Bayesian Calibration in Electrical Conductivity Reaction and Electrode Modeling

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Introduction:

We used the Bayesian method to interpret ECR and SIMS data appearing in literature. Using this method, we were able to quantify uncertainty due to data fitting of the estimates of k* and D*, the effective surface exchange and diffusion coefficients. Although the technique does not require it, we used analytical solution where available. Using our methodology, we resolved a question of parameter identifiability raised by two previous studies with widely different estimated parameters.

Bayesian Method

The Bayesian method is based upon Bayes' theorem which gives the probability of an event B, with P(B) occurring given that A, P(A), has occurred:

$$P(A|B) = \frac{P(B|A)P(A)}{P(B)}$$

This also valid for probability distribution functions as well. We assume that the observable theta has a fixed value that we may only measure with an error epsilon, or: $B = Y(\theta) + \epsilon(\psi)$ Therefore, we write Bayes' theorem as:

[illegible]

With this, we choose a prior for our B, and obtain the posterior distribution.

Secondary Ion Mass Spectrometry (SIMS)

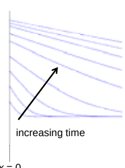
The isotope profile depends on the parameters for D^* and k^*. If the ion profile is known, it can be fitted to a model to obtain the reaction-diffusion parameters.

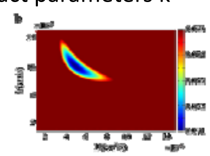
$$\frac{c(x)-c_b}{c_g-c_b} = \mathrm{erfc}\left(\frac{x}{2\sqrt{D^* t}}\right) - \exp(lx + l^2 D^* t)\,\mathrm{erfc}\left(\frac{x}{2\sqrt{D^* t}} + l\sqrt{D^* t}\right)$$

Using isotopes, the profile can be measured directly by a combination of focused ion beam milling and secondary ion mass spectrometry (SIMS).

Electrical Conductivity Relaxation (ECR)

ECR uses the electrical conductivity as a proxy for ion vacancy. When a change of the partial pressure of a gas leads to a change in bulk conductivity, the conductivity's relaxation rate is controlled by the surface and diffusion rates. Therefore, we can extract parameters k^* and D^* using a model for conductivity as a function of ion profile.

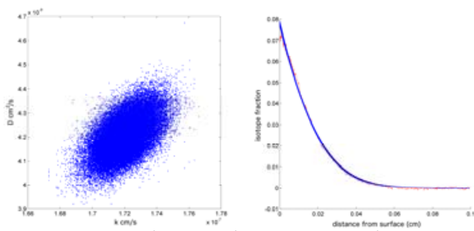




Y. Li, et al., Solid State Ionics 204-205 (2011) 104.

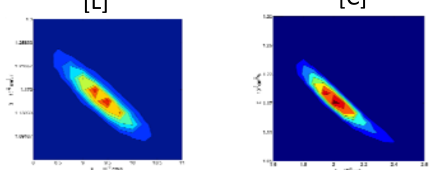
Discussion

Using experimental SIMS data, we obtained the posterior distribution of k^* and D^*.



Each sampled point in the figure on the left represents one possible fit to the data. On the right the experimental data vs. the family of curves that we generate.

The ECR studies of Lane et al. [L] and Cox-Galhotra et al. [C], resulted in a very large differences in fitting parameters, that they attributed to fitting error. Using a Bayesian analysis, we found that the distribution for the D^* is similar, but the distribution of k^* is different. The discrepancy is probably due to the surface treatment, since this is crucial to the surface structure, which in turn controls the catalytic activity.



Ref.	k^*_{mode} (cm/s)	D^*_{mode} (cm²/s)	k^*_{min}	k^*_{max}	D^*_{min}	D^*_{max}
[L]	9.53×10[illegible]	1.15×10[illegible]	8.40×10[illegible]	1.08×10[illegible]	1.10×10[illegible]	1.20×10[illegible]
[C]	2.00×10[illegible]	1.18×10[illegible]	1.70×10[illegible]	2.60×10[illegible]	1.07×10[illegible]	1.28×10[illegible]

The method results in a sample-based joint posterior distribution for k*, D* and the observation error variance.

Calibration Model

In our current study, we are using Bayesian calibration to obtain the posterior distribution of the parameters of the following reactions of a LSM/YSZ:

$$O_{ad}^{-} + V_{O,LSM}^{\bullet\bullet} \rightarrow O_{O,LSM}^{\times} + h^{\bullet}$$

$$\tfrac{1}{2}O_2 + S \rightarrow O_{ad}^{-} + h^{\bullet}$$

$$O_{ad}^{-} + V_{O,YSZ}^{\bullet\bullet} \rightarrow O_{O}^{\times} + S + h^{\bullet}$$

$$O_{O,LSM}^{\times} + V_{O,YSZ}^{\bullet\bullet} \rightarrow O_{O,YSZ}^{\times} + V_{O,LSM}^{\bullet\bullet}$$

Our model is a 1-D porous electrode model (the microstructure data comes from Dr. Salvador's group at CMU) with a set of non-linear equations describing the equilibrium conditions and a set of linearized rate equations. We will obtain our model's impedance response using phasors, and calibrate that to the impedance data from Dr. Finklea's group

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