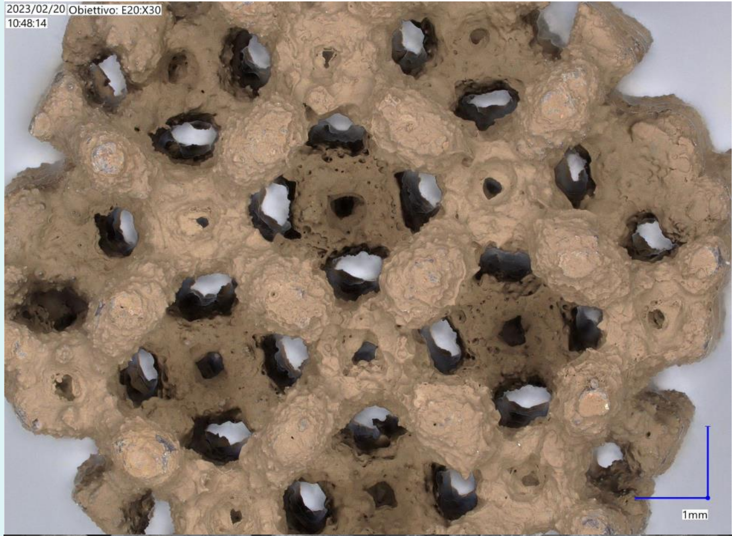
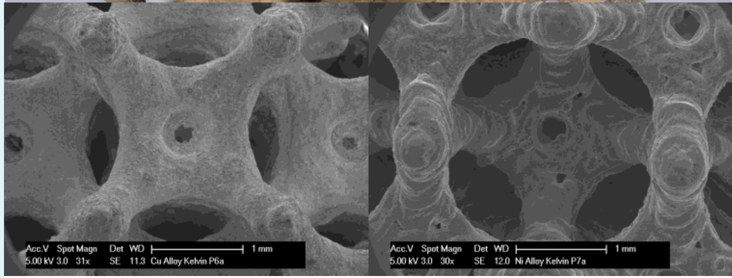
Catalytic activation of Periodic Open Cellular Structures (POCSs) for the integration with membranes to enhance ammonia synthesis in membrane reactors





Cristina Italiano[1], Assia Saker[2], Lidia Pino[1], Massimo Laganà[1], Minju Thomas[1], Gabriel Marino[1], Benjamin Hary[3], Steve Nardone[3], Nicolas Meynet[2], Alvaro Ramirez Santos[2], ***Antonio Vita[1]***

[1] *Institute CNR-ITAE, Via Salita S. Lucia sopra Contesse n. 5, 98126 S. Lucia, Messina, Italy*

[2] *2ENGIE Lab CRIGEN, 4 Rue Joséphine Baker, Stains, France*

[3] *ENGIE Laborelec, Rodestraat 125, 1630 Linkebeek, Belgium*

16th International Conference on Catalysis in Membrane Reactors (ICCMR16-2023)

Donostia-San Sebastián, Spain
October 16-18

Green ammonia production for long-term H_2 storage

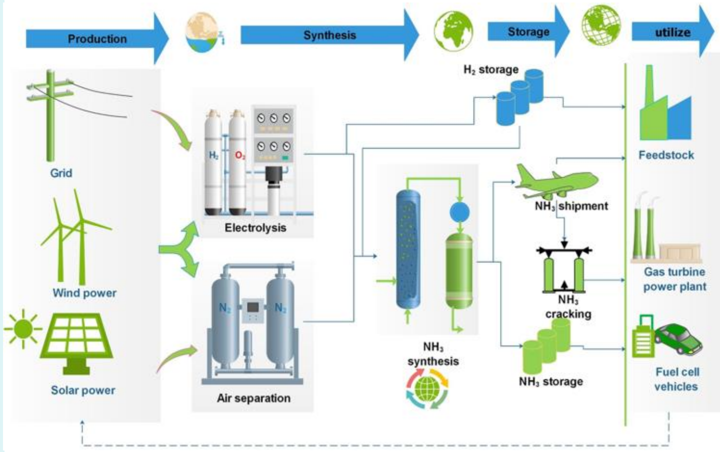
Ammonia	121 kg H_2/m^3
Methanol	99 kg H_2/m^3
Liquid Hydrogen	71 kg H_2/m^3
LOHC	57 kg H_2/m^3

Highest energy density

Cost advantage for long-distance transportation

Existing infrastructure for ammonia transportation

Current NH_3 production has the lowest CCS cost (due to the CO_2 separation step) (blue ammonia)



Conversion to ammonia is the most cost-competitive solution for long-distance hydrogen transportation

Distributed ammonia plant will offer liquid storage of renewable electricity at ambient pressure and low boil-off conditions. Ammonia can then be safely transported by road or rail to the user or used locally giving birth to local industrial ecosystems.

GREENING OF AMMONIA PRODUCTION
HABER-BOSCH DRAWBACKs

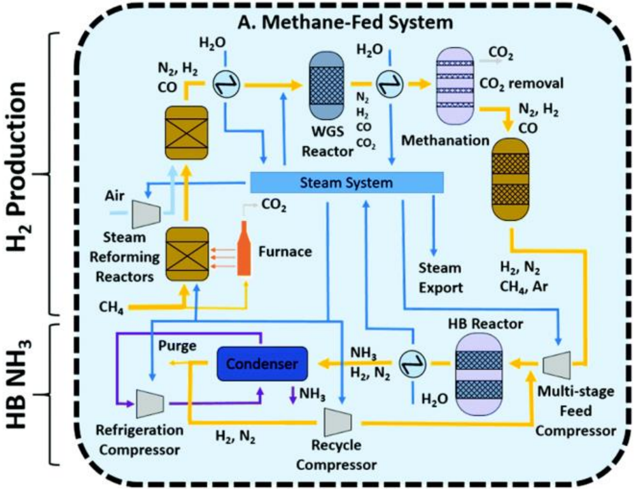
$3H_2 + N_2 \rightarrow 2NH_3$, ΔH = -92 Kj/mol

Ammonia synthesis is deceptively simple

Nearly 80% of every breath we take is nitrogen (N_2)

N≡N **Easy to find, hard to use** *(limiting step: activation of the stable N≡N bond, 945 kJ mol*$^{-1}$*)*

Under pressure and temperature
(150 – 200 bar, ≈ 500°C)



$6H_2O + 3CH_4 + 4N_2 \rightarrow 3CO_2 + 8NH_3$

1.2% of anthropogenic CO_2 emissions

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

Ammonia and MOF Based Hydrogen storagE for euRope

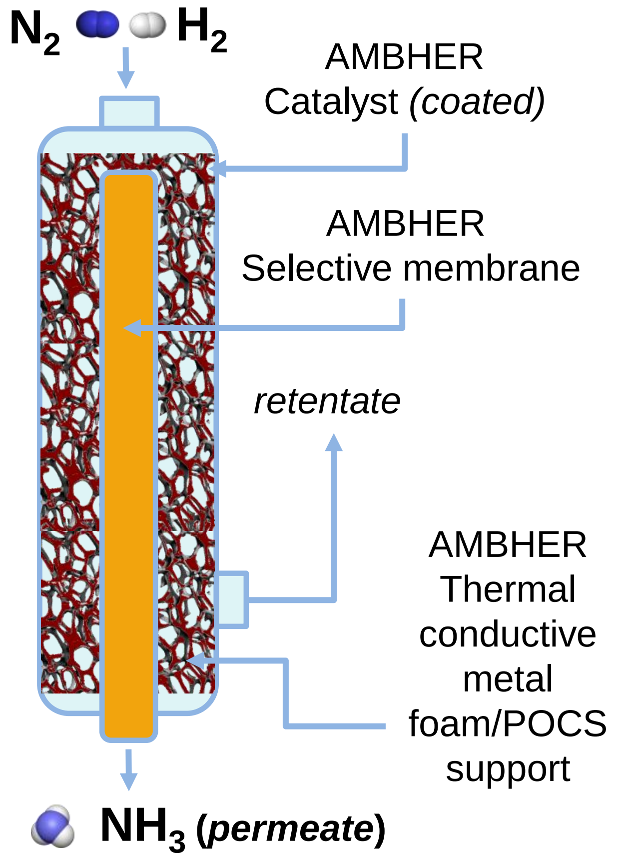
AMBH2ER

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 3.3.2: *Catalytic activation, characterization and performances of thermal conductive open-cell foams and POCS with commercial reference catalyst (1st generation)*

Integration of POCS catalysts with membranes in a membrane reactor



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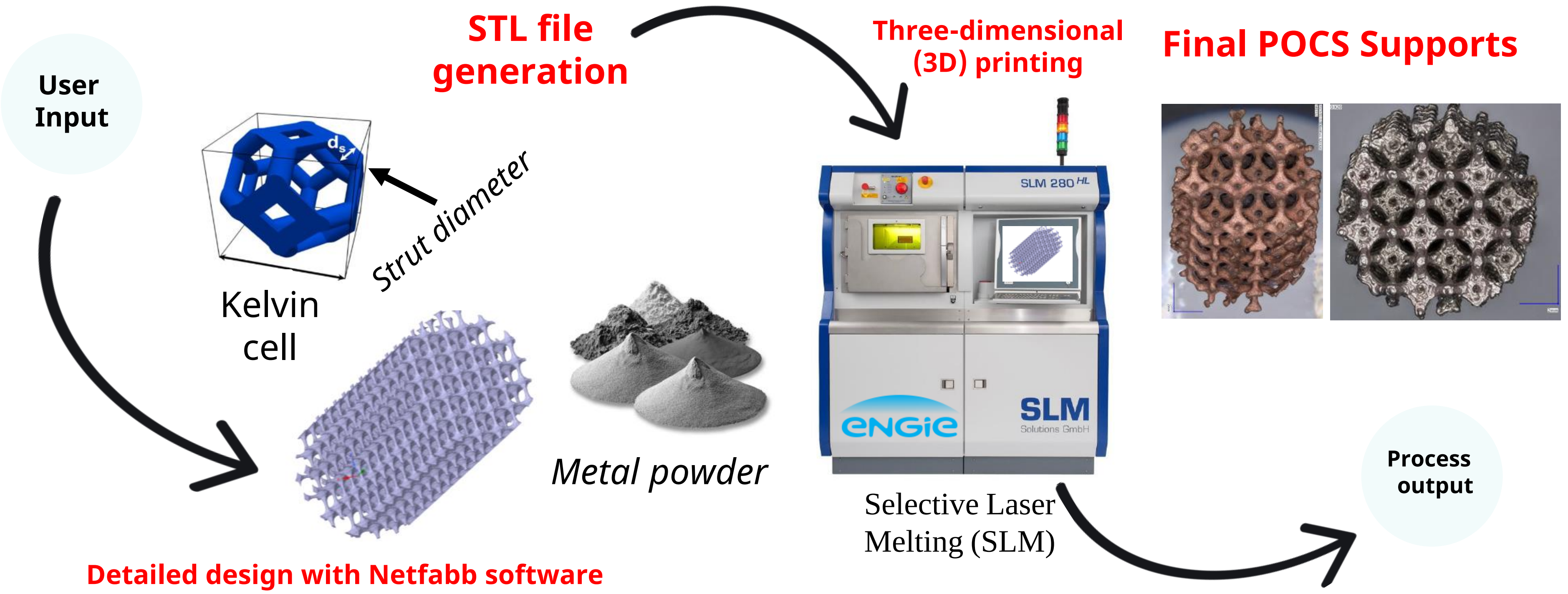
POCSs Manufacturing

- **_Schematic sequence of POCSs manufacturing process_**



POCSs Manufacturing

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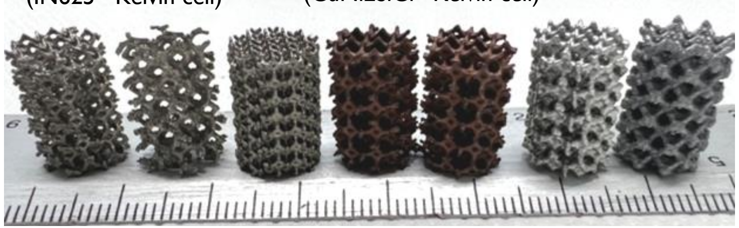
Material	Cell type	Cell size (mm)	Strut diameter (mm)	Volume (cm³)	Surface (cm²)	Surface/ Volume ratio	Theor. Relative Density	Sample name
Al alloy (AlSi10Mg)	BCC	3	0.6	0.220	12.94	58.82	0.17	**4a-4b-4c-4d-4e-4f**
	Kelvin	3	0.6	0.290	15.23	52.52	0.21	**5a-5b-5c-5d-5e-5f**
Cu alloy (CuNi2SiCr)	Kelvin	3	0.6	0.290	15.23	52.52	0.21	**6a-6b-6c-6d-6e**

Material	Cell type	Cell size (mm)	Strut diameter (mm)	Volume (cm³)	Surface (cm²)	Surface/ Volume ratio	Theor. Relative Density	Sample name
Ni alloy (IN625)	Kelvin	3	0.6	0.290	15.23	52.52	0.21	**7a**
		4	0.6	0.153	9.08	59.37	0.11	**7b**
		3	0.8	0.518	16.93	32.68	0.36	**7c**
		3	0.4	0.126	11.21	88.97	0.10	**7d**
		1.5	0.3	0.292	29.79	102.02	0.23	**7e**
		4	0.8	0.278	11.39	40.97	0.19	**7f**
		2	0.4	0.288	22.46	78.00	0.22	**7g**
		2	0.6	0.631	25.20	39.94	0.45	**7h**

- Al Alloy AlSi10Mg

(Kelvin c.) (BCC c.)

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



Ø = 1cm, L = 1.5cm

POCS Supports Characterization

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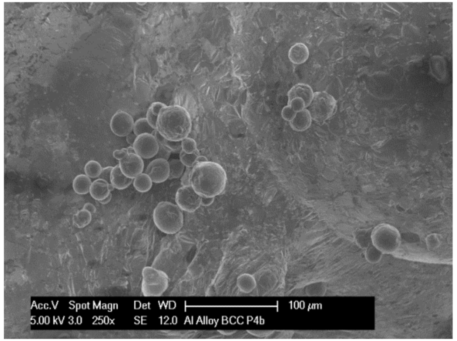
❑ *Morphological characterizations and porosity*

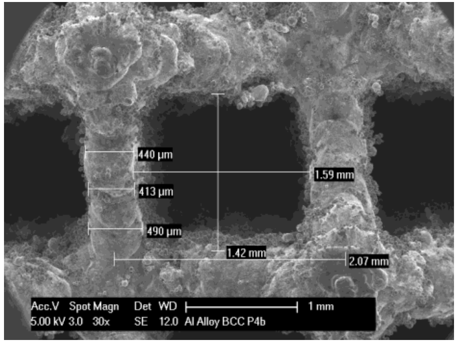
Material	Cell type	Cell size (mm)	Strut diameter (mm)	** Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	** Geom. density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
IN625	BCC	2 (2*)	0.4 (0.41*)	0.219	10.87	9.45	82.9	2.80	87.03	0.17
IN625	BCC	2 (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*

Elium pycnometer (Model 1305 Multivolume, Micromeritics)

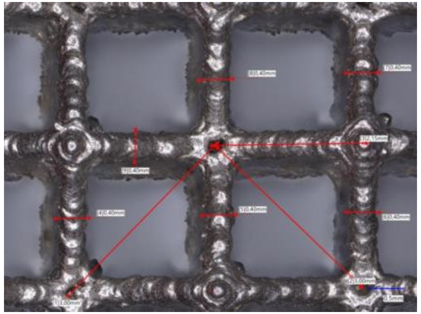
- **SEM micrographs**



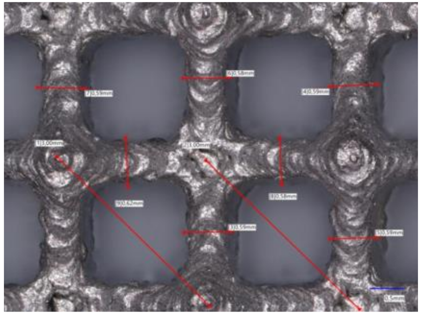


- **Optical microscope images of as-built BCC Ni-alloy POCS**

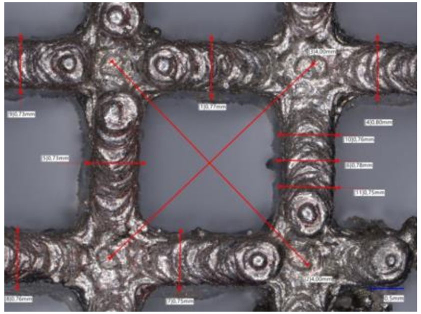
Cell Type = 3, Ø Strut =0.4mm,
SSA = 95.66 cm^2/cm^3, Porosity = 92%



Cell Type = 3, Ø Strut =0,6 mm,
SSA = 58,82 cm^2/cm^3, Porosity = 83,3%



Cell Type = 3, Ø Strut =0,8 mm,
SSA = 39,01 cm^2/cm^3, Porosity = 71,3%



POCS Supports Characterization

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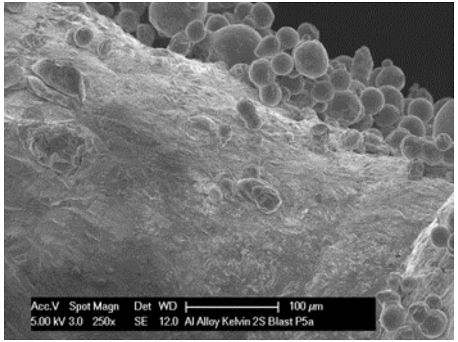
❑ *Morphological characterizations and porosity*

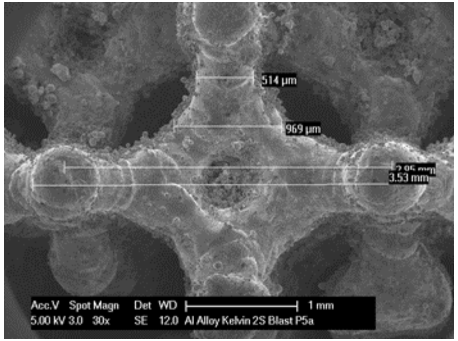
Material	Cell type	Cell size (mm)	Strut diameter (mm)	**Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	** Geom. density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
IN625	KELVIN	2 (2*)	0.6 (0.4*)	0.631	9.30	25.20	54.5	4.99	39.94	54.5
IN625	KELVIN	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*

Elium pycnometer (Model 1305 Multivolume, Micromeritics)

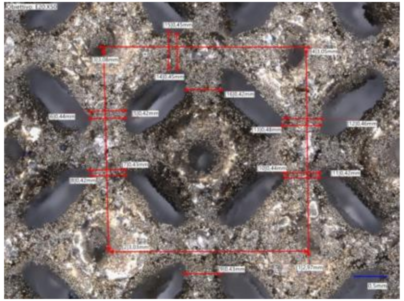
- **SEM micrographs**



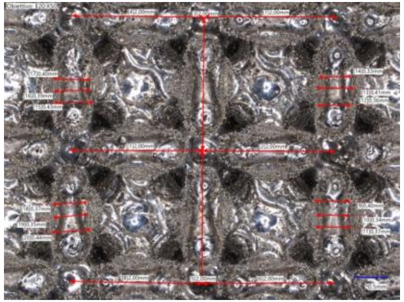


- **Optical microscope images of as-built kelvin Ni-alloy POCS**

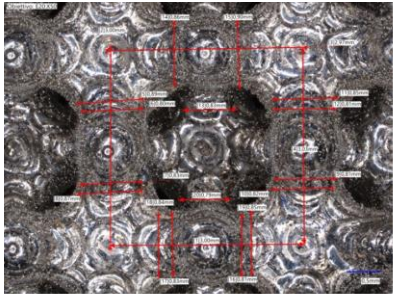
Cell Type = 3, Ø Strut =0.4mm, SSA = 88.9 cm^2/cm^3, Porosity = 90.4%



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%



POCS Supports Characterization

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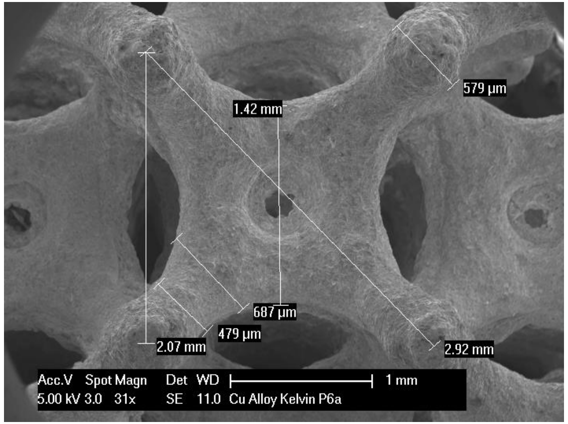
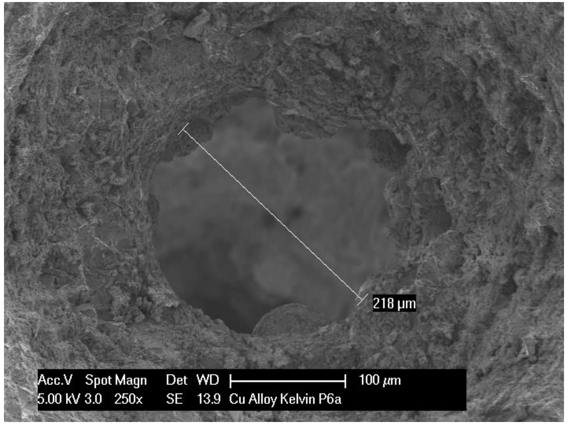
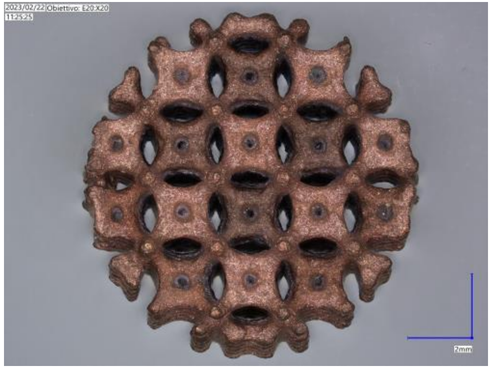
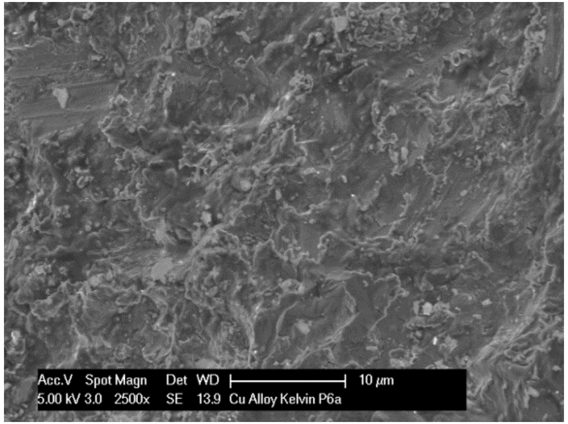
❑ *Morphological characterizations*

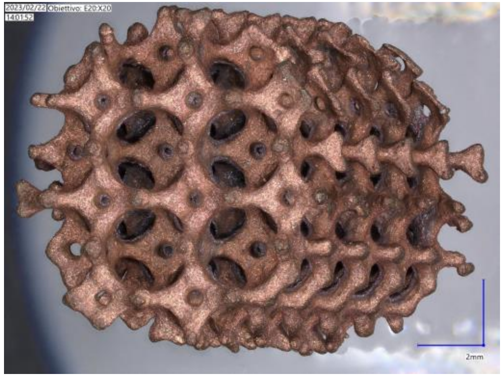


Cu alloy; kelvin (sand - blasted)









POCS Supports Characterization

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❑ *Morphological characterizations and porosity*

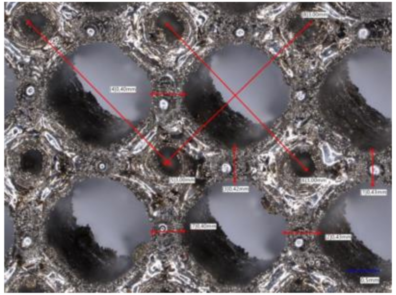
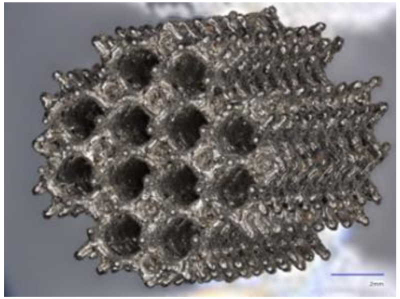
Material	Cell type	Cell size (mm)	Strut diameter (mm)	** Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	Geom.** density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
IN625	HEXA	2 (2*)	0.4 (0.42*)	0.336	10.33	26.15	73.8	2.95	77.83	73.8
IN625	HEXA	2 (2*)	0.6 (0.61*)	0.745	8.16	29.78	44.8	5.16	39.97	44.8
IN625	HEXA	3 (3*)	0.4 (0.42*)	0.142	11.27	12.74	89.1	1.36	89.72	89.1
IN625	HEXA	3 (3*)	0.6 (0.61*)	0.326	8.53	17.28	75.4	2.36	53.01	75.4
IN625	HEXA	3 (2.98*)	0.8 (0.82*)	0.582	7.32	19.68	58.3	3.62	33.81	58.3
IN625	HEXA	4 (3.96*)	0.6 (0.6*)	0.182	9.01	10.53	86.3	1.39	57.86	86.3
IN625	HEXA	4 (4*)	0.8 (0.76*)	0.332	8.10	13.10	76.2	2.28	39.46	76.2
IN625	HEXA	1.5(1.5*)	0.3 (0.33*)	0.338	11.36	34.68	73.5	3.26	102.60	73.5

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

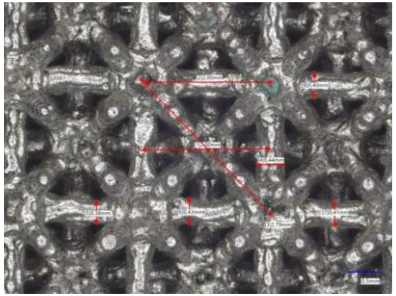
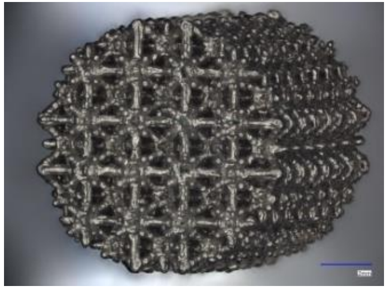
Material	Cell type	Cell size (mm)	Strut diameter (mm)	** Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	Geom.** density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
IN625	TETRA	2 (2*)	0.4 (0.4*)	0.326	11.04	25.56	74.9	3.06	78.40	0.25
IN625	TETRA	2 (2*)	0.6 (0.58*)	0.710	8.68	28.12	51.5	5.23	39.60	0.49
IN625	TETRA	3 (3*)	0.4 (0.42*)	0.147	11.90	13.14	88.8	1.49	89.39	0.11
IN625	TETRA	3 (3*)	0.6 (0.57*)	0.325	9.75	16.82	76.1	2.69	51.75	0.24
IN625	TETRA	3 (3*)	0.8 (0.76*)	0.563	9.36	18.74	61.6	4.48	33.29	0.38
IN625	TETRA	4 (3.99*)	0.6 (0.6*)	0.179	8.99	10.95	86.7	1.37	61.20	0.13
IN625	TETRA	4 (4.03*)	0.8 (0.77*)	0.322	8.23	13.43	77.8	2.25	41.70	0.22
IN625	TETRA	1.5(1.5*)	0.3 (0.3*)	0.317	12.81	33.34	75.3	3.45	105.17	0.25

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

- **Optical microscope images of as-built HEXA Ni-alloy POCS**

Cell Type = 3, Ø Strut =0.4mm, SSA = 89.7 cm^2/cm^3, Porosity = 89.1%

Cell Type = 3, Ø Strut =0.4mm, SSA = 89.3 cm^2/cm^3, Porosity = 88.8%

POCS Supports Characterization

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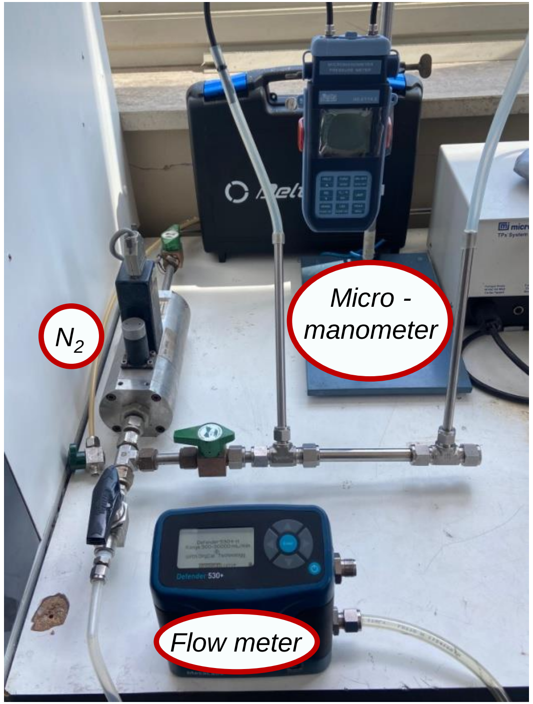
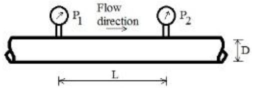
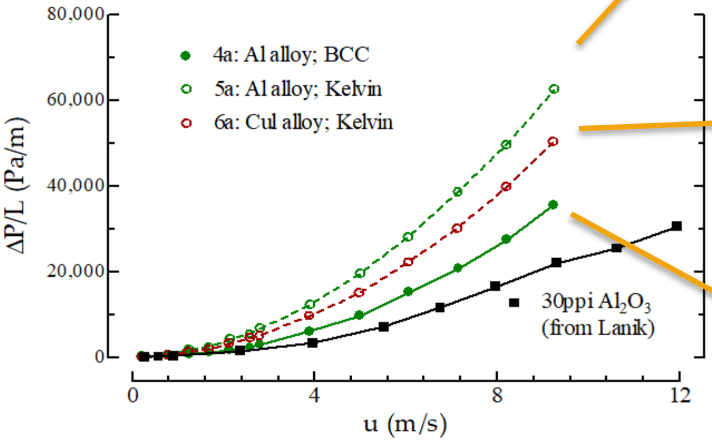
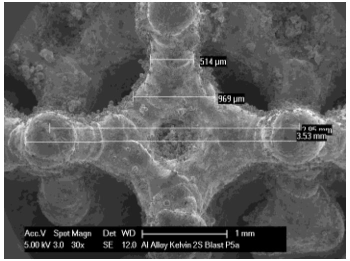
❑ *Pressure drop*



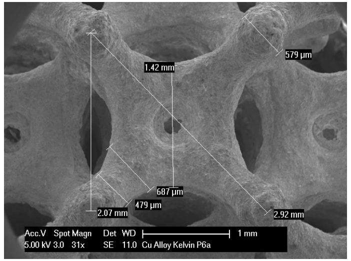
$$\frac{\Delta P}{L} = au + bu^2$$



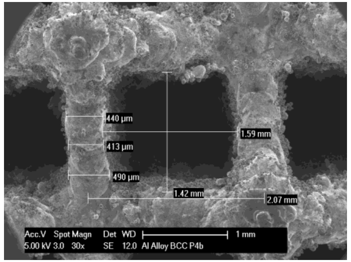




Al alloy; Kelvin (as built)



Cu alloy; kelvin (sand - blasted)



Al alloy; BCC (as built)

POCS Supports Characterization

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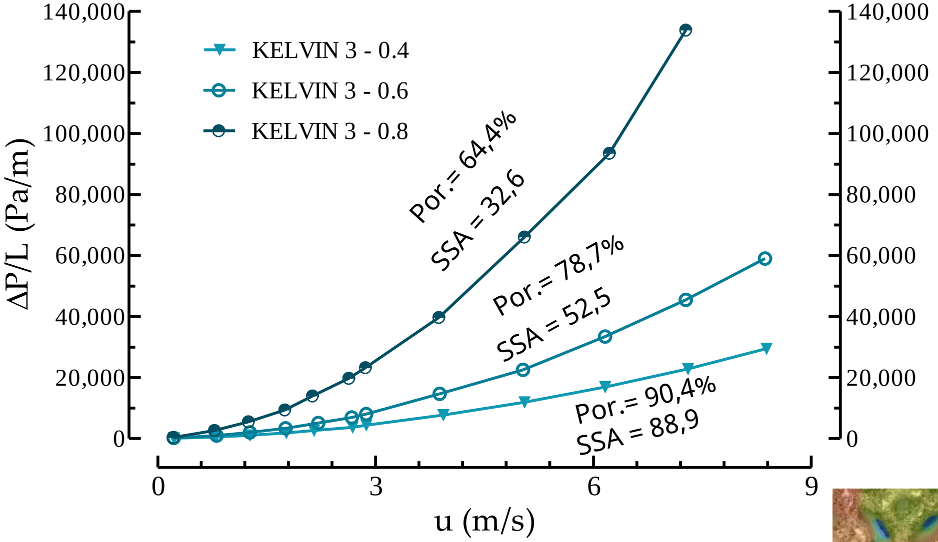
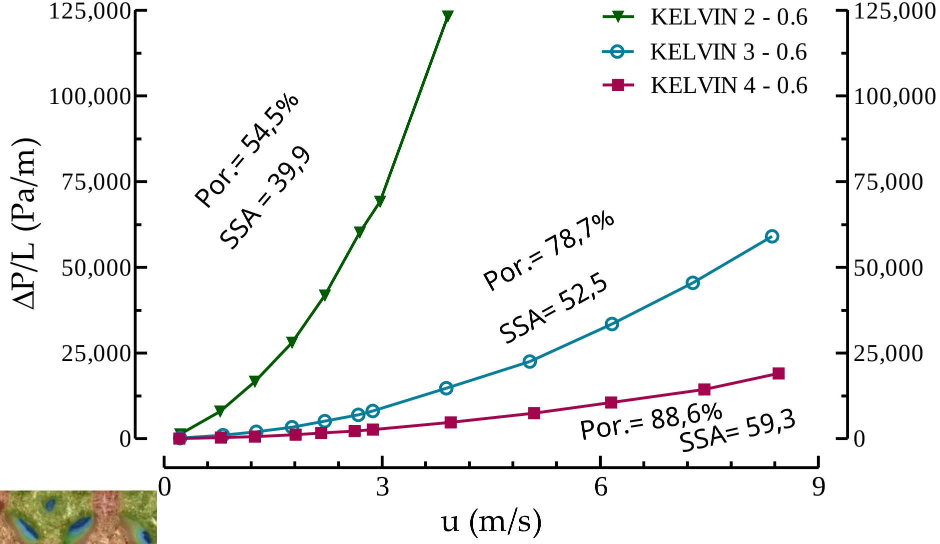
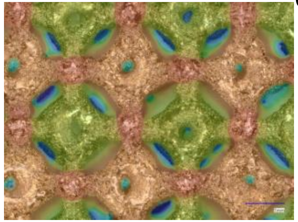
Pressure drop







POCS Supports Characterization

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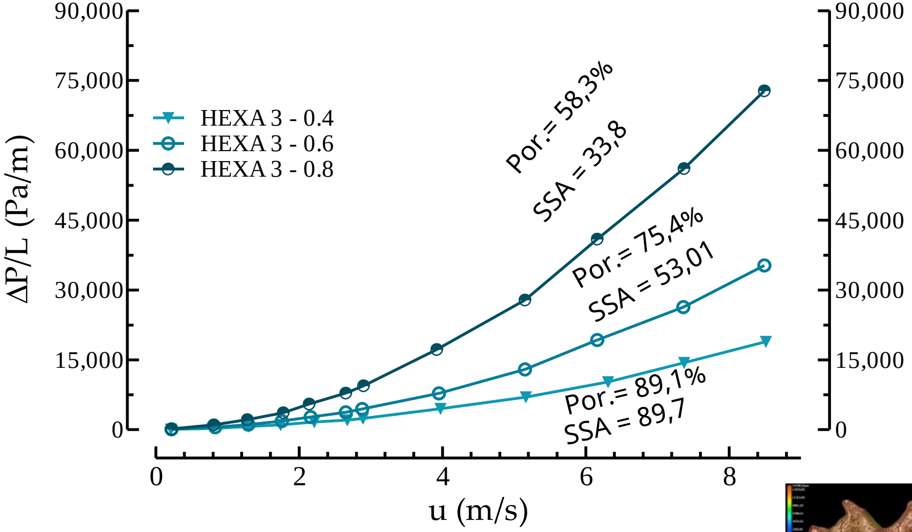
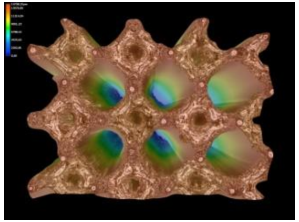
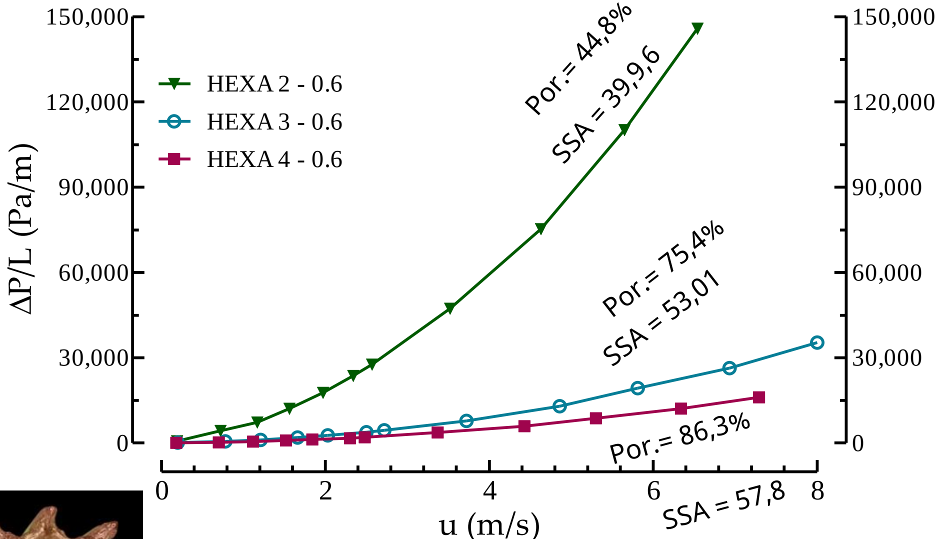
❑ *Pressure drop*







POCS Supports Characterization

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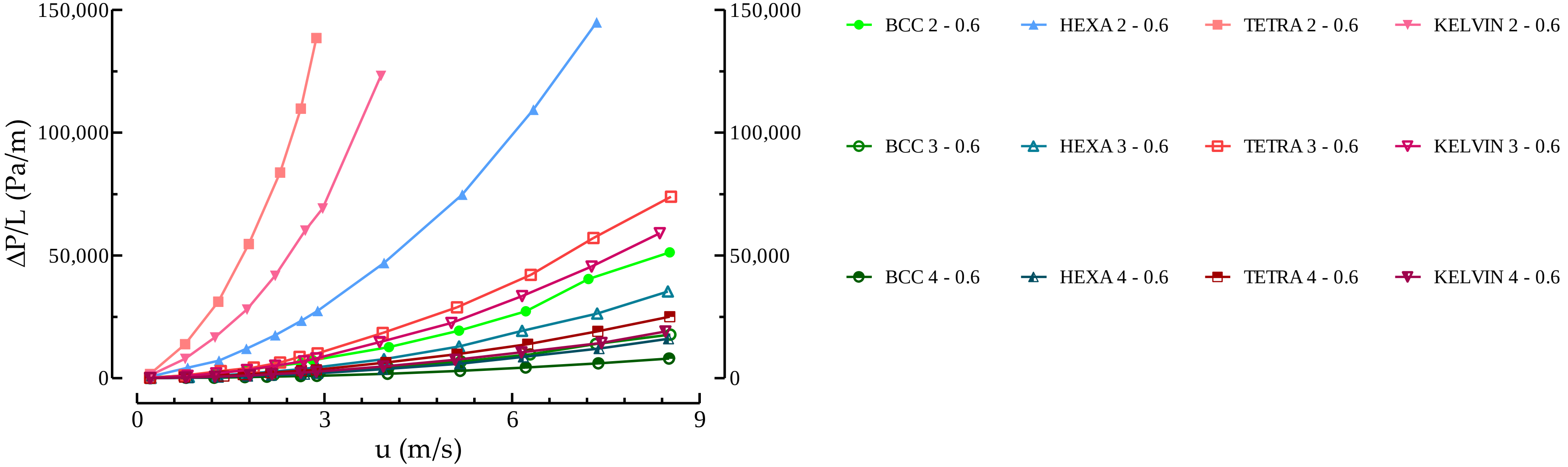
Pressure drop



Activation of Al-Alloy POCSs by combined dip/spin coating method

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1a – Structured substrate manufacturing (POCSs)
- Laser Powder Bed Fusion (LPBF)
- POCSs Cleaning

1b – Catalytic powder synthesis
- Solution combustion synthesis (SCS)
- 7wt% Ni/CeO_2 & 7wt%Ni/CeO_2-Al_2O_3

2a – Substrate pretreatment
- Thermal treatment
- Anodization
- Thermal treatmet / primer deposition
- Thermal treatment / anodization

2b – Slurry preparation
- Powder ball milling
- Slurry (PVA + GLY + powder) water solution ball milling

3a – Slurry deposition (dip – spin coating)

Coating step → Flash Drying → Load after Flash Drying → Is load enough? — NO → Coating step; YES → Calcination

Principal Equipment (easily scalable)

Planetary mono ball mill (PULVERISETTE 6)
Particle size reduction
(<10μm) - (cat.g.= 5 g)

Rheometer (MCR72)
Rheological behavior of slurry formulations
(Slurry Vol. = 12ml)

Spin coater (SPIN 150 SPS)
Rotation time (20 s)
Rotation speed (1000 s^{-1})
Acceleration (1000 rpm/s^2)
Max POCS size (L=1 – 2cm, Ø=1-4cm)

Furnace (Nabertherm)
Max Temp. (1200° C)
Capacity (14.9 Liters)

Main steps involved in the preparation of a POCS catalysts by washcoating

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AMBHER

Activation of Al-Alloy POCSs by combined dip/spin coating method

❑ *Method 1 (Thermal treatment based)*

1a Support pre-treatment

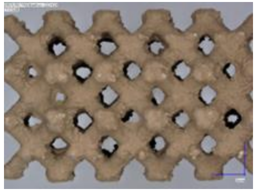
- Surface Cleaning
  - *Sonication (Wat./Ac. – 50/50), 30 min → drying 120°C, 1h.*
  - *NaOH (1M), 2 min.*
- Thermal treatment
  - *300°C, 3 h.*

1b Slurry preparation

- Powder ball milling
  - *300 rpm, 3 h.*
- Suspension ball milling
  - *200 rpm, 24 h.*

2 Washcoating

- Primer deposition
  - *Dip/Spin coating, 1000 rpm, 0.04g/cm³*
- Slurry deposition
  - Dip/Spin coating, 1000 rpm, 0.1-0.25g/cm³



3 Flash drying

- 450°C, 10 min.

Is load enough ?

No → Slurry deposition

Yes → **4 Calcination**

- 450°C, 6h.

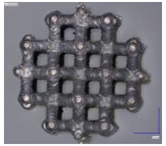
Method 1

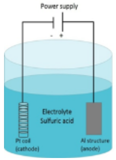
Schematic representation of the typical steps of the washcoating process

Funded by the European Union

Activation of Al-Alloy POCSs by combined dip/spin coating method

❑ *Method 1 (Anodization based)*





1a Support pre-treatment

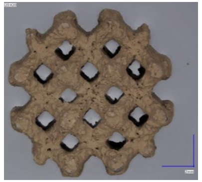
- Surface Cleaning
  - *Sonication (Wat./Ac. – 50/50), 30 min → drying 120°C, 1h.*
  - *NaOH (1M), 2 min.*
- Thermal treatment
  - *300°C, 3 h.*
- Anodization
  - *0.2 mA/cm^2, 30 min.*

1b Slurry preparation

- Powder ball milling
  - *300 rpm, 3 h.*
- Suspension ball milling
  - *200 rpm, 24 h.*

2 Washcoating

- Primer deposition
  - *Dip/Spin coating, 1000 rpm, 0.04g/cm^3*
- Slurry deposition
  - Dip/Spin coating, 1000 rpm, 0.1-0.25g/cm^3



3 Flash drying

- 450°C, 10 min.

Is load enough ? — No → Slurry deposition; Yes → Calcination

4 Calcination

- 450°C, 6h.

Method 2

Schematic representation of the typical steps of the washcoating process

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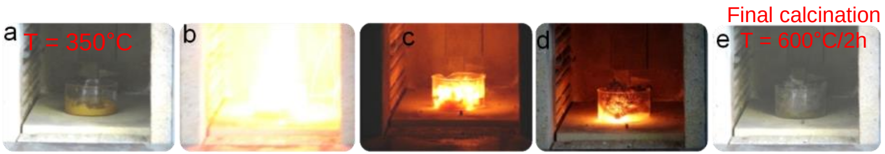
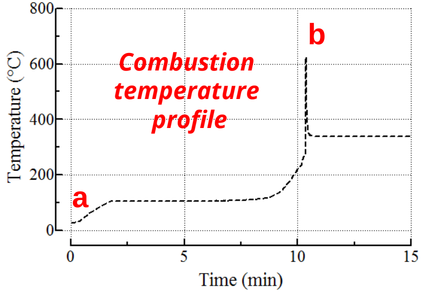
Activation of Al-Alloy POCSs by combined dip/spin coating method

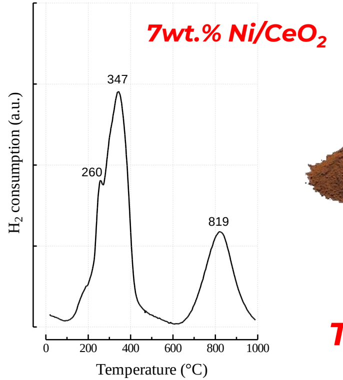
Consiglio Nazionale delle Ricerche
ENGIE

❑ *Catalysts preparation and characterization*



Solution Combustion synthesis sequence: *a) muffle introduction of water precursors and fuel mixture; b) reaction initiation; c and d) cooling phase; c) final catalyst (fine powder)*



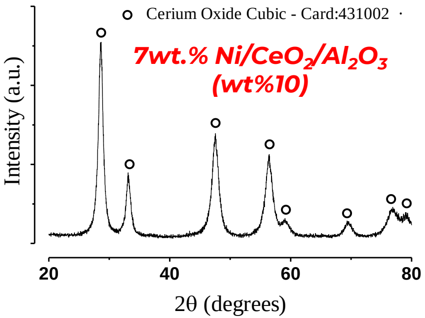


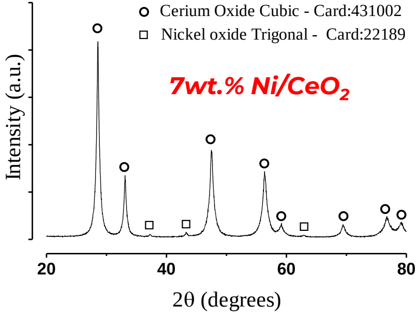
TPR

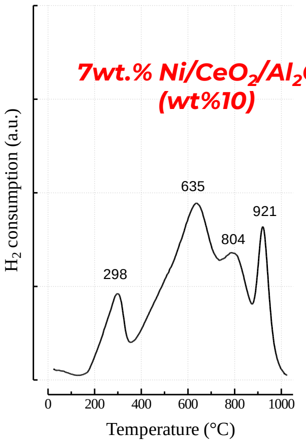
Ce Precursor	Ni Precursor	Fuel
Ce(NO$_3$)$_3$· 6H$_2$O	Ni(NO$_3$)$_6$· *6H$_2$O*	*Urea*

Ce Precursor	Ni Precursor	Fuel
Ce(NO$_3$)$_3$· 6H$_2$O	Ni(NO$_3$)$_6$· *6H$_2$O*	*Urea*
Al Precursor	Al(NO3)$_3$	

XRD







*Main textural and structural properties of synthesized catalysts (*XRD, ** He-pycnometer)*

Sample	*Ceria 2ɵ (111)	*Ceria lattice paramiter (Å)	*Ceria Cristal size nm (111)	*Nickel Cristal size (nm)	**True density (g/cm^3)
7wt%Ni/CeO$_2$	28.576	5.409	16.66	22.8	16.32
7wt%Ni/CeO$_2$ – Al$_2$O$_3$	28.605	5.407	9.1	-	26.97

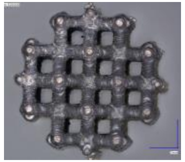
Funded by the European Union
AMBHER$_2$

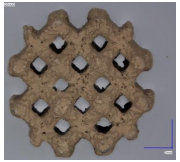
Activation of Al-Alloy POCSs by combined dip/spin coating method

Consiglio Nazionale delle Ricerche

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*





On coating quality and mechanical stability

Slurry optimization

Catalysts (CNR)	Solid density (cm^3/g)
7wt%Ni CeO_2	16.32
7wt%Ni CeO_2-Al_2O_3	26.97

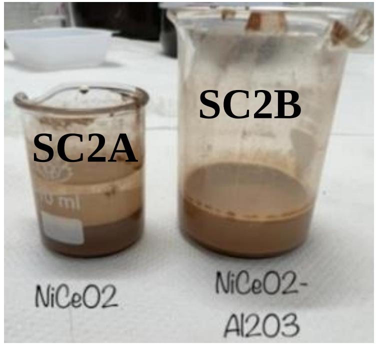
DISPERAL P2
highly dispersible
Boehmite (aluminium oxide
hydroxide, γ-AlO(OH)
powders

sasol

Single deposition step

Composition of the different slurry prepared.

Slurry	Catalyst formulation	Powder Catalyst (%)	Glycerol (%)	PVA (%)	Water (%)	Disperal P2® Boehmite (%)
SC1	Ni/CeO_2	24.03	45.65	1.49	28.83	-
SC2A	Ni/CeO_2	22.40	42.50	1.50	33.60	-
SC3	Ni/CeO_2	25.36	48.18	1.46	25.00	-
SC2B	Ni/CeO_2-Al_2O_3	22.40	42.50	1.50	33.60	-
SC2C	Ni/CeO_2	20.14	42.50	1.50	33.60	2.26



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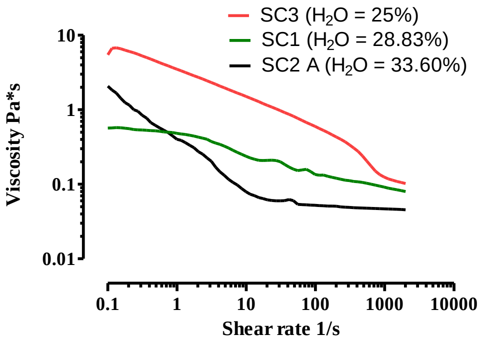
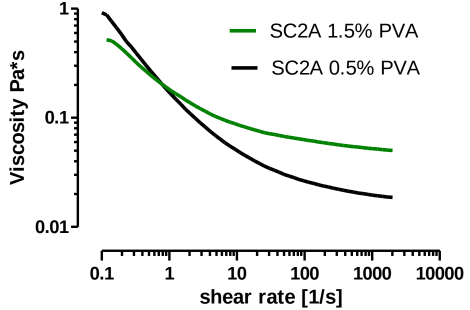
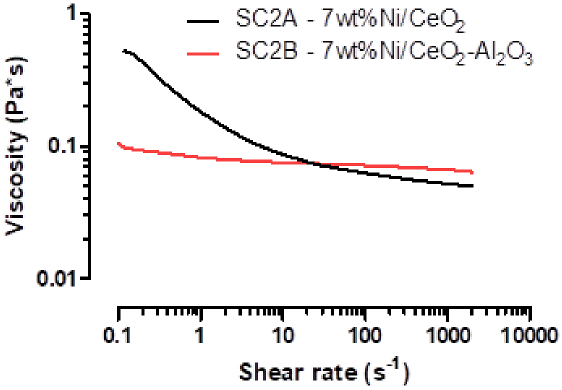
Activation of Al-Alloy POCSs by combined dip/spin coating method

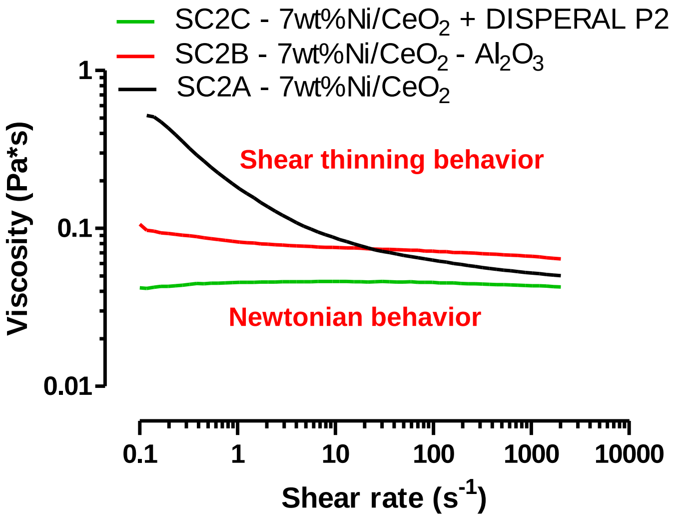




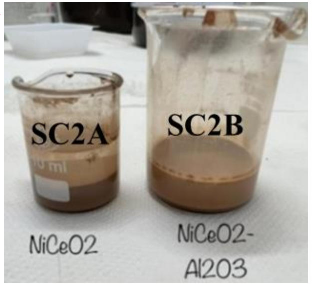
Flow curves



❑ *Slurry optimization: Rheology*



Slurries stability after one week



Slurry	Catalyst formulation	Powder catalyst (%)	Glycerol (%)	PVA (%)	Water (%)	Disperal P2® (%)
SC1	Ni/CeO_2	24.03	45.65	1.49	28.83	-
SC2A	Ni/CeO_2	22.40	42.50	1.50	33.60	-
SC3	Ni/CeO_2	25.36	48.18	1.46	25.00	-
SC2B	Ni/CeO_2-Al_2O_3	22.40	42.50	1.50	33.60	-
SC2C	Ni/CeO_2	20.14	42.50	1.50	33.60	2.26

Composition of the different slurry prepared.

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Activation of Al-Alloy POCSs by combined dip/spin coating method

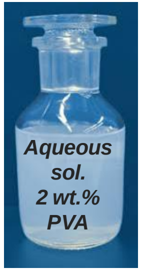
❑ *Method 1*

Influence of :

1. *Slurry composition;*
2. ***Support Thermal Treatment;***
3. *Catalyst formulation;*
4. ***Primer (Disperal P2) utilization***

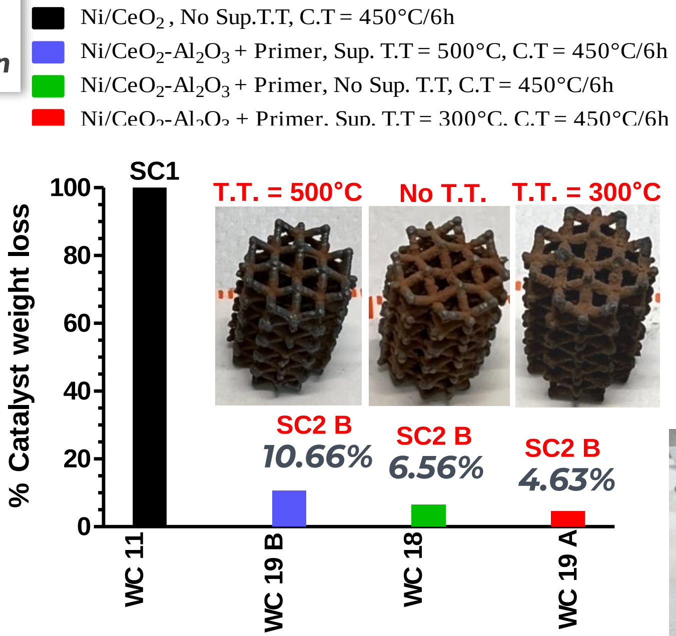
Mechanical Stability

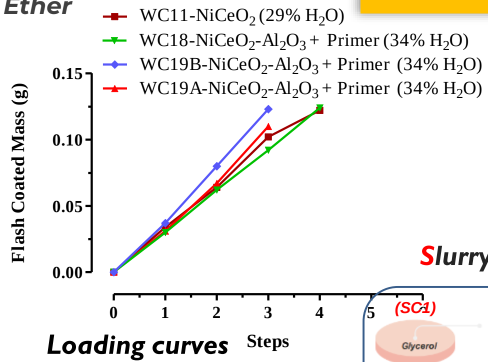
Sonication for 30min, 45kHz in Petroleum Ether



DISPERAL P2
highly dispersible
Boehmite (aluminium oxide hydroxide, γ-AlO(OH) powders

Single deposition step

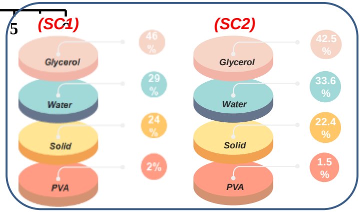


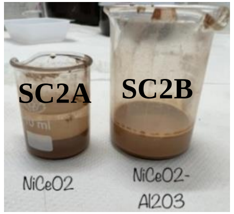


Loading curves

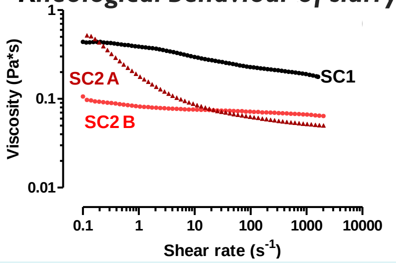
Cat. loading: 0.1 g/cm³

Slurry Composition





Rheological behaviour of slurry



Catalyst	True density (g/cm³)
7wt%Ni/CeO_2	16.32
7wt%Ni/CeO_2 – Al_2O_3	26.97

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AMBHER H2

Activation of Al-Alloy POCSs by combined dip/spin coating method

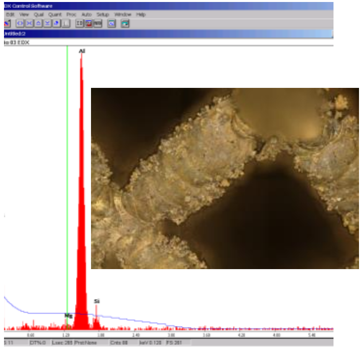
Method 1

Influence of Thermal Pre -Treatment of BCC support

Al alloy; BCC (as built)

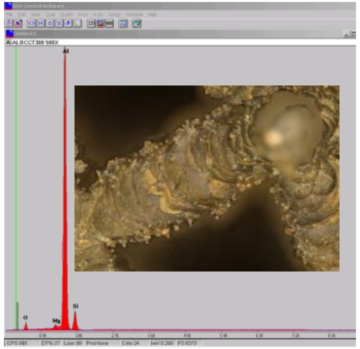
Energy-dispersive X-ray spectroscopy (EDAX)

WC 11 - BCC as built and cleaned



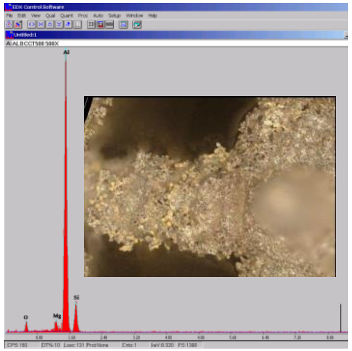
Elements	Wt %	At %
O K	3,30	5.80
MgK	0,36	0,44
AlK	85.11	83,24
SiK	11,23	10,58

WC 19A - cleaned -T.T. = 300°C/3h

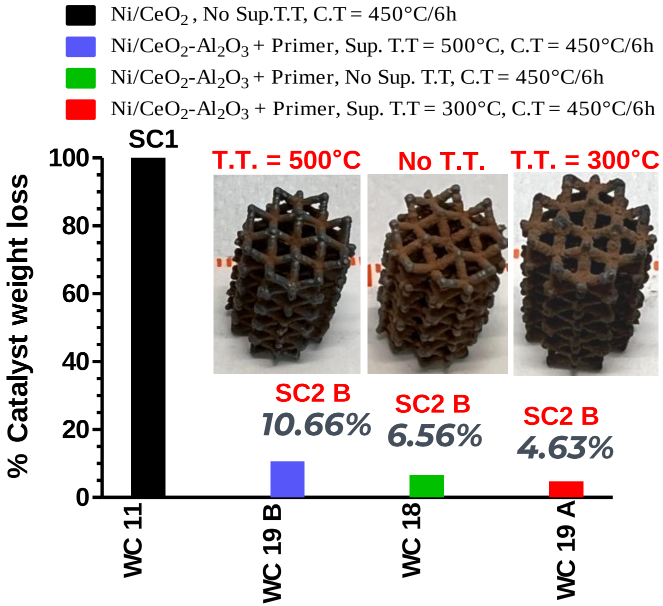


Elements	Wt %	At %
O K	8.46	13.55
MgK	1.11	1.17
AlK	75.58	71.75
SiK	14.84	13.54

WC 19B – cleaned - T.T. = 500°C/3h



Elements	Wt %	At %
O K	11.07	17.43
Mg K	2.78	2.88
Al K	65.95	61.57
Si K	20.20	18.11



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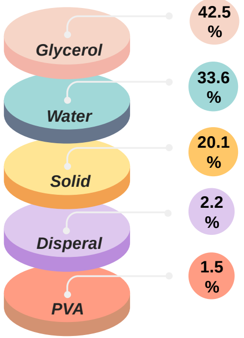
Activation of Al-Alloy POCSs by combined dip/spin coating method

Method 1

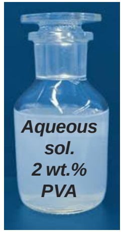
Influence of :

1. *DISPERAL in the slurry preparation;*
2. *Catalyst formulation*

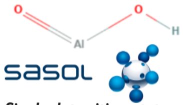
Slurry Composition (SC2 C)



Primer



DISPERAL P2 highly dispersible Boehmite (aluminium oxide hydroxide, γ-AlO(OH) powders



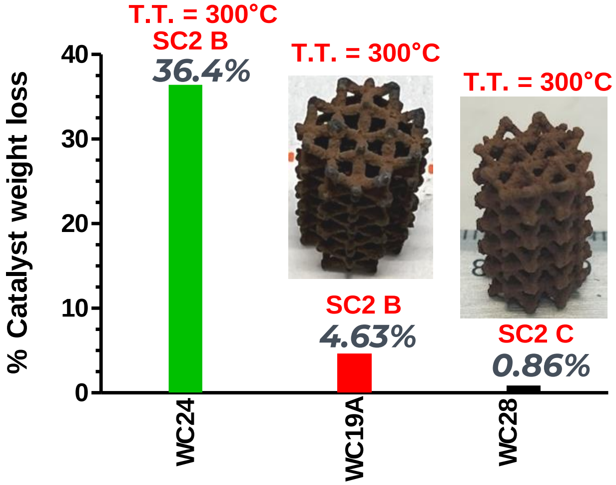
Single deposition step

Catalyst	True density (g/cm^3)
7wt%Ni/CeO_2	16.32
7wt%Ni/CeO_2– Al_2O_3	26.97

Mechanical Stability

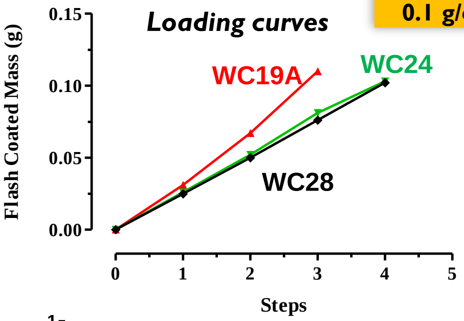
Sonication for 30min, 45kHz in Petroleum Ether

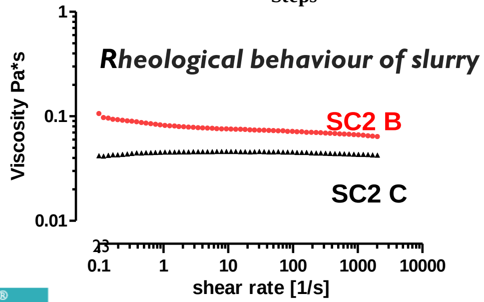
- Green: Ni/CeO_2, Primer, Sup. T.T =300°C, C.T = 450°C/6h
- Red: Ni/CeO_2-Al_2O_3, Primer, Sup. T.T = 300°C, C.T = 450°C/6h
- Black: Ni/CeO_2, Pimer + T.T =300°C, C.T = 450°C/6h, **Slurry + DISPERAL**



Al-alloy; BCC (as built)

Cat. loading: 0.1 g/cm^3





Slurry	Catalyst formulation	Powder catalyst (%)	Glycerol (%)	PVA (%)	Water (%)	Disperal P2® Boehmite (%)
SC2B	Ni/CeO_2-Al_2O_3	22.40	42.50	1.50	33.60	-
SC2C	Ni/CeO_2	20.14	42.50	1.50	33.60	2.26

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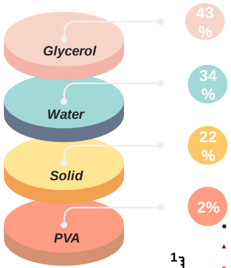
Activation of Al-Alloy POCSs by combined dip/spin coating method

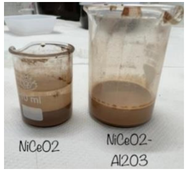
Consiglio Nazionale delle Ricerche — ENGIE

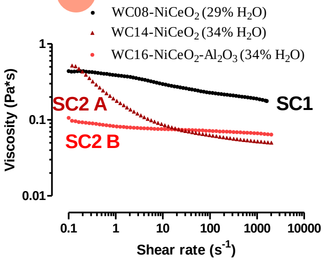
Influence of :

(1) Alumina (10wt%) in the formulation, powder ball milling, slurry ball milling time.
(2) Thermal Treatment time.
(3) Primer (Disperal P2) utilization.
(4) Anodization after Thermal Treatment



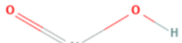
1 *Surry stability After 1 day*





2 *Thermal Treatment time 4 ➔ 6 h*

3 *DISPERAL P2 highly dispersible Boehmite (aluminium oxide hydroxide, γ-AlO(OH)) powders*

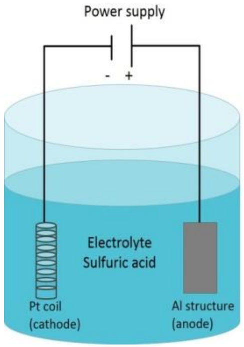


sasol

Single deposition step

❑ Method 2

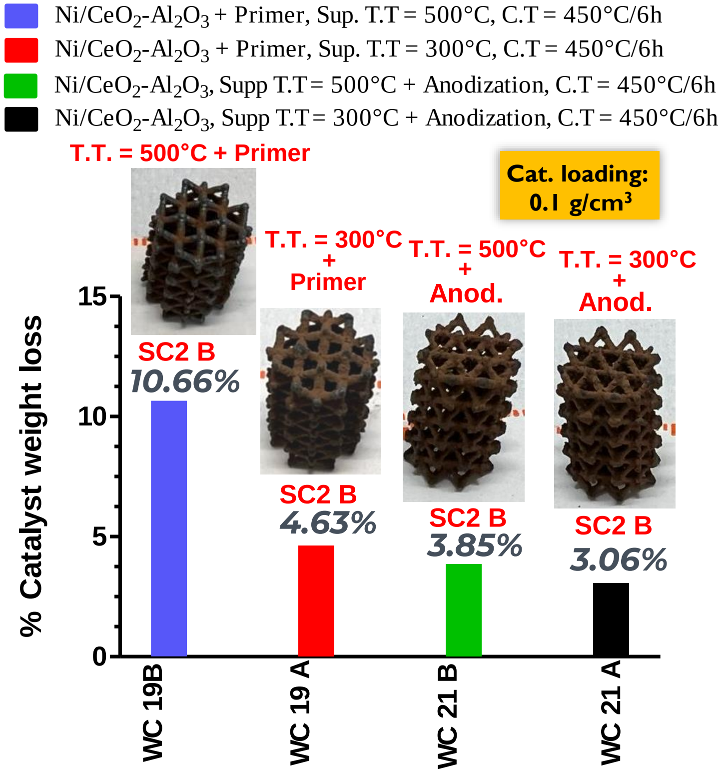
4 *Anodization after Thermal Treatment*



Galvanostatic anodization

- H_2SO_4 1.63 M (15Wt%)
- Temperature : 20°C
- V: 40, A: 0.251
- Current density 0.2 mA/cm^2
- Time: 30 min

Al-alloy; BCC (as built)



Sonication for 30min - 45kHz in Petroleum Ether

Funded by the European Union

AMBHER2

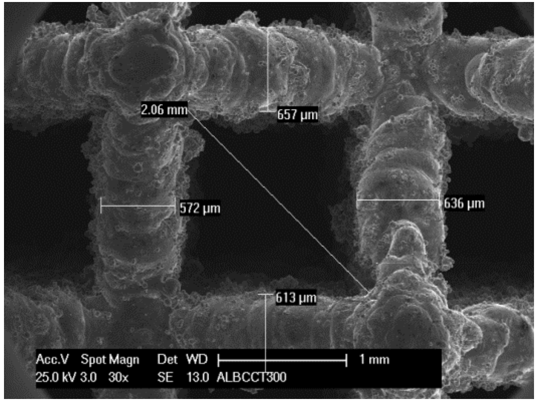
Activation of Al-Alloy POCSs by combined dip/spin coating method

Al-alloy; BCC (as built)

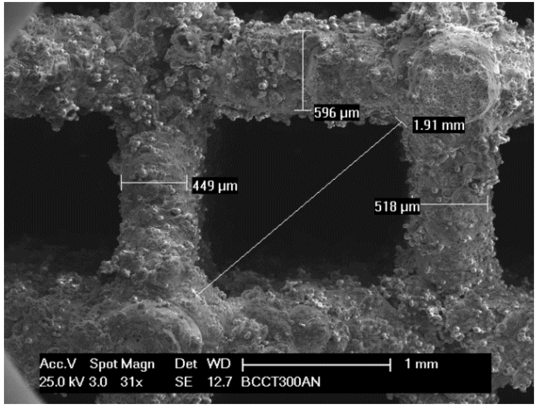
Anodization after Thermal Treatment

SEM micrographs

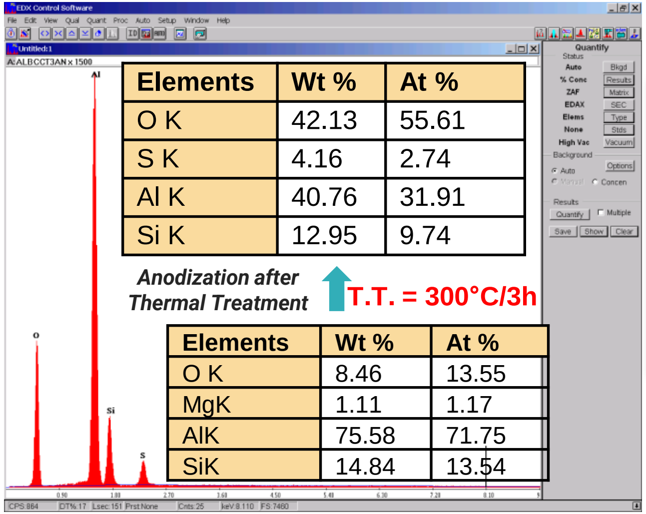
WC 19A - cleaned -T.T. = 300°C/3h



WC 19A - cleaned -T.T. = 300°C/3h - anodized



Method 2

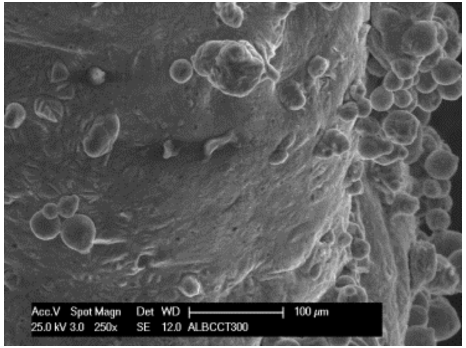


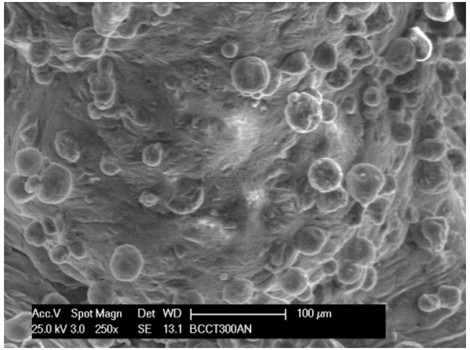
Elements	Wt %	At %
O K	42.13	55.61
S K	4.16	2.74
Al K	40.76	31.91
Si K	12.95	9.74

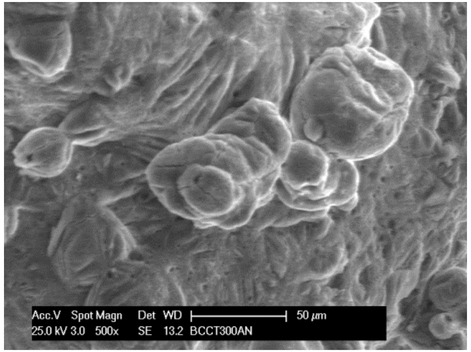
Anodization after Thermal Treatment T.T. = 300°C/3h

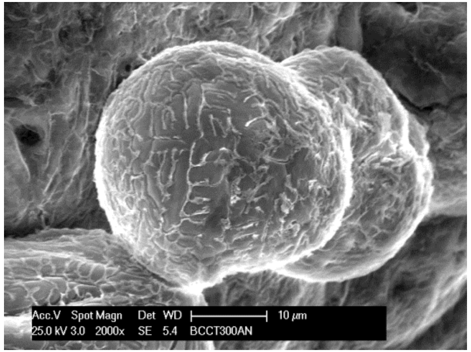
Elements	Wt %	At %
O K	8.46	13.55
MgK	1.11	1.17
AlK	75.58	71.75
SiK	14.84	13.54

EDAX analysis









Activation of Al-Alloy POCSs by combined dip/spin coating method

Consiglio Nazionale delle Ricerche

ENGIE

❑ *Method 1*

Influence of :

1. *DISPERAL in the slurry preparation;*
2. *POCS pretreatment (sand-blasted);*
3. *POCS geometry (BCC, Kelvin)*

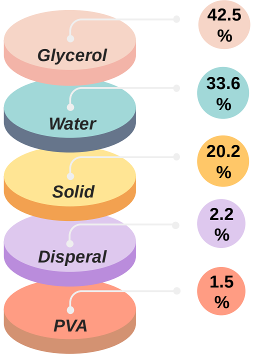
Mechanical Stability

Sonication for 30min, 45kHz in Petroleum Ether

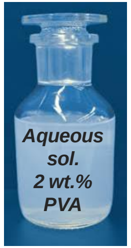
Cat. loading: 0.1 g/cm³

Al-alloy; BCC & kelvin

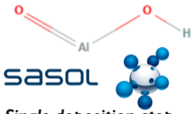
Slurry Composition (SC2 C)



Primer



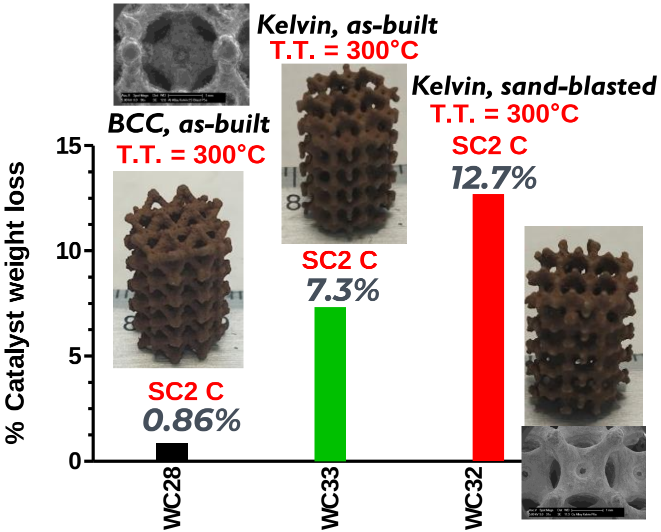
DISPERAL P2 highly dispersible Boehmite (aluminium oxide hydroxide, γ-AlO(OH) powders

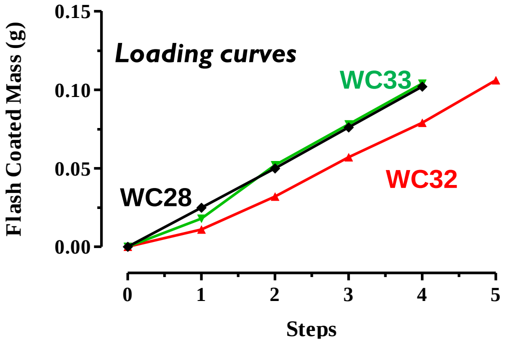


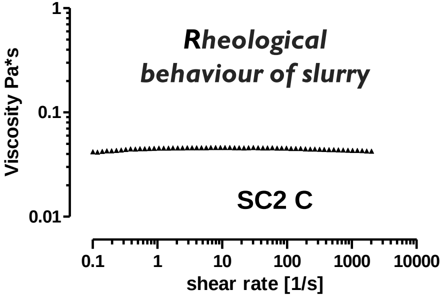
sasol

Single deposition step

Catalyst	True density (g/cm³)
7wt%Ni/CeO_2	16.32







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Activation of Al-Alloy POCSs by combined dip/spin coating method

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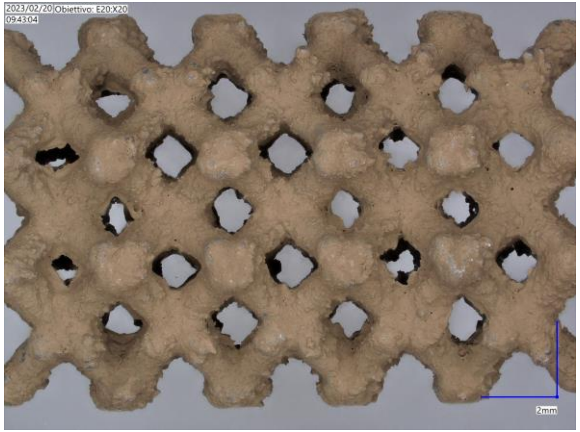
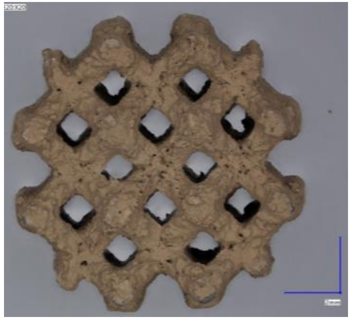
Method 1

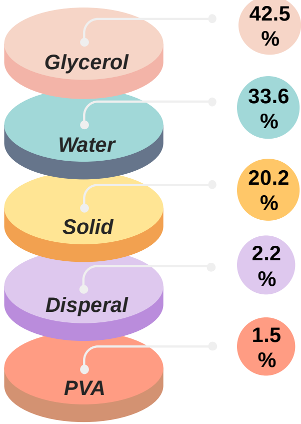
BCC





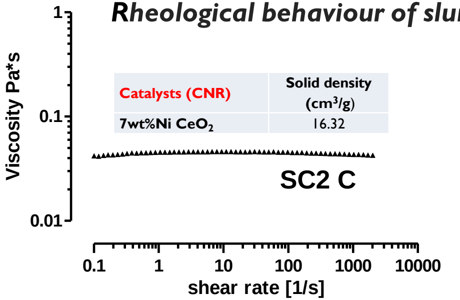
Cell Type = 3, Ø Strut =0,6 mm,
SSA = 58,82 cm^2/cm^3, Porosity = 83,3%

Slurry Composition (SC2 C)



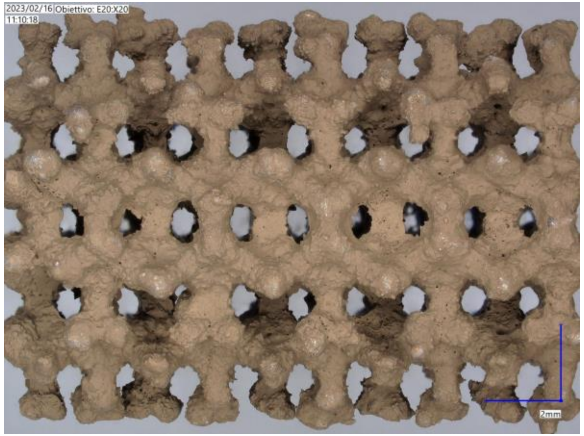
Cat. loading: 0.1 g/cm³

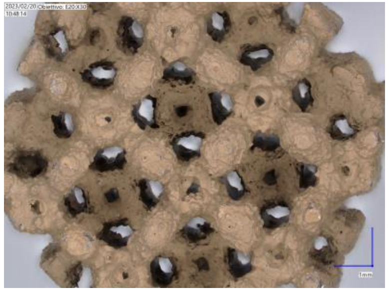
Rheological behaviour of slurry



Catalysts (CNR)	Solid density (cm^3/g)
7wt%Ni CeO_2	16.32

KELVIN





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

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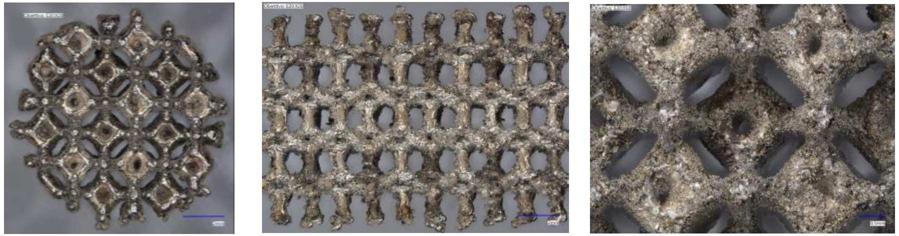
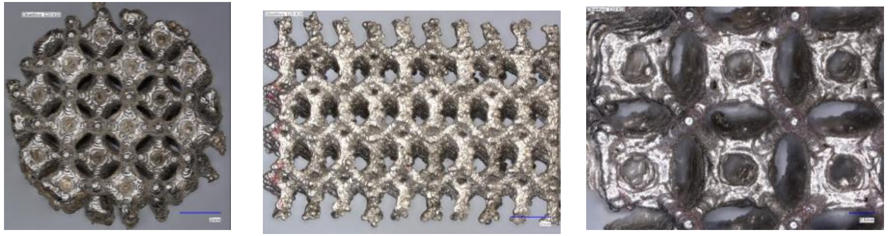
Activation of Ni-Alloy POCSs by combined dip/spin coating method

Consiglio Nazionale delle Ricerche

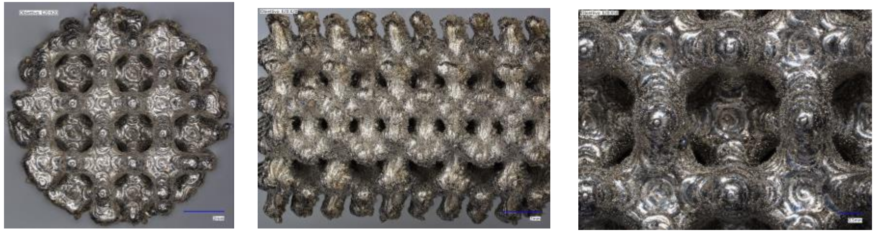
Method 1



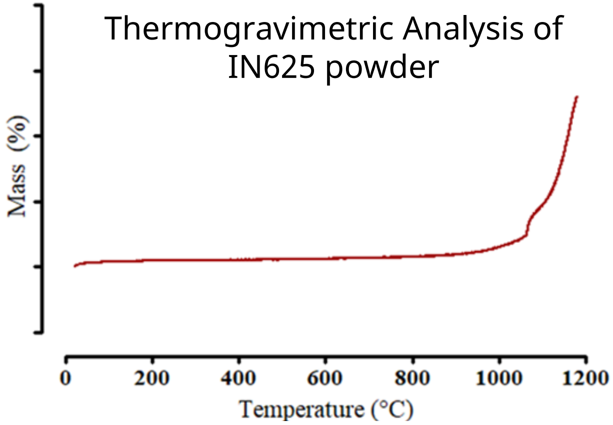
Cell Type = 3, Ø Strut =0,4 mm, SSA = 58,82 cm^2/cm^3, Porosity = 83,3%

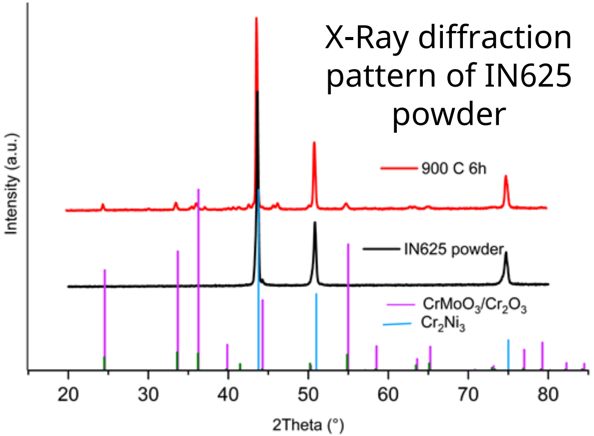


Cell Type = 3, Ø Strut =0,6 mm, SSA = 52,52 cm^2/cm^3, Porosity = 78,7%



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





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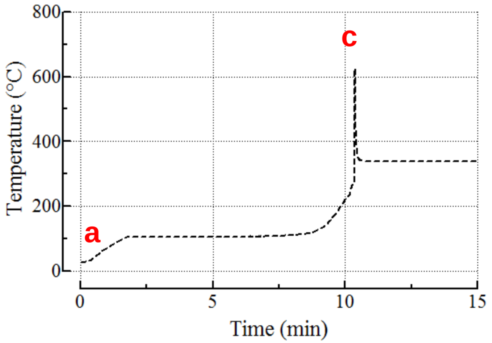
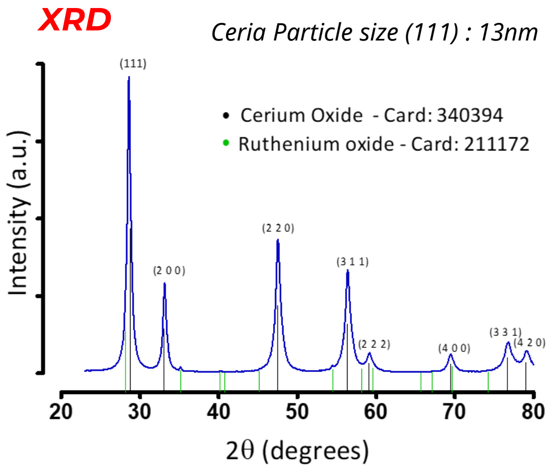
Activation of Ni-Alloy POCSs by combined dip/spin coating method

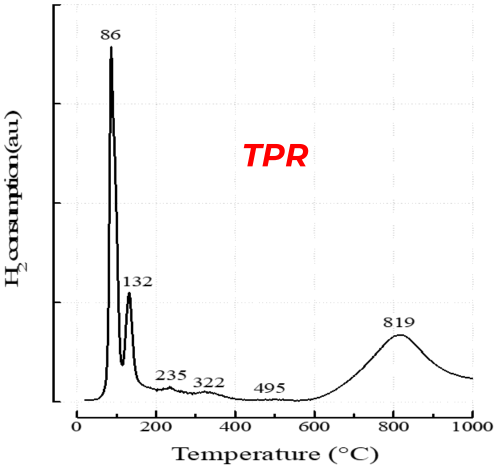
❑ Catalysts preparation and characterization (4wt%Ru/CeO_2)

Solution Combustion synthesis sequence: *a) muffle introduction of water precursors and fuel mixture; b) reaction initiation; c and d) cooling phase; c) final catalyst (fine powder)*



Combustion temperature profile





Ce Precursor	Ru Precursor	Fuel
$Ce(NO_3)_3 \cdot 6H_2O$	Ru(NO)(NO3)x(OH)y, x+y=3	*Urea*

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Activation of Ni-Alloy POCSs by combined dip/spin coating method

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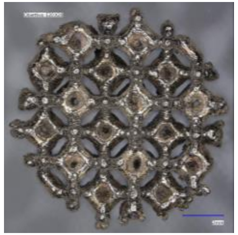
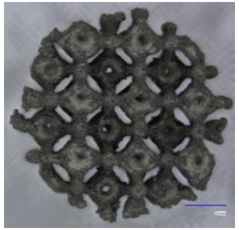
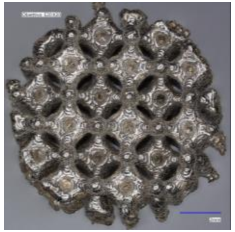


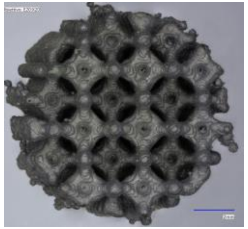
Thermal pre–treatment at 900 ℃ / 6h



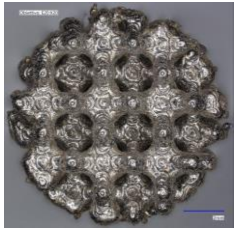
Cell Type = 3, Ø Strut =0,4 mm, SSA = 58,82 cm^2/cm^3, Porosity = 83,3%



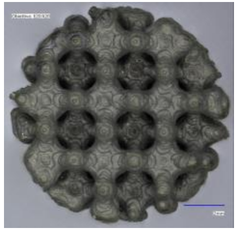
Thermal pre–treatment at 900 ℃ / 6h



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



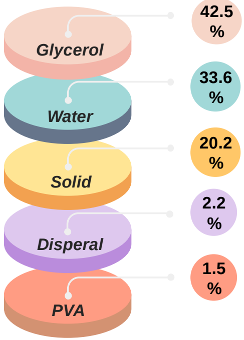
Thermal pre–treatment at 900 ℃ / 6h



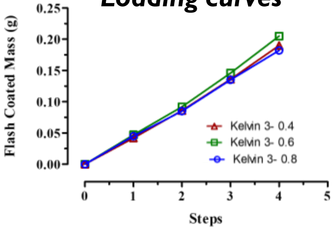
Cell Type = 3, Ø Strut =0,8 mm, SSA = 32,68 cm^2/cm^3, Porosity = 64.4%

Method 1

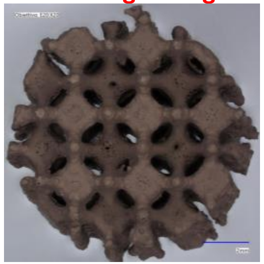
Slurry Composition (SC2 C)



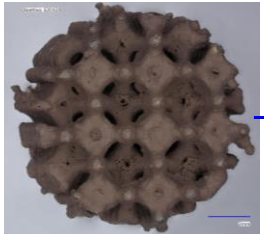
Loading curves



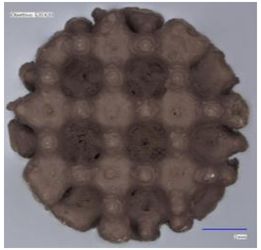
Cat. loading: 0.16 g/cm^3



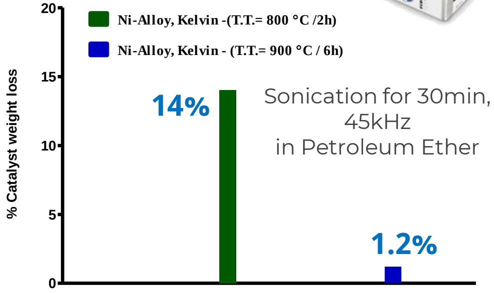
Cat. loading: 0.17 g/cm^3

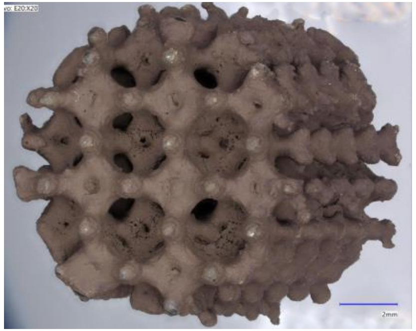


Cat. loading: 0.16 g/cm^3



Mechanical Stability





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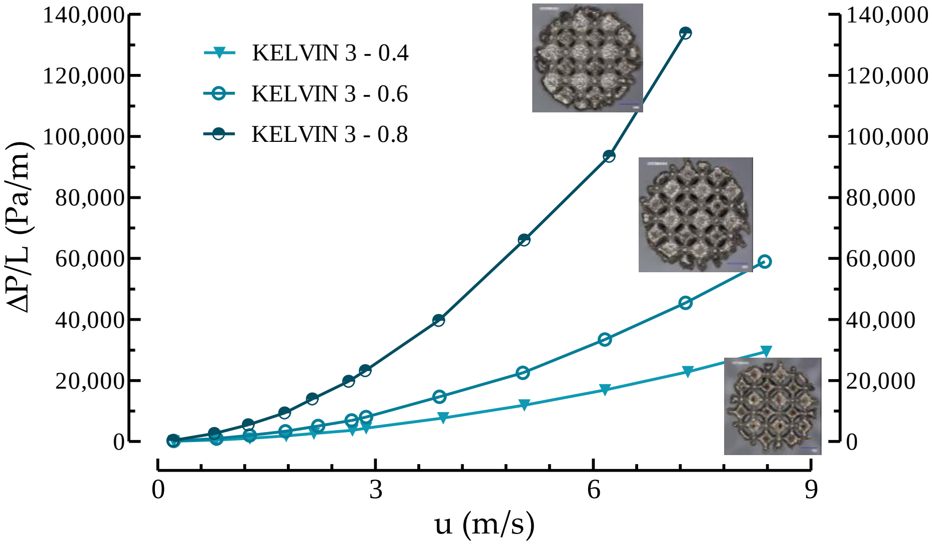
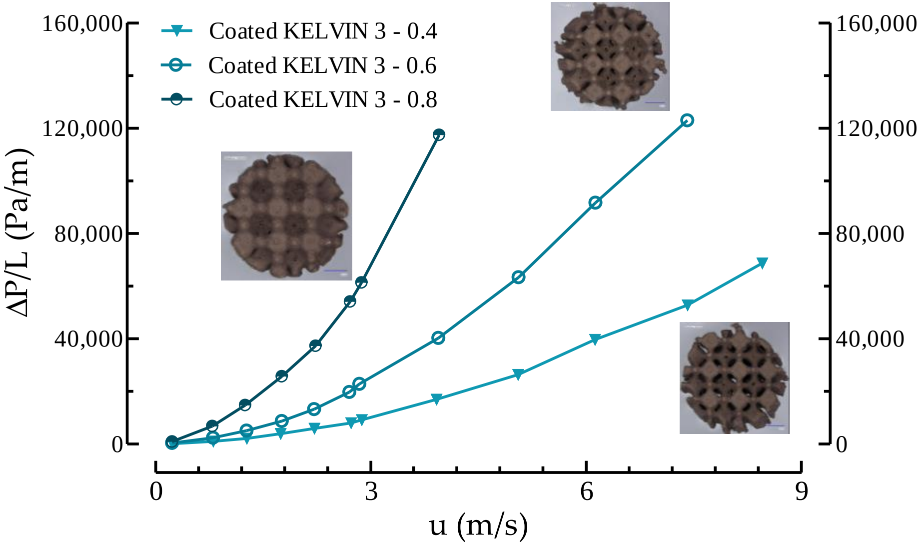
Activation of Ni-Alloy POCSs by combined dip/spin coating method

❑ *Pressure drop*





Cell Type = 3, Ø Strut =0,4 mm, SSA = 58,82 cm^2/cm^3, Porosity = 83,3%

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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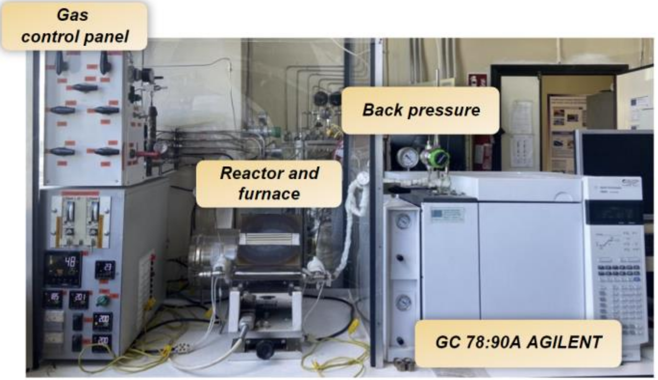
Activation of Ni-Alloy POCSs by combined dip/spin coating method

Consiglio Nazionale delle Ricerche

❑ *Ammonia synthesis: Preliminary catalytic activity*

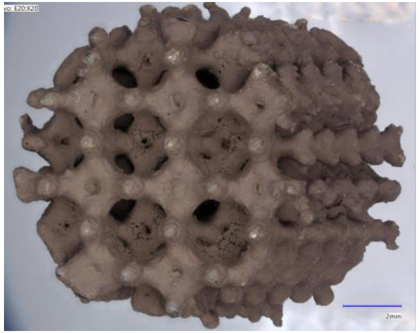


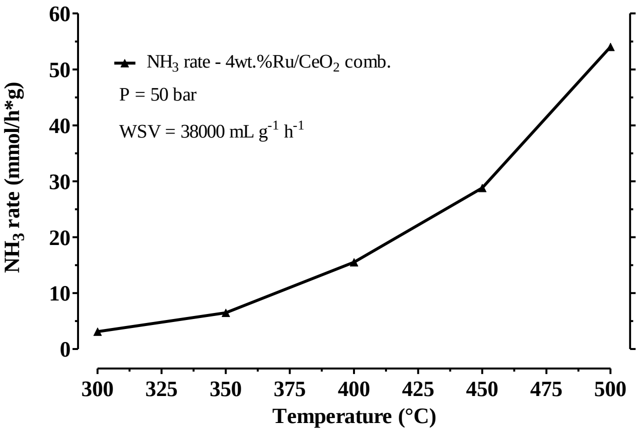
Test rig for the evaluation of catalytic performances of catalysts towards the ammonia synthesis up to 50 bar

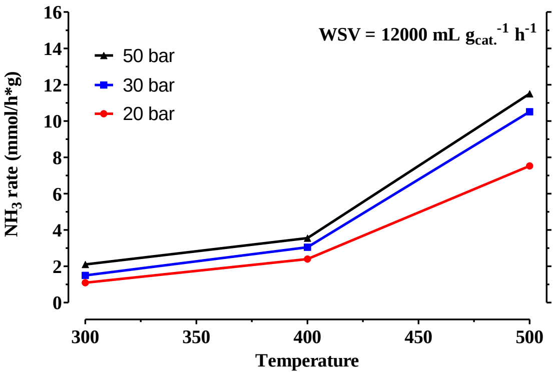
Operative conditions	
Temperature	300 - 500 (°C)
Pressure	20 – 30 - 50 (bar)
WSV	12000 ($cm^3\ g_{cat}^{-1}\ h^{-1}$) 38000 ($cm^3\ g_{cat}^{-1}\ h^{-1}$)
Total IN Flow	41 cm^3/min 130 cm^3/min
H_2/N_2	3:1
Catalyst	4wt%Ru/CeO_2 (loading = 0,17 g/cm^3, 0.2g)

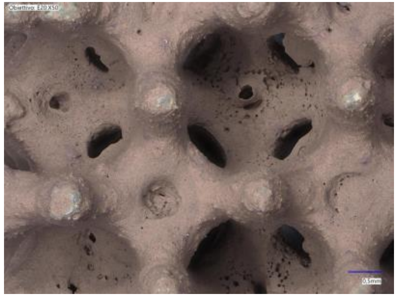
Cell Type = 3, Ø Strut =0,6 mm,
SSA = 52,52 cm^2/cm^3 , Porosity = 78,7%

Ø = 1cm
L = 1,5cm









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AMBH2ER

Work in progress .....

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Scale–up of the dip/spin coating method

Catalyst amount for slurry preparation: 5g

Catalyst amount for slurry preparation: 50-500g

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

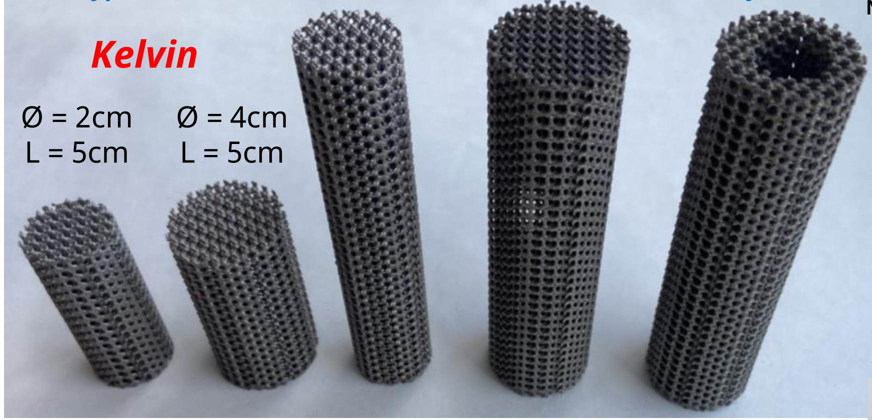
POCS size: Ø= 1cm, L=1.5

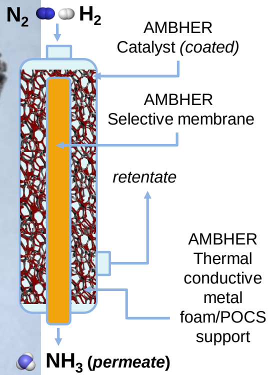
Spin coater

POCS size: Ø= 1- 5cm, L=5-15cm

Ø = 2cm L = 10cm | Ø = 4cm L = 10cm | Ø = 2,66cm L = 10cm

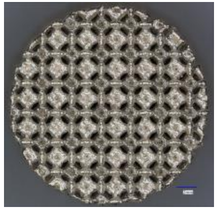
Cell Type = 3, Ø Strut =0,6 mm, SSA = 52,52 cm^2/cm^3, Porosity = 78,7%





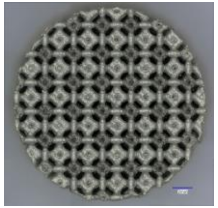
First sample

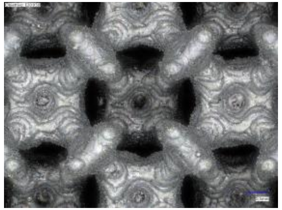
Ø = 2cm, L = 5cm



Thermal pre–treatment at 900 ℃ / 6h

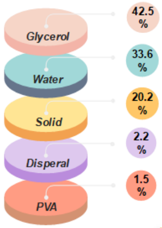
0,5wt%Ru/Al_2O_3(commercial)

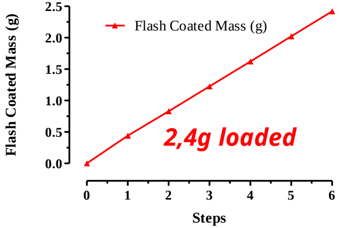




Method 1

Slurry Composition (SC2 C)





Weight loss = 2,3%

Ø = 2cm, L = 5cm

CONCLUSIONS

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POCSs Manufacturing

1. Additive Manufacturing (AM) is a powerful tool for preparing conductive Periodic Open Cellular Structures (POCS) with potentially infinite geometries characterized by high porosities and Specific Surface Area;
2. It is also cost-effective, as it requires less material than traditional manufacturing methods;
3. It can be used to create parts with complex geometries that would be difficult or impossible to produce using traditional methods and also allows for better control of porosity and pressure drop, enabling parts to be made with higher precision and accuracy.
4. Between the different 3D-printed geometries studied, the BCC and KELVIN showed the lowest pressure drop

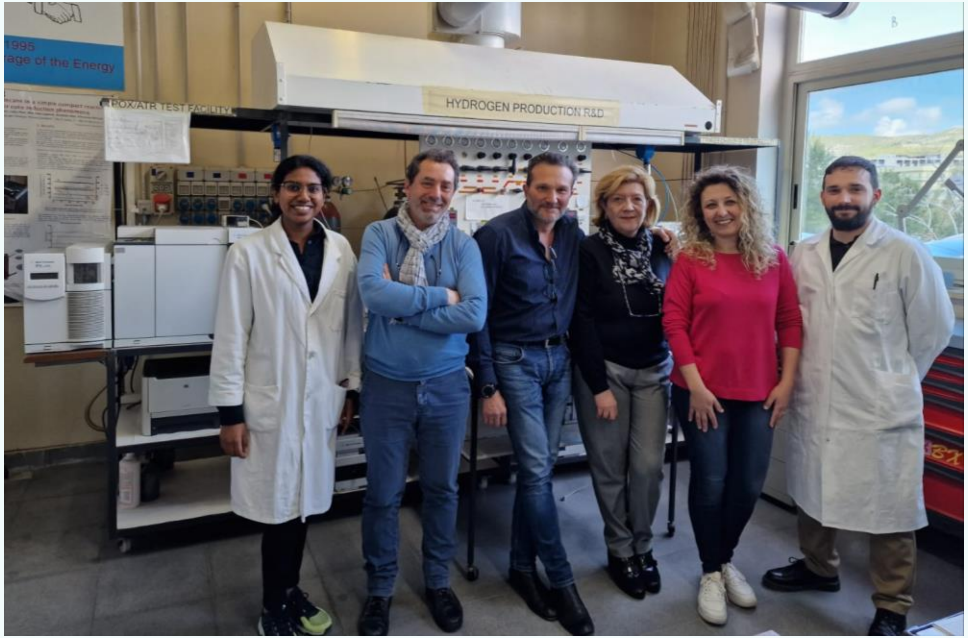
Coated POCSs

1. Dip/Spin coating is an attractive option for the catalytic activation of metallic 3D printed POCSs;
2. The method allows for control of the thickness (20-40µm) and the homogeneity of the resulting coated layers by adjusting slurry viscosity and coating parameters such as rotation speed and rotation time;
3. The catalytic layer deposited resulted well anchored to the POCS surface;
4. The presence of anchoring points, the thermal or anodization pre-treatment (or both) of supports or the primer (DISPERAL P2) utilization (both in the slurry and coated on the supports) play a crucial role in achieving high mechanical stability;
5. No pore-clogging phenomena were observed irrespective of the geometry used;
6. The method is potentially easily scalable

Catalytic activity towards ammonia synthesis

1. Preliminary catalytic activity carried out with a kelvin POCS coated with 4wt%Rh/CeO_2 has demonstrated promising results at high WSV.

Staff involved



Thanks!

Consiglio Nazionale delle Ricerche

Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (ITAE)

Antonio Vita
Senior Researcher
Head of FPMaT,
antonio.vita@itae.cnr.it

Massimo Laganà
Technician,
Test facilities design,
laboratory activities
massimo.lagana@itae.cnr.it

Lidia Pino
Researcher Manager
Catalyst design
lidia.pino@itae.cnr.it

Minju Thomas
Postdoctoral Researcher,
Laboratory activities
thomas@itae.cnr.it

Cristina Italiano
Researcher
Catalyst design ,
Responsible of the laboratory
cristina.italiano@itae.cnr.it

Gabriel Marino.
Research fellow
Laboratory activities
marino@itae.cnr.it

Dr. Antonio Vita

Fuel Processing Materials and Technologies (FPMaT)

antonio.vita@itae.cnr.it

HYCELTEC 2024
IX Symposium on Hydrogen, Fuel Cells and Advanced Batteries
Milazzo, Italy, 30 June-3 July 2024

We are pleased to invite you to participate in the IX Symposium on Hydrogen, Fuel Cells and Advanced Batteries, HYCELTEC 2024. The conference will take place **from June 30th to July 3rd, 2024, in Milazzo (Messina, Italy)**, a lovely sicilian town facing the Aeolian Islands. The venue will be the impressive hilltop **Castle of Milazzo**.

HYCELTEC 2024 will be certainly an interdisciplinary forum for discussion of topics related to fuel cells, hydrogen and batteries, bringing together researchers from academia, technological centers and industry.

Please visit the website: www.hyceltec2024.it (under construction)

Topics

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1. Hydrogen
a) Production
b) Carriers
c) Storage and transportation
d) Integration with renewable source energies
e) Environmental and social impacts
f) Other related subjects

2. Fuel Cells
a) Low and high temperature
b) Applications
c) Development of components and materials
d) Degradation mechanisms
e) Device integration

3. Advanced Batteries
a) Liquid-, fused-, solid-state and polymeric batteries
b) Redox flow batteries
c) Supercapacitors
d) Electrochromic energy storage devices