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Project Title:	Toward next-generation 3D printed materials for space applications: hierarchical nanoporous structures with engineered macro-architectures		
Project Number	4000135470	Start date	End date
		01-09-2021	30-04-2023
Period	M1-M18		
Author(s)	Dr. A. (Ahmad) Zafari Dr. D. (Davoud) Jafari Dr. A. (Antoni) Forner Cuenca Dr. S. (Salome) Sanchez Dr. K (Kiran) Bhatia		

Document Type	Name	Description	Milestone	WP no.	Delivery date (in month)
R	D0.5.	Final Presentation slides	End of WP6	0	M18

	Prepared & verified	Approved	Authorized
Name	D. Jafari		
Date	12-05-2023		
Signature			

Revision Index		
Issue	Prepared/Date	Remarks
8.0	D. Jafari 12-05-2022	First version

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Minutes of Meeting - Project Closure Meeting

Date: 11 May 2023

Time: 14:30

Location: ESTEC, Noordwijk, The Netherlands

Attendees:

Malgorzata Holynska, ESA

Malgorzata Holynska

Digitally signed by Malgorzata Holynska
Date: 2023.05.12 13:05:49 +02'00'

Adam Mitchell, ESA

Advenit Makaya, ESA

Davoud Jafari, University of Twente

Ahmad Zafari, University of Twente

Salome Sanchez, University of Twente

Antoni Forner Cuenca, Eindhoven University of Technology

Kiran Bhatia, Eindhoven University of Technology

Agenda:

Project Overview, objectives, deliverables

Lessons learned 1 – laser powder bed fusion of Ti-6Al-4V and In-718 porous materials

Lessons learned 2 – Electrodeposition and electrochemical performance

Project closure and handover

Next steps and a follow-up project

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Minutes:

Project Overview and Accomplishments

- Davoud Jafari provided a brief summary of the project objectives and goals.
- Ahmad Zafari discussed the overall progress of the project, highlighting key achievements in laser powder bed fusion of Ti-6Al-4V and In-718 porous materials
- Kiran Bhatia discussed the overall progress of the project, highlighting key achievements in electrodeposition and electrochemical performance of porous materials
- The team expressed satisfaction with the outcomes and acknowledged the efforts of all project members.
- Davoud Jafari shared project deliverables.

Lessons Learned (slides are presented in the following sections)

- The team engaged in a discussion to identify lessons learned throughout the project lifecycle.
- The lessons learned were documented and shared for future reference.
- Participants' suggestions for enhancing the performance materials were discussed

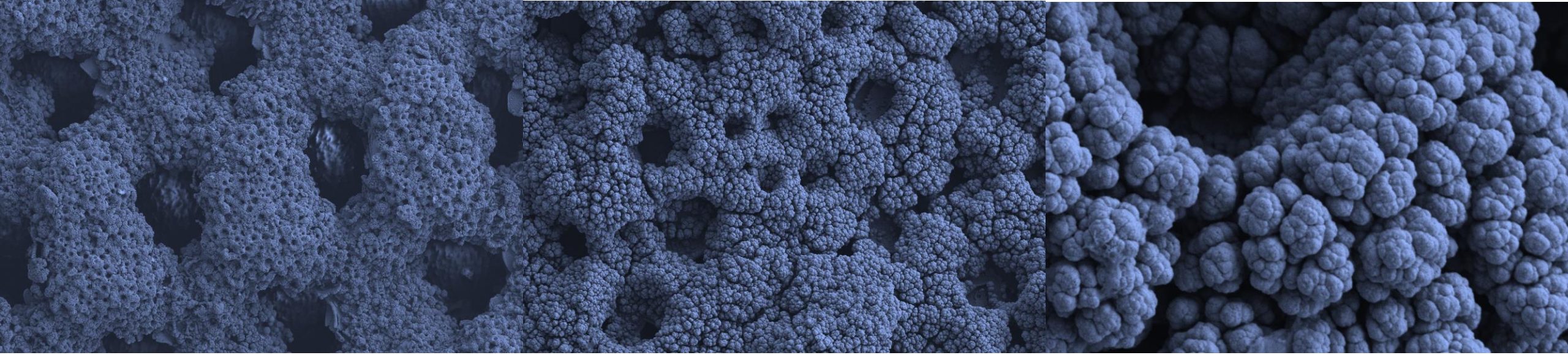
Next Steps and a Follow-up Project

The recommendations for a follow-up project were documented and could be as follows:

- Further investigation to assess the printability of lattice structures of < 300 µm by modifying designs, laser parameters, and materials.
- Fabrication of electrodes from materials with higher melt pool stability (e.g., stainless steel).
- Further study on the microstructure of the substrate including microscopic phases and particles attached to the struts and walls to understand how they influence the coating quality, and thus, electrochemical properties.
- Extend the study to other materials with potentially better electrochemical properties. This can be expanded to difficult-to-print materials, such as Mo and MoS2 - The main focus has thus far been on Ti-64, and In718.
- Surface engineering and further study on the coating methods and chemistry of the catalysts to maximize electrochemical efficiency

The team agreed that no further meetings were required for project closure. However, participants acknowledged the importance of maintaining communication channels for future collaboration and a follow-up project.

Note: These minutes are intended as a record of discussions and decisions made during the project closure meeting.



Summarising the main results of the Project No. 4000135470/21/NL/GLC/ov

Toward next generation 3D printed materials for space applications: hierarchical nano-porous structures with engineered macro-architectures

Kiran Bhatia, Antoni Forner Cuenca, Salomé Sanchez, Ahmad Zafari, Davoud Jafari

TU/e UNIVERSITY OF TWENTE. esa

Agenda

- 14:30 – 14:40 Opening.
- 14:40 – 15:10 Presentation by UTwente
- 15:15 –15:45 Presentation by TU/e
- 15:45 – 16:00 Wrap-up

Project Objectives

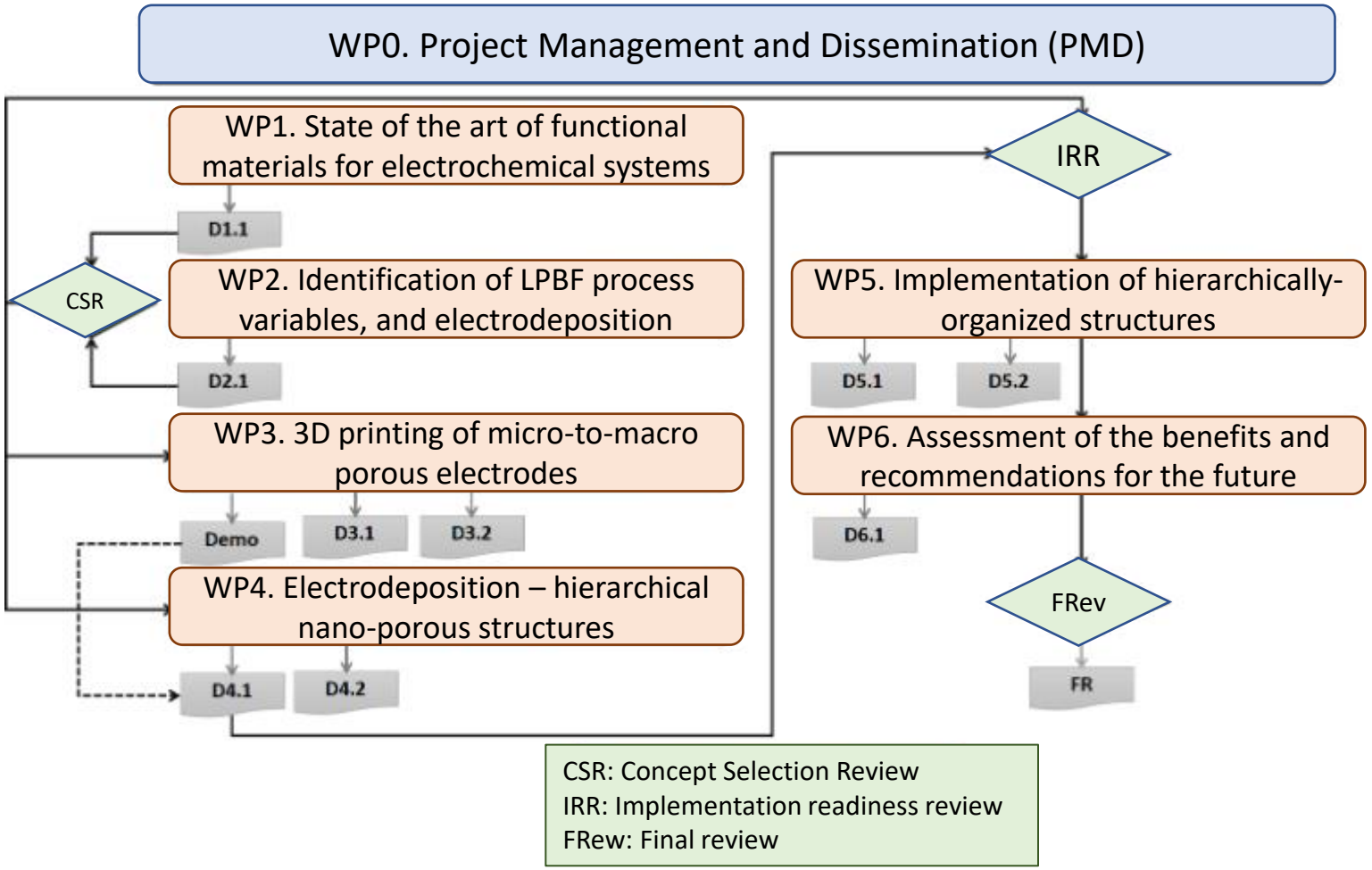
✓ **Key Objective:**

To develop 3D printed metal hierarchical nanoporous electrochemical interfaces with engineered macro-architectures to be implemented in electrochemical systems as a porous electrode.

✓ **Main Technical Objectives:**

- ❑ Material Design – design of high-performance porous materials customizable for an integrated powder-bed AM and coating technology based on electrochemically-controlled metals.
- ❑ AM Process – Development of experimental methodology (design of experiment) to produce tailored 3D micro-to-macro pore structures.
- ❑ Coating – Levering electrochemical methods to control coating composition and morphology to enable tailored interfaces with controlled catalytic activity, surface area, wettability and mass transport characteristics.
- ❑ Proof of concept – test featuring tailored porous material in terms of electrochemical performance.

Workflow



Key Deliverables :

D.1.1: State of the art of metal 3D printing and electrodeposition and dealloying concept

D2.1: Identification of powder bed AM key process variables

D3.1: Experimental results for selected metal materials

D3.2: Characterization results of 3DP porous materials

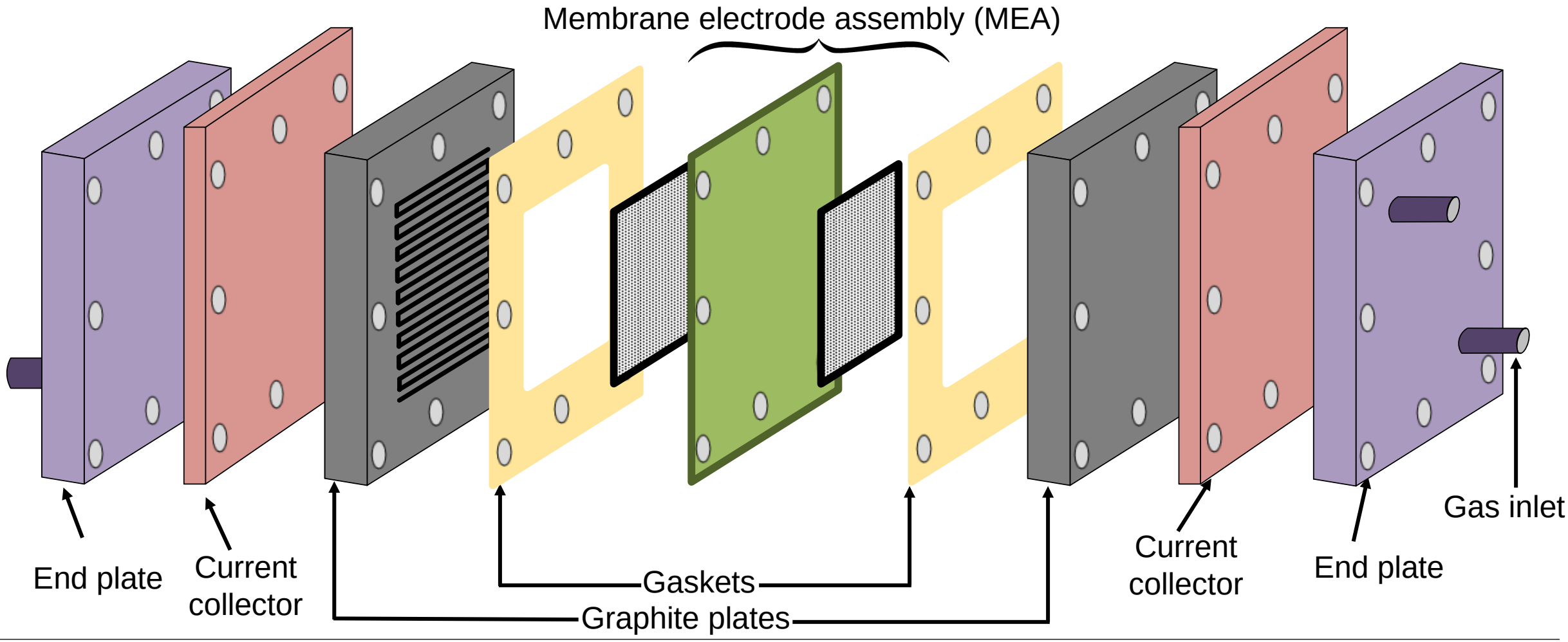
D4.1: A strategy for optimized coating compositions using flat

D4.2: Strategies for translating to porous scaffolds

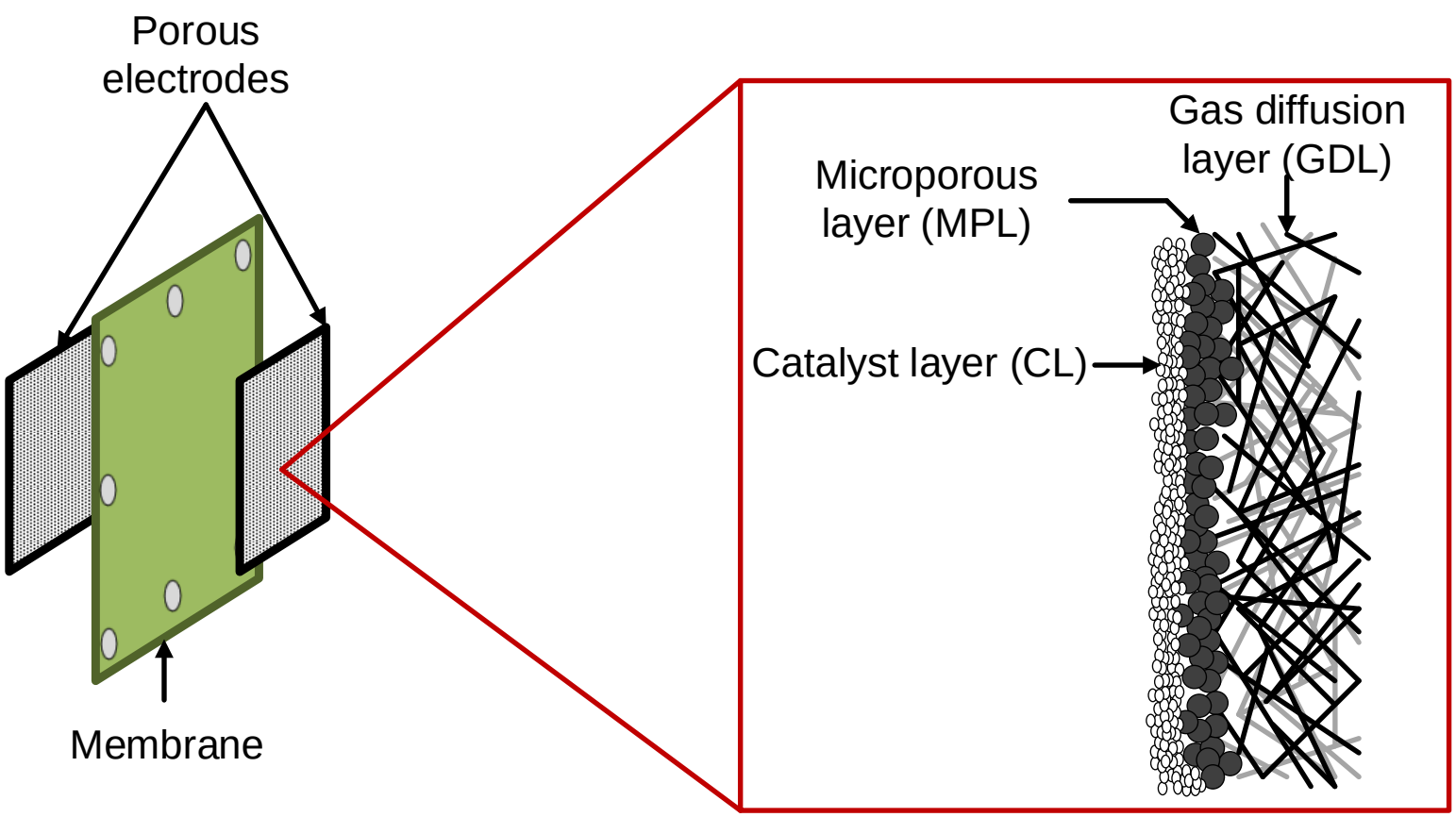
D5.1 and 5.2: Experimental results/data of electrodes which are tested on a small scale (5 cm2) RFCs

D6.1: Assessment of the benefits and recommendations for the future

Reversible fuel cells: Membrane electrode assembly

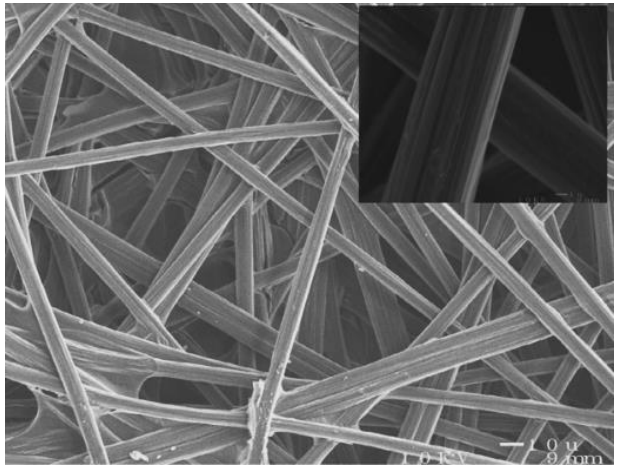


Membrane Electrode Assembly (MEA)



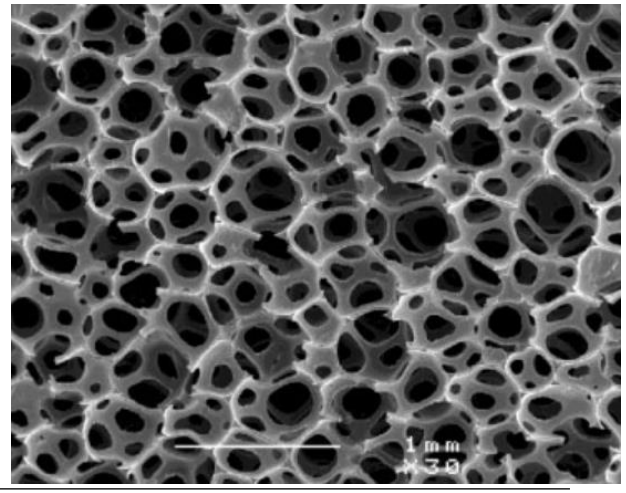
Carbon paper

Nanotechnol 18 (2007) 035202



Ni foam

Environ. Sci. Technol. 54 (2020) 12511–12520

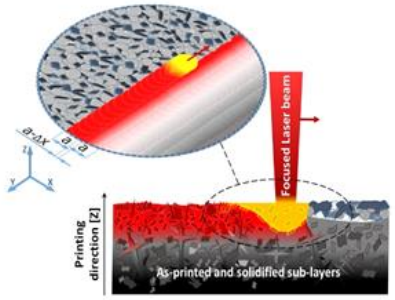


Project in a nutshell

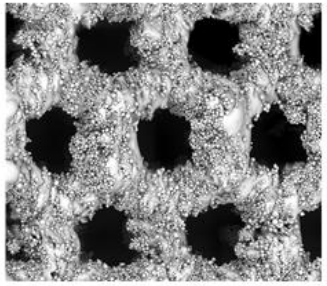
Fabrication of gas diffusion layer (Ti-6Al-4V and Inconel 718)

Functionalisation (catalyst deposition)

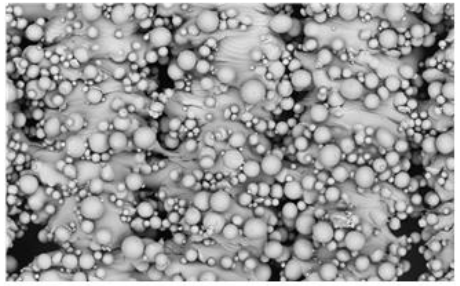
Laser powder bed fusion



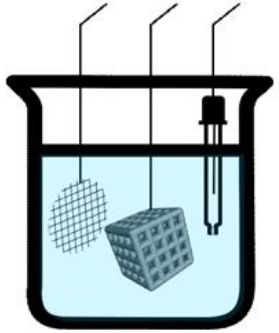
Lattice structures



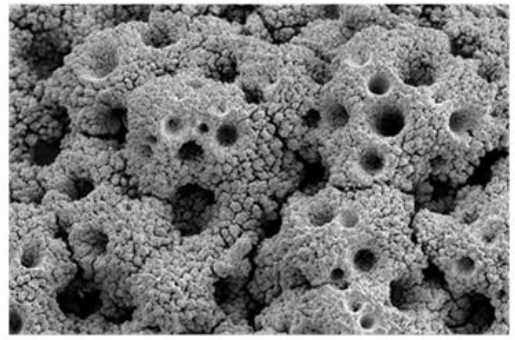
Thin walled structures



Electrochemical depositon



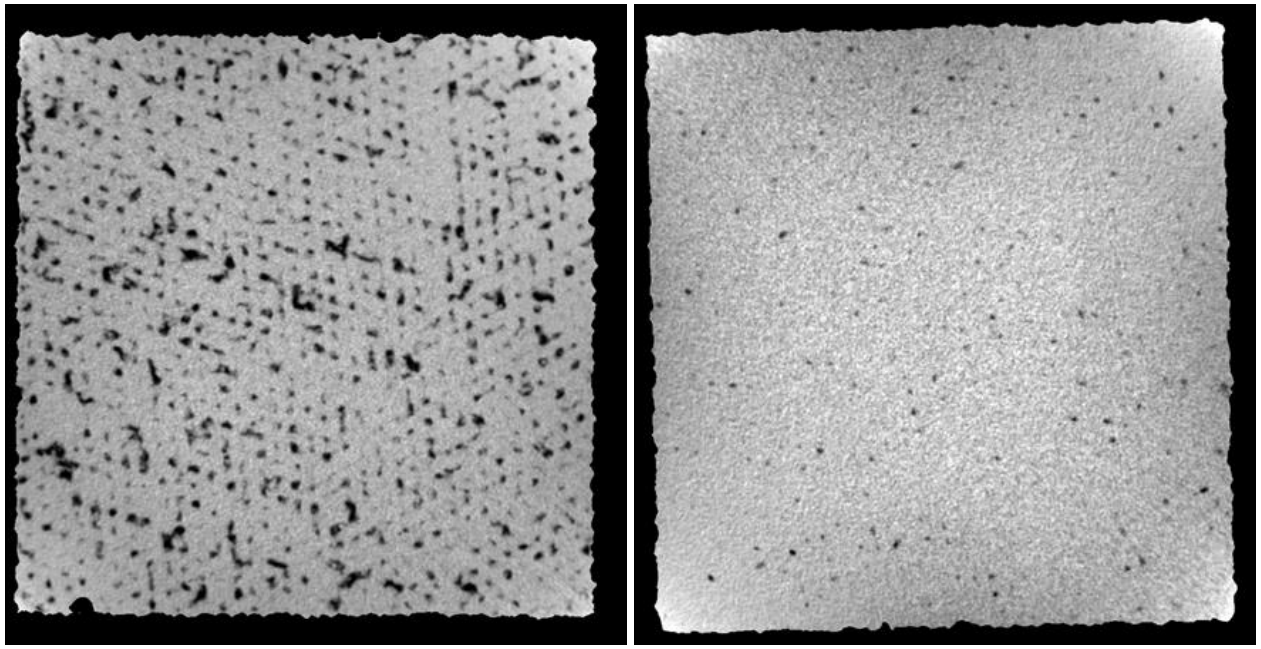
Nickel deposition



Order of 0.01-1 mm **Pore size reduction** Order of 0.1-1 µm

Additive manufacturing of electrodes: Two different types of porosity

Geometrically undefined porosity



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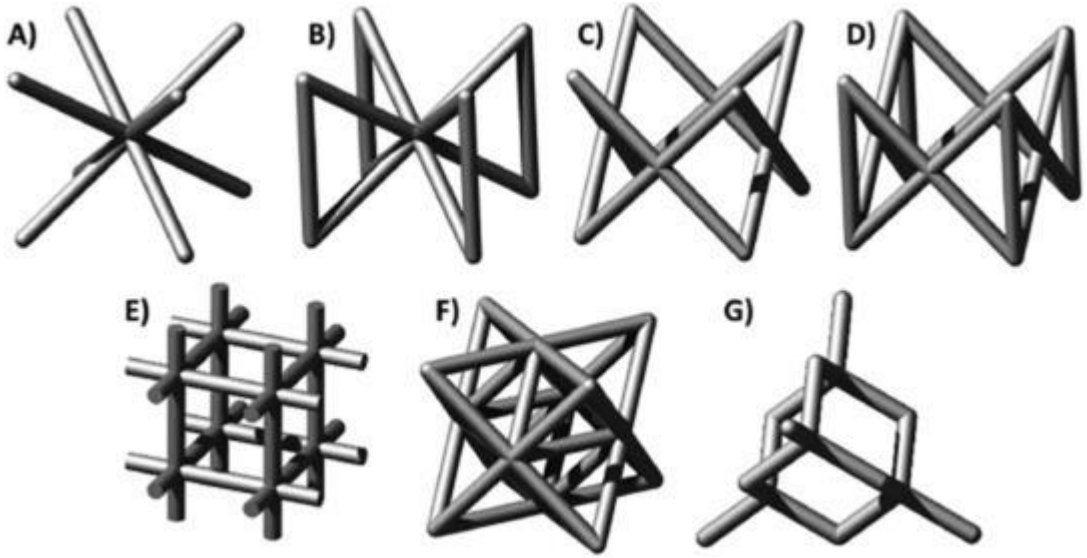
Geometrically defined lattice structure porosity



Mater Des 183 (2019) 108137

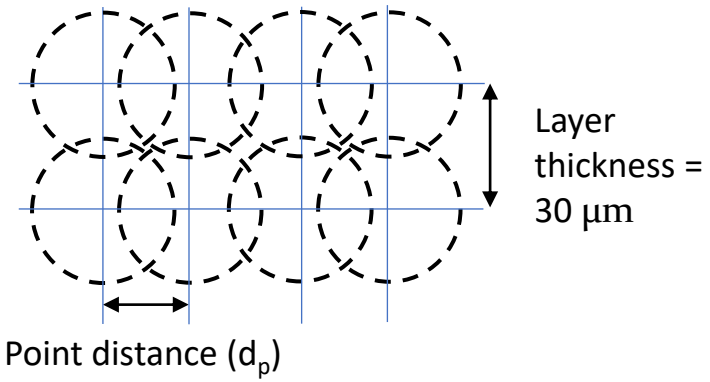
Laser powder bed fusion of thin walled porous structures

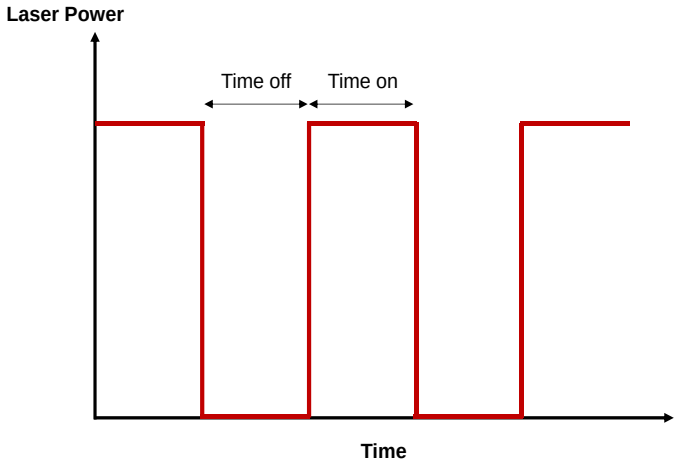
Geometrically undefined porosity

-Material: Ti-6Al-4V

-Single laser track per layer → Walls of 100-180 µm

-Porosity of ~30-60%

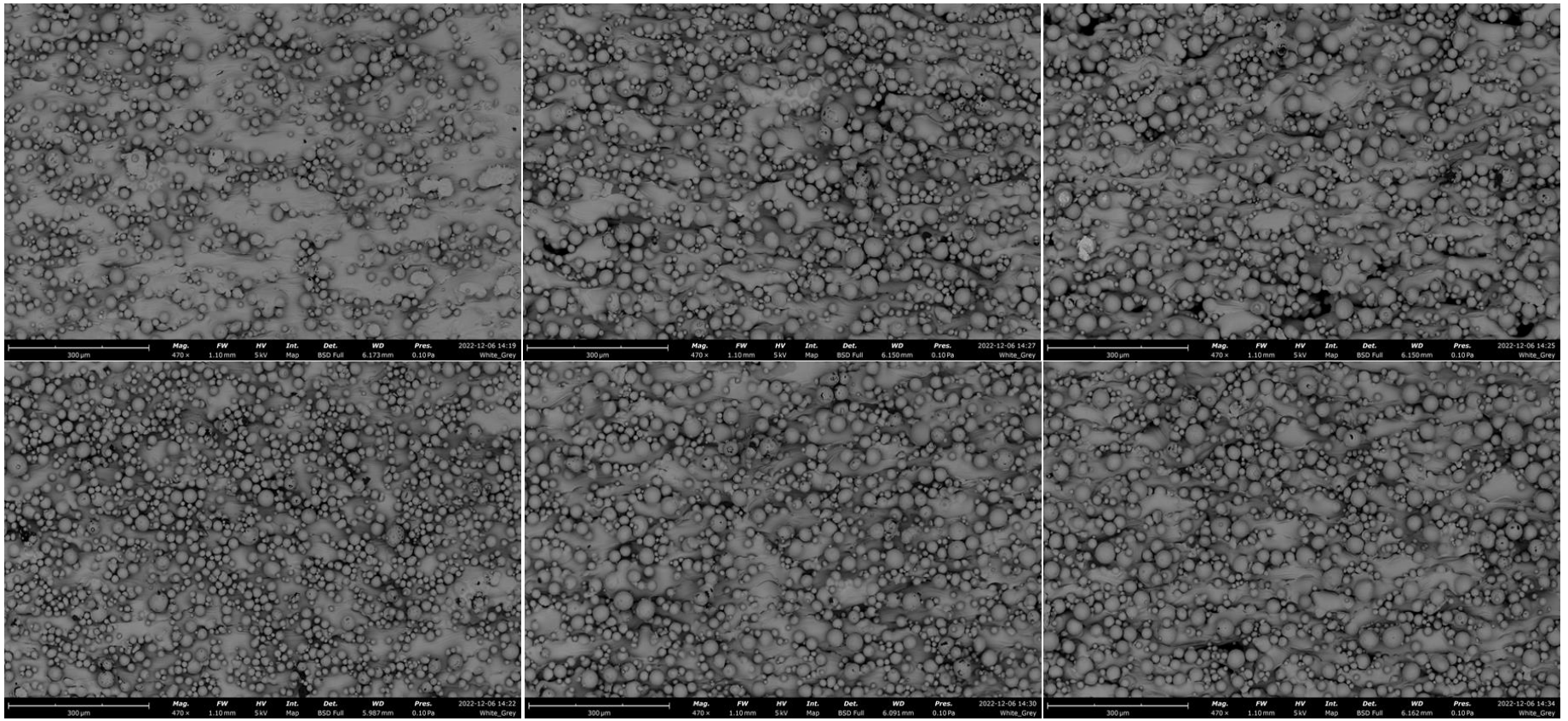




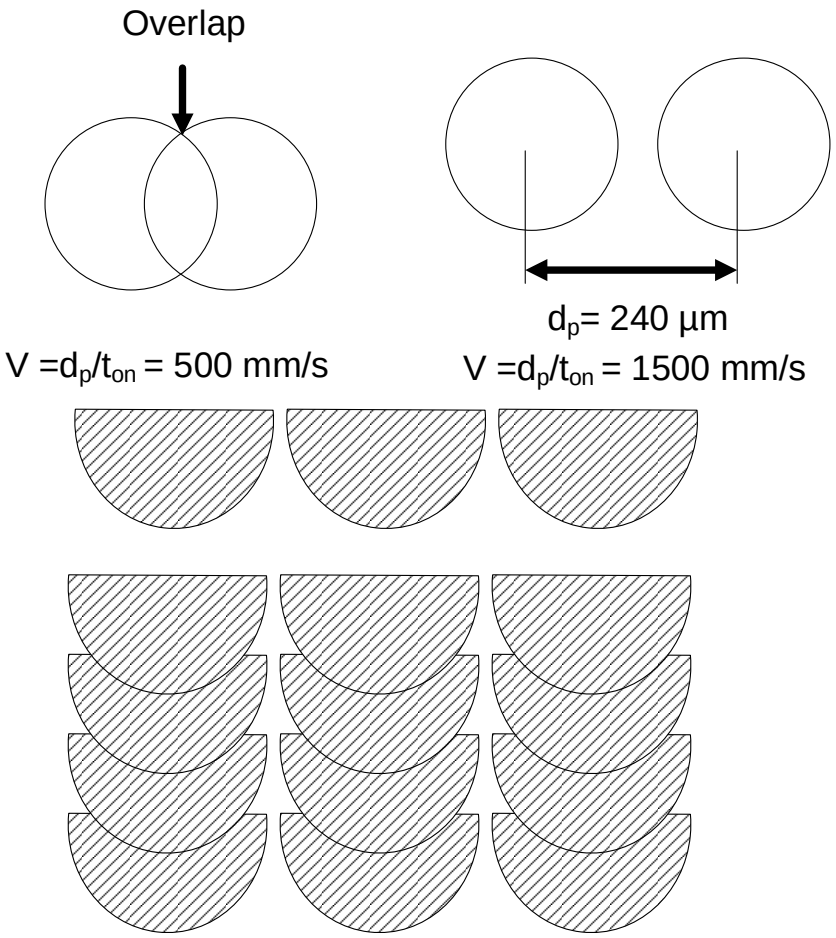
$$\delta = \frac{t_{on}}{t_{on} + t_{off}} \qquad v = \frac{d_p}{t_{on}}$$

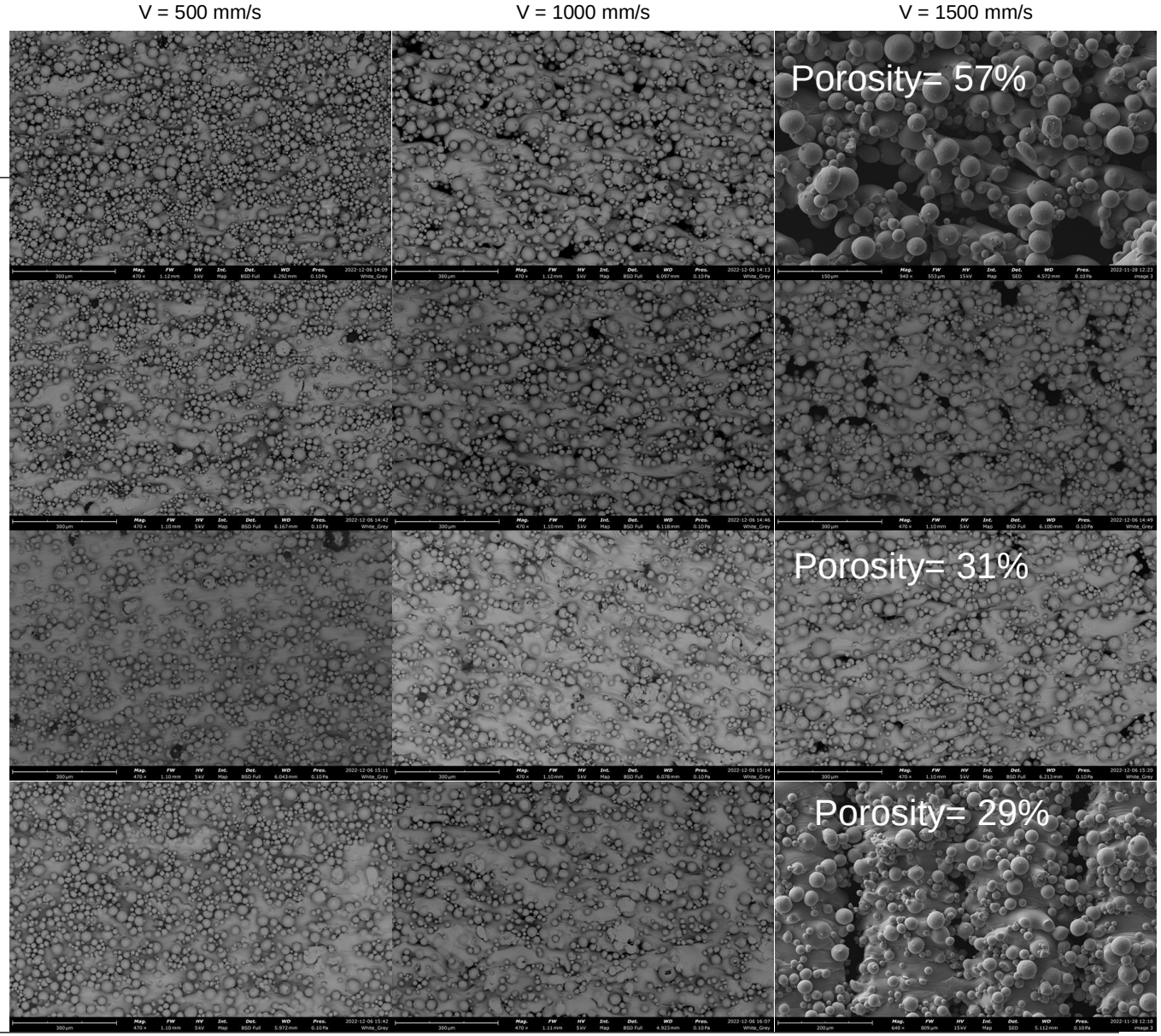
Variables:
Power = 100-200 W
v: scanning speed = 500-1500 mm/s
δ: duty cycle = 50-87.5%

SEM analysis: Powers of 150 and 200 W



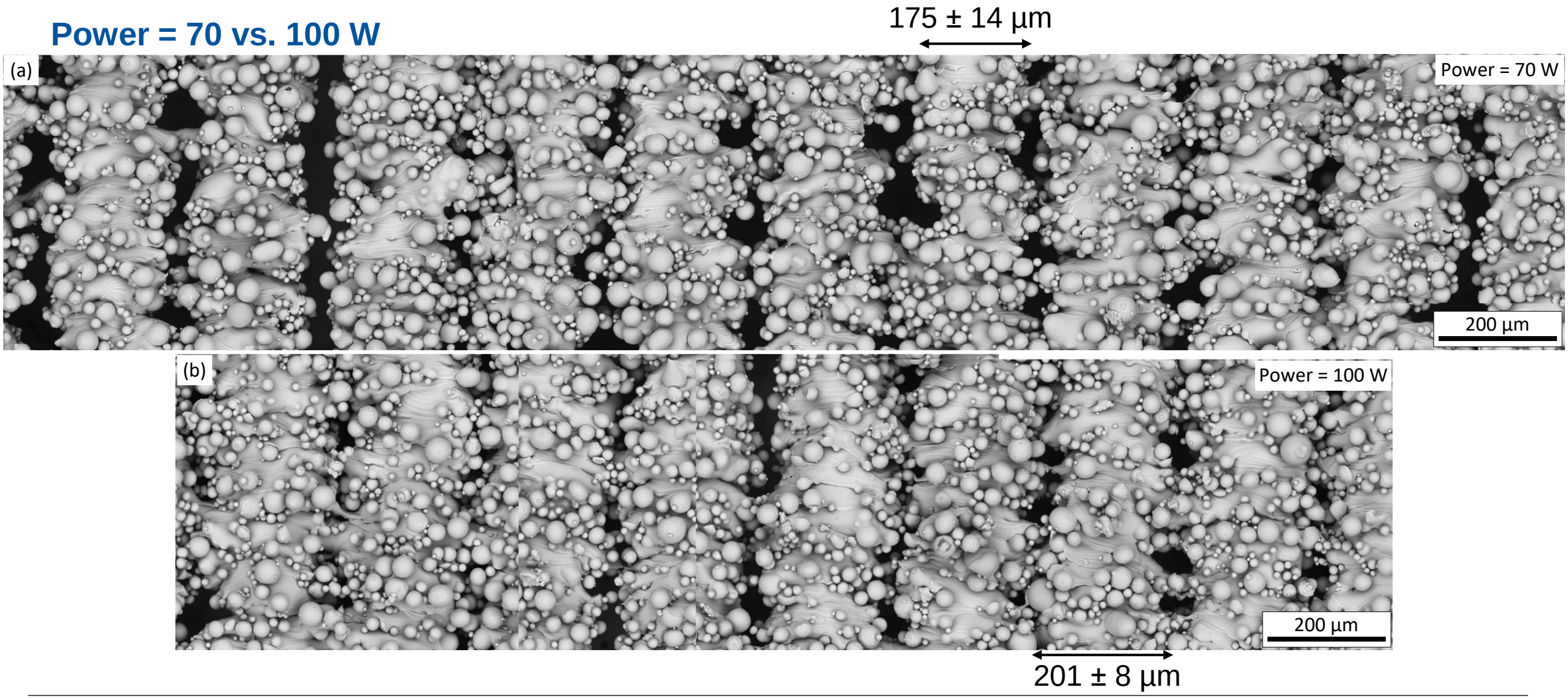
SEM analysis: Power of 100 W





DC = 87.5%; V = 1500 mm/s

Power = 70 vs. 100 W



Design of macro porosity

Geometrically defined lattice structure porosity

-Material: Ti-6Al-4V

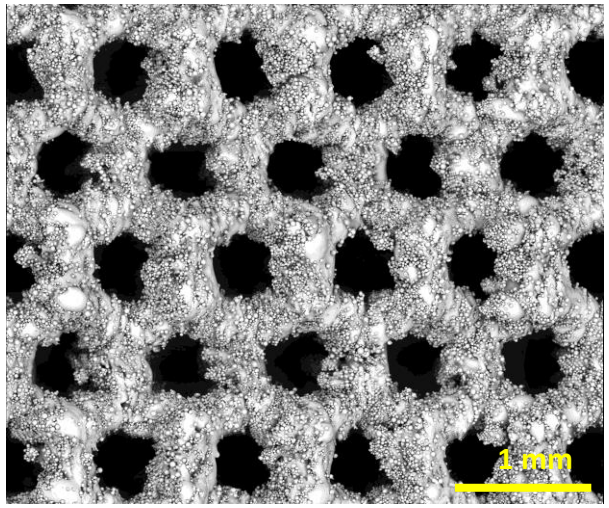
Variables:

-Lattice type: body cantered cubic (Bcc), octet, hexagon

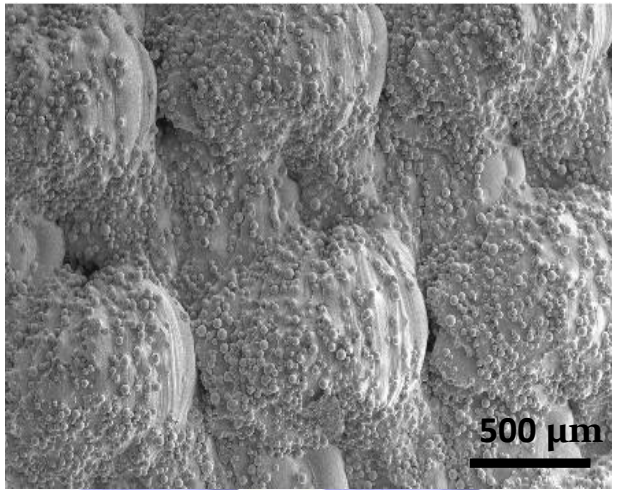
-Strut diameter: 0.15-0.4 mm

-Unit cell size: 0.5-1.5 mm

-Cell thickness: 0.5-1 mm



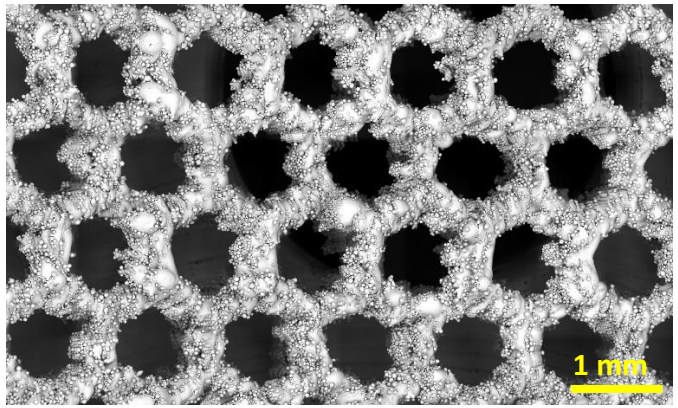
Hexagon
Unit cell: 1.2 × 1.5 × 1.5 mm
Strut: 0.25 mm



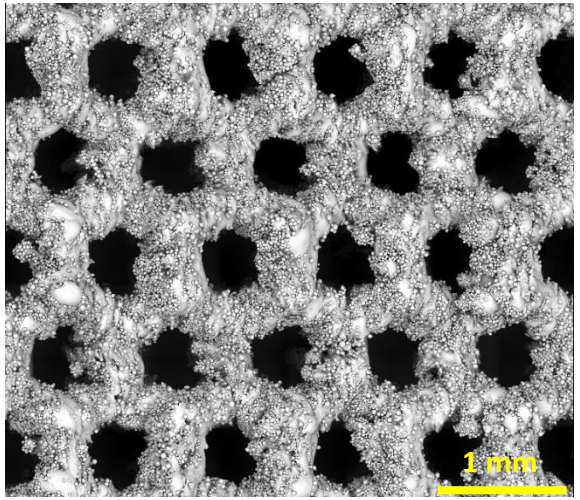
BCC
Unit cell: 1 mm
Strut: 0.4 mm

Geometrically defined lattice structure porosity

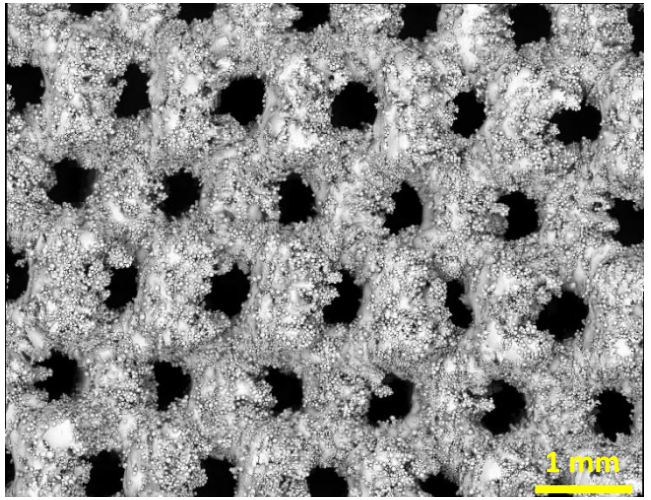
Hexagon unit cells of 1.2 × 1.5 × 1.5 mm; Struts of 0.15-0.35 mm



Strut thickness = 0.15 mm



Strut thickness = 0.25 mm

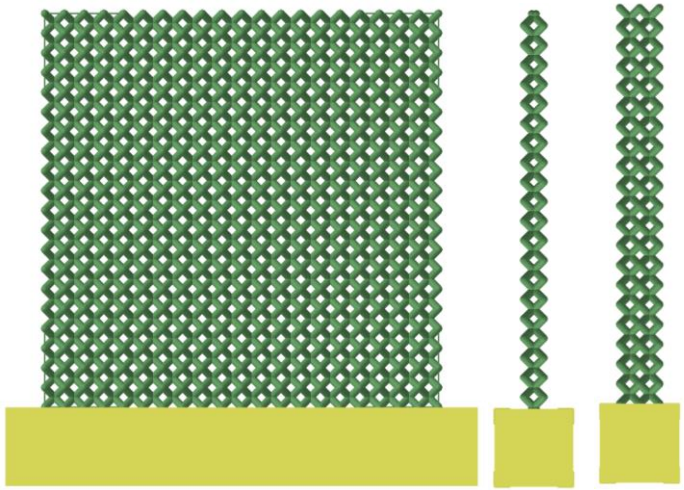


Strut thickness = 0.35 mm

Designed strut thickness (mm)	0.15	0.25	0.35
Measured pore diameter (mm)	0.77±0.04	0.47±0.04	0.42±0.08
Measured strut thickness (mm)	0.37±0.05	0.43±0.04	0.70±0.06

LPBF of Inconel 718 (In718): Design and laser parameters

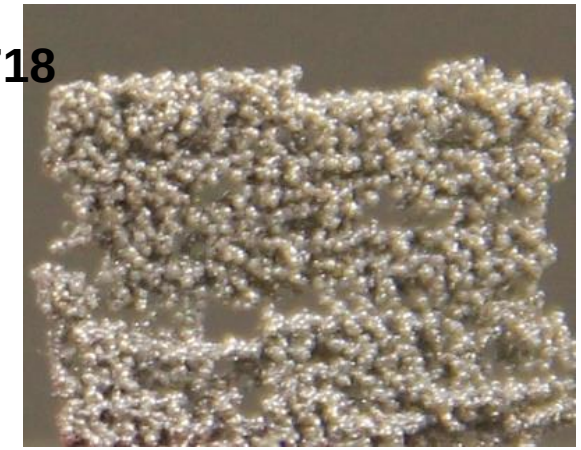
Cell (µm)	Strut, Ø (µm)	Thickness (µm)
500	100	500 (single layer)
500	100	1000 (double layer)
500	200	500 (single layer)
300	100	600 (double layer)
200	100	400 (double layer)



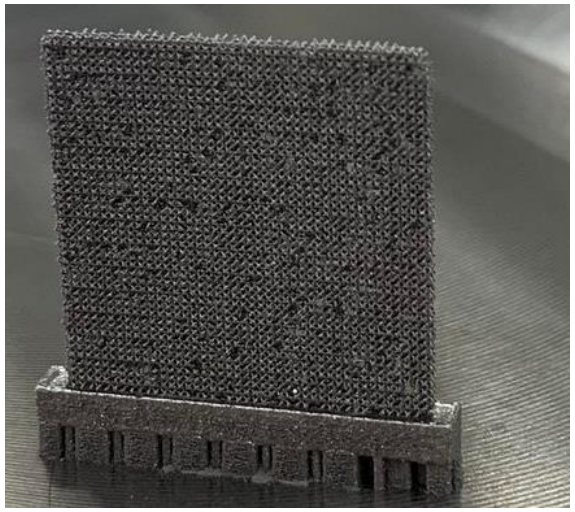
Power (W)	Exposure time (µs)	Point distance (µm)	VED (J/mm3)	Relative density (%)
70-200	40-100	50-90	10-40	80 to > 99

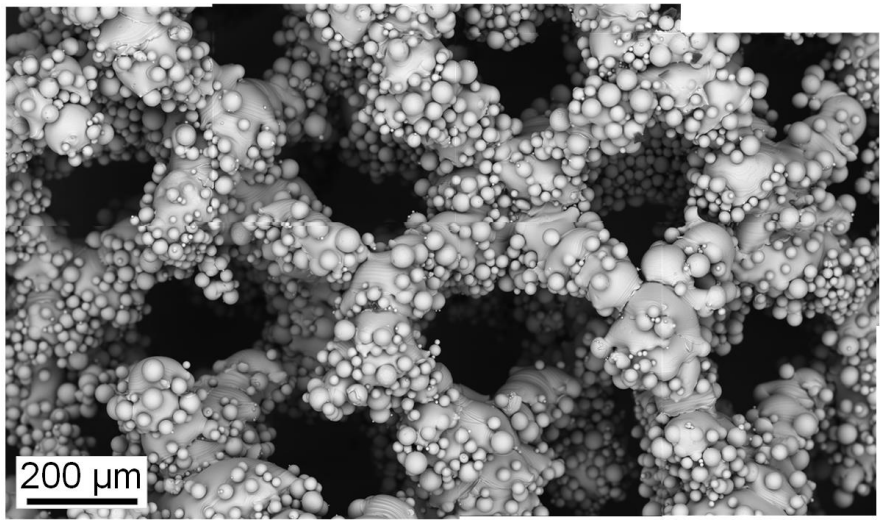
Unit cell= 0.5 mm, strut = 0.1 mm; double layers: Ti-6Al-4V vs. Inconel 718

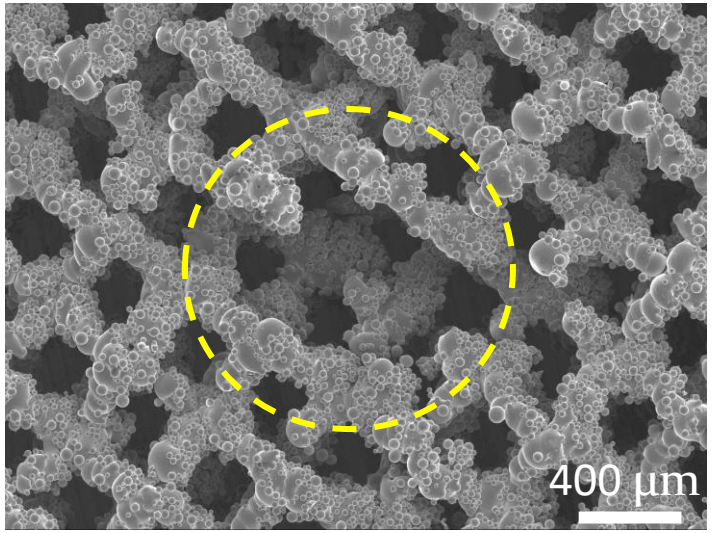
Inconel 718



Ti-6Al-4V



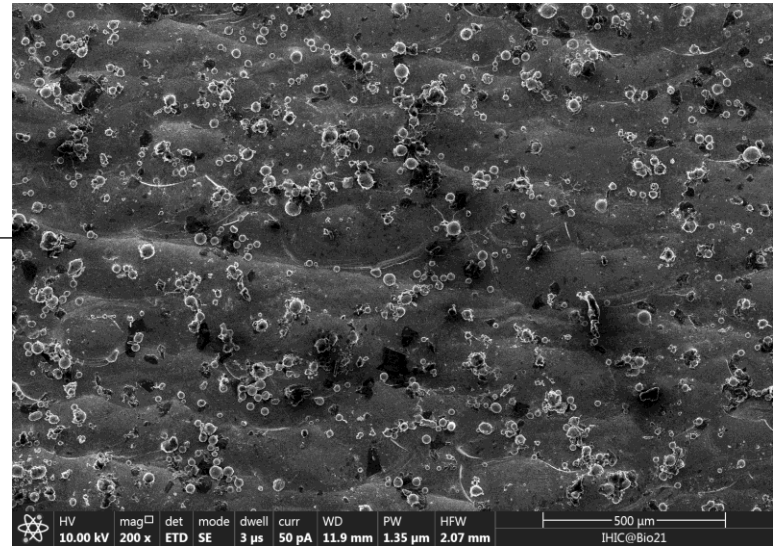


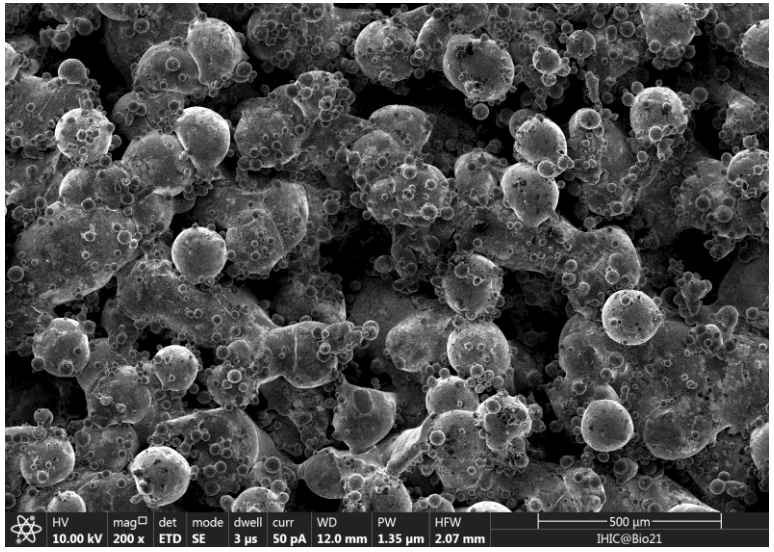


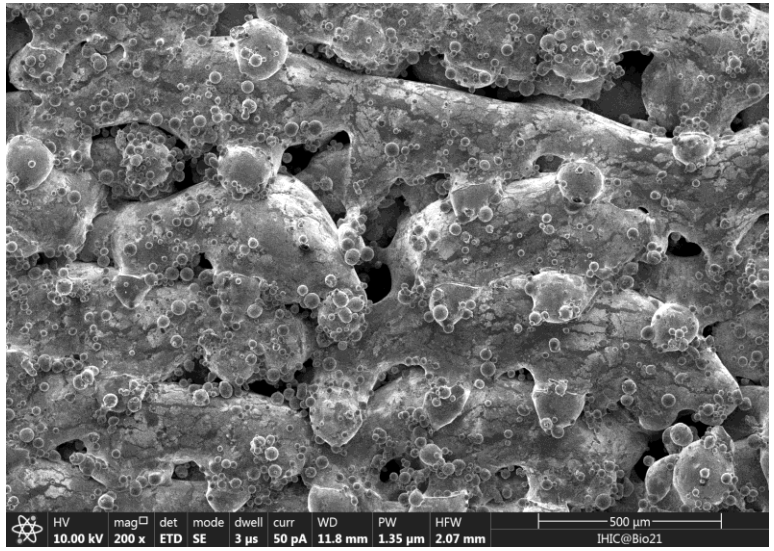
Double layers: Unit cells of < 500 µm; struts of 100 µm

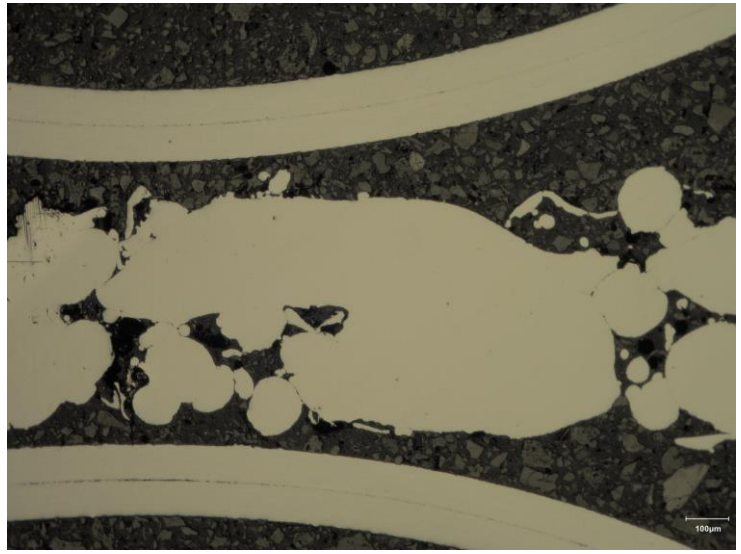
In-718: cell = 0.2 mm; strut: 0.1 mm, thickness = 0.4 mm (double layer)

Solid wall





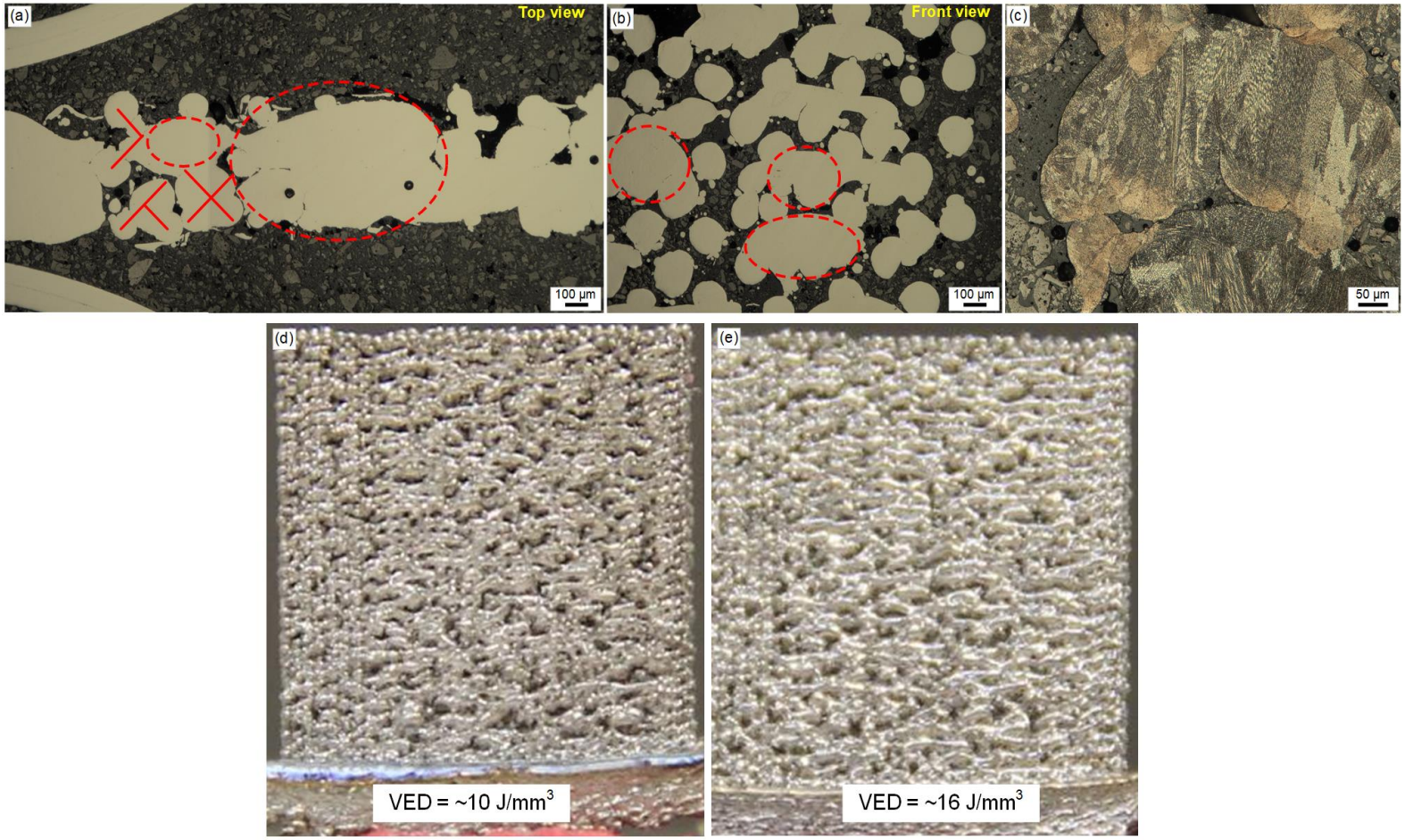




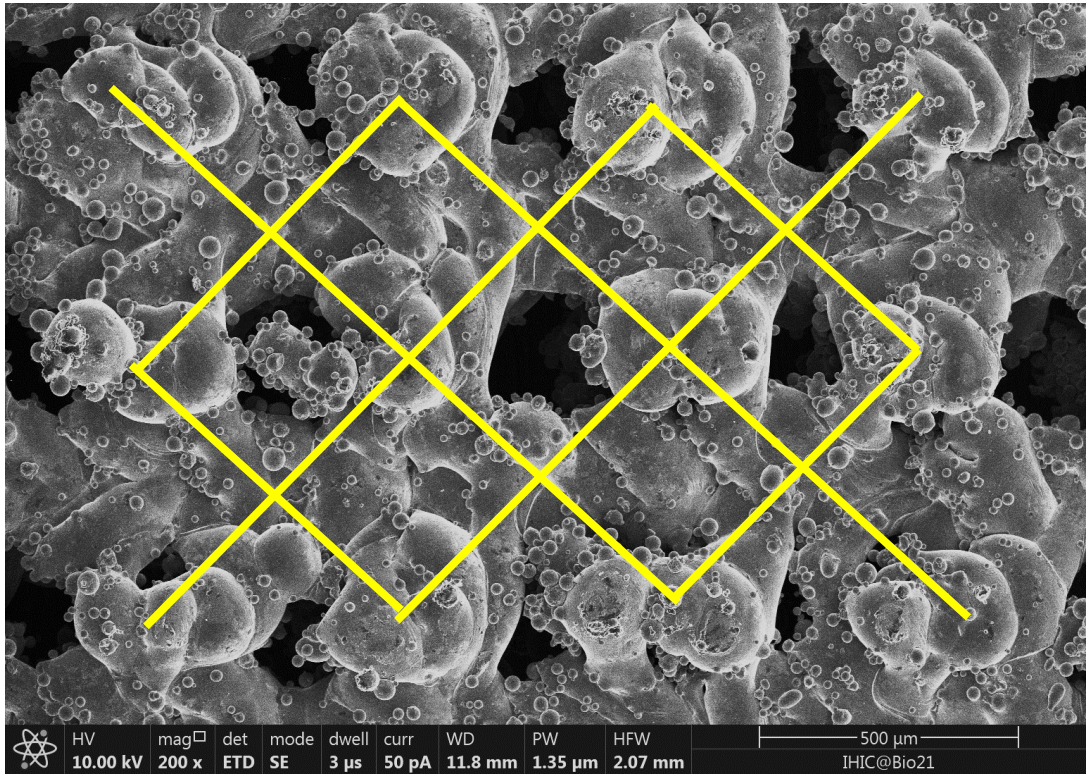
In718: cell = 0.3 mm; strut: 0.1 mm, thickness = 0.6 mm (double layer)

Coalescence of cells → Uneven cell/pore distributions

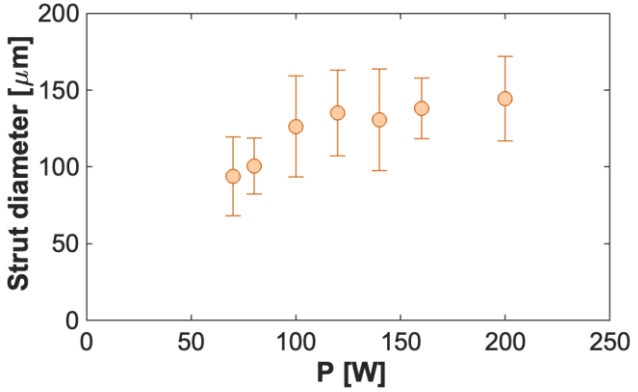
Microstructure and LPBF at low energy inputs: Unit cell = 300 µm

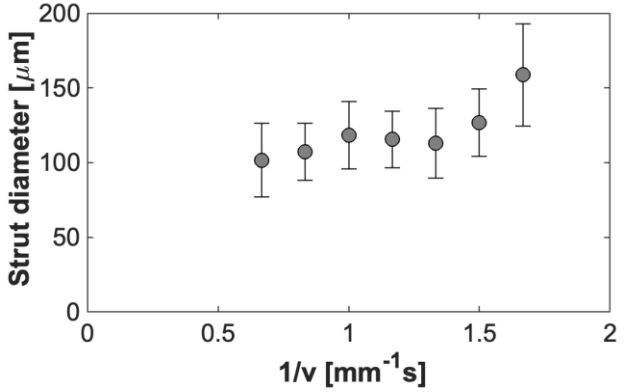


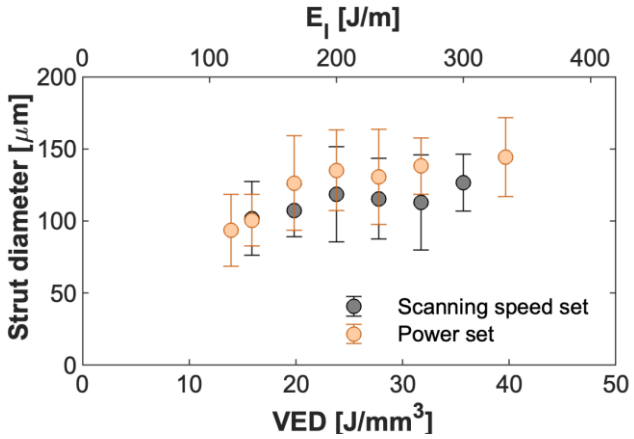
Single layers: Unit cells of 500 µm; struts of 200 µm

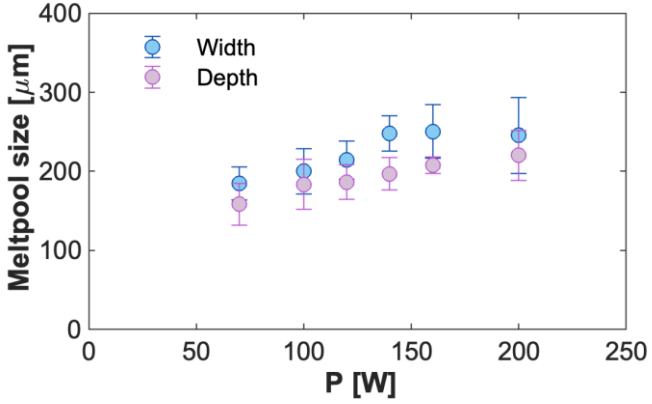


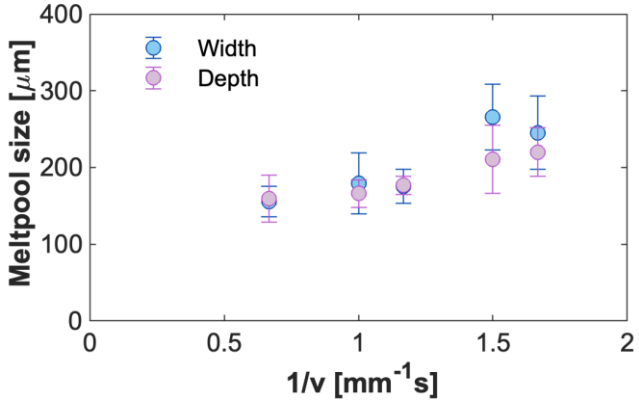
Effects of laser energy density on structure and microstructure characteristics

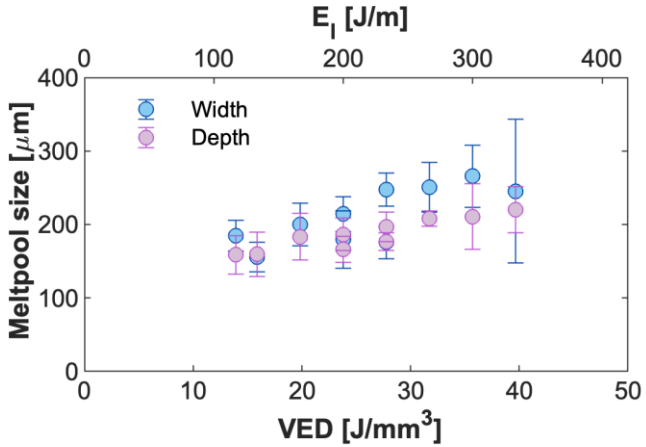




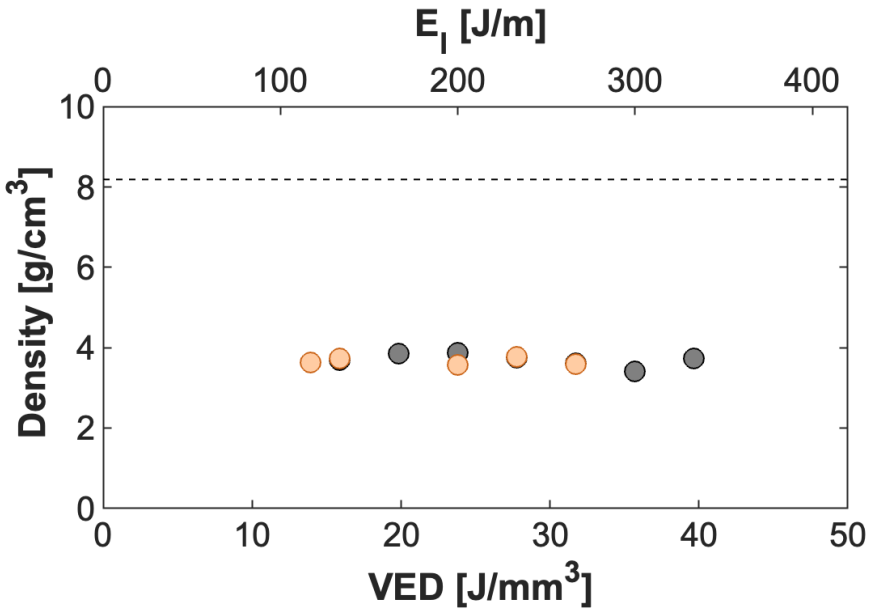


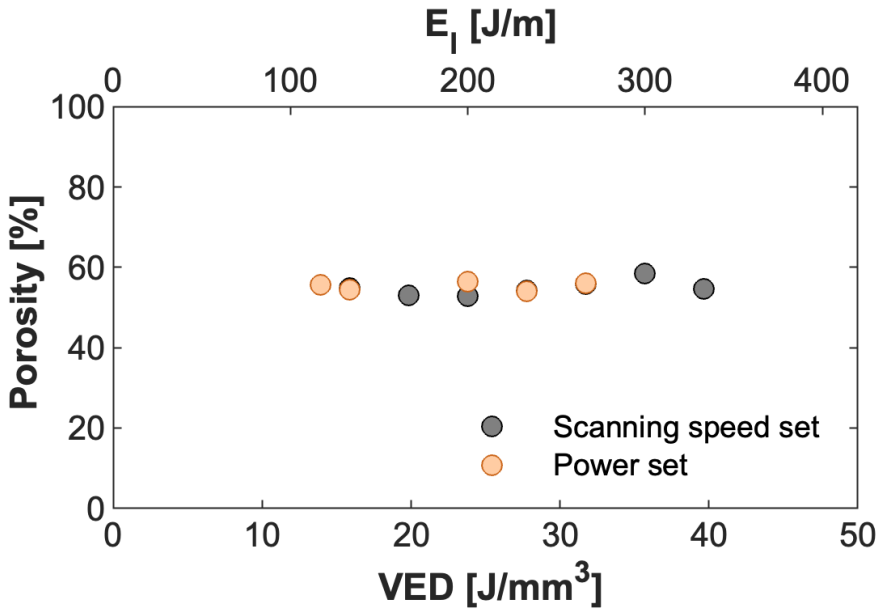




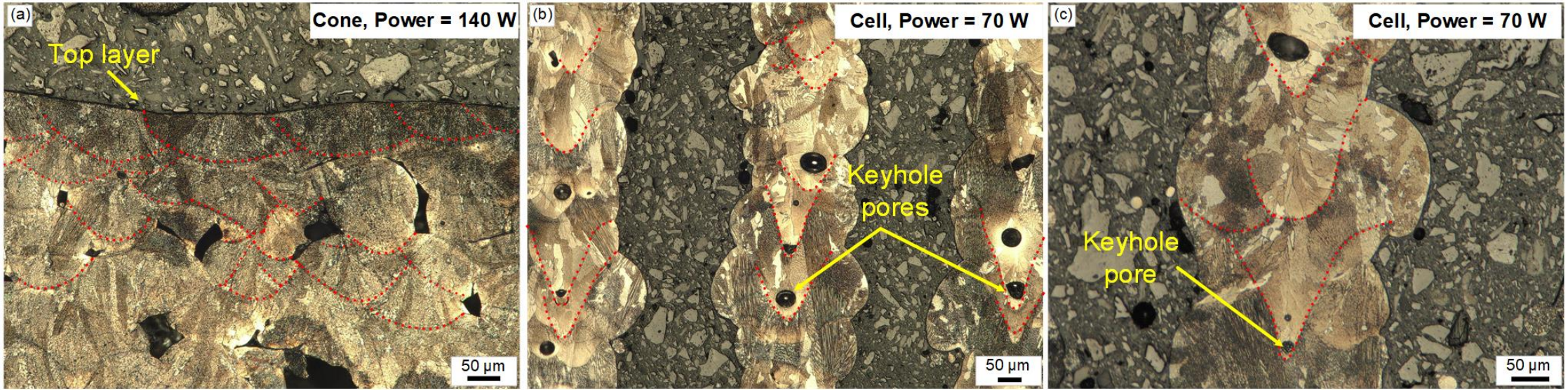


Porosity


E_l [J/m]
0
100
200
300
400
10
8
6
4
2
0
Density [g/cm^3]
0
10
20
30
40
50
VED [J/mm^3]


E_l [J/m]
0
100
200
300
400
100
80
60
40
20
0
Porosity [%]
0
10
20
30
40
50
VED [J/mm^3]
Scanning speed set
Power set

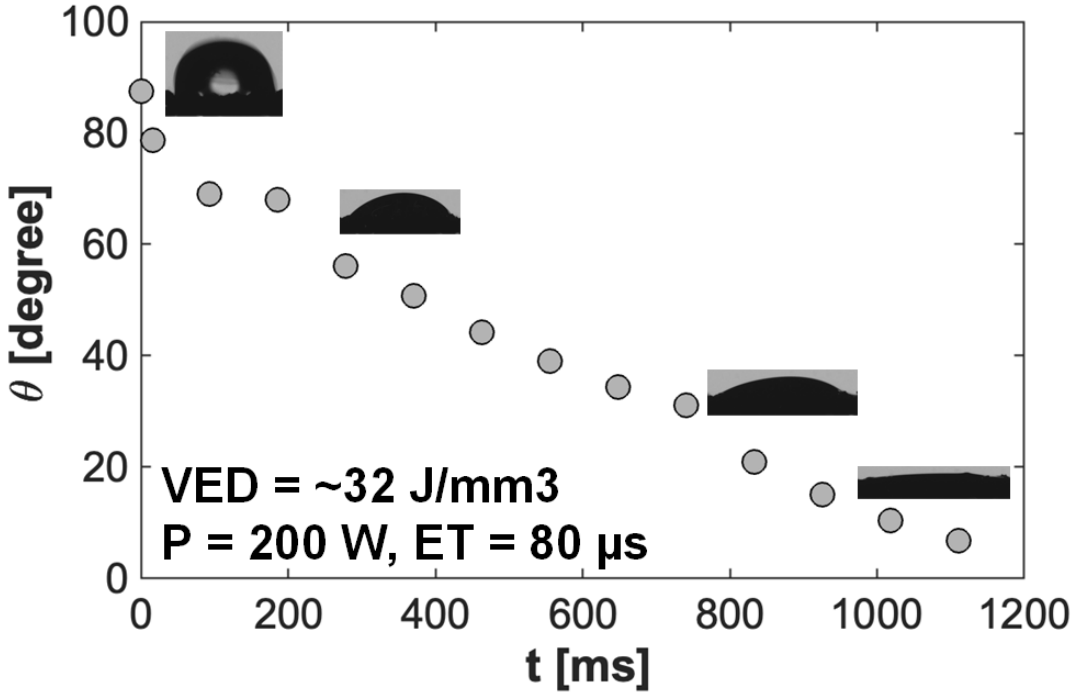
Strut-based lattice structure vs. bulk

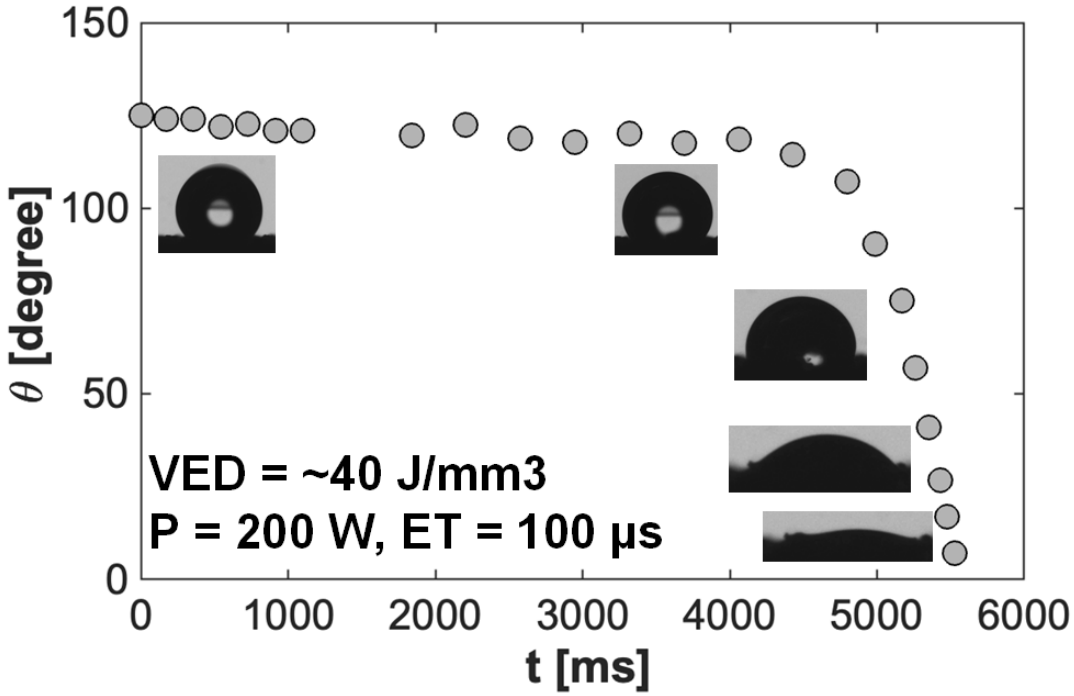


Bulk at P = 140 W
Depth = ~109.8±23
Width = ~227.5±37

Lattice/cell at P = 70 W
Depth = ~156±26
Width = ~185±20

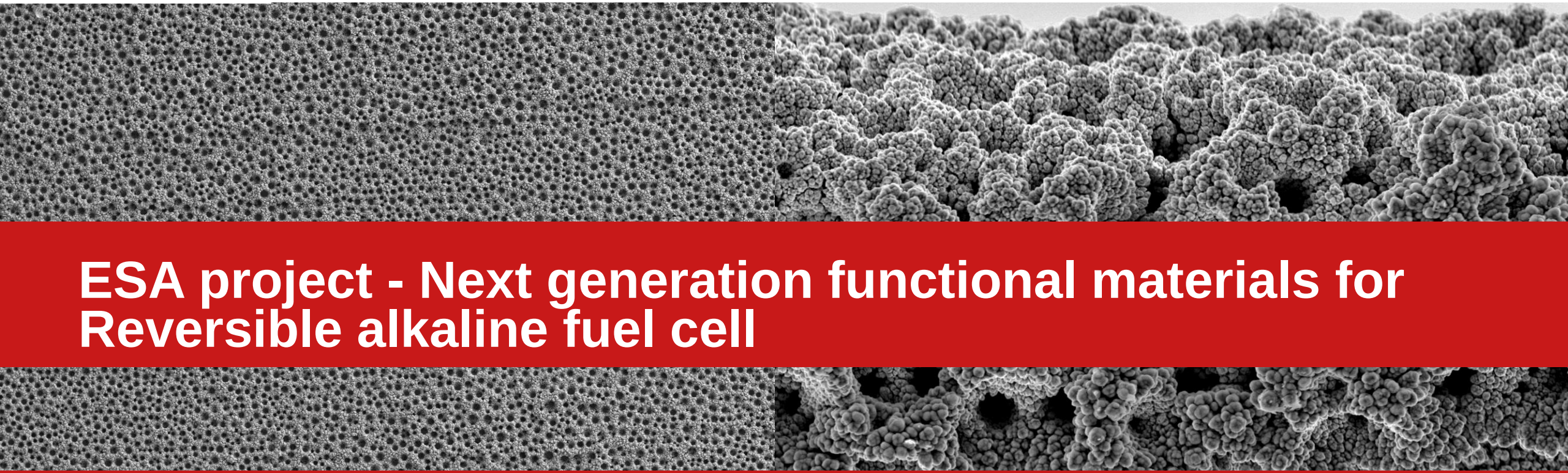
Wettability





Summary

- Laser parameters, particularly power and point distance, played important roles in fabricating regularly spaced pores/free spaces in thin electrodes (GDL) with great repeatability.
- Geometrically undefined pores of a few micrometres were much finer than those obtained from cellular structures in the range of > 100 µm.
- Design of unit cells and struts directly affected the pore sizes and porosity in strut-based lattice structures.
- Thinnest electrodes of 100-200 µm were obtained from thin walled Ti-6Al-4V, while the lattice structures were 0.5-1 mm in thickness.
- Laser parameters could affect wettability of lattice structures, although their effects on pore sizes and porosity were insignificant.



ESA project - Next generation functional materials for Reversible alkaline fuel cell

Ahmad Zafari, Salome Sanchez, Davoud Jafari, Inmaculada Gimenez Garcia, Antoni Forner Cuenca, Kiran

11.05.2023

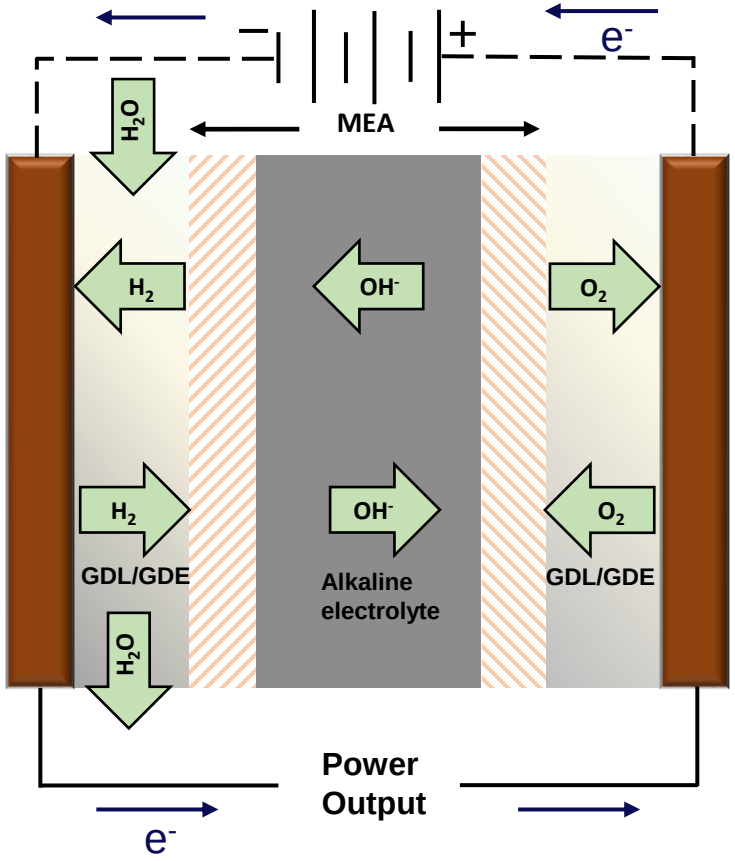
Membrane Materials & Processes

ELECTROCHEMICAL MATERIALS AND SYSTEMS

Department of Chemical Engineering and Chemistry

Reversible fuel cell operation

Electrc RAFC C) mode



	Cathode	Anode
EC Mode	$2\,H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2\,OH^- \rightarrow H_2O + 1/2O_2 + 2e^-$
FC Mode	$H_2 + 2OH^- \rightarrow 2\,H_2O + 2e^-$	$H_2O + 1/2\,O_2 + 2e^- \rightarrow 2\,OH^-$

H2 production: Methods

Technology	Energy source	Feedstock	Efficiency	Maturity
Steam reforming	Thermal	Hydrocarbons	70–85% [a]	Commercial
Partial oxidation	Thermal	Hydrocarbons	60–75% [a]	Commercial
Plasma reforming	Electric	Hydrocarbons	9–85% [b]	Long term
Ammonia reforming	Thermal	Ammonia	NA [c]	Near term
Biomass gasification	Thermal	Biomass	35–50% [a]	Commercial
Photolysis	Solar	Water	0.5% [d]	Long term
Dark fermentation	Biochemical	Biomass	60–80% [e]	Long term
Microbial electrolysis cell	Electric	Biomass	78% [g]	Long term
Alkaline electrolyzer	Electric	Water	50–60% [h]	Commercial
PEM electrolyzer	Electric	Water	55–70% [h]	Commercial
Solid oxide electrolysis cell	Electric+Thermal	Water	40–60% [i]	Mid term
Thermochemical water splitting	Thermal	Water	NA [c]	Long term
Photoelectrochemical water splitting	Solar	Water	12.4% [d]	Long term

[a] Thermal efficiency, based on the Higher Heating Values (HHV).
[B] Based on efficiency equation from [27].
[C] Not available.
[d] Solar to hydrogen via water splitting and does not include hydrogen purification.
[e] Percent of 4 mol H2 per mole glucose theoretical maximum.
[g] Overall energy efficiency including the applied voltage and energy in the substrate. It does not include hydrogen purification.
[h] Lower heating value of hydrogen produced divided by the electrical energy to the electrolysis cell.
i High-temperature electrolysis efficiency is dependent on the temperature the electrolyzer operates at and the efficiency of the thermal energy source.

Advances in alkaline water electrolyzers: A review https://doi.org/10.1016/j.est.2019.03.001

Functional materials: electrodeposition based

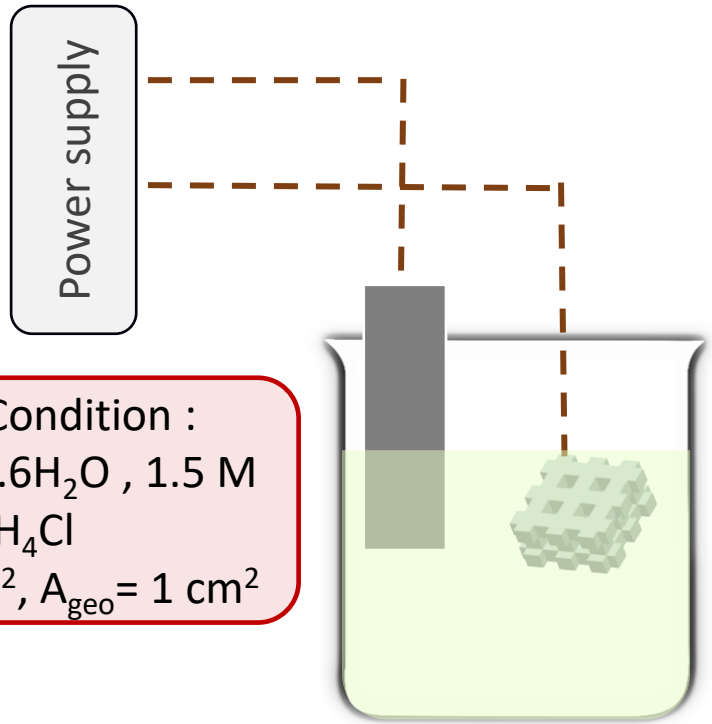
Material/ catalyst	Substrate	Method	Conditions/ Ref.
Ni-Se	Ni foam	Pulse electrodeposition	Square wave 0-0.8$_{SCE}$ [1]
Pt@GO@Ni-Cu@NF	Ni foam	Reverse Pulse electro- deposition	-0.4V_{SCE} for 120s [2]
Ni-Cu@NF	Ni foam	Electrodeposition	2A/cm^2 , 120s [3]
Ni-P	Ti foil	Pulse electrodeposition	-1V_{SCE} for t_{on} 10ms for 30 min [4]
3D-NiFe layered double hydroxide	3D printed graphene		-1.3 V vs SCE for 15 min at 10° C [4]
3D-NiMo	-	3D Printing	resorcinol-based polymer [5]
Ni_xCu_{1-x} /Porous Ni	-	Electrodeposition and de-alloying	-0.75 V to -1.0 V, deposition charge 3C/cm^2 [6]
Ni foam	Cu foil	Electrodeposition	Applied current/potential, time of deposition varied [7]
NiFe alloy	Cu plate	Electrodeposition	Galvanostatic for 900s [8]

References:

1. Esmailzadeh, S.S., T. Barati Darband, Gh Yaghoubinezhad, Y. , *Pulse electrodeposition of nickel selenide nanostructure as a binder-free and high-efficient catalyst for both electrocatalytic hydrogen and oxygen evolution reactions in alkaline solution.* 2020. **334**.
2. Lotfi, N.S., T. Yaghoubinezhad, Y. Darband, Gh Barati *Direct electrodeposition of platinum nanoparticles@graphene oxide@nickel-copper@nickel foam electrode as a durable and cost-effective catalyst with remarkable performance for electrochemical hydrogen evolution reaction.* 2020. **505**.
3. Lotfi, N.S., T. Yaghoubinezhad, Y. Barati Darband, Gh, *Electrodeposition of cedar leaf-like graphene Oxide@Ni–Cu@Ni foam electrode as a highly efficient and ultra-stable catalyst for hydrogen evolution reaction.* 2019. **326**.
4. Kim, H.P., Hyanjoo Kim, Dong Kwon Choi, Insoo Kim, Soo Kil, *Pulse-electrodeposited nickel phosphide for high-performance proton exchange membrane water electrolysis.* 2019. **785**: p. 296-304.
5. Sullivan, I., et al., *3D printed nickel-molybdenum-based electrocatalysts for hydrogen evolution at low overpotentials in a flow-through configuration.* 2021. **13**: p. 20260-20268.
6. Sun, L., C.-L. Chien, and P.C. Searson, *Fabrication of Nanoporous Nickel by Electrochemical Dealloying.* Chemistry of Materials, 2004. **16**(16): p. 3125-3129.
7. Sengupta, S., et al., *A Study on the Effect of Electrodeposition Parameters on the Morphology of Porous Nickel Electrodeposits.* Metallurgical and Materials Transactions A, 2018. **49**.
8. Ullal, Y. and A.C. Hegde, *Electrodeposition and electro-catalytic study of nanocrystalline Ni–Fe alloy.* International Journal of Hydrogen Energy, 2014. **39**(20): p. 10485-10492.

Foam deposition: DHBT

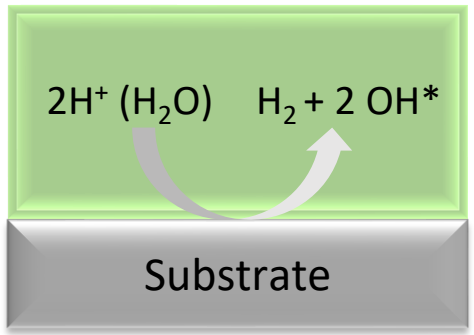
(a)

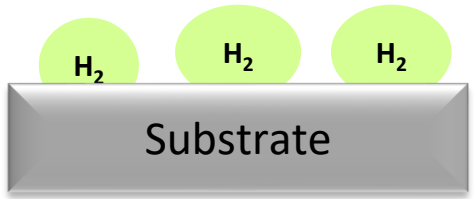


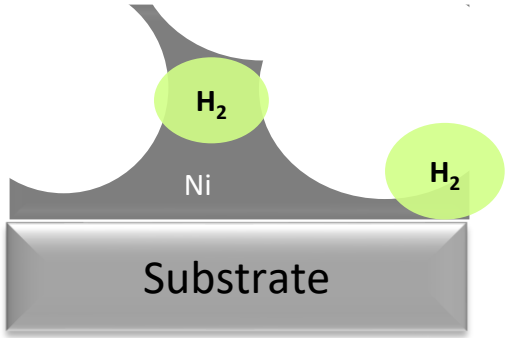
Plating Condition :
0.1 M $NiCl_2.6H_2O$, 1.5 M NH_4Cl
i = - 3 A cm^{-2}, A_{geo}= 1 cm^2

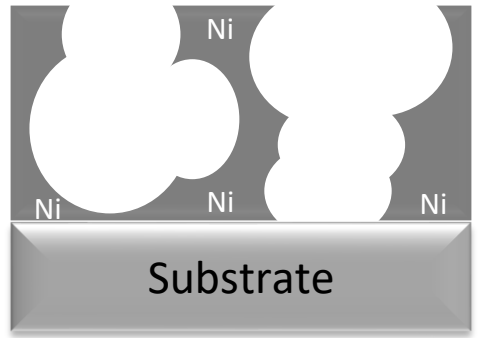
(b)

TiAlV (T2)









❑ Effect of pore size distribution and loading?

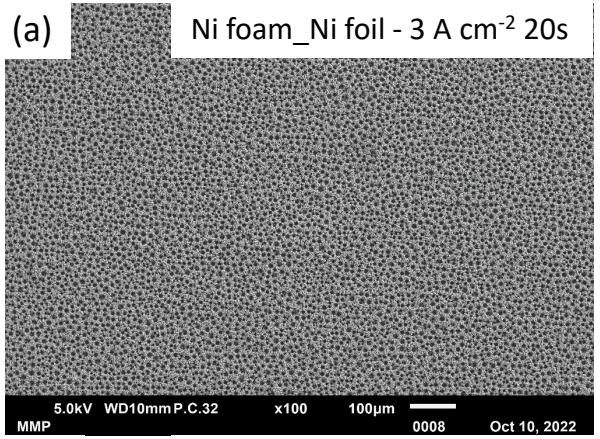
❑ Applied Deposition current density

❑ Deposition Time

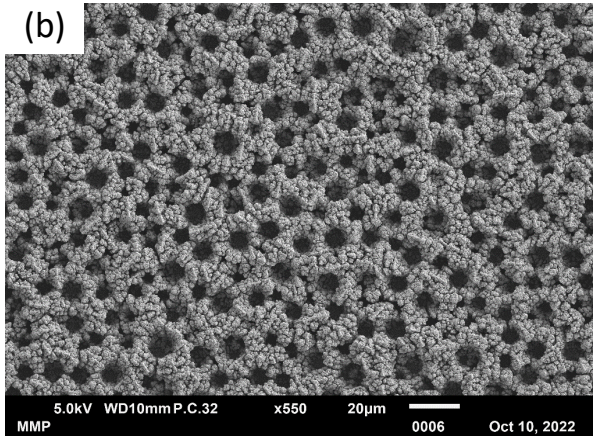
Pore size distribution : constant applied current density

Increasing deposition time

(a) Ni foam_Ni foil - 3 A cm^{-2} 20s



(b)



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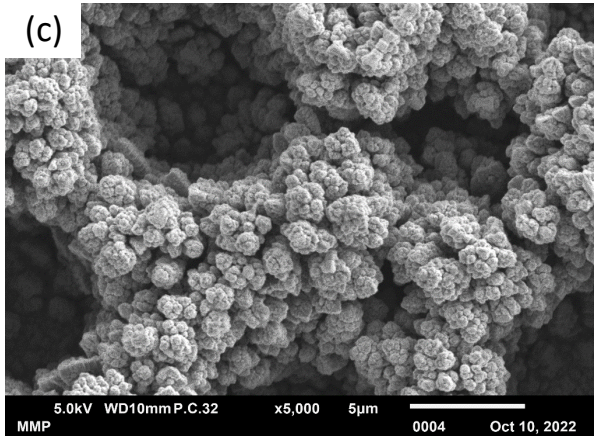
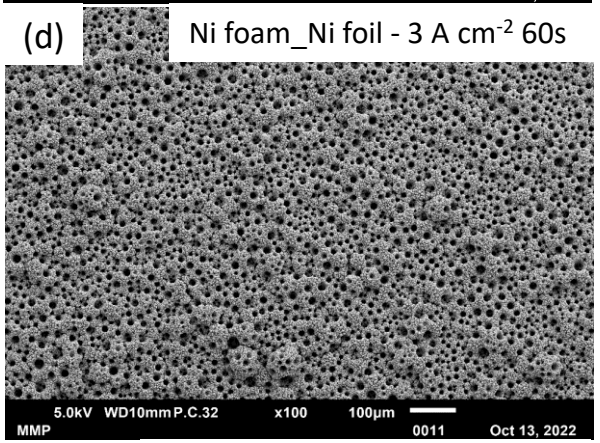


(d) Ni foam_Ni foil - 3 A cm^{-2} 60s



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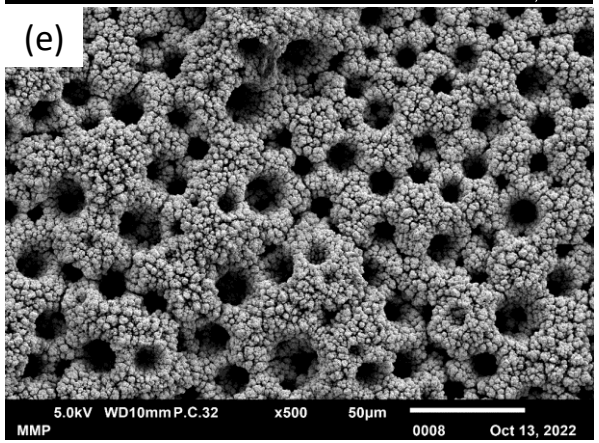

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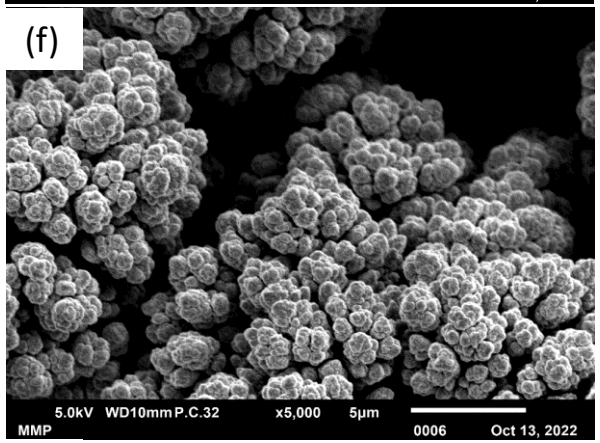
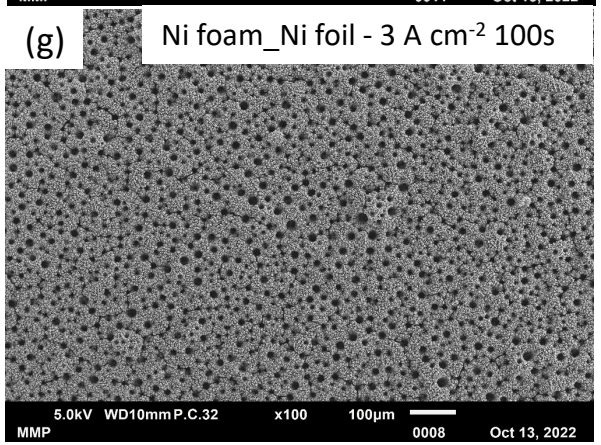


(g) Ni foam_Ni foil - 3 A cm^{-2} 100s



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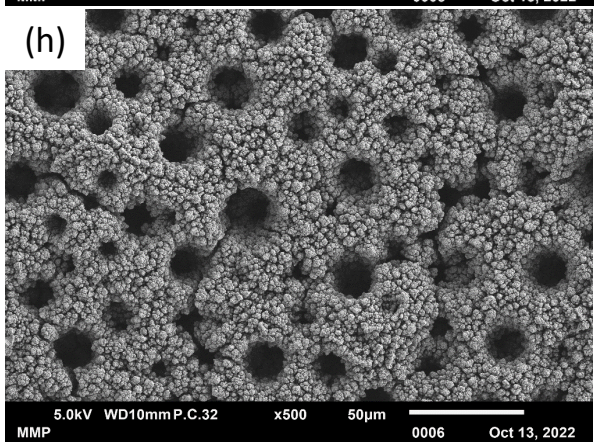
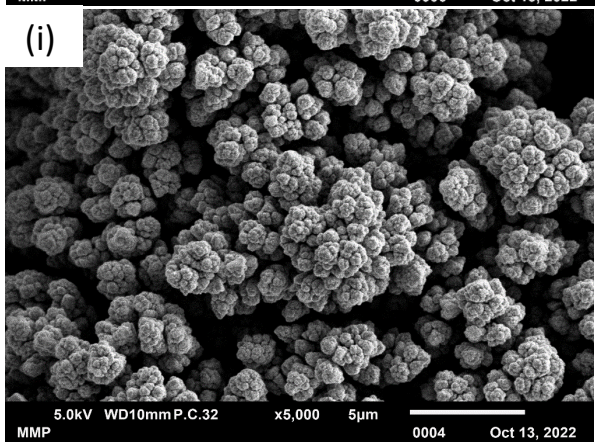
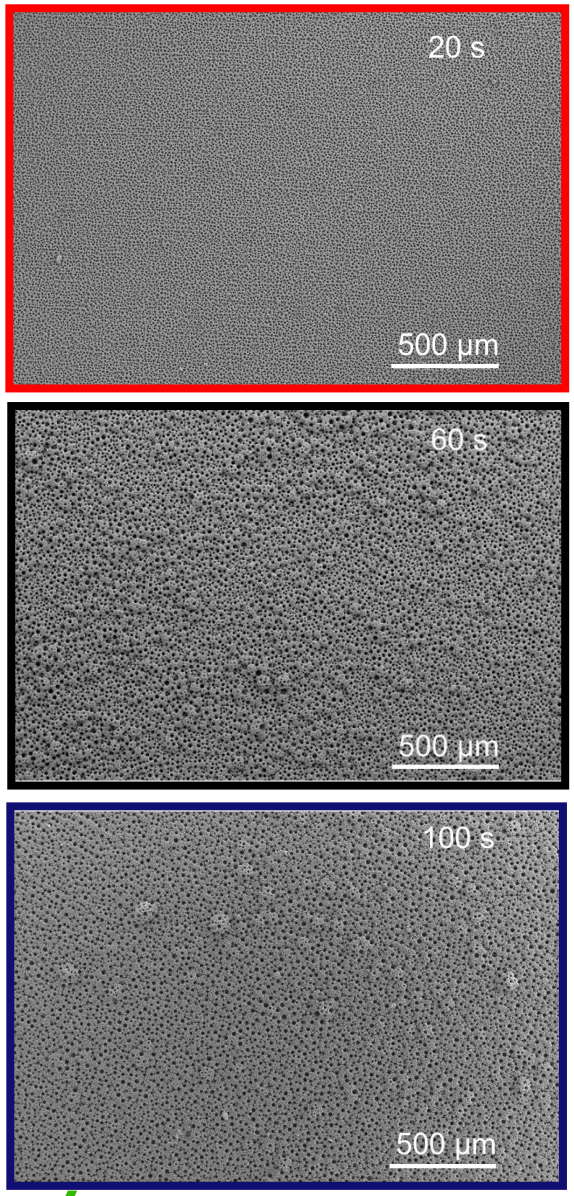


(i)

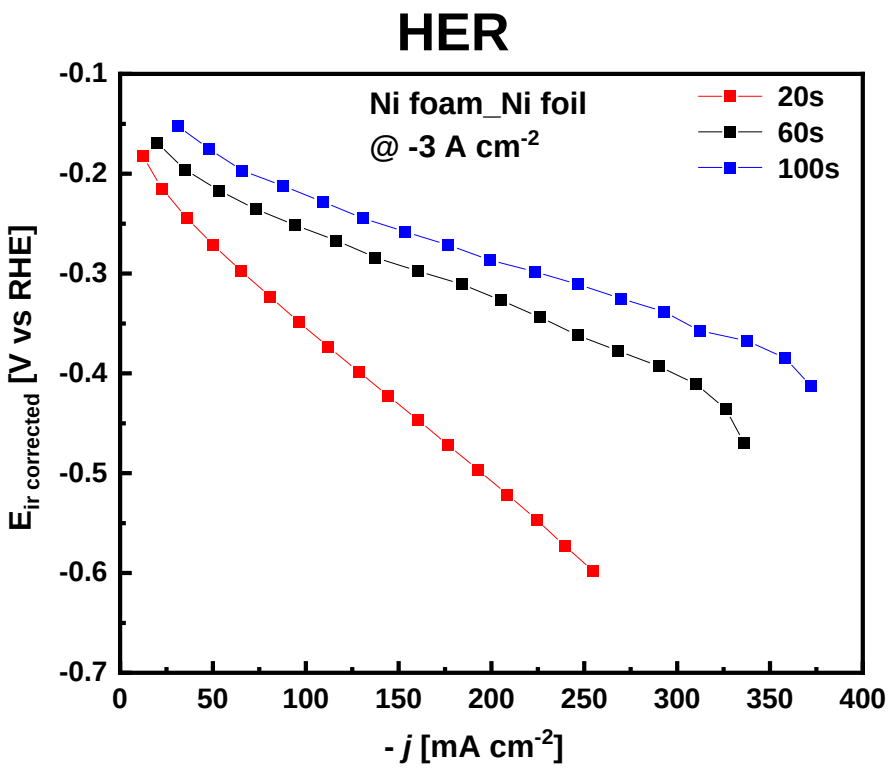


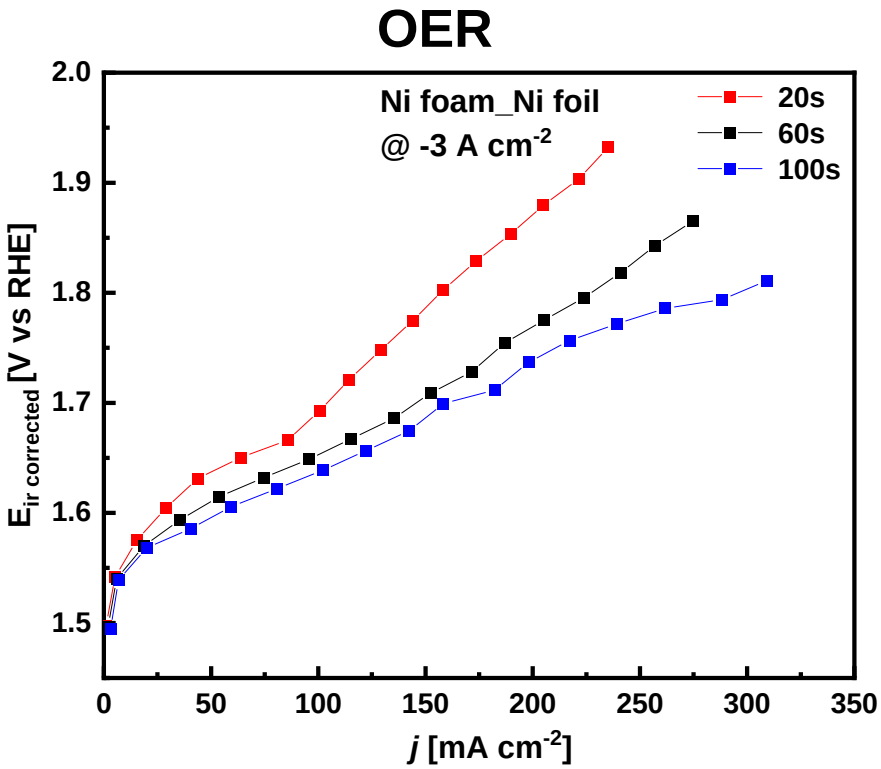
Increasing pore size

Electrochemical Analysis: Constant applied current density



Polarization Curves





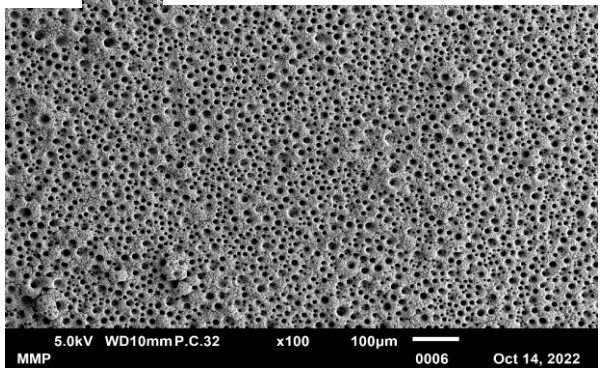
- Higher deposition times results in higher loading, in turn increasing ECSA leading to better performance towards HER and OER.

Pore size distribution : constant deposition time

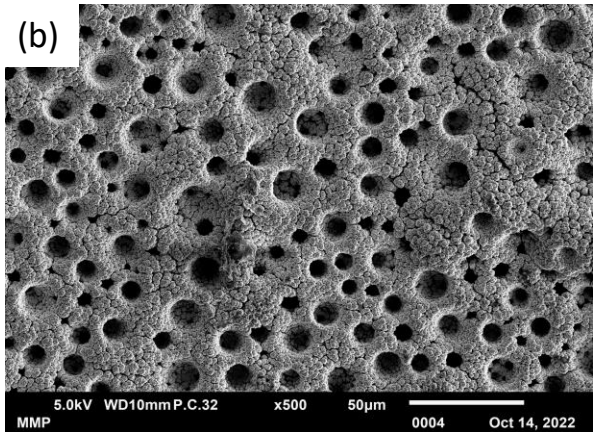
Applied current density

Increasing pore size

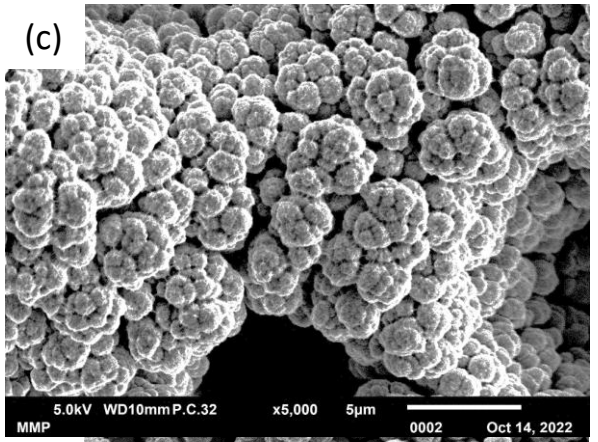
(a) Ni foam_Ni foil - 1 A cm^{-2} 100s



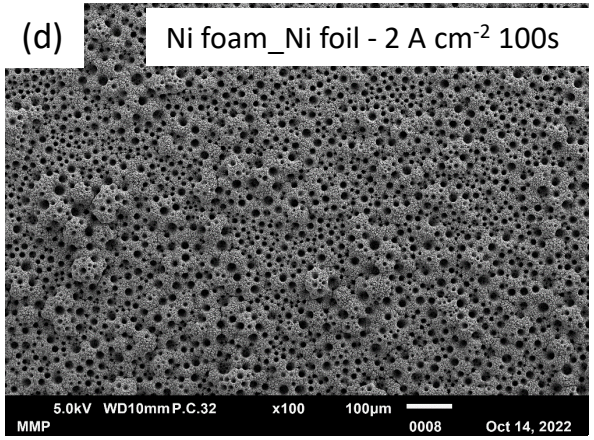
(b)



(c)



(d) Ni foam_Ni foil - 2 A cm^{-2} 100s



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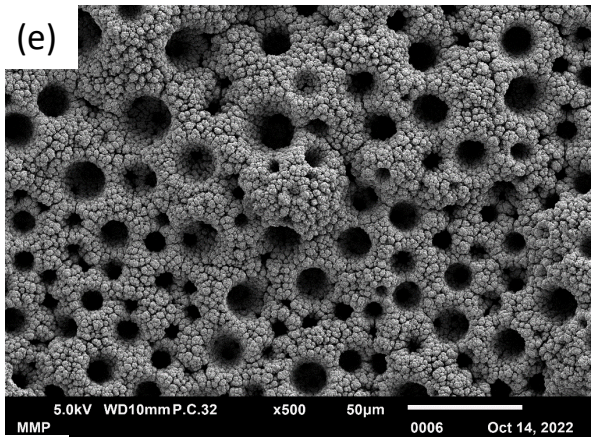
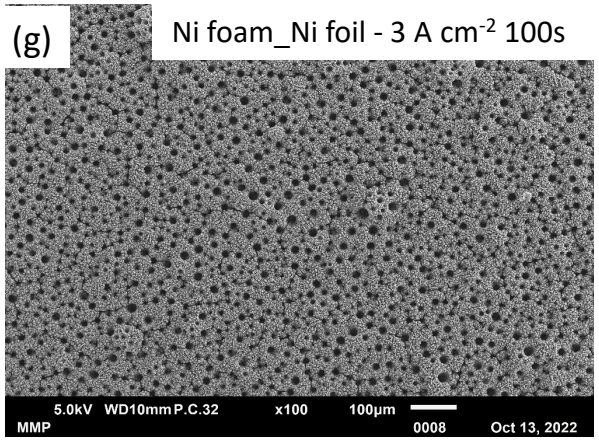
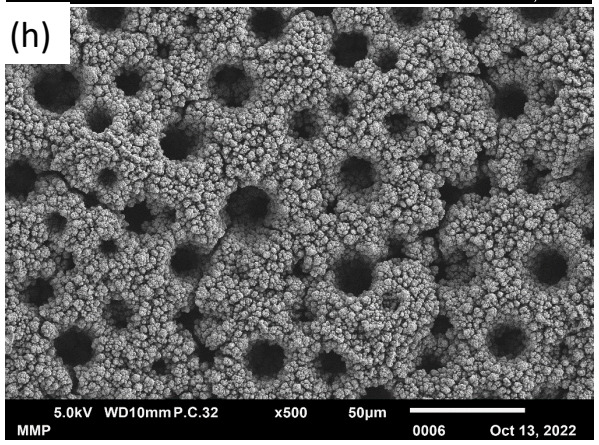


(f)

(g) Ni foam_Ni foil - 3 A cm^{-2} 100s



(h)



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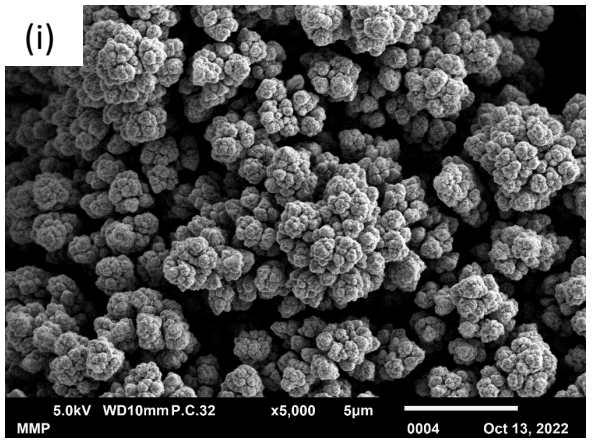
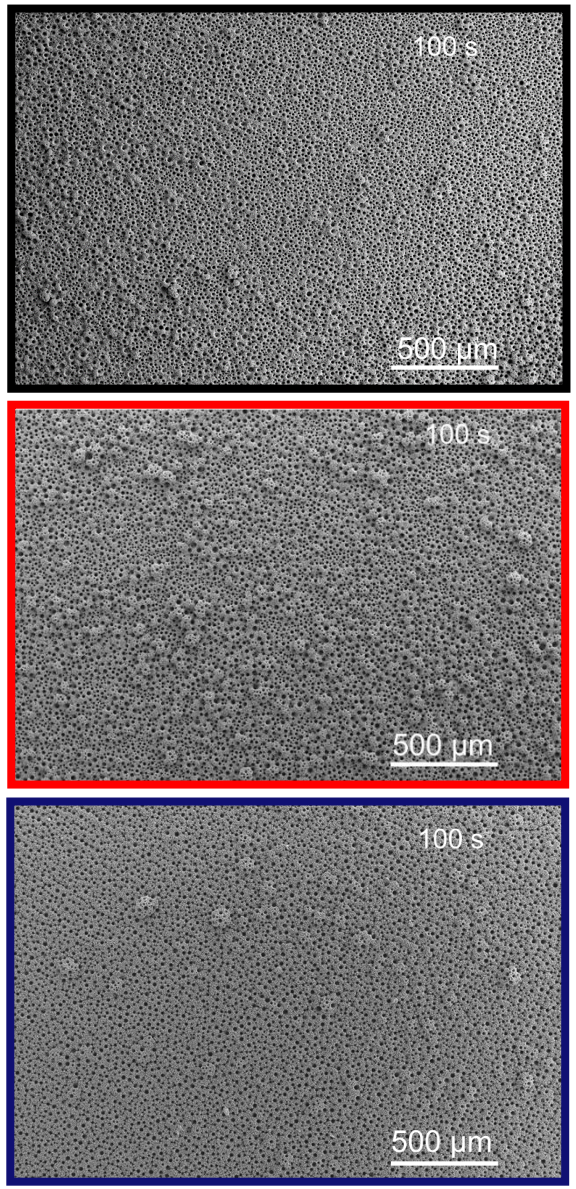


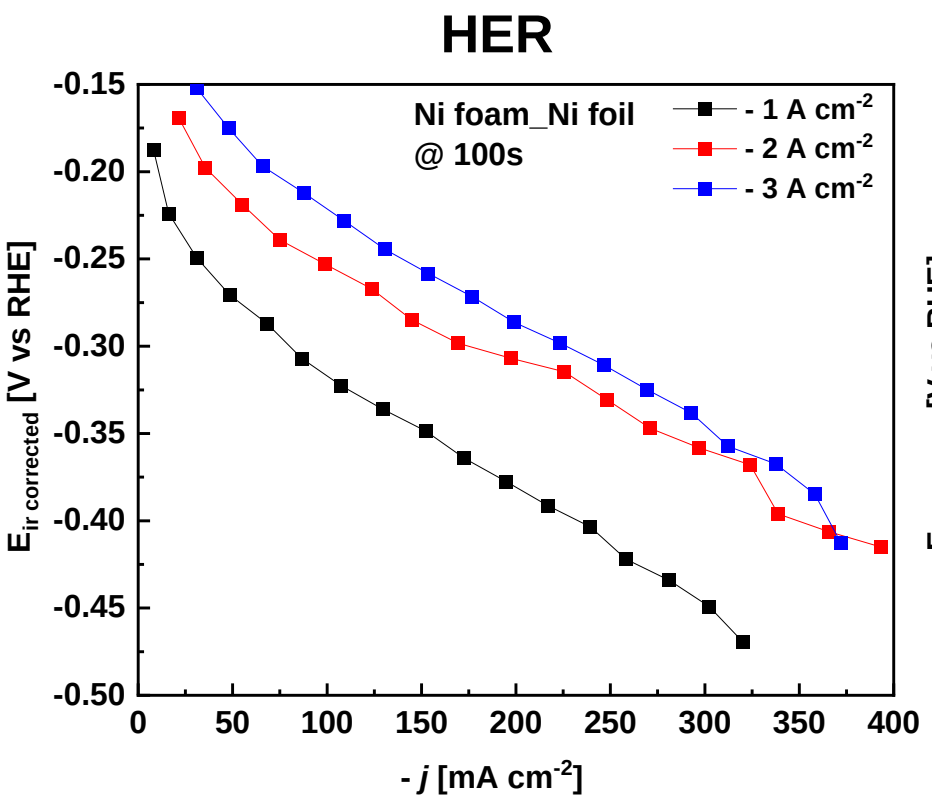
MM/P

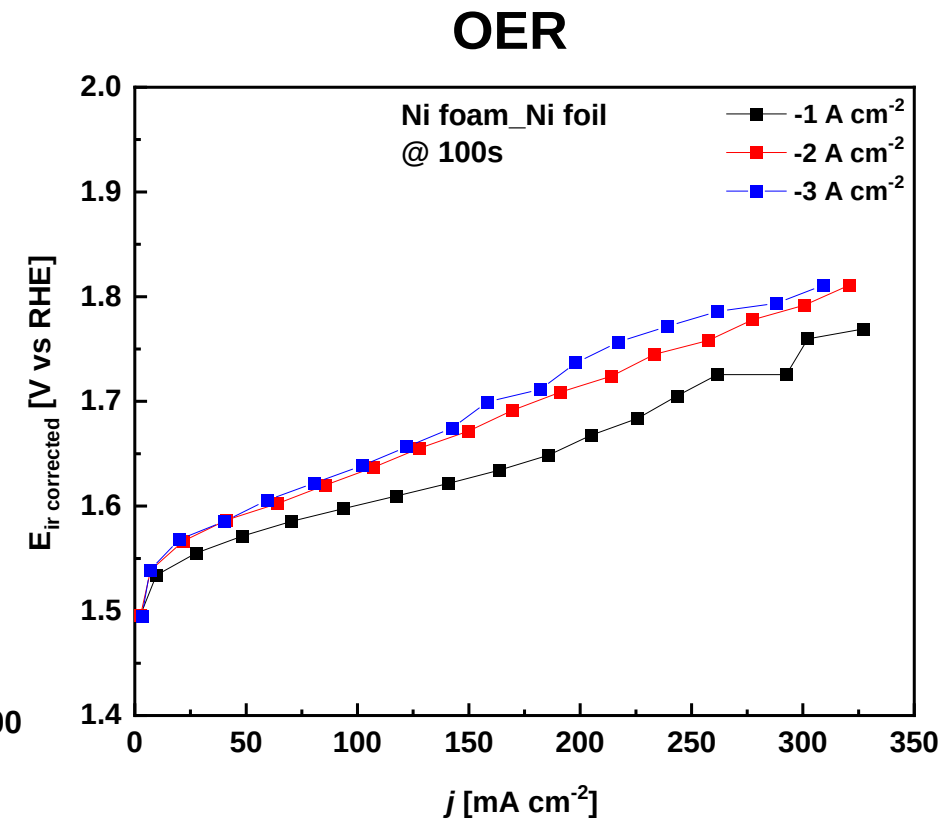
TU/e

Electrochemical Analysis: Constant deposition time



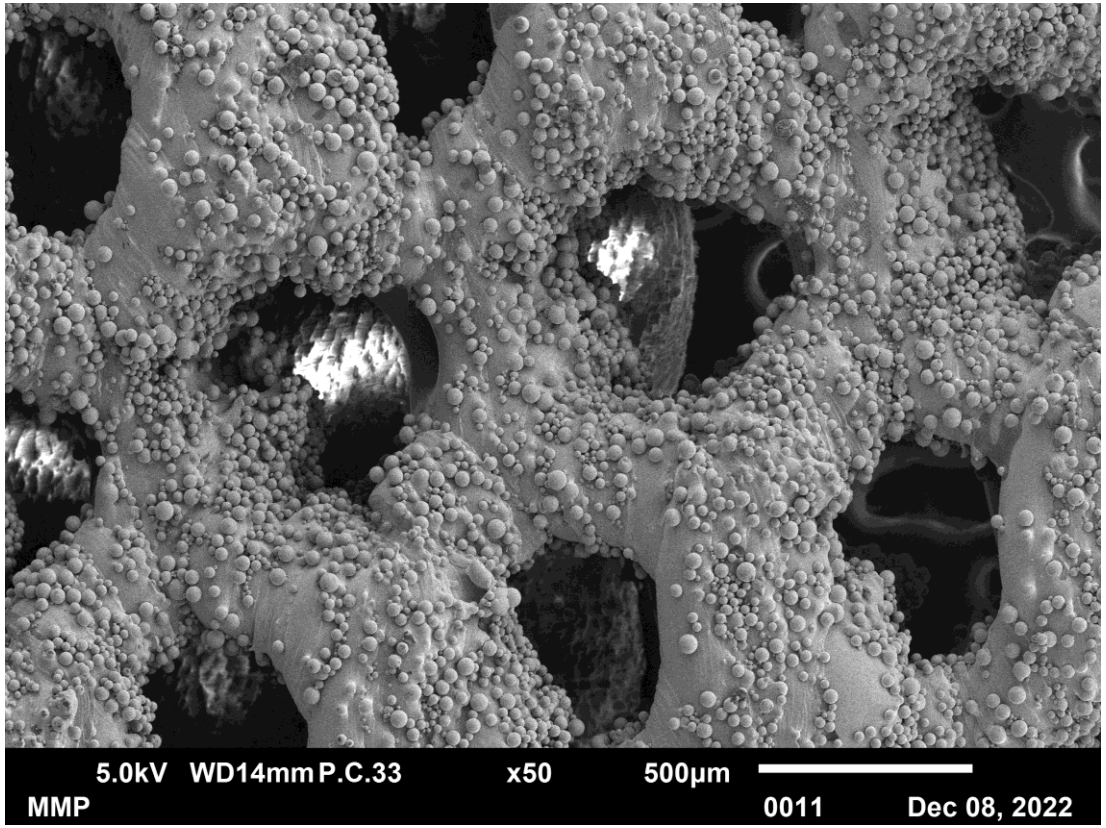
Polarization Curves





- Applied deposition current affects the loading of the catalyst layer, in turn affecting the performance towards HER and OER.

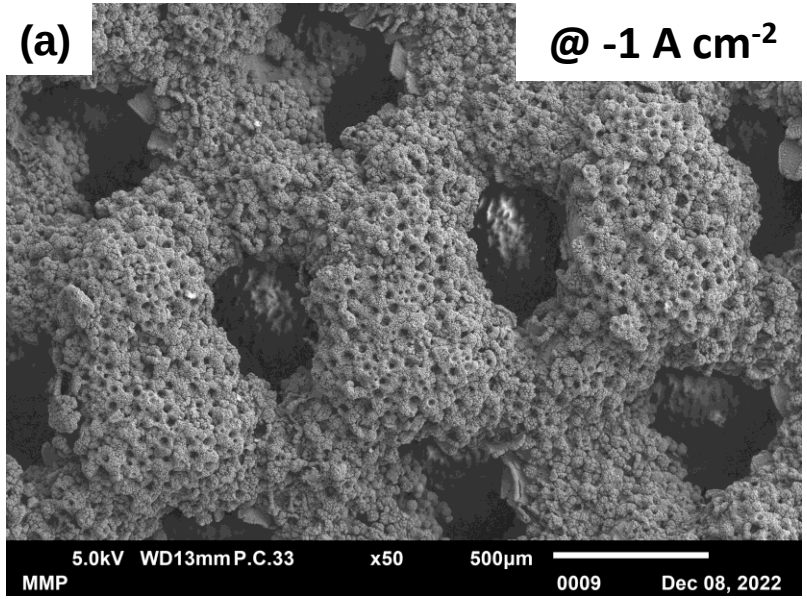
❑ Transferable to 3D printed metal scaffolds?



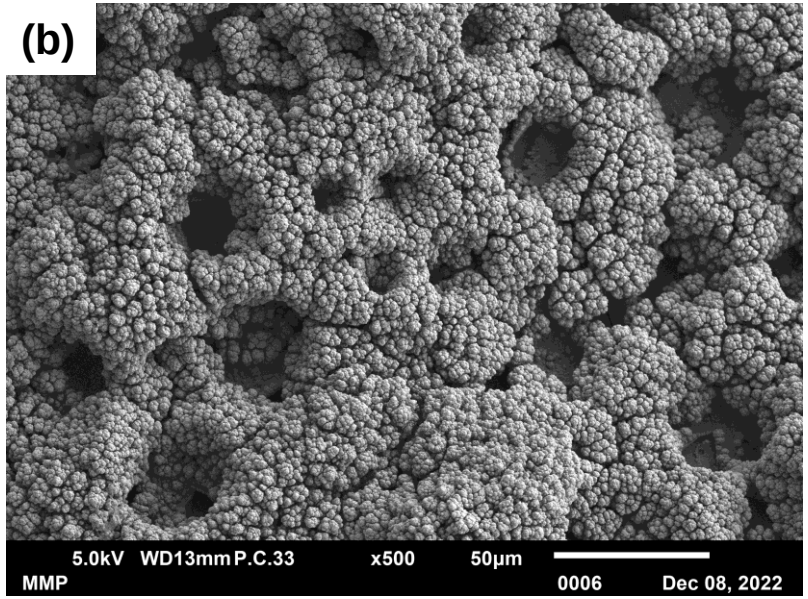
Morphological analysis

Ni-coated Ti-6Al-4V (350 µm L2 structure)

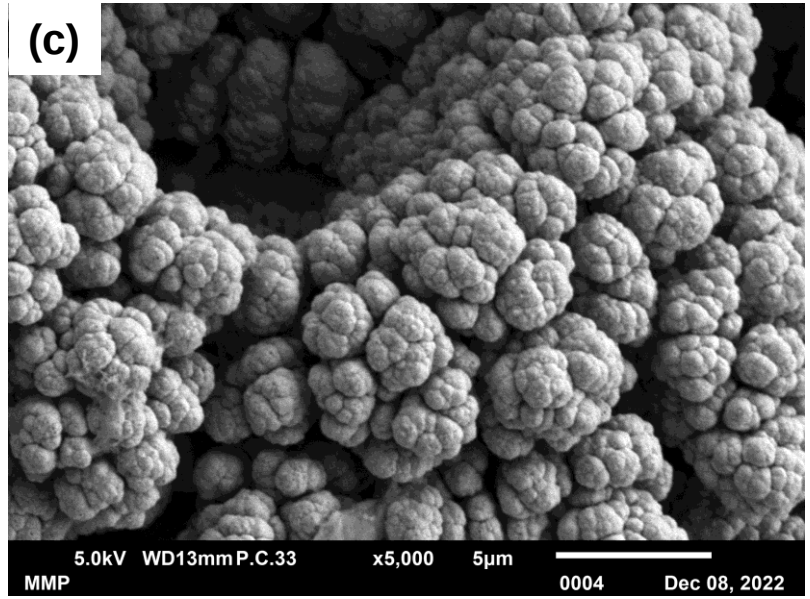
(a) @ -1 A cm^{-2}



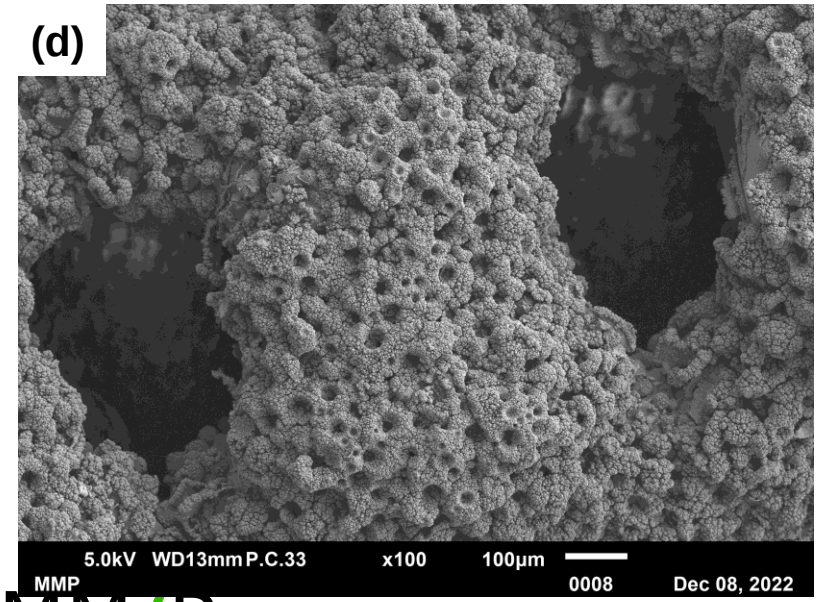
(b)



(c)



(d)



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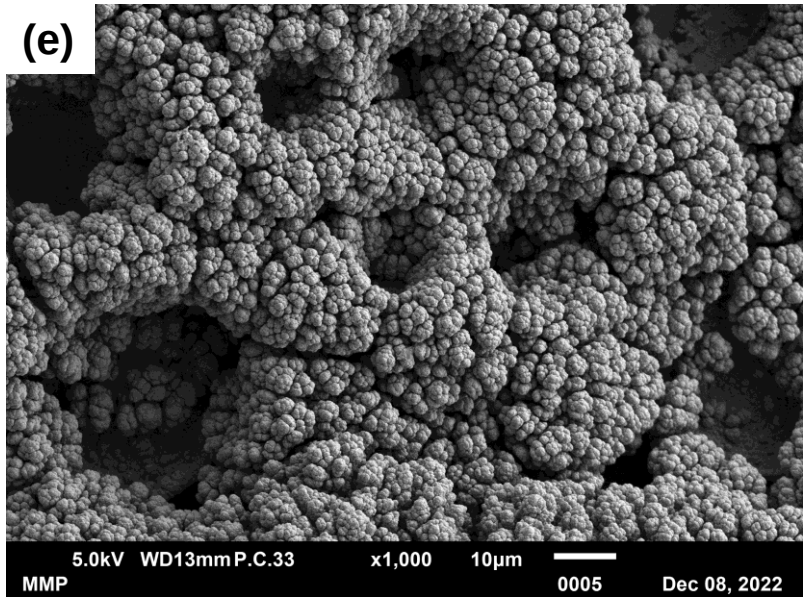

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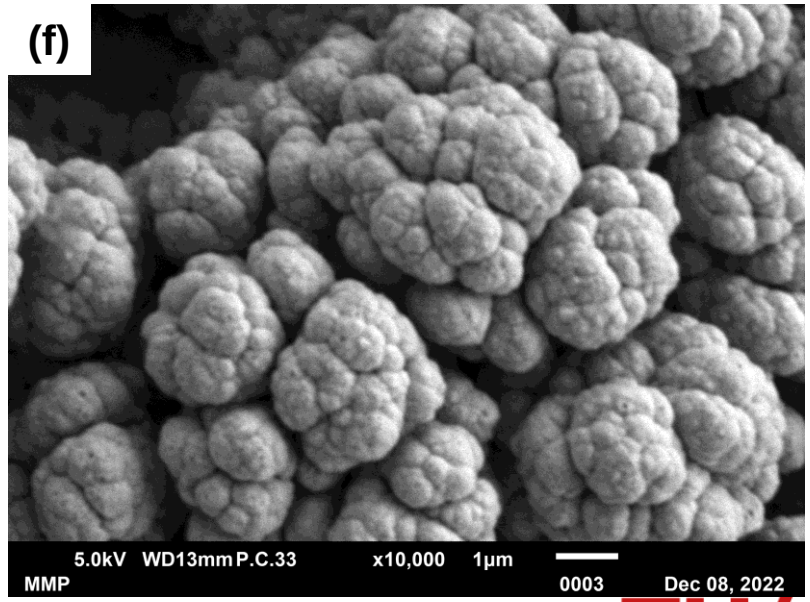
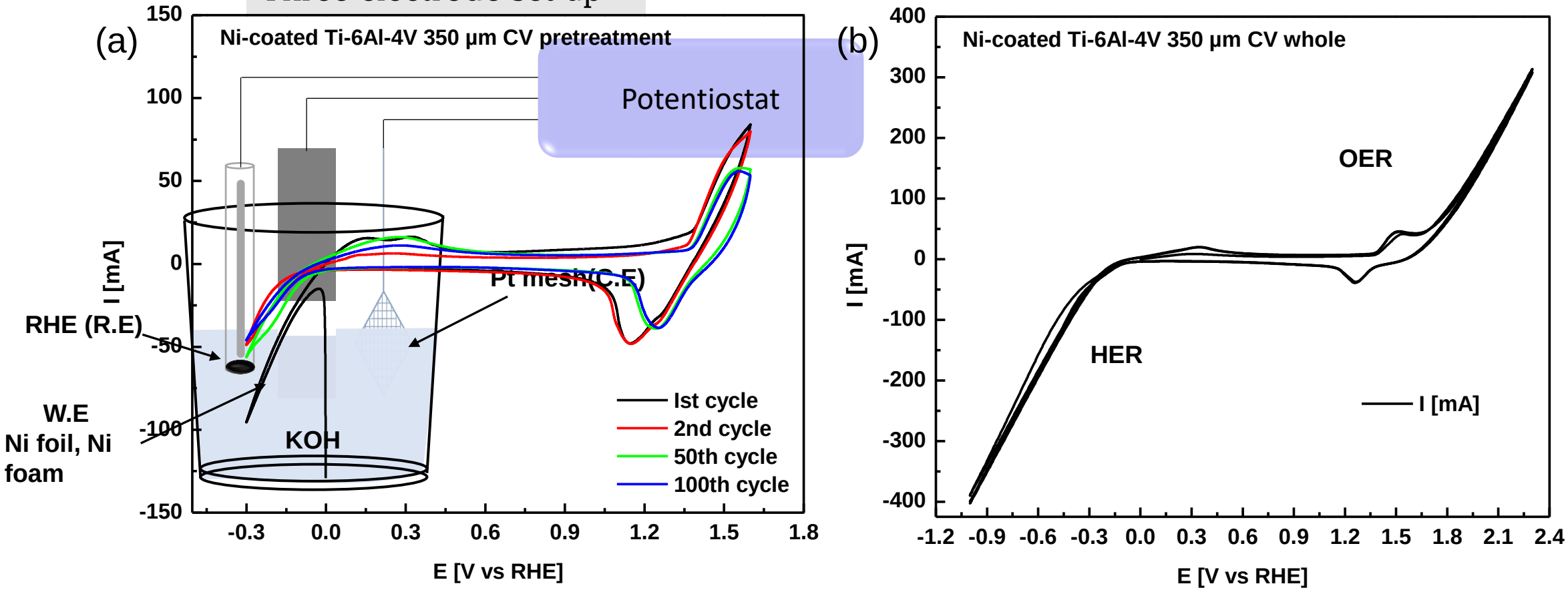


Electrochemical Set up and Analysis: Protocol

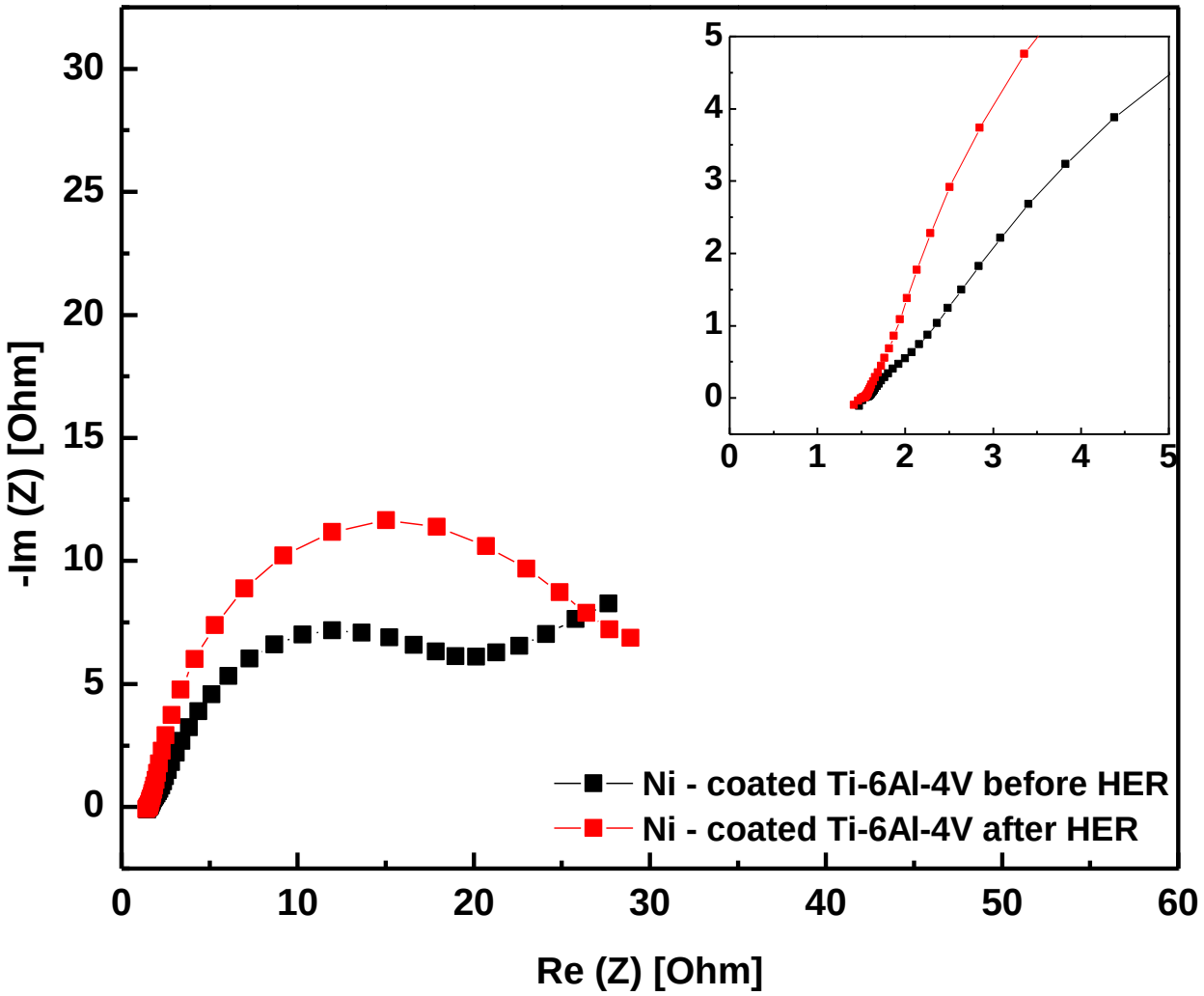
Three electrode set up

Cyclic Voltammetry



❑ After few cycles of pretreatment, system becomes stable.

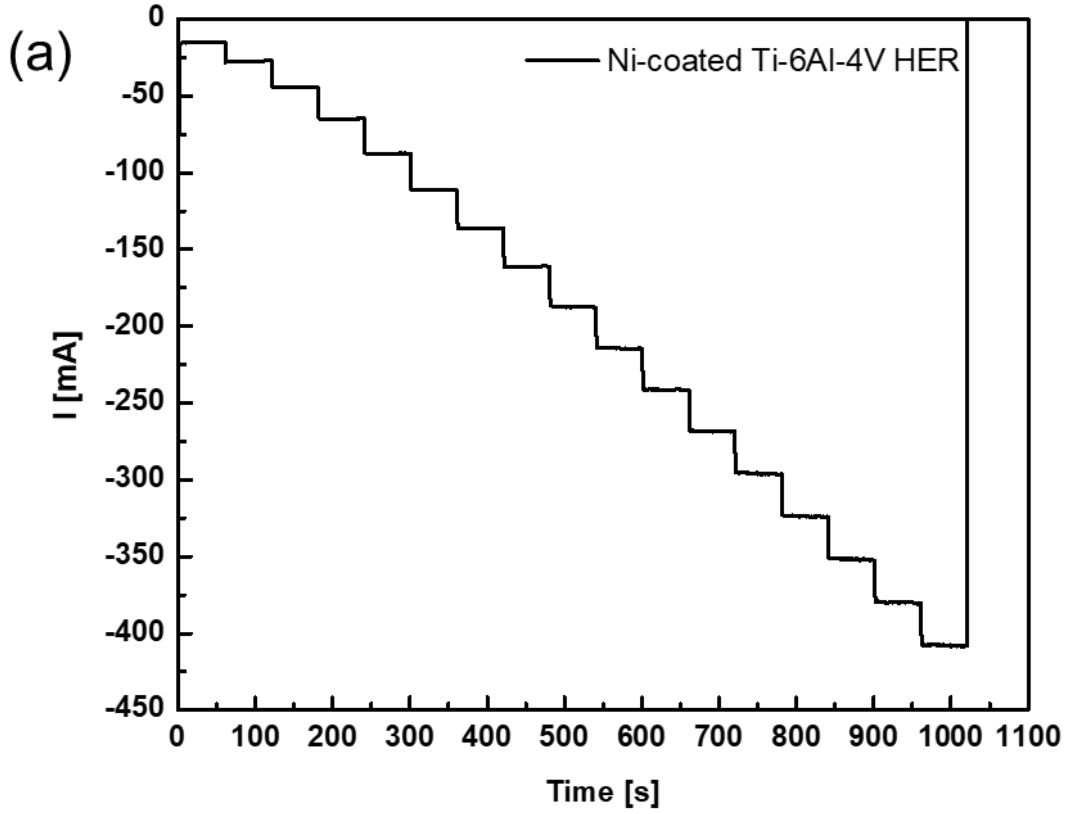
Electrochemical Set up and Analysis: Protocol



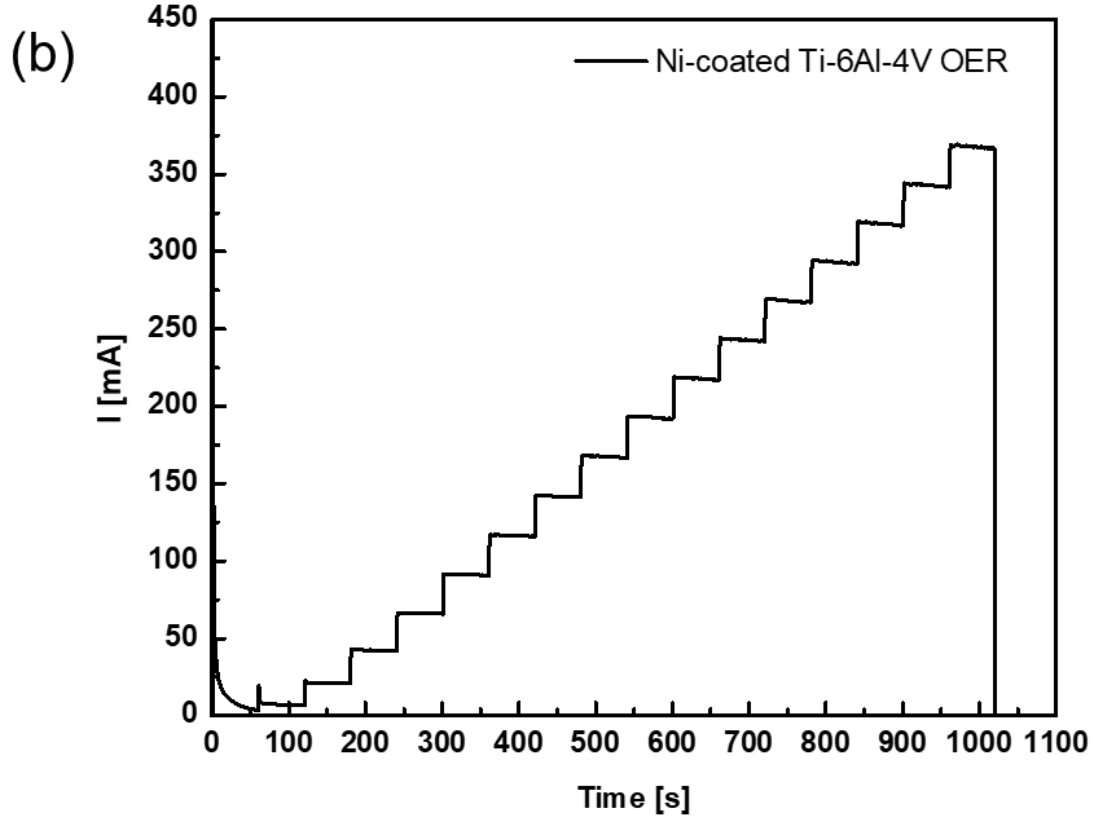
- Ohmic resistance doesn't change before and after measuring HER.

Electrochemical Set up and Analysis: Protocol

HER



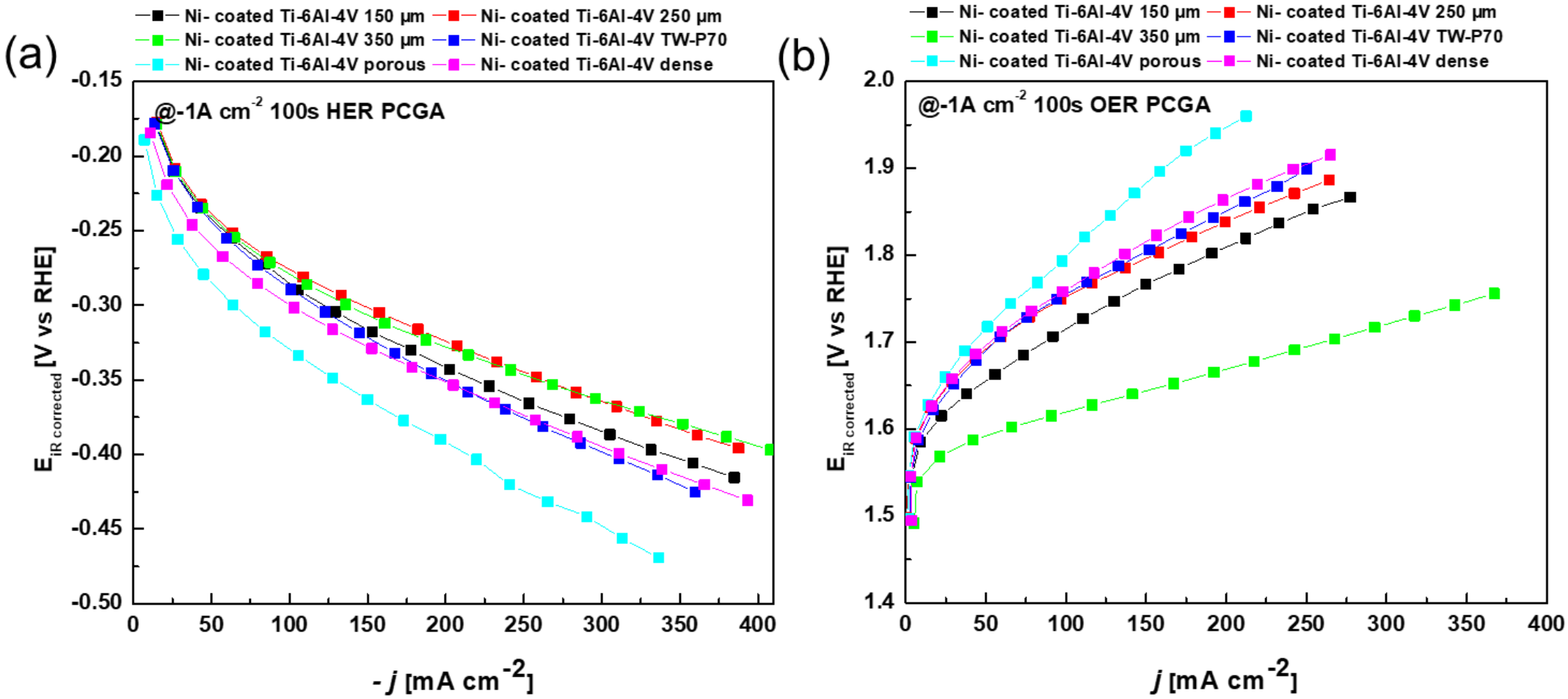
OER



- Obtained current response for HER (-0.2 to -1 V vs RHE) and OER (1.5 to 2.3 V vs RHE)

Electrochemical Analysis: Comparison

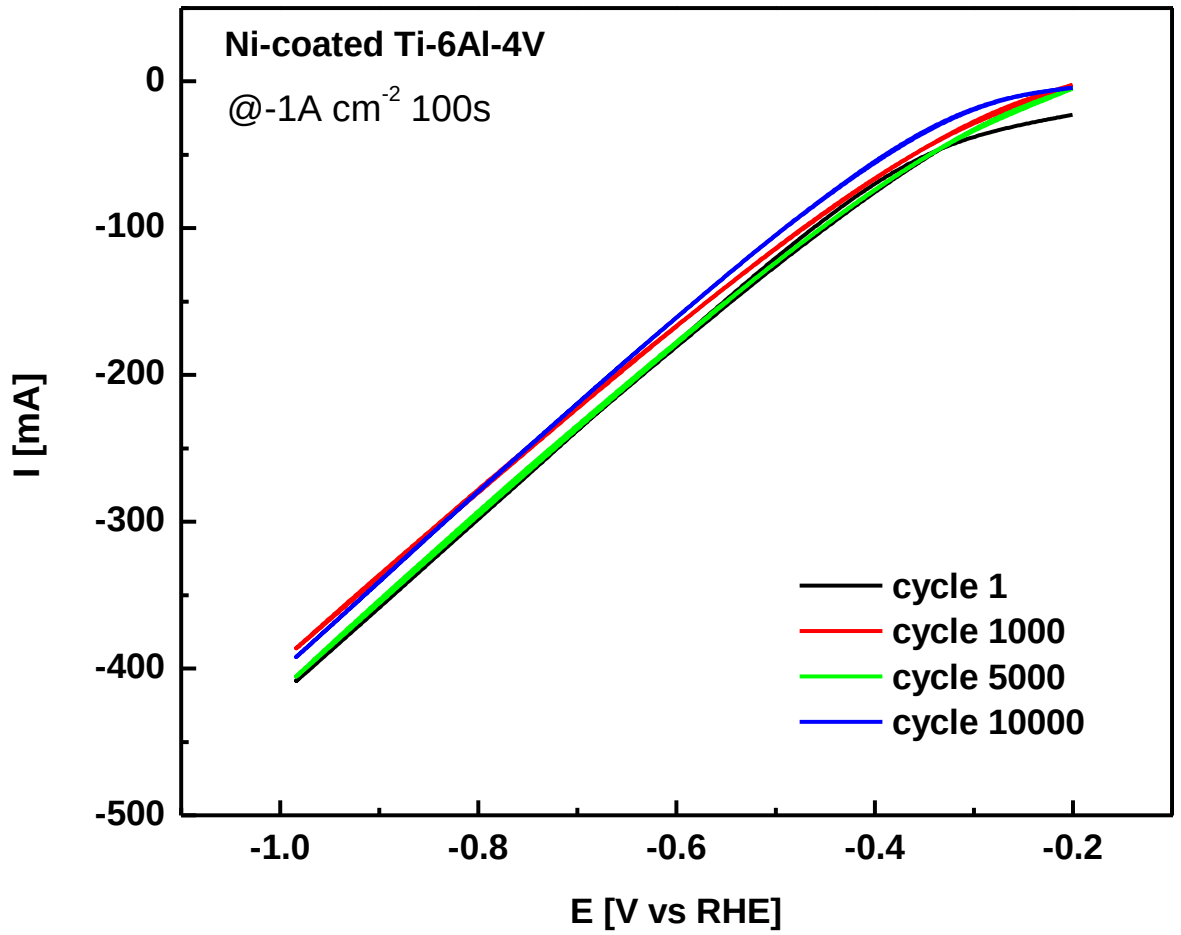
Polarization Curves



- Ni foam@ Ti-6Al-4V 350 µm gives better performance compared to other tested electrodes in the same conditions.

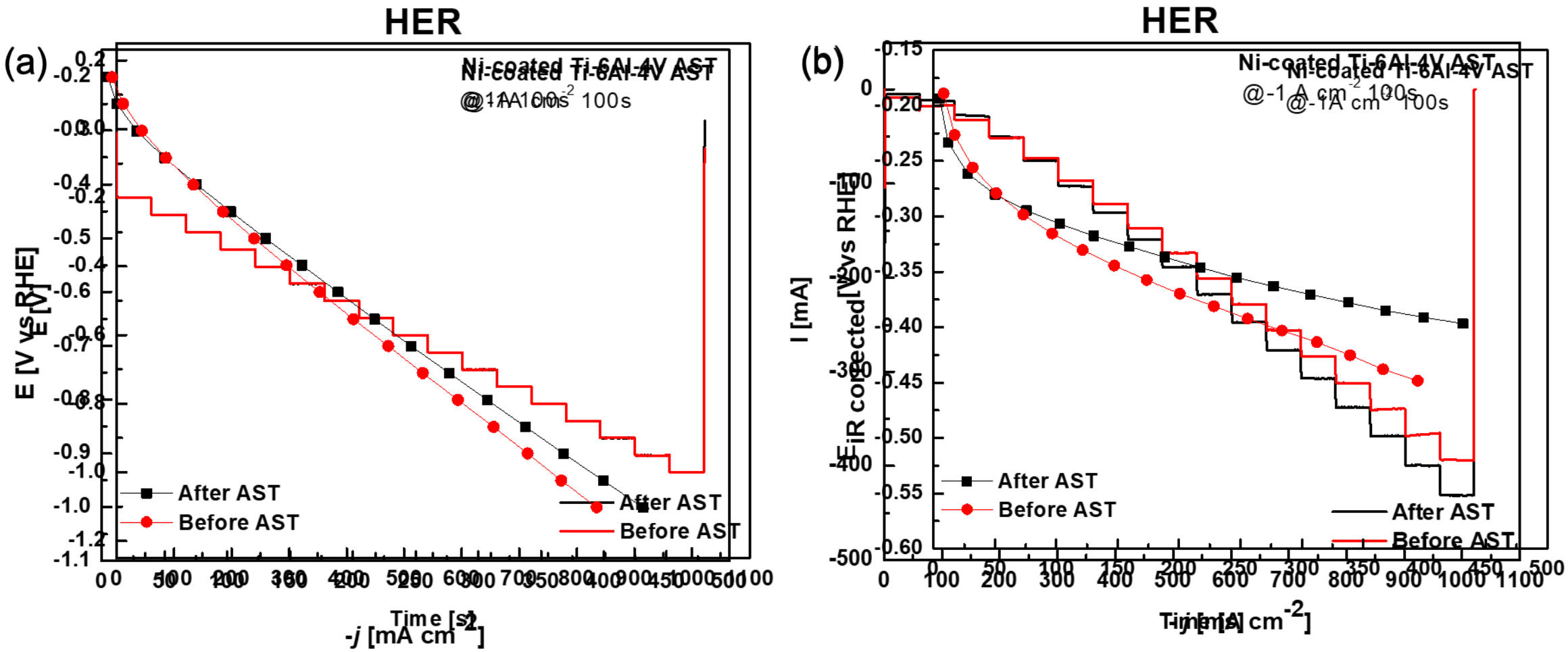
Electrochemical Analysis: Stability AST

Accelerated Stress Testing



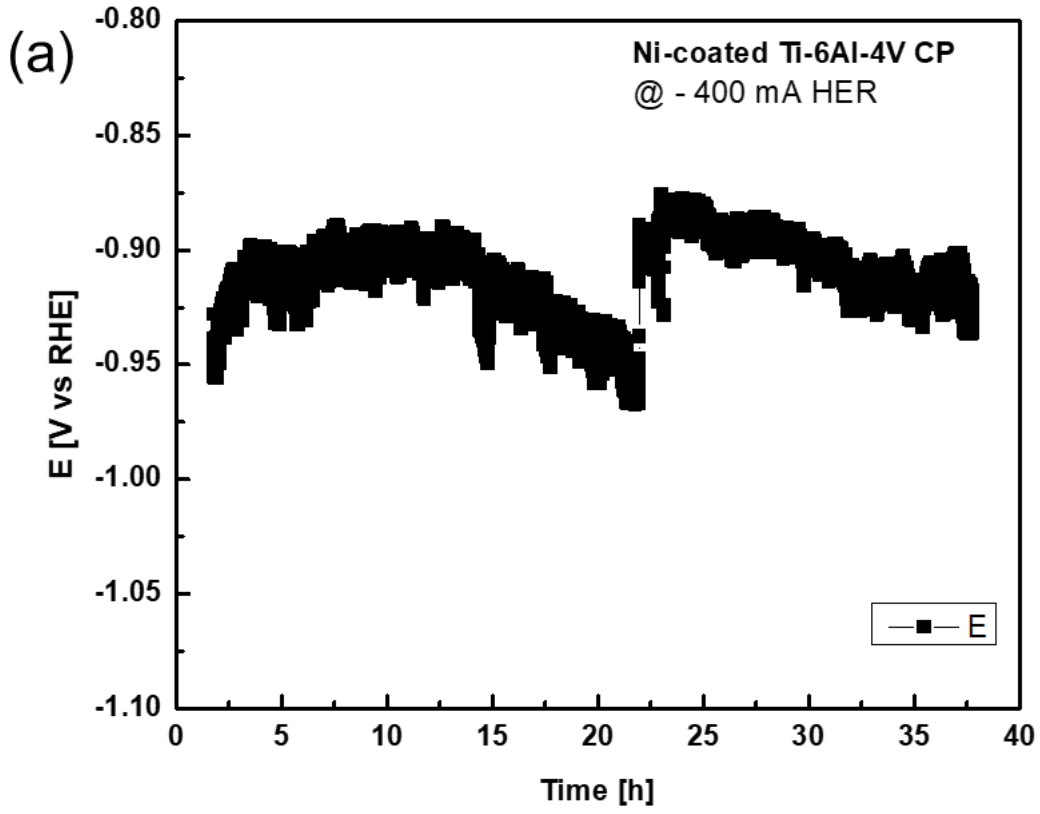
- AST shows the stability of the electrode in HER region.

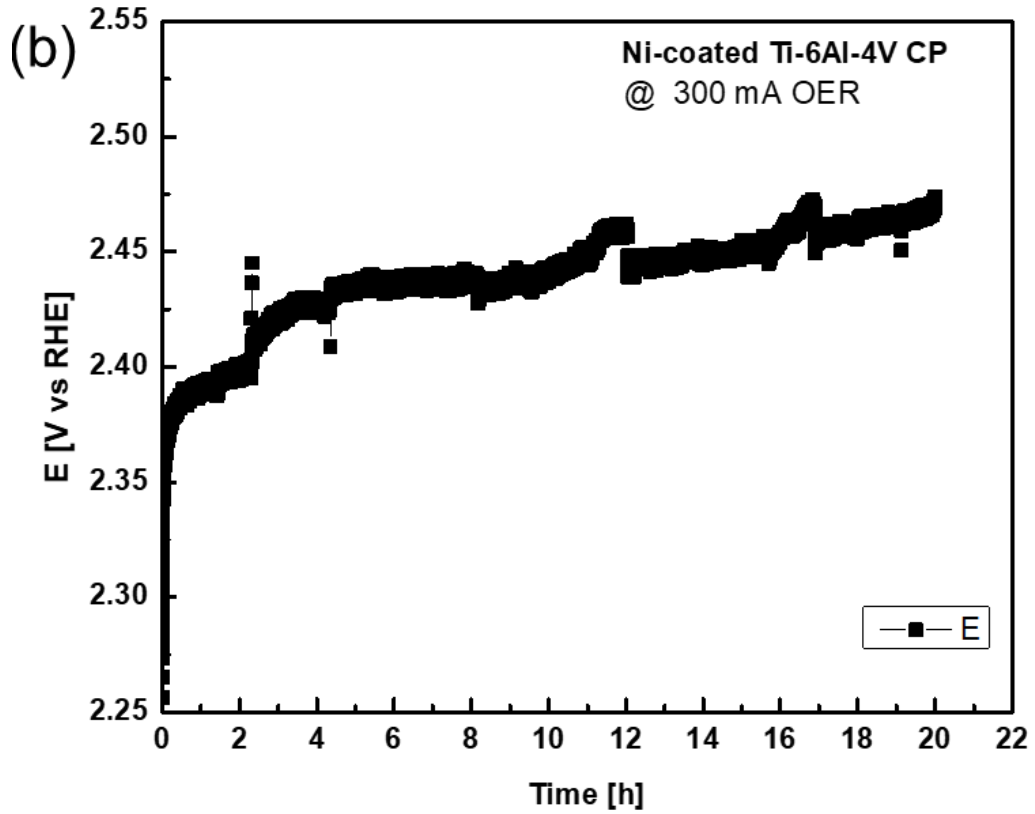
Electrochemical Analysis: Stability AST



- A slight improvement in the performance was observed after AST.

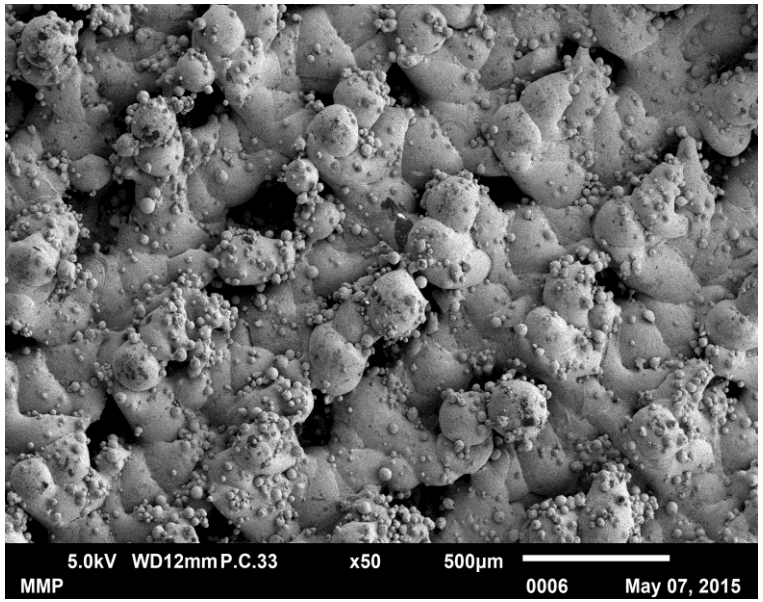
Electrochemical Analysis: continuous electrolysis



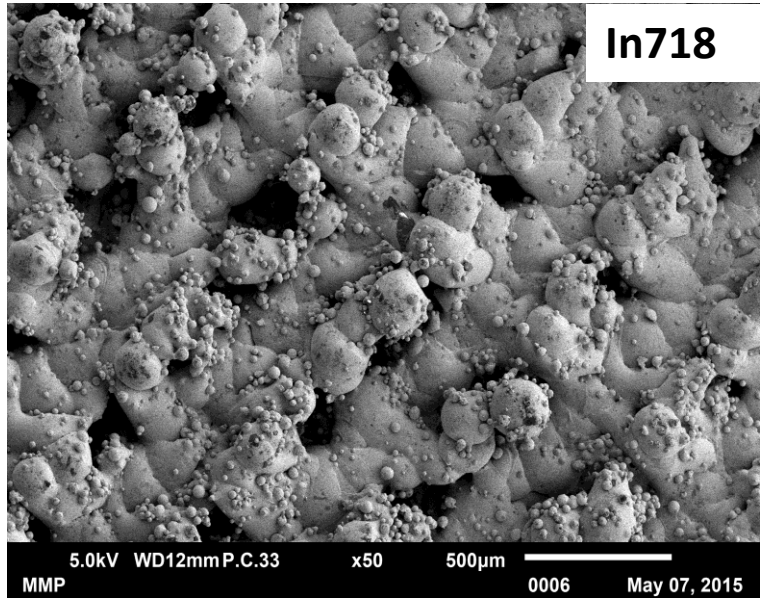


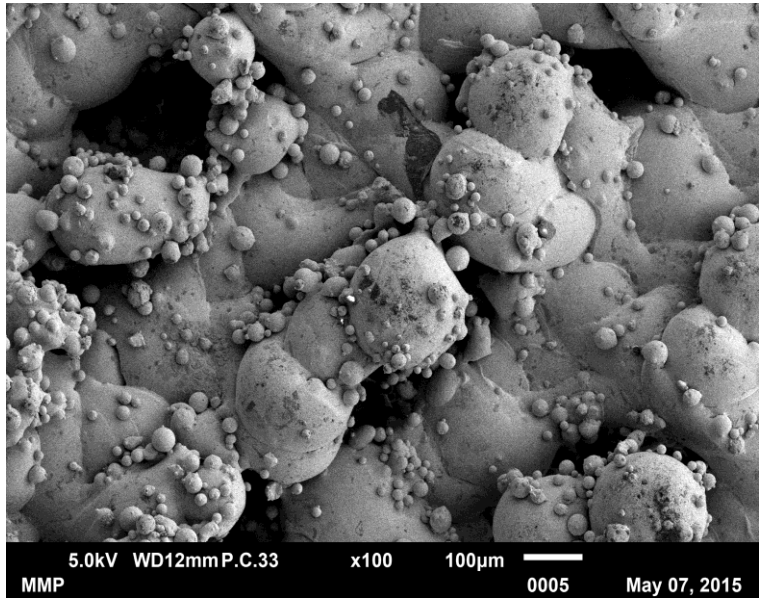
- Chronopotentiometry showed stability of electrodes at relatively higher current densities for HER and OER.

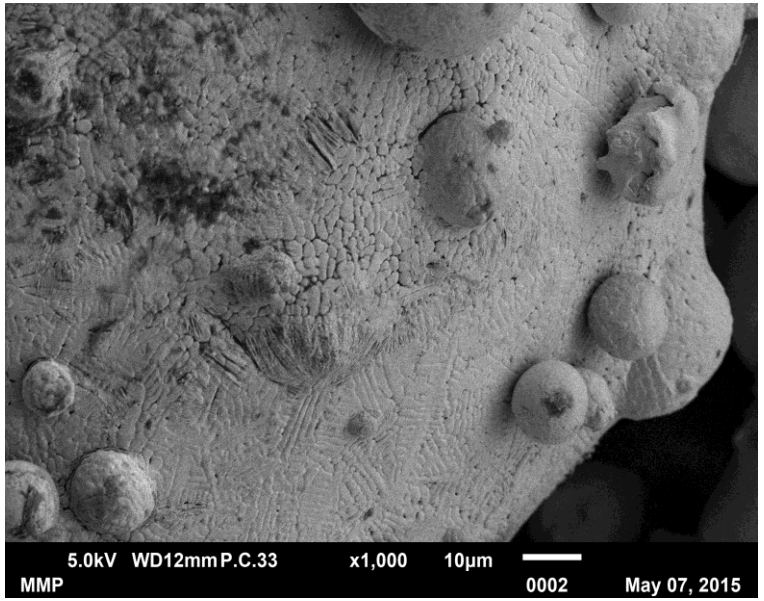
❑ Analysis of Ni-coated inconel

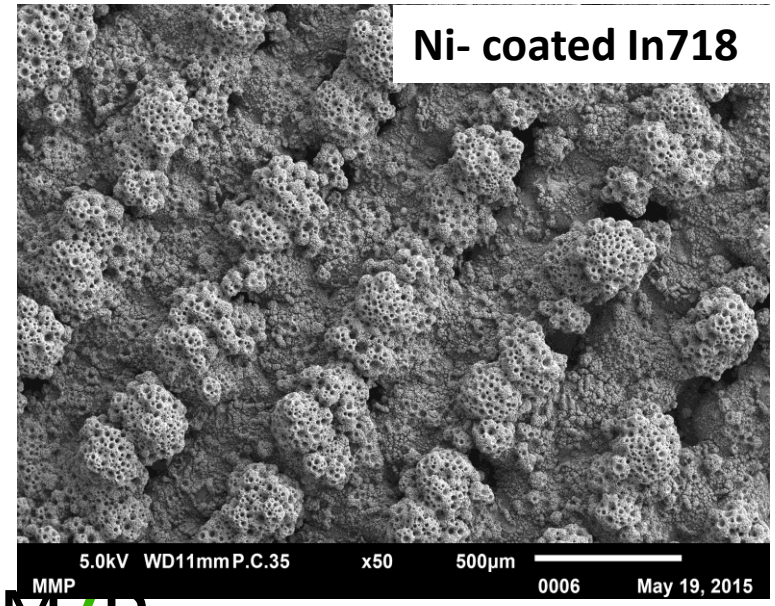


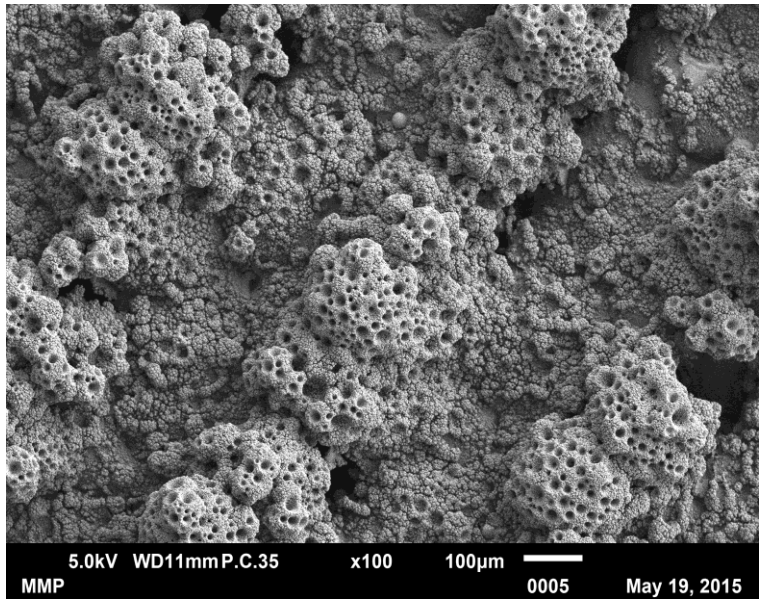
Morphological Analysis: Comparison

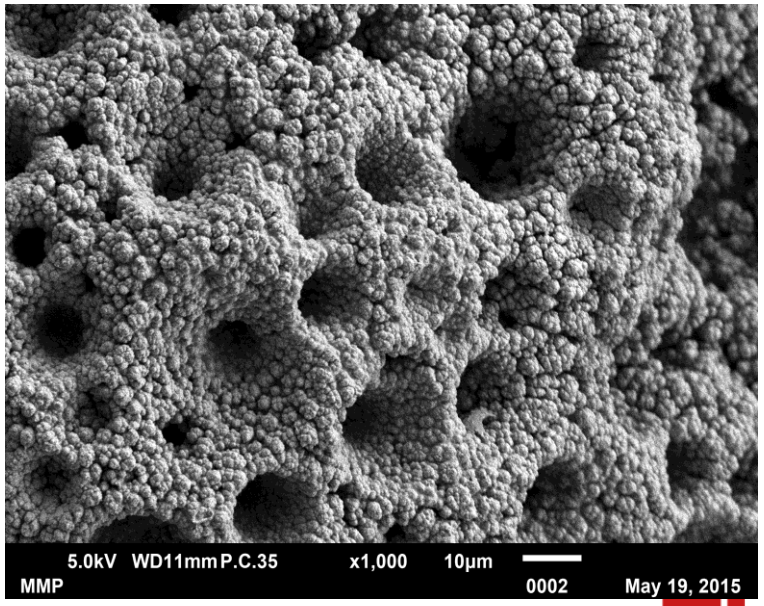




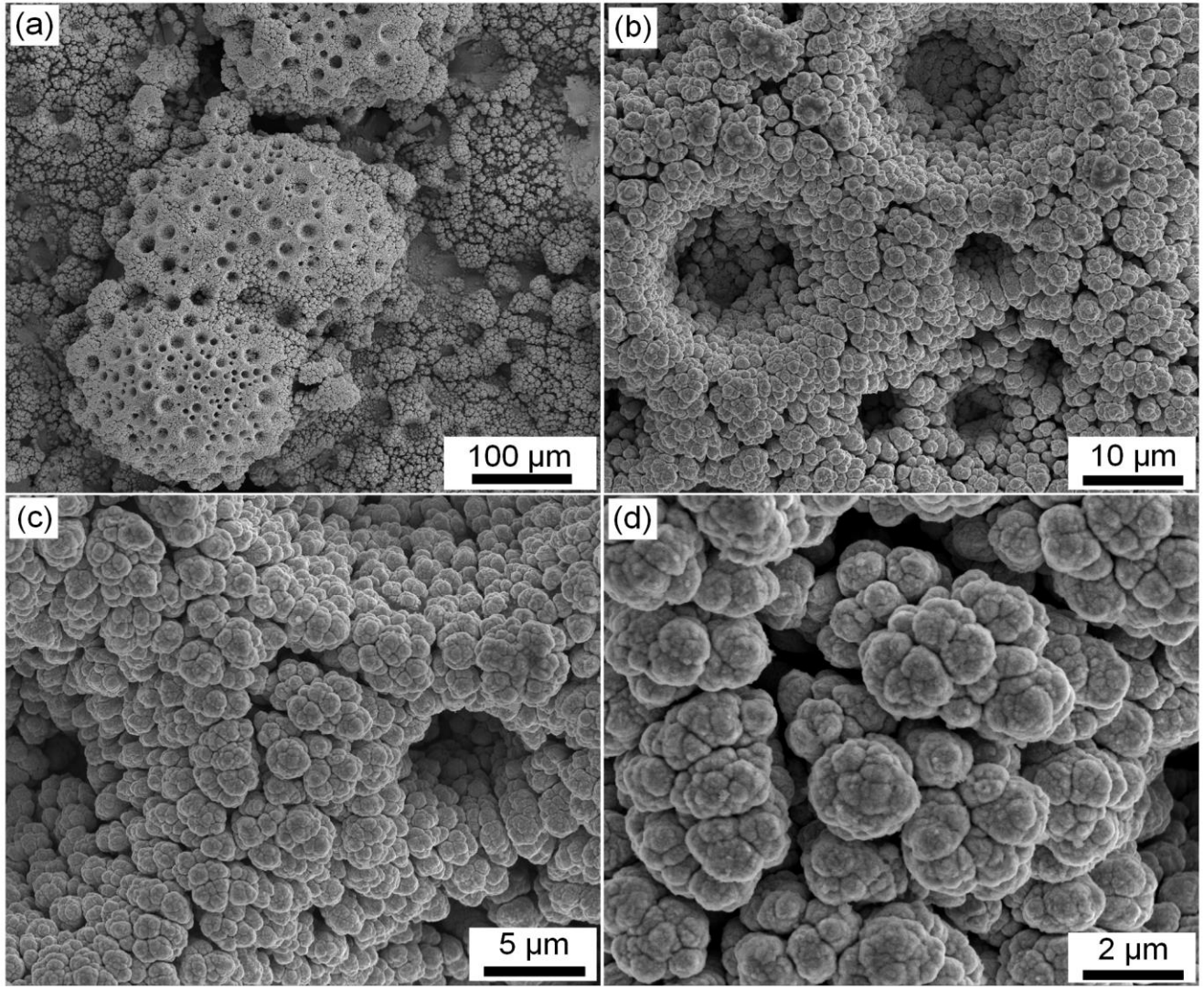








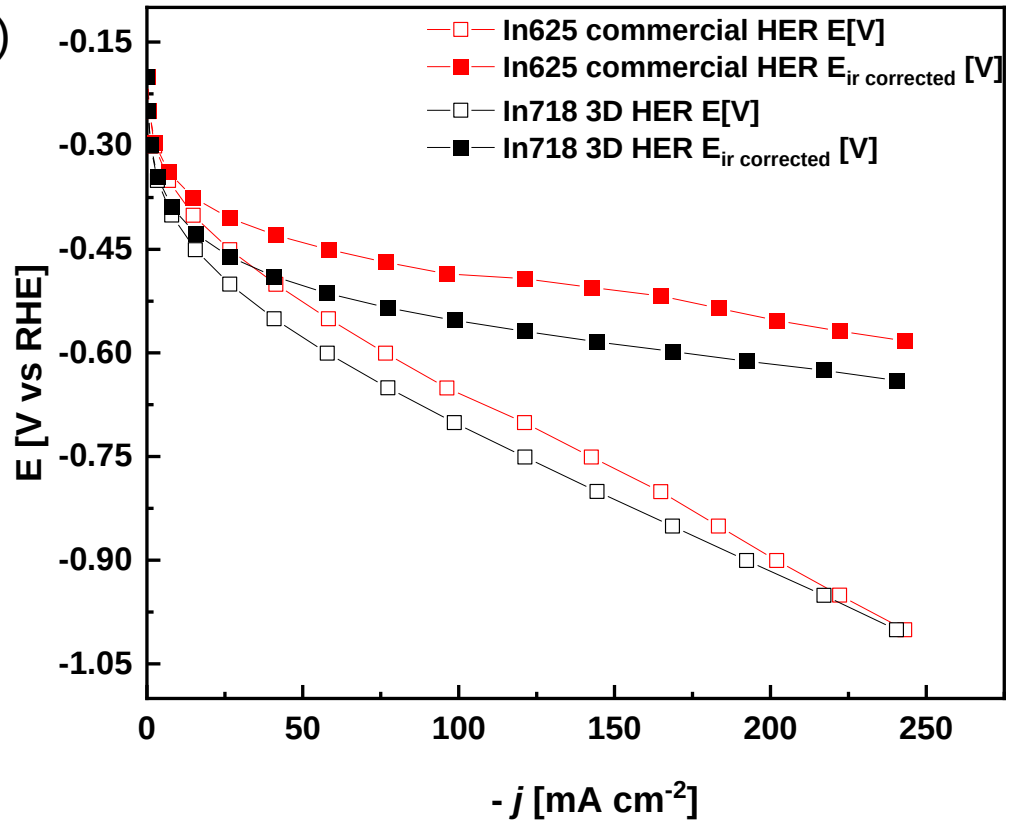
Morphological Analysis: High magnification



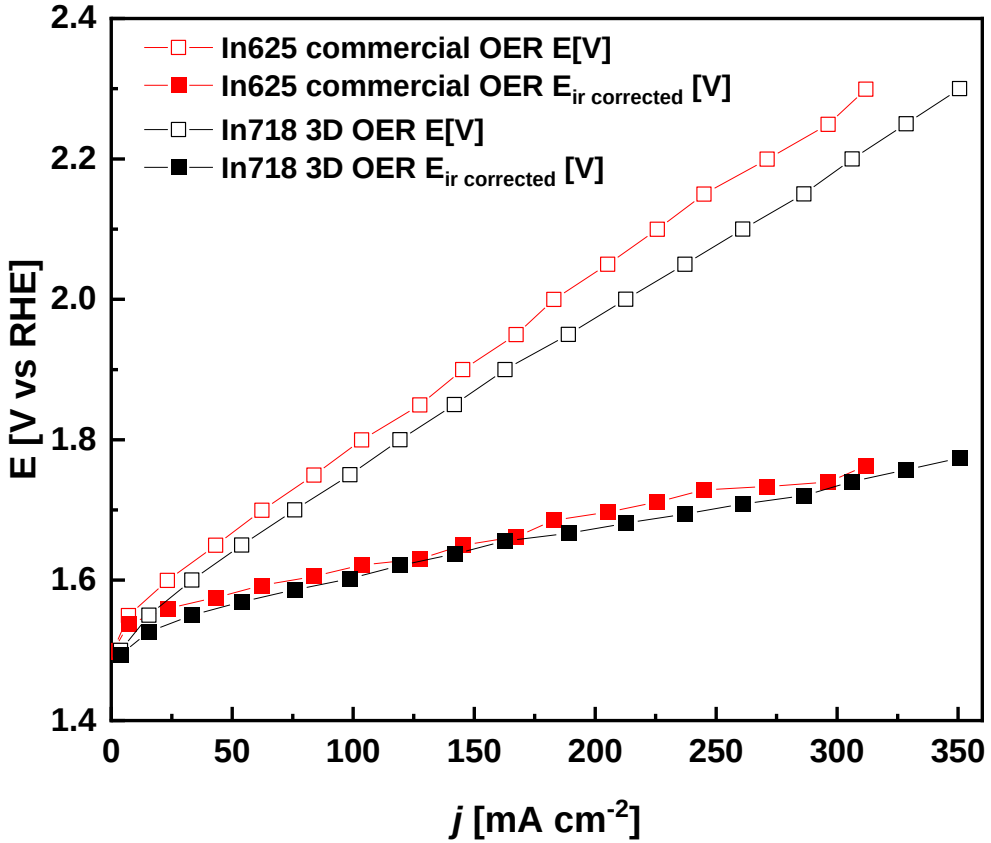
- Deposited structure was like that obtained on Ti-6Al-4V.

Electrochemical Analysis: Comparison

(a)

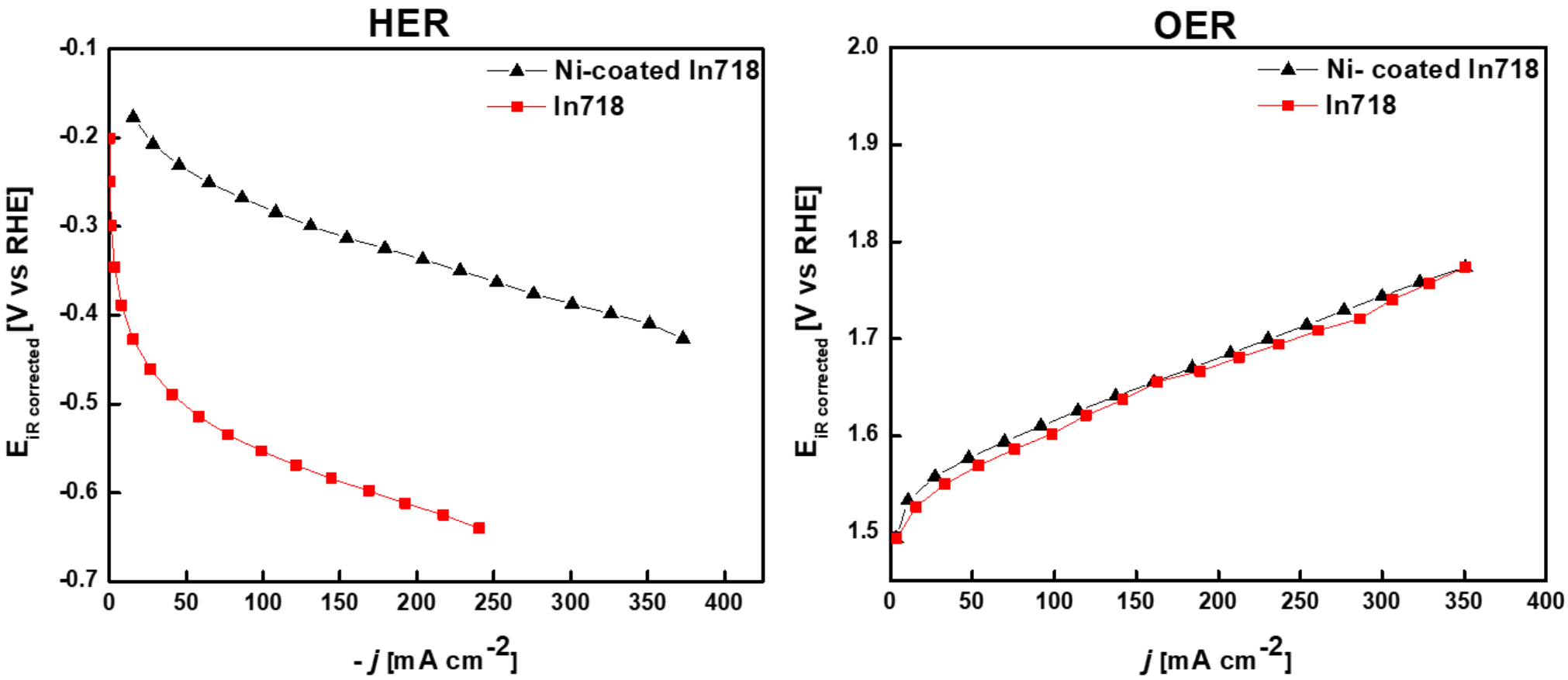


(b)



- Similar performance was obtained with prinstine LPBF- Inconel 718 and Inconel 625 commercial foil.

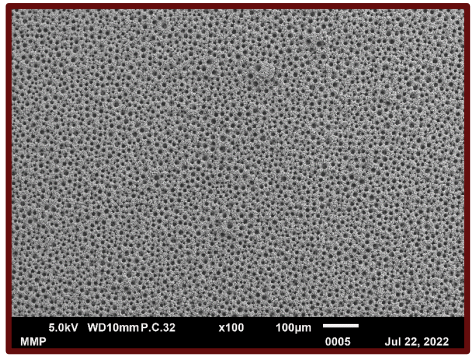
Electrochemical Analysis: Comparision

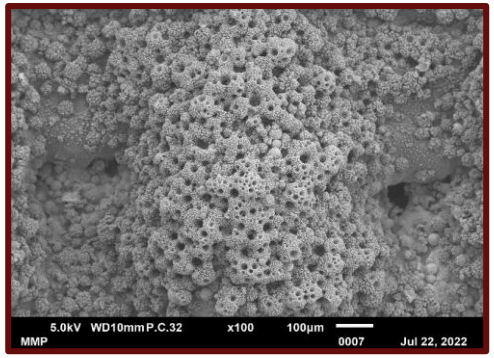


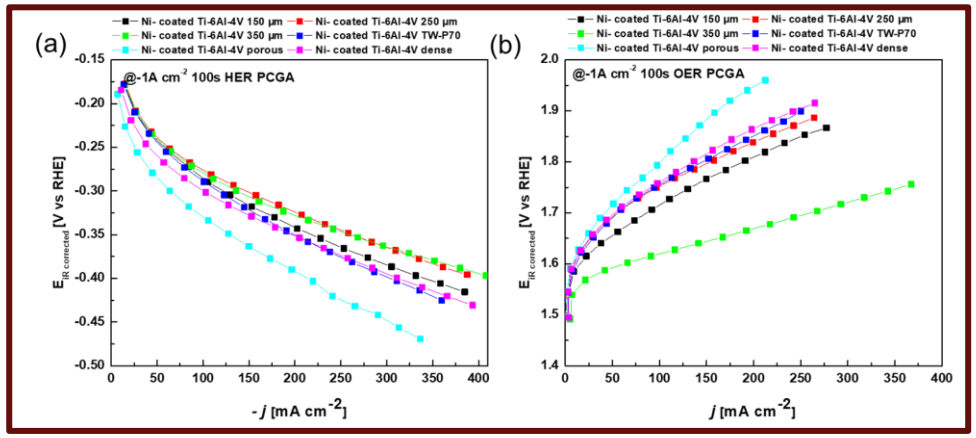
- Ni coated Inconel 718 exhibit better performance for HER however no significant changes has been observed for OER.

Key message

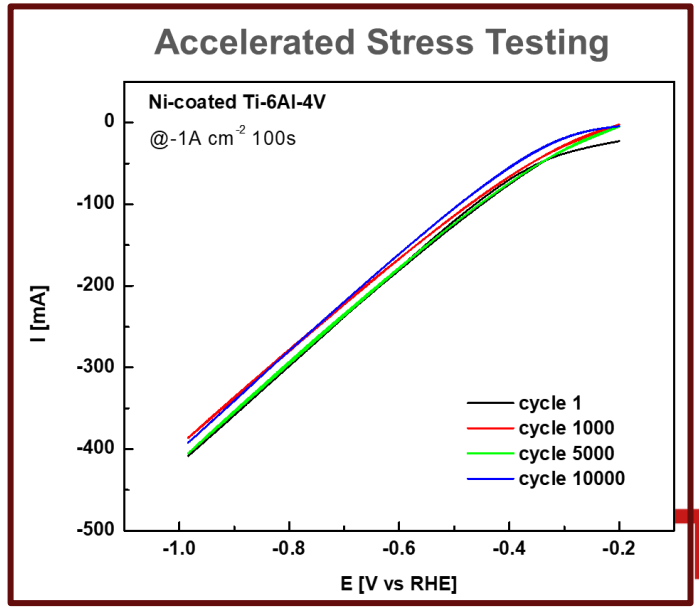
- ✓ Hierarchical porous Ni foam was obtained by electrodeposition process.
- ✓ Transferable to 3D printed structures i.e Ti-6Al-4V and Inconel 718







- ✓ Relatively higher current densities were achieved for Ni-coated Ti-6Al-4V 350 µm.



- ✓ Stability of the electrode for at least 10k cycle for HER.

Future targets and activities

- ✓ Further investigation to assess printability of lattice structures of < 300 µm by modifying designs, laser parameters, and materials.
- ✓ Fabrication of electrodes from materials with higher melt pool stability (e.g., stainless steel).
- ✓ Further study on microstructure of the substrate including microscopic phases and particles attached to the struts and walls to understand how they influence coating quality, and thus, electrochemical properties.
- ✓ Extend the study to other materials with potentially better electrochemical properties. This can be expanded to difficult-to-print materials, such as Mo and MoS2 - The main focus has thus far been on Ti-64, and In718.
- ✓ Surface engineering and further study on the coating methods and chemistry of the catalysts to maximise electrochemical efficiency.