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A Bayesian approach to electrical conductivity relaxation and isotope exchange/secondary ion mass spectrometry

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ABSTRACT

A Bayesian method for interpretation of electrical conductivity relaxation and isotope exchange/secondary ion mass spectrometry data is presented and demonstrated on data appearing in the literature. The new method enables quantification of uncertainty due to data fitting in estimates for the effective surface exchange coefficient k^* and the effective diffusion coefficient D^*. The standard infinite series solutions to the semi-infinite diffusion problem with linearized chemical kinetics at the boundary are utilized, although the Bayesian technique does not depend on the existence of analytical solutions. The methodology is demonstrated in the analysis of data appearing in the literature, both for isotope exchange/secondary ion mass spectrometry and electrical conductivity relaxation. In particular, the utility of the technique in definitively resolving questions of parameter identifiability is demonstrated in a comparison of two literature studies on the same bulk material that lead to widely different estimated parameters using the standard nonlinear least squares fit.

1. Introduction

Due to the minority carrier status and relatively slow transport kinetics of ionic species in most mixed ionic–electronic conductors (MIECs), the measurement of ionic transport properties in mixed conductors is often a challenge. Perhaps the most direct method of measurement is the introduction of a labeled ion through the exposure of the material to a gaseous isotope of low natural abundance, followed by quenching. The profile of isotope concentration as a function of distance from the exposed surface can then be measured through a combination of focused ion beam milling and secondary ion mass spectrometry (SIMS). This isotope profile contains information about both the rate of diffusion and the rate of exchange at the surface, and material properties characterizing the rate of these processes can be estimated by fitting a reaction–diffusion model to the data [1–3].

The isotope exchange/SIMS route (IE-SIMS) requires specialized equipment that is difficult both to obtain and to operate. A more feasible (if less accurate) alternative for many investigators is electrical conductivity relaxation (ECR), which takes advantage of the ambipolar nature of diffusion in mixed conductors, using the electrical conductivity as a proxy for the ion vacancy concentration [4,5]. Generally a step change in the partial pressure of the gas leads to a change in the bulk conductivity, the rate of which is controlled by surface exchange and ion diffusion. The reaction–diffusion model applied to IE-SIMS can be modified to account for this rate, and then fitted to time-dependent conductivity data to estimate exchange and diffusion parameters. The ECR experiment requires only the ability to control the atmosphere and measure the bulk conductivity. However, a single ECR experiment provides considerably less information than IE-SIMS and is burdened by a larger number of assumptions.

Model identifiability is a frequent hurdle encountered in experiments that involve fitting a multi-parameter model to experimental data. Model identifiability problems arise when the model is not sensitive to certain types of parameter changes, thus rendering the unique determination of parameter values difficult or impossible. In the ionics field, where many parameters of interest are not subject to direct observation, the issue of model identifiability has been addressed by several investigators. Mitterdorfer and Gauckler addressed the issue in the context of electrode model fitting to impedance data, using an *ad hoc* model analysis to show global identifiability for the particular model studied [6]. Bessler used a sensitivity analysis to exclude potentially problematic parameters before optimization [7]. Mebane, et al. assessed the local sensitivity of the cost function used in the fitting of an MIEC defect model to thermogravimetry data in the neighborhood of the optimum [8]. Ciucci, et al. developed a formal method of optimal experimental design (OED) for electrochemical experiments, which improves confidence for parameter estimates [9–12].

The IE-SIMS and ECR experiments seek to estimate two effective material properties: the effective surface exchange coefficient k^* and the effective bulk oxygen diffusivity D^*. Because the oxygen incorporation reaction occurs at the boundary of the reaction–diffusion system, the profile of oxygen ions (or vacancies) measured by IE-SIMS or ECR (the latter in an average sense), it is possible for one process or the

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other (diffusion or surface exchange) to be rate-limiting: that is, either experiment may contain a significant amount of information about that parameter which is associated with the slower, rate-limiting step, while containing relatively little information about the faster step. It is also possible for the two processes to be co-limiting. Clearly, an optimal solution is to use sample geometries that pertain to both surface-controlled or diffusion-controlled regimes, fitting single-parameter models to each. The potential problem with this approach is that, depending on the material properties, it may be very difficult to make a measurement on a material with a small enough thickness to uniquely isolate surface exchange properties. Thin films may be used [13–15], but films may have different exchange and transport properties from the corresponding bulk materials due to substrate effects. Armstrong, et al. developed a methodology for gathering isotope exchange data on small particles, called isothermal isotope exchange (IIE), that treats a powder sample like a packed bed, inferring rates of exchange and transport through analysis of isotope concentrations flowing through the bed [16]. But even this innovative technique may reach physical limits depending on material properties.

It may also be possible to increase confidence in estimates using a number of measurements in different co-limited regimes and a sophisticated statistical approach. Toward this goal, Ciucci has extended the OED formalism to both IE-SIMS [10] and ECR [11] experiments. This is a powerful methodology that demonstrates the potential for statistical analysis to extract rich information from standard experiments. The OED technique relies, however, on a linearization of the cost function in its estimates of parameter uncertainty. While this is not a significant impediment to the minimization of uncertainty that is the focus of OED, the work of Li, et al., in which the cost function for ECR analysis was mapped in parameter space, demonstrates that the nonlinearity of the function may lead to higher moments in the posterior distributions for the estimated parameters [17]. It is therefore warranted to introduce a method for uncertainty quantification and propagation in IE-SIMS and ECR that retains nonlinearities in the cost functions.

A fully Bayesian approach to model calibration is presented and demonstrated in this work for both IE-SIMS and ECR. It can be used in tandem with an approach to experimental design such as OED, or as a standalone method for uncertainty quantification. The method is relatively straightforward theoretically, and its numerical implementation well-suited for packaging and distribution as software.

2. Theory and implementation

2.1. Bayesian calibration

The Bayesian approach to calibration [18,19] arises from the philosophy of epistemic uncertainty. This views the parameters of interest θ as possessing a single true value which is unknown, and a probability distribution quantifies beliefs about what the parameters are. Thus Bayes' theorem – in fact a quite general result derived from basic probability theory – takes on the role of a transformation from a prior probability distribution existing before data is considered to a posterior distribution which takes data into account. A useful representation of Bayes' theorem is

$$\Omega(\theta|B) = \mathcal{L}(B|\theta)p(\theta)\left[\int \mathcal{L}(B|\theta)p(\theta)d\theta\right]^{-1}. \tag{1}$$

Here Ω is the posterior distribution for the parameters $\theta = \{k^*, D^*\}$ given the data B, $\mathcal{L}$, called the likelihood function, is the probability of obtaining the data B given a parameter set, and p is the prior distribution. The likelihood may be understood in terms of a stochastic model for the data. In this case we use

$$\mathcal{B} = Y(\theta) + \epsilon(\psi) \tag{2}$$

where Y is the deterministic model pertaining to the experiment, and ϵ is Gaussian white noise with variance ψ. Given a dataset B, the difference between the model and dataset $B - Y(\theta)$ is thus independently and identically normally distributed, with mean zero and covariance equal to the identity times ψ:

$$\mathcal{L}(\theta|B) = \frac{1}{(2\pi)^{N/2}\psi^{N/2}} exp\left[-\frac{(B-Y(\theta))^T(B-Y(\theta))}{2\psi}\right]. \tag{3}$$

Ideally, the observation error variance ψ would be known and fixed. However, this is generally not the case — indeed, the source and extent of errors may be known *a priori* only vaguely. It is therefore useful to estimate ψ at the same time as k^* and D^*. Eq. (1) is then rewritten as

$$\Omega(\theta,\psi|B) = \mathcal{L}(B|\theta,\psi)p(\theta)p(\psi)\left[\int \mathcal{L}(B|\theta,\psi)p(\theta)p(\psi)d\theta d\psi\right]^{-1} \tag{4}$$

and the posterior is now a joint distribution over θ and ψ. Integration over ψ then recovers a distribution joint over just the physical parameters k^* and D^*.

Prior distributions for k^* and D^* can be anything physically justifiable. Generally it will be relatively easy to justify strict bounds on both parameters — a uniform distribution is the simplest distribution incorporating such bounds, and is the type of prior distribution that will be used in the rest of this work for both physical parameters. If the bounds do not intersect the heart of the posterior distribution, then such priors are deemed "uninformative" — that is, they do not influence the estimate of parameters at all. Informative priors for the physical parameters may arise through prior experience or through *ab initio* calculations [19]. However, uninformative priors were used in the present study.

For ψ, it is computationally advantageous to use an inverse gamma (IG) prior, since the IG distribution is "conjugate" to the likelihood (Eq. (3)) for fixed θ, meaning that there is an analytical solution for the conditional posterior distribution given θ. The support of the IG distribution is also strictly positive, which is in accord with the strictly positive nature of the variance. Parameters for the IG distribution may be estimated through knowledge of the sources of error in the experiments, or broad "vaguely informative" prior distributions may be employed, which allows the data to dominate the estimation of the parameter. This study conforms to the latter case.

2.2. Models

Models applied to both IE-SIMS and ECR datasets were the appropriate analytical solutions to the linearized one-dimensional semi-infinite reaction–diffusion model as found in Crank [20]. For IE-SIMS, this is

$$\frac{c(x)-c_b}{c_g-c_b} = \operatorname{erfc}\left(\frac{x}{2\sqrt{D^*t}}\right) - exp\left(lx + l^2D^*t\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{D^*t}} + l\sqrt{D^*t}\right) \tag{5}$$

where $l = k^*/D^*$, $c(x)$ is the isotope fraction at a distance x away from the surface, c_g is the isotope fraction in the enriched gas, and c_b is the background isotope fraction. For ECR, the model frequently pertains to a parallelepiped geometry [5]:

$$\frac{\sigma(t)-\sigma_\infty}{\sigma_0-\sigma_\infty} = 1-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}\frac{2l_1 exp\left(-\beta_{1i}^2D^*t/x_1^2\right)}{\beta_{1i}^2(\beta_{1i}^2+l_1^2+l_2)}\frac{2l_2 exp\left(-\beta_{2j}^2D^*t/x_2^2\right)}{\beta_{2j}^2\left(\beta_{2j}^2+l_2^2+l_2\right)} \times \frac{2l_3 exp\left(-\beta_{3k}^2D^*t/x_3^2\right)}{\beta_{3k}^2(\beta_{3k}^2+l_3^2+l_3)} \tag{6}$$

where $\sigma(t)$ is the measured conductivity at time t, σ_0 is the conductivity before the pO_2 change, and σ_∞ is the conductivity at an infinite time after the pO_2 change; x_p is the half-width of the sample in