Supporting Information

Ion Selective Redox Cycling in Zero-Dimensional Nanopore Electrode Arrays at Low Ionic Strength

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Table S1. Half wave potential of four redox mediators in aqueous media.

Redox mediator	$E_{1/2}$ (V*vs.* Ag/AgCl)
$AQMS^{0/-}$	-0.670 V
$Ru(NH_3)_6^{3+/2+}$	-0.184 V
Fc^+/Fc	0.193 V
$Ru(CN)_6^{4-/3-}$	0.822 V

Finite-Element Simulations.

Finite-element simulations (FES) were performed on a DELL OptiPlex 790 equipped with a quad-core Intel i7-2600 processor (3.4 GHz) and 8 GB of RAM, running on a Windows 7 64-bit operating system. Simulations were carried out using COMSOL Multiphysics v5.2. We used the 'Electroanalysis', 'Electrostatics', and 'Transport of Diluted Species' physics of COMSOL in a time-dependent mode to obtain the electrochemical behavior of the all species.

Mass transport and electric fields in the NEA geometry are described by the Poisson-Nernst-Planck equations.[1,2] Transport to the NEAs is governed by the Nernst-Planck equation,

$$\frac{\partial C_i}{\partial t} = \nabla \cdot D_i\left[\nabla \mathrm{C}_i + \frac{z_i F}{RT} C_i \nabla \Phi\right] \tag{S1}$$

where F is the Faraday's constant, R is the gas constant, T = 298.15K is the absolute temperature, Φ is the electrical potential, and D_i, C_i and z_i are the diffusion coefficient, concentration, and charge of the species i ($Ru(NH_3)_6^{3/2+}$, $Ru(CN)_6^{4/3-}$, K^+, Cl^-). The electric field is determined via the Poisson equation,

$$\nabla^2 \Phi = \frac{\rho}{\varepsilon_0 \varepsilon_R} \tag{S2}$$

where ε_0 and ε_R are the permittivity of space and the dielectric constant of the medium, respectively. The space charge density, ρ, in Eqn. 3 is determined by the concentration of charged species in the solution via,

$$\rho = F\sum_i z_i C_i \tag{S3}$$

Combining Eqns. S1-S3 produces the Poisson-Nernst-Planck equations, which govern molecular transport and electric field strength in the NEA geometry and which were used to obtain the simulation results reported here.

The simulated geometry consists of ten rectangular nanopores surrounded by a large (1000 μm x 1000 μm) reservoir. Such a large reservoir region is necessary to remove any residual effects of the reservoir boundaries on the solution. The nanopores are 460 nm deep with a dielectric layer (h = 60 nm), a top-ring electrode (h = 100 nm), and a top dielectric layer (h = 300 nm). This geometry is an approximation to that used in experiments. A view of the nanopore region in the simulated geometry is shown in **Figure S1**. The boundaries of the reservoir region are set to a constant bulk concentration, such that $C = C_0$. In this work, the SiN_x and SiO_2 pore walls are assigned zero molecular flux and a surface charge density, $\rho_{surface}$ = –1 mC/m^2.

Calculations in **Figure 2B** (in the main text) were performed over the concentration range 100 nM < [$Ru(NH_3)_6^{3+}$] < 10 mM using physical parameters discussed above. To compare simulation to experiment, the limiting current, i_L, for the total array is calculated and scaled by the ratio of the number of experimental pores to the number of simulated pores (ratio = 22,500) for comparison to experimental i_L values. Mesh elements were chosen to be ≤10 nm in the nanopores to improve the reliability of the solution. Mesh quality is particularly important, because very large concentration and potential gradients are present in the nanopores in the

absence of supporting electrolyte. Although some computational accuracy must be sacrificed to make the system computationally tractable, the finite element calculations corroborate experimental observations in low ionic strength samples.

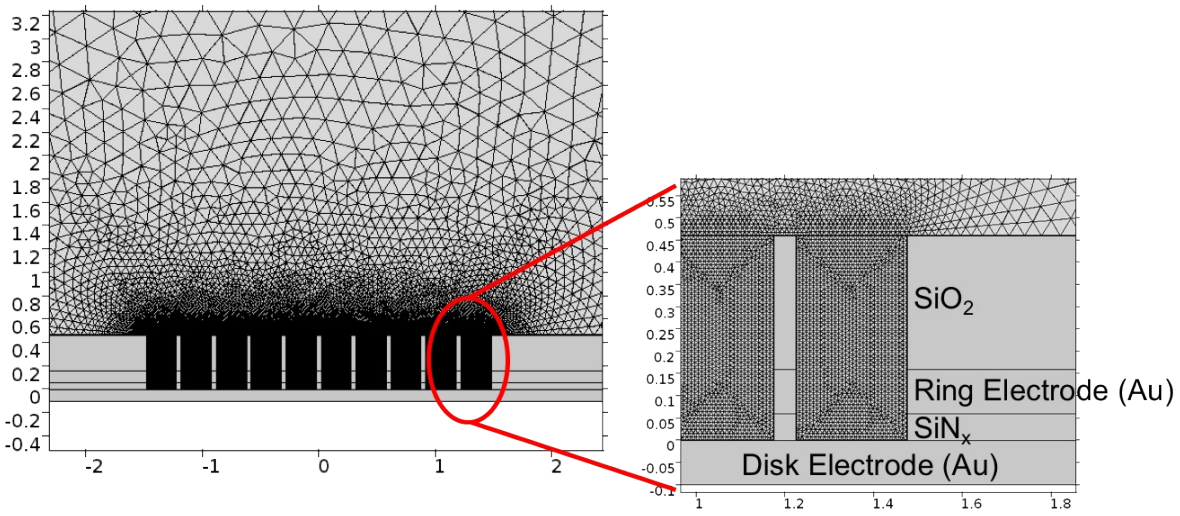


Figure S1. View of a meshed simulation geometry containing recessed ring disk electrodes. *Inset*: magnified view of refined mesh a single nanopore.

References

(1) J. D. Norton, H. S. White and S. W. Feldberg, *J. Phys. Chem.*, 1990, **94**, 6772-6780.

(2) I. Streeter and R. G. Compton, *J. Phys. Chem. C,* 2008, **112**, 13716-13728.

COMSOL Simulation Report

The following is a detailed description of the finite element model as created by the Comsol 'report' function for the case of 10 μM $Ru(NH_3)_6^{3+}$ without supporting electrolyte. It details the creation of the geometry and the mesh, the parameters used within the model and the equations solved.

1 Global Definitions

1.1 Parameters 1

Parameters

Name	Expression	Value	Description
DR	6.5e-6[cm^2/s]	6.5E−10 m²/s	Diffusion coefficient, R
DO	6.5e-6[cm^2/s]	6.5E−10 m²/s	Diffusion coefficient, O
F	96485.3[C/mol]	96485 C/mol	Fataday's constant
R	8.314[J/(mol*K)]	8.314 J/(mol·K)	Gas constant
T	298.15[K]	298.15 K	Temperature
RT	R_const*T	2479 J/mol	Molar gas constant * Temperature
DSC	1.957e-5[cm^2/s]	1.957E−9 m²/s	Diffusion coefficient, K+
DSA	2.032e-5[cm^2/s]	2.032E−9 m²/s	Diffusion coefficient, Cl-
zR	2	2	Charge of R
zO	3	3	Charge of O
zSC	1	1	Charge of K+
zSA	-1	−1	Charge of Cl-
alpha	0.5	0.5	Charge transfer coefficient
cSC	0[mol/L]	0 mol/m³	Concentration of supporting electrolyte, K+
cSA	3e-5[mol/L]	0.03 mol/m³	Concentration of supporting electrolyte, Cl-
cO	1e-5[mol/L]	0.01 mol/m³	Initial concentration, O
cR	0 [mol/L]	0 mol/m³	Initial concentration, R
V_therm	RT/F	0.025693 V	Thermal voltage
eps_H2O	80	80	Relative permittivity of water
delta	0.1	0.1	Dimensionless Stern layer thickness

Name	Expression	Value	Description
k0	1[cm/s]	0.01 m/s	Heterogeneous rate constant
Ef	-0.1[V]	−0.1 V	Formal potential
Er	0.1[V]	0.1 V	Potential of ring electrode
Istr_bulk	0.5*((cO*zO^2) + (cSA*zSA^2) + (cSC*zSC^2) + (cR*zR^2))	0.06 mol/m³	Bulk ionic strength
phiM	-0.1[V]	−0.1 V	Voltage of electrode vs PZC
lambdaD	sqrt(epsilon0_const *eps_H2O*V_therm/(2*F*Istr_bulk))	3.9646E−8 m	Debye length
lambdaS	delta*lambdaD	3.9646E−9 m	Stern layer thickness

2 Component 1

2.1 Definitions

2.1.1 Variables

Variables 1

Selection

Geometric entity level	Entire model

Name	Expression	Unit	Description
rho_surf_WE	epsilon0_const*eps_H2O*deltaphi_d/lambdaS	C/m^2	
deltaphi_d	phiM - V1	V	

2.1.2 Component Couplings

Integration 1

Coupling type	Integration
Operator name	intop1

Integration 2

Coupling type	Integration
Operator name	intop2

2.1.3 Selections

Electrolyte

Selection type
Explicit

Selection
Domains 5–7, 11, 15, 19, 23, 27, 31, 35, 39, 43

WE1_Surface_Domain

Selection type
Explicit

Selection
Domain 1

WE1_Surface_Boundary

Selection type
Explicit

Selection
Boundaries 15, 27, 39, 51, 63, 76, 88, 100, 112, 124

WE2_Surface_Domain

Selection type
Explicit

Selection
Domains 3, 9, 13, 17, 21, 25, 29, 33, 37, 41, 45

WE2_Surface_Boundary

Selection type
Explicit

Selection
Boundaries 16, 21, 28, 33, 40, 45, 52, 57, 64, 69, 77, 82, 89, 94, 101, 106, 113, 118, 125, 130

Insulator Surface_Boundary

Selection type
Explicit

Selection
Boundaries 14, 17, 19, 23, 26, 29, 31, 35, 38, 41, 43, 47, 50, 53, 55, 59, 62, 65, 67, 71, 75, 78, 80, 84, 87, 90, 92, 96, 99, 102, 104, 108, 111, 114, 116, 120, 123, 126, 128, 132

Nanopores

Selection type
Explicit

Selection
Domains 6–7, 11, 15, 19, 23, 27, 31, 35, 39, 43

Nanopore_Boundray

Selection type
Explicit

Selection
No boundaries

Au Surface

Selection type
Explicit

Selection
Boundaries 15–16, 21, 27–28, 33, 39–40, 45, 51–52, 57, 63–64, 69, 76–77, 82, 88–89, 94, 100–101, 106, 112–113, 118, 124–125, 130

2.1.4 Coordinate Systems

Boundary System 1

Coordinate system type	Boundary system
Tag	sys1

2.1.5 Domain Properties

Infinite Element Domain 1

Tag	ie1

Selection

Geometric entity level	Domain

Selection	No domains

2.1.6 Coordinate Systems

Material XY-Plane System

Coordinate system type	Base vector system
Tag	comp1_xy_sys

Material YZ-Plane System

Coordinate system type	Base vector system
Tag	comp1_yz_sys

Material ZX-Plane System

Coordinate system type	Base vector system
Tag	comp1_zx_sys

Material YX-Plane System

Coordinate system type	Base vector system
Tag	comp1_yx_sys

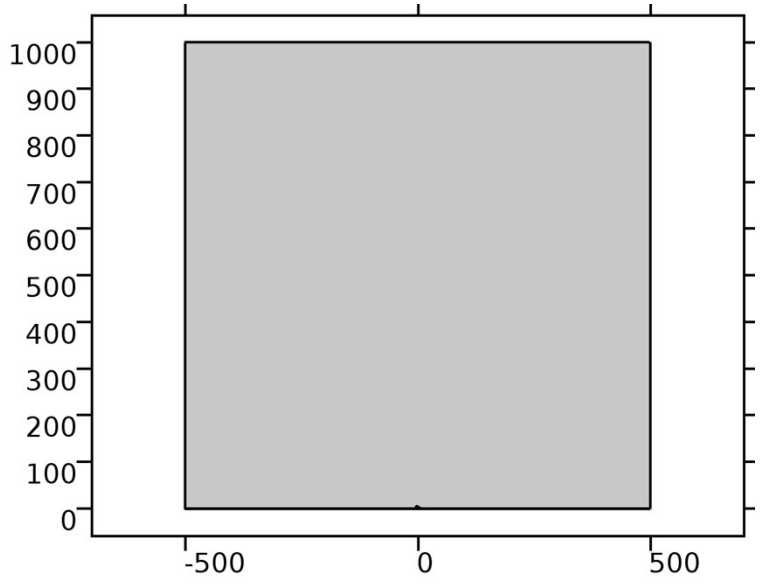
Material XZ-Plane System

Coordinate system type	Base vector system
Tag	comp1_xz_sys

Material ZY-Plane System

Coordinate system type	Base vector system
Tag	comp1_zy_sys

2.2 Geometry 1



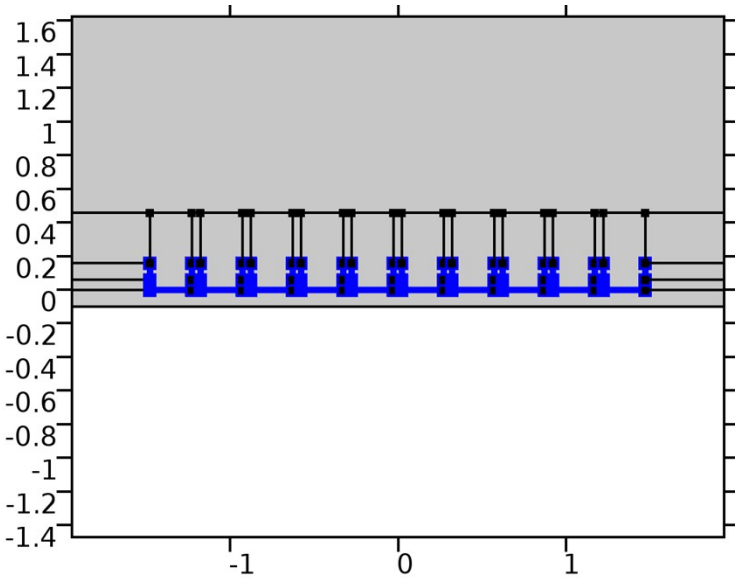
Geometry 1

Units

Length unit	µm
Angular unit	deg

2.3 Materials

2.3.1 Au - Gold

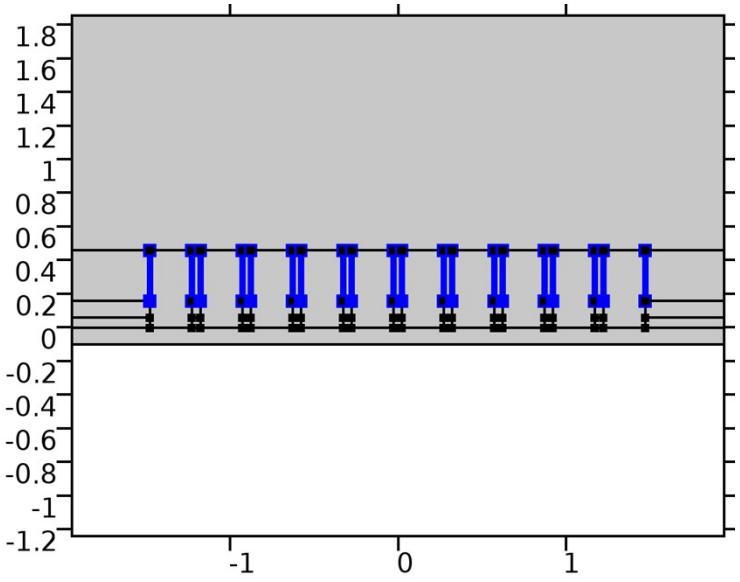


Au - Gold

Selection

Geometric entity level	Boundary
Selection	Boundaries 15–16, 21, 27–28, 33, 39–40, 45, 51–52, 57, 63–64, 69, 76–77, 82, 88–89, 94, 100–101, 106, 112–113, 118, 124–125, 130

2.3.2 SiO2 - Silicon oxide

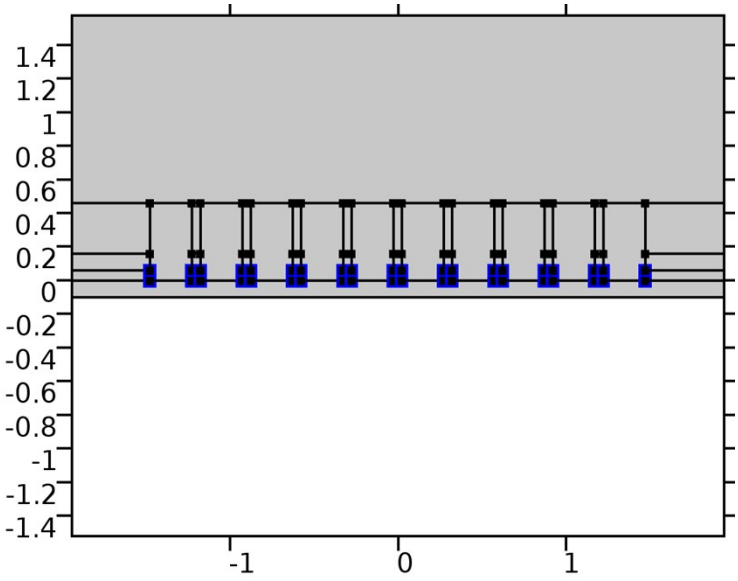


SiO2 - Silicon oxide

Selection

Geometric entity level	Boundary
Selection	Boundaries 17, 23, 29, 35, 41, 47, 53, 59, 65, 71, 78, 84, 90, 96, 102, 108, 114, 120, 126, 132

2.3.3 Si3N4 - Silicon nitride

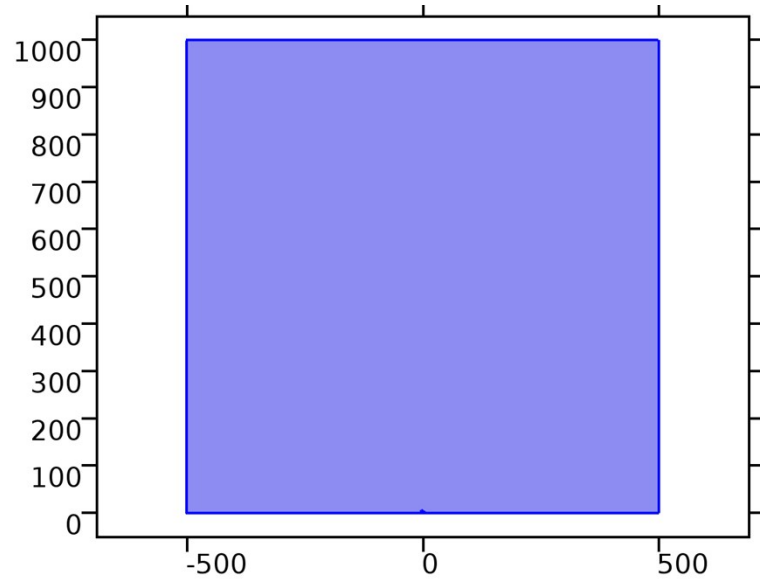


Si3N4 - Silicon nitride

Selection

Geometric entity level	Boundary
Selection	Boundaries 14, 19, 26, 31, 38, 43, 50, 55, 62, 67, 75, 80, 87, 92, 99, 104, 111, 116, 123, 128

2.4 Electroanalysis



Electroanalysis

Equations

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l) = R_i$$
$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l$$

Features

Transport Properties 1
No Flux 1
Initial Values 1
Electrode Surface 1
Electrode Surface 2
Concentration 1

2.4.1 Transport Properties 1

Equations

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l) = R_i$$
$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l$$

2.4.2 No Flux 1

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = 0$$

2.4.3 Electrode Surface 1

Equations

$$i_{total} = \sum_m i_{loc,m} + i_{dl}$$
$$-\mathbf{n} \cdot \mathbf{N}_i = R_{i,tot}, \quad R_{i,tot} = \sum_m R_{i,m}$$

Electrode Reaction 1

Equations

$$\eta = \phi_{s,ext} - \phi_l - E_{eq}$$

2.4.4 Electrode Surface 2

Equations

$$i_{total} = \sum_m i_{loc,m} + i_{dl}$$

$$-\mathbf{n}\cdot\mathbf{N}_i = R_{i,\mathrm{tot}},\quad R_{i,\mathrm{tot}} = \sum_m R_{i,m}$$

Electrode Reaction 1

Equations

$$\eta = \phi_{s,\mathrm{ext}} - \phi_l - E_{\mathrm{eq}}$$

2.4.5 Concentration 1

Equations

$$c_i = c_{0,i}$$

2.5 Electrostatics

Electrostatics

Equations

$$\nabla\cdot\mathbf{D} = \rho_v$$

$$\mathbf{E} = -\nabla V$$

Features

Charge Conservation 1
Zero Charge 1
Initial Values 1
Space Charge Density 1
Surface Charge Density 2

Surface Charge Density 3
Ground 1

2.5.1 Charge Conservation 1

Equations

$$\mathbf{E} = -\nabla V$$
$$\nabla \cdot (\epsilon_0 \epsilon_r \mathbf{E}) = \rho_v$$

2.5.2 Zero Charge 1

Equations

$$\mathbf{n} \cdot \mathbf{D} = 0$$

2.5.3 Space Charge Density 1

Equations

$$\nabla \cdot \mathbf{D} = \rho_v$$

2.5.4 Surface Charge Density 2

Equations

$$\mathbf{n} \cdot (\mathbf{D}_1 - \mathbf{D}_2) = \rho_s$$

2.5.5 Surface Charge Density 3

Equations

$$\mathbf{n} \cdot (\mathbf{D}_1 - \mathbf{D}_2) = \rho_s$$

2.5.6 Ground 1

Equations

$$V = 0$$

2.6 Transport of Diluted Species

Transport of Diluted Species

Equations

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V) = R_i$$
$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V$$

Features

Transport Properties 1
No Flux 1
Initial Values 1
Concentration 1

2.6.1 Transport Properties 1

Equations

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V) = R_i$$
$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla V$$

2.6.2 No Flux 1

Equations

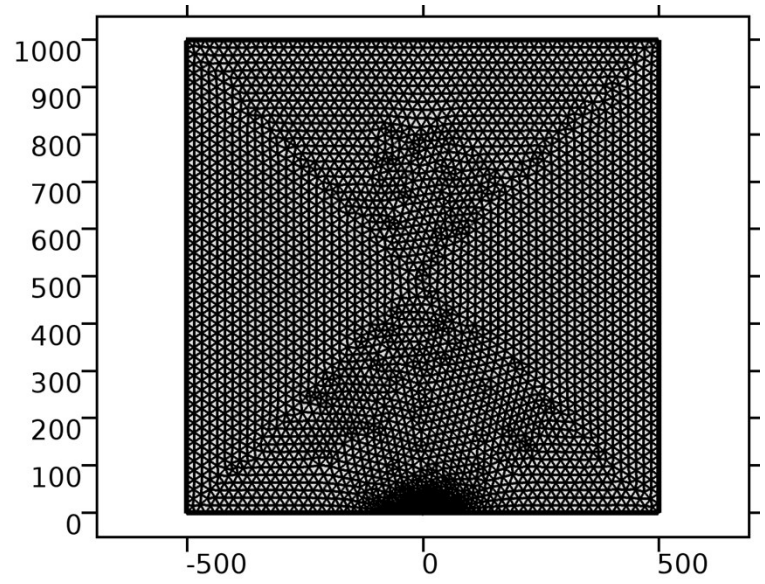
$$-\mathbf{n} \cdot \mathbf{N}_i = 0$$

2.6.3 Concentration 1

Equations

$c_i = c_{0,i}$

2.7 Mesh 1



Mesh 1

3 Study 1

3.1 Cyclic Voltammetry

Study settings

Description	Value
Include geometric nonlinearity	Off

Physics and variables selection

Physics interface	Discretization
Electroanalysis (elan)	physics
Electrostatics (es)	physics
Transport of Diluted Species (tds)	physics

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

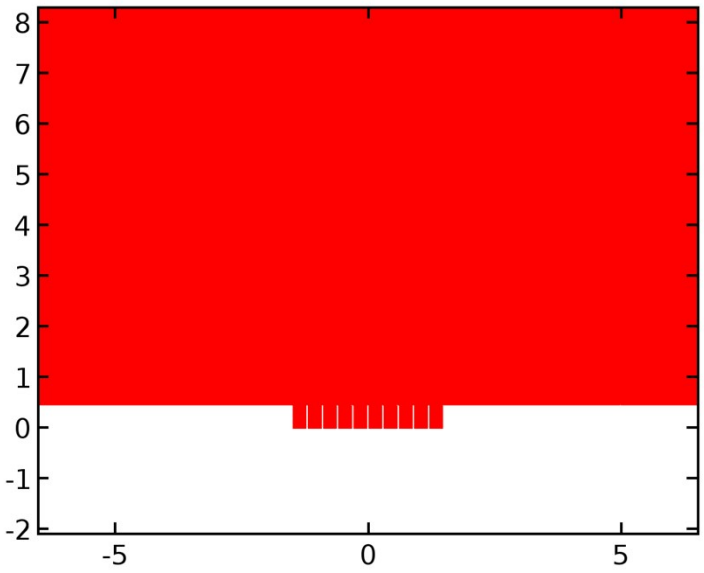
4 Results

4.1 Data Sets

4.1.1 Study 1/Solution 1

Solution

Description	Value
Solution	Solution 1
Component	Save Point Geometry 1



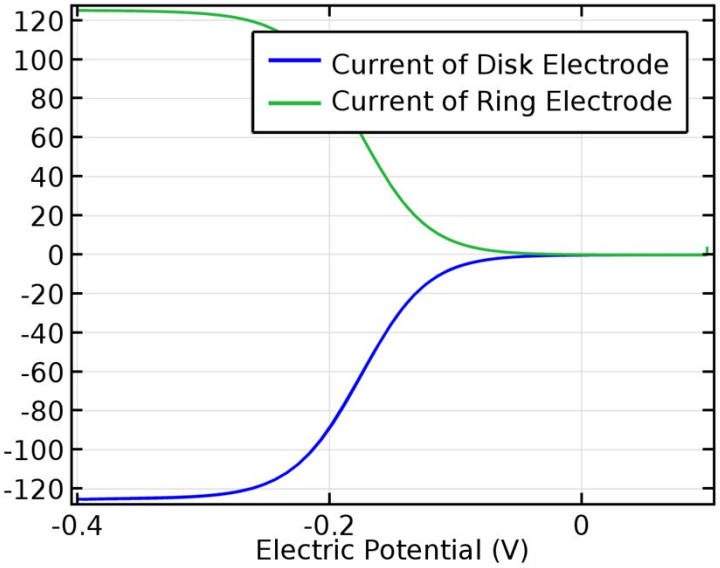
Data set: Study 1/Solution 1

4.2 Tables

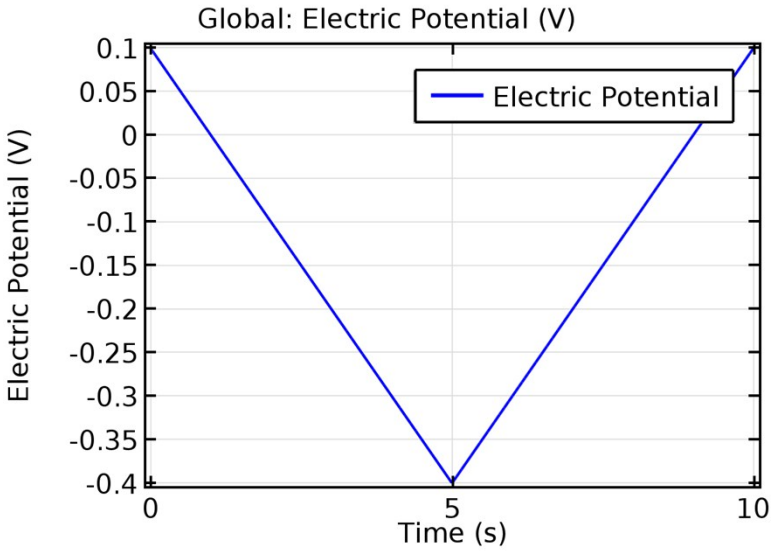
4.2.1 Table 1

4.3 Plot Groups

4.3.1 Cyclic Voltammograms (elan)

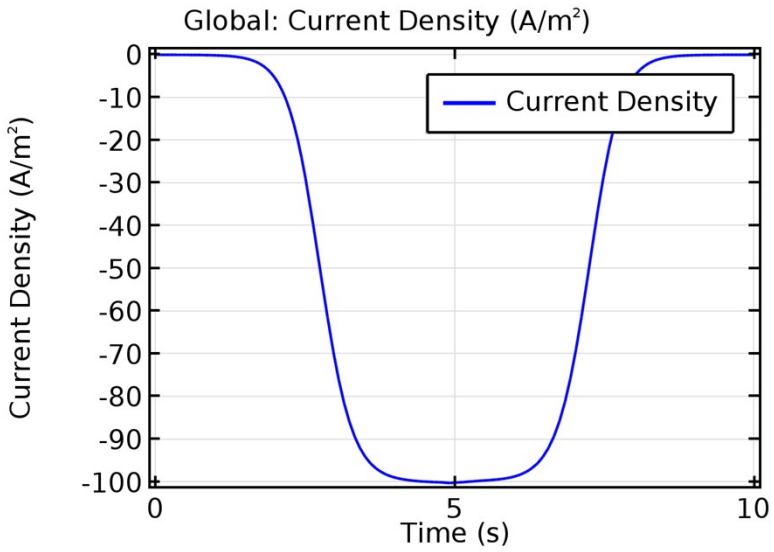


4.3.2 Electrode Potential (elan)



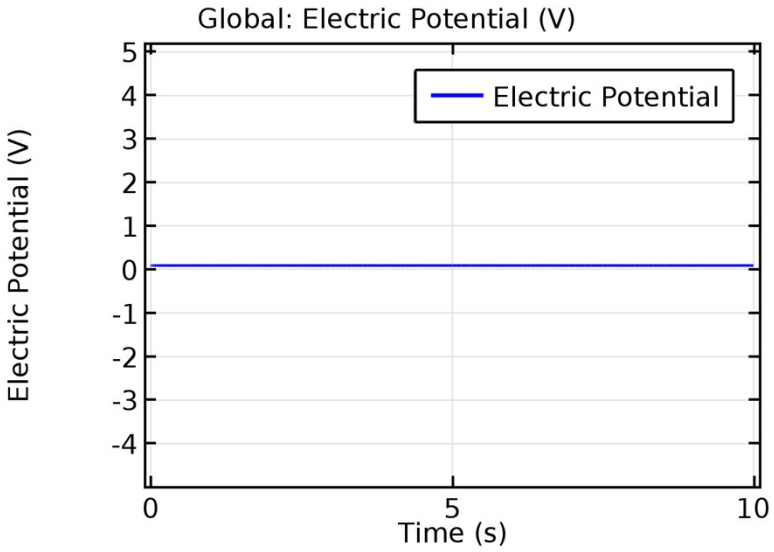
Global: Electric Potential (V)

4.3.3 Average Current Density (elan)



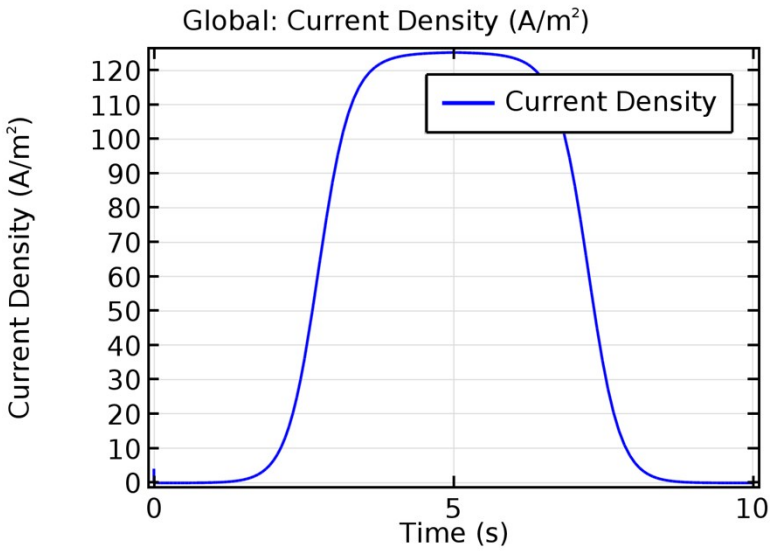
Global: Current Density (A/m²)

4.3.4 Electrode Potential (elan) 1



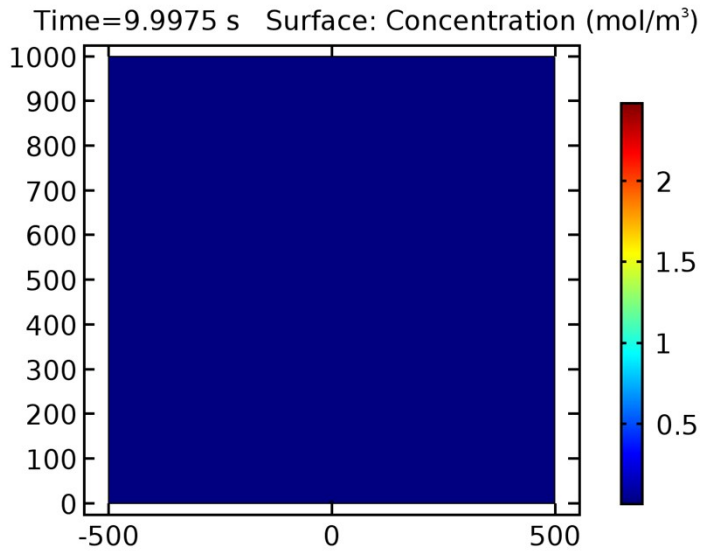
Global: Electric Potential (V)

4.3.5 Average Current Density (elan) 1



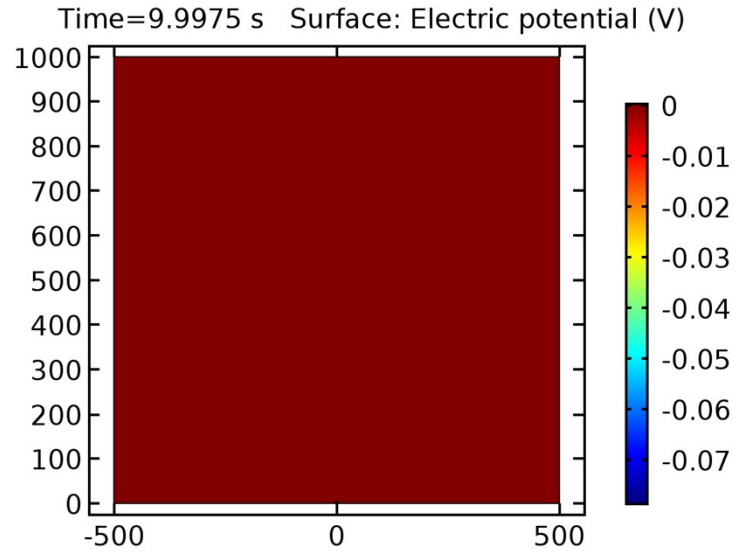
Global: Current Density (A/m²)

4.3.6 Concentration (elan)



Time=9.9975 s Surface: Concentration (mol/m³)

4.3.7 Electric Potential (es)



Time=9.9975 s Surface: Electric potential (V)