Advanced Measurement and Modeling Tools for Improved SOFC Cathodes

Yunxiang Lu, Jamie R. Wilson, Lilya Dunyushkina, Stuart B. Adler
University of Washington

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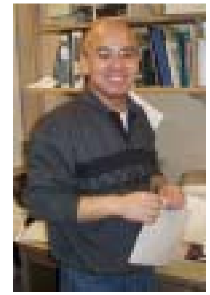

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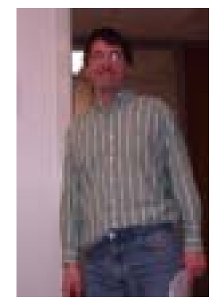

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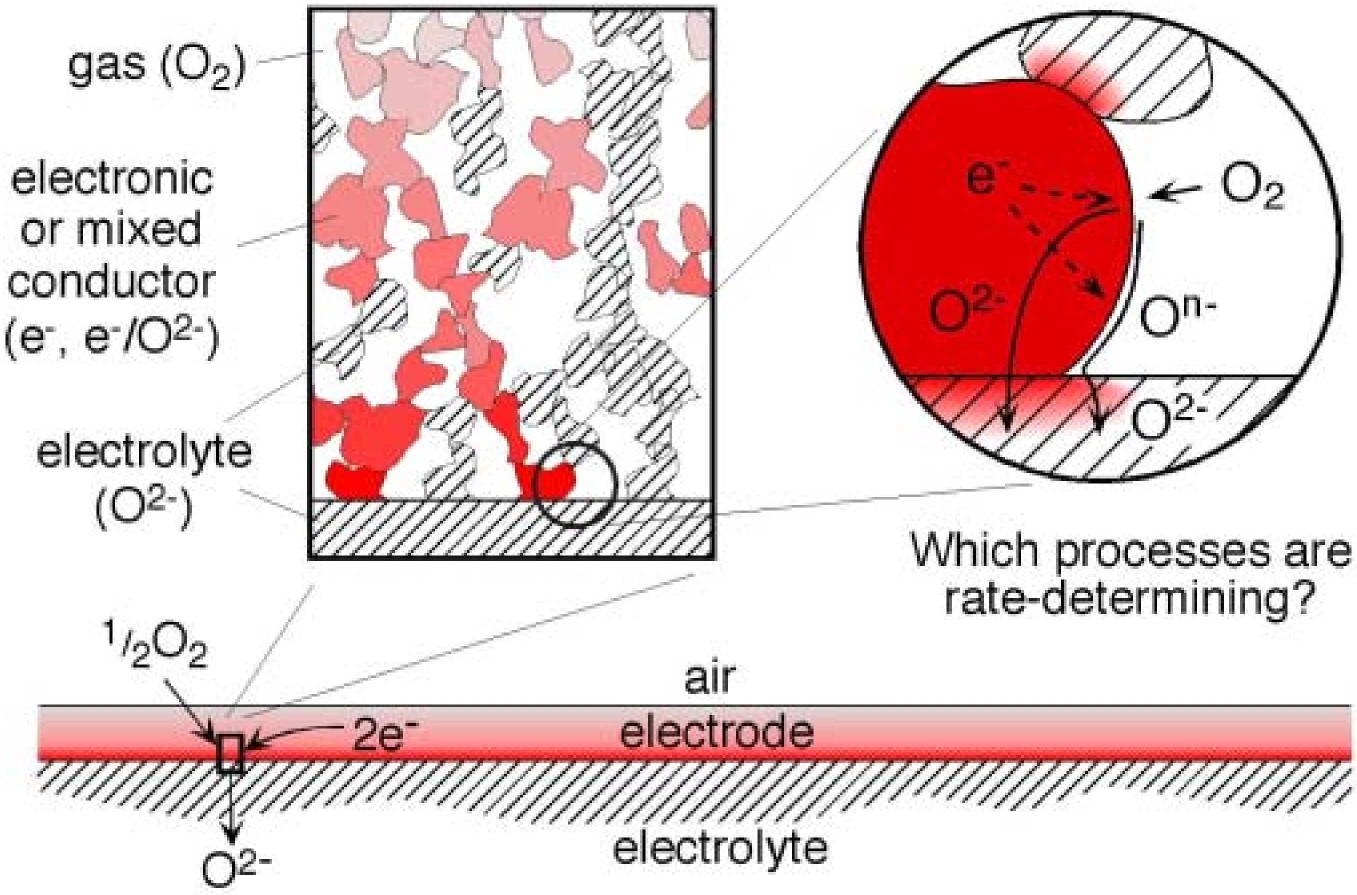
Motivation: How do we identify and improve physical processes limiting electrode performance?



The Problem

Current electrochemical techniques are limited in the information they can provide.

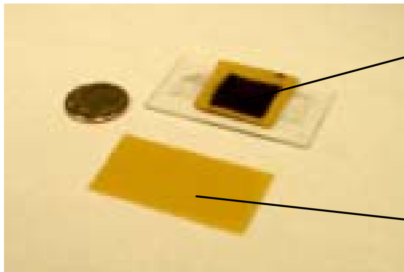
- Difficulty isolating the electrode in a meaningful environment.
- Limitations of impedance spectroscopy (*i.e*. “interpreting blobs”).
- Lack of models linking performance to properties, microstructure.
- Inability to implement broadly in a development environment.

Our Approach

- Microelectrodes for improved cathode measurements
  - Better resolution and isolation than standard half-cells.
  - Allows testing under more realistic conditions.
  - Higher experimental throughput via. miniaturization.
- Analysis of nonlinear harmonics (NLEIS, EFM)
  - Helps identify physical processes via. *nonlinearity*.
  - Broader spectrum of information without more experiments.
- Mechanistic modeling using finite element analysis
  - Quantitative evaluation of proposed mechanisms (based on data).
  - Includes nonlinear and 3-D effects.
  - Links performance to properties and microstructure.

Materials of Interest

Porous Perovskite Electrodes:

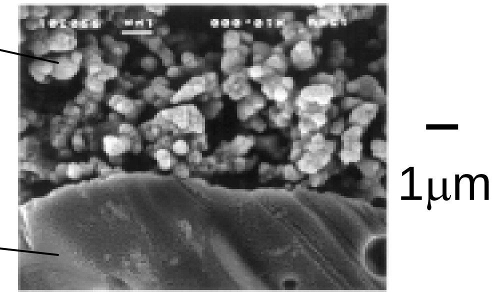


electrode

$La_{1-x}Sr_x(Co,Fe)O_{3-\delta}$

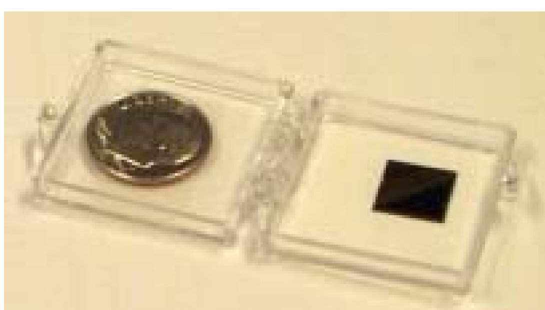
electrolyte

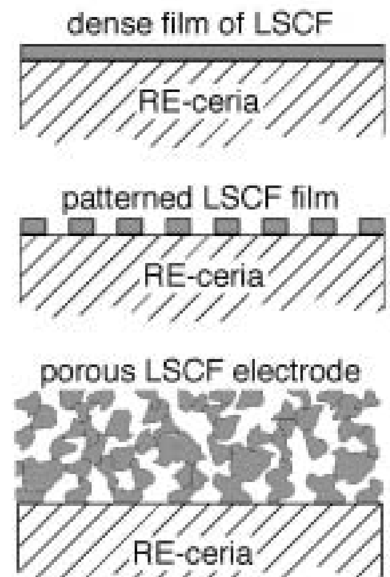
$Ce_{0.8}Sm_{0.2}O_{2-x}$



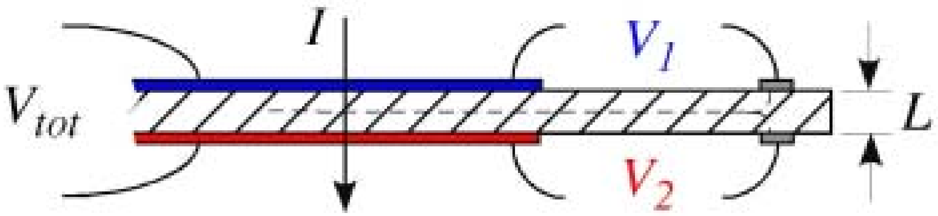
Thin-Film and patterned electrodes:

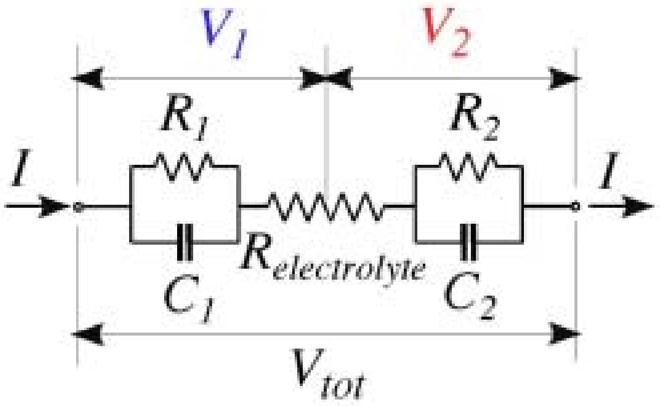
$La_{0.5}Sr_{0.5}CoO_{3-d}$
on single-crystal YSZ





Purpose of a half-cell measurement

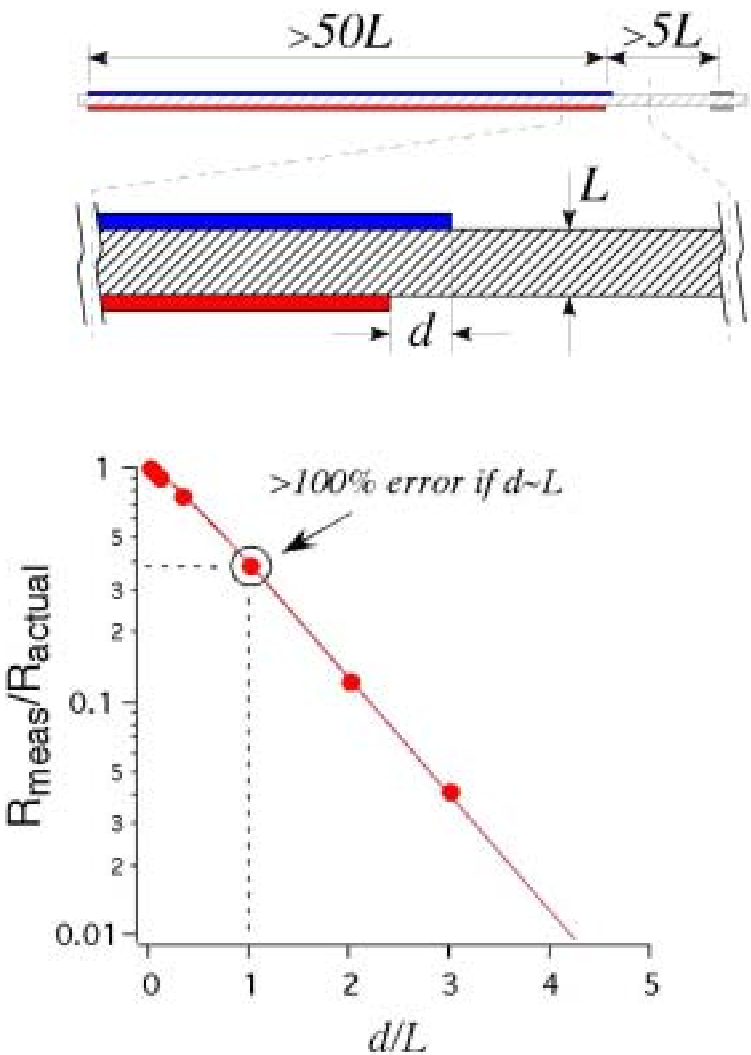




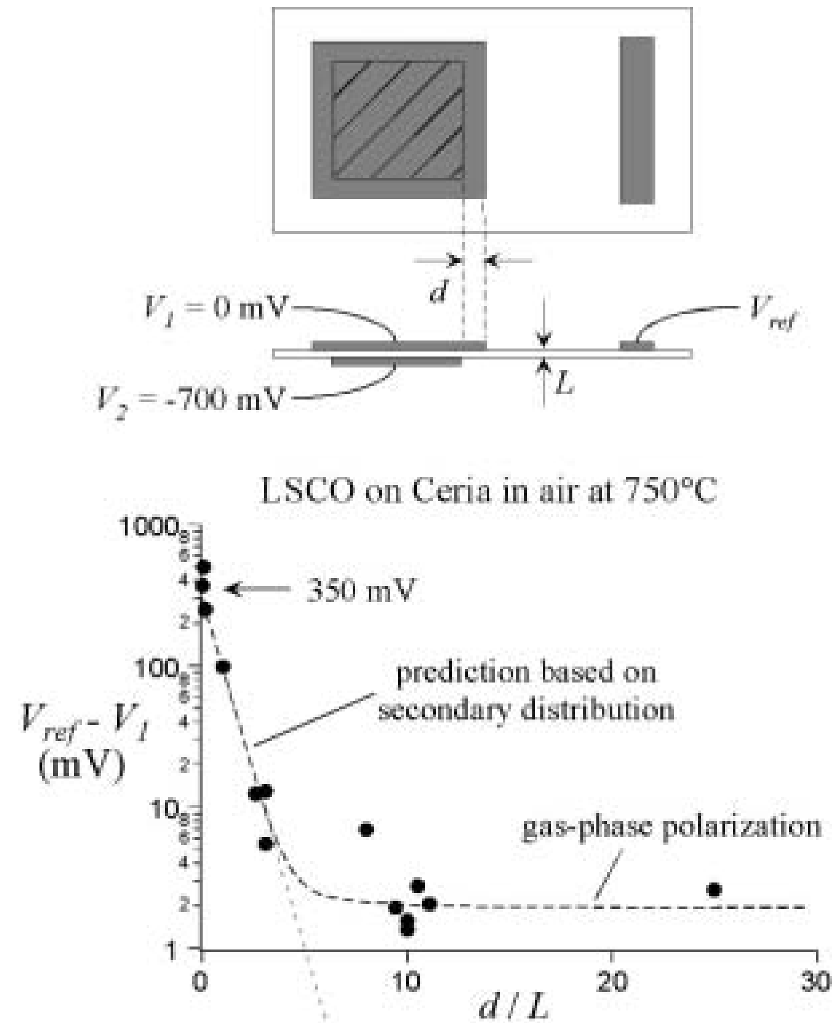
Typical Experimental Goals:

- Measure voltage loss associated with a particular electrode in an operating fuel cell.
- Test an electrode under a current load in a particular environment.
- Isolate the electrode frequency response (impedance).

Reference Electrodes are Prone to Error on Thin Cells

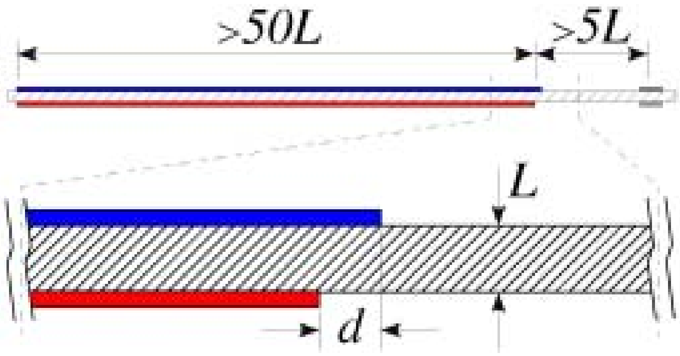


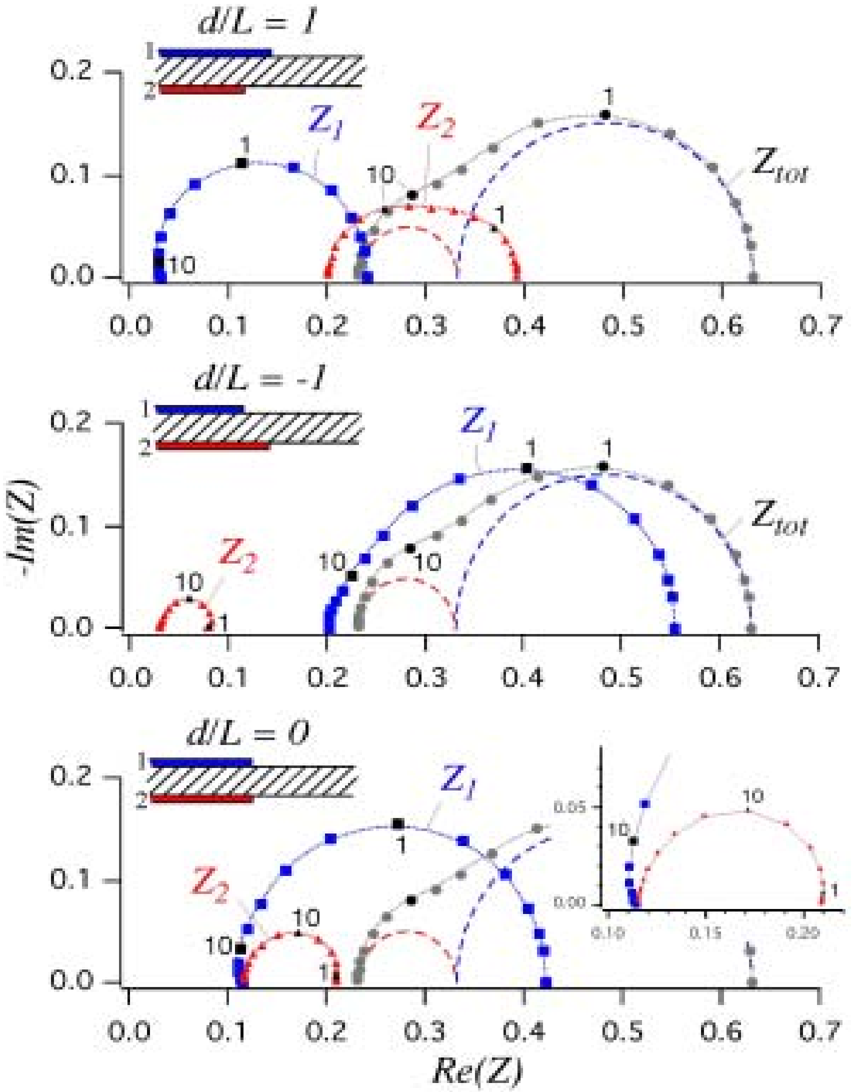
FEA calculation



Measured Error

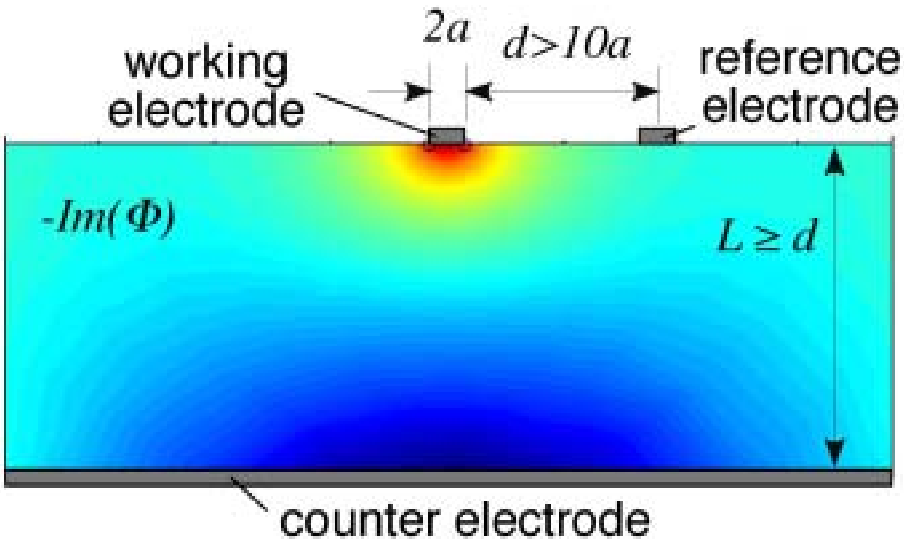
Error Includes Distortion of Impedance Spectra

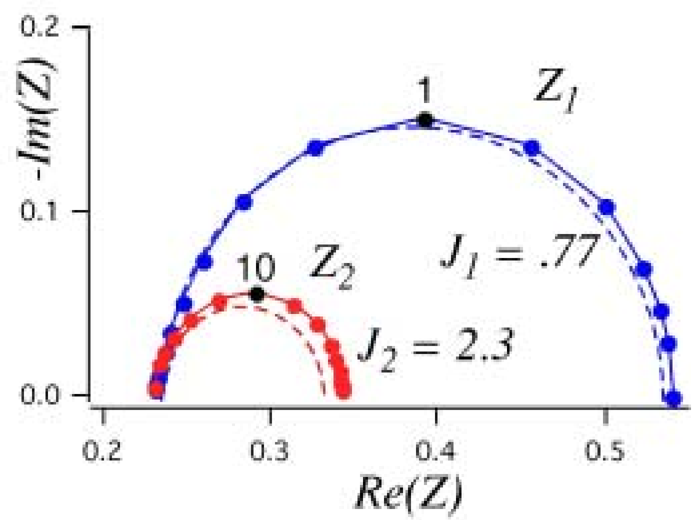




- "Cross-contamination" of WE and CE response.
- Distortion even with perfect electrode alignment.
- Impossible to avoid with thin cells having 1-D geometry.

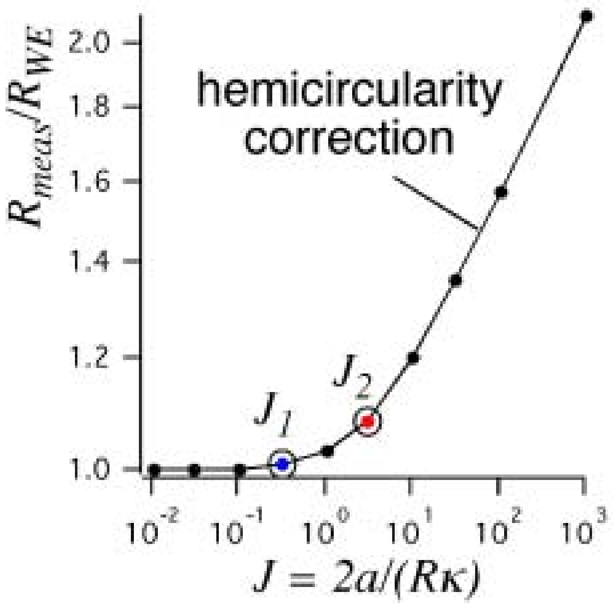
Principle of a 2-D "strip" microelectrode



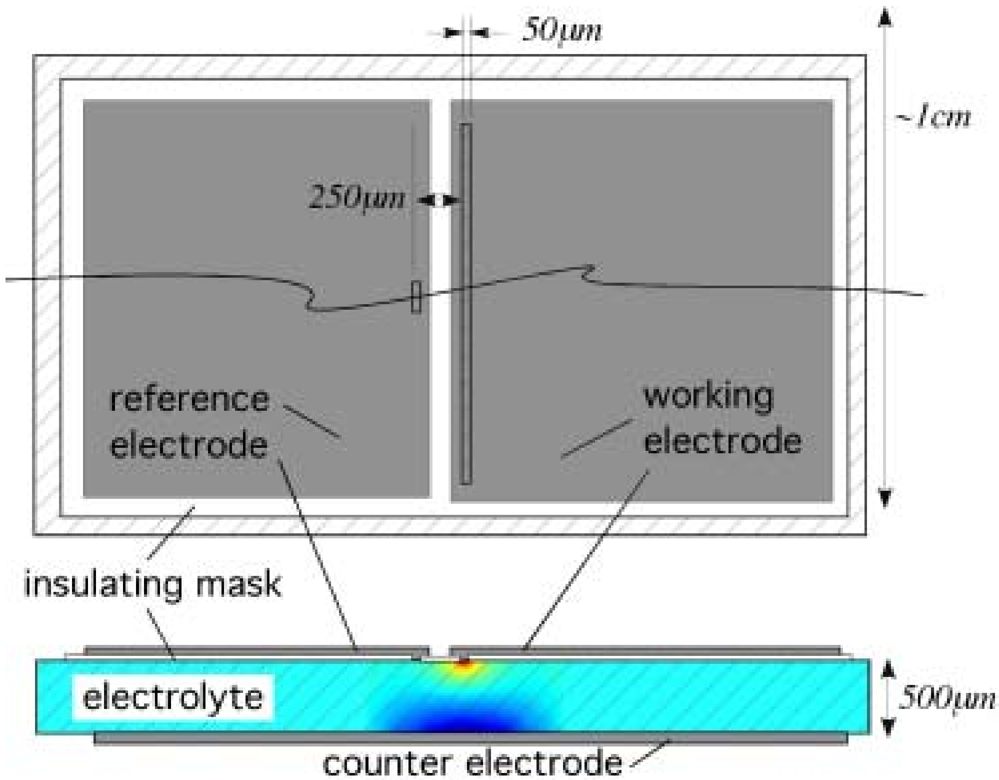


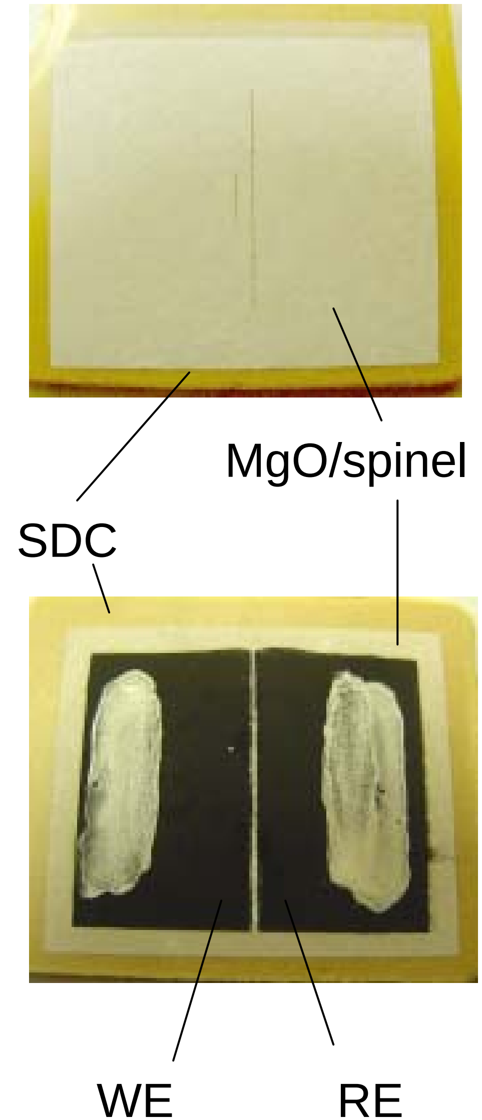
Potential benefits:

- Excellent isolation of WE.
- Representative materials.
- Ability to test at high bias.
- Reduced IR and inductive effects.
- Multiplicity through miniaturization.

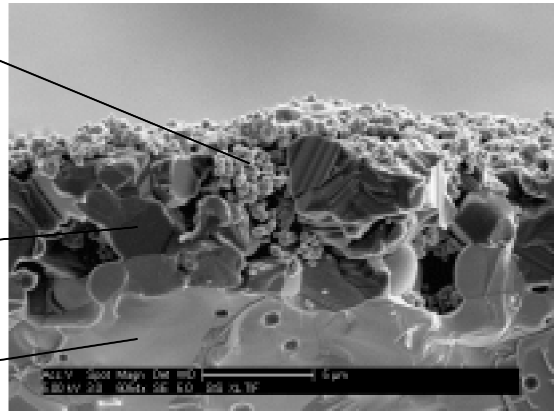


Phase 1 Cell Design and Implementation





Search for a Better Mask Material



Problems with MgO/spinel:

- Voids allow some electrode contact.
- Must be >50 micron thick.
- Must align multiple layers.
- Too course to pattern well.

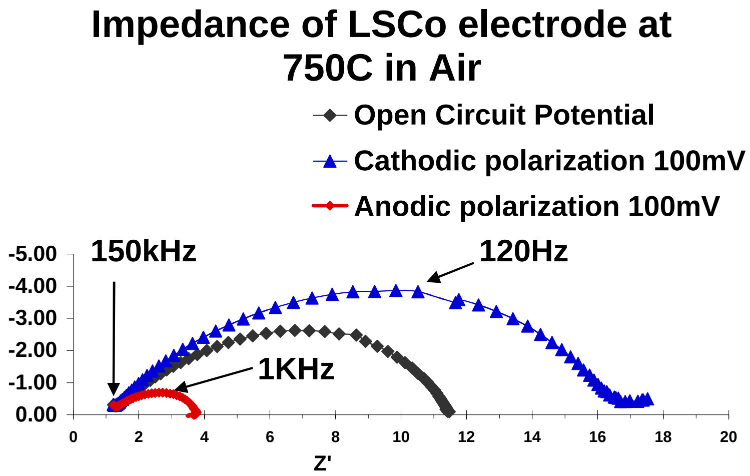
Current solution: colloidal MgO powder.

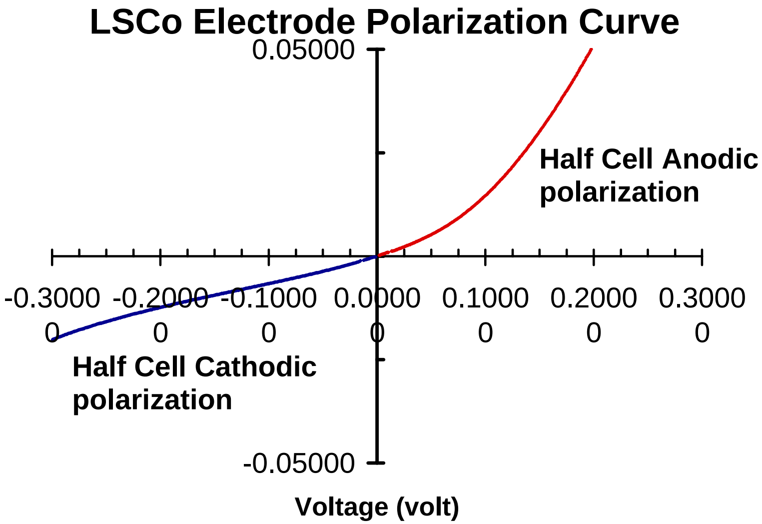
- 10 times better insulation with one layer.
- Only 10 microns thick.
- Results more repeatable.
- Less reactive with SDC.

Phase 2: Sputtered MgO films

Mask material	Resistance (Ω-cm^2)
MgO/spinel (1 layer)	3000
MgO/spinel (3 layers)	25,000
c-MgO (1 layer)	200,000
c-MgO (2 layers)	220,000

Preliminary results with LSCO on SDC.



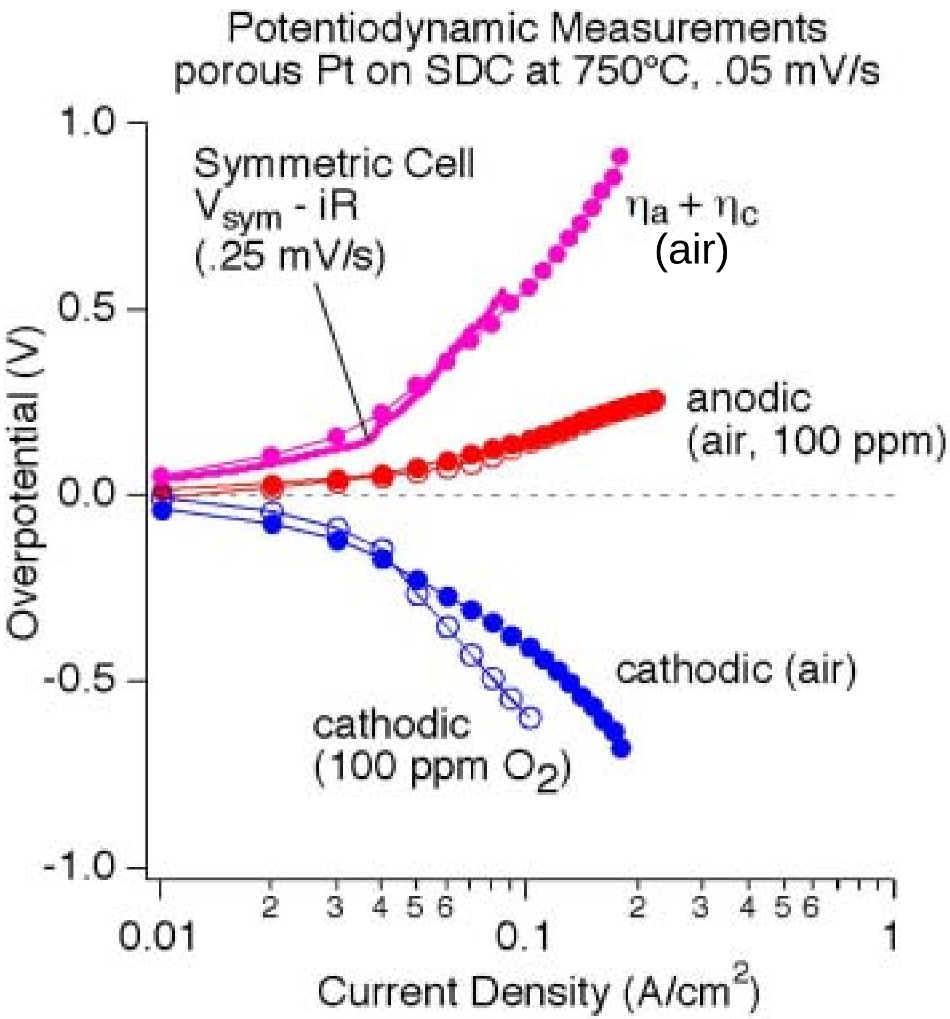


- Microelectrodes clearly reveal differences between cathodic and anodic polarization.
- Impedance exhibit clean and repeatable ohmic intercepts, indicating good frequency isolation and reduced effect of lead induction.
- Technique not quantitative with MgO/spinel mask.

Verification of Microelectrode Overpotentials

Procedure:

1) Measure *i-V* characteristics of microelectrode.
2) Subtract iR losses (based on impedance).
3) Add anode and cathode OP.
4) Compare to V(i)-iR for a full-sized symmetric cell having the same electrodes.



Conclusions:

- Sum of anode & cathode OP's yield values close to a symmetric cell.

- Anode and Cathode OP's have behavior consistent with literature observations.

Applications and Future Work

- Incorporate Microelectrodes into our perovskite electrode studies.

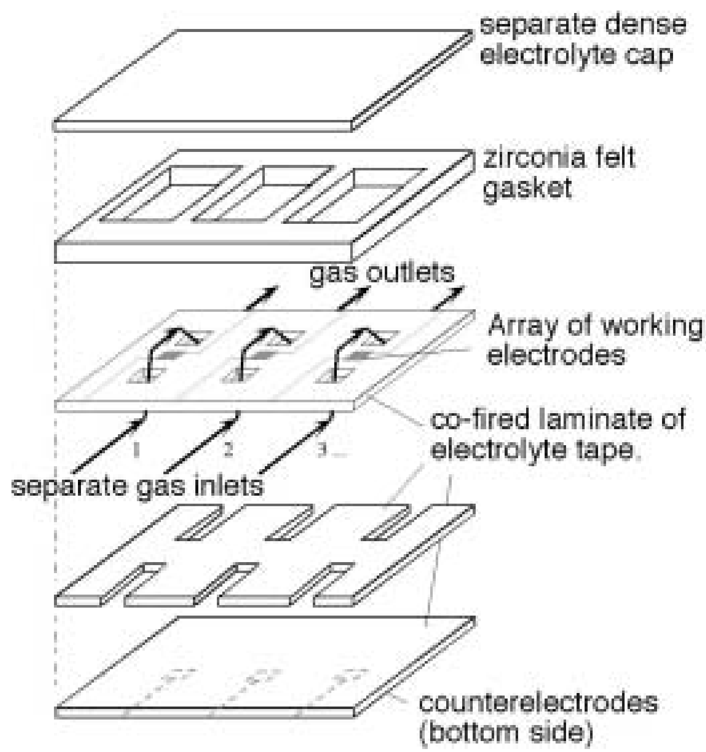
  - Mechanistic studies employing controlled microstructure.
  - Development of tailored microstructures for improved cathode performance.
  - Co-development of NLEIS and EFM.

- Sputtered thin-film mask

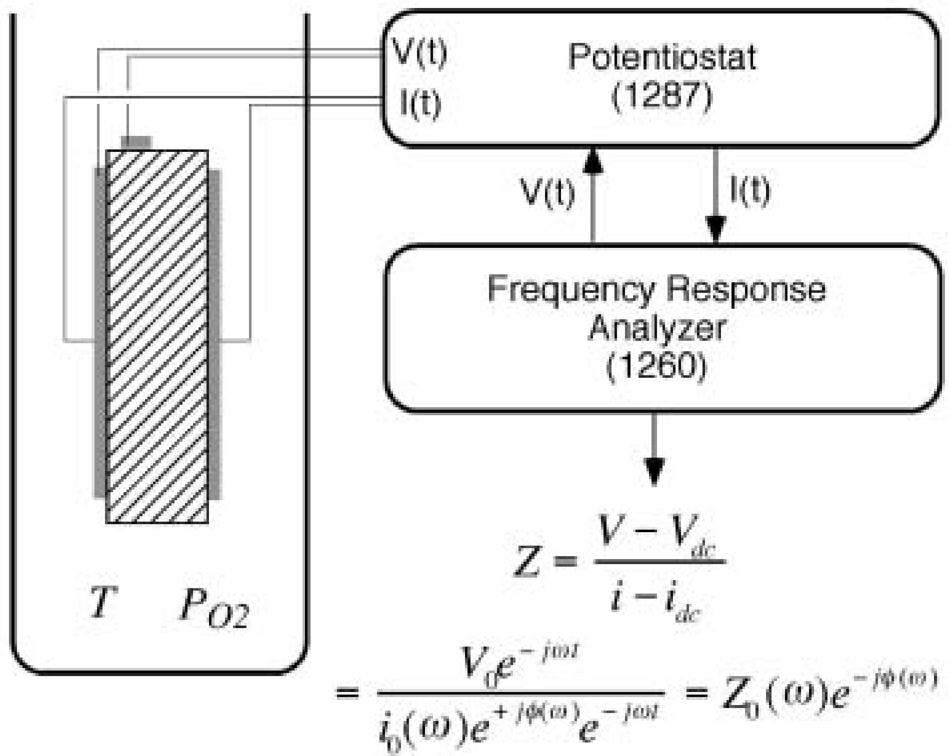
  - Thin mask = smaller dimensions.
  - Reduced risk of geometric effects.
  - Thinner electrolytes

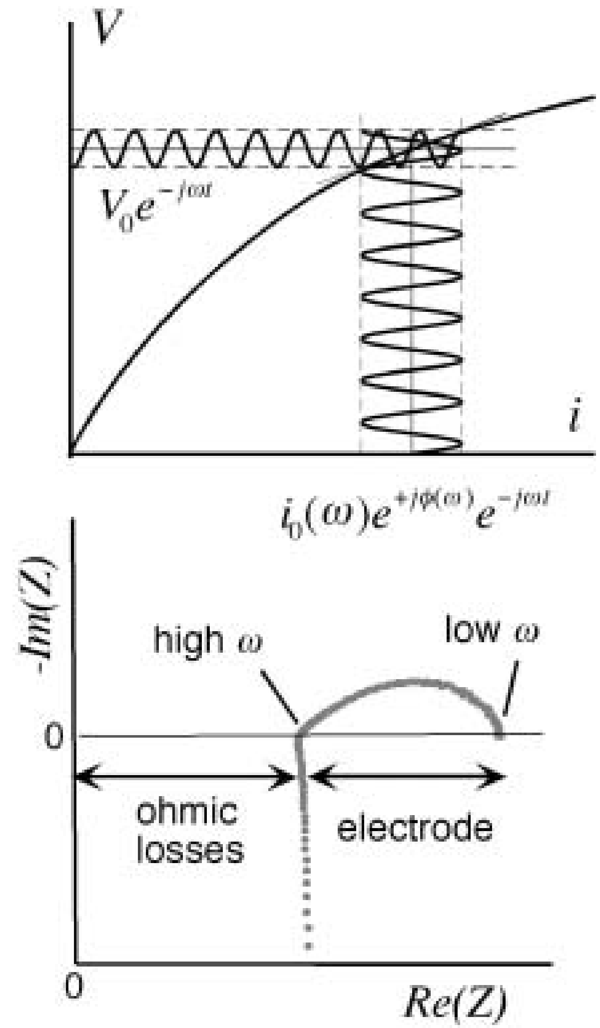
- Develop methods to test multiple cells on a single substrate.

  - Materials Screening
  - Massively Parallel Testing
  - Design of Experiments
  - Long-term Degradation



How Electrochemical Impedance Spectroscopy (EIS) works

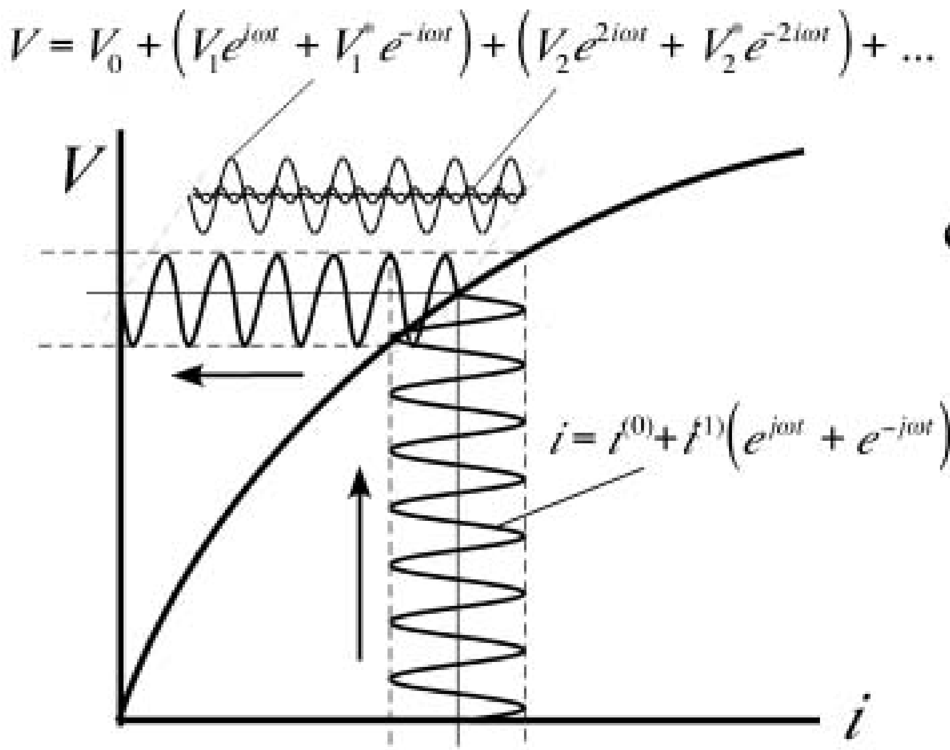




Plus: EIS facilitates separation of complex overlapping physics via. *time scale.*

Minus: multiple models tend to predict similar (or identical) linearized response.

What are harmonics, and why measure them?



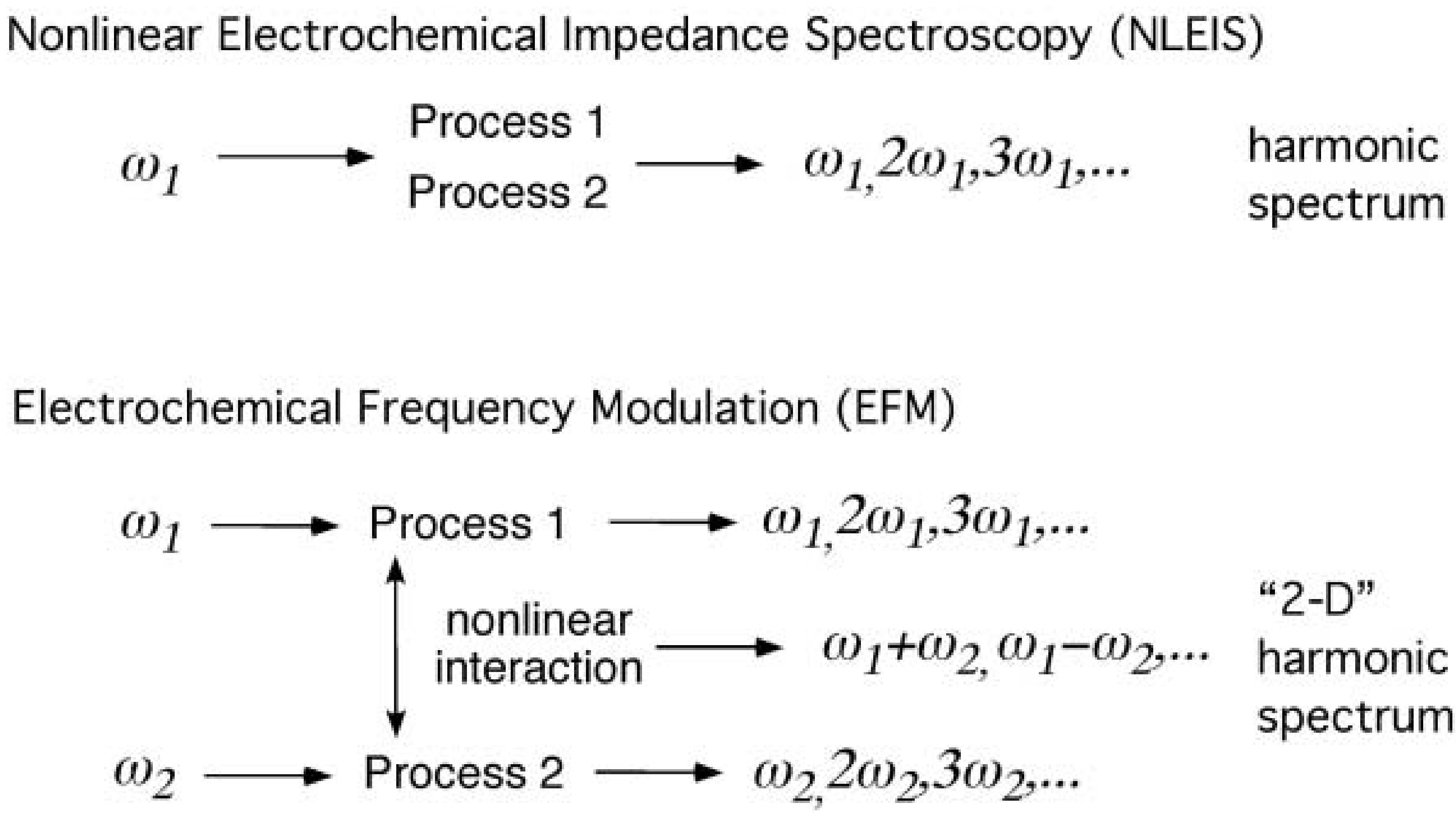
$\cos(\omega t)$ → $\dfrac{\partial c}{\partial t}$, $\cos(\omega t)$ → $\dfrac{\partial^2 c}{\partial y^2}$, $\cos^2(\omega t)$ → $\dfrac{\partial c}{\partial y}$

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial y^2} - \nu \frac{\partial c}{\partial y}$$

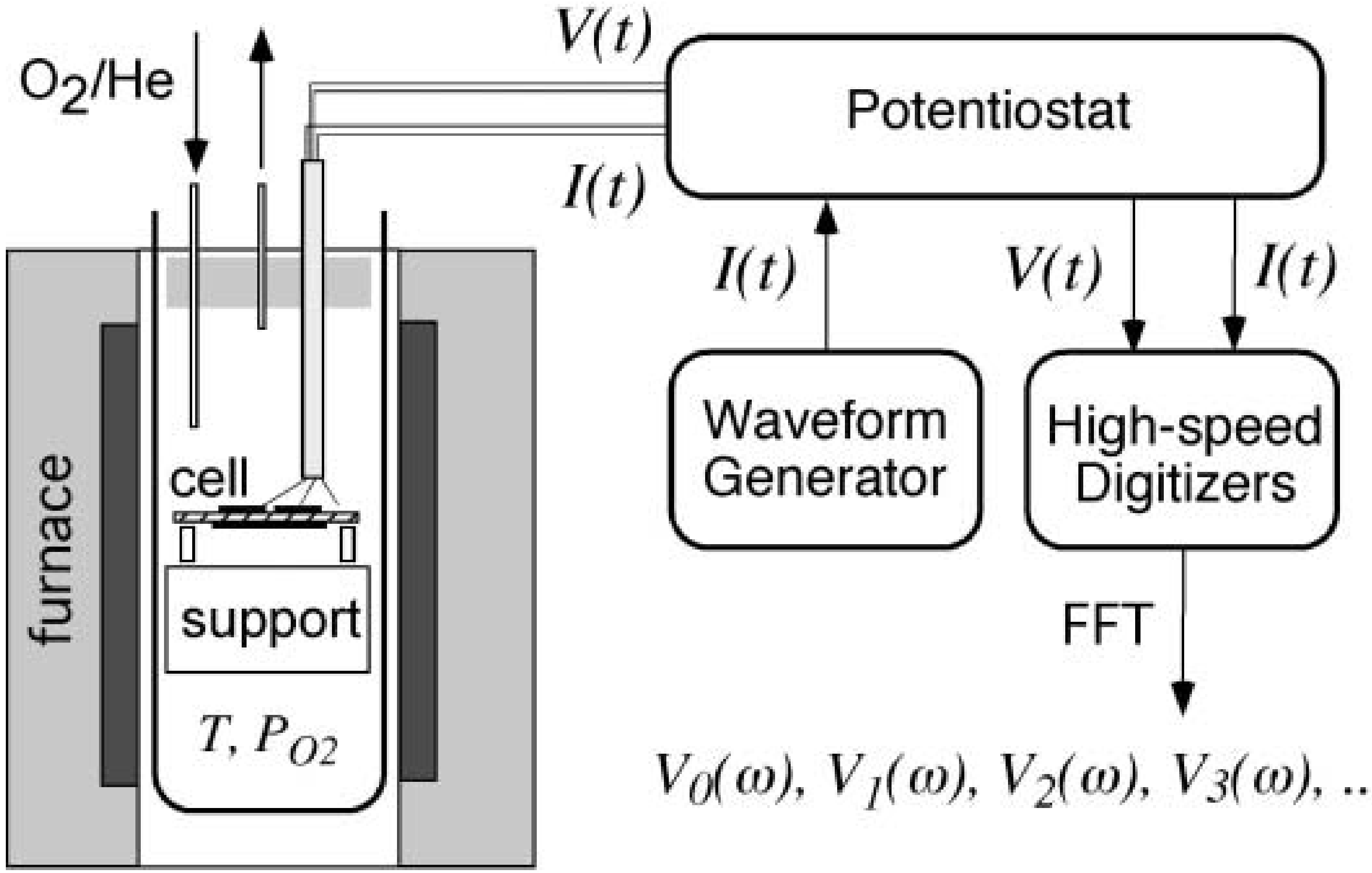
$$\cos^2(\omega t) = \frac{1}{2} + \frac{1}{2}\cos(2\omega t)$$

- All nonlinear systems generate responses at multiples of the excitation frequency (harmonics).
- The magnitude, sign, and phase of the harmonics are highly sensitive to the details of the underlying physics.

Types on nonlinear harmonic measurements

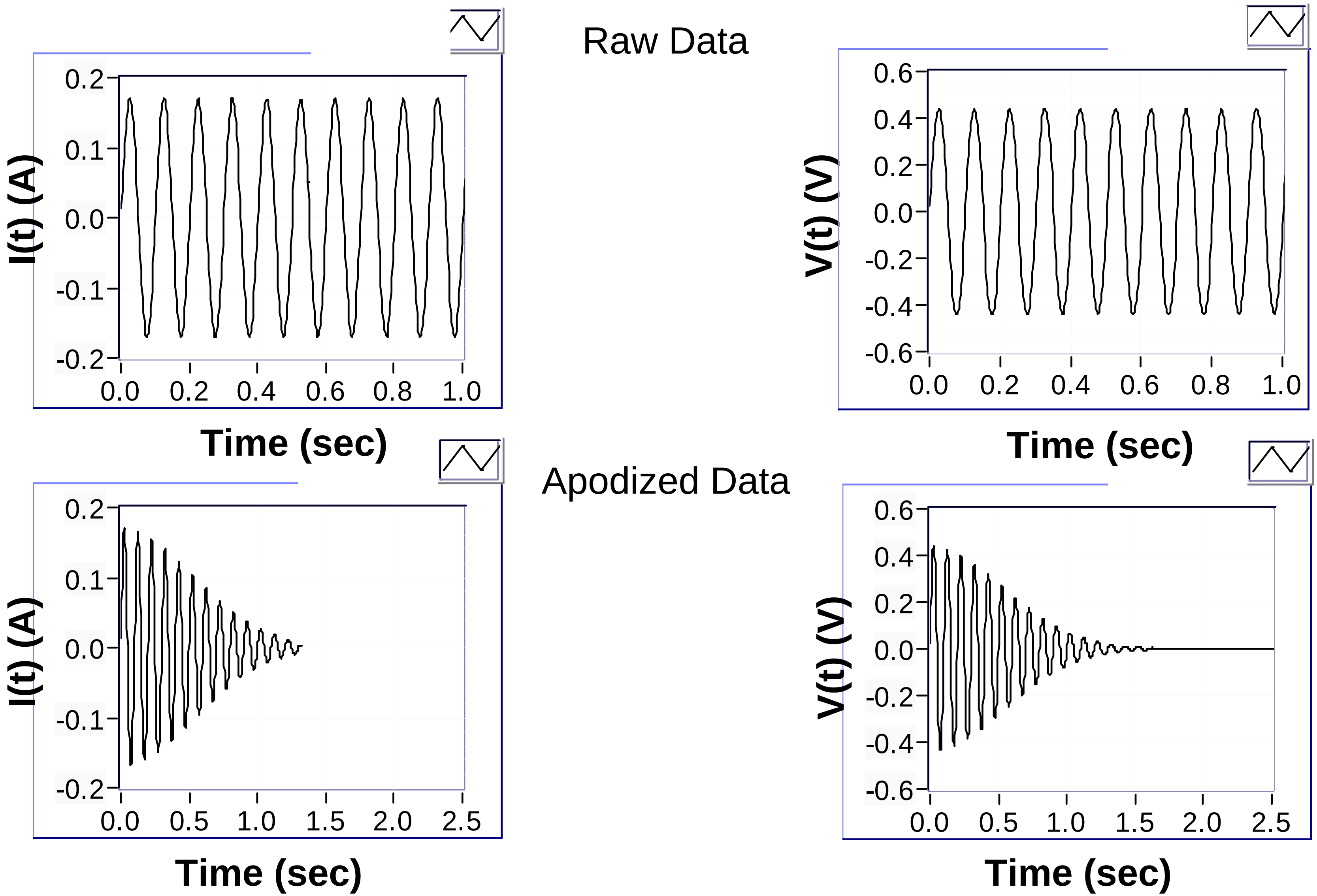


Our apparatus for NLEIS and EFM measurements



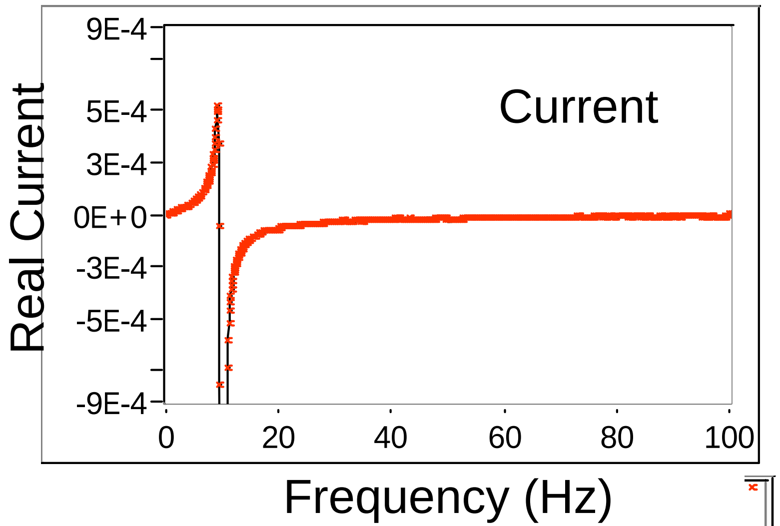
How NLEIS Data is Acquired and Processed

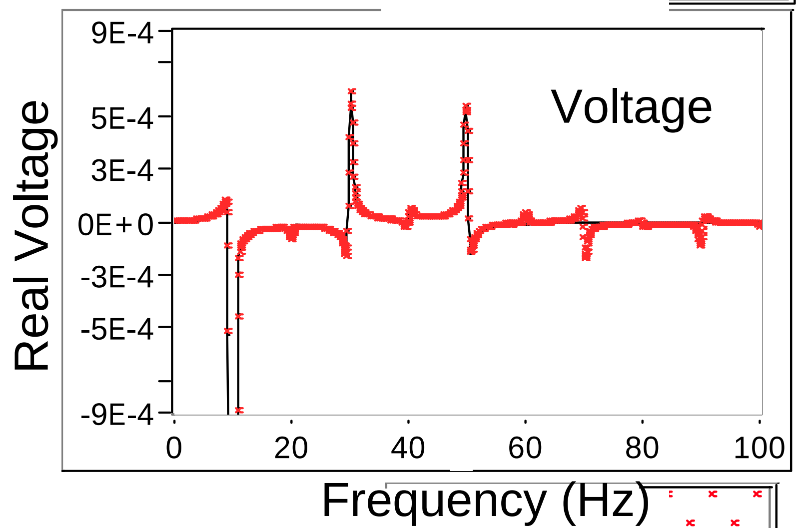
(example: LSCO on SDC at 750°C in air, 10 Hz)

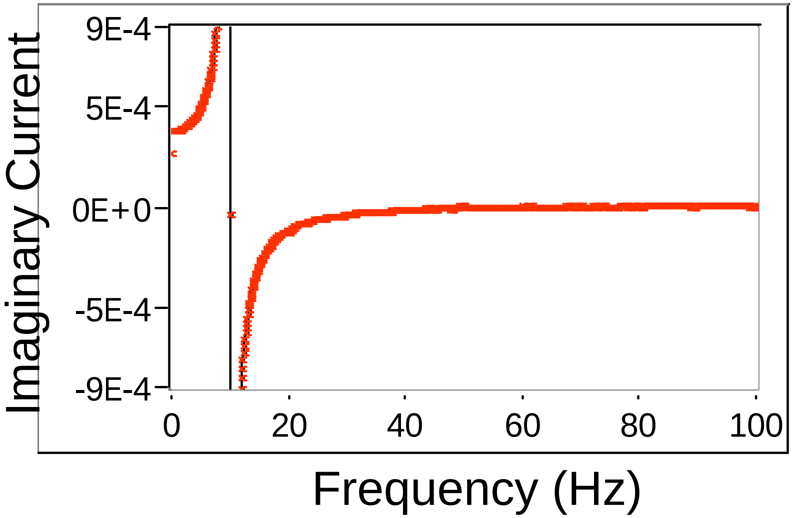


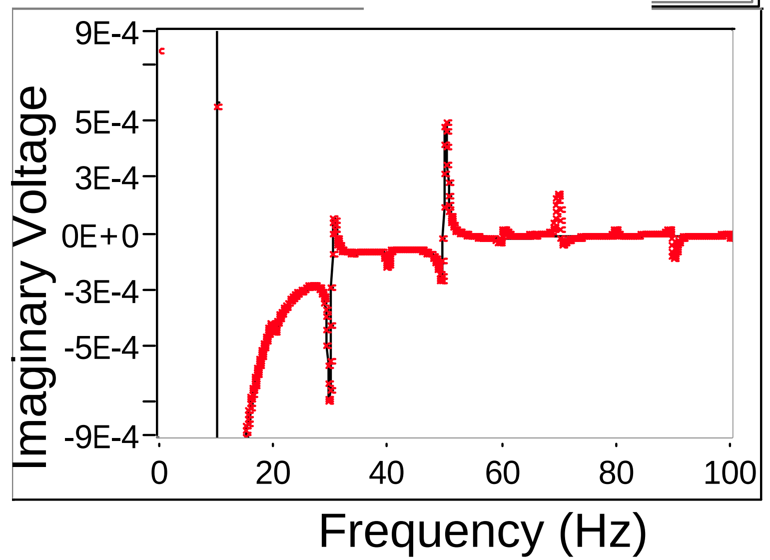
How NLEIS Data is Acquired and Processed

Complex Fourier Transformed Data



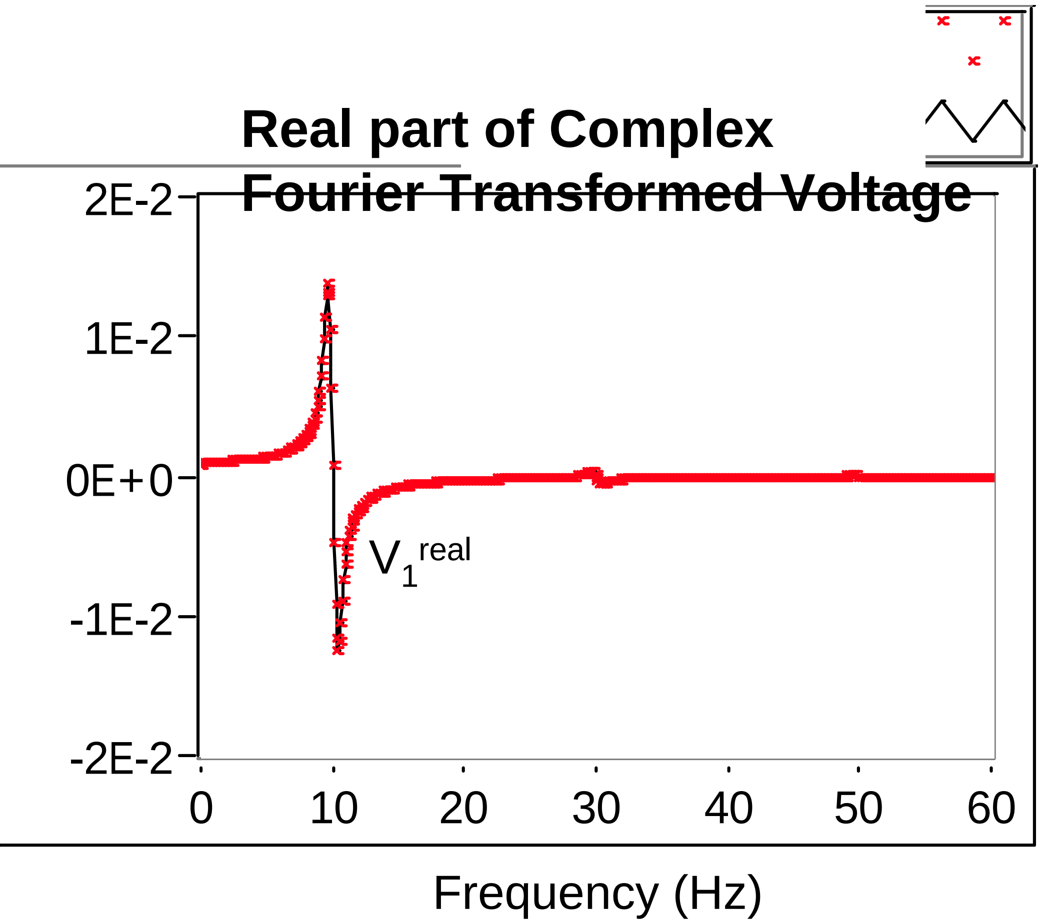


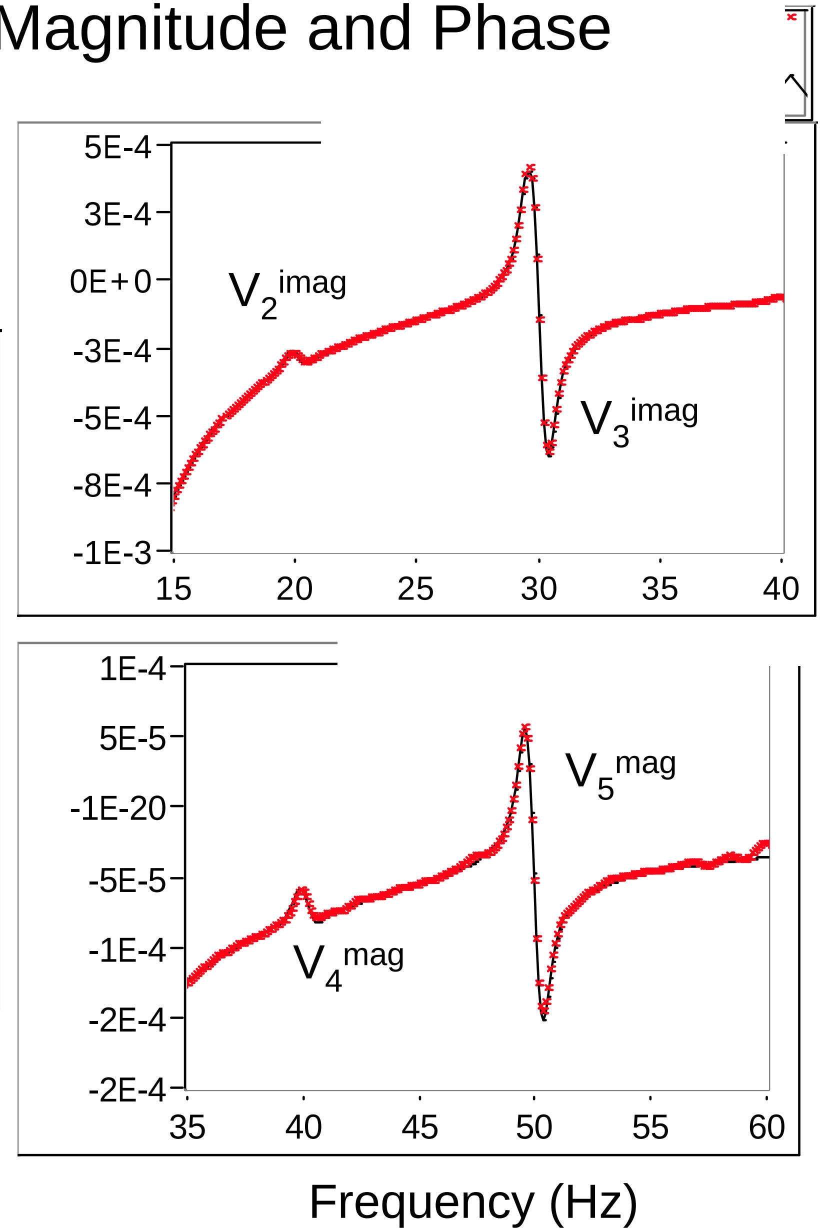




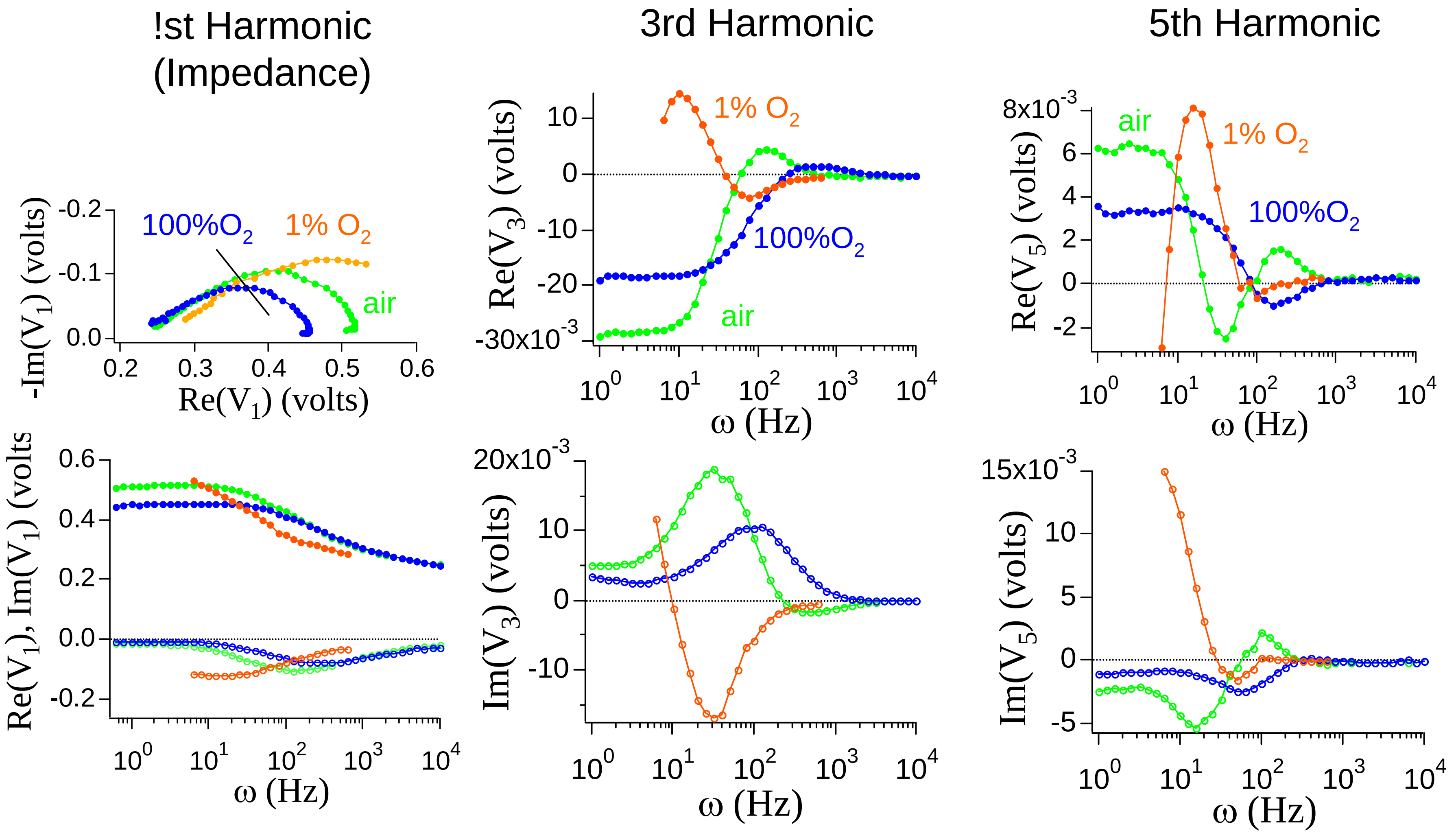
Gaussian Fit to Determine Magnitude and Phase

Real part of Complex Fourier Transformed Voltage





Harmonic Response of LSF-82 on SDC at 750°C (symmetric cell)



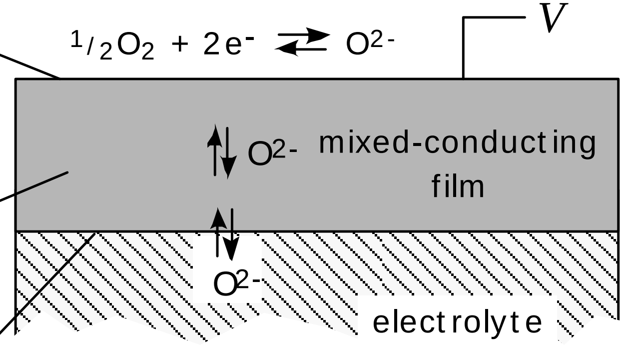
Possible sources of nonlinearity in a perovskite cathode.

$$\mathbf{n}\cdot\mathbf{N}_v\big|_{y=L} = k\left(\frac{(P_{O_2}^{gas})^n}{(P_{O_2}^{solid})^m} - (P_{O_2}^{solid})^{n-m}\right)$$

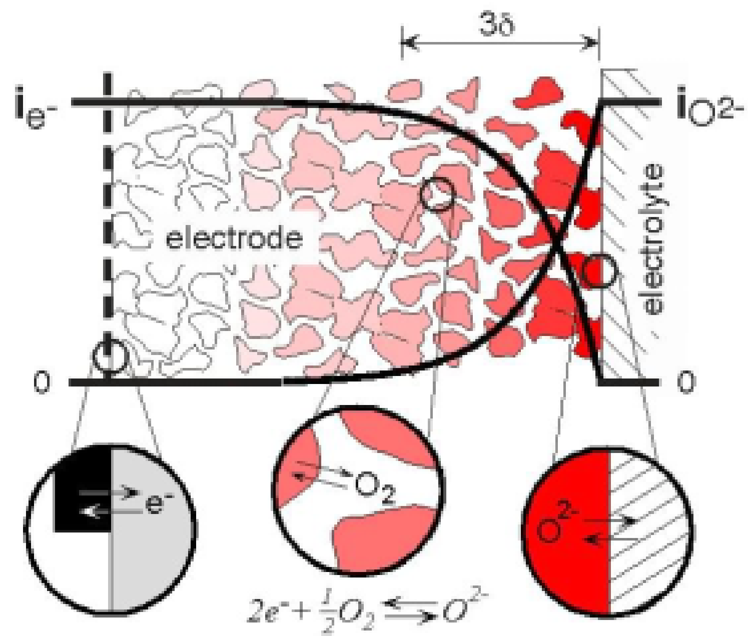
$$\frac{\partial x_v}{\partial t} = \frac{D_v}{RT}\nabla\cdot\left(-\frac{1}{2}\frac{\partial \ln P_{O_2}^{solid}}{\partial \ln x_v}\nabla x_v\right)$$

$$i = 2F(\mathbf{n}\cdot\mathbf{N}_v\big|_{y=0}) = i_{\pm}\left(e^{\frac{\alpha_1 F\eta_{int}}{RT}} - e^{\frac{-\alpha_2 F\eta_{int}}{RT}}\right) + C\frac{\partial \eta_{int}}{\partial t}$$

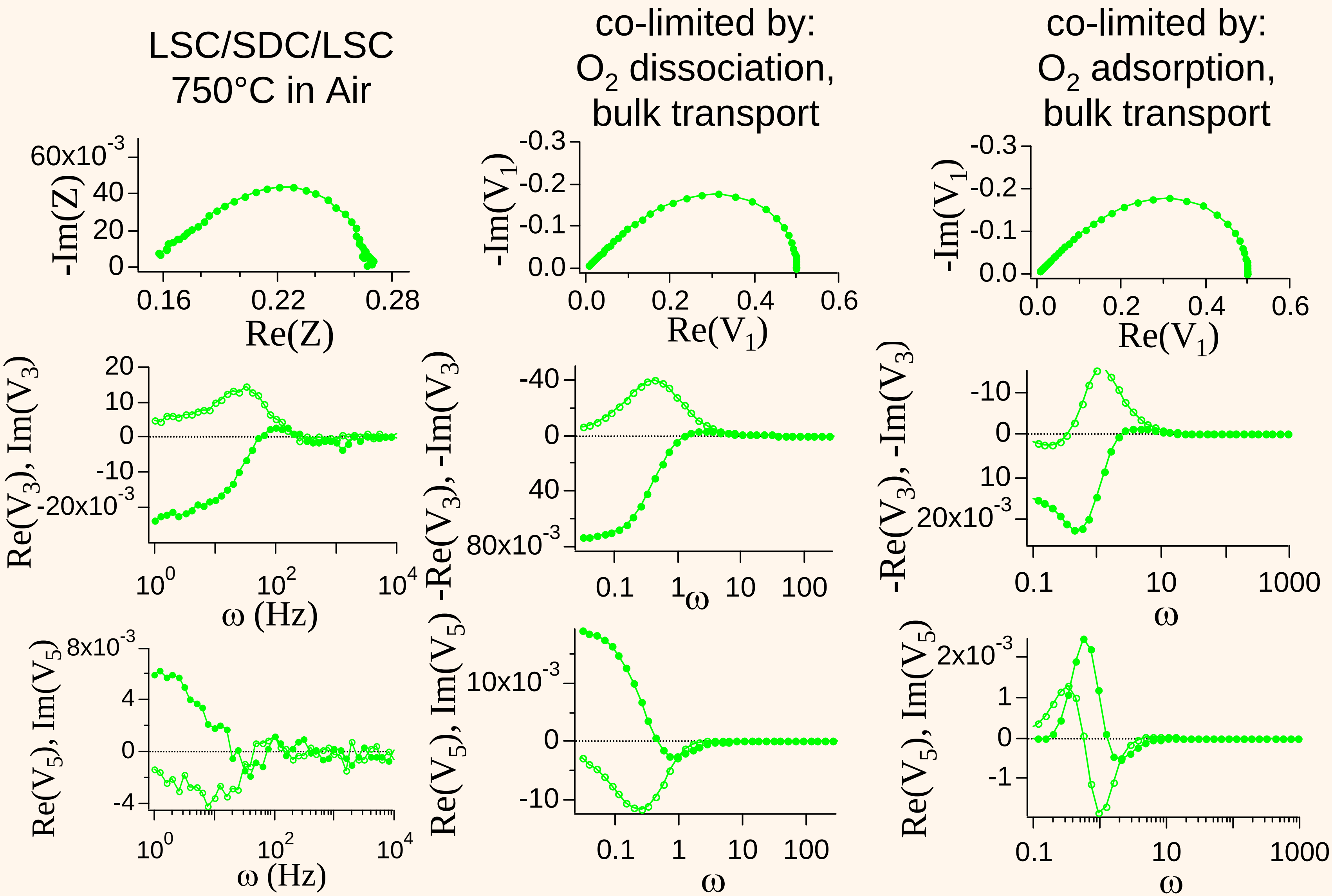
Dense Thin Film
Mixed-Conducting Electrode



Can be solved in 1-D, 2-D, or 3-D
using Finite Element Analysis (FEA)



Numerical FEA Modeling of Porous LSCO on SDC



Applications and Future Work

- NLEIS measurements on half-cell LSF/SDC microcathodes.
  - 2nd and 4th harmonics.
  - Higher S/N and reduced inductive effects at high frequency.

- Measurements and modeling of patterned electrodes (collaborative with PNNL and U Houston).

- Application to developing new materials and microstructures for cathodes (joint with MSE at UW).

- NLEIS as an alternative method for characterization and diagnosis of cells/stacks, with no additional experimental effort/time.
  - Look at materials in industrial development.
  - Build a database of characteristic behavior.

Summary

- Microelectrodes potentially offer a more reliable vehicle for both measurement and development testing.
- It may be possible to use microelectrodes for for design-of-experiments or other combinatorial applications.
- NLEIS appears to be a promising method for both electrode analysis and characterization/diagnosis of cells/stacks, with no additional experimental effort/time.
- These tools will be used in subsequent work to develop a deeper understanding of electrode mechanisms, and new materials and microstructures for cathodes.