Supporting information - Choosing the Right Electrode Representation for Modeling Real Bioelectronic Interfaces: A Comprehensive Guide

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Choosing the Right Electrode Representation for Modeling Real Bioelectronic Interfaces: A Comprehensive Guide

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1. Convergence of the CPE integral

The CPE integral:

$$\sigma_{CPE}(t) = \int_0^t \frac{Q_{SPEC}}{\Gamma(1-\alpha)} \frac{V_{WE}}{(t-\tau)^\alpha}\, d\tau \qquad t > 0;\;\; 0 < \alpha < 1$$

Is a convergent integral of a divergent function for $\tau = t$ which creates problems for COMSOL's numerical integration algorithm and yields an error for division with zero. To solve this problem, we separate the integral in two parts:

$$\sigma_{CPE}(t) = \int_0^{t-\Delta t} \frac{Q_{SPEC}}{\Gamma(1-\alpha)} \frac{V_{WE}}{(t-\tau)^\alpha}\, d\tau + \int_{t-\Delta t}^{t} \frac{Q_{SPEC}}{\Gamma(1-\alpha)} \frac{V_{WE}}{(t-\tau)^\alpha}\, d\tau$$

Where Δt is a small time interval comparable with the time stepping of the simulation. Now the first integral does not have divergence issues as we got rid of the $\tau = t$ point. For the second integral, because Δt is a very small time interval comparable to the time resolution of the simulation, we can assume the functions Q_{SPEC}, V_{WE} and α are constant for the time Δt and assign them the value for $\tau = t$. We can thus take the functions out of the integral to obtain:

$$\sigma_{CPE}(t) = \int_0^{t-\Delta t} \frac{Q_{SPEC}}{\Gamma(1-\alpha)} \frac{V_{WE}}{(t-\tau)^\alpha}\, d\tau \; + \; \frac{Q_{SPEC}(t)\, V_{WE}(t)}{\Gamma(1-\alpha(t))} \int_{t-\Delta t}^{t} \frac{1}{(t-\tau)^\alpha}\, d\tau$$

The second integral can now be solved analytically for $\alpha < 1$ to get the final expression:

$$\sigma_{CPE}(t) = \int_0^{t-\Delta t} \frac{Q_{SPEC}}{\Gamma(1-\alpha)} \frac{V_{WE}}{(t-\tau)^\alpha}\, d\tau \; + \; \frac{Q_{SPEC}(t)\, V_{WE}(t)}{\Gamma(1-\alpha(t))} \frac{\Delta t^{1-\alpha}}{1-\alpha} \qquad t > \Delta t;\;\; 0 < \alpha < 1$$

That is numerically stable and does not cause problems in COMSOL Multiphysics. Care must be taken to make sure that the time Δt is much smaller than the time scale relevant for the evolution of the system in question.

2. Additional implementation details

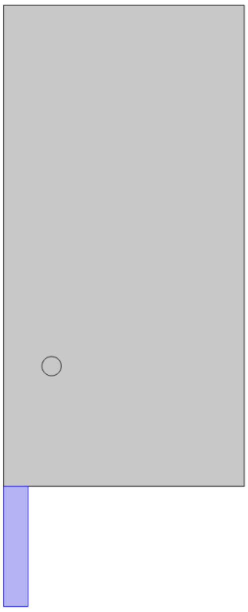


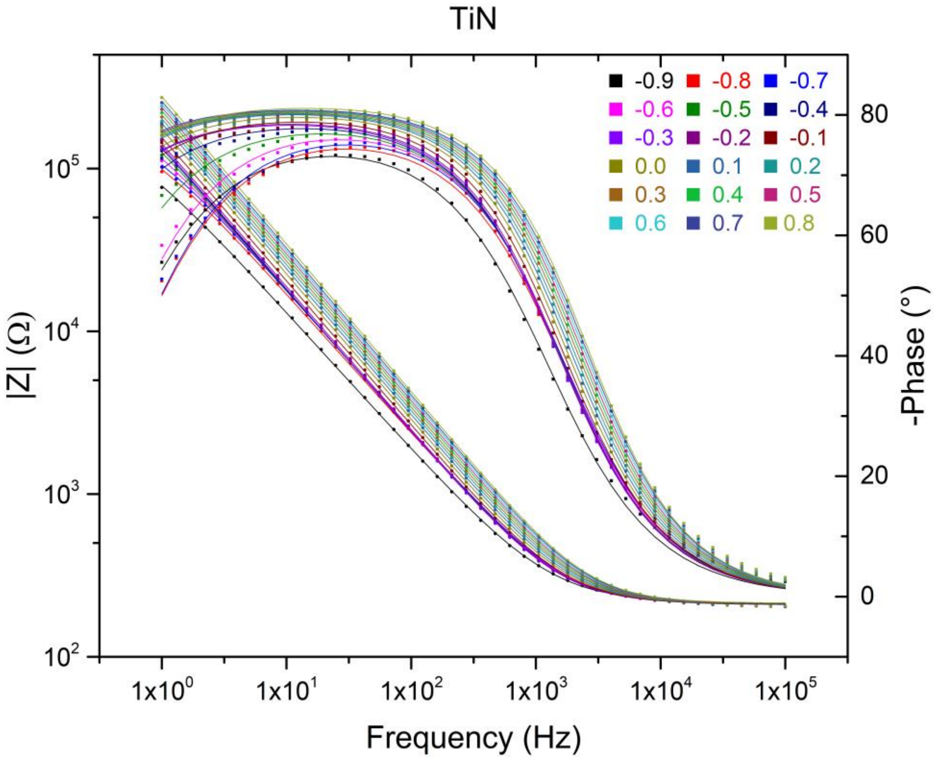
Figure S1 Additional geometry (highlighted in blue) for mapping the potential from time to space via the Stabilized Convection-Diffusion Equation. The entire electrode computed potential history at each electrode node is mapped vertically to spatial geometry

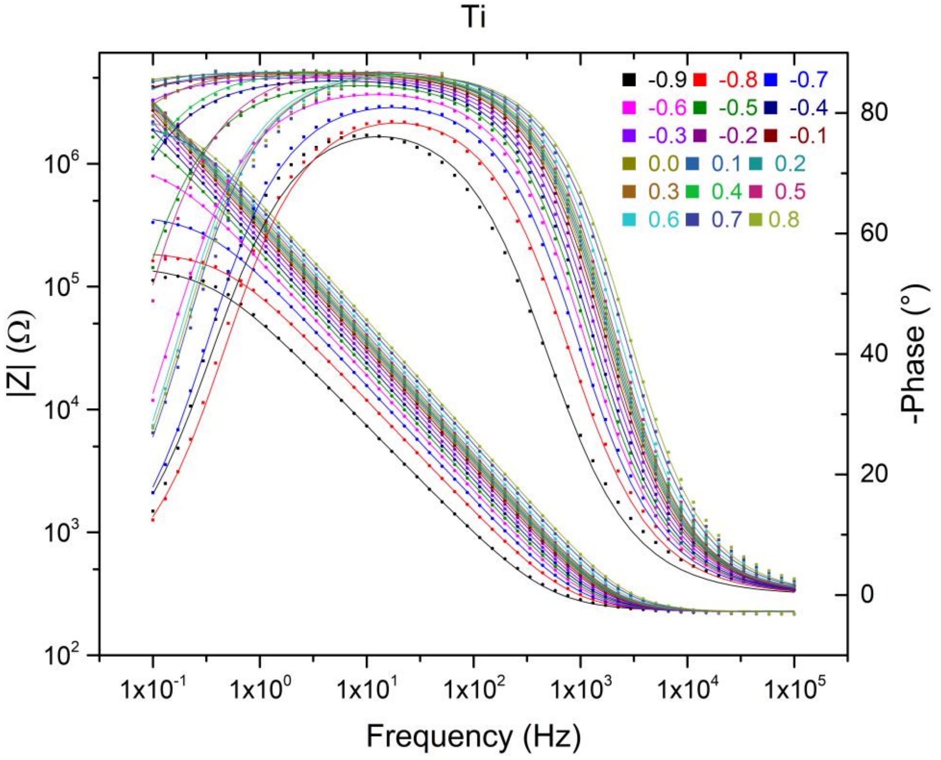
We use a convection (advection) differential equation for mapping the calculated potential history. The convection equation is a special case of the generalized convection–diffusion differential equation:

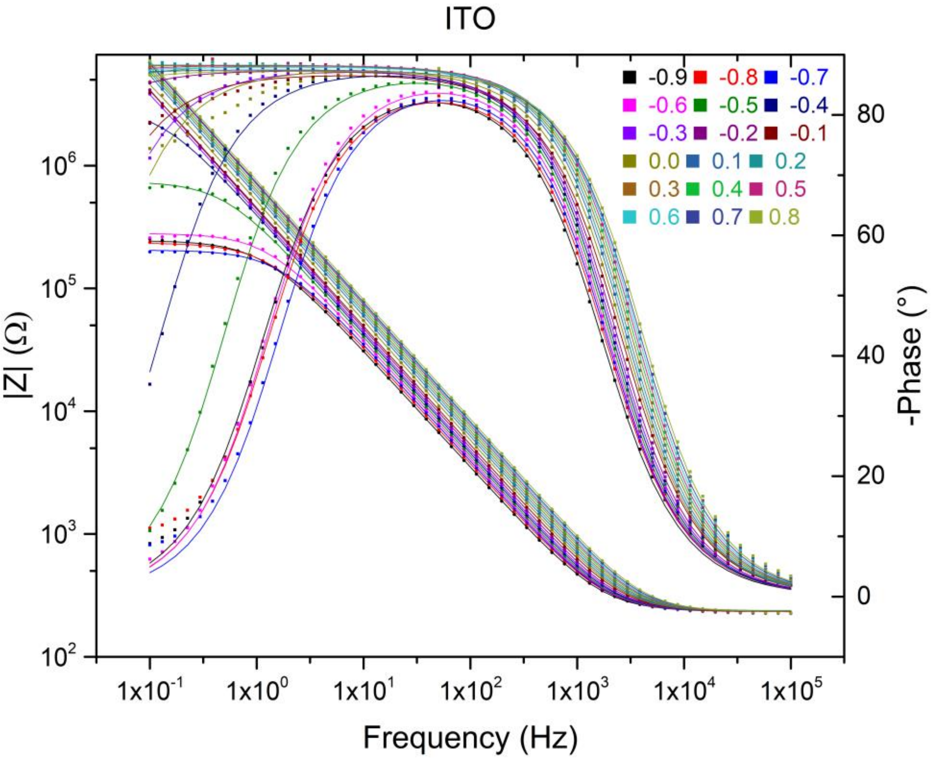
$$\frac{\partial U}{\partial t} + \nabla \cdot (\beta\, U) = \nabla \cdot (c \nabla U) + F$$

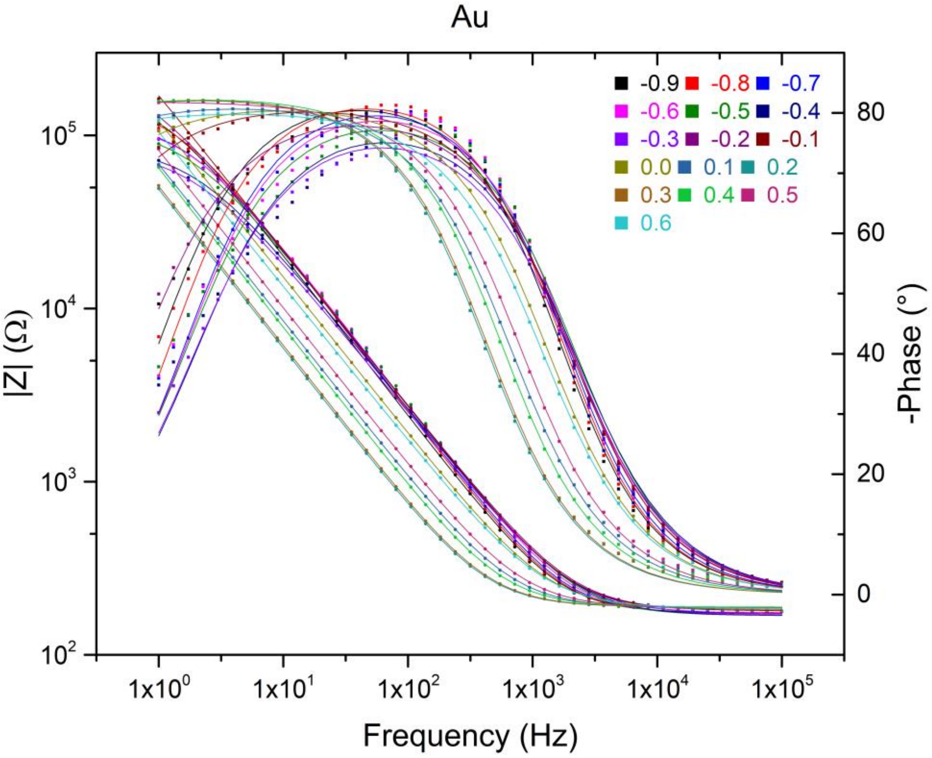
where U is the mapping variable, c is the diffusion coefficient, β is the convection velocity, F represents sources or sinks of the quantity U and ∇ and $\nabla \cdot$ represent gradient and divergence operator respectively. We obtain the desired mapping equation by setting the diffusion coefficient and sources term to zero and by setting the value of the convection velocity to be constant.

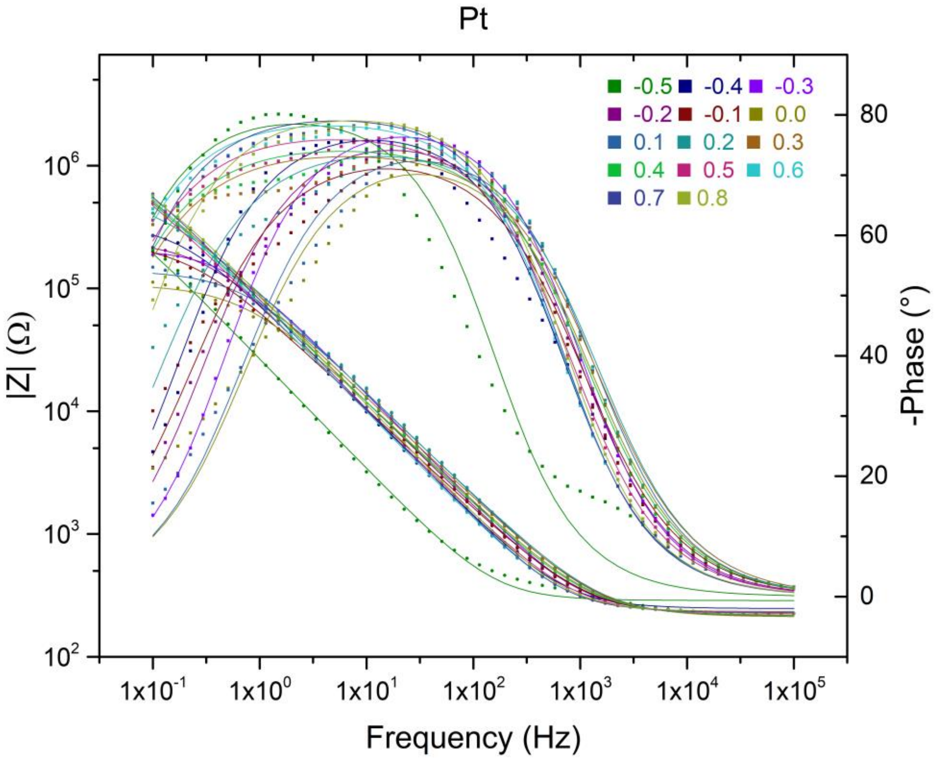
3. EIS measurements and fits

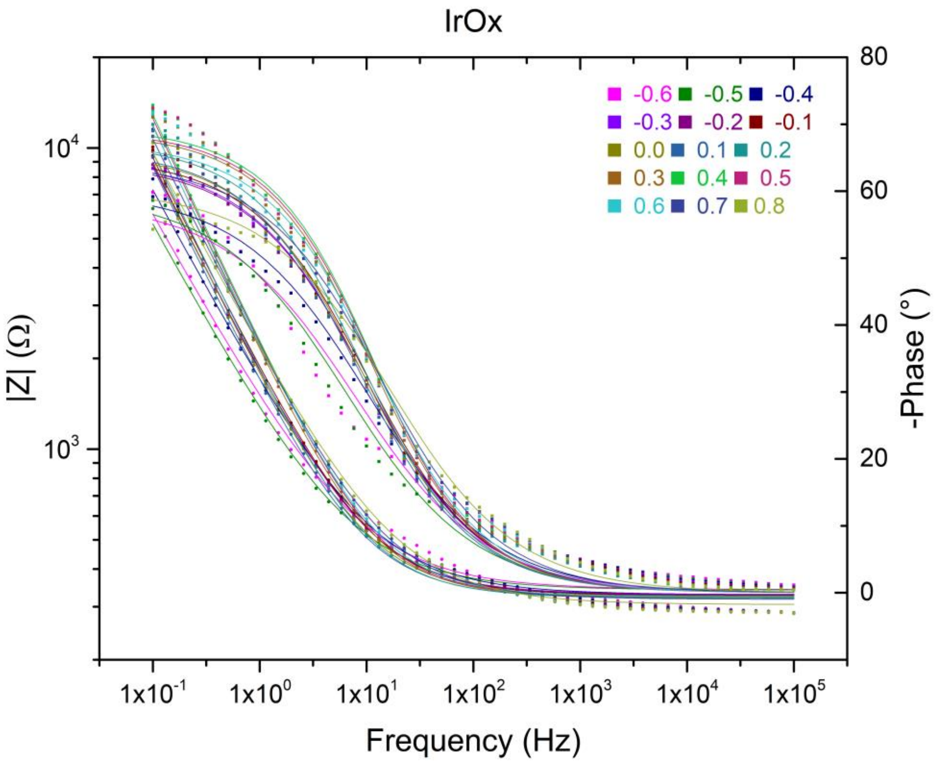





ITO
-0.9 -0.8 -0.7
-0.6 -0.5 -0.4
-0.3 -0.2 -0.1
0.0 0.1 0.2
0.3 0.4 0.5
0.6 0.7 0.8
|Z| (Ω)
10^2
10^3
10^4
10^5
10^6
-Phase (°)
0
20
40
60
80
1x10-1
1x100
1x101
1x102
1x103
1x104
1x105
Frequency (Hz)


Au
-0.9 -0.8 -0.7
-0.6 -0.5 -0.4
-0.3 -0.2 -0.1
0.0 0.1 0.2
0.3 0.4 0.5
0.6
|Z| (Ω)
10^2
10^3
10^4
10^5
-Phase (°)
0
20
40
60
80
1x100
1x101
1x102
1x103
1x104
1x105
Frequency (Hz)





Figures S2 – S7 Electrochemical impedance spectroscopy measured and fitted data to a single domain Randles (CPE) circuit (Figure 2b) for studied materials. Measured data is marked by points and fitted data by lines. Impedance values are depicted with circles and negative phase values with squares. Raw data in .csv form is available from the institutional repository referenced in the Supporting Information section. Color legend is the DC bias in V vs Ag/AgCl reference electrode.

4. CV measurements

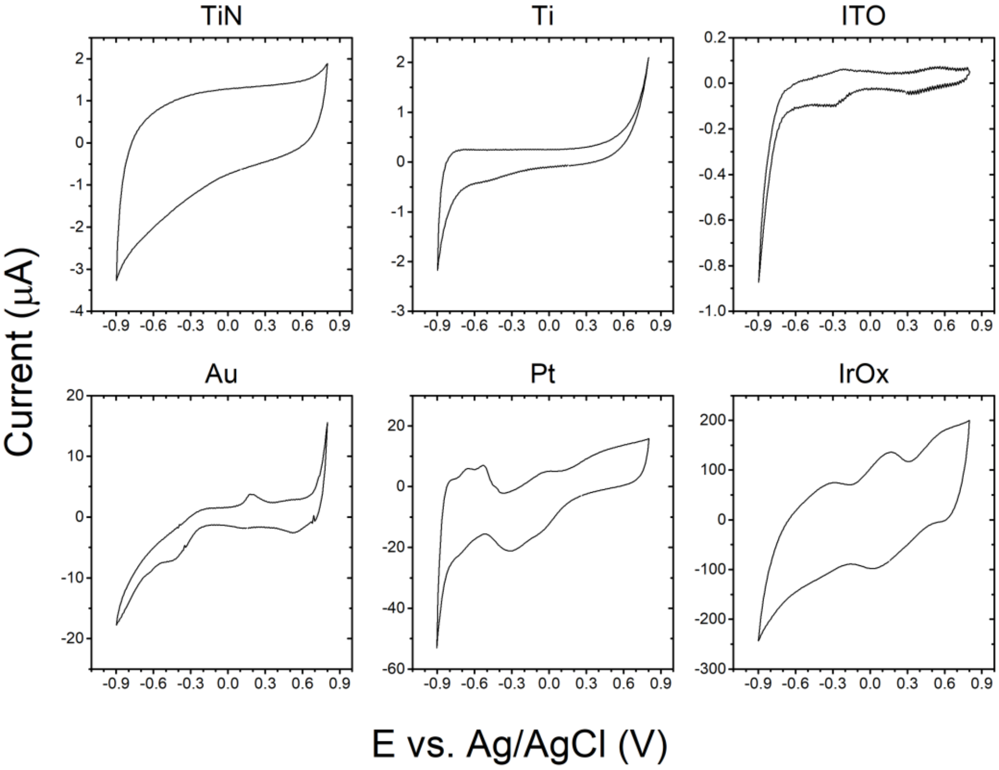


Figure S8 Cyclic Voltammetry measurements for the studied materials. Measurements are performed in the voltage range from -900 mV *to 800* mV *vs. Ag/AgCl reference with a scan rate of 1* V/s.

5. Relative error for RC and CPE implementation

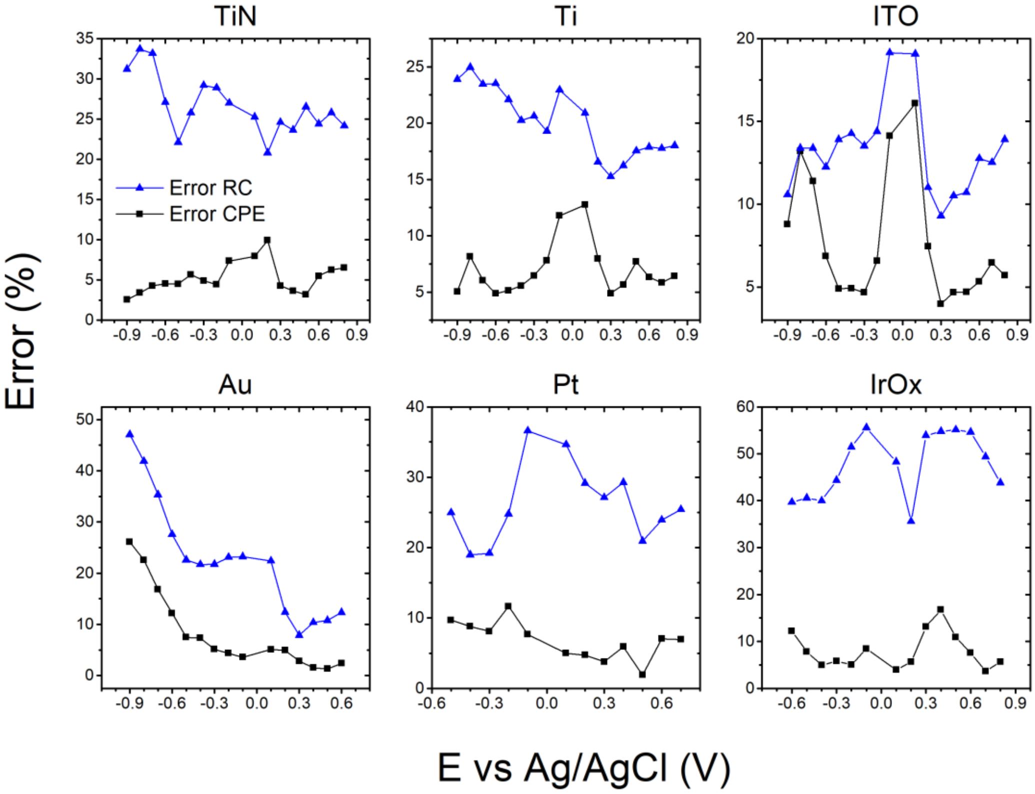


Figure S9 Relative error for RC and CPE implementation for each material and pulse voltage.