Separating Rate-controlling Factors in Solid Oxide Fuel Cell Cathodes

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7th Annual SECA Workshop

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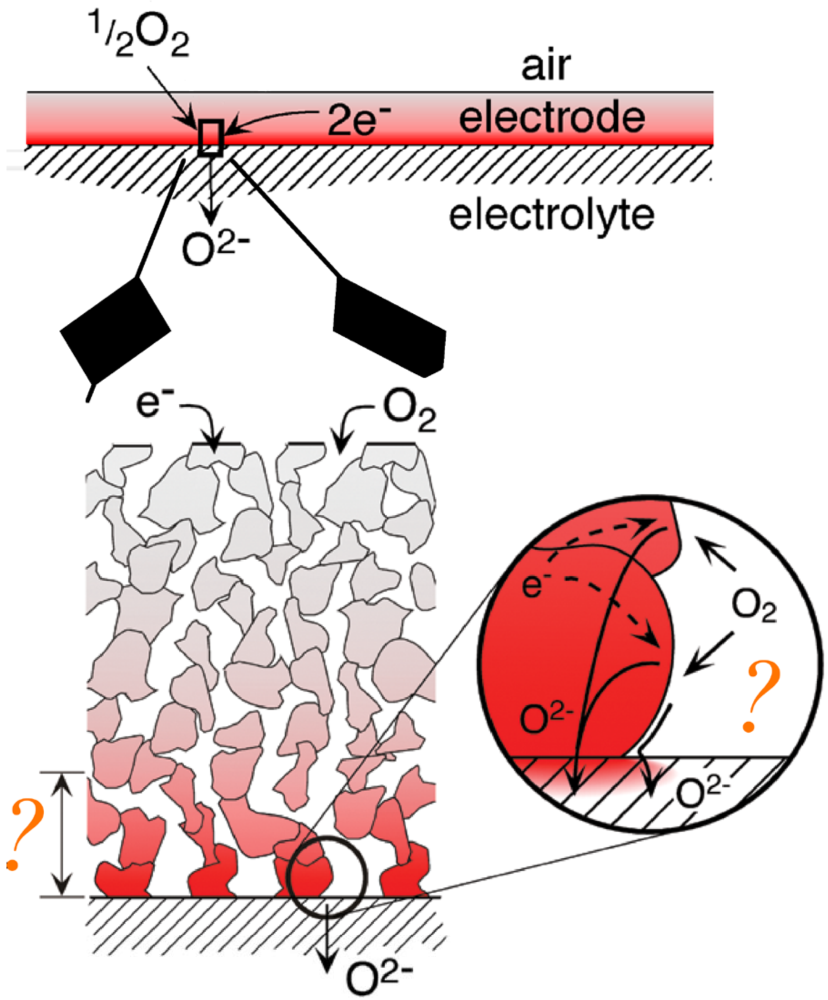
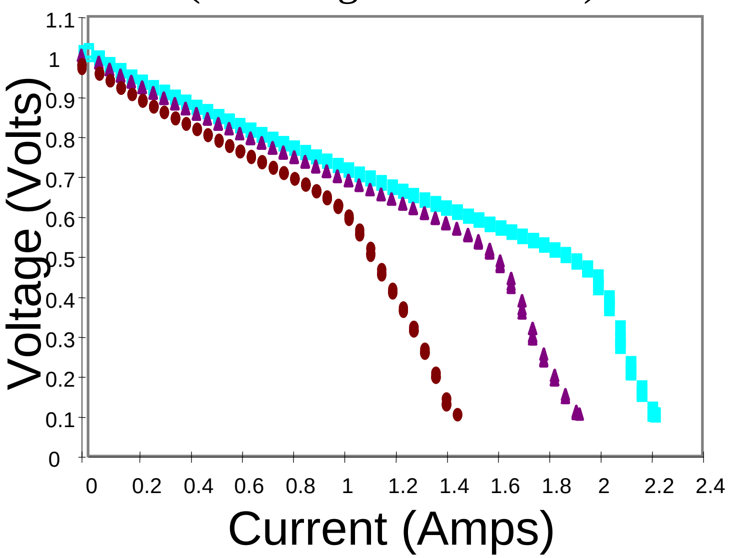
Support
SECA Core Technology Program
NSF: Chemical and Transport Systems, Collaborative Research (DMR-Ceramics),

What factors govern SOFC cathodes?



Why can't we just measure *i-V* characteristics vs. *T*, P_{O2}, etc., and then fit to a model?

PNNL button cell test*
(various gas conditions)



**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.

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

Why can't we just measure *i*-*V* characteristics vs. T, P_{O2}, etc., and then fit to a model?

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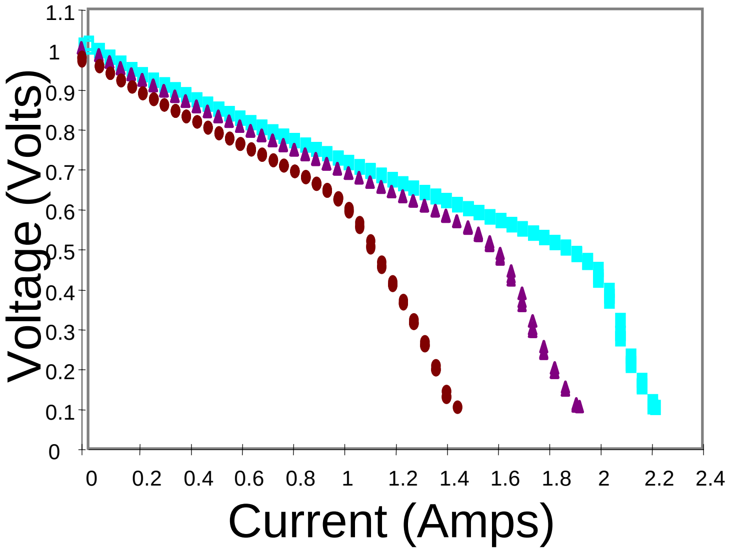

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Outline/Conclusions

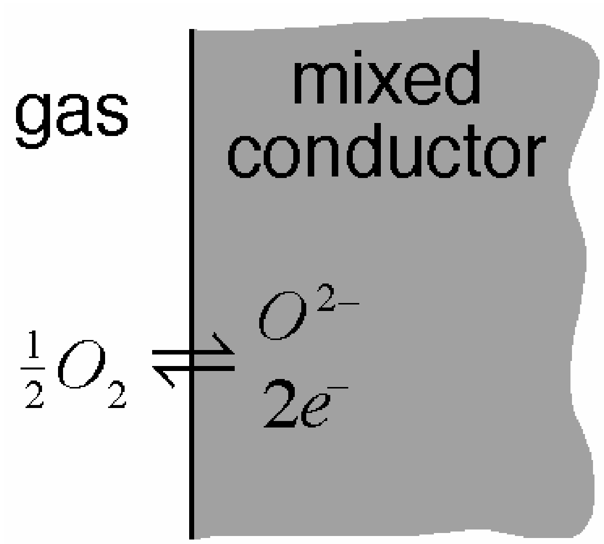
- ***Isolating O_2 reduction***: studies of $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) thin-film electrodes using nonlinear impedance.

    - 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 $La_{1-x}Sr_xCoO_{3-\delta}$ electrodes using FIB-SEM.

    - 3D microstructural data *may allow quantitative analysis of porous electrodes.*

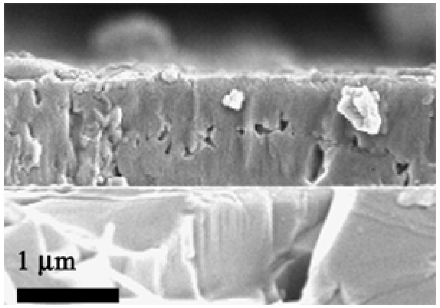
How does one isolate O_2 reduction rates?



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

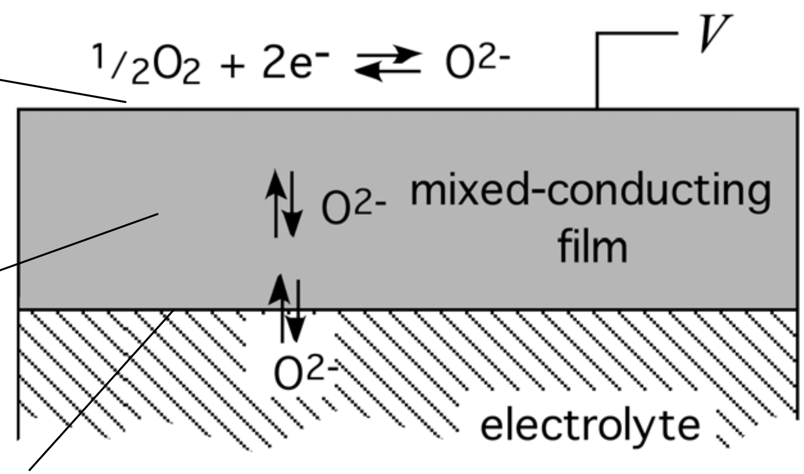


- Dense films of $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) made by pulsed laser deposition (500~1000 nm thickness)

- LSC (x=0.4) on polished polycrystalline Gd-doped ceria (Tohoku University)
- LSC (x=0.5) on single-crystal YSZ (University of Houston)

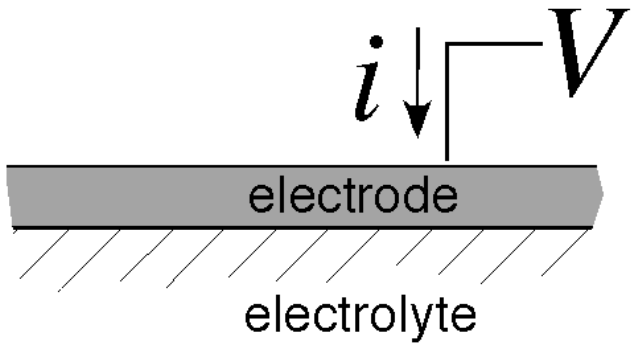
Resistance dominated by O_2 exchange kinetics

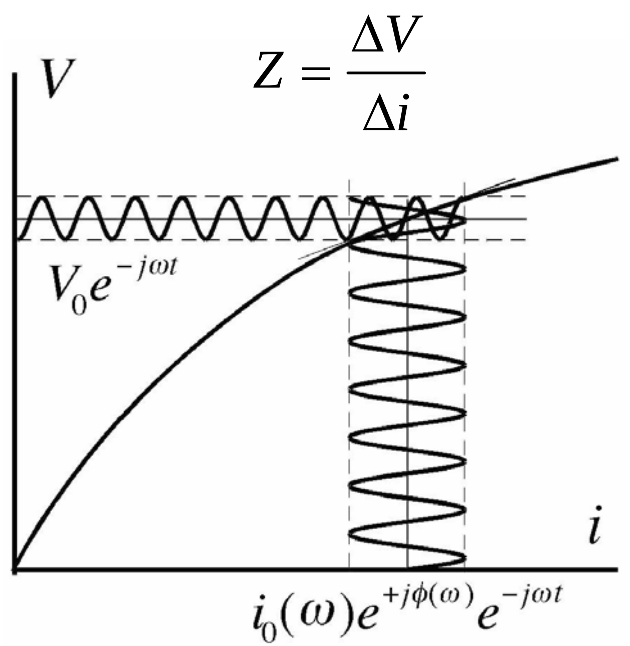
Diffusion is fast (film acts as well-mixed oxygen reservoir)

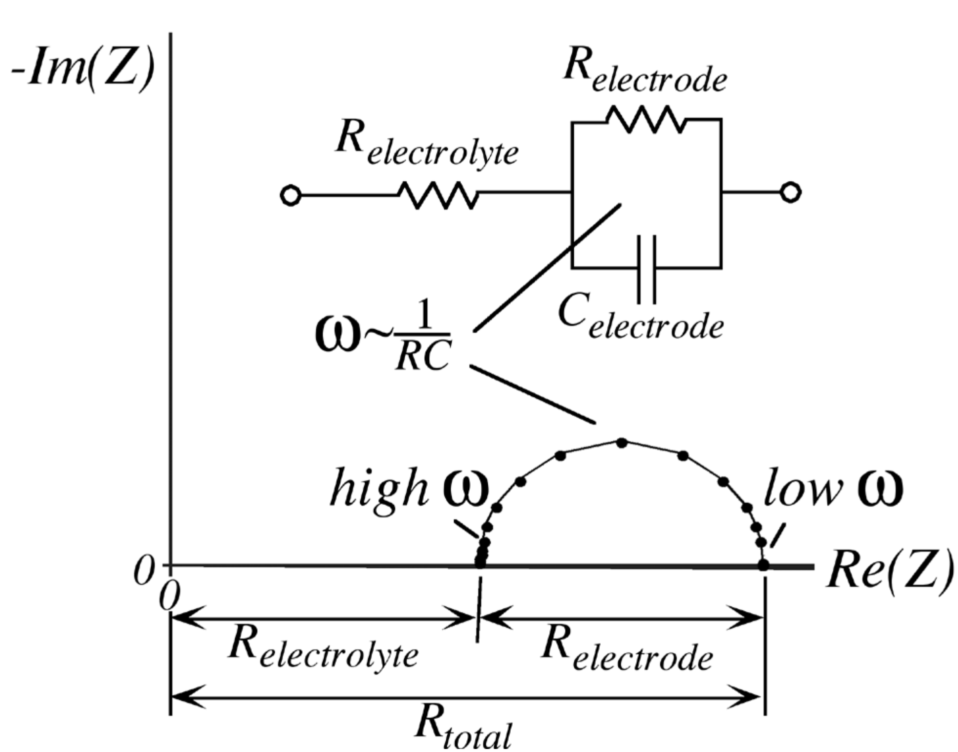


Interfacial resistance is small (2-3%).

Electrochemical Impedance Spectroscopy (EIS)

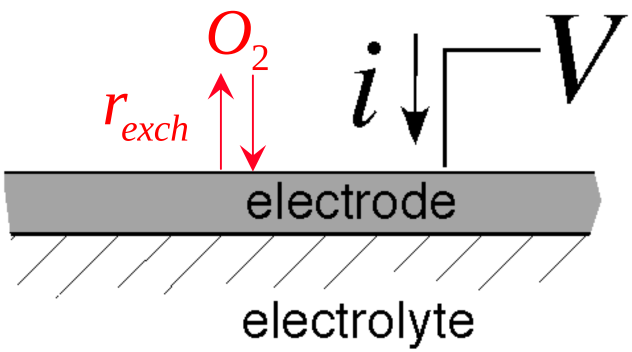


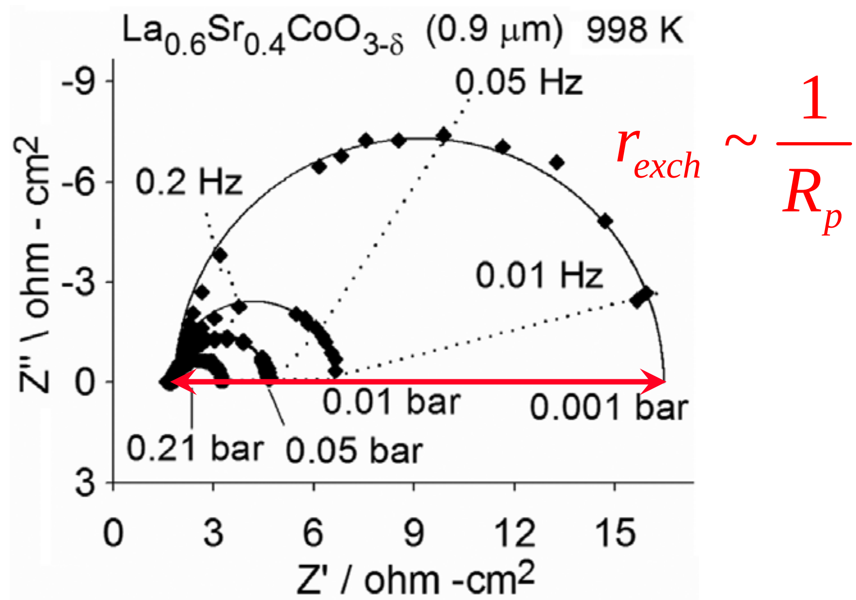


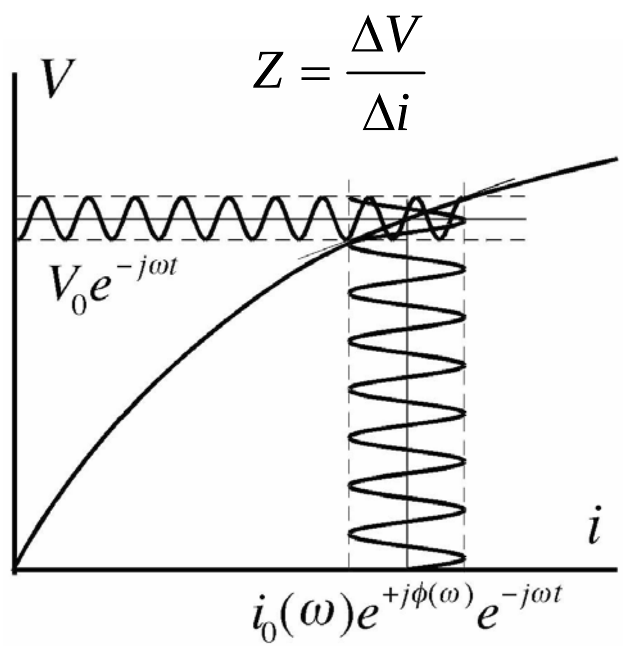


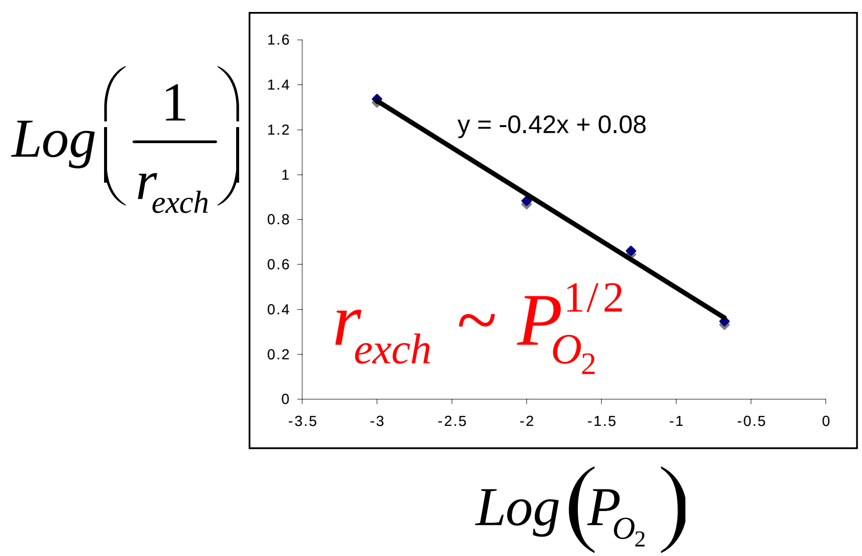
EIS attempts to identify overlapping mechanisms via ***time scale.***

Electrochemical Impedance Spectroscopy (EIS)









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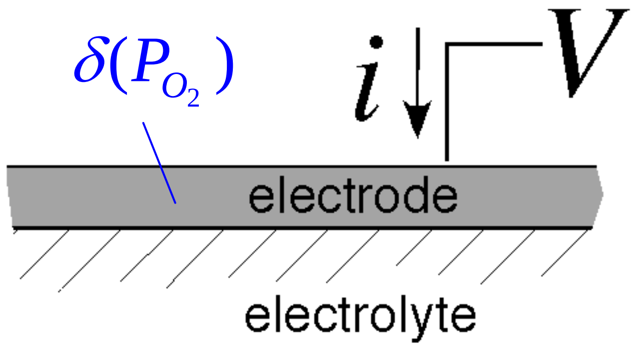
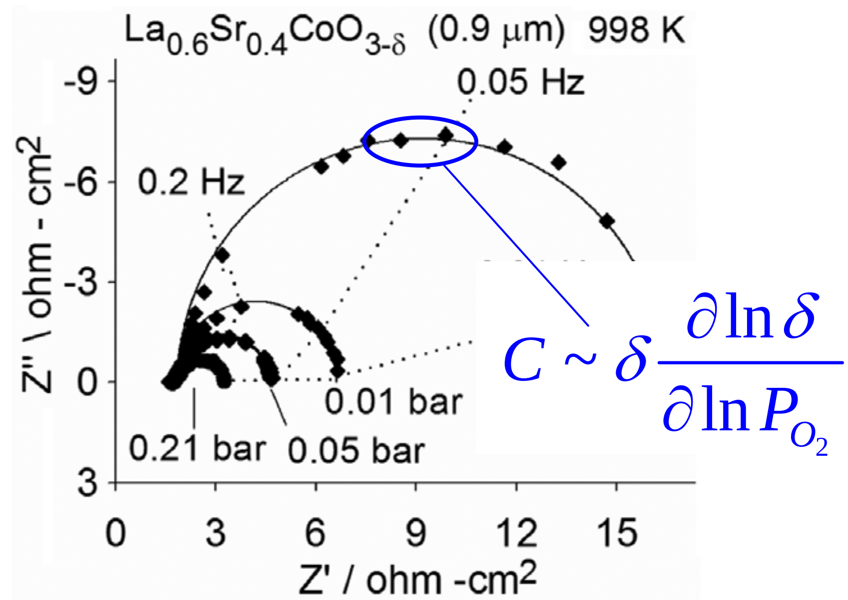
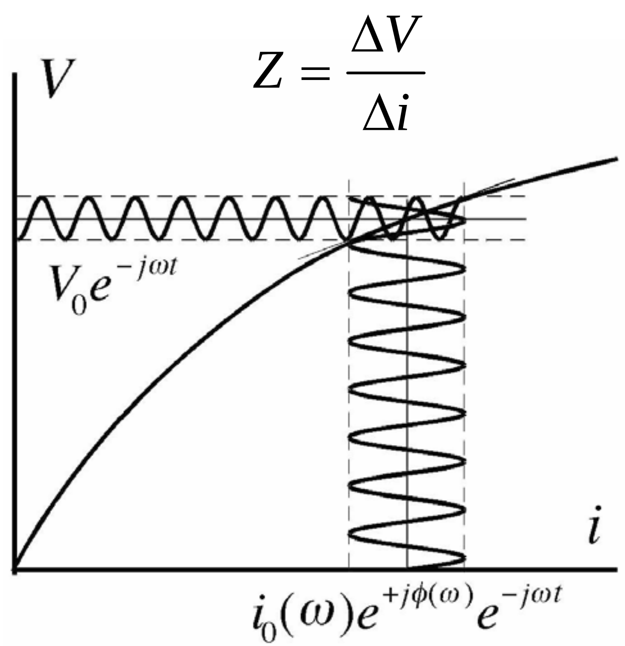
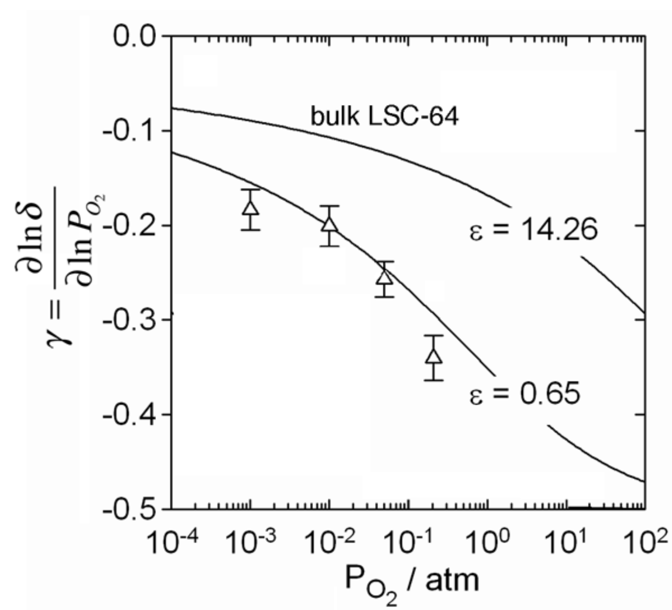


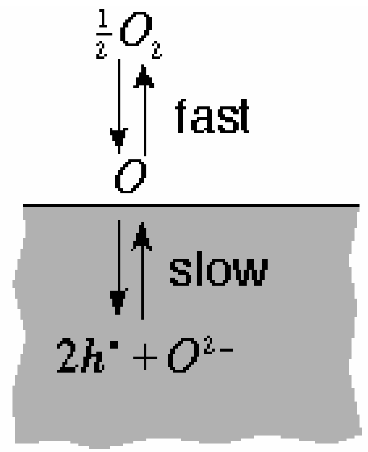






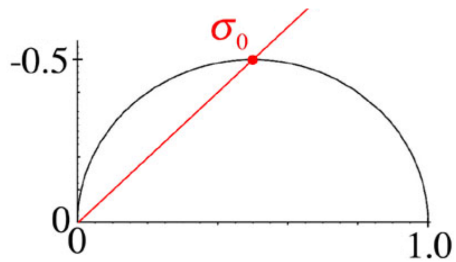
What mechanisms are consistent with $r_{exch} \sim (P_{O2})^{1/2}$?

Limited by consumption of reactive intermediate



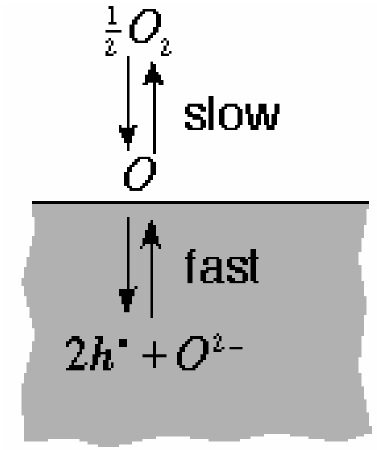
$$r_{ads} = k_1\left(\left(P_{O_2}^{gas}\right)^{\frac{1}{2}} - \left(f_{O_2}^{solid}\right)^{\frac{1}{2}}\right)$$

$$r_{exch} = k_1\left(P_{O_2}\right)^{\frac{1}{2}}$$



Same Response!

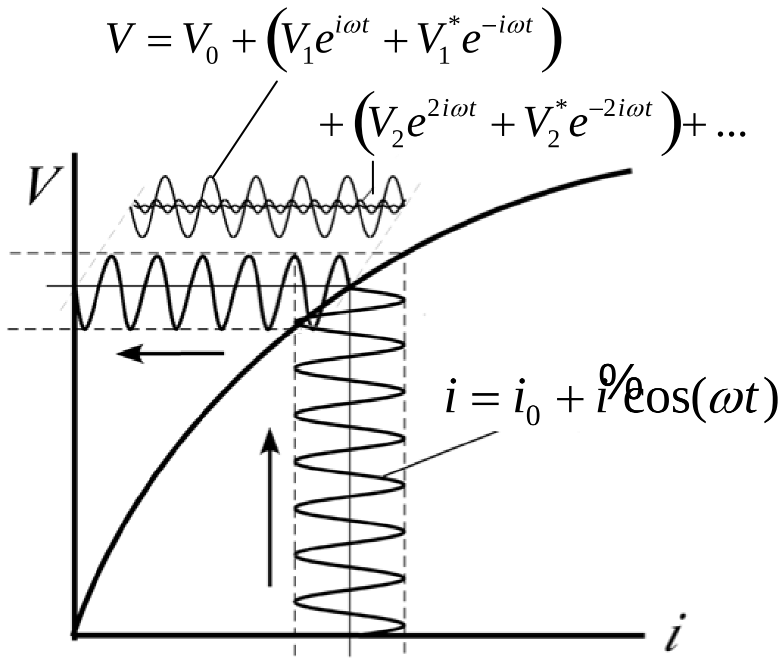
Limited by formation of reactive intermediate



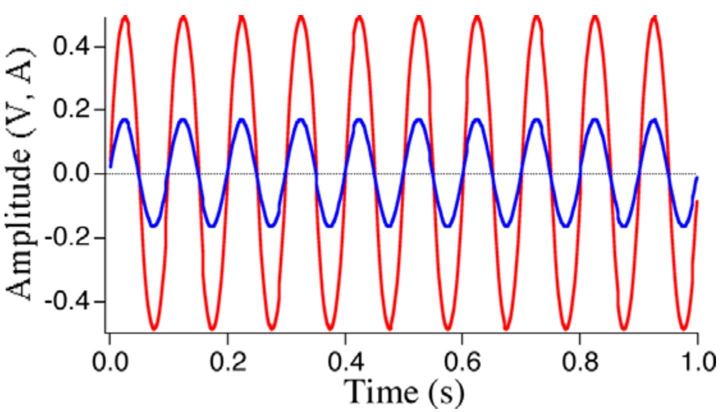
$$r_{ads} = k_1\left(\frac{\left(P_{O_2}^{gas}\right)}{\left(f_{O_2}^{solid}\right)^{\frac{1}{2}}} - \left(f_{O_2}^{solid}\right)^{\frac{1}{2}}\right)$$

$$r_{exch} = k_1\left(P_{O_2}\right)^{\frac{1}{2}}$$

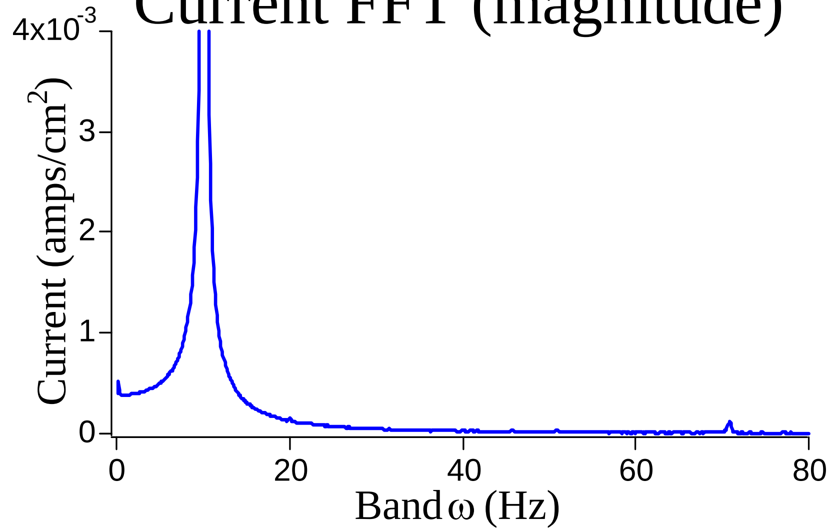
Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)



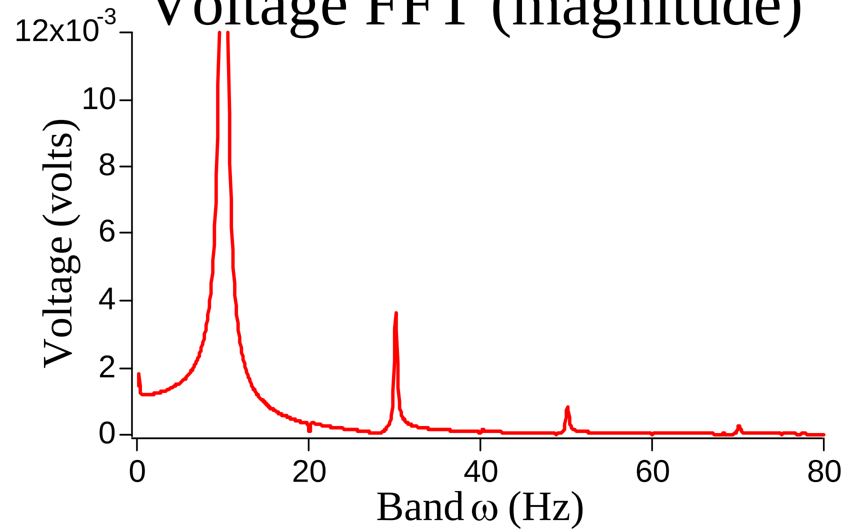
LSF/ceria/LSF cell at 750°C in air (10 Hz)



Current FFT (magnitude)

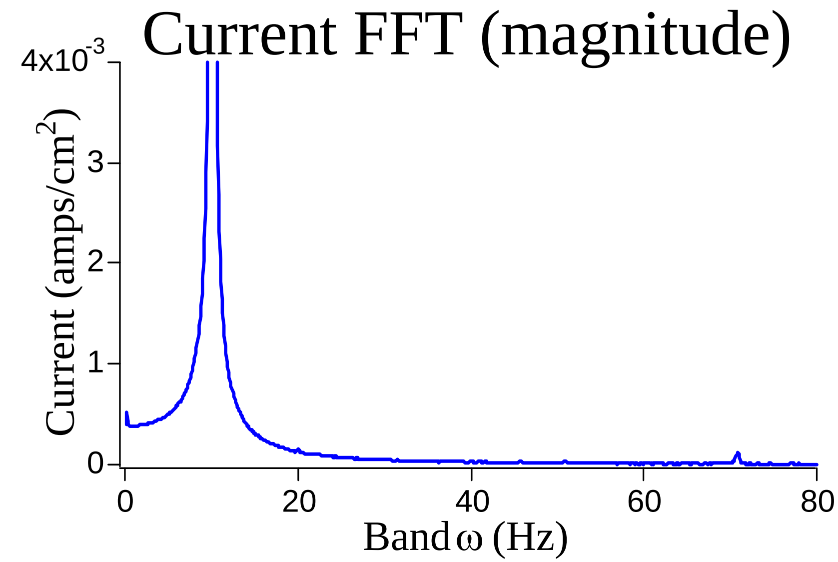


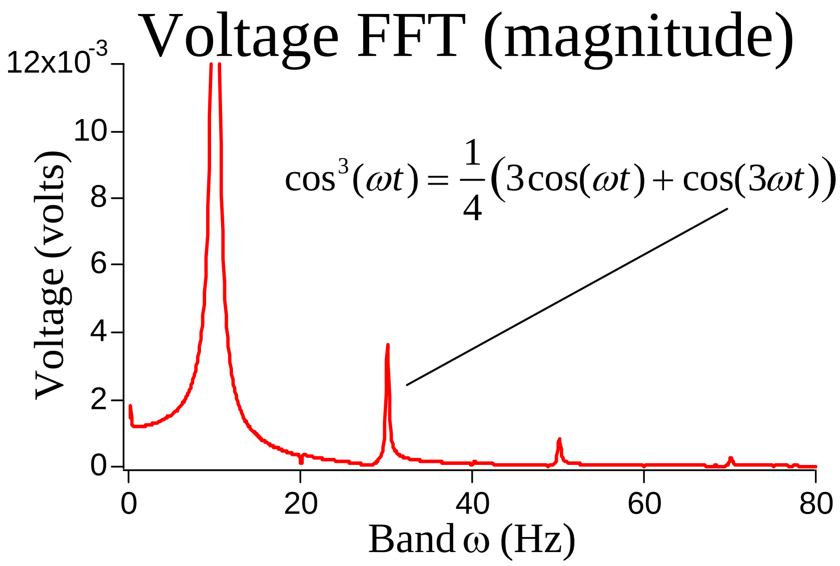
Voltage FFT (magnitude)



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.



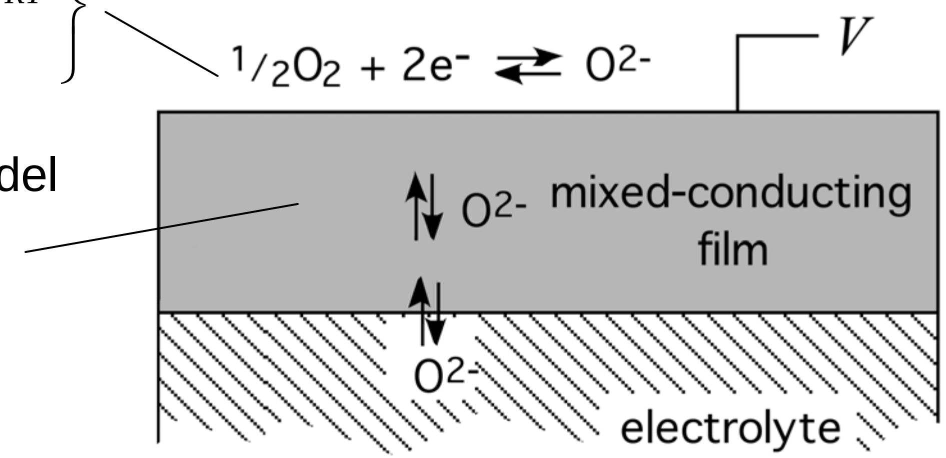


Sources of Nonlinearity in a Mixed Conducting Oxide Film.

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

$\delta(f_{O_2}^{solid})$ obeys Lankhorst's model

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



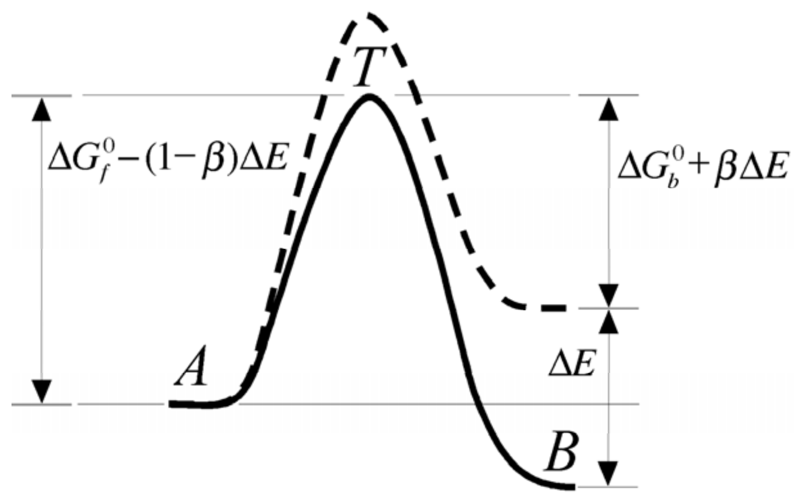
Sources of Nonlinearity in a Mixed Conducting Oxide Film.

Adsorption: $$O_2 + V_{O_s}^{q_s \bullet} + q_{ads} e^- \rightleftharpoons (O_2)_{O_s}^{q_{O_2} \bullet}$$

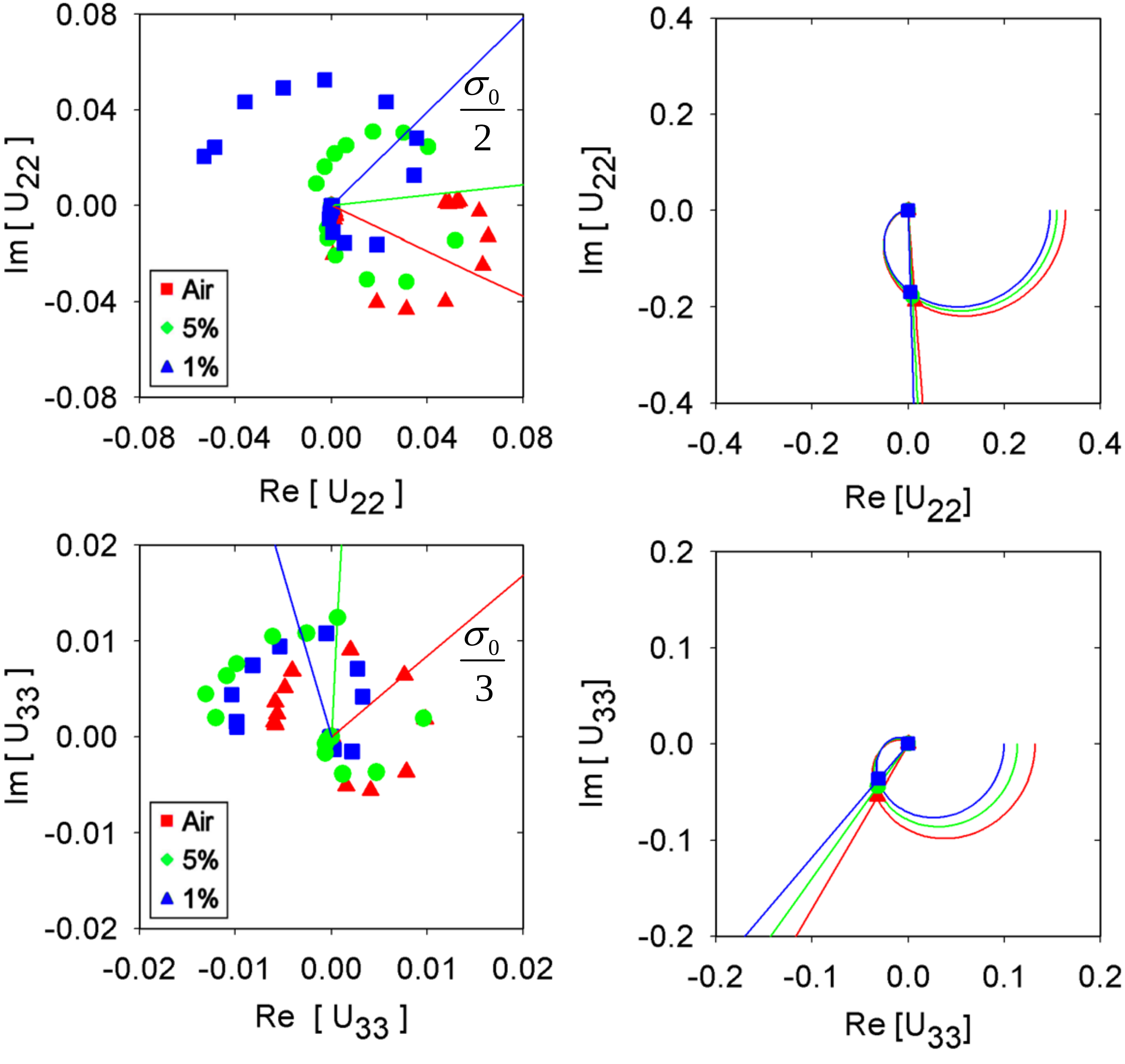
Dissociation: $$(O_2)_{O_s}^{q_{O_2} \bullet} + V_{O_s}^{q_s \bullet} + q_{diss} e^- \rightleftharpoons 2 O_{O_s}^{q_O \bullet}$$

Incorporation: $$O_{O_s}^{q_O \bullet} + V_{O_b}^{\bullet\bullet} + q_{incorp} e^- \rightleftharpoons O_{O_b}^{X} + V_{O_s}^{q_s \bullet}$$

Non-ideal thermodynamics requires that transition states depend on driving force.



Harmonic Response of a $La_{0.6}Sr_{0.4}Co_{3-\delta}$ film on Gd-doped ceria at 725°C vs. P_{O2}



Model: limited by dissociation of chemisorbed intermediate

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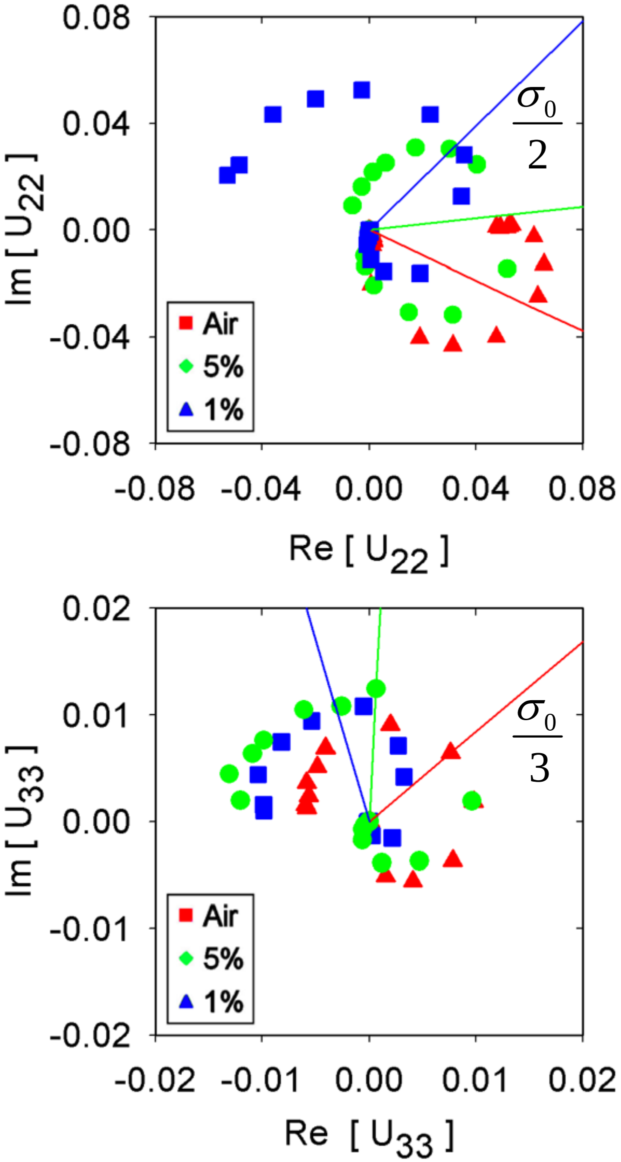

Possible rate limiting phenomena

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

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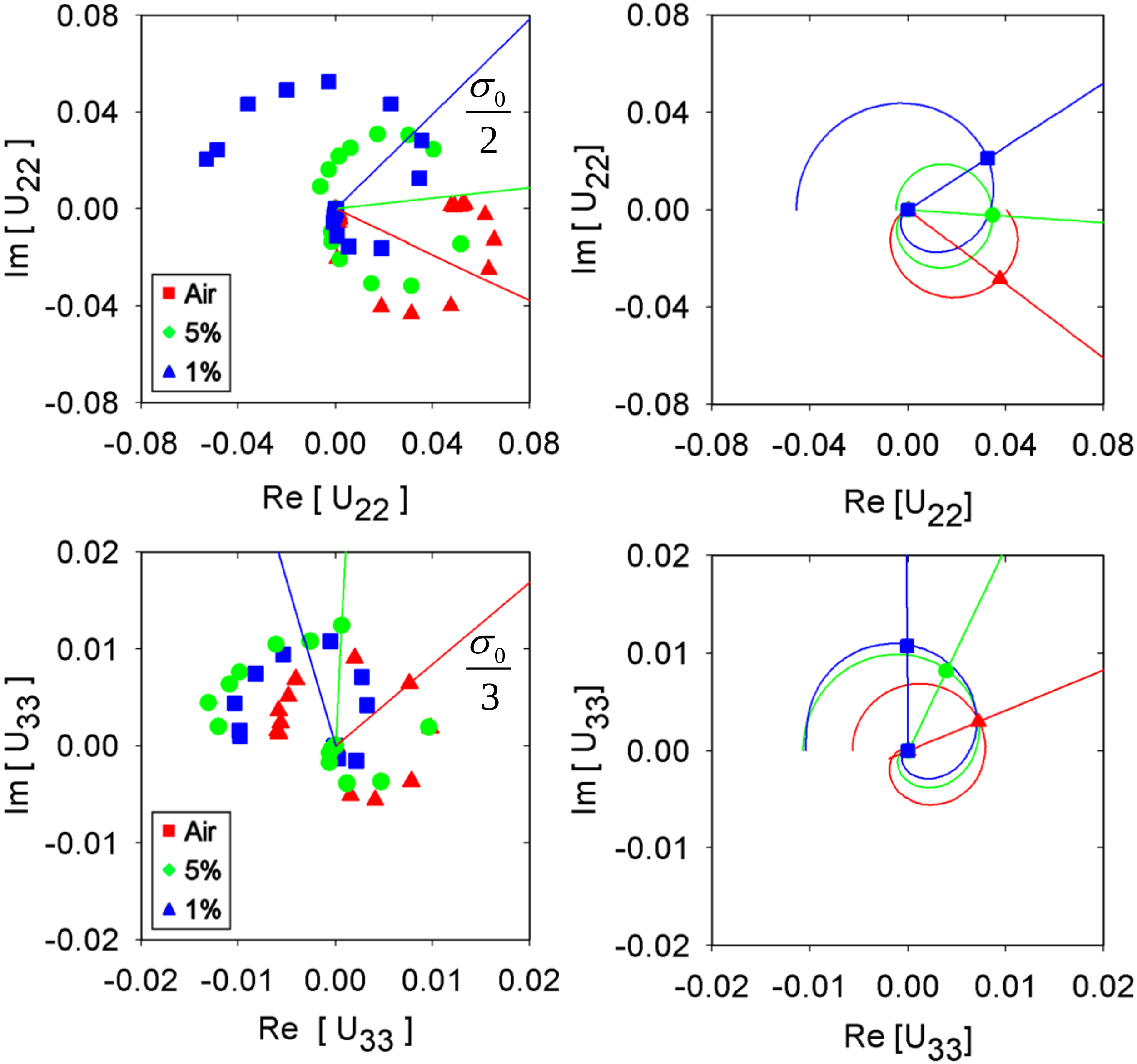

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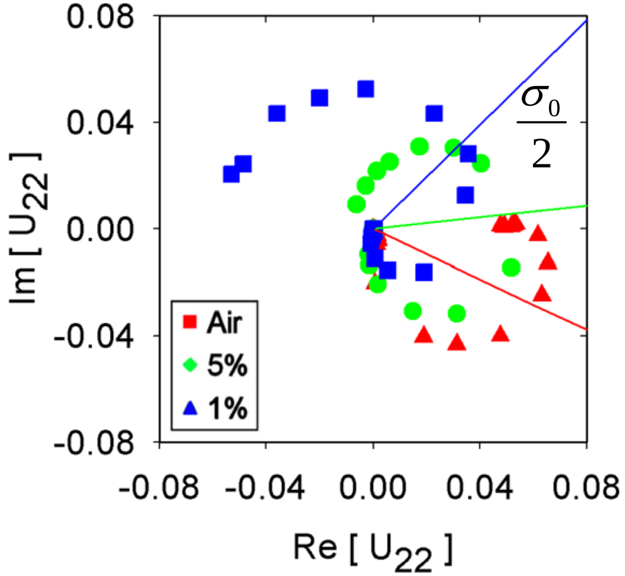
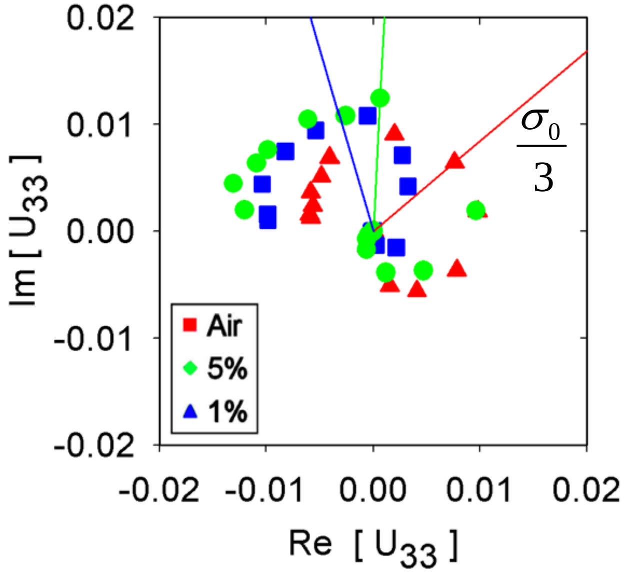
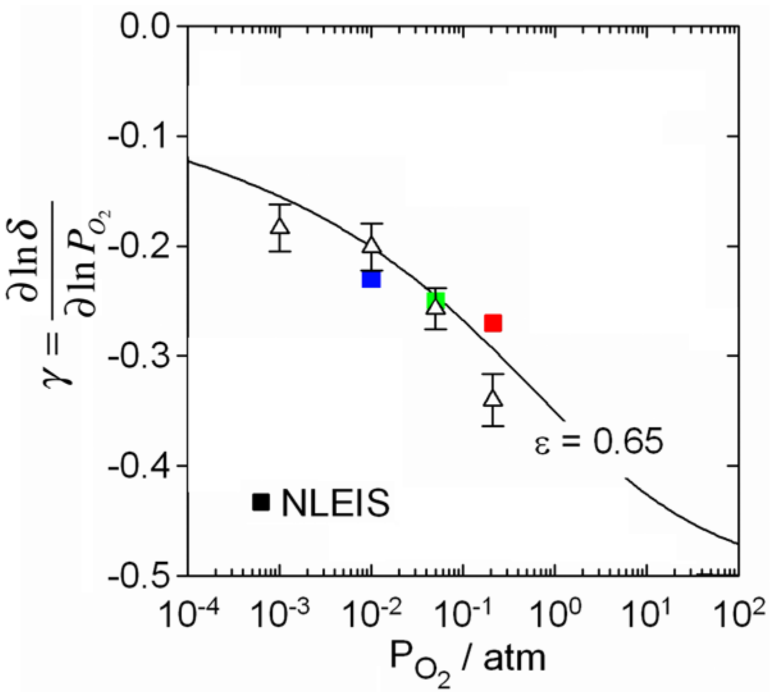




Thermodynamic factor assuming limited by dissociative adsorption



Physical Interpretation of the Observed Kinetics

"dissociative adsorption"

Adsorption: $O_2 + V_{O_s}^{q_s \bullet} + q_{ads} e^- \rightleftharpoons (O_2)_{O_s}^{q_{O_2} \bullet}$

Dissociation: $(O_2)_{O_s}^{q_{O_2} \bullet} + V_{O_s}^{q_s \bullet} + q_{diss} e^- \rightleftharpoons 2O_{O_s}^{q_O \bullet}$

Incorporation: $O_{O_s}^{q_O \bullet} + V_{O_b}^{\bullet\bullet} + q_{incorp} e^- \rightleftharpoons O_{O_b}^{X} + V_{O_s}^{q_s \bullet}$

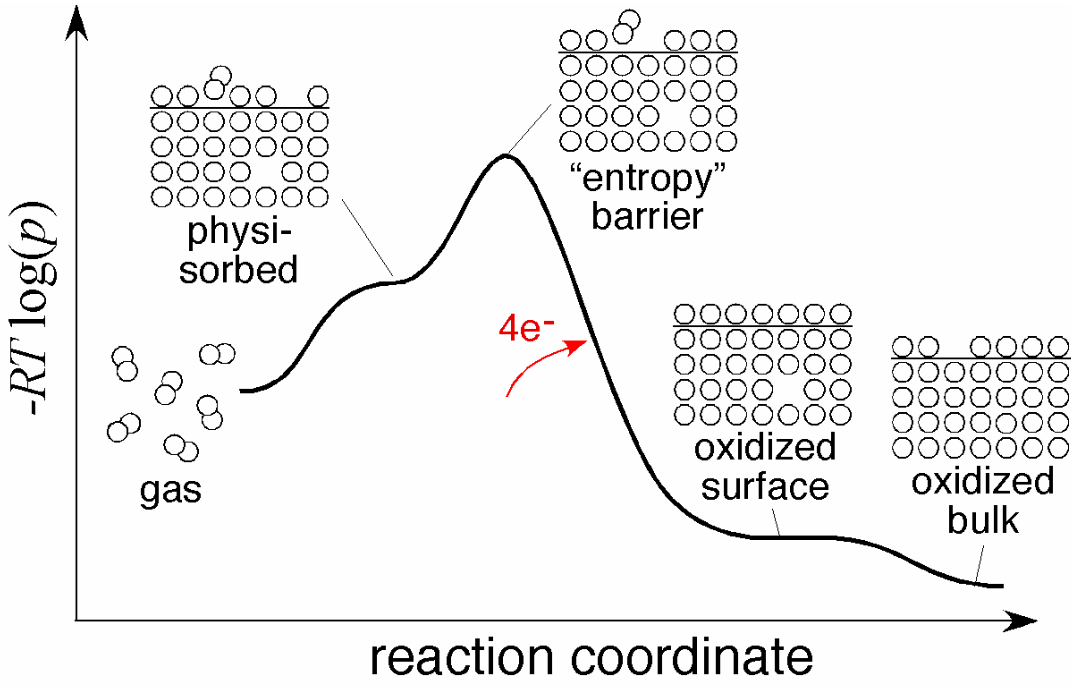
$q_{diss} = 4$,

$\beta = 1$

Implies:

- O_2 only exists as a molecule, or fully reduced on surface.
- Forward rate obeys mass action (no energy barrier).

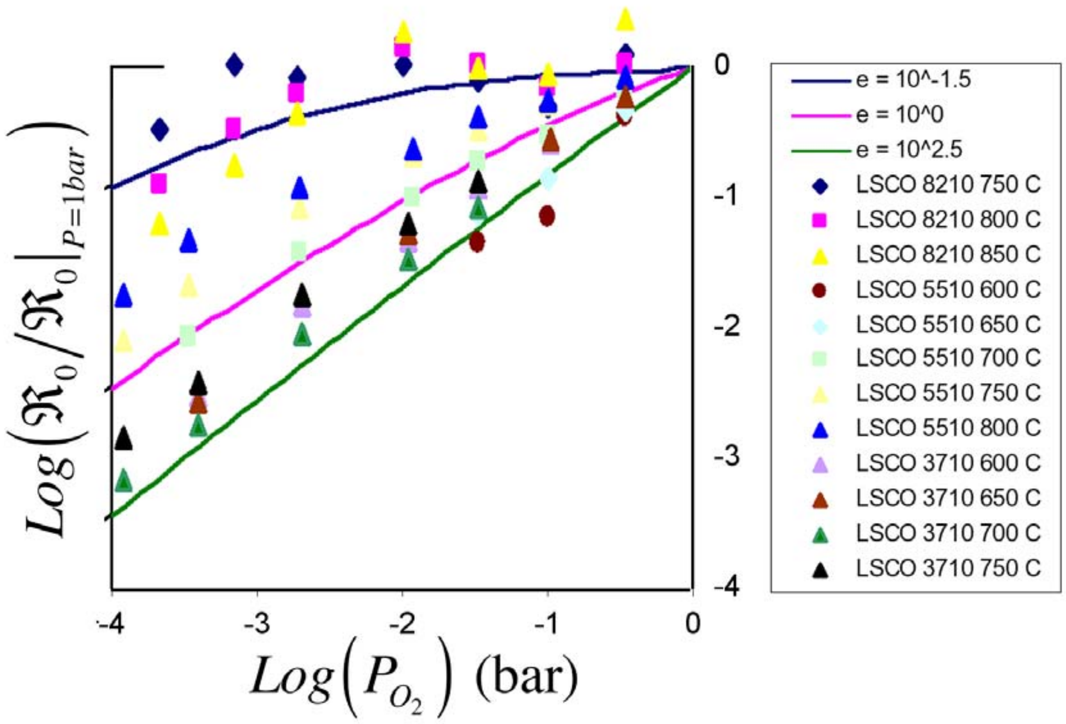
Physical Interpretation of the Observed Kinetics



- 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

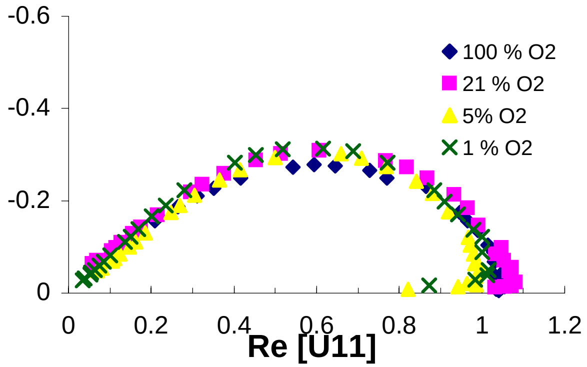


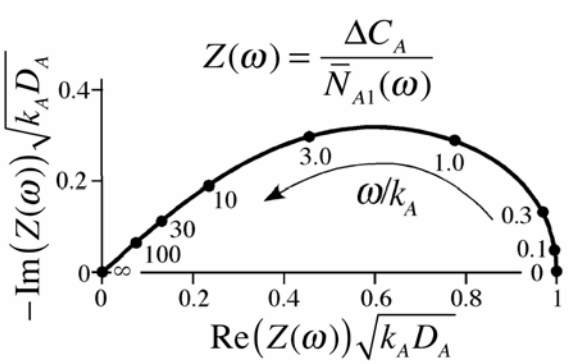
- Proposed model explains O_2 exchange measurements on bulk $La_{1-x}Sr_xCoO_{3-\delta}$ over a wide range of x, T and P_{O2}.

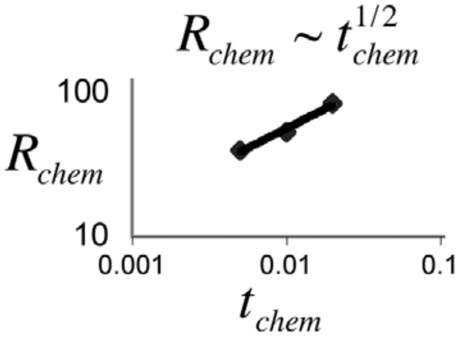
- Metallic band structure appears to be important for stabilizing physisorbed O_2, leading to faster rates.

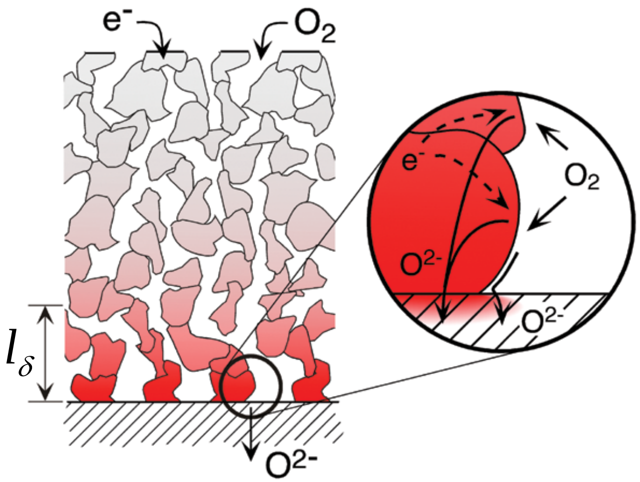
(Pr,Ba)CoO_y, (Ba,Sr)(Co,Fe)O_y?

NLEIS of a Porous $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ Electrode at 725°C vs. P_{O2}









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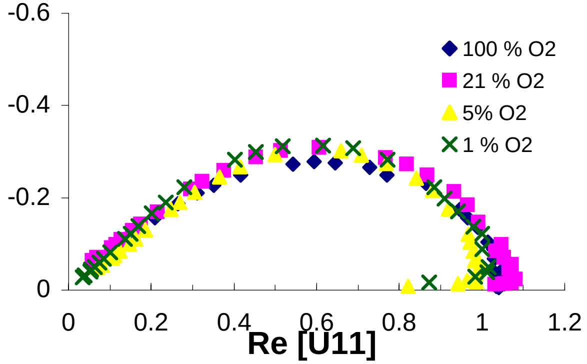
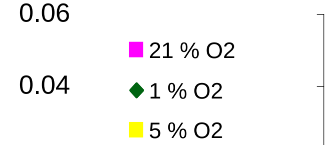
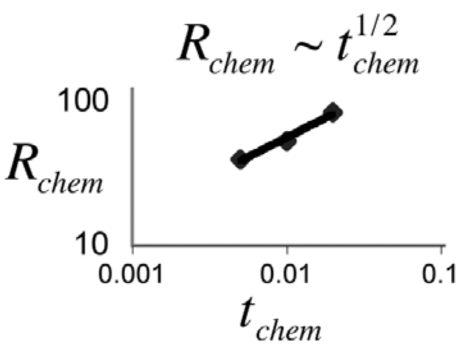
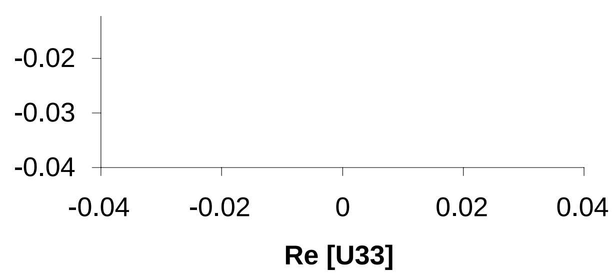




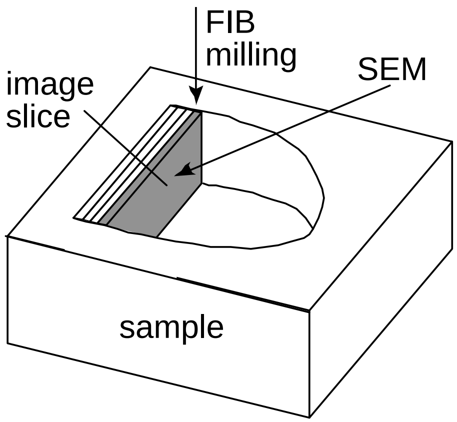
- Simple 1-D models don't explain higher harmonic data very well.

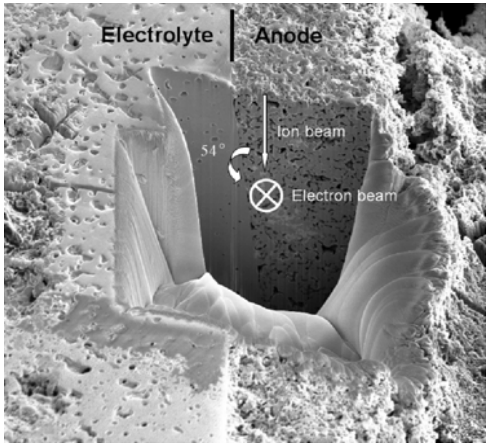


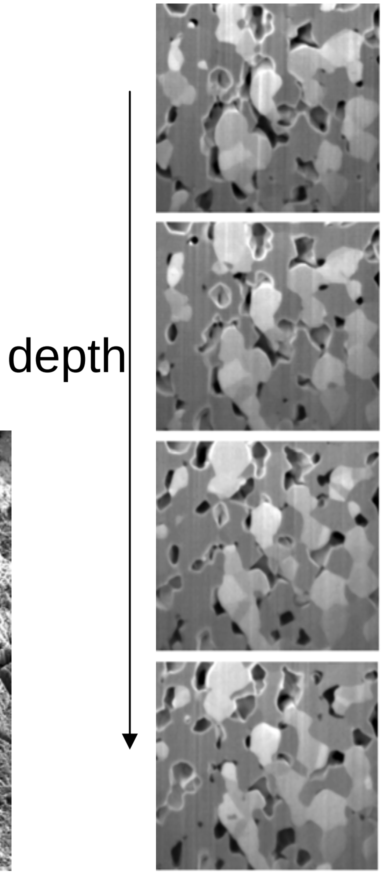
- Many uncertainties related to the details of microstructure.

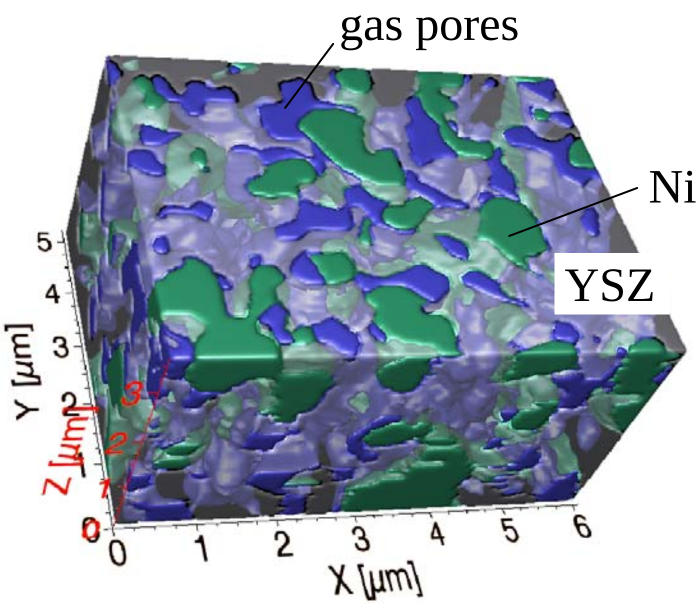


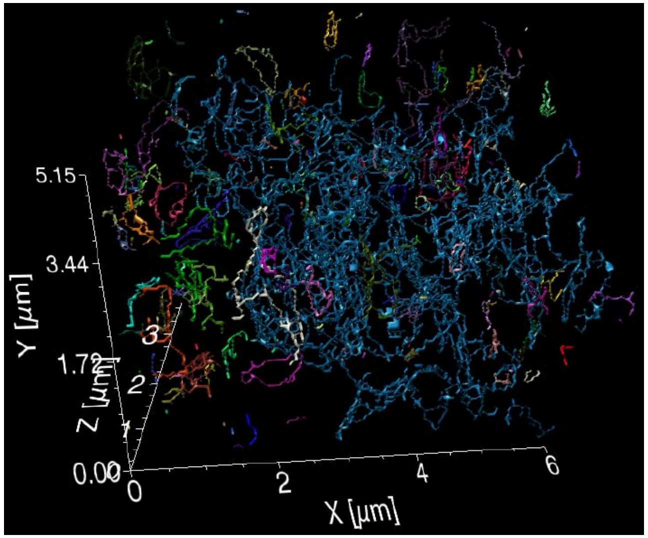
3D Imaging of SOFC Electrodes with FIB-SEM





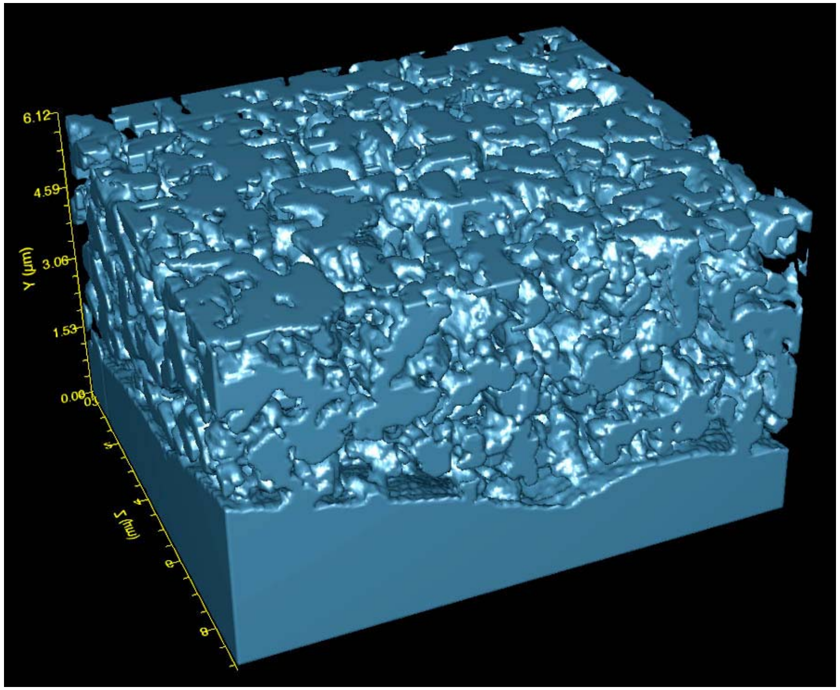






NSF Collaborative Research, Ceramics-DMR
Barnett and Voorhees (Northwestern)
Thornton (U. Michigan), Adler (U. Washington)
J.R. Wilson et al., *Nature Materials*, July 2006

3D Images of a Porous $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ Electrode



Electrode area: 2.23 um^{-1} = 22,300 cm^2/cm^3

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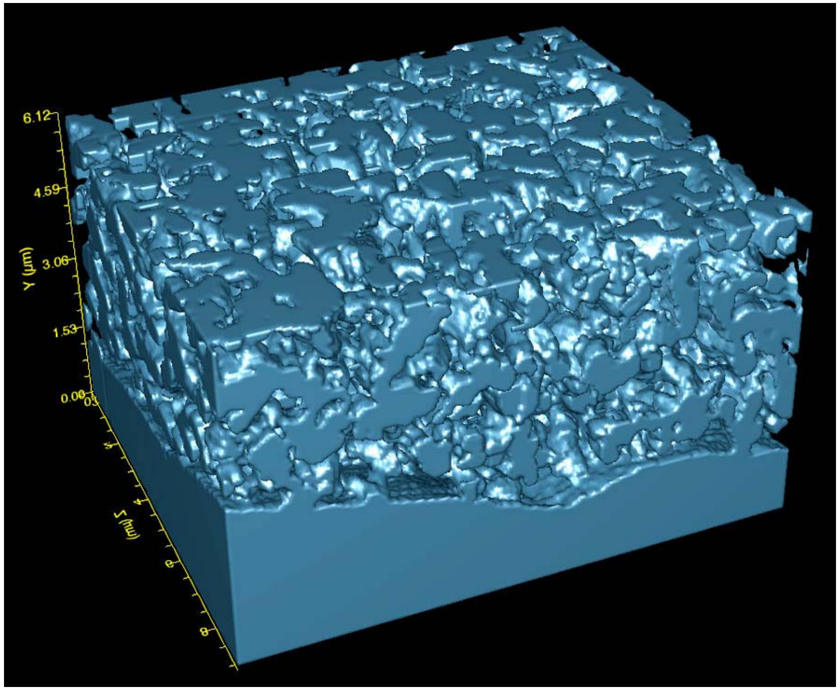

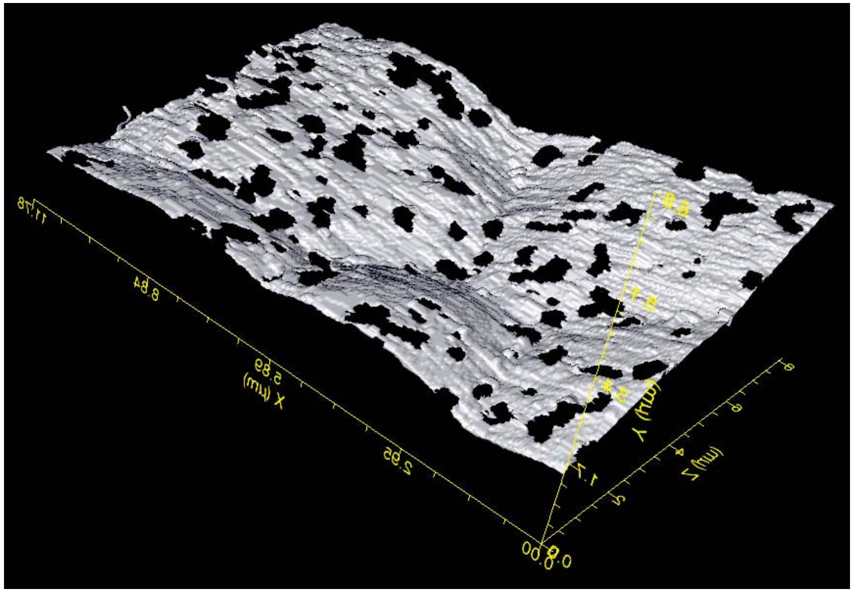

Electrode area: 2.23 um^{-1} = 22,300 cm^2/cm^3

Extent of electrode/electrolyte contact: 20.5%

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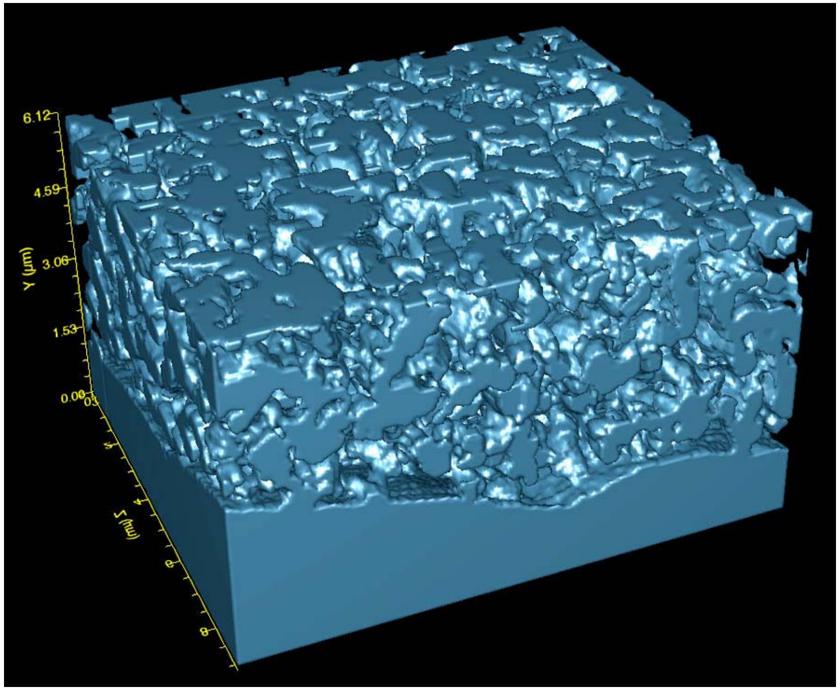
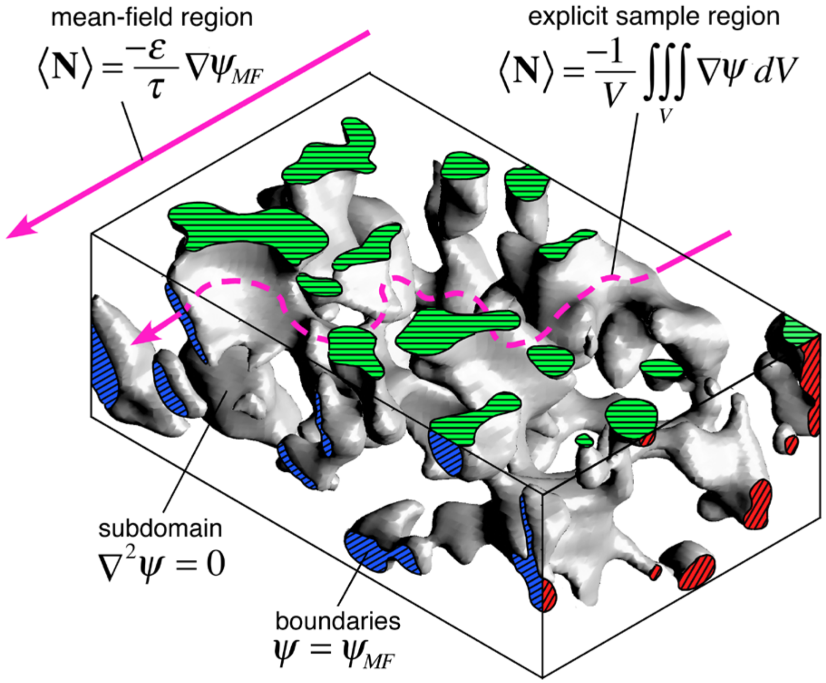
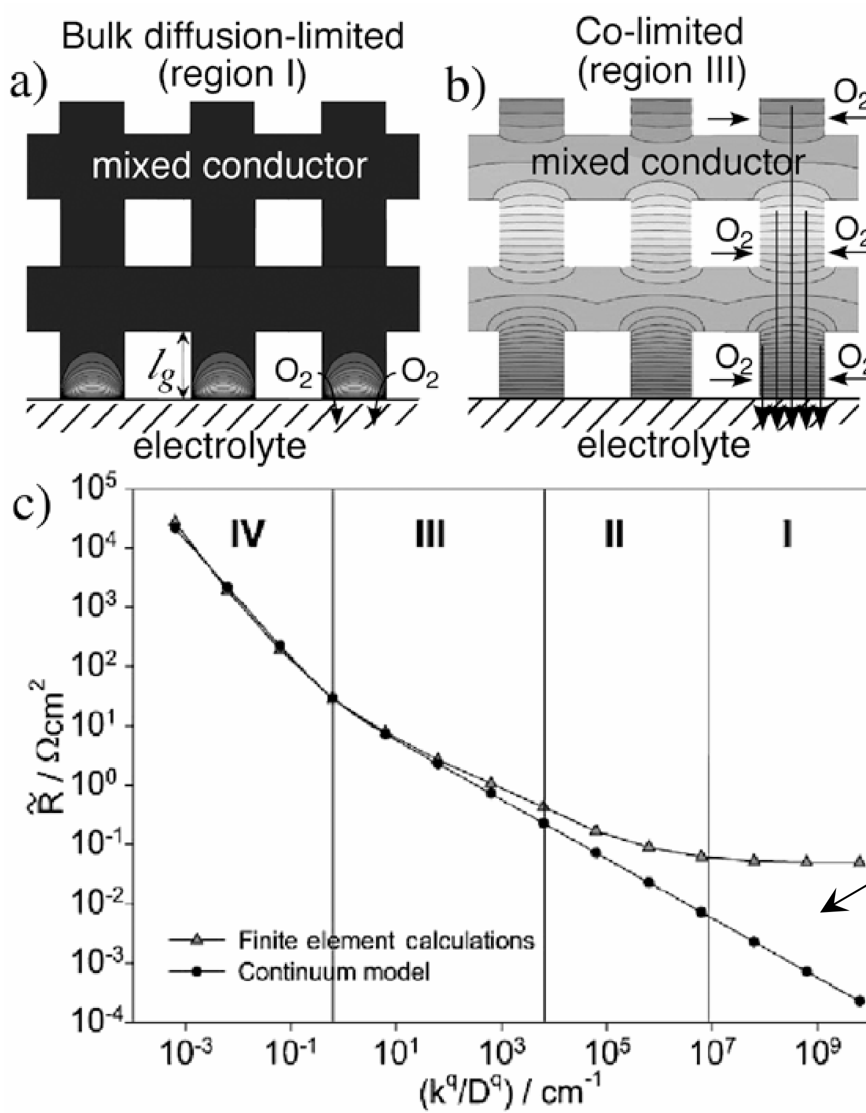




Electrode area: 2.23 um^{-1} = 22,300 cm^2/cm^3
Extent of electrode/electrolyte contact: 20.5%
Transport tortuosity factors.

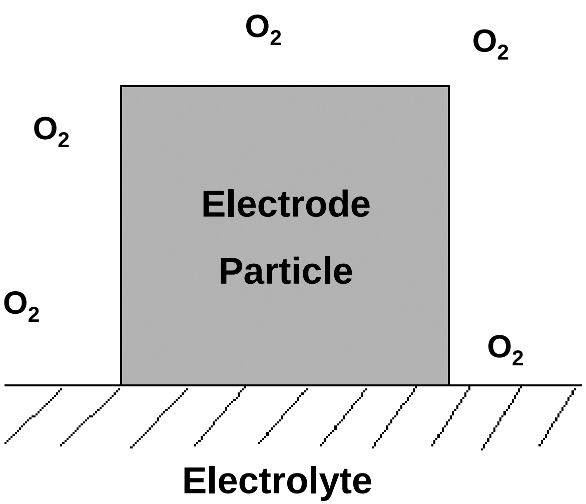
When are macrohomogeneous properties valid?

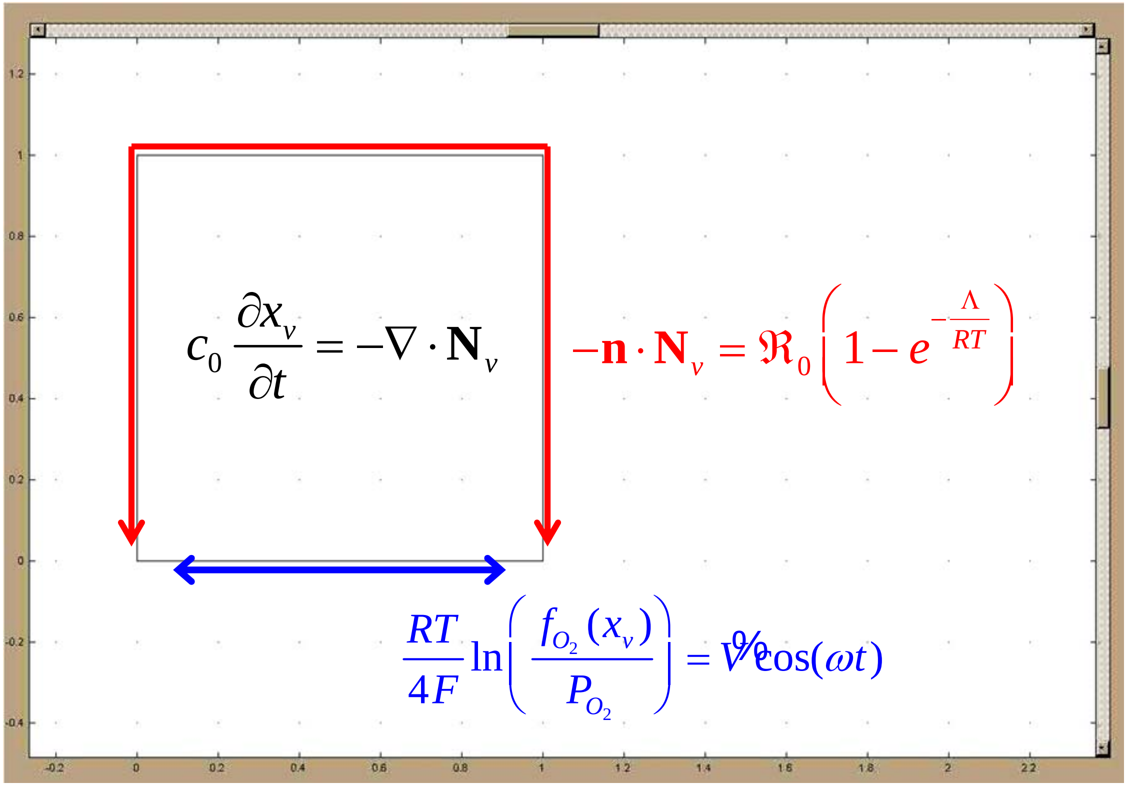


Juergen Fleig
Annu. Rev. Mat. Sci., 2003.

Must apply models to actual 3D geometry

Baby steps: a cubic electrode particle



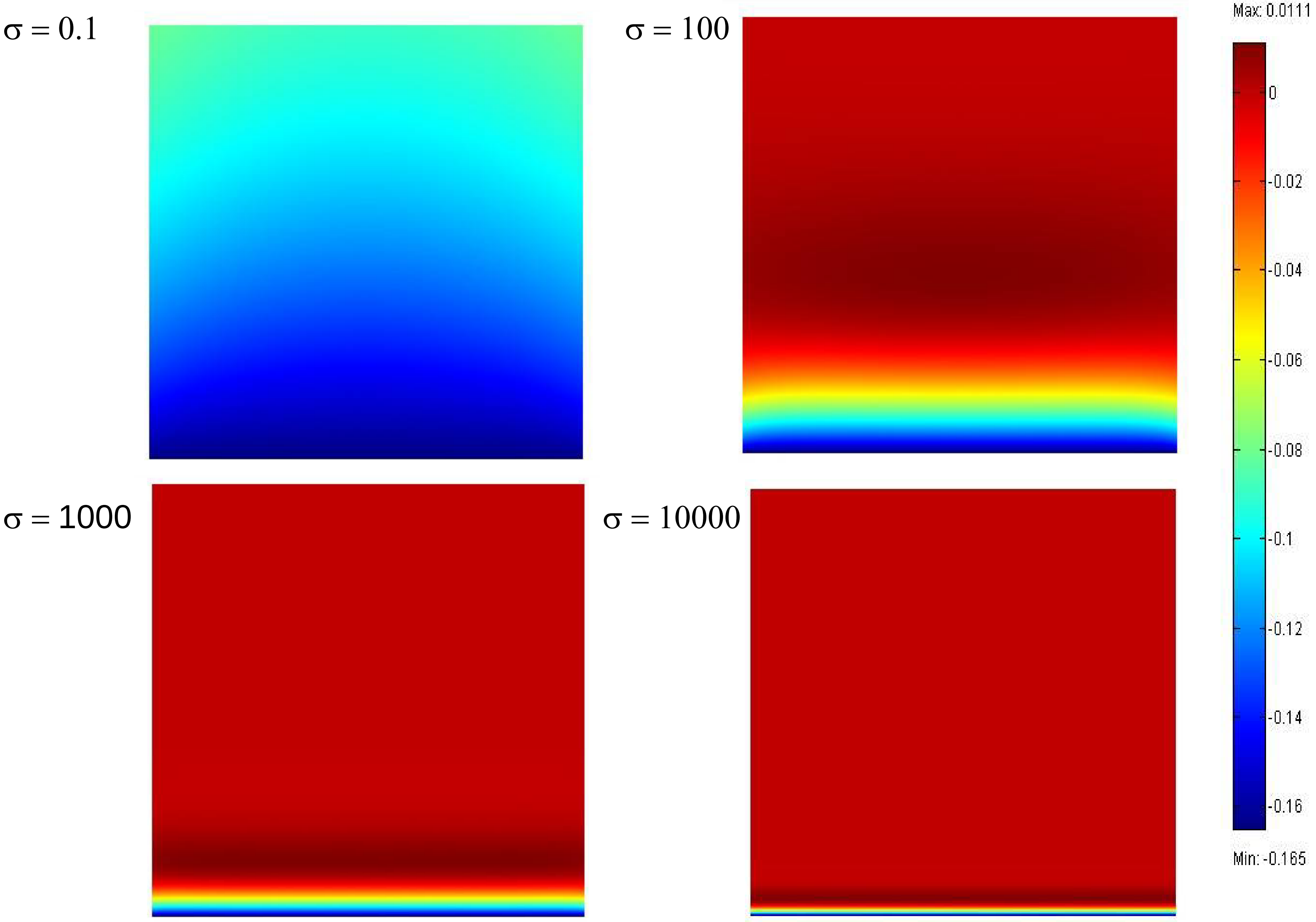


$$c_0 \frac{\partial x_v}{\partial t} = -\nabla \cdot \mathbf{N}_v$$

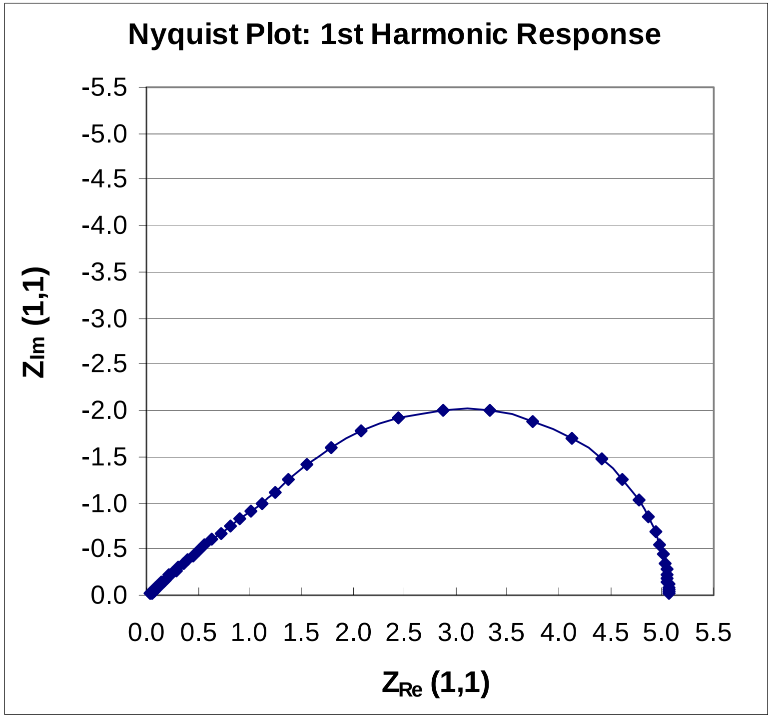
$$-\mathbf{n} \cdot \mathbf{N}_v = \Re_0 \left(1 - e^{-\frac{\Lambda}{RT}} \right)$$

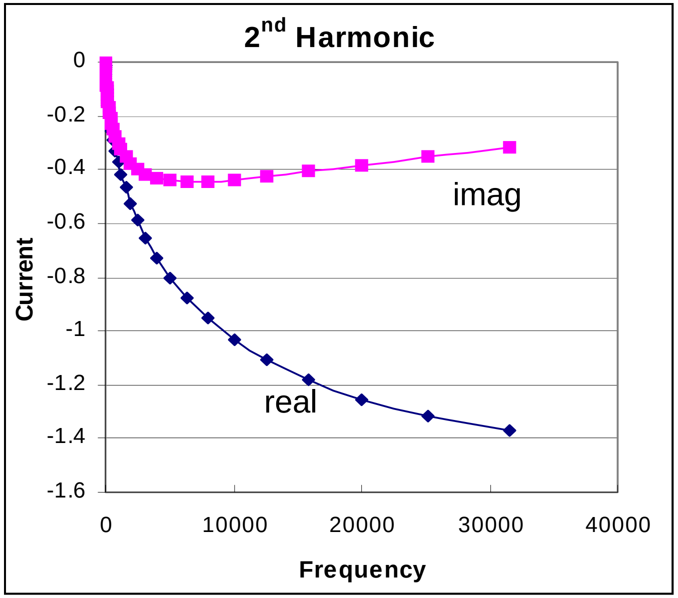
$$\frac{RT}{4F} \ln\left(\frac{f_{O_2}(x_v)}{P_{O_2}} \right) = \tilde{V}\cos(\omega t)$$

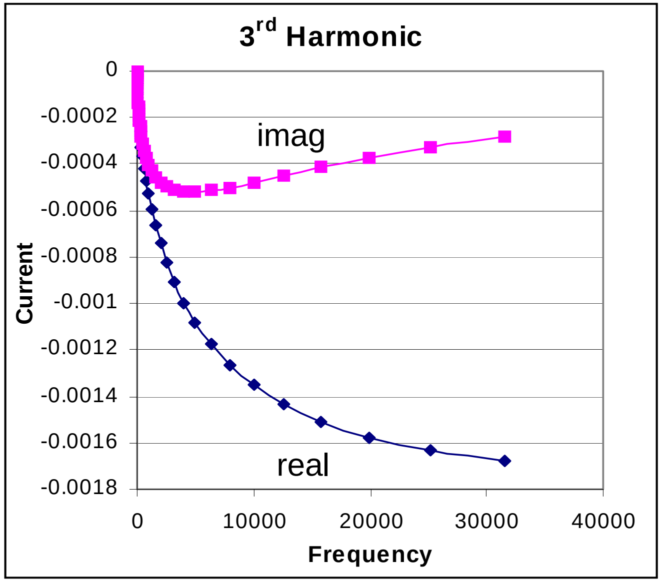
Concentration Profiles of Increasing Perturbation Frequency



Higher Order Harmonic Data







Conclusions

- By resolving both timescale and nonlinearity, NLEIS appears to be a promising technique for analyzing electrode kinetics.
- For metallic $La_{1-x}Sr_xCoO_{3-\delta}$, 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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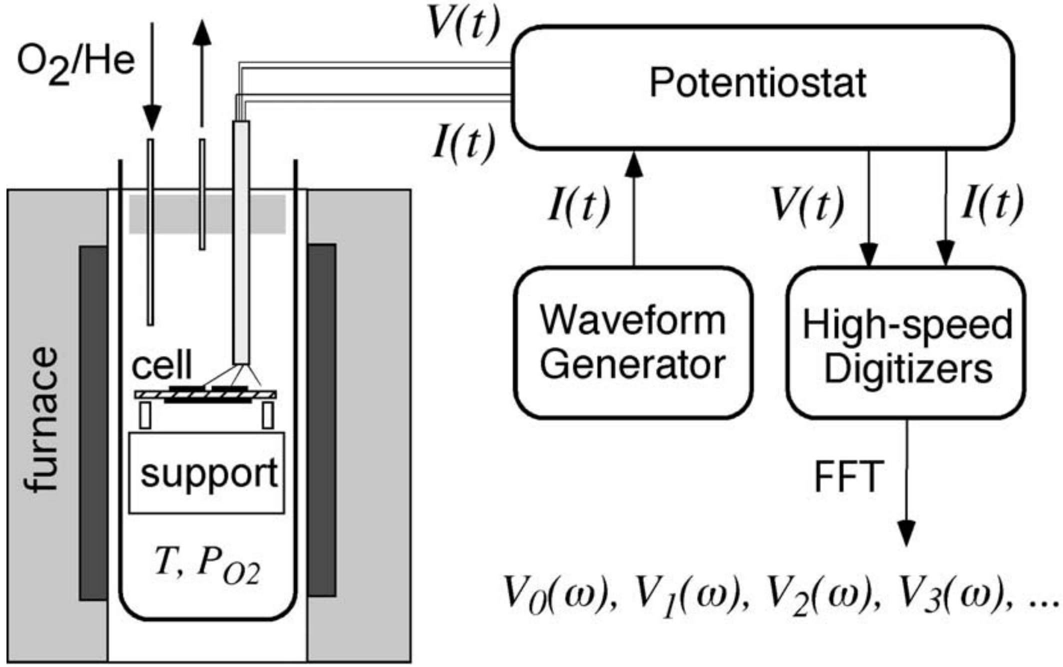
Thank You

NLEIS measurements



Power Series Expansion of Harmonic Response

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

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

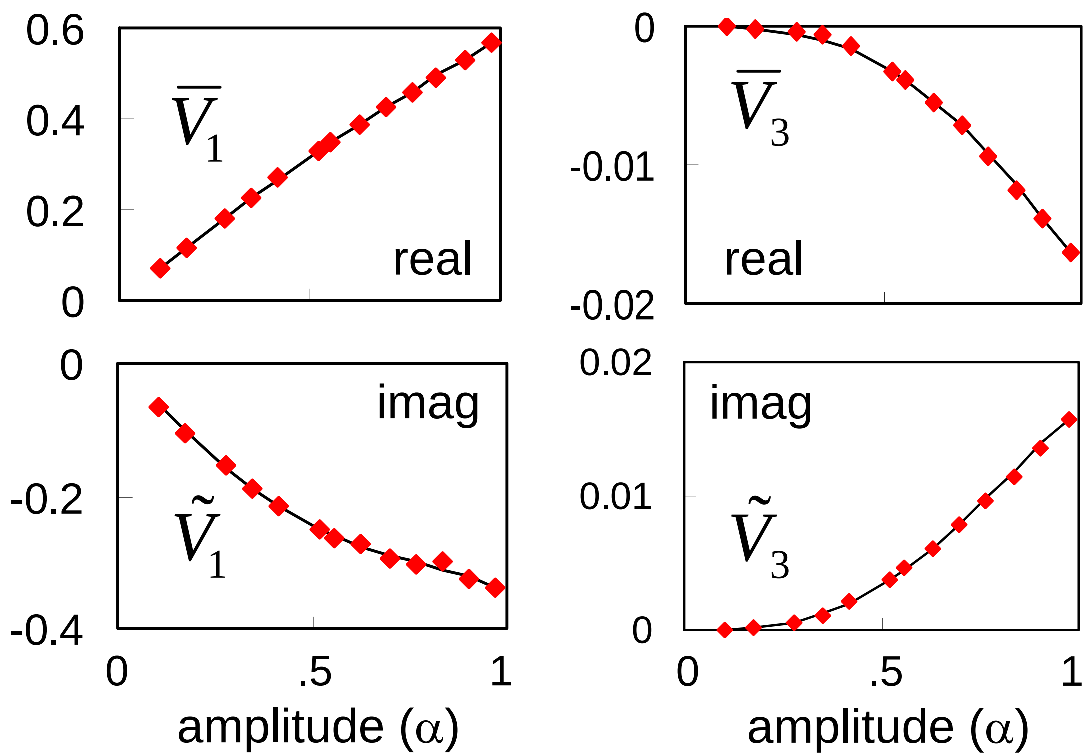
Least Squares Fit

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

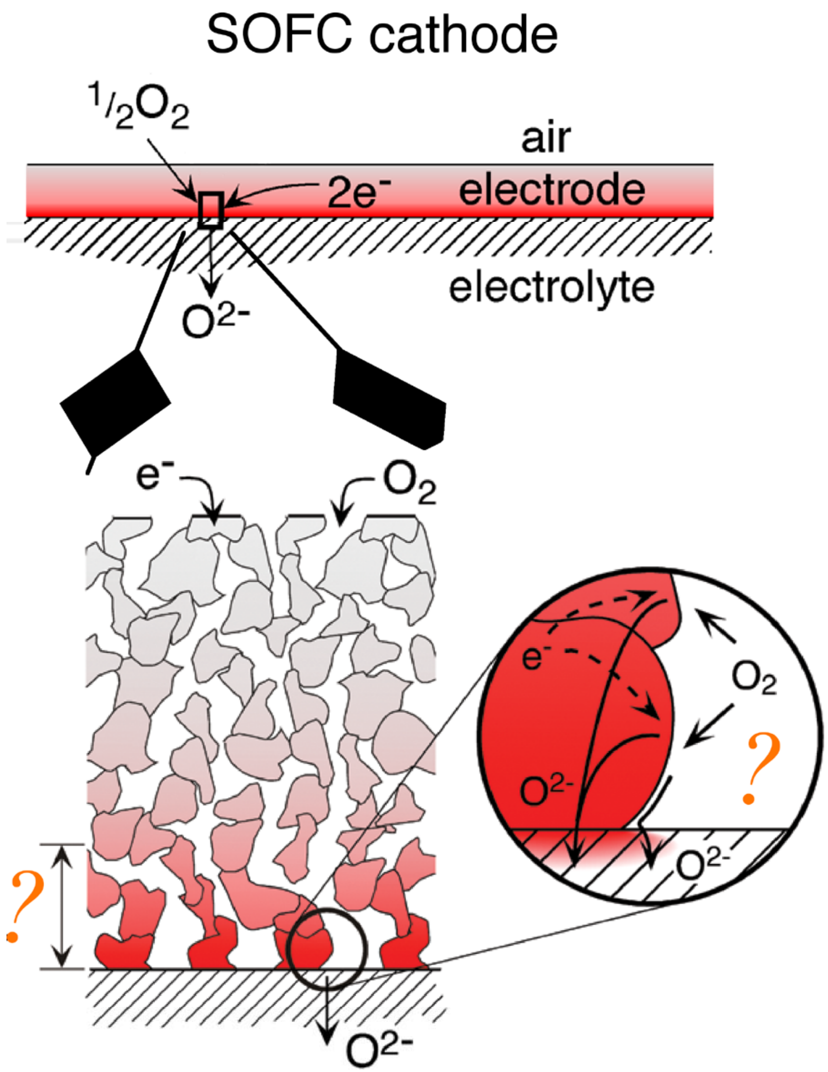
$\overline{V}_k$ = Real Part of the Response

$\tilde{V}_k$ = 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.