Interpretation of Impedance Spectroscopy Data on Porous LSM Electrodes

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Introduction:

This study uses Bayesian Analysis in conjunction with microstructural data from X-ray tomography to analyze impedance data from a symmetric porous LSM electrode button cell

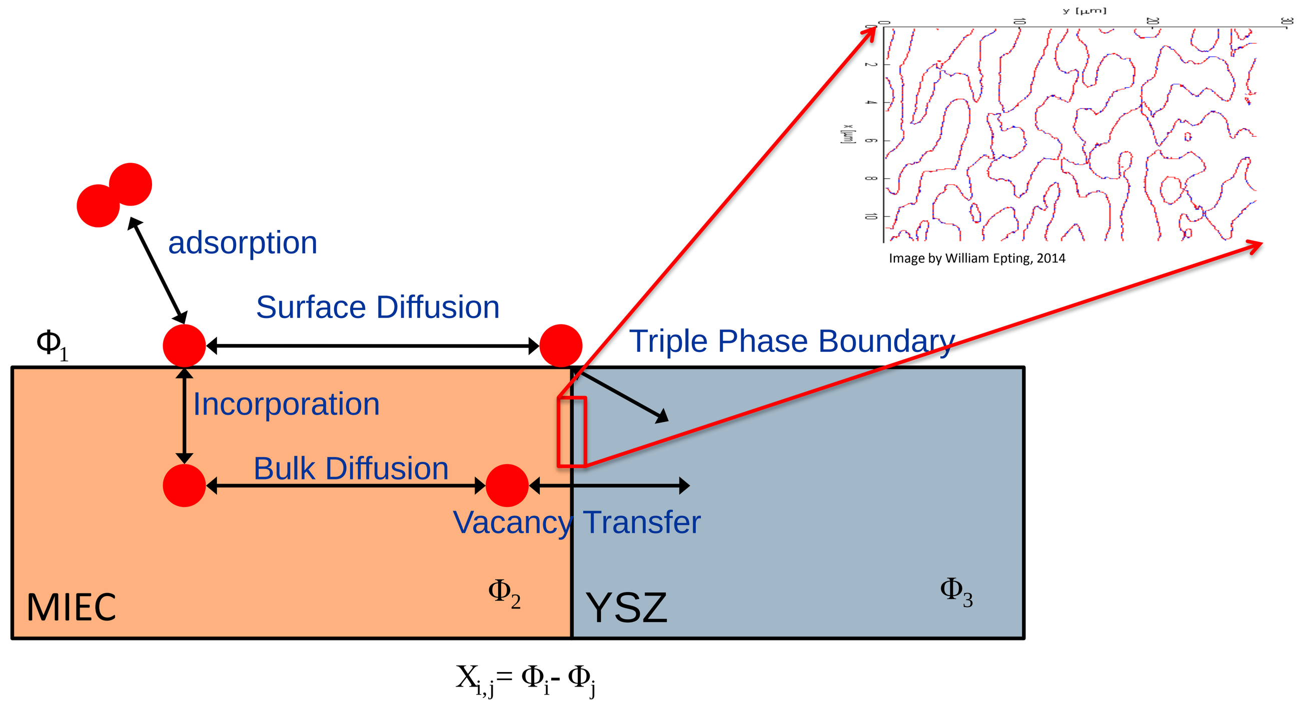

Figure 1: Schematic of the electrochemical cell. The TPB length is obtained through X-ray tomography.

Electrochemical Model:

A finite volume one dimensional model solved in phase space using the Nernst-Planck equations for species' migration and linearized kinetic equations.

Dissociative adsorption:

$$\tfrac{1}{2}O_2(g) + Mn_B^x + V_{ad}^x \longleftrightarrow O'_{ad} + Mn_B^{\cdot}$$

Incorporation:

$$O'_{ad} + V_O^{\cdot\cdot} + Mn_B^x \longleftrightarrow O_O^x + Mn_B^{\cdot} + V_{ad}^x$$

Vacancy Transfer:

$$O_O^x + V_{O,YSZ}^{\cdot\cdot} \longleftrightarrow O_{O,YSZ}^x + V_O^{\cdot\cdot}$$

Triple Phase Boundary:

$$O'_{ad} + V_{O,YSZ}^{\cdot\cdot} + Mn_{Mn}^x \longleftrightarrow V_{ad}^x + O_{O,YSZ}^x + Mn_{Mn}^{\cdot}$$

Schottky:

$$\text{nil} \longleftrightarrow 3V_O^{\cdot\cdot} + V_{La}''' + V_{Mn}'''$$

Figure 2: These chemical equations' thermodynamic and linearized kinetic equations were used.

Bayesian Analysis:

Bayes' theorem provides a way to update prior belief given a experimental data to obtain a posterior

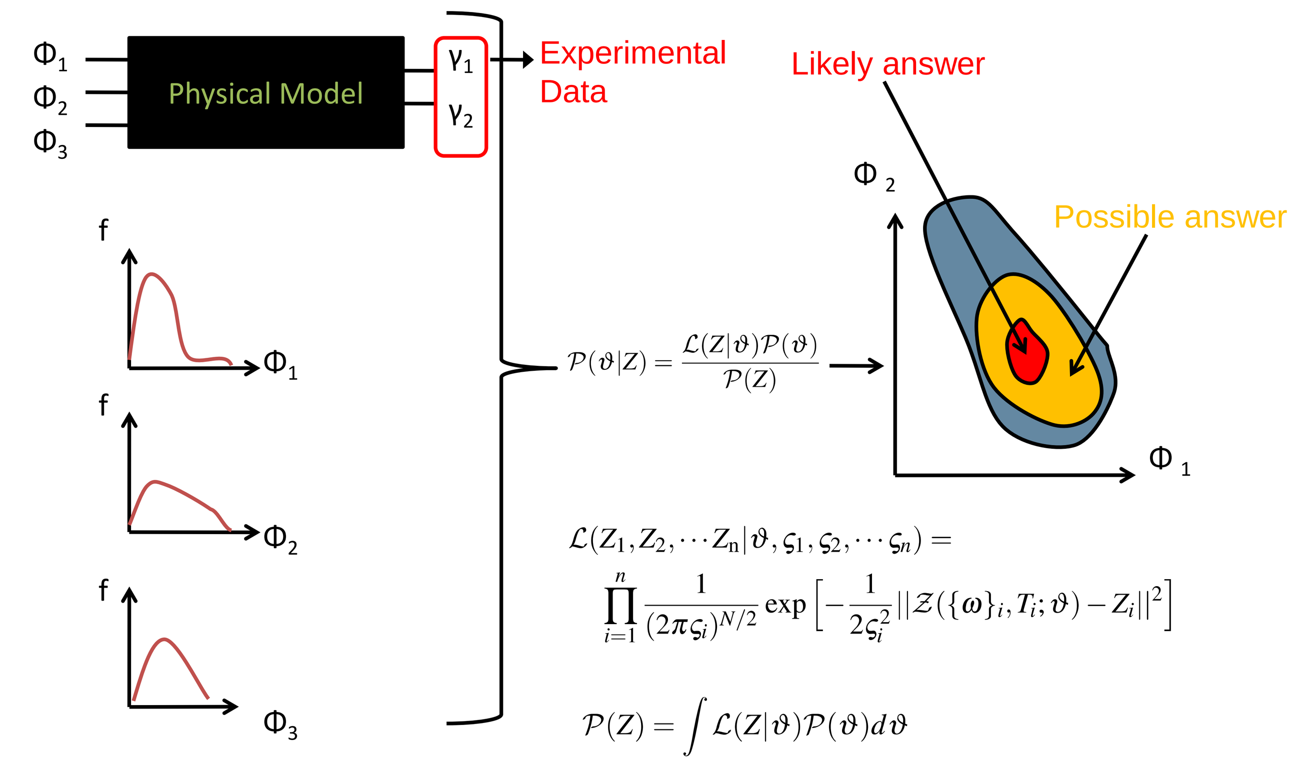

Figure 3: Bayes' theorem ties together experimental data, a physical model and a set of Priors to obtain a posterior distribution.

Priors:

The probability distribution of a model's parameter (the unconditional probability)

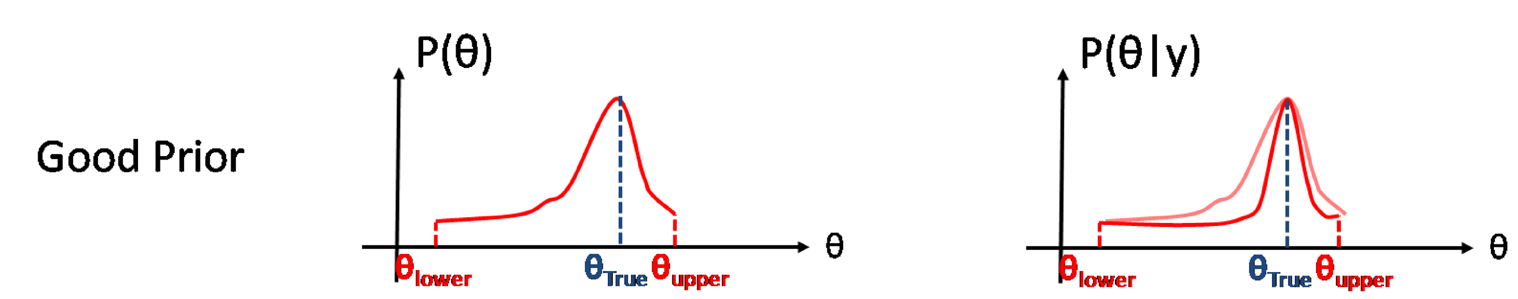

Figure 4: Good priors accelerate the search in parameter space and produce better results.

Parameter	Units	Prior	Bounds	Parameter	Units	Prior	Bounds
ΔH_{ads}	eV	N(-1.5,0.5)	-3 to 0	$\Delta H_{3PB}^{\ddagger}$	eV	Uniform	0 to 6
ΔS_{ads}	J/molK	N(-200,25)	-250 to -100	$\Delta S_{3PB}^{\ddagger}$	J/molK	Uniform	-500 to 10
ΔH_{inc}	eV	N(-1,0.5)	-3 to 1	$\Delta H_{2PB}^{\ddagger}$	eV	Uniform	0 to 3
ΔS_{inc}	J/molK	Uniform	-100 to 100	$\Delta S_{2PB}^{\ddagger}$	J/molK	Uniform	-500 to 10
$\Delta H_{ads}^{\ddagger}$	eV	Uniform	0 to 4	Q_θ	eV	Uniform	0 to 3
$\Delta S_{ads}^{\ddagger}$	J/molK	Uniform	-150 to 200	K_θ	m^2/s	Uniform	10^{-5} to 100
$\Delta H_{inc}^{\ddagger}$	eV	Uniform	0 to 5	Q_v	eV	N(0.65,0.2)	0.1-1
$\Delta S_{inc}^{\ddagger}$	J/molK	Uniform	-100 to 200	K_v	m^2/s	Uniform	10^{-3} to 10
$\Delta H_{schottky}$	eV	N(4.5,0.25)	3 to 5.5	$C_{miec\text{-}YSZ}$	F/m^2	N(1e-3,3e-3)	10^{-10} to 10^{-2}
$\Delta S_{schottky}$	J/molK	Uniform	-30 to 100	$C_{miec\text{-}gas}$	F/m^2	N(0.01,0.05)	10^{-5} to 0.1

Table 1: The priors used to obtain figure 6. Note that some priors are uninformed.

Posterior:

The probability distribution of a parameter given data. This is obtained once a good fit to the experimental data is obtained

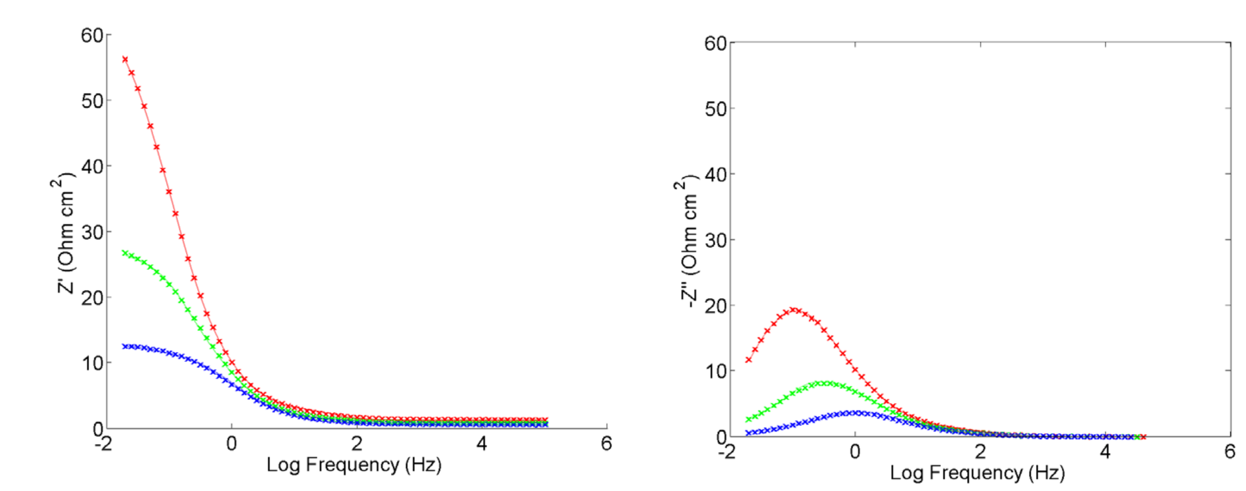

Figure 5: A family of well fitting parameters (posterior) were found using priors that were too broad.

Parameter	Units	Old Value	Parameter	Units	Old Value
ΔH_{ads}	eV	-0.87	$\Delta H_{3PB}^{\ddagger}$	eV	1.34
ΔS_{ads}	J/molK	-163	ζ_{3PB}	mol/m^2	2.1e-16
ΔH_{inc}	eV	-2.55	$\Delta H_{2PB}^{\ddagger}$	eV	1.78
ΔS_{inc}	J/molK	-99.0	ζ_{2PB}	mol/m^2	3.9e-9
$\Delta H_{ads}^{\ddagger}$	eV	1.88	Q_θ	eV	1.42
ζ_{ads}	mol/m^2	1.0e-6	K_θ	m^2/s	3.8e-9
$\Delta H_{inc}^{\ddagger}$	eV	0.99	Q_v	eV	1.73
ζ_{inc}	mol/m^2	2.55e-11	K_v	m^2/s	2.1e-9
$\Delta H_{schottky}$	eV	3.85	$C_{miec\text{-}YSZ}$	F/m^2	1.60e-3
$\Delta S_{schottky}$	J/molK	23.6	$C_{miec\text{-}gas}$	F/m^2	35

Table 2: The mean of the parameters' posterior used in figure 5.

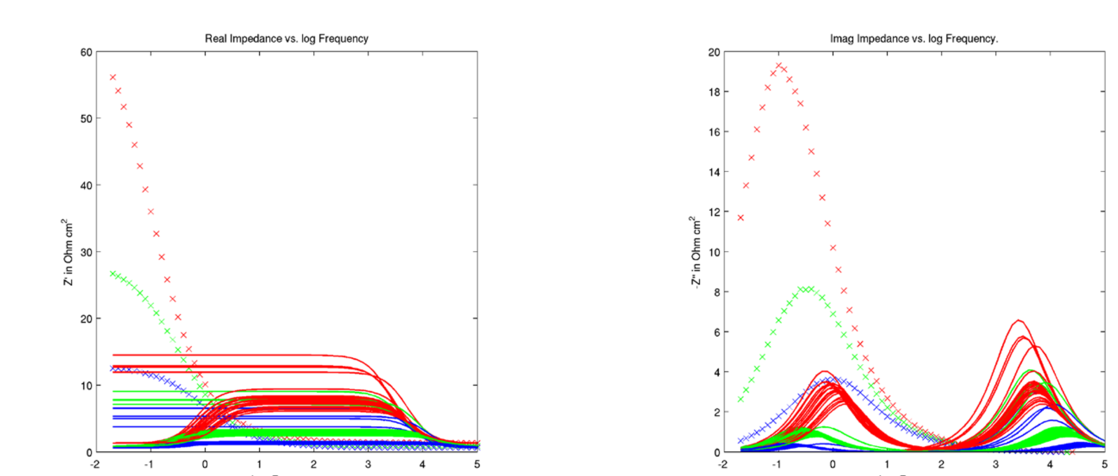

Figure 6: The search for a solution is a random walk. A low frequency peak is starting to emerge

Conclusions:

Previously, the solution found had a large capacitance and activation energy (30 F/m^2 and 1.7 eV). A new solution is currently being found.

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