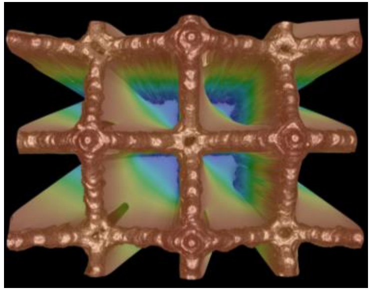
Cell Type = 3,
Ø Strut =0.4mm,
SSA = 20.4 cm^2/cm^3,
Porosity = 79%

KELVIN



Cell Type = 3,
Ø Strut =0,4 mm,
SSA = 88,97 cm^2/cm^3,
Porosity = 90,4%

BCC

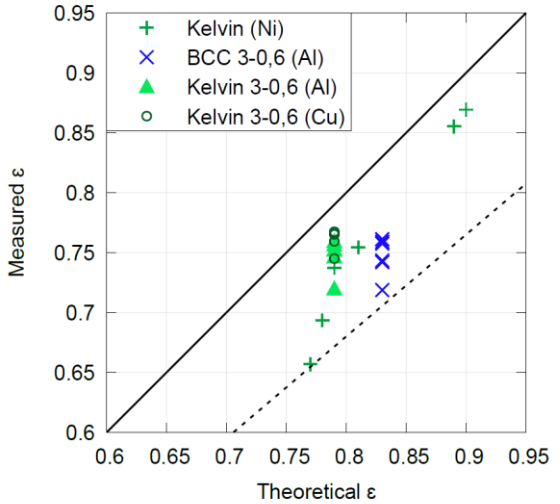


Cell Type = 3,
Ø Strut =0,4 mm,
SSA = 95,66 cm^2/cm^3,
Porosity = 92,1%

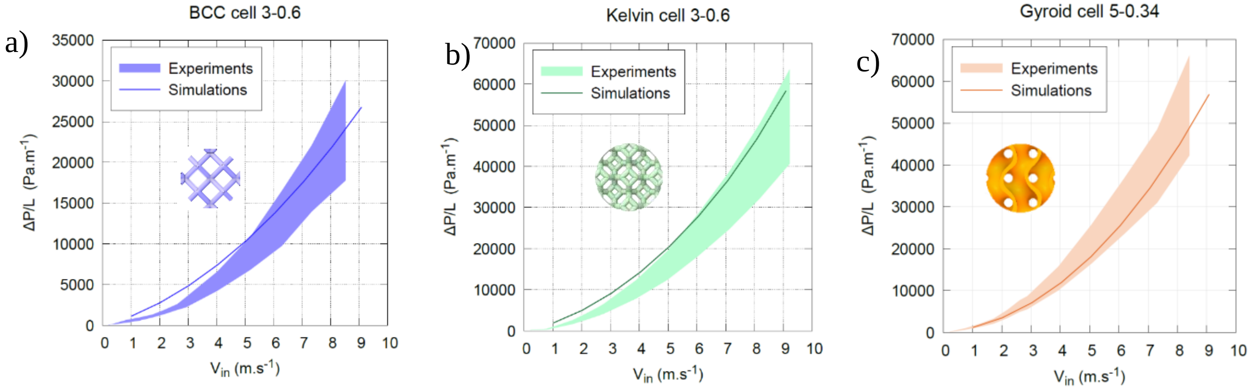
3D PRINTED SUPPORTS CHARACTERIZATION

Funded by the European Union

❑ *Experimental validation of CFD model a) BCC b) Kelvin c) Gyroid*



Comparison of experimental hydrodynamic porosity vs. theoretical porosity. The 15% error margin is indicated by a dashed line.



Pressure drop comparison on various structures

The printed samples closely resemble their CAD counterparts

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Comparison of thermo-hydraulic performance among different 3D printed periodic open cellular structures

S. Richard [a,d,*], D. Tasso [a], M. Rajana [a], A Saker [a], A. Ramirez Santos [a], C. Makhloufi [a], N. Meynet [a], B. Hary [b], S. Nardone [b], G. Marino [c], M. Thomas [c], C. Italiano [c], A. Vita [c], F. Gallucci [d]

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[b] ENGIE Laborelec, Rodestraat 125, 1630 Linkebeek, Belgium
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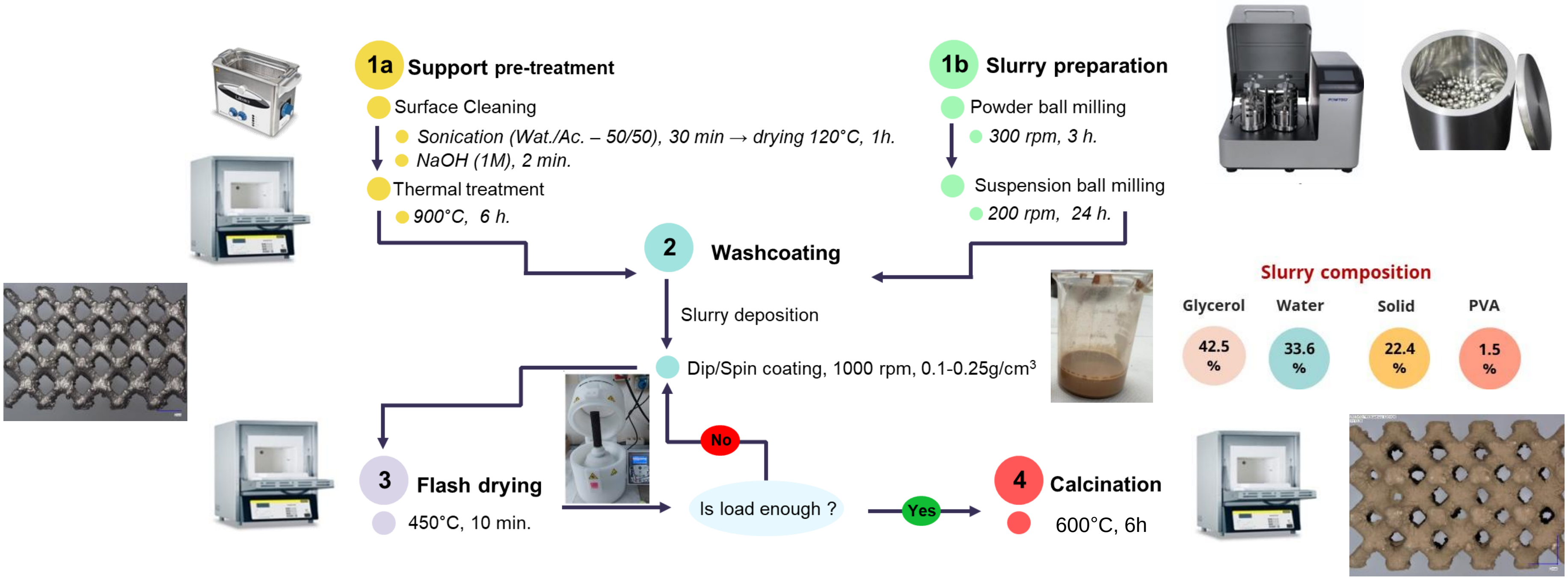
ACTIVATION OF NI-ALLOY POCS BY COMBINED DIP/SPIN COATING METHOD

❑ *Optimized dip/spin coating method*



Main steps involved in the preparation of structured catalysts by washcoating

CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

❑ Activation of Ni-Alloy POCS and TPMS by combined dip/spin coating method

Slurry preparation with a 5wt%Ru/Al_2O_3 catalyst for the activation of KELVIN, BCC and GYROYD structures

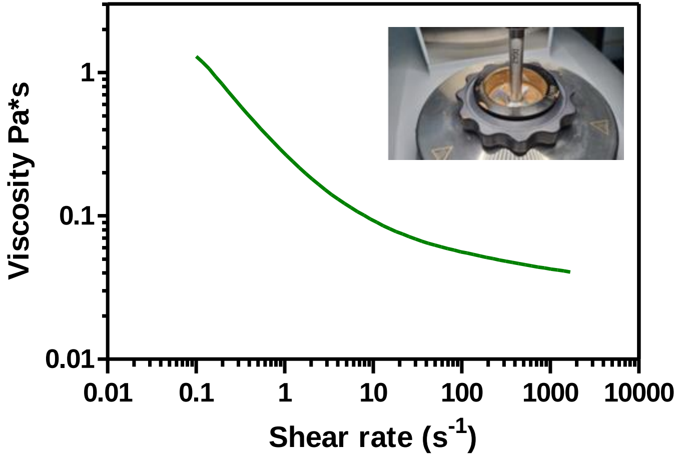
Slurry Composition

Glycerol: 42.5 %

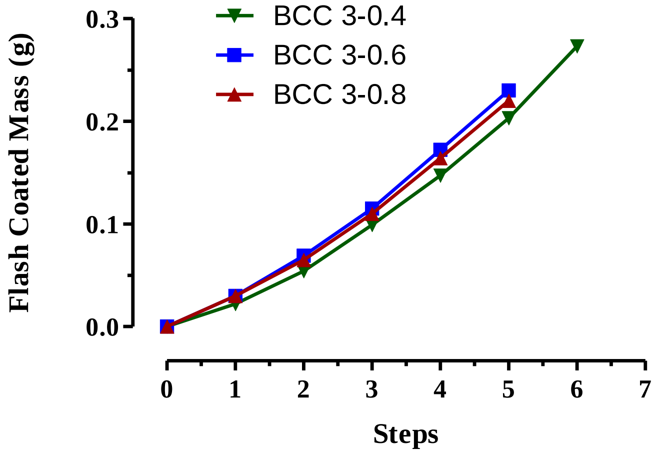
Water: 33.6 %

Solid: 22.4 %

PVA: 1.5 %



Rheological behaviour of slurry formulation (flow curve)



Loading curves

	Catalyst (g)	PVA (g)	Glycerol (g)	Water (g)	Ethanol (g)	No. Balls (1cm)	Volume of slurry (ml)
Batch 1	5	0.34	9.5	7.5	2	7	~16

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CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

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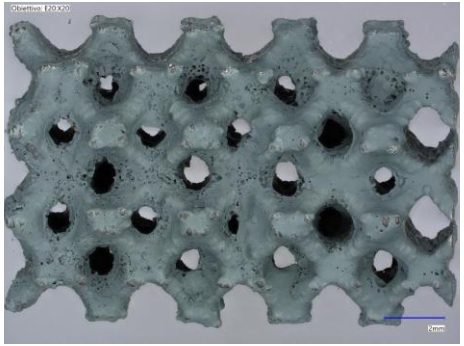
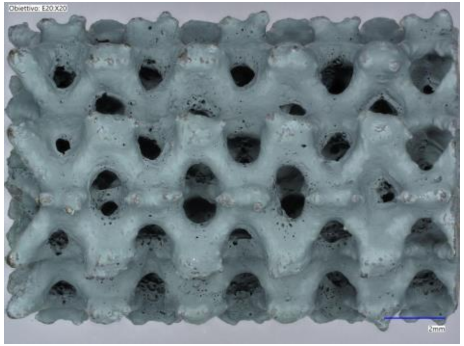
❑ *Coating of BCC Ni-Alloy POCS with a commercial 5wt%Ru/Al_2O_3 catalyst*

Cat. loading: 0,272g (0.23 g/cm³, 0.014g/cm²)



Cell Type = 3, Ø Strut =0,4 mm, SSA = 95,66 cm²/cm³, Porosity = 86,17%

Cat. loading: 0,232 (0.19 g/cm³, 0.012 g/cm²)



Cell Type = 3, Ø Strut =0,6 mm, SSA = 58,82 cm²/cm³, Porosity = 75,89%

Cat. loading: 0,241 (0.20 g/cm³, 0.015g/cm²)

Cell Type = 3, Ø Strut =0,8 mm, SSA = 39,01 cm²/cm³, Porosity = 66.61%

Ø = 1cm, L = 1.5cm

Slurry Composition

- Glycerol: 42.5 %
- Water: 33.6 %
- Solid: 22.4 %
- PVA: 1.5 %

$$\text{Catalyst Thickness} = \frac{m_{\text{catalyst}}}{\text{SSA}_{\text{POCS}} \times V_{\text{POCS}} \times d_{\text{layer}}}$$

POCS type	Cell size (mm)	Strut diameter (mm)	Solid Volume (cm³)	Surface (cm²)	Surface/Volume ratio (cm²/cm³)	Geometric V_{POCS} (cm³)	Catalyst loaded (g)	Density cat. layer ($g_{cat.}$/cm³)	Thickness (μm)
BCC	3	0,4	0,099	9,47	95,66	1,178	0,272	1,4	17,24
BCC	3	0,6	0,220	12,94	58,82	1,178	0,232	1,4	23,92
BCC	3	0,8	0,395	15,41	39,01	1,178	0,241	1,4	37,46

CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

Funded by the European Union

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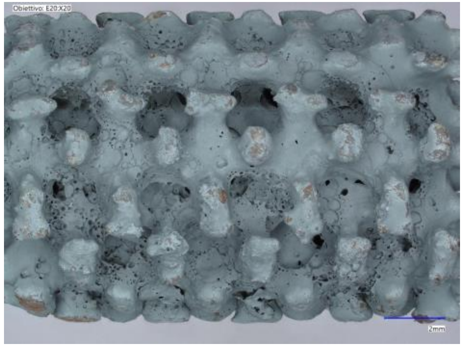
AMBHER ENGIE

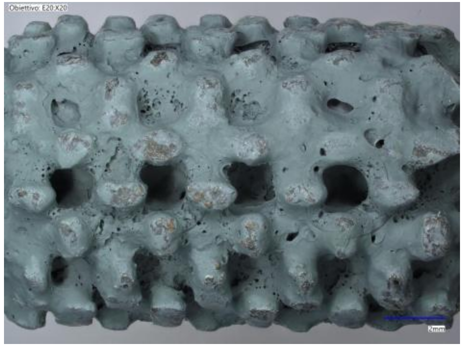
❑ *Coating of KELVIN Ni-Alloy POCS with a commercial 5wt%Ru/Al_2O_3 catalyst*

Cat. loading: 0,202g (0.17 g/cm³, 0.014g/cm²)



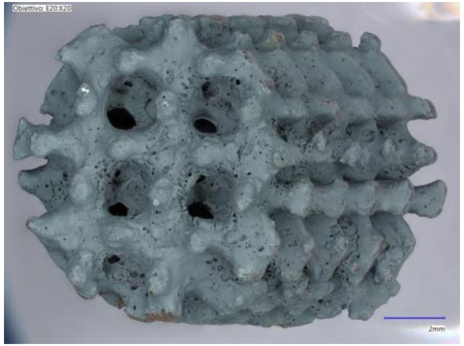
Cell Type = 3, Ø Strut =0,4 mm, SSA = 88,96 cm²/cm³, Porosity = 81,9%

Cat. loading: 0,234 (0.20 g/cm³, 0.012 g/cm²)



Cell Type = 3, Ø Strut =0,6 mm, SSA = 52,52 cm²/cm³, Porosity = 70,75%

Cat. loading: 0,225 (0.19 g/cm³, 0.01g/cm²)



Cell Type = 3, Ø Strut =0,8 mm, SSA = 32,68 cm²/cm³, Porosity = 51.54%

Ø = 1cm, L = 1.5cm

Slurry Composition

- Glycerol: 42.5 %
- Water: 33.6 %
- Solid: 22.4 %
- PVA: 1.5 %

$$\text{Catalyst Thickness} = \frac{m_{catalyst}}{SSA_{POCS} \times V_{POCS} \times d_{layer}}$$

POCS type	Cell size (mm)	Strut diameter (mm)	Solid Volume (cm³)	Surface (cm²)	Surface/Volume ratio (cm²/cm³)	Geometric V_{POCS} (cm³)	Catalyst loaded (g)	Density cat. layer ($g_{cat.}$/cm³)	Thickness (μm)
Kelvin	3	0,4	0,126	11,21	88,97	1,178	0,202	1,4	13,77
Kelvin	3	0,6	0,290	15,23	52,52	1,178	0,234	1,4	27,02
Kelvin	3	0,8	0,518	16,93	32,68	1,178	0,225	1,4	41,74

CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

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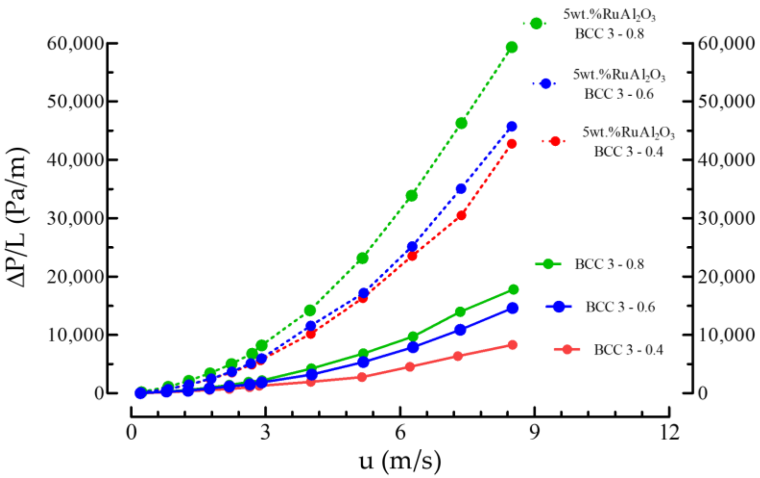
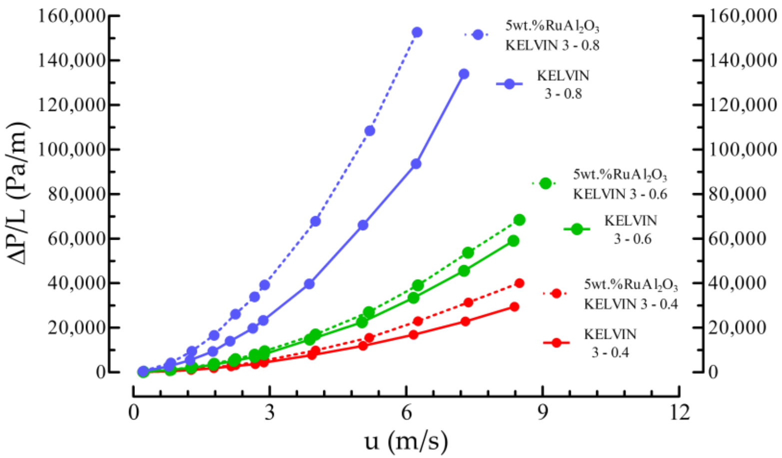
- ***Pressure drop (comparison Gyroid, Kelvin, BCC) influence of coating***





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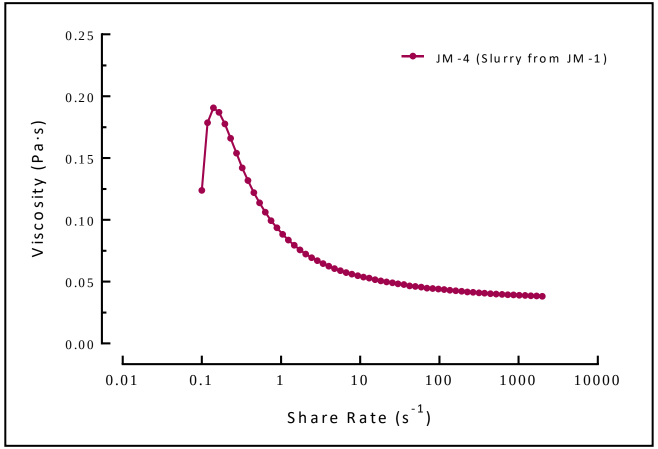
CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

Funded by the European Union

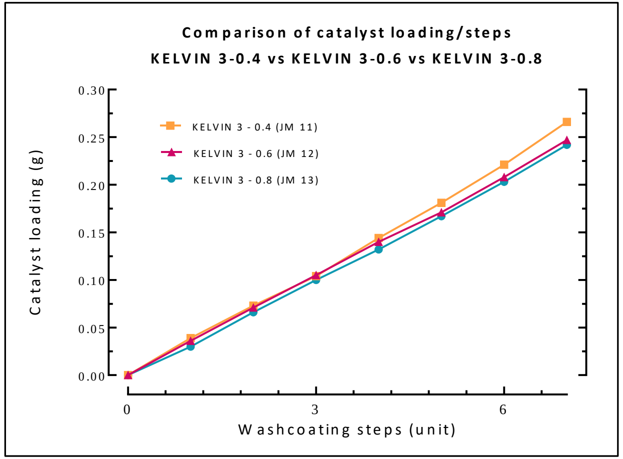
- *Slurry preparation with novel JM catalyst (Ru-based) for the activation of KELVIN, BCC and GYROYD structures*

Slurry Composition

Glycerol	Water	Solid	PVA
42.5 %	33.6 %	22.4 %	1.5 %



Rheological behaviour of slurry formulation (flow curve)



Loading curves

	Catalyst (g)	PVA (g)	Glycerol (g)	Water (g)	Ethanol (g)	No. Balls (1cm)	Volume of slurry (ml)
Batch 1	5	0.34	9.5	7.5	2	7	~16

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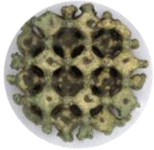
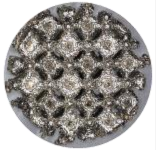
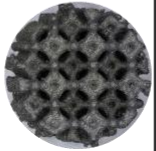
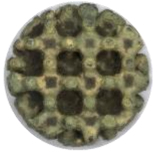
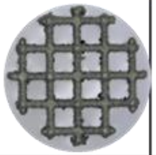
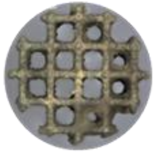
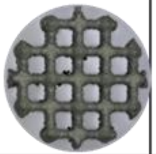
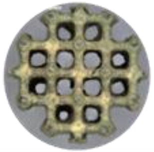
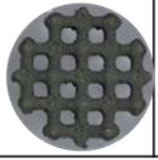
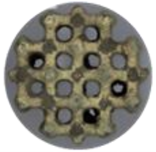
CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

Funded by the European Union

- ***Slurry preparation with novel JM catalyst (Ru-based) for the activation of KELVIN, and BCC POCS***

Ø = 1cm, L = 1.5cm

Support	Bare	Calcined	Washcoated	Calcined WC
KELVIN Cell size: 3 Strut size: 0.4 (mm)				
KELVIN Cell size: 3 Strut size: 0.6 (mm)				
KELVIN Cell: 3 Strut size: 0.8 (mm)				

Support	Bare	Calcined	Washcoated	Calcined WC
BCC Cell size: 3 Strut size: 0.4 (mm)				
BCC Cell size: 3 Strut size: 0.6 (mm)				
BCC Cell size: 3 Strut size: 0.8 (mm)				

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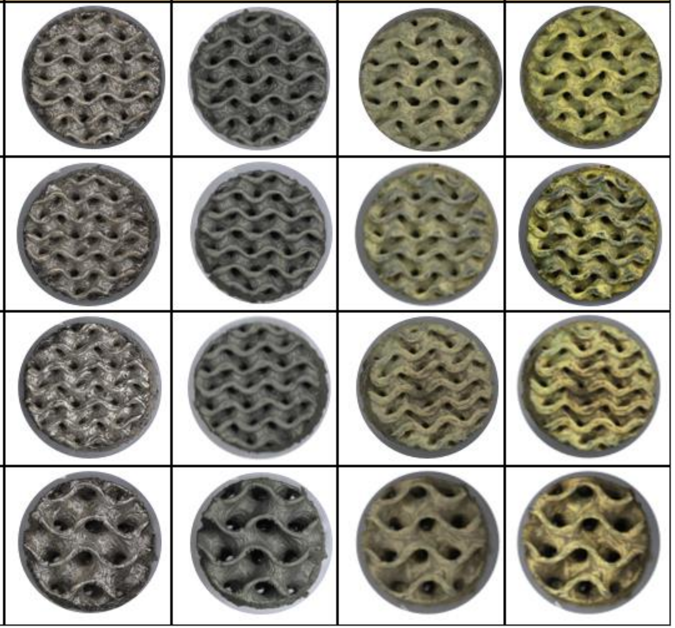
CATALYTIC ACTIVATION OF NI-ALLOY STRUCTURED SUPPORTS

Funded by the European Union

- *Slurry preparation with novel JM catalyst (Ru-based) for the activation of Triply Periodic Minimal Surface (TPMS) GYROYD structures*

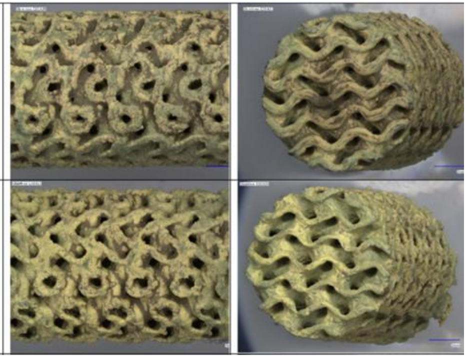
Ø = 1cm, L = 1.5cm

Support	Bare	Calcined	Washcoated	Calcined WC
GYROID Cell size: 3 Sheet size: 0.2 (mm)				
GYROID Cell size: 3 Sheet size: 0.3 (mm)				
GYROID Cell size: 3 Sheet size: 0.4 (mm)				
GYROID Cell size: 5 Sheet size: 0.34 (mm)				



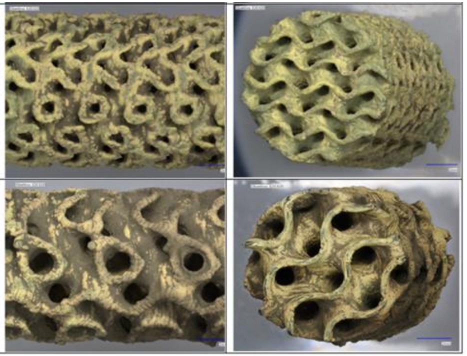
Coated GYROID Cell size: 3 Sheet size: 0.2 (mm)

Coated GYROID Cell size: 3 Sheet size: 0.3 (mm)



Coated GYROID Cell size: 3 Sheet size: 0.4 (mm)

Coated GYROID Cell size: 5 Sheet size: 0.34 (mm)



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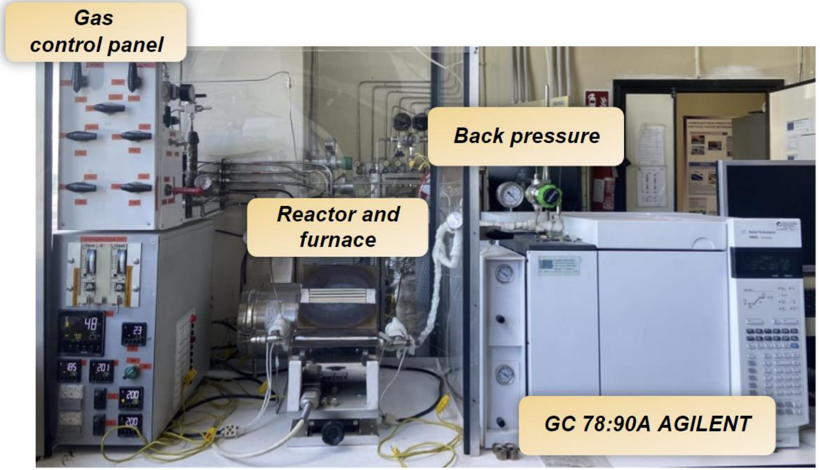
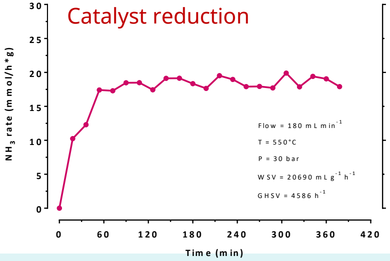
CATALYTIC ACTIVITY – AMMONIA SYNTHESIS

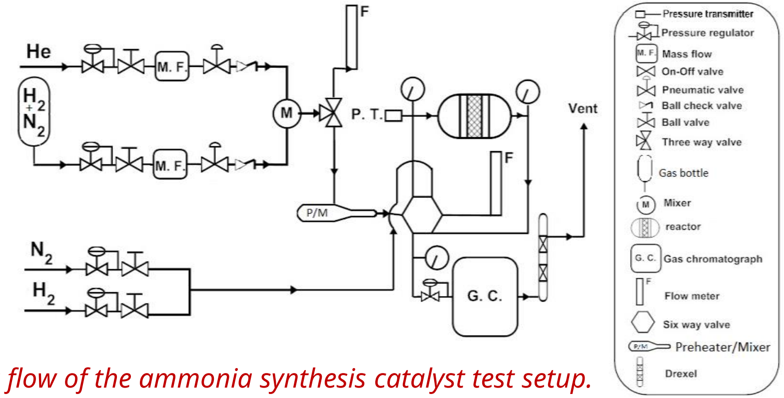
- ***Catalytic activity (test set up)***



Test rig for the evaluation of catalytic performances of catalysts towards the ammonia synthesis up to 50 bar

Operative conditions	
Temperature	300 - 550 (°C)
Pressure	20 (bar)
WSV	41379 ($cm^3\ g_{cat}^{-1}\ h^{-1}$)
GHSV	9172 (h^{-1})
Total IN Flow	90 - 540 cm^3/min
H_2/N_2	3:1 (H2 = 75%, N2 = 25%)
Catalyst	JM (Ru) –based AN5750





Schematic flow of the ammonia synthesis catalyst test setup.

CATALYTIC ACTIVITY – AMMONIA SYNTHESIS

AMBHER · Consiglio Nazionale delle Ricerche · ENGIE · JM

❑ *Catalytic tests at microscale with JM catalyst coated on POCS – Influence of geometry (KELVIN)*

Ø = 1cm, L = 1.5cm

JM-11 (KELVIN 3-0.4)

Pressure (bar)	GHSV (h-1)	WSV (cm³ g_{cat}^{-1} h⁻¹)	Flow (mL/min)
20	9172	40602	180

$N_2 + 3 H_2$ →

g_{cat}	Vol (cm3)	g/cm3
0.266	1,178	0,223

→ 2 NH_3

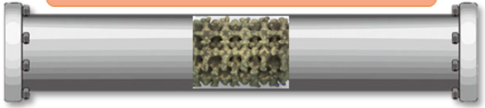
P = 20 bar					
χ H_2			NH_3 rate (mmol g^{-1} h^{-1})		
T 400	T 450	T 500	T 400	T 450	T 500
1.37	4.16	4.45	12.27	36.26	39.12

JM-12 (KELVIN 3-0.6)

Pressure (bar)	GHSV (h-1)	WSV (cm³ g_{cat}^{-1} h⁻¹)	Flow (mL/min)
20	9172	43725	180

$N_2 + 3 H_2$ →

g_{cat}	Vol (cm3)	g/cm3
0.247	1,178	0,210



→ 2 NH_3

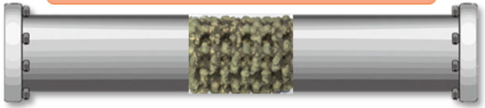
P = 20 bar					
χ H_2			NH_3 rate (mmol g^{-1} h^{-1})		
T 400	T 450	T 500	T 400	T 450	T 500
0.77	2.90	4.15	7.62	27.29	39.81

JM-13 (KELVIN 3-0.8)

Pressure (bar)	GHSV (h-1)	WSV (cm³ g_{cat}^{-1} h⁻¹)	Flow (mL/min)
20	9172	44628	180

$N_2 + 3 H_2$ →

g_{cat}	Vol (cm3)	g/cm3
0.266	1,178	0,206



→ 2 NH_3

P = 20 bar					
χ H_2			NH_3 rate (mmol g^{-1} h^{-1})		
T 400	T 450	T 500	T 400	T 450	T 500
0.62	2.16	3.74	6.02	20.74	35.86

CATALYTIC ACTIVITY – AMMONIA SYNTHESIS

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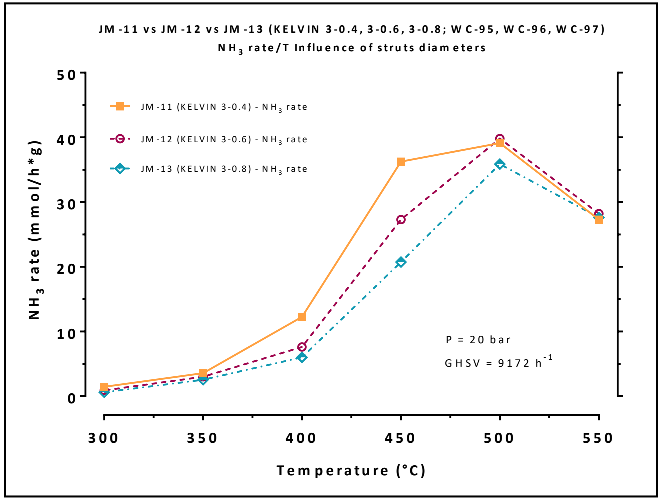
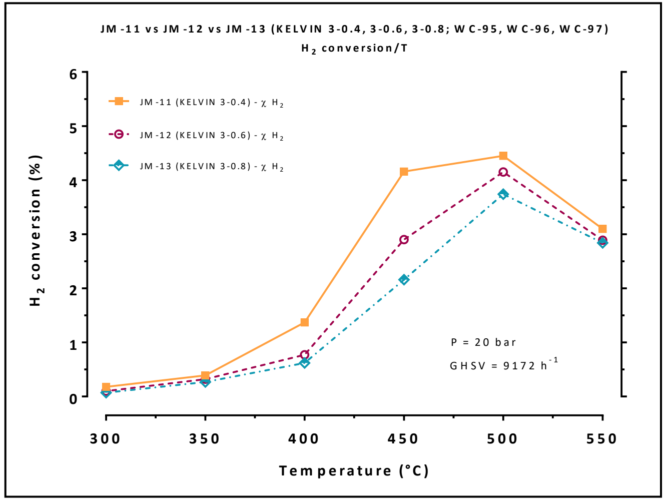
❑ *Catalytic tests at microscale with JM catalyst coated on POCS – Influence of geometry (KELVIN)*





Coating	Cell type	Solid Volume (cm^3)	Solid Density (g/cm^3)	Porosity (%)	WC g_{cat} (g) g_{cat}/V_{pyc} (g/cm^3)
JM-4	KELVIN 3-0.4	0.248**	8,2497**	78.91**	0.266 1.071**
JM-4	KELVIN 3-0.6	0.382**	8,2924**	67.59**	0.247 0.647**
JM-4	KELVIN 3-0.8	0.607**	8.4046**	48.46**	0,242 0.399**

Material	Cell type	Cell Size (mm)	Strut Diameter (mm)	Solid Volume (cm^3)	Solid Density (g/cm^3)	Internal Surface area (cm^2)	Porosity (%)	Geom. Density (g/cm^3)	Specific Surf. Area (cm^2/cm^3)	Relative density	WC g_{cat} g_{cat}/V_{geom}
IN625	KELVIN	3 (3.01*)	0.4 (0.42*)	0.126 (0.217**)	14.21 (8.2386**)	11.21	90.4 (81.94**)	1.52	88.97	0.10	0.266 0.226***
IN625	KELVIN	3 (3*)	0.6 (0.6*)	0.290 (0.350**)	10.14 (8.3484**)	15.23	78.7 (70.75**)	2.50	52.52	0.21	0.247 0.210***
IN625	KELVIN	3 (3*)	0.8 (0.81*)	0.518 (0.577**)	9.42 (8.4166**)	16.93	64.4 (51.64**)	4.14	32.68	0.36	0,242 0,206***

CATALYTIC ACTIVITY – AMMONIA SYNTHESIS

- *Catalytic tests at microscale with JM catalyst coated on POCS – Influence of geometry (KELVIN, BCC, GYROID)*

Ø = 1cm, L = 1.5cm

JM-11 (KELVIN 3-0.4)

Pressure (bar)	GHSV (h^{-1})	WSV ($cm^3\ g_{cat}^{-1}\ h^{-1}$)	Flow (mL/min)
20	9172	40602	180

$N_2 + 3\ H_2$ →

g_{cat}	Vol (cm3)	g/cm3
0.266	1,178	0,223

→ $2\ NH_3$

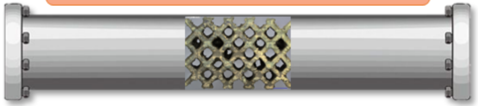
P = 20 bar					
χ H_2			NH_3 rate ($mmol\ g^{-1}\ h^{-1}$)		
T 400	T 450	T 500	T 400	T 450	T 500
1.37	4.16	4.45	12.27	36.26	39.12

JM-14 (BCC 3-0.4)

Pressure (bar)	GHSV (h^{-1})	WSV ($cm^3\ g_{cat}^{-1}\ h^{-1}$)	Flow (mL/min)
20	9172	41379	180

$N_2 + 3\ H_2$ →

g_{cat}	Vol (cm3)	g/cm3
0.261	1,178	0,222



→ $2\ NH_3$

P = 20 bar					
χ H_2			NH_3 rate ($mmol\ g^{-1}\ h^{-1}$)		
T 400	T 450	T 500	T 400	T 450	T 500
2.01	4.63	4.52	17.82	41.02	40.47

JM-24 (GYROID 5-0.34)

Pressure (bar)	GHSV (h^{-1})	WSV ($cm^3\ g_{cat}^{-1}\ h^{-1}$)	Flow (mL/min)
20	9172	41538	180

$N_2 + 3\ H_2$ →

g_{cat}	Vol (cm3)	g/cm3
0.260	1,178	0,221

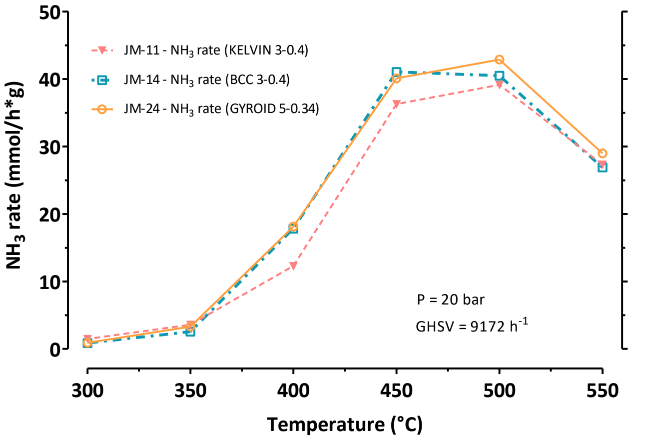
→ $2\ NH_3$

P = 20 bar					
χ H_2			NH_3 rate ($mmol\ g^{-1}\ h^{-1}$)		
T 400	T 450	T 500	T 400	T 450	T 500
2.02	4.43	4.82	18.13	40.08	42.86

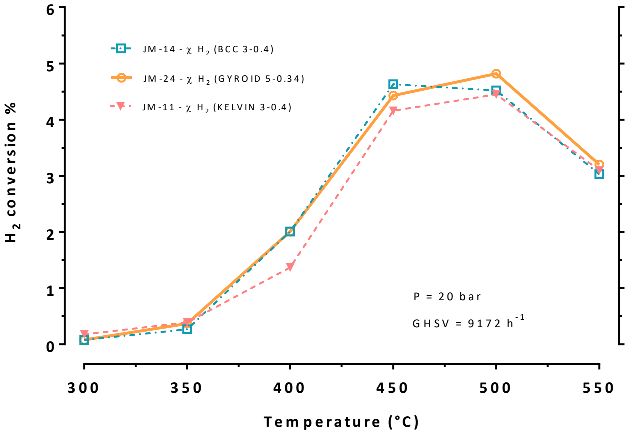
CATALYTIC ACTIVITY – AMMONIA SYNTHESIS

- ***Catalytic tests at microscale with JM catalyst coated on POCS – Influence of geometry (KELVIN, BCC, GYROID)***

JM-11 (KELVIN 3-0.4 WC-95) vs JM-14 (BCC 3-0.4 WC-98) vs JM-24 (GYROID 5-0.34 WC-107)
NH_3 rate/T Influence of geometry



JM-11 (KELVIN 3-0.4 WC-95) vs JM-14 (BCC 3-0.4 WC-98) vs JM-24 (GYROID 5-0.34 WC-107)
H_2 conversion Influence of geometry

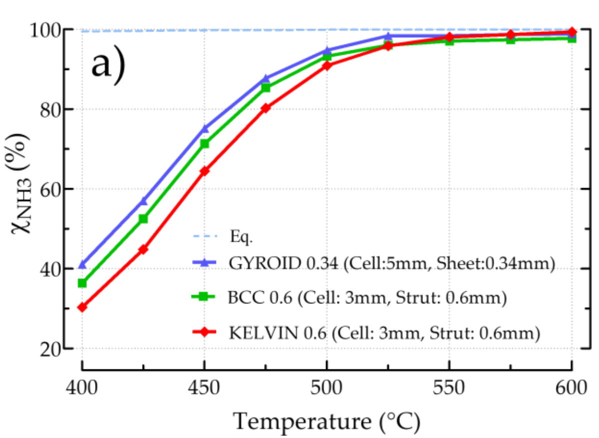


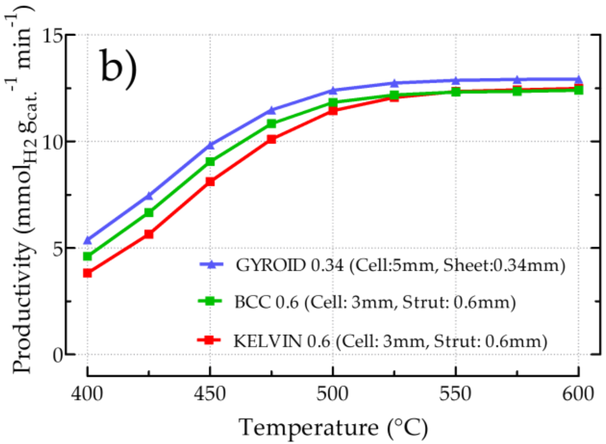
Coating	Cell type	Solid Volume (cm^3)	Solid Density (g/cm^3)	Porosity (%)	WC g_{cat} (g) g_{cat}/V_{pyc} (g/cm^3)
JM-4	KELVIN 3-0.4	0.248**	8,2497**	78.91**	0.266 1.071**
JM-4	BCC 3-0.4	0.165**	8,2134**	83.46**	0.261 1.071**
JM-4	GYROID 5-0.34	0.3577**	8.4203**	69.62**	0.260 0.727**

Material	Cell type	Cell Size (mm)	Strut Diameter (mm)	Solid Volume (cm^3)	Solid Density (g/cm^3)	Internal Surface area (cm^2)	Porosity (%)	Geom. Density (g/cm^3)	Specific Surf. Area (cm^2/cm^3)	Relative density	WC g_{cat} g_{cat}/V_{geom}
IN625	KELVIN	3 (3.01*)	0.4 (0.42*)	0.126 (0.217**)	14.21 (8.2386**)	11.21	90.4 (81.94**)	1.52	88.97	0.10	0.266 0.226***
IN625	BCC	3 (3*)	0.4 (0.4*)	0.099 (0.165**)	11.31 (8.213**)	19.06	92.1 (86.01**)	3.65	95.66	0.08	0.261 0.222***
IN625	GYROID	5 (5.18*)	0.34 (0.34*)	(0.325**)	(8.4966**)	14.51	(72.40**)	Not reported	59.22	0.791	0.260 0.221***

CATALYTIC ACTIVITY – AMMONIA DECOMPOSITION

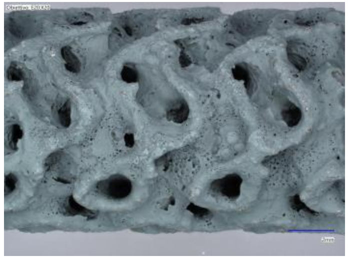
- ***Catalytic tests at microscale with 5wt%Ru/CeO$_2$ – Influence of geometry (KELVIN, BCC, GYROID)***

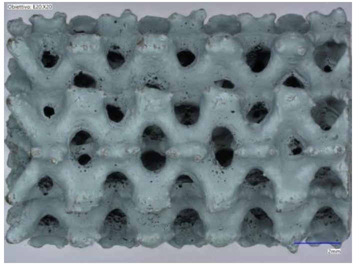


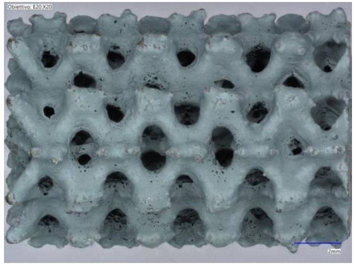


Performances of Ni-Alloy structures activated by 5wt%Ru/Al2O3, influence of Strut size (0.4, 0.34mm) and cell size (5, 3mm). GYROID 0.34: (Cell size = 5, catalyst loading = 0.225g, 0.19g/cm3, WSV = 27067cm3gcat-1 h-1), BCC 0.6: (catalyst loading = 0.232g, 0.2g/cm3, WSV = 26250 cm3gcat-1 h-1), KELVIN 0.6: (catalyst loading = 0.234g, 0.2g/cm3, WSV = 26154 cm3gcat-1 h-1). Operating conditions: He = 54%vol., NH3 = 46%vol., P = 1 bar, T = 400-600°C, total flow = 102 cm3 min-1, GHSV = 5172 h-1.

Cell type	Cell Size (mm)	Strut/sheet Size (mm)	Solid Volume (cm³)	Solid Density (g/cm³)	Internal Surface area (cm²)	Porosity (%)	Surface/Solid Vol. (cm²/cm³)	Cat. Layer thickness (µm)
BCC 0.6	3 (3*)	0.6 (0.59*)	0.220 (0.284**)	8.86 (8.40**)	12.94	83.3 (75.89***)	58.82	(23.92****)
KELVIN 0.6	3 (3*)	0.6 (0.61*)	0.290 (0.344**)	10.14 (8.50**)	15.23	78.7 (70.75***)	52.52	(27.02****)
GYROID 0.34	5 (5.18*)	0.34 (0.34*)	0.245 (0.325**)	11.26 (8.49**)	14.51	79.2 (72.40***)	59.22	(26.11****)







SCALE UP OF STRUCTURED CATALYSTS

Funded by the European Union

❑ *Scale–up of the dip/spin coating method (second generation of POCS)*

Catalyst amount for slurry preparation: 5g

Catalyst amount for slurry preparation: 50-500g

Planetary Ball Mill BM40 220V, 50Hz, with 4 grinding stations

POCS size: Ø= 1cm, L=1.5

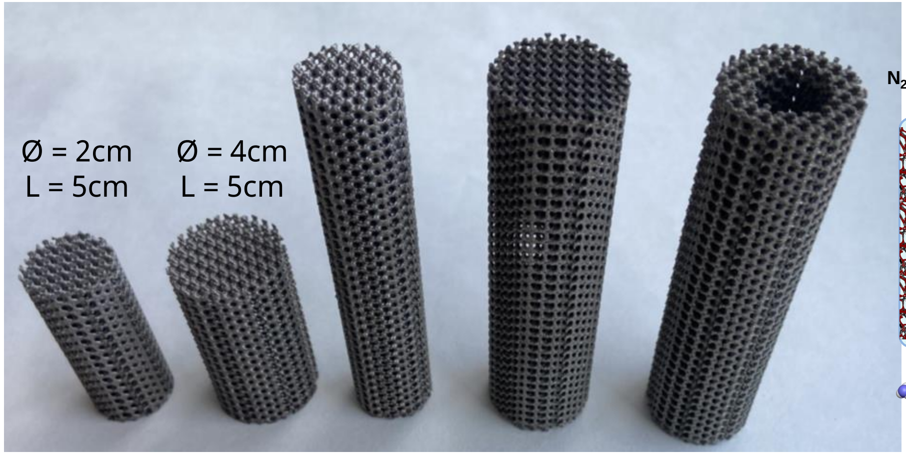
POCS size: Ø= 1- 5cm, L=5-15cm

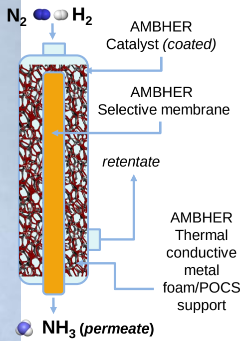
Spin coater

Ø = 2cm L = 10cm

Ø = 4cm L = 10cm

Ø = 2,66cm L = 10cm





SCALE UP OF STRUCTURED CATALYSTS

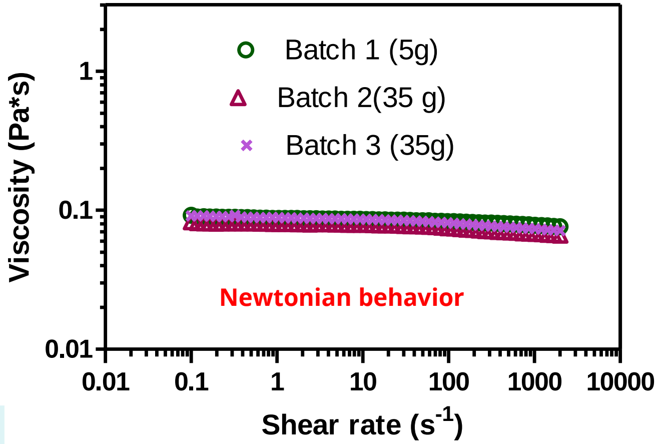
Funded by the European Union

❑ *Scale–up of the dip/spin coating method (second generation of POCS)*

Slurry composition

Glycerol	Water	Solid	PVA
42.5 %	33.6 %	22.4 %	1.5 %

Catalyst: Commercial 0.5wt%Ru/Al_2O_3



Rheological behaviour of slurry formulations (flow curves)

	Catalyst (g)	PVA (g)	Glycerol (g)	Water (g)	Ethanol (g)	No. Balls (1cm)	Volume of slurry (ml)
Batch 1	5	0.34	9.5	7.5	2	7	~16
Batch 2	10	0.68	19	15	4	14	~32
Batch 3	35	2.38	66.5	52.5	14	50	~155

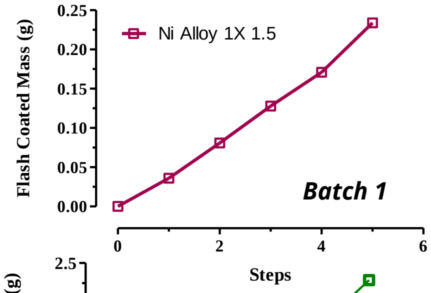
Batch 2 and 3 were used for coating large supports

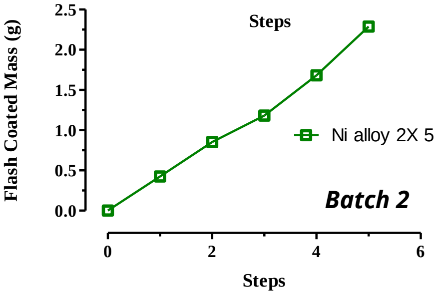
SCALE UP OF STRUCTURED CATALYSTS

Funded by the European Union

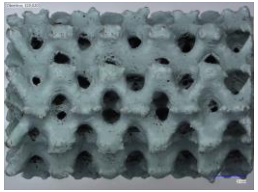
❑ *Scale–up of the dip/spin coating method*

Loading curves

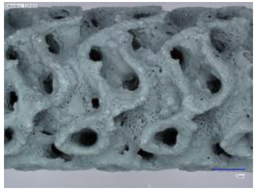




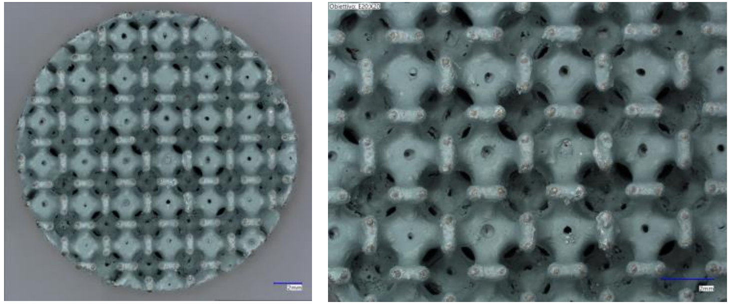
BCC



Gyroid



Kelvin



Catalyst: ***Commercial 0.5wt%Ru/Al_2O_3***

	Catalyst (g)	PVA (g)	Glycerol (g)	Water (g)	Ethanol (g)	No. Balls (1cm)	Volume of slurry (ml)
Batch 1	5	0.34	9.5	7.5	2	7	~16
Batch 2	10	0.68	19	15	4	14	~32
Batch 3	35	2.38	66.5	52.5	14	50	~155

SCALE UP OF STRUCTURED CATALYSTS

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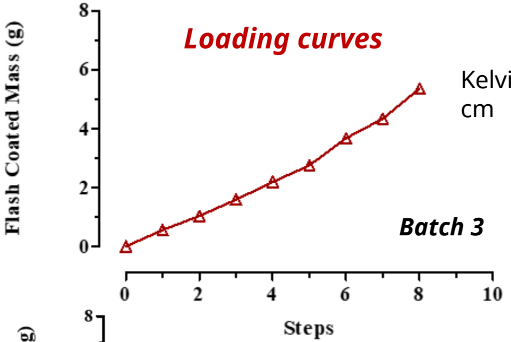
ENGIE

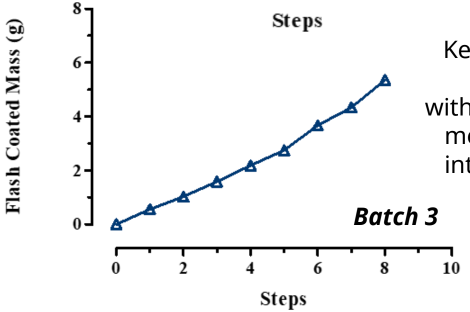
❑ *Scale–up of the dip/spin coating method (second generation of POCS)*

Catalyst: *Commercial 0.5wt%Ru/Al_2O_3*

Loading curves

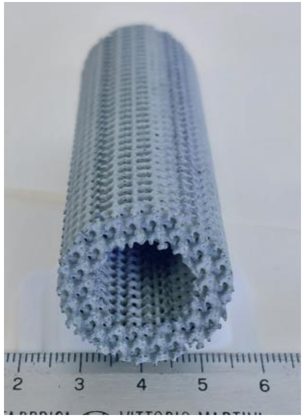


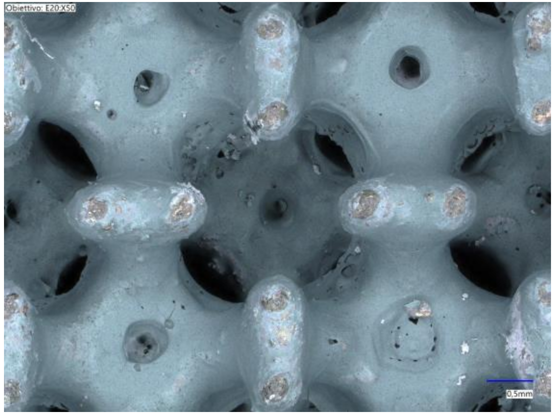
Kelvin 2x10 cm

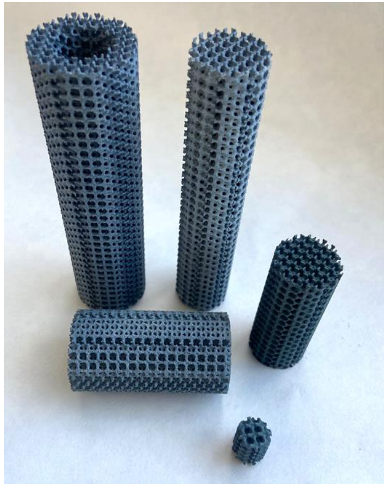


Kelvin 2x10 cm with a hole for membrane integration

	Catalyst (g)	PVA (g)	Glycerol (g)	Water (g)	Ethanol (g)	No. Balls (1cm)	Volume of slurry (ml)
Batch 1	5	0.34	9.5	7.5	2	7	~16
Batch 2	10	0.68	19	15	4	14	~32
Batch 3	35	2.38	66.5	52.5	14	50	~155







SCALE UP OF STRUCTURED CATALYSTS

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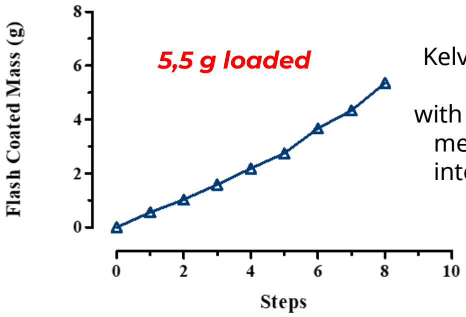
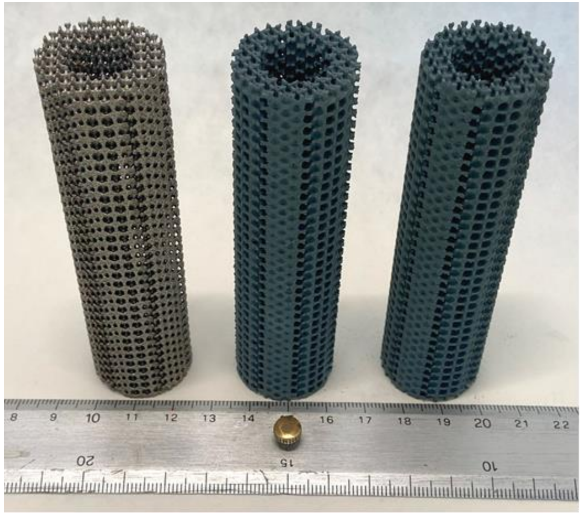
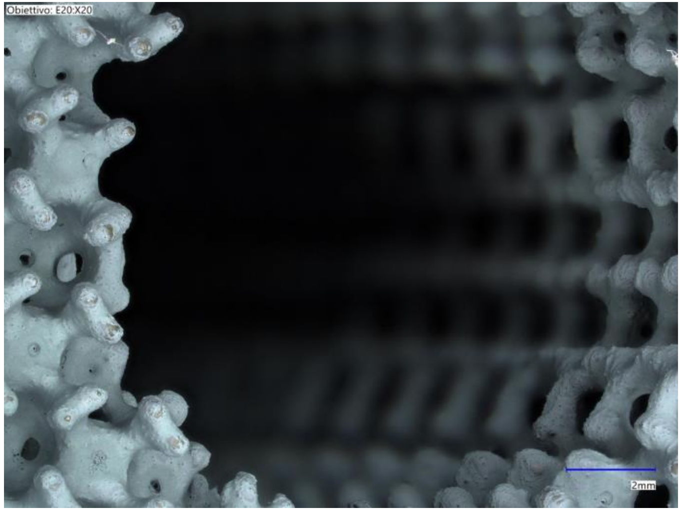
❑ *Scale–up of the dip/spin coating method (second generation of POCS)*

Catalyst: Commercial 5wt%Ru/Al_2O_3



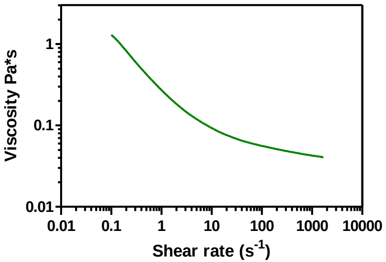
Kelvin 2.5x10 cm
with a hole for membrane integration





Slurry Composition

Glycerol	Water	Solid	PVA
42.5 %	33.6 %	22.4 %	1.5 %



Rheological behaviour of slurry formulation (flow curve)

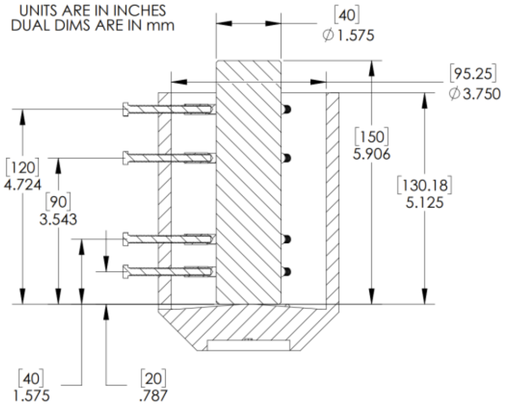
	Catalyst (g)	PVA (g)	Glycerol (g)	Water (g)	Ethanol (g)	No. Balls (1cm)	Volume of slurry (ml)
Batch 3	35	2.38	66.5	52.5	14	50	~155

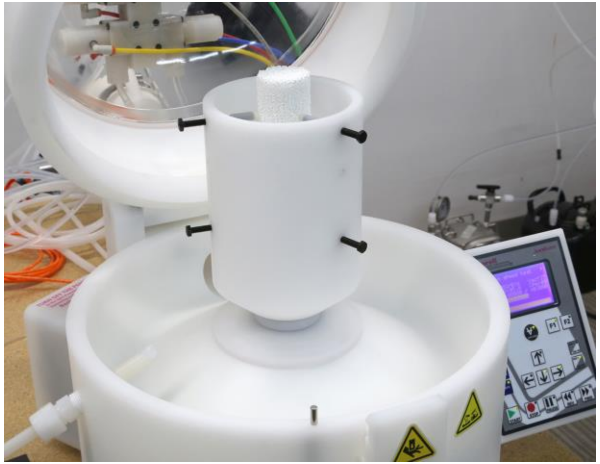
SCALE UP OF STRUCTURED CATALYSTS

Funded by the European Union

Scale–up of the dip/spin coating method (third generation of BCC and GYROID)

- *Design and realization of a new specimen holder for the spin-coater to host supports with size for the demonstrator*





Work in progress …..

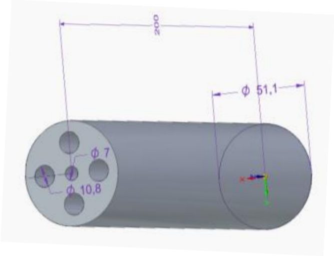
SCALE UP OF STRUCTURED CATALYSTS

Funded by the European Union

- ***Scale–up of the dip/spin coating method (third generation of BCC and GYROID)***

  - ***Sizes***

Type	Size	BCC Cell/Strut (mm)	Gyroïd Cell/Strut (mm)
Single-membrane BCC/GYROID (for washcoating)	H=100 mm / Φint = 15,2 mm , Φext = 26,6mm	3/0,4	3/0,6
Single-membrane supports with outer skin (for packed – BCC/GYROID)	H=100 mm / Φint = 15,2 mm , Φext = 26,6mm	3/0,4	3/0,6
Demonstrator: BCC/GYROID for washcoating (4 membranes + 1 thermocouple)	H=100 mm / Φholes = 15,2 mm, Φext = 51,1 mm, Φtherm = 7 mm	3/0,4	3/0,6
Demonstrator with outer skin: for packed – BCC/GYROID (4 membranes + 1 thermocouples)	H=100 mm / Φholes = 15,2 mm, Φext = 51,1 mm, Φtherm = 7 mm	3/0,4	3/0,6



SCALE UP OF STRUCTURED CATALYSTS

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❑ *Scale–up of the dip/spin coating method (third generation of BCC and GYROID)*

- ***Amount of catalyst required***

Catalyst Features		COATED POCS Features (Micro-scale)					COATED POCS Features (Prototype) Note: The volume of the holes to host membranes was not removed			
Catalyst code	Formulation	POCS/TPMS Type	POCS/TPMS Volume (cm^3)	Catalyst loaded		Slurry Vol.	POCS/TPMS Type	POCS/TPMS Volume (cm^3)	Catalyst loaded	
				g	g/cm^3	cm^3			g	g/cm^3
JM (AN4750)	Ru-based	BCC Cell=3, Strut= 0.4mm, L=1.5cm; Ø=1cm	1,1775	0,261	0,222	16 (for 8-10 POCS) -5g of catalyst	BCC Cell=3, Strut= 0.4mm, L=20 cm; Ø=5,11cm	409,96	90	0,220
JM (AN4750)	Ru-based	GYROID Cell=5, Strut= 0.34mm, L=1.5cm; Ø=1cm	1,1775	0,260	0,221	16 (for 8-10 POCS) - 5g catalyst	GYROID Cell=5, Strut= 0.34mm, L=20cm; Ø=5,11cm	409,96	90	0,220
JM (AN4750)	Ru-based	SINGLE MR - BCC Cell=3, Strut= 0.4mm, L=10cm; Ø=2.66cm with hole (1,08cm)	46,38722	10,200	0,220	155 (For 3-4 POCS), 35g catalyst				

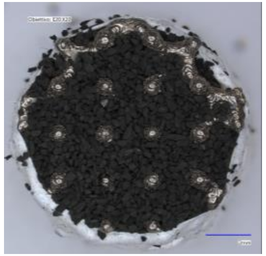
SCALE UP OF STRUCTURED CATALYSTS

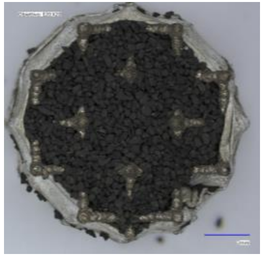
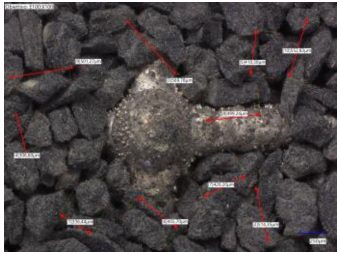
Funded by the European Union

❑ *Scale–up of packing method (third generation of BCC and GYROID)*

- ***Amount of catalyst required***

Catalyst Features		PACKED POCS Features (Micro-scale)					PACKED POCS Features (Prototype) Note: The volume of the holes to host membranes was not removed				
Catalyst code	Formulation	POCS Type	POCS Volume (cm^3)	Pellets size	Catalyst loaded g	Catalyst loaded g/cm^3	POCS Type	POCS Volume (cm^3)	Pellets size	Catalyst loaded g	Catalyst loaded g/cm^3
JM (AN4750)	Ru-based	BCC Cell=3, Strut= 0.4mm, L=1.5cm; Ø=1cm	1,177	50-70 mesh – 0,297-0,210mm	1,172	0,995	BCC Cell=3, Strut= 0.4mm, L=20cm; Ø=5,11cm	409,96	50-70 mesh - 0,297-0,210 mm	406	0,990
JM (AN4750)	Ru-based	SINGLE MR – BCC Cell=3, Strut= 0.4mm, L=10cm; Ø=2.66cm with hole (1,08cm)	46,38	50-70 mesh – 0,297-0,210mm	46,10	0,994					



CONCLUSIONS

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Support manufacturing activation and scale-up

- AM can manufacture complex parts allowing more freedom of design optimisation for catalytic reactors compared with traditional manufacturing techniques;
- The combined dip/spin coating method can be used to obtain Structured catalysts with homogeneous and stable catalytic layers (thickness ≈ 17-41μm), no pore-clogging phenomena were observed irrespective of the geometry used;
- The presence of anchoring points, and the thermal pre-treatment of supports play a crucial role in achieving high mechanical stability;
- The structured catalytic systems obtained by combining AM with the whashcoating technique are characterized by higher porosity (88 -90%), higher SSA (50-115 cm^2/cm^3) and lower pressure drops with respect to the conventional packed bed reactor.
- The coating method can be easily scaled up without requiring adjustments compared to samples prepared on a smaller scale

Catalytic activity

- The BCC and Gyroid based catalysts have shown promising catalytic performances towards ammonia synthesis and decomposition;
- In particular, the GYROID structure, with its labyrinthine network of channels, provided efficient mass transfer pathways;
- The Gyroid structure enabled the design of lighter and more compact reactors, addressing weight and volume constraints in applications like distribute hydrogen production and ammonia synthesis.
- Overall, this comparative analysis highlights the importance of structural design in catalytic processes and underscores the potential of GYROID structures for advancing reactor efficiency and compactness.

Staff involved

Thanks!

Consiglio Nazionale delle Ricerche

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