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## **Understanding Reaction Mechanisms Using Dynamic Electrochemical Impedance Spectroscopy: Modeling of Cyclic Voltammetry and Impedance Spectra**

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The fitting of reaction models consisting of elementary reaction steps to experimental data constitutes a method for verification of the reaction models and the possibility of finding the kinetic parameters of a system. However, due to the complexity that easily arises due to numerous reaction steps, it is notoriously difficult to pose a problem and optimize it to a single solution. Therefore, the successful fitting of a reaction model is not proof since several models can potentially be fit successfully to the same experimental dataset. A possible solution to this problem is to fit the reaction models to one dataset and verify the results by using a complementary experimental technique under the same conditions. Dynamic electrochemical impedance spectroscopy (dEIS) is uniquely suited for such an approach. In this work, a method for fitting and optimizing kinetic parameters in a reaction mechanism to experimental data from cyclic voltammetry is described. Subsequently, the optimized kinetic parameters are used to calculate corresponding dEIS results. Methanol oxidation on Pt at elevated temperatures is used as an example of the application of this method.

### **Introduction**

Electrochemical impedance spectroscopy (EIS) is a suitable tool for mechanistic studies due to the amount of data that is accessible through this technique (1). However, even if the frequency range is wide, the mechanistic information is convoluted making the interpretation complicated. Therefore, data analysis of impedance data is often limited to pattern recognition and fitting of equivalent circuits. Methods for calculating EIS spectra from a stated mechanism are readily available (2, 3). However, the system under study needs to be well understood so that realistic reaction mechanisms can be formulated.

Quantitative analysis using EIS data is a goal as it can utilize information that is readily available experimentally to enhance mechanistic analysis. The use of dEIS is an ideal tool for this purpose because dEIS is collected simultaneously with a pseudo steady-state technique such as slow cyclic voltammetry, allowing for the simultaneous collection of direct current (dc) and alternating current (ac) data. In practical cases, models of different reaction mechanisms have yielded similar results for steady-state techniques making the results ambiguous (4). In our case, with the combination of dEIS and cyclic voltammetry, a reaction mechanism can be fitted to experimental cyclic voltammograms, and the

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calculated dEIS spectra can be used to distinguish between mechanisms that have similar modeled cyclic voltammograms. This combination offers a superior path for performing a mechanistic analysis.

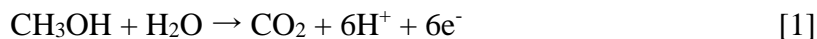
In this work, we present a systematic method to deduce a reaction model from experimental data. The method uses a dc technique, i.e., cyclic voltammetry, to fit kinetic parameters through an iterative optimization process. Subsequently, EIS spectra at any potential can be calculated and compared to the experimental data. This routine makes it possible to use the large amount of information found in dEIS data sets in a mechanistic analysis. Examples from studies of methanol oxidation are used to illustrate the technique.

### **Problem statement**

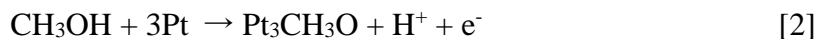
The fitting of a reaction mechanism to experimental data is a general problem in electrochemistry. However, few established methods exist where the kinetic parameters can be quickly optimized. The general statement of the optimization problem is given below for the case of methanol oxidation through adsorbed CO. Experimental data at higher temperatures are used to support the assumption that this reaction pathway dominates the overall mechanism (7). The purpose is to explain the methodology, and show that realistic reaction mechanisms can be proposed.

#### Methanol oxidation

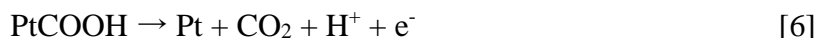
Methanol oxidation in acidic conditions is known to proceed through a dual pathway mechanism, a direct pathway producing formaldehyde, formic acid, and CO<sub>2</sub>, and an indirect pathway through adsorbed CO producing CO<sub>2</sub> (8). At temperatures above 100°C, the indirect pathway dominates the current, and the overall reaction mechanism can be simplified (7). The half-cell reaction of methanol to CO<sub>2</sub> is given in Eq. (1).



The total reaction can be separated into two steps in the indirect pathway: CO production and CO oxidation. For the CO production step(s), it is assumed that three Pt sites are necessary to adsorb methanol on Pt in accordance with the literature (9-11). Therefore, the CO production steps can be written as in Eqs. (2)-(3).



Similarly, for the CO oxidation steps, a chemical surface reaction is assumed, i.e., a so-called Kauranen-step (13), giving the steps in Eqs. (4)-(6) as the CO oxidation mechanism.



In addition to all the steps related to methanol oxidation, platinum oxidation will proceed at higher potentials; this reaction is simplified as Eq. (7).



The mechanism consisting of Eqs. (2)-(7) thus constitutes a model for indirect oxidation of methanol on Pt.

### Reversible OH/O reactions

The water adsorption step, Eq. (4), is commonly assumed to be reversible. This makes the reaction infinitely fast, and hence, the kinetics of the reaction does not contribute to the shape of the impedance spectra. To simplify the calculation further and to minimize the influence of the platinum oxidation reaction, Eq. (7), this step is assumed to be reversible as well. Following these assumptions, the surface coverages of OH and PtO can be found from Eqs. (8)-(9).

$$\theta_{\text{OH}}/\theta_{\text{Pt}} = K_{\text{OH}} \exp(F\eta/RT) \quad [8]$$

$$\theta_{\text{PtO}}/\theta_{\text{OH}} = K_{\text{PtO}} \exp(F\eta/RT) \quad [9]$$

Here,  $\theta_i$  is the surface coverage species  $i$  defined as  $\theta_i = \Gamma_i/\Gamma_{\text{tot}}$ , where  $\Gamma_i$  is the surface density of species  $i$  (see Eq. (10)),  $K_{\text{OH}}$  is the equilibrium constant for OH adsorption ( $= k_{\text{OH}}/k_{-\text{OH}}$ ),  $K_{\text{PtO}}$  is the equilibrium constant of platinum oxidation ( $= k_{\text{PtO}}/k_{-\text{PtO}}$ ),  $F$  is the Faraday constant,  $R$  is the gas constant,  $T$  is the temperature, and  $\eta$  is the overpotential relative to 0 V vs RHE.

### System of ordinary differential equations (ODEs)

The mechanism described above has 6 adsorbates ( $\text{CH}_3\text{O}$ ,  $\text{CO}$ ,  $\text{COOH}$ ,  $\text{OH}$ ,  $\text{PtO}$ , and Pt sites), and the total coverage is equal to 1 according to Eq. (11). Note that the  $\text{CH}_3\text{O}$  adsorbate takes up 3 Pt sites.

$$\Gamma_{\text{Pt}} + 3\Gamma_{\text{CH}_3\text{O}} + \Gamma_{\text{CO}} + \Gamma_{\text{COOH}} + \Gamma_{\text{PtOH}} + \Gamma_{\text{PtO}} = \Gamma_{\text{tot}} \quad [10]$$

$$\theta_{\text{Pt}} + 3\theta_{\text{CH}_3\text{O}} + \theta_{\text{CO}} + \theta_{\text{COOH}} + \theta_{\text{PtOH}} + \theta_{\text{PtO}} = 1 \quad [11]$$

The rate of each step is given in Eqs. (12)-(17). The units of the reaction constants,  $k_i$ , and the rates,  $v_i$ , are  $\text{s}^{-1}$  and can be turned into flux ( $\text{mol cm}^{-2} \text{s}^{-1}$ ) by dividing by the total surface density of Pt atoms,  $\Gamma_{\text{tot}}$  ( $2.28 \text{ nmol cm}^{-2}$ ).

$$v_{\text{CH}_3\text{O}} = k_{\text{CH}_3\text{O}} C_{\text{CH}_3\text{OH}} \theta_{\text{Pt}}^3 \exp((1-\beta_{\text{CH}_3\text{O}})F\eta/RT) \quad [12]$$

$$v_{\text{CO}} = k_{\text{CO}} \theta_{\text{CH}_3\text{O}} \exp((1-\beta_{\text{CO}})F\eta/RT) \quad [13]$$

$$v_{\text{OH}} = k_{\text{OH}} \theta_{\text{Pt}} \exp((1-\beta_{\text{OH}})F\eta/RT) - k_{-\text{OH}} \theta_{\text{OH}} \exp(-\beta_{\text{OH}}F\eta/RT) \quad [14]$$

$$v_{\text{COOH}} = k_{\text{COOH}} \theta_{\text{OH}} \theta_{\text{CO}} \quad [15]$$

$$v_{\text{CO}_2} = k_{\text{CO}_2} \theta_{\text{COOH}} \exp((1-\beta_{\text{CO}_2})F\eta/RT) \quad [16]$$

$$v_{\text{PtO}} = k_{\text{PtO}} \theta_{\text{OH}} \exp((1-\beta_{\text{PtO}})F\eta/RT) - k_{-\text{PtO}} \theta_{\text{PtO}} \exp(-\beta_{\text{PtO}}F\eta/RT) \quad [17]$$

Here,  $C_{\text{CH}_3\text{OH}}$  is the concentration of methanol (normalized as a unitless parameter). The differential equations for the model can then be defined for each adsorbate as given in Eqs. (18)-(23).

$$d\theta_{\text{Pt}}/dt = -3\nu_{\text{CH}_3\text{O}} + 2\nu_{\text{CO}} - \nu_{\text{OH}} + \nu_{\text{COOH}} + \nu_{\text{CO}_2} \quad [18]$$

$$d\theta_{\text{CH}_3\text{O}}/dt = \nu_{\text{CH}_3\text{O}} - \nu_{\text{CO}} \quad [19]$$

$$d\theta_{\text{CO}}/dt = \nu_{\text{CO}} - \nu_{\text{COOH}} \quad [20]$$

$$d\theta_{\text{COOH}}/dt = \nu_{\text{COOH}} - \nu_{\text{CO}_2} \quad [21]$$

$$d\theta_{\text{OH}}/dt = \nu_{\text{OH}} - \nu_{\text{COOH}} - \nu_{\text{PtO}} \quad [22]$$

$$d\theta_{\text{PtO}}/dt = \nu_{\text{PtO}} \quad [23]$$

By solving this system of ODEs, with the initial conditions  $\theta_{\text{Pt}}(t=0) = \theta_{\text{PtO}}(t=0) = 0.5$  and other coverages zero, the current density,  $j$ , can be calculated at any point in the cyclic voltammogram by using Eq. (24) and the relationship between the potential and the time as given by Eq. (25).

$$j = F\Gamma_{\text{tot}}(\nu_{\text{CH}_3\text{O}} + 3\nu_{\text{CO}} + \nu_{\text{OH}} + \nu_{\text{CO}_2} + \nu_{\text{PtO}}) \quad [24]$$

$$E(t) = E_{\text{init}} + \nu t \quad [25]$$

The initial potential,  $E_{\text{init}}$ , is here 0 V vs RHE, and the sweep rate,  $\nu$ , is 5 mV s<sup>-1</sup> in all of our experiments.

## Experimental

Optimization of kinetic parameters was done using Maple 2017 and a computer with 16 Gb RAM, Intel Core i7-7700T CPU @ 2.90 GHz, and Windows 10 64 bit.

### Optimization procedure

Nominally, the problem stated above has 8 rate constants,  $k_i$ , and 5 symmetry factors,  $\beta_i$ . To simplify the optimization problem, the symmetry factors were fixed at 0.5 except for  $\beta_{\text{CH}_3\text{O}}$ , which was fixed at 0.25 (12). This reduced the number of parameters to 8. Due to the exponential relationship inherent in electrochemical systems, the objective function to be minimized was taken as the logarithm of the current, i.e., as given in Eq. (26).

$$RSS = \sum_t (\ln(j_{\text{exp}}(t)) - \ln(j_{\text{mod}}(t)))^2 \quad [26]$$

The optimization of the rate constants was also done in the logarithmic state, i.e.,  $\log(k_i)$  were the actual optimized parameters. This is important as it simplifies the choice of optimization procedure when the fitted parameters range over values between -20 and 20 instead of the exponential equivalent.

This optimization problem is significantly more complicated than usual because the set of ODEs must be solved numerically every time the optimization routine needs to evaluate the objective function. As the system of differential equations is solved numerically, the gradient is not accessible. Therefore, gradient-free optimization methods are necessary. Built into Maple's NLPSolve command, two methods are especially relevant, the non-linear simplex method and the branch-and-bound method. If successful, the non-linear simplex method is the ideal choice as it does not depend on the initial value and does not need bounds of the solution. On the other hand, the bounds can be given to the branch-and-bound method to ensure that realistic values are obtained. However, this method is slower, increasing the optimization time. To ensure maximum stability, the branch-and-bound

method was used for all single parameter optimizations. For the reversible steps, Eqs. (4) and (7), both the forward and back reaction should be optimized simultaneously. This is only possible with the non-linear simplex method, and therefore, the simplex method was used in those cases.

In summary, the optimization procedure works as follows: Every single parameter is optimized by the branch-and-bound method with the value from the previous iteration as the starting point and bounded by  $\pm 1$  in the  $\log_{10}$  state, i.e., spanning 3 orders of magnitude. The steps with both forward and back reaction,  $k_{\text{OH}}/k_{-\text{OH}}$  and  $k_{\text{PtO}}/k_{-\text{PtO}}$ , are optimized by the non-linear simplex method with the value from the previous iteration as the starting point. The parameters were fitted in sequence, i.e.,  $k_{\text{CH}_3\text{O}} - k_{\text{CO}} - k_{\text{OH}}/k_{-\text{OH}} - k_{\text{COOH}} - k_{\text{CO}_2} - k_{\text{PtO}}/k_{-\text{PtO}}$ , until convergence was reached. Successful convergence was defined as  $(\text{RSS}_i - \text{RSS}_{i+1})/\text{RSS}_i < 0.00001$  for the fitting of experimental data, and as  $\text{RSS} < 10^{-4}$  for synthetic data, where the subscript  $i$  denotes the iteration number.

After posing the problem and choosing the optimization procedure, it remains to determine suitable initial values. Unfortunately, there is, to the authors' knowledge, no appropriate method to determine the initial values except for trial and error. The difficulty is accentuated by the fact that the problem will rarely converge unless the initial values are relatively close to the optimum values. The strategy chosen to find the initial values in this work was to use the experimental data set from cyclic voltammetry and the expected development in coverages from the literature (14), and then manually fit the model until it closely resembled the experimental results. From this coarse result, the optimization procedure was used to find the exact parameter values. As always, there is uncertainty about whether a global minimum is achieved, but getting the correct feature in the dEIS and a close resemblance with experimental IR spectroscopy data of coverages gives confidence that we are not in a local minimum far from the correct solution. In the subsequent section, the method described is used to optimize synthetically-generated data from the given model of methanol oxidation.

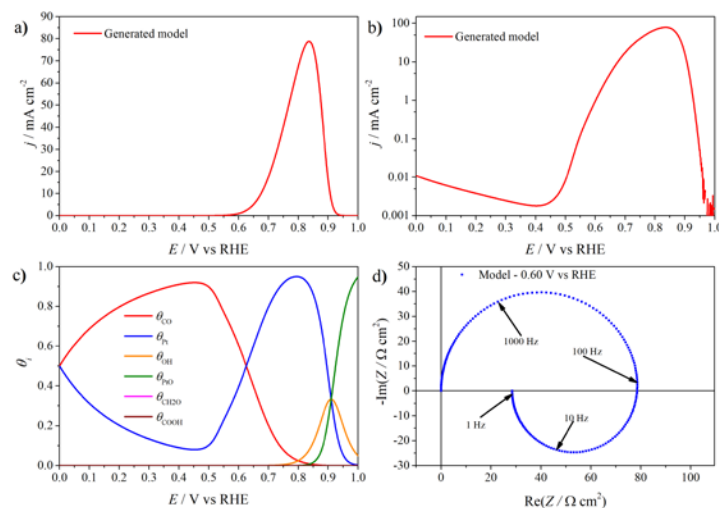


Figure 1. The generated model data from the methanol oxidation model: (a) cyclic voltammogram at  $5 \text{ mV s}^{-1}$  and  $80^\circ\text{C}$  temperature, (b) cyclic voltammogram with logarithmic scale of the current, (c) adsorbate coverage as a function of potential, and (d) representative Nyquist plot of EIS data at  $0.60 \text{ V vs RHE}$ .

## Results and Discussion

### Sensitivity analysis

A sensitivity analysis is necessary to estimate the confidence we will have in the fitted parameters. In our case, we generated a synthetic data set with 101 data points between 0.40 and 0.90 V by calculating the cyclic voltammogram at a  $5 \text{ mV s}^{-1}$  sweep rate and  $80^\circ\text{C}$  temperature from the model of methanol oxidation with known rate constants. The simulated data are shown in Fig. 1 giving the (a)-(b) cyclic voltammogram, (c) the calculated adsorbate coverages as a function of potential, and (d) as a representative Nyquist plot of impedance at 0.60 V vs RHE. Notably, the simulated data is qualitatively similar to reported cyclic voltammograms (15,16), reported coverages from IR spectroscopy data (14), and reported EIS spectra (3,16).

To test the efficiency and sensitivity of the optimization procedure, a single parameter was changed from the known global minimum, and the optimization routine was allowed to run until convergence. This type of study is useful to i) identify the parameters that the model is sensitive towards and which parameters that can be determined confidently, ii) determine if the optimization routine can find the global minimum or will be going towards a local minimum, and iii) understand the convergence of the optimization routine and identify ways to improve this. A total number of 21 tests were run with different initial values to analyze the model. The total time for each iteration was about 7-9 mins. A summary of the different tests is shown in Table 1, and the resulting optimized parameters for each test are shown in Table 2.

**TABLE 1.** Initial values for rate constants in the sensitivity analysis. All units are in  $\text{s}^{-1}$  and the values are given as the base 10 logarithm of the rate constant.

Number	Code	$k_{\text{CH}_3\text{O}}$	$k_{\text{CO}}$	$k_{\text{OH}}$	$k_{\text{COOH}}$	$k_{\text{CO}_2}$	$k_{\text{PtO}}$	$k_{\text{OH}}$	$k_{\text{PtO}}$
Initial		-1	10	-3	5	10	1	10	13
1	000000	-1	10	-3	5	10	1	10	13
2	100000	<b>0</b>	10	-3	5	10	1	10	13
3	010000	-1	<b>11</b>	-3	5	10	1	10	13
4	001000	-1	10	<b>-2</b>	5	10	1	10	13
5	000100	-1	10	-3	<b>6</b>	10	1	10	13
6	000010	-1	10	-3	5	<b>11</b>	1	10	13
7	000001	-1	10	-3	5	10	<b>2</b>	10	13
8	-100000	<b>-2</b>	10	-3	5	10	1	10	13
9	0-10000	-1	<b>9</b>	-3	5	10	1	10	13
10	00-1000	-1	10	<b>-4</b>	5	10	1	10	13
11	000-100	-1	10	-3	<b>4</b>	10	1	10	13
12	0000-10	-1	10	-3	5	<b>9</b>	1	10	13
13	00000-1	-1	10	-3	5	10	<b>0</b>	10	13
14	005000	-1	10	<b>-2.5</b>	5	10	1	10	13
15	000500	-1	10	-3	<b>4.5</b>	10	1	10	13
16	00-5000	-1	10	<b>-3.5</b>	5	10	1	10	13
17	000-500	-1	10	-3	<b>5.5</b>	10	1	10	13
18	00(25)000	-1	10	<b>-2.75</b>	5	10	1	10	13
19	000(25)00	-1	10	-3	<b>4.75</b>	10	1	10	13
20	00(-25)000	-1	10	<b>-3.25</b>	5	10	1	10	13
21	000(-25)00	-1	10	-3	<b>5.25</b>	10	1	10	13

From Table 2, it is evident that the models where the  $k_{\text{OH}}$  and  $k_{\text{COOH}}$  parameters were changed did not converge as quickly. To assess the optimization of these parameters, a change of 0.5 or 0.25 (in log form) was made in models 14-21. This was more successful than the fitting of the larger change, i.e., models 4, 5, 10, and 11. However, it is clear that a reasonable estimate of the initial value for these parameters is critical to ensure convergence. The accuracy of the optimized parameters was estimated by taking the average of the optimized parameter values for the models that converged successfully. This is summarized in Table 3. From this result, it is clear that 4 parameters can be reasonably confidently estimated in this model; these are the single parameters  $k_{\text{CH}_3\text{O}}$  and  $k_{\text{COOH}}$ , and the two reversible ratios,  $k_{\text{OH}}/k_{-\text{OH}}$  and  $k_{\text{PtO}}/k_{-\text{PtO}}$ . Notably, this list of parameters indicate that for the reversible steps, the confidence is in the ratios of the forward and back rate constants,  $k_{\text{OH}}/k_{-\text{OH}}$  (or  $k_{\text{PtO}}/k_{-\text{PtO}}$ ). Thus, an order of magnitude increase in the  $k_{\text{OH}}$  parameter is similar to an order of magnitude decrease in the  $k_{-\text{OH}}$  parameter, and it is not necessary to have a sensitivity analysis for both of these parameters. The  $k_{\text{CO}}$  and  $k_{\text{CO}_2}$  parameters cannot be estimated in this model and this is evident from the assumptions that go into the determination of the initial values, i.e., that these steps are highly irreversible because adsorbed methanol and COOH are not detected in IR spectroscopy studies of methanol oxidation.

TABLE 2. Rate constants after convergence for the different models in the sensitivity analysis. All units are in  $\text{s}^{-1}$  and the values are given as the base 10 logarithm of the rate constant.

Number	Code	$k_{\text{CH}_3\text{O}}$	$k_{\text{CO}}$	$k_{\text{OH}}$	$k_{\text{COOH}}$	$k_{\text{CO}_2}$	$k_{\text{PtO}}$	$k_{-\text{OH}}$	$k_{-\text{PtO}}$	Number of iterations	Convergence
Initial		-1	10	-3	5	10	1	10	13	n/a	n/a
1	000000	-1.00	6.83	-3.00	5.00	9.26	0.01	10.0	13.0	5	Y
2	100000	-1.00	7.43	-3.00	5.00	5.26	0.01	10.0	13.0	5	Y
3	010000	-1.00	8.80	-3.00	5.00	7.18	0.00	10.0	13.0	3	Y
4	001000	-1.00	6.44	-5.61	5.00	-0.65	2.55	7.38	15.6	345	Y
5	000100	-1.04	14.2	2.40	5.98	9.57	1.45	16.4	13.1	12	N
6	000010	-1.00	6.83	-3.00	5.00	10.5	0.01	10.0	13.0	5	Y
7	000001	-1.01	10.9	-3.14	5.11	6.88	7.38	9.98	20.1	10	N
8	-100000	-1.00	8.80	-3.00	5.00	6.62	0.00	10.0	13.0	4	Y
9	0-10000	-1.00	4.72	-3.00	5.00	4.97	0.01	10.0	13.0	7	Y
10	00-1000	-1.00	6.44	-6.29	5.00	-0.54	-1.32	6.71	11.7	317	Y
11	000-100	-0.88	-1.50	-6.10	4.78	-2.54	-5.95	6.65	60.5	80	N
12	0000-10	-1.00	4.72	-3.00	5.00	2.88	0.01	10.0	13.0	10	Y
13	00000-1	-1.00	6.83	-3.00	5.00	7.06	0.01	10.0	13.0	5	Y
14	005000	-1.00	5.28	-3.47	5.00	-0.47	2.31	9.53	15.3	288	Y
15	000500	-1.03	14.0	-3.83	5.39	8.89	4.86	9.56	17.2	80	N
16	00-5000	-1.00	10.4	-5.36	5.00	11.0	-0.74	7.64	12.3	256	Y
17	000-500	-0.96	4.56	-8.70	4.81	-2.16	-6.80	4.10	49.5	72	N
18	00(25)000	-1.00	6.42	-4.65	5.00	-0.22	1.92	8.35	14.9	274	Y
19	000(25)00	-1.02	7.89	-4.47	5.17	8.36	7.22	8.70	19.9	80	N
20	00(-25)000	-1.00	10.4	-4.65	5.00	9.56	1.58	8.35	14.6	213	Y
21	000(-25)00	-0.96	4.61	-4.14	4.81	-2.14	7.92	8.66	50.4	71	N



TABLE 3. The average value and the standard deviation of the optimized values for the models that converged successfully ( $RSS < 10^{-6}$ ). All units are in  $s^{-1}$  and are given as the base 10 logarithm of the rate constant.

Number	$k_{CH3O}$	$k_{CO}$	$k_{OH}$	$k_{COOH}$	$k_{CO2}$	$k_{PiO}$	$k_{-OH}$	$k_{-PiO}$	$k_{OH}/k_{-OH}$	$k_{PiO}/k_{-PiO}$
Average value	-1.00	7.17	-3.86	5.00	5.17	0.45	9.14	13.5	-13.0	-13.0
Standard deviation	$4.3 \cdot 10^{-4}$	>1	>1	$1.7 \cdot 10^{-3}$	>1	>1	>1	>1	$1.8 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$

The observations from the converged results are further supported by plotting the error function,  $RSS$ , as a function of iteration number in Fig. 2. Here, the models with changes in the  $k_{OH}$  and  $k_{COOH}$  parameters use more iterations to converge successfully (if ever). This indicates that these parameters are dependent on each other, and that a wrong parameter can be compensated by the other parameters to reach lower  $RSS$  without necessarily reaching the global minimum (or very slowly going towards the global minimum). Complementary methods to estimate these values would be useful to improve the stability of the optimization procedure.

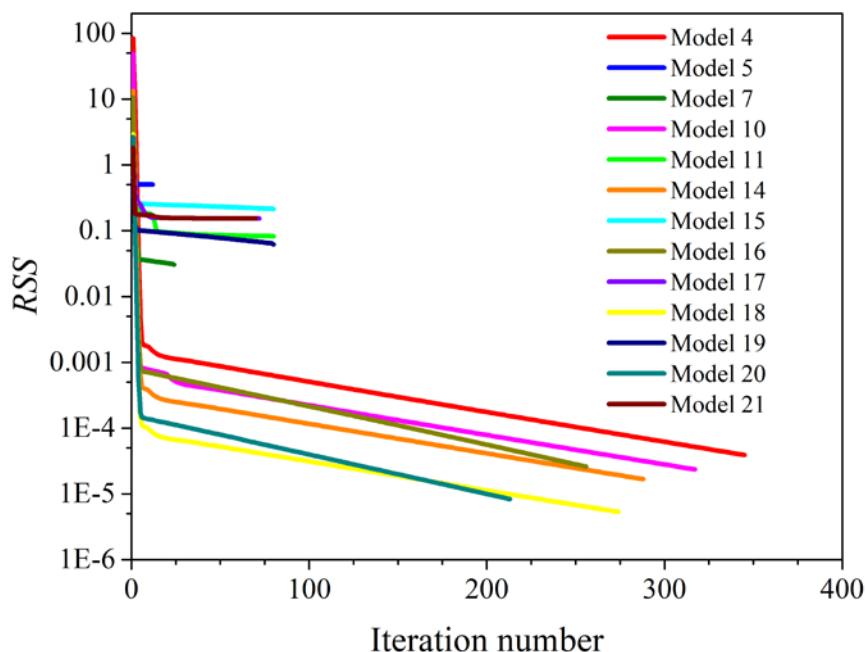


Figure 2. Error function vs number of iterations for the models used in this work. The models that converged very quickly (1, 2, 3, 6, 8, 9, and 13) were omitted for clarity.

### Improvement of the method

The method to optimize the parameters here to an experimental cyclic voltammogram is suitable for many important electrochemical reactions. The method converges relatively slowly, so it is important to have a reasonable estimate of the initial values to ensure economic calculation. Complementary methods to estimate the initial values would be desirable, and at the very least, a qualitative estimate of the adsorbate coverages from IR spectroscopy is a necessity. This data is available in the literature for commonly studied oxidation reactions. Another approach is to use the dEIS data in the optimization. For example, the low-frequency intercept has been suggested as an additional parameter in the optimization (17). However, in many cases, the low-frequency intercept is not necessarily

available experimentally within a reasonable frequency range for dEIS (1 Hz – 100 kHz) making this only useful in some cases.

To ensure faster convergence, the simultaneous optimization of several parameters would be useful. To identify the more important parameters, a sensitivity analysis can be used to identify the critical parameters, i.e.,  $k_{\text{CH}_3\text{O}}$ ,  $k_{\text{COOH}}$ ,  $k_{\text{OH}}/k_{-\text{OH}}$ , and  $k_{\text{PtO}}/k_{-\text{PtO}}$  in our case. Subsequently, multi-parameter optimization can be used on this subset of parameters. We briefly attempted this with some success. The main challenge with doing this is to ensure that the optimization procedure is able to explore the parameter space successfully. As this type of optimization can only be done using the non-linear simplex method in Maple, it would be useful to limit the parameter space explored to ensure some stability.

The method described in this paper was used to model experimental data of methanol and formic acid oxidation on Pt with 6 and 8 different models, respectively. The reader is referred to these publications (18,19) for further demonstration of this method.

## Conclusions

A method was developed for numerical optimization of kinetic parameters and calculation of EIS spectra. Synthetic data appropriate for methanol oxidation on platinum at 80°C were used as an example. A reasonable mechanism of methanol oxidation was suggested, and the sensitivity of the relevant parameters was assessed. The method is uniquely suited to help in the interpretation of experimental data when dEIS is measured simultaneously with a pseudo steady-state dc technique, here: cyclic voltammetry. The procedure described in this work is an improvement to existing methods of parameter optimization in electrochemical problems both in terms of the type of data optimized and the amount of information that can be extracted from the optimized models.

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