Application of a State-Space Model to Patterned Cathodes of $(La_{0.87}Ca_{0.13})_{0.95}MnO_3$

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Abstract:

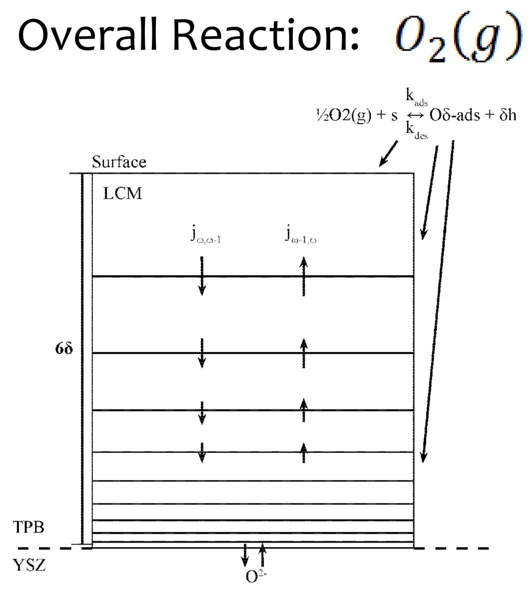
Our aim is to understand the kinetics of the oxygen reduction reaction (ORR) which occurs on solid oxide fuel cell (SOFC) cathodes. Under normal operating conditions this reaction is slow and is responsible for the largest polarization losses in the cell. In this study a state-space model (SSM) has been used to identify key kinetic parameters associated with the ORR.

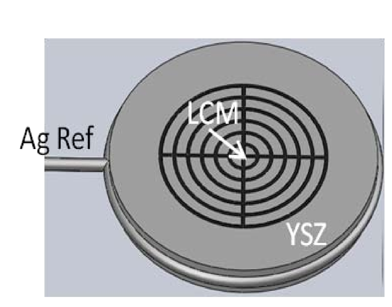
By fitting our electrochemical impedance spectroscopy results collected at temperatures from 600-800°C and oxygen partial pressures (pO_2) from 10^{-3} – 1.0 atm, using impedance generated from the SSM, we have determined the surface coverage and temperature dependence of the parameters: p = [k_{ad}, k_{des}, D_S, k_{1c}]. This is a superior approach to equivalent circuit modeling since simulated impedance spectra are produced directly from a kinetic model instead of indirectly relating kinetic processes to circuit elements.

Introduction:

The ORR is thought to occur according to the schematic shown below. However whether the "bulk path" or "surface path" dominates depends on the ionic conductivity of the cathode.

Overall Reaction: $O_2(g) + 4e' = 2O^{2-}$





For this study we used a cathode with composition: $(La_{0.87}Ca_{0.13})_{0.95}MnO_3$ which is predominately an electronic conductor, so it was analyzed with the following three elementary reaction steps:

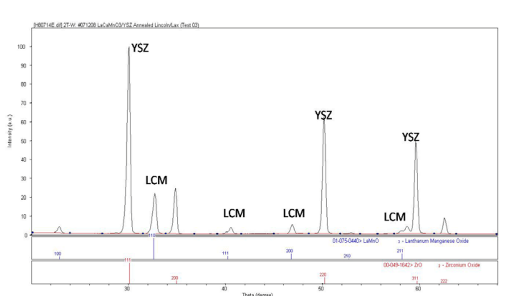
Dissociative Adsorption: $O_2 + 2s \underset{k_{des}}{\overset{k_{ad}}{\leftrightarrow}} 2O^{ad}$

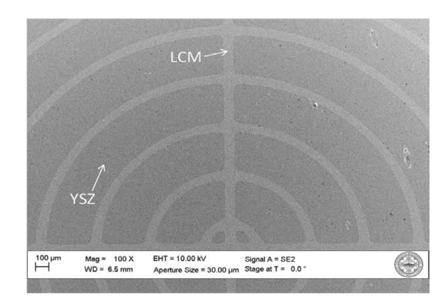
Surface Diffusion: $\frac{d\theta}{dt} = D(\theta)\frac{d\theta}{dx}$

Charge Transfer: $O^{ad} + V_O^{YSZ} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} O_O^{x-YSZ} + h + s$

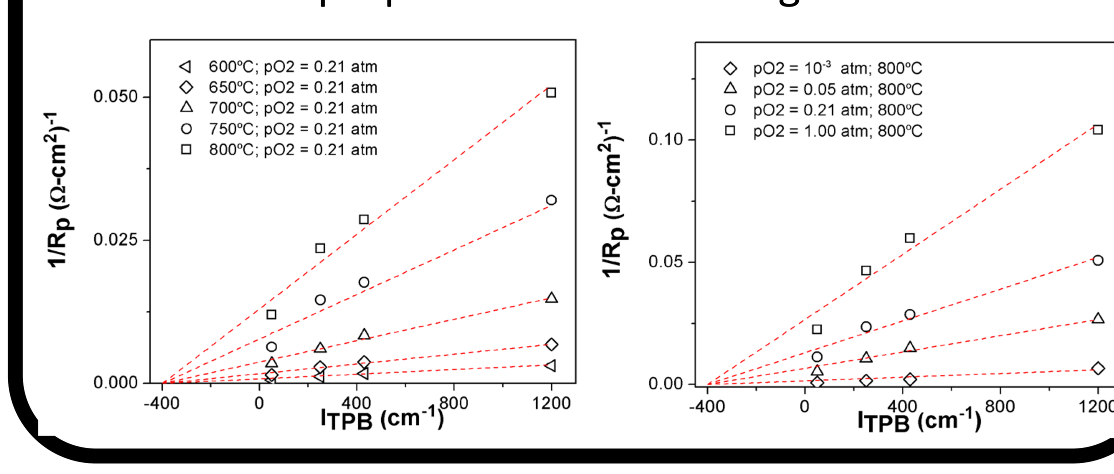
Sample Preparation

Conventional photolithographic techniques were used to produce half-cells with a well-defined geometry. We kept a constant cathode-electrolyte contact area (0.8 cm²) but varied the TPB length from 50 – 1200 cm⁻¹.





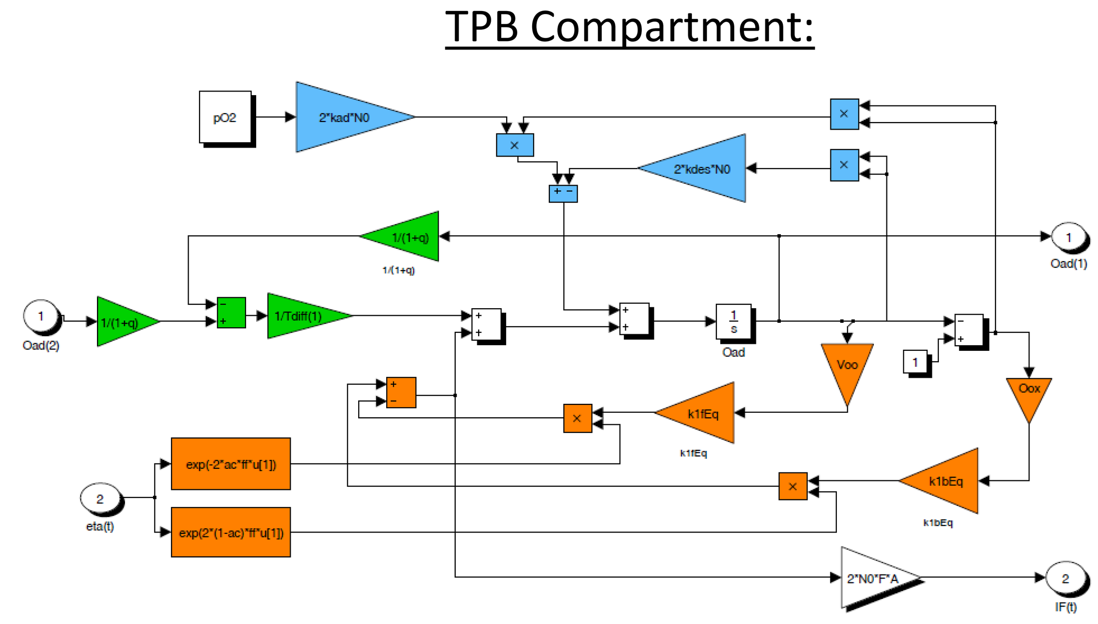
Polarization Resistance, R_p , is inversely proportional to TPB Length.



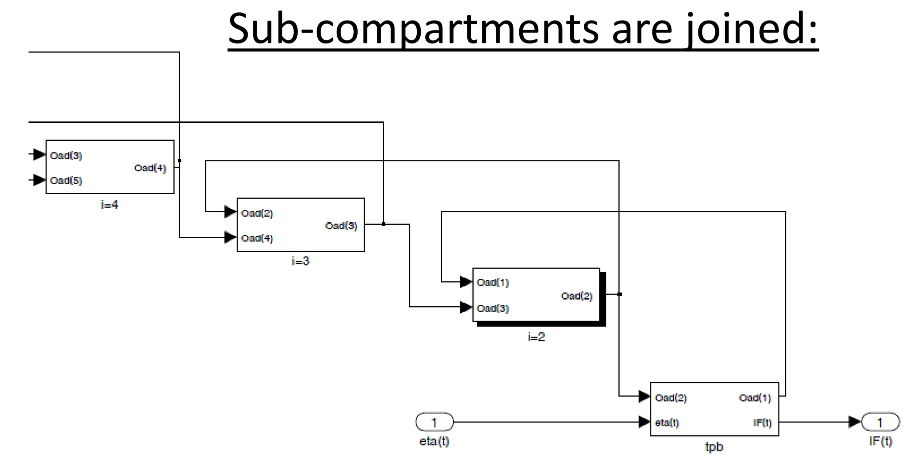
State Space Model

A 1-D finite difference scheme was used to model the mass balance with diffusion to TPB. Charge transfer and incorporation occur in TPB compartment. Other compartments just have adsorption/desorption and diffusion. Simulink and Matlab was used to generate impedance spectra.

TPB Compartment:

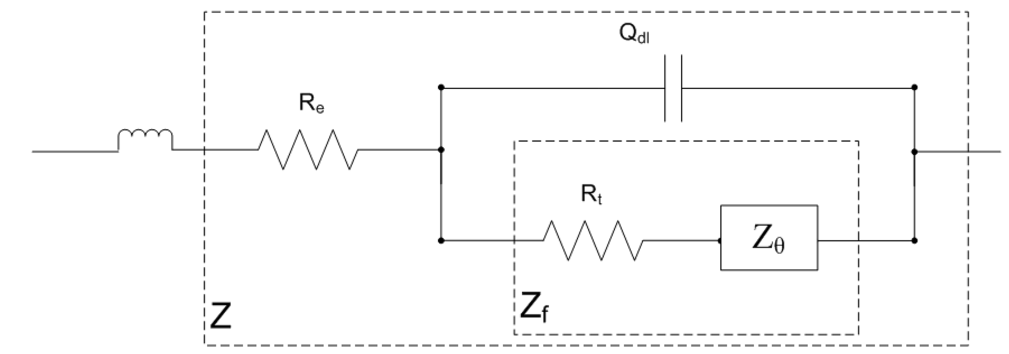


Sub-compartments are joined:

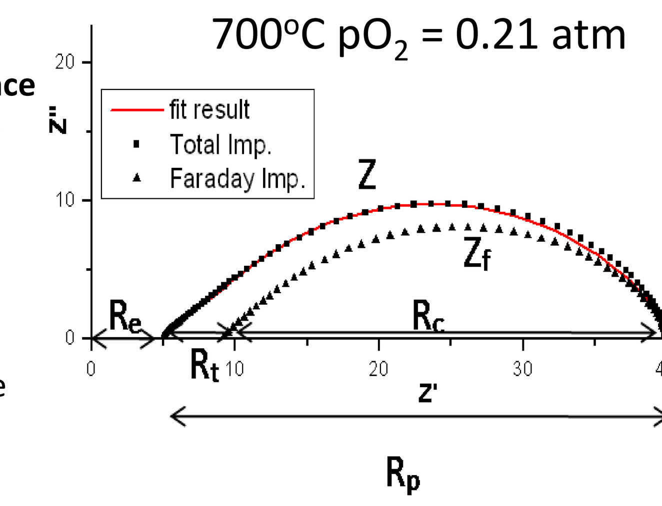


General Equivalent Circuit :

The SSM simulated the Faradaic Impedance: Z_F, but from EIS we measure the total impedance, Z, containing ohmic resistance R_e, and Z_F in parallel with a double layer CPE.

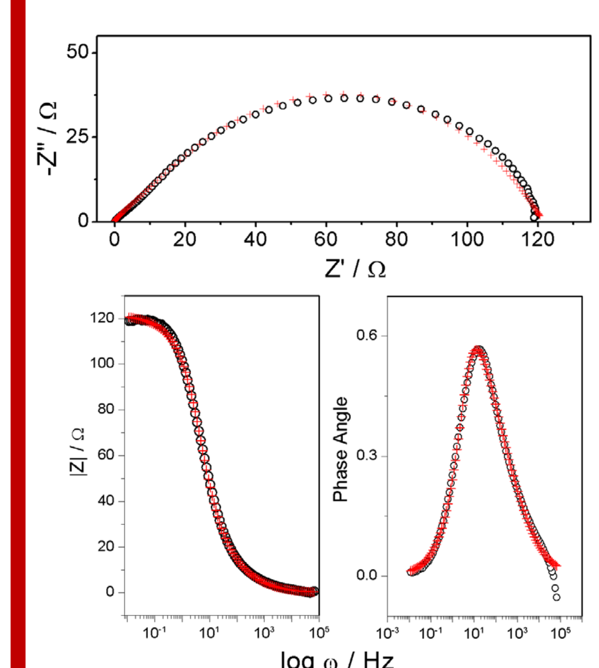


Where:
- Z: Total Impedance
- **Z_f: Faradaic Impedance**
- R_e: Ohmic Resistance
- Q_{dl}: Double Layer Capacitance or CPE
- R_t: Charge Transfer Resistance
- Z_θ: concentration dependent impedance



Results:

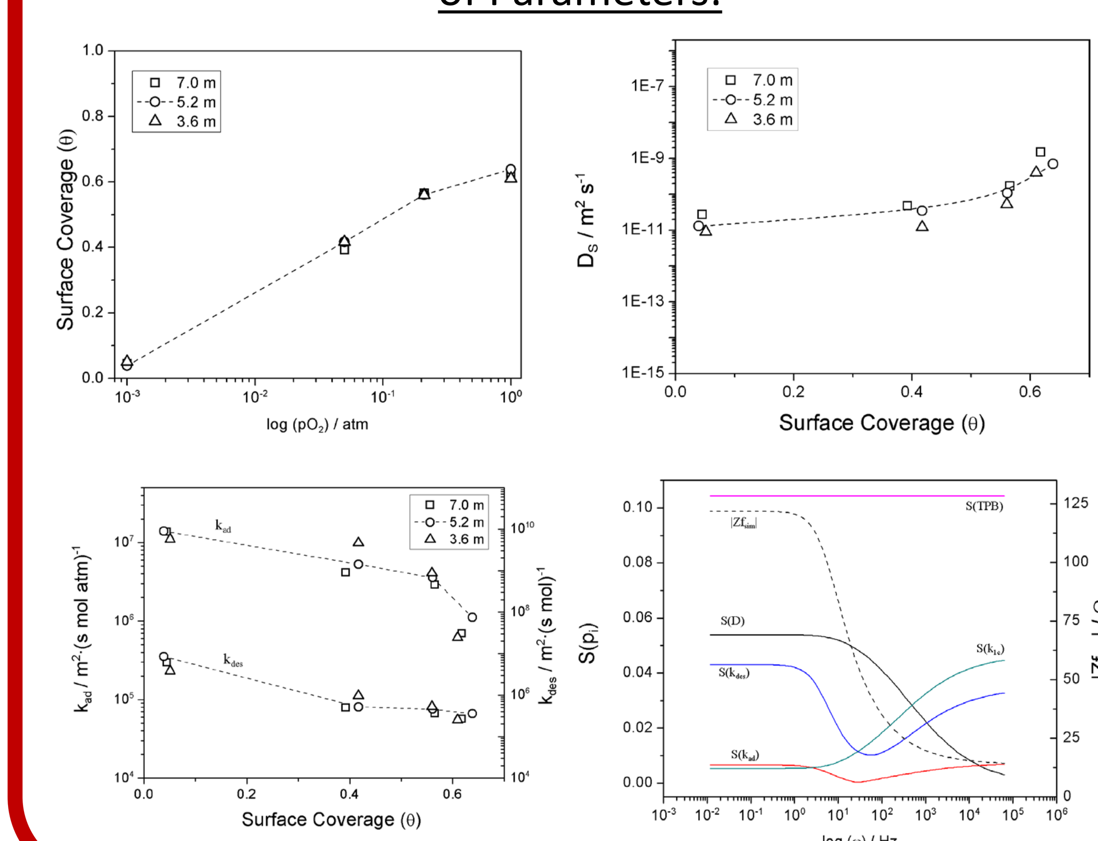
Fitting Results 700C, pO_2 = 0.21, tpb = 7m



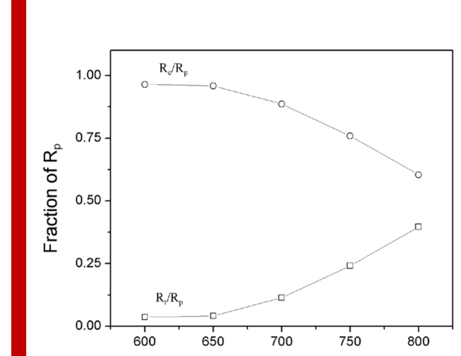
Parameter Estimates:

1. k_{ad} = 2.89·10⁶ m²·(s mol atm)⁻¹
2. k_{des} = 3.58·10⁵ m²·(s mol)⁻¹
3. D_S = 1.69·10⁻¹⁰ m² s⁻¹
4. k_{1c} = 2.87·10⁷ m³ (mol s)⁻¹
5. Q^o = 7.15·10⁻⁴
6. n = 0.63
7. θ = 0.57
8. f(p) = 1.2

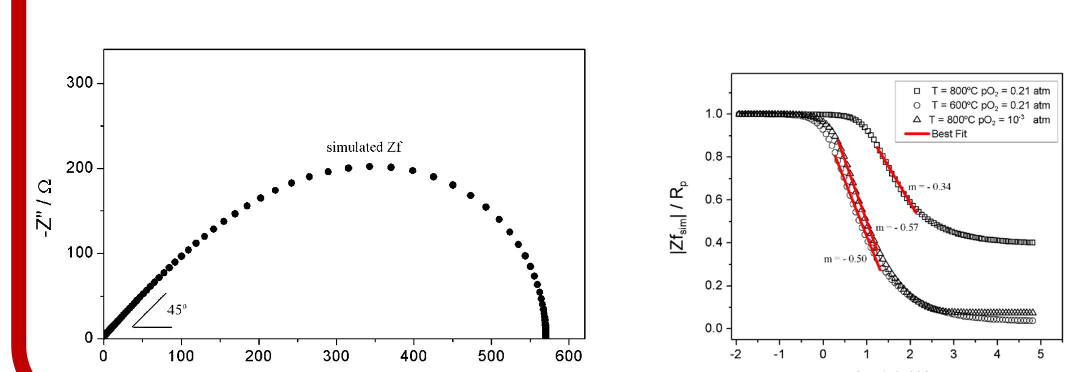
Surface Coverage Dependence and Sensitivity of Parameters:



Rate-limiting regions identified:

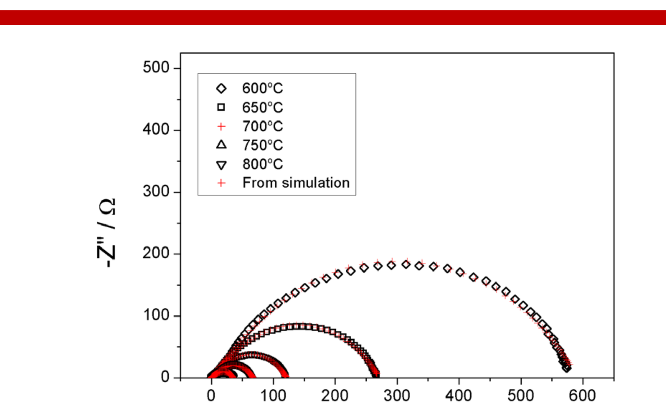


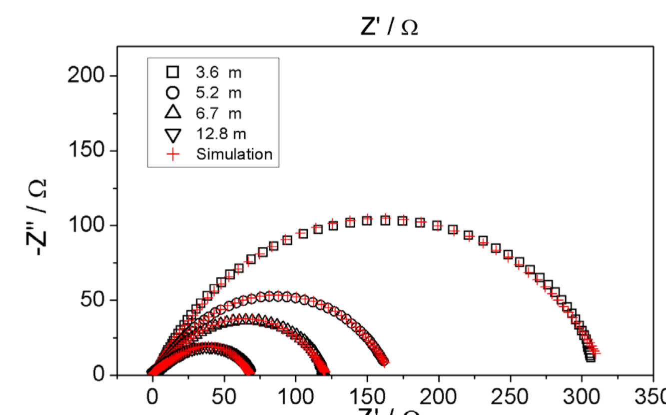
1. 600⁰C and below 0.05 atm oxygen: **Surface Rxn. Ltd.**
2. 600 – 750⁰C at most pO2s: **Surface Diffusion Ltd.**
3. Above 750⁰C and 0.21 atm oxygen: **Charge Transfer Ltd.**



Conclusions:

Patterned half-cells were fabricated of LCM on polycrystalline YSZ substrates. By tightly controlling the TPB length we were able to model our EIS spectra with a SSM to find rate limiting steps occurring at different operating temperatures and pO_2. Above 750⁰C and 0.21 atm oxygen, we see mixed charge transfer/surface process limiting behavior. Otherwise it is purely surface process controlled. We can separate the surface processes into reaction (i.e. adsorption/dissociation) and surface diffusion limiting behavior. One way to separate these is to analyze the bode plot data where a slope of -1/2 corresponds to surface diffusion limitation, whereas a -1 slope indicates reaction controlled. The -1/2 slope is apparent at 0.21 atm at temperatures below 750⁰C. A slope of -0.57 is evident at 600⁰C and 10⁻³ atm oxygen.





Fitting Results for at pO_2 = 0.21 atm and a) different temperatures , and b) different TPB lengths

Future Work:

- The feasibility of applying the SSM to mixed ionic and electronic conducting cathodes is being explored. Patterned cathodes with and without a surface blocking layer will be made.
- The 1-D SSM will be modified to include incorporation away from TPB and used to extract Surface Diffusivity, and other parameters.
- These will be used in a 2-D model.