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Supporting Information

Lifting the Lid on the Potentiostat: A Beginner's Guide to Understanding Electrochemical Circuitry and Practical Operation

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SI 1: Estimating the maximum current that should be passed in a two-electrode system

Consider a typical reference electrode where the chloridised silver wire (i.e. a solid cylinder) is 10 mm in length × 0.3 mm diameter (area of wire = 9.50×10^{-6} m^2) immersed in 3 M $KCl_{(aq)}$. Typical values for the exchange current density of Ag/Ag^+ in chloride media, j_0, fall in the range 1.0- 2.0 A m^{-2}.[1]

Silver chloride is scarcely soluble in water. Its solubility equilibrium in a saturated solution can be represented by:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) \qquad \text{(S1)}$$

The solubility product, K_{sp} is defined as:

$$K_{sp} = a_{Ag^{+}}.a_{Cl^{-}} \qquad \text{(S2)}$$

where a is the activity of each species. K_{sp} for AgCl is 1.77×10^{-10} at 298 K (25 °C)[2,3]

The reaction that defines the potential is:

$$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s) \qquad \text{(S3)}$$

The corresponding Nernst equation is:

$$E = E°_{Ag/Ag^{+}} - \frac{RT}{F} ln\left(\frac{1}{a_{Ag^{+}}}\right) \qquad \text{(S4)}$$

R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature in Kelvin and F is Faraday's constant (96485 C mol^{-1}). RT/F can also be represented in units of volts.

Substituting for the activity of the silver ion from (S2) gives:

$$E = E°_{Ag/Ag^{+}} - \frac{RT}{F} ln\left(\frac{a_{Cl^{-}}}{K_{sp}}\right) \qquad \text{(S5)}$$

At a constant temperature the potential will depend only on the chloride ion activity. Since K_{sp} is constant at a constant temperature, this term can be combined with the standard potential;

$$E = E°_{Ag/Ag^{+}} + \frac{RT}{F} ln(K_{sp}) - \frac{RT}{F} \ln(a_{CL^{-}}) = E°_{Ag/AgCl} - \frac{RT}{F} ln(a_{Cl^{-}}) \qquad \text{(S6)}$$

where $E°_{Ag/AgCl} = E°_{Ag/Ag^{+}} + \frac{RT}{F} ln(K_{sp})$. Since the standard reduction potential of Ag^+ = 0.80 V, $E°_{Ag/AgCl} = 0.223$.[4]

The equilibrium potential for Ag/AgCl can be calculated from the Nernst equation:

$$E = E^0{}_{Ag/AgCl} - \frac{RT}{F}\ \mathrm{ln}a_{Cl^-} \qquad \text{(S7)}$$

For 3 M KCl, the activity coefficient of Cl^- is 0.539 at 298 K (the activity of chloride is 1.617).[5] This gives an E value of 0.211 V.

The Butler-Volmer equation defines the empirical relationship between equilibrium potential and current density which for a single electron transfer is given by:

$$j = j_0\left\{exp\left[\frac{\alpha_a F}{RT}\left(E - E_{eq}\right)\right] - exp\left[-\frac{\alpha_c F}{RT}\left(E - E_{eq}\right)\right]\right\} \qquad \text{(S2)}$$

α_c and α_A are the transfer coefficients (symmetry factors) for the cathodic and anodic reaction respectively.[6] Taking the transfer coefficients to be 0.5 and defining $E - E_{eq}$ as η, the overpotential, gives:

$$\eta = \frac{RT}{F} ln\left(\frac{j}{j_0}\right) \qquad \text{(S3)}$$

which enables the potential shift from equilibrium to be calculated when a defined value of j is passed through an electrode (for a known j_0).

To keep the shift in reference electrode potential below an acceptable reference electrode error of $\pm\ \eta$:

$$j < j_0 exp\left(\frac{F\eta}{RT}\right) \qquad \text{(S4)}$$

If it is decided that an acceptable voltage error is ± 1 mV, i.e. 10^{-3} V, then j would need to be below 1.04 j_0. For the dimensions given above, area = 9.5×10^{-6} m^2, and taking the lower end of the exchange current density for Ag/ Ag^+ of 1 A m^{-2} the maximum tolerable current would be 9.8 μA.

SI 2: Finite Element modelling of cyclic voltammetry incorporating Ohmic drop

Numerical simulations were formulated to model the influence of uncompensated resistance, $R_{u,}$ on the voltammetric response of a reversible redox couple using COMSOL Multiphysics 5.5^{TM} (COMSOL AB, Sweden). The generalised design of the model means that it can be easily adapted for another redox couple/electrode system. The reaction considered is the one-electron reduction of $[Ru(NH)_3]^{3+}$, eq. S5.

$$[Ru(NH_3)_6]^{3+} + e^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Ru(NH_3)_6]^{2+} \tag{S5}$$

where the rate of electron transfer constants for the forward (k_f) and backward (k_b) reactions are defined by Butler-Volmer kinetics. The mass transport of the redox species ($[Ru(NH)_3]^{3+/2+}$), is defined in the model as *cOx* and *cRed* respectively, to and away from the electrode surface was modelled by solving the Nernst-Planck partial differential equation. This is implemented by using the transport of dilute species node in COMSOL. The flux *J*, of species *i* ($[Ru(NH)_3]^{3+/2+}$) is determined by eq. S6 which describes mass transport by diffusion. Mass transport due to convection and migration in solution is omitted as the solution is unstirred and electroneutrality is assumed at every point in solution. This assumes a sufficiently high ionic strength, so the double layer has a negligible influence. The diffusion coefficients for both the oxidized and reduced species are assumed to be equal.

$$J_i = -D_i \nabla c_i \tag{S6}$$

where D_i is the diffusion coefficient of species *i*, c_i is the concentration of species *i*.

Geometry

For this model, we use a disk electrode radius of 0.5 mm, insulated within a glass sheath as shown by Fig. S1. The system is described using 2D axisymmetric cylindrical geometry with the axis of symmetry defined at the centre of the electrode, Fig. S1. Mass transport of species, *i*, by diffusion is solved using eq. S7.

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r}\frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right) \tag{S7}$$

where *t* is time, *r* is the radial distance from the centre of the electrode and *z* is the distance normal to the r axis.

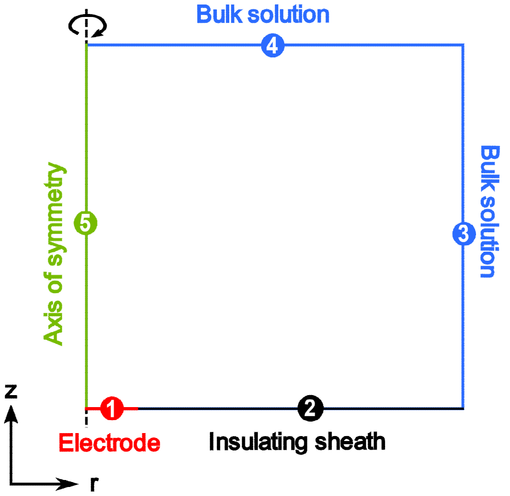

Figure S1. – Schematic diagram of the 2D antisymmetric geometry used for simulating the diffusion of $[Ru(NH)_3]^{3+/2+}$.

Initial and Boundary Conditions

The initial concentration of species in the domain as well as boundaries 3 and 4 was set to represent initially scanning in the cathodic direction. The initial concentrations were set to $[Ru(NH)_3]^{3+} = c_{ox} = 1$ mM and $[Ru(NH)_3]^{2+} = c_{Red} = 0$. The boundary conditions for the model are described in Table S1.

Table S1 – Summary of boundary conditions

Label	Boundary Type	Coordinates (r, z) / mm	Boundary Conditions
1	Electrode	(0,0) – (0.5, 0)	$D_{Ox}\frac{\partial c_{Ox}}{\partial t} = -k_f \times c_{Ox} + k_b \times c_{Red}$ $D_{Red}\frac{\partial c_{Red}}{\partial t} = k_f \times c_{Ox} - k_b \times c_{Red}$
2	Insulating sheath	(0.5,0) – (10, 0)	$0 = \nabla c_i.\boldsymbol{n}$
3	Bulk Solution	(10,0) – (10, 10)	$c_i = c_{b,i}$
4	Bulk Solution	(10, 10) – (0, 10)	$c_i = c_{b,i}$
5	Axis of 2D symmetry	(0, 10) – (0, 0)	$0 = \nabla c.\boldsymbol{n}$

The voltage drop ($V = -iR_\mathrm{u}$) due to uncompensated resistance (R_u) has been added into the Butler-Volmer equations used to describe the forward (k_f) and backward (k_b) reaction rate constants defined by eq. S8 and eq. S9, respectively:

$$k_f = k^0 exp\left(-\frac{\alpha nF}{RT}(E - E^{0\prime} - iR_\mathrm{u})\right) \qquad (S8)$$

$$k_b = k^0 exp\left(\frac{(1-\alpha)nF}{RT}(E - E^{0\prime} - iR_u)\right) \qquad (S9)$$

where k^0 is the standard rate constant, $E^{0\prime}$ is the formal electrode potential, E is the applied potential, α is the transfer coefficient (assumed to be 0.5), n is the number of electrons transferred, T = 298.15K and i is the measured current. The value for $E^{0\prime}$ (-0.160 V) vs SCE was taken from literature.[7] For the simulations described here the electron transfer kinetics were assumed to be sufficiently fast (k^0 = 1 cm^{-1}), such that the rate of mass transport is rate-limiting. The potential waveform was applied using a piecewise function with a scan rate of 0.1 V/s, across a potential range that is defined as ± 0.5 V from $E^{0\prime}$ (-0.660 V to 0.340 V with respect to SCE). Full details on the COMSOL model are included in the COMSOL generated model report, **SI 2b**. A true linear CV waveform is applied in place of a staircase CV waveform to simplify implementation. A boundary probe definition is used to calculate i by integrating the normal flux of the oxidised species (J_{ox}) to the electrode surface, eq. S10:

$$i = -nF \int \underline{n}.J_{Ox} \qquad (S10)$$

where $\underline{n}$ is the inward-pointing unit normal to the electrode boundary.

Mesh

The equations were discretised over a mesh such as those in Fig. S2, which is finest at the edge of the electrode measuring 10 nm. Full details of the mesh can be found in **SI 2b**. The concentration distribution of species was described using linear Lagrange elements. The accuracy of the calculated solutions was confirmed when no appreciable changes were observed when using finer mesh elements or higher solver tolerances. The size of the domain was chosen such that there was no change in the concentration of species from the boundary condition near boundaries 3 and 4.

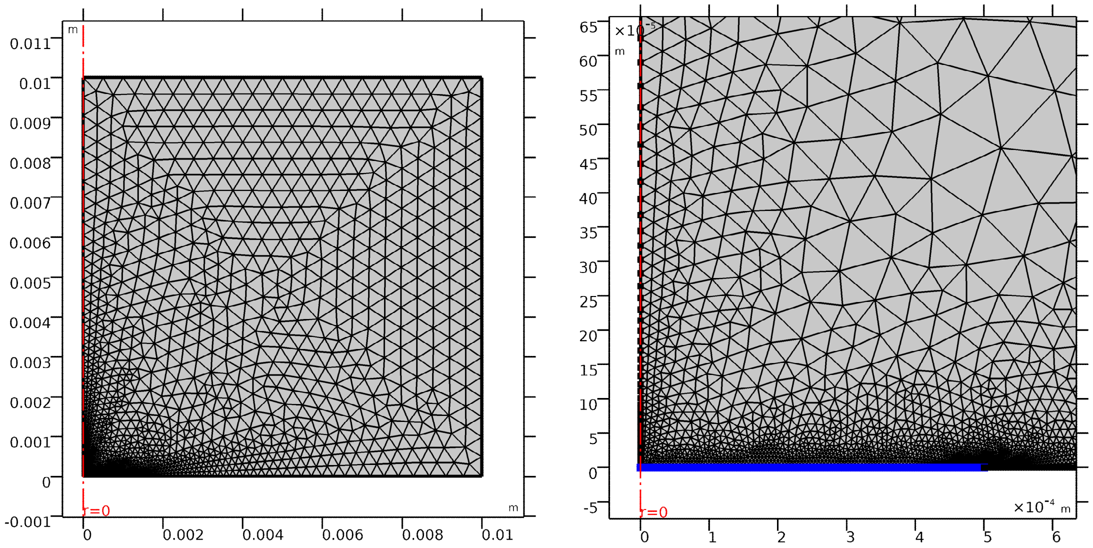

Figure S2. Example mesh used for finite element simulations of a 0.5 mm electrode. Left: full domain; right: zoom-in to the electrode.

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SI 3: Electronic Circuit for a Two Electrode Set-up

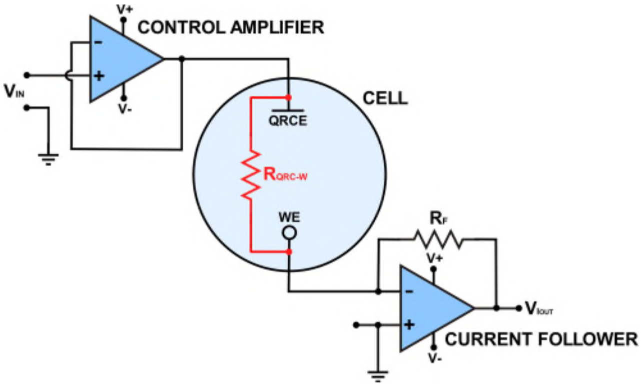

Figure S3: Electronic circuit for a two-electrode configuration.

Fig. S3 shows an exemplar op-amp circuit diagram for a two-electrode set-up. Here the control amplifier is now a simple voltage follower circuit to provide the cell drive voltage and current is measured with a conventional current follower. The input voltage at V_{in} (+) is outputted to the QRCE and current flows from the QRCE to the WE through $R_{\mathrm{QRC\text{-}W}}$; the latter which contains contributions from R_{ct} and R_{u}. Whilst R_{ct} at the QRCE is usually negligible, due to electron transfer being so fast, blocked RE frits must be avoided.

SI 4: Electrical Noise Testing and Reduction

This section aims to provide practical tools for students to utilise when checking for noise in their potentiostat set-up and how to evaluate the influence of the mitigation strategies covered in the main article.

a. Safety

While there is no wet electrochemistry covered in this section and low currents are being employed, users should be aware of the "live" nature of the set-up when the potentiostat cell is turned on.

b. Equipment and Materials

- Potentiostat set-up used for the electrochemical measurements e.g. potentiostat, Faraday cage.
- A resistor (1% tolerance or lower preferred) that will provide the approximate current range of the electrochemical measurement intended. In the examples provided, we are utilising a 10 MΩ resistor to achieve a current in the 10's nA range, across a voltage range of -0.5 to 0.5 V at a sensitivity of 10 nA/V.
- A digital multimeter that can make resistance measurements of a few Ω.

c. General Procedure

Here we describe how to set-up a two-electrode resistor cell to measure the overall noise pickup in the system.

- Connect only the WE to one end of the resistor and the CE and RE to the other. By using a single resistor and connecting the CE and RE to the same point, the control amplifier has unity gain and any noise picked up prior to this will not be amplified.
- If operating in a Faraday cage, ensure that neither the resistor nor connections are in contact with the cage, which would provide an alternative low resistance current path.
- Start by running a sweep CV between -0.5 to 0.5 V at the appropriate sensitivity for the resistor selected. Ensure that the reciprocal gradient of the line ($\boldsymbol{i} = V \times \mathbf{1/\boldsymbol{R}}$) corresponds to the value of the resistor you intend to use within its tolerance. See if there is any visible noise on the curve, e.g. as shown in Fig. S4 in the examples section.

- Record the current, *i* as a function of time, *t*, for a fixed potential. Here we have used 0.5 V so that the current falls in the middle of the 10 nA/V (for a 10 MΩ resistor) current range of the ADC.
- Care should also be taken when selecting the sampling rate for the current, as noise pickup from power lines may be present. The sampling rate should be double your local mains (line) frequency to provide a faithful representation and to avoid aliasing.
- The recorded CVs and *i*-t responses will establish a baseline for the noise of the starting set-up to enable comparisons of the merit of any mitigation strategies you investigate. It is also worth playing around with the parameters which control the sampling rate for both scenarios. However, do ensure that the same parameters are used when comparing different set-ups.

d. Checking the Faraday Cage is fully grounded

As discussed in the main article, the Faraday cage is made of a conductive material and is utilised to block the ingress of electromagnetic fields. The Faraday cage should be grounded to the same "common or star earth" ground point as the potentiostat to ensure the whole system is at the same constant potential. If the build of the Faraday cage uses joints between the metal plates made of a non-conductive material such as anodised aluminium, only the plate directly connected to the ground will likely have a reliable connection to ground. You may therefore wish to check that all panels of the cage are properly connected to the same ground point.

- First, check the resistance between two test probes. The test probes of a laboratory DVM will suffice as the DVM can also function as an ohmmeter. Bring the ends of the probes into contact; the contact resistance should be on the order of a few tenths of an Ω.
- Contact one test probe to your grounding point, and the other to the Faraday cage. Our grounding point is a home-built mains plug which contains only an earth point and connects to the Faraday cage via a wire. For the purpose of the measurement, the plug has been pulled out of the socket to ensure we are measuring the resistance of the primary Faraday cage ground connection alone. If properly grounded the resistance between the two points should be similar to the resistance you recorded for the test probes earlier. Checking the earth integrity of anodized elements of the cage may require forceful application of the test probes in order to break through the insulating oxide layer.
- Check that all six panels of the cage, the frame and the breadboard, if appropriate, meet this criterion. High resistance values may indicate that a panel is not connected properly.

This can be remedied as a stop-gap measure by the addition of copper tape to contact one panel to another or the more permanent addition of screwed earth bonding straps.

Examples

Here we provide examples where we have used the procedure discussed above in SI 4c, to evaluate the influence of three noise mitigation strategies discussed in the main article. These include 1) the use of a Faraday cage, 2) grounding of the potentiostat and 3) how to minimise noise arising from mains powered equipment that may be required in conjunction with the electrochemical measurement. *Students are encouraged to explore the full range of potential noise sources in their system and evaluate the merits of mitigation strategies for their system.*

1) Use of a Faraday cage

A Faraday cage should be employed for low current, high resistance measurements, with the door closed and all gaps sealed. Fig. S4 shows an example of utilising CV for investigating noise pickup in the system and the influence a Faraday cage has on its magnitude. The inset of Fig. S4 shows a magnified section of the *i*-V response when the resistor was placed inside (black) and outside (red) a grounded potentiostat/Faraday cage (black). The noise measured at the current sensitivity of 10 nA/V is undetectable with the resistor placed inside the cage. In contrast, outside the cage, the noise is measurable, displaying a frequency of 50 Hz and a maximum amplitude of approximately 1.2 nA.

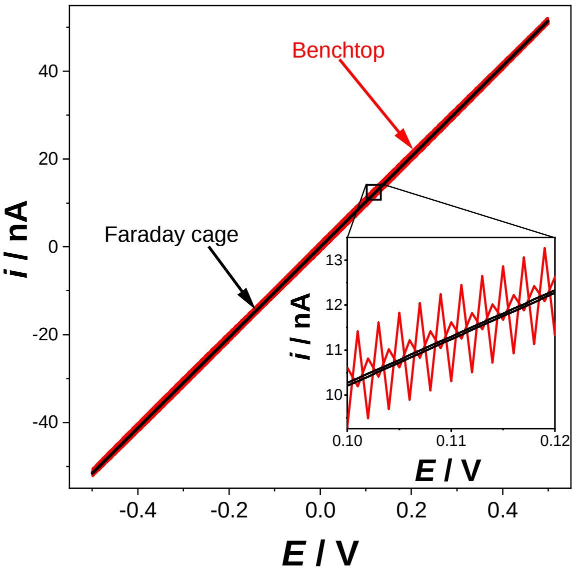

Figure S4. CV noise-pick up with a 10 MΩ two-electrode resistor cell recorded on a CHI760C Potentiostat at a sensitivity of 10 nA/V inside a grounded Faraday cage (black) and on the benchtop (red). The potential was scanned at 0.1 V/s with a potential step size of 1 mV.

Moving to the *i-t* technique provides a method for viewing more subtle changes in the noise. For example, Fig. S5 shows the impact of running the measurement on the bench (red line) versus inside the grounded potentiostat/Faraday cage (black line). The source of the noise can be further investigated by performing a Fast Fourier transform (FFT) of the data to obtain information on the characteristic frequencies present in the data: here the potentiostat software was employed. Fig. S5b is an FFT of the data in Figure S5a. A large peak is seen corresponding to 50 Hz noise pick up from power lines when the resistor cell is placed on the benchtop. In some cases, smaller peaks may be seen due to the aliasing of higher frequencies, dependent on the sampling frequency employed.

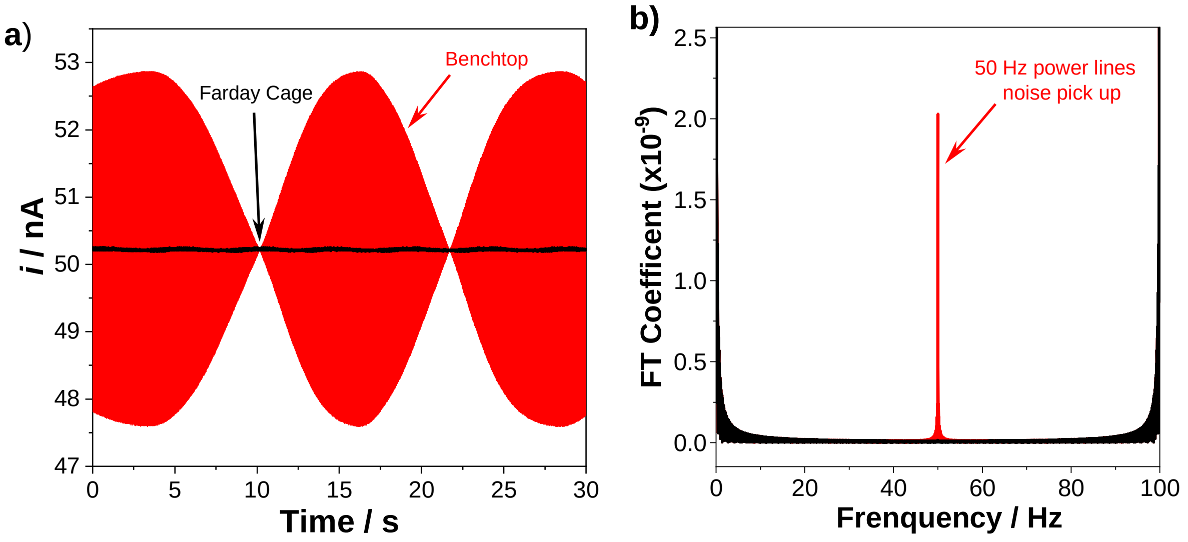

Fig. S5 (a). *i*-t data for a 10 MΩ two-electrode resistor cell and (b) the corresponding FFT, recorded on a CHI760C potentiostat inside a grounded Faraday cage (black) and the benchtop (red). The current was sampled at 0.01s intervals equivalent to a sampling rate of 100 Hz and the initial potential was 0.5V at a sensitivity of 10 nA/V.

With low current measurements, it is also important to note that moving near the two electrode resistor cell set-up will add additional noise when the cell is not properly shielded; here the Faraday cage door was deliberately left open. Movement in front of the open cage is shown by the increased current signals in Fig. S6. The clothed human body is isolated from earth and thus acts as an aerial. One remedy would be to stand naked on a grounded metal plate but this is not advised when shutting the door is a far easier and much more sensible solution!

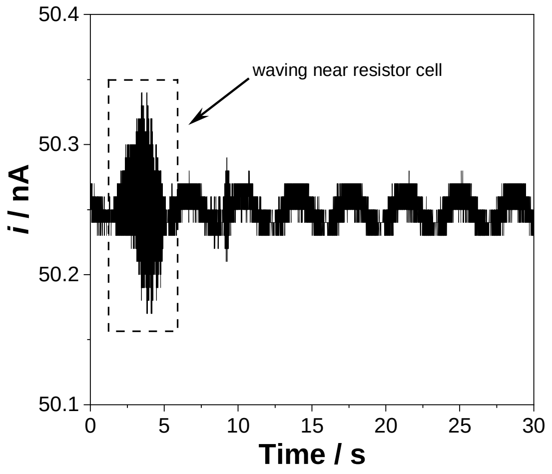

Fig. S6. *i-t* data for a 10 MΩ two-electrode resistor cell recorded on a CHI760C potentiostat in a Faraday cage with the door left open. The current was sampled at 0.01 s intervals equivalent to a sampling rate of 100 Hz and the initial potential was 0.5 V at a sensitivity of 10 nA/V.

2) Grounding the Potentiostat

Here we consider the importance of grounding the potentiostat to the common earth (star earth) and not letting the grounding cable provided by the potentiostat manufacturer hang free. This is shown by Fig. S7 for both (a) CV (black grounded, red ungrounded) and (b) *i-t* data (black grounded, red ungrounded) with the resistor set-up inside a closed Faraday cage. In Fig. S6a inset, noise on the signal is visible on the curve and can be seen in greater detail in the *i*-t data, Fig. S6b.

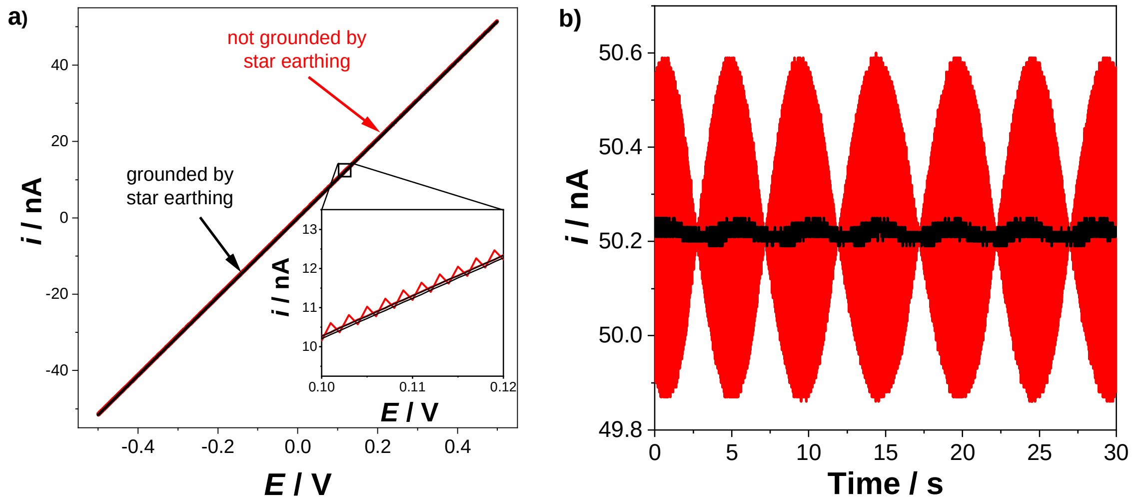

Figure S7. Examples of the noise measurements with a 10 MΩ two-electrode resistor cell recorded on a CHI760C Potentiostat when the potentiostat is grounded to the Faraday cage (black) the ground cable is unclipped (red). a) CV a sensitivity of 10 nA/V at a scan rate of 0.1V/s with a potentials step size of 1 mV. b) *i*-t curve where the current was sampled at 0.01s intervals equivalent to a sampling rate of 100 Hz and *E* = 0.5 V.

3) Working with other mains powered equipment nearby

Most laboratories will contain a range of mains powered equipment that might introduce noise into electrochemical measurements. Fig. S8 shows (a) the CV and (b) *i-t* data when a mains powered glass pH probe is introduced into the Faraday cage (red lines). In this experiment, the pH meter is plugged in at the mains, with the mains switched on but the meter switched off. The meter sits outside the cage, and the probe and cable are fed into the cage through an appropriately sized hole. The mains cable is unshielded, whilst the probe cable is shielded but not grounded to the Faraday cage. The red line shows the data when the pH probe is ~5 cm from the two-electrode resistor cell, whilst the black shows the data when the probe has been removed from the cage. Noise is on a similar nA scale to Fig. S4 when no Faraday cage is used! This is likely due to capacitive coupling from the mains supply noise picked up by the cables despite the instrument itself not being turned on. The data emphasises that equipment not being used should be removed from the Faraday cage, unplugged from the mains and moved far away. It would also have been possible to ameliorate the noise by grounding the shielded probe cable to the cage or placing the unplugged equipment, mains and probe cables inside the Faraday cage.

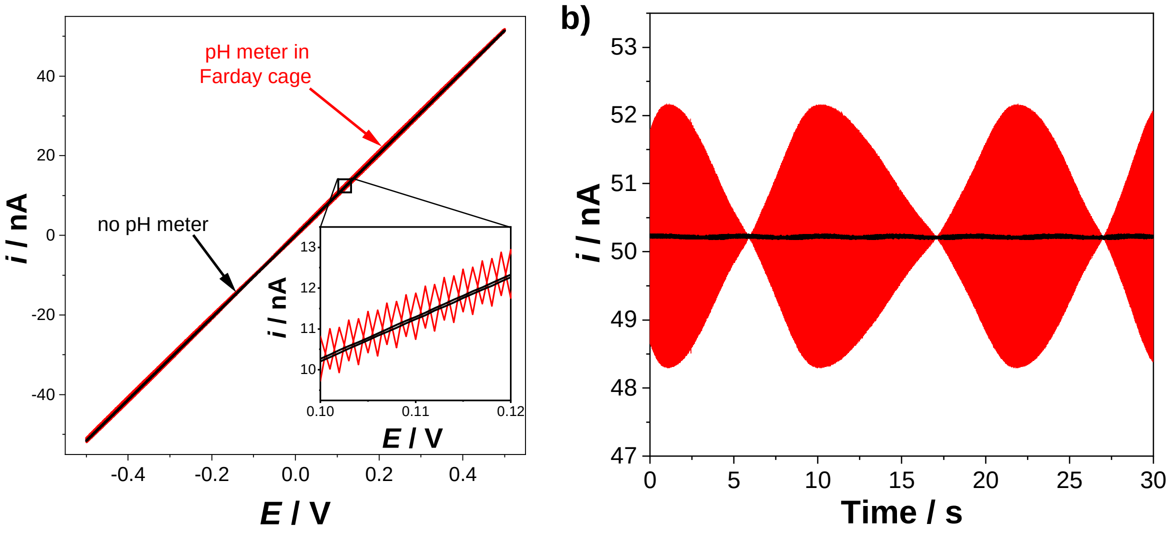

Figure S8. Examples of the noise measurements with a 10 MΩ two-electrode resistor cell recorded on a CHI760C Potentiostat when a mains powered glass pH probe is placed ~5 cm from the resistor cell (red lines) and without (black lines). a) CV a sensitivity of 10 nA/V at a scan rate of 0.1 V/s with a potentials step size of 1 mV. b) *i*-t data when the current was sampled at 0.01s intervals equivalent to a sampling rate of 100 Hz and E = 0.5 V.

If the pH meter were to be used at the same time as making the electrochemical measurement, then for low noise it is best to have the mains powered equipment outside the cage and run the probe shielded cable through an appropriately sized hole in the wall of the Faraday cage, taking care to ground the shielded cable to the cage at the entry point. This also applies to other mains powered equipment connecting to probes used in the cage. Use of a double ended panel connector is preferred but if not possible and the shielded cable contains an outer insulating layer it will be necessary to partially remove a section of this layer in order to make an electrical contact to the cable. For heated cell experiments, placing a high power hot plate in the cage is not recommended, as the mains cable is unshielded and the system generates lots of noise. The better way is to have a mains powered water bath outside the cage and flow solution into the cage, into a jacketed glass cell. However, ideally the point of entry of solution into the cage needs to be grounded requiring the use of chemically inert metal pipes.

Running the *i-t* response using a resistor cell provides a useful diagnostic for reducing noise in your electrochemical set-up.

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