Supplementary Information

Pulsed Electrolysis-explained

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S1 Derivation of the Frequency Response Functions

The general procedure for the derivation of the frequency response functions is straightforward and well-explained in literature, for example [1,2,3]. It consists of seven steps, and here it is exemplified for the reaction system studied in this contribution.

Step 1. Definition of basic kinetic and mass transport equations and dynamic material and charge balances

The charge balance at the electrode surface where two parallel reactions take place (hydrogen evolution reaction (HER) and carbon dioxide reduction reaction (CO2RR)) is defined as:

$$C_{dl}\frac{dE(t)}{dt} = i(t) - \left(i_{f,H_2}(t) + i_{f,CO}(t)\right) \qquad \text{(Eq.S1)}$$

where C_{dl} is the double layer capacity (F m^{-2}), $E(t)$ electrode potential (V), t time (s), $i(t)$ current density (A m^{-2}), $i_{f,i}(t)$ is partial current density (A m^{-2}), and $i = H_2, CO$ stands for HER and CO2RR, respectively.

Tafel expressions are used to describe the kinetics of both reactions:

$$i_{f,H_2}(t) = -i_{0,H_2}exp(-\alpha_{H_2}fE(t)) \qquad \text{(Eq.S2)}$$
$$i_{f,CO}(t) = -i_{0,CO}exp(-\alpha_{CO}fE(t)) \qquad \text{(Eq.S3)}$$

where $i_{0,i}$ is the exchange current density of reaction i (A cm^{-2}), α_i the charge transfer coefficient of reaction i, and $f = \dfrac{F}{RT}$, with F being Faraday's constant (C mol^{-1}), R the universal gas constant (J mol^{-1} K^{-1}), and T temperature (K).

In the next step input and output variables are defined. Only the derivation of frequency response functions (FRFs) with the potential as an input is shown. Procedure for current as a modulated input is analogous.

Step 2. Definition of input and output variables

The input is defined as a cosine wave:

$$\Delta E(t) = (E(t) - E_{ss}) = A\cos(\omega t) = \frac{A}{2}(e^{j\omega \cdot t} + e^{-j\omega \cdot t})$$ (Eq.S4)

where A is the input amplitude (V), E_{ss} is the steady-state potential (V) value, j is the imaginary unit, and ω is the frequency (rad s^{-1}).

The output signal, cell current density, is defined as:

$$\Delta i(t) = (i(t) - i_{ss}) = \left(\frac{A}{2}\right)\{G_1(\omega)e^{j\omega \cdot t} + G_1(-\omega)e^{-j\omega \cdot t}\} +$$
$$\left(\frac{A}{2}\right)^2\{G_2(\omega,\omega)e^{j \cdot 2\omega \cdot t} + 2 \cdot G_2(\omega, -\omega)e^0 + G_2(-\omega, -\omega)e^{-j \cdot 2\omega \cdot t}\} + \dots$$ (Eq.S5)

where i_{ss} is the steady-state current density (A m^{-2}), $G_1(\omega)$ is the 1st-order FRF, $G_2(\omega,\omega)$ symmetrical 2nd-order FRF, and $G_2(\omega, -\omega)$ is the asymmetrical 2nd-order FRF.

Step 3. Taylor approximation of the nonlinear terms of the model around the steady state

The only nonlinear terms of the model defined in the Step 1 are the kinetic terms (Eq. S2 ans S3). The Taylor approximation of these terms up to the 2nd order is:

$$\Delta i_{f,i}(t) = i_{f,i}(t) - i_{f,i,ss} = K_{i,1}\Delta E(t) + K_{i,2}\frac{\Delta E(t)^2}{2}$$ (Eq.S6)

where $i_{f,i,ss}$ represents the steady-state value of the partial current. The constants $K_{i,1}$ and $K_{i,2}, i = H_2, CO$ are defined as:

$$K_{i,1} = \frac{\partial i_{f,i}}{\partial E} = i_{0,i}\alpha_i f \exp(-\alpha_i f E_{ss})$$ (Eq.S7)

$$K_{i,2} = \frac{\partial^2 i_{f,i}}{\partial E^2} = -i_{0,i}\alpha_i^2 f^2 \exp(-\alpha_i f E_{ss})$$ (Eq.S8)

Step 4. Substituting the Taylor polynomial into the mathematical model defined in Step 1

Eq.S6 is substituted in Eq.S1:

$$C_{dl}\frac{dE(t)}{dt} = i(t) - \left(K_{H_2,1}\Delta E(t) + K_{H_2,2}\frac{\Delta E(t)^2}{2} + K_{CO,1}\Delta E(t) + K_{CO,2}\frac{\Delta E(t)^2}{2}\right)$$ (Eq.S9)

Step 5. Substituting the input and outputs into the equations obtained in Step 4.

Eq.S4 and S5 are substituted in Eq.S9. The following equation is obtained:

$$C_{dl}\frac{A}{2}(j\omega e^{j\omega \cdot t} - j\omega e^{-j\omega \cdot t}) = \left(\frac{A}{2}\right)\{G_1(\omega)e^{j\omega \cdot t} + G_1(-\omega)e^{-j\omega \cdot t}\} +$$ (Eq.S10)

$$\left(\frac{A}{2}\right)^2\{G_2(\omega,\omega)e^{j\cdot 2\omega\cdot t} + 2\cdot G_2(\omega,-\omega)e^0 + G_2(-\omega,-\omega)e^{-j\cdot 2\omega\cdot t}\}$$

$$-\left\{K_{H_2,1}\frac{A}{2}(e^{j\omega\cdot t} + e^{-j\omega\cdot t}) + \frac{K_{H_2,2}}{2}\left(\frac{A}{2}\right)^2(e^{2j\omega\cdot t} + 2e^0 + e^{-j2\omega\cdot t}) + \right.$$

$$+ ....$$

Step 6. Applying harmonic probing

Harmonic probing is done by collecting all the terms of the same frequencies from equation Eq.S10. The terms of frequency ω result in equation:

$$C_{dl}\frac{A}{2}j\omega e^{j\omega\cdot t} = \left(\frac{A}{2}\right)G_1(\omega)e^{j\omega\cdot t} - \left\{K_{H_2,1}\frac{A}{2}e^{j\omega\cdot t} + K_{CO,1}\frac{A}{2}e^{j\omega\cdot t}\right\} \qquad \text{(Eq.S11)}$$

Then, by collecting the terms with frequencies 2ω and 0, one obtains:

$$0 = \left(\frac{A}{2}\right)^2 G_2(\omega,\omega)e^{j\cdot 2\omega\cdot t} - \left\{\frac{K_{H_2,2}}{2}\left(\frac{A}{2}\right)^2 e^{2j\omega\cdot t} + \frac{K_{CO,2}}{2}\left(\frac{A}{2}\right)^2 e^{2j\omega\cdot t}\right\} \qquad \text{(Eq.S12)}$$

$$0 = \left(\frac{A}{2}\right)^2 \cdot 2 \cdot G_2(\omega,-\omega)e^0 - \left\{\frac{K_{H_2,2}}{2}\left(\frac{A}{2}\right)^2 \cdot 2e^0 + \frac{K_{CO,2}}{2}\left(\frac{A}{2}\right)^2 \cdot 2e^0\right\} \qquad \text{(Eq.S13)}$$

Step 7. Solving the equations derived in Step 6

By solving equations S11-S13, the analytical expressions for FRFs are obtained:

$$G_1(\omega) = C_{dl}j\omega + \left(K_{H_2,1} + K_{CO,1}\right) \qquad \text{(Eq.S14)}$$

$$G_2(\omega,\omega) = \frac{K_{H_2,2} + K_{CO,2}}{2} \qquad \text{(Eq.S15)}$$

$$G_2(\omega,-\omega) = \frac{K_{H_2,2} + K_{CO,2}}{2} \qquad \text{(Eq.S16)}$$

Similarly, the partial currents can be defined as auxiliary outputs:

$$i_{f,i}(t)$$

$$= i_{f,i,ss} + \left(\frac{A}{2}\right)\{G_{1,i}(\omega)e^{j\omega\cdot t} + G_{1,i}(-\omega)e^{-j\omega\cdot t}\} + \left(\frac{A}{2}\right) \qquad \text{(Eq.S17)}$$

$$+ ...$$

By repeating Steps 3-7, the FRFs for partial currents are calculated as:

$$G_{1,i}(\omega) = K_{i,1} \qquad \text{(Eq.S18)}$$

$$G_{2,i}(\omega,\omega) = \frac{K_{i,2}}{2} \qquad \text{(Eq.S19)}$$

$$G_{2,i}(\omega,-\omega) = \frac{K_{i,2}}{2} \qquad \text{(Eq.S20)}$$

S2 Analysis of the dynamic CO FE with current as a periodic input

In case of the current as a periodic input, the dynamic CO FE is different than the steady-state one:

$$FE_{CO,dyn} = FE_{CO,ss} + \frac{2}{i_{ss}}\left(\frac{A}{2}\right)^2 G_{2,CO}(\omega, -\omega)$$ (Eq.S21)

where $G_{2,CO}(\omega, -\omega)$ is the asymmetrical 2nd-order FRF for partial current of CO defined as:

$$G_{2,CO}(\omega, -\omega) = \frac{\left(K_{H_2,1}K_{CO,2} - K_{CO,1}K_{H_2,2}\right)}{\left(K_{H_2,1} + K_{CO,1}\right)\left(C_{dl}^2\omega^2 + \left(K_{H_2,1} + K_{CO,1}\right)^2\right)}$$ (Eq.S22)

Having in mind that i_{ss} is always negative (reduction current is negative based on the convention), the asymmetrical 2nd-order CO FRF (Eq.S22) has to be negative in order for the dynamic CO FE to be higher than the steady-state one. Based on the definition, coefficients $K_{i,1}$ are always positive, meaning that the denominator of Eq.S22 will also always be positive. Thus, the assymetrical 2nd-order FRF will be negative if the inequality in Eq.S23 is satisfied.

$$K_{H_2,1}K_{CO,2} - K_{CO,1}K_{H_2,2} < 0$$ (Eq.S23)

From Eqs. S7 and S8, it follows:

$$K_{i,2} = -\alpha_i f K_{i,1}$$ (Eq.S24)

By substituting Eq.S24 in the Eq.S23 and rearanging, one obtaines:

$$K_{H_2,1}K_{CO,1}f\left(\alpha_{H_2} - \alpha_{CO}\right) < 0$$ (Eq.S25)

Considering that the coefficients in Eq.S25 are always positive, the values of the charge transfer coefficients of the two parallel reactions determines the sign of the asymmetrical 2nd-order FRF.

Thus, to achieve an increase of the CO FE under the dynamic operation compared to the steady state, the charge transfer coefficient of CO2RR should be greater than the one of HER.

References

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