

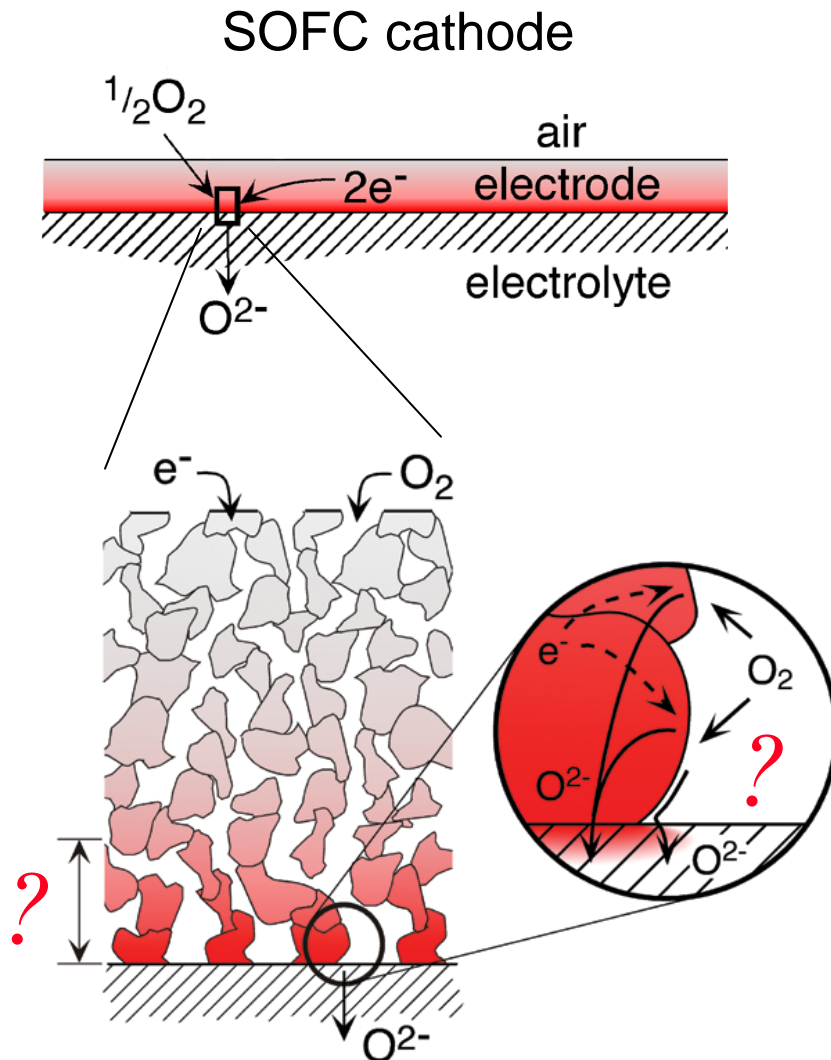
Mechanisms Governing Mixed Conducting SOFC Cathodes

Stuart B. Adler, Dinesh Baskar, Xiyong Chen,
Yunxiang Lu, Jamie R. Wilson

University of Washington

8th Annual SECA Workshop
August 9, 2007

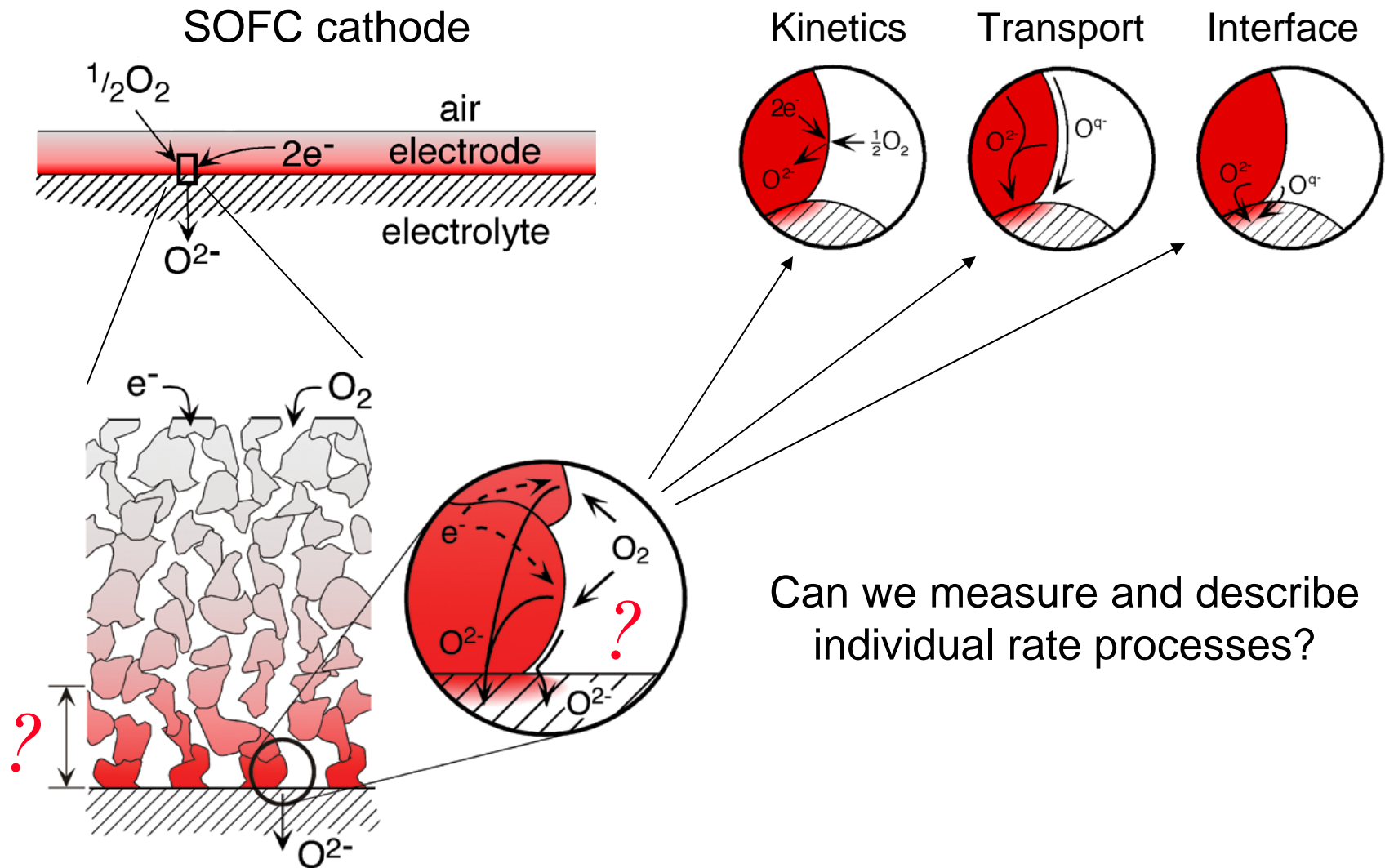
Mixed-conducting SOFC Cathodes



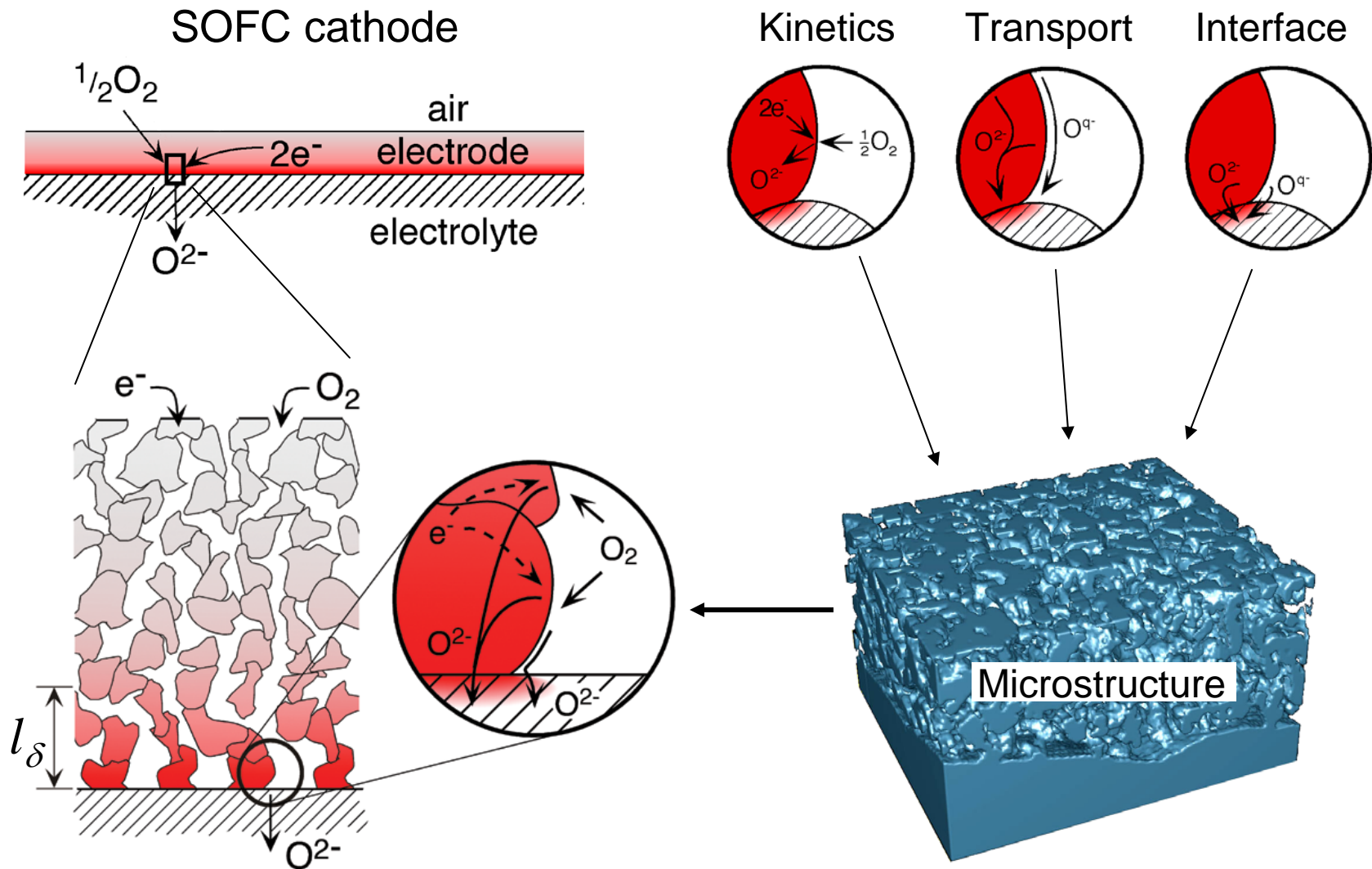
Why our understanding remains largely empirical:

- Many models fit i - V and impedance data equally well.
- Poor *ex-situ* understanding of individual rate processes.
- Inherent convolution of rates.
- Lack of quantitative information about the microstructure.

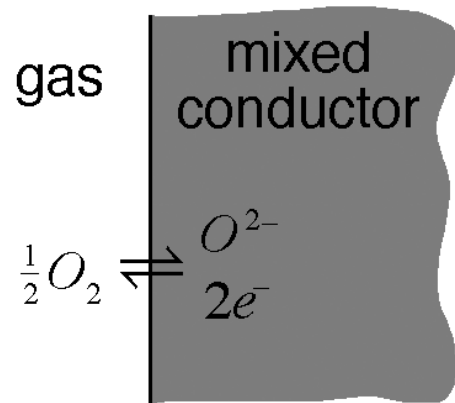
Mixed-conducting SOFC Cathodes



Mixed-conducting SOFC Cathodes

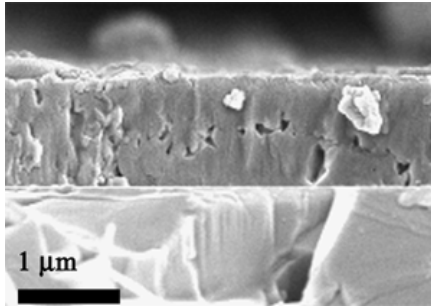


Isolating the Kinetics



This is a difficult reaction to measure and describe.

Isolating the Kinetics



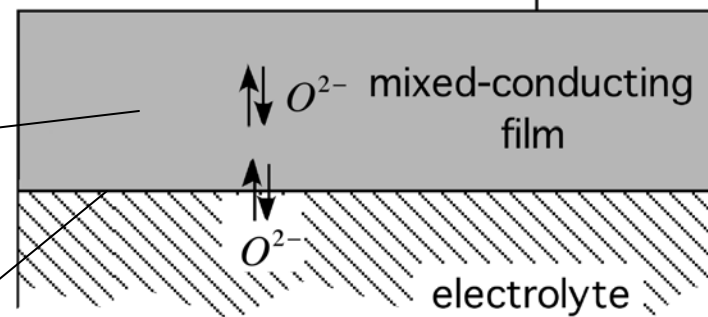
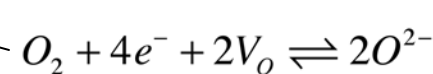
Tohoku University (Maya Sase, Tatsuya Kawada)

- Pulsed laser-deposited films of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC-64) on Gd-doped ceria (GDC).
- Uniform thickness (500~1000 nm) and composition.
- Laterally polycrystalline, but 100 oriented (pseudocubic).

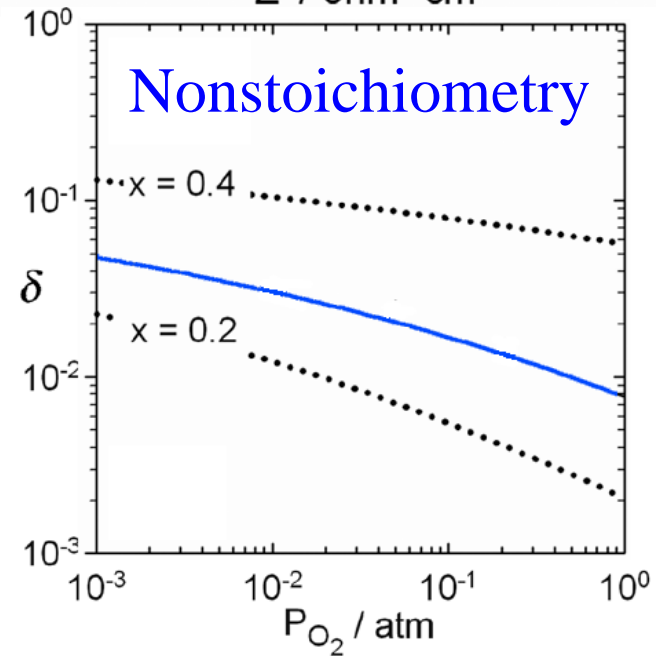
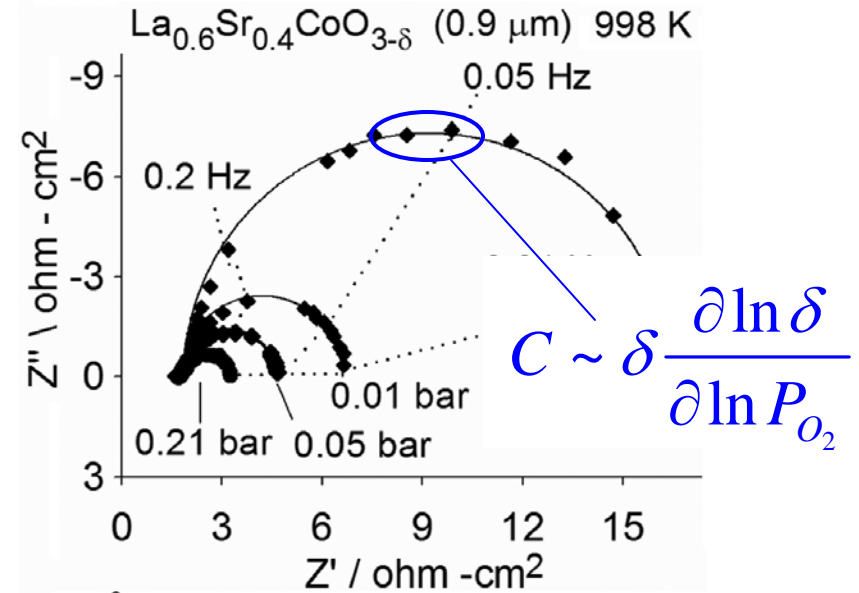
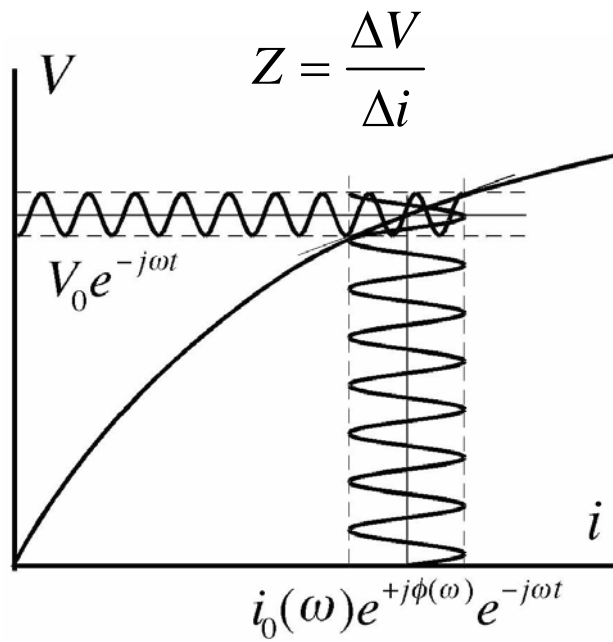
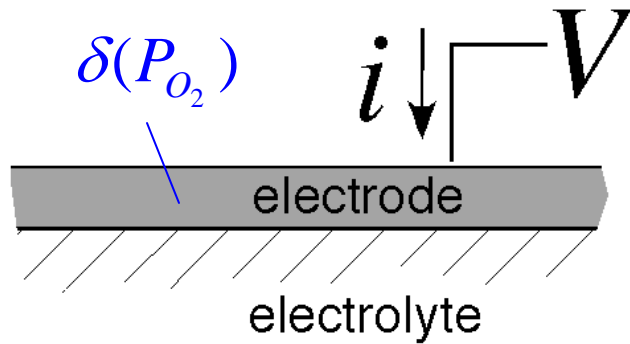
Resistance dominated by
 O_2 exchange kinetics

Fast bulk diffusion
(film acts well-mixed)

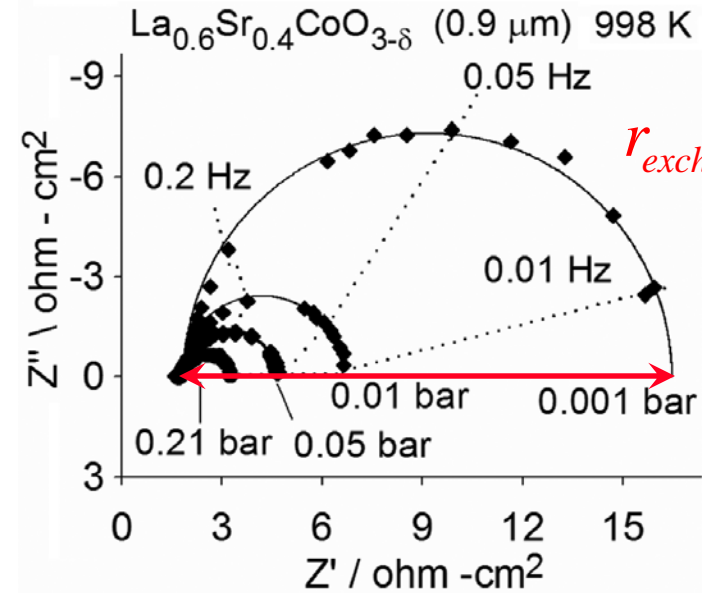
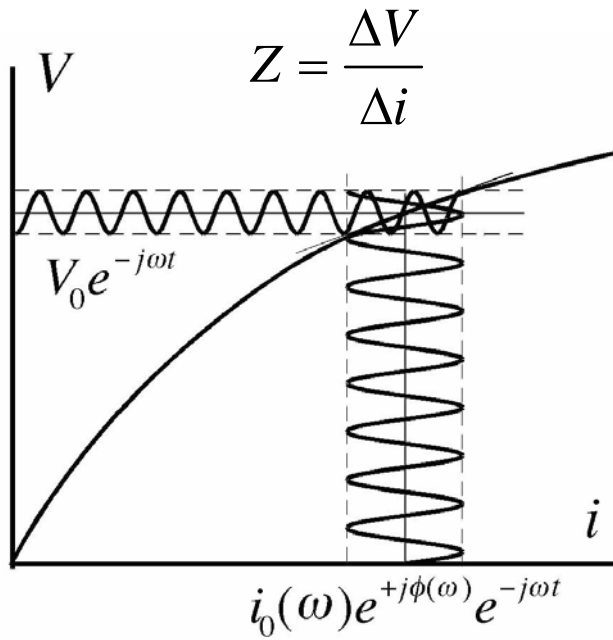
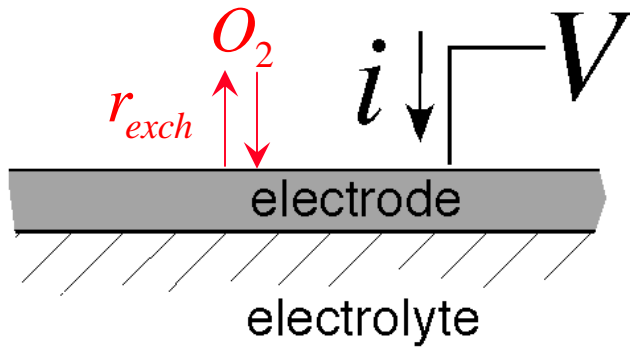
Small interfacial
resistance (2-3%).



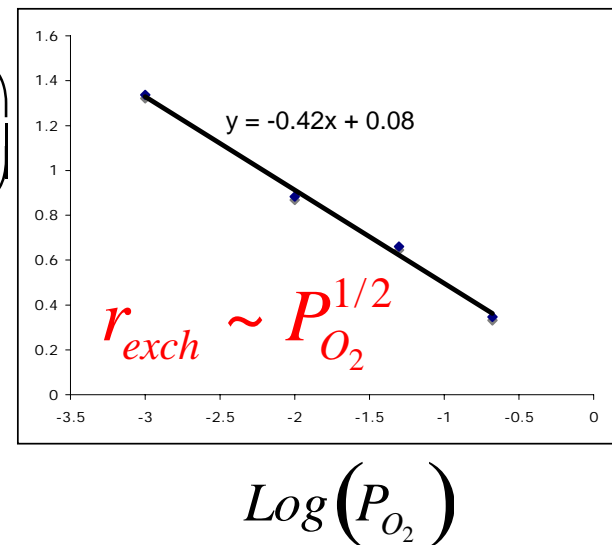
Electrochemical Impedance Spectroscopy (EIS)



Electrochemical Impedance Spectroscopy (EIS)



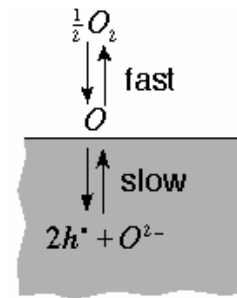
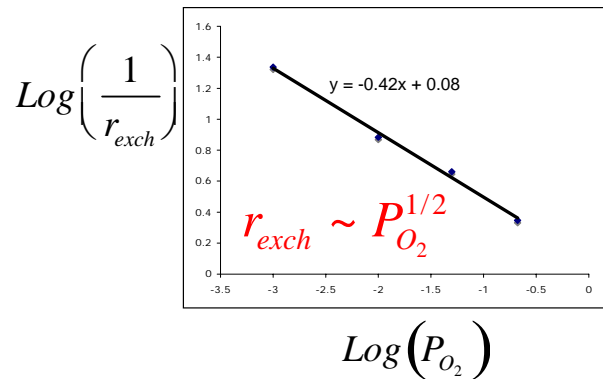
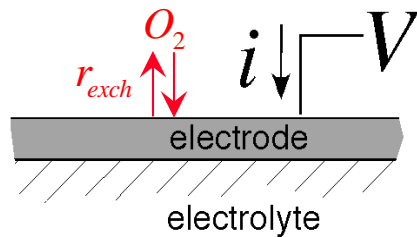
$$\text{Log} \left(\frac{1}{r_{exch}} \right)$$



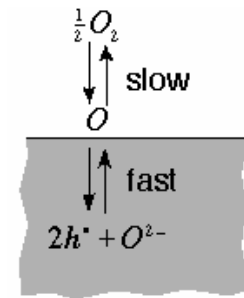
Limitations of linearized rate measurements

What mechanism explains a power-law P_{O_2} dependence?

Multiple models predict similar T and P_{O_2} dependence of r_{exch} .



$$r = k(P_{O_2}^{1/2} - f_{O_2}^{1/2})$$

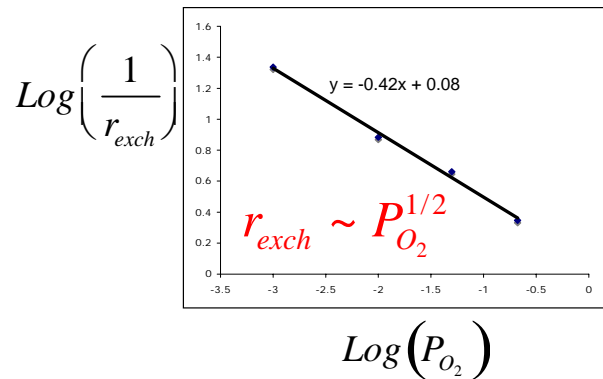
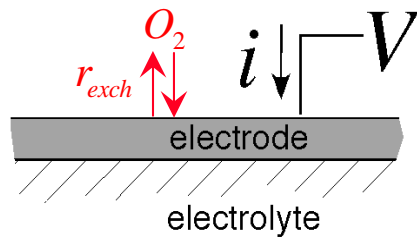


$$r = k\left(\frac{P_{O_2}}{f_{O_2}^{1/2}} - f_{O_2}^{1/2}\right)$$

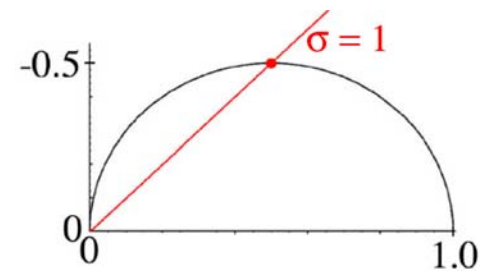
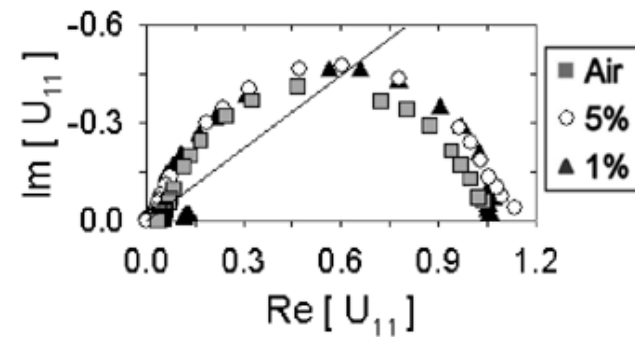
$$r_{exch} = kP_{O_2}^{1/2}$$

Limitations of linearized rate measurements

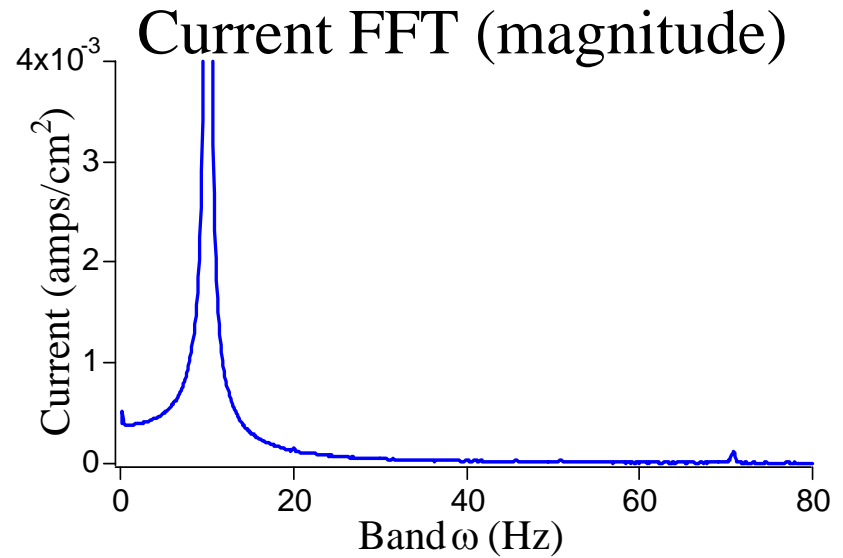
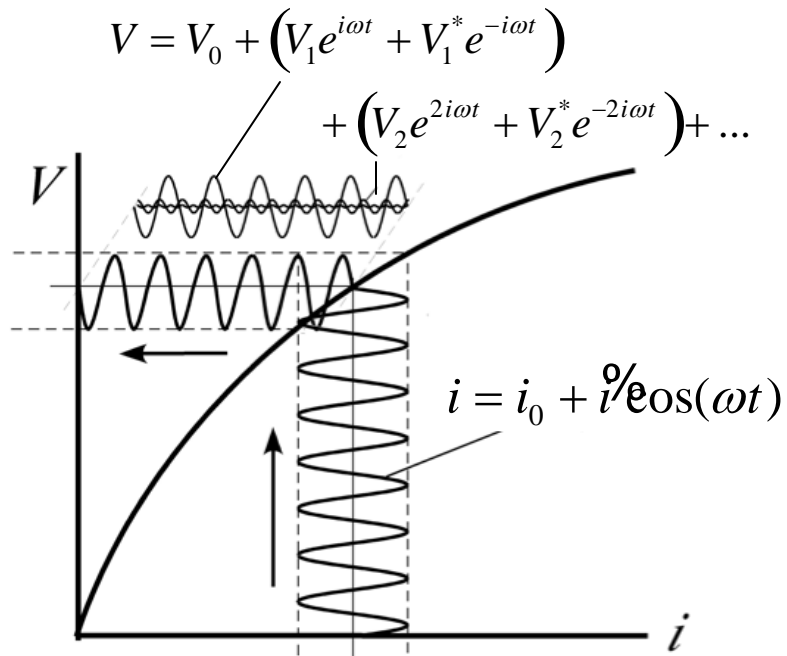
What mechanism explains a power-law P_{O_2} dependence?



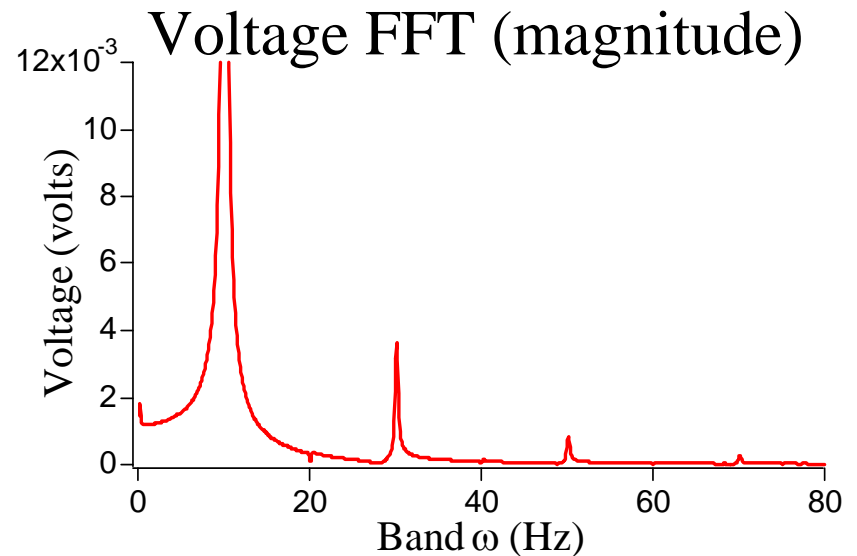
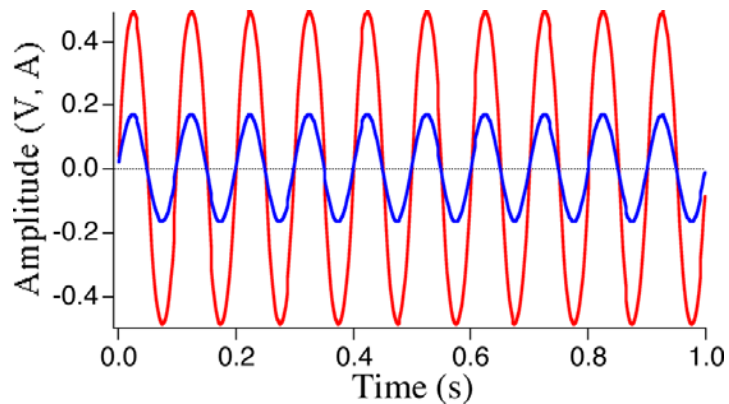
EIS data lack mechanism-specific characteristics



Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)

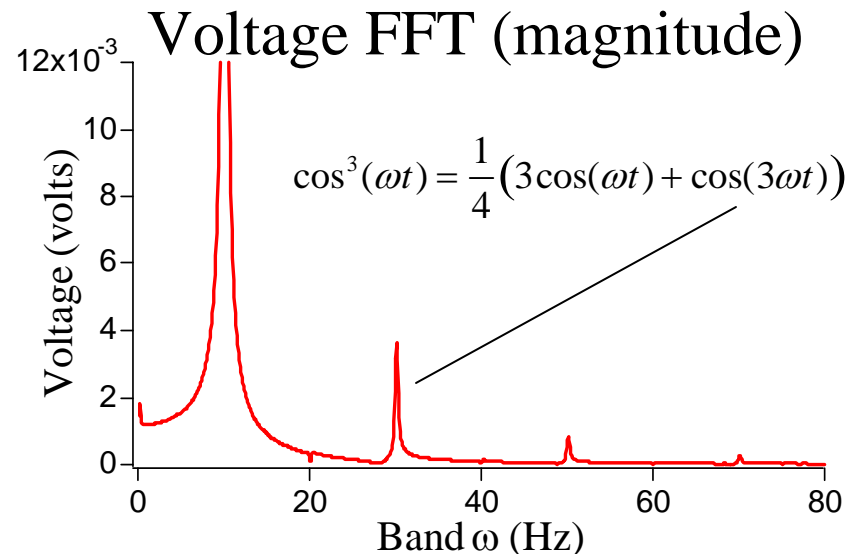
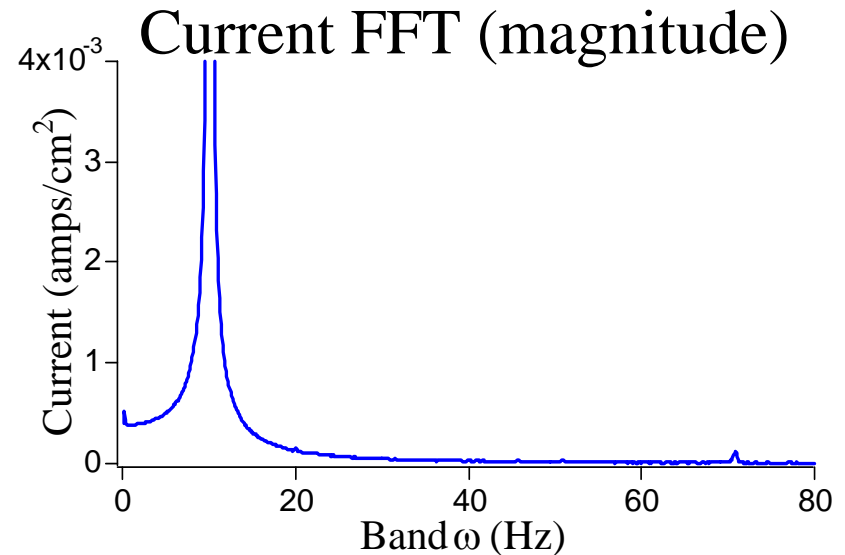


LSF/ceria/LSF cell at 750°C in air (10 Hz)

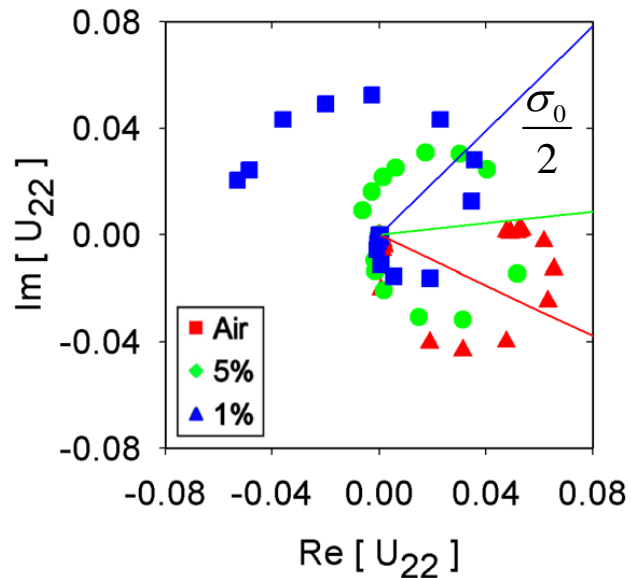


Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)

- Magnitude, sign, and phase of the higher harmonics are tied to nonlinearities of the underlying physics.
(analogy: music).
- Small nonlinearities appear as separate peaks, allowing precise quantification.
- Noise and systematic errors uncorrelated to the input perturbation are automatically filtered.

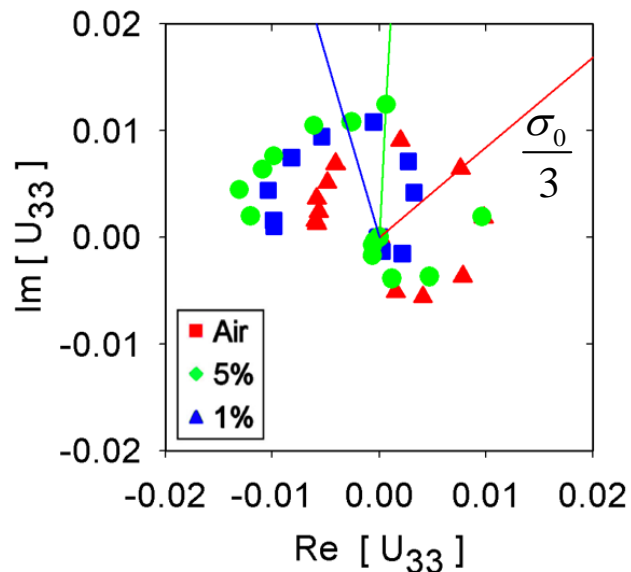


Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. P_{O_2}



Observations:

- The harmonic signals are small - difficult to isolate by other means.
- Unlike EIS, higher harmonics are sensitive to changes in P_{O_2} .



How do we interpret the harmonic response in terms of mechanism?

Sources of Nonlinearity in a Mixed Conducting Oxide Film

$$r = \Re_0 \left(P_{O_2}^{gas}, f_{O_2}^{solid} \right) \left\{ 1 - e^{\frac{-\Lambda}{RT}} \right\}$$

$\delta(f_{O_2}^{solid})$ obeys rigid band model

$$-\frac{1}{2} \frac{\partial \ln f_{O_2}^{solid}}{\partial \ln \delta} = 1 + \frac{4\delta}{g_0 RT}$$

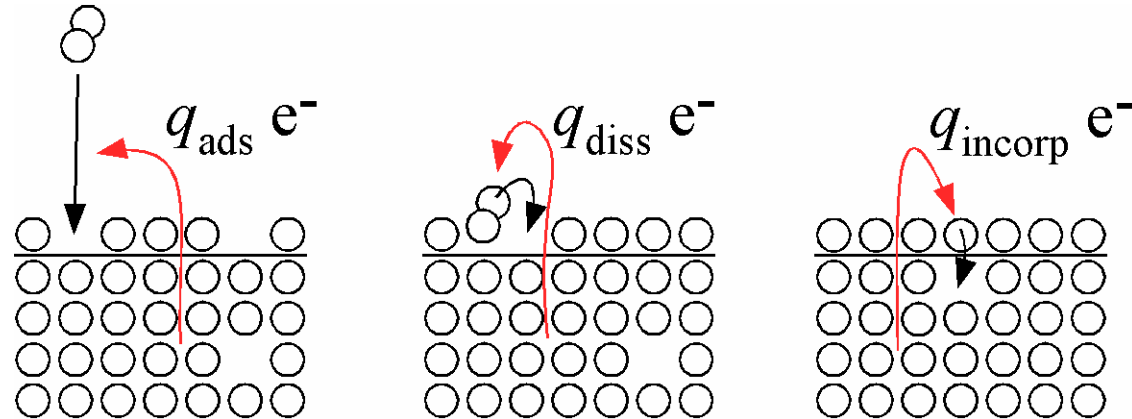
$O_2 + 4e^- + 2V_o \rightleftharpoons 2O^{2-}$

V

O^{2-} mixed-conducting film

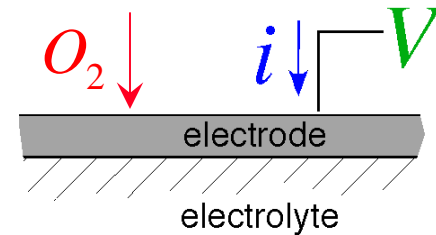
O^{2-} electrolyte

Possible rate-limiting elementary steps

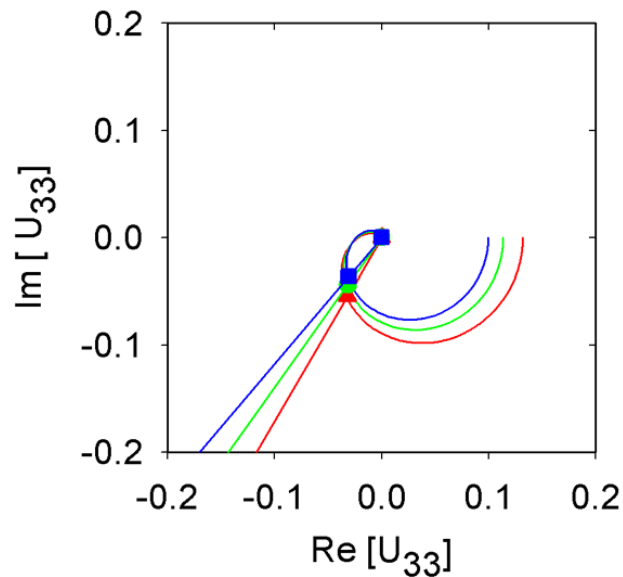
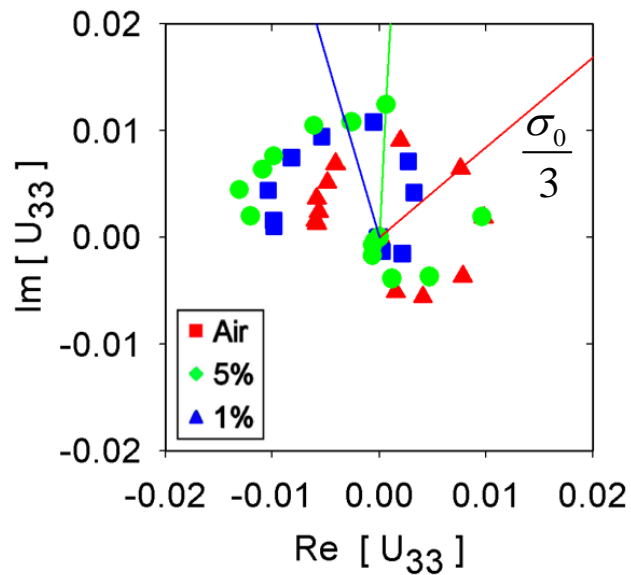
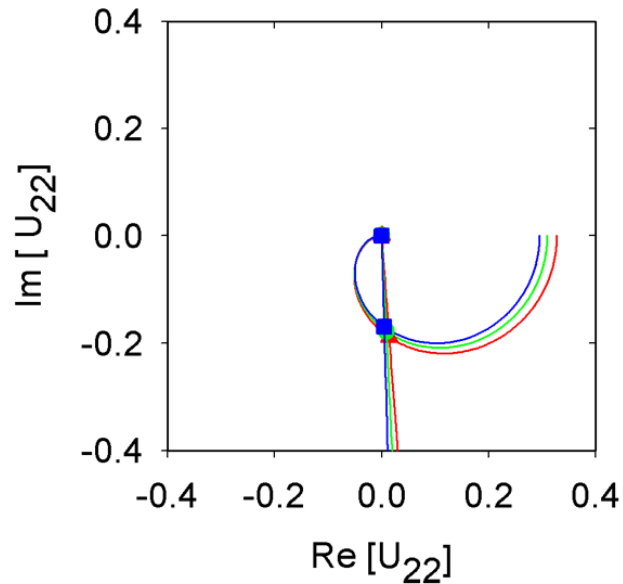
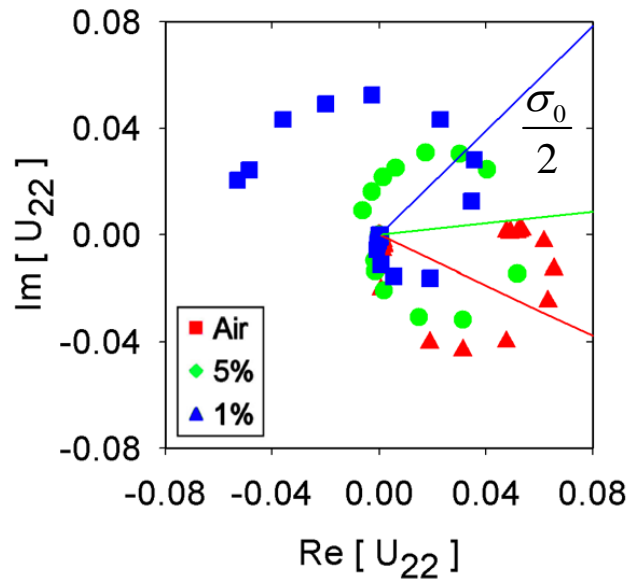


$$\frac{Lc_o}{3} \frac{d\delta}{dt} = -\frac{i_{\text{cos}}(\delta)}{2F} - 2R_0 \left[1 - e^{\frac{-\Lambda}{\lambda RT}} \right]$$

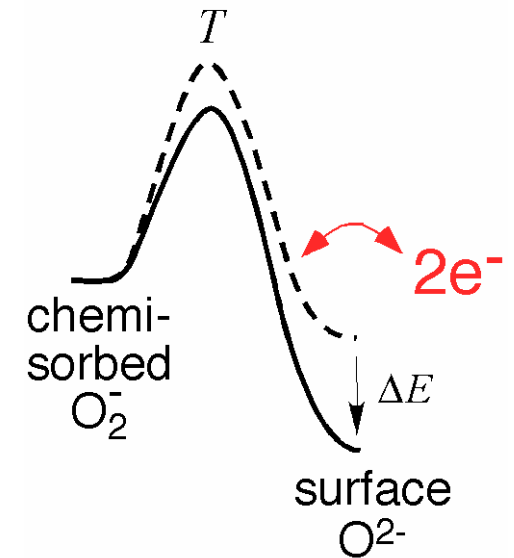
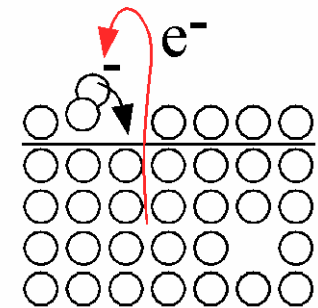
$$V = \frac{RT}{4F} \ln \frac{f_{O_2}(\delta)}{P_{O_2}^{(\text{gas})}}$$



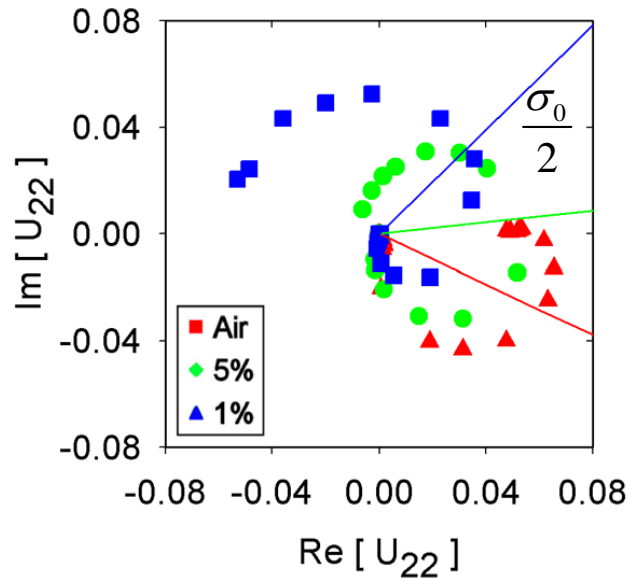
Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. P_{O_2}



Model:
charge-transfer-
limited dissociation

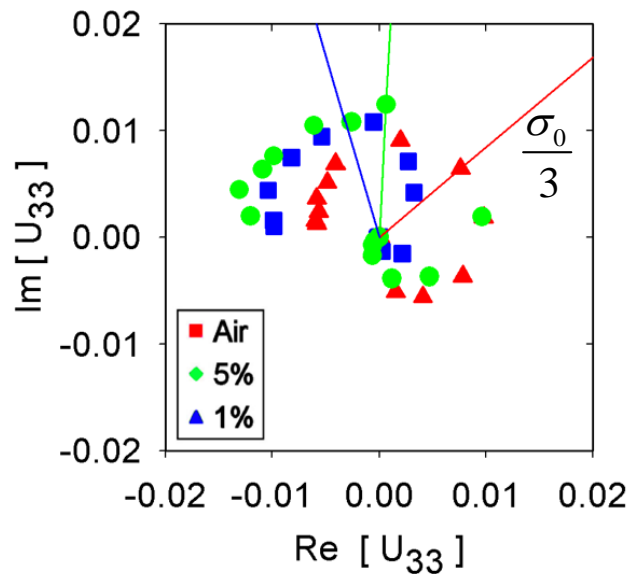


Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. P_{O_2}

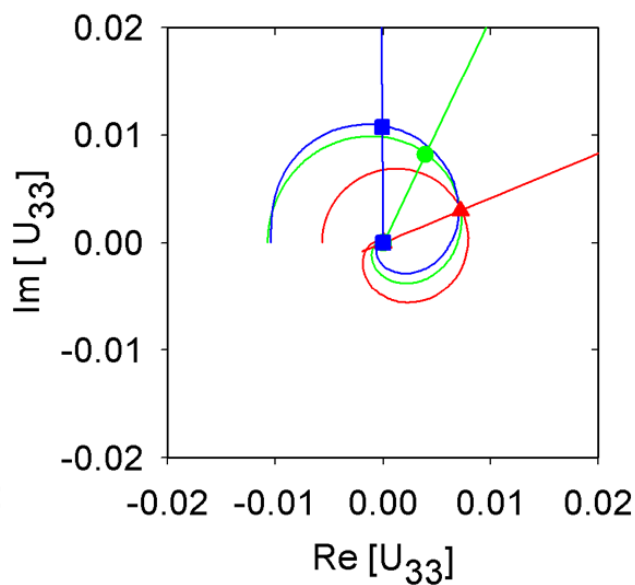
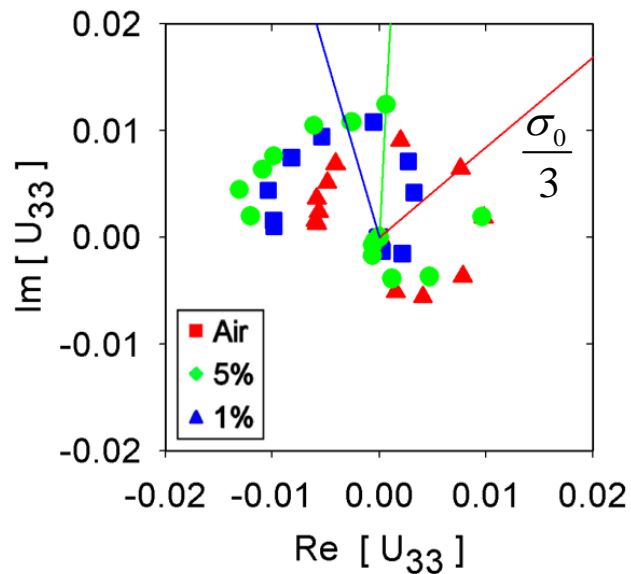
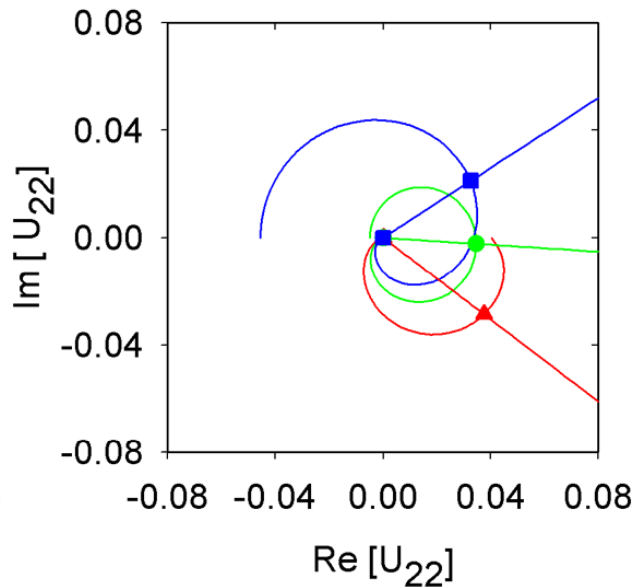
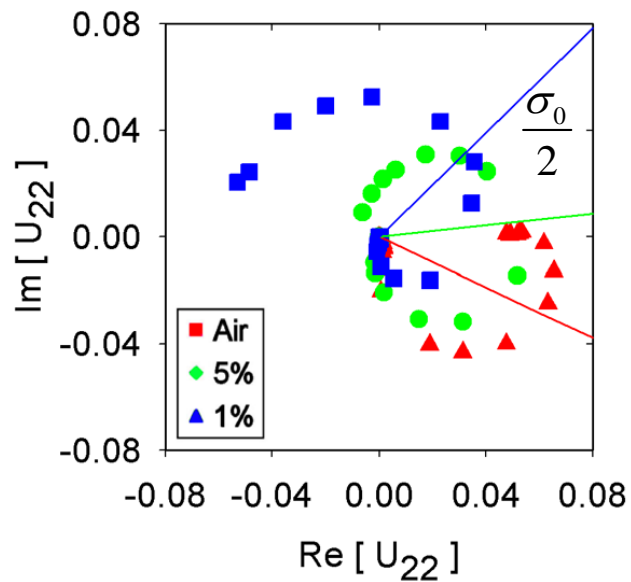


Possible rate limiting phenomena

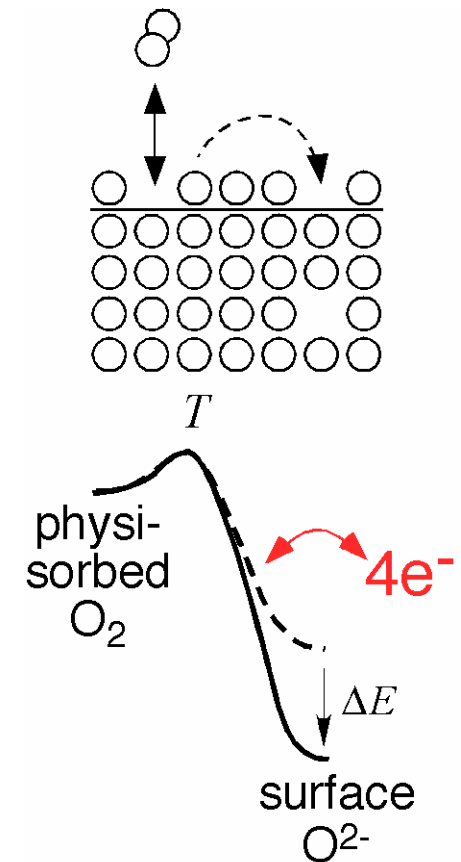
- ~~• dissociation of chemisorbed intermediate~~
- ~~• molecular adsorption~~
- ~~• atomic incorporation into solid~~



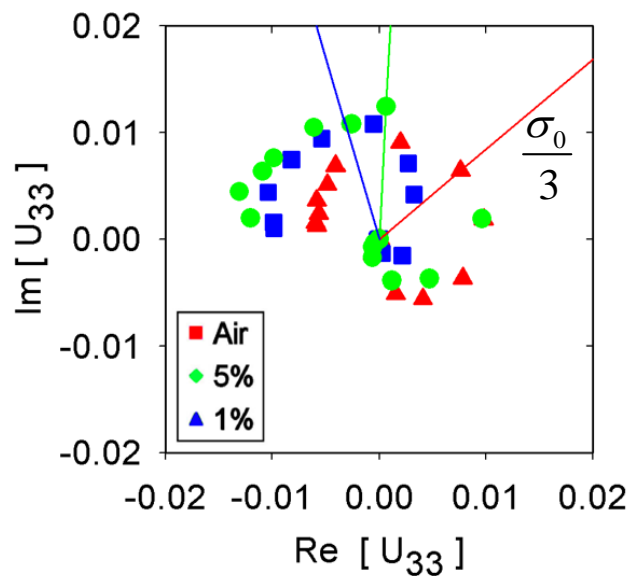
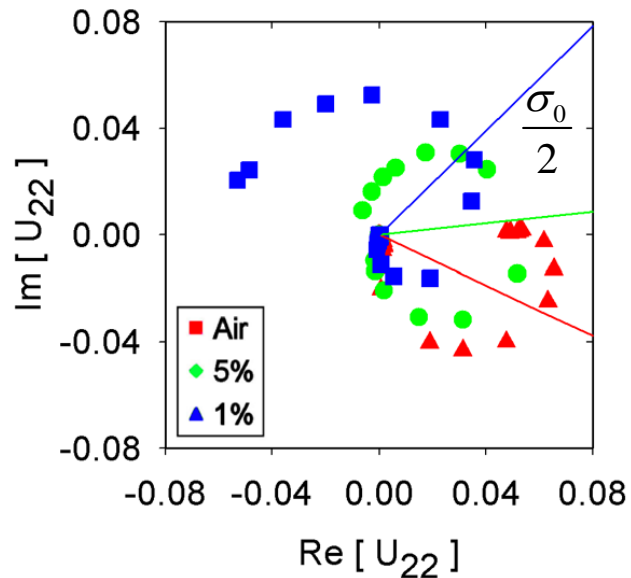
Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. P_{O_2}



Model:
dissociative-
adsorption limited

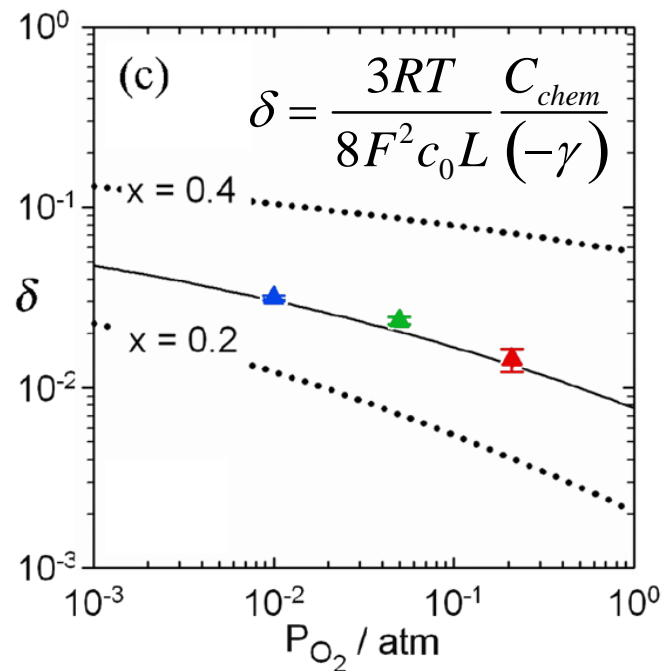


Harmonic Response of a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{3-\delta}$ film on Gd-doped ceria at 725°C vs. P_{O_2}

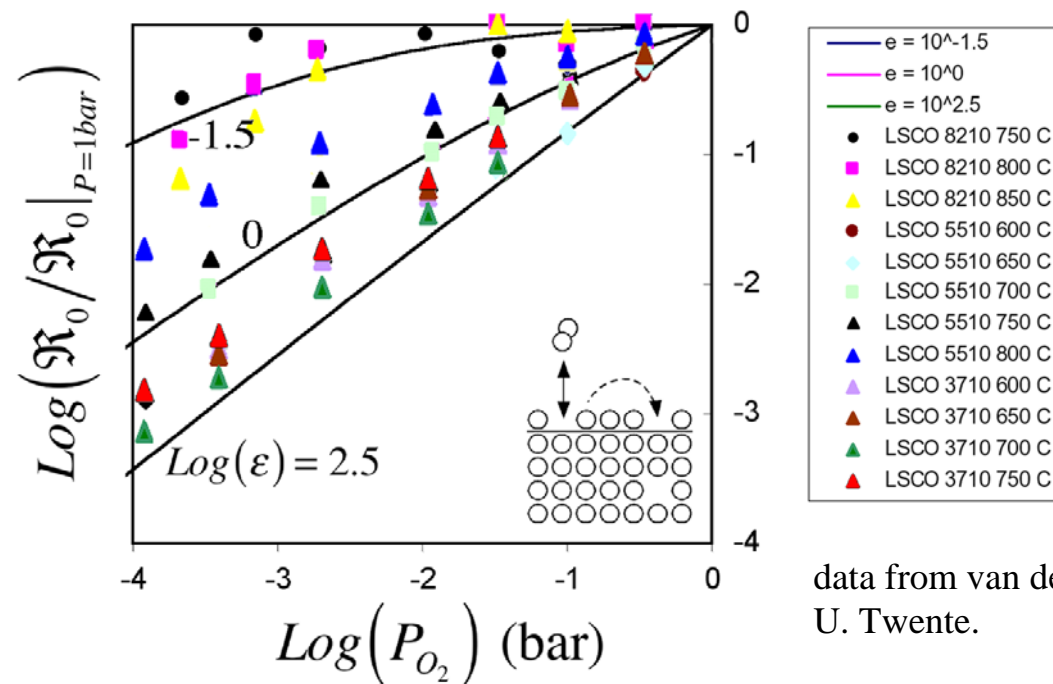
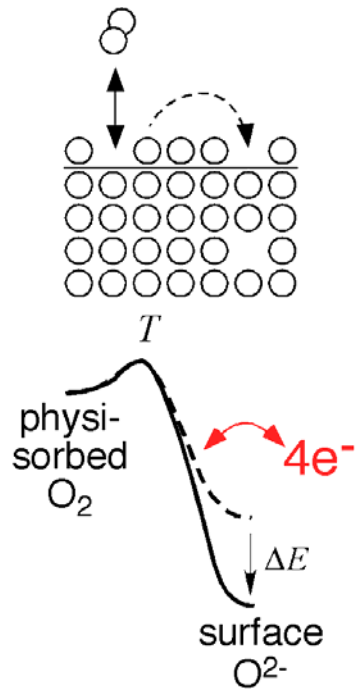


$$\gamma = \frac{\partial \ln \delta}{\partial \ln P_{\text{O}_2}} = -0.27 \sim -0.23$$

Nonstoichiometry calculated from the thermodynamic factor



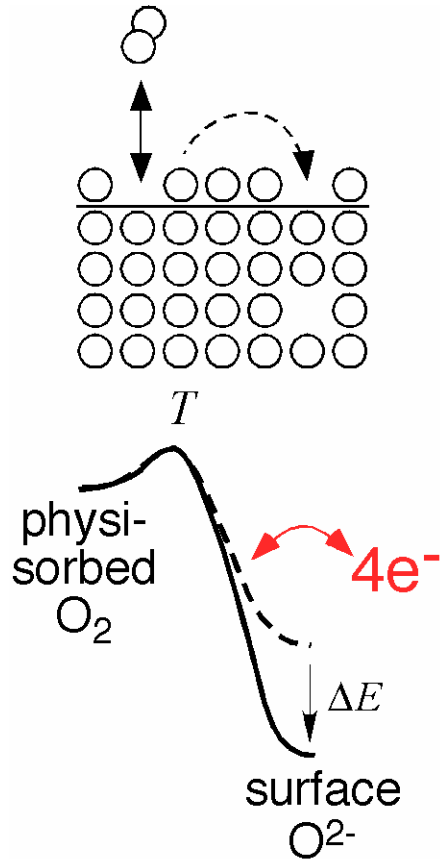
Consistency with equilibrium exchange rates



data from van der Haar *et al*,
U. Twente.

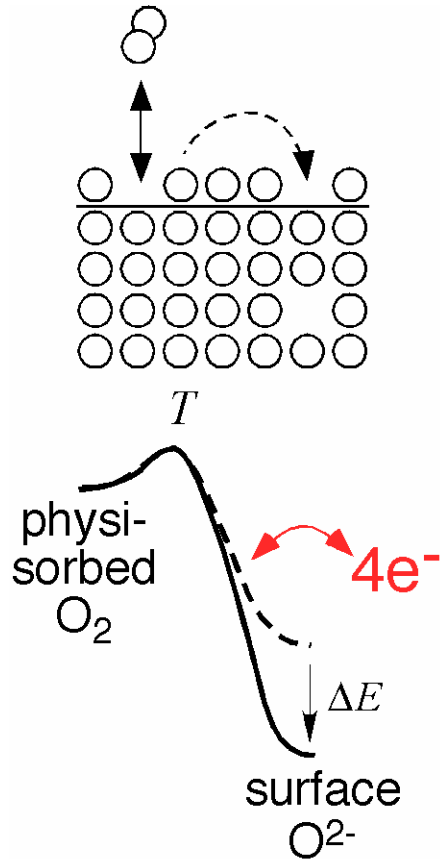
- Dissociative adsorption explains O_2 exchange measurements on bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ over a wide range of x , T and P_{O_2} .

Physical Interpretation of the Observed Kinetics



- The bottleneck is not charge-transfer - reaction is limited by adsorbate lifetime and configurational probability.
- A strong Arrhenius dependence does not imply an activation barrier! In this case a strong T dependence arises from a large negative enthalpy of adsorption.
- O_2 exchange “power law” varies from zeroth to first order, depending on thermodynamic conditions.

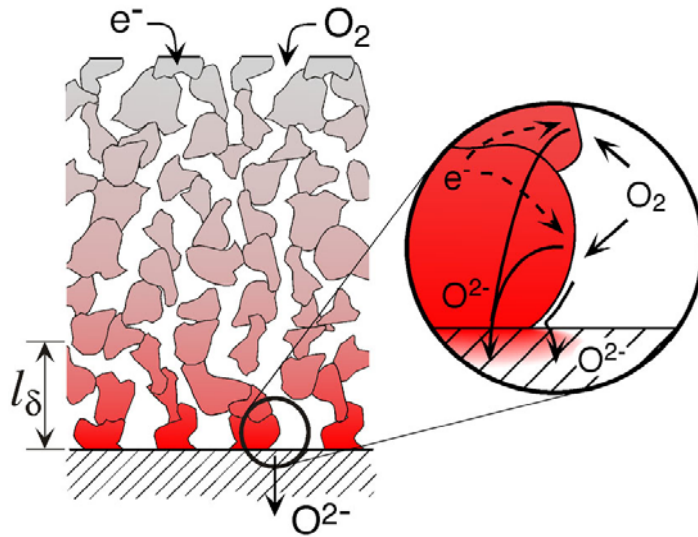
Physical Interpretation of the Observed Kinetics



Possible implications for porous electrodes

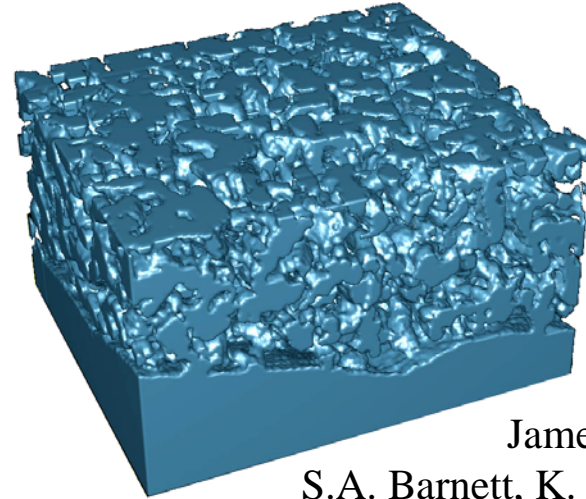
- Surface and bulk are in equilibrium, even though gas and surface are not.
- Any surface diffusion is downstream of reaction barriers.
- No further reduction occurs at the TPB (only ion transfer).

Extension to porous $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ electrodes



macrohomogeneous model

- microstructure described in terms of average porosity and area (ε , a).
- requires $l_\delta \gg d_p$.

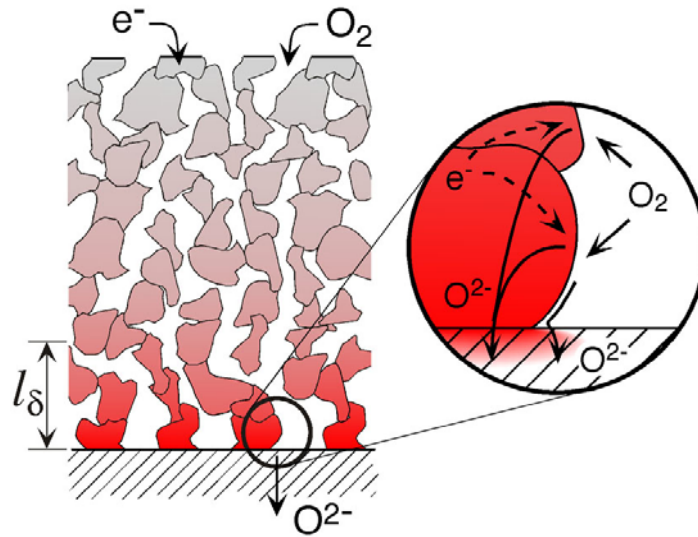


James Wilson
S.A. Barnett, K. Thornton

3-dimensional model

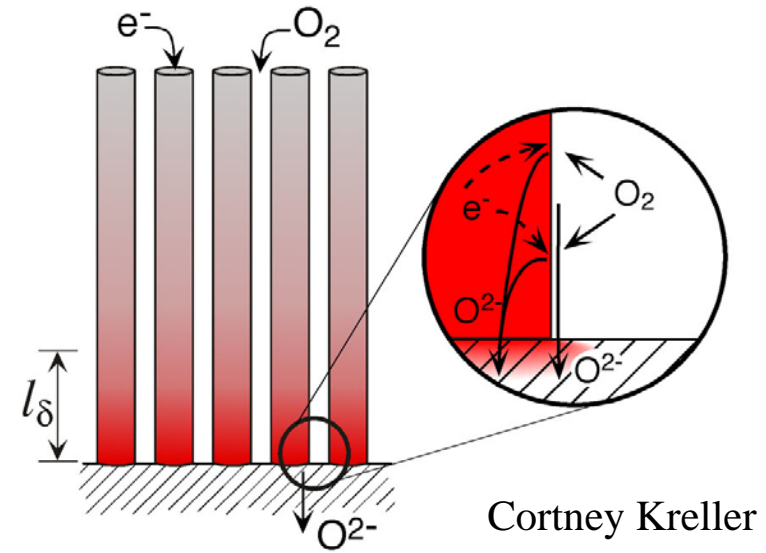
- measured microstructure represented by continuous finite element domain.
- can model 3-D gradients.

Extension to porous $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ electrodes



macrohomogeneous model

- microstructure described in terms of average porosity and area (ε , a).
- requires $l_\delta \gg d_p$.

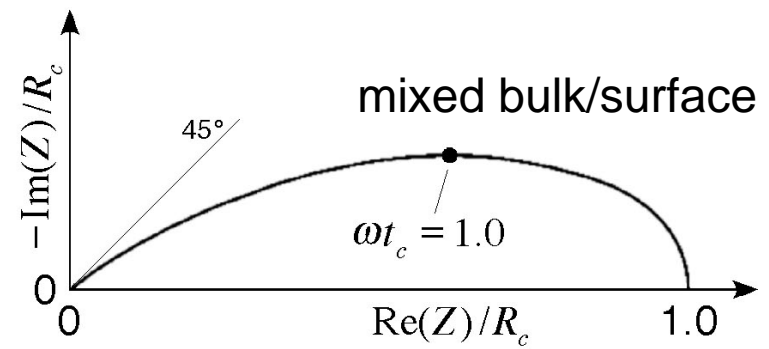
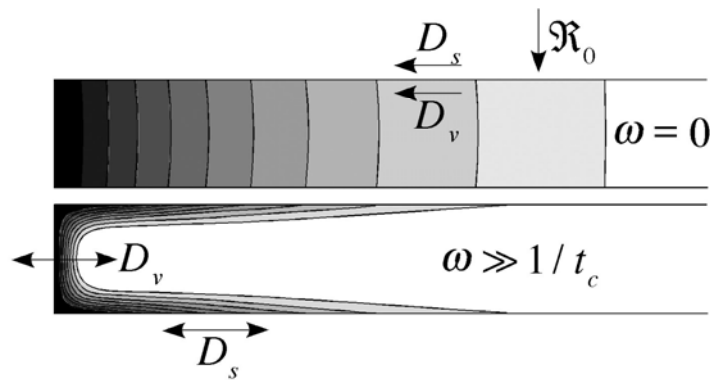
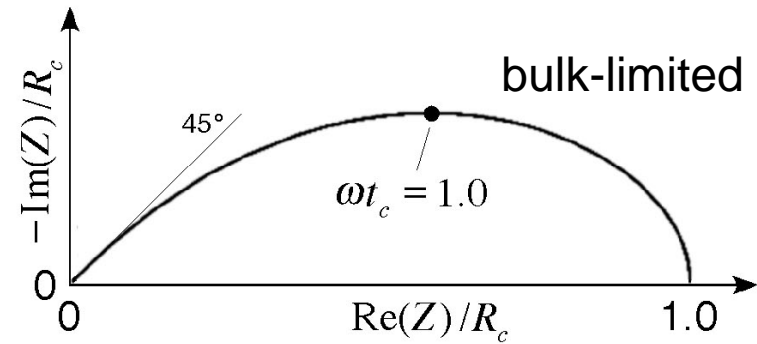
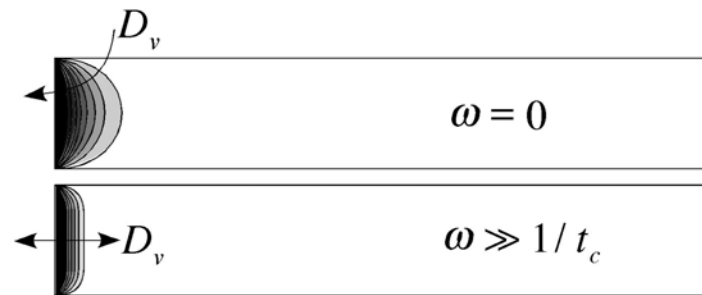
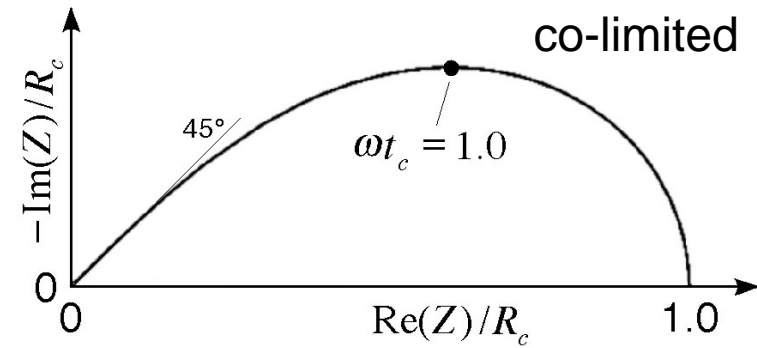
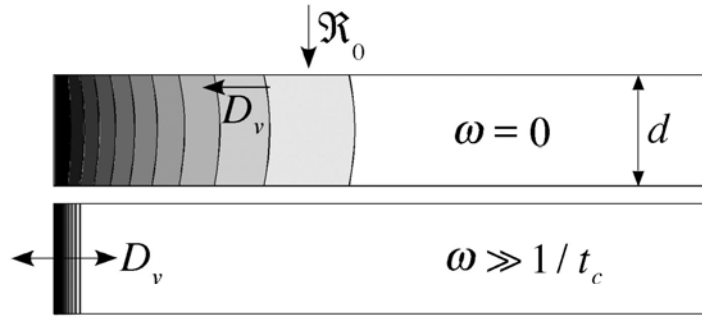


Cortney Kreller

pseudo 3-dimensional model

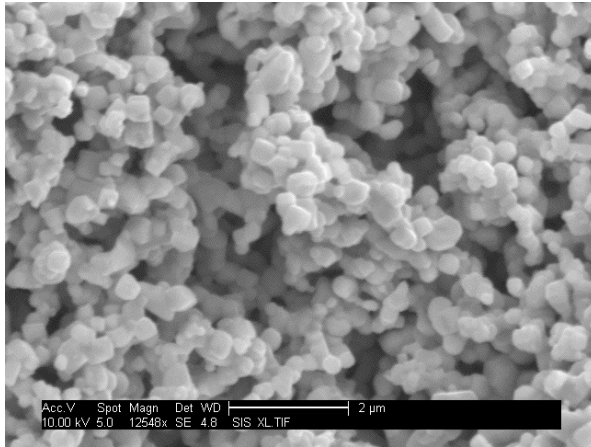
- microstructure replaced by simplified structural elements having same ε , a .
- can model 2-D gradients.

Extension to porous $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ electrodes

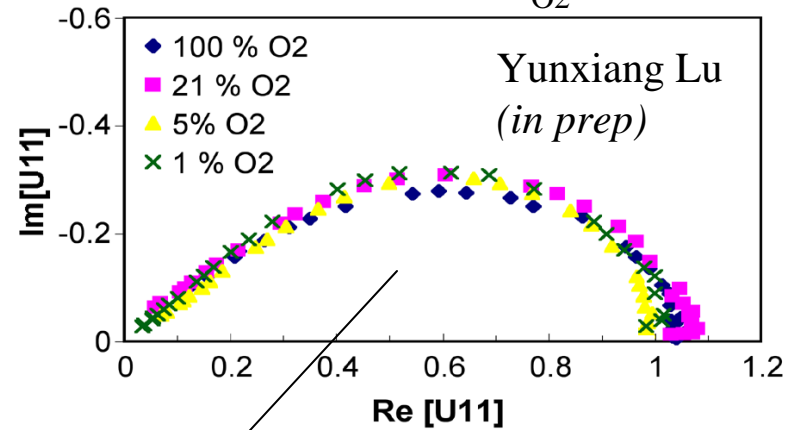


Extension to porous $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ electrodes

$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ on SDC
(sintered at 1000°C)



1st harmonic (impedance) of
porous LSC-82 on SDC at
 725°C vs. P_{O_2}



model

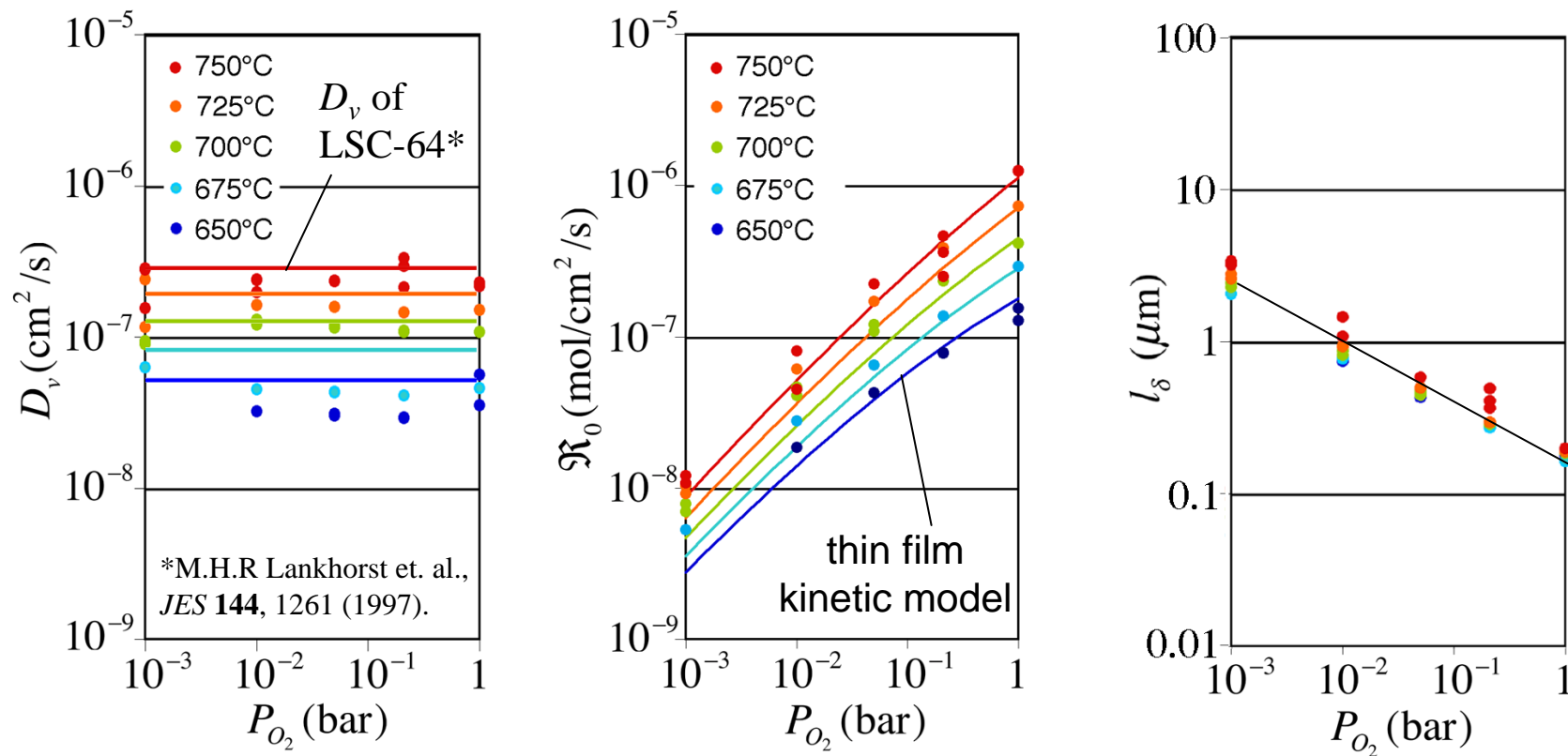
data

$$\begin{bmatrix} R_c \left(\mathfrak{R}_0, D_v, D_s(T), \delta(x, T, P_{\text{O}_2}), \begin{Bmatrix} \varepsilon \\ a \end{Bmatrix} \right) \\ t_c \left(\mathfrak{R}_0, D_v, D_s(T), \delta(x, T, P_{\text{O}_2}), \begin{Bmatrix} \varepsilon \\ a \end{Bmatrix} \right) \end{bmatrix} = \begin{bmatrix} R_c(x, T, P_{\text{O}_2}) \\ t_c(x, T, P_{\text{O}_2}) \end{bmatrix}$$

Possible surface diffusion mechanisms:

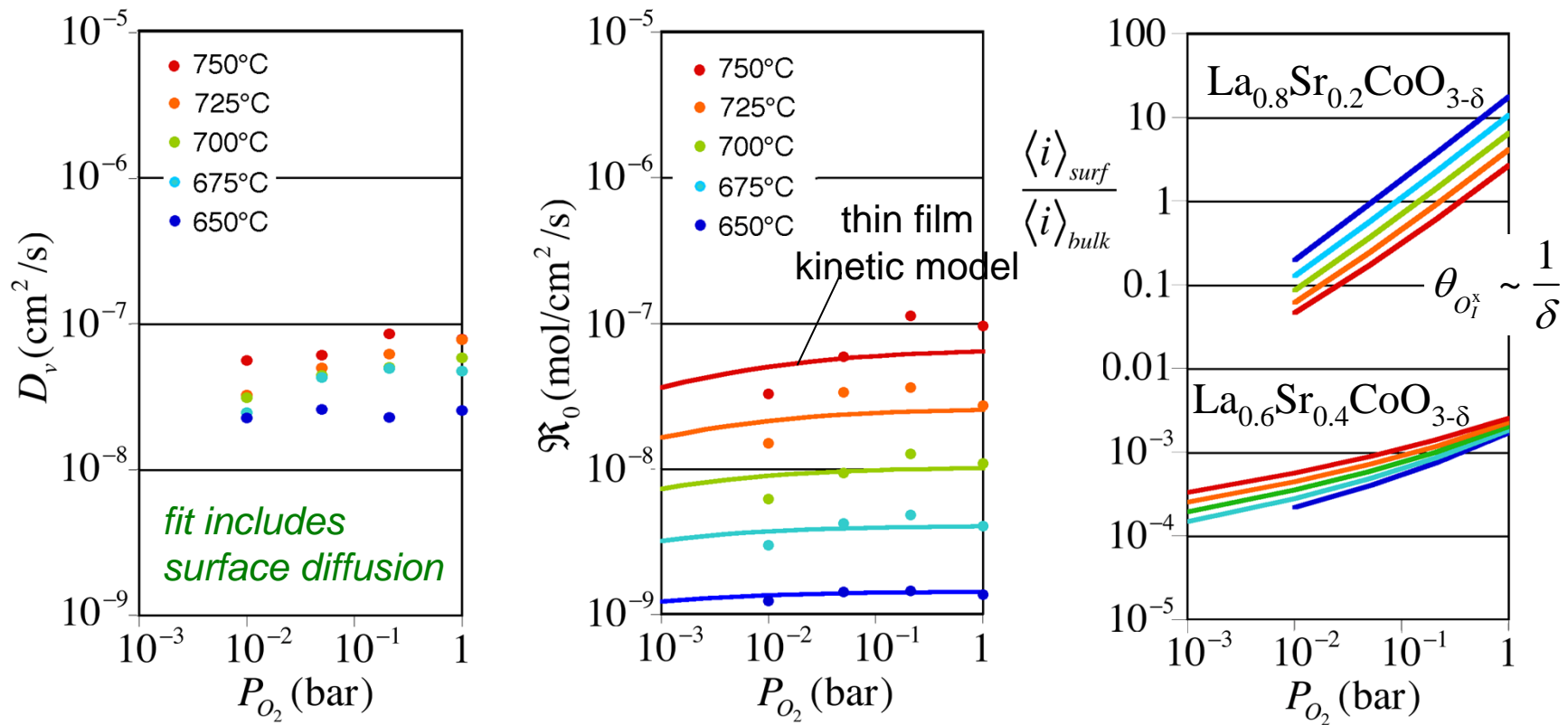
- oxygen vacancies
- oxide ion interstitials

Results: Impedance of Porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$



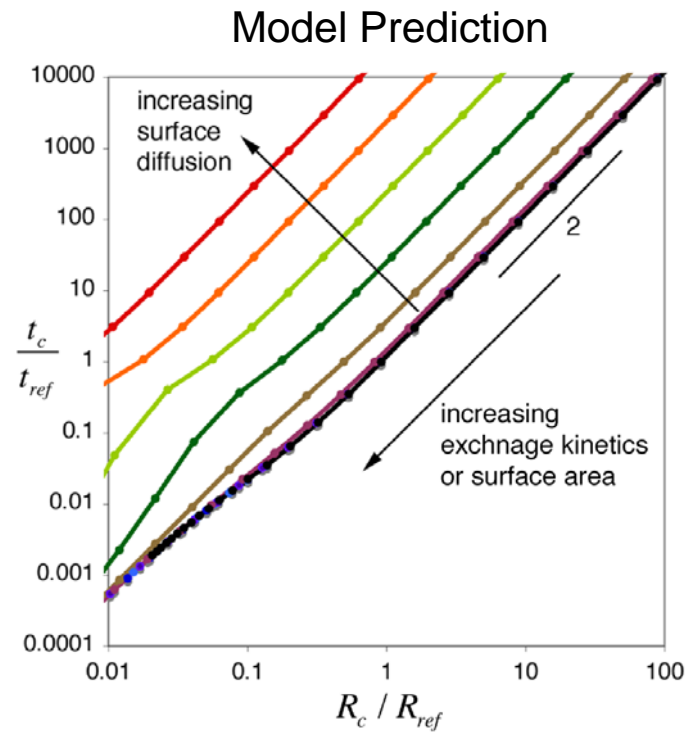
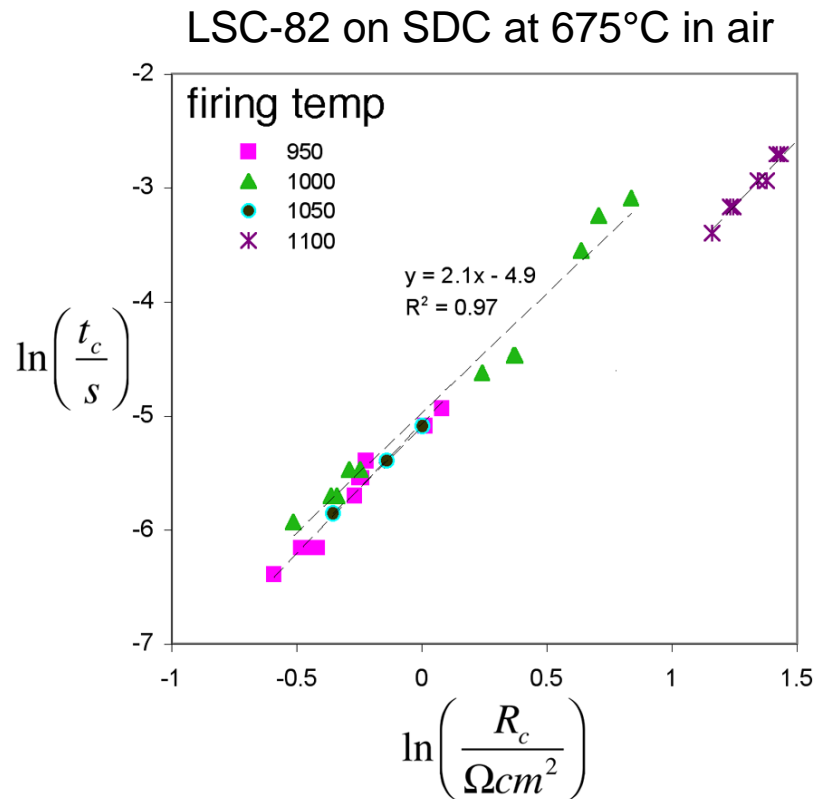
- Bulk transport dominates; D_v matches independent measurement.
- Apparent exchange kinetics match thin film within a scaling factor.
- Utilization region is sub-micron under typical IT-SOFC conditions.

Results: Impedance of Porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$



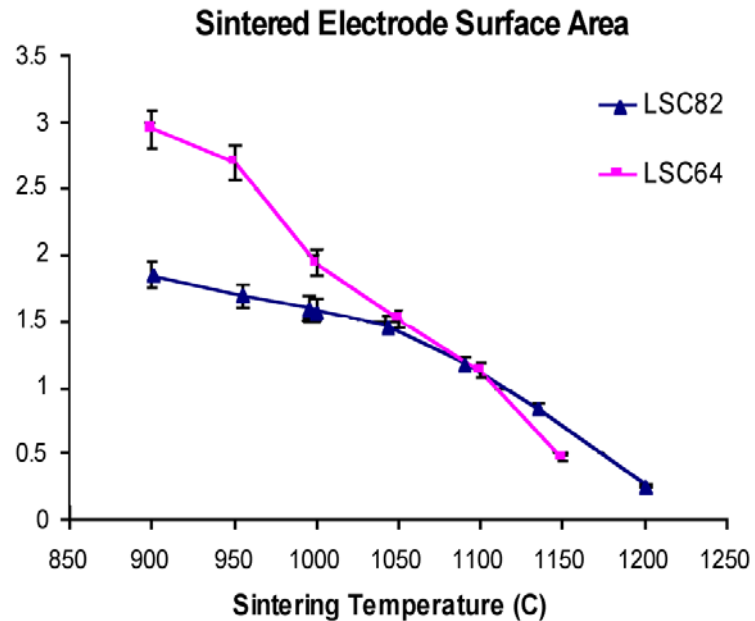
- Must include surface diffusion to yield reasonable values of D_v .
- Apparent exchange kinetics match thin film within a scaling factor.
- Surface diffusion plays a significant role under IT-SOFC conditions and appears to occur by an “interstitial” mechanism (?!).

Results: Electrode Firing Temperature

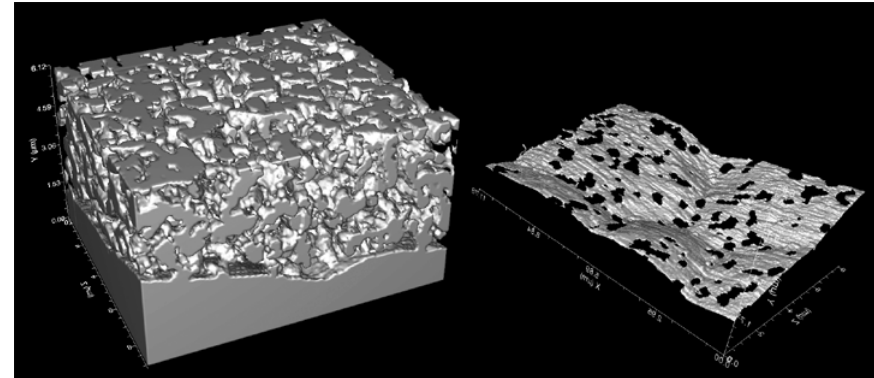


- Above ~950°C, increased firing temperature reduces performance.
- $t_c \sim (R_c)^2$ scaling implies reduced surface area or exchange kinetics.

Results: Electrode Firing Temperature



FIB-SEM reconstruction and analysis

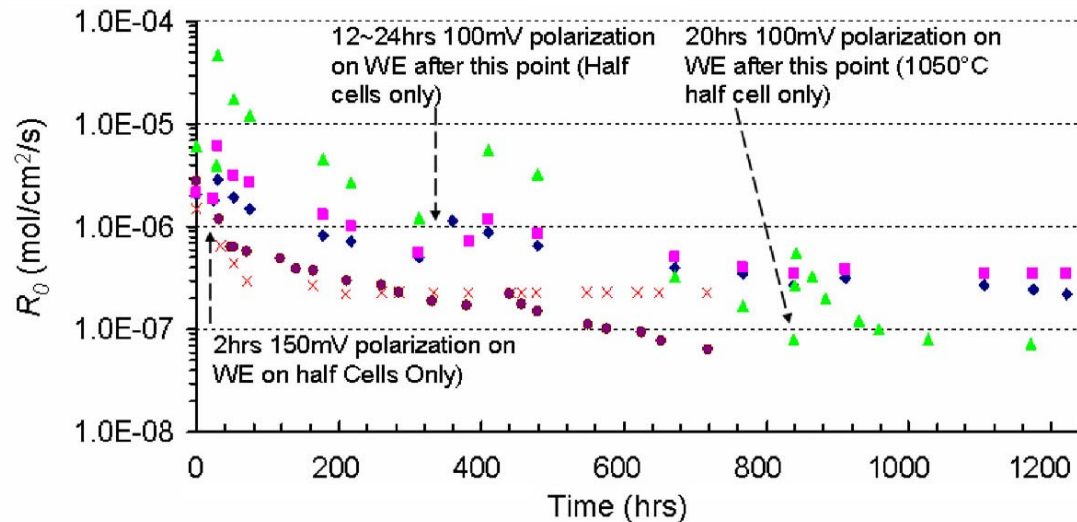
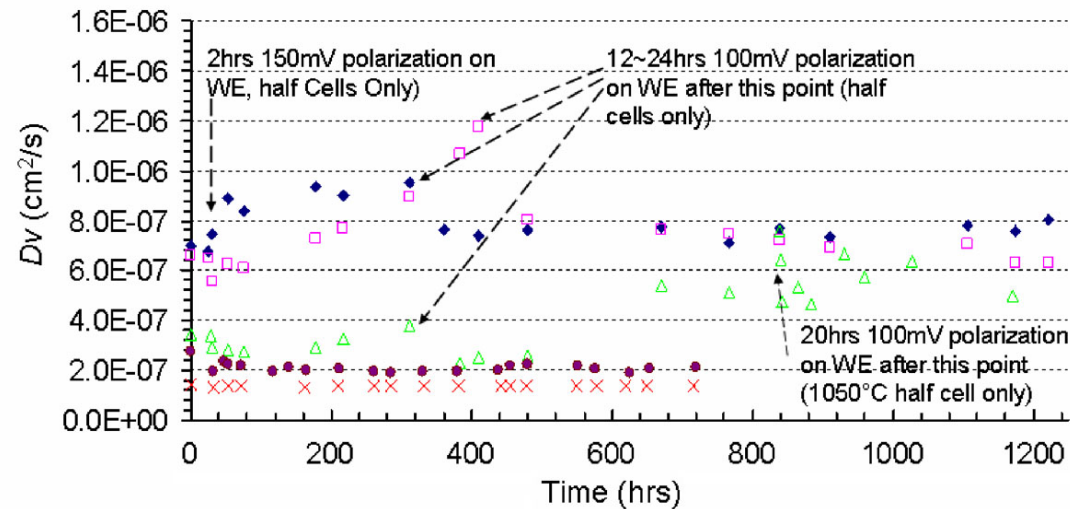


Firing Temp.	Porosity	Volumetric Surface Area	Fraction of Electrolyte Bonded to LSC	Tortuosity for Bulk Ion Transport in LSC	Tortuosity for Gas-Phase Mass Transfer
950/4C	42 %	2.7 μm^{-1}	22 %	1.4	1.6
1100/4C	46 %	2.8 μm^{-1}	21 %	1.3	1.7

- Changes in surface area cannot explain the 50x variation in rate.
- Sample variability is much greater than effect of firing temperature.
- Firing conditions appear to influence catalyst chemistry much more significantly than morphology.

Results: Electrode Degradation

Degradation of various LSC-82 cells in air at 750°C.



Electrode degradation also appears to be tied to surface kinetics.

Summary

- The rate of O_2 reduction on $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) has been isolated from other rates using thin film electrodes and NLEIS, and used to rationalize porous electrode performance using a mechanistic model.
- O_2 reduction on LSC appears to be limited by dissociative adsorption. This result explains previous O_2 exchange measurements vs. x , T , P_{O_2} , and also explains impedance of porous LSC electrodes over a wide range of conditions.
- Porous LSC electrodes are dominated by a bulk transport path at high vacancy concentration. Lower Sr doping and temperatures lead to significant involvement of surface transport at high P_{O_2} . Materials like LSM are almost certainly surface dominated.
- Surface catalytic activity is very sensitive to firing conditions and time (degradation). The origin of these effects appears to be mostly surface chemistry, not morphology. Further work that can identify changes in surface structure/composition is needed.

Acknowledgements

University of Washington

Jamie Wilson (PhD student, ChE)
Dinesh Baskar (PhD student, ChE)
Cortney Kreller (PhD student, ChE)
Dan Schwartz (Faculty, ChE)

Tohoku University

Maya Sase (PhD student, Tohoku)
Tatsuya Kawada (Faculty, Tohoku)

Northwestern/University of Michigan

James Wilson (PhD student, Northwestern MSE)
Scott Barnett, Peter Voorhees (Northwestern MSE)
Hsun Yi (PhD student, Michigan MSE)
Roberto Mendoza, Katsuyo Thornton (Michigan MSE)

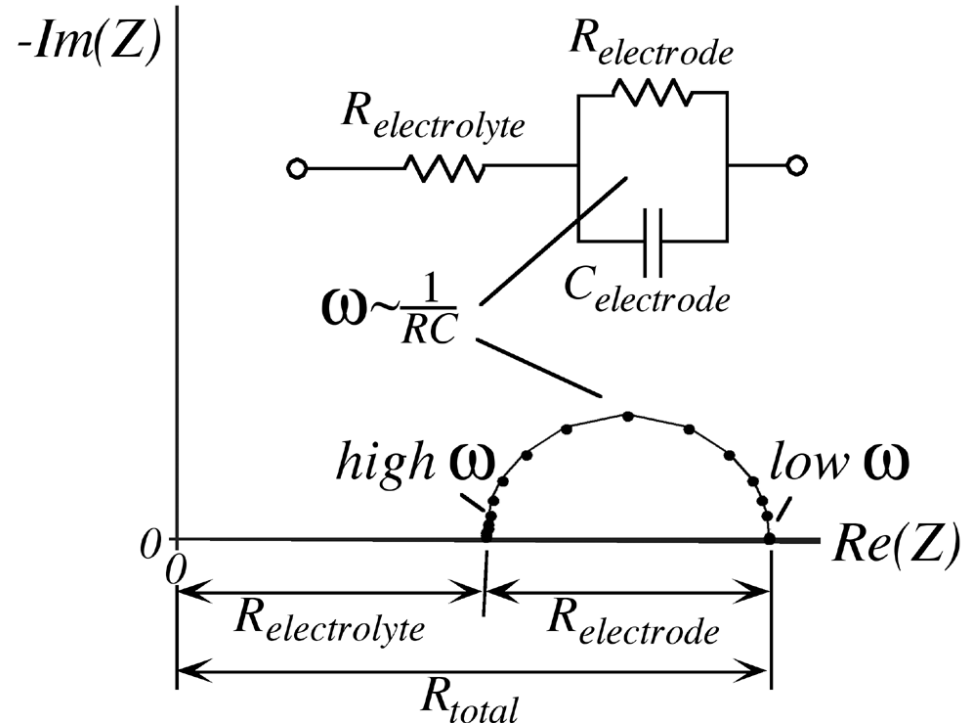
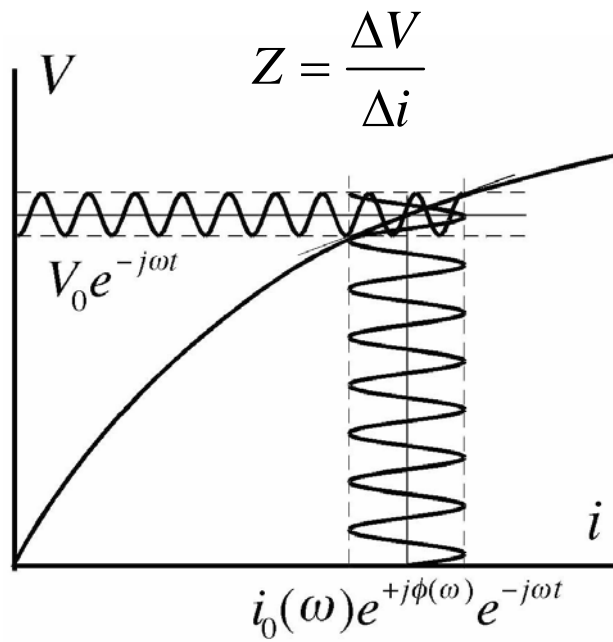
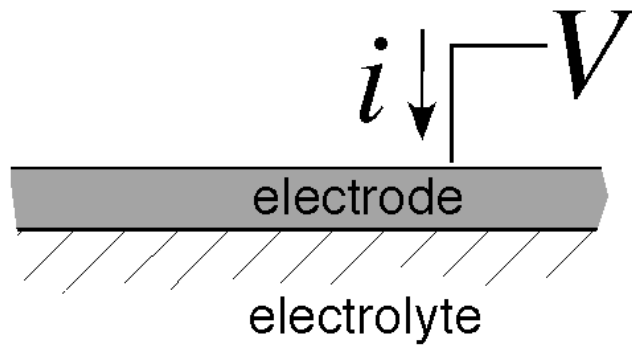
Support

DOE SECA Core Technology Program
NSF: DMR-Ceramics, CTS

Thank You

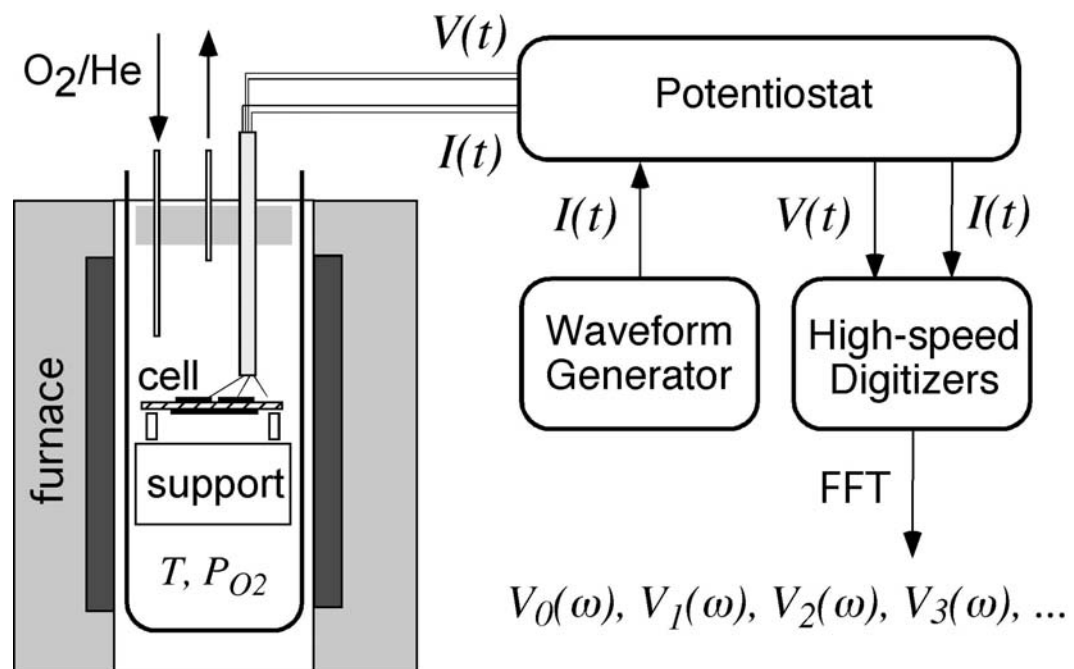


Electrochemical Impedance Spectroscopy (EIS)

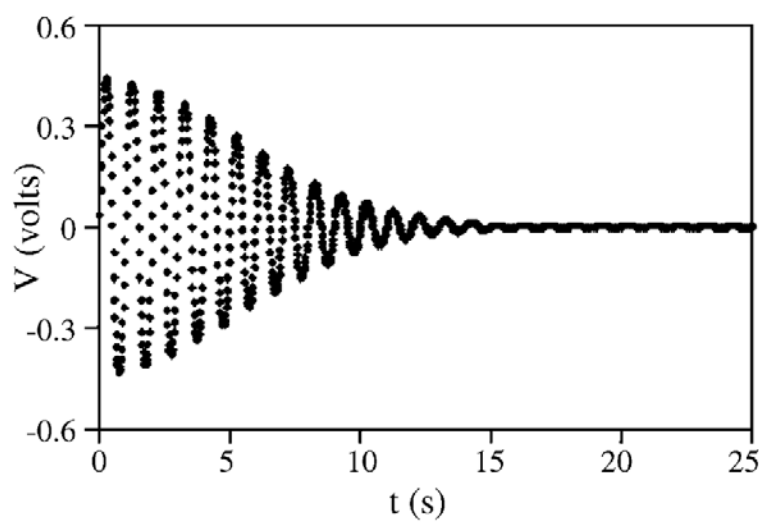


EIS probes **linearized rate** and **faradaic capacitance**.

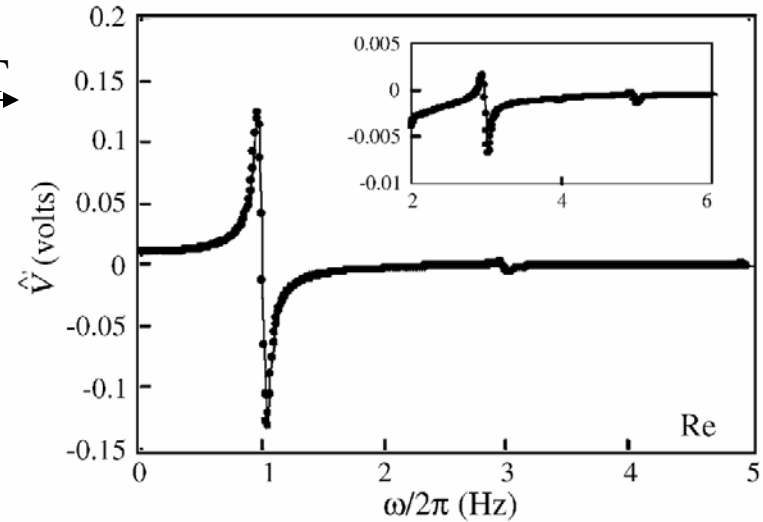
NLEIS measurements



Voltage Signal Involves both Amplitude and Phase Shift



FFT

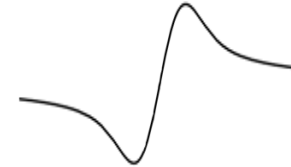
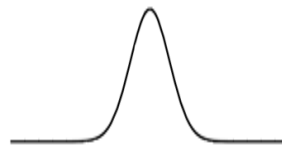


$$V(\alpha, \omega_0, t) = e^{-\frac{\omega_1^2 t^2}{4}} \sum_{k=1}^{\infty} \bar{V}_k(\alpha, \omega_0) e^{jk\omega_0 t} + \bar{V}_k^*(\alpha, \omega_0) e^{-jk\omega_0 t}$$

$$\bar{V}_k = \hat{V}_k + j\tilde{V}_k$$

FFT

$$\text{Re}(\bar{V}(\alpha, \omega_0, \omega)) = \sqrt{2} \sum_{k=1}^{\infty} \hat{V}_K(\alpha, \omega_0) \frac{e^{-\frac{(\omega \mp k\omega_0)^2}{\omega_1^2}}}{\omega_1} - \tilde{V}_K(\alpha, \omega_0) \frac{e^{-\frac{(\omega \mp k\omega_0)^2}{\omega_1^2}}}{\omega_1} \text{erfi}\left[\frac{\omega \mp k\omega_0}{\omega_1}\right]$$



Power Series Expansion of Harmonic Response

$$\bar{V}_1(\alpha, \omega_0) = \alpha \bar{V}_{1,1}(\omega_0) + \alpha^3 \bar{V}_{1,3}(\omega_0) + \alpha^5 \bar{V}_{1,5}(\omega_0)$$

$$\bar{V}_3(\alpha, \omega_0) = \alpha^3 \bar{V}_{3,3}(\omega_0) + \alpha^5 \bar{V}_{3,5}(\omega_0)$$

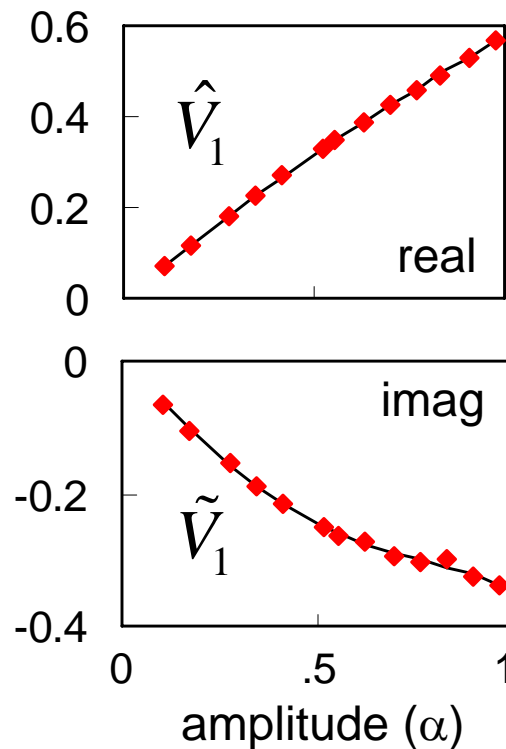
Least Squares Fit

$$\bar{V}_k = \hat{V}_k + j\tilde{V}_k$$

\hat{V}_k = Real Part
of the Response

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

First Harmonic:



Third Harmonic:

