Electrochemical noise analysis to obtain the $R_{sn}$ value via FFT using Excel

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The Supplementary Information 1 describes the procedures to calculate $R_{sn}^0$ using Origin® software and to obtain electrochemical noise data, and a file .xls with the experimental data used to applied the described routine.

How can ENA data be analyzed using Origin® software?

To make the same analysis, described in the main text, using Origin® software follows the steps below:

Copy the data of time ($t$), potential ($E(t) - y_E(t)$) and current ($I(t) - y_I(t)$) in the first three columns (A, B and C). Divide the current values by the electrode area and put the results in column D (select the column D and follows the commands: Column \rightarrow Set Columns Values \rightarrow in the box, type Col(C)/area value \rightarrow Ok).

Select the potential column and follows the commands: Analysis \rightarrow Signal Processing \rightarrow FFT \rightarrow FFT \rightarrow Open Dialog (Fig. S1a). In the window that appears, choose the option Window Hanning \rightarrow uncheck Shift \rightarrow in Spectrum Type box, choose One-sided \rightarrow uncheck Result Graph Sheet \rightarrow Ok (Fig. S1b). If you do not use the Hann window, mark Window Rectangle, as in Fig. S1c:
Figure S1. FFT Origin® command with (B) and without (C) Hann window.

A new tab is created (FFTResultData1) that has all necessary information to potential analysis, including frequency and PSDs, which is in column of “Power as MSA”. Repeat the proceeding for the column of the current. The Fig. S2 shows the tab FFTResultData1.
Figure S2. Results of the FFT routine applied to Potential data using Origin®.

Copy the column “Power as MSA” of the tab FFTResultData1 (PSD_E) and paste it in column E of the Sheet1 and repeat the proceeding for Current density (i), pasting the PSD_i in column F of the Sheet1.

Select the column G in the Sheet1 and follow the commands: Column → Set Columns Values → in the box, type \( \text{Sqrt}(\text{Col(E)/Col(F)}) \) → Ok, to calculate \( R_{sn} \). Figure S3 shows this proceeding.

Figure S3. Command to calculate \( \frac{\text{PSD}_E}{\text{PSD}_I} \).

Copy the frequency column (Freq(X)) of the tab FFTResultData1 and paste it in column H of the Sheet1. In the column I calculate \( \log f \) making: select the column I → Column → Set Columns Values → in the box, type \( \log(\text{Col(H)}) \) → Ok. Use the same proceeding to calculate \( \log(R_{sn}) \) in the column J. Your folder Sheet1 should look like Fig. S4.

Figure S4. Table of sheet1 with necessary values to calculate \( R_{sn}^0 \).
To make the graph select the column I → Column → Set as $X$; select the column J → Column → Set as $Y$. How the study is made in low frequency, select only the values of interesting to make the fit. In this case, the interval between row 2 and 29 was chosen to compare with Excel results (using Hann window). Make the graph using the commands: Plot → Line → Line (see Fig. S5).

Figure S5. Commands to make a graph using line.

Fit the straight line to graph (linear regression) by commands: Analysis → Fitting → Linear Fit → Ok. A new tab will be open, and the values of slope and intercept are presented in Parameters, like in the Fig. S6. Use these parameters to calculate $R_0$, as described in the paper.

Figure S6. Results of the linear regression.

Obtention of electrochemical noise data

Current and potential noise data were obtained in a Potentiostat / Galvanostat Reference 600 using the ESA410 software, from GAMRY Instruments®. The data contained in the spreadsheets were treated with the Excel software and compared with the treatment made with the Origin® software, with and without the Hann window option.

Electrochemical noise measurements were carried out using carbon paste electrodes modified with chalcopyrite powder. The powdered chalcopyrite ($\phi_{\text{average}} = 38$ $\mu$m) stored in argon atmosphere was mixed with graphite powder (Alfa Aesar, $\phi_{\text{average}} = 42$ $\mu$m) in the proportion of 50 wt.-% plus a drop of binder (mineral oil) and 0.6 mL of chloroform, according to the literature. The resulting paste was placed on a cavity electrode, constituting the carbon paste electrode (CPE), expounding an area of 0.282 cm$^2$ to the solution.

The solution A of the T&K medium containing 0.5 g L$^{-1}$ of each of Mg$^{2+}$ and NH$_4^+$ sulfate and potassium phosphate salts, 0.08 mol L$^{-1}$ ionic strength, pH 1.8 (adjusted with diluted H$_2$SO$_4$) plus 0.020 mol L$^{-1}$ CuSO$_4$ was used as electrolyte.

The electrochemical cell (Fig. S7) consisted of a glass cylinder placed horizontally, having two similar CPE electrodes fixed to the opposite sides of the cylinder and a reference electrode of Ag/AgCl/KCl3mol L$^{-1}$ in a Lugging capillary positioned close to one of the CPE electrodes. Once the electrochemical cell was connected to the potentiostat, all current and potential filters were activated for automatic scaling. The electrochemical cell was switched on and the potential and current noise were expected to stabilize before starting to record the 2048 points at the frequencies of 1 Hz. The experiments lasted 34 min and 8 s (1 Hz). Experimental data are in Excel in Supplementary information 2.
Figure S7. Electrochemical cell for obtaining the ENA data.

References

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[2] Tuovinen, O. H., Kelly, D. P., 1973. Studies on the growth of Thiobacillus ferrooxidans, Archiv für Mikrobiologie 88 (4) (1973) 285-298. https://doi.org/10.1007/BF00409941.