Additive Manufacturing of Anode-Supported SOFCs through Aerosol Deposition

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Introduction

Objectives

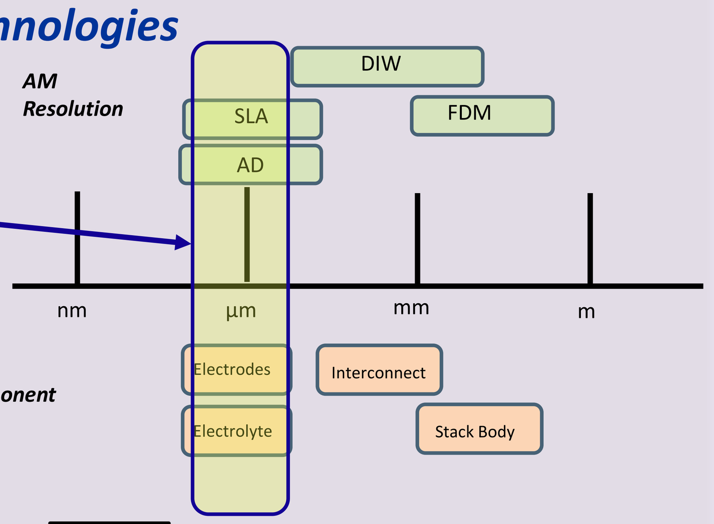
- Manufacture all components of anode–supported SOFC using 3-D automated process
  - Anode Functional Layer
  - Electrolyte
  - Cathode
- Achieve higher resolutions of deposition size and thickness
  - Decrease width and thickness of deposition
  - Less than 20 µm resulting thickness
- Develop method for creating highly customizable and repeatable microstructures
  - Composition
  - Grain Size
  - Density and Porosity
  - Arrangement of ionic and electronic conductors in multiple dimensions

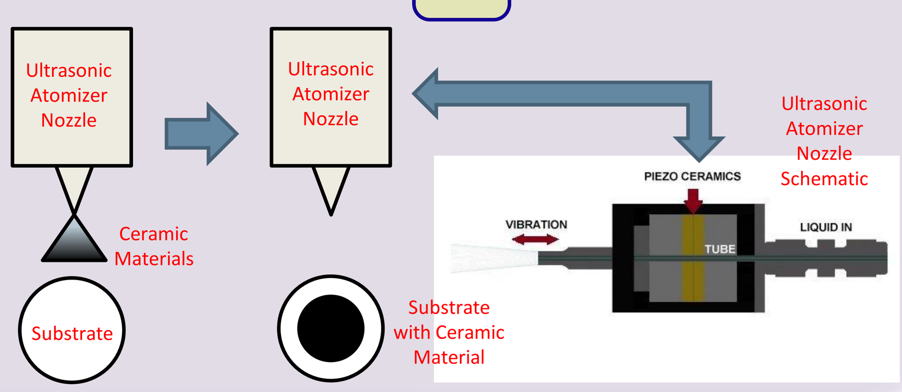
Benefits of Additive Manufacturing

- Offers the ability to in-situ change compositions and microstructure within 3-dimensions
- Higher degree of manufacturing resolution allows for more customizable patterns and designs
- Coupled with machine learning system can provide route to rapidly prototype components to evaluate how variables alter electrochemical performance

Additive Manufacturing Technologies

- **Fused Deposition Manufacturing (FDM)**- Degree of resolution is limited and can not in-situ change material compositions
- **Stereolithography (SLA)**- Very high resolution is desirable for printing electrodes and electrolyte but difficulties in-situ changing material composition
- **Direct Ink Writing (DIW)**- Can reach desirable resolution for electrodes and electrolyte along with in-situ changing material composition but has difficulties with nozzle clogging due to high viscosity inks
- **Aerosol Deposition (AD)**- Degree of resolution is desirable for manufacturing electrodes and electrolyte (less than 20 µm) along with having the ability to in-situ change chemical composition due to multi-pump set up





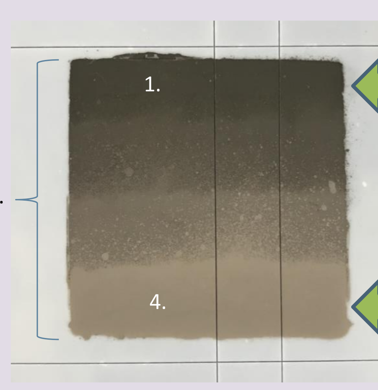
Multi-Dimensional Depositions

- What makes Aerosol Deposition unique to other methods of manufacturing SOFCs?
  - Ability to manufacture thin layers of components
  - Potential for high-customizability with the microstructure of components
- To demonstrate advantages that Aerosol Deposition has over other additive manufacturing techniques, a cathode with changes of microstructure within multiple dimensions was manufactured.
- Two different designs were utilized to manufacture a cathode with changes of composition in multiple dimensions

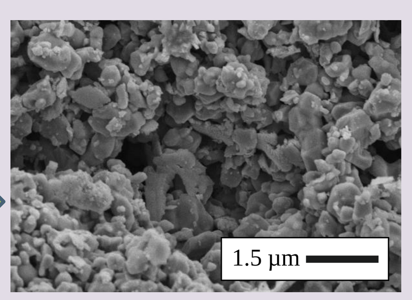
Design #1

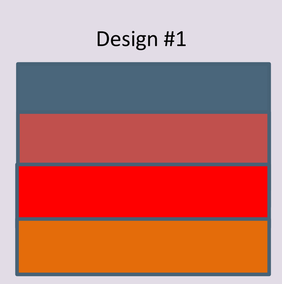
- *Average Grain Size- 0.84 µm*

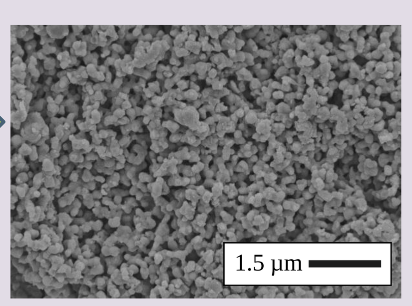
Location #1- 100% LSCF and 3 µm PMMA



5 cm.





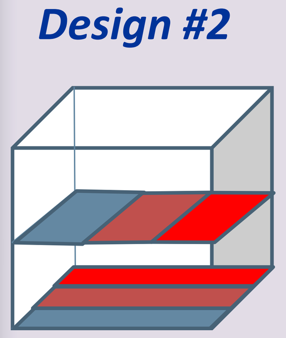


- *Average Grain Size- 0.71 µm*

Location #4- 25/75 vol% LSCF/YSZ and 3 µm PMMA

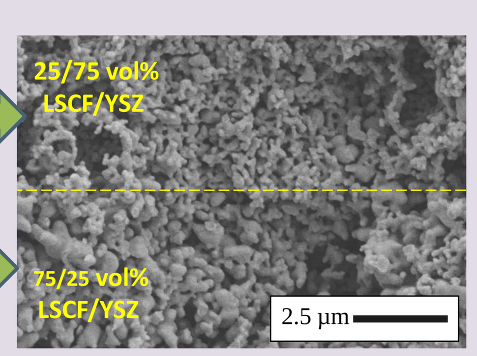
- Goal is to demonstrate that system can also change composition in x-y direction
- Total of 4 different compositions were deposited
- Starting particle sizes for LSCF & YSZ
  - LSCF: ~0.7-1.1 µm
  - YSZ: ~0.4-0.7 µm

Design #2

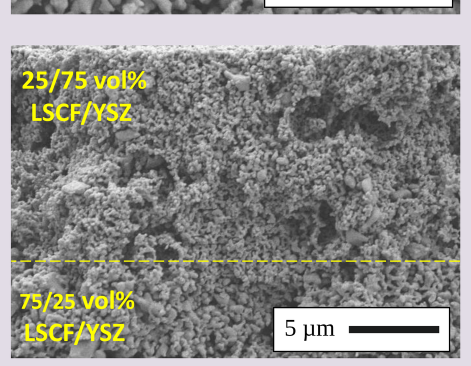


Average Grain Size Top Layer- 0.68 µm

Average Grain Size Bottom Layer- 0.71 µm



5 cm.

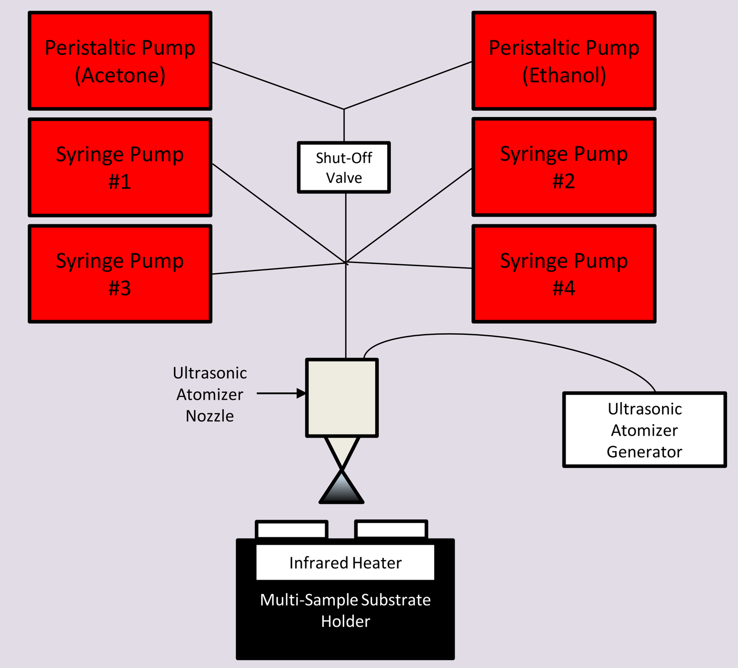


- Top Layer: 25/75 LSCF/YSZ & 3.0 µm PMMA
- Bottom Layer: 75/25 LSCF/YSZ & 3.0 µm PMMA
- Sintered to 1100 °C
- Starting particle sizes for LSCF & YSZ
  - LSCF: ~0.7-1.1 µm
  - YSZ: ~0.4-0.7 µm

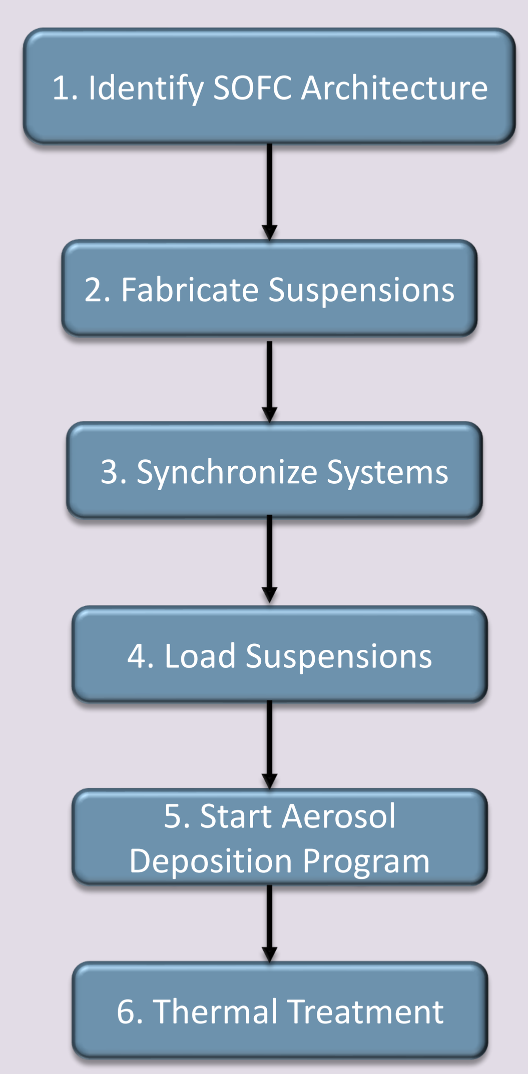
Aerosol Deposition System

System Components

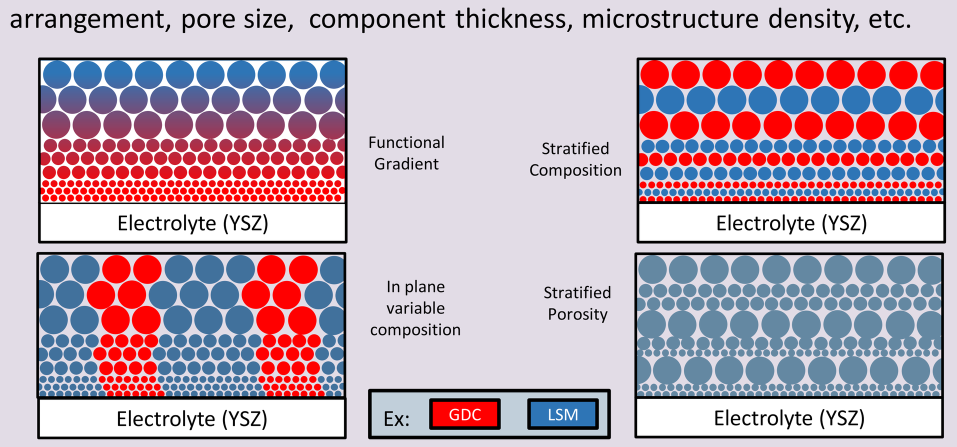
- **Cleaning Pumps-** Two peristaltic pumps are utilized to supply acetone and ethanol throughout system which clean and clear suspension tubing of any residual material
- **Syringe Pumps-** Four programmable syringe pumps inject suspensions through tubing to the ultrasonic atomizer for consistent flow. Programmable syringe pumps have the capability to alter flow rate for system optimization
- **User-Friendly Interface-** Syringe pumps are controlled through Labview software that can alter flow rate, run time, and sequence order of designated pumps
- **Ultrasonic Atomizer Nozzle-** Converts stream of suspension into a fine mist through mechanical vibrations. Mechanical vibrations are produced by converting the electrical signal supplied from the ultrasonic atomizer generator to mechanical vibrations through piezoceramics
- **Flexible Automation System-** An array of stepper motors accompanied with alignment tracks allow the ultrasonic atomizer nozzle to move in any direction within the x-y plane. Flexible automation system is controlled with CNC programming language to create unique print pathways
- **Multi-Sample Substrate Holder-** Offers the ability to hold multiple substrates for mass production of samples. Also contains an infrared heater within the interior of substrate holder for proximity to substrates for increased drying rate of depositions



Aerosol Deposition Process



1. Identify SOFC Architecture- Identify desired parameters for specific SOFC component such as material arrangement, pore size, component thickness, microstructure density, etc.



2. Fabricate Suspensions- Suspensions utilized within aerosol deposition consist of several different components:
- Solvent: Ethanol/Water mixture, mixture is predominantly ethanol for faster drying time
- Ceramic Solids: Ionic or electronic conductor depending on desired component
- Dispersant: Variety of nonionic and anionic dispersants available to keep solids from agglomerating within suspension
- Binder: Polyethylene Glycol and Glycerol, utilized to give 3-D printed green part strength
- Pore Former: PMMA, an organic polymer is used to achieve desired pore size within the microstructure

3. Synchronize Systems- Sync the timing of gCode pattern for flexible automation and Labview program for syringe pumps to achieve desired design

4. Load Suspensions- Load fabricated suspensions into proper syringe pumps for proper deposition pattern

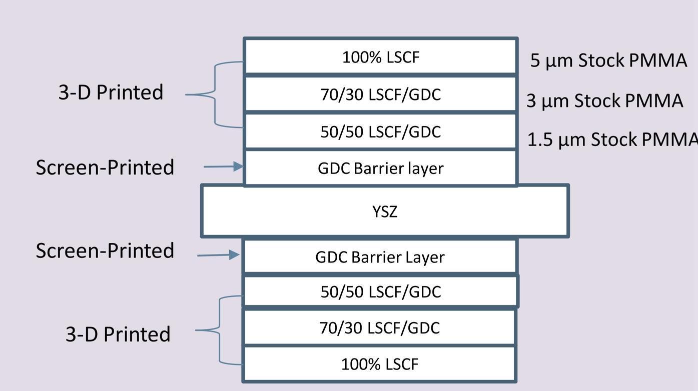
5. Start Aerosol Deposition Program- Once suspensions have been loaded, program can be started by clicking "Start" which begins the heating process of the infrared heater to a desired temperature for drying depositions. Once heater is brought up to proper temperature, deposition process begins where syringe pumps supply suspensions to ultrasonic atomizer and is deposited on substrates.

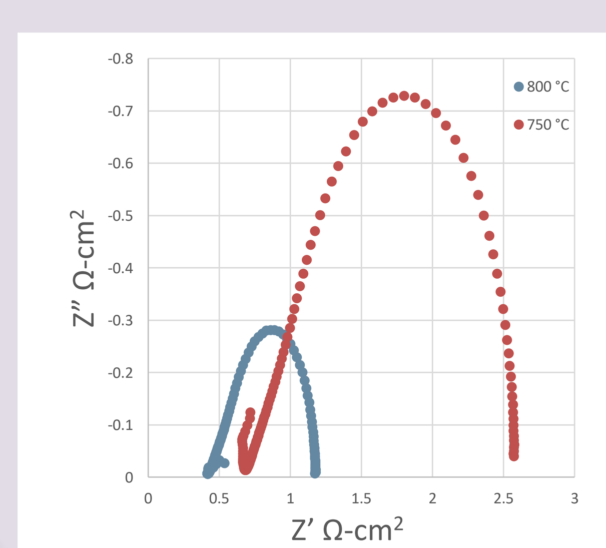
6. Thermal Treatment- Once suspensions are deposited and dried, thermal treatment of depositions is completed to strengthen the 3-D printed SOFC component

EIS Results

- **EIS- Electrochemical Impedance Spectroscopy is used to characterize the electrical performance of the fuel cell**
- **Initial development of the electrical performance of cathodes manufactured via aerosol deposition utilized LSCF/YSZ within a comparative study to evaluate how different variables changed the performance**
- **Variables evaluated:**
  - Sintering temperature
  - Porosity architecture
  - Type of dispersant
  - LSCF/YSZ ratios
  - hydroxyl modified PMMA vs. Stock PMMA
- **From the results of the comparative study, the baseline cathode structure was identified to represent the best performing variables from the study**
- **Composite materials for the cathode was also changed to LSCF/GDC to reflect EIS values commonly found in literature**
- **Observations**
  - At 800 °C, polarization resistance of 0.377 $\Omega \cdot cm^2$ and ohmic resistance of 0.425 $\Omega \cdot cm^2$ are measured
  - A large diffusional peak can be observed in the bode plot around 1 Hz

LSCF/GDC Baseline Cathode



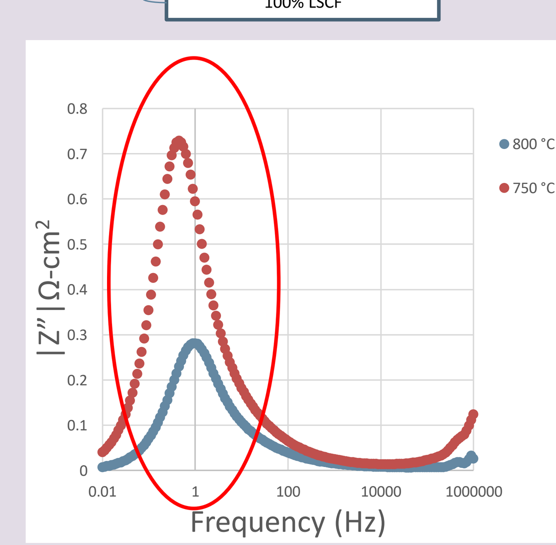


Polarization Resistances
800°C- 0.377 $\Omega \cdot cm^2$
750°C-0.94 $\Omega \cdot cm^2$

Frequency Peaks
800°C- 1 Hz
750°C- 0.45 Hz

Ohmic Resistances
800°C- 0.425 $\Omega \cdot cm^2$
750°C- 0.685 $\Omega \cdot cm^2$

Electrolyte Thickness
0.27 mm.

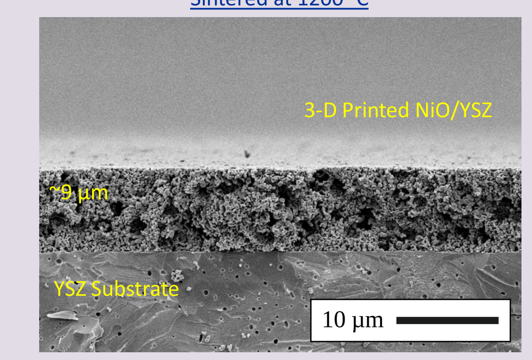


Components Development through Aerosol Deposition

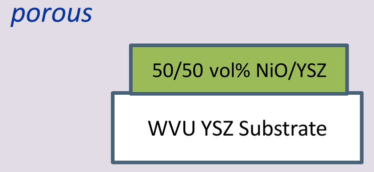
Anode Functional Layer

- **50/50 vol% NiO/YSZ and 1.5 µm hydroxyl modified PMMA was incorporated within a suspension and deposited onto a YSZ substrate**
- **Resulting depositions were sintered at various temperatures to evaluate thickness, and microstructure density/porosity**
- **Observations-** Homogenous depositions with thicknesses less than 10 µm were observed along with a suitable amount of porosity for the anode functional layer

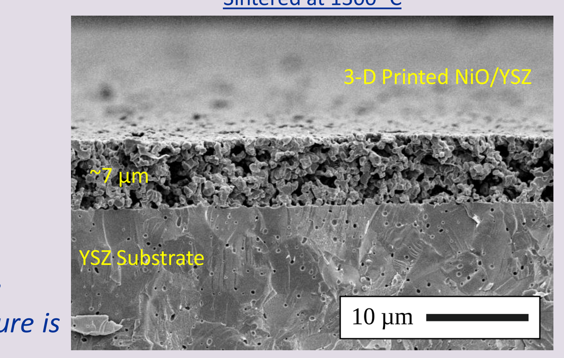
Sintered at 1200 °C



~18% of the microstructure is porous



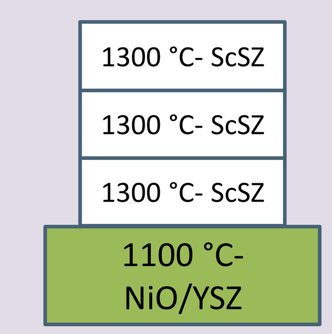
Sintered at 1300 °C

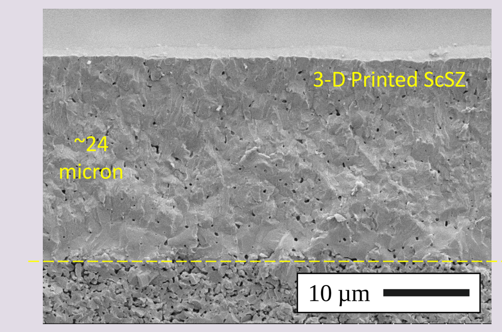


~23% of the microstructure is porous

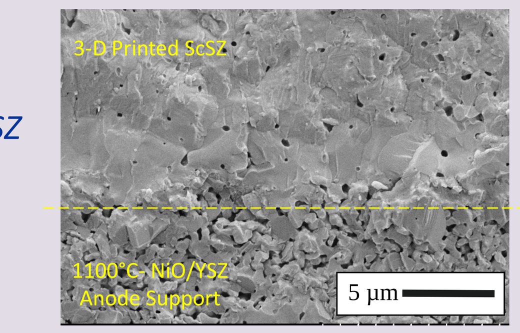
Electrolyte

- **100 vol% ScSZ was incorporated within a suspension and deposited onto NiO/YSZ anode supports with varying sintering temperatures**
- **ScSZ depositions were sintered to 1300 °C to evaluate density of microstructure**





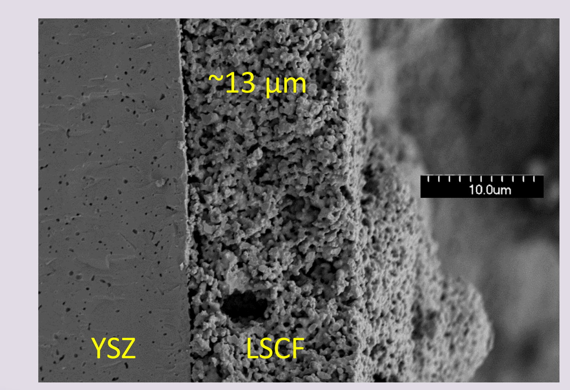
~0.54% of the ScSZ microstructure is porous



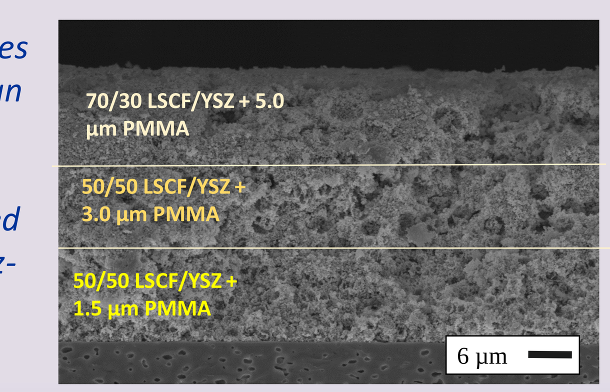
- Observations
  - Resulting thickness is ~24 µm with 3 layers of deposited ScSZ
  - Smaller thicknesses of electrolyte are possible with altered Aerosol Deposition process
  - Minimal porosity can be observed within the ScSZ microstructure
  - No connected porosity within the microstructure

Cathode

- **100 vol% LSCF was incorporated within a suspension and deposited onto YSZ substrates**
- **Composite cathode of LSCF/YSZ with varied pore size throughout z-direction was also developed**



- *Cathode thicknesses less than 20 µm can be achieved*
- *Potential to manufacture varied microstructure in z-direction was also demonstrated*



~46 µm sprayed thickness

Conclusions & Future Work

Summary
- Various types of additive manufacturing techniques are available
  - Aerosol Deposition offers advantages over types of technologies such as higher resolution, and customizability
- Components of SOFC have been developed through Aerosol Deposition
  - **Anode-** NiO/YSZ anode with 16%-23% porosity have been manufactured by utilizing PMMA pore former
  - **Electrolyte-** Dense ScSZ electrolyte has been manufactured. Type of substrate utilized within system is crucial for resulting thickness and porosity of deposition
  - **Cathode-** Composite cathodes have been manufactured with step gradients in composition and microstructure. Variables have been identified to improve electrical performance of LSCF/GDC baseline cathode
- Demonstrations of the potential of the system to manufacture highly customizable components by changing composition and microstructure in three dimensions was completed

Future Work
- Barrier Layer
  - Follow same development process to implement GDC barrier layer through system
- Higher Resolution
  - Current system has great resolution in the z-direction but deposition width in x-y direction is ~7 mm.
  - Have access to a higher resolution nozzle that can reach deposition widths of ~0.25 mm.
- System Variables
  - Alter system variables to optimize component print quality and evaluate any changes in electrical performance
- In-Situ Mixing
  - Rather than manufacturing changes in composition and microstructure in a "step" design make gradient changes by being able to mix suspensions of LSCF, GDC, NiO, YSZ to in-situ change the suspension composition

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