Supporting Information

Universal Algorithm for Simulating and Evaluating Cyclic Voltammetry at Macroporous Electrodes by Considering Random Arrays of Microelectrodes

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SUPPORTING INFORMATION

S1 ELECTRODE KINETICS, COUPLED HOMOGENEOUS KINETICS AND NON-EQUAL DIFFUSION COEFFICIENTS

This section discusses the combined influence of Butler-Volmer electrode kinetics, electrode geometries, diffusion domains, non-equal diffusion coefficients, limited heterogeneous kinetics and homogeneous chemical kinetics on the CV response. For exemplary calculations only the planar finite random-network diffusion domain model is shown, as the qualitative behavior of the other diffusion models is similar. All calculations were performed with \( d_{av} = 50 \, \mu\text{m} \) and a discretization of the domain of the distribution function into 10 intervals. Fig. S1 depicts the influence of A) Butler-Volmer electrode kinetics with respect to \( k^0 \), B) Butler-Volmer electrode kinetics with respect to \( \alpha \), C) limited heterogeneous electrode kinetics and D) non-equal diffusion coefficients on the CV response in a finite and statistically distributed diffusion domain.
**Fig. S1**: Simulated dimensionless current responses vs. dimensionless potentials for a porous electrode with planar finite geometry. Simulations were performed using the set of parameters given in tab. 9 and changing individual parameters according to the values given in the individual subplots.

From fig. S1A and S1B it can be seen that the well-known influence of Butler-Volmer electrode kinetics also holds in a statistically distributed finite diffusion domain. Consequently, decreasing $k^0$ yields an increased peak-to-peak separation, $\alpha > 0.5$ forces a steeper and $\alpha < 0.5$ a flatter and more rounded forward reaction peak. From fig. S1C it can be seen that finite heterogeneous electron transfer kinetics will result in a decreased peak height and a more broadened peak for the forward as well as for the backward reaction.
However, it should be noted that the peak separation remains similar. Of course, in case of infinitely fast limited electron transfer kinetics, the ordinary Butler-Volmer behavior would be obtained. Fig. S1D depicts the influence of non-equal diffusion coefficients on a CV in a finite and statistically distributed diffusion domain. Whereas it is well-known that in semi-infinite diffusion space at a planar electrode, non-equal diffusion coefficients will just shift the CV along the potential axis according to $\Delta E = \frac{nF}{RT} \ln \left( \frac{D_R}{D_O} \right)$ [4], we demonstrate that non-equal diffusion coefficients will deform the shape of the CV in a finite diffusion domain. It can be seen that changing the ratio $D_R/D_O$ from 1 to 10 by increasing $D_O$ by factor 10 (curve c) introduces only weak changes to the forward reaction peak (here the oxidation peak) as the value of $D_R$ was kept constant with respect to the $D_R = D_O$ (curve a) case. However, the backward reaction peak (here the reduction peak) becomes significantly affected (increased peak height and steeper diffusion tail). This can be illustrated in the following way. While the diffusion zone reaches the wall at distance $d$ from the electrode surface more rapidly, the backward diffusion requires less time, resulting in a more steeply decreasing diffusion tail in the CV.

As the volume and thus the absolute amount of electrochemically active species trapped inside the diffusion domain remains constant, the absolute charge under oxidation and reduction peak has to stay constant as well. Consequently a shortened diffusion tail has to be accompanied by an increased peak height. In case of $D_R = 10D_O$ (curve b), the entire dimensionless current of the CV response is scaled down, as $\chi(\xi)$ is always normalized to the diffusion coefficient of the forward reaction. Upscaling $\chi(\xi)$ by $\sqrt{D_R}$ will consequently result in the opposite trend observed in curve b. It should be noted however, that for the CV simulation in Fig. S1D (as well as in all CV simulations shown in this paper) the forward reaction is an oxidation. If the forward scan would be reductive, the opposite trend will be observed. Nevertheless, it has to be underlined that the deformation of the CV response introduced by non-equal diffusion
coefficients is different from the modification caused by the parameter $\alpha$ (fig. S1A). The latter mainly modifies the exponentially ascending part of the peaks in the CV, whereas unequal diffusion coefficients mainly affect the depleting part, i.e. the diffusion tail. This is of extraordinary importance for differentiating qualitatively between the influences of kinetics and diffusion properties.

Fig. S2 depicts the influence of homogeneous chemical reactions coupled to the electron transfer reaction in a planar finite statistically distributed diffusion domain. Again the CVs for diffusion models deviating from the planar one are not discussed separately, as the qualitative influence of the parameters will be the same. Calculations are performed for three different values of $K_p$ in a reaction sequence of $E \rightleftharpoons R \rightleftharpoons O$ (fig. S2A, S2B and S2C) and $K_f$ in a reaction sequence of $R \rightleftharpoons O \rightleftharpoons P$ (fig. S2D, S2E and S2F) with three different values of $p = k_p + k_{-p}$ and $f = k_f + k_{-f}$ each. It can be seen that the impact of homogeneous chemical reactions on the CV response depends on both, the location of the equilibrium and on the rate at which the equilibrium will be reached. Fig. S2A and S2D depict the cases of $K_p = 10$ and $K_f = 0.1$, corresponding to a preceding equilibrium at the side of species $R$ and a following equilibrium on the side of $O$, respectively. As the equilibrium lies in both cases on the side of the electrochemically active species $R$ and $O$, only small modifications are visible in the CV.
Fig. S2 Simulated CV responses for a statistically distributed planar finite diffusion domain with coupled preceding (A, B, C) and following (D, E, F) homogeneous chemical equilibria at different location and apparent rate constants. Simulated dimensionless current simulations were performed using the set of parameters given in tab. 9.

More significant changes in the CV response are expected, if the preceding equilibrium lies rather on the side of $E$ and the following chemical equilibrium lies rather on the side of $P$. This effect is shown in fig. S2B and S2E with $K_P = 1$ and $K_f = 1$, i.e. a preceding and following chemical equilibrium that lies equally at the side of $E$ and $R$ or $O$ and $P$, and fig. S2C and S2F where $K_P = 0.1$ and $K_f = 10$, i.e. a preceding equilibrium lying at the side of $E$ and following chemical equilibrium lying at the side of $P$. It can be seen that in case of very slow preceding chemical equilibria with an apparent rate constant of $p = 1.1 \cdot 10^{-4} \text{s}^{-1}$ (fig. S2B and S2C, dotted curve) the CV response is scaled down, without significant changes in shape.
This can be assigned to the fact that the rate of the preceding equilibrium is too slow for compensating the loss of species \( R \) by converting \( E \) to \( R \). From fig. S2E and S2F it can be seen that an apparent rate constant of \( f = 1.1 \cdot 10^{-4}s^{-1} \) (dotted curves) only weakly affects the backward reaction without changing the forward reaction, as it is too slow for converting a significant amount of \( O \) into \( P \) at the time scale of the experiment. From fig. S2C, S2D, S2E and S2F it can be seen that at high rate constants of preceding and following chemical equilibria \( (p = f = 1.1 \text{ s}^{-1}, \text{ solid curves}) \) the CV response gets rather similar to the case of an electrochemical reaction without coupled homogeneous chemical kinetics. This can be attributed to the fact that the coupled chemical reactions proceed so fast that the change in the concentration of electrochemically active species will be compensated rapidly. Consequently, in case of coupled homogeneous chemical reactions the most significant distortion of the CV can be expected when the coupled chemical equilibria lie at the side of \( E \) and \( P \), respectively, with rate constants comparable to the rate of the electrochemical reaction. This scenario is depicted by the dashed lines in fig. S2C, S2D, S2E and S2F. In general, while a preceding chemical equilibrium modifies the forward and the backward reaction peak, a following chemical equilibrium mainly affects the backward reaction. This can be explained by the fact that the intensity of the backward reaction depends on both, a) the amount of electrochemically active species generated by a forward reaction and b) on the rate of the backward reaction itself. Consequently, if the forward reaction will be influenced by a preceding chemical equilibrium, also the backward reaction will be affected.
S2 MANUAL FITTING ROUTINE

This section discusses how the fitting process leading to the results shown in fig. 6B and 9A was performed, namely for the random Pt-wire network electrode. It might be used as a quick guide on how to evaluate experimental data with our software. After loading a data file as shown in fig. S3 and choosing a suitable diffusion model (in this case the statistically weighted, external cylindrical finite diffusion model), all parameters marked with an asterisk are mandatory to provide. Therein, \( a, k^0, E^0, T, \nu, A, A, \) and \( D \) have their usual meaning. The entry “Cylinders per \text{mm}^2” corresponds to the value of \( N_i \) (\( i = p, c, s \), here \( N_c \)). The parameter “Intervals of Dist.” represents the number of intervals in which the domain of the distribution function will be split up and thus the number of individual CVs being calculated.

For including non-mandatory parameters, the corresponding checkboxes need to be activated prior to CV simulation. In this manner the option “Modify Distribution function” allows for calculating any desired density distribution function describing the distribution of the microelectrode distance in a porous electrode by editing the parameters \( a, b \) and \( c \) of equation 13 of our theory section. Default values for these parameters, as given in the theory section, are selected automatically with the respective diffusion model unless manual modification is explicitly chosen. The option “Mod_Xi_Resol” allows for editing the increment of the dimensionless potential \( \xi = nF(E - E^0)/RT \) during the CV simulation. As explained in the theory section the value \( \Delta \xi = 0.1 \) is set as default.

For the example provided in this paper, the value of \( E^0 \) vs. the reference electrode potential can be obtained from the literature. Additional information about the electrode morphology perhaps obtained from microscopic images of the electrode material, allows one to estimate \( N_i \) as well as electrode fiber radii. Based on the latter two parameters, also a rough estimate of internal electrode surface areas can be obtained that can be used as starting values in the simulations.
Suitable values for diffusion coefficients of electrochemically active species may be available from the literature, in the present case from ref [42]. Otherwise, values for $D$ in aqueous media are usually of the order of $10^{-6}\text{cm}^2/\text{s}$ to $10^{-5}\text{cm}^2/\text{s}$. Next, the remaining yet unknown parameters need to be estimated. It turned out to be an effective strategy to adjust the value of $k^0$ to roughly fit the peak positions and subsequently to adjust $\alpha$ to roughly fit the ascending part of both CV peaks. By considering the symmetry of the imported CV data (fig. S3 or fig. 6), the initial guess of $\alpha = 0.5$ was chosen. The initial value of the standard rate constant was set to be $k^0 = 10^{-4}\text{cm/s}$, leading to a calculated CV response poorly fitting the measured data as shown in fig. S4A. Adjusting the value of $k^0 = 10^{-3}\text{cm/s}$ yields already to a much better fit as shown in fig. S4B. By scaling the electrode area the first fitting iteration is obtained as shown in fig. S4C. In the following steps all parameters are adjusted more precisely so as to fit the measured CV curve as closely as possible. Hence one can successfully attempt to minimize the standard deviation between simulated and measured data as shown in fig. S4D. However, it has to be underlined that during this fitting process all individual parameters have to be kept at realistic values in order to provide meaningful data evaluation. Thus, the initial guess of parameters is a mandatory and the most crucial step. Nevertheless, we suggest that this strategy can be used to evaluate CV data, even of porous electrodes, such that reliable information about electrode kinetics can be obtained.
Fig. S3: Importing a data file for evaluation via Polarographica and setting the initial parameters for CV calculation.
Fig. S4: Manual fitting process for experimentally acquired CV data of the ferro/ferricyanide redox couple at a folded Pt mesh electrode (assumed as an array of cylindrical microelectrodes). Measurements were conducted at 25°C with a sweep rate of 2 mV/s in a 0.01 M $K_4[Fe(CN)_6]$ solution containing 0.1 M KCl supporting electrolyte using a Gamry Ref600 potentiostat (Gamry Instruments).
Tab. SI: Kinetic, hydrodynamic and geometric parameters of the VO$_2^+$/VO$_2^{2+}$ redox couple obtained from the fitting of the CV of the carbon felt electrode in fig. 7.

| $n$ | $T[K]$  | $A[cm^2]$ | $c[mol/L]$ | $D_R[cm^2/s]$ | $D_0[cm^2/s]$ | $a[\mu m]$ | Cyl. Per mm$^2$ |
|-----|---------|-----------|------------|---------------|---------------|------------|----------------|
| 1   | 298.15  | 28        | 0.16       | 2.7·10$^{-5}$ | 3.2·10$^{-5}$ | 4.2        | 722            |
| $\alpha$ | $k^0[cm/s]$ | $k_p[s^{-1}]$ | $k_{-p}[s^{-1}]$ | $k_f[s^{-1}]$ | $k_{-f}[s^{-1}]$ | $\nu[mV/s]$ | $E^0$ vs. $E_{Ag/AgCl}$ [V] |
| 0.42 | 2.6·10$^{-4}$ | 0.0028 | 0.0015 | 0.0008 | 0.0003 | 2, 3, 4, 5, 6, 7 | 0.882 |