

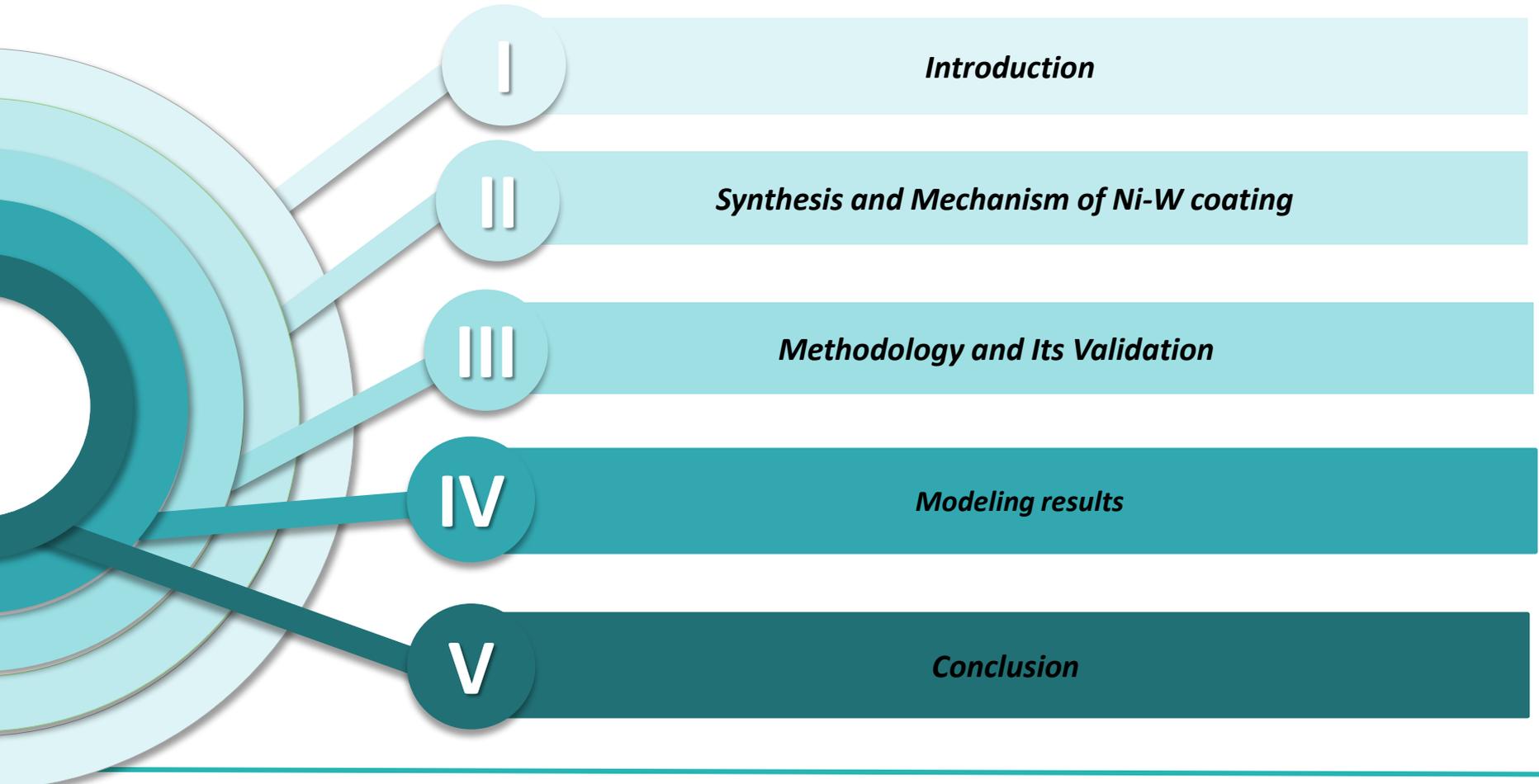


Ni-based Ferromagnetic Coatings with Enhanced Efficiency to Replace
Pt in Energy & Digital Storage Applications

Develop of a mathematical model to simulate the electrodeposition process

Presented by: Parisa Molaei

Colleague's Name: Bart van den Bossche, Roger de paz castany, Eva Pellicer,
Annick Hubin, Mesfin Haile Mamme



Introduction



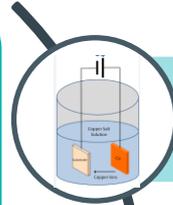
Co-funded by
the European
Commission

Ensure high
efficiency in key
applications.

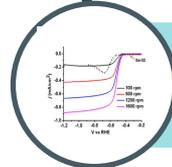


Replace the
scarce and
costly Platinum

Develop novel
ferromagnetic
Ni-based coating



Mechanism of electrodeposition of
Ni-W



Kinetic Parameters in Ni-W
Electrodeposition



Modelling of Ni-W electrodeposition

Synthesis and Mechanism of Ni-W coating

> > > > > > > > > >

Definition of Electrochemical reaction

Bath formulation	M
NiSO ₄ (M)	0.11
Na ₂ WO ₄ (M)	0.05
Sodium gluconate (M)	0.5
H ₃ BO ₃ (M)	0.65



1	Ni reduction	$NiGlu^+ + 2e^- \rightarrow Glu^- + Ni(s)$
2	W reduction	$WO_4^{2-} + 4H_2O + 6e^- \rightarrow W + 8OH^-$
3	H production	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Understanding of Mass Transport

Model Validation



Diffusion Coefficient of Ni in the bath

Based on the literature

Experimentally

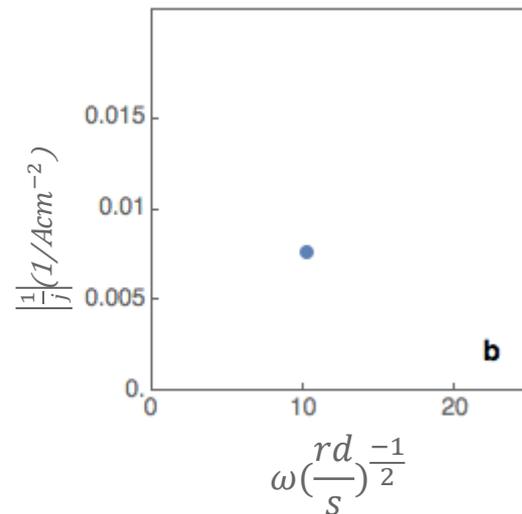
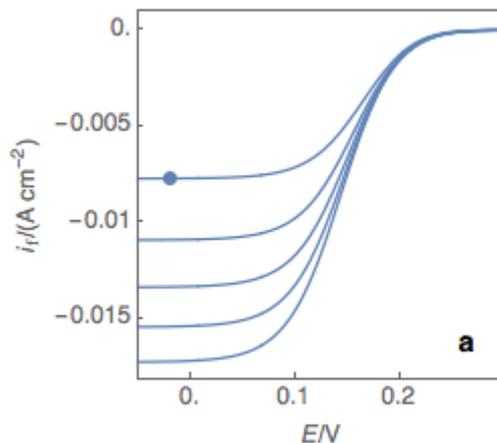
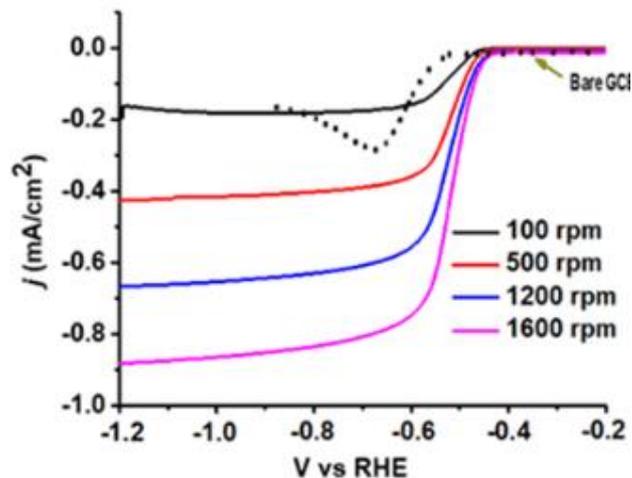
1.27E-9
7.6E-10
6.61E-10 m²/s



Linear Sweep Voltammetry

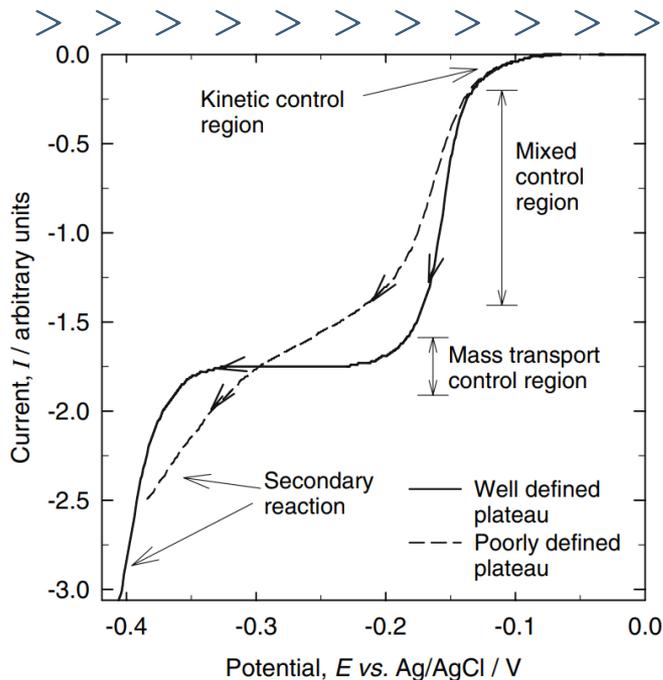
> > > > > > > > > > >

In theory



Koutecky-Levich equation
$$\frac{1}{j} = \frac{1}{j_k} + \left(\frac{1}{0.62nFD^{2/3}v^{-1/6}C} \right) \omega^{-1/2}$$

Linear Sweep Voltammetry

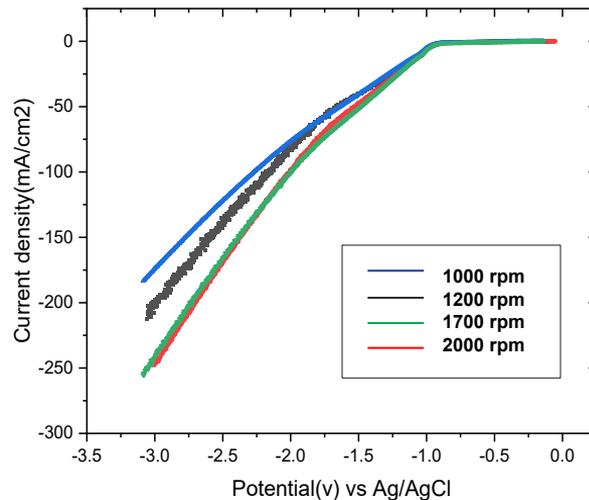


In reality

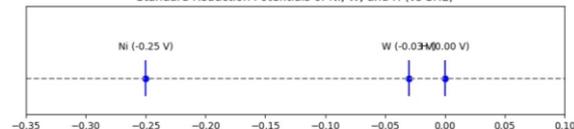
Secondary Reactions and Hydrogen Bubble Formation

Increase of the electrode area due to metal deposition

Uneven current and/or Potential distribution



Standard Reduction Potentials of Ni, W, and H (vs SHE)



Ponce-de-Leon, C., Low, C.T.J., Kear, G. and Walsh, F.C., 2007. Strategies for the determination of the convective-diffusion limiting current from steady state linear sweep voltammetry. *Journal of Applied Electrochemistry*, 37(11), pp.1261-1270.

Methodology

> > > > > > > > > >

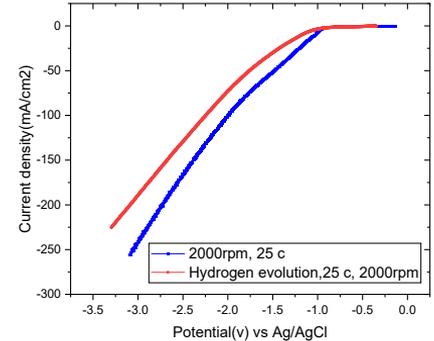
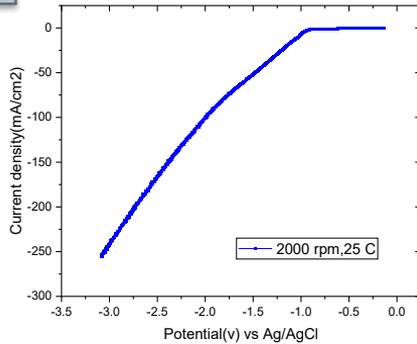
1	Ni reduction	$NiGlu^+ + 2e^- \rightarrow Glu^- + Ni(s)$
2	W reduction	$WO_4^{2-} + 4H_2O + 6e^- \rightarrow W + 8OH^-$
3	H production	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Bath formulation	M
NiSO₄ (M)	0.11
Na₂SO₄ (M)	0.05
Sodium gluconate (M)	0.5
H ₃ BO ₃ (M)	0.65

Reduction of Ni and hydrogen evolution

Bath formulation	M
NiSO₄ (M)	0.11
Na₂SO₄ (M)	0.05
Sodium gluconate (M)	0.5
H ₃ BO ₃ (M)	0.65

Hydrogen evolution



Methodology



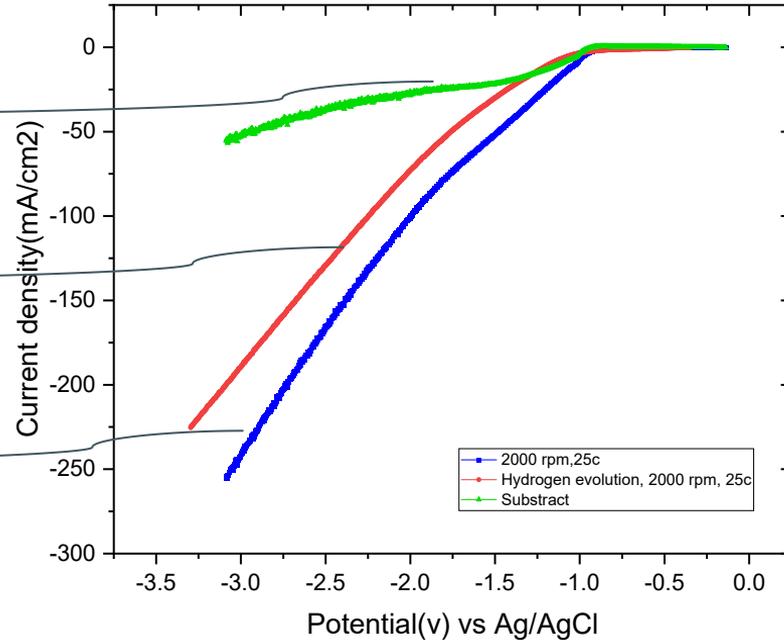
Only reduction of Ni



Only hydrogen evolution



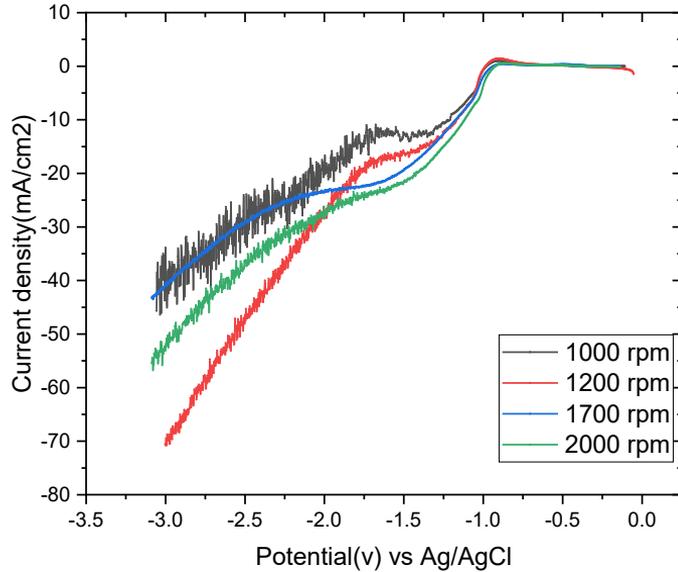
Reduction of Ni+side
reaction



Methodology

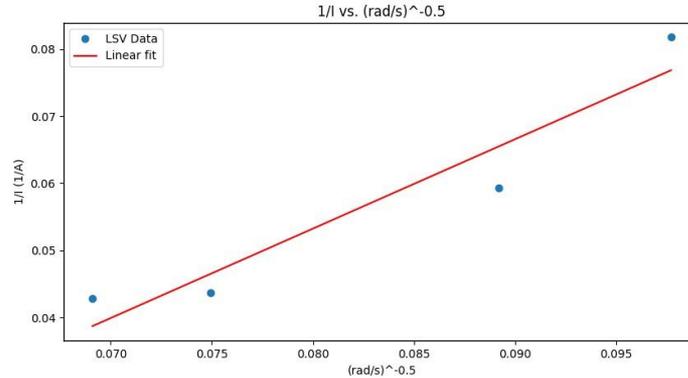


Subtracted results: Ni reduction in different rpm at **25 °C**



$$k = \frac{i_k}{nFAC}$$

$$D = \left(\frac{i_{mt}}{0.620 nFAv^{-1/6}C} \right)^{2/3}$$



R-squared: 0.91
Slope: 1.33

D: 9.8e-10 m²/s
K:0.25

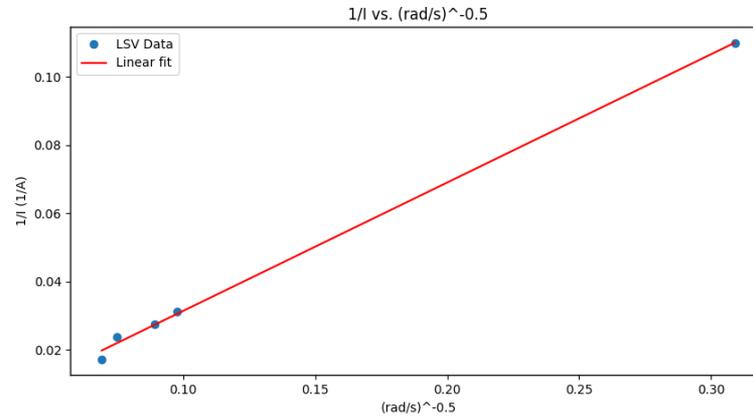
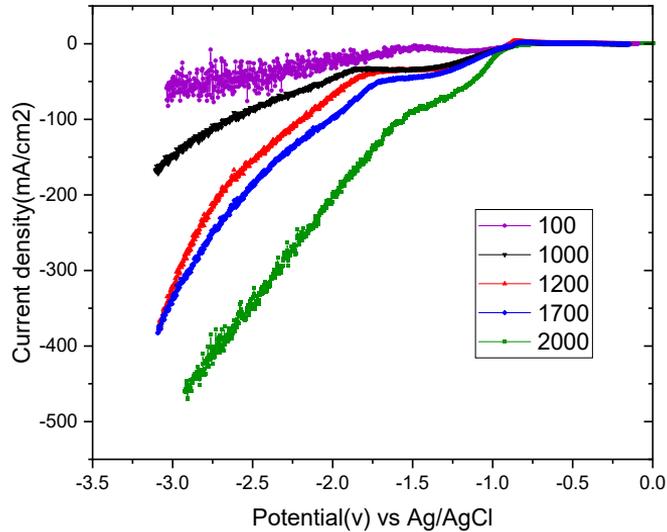


$$\frac{1}{j} = \frac{1}{j_k} + \left(\frac{1}{0.62nFD^{2/3}v^{-1/6}C} \right) \omega^{-1/2}$$

Methodology



Subtracted results: Ni reduction in different rpm at **62°C**



R-squared: 0.99
Slope: 0.37

D: 6.5e-9 m²/s
K:1.3

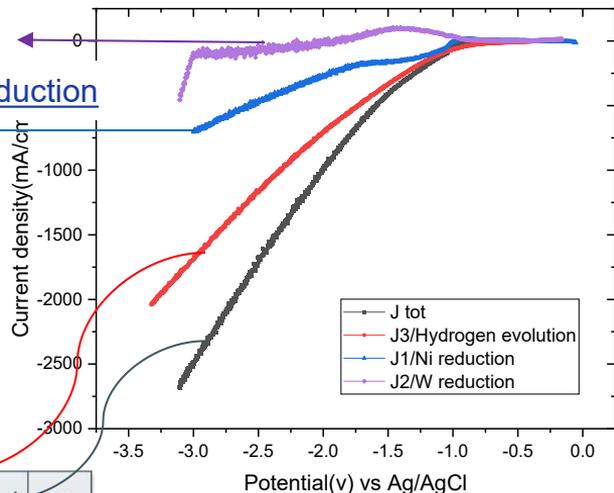


Validation of Methodology

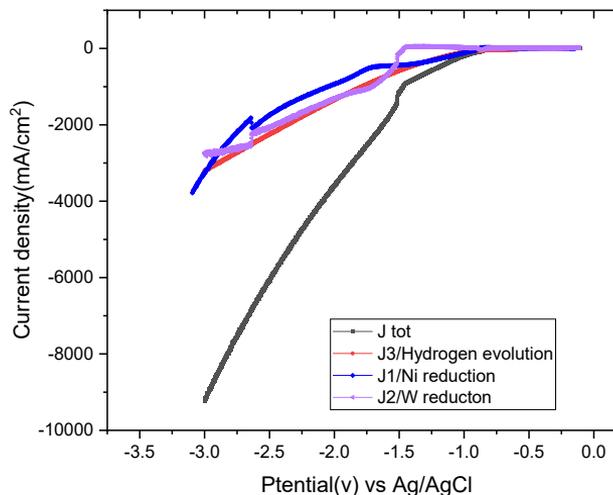
> > > > > > > > > >

Only by calculation

Only Ni reduction



25 °C, 1200 RPM



62 °C, 2000 RPM

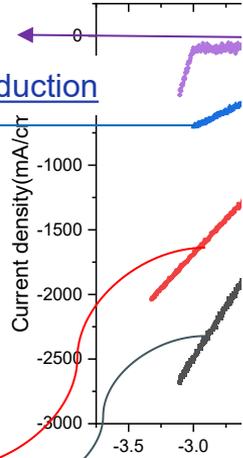
Bath formulation	M
Ni (M)	0.11
Na (M)	0.05
Sodium gluconate (M)	0.5
H ₂ BO ₃ (M)	0.65

Validation of Methodology

> > > > > >

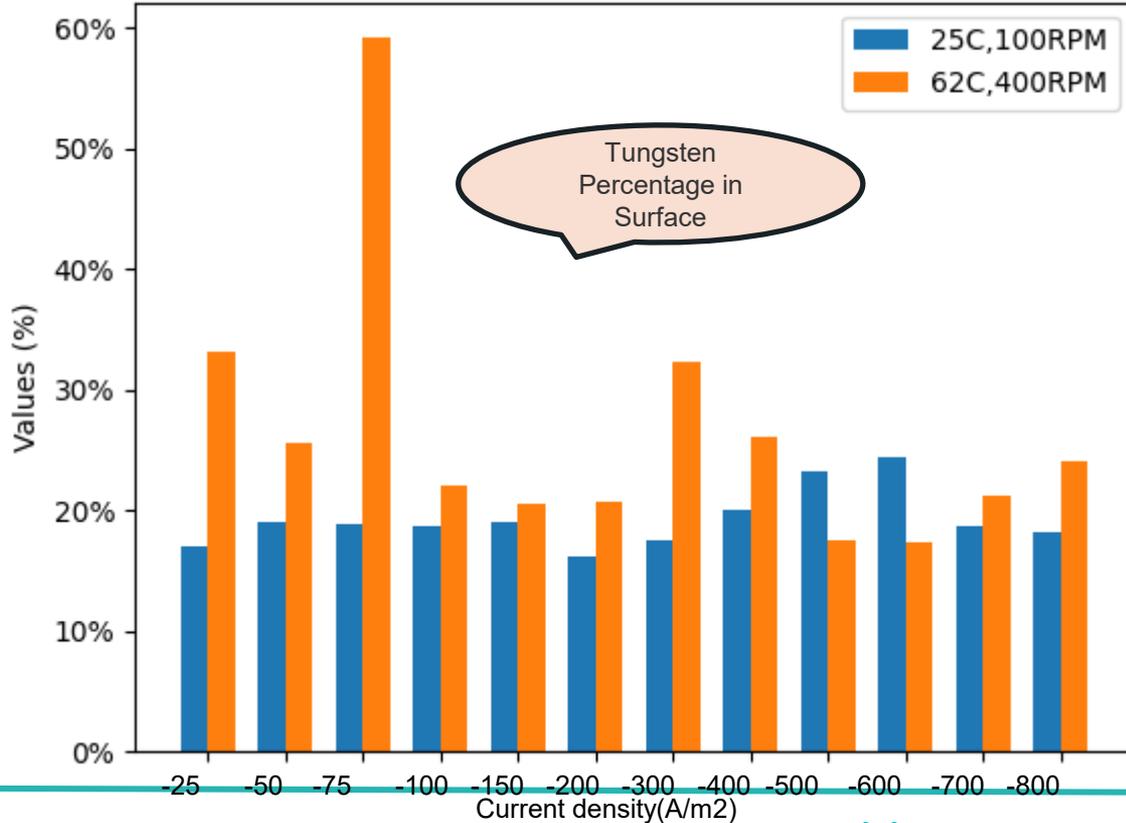
Only by calculation

Only Ni reduction

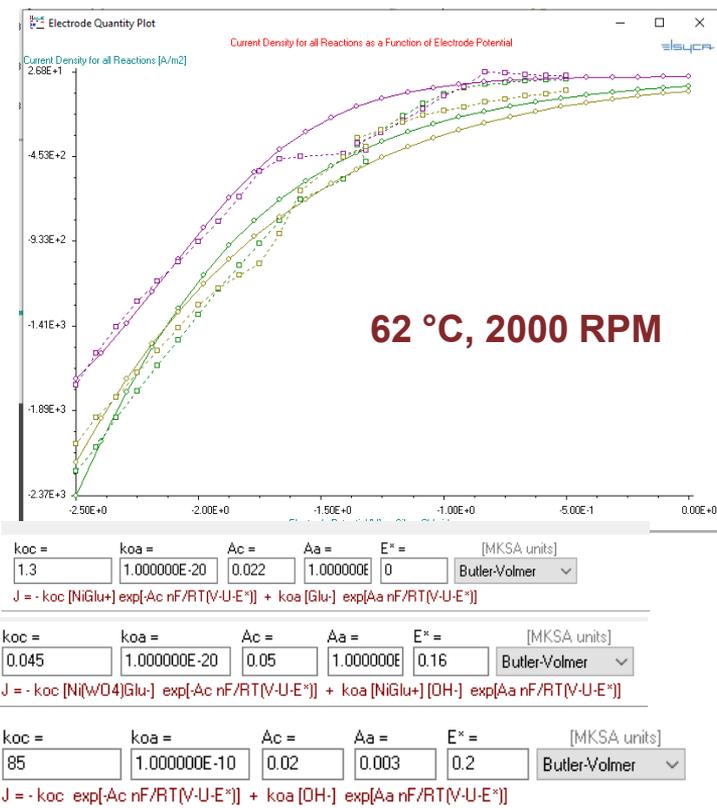
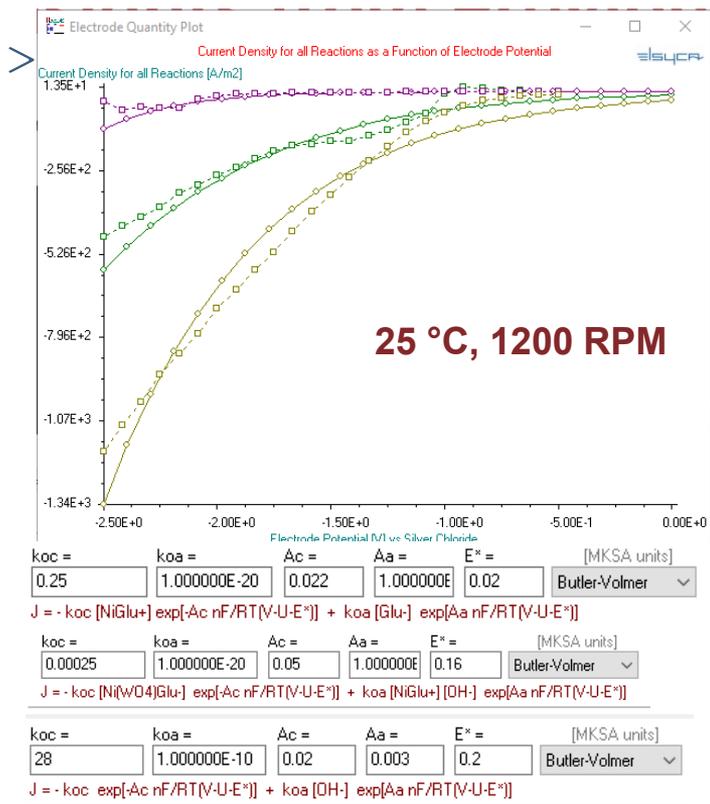


25 °C

Bath formulation	M
Ni²⁺ (M)	0.11
Na⁺ (M)	0.05
Sodium gluconate (M)	0.5
H ₂ BO ₃ (M)	0.65

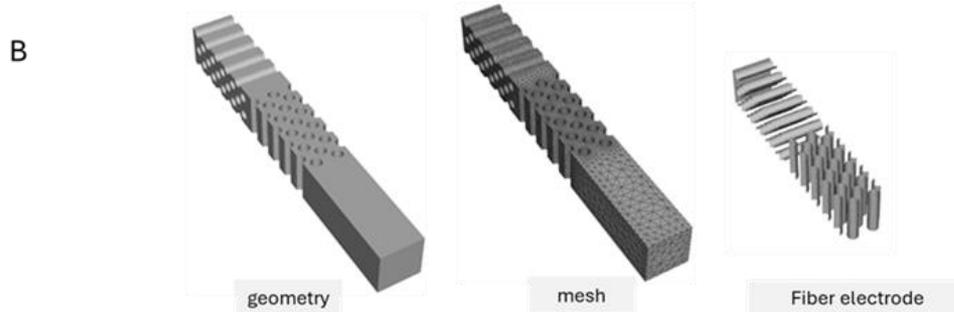
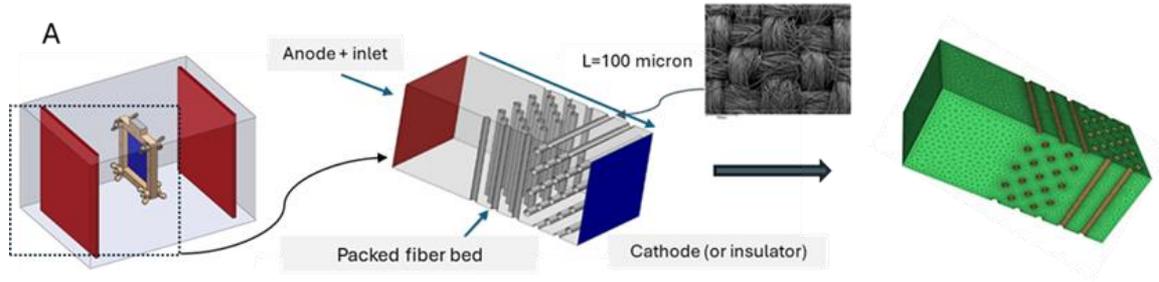


Simulation results



Task 4.2: Main achievements

> > > > > > > > > > > 3D fiber cloth model



Task 4.3. Main achievements

> > > > > > > > > > >

➤ experiments Ni-W 5 V (45 min/ 2.8 A*h) – cloth sample

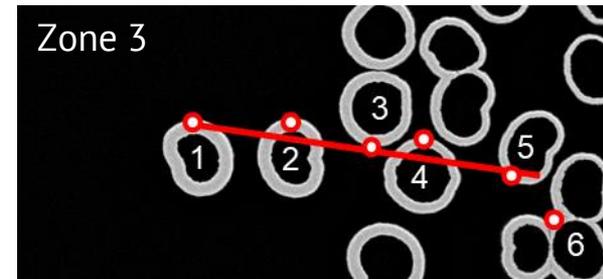
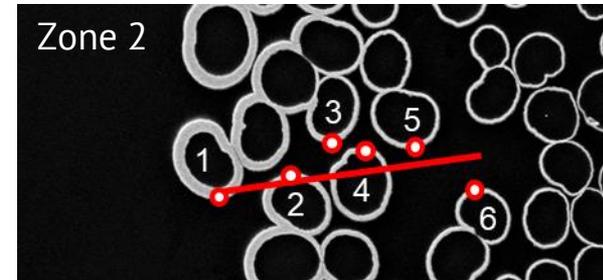
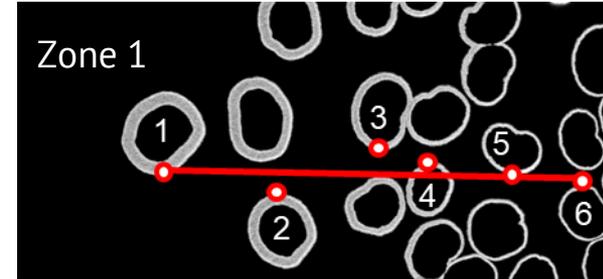
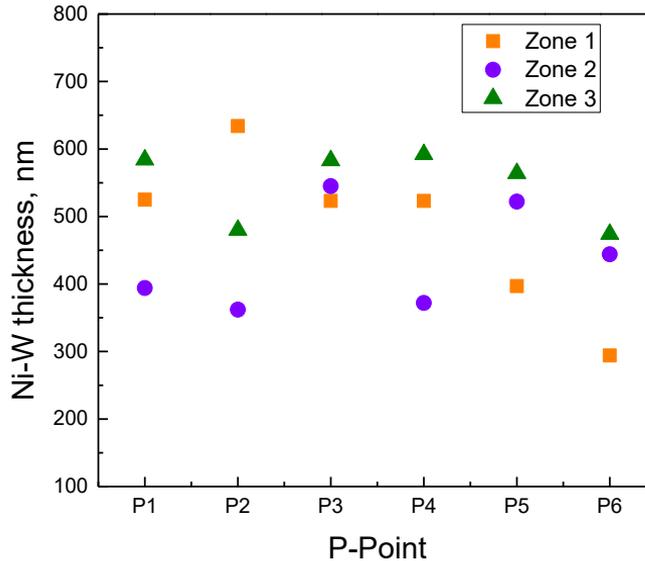
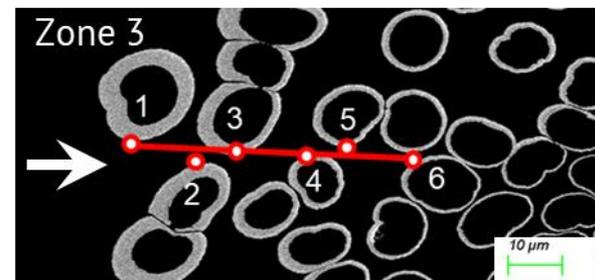
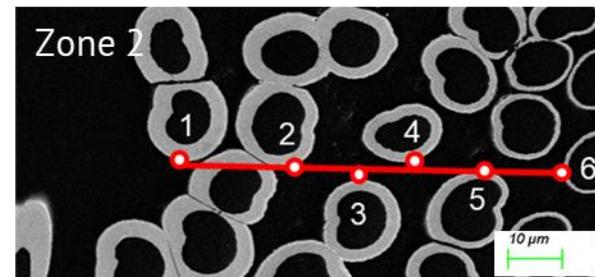
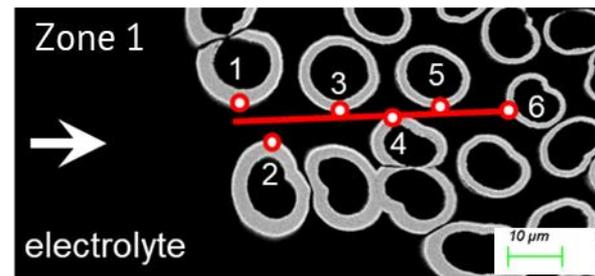
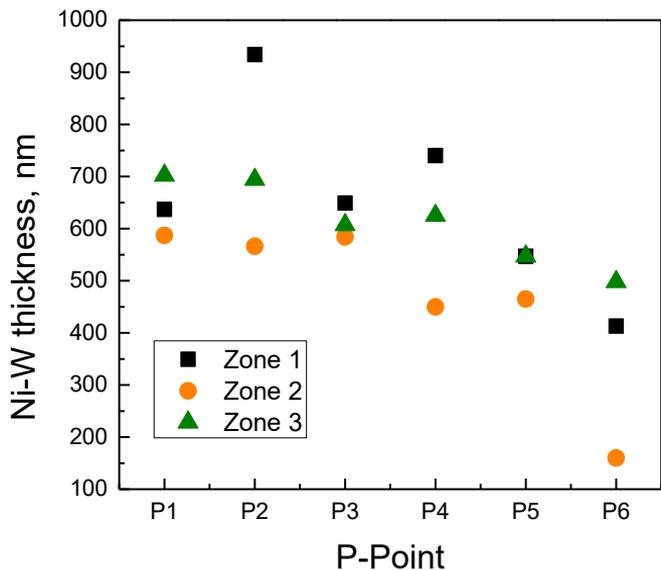


Image analysis at 20 kV. Very low contrast between the two layers (due to low W content). Large errors expected. Analysis will be repeated on freshly polished surface

Task 4.3. Main achievements

> > > > > > > > > > >

➤ experiments Ni-W 10 V (15 min/ 2.8 A*h) – cloth sample



Task 4.3. Main achievements

> > > > > > > > > > >

➤ experiments Ni-W 15 V (8 min/ 2.3 A*h) – cloth sample

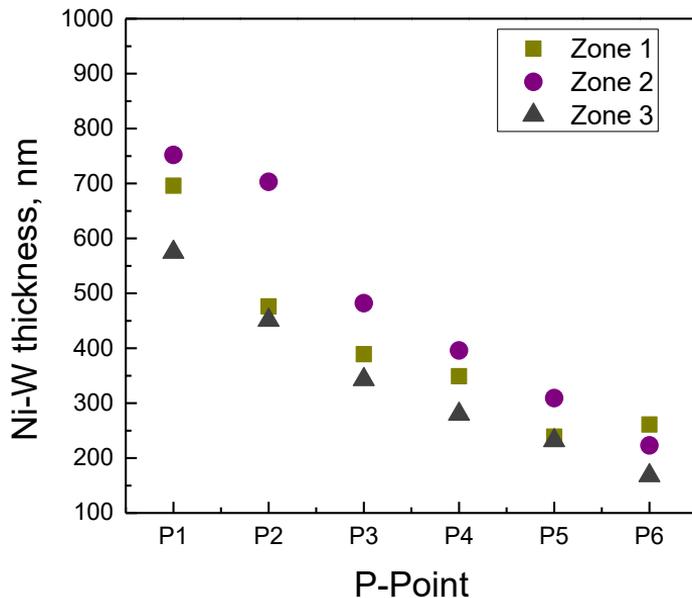
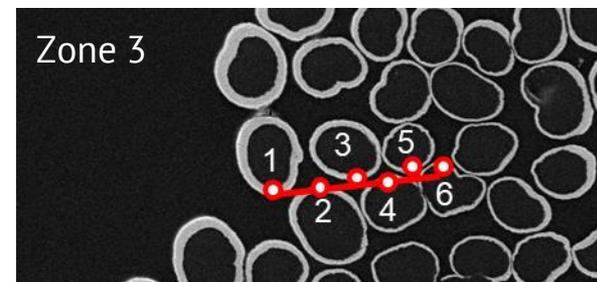
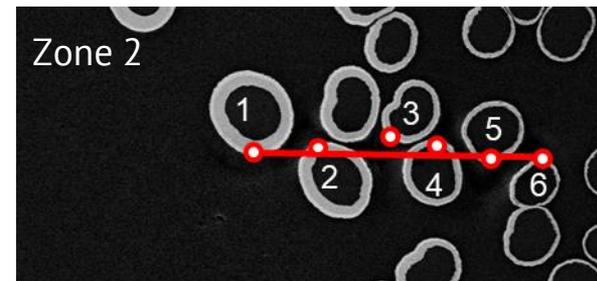


Image analysis at 10 kV.

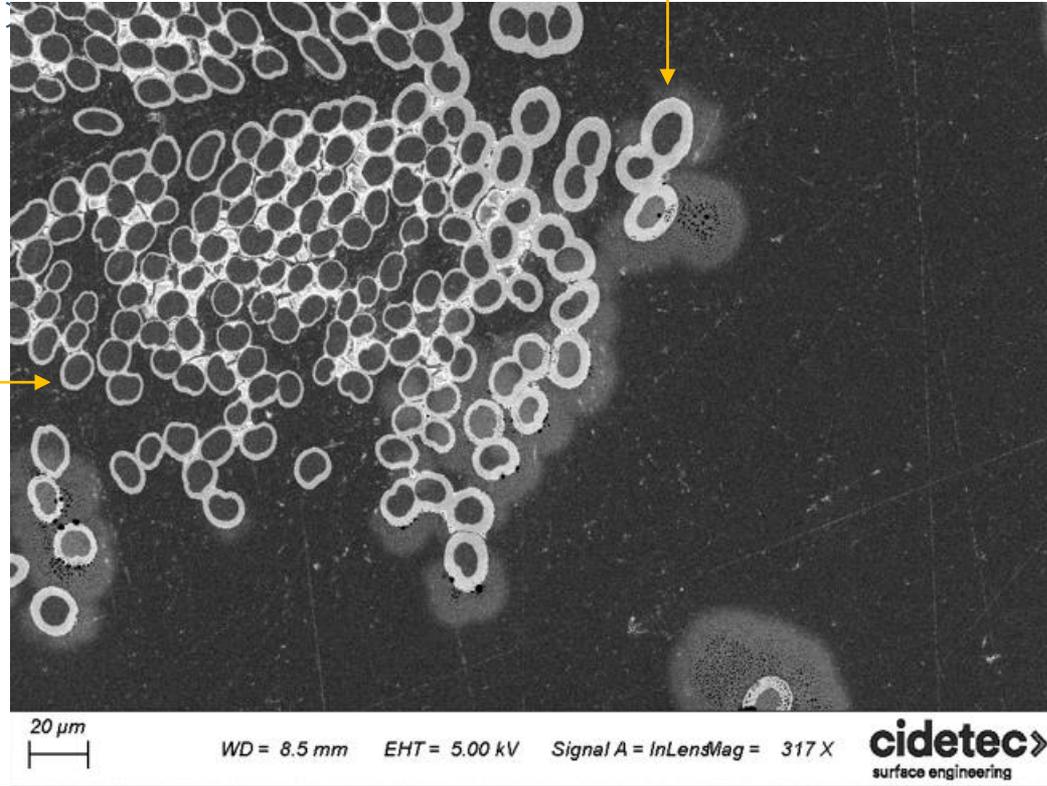


Task 4.3: Model validation

> > > > > >

only NiP

NiW + NiP



Task 4.3. Main achievements

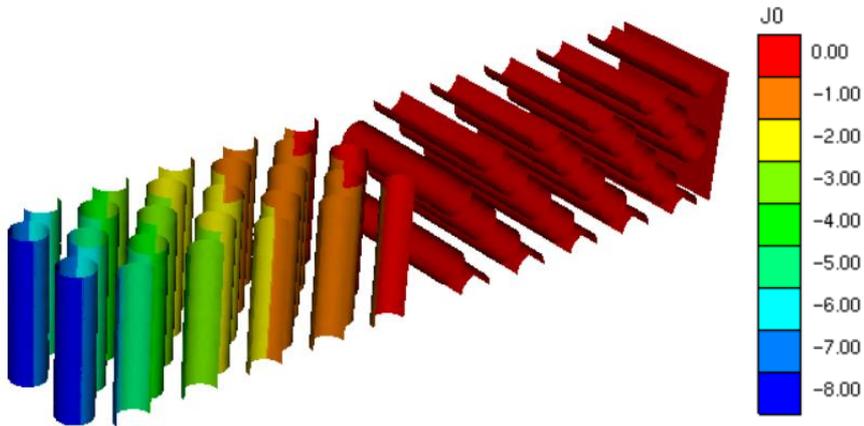
> > > > > > > > > >

➤ simulation results – current density micro-scale

Dt [s]	ΔV main [V]
2700	5
I fabric [A]	j avg [ASM]
1.21	-200

1 Ni reduction $\text{NiGlu}^+ + 2\text{e}^- = \text{Ni} + \text{Glu}^-$

2 NiW reduction $\text{Ni}(\text{WO}_4)\text{Glu}^- + 4\text{H}_2\text{O} + 8\text{e}^- = \text{Ni} + \text{W} + \text{Glu}^- + 8\text{OH}^-$

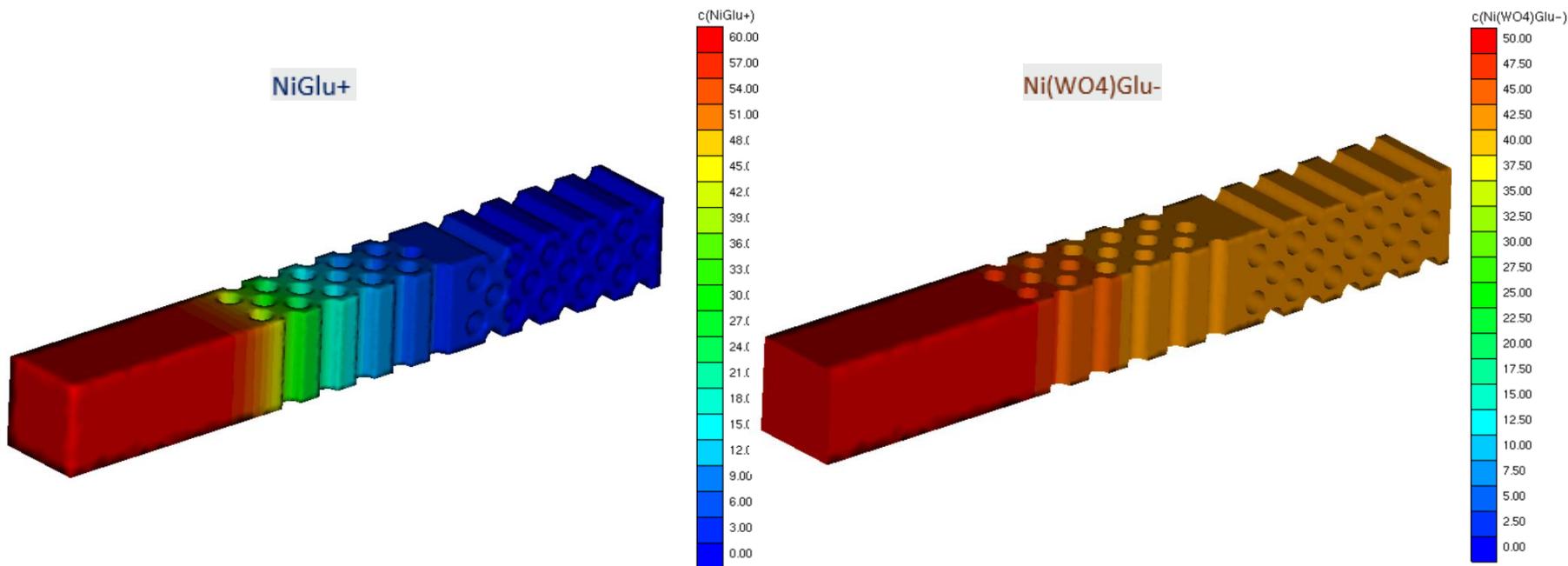


Task 4.3. Main achievements

> > > > > > > > > > >

➤ simulation results – Ni ion concentration profiles micro-scale

Dt [s]	ΔV main [V]
2700	5
I fabric [A]	j avg [ASM]
1.21	-200



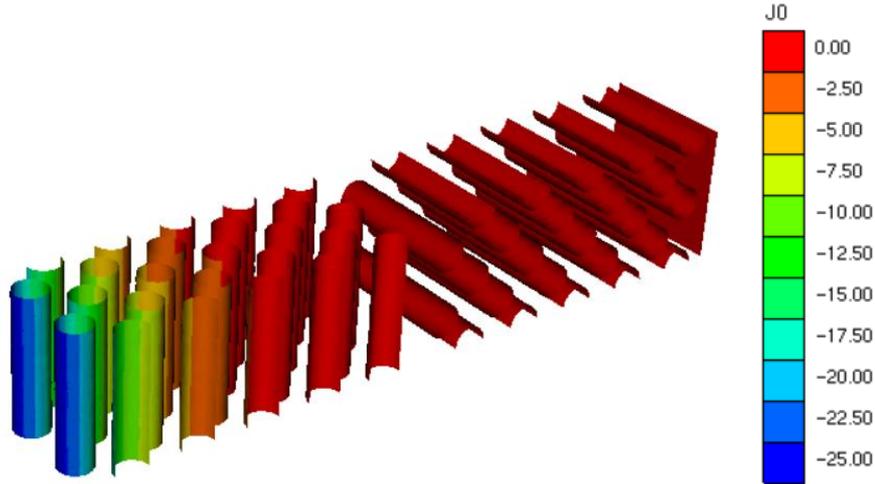
Task 4.3. Main achievements

> > > > > > > > > >

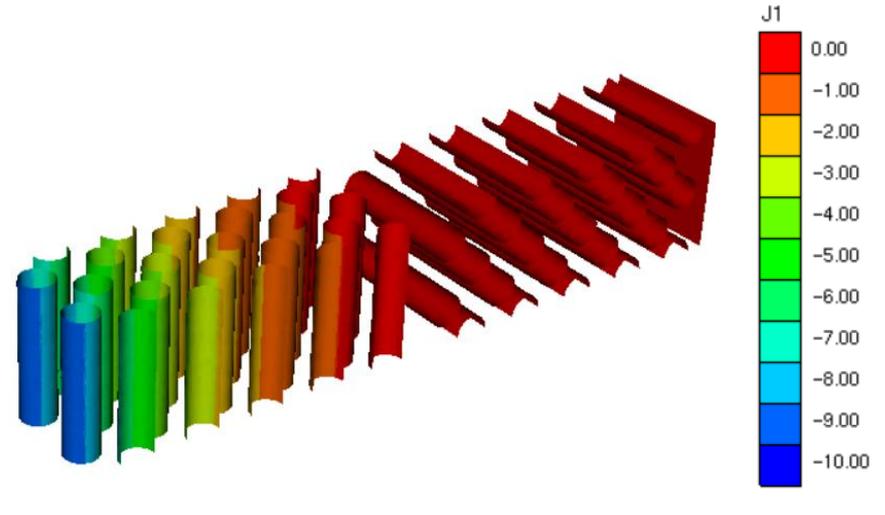
➤ simulation results – current density micro-scale

Dt [s]	ΔV main [V]
900	10
I fabric [A]	j avg [ASM]
2.61	-432

1 Ni reduction $\text{NiGlu} + 2\text{e}^- = \text{Ni} + \text{Glu}^-$



2 NiW reduction $\text{Ni}(\text{WO}_4)\text{Glu}^- + 4\text{H}_2\text{O} + 8\text{e}^- = \text{Ni} + \text{W} + \text{Glu}^- + 8\text{OH}^-$

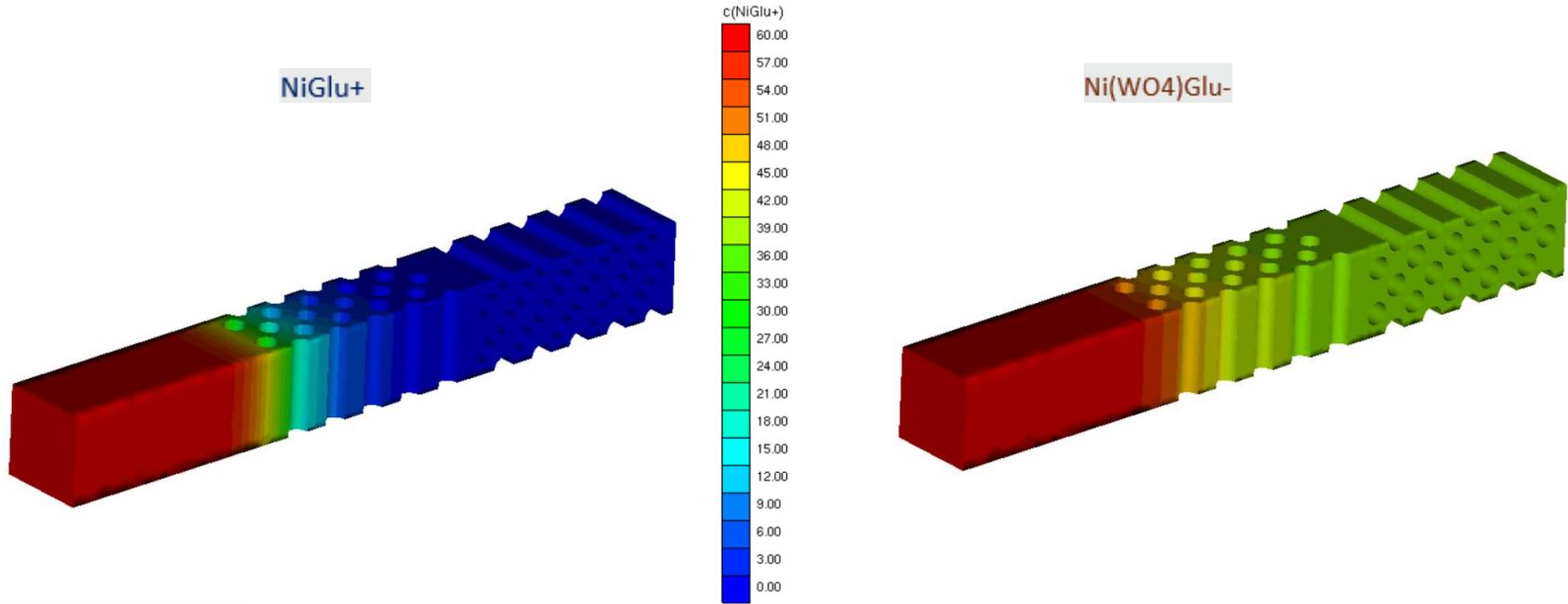


Task 4.3. Main achievements

> > > > > > > > > > >

➤ simulation results – Ni ion concentration profiles micro-scale

Dt [s]	ΔV main [V]
900	10
I fabric [A]	j avg [ASM]
2.61	-432

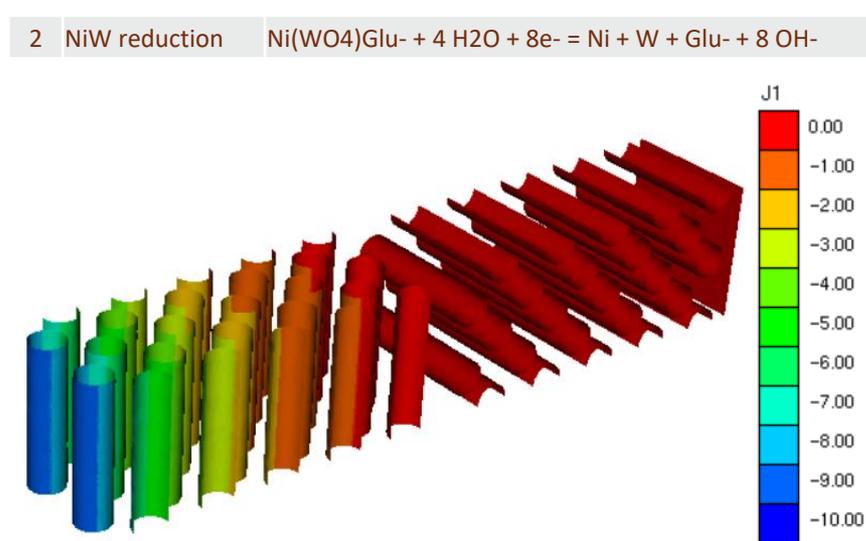
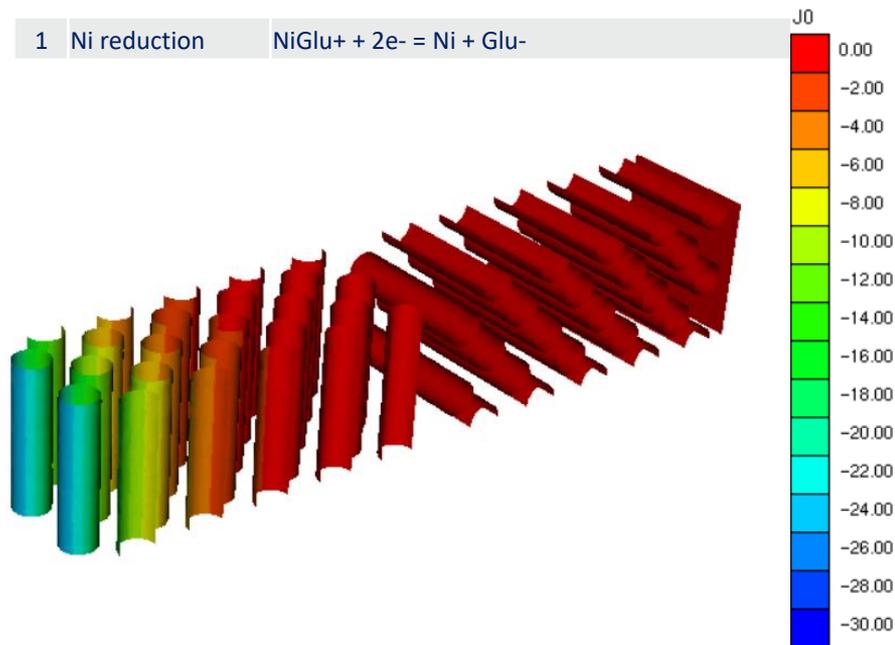


Task 5.1. Main achievements

> > > > > > > > > >

➤ simulation results – current density micro-scale

Dt [s]	ΔV main [V]
480	15
I fabric [A]	j avg [ASM]
3.46	-572

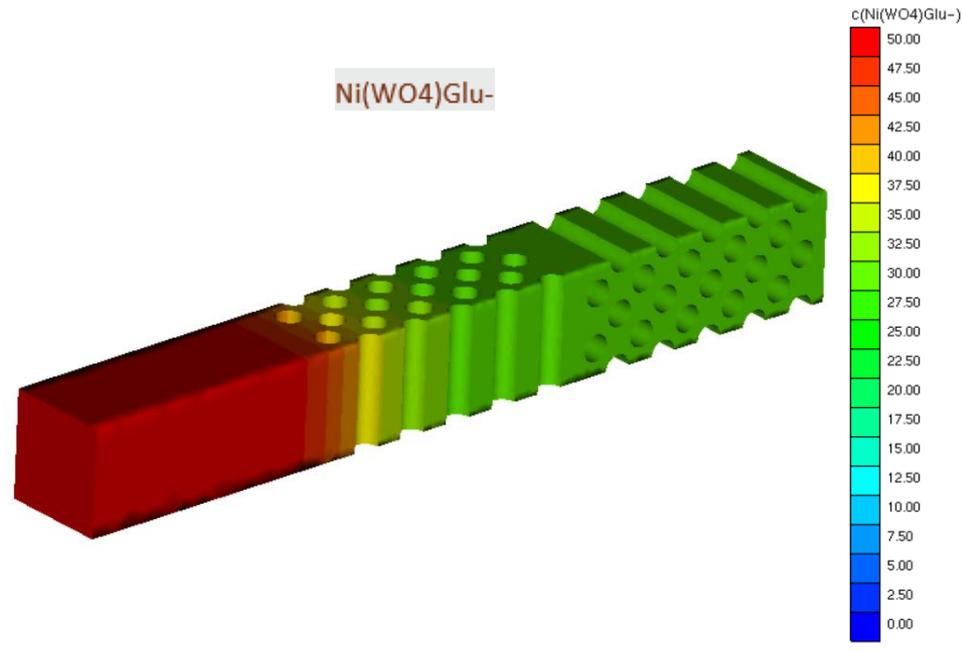
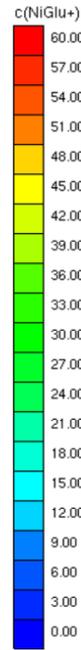
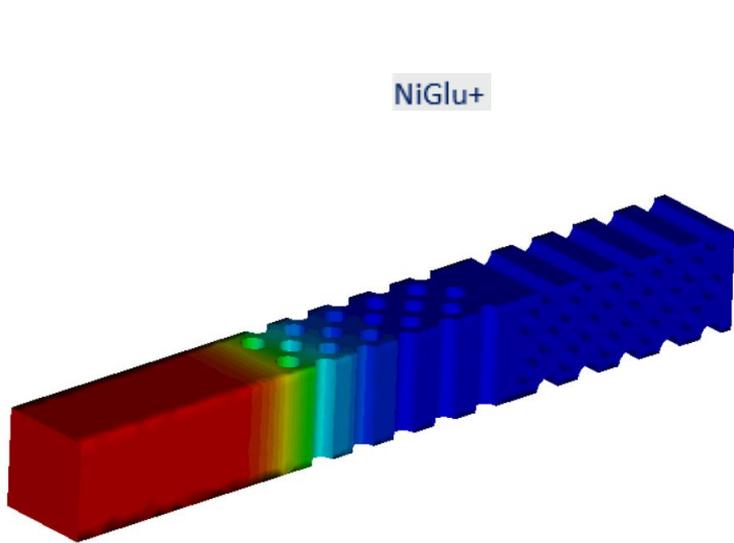


Task 4.3. Main achievements

> > > > > > > > > > >

➤ simulation results – Ni ion concentration profiles micro-scale

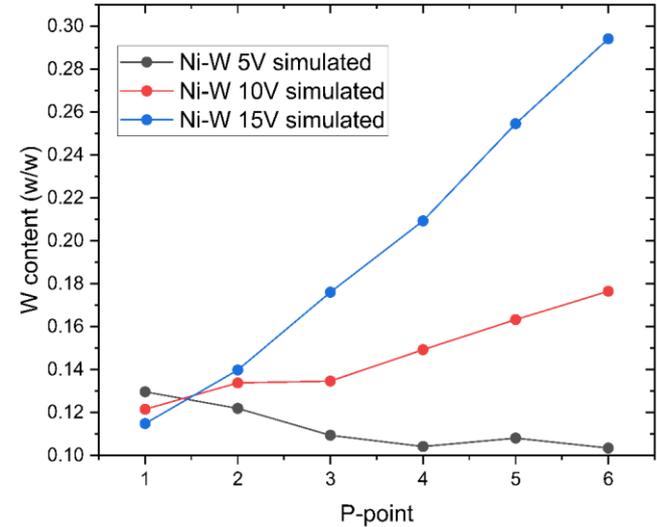
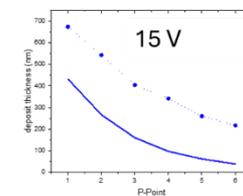
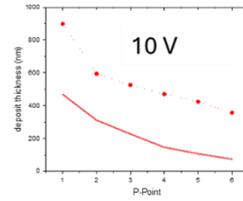
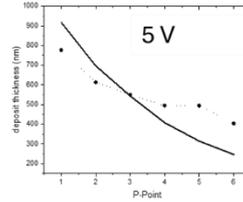
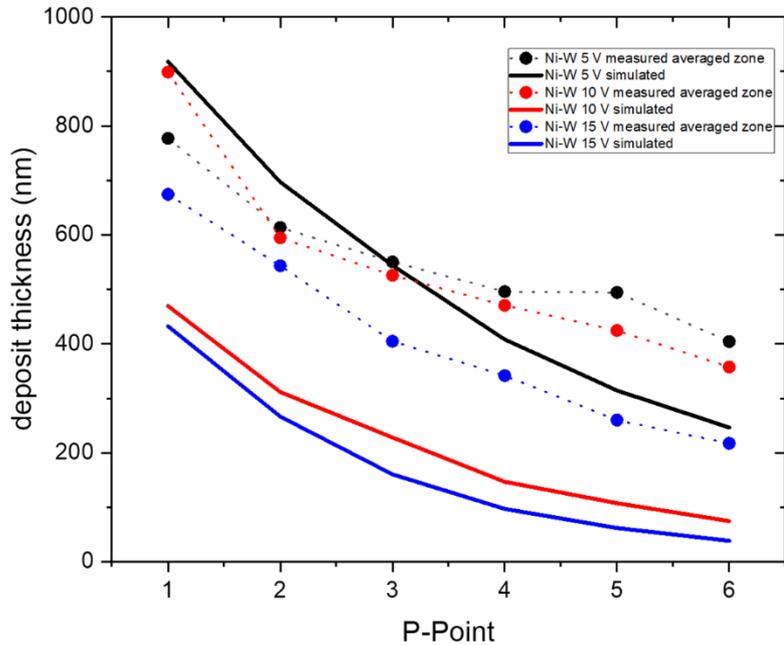
Dt [s]	ΔV main [V]
480	15
I fabric [A]	j avg [ASM]
3.46	-572



Task 4.3. Main achievements

> > > > > > > > > >

➤ validation – deposit thickness and W content



Thank you for your attention!



www.nickeffect.eu



Funded by
the European Union

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HADEA). Neither the European Union nor the granting authority can be held responsible for them.