DEVELOPMENT OF HIGH PRESSURE SOFC TEST STAND AND IN-SITU CHARACTERIZATION OF ANODE SUPPORTED CELLS USING TIME DOMAIN IMPEDANCE SPECTROSCOPY

By

Nathanael Royer

Outline

- ***Introduction***
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- Co-Mn Spinel Coatings
- Time Domain Impedance Spectroscopy
  - Motivation/Background
  - Device Theory of Operation
  - Software/Hardware Validation
  - Application to Pressurized SOFCs
- Conclusions

Why Pressurization?

- Pressurization of SOFCs can be beneficial in the following ways:
  - Increased Performance
    - Higher Nernst potential
    - Reduced activation and gas diffusion losses
  - System Integration Benefits
    - SOFC-GT hybridization
    - Co-Electrolysis and methanation
    - Hydrogen production at storage/use pressure

Research Questions

Overall:

- How does pressurization effect performance of anode supported SOFC's in a realistic stack environment?

Specific Objectives:

- Design and build a test station capable of characterizing pressurized SOFC's.
- Create a stack arrangement which closely mimics commercial technology.
- Quantify the performance benefits, if any, of pressurization.
- Determine what specific mechanisms are contributing to performance benefits.

Outline

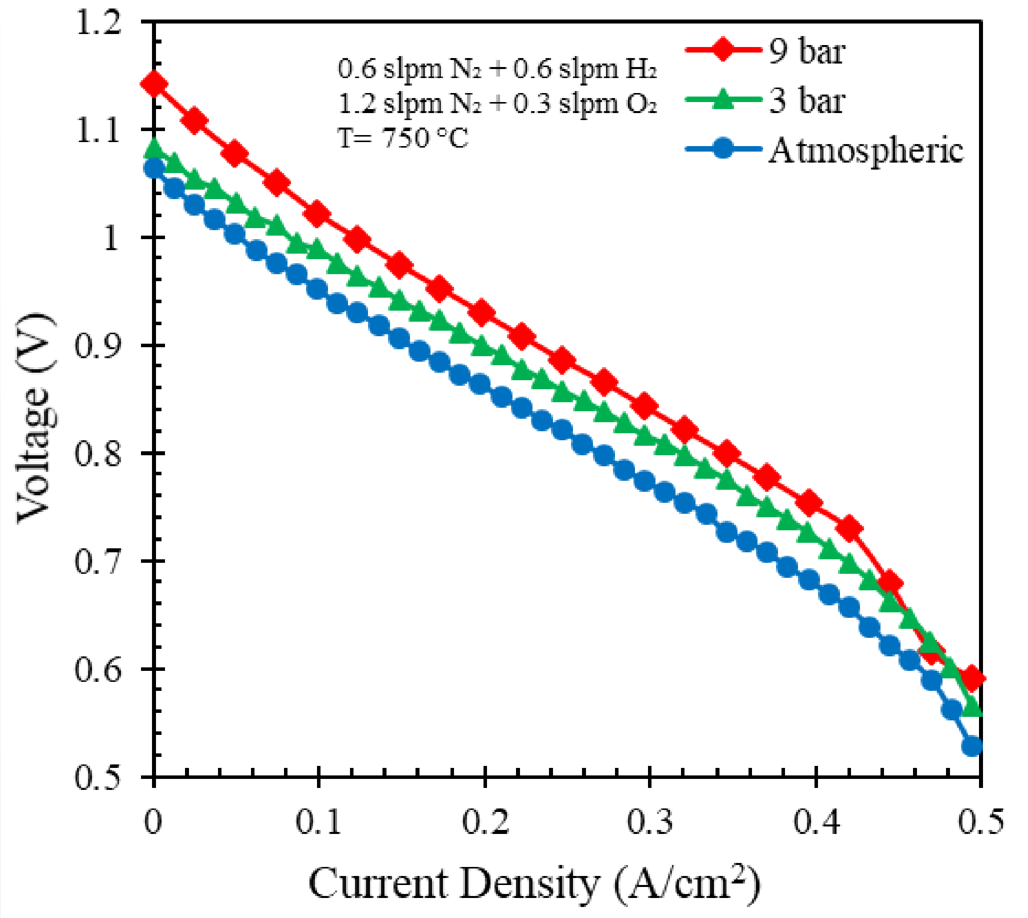
- Introduction
  - Motivation and Objectives
- ***Pressurized SOFC Test Stand***
- Co-Mn Spinel Coatings
- Time Domain Impedance Spectroscopy
  - Motivation/Background
  - Device Theory of Operation
  - Software/Hardware Validation
  - Application to Pressurized SOFCs
- Conclusions

Test Station Design

- Furnace rating: 10 bar, 1000 ˚C
- Bronkhorst mas flow meters with 50:1 turndown ratio:
  - Anode: 5slpm N2, 5slpm H2, 0.2 slpm CO2, 2 slpm CO, and 5slpm CH4
  - Cathode: 10slpm N2 and 10slpm O2
- Independent/coupled back pressure control to 10 bar for cathode/anode/furnace
- A hydraulic ram assembly to provide stack compression for sealing

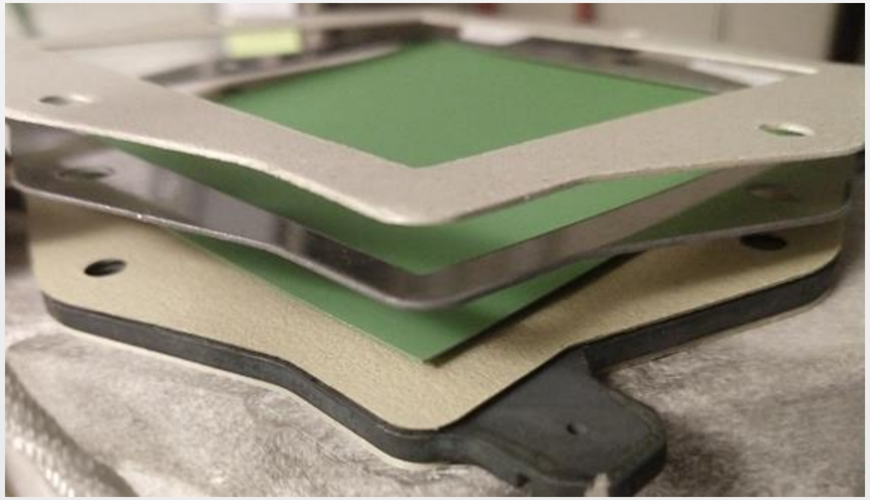
Initial Results

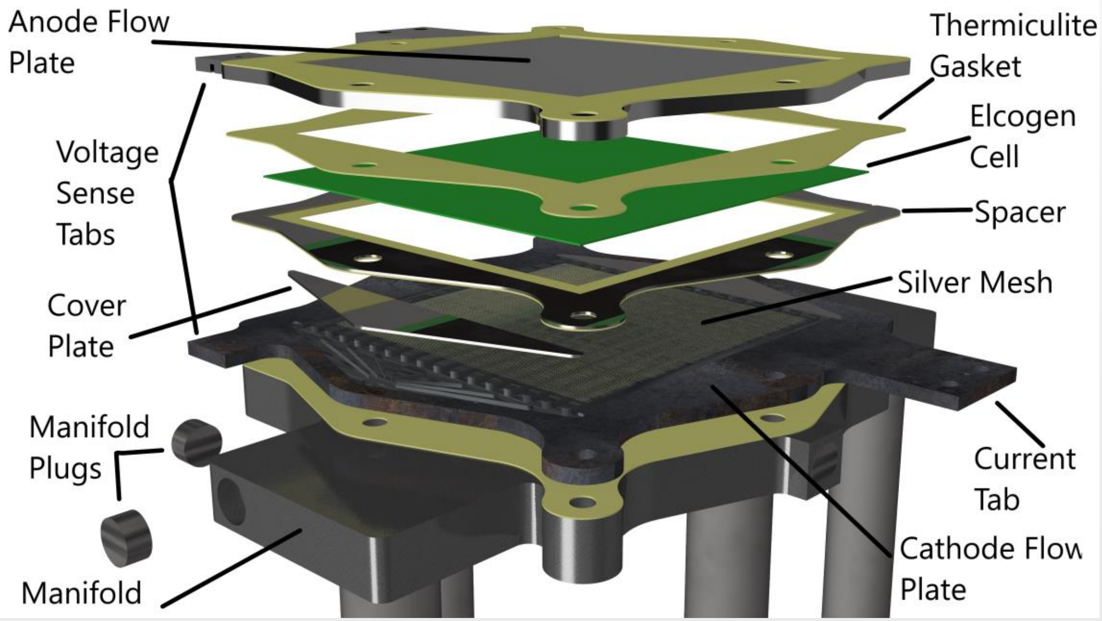
- Low OCV indicates leakage
- Power density at 0.85 V saw a 37.3% increase from atmospheric to 9 bar
- Clear indications of concentration limiting behavior at high current densities
- ASR varied from1.01 Ω cm² at atmospheric pressure, to 0.82 Ω cm² at 9 bar



Redesigned Stack

- Replaces glass seal with thermiculite 870
- Reduces total part count
- Mass Produced, disposable flow plates for repeatability & cost effectiveness
- Reduces compressive load by order of magnitude
- Dedicated voltage sense tabs
- Single manifold with separate inlets/outlets





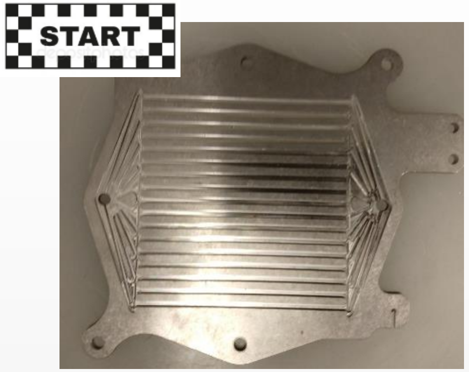
Outline

- Introduction
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- ***Co-Mn Spinel Coatings***
- Time Domain Impedance Spectroscopy
  - Motivation/Background
  - Device Theory of Operation
  - Software/Hardware Validation
  - Application to Pressurized SOFCs
- Conclusions

Co-Mn Coatings Background/Motivation

- Why Develop in house coatings?
  - Coating large numbers of plates for disposable stack was cost prohibitive
  - Having in house coating method allows flexibility in testing new flow plate designs/materials
  - Improved/less expensive cathode interconnect coatings necessary for wider adoption of SOFC technology
- Co-Mn spinel coatings have received extensive attention due to their low resisitivity, excellent chrome blocking capability, and close COE match to stainless steel.
- Electrolytic deposition is a simple, inexpensive method capable of coating complex geometries.
- The general procedures found in Wu et al were followed, which involved co-deposition of Co-Mn from a simple sulfate bath followed by thermal annealing to produce Co-Mn spinel.

Co-Mn Coating Process



As received CNC Milled 430 SS flow plate

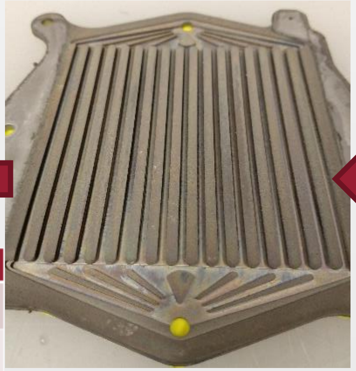
Sandblast coating area thoroughly

Ultrasonically Clean 30 min each:
- Acetone
- 50/50 Ethanol/D.I water
- D.I water

Mask all non-coated area

Etch plate for 60 sec in 50 v/v % sulfuric acid bath

Adjust DC Voltage to -7.5 V and run for 3 hrs



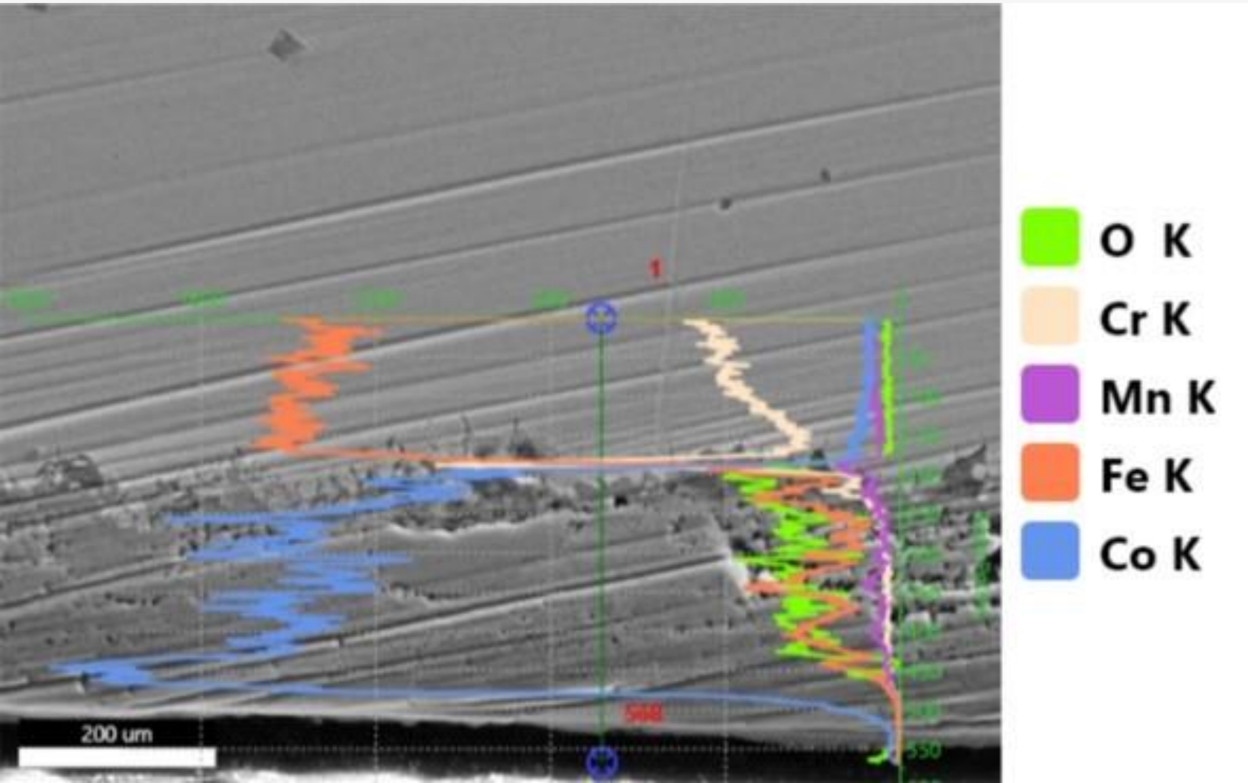
Remove tape and allow to dry

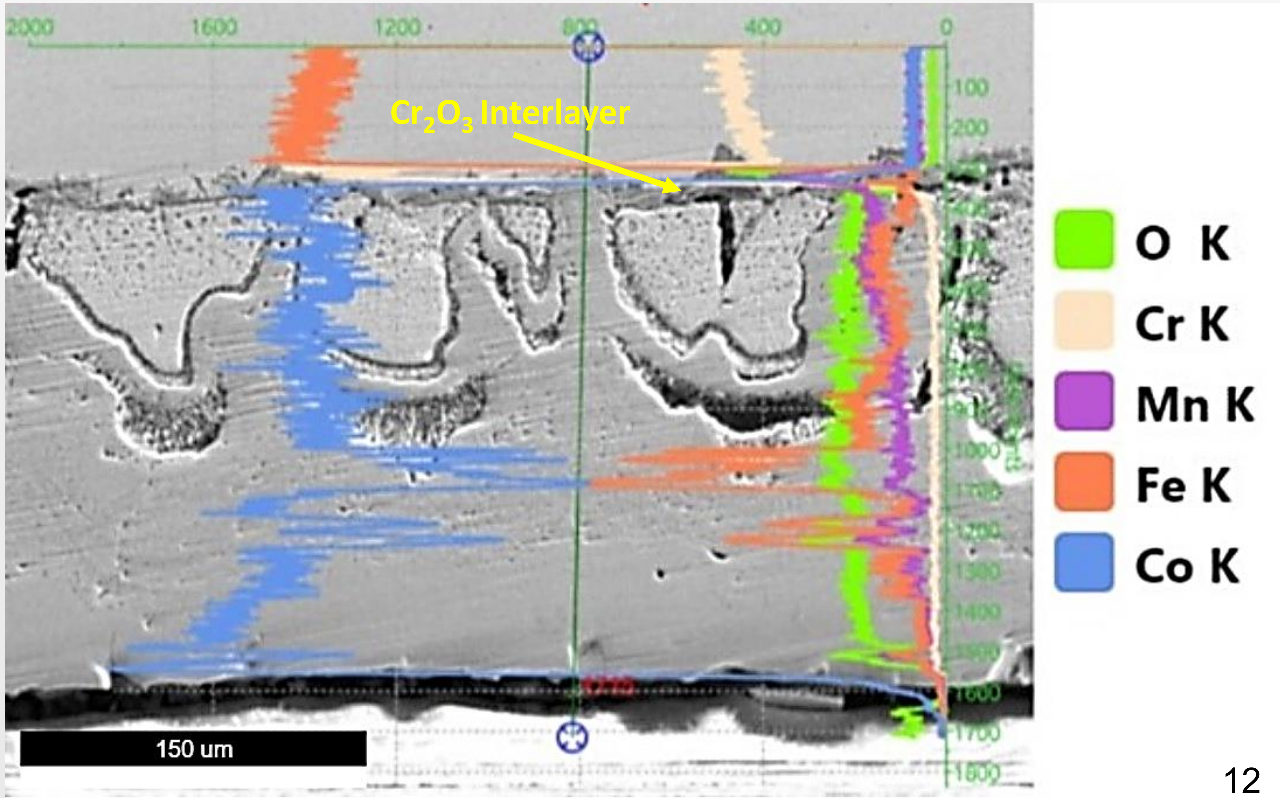
Temperature	Time	Flows
25°C-1000°C	08:22	0.2 CFH H_2 & 4 CFH N_2
1000°C-1000°C	02:00	0.2 CFH H_2 & 4 CFH N_2
1000°C-900°C	00:50	4 CFH N_2
900°C-900°C	02:30	0.85 CFH O_2 & 4 CFH N_2
900°C-25°C	07:17	4 CFH N_2

Finished Co-Mn Spinel Coating

Bottom of Channel:
- Coating is continuous and roughly 50 µm thick.
- Mn content still very low.
- The Fe impurity seems to have diffused inward.
- Outer shell appears to be pure Co oxide.

Top of Channel (Contact point of cell):
- Coating is continuous, no cracking.
- Surface is very uniform and even, roughly 220 µm.
- Uneven deposits present close to substrate.
- Spike in Cr between coating and substrate evidence of a thin Cr_2O_3 interlayer.





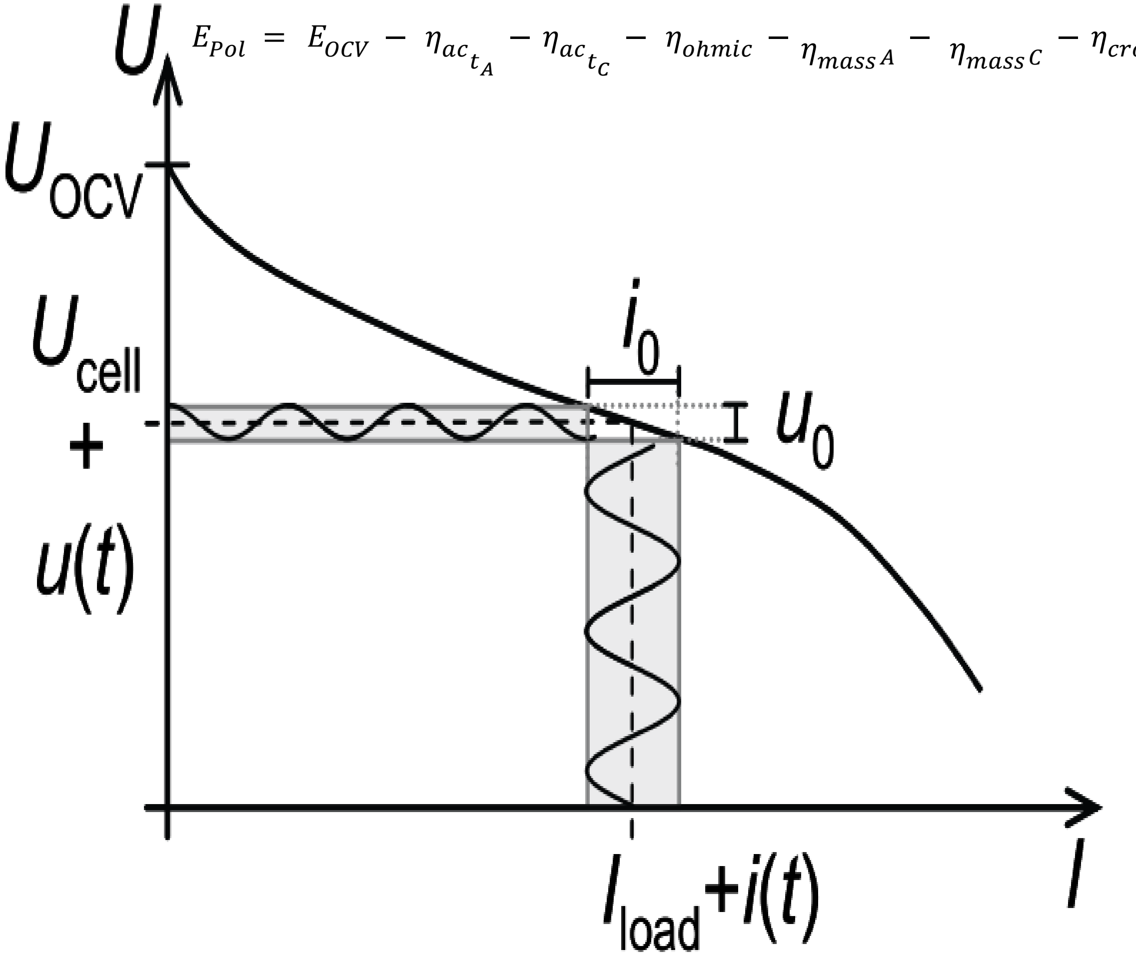
Outline

- Introduction
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- Co-Mn Spinel Coatings
- ***Time Domain Impedance Spectroscopy***
  - ***Motivation/Background***
  - Device Theory of Operation
  - Software/Hardware Validation
  - Application to Pressurized SOFCs
- Conclusions

EIS Introduction

- Electrochemical Impedance Spectroscopy (EIS) is primarily used to separate individual polarization mechanisms from the overall impedance.
- This is commonly achieved using a Frequency Response Analyzer (FRA).
  - FRA's typically apply a single frequency excitation of voltage/current to the cell and measure the phase shift and amplitude of the resulting current/voltage at that frequency.
- The full impedance spectrum is obtained by varying the frequency over a wide range, for electrochemical systems usually from 1 MHz to 1 mHz.

$$E_{Pol} = E_{OCV} - \eta_{ac_{t_A}} - \eta_{ac_{t_C}} - \eta_{ohmic} - \eta_{mass\,A} - \eta_{mass\,C} - \eta_{cross}$$

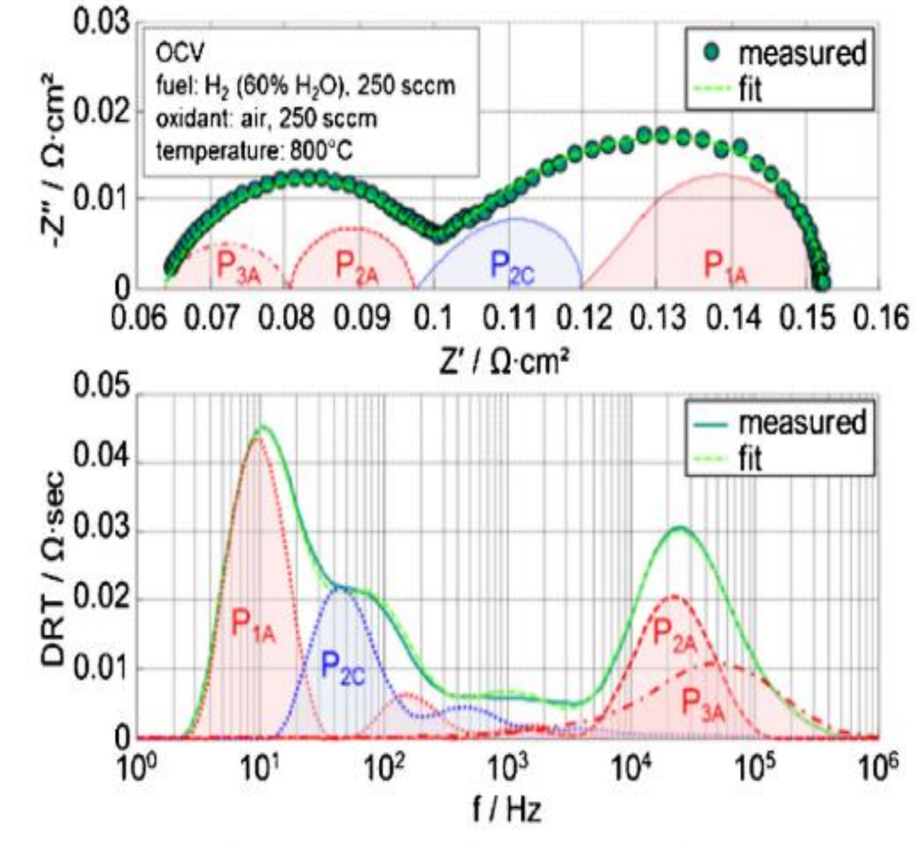


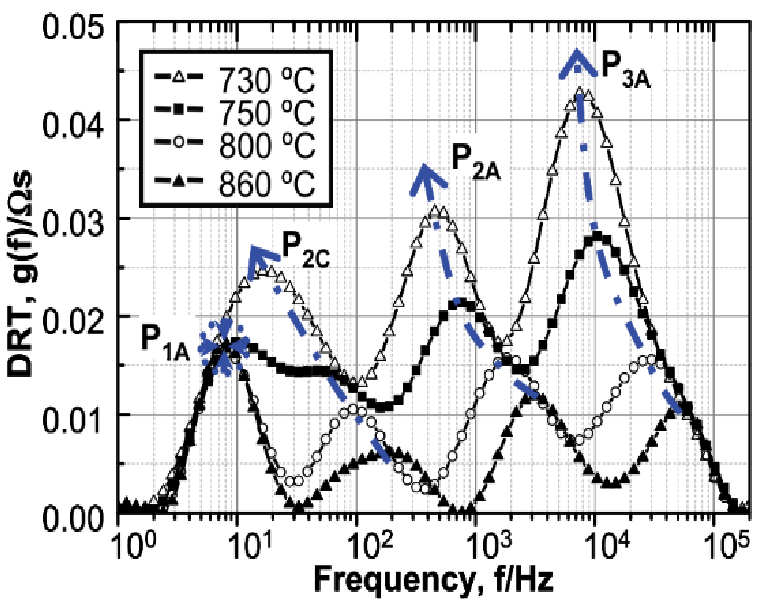
$$Z(\omega) = \frac{u_0 e^{j\omega t}}{i_0 e^{j\omega t - j\theta}} = \frac{u_0}{i_0} e^{j\theta} = Z_0(\cos\theta + j\sin\theta) = Z_{re} + jZ_{im}$$

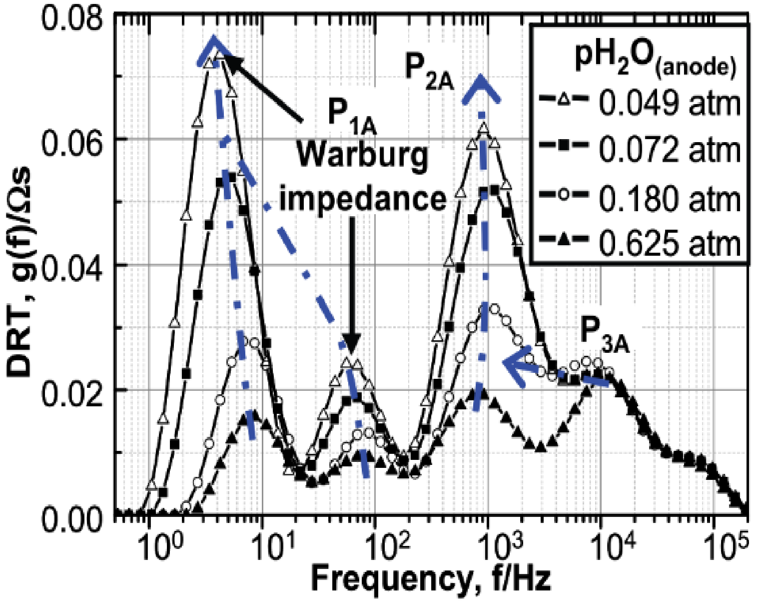
A. Leonide, V. Sonn, A. Weber, and E. Ivers-Tiffée, "Evaluation and Modeling of the Cell Resistance in Anode-Supported Solid Oxide Fuel Cells," J. Electrochem. Soc., vol. 155, no. 1, p. B36, 2007

DRT Introduction

- One way to interpret impedance spectra is through a Distribution of Relaxation Times (DRT) analysis.
- The impedance spectrum is deconvoluted to further resolve individual polarization processes.
- This technique has been used to learn more about the effects of different fuels, coking, long term degradation, separation of anode vs. cathode processes, etc.
- System variables such as temperature, fuel utilization, cathode oxygen partial pressure, and system pressure can be varied and the corresponding effects on the peaks can be analyzed.







[1] E. IVERS-TIFFÉE and A. WEBER, "Evaluation of electrochemical impedance spectra by the distribution of relaxation times," *J. Ceram. Soc. Japan*, vol. 125, no. 4, pp. 193–201, 2017.

[2] A. Leonide, *SOFC modelling and parameter identification by means of impedance spectr* Technische Informationsbibliothek u. Universitätsbibliothek, 2010.

Initial Motivation for Alternative EIS Technique

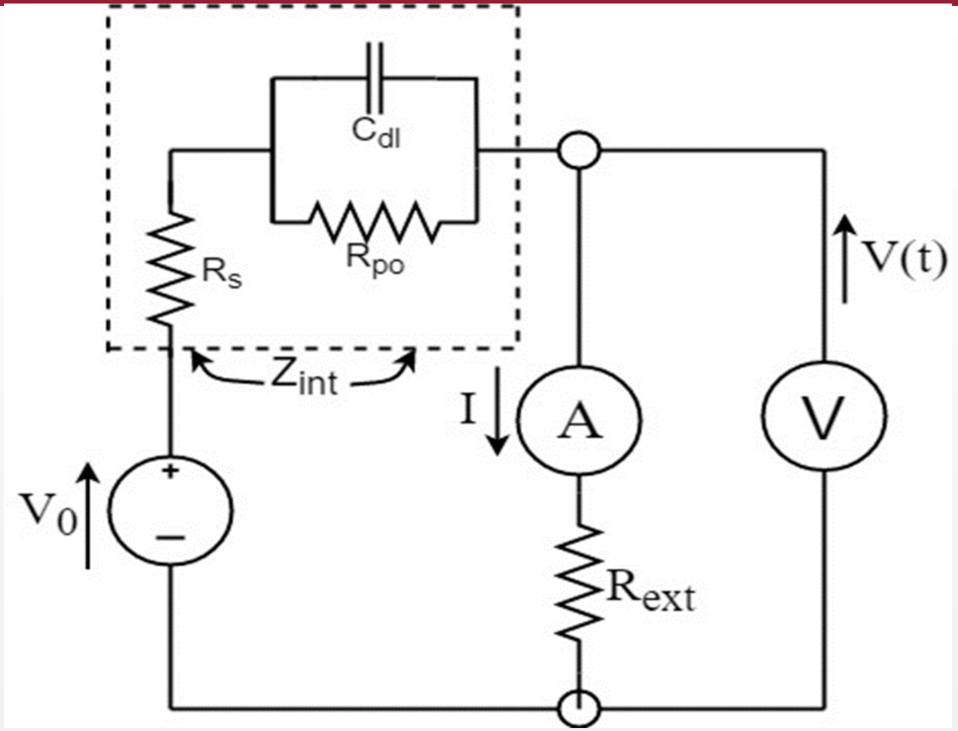
- While EIS gives a wealth of diagnostic information on an electrochemical cell, the FRA equipment used to perform EIS struggles with larger cells.
- Commercially available FRA's have a current limitation of around 0.5-2 amps typically.
  - For low impedance cells <10 mΩ, a typical perturbation voltage of about 10 mV will cause a response from the cell which may exceed the capacity of the FRA.
  - The only work around for this is to add a booster potentiostat to extend the instruments measurement range.
- Barsoukov et al developed the mathematical framework for a technique he called "Passive Load Excitation" (PLE), which has the potential to drastically simplify impedance measurements of even very large/low impedance cells.

E. Barsoukov, S. H. Ryu, and H. Lee, "A novel impedance spectrometer based on carrier function Laplace-transform of the response to arbitrary excitation," *J. Electroanal. Chem.*, vol. 536, no. 1–2, pp. 109–122, Nov. 2002.

Passive Load Excitation Overview

How Does It Work?

- Utilizes a constant load step as a perturbation.
- Easily accomplished by instantaneously connecting a resistor across the terminals of an electrochemical cell
- After perturbation, the voltage drops as current flows.
- Transient voltage and current response is measured and logged.
- This time domain response can be transformed into the frequency domain to obtain the impedance spectrum.



How Has This Technique Been Used?

- While Barsoukov developed the theory behind the technique, he did not show an actual hardware implementation of it.
- In fact, despite its simplicity it appears only one (unsuccessful) attempt has been made to develop and test a device using PLE.
- Hoff et al developed a device to characterize SOFC’s using PLE, however due poor resolution of his device and a faulty theoretical understanding of the method led prevented him from extracting the impedance spectrum from the time domain transients.

[3] B. R. I. A. N. D. A. V. I. D. HOFF, “A TIME TRANSIENT TECHNIQUE FOR P E R F O R M A N C E C H A R A C T E R I Z A T I O N A N D D E G R A D A T I O N DIAGNOSTICS,” no. August, 2004.

Mathematical Theory

$$V(t) = \sum_{i=0}^{n} k_i \cdot e^{\frac{-t}{\tau_i}}$$

- A sum of exponentials is fit to the time voltage and current response using a CNLS solver.

$$V(s) = \sum_{i=0}^{n} \frac{k_i}{s + \frac{1}{\tau_i}}$$

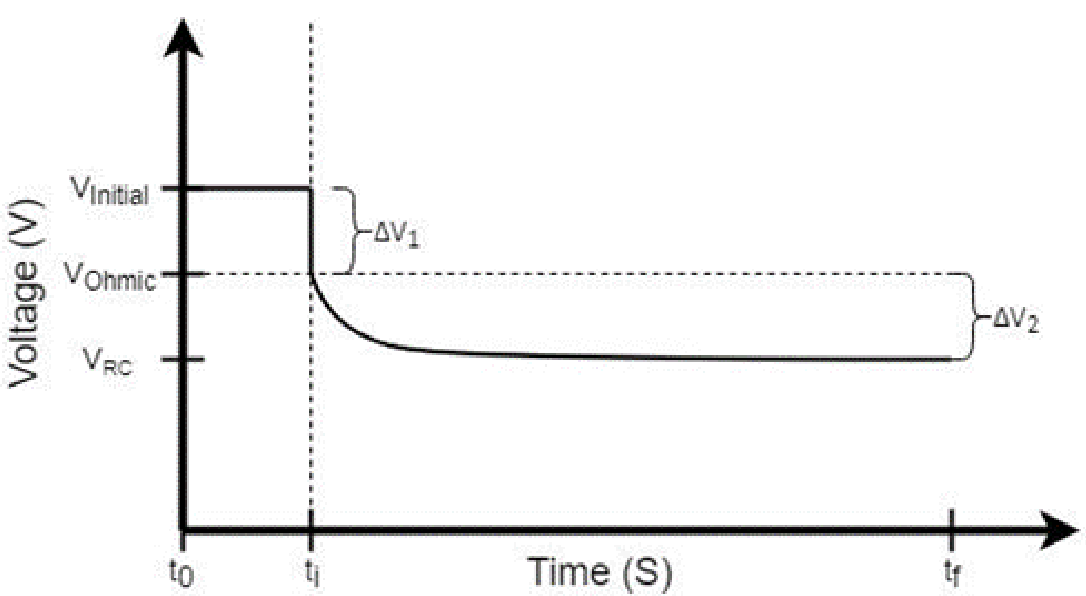
- The exponential sum is Laplace Transformed into the S-Domain where $s = \omega i$.

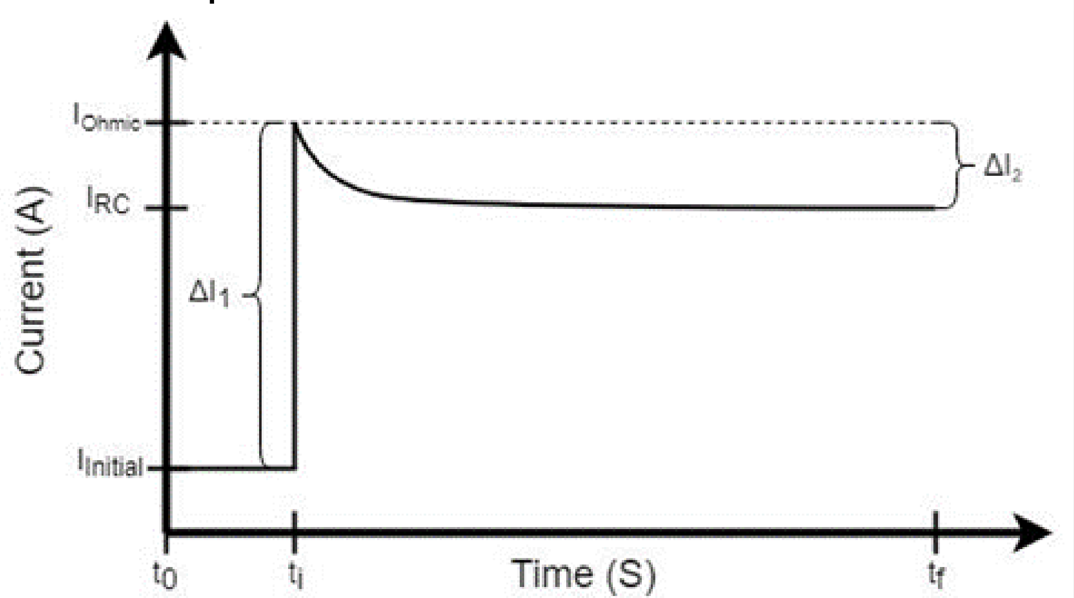
$$Z(s) = \frac{L\{V(t)\}}{L\{I(t)\}}$$

- Complex Impedance is calculated from the complex voltage and current response.

$$Z(s) = \left(\frac{V_0}{s} - V(s)\right) \cdot \left(\frac{s}{I(s)}\right)$$

- For a system at an initial voltage of V_0 Complex impedance will take the above form.





Traditional Method vs. Passive Load Excitation

Traditional EIS (FRA Method)

- Complex/expensive hardware such as signal generators and phase sensitive detectors.
- Long measurement times at low frequency.
- Measurement of large/low impedance batteries and fuel cells requires complex and expensive high-power booster potentiostat.
- Can be used to characterize materials and interfaces in addition to power sources.

Passive Load Excitation

- Lack of active circuitry makes hardware simple/inexpensive.
- Theoretically minimum measurement times obtainable. 12% of traditional method.
- Cell provides the power for the perturbation, no potentiostat needed.
- Highly portable.
- Only capable of measuring impedance of devices with an internal power source.

Additional Motivations

- After studying this technique it was realized that the PLE method has the potential to solve a host of problems beyond those encountered in this work.
  - Christensen et al identified a need for on board impedance measurements in battery electric vehicles to improve State of Health (SoH) estimation, balancing, battery ageing, and second life.
  - Cooper et al noted that fast, low power measurement techniques are needed for space applications and measurement of large electrode arrays.
  - Din et al studied battery management systems for grid scale battery energy storage and found a need for improved EIS techniques for large battery measurements.
- **Many applications for a low cost, portable, fast, and low power draw impedance measurement devices exist, and PLE is an ideal solution.**

A. Christensen and A. Adebusuyi, "Using on-board electrochemical impedance spectroscopy in battery management systems," in *2013 World Electric Vehicle Symposium and Exhibition, EVS 2014*, 2014.

B. K. R. Cooper, M. Smith, and D. Johnson, "Development and demonstration of measurement-time efficient methods for impedance spectroscopy of electrode and sensor arrays," *Sensors*, vol. 8, no. 3, pp. 1774–1796, 2008.

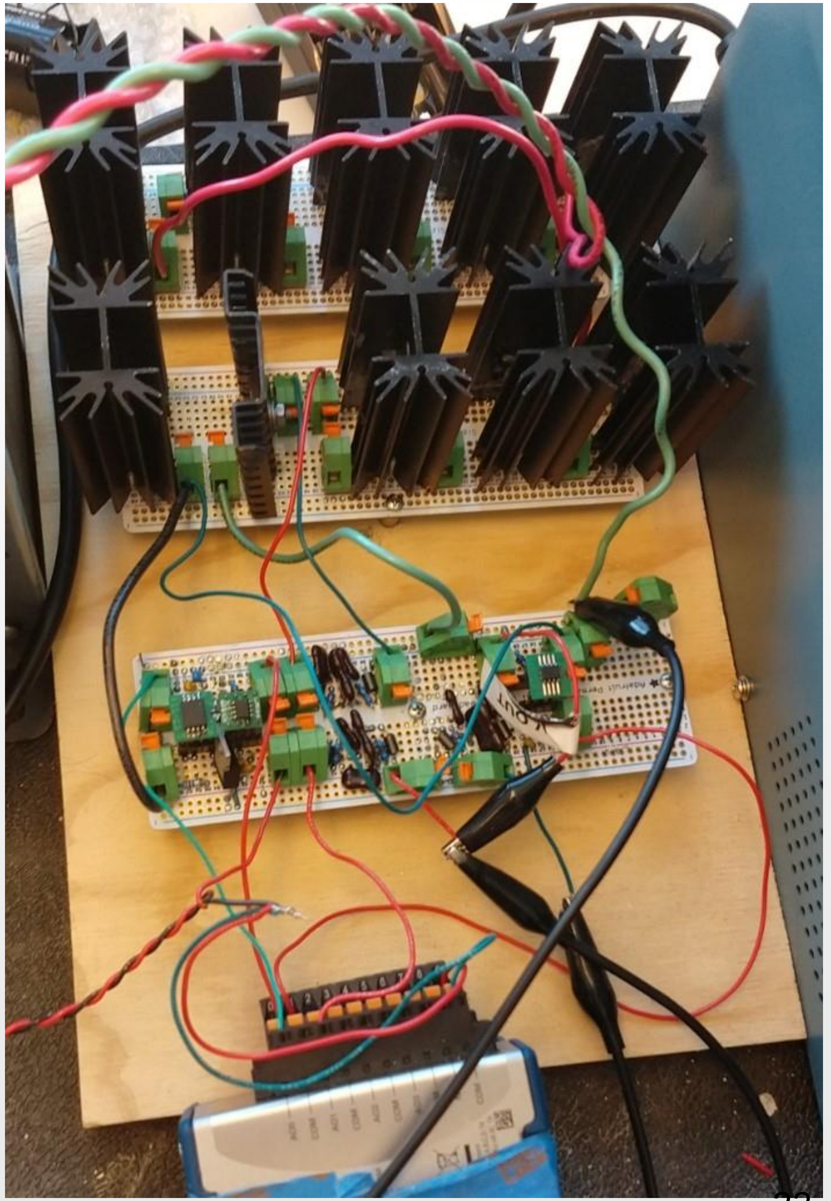
C. E. Din, C. Schaef, K. Moffat, and J. T. Stauth, "A scalable active battery management system with embedded real-time electrochemical impedance spectroscopy," *IEEE Trans. Power Electron.*, vol. 32, no. 7, pp. 5688–5698, Jul. 2017.

Outline

- Introduction
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- Co-Mn Spinel Coatings
- ***Time Domain Impedance Spectroscopy***
  - Motivation/Background
  - ***Device Theory of Operation***
  - Software/Hardware Validation
  - Application to Pressurized SOFCs
- Conclusions

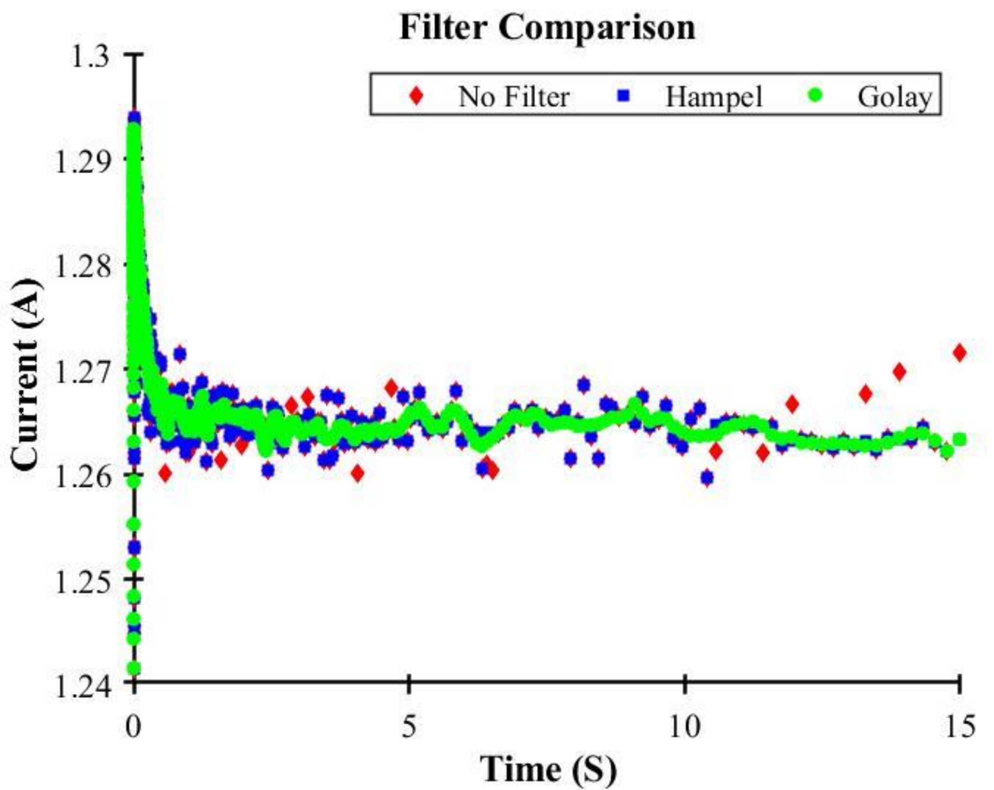
Hardware Implementation

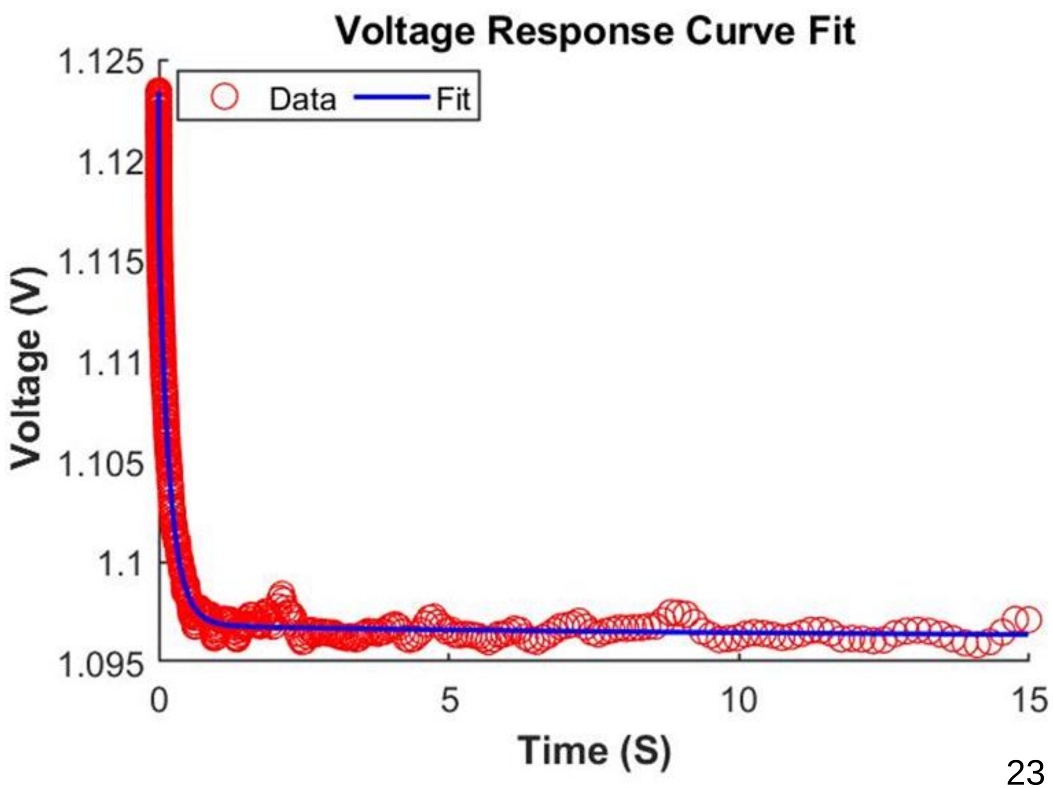
- An NI-9201 ADC samples current and voltage at a rate of 250k samples per second.
  - From Nyquist theorem highest frequency achievable is 125 kHz.
  - Lowest frequency is determined by length of perturbation according to $\frac{1}{t_{min}}$
- A NI-9263 DAC triggers the mosfet switch and supplies a reference voltage.
- Hand soldered analog pre-processing board amplifies and filters signal to get best resolution from ADC.
- Adjustable resistor bank allows different amplitude perturbations.
  - Typically a voltage drop of 20-40 mV is best.



Software Implementation

1. Steady state voltage and current of the cell is measured to establish initial conditions.
2. Waveforms are filtered digitally with hampel and savitsky golay filters.
3. Data is truncated at the exact moment the current waveform goes from low to high.
4. The CNLS solver uses the trust region reflective algorithm and the multistart function to fit the voltage and current waveform with a sum of exponentials.
5. Fit response is Laplace transformed and the impedance spectrum as a function of frequency is computed.





Outline

- Introduction
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- Co-Mn Spinel Coatings
- ***Time Domain Impedance Spectroscopy***
  - Motivation/Background
  - Device Theory of Operation
  - ***Software/Hardware Validation***
  - Application to Pressurized SOFCs
- Conclusions

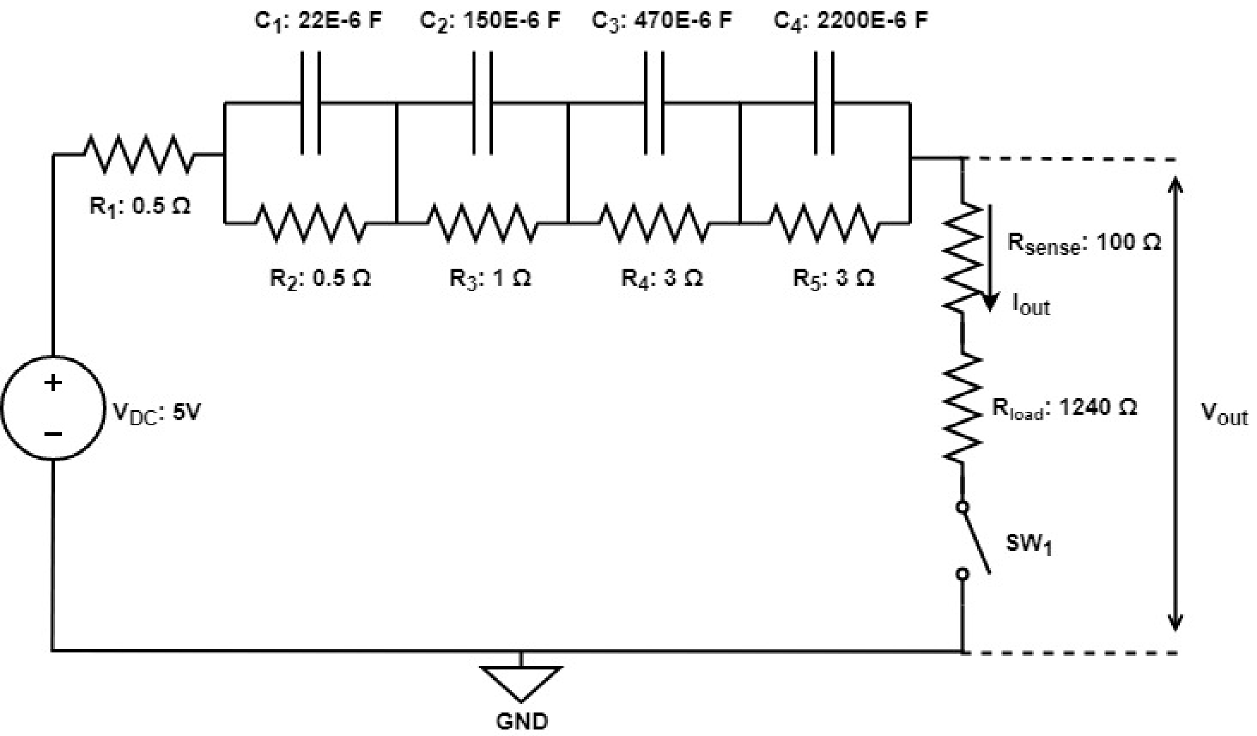
Dummy Cell Simulation

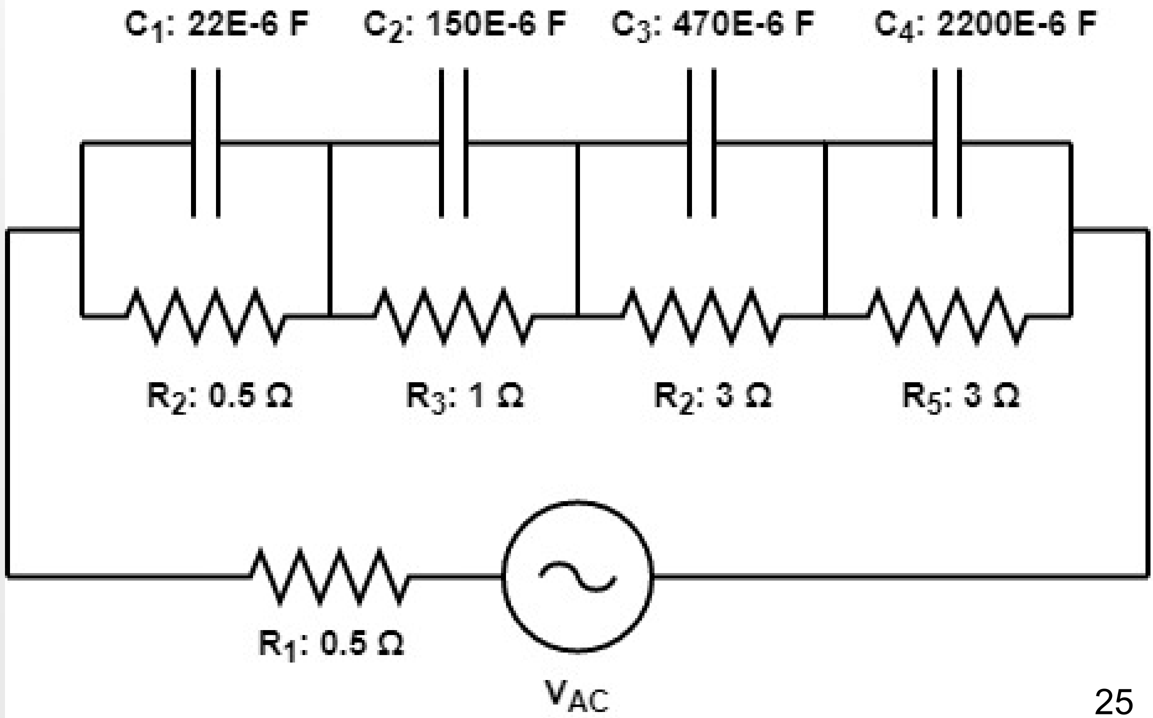
Passive Load Excitation RC Simulation

- Ideal voltage source in series with dummy cell.
- Transient response to switch SW_1 closing is sampled at 250 kHz.
- Results are processed using Custom Matlab script and transformed to frequency domain.

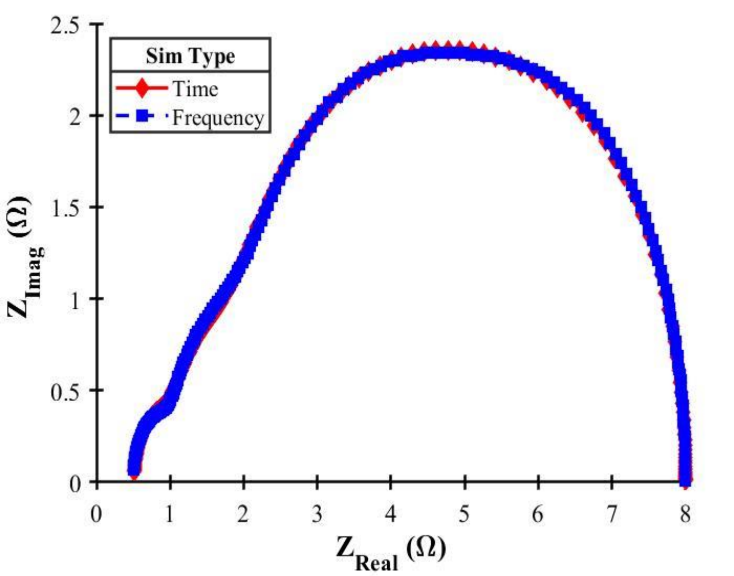
Frequency Domain RC Simulation

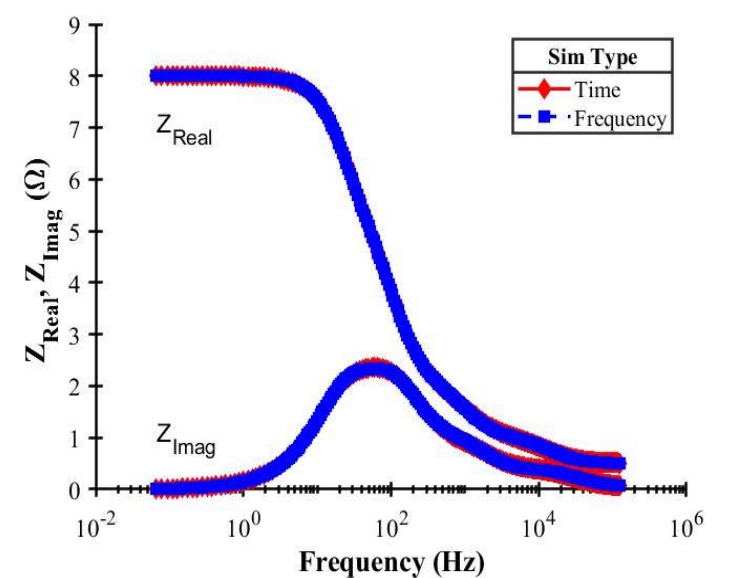
- Cell is perturbed by AC voltage of 0.1 mV and the corresponding frequency response of current and voltage is sampled at 44 pts/decade.
- Impedance is computed from Z = V/I
- Represents theoretical Impedance of RC circuit, with resolution of 44 pts/decade being close to practical upper limit for best DRT deconvolution.





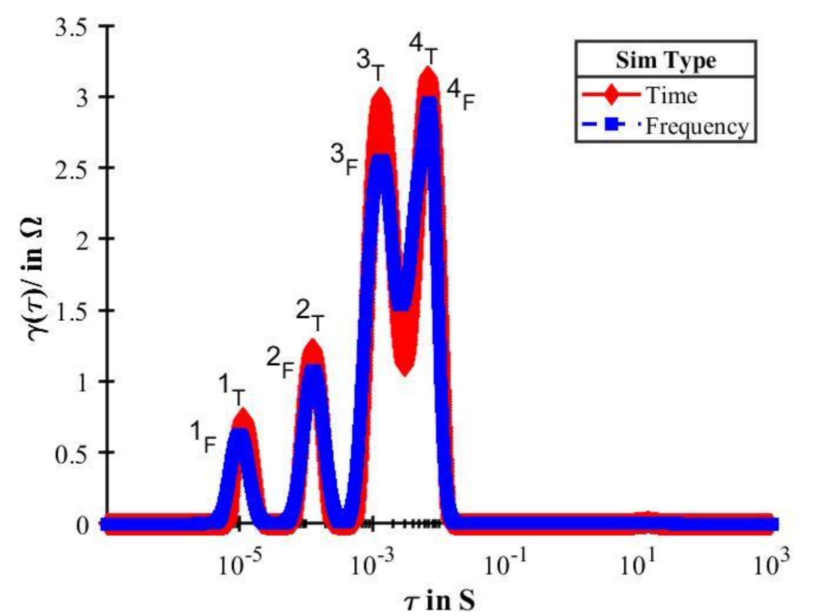
Software Validation





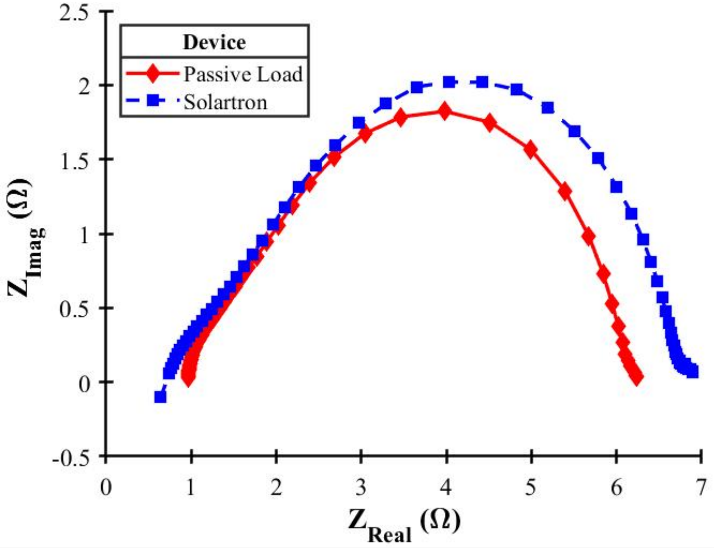
- Impedance results for Time and Frequency Simulations are largely indistinguishable from one another.
- The DRT spectrum of both simulations was deconvoluted using the free MATLAB toolbox DRTTOOLS.
- Both methods deconvoluted the spectrum for all four RC couples with reasonable accuracy.
- This demonstrates that the software is functioning properly, although it does slightly increase error.

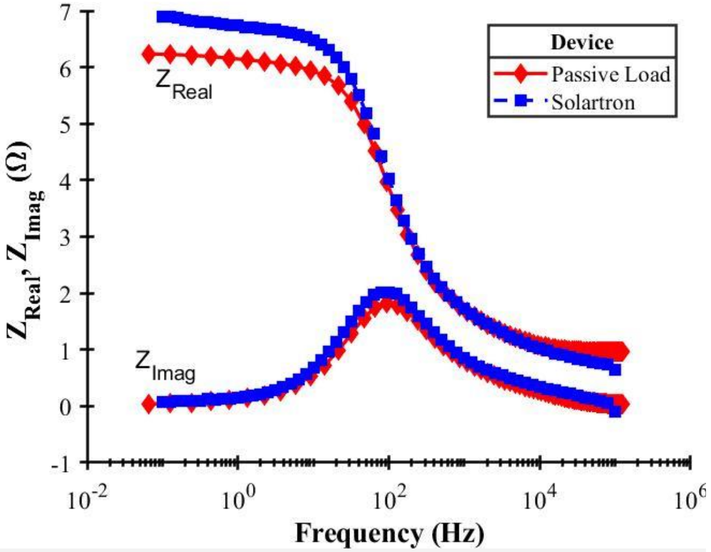
PARAMETER	AVG. % ERROR TIME SIM.	AVG. % ERROR FREQUENCY SIM.
T(S)	7.57	4.56
R(Ω)	19.1	12.37
C(F)	17.16	12.32

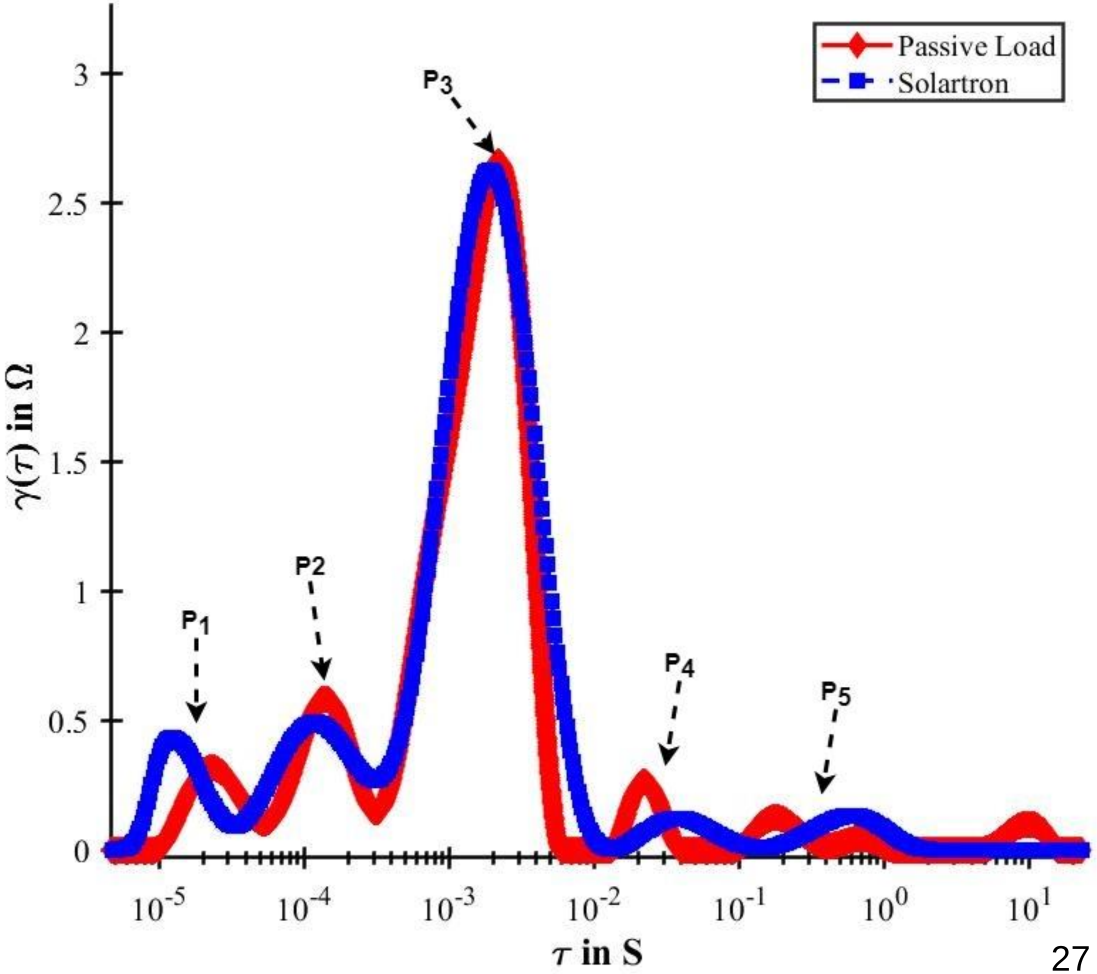


Peak		τ(s)	R(Ω)	C(F)
1	Time	$1.14x10^{-5}$	0.742	$15.4x10^{-6}$
	Frequency	$9.94x10^{-6}$	0.623	$16.0x10^{-6}$
	Actual	$1.10x10^{-5}$	0.500	$22.0x10^{-6}$
2	Time	$1.26x10^{-4}$	1.23	$102x10^{-6}$
	Frequency	$1.28x10^{-4}$	1.07	$120x10^{-6}$
	Actual	$1.50x10^{-4}$	1.00	$150x10^{-6}$
3	Time	$1.32x10^{-3}$	2.99	$441x10^{-6}$
	Frequency	$1.34x10^{-3}$	2.55	$525x10^{-6}$
	Actual	$1.41x10^{-3}$	3.00	$470x10^{-6}$
4	Time	$6.88x10^{-3}$	3.14	$2190x10^{-6}$
	Frequency	$7.04x10^{-3}$	2.96	$2380x10^{-6}$
	Actual	$6.60x10^{-3}$	3.00	$2200x10^{-6}$

Hardware Validation

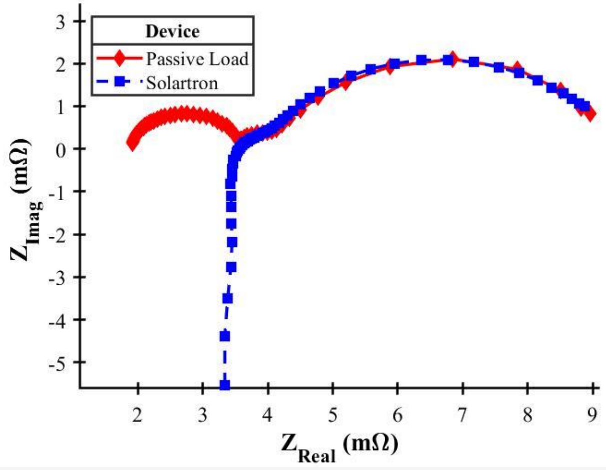


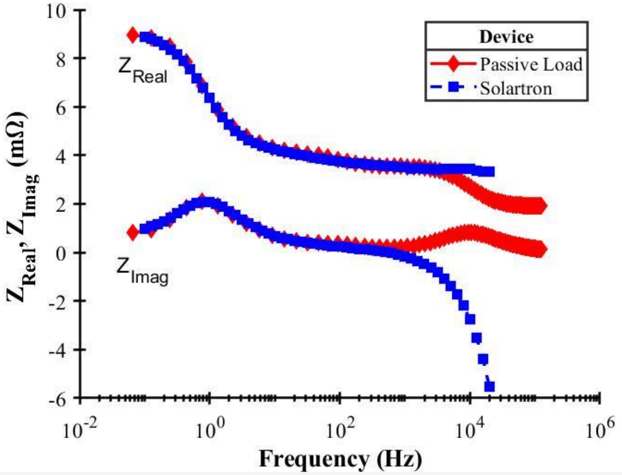




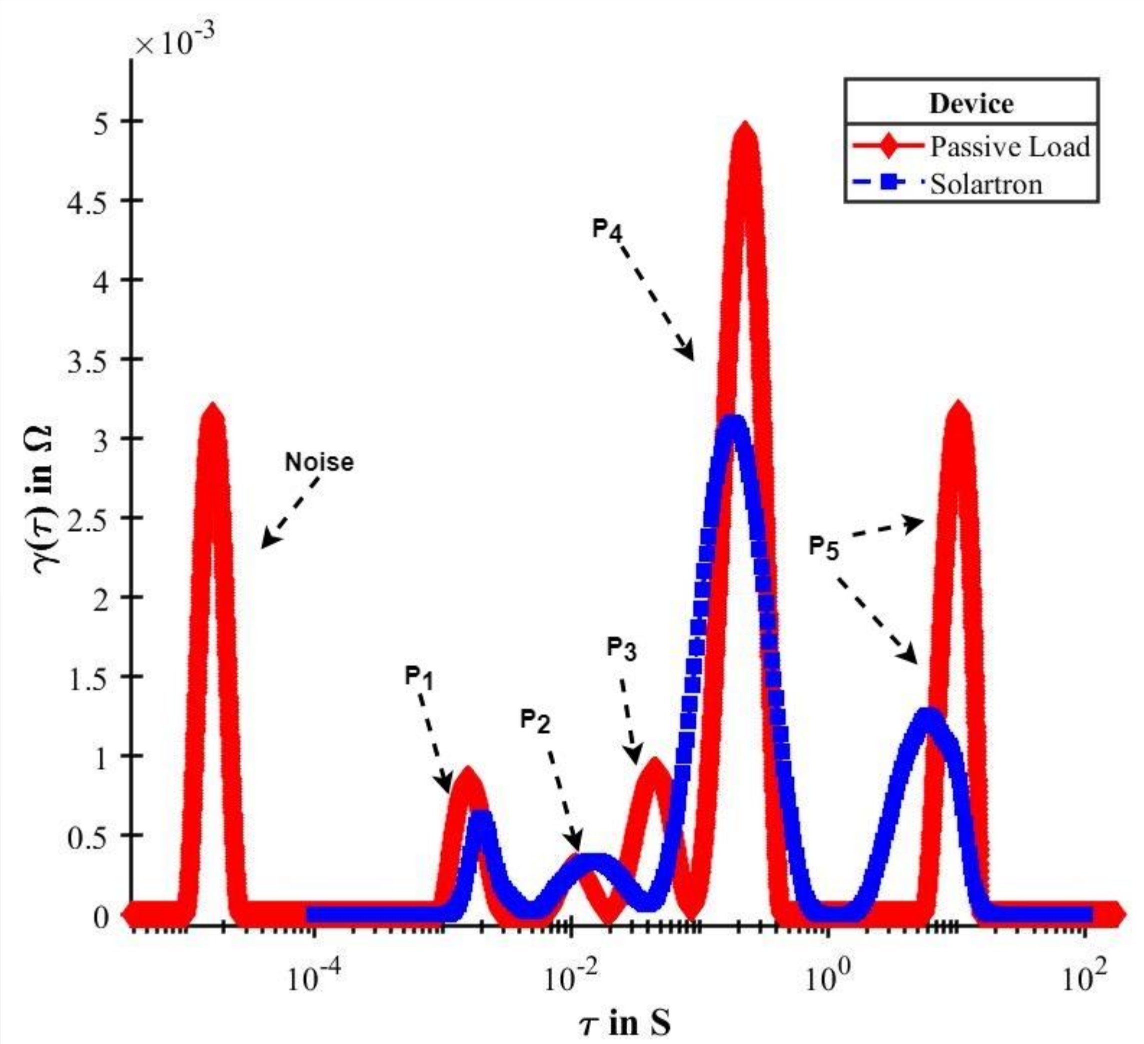
- A Solartron 1260+1287 is used to validate the measurement method.
- SOFC button cell is measured by both devices.
- General agreement between the two methods, although high and low frequency region shows clear divergence.
- This may be related to size/type of perturbation, as impedance of SOFC is very sensitive to H_2O content.
- Solartron uses 10 mV perturbation, Passive Load method uses 30-40 mV.
- DRT spectrum shows close agreement.

Hardware Validation



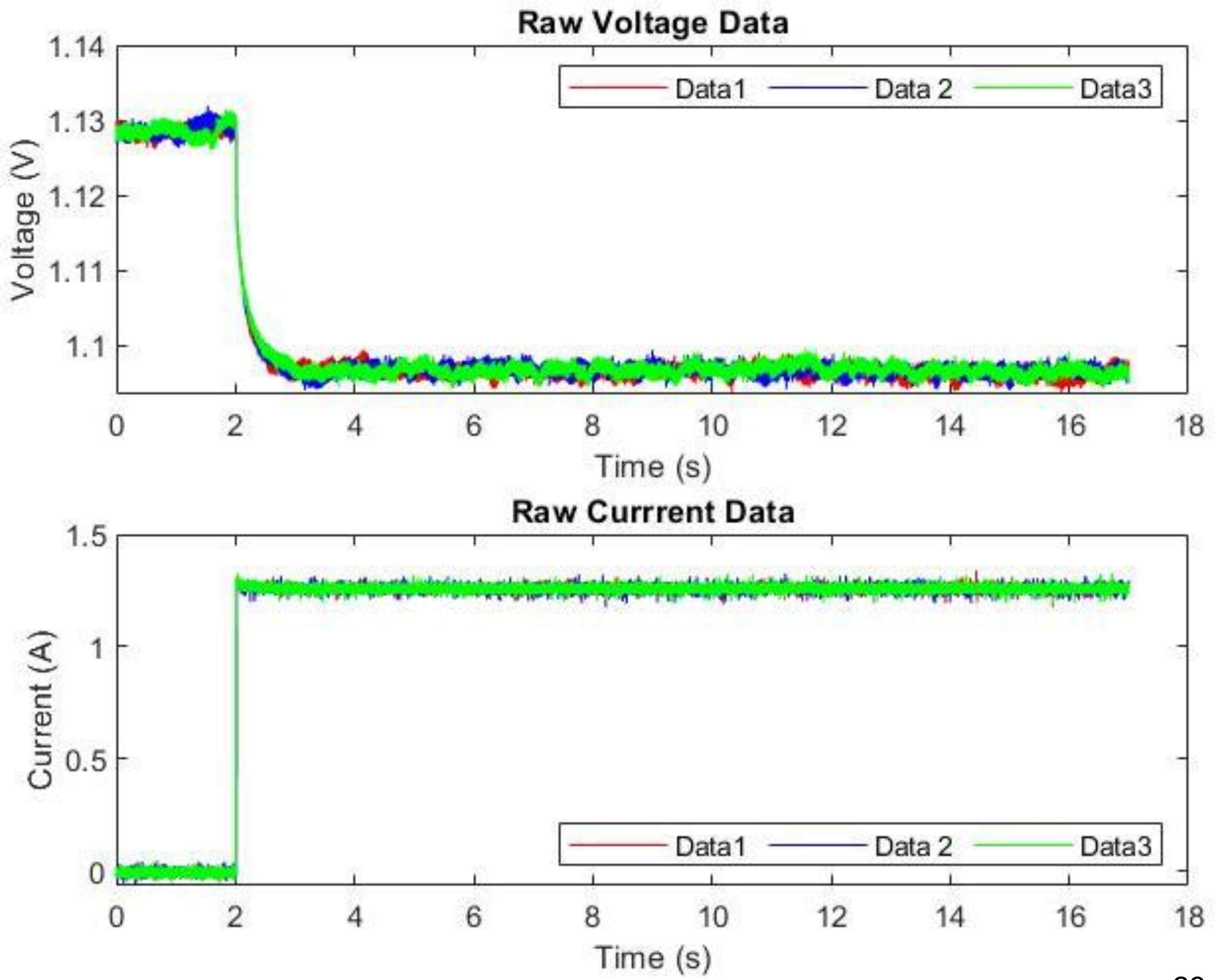


- A battery pack of 8 NiMH AA batteries were combined in parallel to simulate a cell with low impedance.
- This pushes the solartron to its rated limit.
- The solartron reads a huge amount of inductance which distorts the high frequency region.
- The passive load method has an extra process in the high frequency region. This is belived to be caused by inductive ringing.
- DRT shows good qualitative agreement



Measurement Repeatability

- Three measurements are taken, spaced 1 min. apart.
  - The time in-between measurements can be increased or decreased based on cell response.
- Multiple measurements ensure the cell is stable and the response is unvarying.
- The three measurements are averaged to increase accuracy.

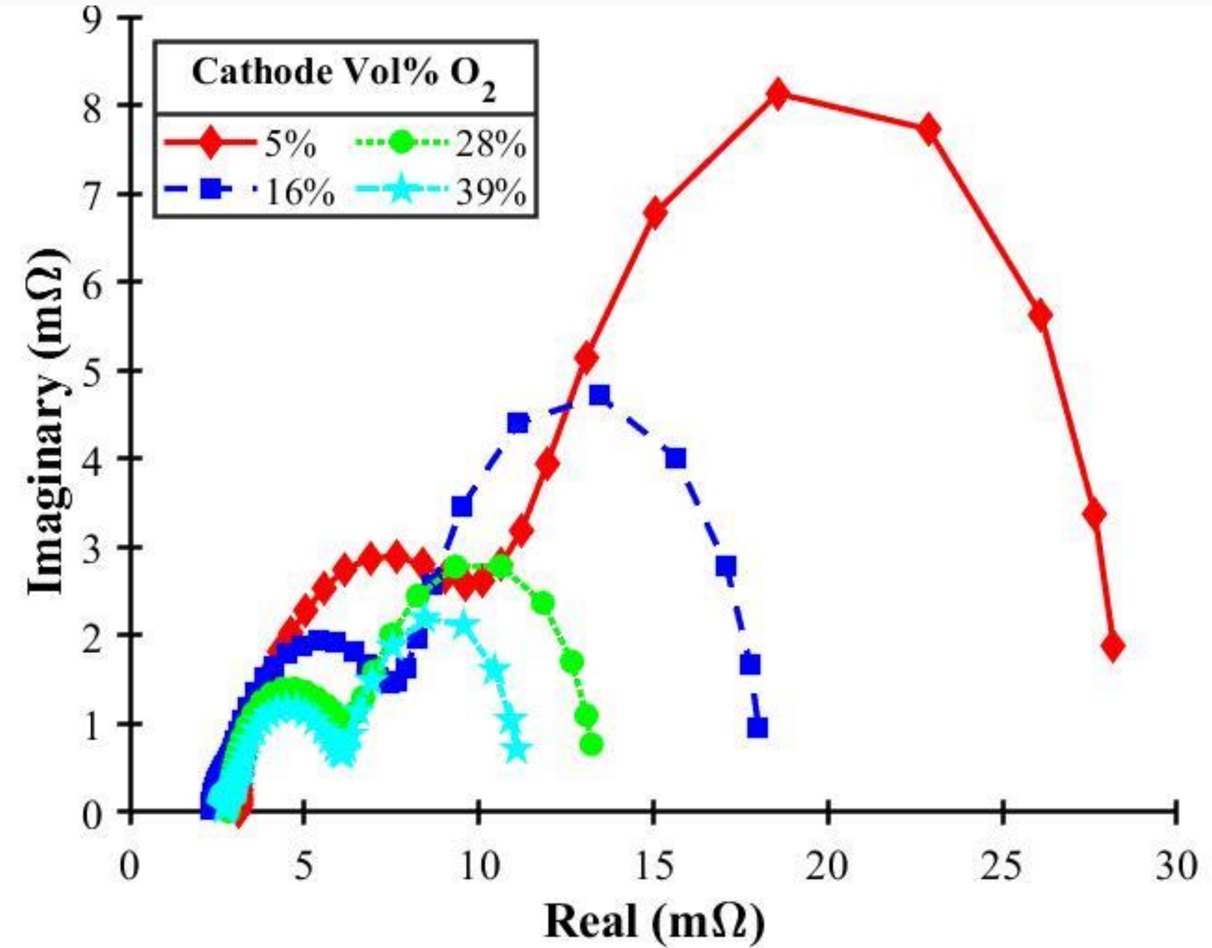


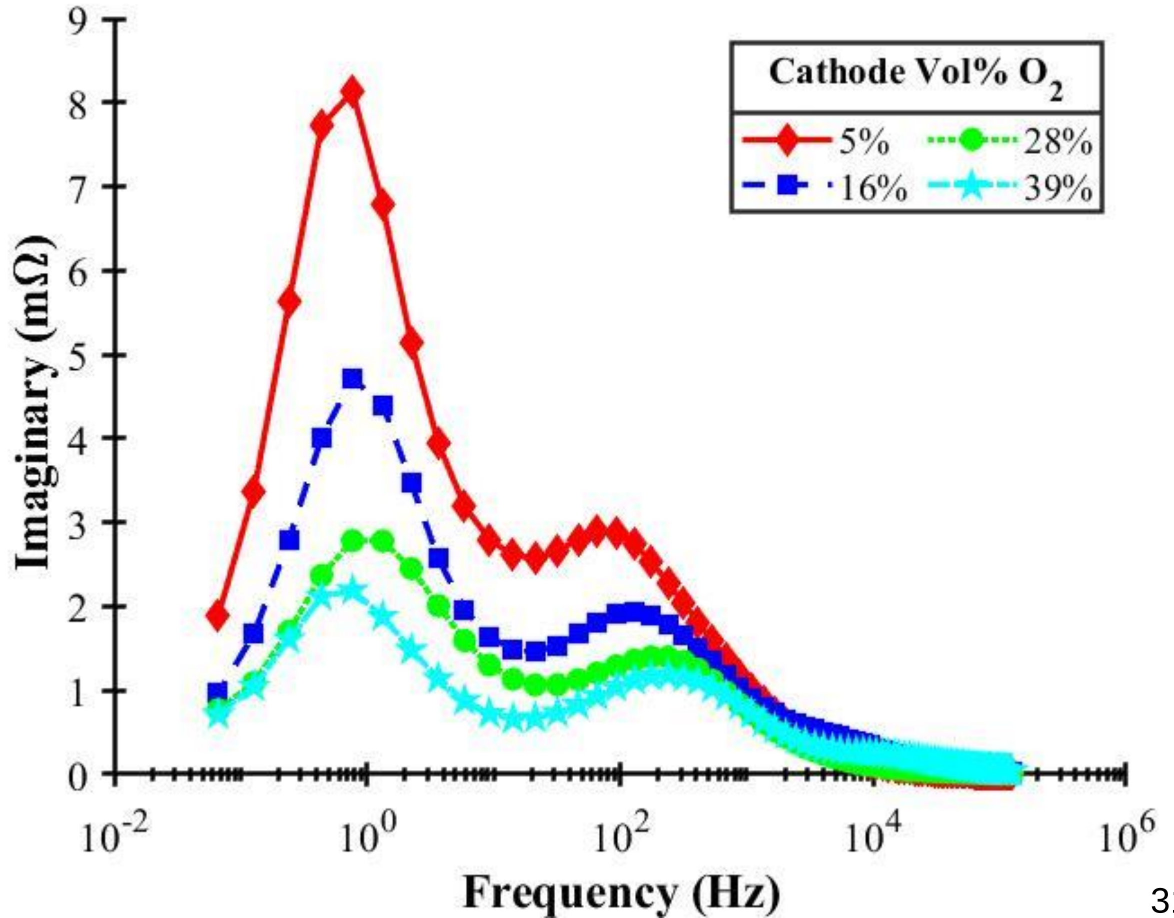
Outline

- Introduction
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- Co-Mn Spinel Coatings
- ***Time Domain Impedance Spectroscopy***
  - Motivation/Background
  - Device Theory of Operation
  - Software/Hardware Validation
  - ***Application to Pressurized SOFCs***
- Conclusions

pO_2 Sweep

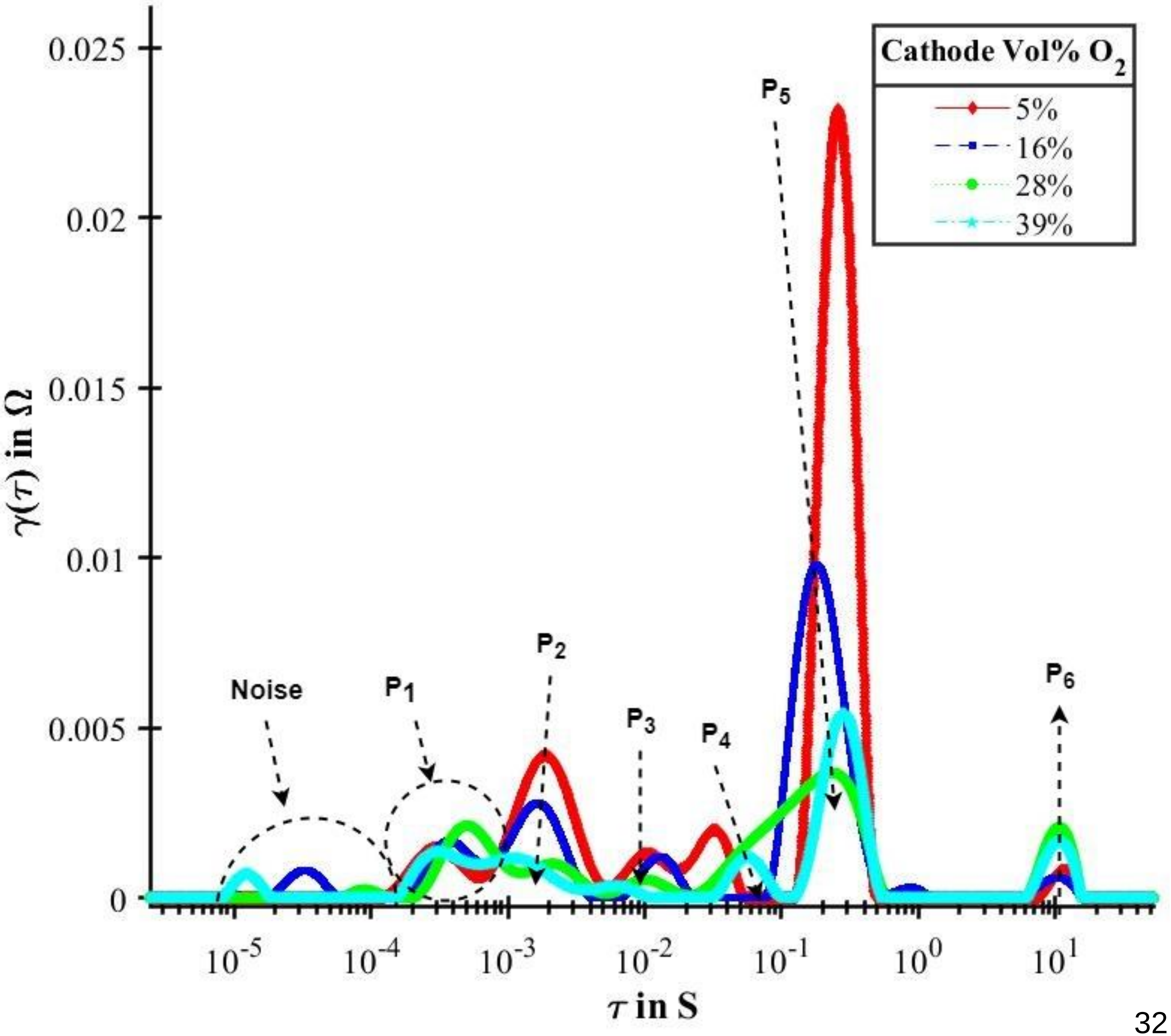
- Oxygen content was varied from 5% to 39%, with the balance being nitrogen. Total flow rate was kept constant to avoid temperature fluctuations.
- There is a clear trend of reduced gas diffusion and activation losses with increased oxygen content.
- The dependence of activation losses on pO_2 is a likely indicator of a leak.





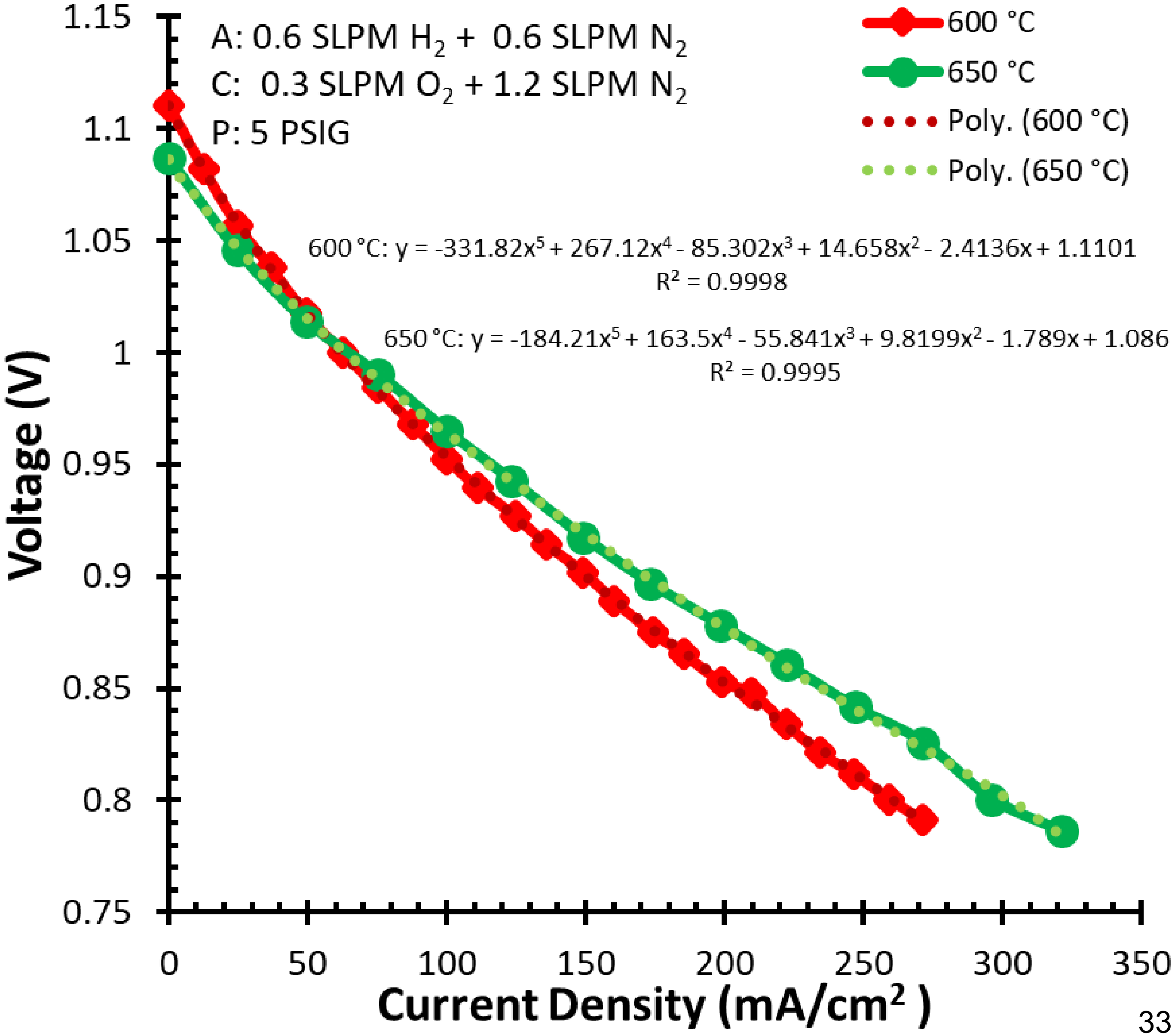
pO_2 sweep DRT

- The DRT of the pO_2 sweep shows six distinct peaks.
- Peaks 1-3 occur at high frequency (small time) and span roughly the same frequency range as the first semicircle, indicating these peaks are associated with activation losses
- The other three peaks, P_4-P_6, occur at lower frequencies, indicating they are related to gas diffusion.



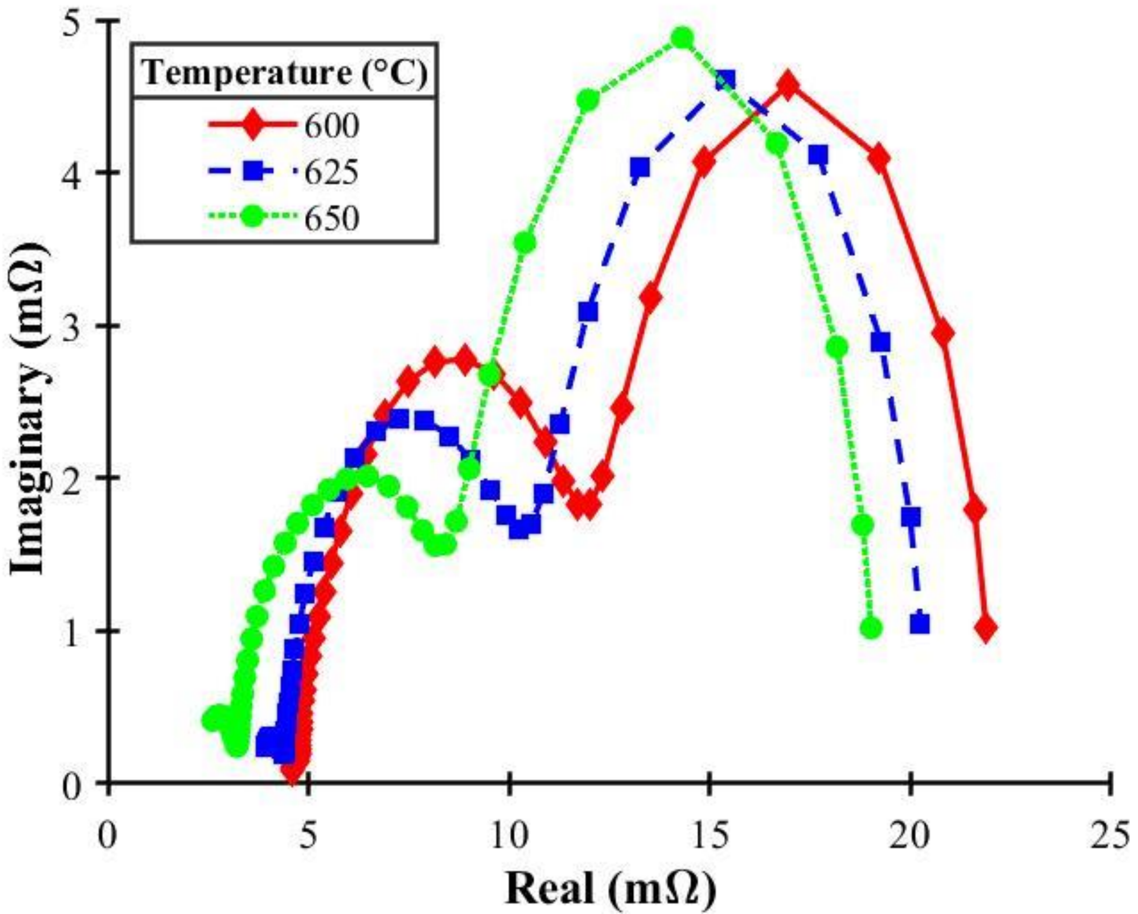
Temperature Sweep

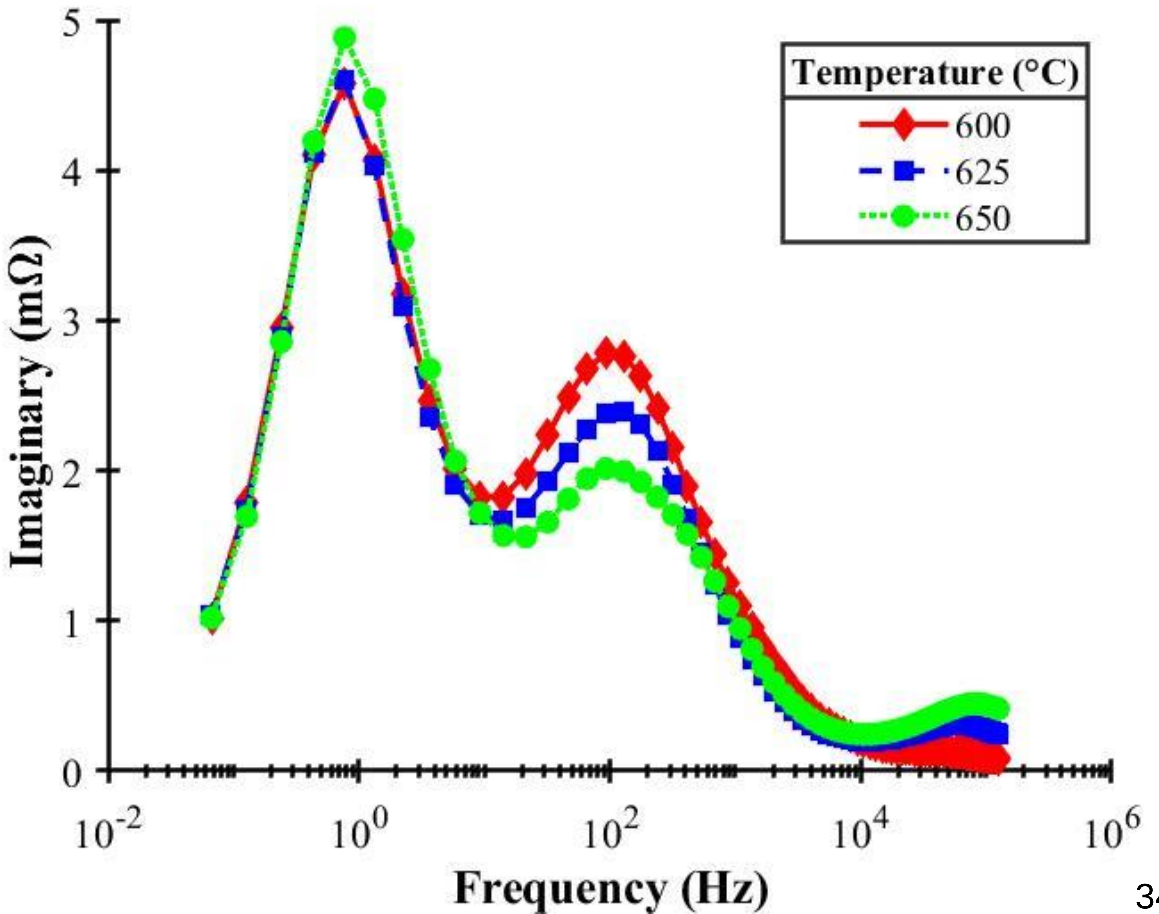
- Temperature of the cathode inlet is varied from 600-650 ˚C
- Low OCV further indicates leakage. OCV @ 650 ˚C is 1.087 V, from Nernst it should be roughly 1.184 V.
- Increasing temperature caused a drop of 24 mV, theory only predicts a 5.2 mV drop.
- Increased temperature caused worse leakage.



Temperature Sweep

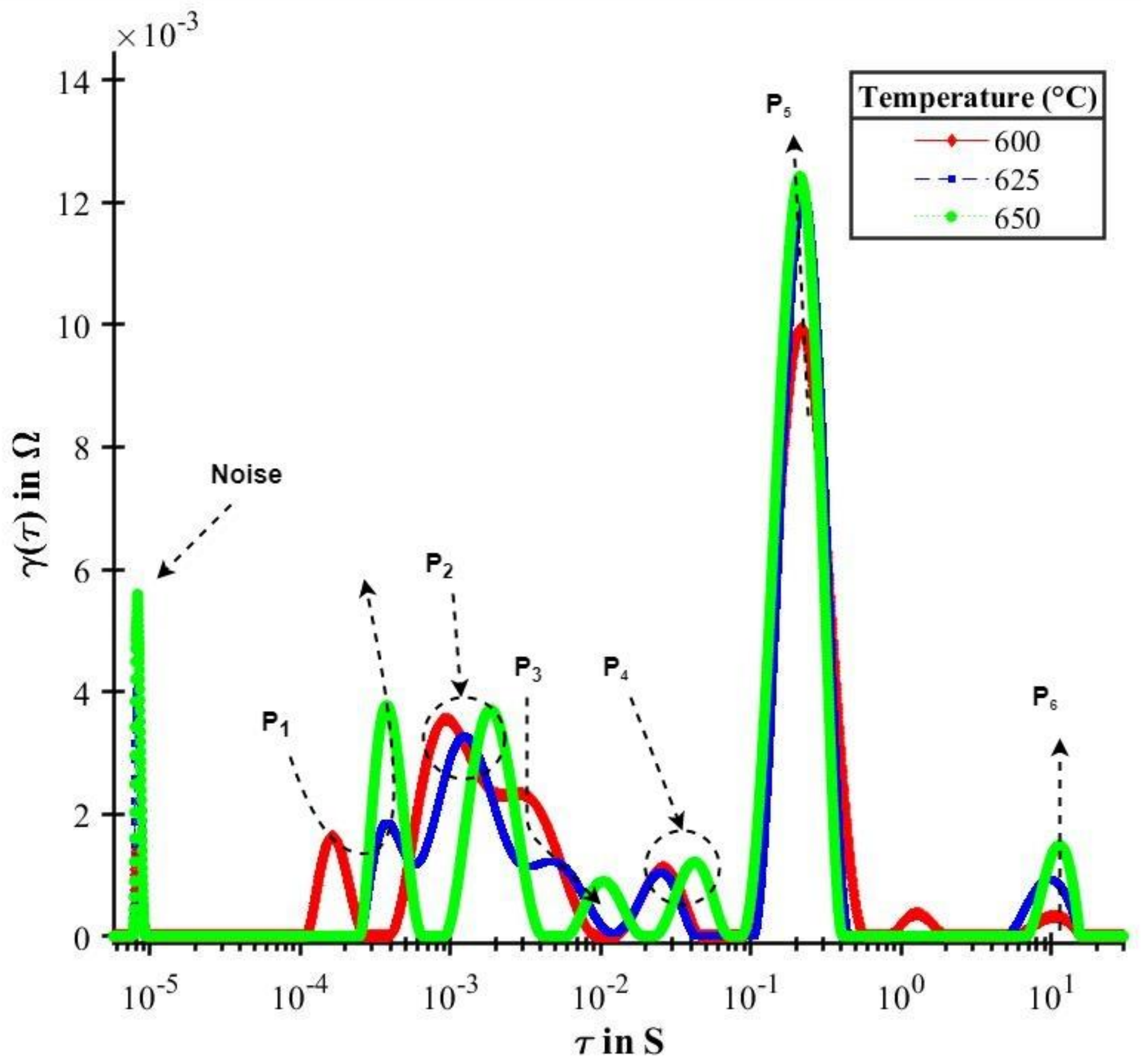
- Impedance results show a decrease in ohmic and activation losses as expected.
    - Ohmic resistance decrease from about 5 mΩ to about 3 mΩ
- Gas diffusion losses remain roughly the same.





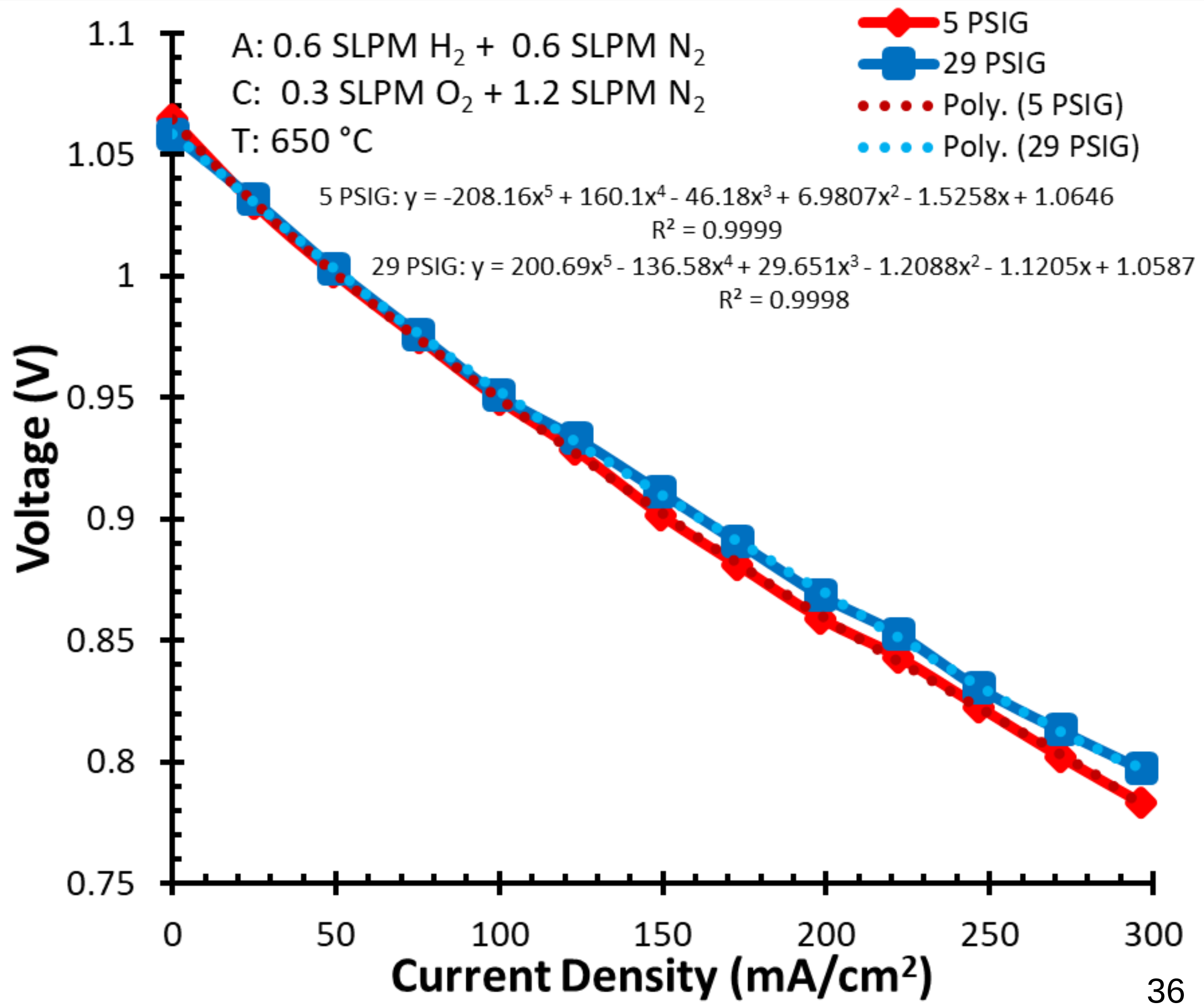
Temperature Sweep

- Temperature variation has caused P_1, P_5, and P_6 to grow larger, indicating that temperature is having a negative effect on these processes.
- Result is unexpected as temperature variations normally only have positive (or neutral) effects.
  - Further evidence that the cell leakage must be sensitive to temperature variations.
- Only P_3 shows a strong positive dependency on temperature, while P_2 and P_4 seem unaffected.



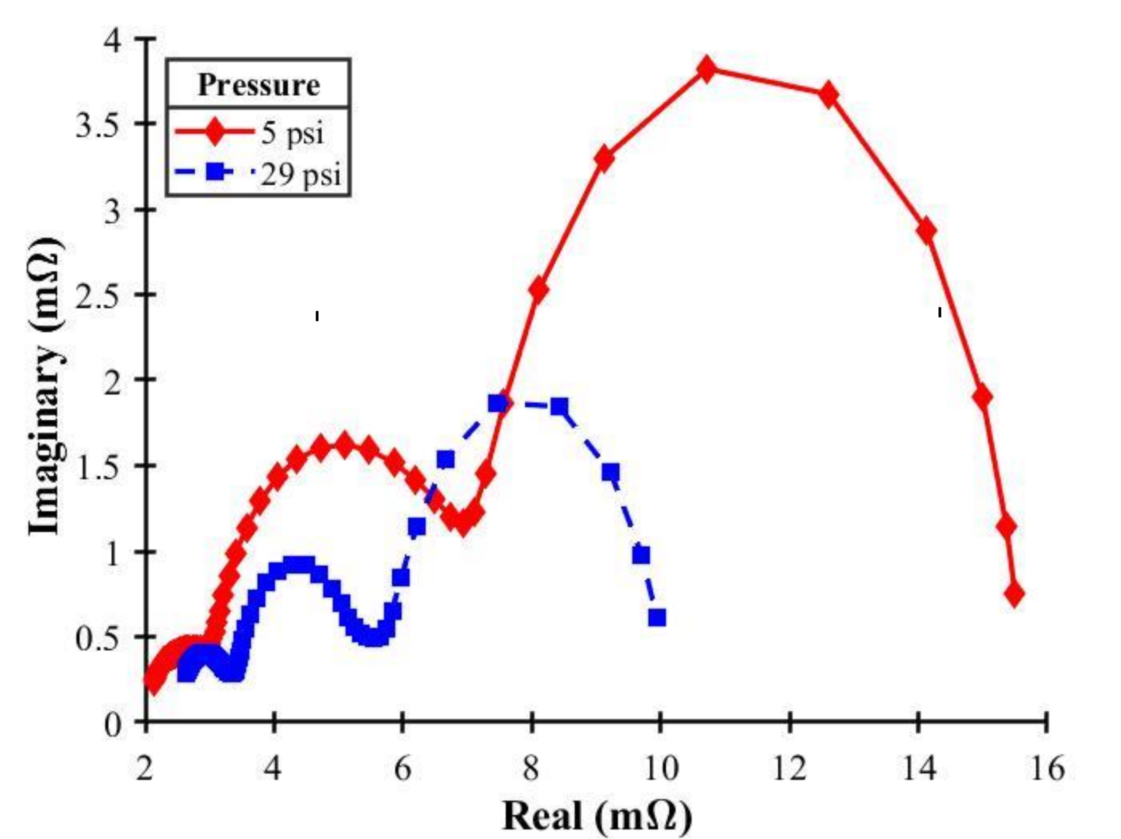
Pressure Sweep IV Curves

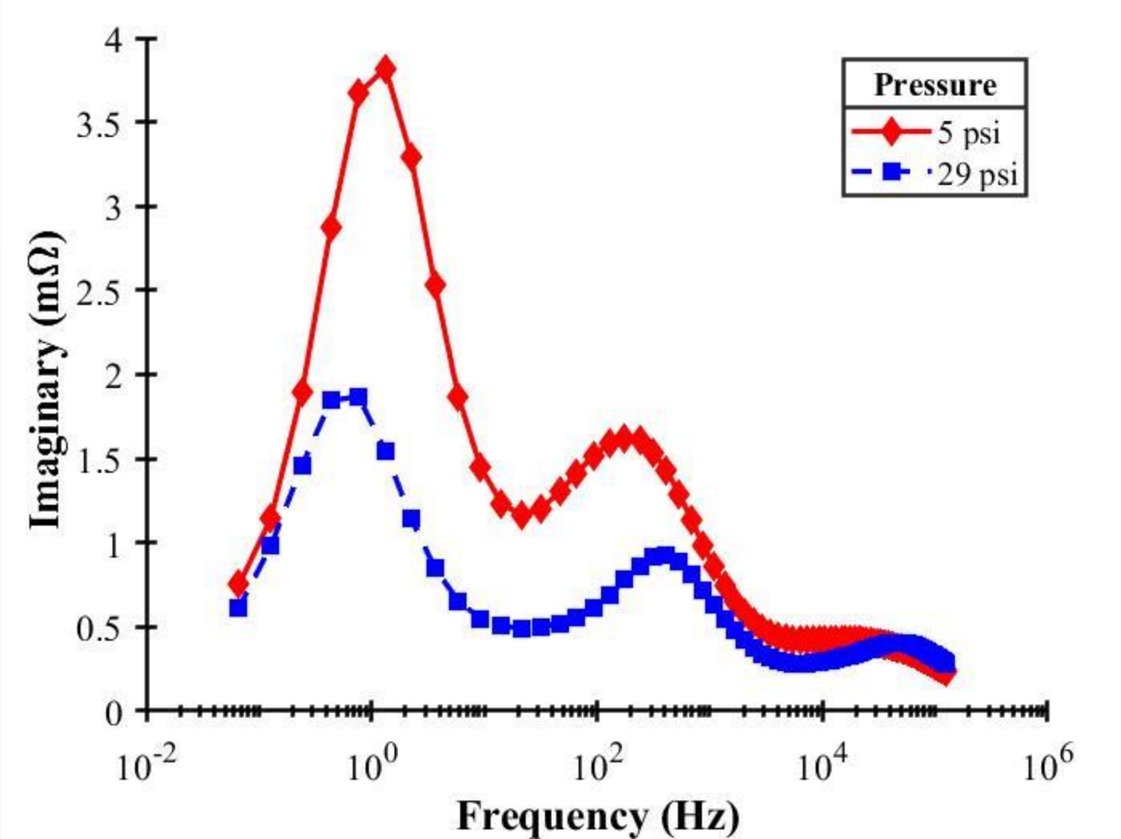
- The IV curve showes only mild improvement wth pressurization with ASR only decreasing by 6 mΩ·cm^2.
- OCV again had a slight decrease of 7 mV.
- Previous testing saw large improvements in performance with pressure.
  - Could be related to hydrogen developed a leak to atmosphere after the humidifer overheated and damaged the O-ring seal



Pressure Sweep Impedance

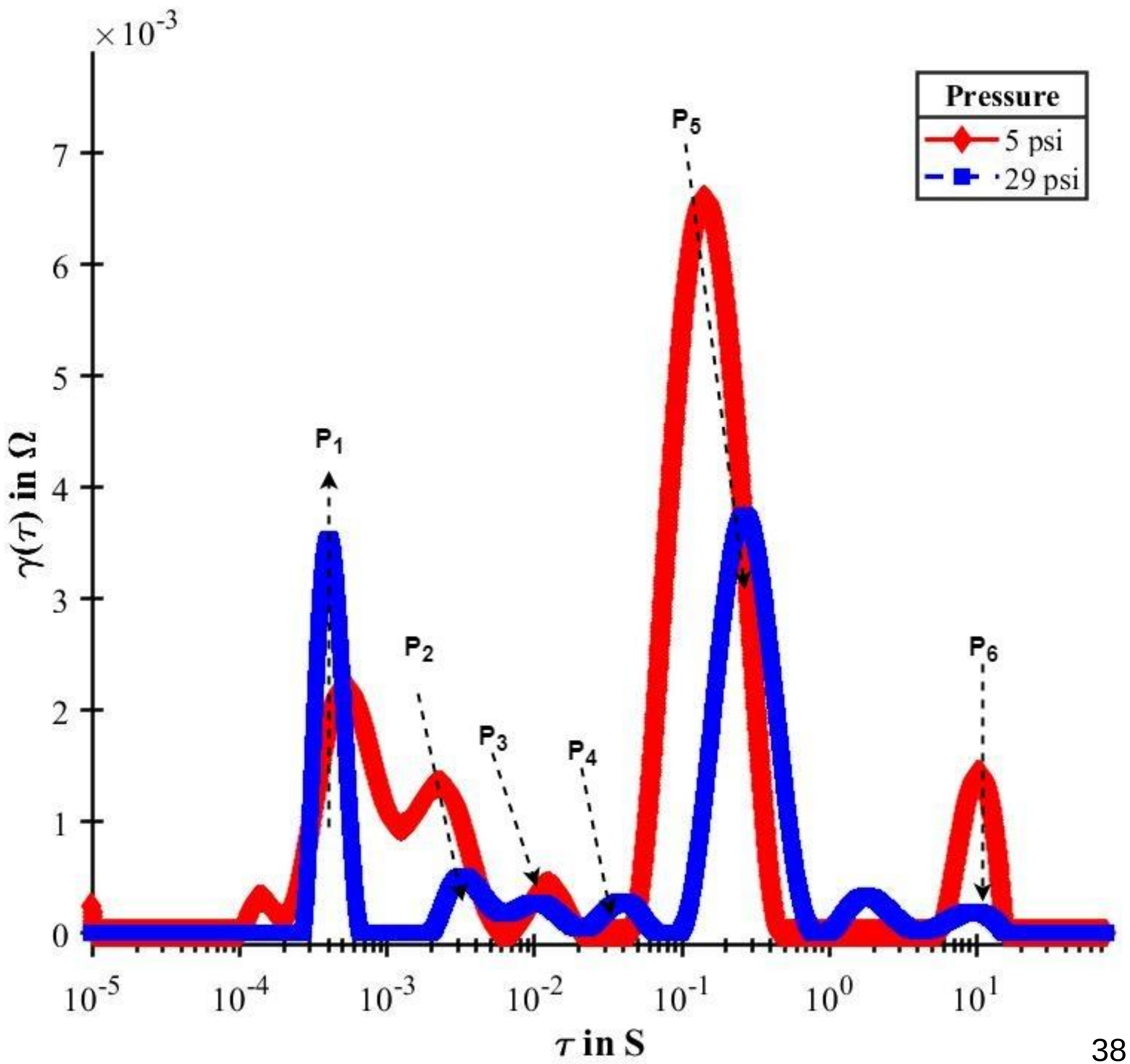
- Pressurization caused a large reduction in gas diffusion and activation losses.
- Increase of ohmic resistance at higher pressure, about 0.5 mΩ.
    - Previous studies have found no dependence of ohmic resistance with increased pressure





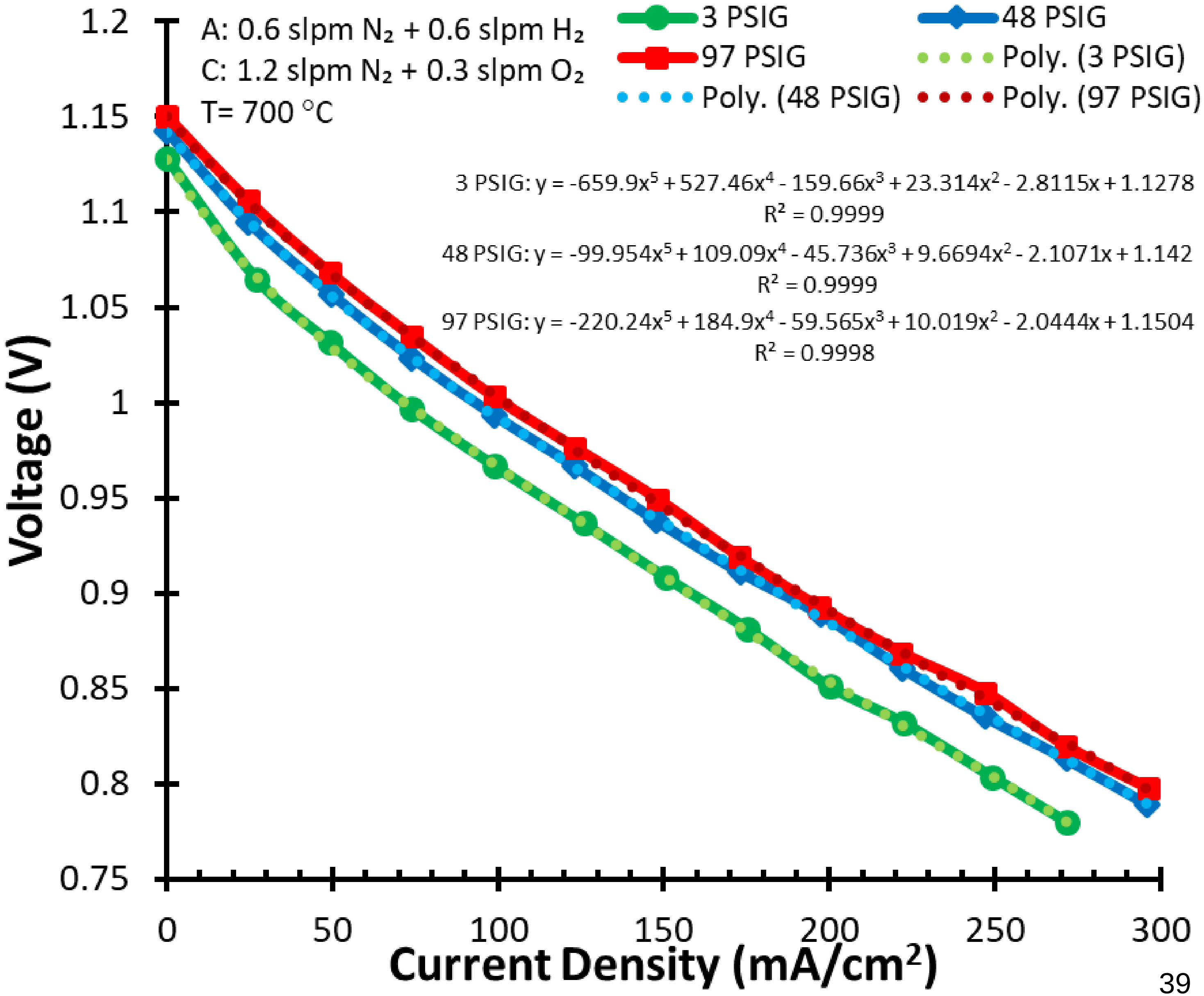
Pressure Sweep DRT

- The DRT shows a decrease across all peaks with the exception of P_1, which shows a sharp increase.
- P_1 has been associated with reactions at triple-phase sites, indicating pressurization led to worsening performance of these sites.
- Increase of P_1 and ohmic losses is partially offsetting the decrease of the polarization losses.
- Cell was shut down after 29 PSIG for safety reasons due to leakage of hydrogen from bad O-ring seal.



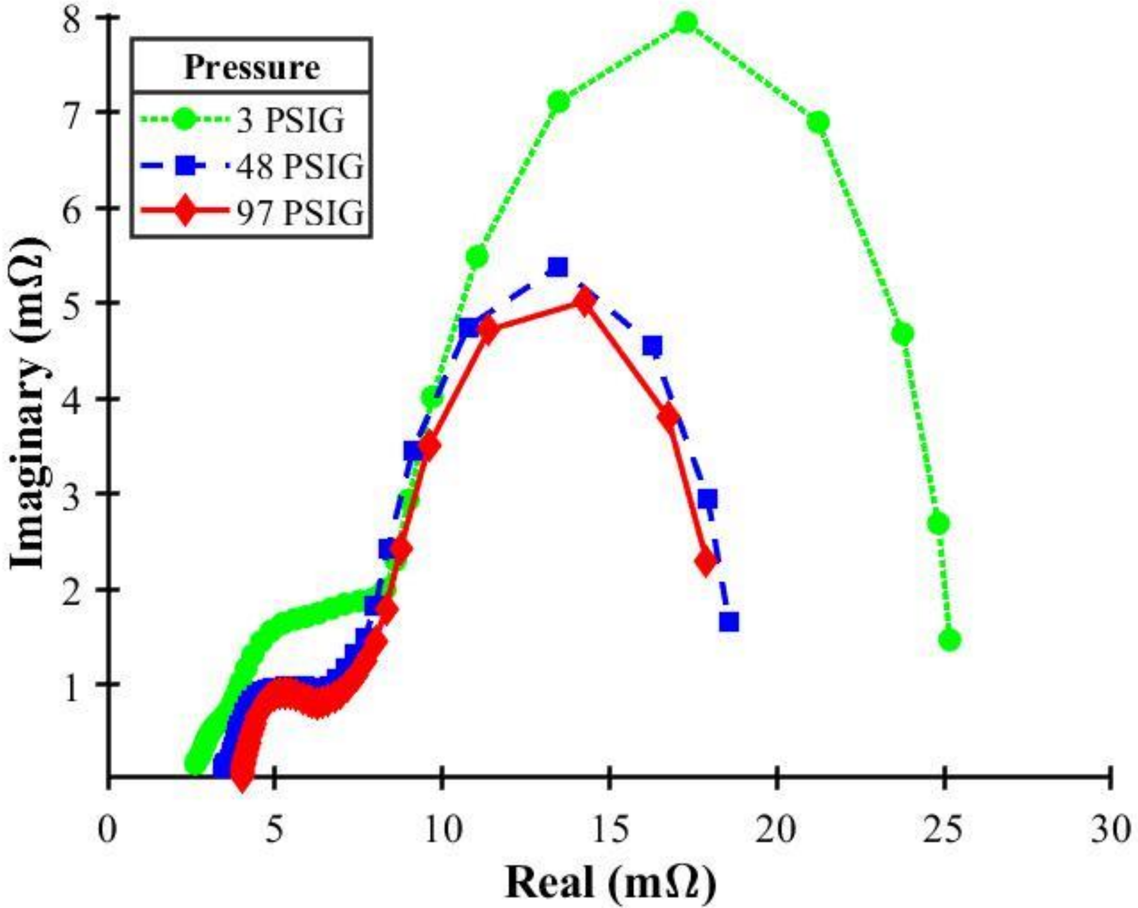
Pressure Sweep

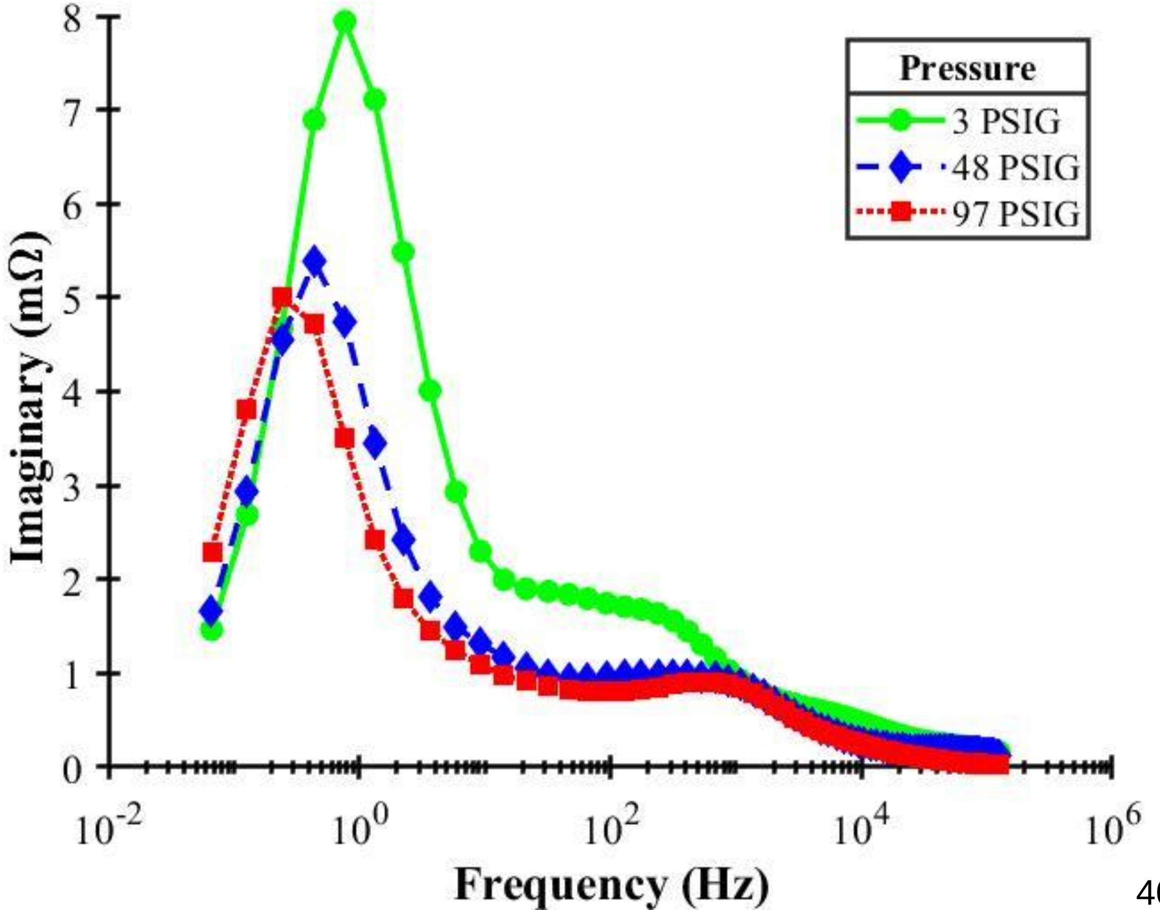
- VI curve shows a 4.4% increase in power density from 3 PSIG (atmospheric) to 97 PSIG.
- Performance improvements level off after about 48 PSIG.
- Some leakage still present with a 42 mV deviation from Nernst.
  - Previously 97 mV deviation.
- Test ended at 120 psi after unexpected seal failure on furnace.



Pressure Sweep

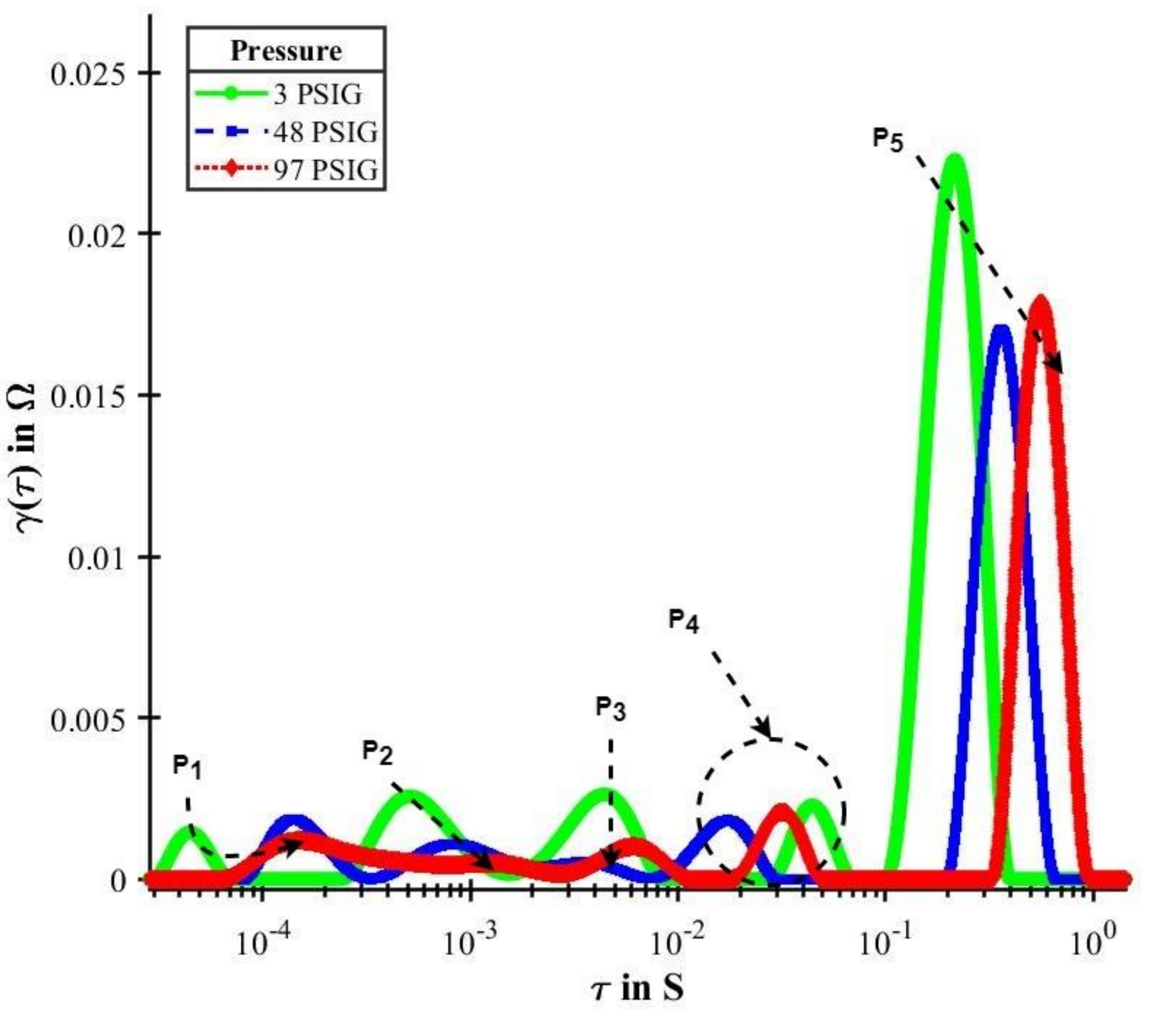
- Impedance results show an increase in ohmic and polarization losses compared to previous cell despite operating 50 °C hotter.
- ASR@ 200 mA/cm^2 increases by roughly 30% from the previous test.
  - This indicates that coatings were highly beneficial for cell performance.
- Pressurization shows a clear decrease in gas diffusion and activation losses and an increase in ohmic.





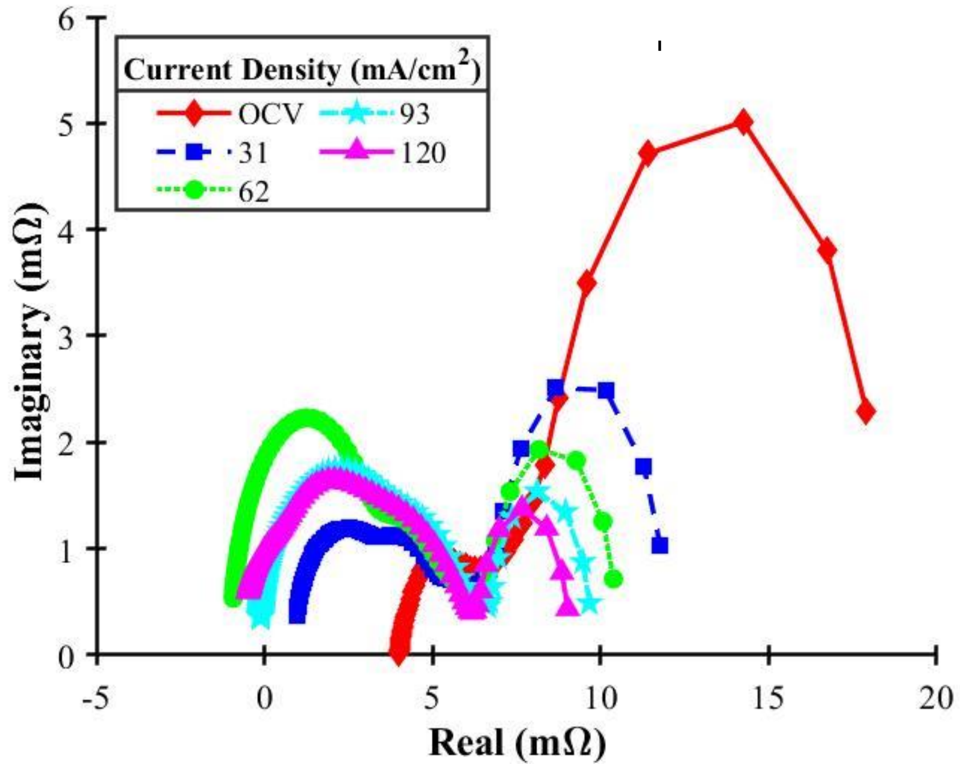
Pressure Sweep

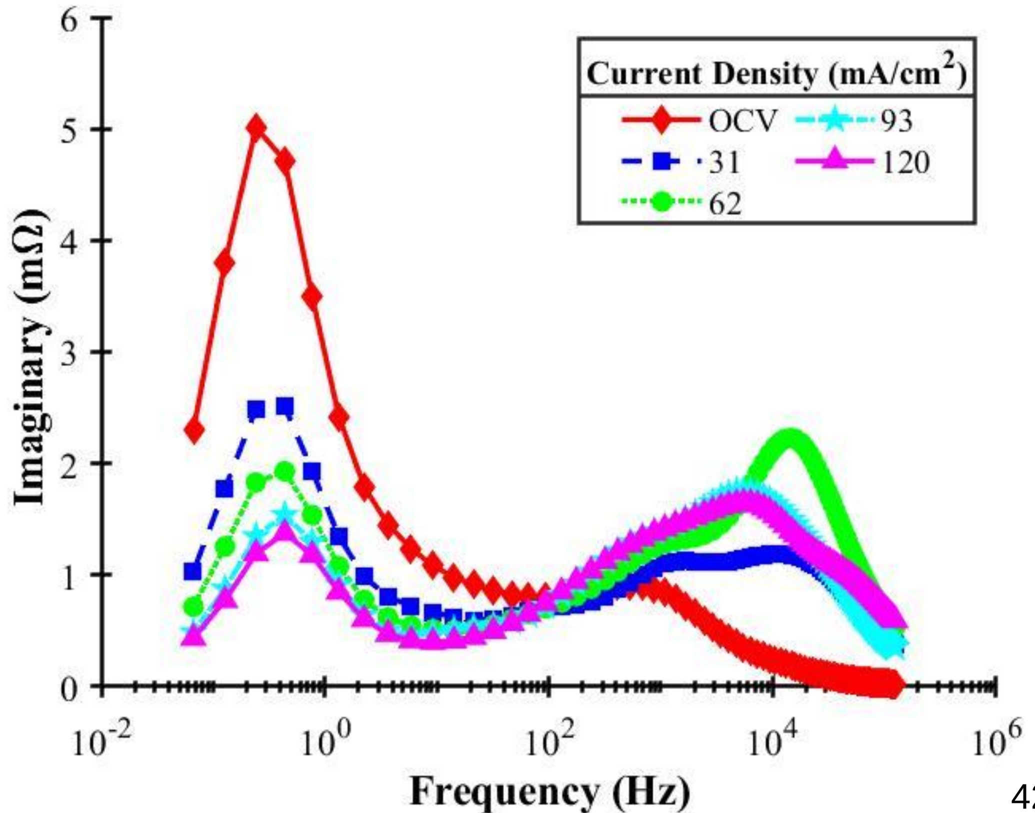
- Pressurizing from 5 PSIG to 48 PSIG flattened peaks P_2, P_3 and P_5, but P_1 and P_4 remain at roughly the same magnitude.
- Unlike previous run, P_1 does not show an increase with pressure.
- Pressurization seems to bring polarization processes closer in frequency.



Under Load Impedance Results

- By adding a resistor in parallel to the PLE instrument, Impedance measurements under load can be obtained.
- Impedance measurements under load are useful for determining dominant losses over full operating range.
- Higher frequencies Obviously distorted/noisy, likely due to increased inductance.
- Lower frequencies show expected trend.





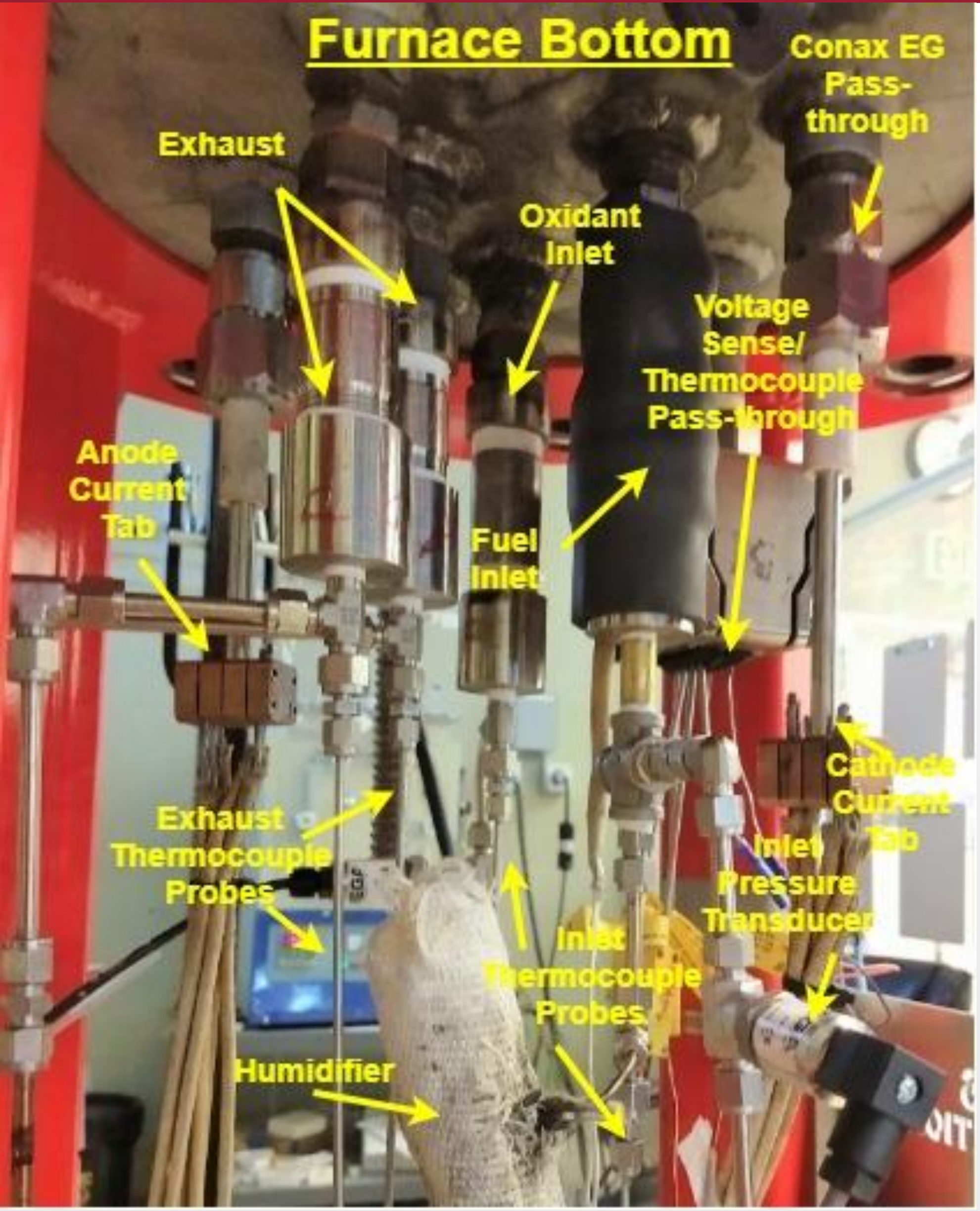
Outline

- Introduction
  - Motivation and Objectives
- Pressurized SOFC Test Stand
- Co-Mn Spinel Coatings
- Time Domain Impedance Spectroscopy
  - Motivation/Background
  - Device Theory of Operation
  - Software/Hardware Validation
  - Application to Pressurized SOFCs
- ***Conclusions***

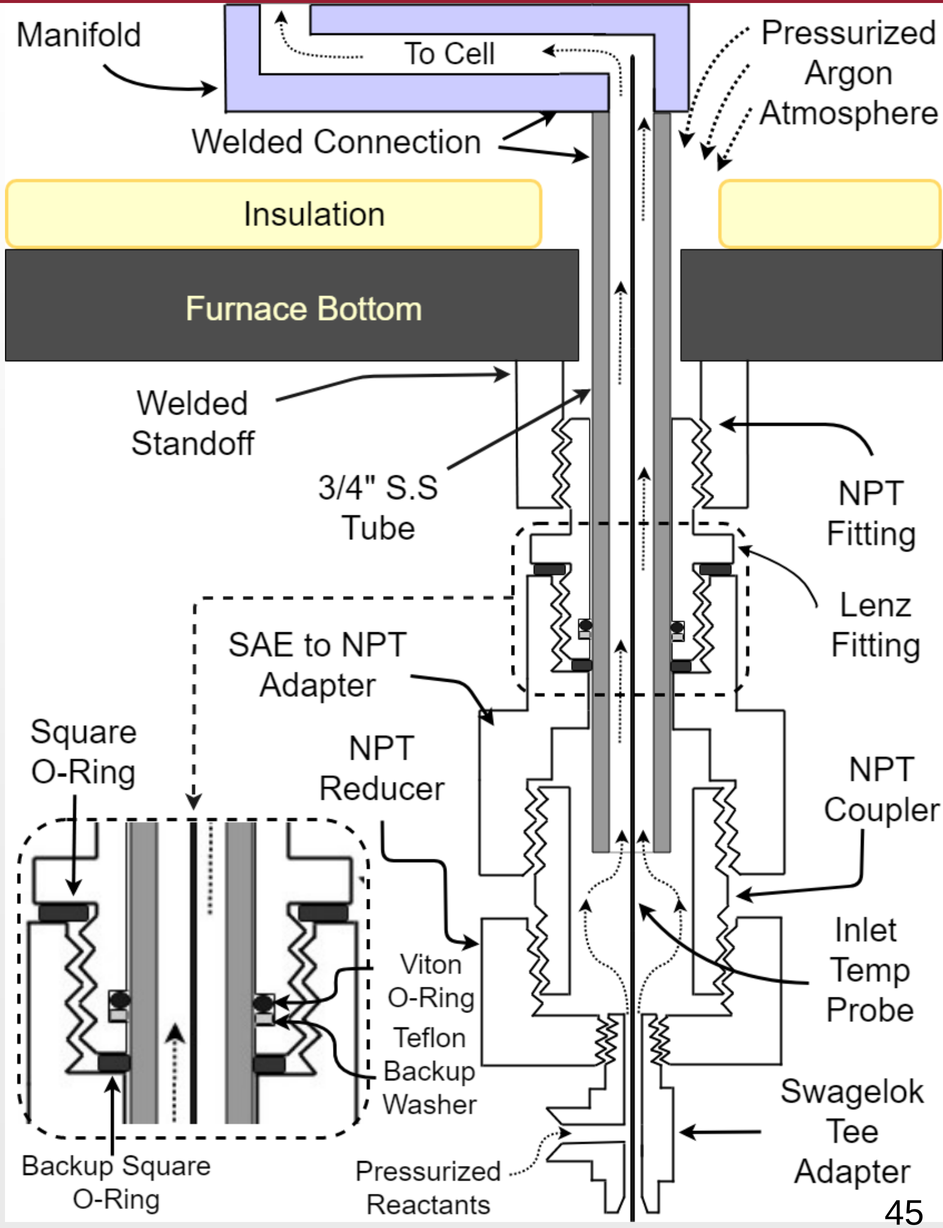
Conclusions

- Time Domain methods are faster, and less complicated/expensive than frequency domain methods.
  - Passive Load Excitation could allow for highly portable impedance spectrometers capable of measuring high power electrochemical cells.
  - I have designed and constructed a “Passive Load” impedance spectrometer and validated it against a commercial instrument.
  - The instrument has been used to measure the impedance spectrum of a pressurized SOFC cell that traditional methods would struggle with.
- Pressurization of SOFC’s can result in significant power increases.
  - This is accomplished through reduction of activation and gas diffusion losses.
  - Performance increases show a distinct leveling off effect with pressure.
- Benefits of pressurization can vary widely based on stack and cell design.

Reactant Pass-Through Design



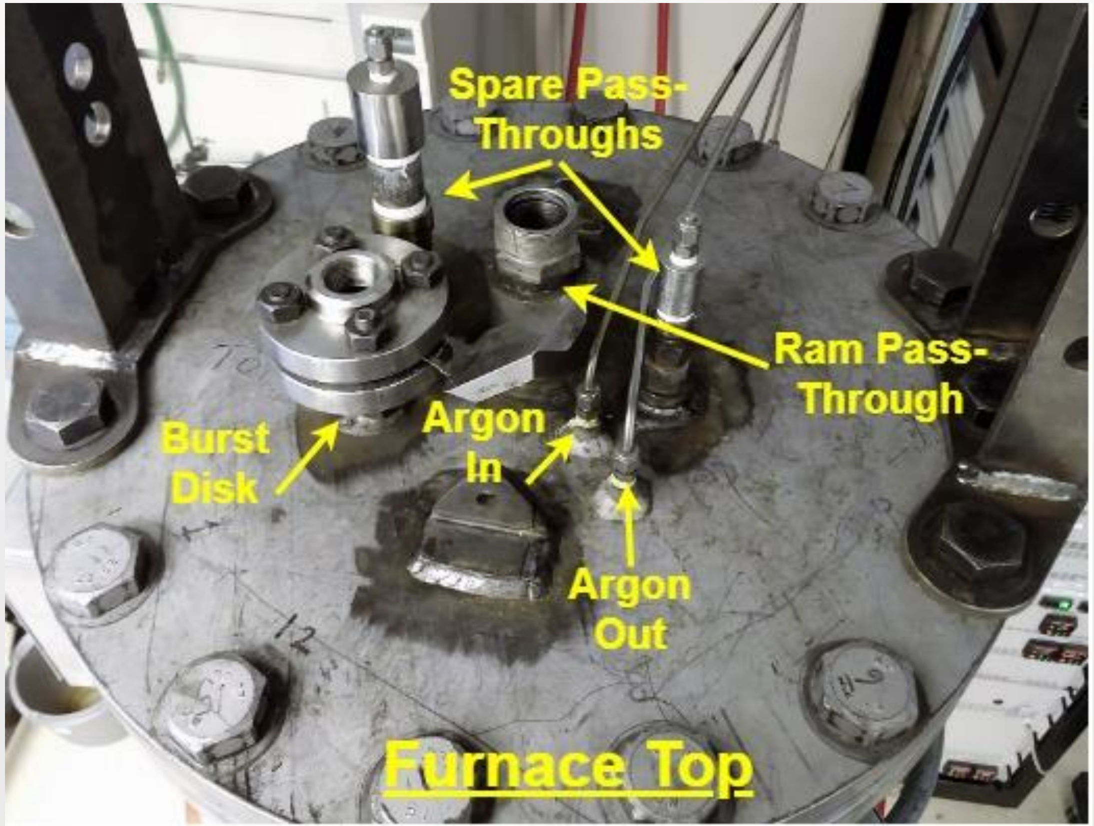
- Inlet/outlet pressure & temperature are monitored.
- Copper cored electrodes draw current from the stack.
- Nichrome voltage sense probes for accurate cell voltages.
- Redundant O-Rings help prevent failure and cross leaking
- Pass throughs allow easy change out of manifolds and work with ceramic/metal.
- Steam can be metered to experiment using 1 kw humidifier, insulation ad heating tape prevents condensation.

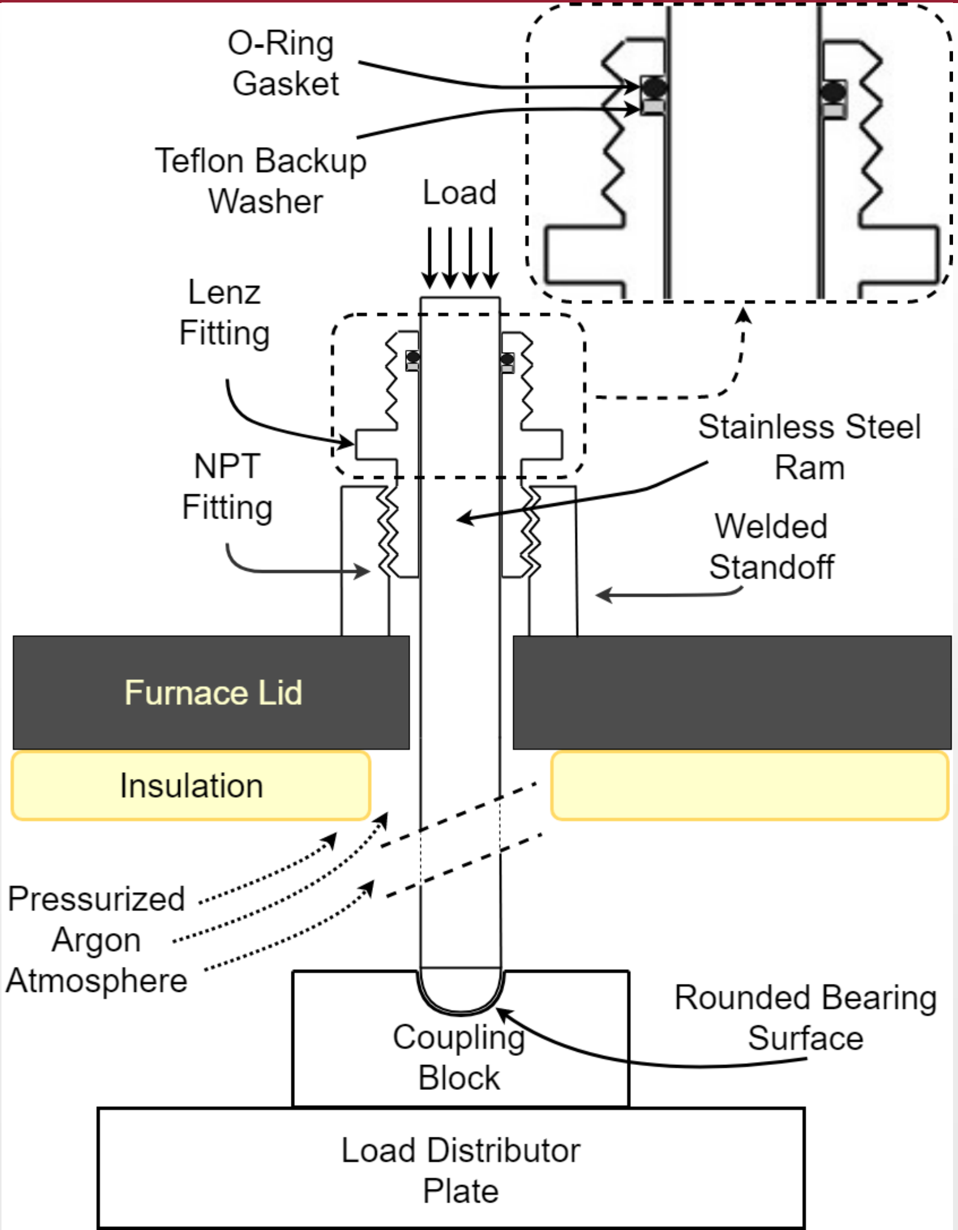


Ram Pass-Through

- Burst disk rated to about 11 bar prevents unsafe pressurization of the furnace.

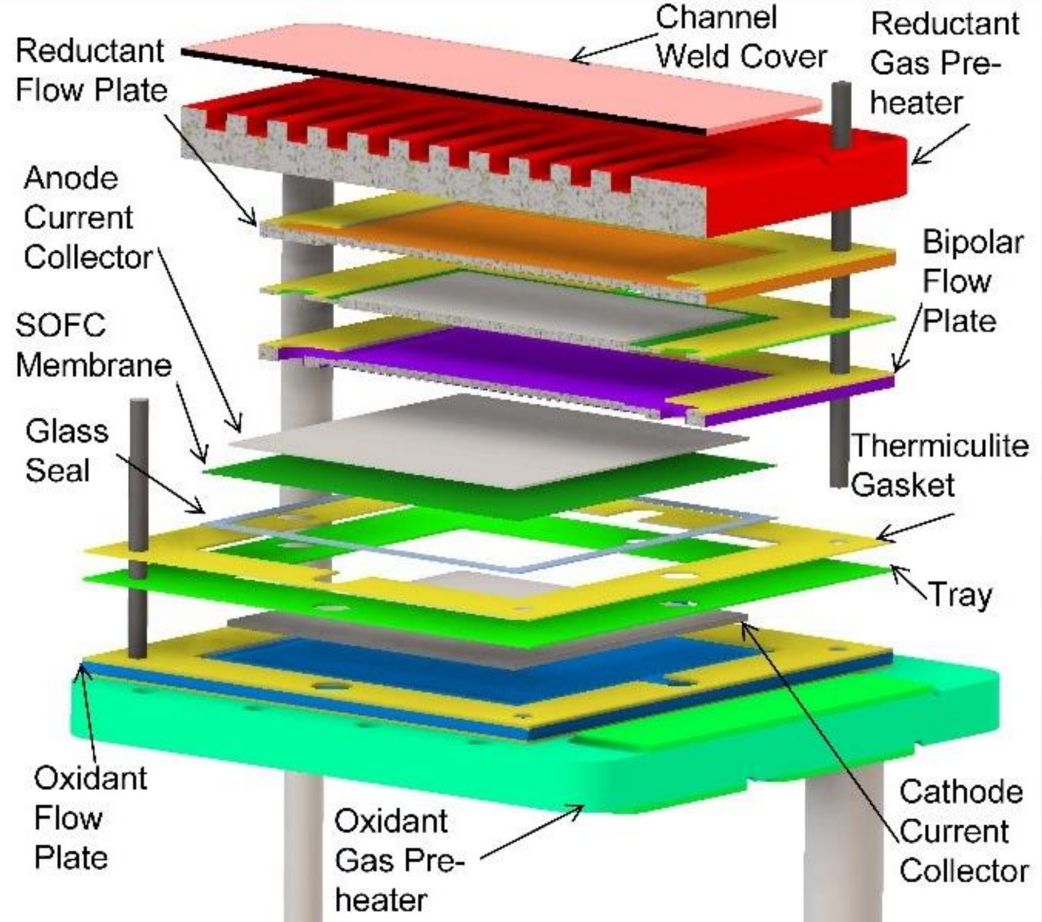
- Constant purge of 0.5 slpm Argon prevents unsafe mixing of reactants in case of leakage.
- Ram is routed through center of furnace for stack compression.





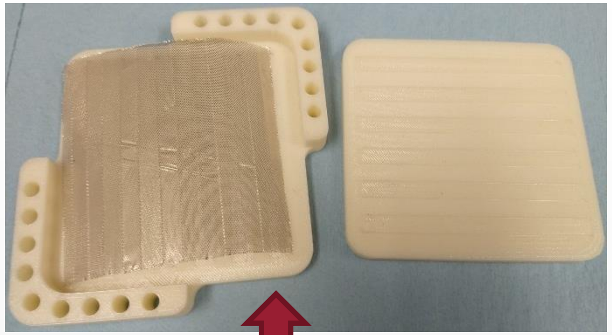
V1 Stack Design

- "Window frame" design uses Kerafol glass to seal cell to stainless steel tray
- Flexitallic's Thermiculite 866 seals tray to interconnect and interconnect to manifold
- Compressed to 10 MPa with external press



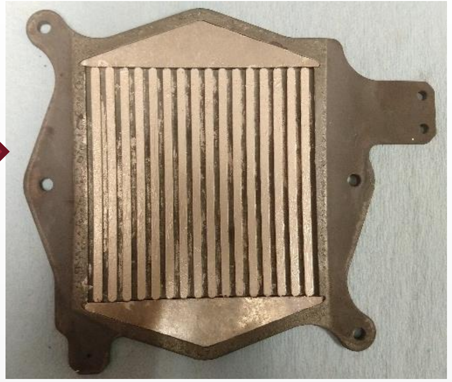
- Two separate Inconel manifolds preheat and route reactants to cell.
- Concentric piping used to reduce # of pass throughs necessary.
- Preheaters coated with Alumina spinel.
- Cathode interconnect coated with Co-Mn using a commercial thermal spray.

V2 Stack Build



Silver mesh is corrugated using 3D printed stamp

Silver paint is applied to ridges for better contact



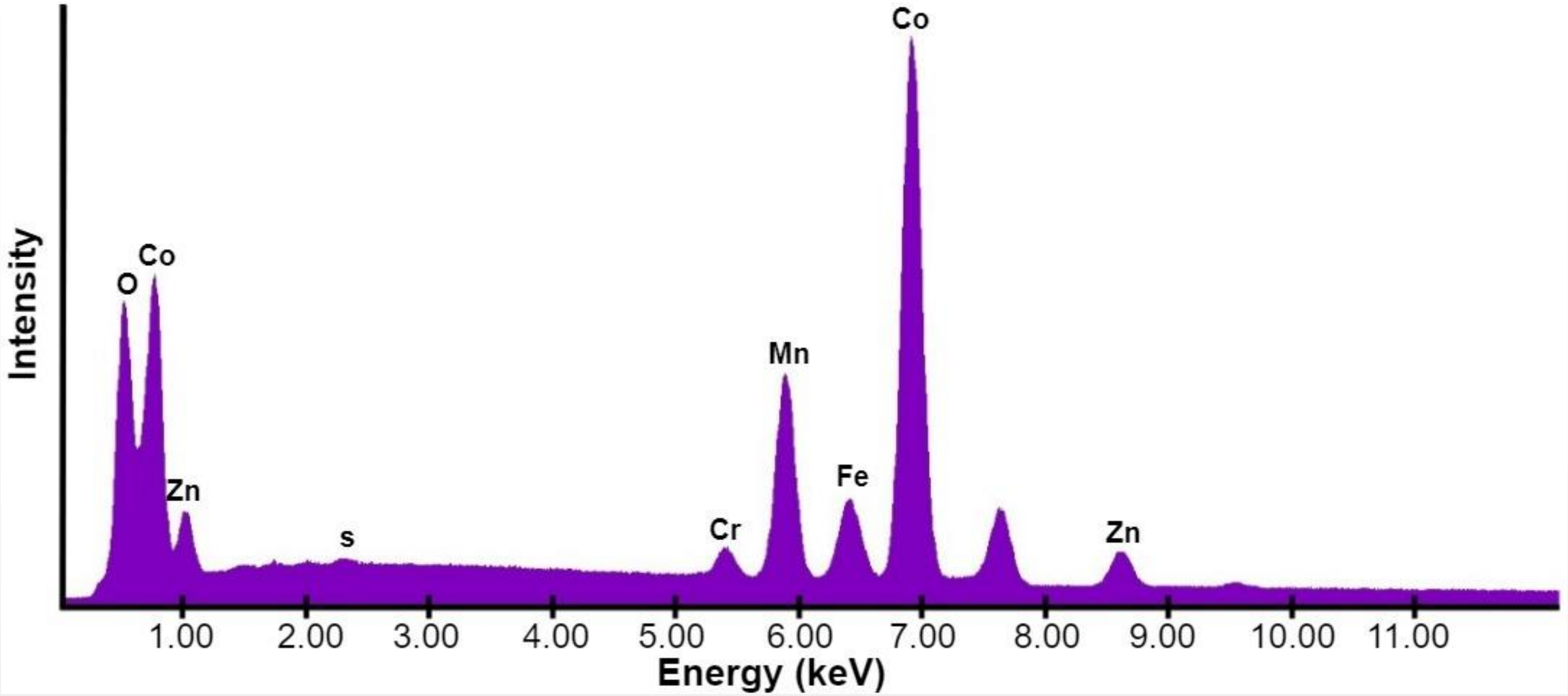
Twisted pair wires with silica sheathing are added for impedance measurements

Stack components laid out prior to build

Revised Stack Testing

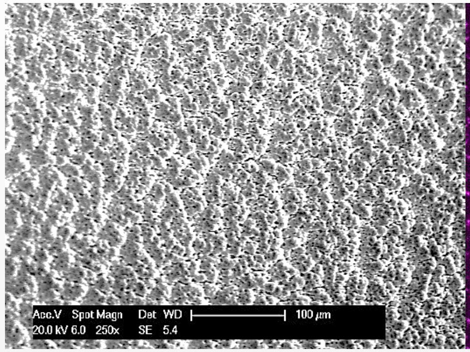
- New manifold made from 0.5 in. 304 S.S.
- Allows for inlet/outlet temps to be measured with removal of concentric piping.
- Two tests were run, one with a coated cathode plate and one without to give comparison.

As Plated SEM/EDS Surface Scans

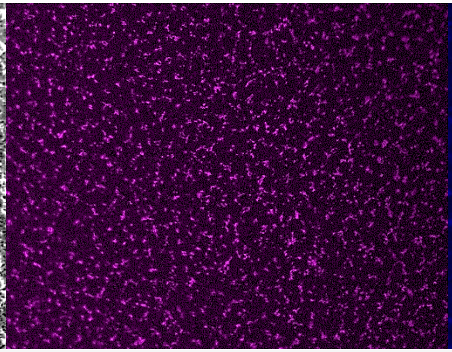


- Scans performed on 1 cm^2 sample
- Mn & Co cover most of the surface
- Fe & Cr are present where Mn & Co are not
- Zinc exists as a trace impurity

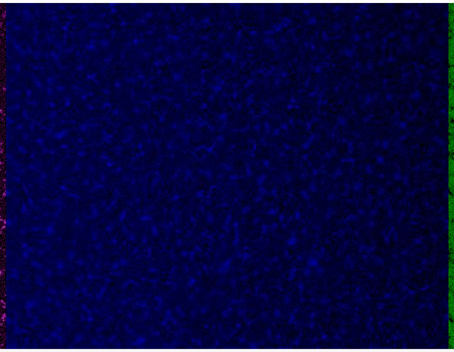
As Plated SEM/EDS Surface Scans



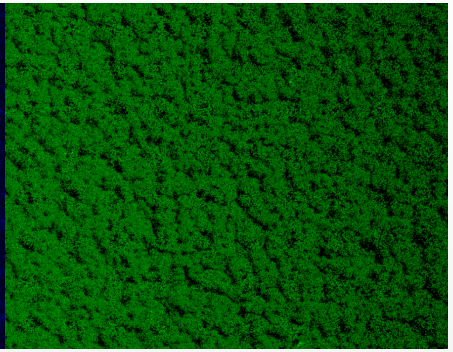
SEM Secondary Image



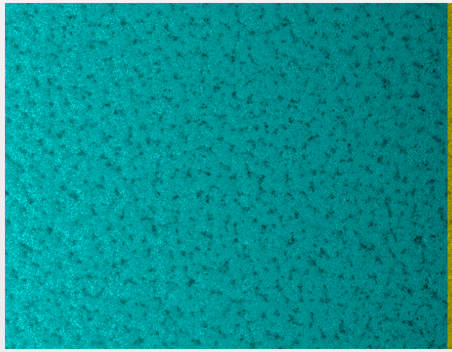
Fe K-α



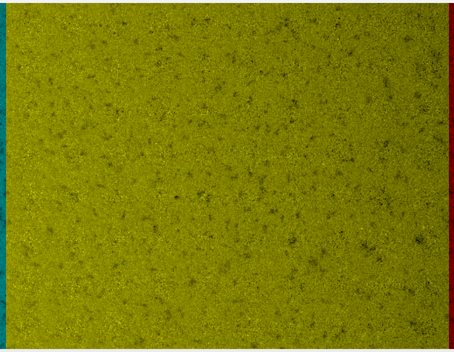
Cr K-α



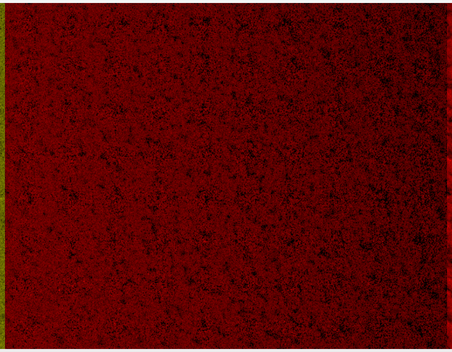
S K-α



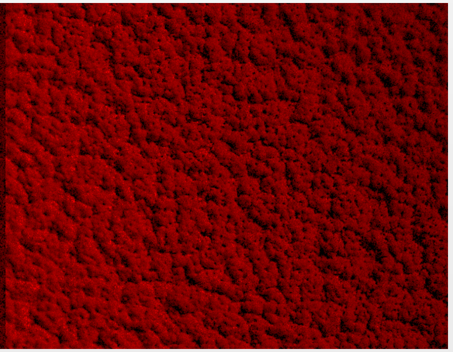
Co K-α



Mn K-α



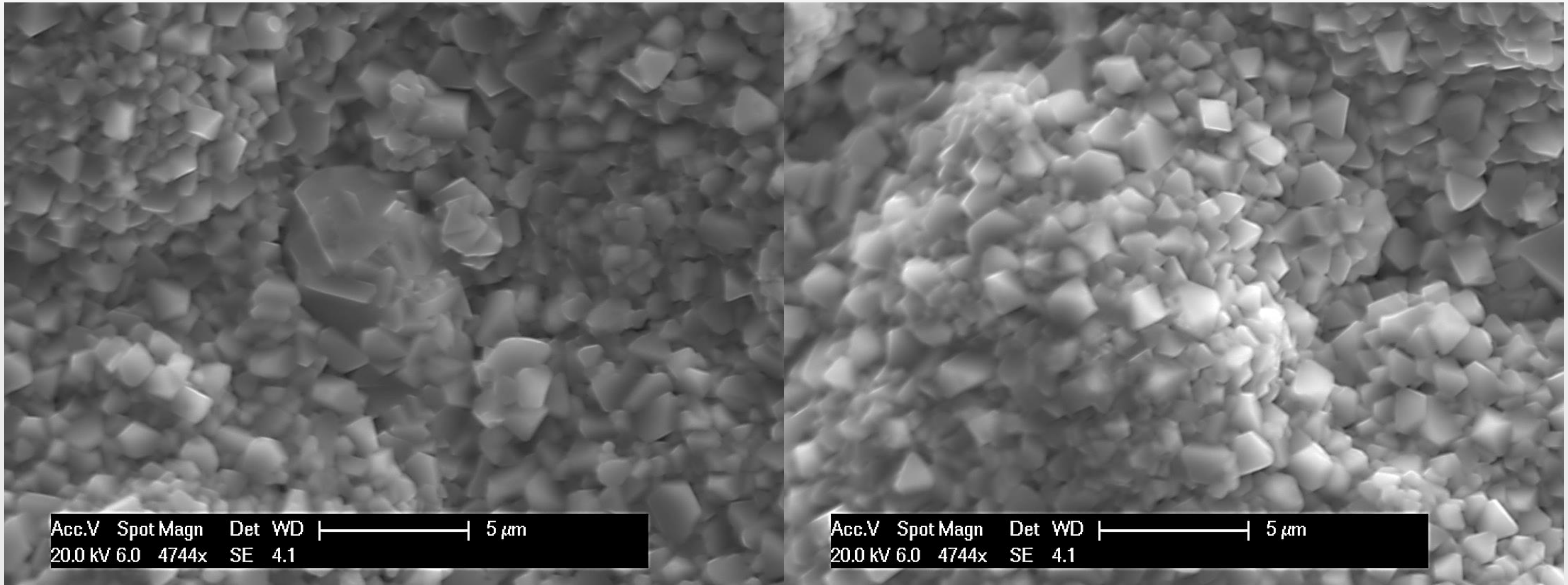
Zn K-α



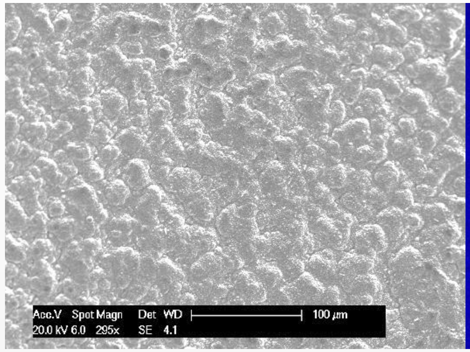
O K-α

Sintered Mn-Co Spinel Coatings

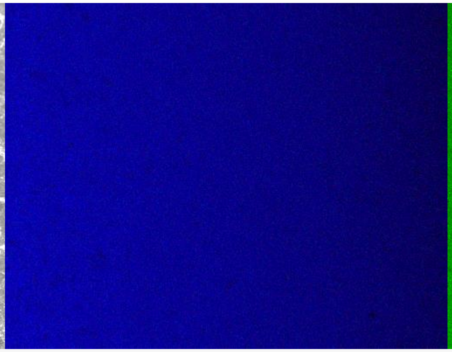
- Surface is well crystallized and relatively uniform in coverage
- No signs of spalling
- Highly conductive at operating temperatures of 650 ˚C



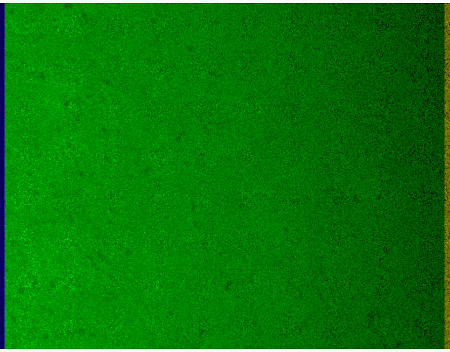
Sintered Mn-Co Spinel Coatings



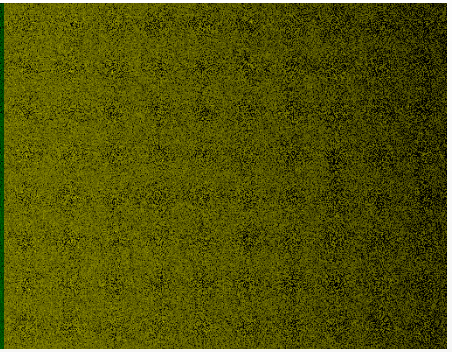
SEM Secondary Image



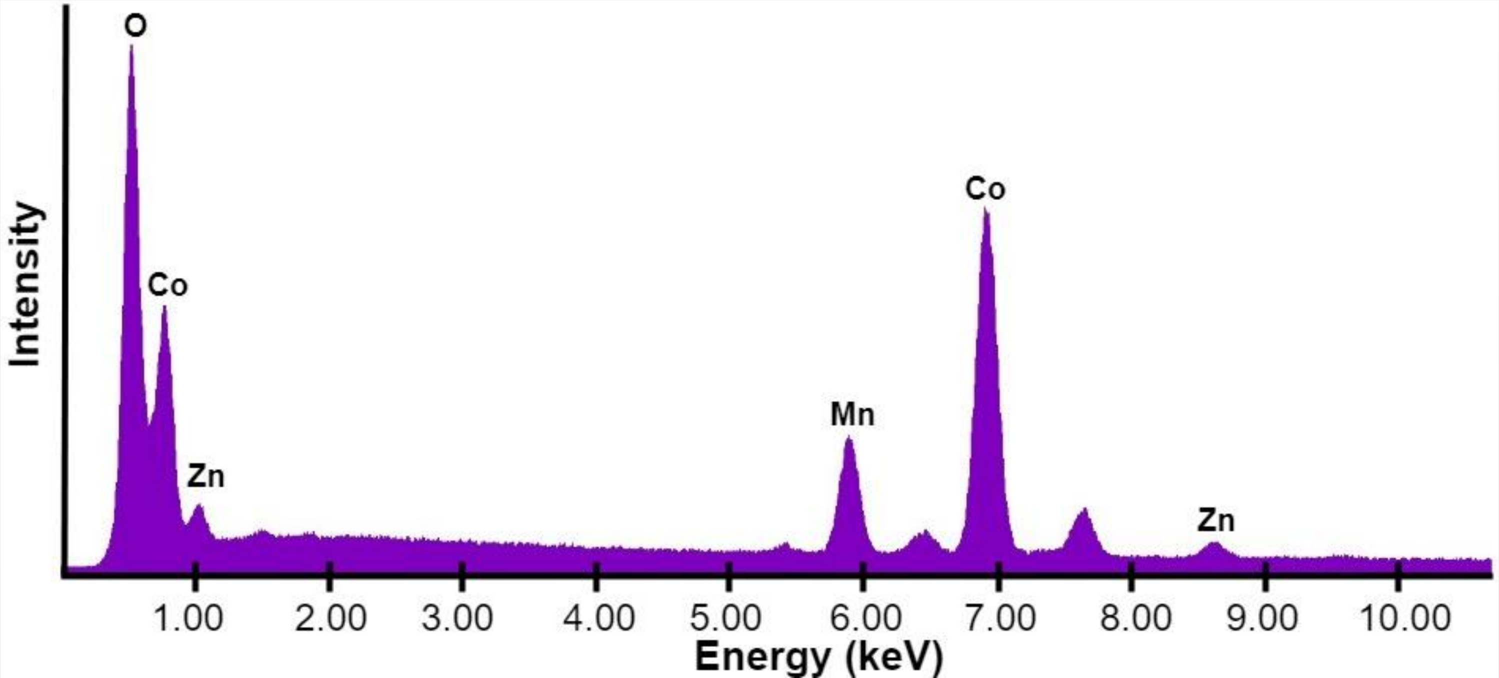
Co K-α

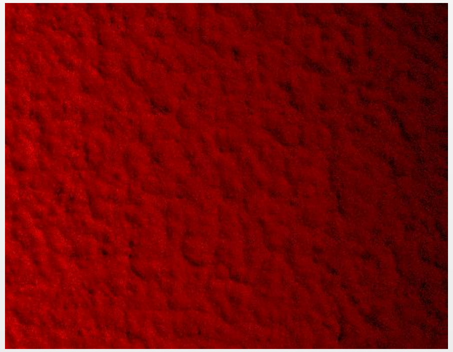


Mn K-α



Zn K-α

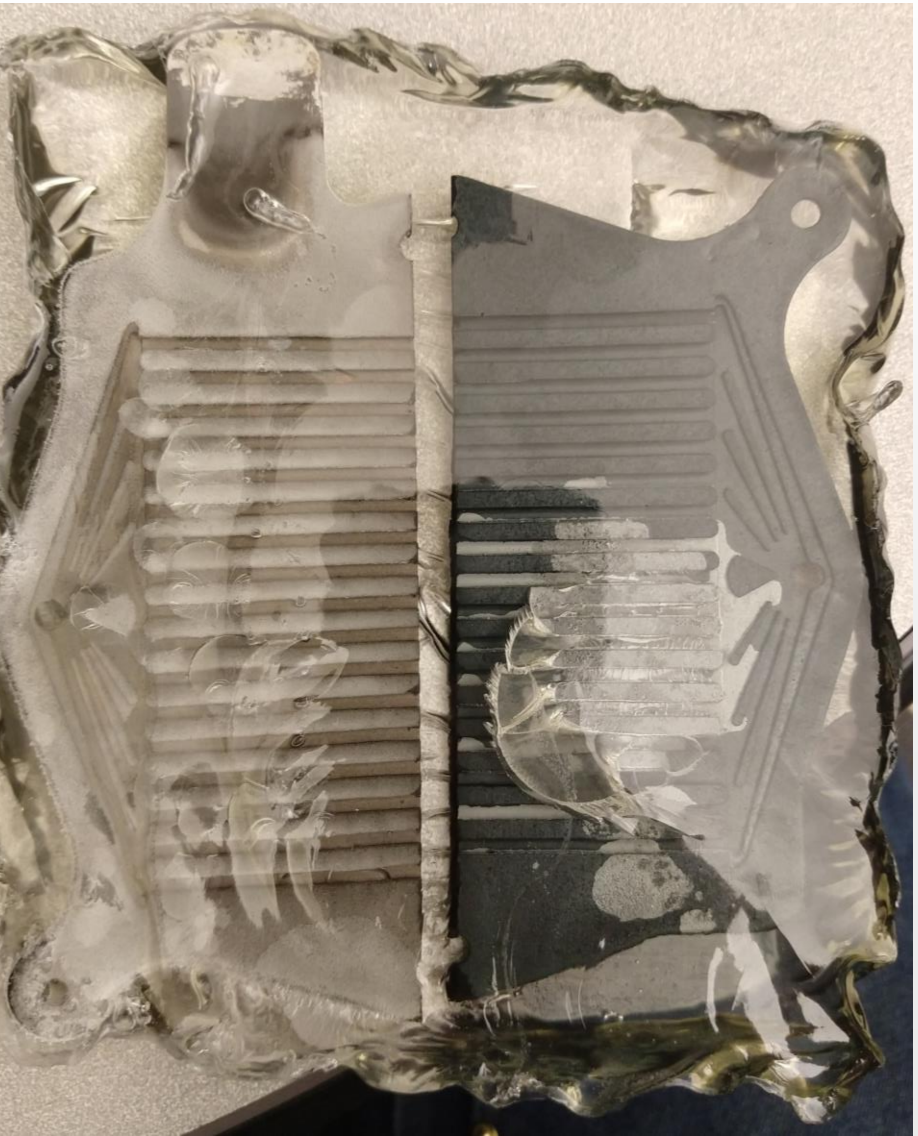




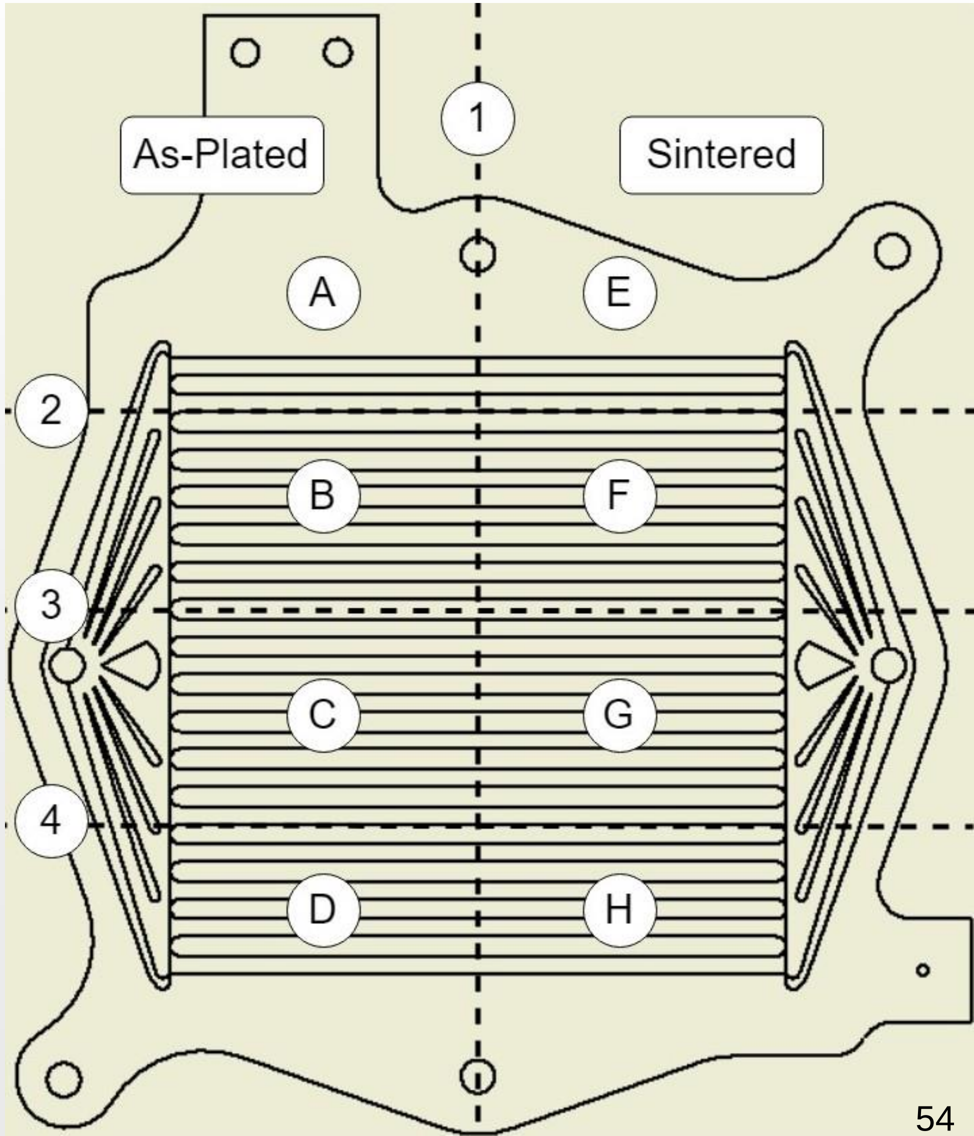
Cr L-α

(Likely O K-α)

Full Scale Interconnect Characterization



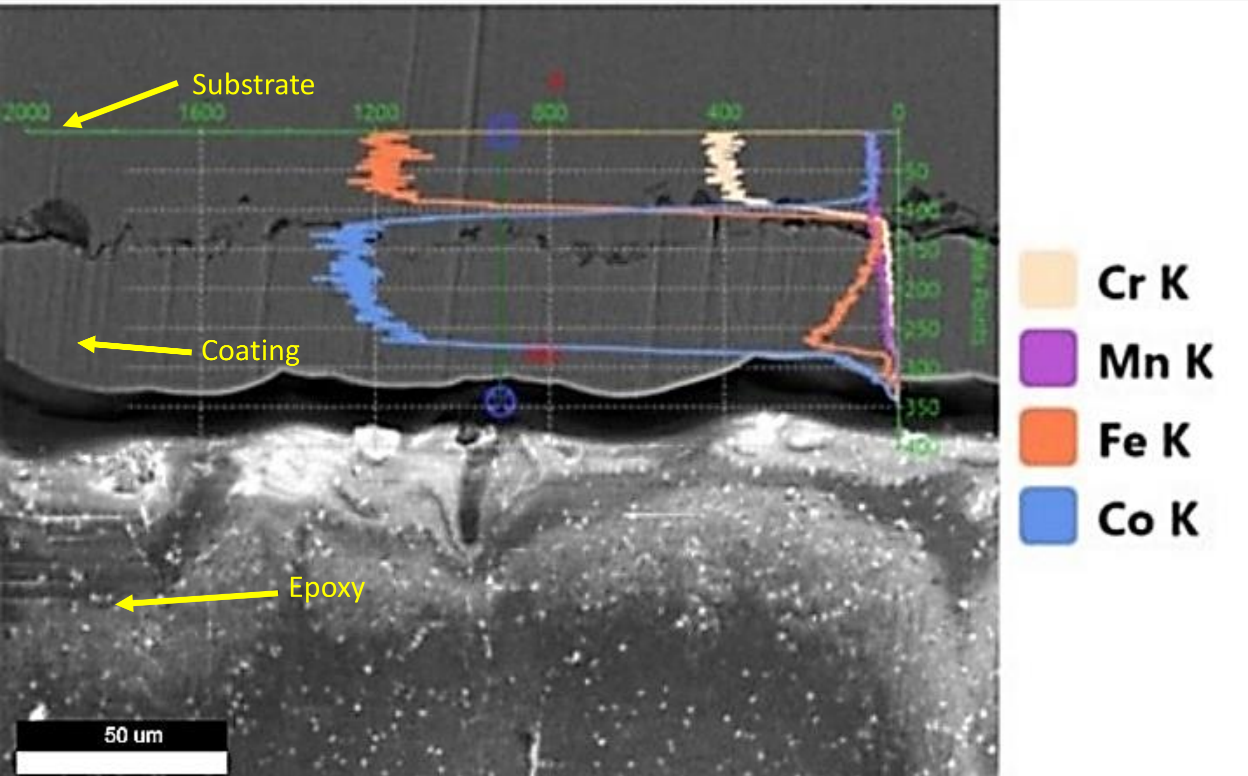
- Full Size Interconnect plate is electroplated and then cut in two using a bandsaw.
- One half is sintered to convert to Mn-Co Spinel
- Both halves are epoxy mounted and sectioned into smaller pieces.
- Sections C & G are characterized via SEM/EDS along line one.



As Plated

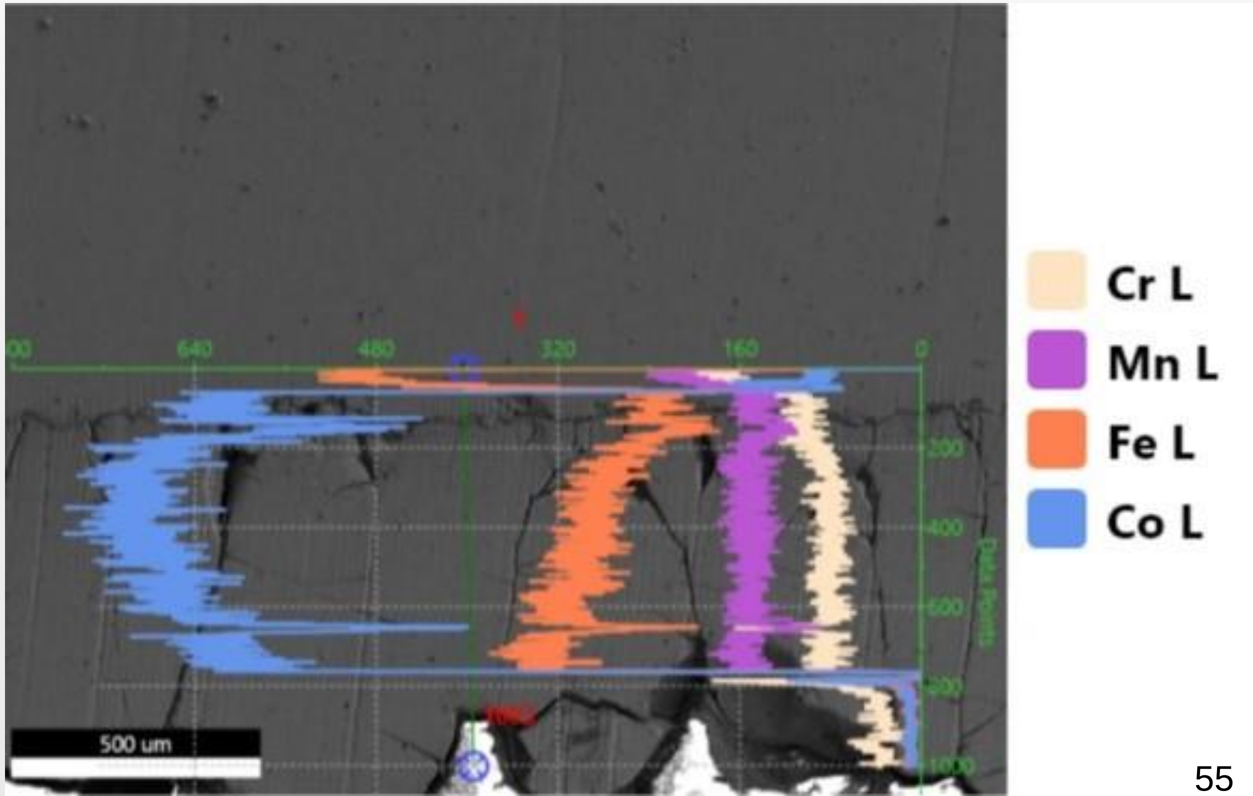
Bottom of Channel:

- Coating is continuous and roughly 35 µm thick.
- Mn content throughout the coating is very low, almost not present.
- Unexpected Fe in the coating, which increases linearly with coating thickness



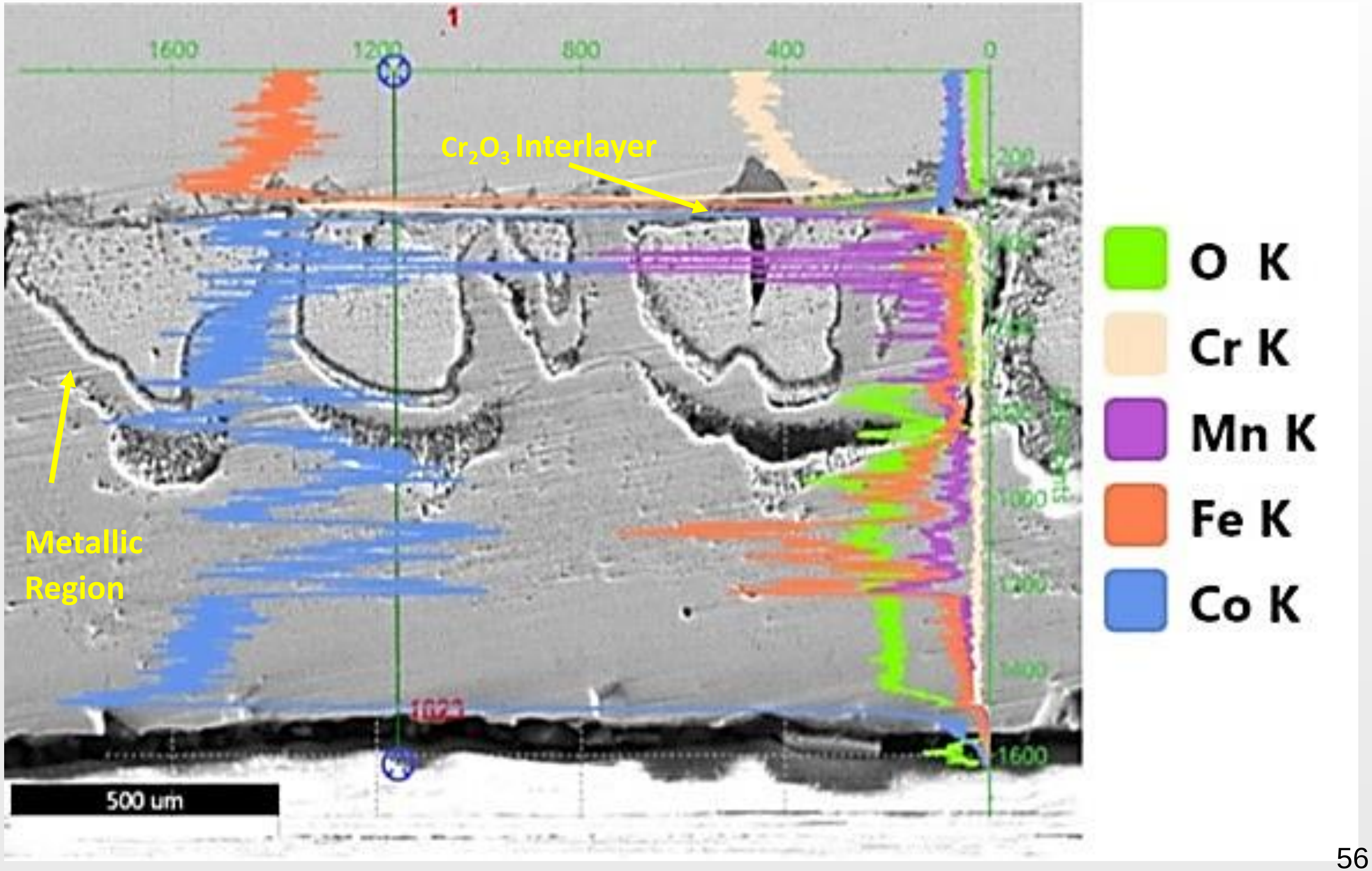
Top of Channel (Contact point of cell):

- Coating shows cracking.
  - This is believed to be caused by mechanical damage during cutting/grinding.
- Coating surface uneven, thickness is roughly 125 µm
- Mn content throughout the coating higher than on bottom of channel.



Sintered

- Second scan was performed adjacent to one of the formations to investigate further.
- Deposits show very high levels of Mn and almost no O_2.
- This indicates a metallic region still present.
- Further verified by shiny surface in optical microscope.



In-Situ Stack Compression Verification

- After the previous test, a new method for determining the appropriate amount of stack compression was developed.
- This method is performed in-situ during stack compression at room temperature using the Solartron 1260.
- The impedance response is measured as a function of applied gasket stress.
- The data shows a clear “leveling off” as pressure increases. The impedance spectrum no longer changes significantly.
- The strongest response seen at lower frequencies, where capacitive effects will dominate.