Electrical Conductivity Relaxation Measurements:
Statistical Investigations using Sensitivity Analysis,
Optimal Experimental Design and ECRTOOLS

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KEYWORDS: Diffusion, Surface Exchange, Electrical Conductivity Relaxation, Identification,
Robustness, Optimal Experimental Design

ABSTRACT

Mixed ionic and electronic conductors (MIECs) can be found in many applications of interest
to solid state ionics, ranging from separation membranes, to solid oxide fuel cells and oxygen
sensors. The performance of such MIEC-based devices is closely linked to fundamental transport
and electrocatalytic properties such as the oxygen diffusion coefficient $D$ and oxygen exchange
rate $k$, which can be estimated using Electrical Conductivity Relaxation (ECR).

In this article, the statistical quality of $k$ and $D$ obtained using ECR is studied via asymptotic
statistical methods. In particular, Optimal Experimental Design (OED) is used to design
experiments, which minimize the uncertainty on the estimated $k$ and $D$, by selecting optimal
sample size and experimental timespan. Furthermore, robust OED is introduced as a tool to reduce the uncertainty on the estimated $k$ and $D$ when some prior information on the two quantities is available such as their literature values or their bounds in a given temperature range. In addition, it is shown that the sensitivity analysis can be used as a graphical tool to investigate the measurability of $k$ and $D$ and that the parameters governing the sensitivity are linked to the Biot number, the diffusion and reaction timescales. Similarly, flush time limitations can be linked to the Biot number and the ratio between the characteristic timescale of the flush process. All calculations are carried out with ECRTOOLS a freely available MATLAB toolbox which allows the estimation of $k$ and $D$ from ECR data, the evaluation of the quality of the estimated parameters and OED.

1 Introduction

Mixed ionic and electronic conductors (MIECs) [1] are of great significance in the field of solid ionics because they are employed in separation membranes [2], electrodes of solid oxide fuel cells [3] and oxygen sensors [4]. Generally, transport and kinetics properties determine the performance of such devices [3, 5]. Electrical conductivity relaxation (ECR) is a technique often used in solid-state electrochemistry to determine the transport and kinetic properties of MIECs [6-18]. Thanks to ECR one can estimate the oxygen surface exchange coefficient $k$ and the oxygen diffusivity $D$ [19, 20] by subjecting a MIEC sample at fixed temperature to a step change in oxygen partial pressure [21]. The sudden oxygen pressure change causes oxygen incorporation and migration within the MIEC and in turn changes the MIEC conductivity [20]. If the conductivity is measured as a function of time, then $k$ and $D$ can be estimated by fitting the ECR data against a suitable model [20, 22-24]. The typical model used in ECR analysis is
derived by solving the linear diffusion equation (Fick’s second law) with linear absorbing boundary conditions [9, 19, 20]. While the validity of such a model is limited to “small” pressure step changes, which ensure the linearity of the exchange kinetics [22, 25]; the analytical results can be corrected to account for non-instantaneous pressure response [2, 5] by considering a suitable relaxation of flush time [25, 26].

Recent experimental work of Cox-Galhotra and McIntosh has shown some of the weaknesses of ECR in particular with respect to the unreliability of simultaneous measurement of $k$ and $D$ for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ [27]. Methods for improving ECR analysis have also been published in the literature; Boukamp and collaborators suggested to couple ECR with data analysis in the frequency spectrum [26], while Li and coworkers provided methods to estimate independently the flush time [28]. All these works stress the need for a precise understanding of the nature of the estimation process in ECR.

In spite of the clear importance and significance of ECR for the analysis of solid state ionics systems, the quality of the ECR-based estimates of the parameters $k$ and $D$ have not been addressed yet from a statistical perspective. Literature articles employing ECR rarely discuss the confidence on the estimates, the sensitivity of the measurements with respect to $k$ and $D$, and the limitations of this technique. This article aims at bridging the gap between practice and theory by providing clear guidelines and methods for the analysis of ECR data and for their qualitative and quantitative experimental optimization. The qualitative analysis is performed by sensitivity analysis, while OED-related techniques are used for a quantitative assessment of the uncertainty and its minimization. In addition, robust OED is used to determine a suitable experimental design provided that some range for the physical parameters $k$ and $D$ is given. The mathematical tools discussed are implemented in ECRTOOLS [29], a freely-available MATLAB [30] toolbox.
featuring an intuitive GUI interface. The latter is expected to be a useful platform for ECR practitioner because it can perform graphical parameter fitting, analysis of sensitivity, confidence region estimation and simulated experiments.

The first part of the article reviews the main concepts underpinning ECR modeling and nonlinear regression that are used to identify the ECR parameters $k$ and $D$. This is instrumental for establishing the uncertainty on the estimated quantities. Subsequently, OED and Robust OED are introduced as tools that improve experimental quality and mitigate uncertainty. Then the framework developed in the theory section is applied to simulated ECR experiments, where the theoretical limits of the approach, the link to sensitivity analysis, and applications are also discussed. The impact of geometrical variations is shown and the Biot number is highlighted to be the key parameter governing the identifiability of $k$ and $D$ in ECR and it is further linked to the flush time limitations.

### 2 Theory

#### 2.1 Model

A Cartesian three dimensional MIEC geometry is considered. The latter is taken to be a parallelepiped with rectangular faces of side length $2l_x$, $2l_y$, and $2l_z$ in the $x$, $y$, and $z$ directions respectively. The sample is taken to be initially at equilibrium and it is characterized by concentration $c_0$. The step change in oxygen partial pressure applied in ECR causes incorporation reactions, which are modeled by linearized kinetic boundary conditions [31]:
where $c_\infty$ is the concentration of oxygen in the sample at $t \to \infty$ (this condition corresponds to the equilibrium concentration of oxygen at the post-step oxygen partial pressure).

Concurrent oxygen migration in the sample is modeled by Fickian diffusion

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

(4)

where $c(t,x,y,z)$ is the oxygen concentration at time $t$ and position $(x,y,z)$.

The concentration field $c(t,x,y,z)$ can then be linked to the conductivity $\sigma(t)$ [6] and the normalized conductivity $\sigma_n(t)$

$$\sigma_n = \frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0}$$

(5)

which is a function of the conductivity at time $t$, of the initial conductivity $\sigma_0$ ($t = 0$), and of the final conductivity $\sigma_\infty$ ($t \to \infty$). Specifically, it is given by [9, 27]

$$\sigma_n = 1 - \sum_{p=1}^{\infty} \frac{2L_x^2}{\beta_{p,x}^2 \left( \beta_{p,x}^2 + L_x^2 + L_y^2 \right)} \exp \left( -\frac{\beta_{p,x}^2 D t}{L_x^2} \right)$$

$$\times \sum_{q=1}^{\infty} \frac{2L_y^2}{\beta_{q,y}^2 \left( \beta_{q,y}^2 + L_y^2 + L_z^2 \right)} \exp \left( -\frac{\beta_{q,y}^2 D t}{L_y^2} \right)$$

$$\times \sum_{r=1}^{\infty} \frac{2L_z^2}{\beta_{r,z}^2 \left( \beta_{r,z}^2 + L_z^2 + L_x^2 \right)} \exp \left( -\frac{\beta_{r,z}^2 D t}{L_z^2} \right)$$

(6)

where $L_x = \frac{l_x k}{D}$, $L_y = \frac{l_y k}{D}$, $L_z = \frac{l_z k}{D}$ and the $\beta$’s are the positive roots of the equation $\beta \tan \beta = L_i$ with $i = x, y, z$. The expression (6) is computed numerically by truncating the
summation when the final term is less than a given tolerance \( \frac{2L^2}{\beta^2 (\beta^2 + L^2 + L)} \leq \text{tol} \) (here tol is taken to be \( 10^{-10} \)) or when the number of terms in the summation equals 100 [32].

It is assumed that a measurement is given by the \( \sigma_n(t) \) plus random errors. This corresponds to taking that the measured conductivity \( \sigma_n^{\text{meas}}(t) \) is the outcome of the following stochastic process:

\[
\sigma_n^{\text{meas}}(t) = \sigma_n(t) + \varepsilon
\]

where \( \sigma_n(t) \) is the “true” conductivity (or noiseless measurement), given by (6), and \( \varepsilon \) is the measurement error. One notes that \( \sigma_n^{\text{meas}}(t) \) depends on a set of “true” parameters \( \bar{\theta} = (\bar{k}, \bar{D})^T \) and on a design \( \xi = (l_x, l_y, l_z)^T \). Thus, one can write that \( \sigma_n^{\text{meas}}(t) = \sigma_n^{\text{meas}}(\bar{\theta}, \xi, t) \).

2.2 Parameter Identification

The parameters of the ECR model (6) are typically identified by unweighted nonlinear regression [33]. For this purpose the following sum of squares is defined

\[
S(\theta, \bar{\theta}, \xi) = \sum_{j=0}^{N} \left( \sigma_n(t_j, \theta, \xi) - \sigma_n^{\text{meas}}(t_j, \bar{\theta}, \xi) \right)^2
\]

where \( \theta = (D, k)^T \) is the vector of the parameters that needs to be estimated, \( \bar{\theta} = (\bar{D}, \bar{k})^T \) is the “true” value of the vector of the parameters, \( \xi = (l_x, l_y, l_z)^T \) is the set of the designs, and the \( t_j \)'s are the \( N+1 \) measurement times. From experimental data, one obtains the vector of estimated parameters \( \hat{\theta} = (\hat{D}, \hat{k})^T \) by minimizing the function \( S(\theta, \bar{\theta}, \xi) \). Formally, this is written as
\( \hat{\theta} = \text{arg} \min_{\theta} S(\theta, \bar{\theta}, \xi) \) \hspace{1cm} (9)

If the errors given in (7) are “small”, identically distributed, uncorrelated and Gaussian (\( \varepsilon \sim N(0, \sigma^2_\varepsilon) \)), then \( \hat{\theta} \) is also Gaussian, asymptotically unbiased with respect to the true value \( \bar{\theta} \) [34, 35] and the covariance matrix of \( \hat{\theta} \) can be approximated by the following expression [36] obtained by linearization of the model with respect to \( \theta \) around the “true” value \( \bar{\theta} \) [37, 38]:

\[
V(\bar{\theta}, \xi) = \sigma^2_\varepsilon \left( J(\bar{\theta}, \xi)(J(\bar{\theta}, \xi))^T \right)^{-1}
\]

The derivation of (10) follows from asymptotic frequentist statistics [34]; for a derivation of this formula see [39]. In equation (10) the matrix \( J \) identifies the sensitivity of the measured quantity with respect to the parameters and has the following components:

\[
(J)_{ij} = \frac{\partial \sigma_{\alpha}(t_j, \bar{\theta}, \xi)}{\partial \theta_i}
\]

One notes that \( J \) has dimensions \( \text{dim}(\theta) \times N \), where \( \text{dim}(\theta) \) is the size of the vector \( \theta \).

The covariance matrix \( V(\bar{\theta}, \xi) \) constitutes a measure of the “spread” of the \( \hat{\theta} \)'s obtained from (9), in particular, the “smaller” \( V(\bar{\theta}, \xi) \) is, the greater is the information of the experiment or equivalently the more confident the experimenter is that \( \hat{\theta} \) is close to the “true” \( \bar{\theta} \). The matrix \( V(\bar{\theta}, \xi) \) defines the asymptotic confidence region, which is the area where it is likely to find the majority of estimated parameters \( \hat{\theta} \). The latter region is the set of \( \hat{\theta} \) such that

\[
(\hat{\theta} - \bar{\theta})^T (V(\bar{\theta}, \xi))^{-1} (\hat{\theta} - \bar{\theta}) \leq \gamma .
\]

In analogy with earlier publications \( \gamma = 9 \) and the reader is referred to reviews [36, 40] and monographs [41] for an exhaustive description of the choice of \( \gamma \).
2.3 Optimal Experimental Design

With reference to the expressions (10) and (11), one notices that the value of $V(\bar{\theta}, \xi)$ depends inversely on the sensitivity $\frac{\partial \sigma_n}{\partial \theta}$. In agreement with intuition, this implies that greater sensitivity correlates with greater accuracy. Similarly, the more measurement are taken the “smaller” is the $V(\bar{\theta}, \xi)$.

Since $V(\bar{\theta}, \xi)$ has $(\text{dim}(\theta))^2$ entries, it is of primary importance to define what is meant by “big” and “small” $V(\bar{\theta}, \xi)$. This corresponds to identifying a suitable scalar function $\phi(V(\bar{\theta}, \xi))$, which describes the “size” of the matrix $V(\bar{\theta}, \xi)$. One notes that if $V(\bar{\theta}, \xi)$ is positive definite [42] (the estimated $\hat{\theta}$'s are subjected to finite error), then the covariance region is ellipsoidal. Thus, one can describe how “big” or “small” $V(\bar{\theta}, \xi)$ is, by relating it to a geometrical feature of the ellipsoidal region [36]. For example, the trace of $V(\bar{\theta}, \xi)$ identifies the dimension of the box enclosing the ellipsoid and the determinant of $V(\bar{\theta}, \xi)$ corresponds to the volume of the ellipsoidal region [38]. Those two functions are indicated as $\phi_d(V(\bar{\theta}, \xi)) = \text{tr}(V(\bar{\theta}, \xi))$ and $\phi_D(V(\bar{\theta}, \xi)) = \text{det}(V(\bar{\theta}, \xi))$ respectively. The reader is referred to the specialized literature [38, 40] for more details on possible choices of the scalar function.

By applying optimal experimental design, one minimizes the function $\phi(V(\bar{\theta}, \xi))$ with respect to the design parameters $\xi$ and this leads to increased precision on the estimated $\hat{\theta}$. The optimum design $\xi_{opt}$ can be then written as
\[ \xi_{\text{opt}} = \arg \min_{\xi \in \Xi} \phi \left( V \left( \bar{\theta}, \xi \right) \right) \]  
where \( \Xi \) is the set of allowed designs \( \xi \). It is worthwhile stressing that in order to compute the optimal design the “true” \( \bar{\theta} \) is required.

2.4 Robust Identification

While ECR experiments are typically developed to establish the “true” \( \bar{\theta} = (\bar{k} \ D)^T \), one may be able to leverage on existing publications and prior research experience in order to determine an expected range for \( \bar{\theta} \) [43] for a given material in a certain temperature interval. In addition, one may want to use only one sample to probe its ECR response in a temperature or pressure range, so that both \( k \) and \( D \) are projected to vary under those conditions. It is suggested that this information is then used to develop robust OED [6, 44] for ECR. In general, a robust design can be though as the best design in the worst-case scenario or the best design in the average sense. This general approach overcomes the dependence of the optimum design given in (12) on the unknown parameter \( \bar{\theta} \) providing the design itself with resilience or robustness with respect to the uncertainty on the latter or to variability under the given experimental conditions.

In robust OED one rewrites the worst-case scenario design as the following min-max optimization problem [6, 45]:

\[ \xi_{\min-max}^* = \arg \min_{\xi \in \Xi} \left( \max_{\bar{\theta} \in \Theta} \phi \left( \bar{\theta}, \xi \right) \right) \]  
where \( \Xi \) is the set of allowed designs and \( \Theta \) is the set over which the “true” physical parameters \( \bar{k} \) and \( \bar{D} \) are allowed to vary. By applying (13) one finds the design \( \xi_{\min-max}^* \), which minimizes the confidence region size for the “true” parameters that are least suited for identification. It is important to stress that as it is shown in the literature [29, 44] this approach biases the design since it optimizes the experiment for the \( \bar{\theta} \)’s maximizing \( \phi \left( \bar{\theta}, \xi \right) \). This
condition may occur at the boundary of $\Theta$; if it is the case, then such condition may have little statistical significance [41].

The best average design hypothesizes instead that $\bar{\theta}$ is a random variable with given probability density distribution [42] $f(\bar{\theta})$ within the allowed region $\Theta$. This information is used to minimize the average $\phi(\bar{\theta}, \xi)$ over $\Theta$, which is computed as the expected value of $\phi(\bar{\theta}, \xi)$; the optimization can in turn be written as

$$\xi_{\text{avg}}^* = \arg \min_{\xi \in \Xi} \left( \int_{\Theta \in \Theta} \phi(\bar{\theta}, \xi) f(\bar{\theta}) d\theta \right)$$  \hspace{1cm} (14)

It is important to note that by selecting the design $\xi_{\text{avg}}^*$ one ensures that the size of the confidence region is minimized on average provided that a suitable distribution for $\bar{\theta}$ is given. While the criterion (13) improves the identification outcome under the worst case scenario, the design obtained using (14) optimizes the average outcome of the identification.

### 3 Results

#### 3.1 General Considerations

It is hypothesized that the “true” parameters may vary by one order of magnitude in the set [27] given by

$$\Theta = \{(\bar{k}, \bar{D}) : \ 10^{-3} \text{ cm/s} \leq \bar{k} \leq 10^{-2} \text{ cm/s} \ \& \ \ 10^{-3} \text{ cm}^2/\text{s} \leq \bar{D} \leq 10^{-4} \text{ cm}^2/\text{s} \}$$  \hspace{1cm} (15)

It is also assumed that $N=151$ equally spaced measurements are taken such that

$$t_j = 0, \frac{t_N}{N-1}, \frac{2t_N}{N-1}, \ldots, t_N$$  and that the final time of the experiment is $t_N = 500$ s. Furthermore a cubic sample with 1 mm half-length is considered, i.e., $\xi = (1 \text{ mm} \ 1 \text{ mm} \ 1 \text{ mm})^T$. 


The “true” ECR response $\sigma_n(t)$ (solid line) is plotted in Figure 1 (b) for $D=10^{-3}$ cm$^2$/s and $\bar{k}=10^{-2}$ cm/s. In the same panel one simulated measurement $\sigma_{n,\text{meas}}(t)$ (black circles) is shown. The latter is equal to “true” ECR response plus random Gaussian noise as given by (7) with standard deviation $\sigma_{\epsilon}=1\%$.

Subsequently, the simulated measurement $\sigma_{n,\text{meas}}(t)$ is repeated 1000 times. The vector $\hat{\theta}$ is then estimated by solving (9) for each set of simulated data. From this procedure, one obtains the cloud of points of Figure 1 (a) where it should be emphasized that each dot represents the outcome of the estimation obtained from one simulated experiment. From (10) an ellipsoidal confidence region for the parameters is obtained and it is shown that this domain captures well the stochastic cloud. For this particular choice of parameters the estimate of the parameter $k$ is poor in comparison to the one attainable for $D$. For the former the relative errors are of the order of 60% while for the latter they are less than 10%.

Choosing $D=10^{-4}$ cm$^2$/s and $k=10^{-3}$ cm/s leads to opposite results. While the simulated ECR response of Figure 1 (d) has expected features (larger $D$ implies establishing faster equilibrium conditions and therefore reaching $\sigma_n=1$ in a shorter time), the estimates obtained from 1000 simulated experiments, which are shown in Figure 1 (c), are mostly located in an ellipsoidal region oriented preferentially along the $D$ direction. Therefore the error on the estimated $\hat{D}$ is larger than the one on $\hat{k}$.

The asymptotic error is defined as the projection of the asymptotic confidence ellipsoid onto the relevant axis. For example, the relative error on $\hat{D}$ for the conditions Figure 1 (d), can be retrieved directly from Figure 1 (c) and it corresponds to approximately 40%. Similarly, the
relative error on $\hat{k}$ is approximately 10%. One can also note that a few dots can be found outside the asymptotic confidence region, highlighting the weak nonlinearity of the estimation process.

Subsequently, the relative asymptotic errors on $\hat{k}$ and $\hat{D}$ are reported in Figure 2, panels (a) and (b) respectively, for the whole set $\Theta$ of possible “true” parameters. Within the given range, the true values $\bar{D}=10^{-4}$ cm$^2$/s and $\bar{k}=10^{-3}$ cm/s imply lowest relative confidence on the $\hat{D}$ and greatest on $\hat{k}$. Conversely for $\bar{D}=10^{-5}$ cm$^2$/s and $\bar{k}=10^{-2}$ cm/s, lowest relative confidence on the $\hat{k}$ and greatest on $\hat{D}$ are obtained. It is evident that the relative errors on $\hat{k}$ and $\hat{D}$ have great variability on the selected range. While the former varies approximately from 10% to 60%, the latter ranges from 5% to 40%.

3.2 Robust Design

Since estimated values for parameters chosen within the set $\Theta$ are characterized by great variability, robust identification is addressed with the A-criterion by choosing $\phi(V)=\phi_A(V)$. The min-max problem (13) is then solved by nesting the maximization problem inside the minimization. For this purpose, the NLOPT package [37] is used and

$$\xi^*_{\text{min-max}} \approx (1.03 \text{ mm} \ 1.03 \text{ mm} \ 1.03 \text{ mm})^T$$

is obtained where the three dimensional vector $\xi$ was constrained to be in the box $0.01 \text{mm} \leq l_x, l_y, l_z \leq 5 \text{ cm}$. The obtained min-max value is remarkably close to the one chosen in Section 3.1 and it indicates that the dimensions selected above are essentially robust in the min-max sense. This implies that the design discussed in Section 3.1 augments identifiability in the worst-case scenario.
The minimum of the average \( \phi_A(V) \) is also obtained by choosing \( f(\theta) \) in (14) so that it is uniform within the set \( \Theta \) (every point in \( \Theta \) can be chosen with identical probability), this in turn corresponds to solving

\[
\tilde{\xi}_\text{avg} = \arg \min_{\xi \in \Theta} \left( \int \phi_A(\theta, \xi) d\theta \right)
\]

(16)

where the inner integral is computed using the 2D trapezoidal rule on the uniformly meshed set \( \Theta \) with 30 elements per side, NLOPT is subsequently used to solve (16) and it is found that \( \tilde{\xi}_\text{avg} \approx (1.93 \text{ mm} \ 1.93 \text{ mm} \ 1.93 \text{ mm})^T \), under the same constraints of the min-max design. The overall effect of this second design is to flatten out the function \( \phi(\theta, \xi) \) within the domain \( \Theta \).

In Figure 3 the difference in relative errors on \( k \) and \( D \), panel (a) and (b) respectively, between the \( \tilde{\xi}_{\text{min-max}} \) and the \( \tilde{\xi}_{\text{avg}} \) design is reported. A positive value of relative error difference indicates that the \( \tilde{\xi}_{\text{avg}} \) leads to better estimate of the prescribed variable than \( \tilde{\xi}_{\text{min-max}} \). For \( \bar{D} \geq 2 \times 10^{-5} \text{ cm/s} \), the \( \tilde{\xi}_{\text{avg}} \) design gives a 5\% more accurate \( k \)-estimate than the \( \tilde{\xi}_{\text{min-max}} \) design.

However, \( \tilde{\xi}_{\text{avg}} \) is inferior with respect to the same estimation at the corner of the domain \( \Theta \), near \( \bar{D} = 10^{-5} \text{ cm}^2/\text{s} \) and \( \bar{k} = 10^{-2} \text{ cm/s} \). At this location \( \tilde{\xi}_{\text{min-max}} \) is superior by nearly 10\%. On the other hand, the \( \tilde{\xi}_{\text{avg}} \) design leads to consistently greater accuracy on \( D \) with a relative gain ranging from a few percent to approximately 25\%. It appears that under the chosen \( N \) and \( t_N \), the outcome of the estimation process is the poorest at \( \bar{D} = 10^{-5} \text{ cm}^2/\text{s} \) and \( \bar{k} = 10^{-2} \text{ cm/s} \). For this reason, the sensitivity of the parameters with respect to the model under such conditions is studied below in greater detail.
3.3 Sensitivity as a Qualitative Tool for Identification

The sensitivity of the model with respect to the parameters is defined as the following vector valued function:

\[
S(t, \theta, \xi) = (S_k \quad S_D)^T = \left( k \frac{\partial \sigma_n}{\partial k} \quad D \frac{\partial \sigma_n}{\partial D} \right)^T
\]

(17)

As mentioned above, measurements occurring at conditions for which \( \theta_k \frac{\partial \sigma_n}{\partial \theta_k} \) is large decrease the relative errors on \( \theta_k \). On the other hand lack of sensitivity, i.e., \( \theta_k \frac{\partial \sigma_n}{\partial \theta_k} \approx 0 \), leads to large errors. This makes the concepts of sensitivity and accuracy deeply related.

The worst-case scenario conditions given by \( \tilde{D} = 10^{-5} \ \text{cm}^2 / \text{s} \) and \( \tilde{k} = 10^{-2} \ \text{cm} / \text{s} \) are chosen in order to show how the sensitivity depends on sample size and on experimental time. First, the sensitivity for \( l_x = l_y = l_z = 1 \ \text{mm} \) is computed and reported in Figure 4 (a), where one immediately notes that ECR is quite sensitive to \( D \) in the time interval \( 1 \leq t \leq 100 \ \text{s} \); conversely, \( \sigma_n \) is much less sensitive to \( k \) in the same time span. This finding is in agreement with Figure 2, which shows that while the relative error on \( \hat{k} \) is of the order of 60%, the relative error on \( \hat{D} \) is well below 5%.

More balanced identification can be obtained for a design with \( l_x = l_y = l_z = 5.7 \times 10^{-2} \ \text{mm} \) corresponding to identical maximum sensitivities on the two parameters, see Figure 4 (b). Mathematically this is achieved by selecting a \( \xi \) such that
\[
\max_{t_N} \left( k \frac{\partial \sigma_n}{\partial k} \right) = \max_{t_N} \left( D \frac{\partial \sigma_n}{\partial D} \right)
\]

(18)

where the two functions peak at different times, i.e., \( \arg \max_{t_N} \left( k \frac{\partial \sigma_n}{\partial k} \right) \neq \arg \max_{t_N} \left( D \frac{\partial \sigma_n}{\partial D} \right) \) and that the most sensitive range is shifted in the interval \( 10^{-2} \text{ s} \leq t \leq 1 \text{ s} \), making the chosen time requirement unsuitable (the upper bound of the timespan is \( t_N = 500 \text{ s} \)) for the identification of the parameters.

It makes physical and intuitive sense to ensure that both physical processes described in the model (incorporation and diffusion) are characterized by the same timescales [19]. For this reason one may choose the size of the system so that the characteristic timescales of the incorporation reaction \( \tau_k = \frac{l_{ch}}{k} \) and of diffusion \( \tau_D = \frac{l_{ch}^2}{D} \) are identical, where \( l_{ch} \) is a given characteristic length scale. By setting \( l_{ch} = l_x = l_y = l_z \) and \( \tau_k = \tau_D \), one obtains \( l = l_x = l_y = l_z = \frac{D}{k} = 10^{-2} \text{ mm} \). Figure 4 (c) depicts the sensitivities under these conditions. Since the peak for the sensitivity of \( k \) is higher than the one of \( D \), it is expected that the estimate \( \hat{k} \) is subjected to lower relative error than \( \hat{D} \). In short, if the two timescales are identical, then the sensitivity peak simultaneously but identical errors are not guaranteed. In this example, it is apparent that, contrary to intuition, exact time-scale matching does not lead to maximum measurement quality. This concept is expanded in Section 3.6 using dimensionless groups.

As discussed in the previous section the robust average design \( \xi_{\text{avg}}^* \) is expected to provide less accurate \( k \) values than the \( \xi_{\text{min-max}}^* \) (Figure 3 (a) rightmost corner). This is confirmed in Figure 4 (d) where the derivative with respect to \( k \) is slightly depressed in comparison to the same
quantity in Figure 4 (a). In addition the relevant time range is shown to have shifted into the interval $1 \text{s} \leq t \leq 10^3 \text{s}$.

It is important to stress that the sensitivity analysis provides a pictorial description of the location at which the experiment is sensitive; in addition, it can be computed quickly and within the GUI of ECRTOOLS it can give intuitive trends for experimental optimization.

### 3.4 Theoretical Limits

For completeness, a purely theoretical analysis is performed by relaxing the condition that $t_N$ is fixed and by letting $t_N > 0$. It will be assumed that 151 measurements equally spaced in time from 0 to $t_N$ are taken. First, the following optimization problem is solved

$$t_N = \arg \min_{t_N > 0} \phi \left( \mathbf{V} \left( \mathbf{0}, \mathbf{\xi}, t_N \right) \right)$$

(19)

for $t_N > 0$ and fixed $\mathbf{\xi} = \left( \frac{D}{k}, \frac{\bar{D}}{k}, \frac{\bar{D}}{k} \right)^T$, and where the optimal timespan upper bound is found so that $\phi \left( \mathbf{V} \left( \mathbf{0}, \mathbf{\xi}, t_N \right) \right)$ is minimized with time points given by $t_j = 0, \frac{t_N}{N-1}, \frac{2t_N}{N-1}, \ldots, t_N$. In agreement with the sensitivity curves of Figure 4 (c), the minimum is found in the interval, $0 \text{s} \leq t \leq 10^{-1} \text{s}$. In Figure 5 (b) the “true” $\sigma_n(t)$ is shown alongside with a noise-corrupted measurement $\sigma_n^{\text{meas}}(t)$. By performing parameter estimation on a set of simulated data, one obtains a measurement point in the $k-D$ plane. Repeating numerous simulated measurements leads to a cloud of points which can be conveniently compared to the asymptotic confidence region. For the chosen conditions, the points are contained within the asymptotic confidence region in Figure 5 (a). For reference, the asymptotic confidence region of Figure 1 (a) is also
shown. As anticipated by the sensitivity analysis, it is much more likely that the $\hat{k}$ is closer to $\bar{k}$ than $\hat{D}$ is to $\bar{D}$, this implies that the first parameter can be identified with greater accuracy.

One can further relax the condition above and optimize both the side length of the sample and the timespan by solving the following

$$\left(\xi_{opt}, t_{N}\right)^T = \arg\min_{\xi, t_{N}} \phi\left(V\left(\tilde{\theta}, \xi, t_{N}\right)\right)$$

(20)

where again $\xi \in \Xi$ and $t_{N} > 0$. The minimum is found for $t_{opt} = 1.447$ s and $\xi_{opt} = \left(L_{opt} \quad L_{opt} \quad L_{opt}\right)^T$ with $L_{opt} = 0.1019$ mm. In Figure 6 (b), it is shown show the “true” $\sigma_n$ and the noise-corrupted measurement for $0 \leq t \leq 1.5$ s. In Figure 6 (a) the corresponding confidence ellipsoid (red solid line) and cloud of points is reported. The size reduction is striking in comparison to the base case of Figure 1 (a) (black); this is consistent with a balanced sensitivity of Figure 7. This finding is similar to the one of Figure 4 (d) obtained under condition (18).

Lastly, it is emphasized that, while the analysis provided in this section helps illustrate the methodology, it is purely theoretical because the optimal conditions obtained above are prohibitive in experiments. In particular, the physical and experimental constraints can be taken into account by selecting the design set $\Xi$ and the bounds on time in a suitable manner. In addition, it is expected that the pressure step is non-ideal, therefore flush time limitations will restrict the allowed time span of the experiment [2], this aspect is further studied Section 3.7 of this article.

1 The minimization procedure minimizes the function $\phi$ with respect to the three-dimensional vector $\xi$. 
3.5 Impact of the Geometry

Geometrical effects are known to significantly impact the ECR response. For example, the response of a cube sample and of a thin slab will be significantly different in spite of the same characteristic length scale. This is reported in Figure 8 (a), where the noiseless ECR response is shown for a 1D (slab), 2D (pillar of infinite length with square section) and 3D (cubic sample), and where the characteristic size of the sample is taken to be \( l_{\text{ref}} = 1 \text{ mm} \) and the “true” parameters are \( \bar{k} = 10^{-2} \text{ cm/s} \) and \( \bar{D} = 10^{-5} \text{ cm}^2/\text{s} \). One notices that going from 1D to 3D decreases the overall ECR relaxation time; this is easily understood by noting that the right hand side of (6) depends on the product of three terms less than or equal to 1, if one of those terms is one, all others being identical, then the time converge to 0 will be slower. Thus, a 1D sample will reach steady state conditions in a longer time than a 3D (cubic) sample. This is in turn reflected in the asymptotic confidence regions, shown in Figure 8 (b). The latter are computed in analogous manner as above: the measurement time is taken to be \( t_N = 500 \text{ s} \) and \( N = 151 \) measurement points are considered. In accordance with the results shown earlier in the article, one notices that the limits of the x-axis are wider than the limits of the y-axis indicating greater confidence on the parameter \( D \) than on \( k \). In addition, it is shown that the size of the confidence region increases from the one dimensional to the multidimensional for the given conditions and measurement points.

It is important to note that while Equation (6) describes well the ECR response of parallelepipeds, it is not convenient when one wishes to compute the ECR response of a sample in the slab (1D) or in the pillar (2D) configuration. It is more efficient to set to unity the summation term corresponding to each infinite length. This indicates that the transient term in
the dimensionless conductivity $\sigma_n(t)$ increases with the number of non-infinite dimensions of the sample.

The 1D case should be therefore studied in greater detail. In Figure 9 (a) the $\phi_A(V)$ and the asymptotic errors are shown and compared under the same conditions as above ($t_N = 500 \text{ s}$ and $N = 151$) and for sample sizes between $\frac{1}{10}l_{ref}$ to $10l_{ref}$. From the picture one notices that the thickness that corresponds to the lowest uncertainty on the estimation of $k$ ($l_x = 0.87 \text{ mm}$) is quite close to the one leading to the minimization of $\phi_A(V)$ ($l_x = 0.58 \text{ mm}$); one may also note that the (asymptotic estimate of the) standard deviation on $D$ (approximately $1/3$ of the error) is quite large and it compares well to the $\sqrt{\phi_A(V)}$. If the condition on $t_N$ is relaxed, then $D$ may be established with greater confidence and the overall performance of the estimation process may be improved by minimizing $\phi_A(V)$ with respect to both $t_N$ and $l_x$. This is studied in Figure 9 (b), where the contour plot reports $\log_{10}\sqrt{\phi_A(V)}$ against the two design parameters in the range $50 \text{ s} = \frac{1}{10}t_{ref} \leq t_N \leq 10t_{ref} = 5000 \text{ s}$ and $0.1 \text{ mm} = \frac{1}{10}l_{ref} \leq l_x \leq 10l_{ref} = 10 \text{ mm}$. It is found that, if the $t_N = 50 \text{ s}$ and $l_x = 0.2 \text{ mm}$, then $\sqrt{\phi_A(V)}$ decreases by 40% compared the corresponding minimum shown in Figure 9 (a). This entails that a balanced identification strategy addressing both experimental time and optimal size is needed in order to improve parameter estimates.

Going from 1D to 2D samples, contributes in reducing the confidence region size for the conditions discussed above as shown in Figure 8 (b), where the sample cross section is square. In order to generalize the discussion, pillars with rectangular cross section are studied. As shown in Figure 10 (a), for $l_x = l_y \approx 0.83 \text{ mm}$ one reduces $\phi_A(V)$. Instead, for $l_x = l_y \approx 1.18 \text{ mm}$ the error
on the parameter $D$ is minimized. One notices that the conditions which reduce the uncertainty on the quantities $\hat{D}$ and $\phi_A(V)$ are slightly offset; in other words, improving the identification of $D$ relates to a decrease in the overall experimental quality and vice versa. In addition, in analogy with the results in the previous part of this article, the optimal conditions are achieved for symmetric samples. Furthermore, one notes that the plots of Figure 10 (a) and (b) are symmetric with respect to the $x$ and $y$ axis. However, the minima are quite shallow and similar quality in the data can be achieved for samples of non-rectangular cross section.

It is considerably harder to visualize similar parametric studies for 3D samples due their dependence on three-parameters dimensional space and for this reason only 3 $l_z$ conditions are shown. In Figure 11 $\phi_A(V)$ is reported against $l_x$ and $l_y$ for various values of $l_z$. In particular panel (a) corresponds to $l_z = 0.1 l_{ref}$, panel (b) to $l_z = l_{ref}$ and panel (c) to $l_z = 10 l_{ref}$. In each panel the optimal value is highlighted; in Figure 11 (a) it is positioned in the uppermost right corner, in Figure 11 (b), it is located near the center and in Figure 11 (c) it is slightly displaced with respect to the center of the sample. These plots confirm the earlier result that, for the given conditions, a cubic sample increases the identifiability of the parameters. It must be noted however that nearly identical results may be achieved for samples characterized by different dimensions, i.e., analogously to the 2D case, the minima are shallow.

### 3.6 The Link to the Biot Number

One may notice that Equation (6) essentially depends on two physical parameters, the relaxation times for the diffusion processes, generically written as $\tau_D = \frac{l^2}{D}$, where $l$ is a representative length scale, and the characteristic relaxation time of the exchange reactions, i.e., $\tau_k = \frac{l}{k}$. One
further notices that the quantities $L$ in (6) are the chemical Biot number defined as the ratio of the diffusional and reaction time scales, $\text{Bi} = \frac{\tau_D}{\tau_k}$. For illustration, the value of $\sigma_n(t)$ is reported as a function of the Biot number and the diffusion timescale under the condition that $l_x, l_y \to \infty$ (1D) [25]:

$$\sigma_n(t) = 1 - \sum_{p=1}^{\infty} \frac{2\text{Bi}^2}{\left(\beta_p(\text{Bi})\right)^2 \left[\left(\beta_p(\text{Bi})\right)^2 + \text{Bi}^2 + \text{Bi}\right]} \exp \left(-\left(\beta_p(\text{Bi})\right)^2 \frac{t}{\tau_D}\right)$$  \hspace{1cm} (21)

where it is taken that $\text{Bi} = L_x = \text{Bi}_x = \frac{k l_x}{D} = \frac{\tau_{D,x}}{\tau_{k,x}}$. In Equation (21), it is emphasized that $\beta_p(\text{Bi})$ is the p-th solution of the $\beta_p \tan(\beta_p) = \text{Bi}$, which is also a function of the Biot number. Therefore, one may write that

$$\sigma_n(t) = \sigma_n(t^*, \text{Bi})$$  \hspace{1cm} (22)

where the dimensionless time $t^*$ is such that $t^* = \frac{t}{\tau_D}$. The sensitivity of the ECR with respect to the parameter $k$ can then be rewritten as:

$$S_k = k \frac{\partial \sigma_n}{\partial k}(t^*, \text{Bi}) = k \frac{\partial \text{Bi}}{\partial k} \frac{\partial \sigma_n}{\partial \text{Bi}}(t^*, \text{Bi})$$

$$= \text{Bi} \frac{\partial \sigma_n}{\partial \text{Bi}}(t^*, \text{Bi})$$  \hspace{1cm} (23)

This last equation highlights that the sensitivity $S_k$ of the ECR response with respect to $k$ is equal to the sensitivity with respect to the Biot number. Similarly, the sensitivity $S_D$ with respect to $D$ is given by
\[ S_D = D \frac{\partial}{\partial D} n(t^*, Bi) \]
\[ = D \frac{\partial}{\partial D} Bi \frac{\partial}{\partial Bi} n(t^*, Bi) + D \frac{\partial}{\partial D} Bi \frac{\partial}{\partial Bi} n(t^*, Bi) \]
\[ = t^* \frac{\partial}{\partial t} n(t^*, Bi) - S_k \]

which shows that sum of \( S_D \) and \( S_k \) is equal to the sensitivity with respect to the dimensionless time and it indicates that if the \( S_k \) increases then, all other conditions being constant, the \( S_D \) will decrease.

Figure 12 (a) shows the maximum sensitivity of \( n(t^*) \) with respect to \( k \) and \( D \) in the range \( 10^{-3} \leq t^* \leq 10^3 \). It is apparent that for “large” Biot numbers (\( Bi \geq 20 \)) the \( n(t) \) is sensitive only to \( D \) (the rightmost dashed line corresponds to \( S_k \leq 5\% \)) while for “small” Biot numbers (\( Bi \leq 0.4 \)), the ECR response is sensitive only to \( k \). Both \( k \) and \( D \) are sensitive in the region where Biot number is close to unity (\( 0.4 \leq Bi \leq 20 \)). In particular if the Biot number is exactly unity, the maximum relative error on \( k \) is expected to be smaller than the relative error on \( D \) since the sensitivity on the former is greater than for the latter. When \( Bi \approx 2 \) the two max sensitivities errors are identical and the confidence bands of both parameters are projected to be similar.

Incidentally, this corresponds to enforcing the condition of Equation (18), see Figure 4 (c). The Biot number threshold can be easily understood by recalling that \( Bi = \frac{\tau_D}{\tau_k} \). If \( \tau_D \gg \tau_k \), \( Bi = \frac{\tau_D}{\tau_k} \gg 1 \), then if experimental time is sufficiently long only \( D \) will be identifiable and the peak of the sensitivity occurs at \( t^* \approx 1 \) (or \( t \approx \tau_D \)) as shown in the rightmost part of Figure 12 (b).

Similarly, if i.e., \( \tau_k \gg \tau_D \), i.e., \( Bi = \frac{\tau_D}{\tau_k} \ll 1 \), then only \( k \) is identifiable with peak of the sensitivity occurring at approximately \( t \approx \tau_k \) as it is shown in the left portion of Figure 12 (c).
This trend is easily reconciled with intuition, if the measurement is only sensitive to \( k \), then the best measurement time roughly corresponds to its characteristic timescale \( \tau_k \). Similarly, if the measurement is sensitive only to \( D \), then the best sensitivity is achieved roughly at \( \tau_D \). Again, while \( S_D \) is monotonically increasing with \( Bi \), \( S_k \) is monotonically decreasing evidencing a region where the two sensitivities are comparable. In addition, these findings provide stricter bounds compared to rule of thumb principles found in the literature [25]. The latter state that for \( Bi<0.03 \) only \( k \) can be obtained, for \( Bi>30 \) only \( D \) is accessible, and for \( 0.03<Bi<30 \) both \( k \) and \( D \) may be estimated with good confidence.

Expressions that are analogous to (22) may be found for the pillar (2D) and parallelepiped (3D) configurations; for example in 3D one may write

\[
\sigma_n(t) = \sigma_n(t^*, Bi_x, Bi_y, Bi_z)
\]

where the dimensionless time \( t^* = \frac{t}{\tau_D} \) is taken with diffusion timescale \( \tau_D = \frac{l^2}{D} \) with

\[
\frac{1}{l^2} = \frac{1}{l_x^2} + \frac{1}{l_y^2} + \frac{1}{l_z^2}.
\]

It is important to stress that ECR response depends on \( \tau_D \) but also on the Biot numbers along the directions \( x, y \) and \( z \). This definition is useful to assess the sensitivities, for example in the 2D (pillar) case one may write that

\[
S_k = Bi_x \frac{\partial \sigma_n}{\partial Bi_x}(t^*, Bi_x) + Bi_y \frac{\partial \sigma_n}{\partial Bi_y}(t^*, Bi_y)
\]

and

\[
S_D = t^* \frac{\partial \sigma_n}{\partial t^*}(t^*, Bi) - S_k
\]

The maxima of the sensitivity of the noiseless ECR with respect to \( k \) and \( D \) is computed against \( Bi_x \) and \( Bi_y \) and they are plotted in Figure 13 (a) and (b) respectively. As shown in panel (a), the ECR response is sensitive with respect to the \( k \) parameter if \( Bi_x \ll 1 \) or \( Bi_y \ll 1 \). On the other
hand, Figure 13 (b) shows that good sensitivity in $D$ is achieved if both $\text{Bi}_x \gg 1$ and $\text{Bi}_y \gg 1$. In general, as evidenced in the plot, ECR’s maximum sensitivity is greater for $k$ than it is for $D$. Good sensitivity on the two parameters is obtained at the intersection of the two sensitive regions where either $\text{Bi}_x$ or $\text{Bi}_y$ is close to unity. This provides a qualitative guideline for the experimental design, showing that good identification may be achieved in the region where both $k$ and $D$ are sensitive. As in the 1D case, the $S_k$ and $S_D$ are characterized by the fact that when one decreases the other one increases accordingly.

3.7 Impact of Flush Time

As it was outlined in the first part if this article, flush time limitations can affect in a significant manner the ECR response. In reference to that, publications have reported the response for the slab (1D) and pillar (2D) configuration [25, 26]; here the normalized conductivity is reported for the 1D case:

$$\sigma_n(t) = 1 - \exp\left(-\frac{t}{\tau_f}\right) - \sum_{p=1}^{\infty} \frac{2\text{Bi}^2}{\beta_p^2(\beta_p^2 + \text{Bi}^2 + \text{Bi})} \frac{\tau_p}{\tau_p - \tau_f} \left[\exp\left(-\frac{t}{\tau_p}\right) - \exp\left(-\frac{t}{\tau_f}\right)\right]$$

(28)

where $\tau_f$ is the flush time and $\tau_p = \frac{\tau_D}{\beta_p^2}$. In the right hand side of the last equation, three dimensionless groups may be identified: $\frac{t}{\tau_f}$, $\frac{t}{\tau_D}$ and Bi. In particular, 2 non-dimensional quantities influence the maximum sensitivity; the first is $\frac{\tau_f}{\tau^*}$, where $\tau^*$ is a suitable timescale, and the second is the Biot number. In analogy with Figure 8, the noiseless ECR response of a 1D sample is reported in Figure 14 (a) for three flush times $\tau_f$ and with $l = 1\text{ mm}$, $\bar{k} = 10^{-2}\text{ cm/s}$
and \( D = 10^{-5} \text{ cm}^2 / \text{s} \) in the timespan \( 0 \leq t \leq 2000 \text{s} \). One notices that the flush time affects the ECR response by lowering the noiseless conductivity. Figure 14 (b) reports the corresponding sensitivity with respect to \( D \), which is the only identifiable parameter since the sensitivity on \( k \) is close to 0. As expected, the sensitivity decreases with increasing \( \tau_f \) and one finds that such decrease correlates with a change in the confidence region size. While the \( k \) parameter is significantly affected, the corresponding impact on \( D \) is small even for a flush time of the order 100 s. It should be noted that the asymptotic confidence region is computed analogously as above, i.e., using the expression (10) with inclusion of the derivative with respect to \( \tau_f \). Hence, one needs to compute the sensitivity with respect to \( \tau_f \). These considerations are complemented by contour plots of the maximum sensitivities with respect to the Biot number and \( \frac{\tau_f}{\tau^*} \), where \( \tau^* = \tau_D \), see Figure 15 (a) and (b), or \( \tau^* = \tau_D \text{ Bi}^2 = \frac{D}{k^2} \), see Figure 15 (c) and (d). As shown in the earlier in this article, if the Biot number is large, then \( D \) is measurable with enhanced sensitivity at small \( \frac{\tau_f}{\tau^*} \). The sensitivity with respect to \( k \) is reported in Figure 15 (a) and (c), where one notices that \( k \) is better identifiable for small Biot number and the sensitivity range decreases by increasing the ratio \( \frac{\tau_f}{\tau_D} \), panel (a), one also notes that \( k \) is not identifiable for sufficiently large Biot number. A smaller range where \( k \) is sensitive can be found in panel (c), in this context the peak sensitivity is found at about \( \text{Bi} \approx 10^{-2} \). The discrepancy between the panel

\[ \text{Note that } \tau_D \text{ depends on } l \text{ while } \tau_D \text{ Bi}^2 \text{ is independent of the size of the system.} \]
(a) and (c) may be understood quite simply to be the consequence of the dependence of both $\tau_D$ and Bi on $l$, the half-thickness of the sample. The sensitivity with respect to $D$ is shown in Figure 15 (b) and (d), again, if the Biot number is large, then $D$ is better identifiable; the sensitive range is quite narrow and it decreases by increasing the ratio $\frac{\tau_f}{\tau_D}$, panel (b). If the y-axis is instead $\frac{\tau_f}{D/k^2}$, one observes that the sensitive range broadens out.

Lastly one notes that this insight may be used for the heuristic optimization of the experimental size of the system. For example, if one can obtain from the literature a suitable range for $\tau_f$, $D$ and $k$, one may identify a band in the y axis of Figure 15 (c) and (d) for $\frac{\tau_f}{D/k^2}$, this band in turn shows the maximum sensitivity an ECR experiment may have as a function of the Biot number. One may adjust the Biot number accordingly by modifying the thickness of the sample in order to estimate the desired parameter with increased confidence.

4 Practical Applications

The tools used in this article, which are implemented in a freely available MATLAB toolbox, can be easily applied to ECR design and data analysis. For example, the plots of the confidence region can be used to compute the error bars on the parameters and to establish the limitations of the ECR design. The sensitivity analysis can be used as a graphical empirical tool to establish which times spans are best suited for the given experimental conditions and to determine the most sensitive regions for various sample sizes.

A robust OED can be computed with ECRTOOLS prior to sample fabrication. For example, on the basis of experimental data available on the literature, one may determine the set over which
the true parameters are likely to vary as a function of operation temperature and as a consequence of sample-to-sample variability. Then one can apply the robust optimization criteria outlined above to determine the design conditions, such as experimental time and sample sizes, which maximize the quality of the experimental information for the given set of experimental conditions.

All those applications are explained within the ECRTOOLS manual, which features a GUI for intuitive optimization of ECR data. The GUI allows online sensitivity analysis, confidence ellipse generation and data fitting of empirical data within a variety of optimization algorithms. The demos of ECRTOOLS explain in detail how the features presented here can be used.

5 Conclusions

This article focuses on improving parameter determination in ECR by linking it with sensitivity analysis OED. The asymptotic computation of the covariance matrix and the sensitivity analysis were shown to be powerful tools, which can improve ECR experimental designs. In particular, OED provides a way to robustify the experiments with respect to variability of the experimental parameters. Two robust OED strategies were shown and compared: the min-max approach aims at safeguarding the outcome of the experiment in the worst-case scenario; the average OED design instead improves the average outcome of the experiment.

The sensitivity analysis is used as a graphical tool to test which combination of experimental time span and sample is are most affected by the parameter variability. This is closely linked to the identification. The sensitivity analysis can also be employed to investigate the identifiability of the ECR parameters, establish the most sensitive timescales and qualitatively optimize ECR.
One can immediately appreciate its importance by noting that sensitivity analysis can be employed as a manual, intuitive tool for optimization within a GUI.

This work also highlights the link between Biot number and sensitivity showing that for a small Biot number, the ECR experiment is sensitive only to $k$ and this makes only $k$ identifiable), while for a large Biot number only $D$ is identifiable. The link between the identification of $k$ and $D$ as a function of the Biot number is further analyzed in multiple dimensions and connected by including flush time limitations.
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Funding Sources

The author gratefully acknowledges support from grant DAG12EG06

Acknowledgements

The author thanks Dr. Dengjie Chen for critically reading the manuscripts and providing insightful experimentally oriented comments. The author also gratefully acknowledges early inputs from Prof. Zongping Shao of Nanjing University of Technology.

Additional Note

MATLAB toolbox in this paper, the ECRTOOLS is available at

https://sites.google.com/site/ecrtools/
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<td>Electrical Conductivity Relaxation</td>
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<tr>
<td>OED</td>
<td>Optimal Experimental Design</td>
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<tr>
<td>$k$</td>
<td>Surface exchange coefficient</td>
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<td>$D$</td>
<td>Oxygen diffusion coefficient</td>
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<td>“True” value of the surface exchange coefficient</td>
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<td>Sensitivity with respect to $D$ defined as $D \frac{\partial \sigma_n(t)}{\partial D}$</td>
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REFERENCES

Figure 1

The panels (a) & (c) show plots of the asymptotic confidence regions (solid line) and outcome of the identification of 1000 simulated experiments (cloud of dots). The panels (b) & (d) show the outcome of a typical asymptotic experiment (circles) plotted against the true value of $\sigma_n$. The results in panels (a) & (b) are computed for $D = 10^{-5}$ cm$^2$/s and $k = 10^{-2}$ cm/s while the results in panels (c) & (d) are evaluated for $D = 10^{-4}$ cm$^2$/s and $k = 10^{-3}$ cm/s.
Relative asymptotic errors on the estimated $\hat{k}$ and $\hat{D}$ for $l_x = l_y = l_z = 1 \text{ mm}$ within the domain $\Theta$. 

Figure 2
Figure 3
Difference between the min-max and average design asymptotic errors within the domain \( \Theta \).

The panel (a) shows the relative error difference on the estimated \( \hat{k} \) and (b) shows the difference for \( \hat{D} \). If the difference is positive then the average design leads to better identification than the min-max design since the error with the former design is greater than the error with the latter.
Figure 4

Sensitivity of the ECR signal with respect to $k$ and $D$ within the time interval $10^{-4} \, s \leq t \leq 10^4 \, s$ for (a) $l_x = l_y = l_z = 1 \, \text{mm}$, (b) $l_x = l_y = l_z \approx 5.7 \times 10^{-2} \, \text{mm}$, corresponding to the case where

$$\max_k \left( k \frac{\partial \sigma_n}{\partial k} \right) = \max_D \left( D \frac{\partial \sigma_n}{\partial D} \right),$$

(c) $l_x = l_y = l_z = 10^{-2} \, \text{mm}$, corresponding to $\tau_k = \tau_D$ and (d) $l_x = l_y = l_z = 1.93 \, \text{mm}$ corresponding to robust average design.
Figure 5

In panel (a) the confidence ellipsoid (red solid line) is shown along with the outcomes (cloud of dots) of the identification of 1000 simulated ECR data sets. The confidence ellipsoid of Figure 1 (a) (black solid line) is also shown for reference. In panel (b) the “true” value of the $\sigma_n$ (red solid line) is shown along with $\sigma_n^{\text{meas}}$ (red circles). The conditions are such that $l_x= l_y = l_z = 10^{-2}$ mm ($\tau_k = \tau_D$), $\bar{D} = 10^{-5}$ cm$^2$/s, $\bar{k} = 10^{-2}$ cm/s and the upper limit of the timespan is optimized.
Panel (a) shows the confidence region (solid red line) and outcome of the simulated experiment for the OED optimal condition with $\bar{D} = 10^{-5}$ cm$^2$/s, $\bar{k} = 10^{-2}$ cm/s, $l_x = l_y = l_z = L_{\text{opt}} \approx 0.1019$ mm and an optimized timespan upper bound. In (b) the red solid line is the “true” $\sigma_n$ and the circles indicate $\sigma_n^{\text{meas}}$. 

Figure 6
Figure 7

Sensitivity of the $\sigma_n$ with respect to $k$ and $D$ for $D = 10^{-5}$ cm$^2$/s and $k = 10^{-2}$ cm/s and $l_x = l_y = l_z = L_{opt} = 0.1019$ mm.
Figure 8
Panel (a), ECR response as a function of time for slab (1D), pillar with square cross section (2D) and cube (3D) samples with characteristic length equal to 1 mm. Panel (b), corresponding confidence intervals with N=151 measurement points and measurement error of 1%.
In panel (a), the relative errors on $k$ and $D$ are shown along with

$$\sqrt{\phi_A(V)} = \frac{1}{3} \sqrt{\left(\frac{\text{error}(k)}{k}\right)^2 + \left(\frac{\text{error}(D)}{D}\right)^2}$$

for $N=151$ measurement points and $t_N = t_{\text{ref}} = 500\,s$ and $l_{\text{ref}} = 1\,\text{mm}$. Panel (b) shows $\log_{10} \sqrt{\phi_A(V)}$ with $N=151$ equally spaced measurements times collected in the time interval from 0 to $t_N$; the minimum is highlighted with a yellow dot.
Figure 10

Panel (a), plot of $\sqrt{\phi_A(V)}$ for the pillar (2D) configuration with rectangular cross section as a function of the half side lengths $l_x$ and $l_y$. Panel (b), plot of the error on the estimated $D$ versus $l_x$ and $l_y$. Note that $l_{\text{ref}} = 1$ mm.
Figure 11

Plots of $\log_{10} \sqrt{\phi_a(V)}$ for the parallelepiped (3D) configuration as a function of the half side lengths $l_x$ and $l_y$ for various $l_z$'s. In panel (a), $l_z = 0.1 l_{\text{ref}}$; in panel (b), $l_z = l_{\text{ref}}$; in panel (c), $l_z = 10 l_{\text{ref}}$. 
Figure 12
Panel (a), plot of the maximum sensitivity of the ECR response with respect to k and D as a function of the Biot number. Panel (b), plot of the time at which the maximum sensitivity is achieved versus the Biot number, note that the time is divided by the diffusional characteristic timescale \( \tau_D \). Panel (c), plot of the time at which the maximum sensitivity is achieved, in contrast to panel (b) the time is divided by the chemical reaction characteristic timescale \( \tau_k \). The dashed lines indicate the limits at which the sensitivity is less than 5%.
Figure 13

Panel (a), maximum sensitivity of the ECR with respect to $k$ versus the Biot number along the $x$-direction, $\text{Bi}_x$, and along the $y$-direction, $\text{Bi}_y$, is shown. Panel (b) reports the maximum sensitivity with respect to $D$. The area where the sensitivity is less than 5% is highlighted.
Figure 14

Panel (a), noiseless ECR response for a 1D (slab) sample with $\bar{D} = 10^{-5}$ cm$^2$/s and $\bar{k} = 10^{-2}$ cm/s. Panel (b), sensitivity of the ECR signal with respect to $D$. Panel (c), corresponding confidence regions under the assumption that $k$, $D$, and $\tau_f$ need to be identified.
Figure 15
Contour plot of the maximum sensitivity of the normalized conductivity with respect to $k$, panels (a) and (c), and with respect to $D$, panel (b) and (d), versus normalized flush time and Biot number. The region with sensitivity less than 5% is highlighted. The color bar to the left of panel (b), is matched to (a) and (b) while the color bar to the side of panel (d) linked to both panels (c) and (d).