Separating Rate-controlling Factors in Solid Oxide Fuel Cell Cathodes

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What factors govern SOFC cathodes?

Why can’t we just measure $i$-$V$ characteristics vs. $T$, $P_{O_2}$, etc., and then fit to a model?

*data courtesy of Steve Simner, PNNL*
What factors govern SOFC cathodes?

• Many models fit the data equally well.

• Poor understanding of individual rate-controlling processes.

• Convolution of processes.

• Lack of quantitative information about the microstructure.

Why can’t we just measure $i$-$V$ characteristics vs. $T$, $P_{O_2}$, etc., and then fit to a model?

How do we better isolate the various rate-controlling factors?

*data courtesy of Steve Simner, PNNL*
Outline/Conclusions

• **Isolating O\textsubscript{2} reduction**: studies of La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3-\delta} (LSC) thin-film electrodes using nonlinear impedance.
  - **Dissociative adsorption** appears to be rate-controlling on LSC.
  - **Metallic band structure** may be key to faster catalysis.

• **Quantitative analysis of microstructure**: 3D imaging of porous La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3-\delta} electrodes using FIB-SEM.
  - **3D microstructural data** may allow quantitative analysis of porous electrodes.
How does one isolate O₂ reduction rates?

This is more difficult to measure than you might imagine...

- Kinetics are difficult to isolate from other rates.
- Systems often restricted to linear driving force.
Studies of Thin-film Mixed-conducting Perovskite Electrodes

- Dense films of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) made by pulsed laser deposition (500~1000 nm thickness)
  - LSC ($x=0.4$) on polished polycrystalline Gd-doped ceria (Tohoku University)
  - LSC ($x=0.5$) on single-crystal YSZ (University of Houston)

 Resistance dominated by $\text{O}_2$ exchange kinetics

Diffusion is fast (film acts as well-mixed oxygen reservoir)

Interfacial resistance is small (2-3%).
Electrochemical Impedance Spectroscopy (EIS)

\[ Z = \frac{\Delta V}{\Delta i} \]

EIS attempts to identify overlapping mechanisms via \textit{time scale}.
Electrochemical Impedance Spectroscopy (EIS)

\[ Z = \frac{\Delta V}{\Delta i} \]

\[ V_0 e^{-j \omega t} \]

\[ i_0(\omega) e^{+j \phi(\omega)} e^{-j \omega t} \]

\[ r_{\text{exch}} \sim \frac{1}{R_p} \]

\[ \text{Log} \left( \frac{1}{r_{\text{exch}}} \right) \]

\[ y = -0.42x + 0.08 \]

\[ r_{\text{exch}} \sim P_{O_2}^{1/2} \]

\[ \text{Log} \left( P_{O_2} \right) \]
Electrochemical Impedance Spectroscopy (EIS)

\[ Z = \frac{\Delta V}{\Delta i} \]

\[ V_0 e^{-j\omega t} \]

\[ i_0(\omega) e^{+j\phi(\omega)} e^{-j\omega t} \]

\[ \delta(P_{O_2}) \]

\[ C \sim \delta \frac{\partial \ln \delta}{\partial \ln P_{O_2}} \]
What mechanisms are consistent with \( r_{exch} \sim (P_{O_2})^{1/2} \)?

**Limited by consumption of reactive intermediate**

\[
r_{ads} = k_1 \left( P_{O_2}^{gas} \right)^{1/2} - \left( f_{O_2}^{solid} \right)^{1/2}
\]

\[
r_{exch} = k_1 \left( P_{O_2} \right)^{1/2}
\]

**Limited by formation of reactive intermediate**

\[
r_{ads} = k_1 \left( \frac{P_{O_2}^{gas}}{f_{O_2}^{solid}} \right)^{1/2} - \left( f_{O_2}^{solid} \right)^{1/2}
\]

\[
r_{exch} = k_1 \left( P_{O_2} \right)^{1/2}
\]

Same Response!
Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)

\[ V = V_0 + (V_1 e^{j\omega t} + V_1^* e^{-j\omega t}) + (V_2 e^{2j\omega t} + V_2^* e^{-2j\omega t}) + \ldots \]

\[ i = i_0 + \%\cos(\omega t) \]

Current FFT (magnitude)

Voltage FFT (magnitude)
Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)

- The magnitude, sign, and phase of the harmonics are tied to nonlinearities of the underlying physics (analogy: music).

- Nonlinear harmonic analysis automatically filters out noise and nonperiodic drifts uncorrelated to the input perturbation.
Sources of Nonlinearity in a Mixed Conducting Oxide Film.

\[ r = R_0 \left( P_{O_2}^{\text{gas}}, f_{O_2}^{\text{solid}} \right) \left\{ 1 - e^{-\frac{-\Lambda}{RT}} \right\} \]

\[ \delta(f_{O_2}^{\text{solid}}) \] obeys Lankhorst's model

\[ \frac{\partial \ln \delta}{\partial \ln f_{O_2}^{\text{solid}}} = \frac{-2}{1 + \frac{4\delta}{g_0 RT}} \]
Sources of Nonlinearity in a Mixed Conducting Oxide Film.

Adsorption: \( O_2 + V_{O_s}^{q_s} + q_{ads}e^- \overset{\dot{\mathcal{E}}}{\rightarrow} (O_2)_{O_s}^{q_{O_2}} \)

Dissociation: \( (O_2)_{O_s}^{q_{O_2}} + V_{O_s}^{q_s} + q_{diss}e^- \overset{\dot{\mathcal{E}}}{\rightarrow} 2O_{O_s}^{q_O} \)

Incorporation: \( O_{O_s}^{q_{O}} + V_{O_b}^{q_s} + q_{incorp}e^- \overset{\dot{\mathcal{E}}}{\rightarrow} O_{O_b}^X + V_{O_s}^{q_s} \)

Non-ideal thermodynamics requires that transition states depend on driving force.
Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. $P_{O_2}$

Model: limited by dissociation of chemisorbed intermediate
Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. $P_{O_2}$

Possible rate limiting phenomena

- dissociation of chemisorbed intermediate
- molecular adsorption
- atomic incorporation into solid
Harmonic Response of a La$_{0.6}$Sr$_{0.4}$Co$_{3-\delta}$ film on Gd-doped ceria at 725°C vs. $P_{O_2}$

Model: limited by dissociative adsorption
Harmonic Response of a La$_{0.6}$Sr$_{0.4}$Co$_{3-\delta}$ film on Gd-doped ceria at 725°C vs. $P_{O_2}$

Thermodynamic factor assuming limited by dissociative adsorption
Physical Interpretation of the Observed Kinetics

“dissociative adsorption”

Adsorption: \( O_2 + V_{O_s}^{q_s} \cdot + q_{ads} e^- \hat{E} (O_2)_{O_s}^{q_0} \cdot \)

Dissociation: \( (O_2)_{O_s}^{q_0} \cdot + V_{O_s}^{q_s} \cdot + q_{diss} e^- \hat{E} 2O_{O_s}^{q_0} \cdot \)

Incorporation: \( O_{O_s}^{q_0} \cdot + V_{O_b}^{q_0} \cdot + q_{incorp} e^- \hat{E} O_{O_b}^{\chi} + V_{O_s}^{q_1} \cdot \)

\( q_{diss} = 4, \quad \beta = 1 \)

Implies:
- \( O_2 \) only exists as a molecule, or fully reduced on surface.
- Forward rate obeys mass action (no energy barrier).
Physical Interpretation of the Observed Kinetics

- Reaction is limited by adsorbate lifetime and site availability, not charge transfer.

- Strong Arrhenius dependence corresponds to enthalpy of adsorption (not a true activation barrier).
Physical Interpretation of the Observed Kinetics

- Proposed model explains O$_2$ exchange measurements on bulk La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ over a wide range of $x$, $T$ and $P_{O_2}$.

- Metallic band structure appears to be important for stabilizing physisorbed O$_2$, leading to faster rates.
  
  \[(\text{Pr,Ba})\text{CoO}_y, (\text{Ba,Sr})(\text{Co,Fe})\text{O}_y\]
NLEIS of a Porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ Electrode at $725^\circ\text{C}$ vs. $P_{O_2}$
NLEIS of a Porous La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ Electrode at 725°C vs. $P_{O_2}$

- Simple 1-D models don’t explain higher harmonic data very well.

- Many uncertainties related to the details of microstructure.
3D Imaging of SOFC Electrodes with FIB-SEM

NSF Collaborative Research, Ceramics-DMR
Barnett and Voorhees (Northwestern)
Thornton (U. Michigan), Adler (U. Washington)
J.R. Wilson et al., Nature Materials, July 2006
3D Images of a Porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ Electrode

Electrode area: $2.23 \text{ um}^{-1} = 22,300 \text{ cm}^2/\text{cm}^3$
3D Images of a Porous La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ Electrode

Electrode area: $2.23 \ \text{um}^{-1} = 22,300 \ \text{cm}^2/\text{cm}^3$
Extent of electrode/electrolyte contact: 20.5%
3D Images of a Porous La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ Electrode

Electrode area: 2.23 um$^{-1} = 22,300$ cm$^2$/cm$^3$
Extent of electrode/electrolyte contact: 20.5%
Transport tortuosity factors.
When are macrohomogeneous properties valid?

Juergen Fleig  

Must apply models to actual 3D geometry
Baby steps: a cubic electrode particle

\[ c_0 \frac{\partial x_v}{\partial t} = -\nabla \cdot N_v \]

\[ -n \cdot N_v = \mathcal{R}_0 \left( 1 - e^{-\frac{A}{RT}} \right) \]

\[ \frac{RT}{4F} \ln \left( \frac{f_{O_2}(x_v)}{P_{O_2}} \right) = \varphi \cos(\omega t) \]
Concentration Profiles of Increasing Perturbation Frequency

\[ \sigma = 0.1 \]

\[ \sigma = 100 \]

\[ \sigma = 1000 \]

\[ \sigma = 10000 \]
Higher Order Harmonic Data

Nyquist Plot: 1st Harmonic Response

2nd Harmonic

3rd Harmonic
Conclusions

• By resolving both timescale and nonlinearity, NLEIS appears to be a promising technique for analyzing electrode kinetics.

• For metallic La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, oxygen exchange appears to be limited by dissociative adsorption onto limited vacant surface sites.

• More surface vacancies, metallic band structure may be key to improved kinetics.

• 3D microstructural data stands to allow these methods to be extended to real microstructures.
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NLEIS measurements

\[ V(t) \rightarrow I(t) \rightarrow \text{Potentiostat} \]

\[ I(t) \rightarrow V(t) \rightarrow I(t) \]

\[ \text{Waveform Generator} \]

\[ \text{High-speed Digitizers} \]

\[ \text{FFT} \]

\[ V_0(\omega), V_1(\omega), V_2(\omega), V_3(\omega), \ldots \]
Power Series Expansion of Harmonic Response

\[ \hat{V}_1(\alpha, \omega_0) = \alpha \hat{V}_{1,1}(\omega_0) + \alpha^3 \hat{V}_{1,3}(\omega_0) + \alpha^5 \hat{V}_{1,5}(\omega_0) \]

\[ \hat{V}_3(\alpha, \omega_0) = \alpha^3 \hat{V}_{3,3}(\omega_0) + \alpha^5 \hat{V}_{3,5}(\omega_0) \]

Least Squares Fit

\[ \hat{V}_k = \overline{V}_k + j\tilde{V}_k \]

\( \overline{V}_k \) = Real Part of the Response

\( \tilde{V}_k \) = Imaginary Part of the Response

First Harmonic:

Third Harmonic:
Motivation

• O$_2$ reduction remains a source of polarization and degradation in solid oxide fuel cells.

• To improve cathodes, we must better understand the factors limiting them.