Simulación 3D de la distribución espacial de especies químicas asociadas a la corrosión del par Zn-Fe

3D simulation of the spatial distribution of chemical species associated to the corrosion of the Zn-Fe couple

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Máster Propio Universitario en Simulación Numérica en Ciencia e Ingeniería con COMSOL Multiphysics

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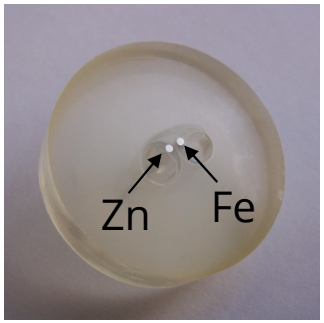
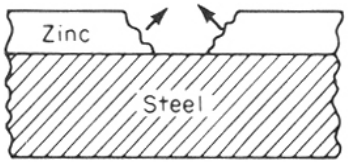
Introduction

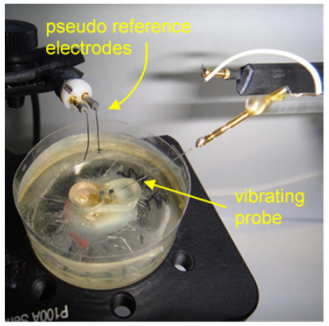


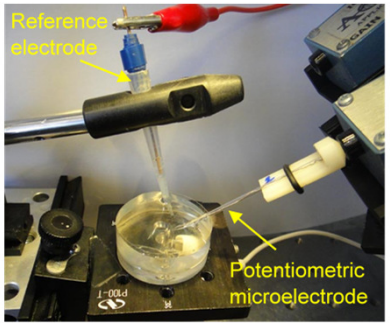
Galvanised steel

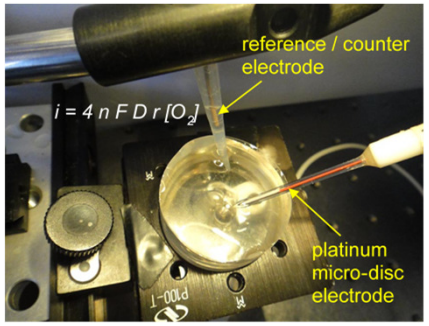


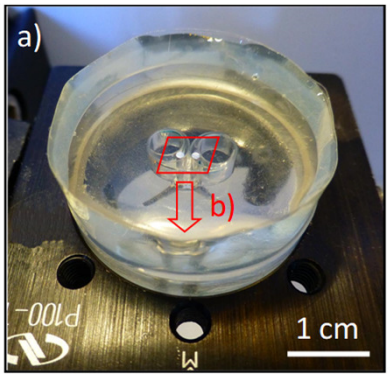
Cathodic protection with
Zn sacrificial anodes

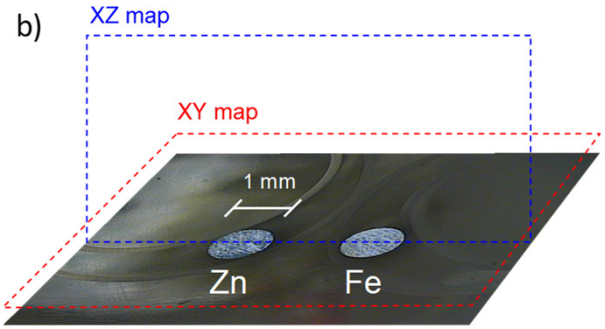
Introduction

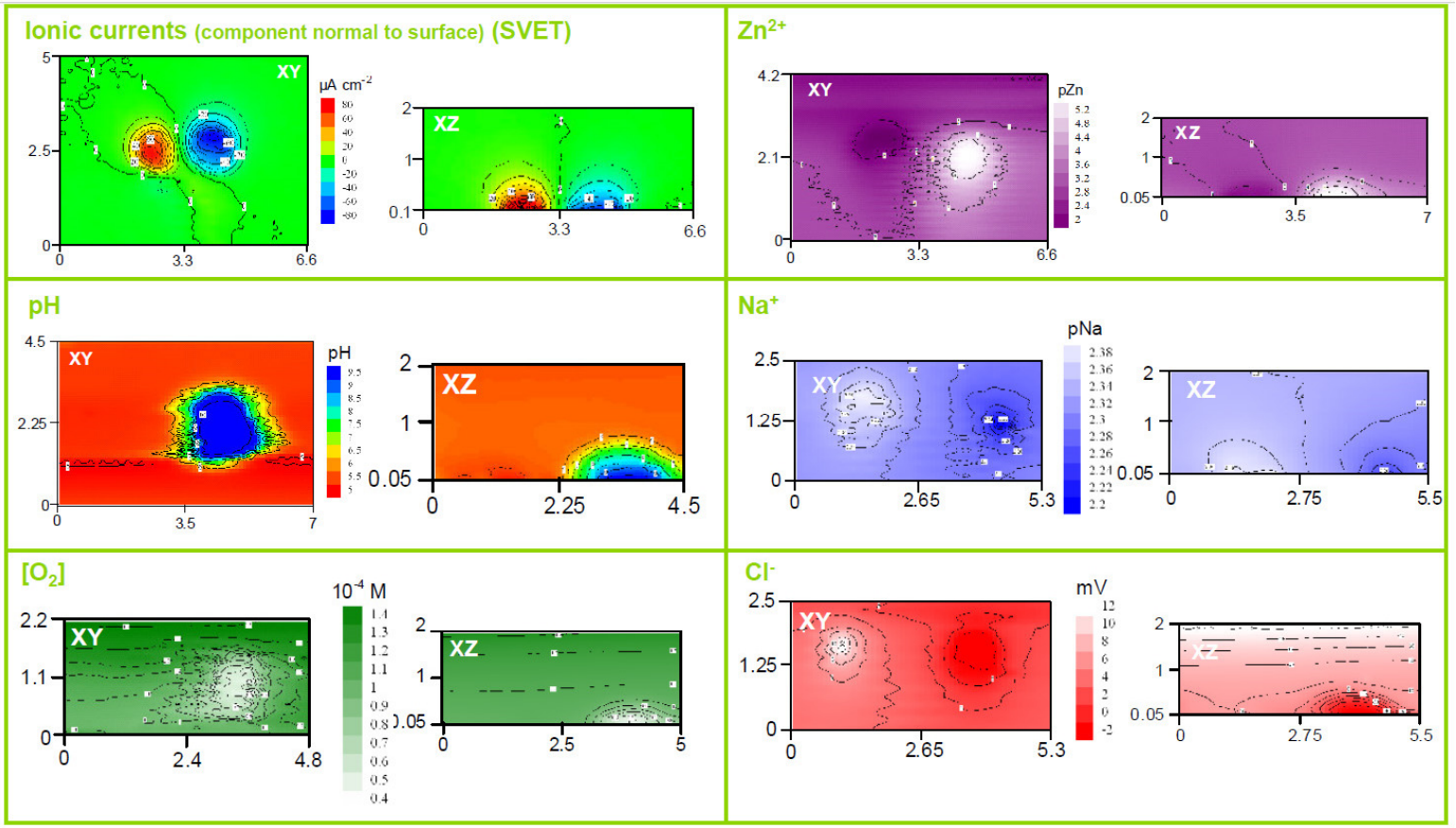




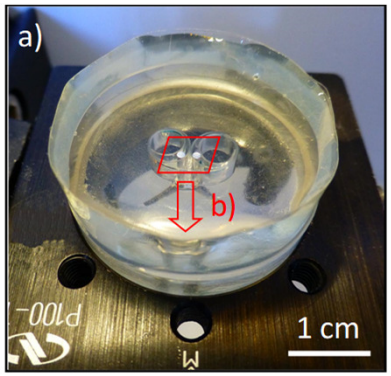


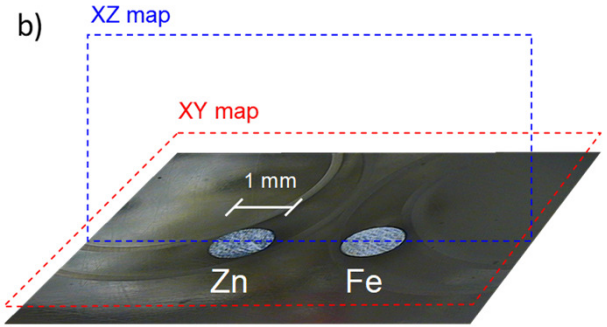


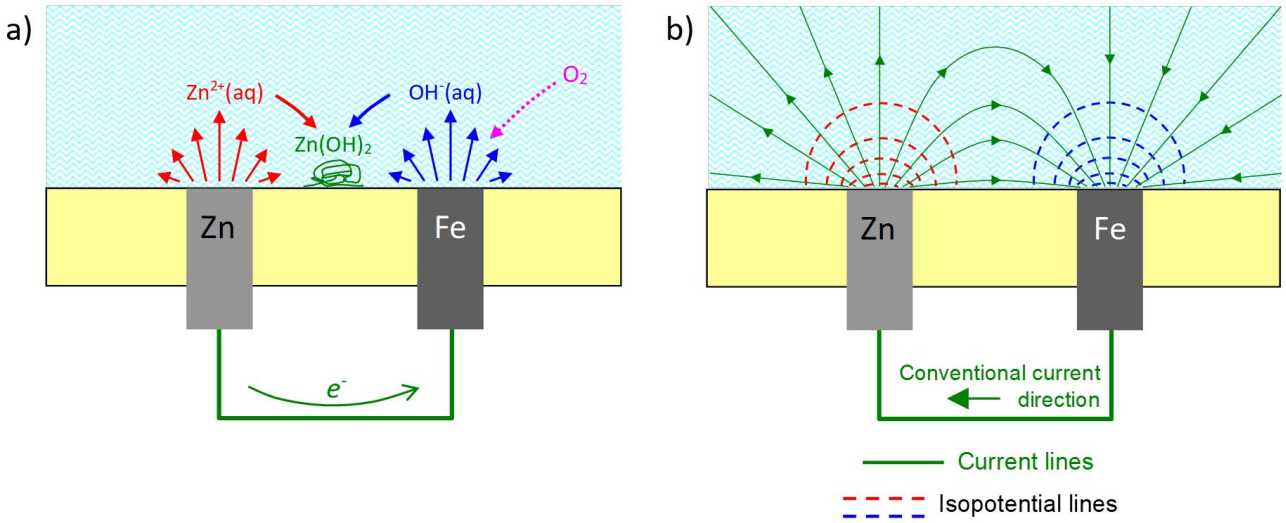




Objective







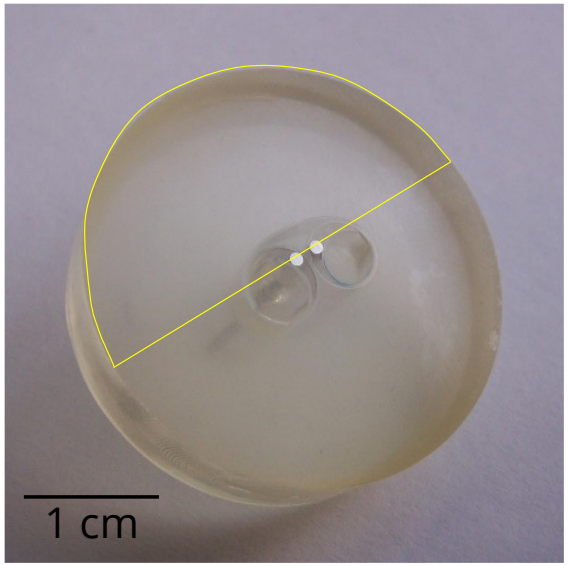
- Go beyond these sketches,
- Be able to numerically simulate the corrosion process,
- Replicate the existing experimental results.

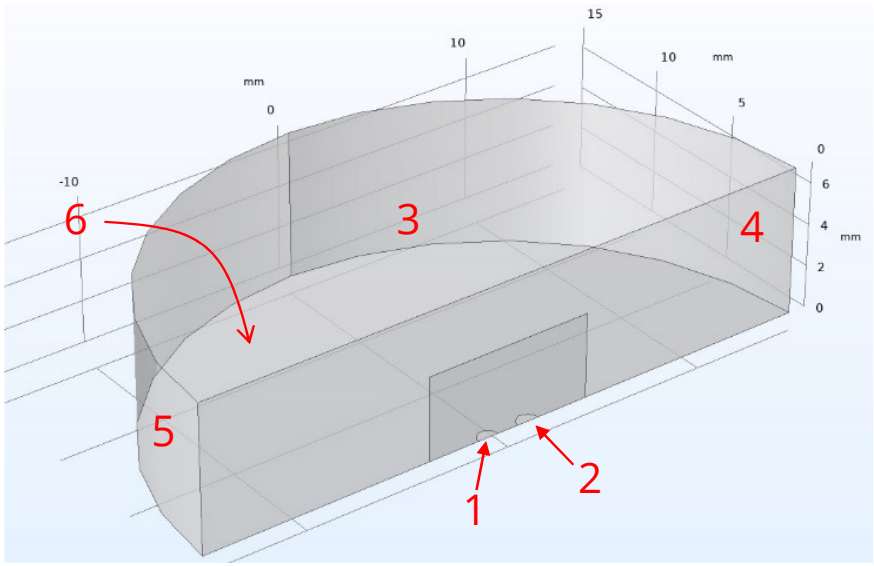
Geometry

Label: Parameters Geometry

Parameters

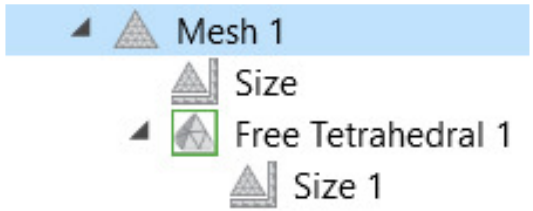
Name	Expression	Value	Description
R1	15[mm]	0.015 m	Radius of electrochemical cell
R2	0.5[mm]	5E-4 m	Radius of electrodes
dist	2[mm]	0.002 m	Distance between the center of electrodes
height	7[mm]	0.007 m	Thickness of the solution layer

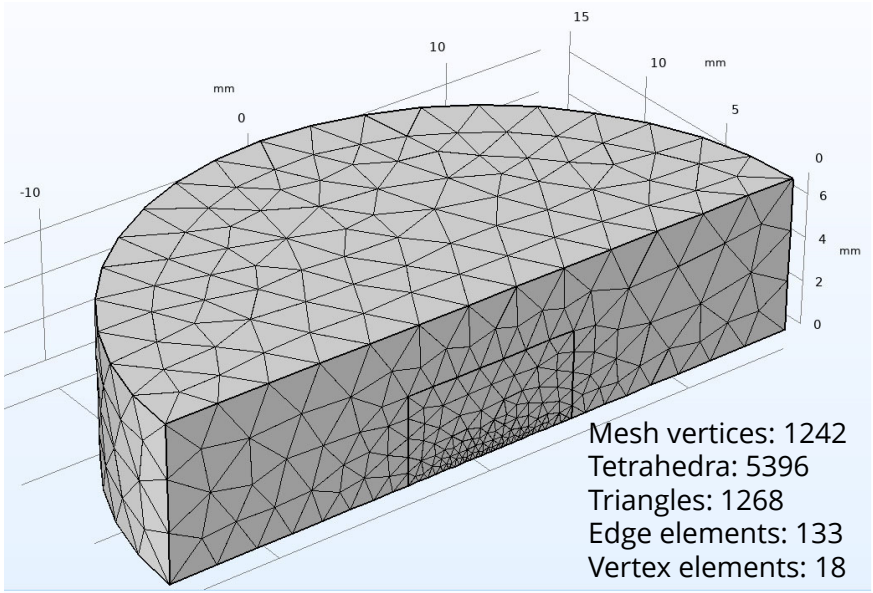




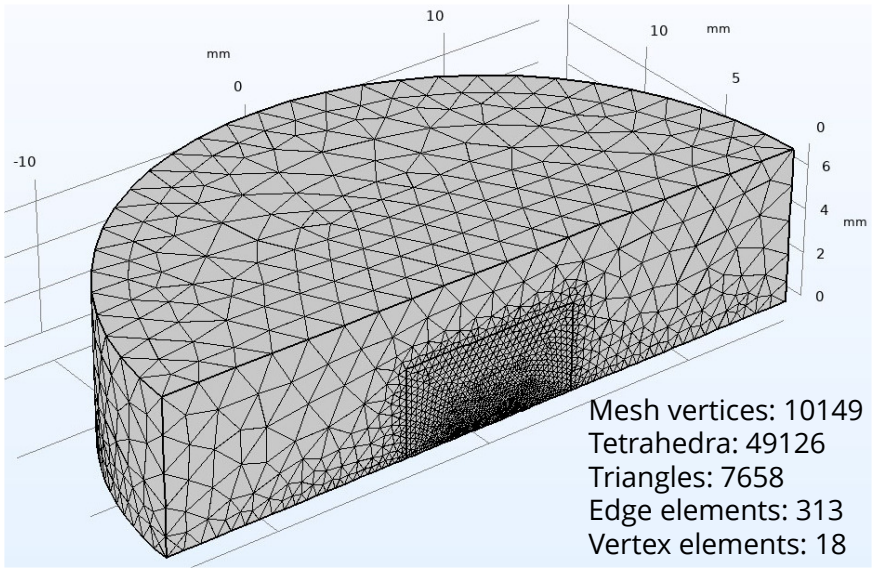
1. Zinc (anode)
2. Iron (cathode)
3. Solution top layer
4. Symmetry plane
5. Cell walls
6. Epoxy mount

Mesh





Mesh vertices: 1242
Tetrahedra: 5396
Triangles: 1268
Edge elements: 133
Vertex elements: 18



Mesh vertices: 10149
Tetrahedra: 49126
Triangles: 7658
Edge elements: 313
Vertex elements: 18

Equations and Physical Interfaces

Tertiary Current Distribution, Nernst-Plank Interface
water-based with electroneutrality charge conservation model

(mass balance of chemical species)

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i + R_i$$

(molar flux, Nernst-Planck equation)

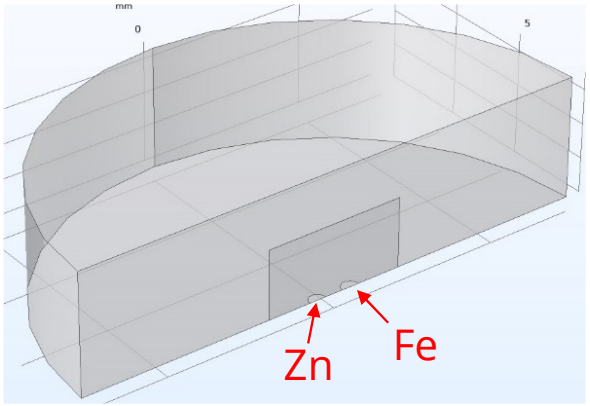
$$J_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi + \cancel{c_i \vartheta}^{\,0}$$

(electroneutrality condition)
maintained by H^+ and OH^- (and Kw)

$$\sum_i^n z_i \, c_i = 0$$

Species	c_i^0 (mol m^{-3})	z_i	D_i (x10^9 m^2 s^{-1})
O_2	0.23	0	1.96
Na^+	5	+1	1.23
Cl^-	5	-1	1.19
H^+	-	+1	9.31
OH^-	-	-1	5.26
Fe^{2+}	10^{-3}	+2	0.65
Zn^{2+}	10^{-3}	+2	0.7

Boundary conditions



Zinc

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$$i_{Zn} = i_{0,Zn}\ 10^{\frac{\eta}{A_{Zn}}}$$

$$\eta = \phi_s - \phi_l - E_{eq}$$

Iron

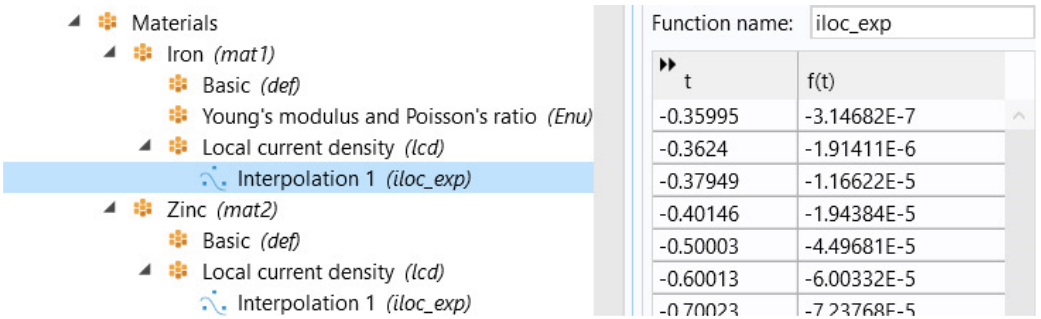
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

$$i_{O_2,Tafel} = -i_{0,O_2}\ 10^{\left(\frac{\eta}{A_{O_2}}\right)}$$

$$i_{O_2} = \frac{i_{O_2,Tafel}}{1 + \left|\frac{i_{O_2,Tafel}}{i_{lim}}\right|}$$

Parameter	Value
E_{Zn}^0	-1.004 V_{SCE}
$i_{0,Zn}$	0.1 A m^{-2}; 4.48 A m^{-2}
A_{Zn}	22 mV, 28±3 mV
E_{Fe}^0	-0.681 V_{SCE}
$i_{0,Fe}$	0.28 A m^{-2}
A_{Fe}	0.154 V
E_{O2}^0	0.650 V_{SCE}
$i_{0,O2\ on\ Zn}$	0.888 x 10^{-4} A m^{-2}
$A_{O2,\ on\ Zn}$	-0.055 V
$i_{0,O2\ on\ Fe}$	0.888 A m^{-2}
$A_{O2,\ on\ Fe}$	-0.055 V
$i_{lim,O2}$	0.2 – 0.5 A m^{-2}

Boundary conditions



Zinc

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

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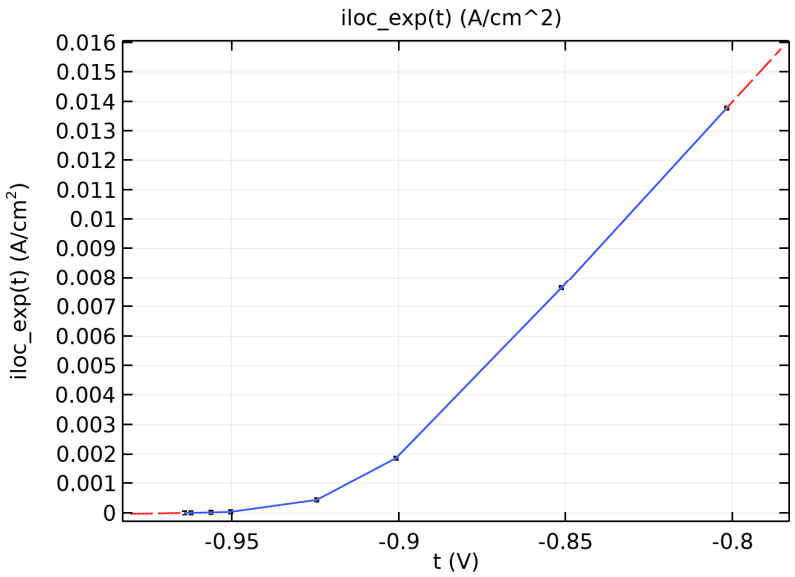
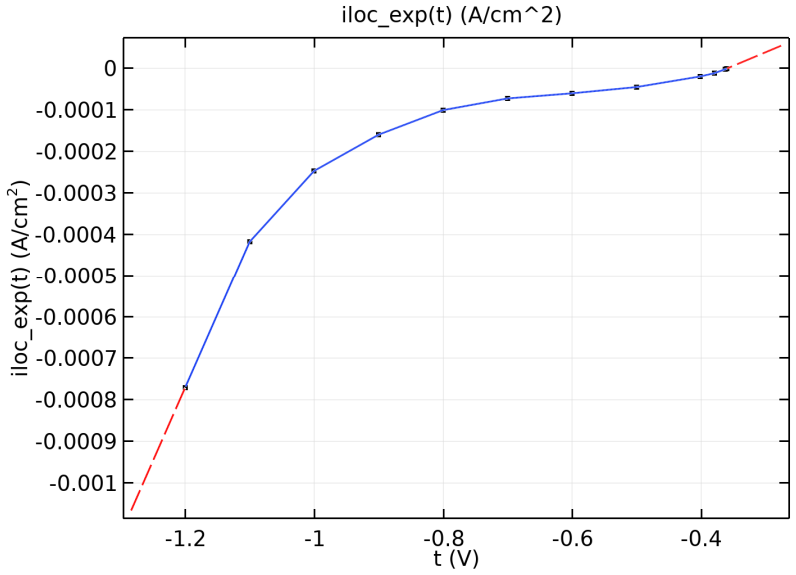
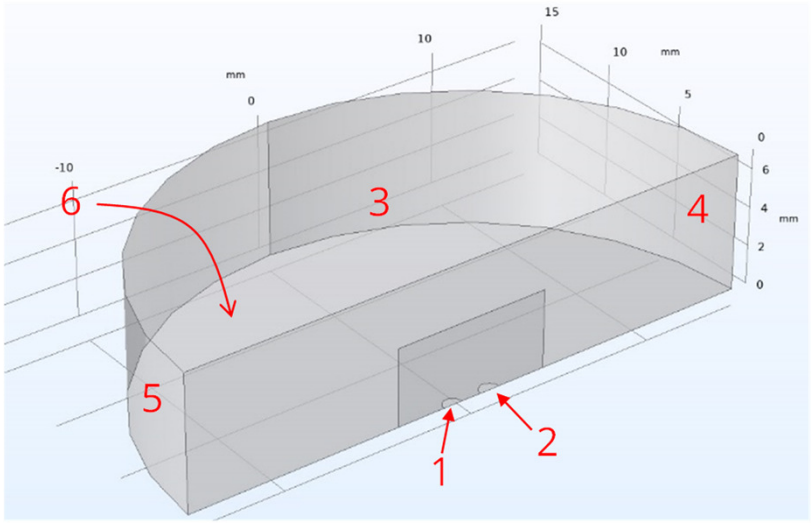




Boundary conditions

- Tertiary Current Distribution, Nernst-Planck *(tcd)*
  - Domain — Electrolyte 1
  - (5,6) — No Flux 1
  - (5,6) — Insulation 1
  - Domain — Initial Values 1
  - (1) — Electrode Surface Zn
  - (2) — Electrode Surface Fe
  - (3) — Concentration 1
  - (4) — Symmetry 1
  - (3) — Flux 1



Insulation: $-\boldsymbol{n} \cdot J_i = 0$

No flux: $-\boldsymbol{n} \cdot i_l = 0$

Flux 1

$$F_{O_2} = \frac{\partial c_{O_2}}{\partial n} = F_{O_2,max}\left(1 - \frac{c_{O_2}}{c_{O_2}^{sat}}\right)$$

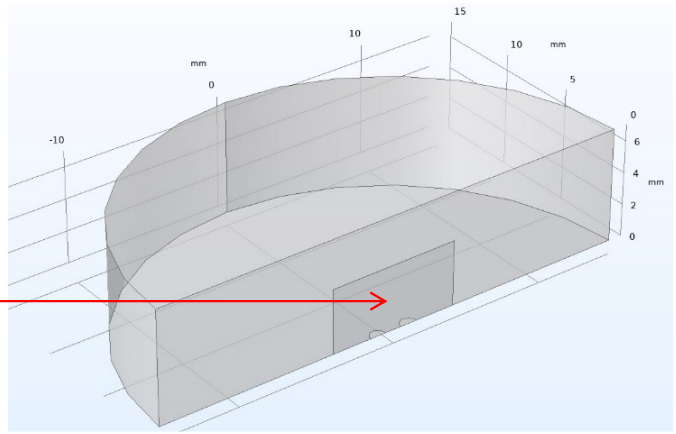
$$c_{O_2}^{sat}(\mathrm{mol/m^3}) = 0.23\, e^{\left(-3.63\times10^{-4} \times c_{Cl^-}\right)}$$

Initial values & Concentration

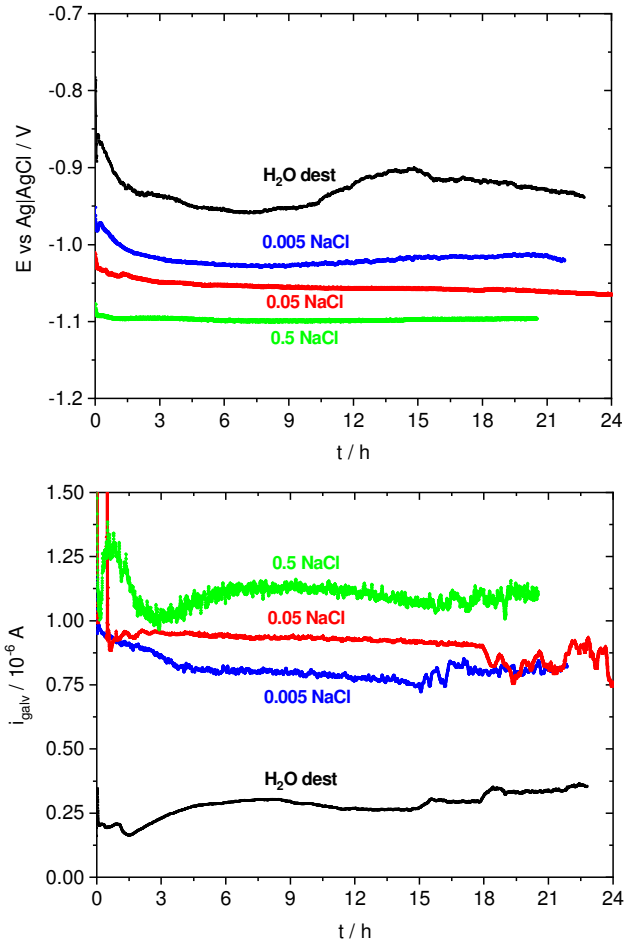
Species	c_i^0 (mol m^{-3})
O_2	0.23
Na^+	5
Cl^-	5
H^+	-
OH^-	-
Fe^{2+}	10^{-3}
Zn^{2+}	10^{-3}

Results

- Results
  - Solution potential
  - Current density in solution (SVET)
  - O2
    - Concentration, O2, Streamline (tcd)
    - Concentration, O2, Surface (tcd)
    - Concentration, O2, maps (tcd) 1
    - 3D Plot Group_O2
  - Zn2+
  - Na+
  - Cl-
  - OH-
  - H+
  - pH
  - Datasets
  - Views
  - Derived Values
    - Surface Integration 1 Zn current
    - Surface Integration 2 Fe current



Results



E_{couple}, I_{galv} and ΔE in solution, from experiments and from numerical modelling.

	Experimental	Polarization curves		Tafel equation	
		Mesh1	*Mesh2*	Mesh1	*Mesh2*
E_{couple} (V_{SCE})	**-1.015**	-0.934	*-0.934*	-1.005	*-1.007*
I_{galv} (10^{-7} A)	**7.5**	7.15	*7.15*	1.86	*1.96*
ΔE (mV)	**12**	17	*17*	7	*7*
Computing time		1 min 40 s	*34 min 34 s*	2 min 54 s	*1 h 43 min 48 s*

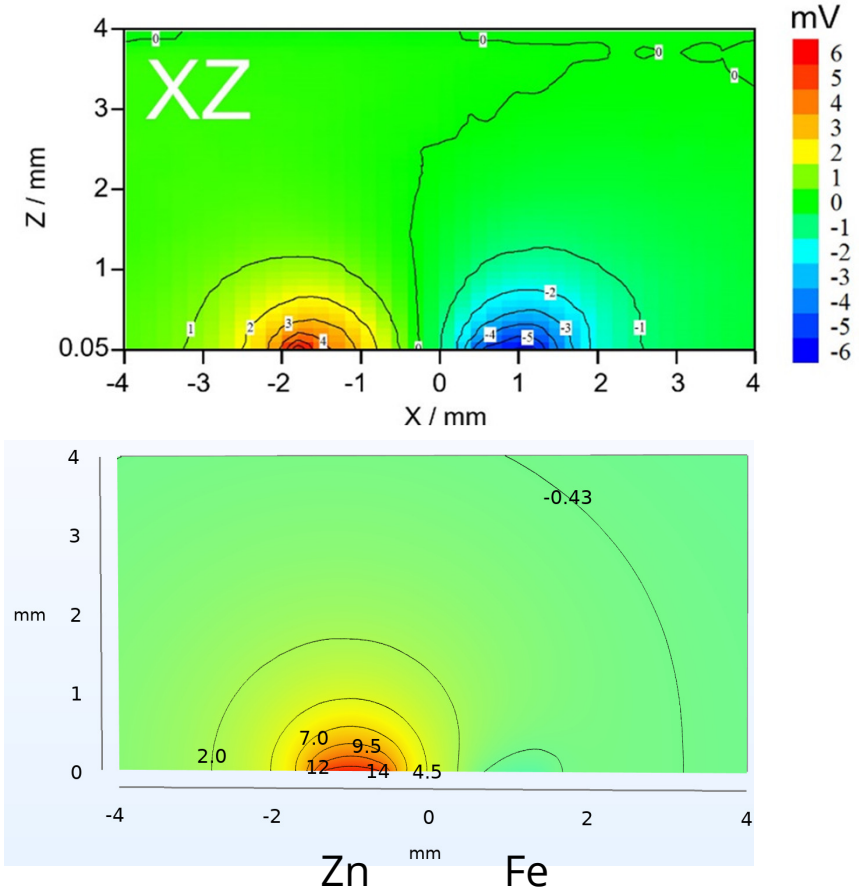
E_{couple}, I_{galv} and ΔE with time: Mesh2 and polarization curves.

Time	Ecouple (V_{SCE})	Igalv (10^{-7} A)	ΔE (mV)
1 µs	-0.9310	6.9967	24
1 ms	-0.9310	6.9965	24
1s	-0.9315	6.9625	23
1 h	-0.9335	7.1208	18
1 d	-0.9340	7.1525	17

E_{couple}, I_{galv} and ΔE with different concentrations of NaCl.

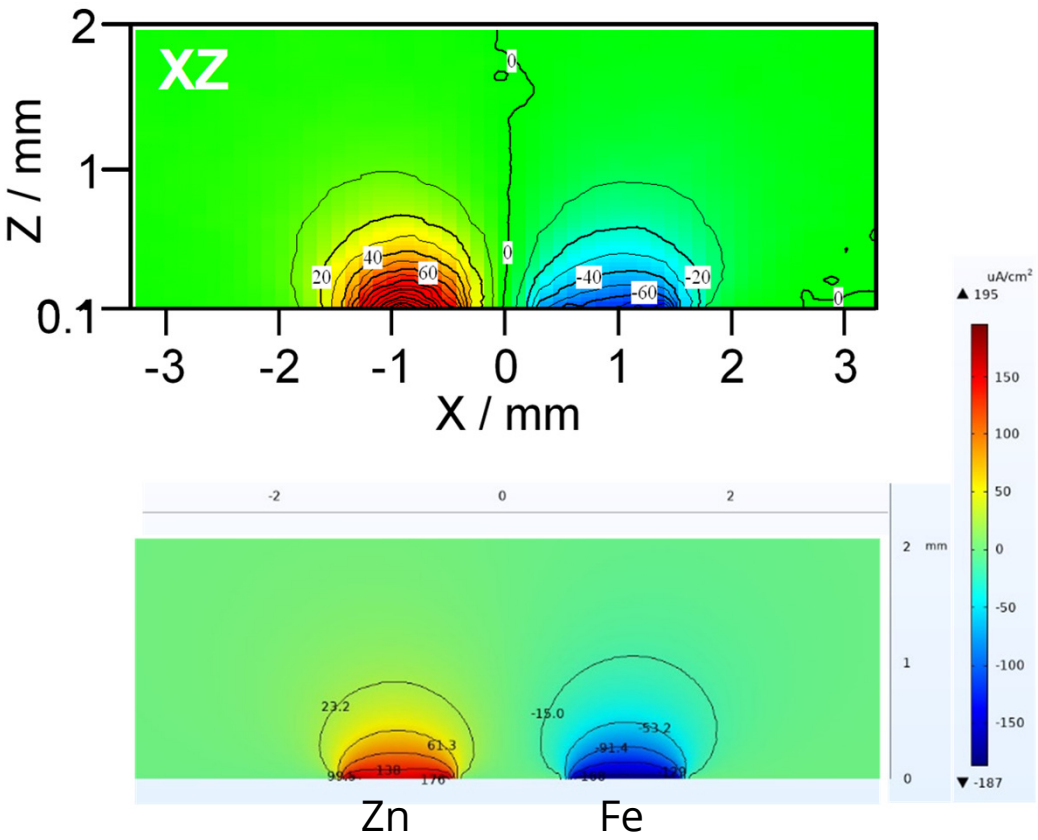
[NaCl] / M	Ecouple (V_{SCE})	Igalv (10^{-7} A)	ΔE (mV)
0.005	-0.934	7.15	17
0.05	-0.939	7.56	3
0.5	-0.940	7.63	0.3

Potential in solution



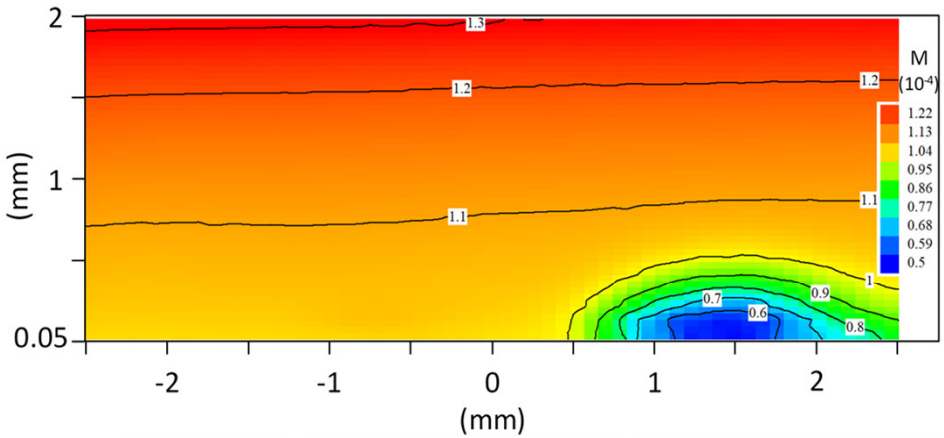
- Location of the map where expected
- Values close to the experimental

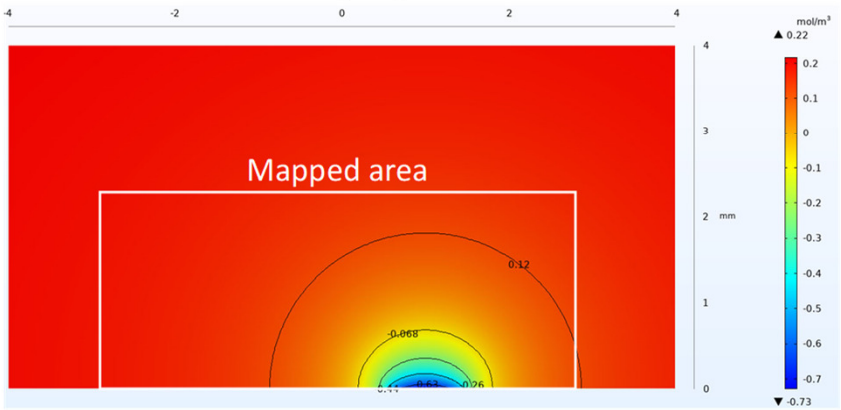
Current density in solution



- Location of the map where expected
- Values close to the experimental

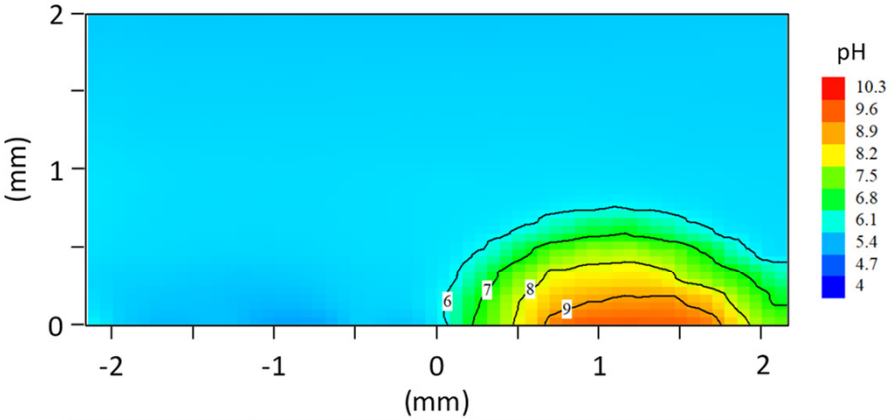
O_2

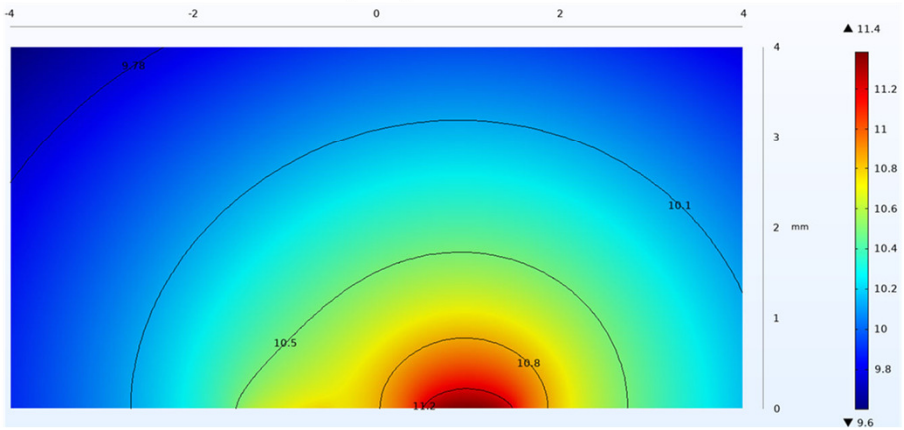




- Location of the maps where expected
- Values close to the experimental

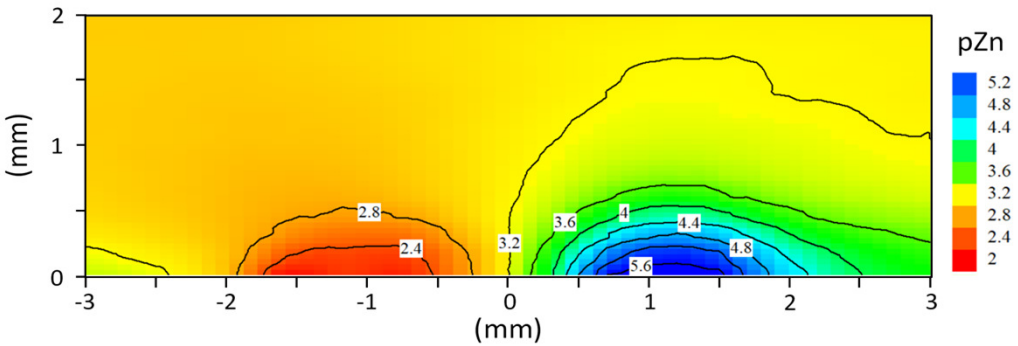
pH

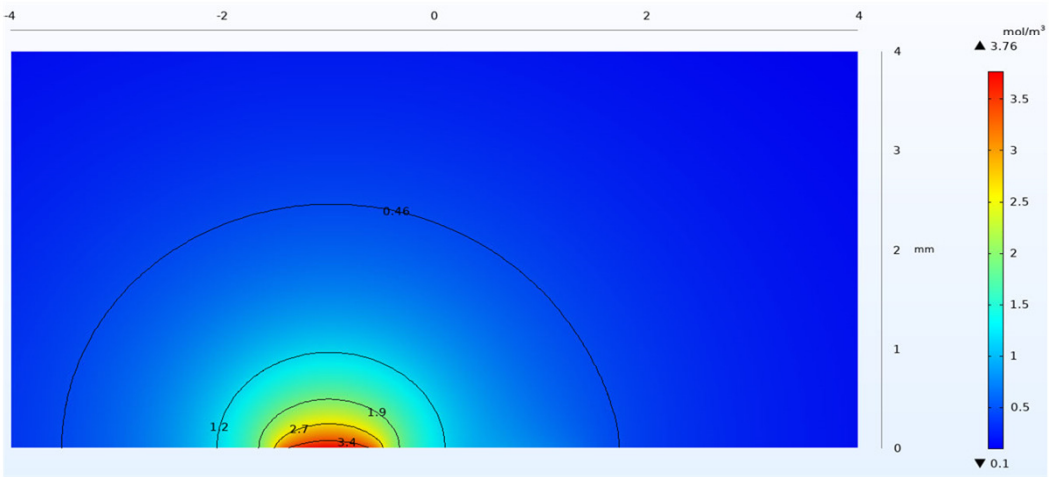


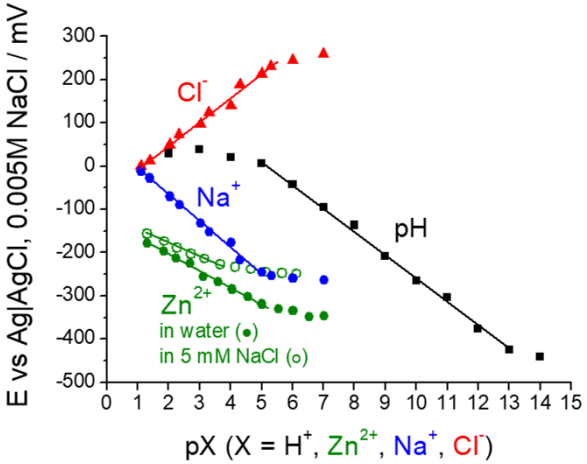


- Round shapes of diffusion path
- Diffusion in the complete simulation domain

Zn^{2+}







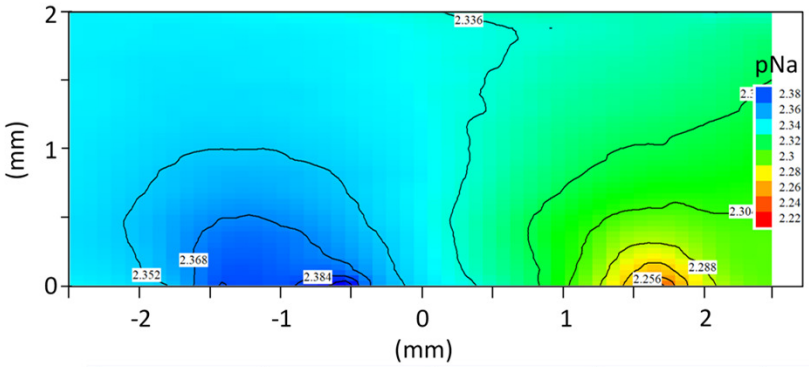
Homogeneous chemical (precipitation) reactions

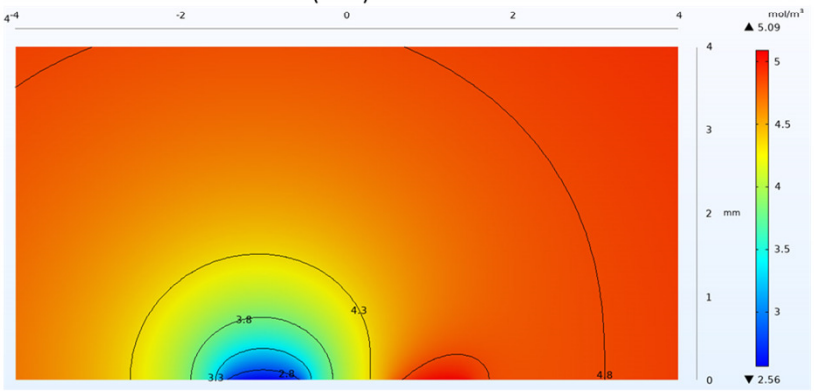
Reaction	log(K) at 25°C
$Zn^{2+} + OH^- \Leftrightarrow Zn(OH)^+$	5.05
$Zn(OH)^+ + OH^- \Leftrightarrow Zn(OH)_2(aq)$	6.06
$Zn(OH)^+ + OH^- \Leftrightarrow Zn(OH)_2(s)$	3.0
$Zn(OH)_2(aq) \Leftrightarrow Zn(OH)_3^-$	2.5

- Zinc produced where expected.
- Values close to the experimental.

- High bulk value in experiment not present in simulation.
- Region of depletion of Zn^{2+} around the cathode seen on experiment not predicted by the simulation.

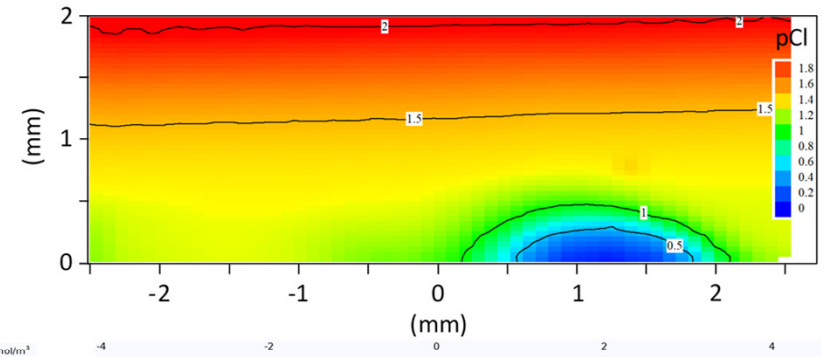
Na^+

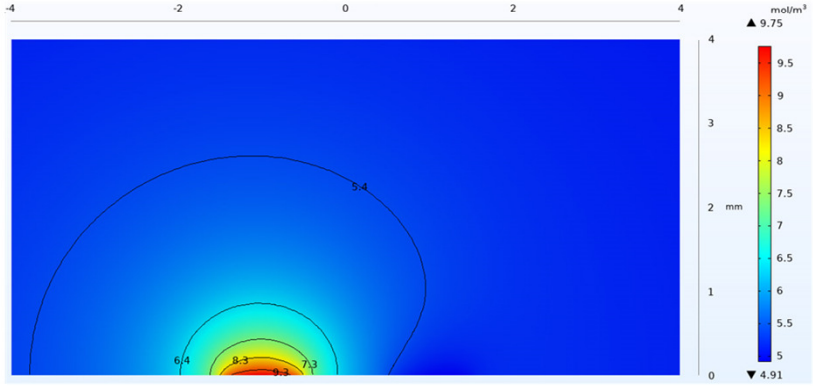




Distribution as expected.

Cl^-





The distribution of Cl- in the experimental map is the opposite of the expected.

Conclusions

This model was able to replicate most of the experimental observations.

The main problem is the lack of natural convection, with the consequent development of a diffusion layer extending to the entirety of the simulation domain.

Divergences were observed in the maps for Zn^{2+} and Cl^{-} but it is possible that the reasons lie on the experimental side (bad microelectrodes response).

A negative concentration appeared in some of the O_2 maps, particularly in the cases with higher current densities.

Future work (improvements)

i) Include natural convection,

ii) Add homogeneous chemical (precipitation) reactions,

iii) Simulations with solution evaporation,

iv) Consider the volume decrease of the corroding metal as it corrodes

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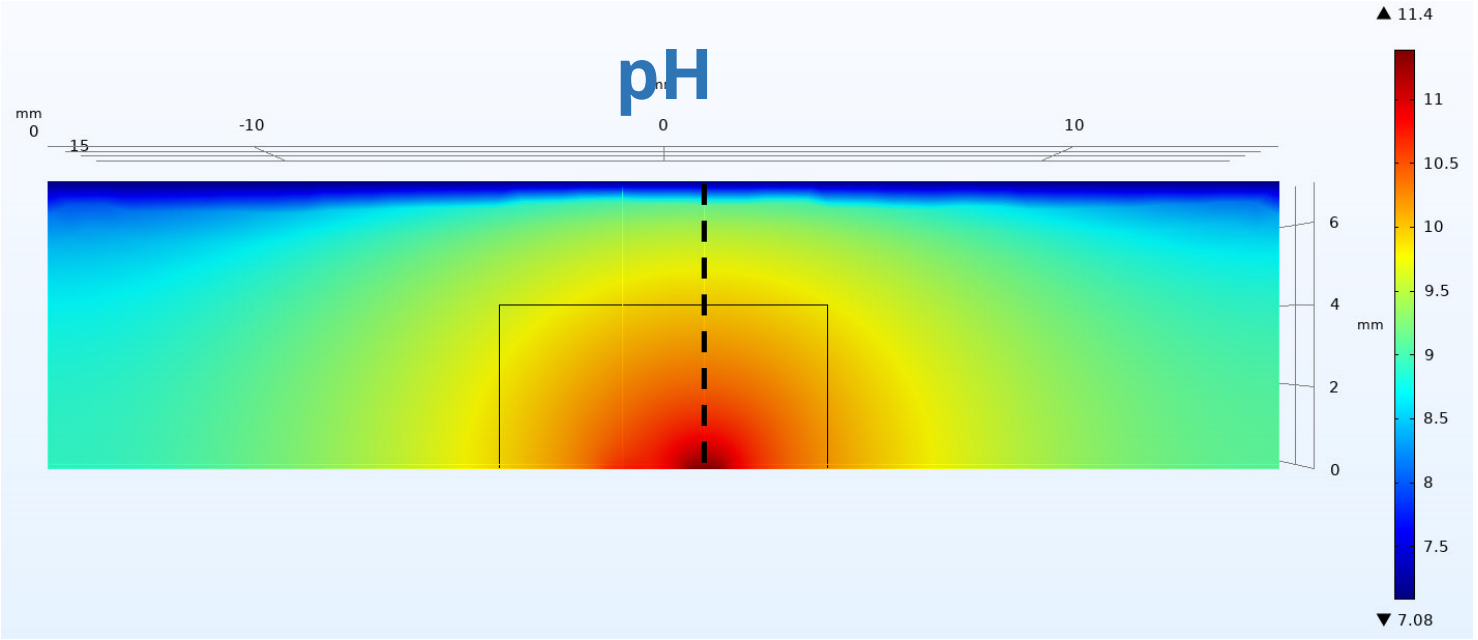

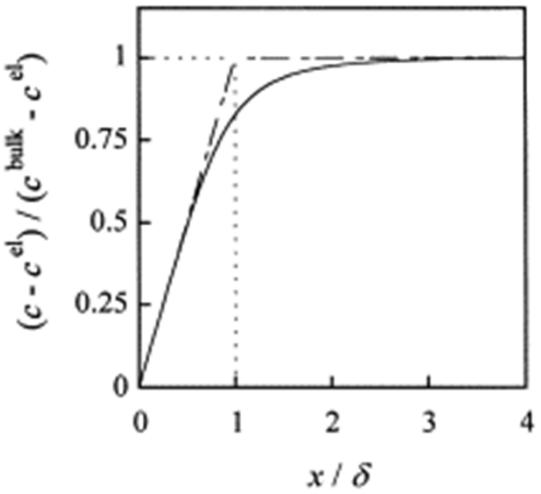

Natural convection

$$J_i = -\left(D_i + D_{\mu conv}^{ref}\right)\nabla c_i - z_i u_i F c_i \nabla\phi$$

$$D_{\mu conv}^{ref} = 1.5072 \cdot D^{ref}\left(\frac{d}{\delta^{ref}}\right)^4$$