SAND2011-7114 C

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Doped Solid Oxide Fuel Cell Electrolytes Produced by a Combination of Suspension Plasma Spray and Very Low Pressure Plasma Spray (VLPPS)

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Thermal Spray Research Laboratory

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Executive Program

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Hamburg, GE

Electrolyte Optimization in SOFCs

- O^{2-} transports across electrolyte and reacts with H_2
- Electrolyte design motivations
  - Maximize O^{2-} conductance
  - Minimize thickness
- Maximize density
- Common electrolyte composition
  - 8 mol% Yttria Stabilized Zirconia (YSZ)

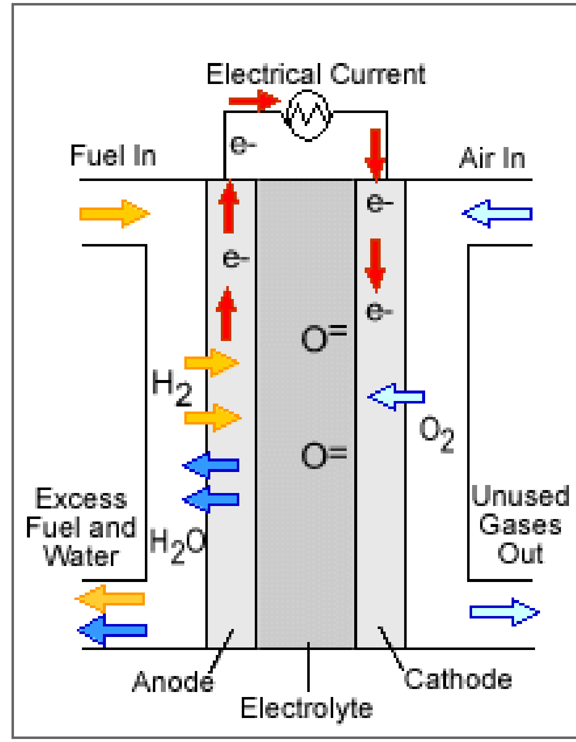

Image taken from U.S. DoE, showing a diagram of SOFC function

Minh, N. Q., Takahashi, T., Science and Technology of Ceramic Fuel Cells, 1995. p. 69-101.
U.S. Department of Energy. *FCT Fuel Cells: Types of Fuel Cells.* 2009.

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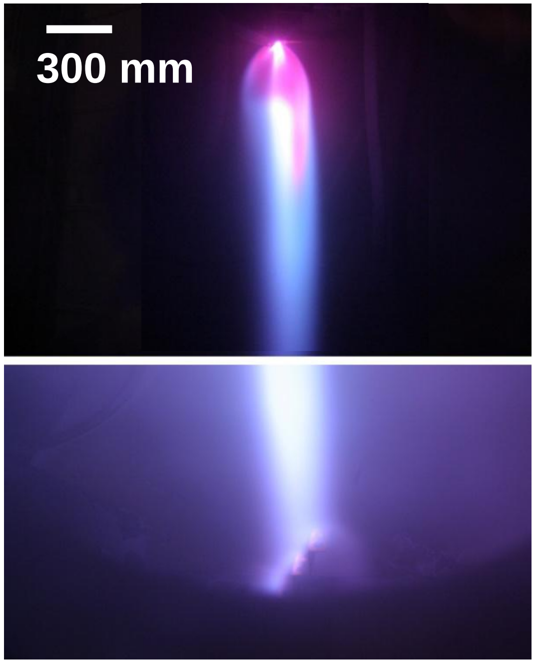
Advantages of Very Low Pressure Plasma Spray (VLPPS) Over Air Plasma Spray (APS)

- Mean free path of particles significantly increased
  - Wide uniform deposition
  - Potential for thinner, denser electrolytes
  - Increased powder residence time in plume



Images of VLPPS/SPS. Note: Chamber pressure ~2 Torr and stand-off distance is 109 cm

Spinhirne, N., *Masters Thesis, New Mexico Institute of Mining and Technology, 2008 p. 13-46.*
G. Mauer, R. Vaßen, D. Stöver, Thin and Dense Ceramic Coatings by Plasma Spraying at Very Low Pressure, *Thermal Spray 2009: Proceedings of the International Thermal Spray Conference*, p 773-778

Advantages of Suspension Plasma Spray (SPS) Over APS (Conventional Powder Feed)

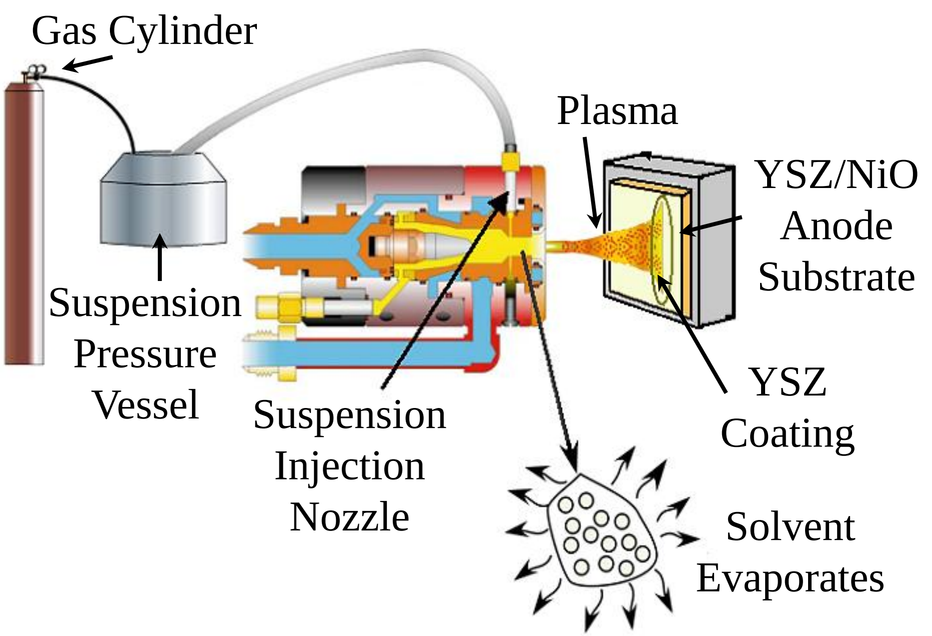


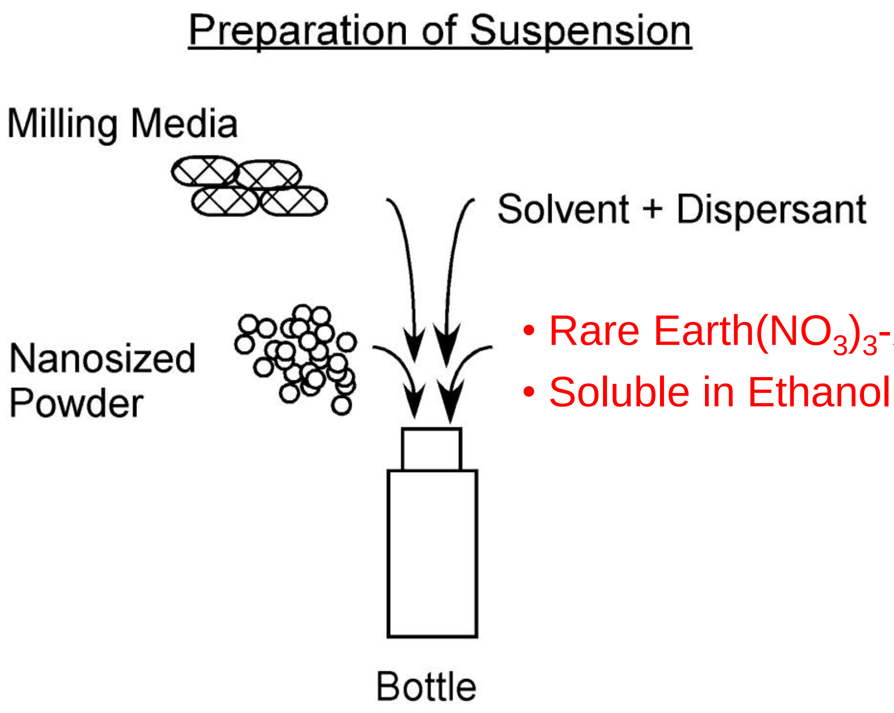
Image adapted from the Ph.D. thesis of Dr. Every, a schematic detailing the SPS process.[4]

Advantages

- relative easy to spray sub-micron particles
- Potential to dope the final coating or electrolyte

Every, Kent, et al, in press, International Journal of Applied Ceramic Technology
Every, Kent, *Ph. D Thesis*, Purdue University, 2009, p. 41.
Irvine et al*, Fuel Cell Technologies: State and Perspectives, 2005, p. 35-47.*

Suspension Plasma Spray (SPS) Doping



- Rare Earth$(NO_3)_3$-XH_2O
- Soluble in Ethanol

- Dopant elements in suspension diffuse into electrolyte
  - $Sc(NO_3)_3*4H_2O$ is initial dopant chosen
    - Sc^{3+} soluble in YSZ
    - SCZ has ~3 times ionic conductivity of YSZ

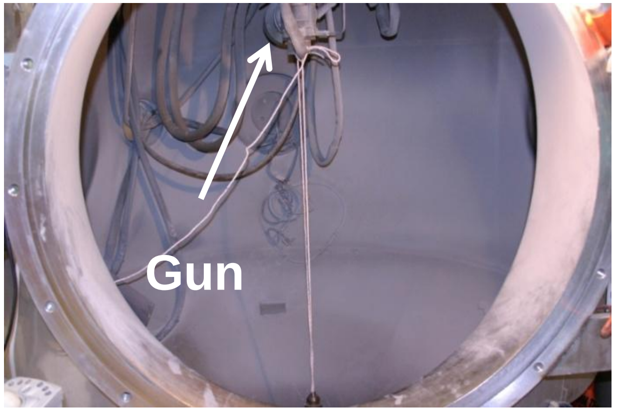
Every, Kent, et al, in press, International Journal of Applied Ceramic Technology
Every, Kent, *Ph. D Thesis*, Purdue University, 2009, p. 41.
Irvine et al, *Fuel Cell Technologies: State and Perspectives, 2005, p. 35-47.*

Suspension Injection Parameters

- 8 mol. Y_2O_3-ZrO_2 (YSZ) powder (d_{50} = 0.5 µm) loaded at 0.25, 0.5, & 1 vol.% in ethanol
  - Phosphate ester dispersant
- 3 & 8 mol % Sc^{3+} in the form of Scandium-Nitrate (note this is 1.5 & 4 mol.% Sc_2O_3) added to 0.5 vol.% YSZ suspensions
- 230 µm diameter straight hole nozzle
  - Allows for laminar flow into plasma
- 414 kPa (60 psi) injection back-pressure
- Injection velocity ~20 m/s
- Mass flow rate of 43 +/- 1 g/min

Sandia National Laboratory Plasma Spray Setup

- Sulzer Metco 03CA plasma gun
  - Operated at 54, 69, 80, & 88 kW
  - 59 slpm Argon, 7 slpm Hydrogen
  - Optionally including 56 slpm Helium
  - 3-10 minute sprays
- YSZ/NiO anode disk substrates
  - 80% dense
  - 50 vol.% NiO/50 vol.% YSZ



Vacuum chamber

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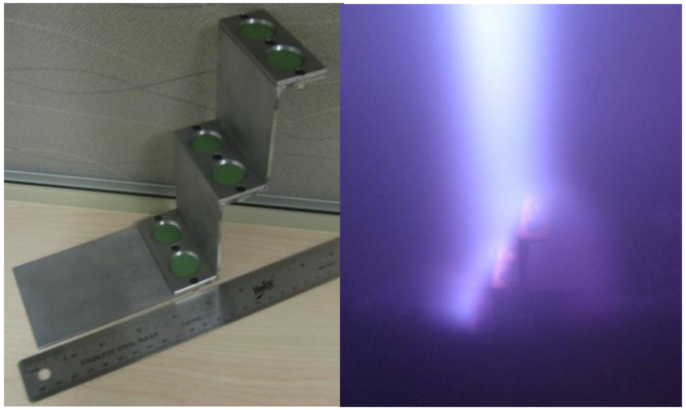
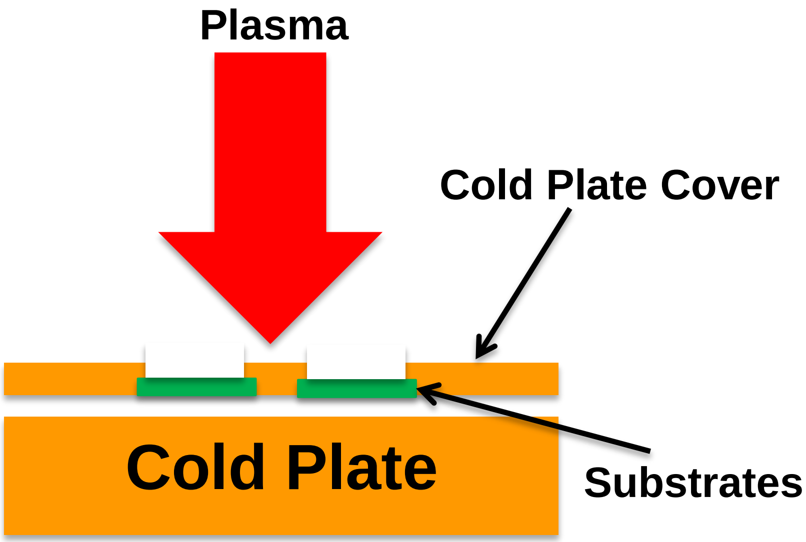
Substrate Holder Designs

- YSZ/NiO anode disk substrates mounted in sample holders
  - Stair-step sample holder used to vary gun-to-substrate distance from 109–125cm in 3 increments
  - Cold plate used at 91 cm

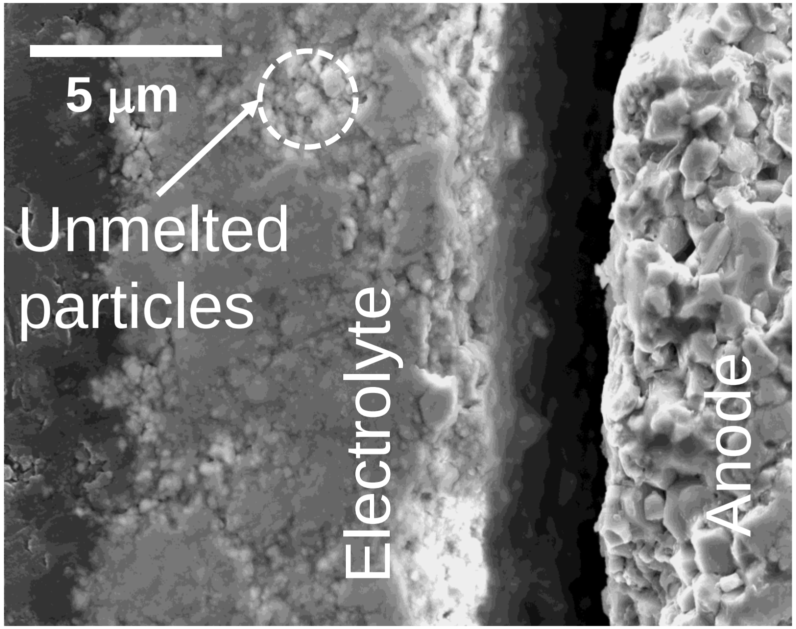


Stair-step substrate holder



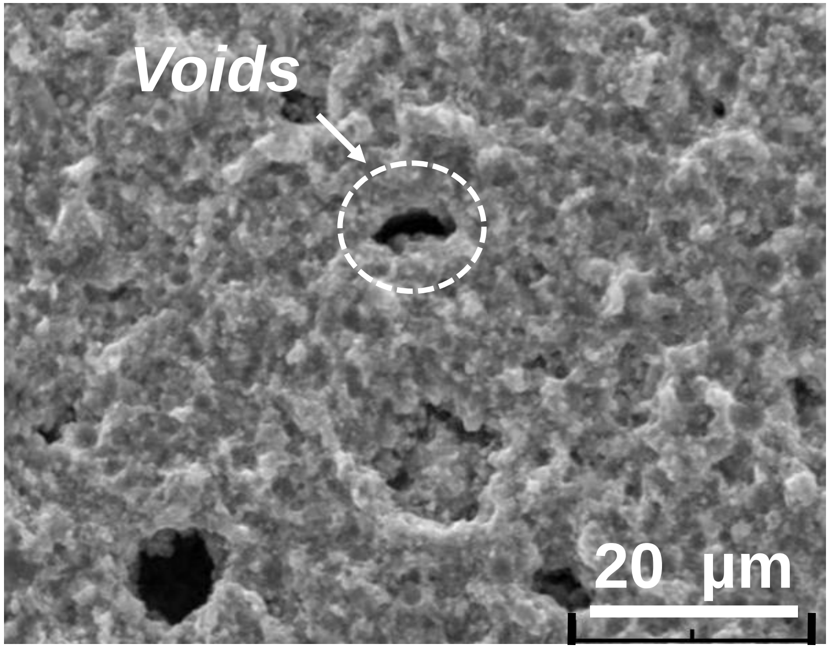
As-Sprayed VLPPS/SPS Electrolyte Microstructures

Cross-Section



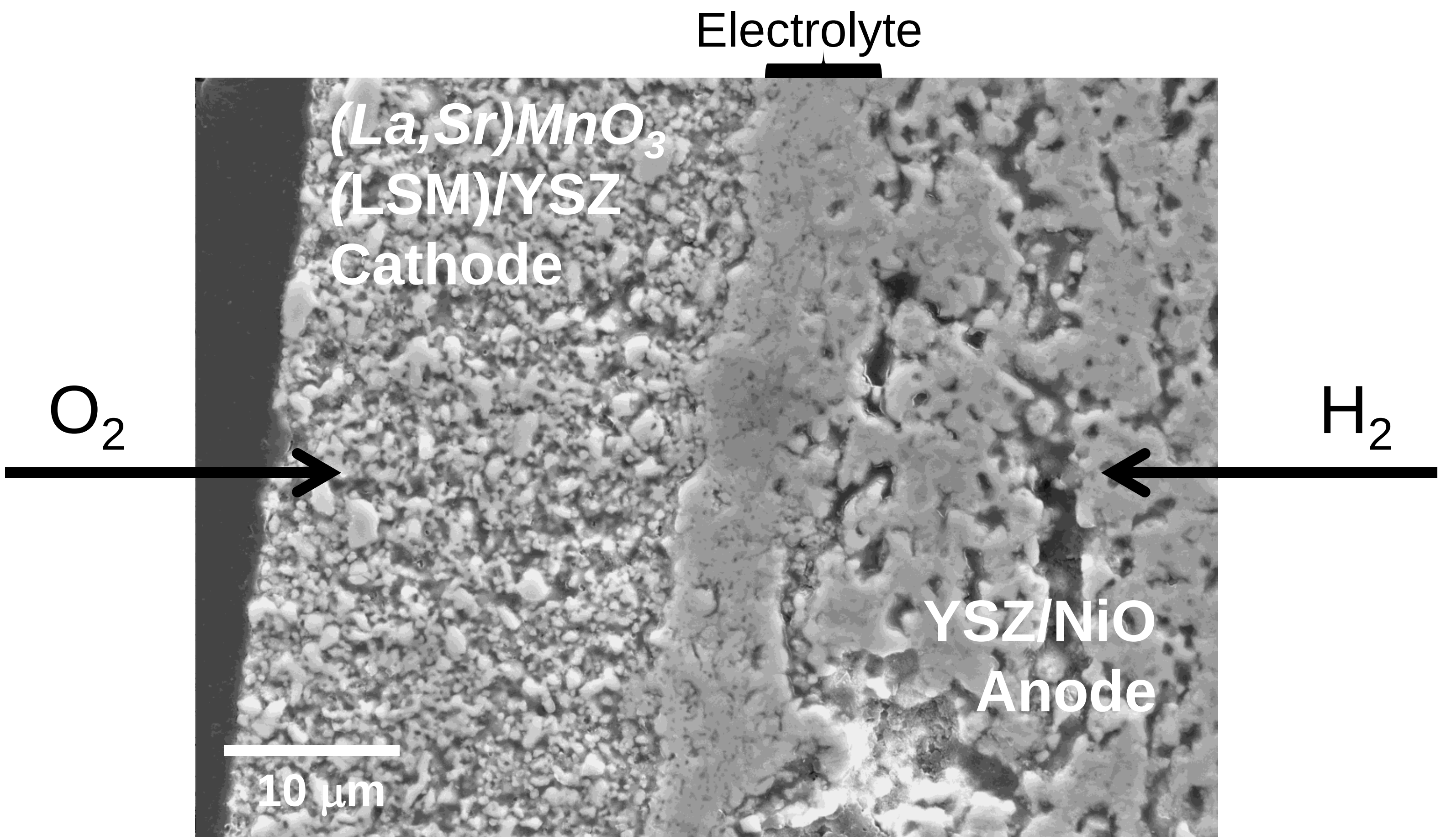
1 vol% YSZ/10 min/117cm/Undoped

Surface



0.5 vol% YSZ/7 min/109cm/3mol %Sc^{3+}

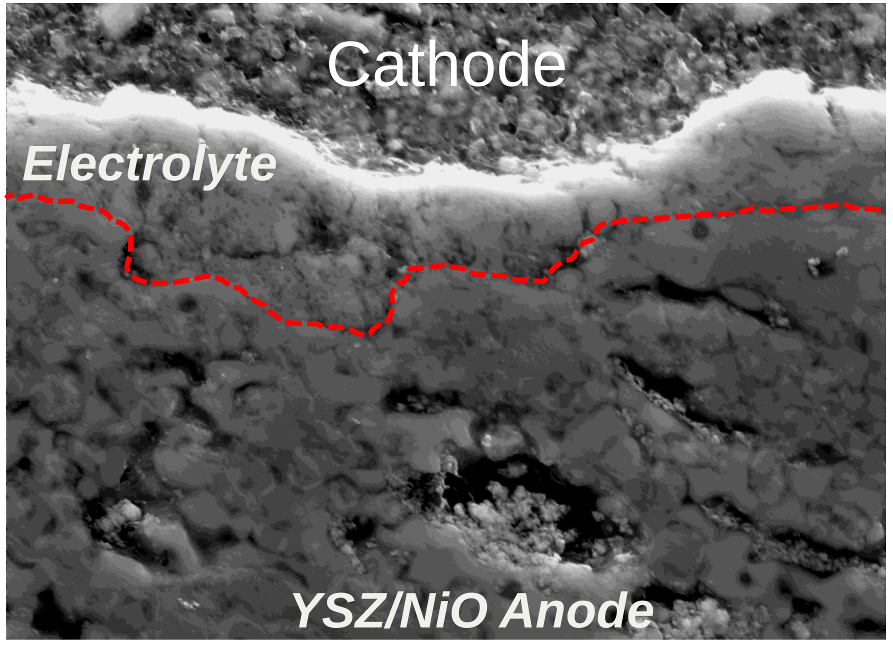
Complete Fuel Cell Microstructure



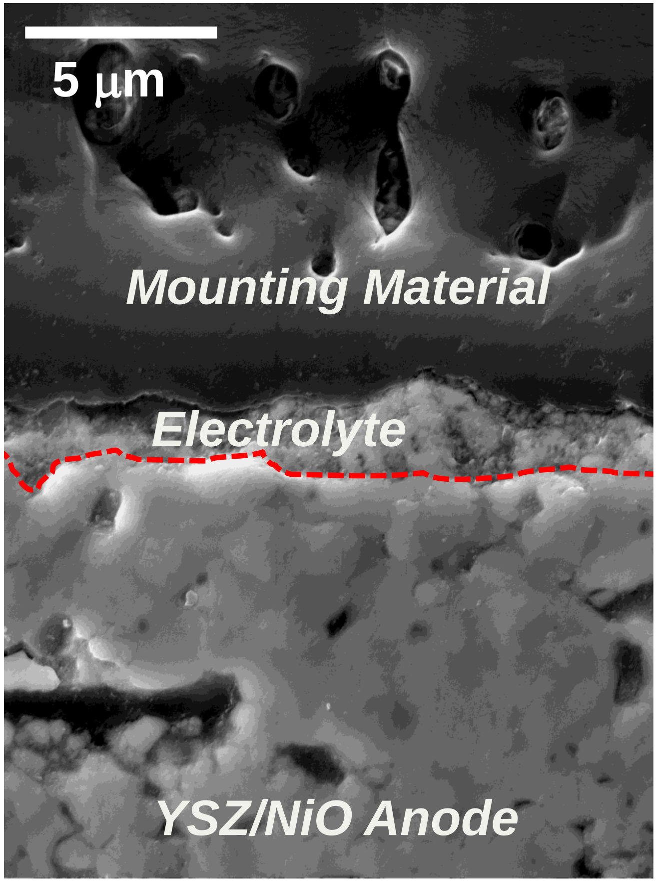
0.5 vol% YSZ/7 min/125cm/8 mol% Sc^{3+}

Effect of Standoff Distance on YSZ-Only Electrolytes

(La,Sr)MnO$_3$ (LSM)/YSZ



109 cm (43”) Standoff



125 cm (49”) Standoff

Powder Loading: 0.5 vol%

Time: 7 min

Cross-Sectional Images

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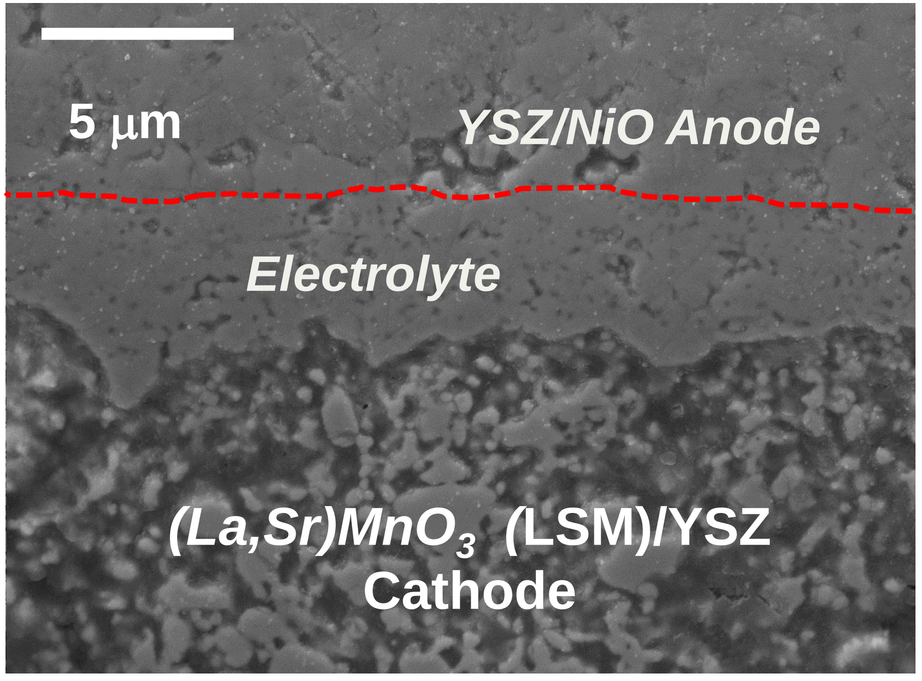
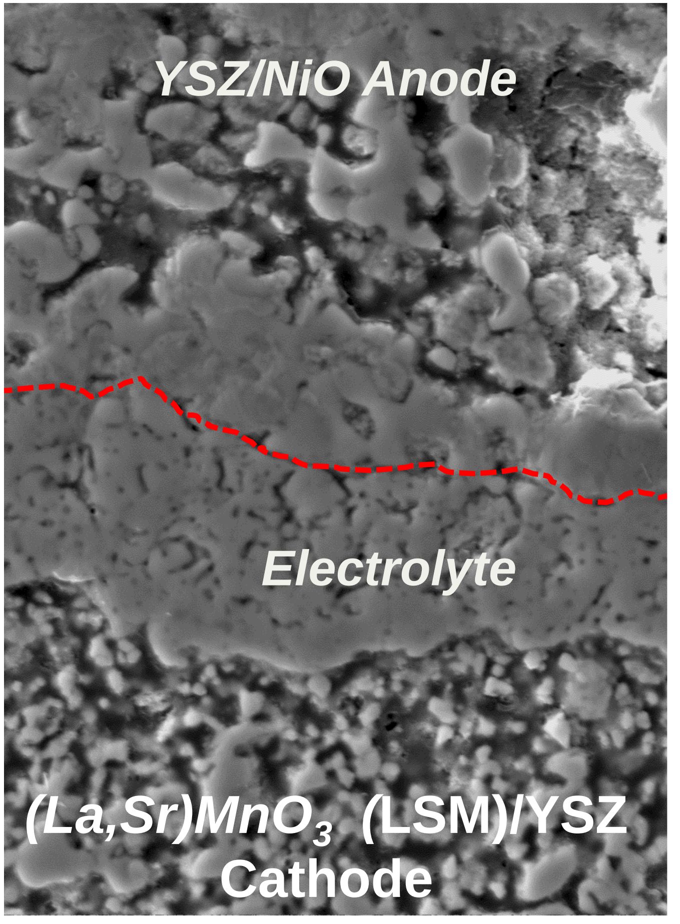
Effect of Standoff Distance on YSZ – 8 mol.% Sc^{3+} Doped Electrolytes

109 cm Standoff



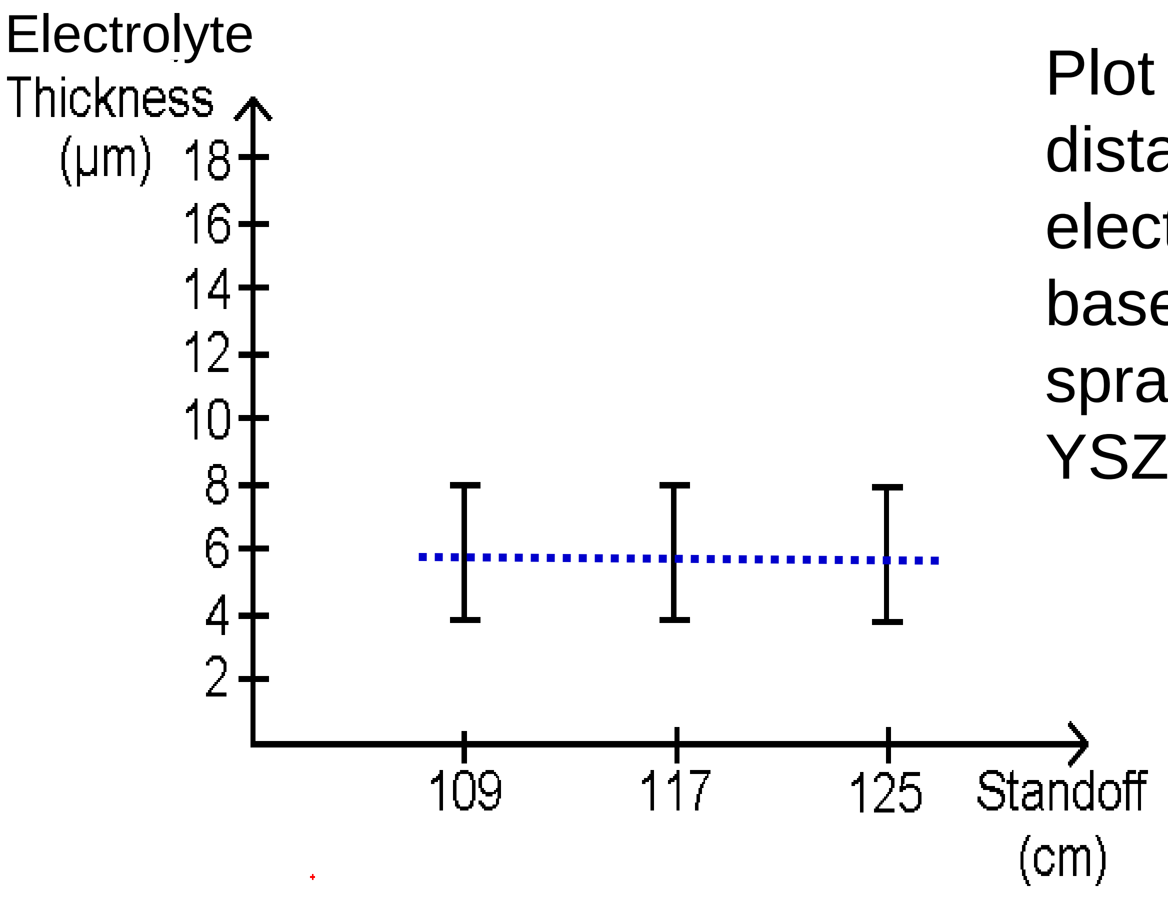
125 cm Standoff



Powder Loading: 0.5 vol%

Time: 7 min

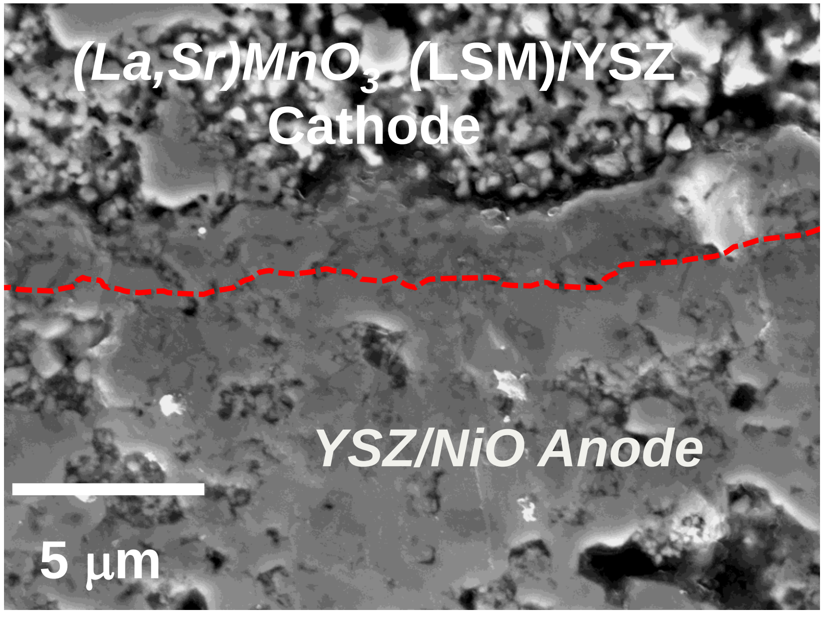
Electrolyte Deposition Thickness Versus Stand-Off Distance



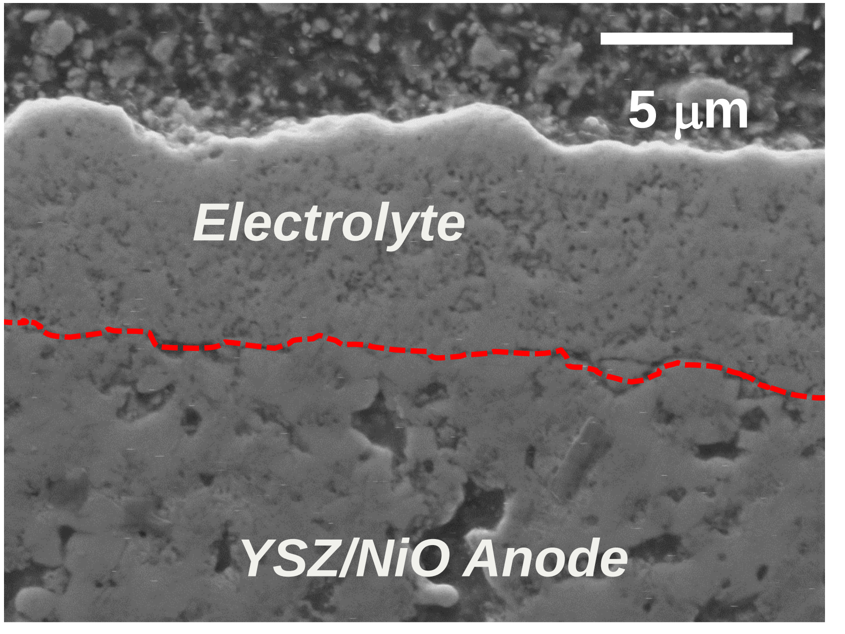
Plot of standoff distance effect on electrolyte thickness, based on 7 minute sprays of 0.5 vol.% YSZ Powder

Effect of Powder Loading on YSZ-Only Electrolyte Formation

0.25 vol% Powder Loading



1.0 vol% Powder Loading



Time: 10 min

Stand-off: 109 cm

Cross-Sectional Images

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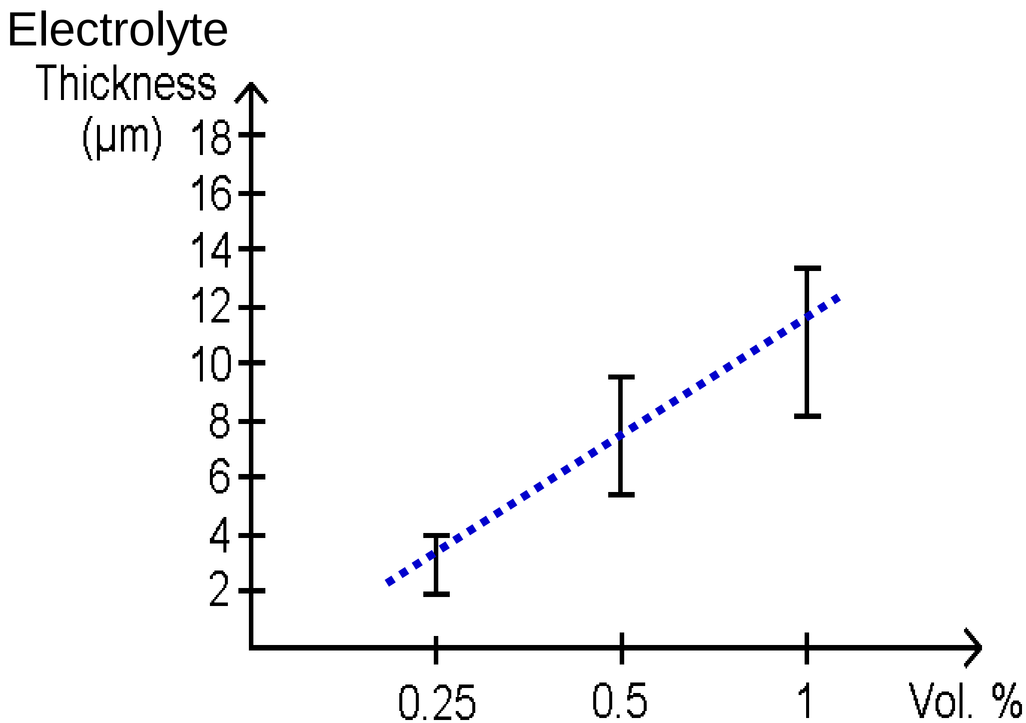
Electrolyte Deposition Thickness versus YSZ Loading in Suspension



Vol.% YSZ in Suspension

- Powder loading effect
  - Deposition rate of ~(1.1 µm/min)*vol.%
- Electrolyte thickness
  - Currently limits minimum thickness to >2 µm

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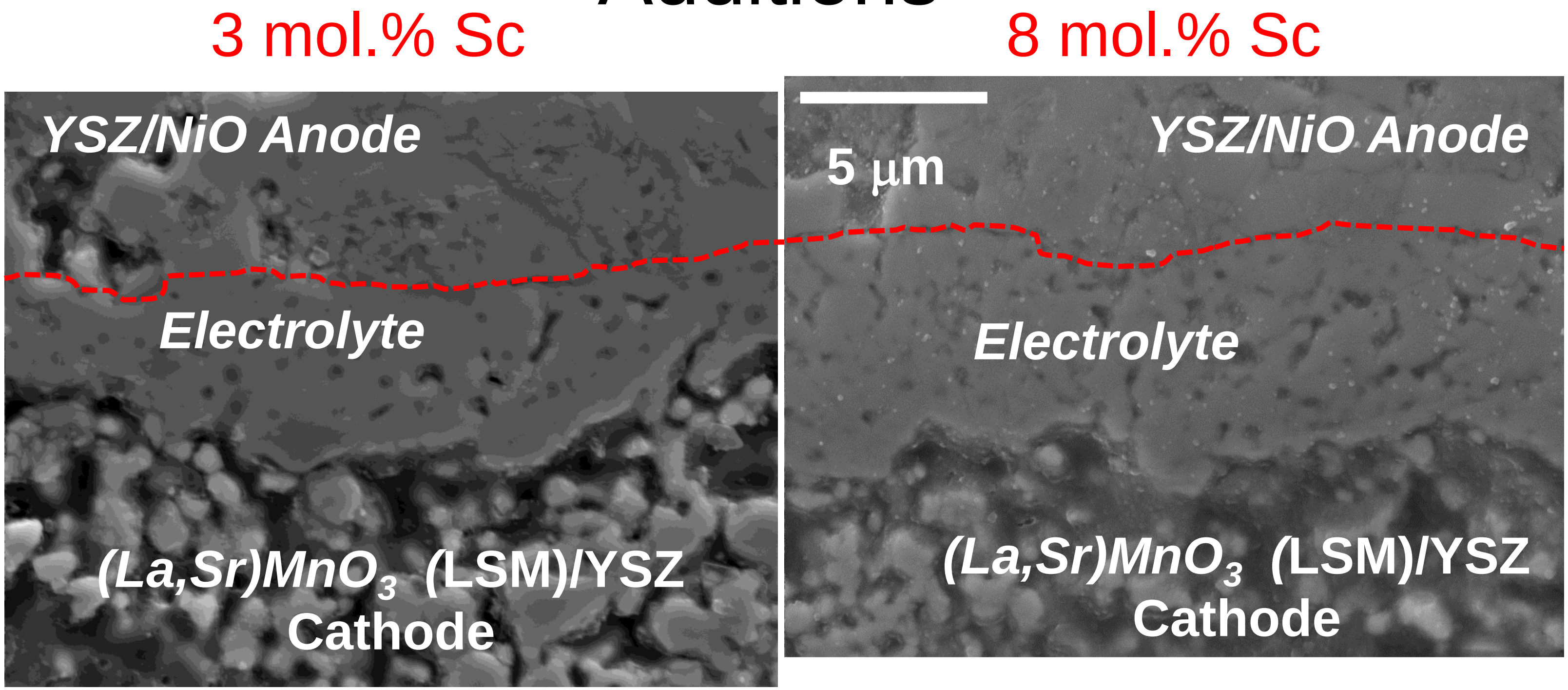
3 mol% Sc^{3+} Vs. 8 mol% Sc^{3+} Dopant Additions



Powder Loading: 0.5 vol.%

Time: 7 min

Stand-off: 109 cm

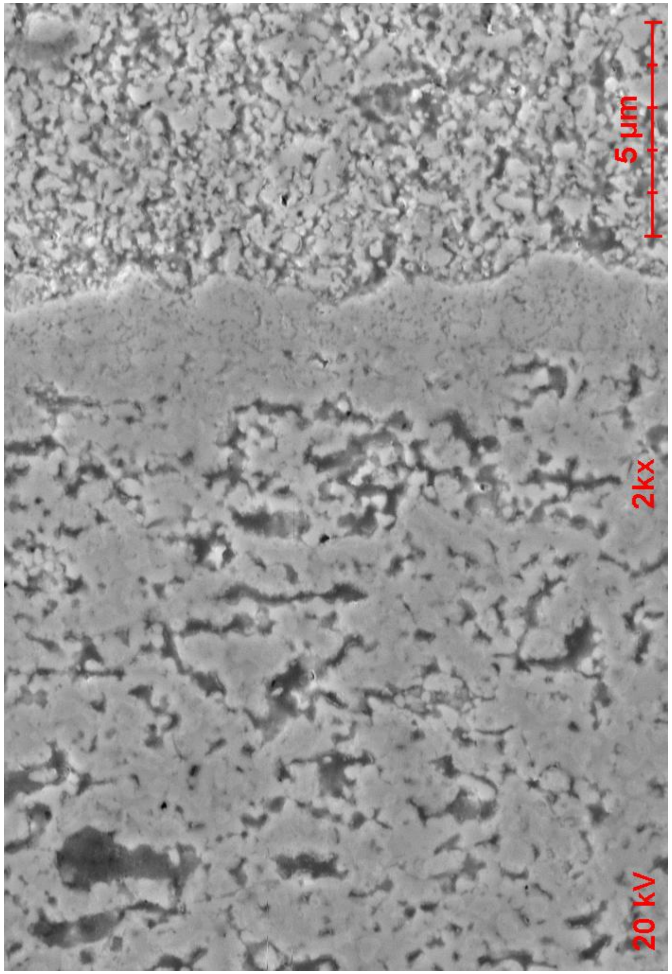
EDS Map of Fuel Cell Microstructure: 8 mol.% Sc^{3+} Doped

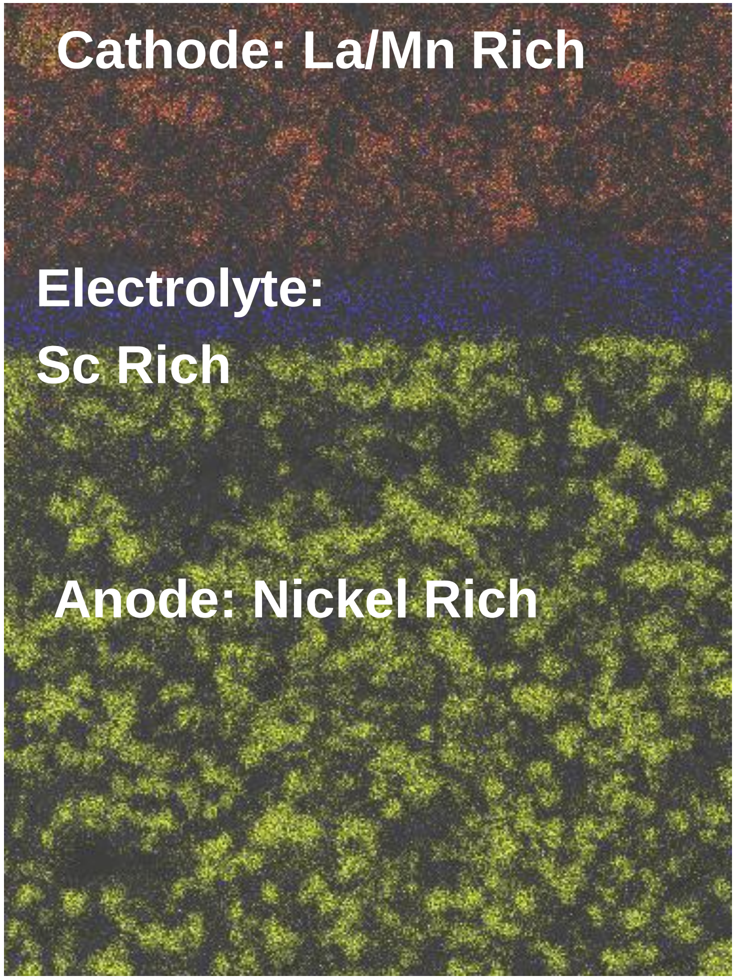
0.5vol%

8-YSZ

7 min

125cm





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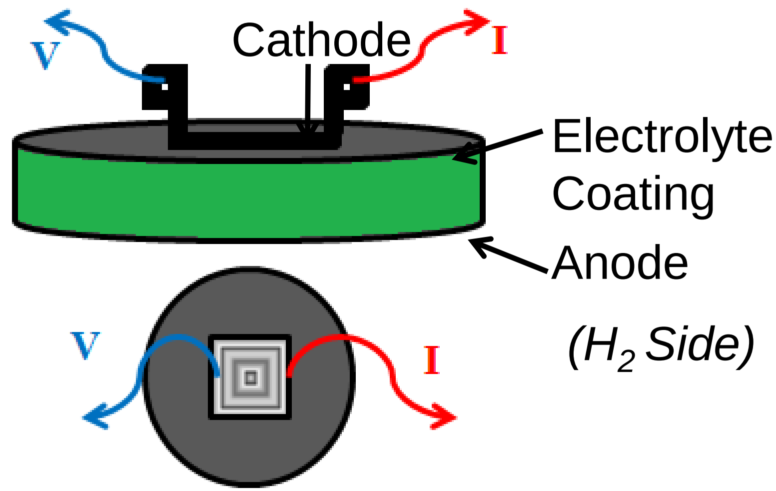
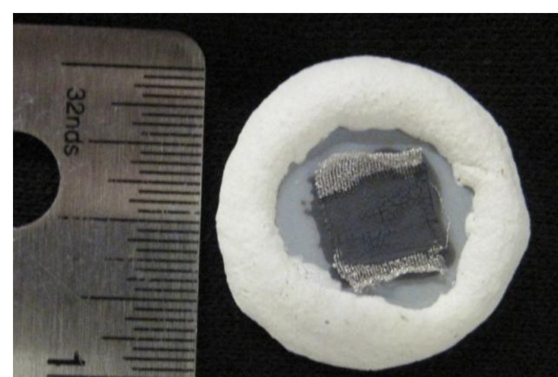
Anode Supported Fuel Cell Design

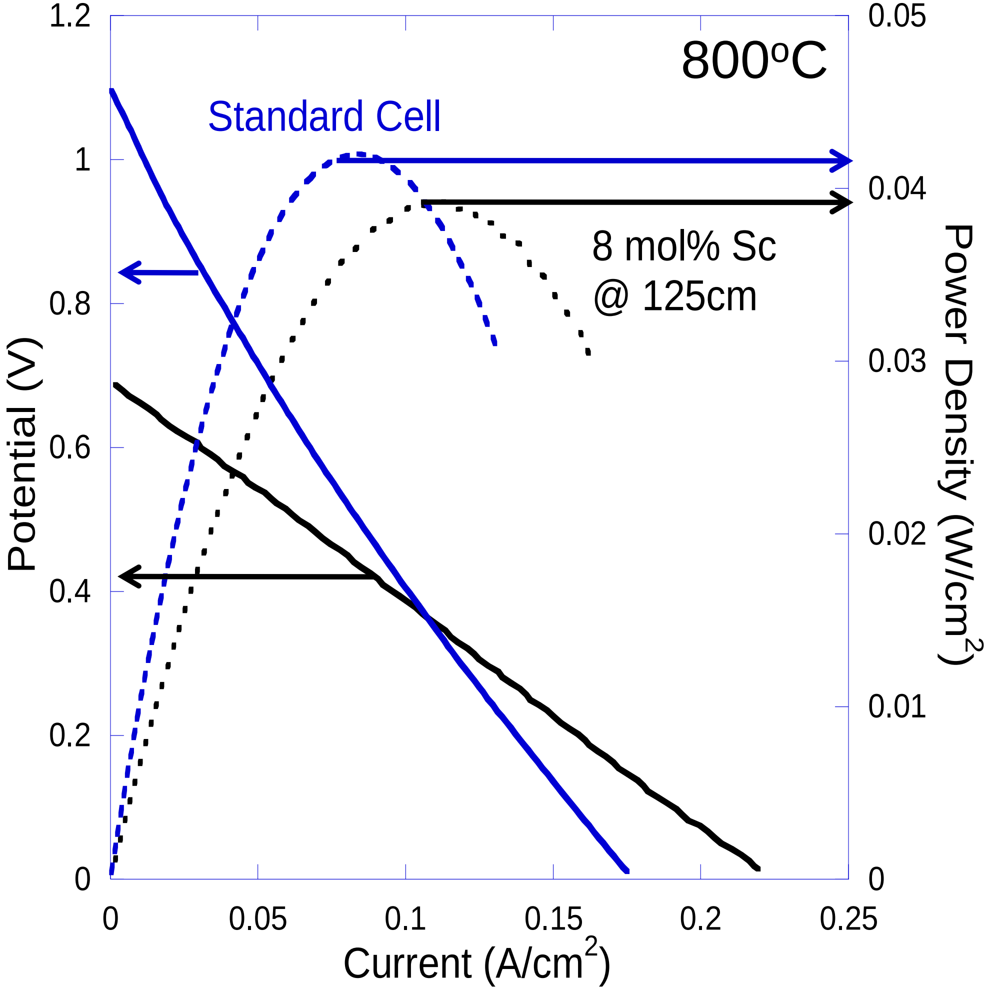
- Anode
  - YSZ/NiO Substrate
  - Platinum mesh & paste are applied on a 1 cm^2 for electrodes
- Electrolyte
  - VLPPS/SPS Coating
- Cathode
  - (La,Sr)MnO_3 (LSM)/YSZ Paste are applied on same 1 cm^2 but on opposite side
  - Platinum mesh pasted into cathode material for electrodes



A schematic of the 4-point IV measurement method employed. Note: the electrodes are attached on both the cathode and anode



SOFC Performance Comparison



Coating	Power Density (W/cm^2)
0.5 vol% YSZ/ 7min/125cm/ 8 mol% Sc^{3+}	0.039
Standard Cell from Fuel Cell Materials, Inc	0.042

Y.J. Leng et al, International Journal of Hydrogen Energy 29 1025-1033 (2004) .

Summary of VLPPS/SPS Electrolyte Development

- Coating thicknesses of 3 +/- 2 µm to 11 +/- 5 µm
- Within the 16 cm window investigated, the stand-off distance was shown to have negligible effect on electrolyte thickness – suggesting a process that can be used to apply electrolytes on non-planar anodes
- Electrolyte thickness is linearly controlled by the effect of powder loading in the suspension
  - ~1.1 µm/min*vol.% of feedstock powder
- Effect of Doping
  - SOFC performance increased withSc^{3+} doping, but results are significantly below a ‘good’ fuel cell and indicate the need for further refinement of the electrolyte application process and fuel cell testing.

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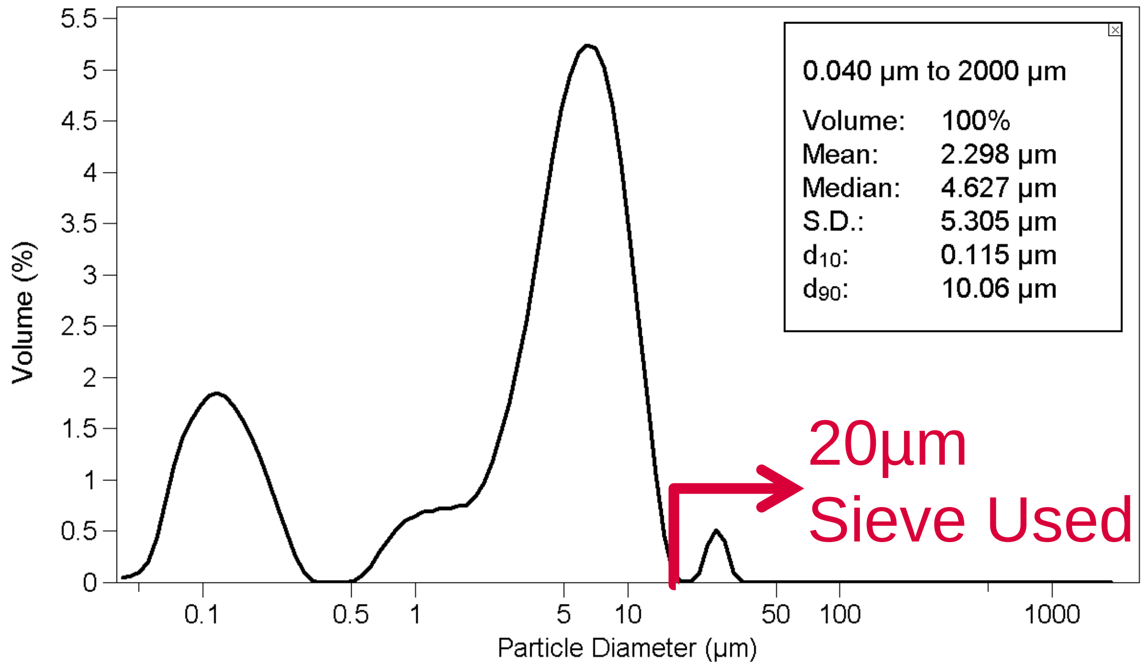
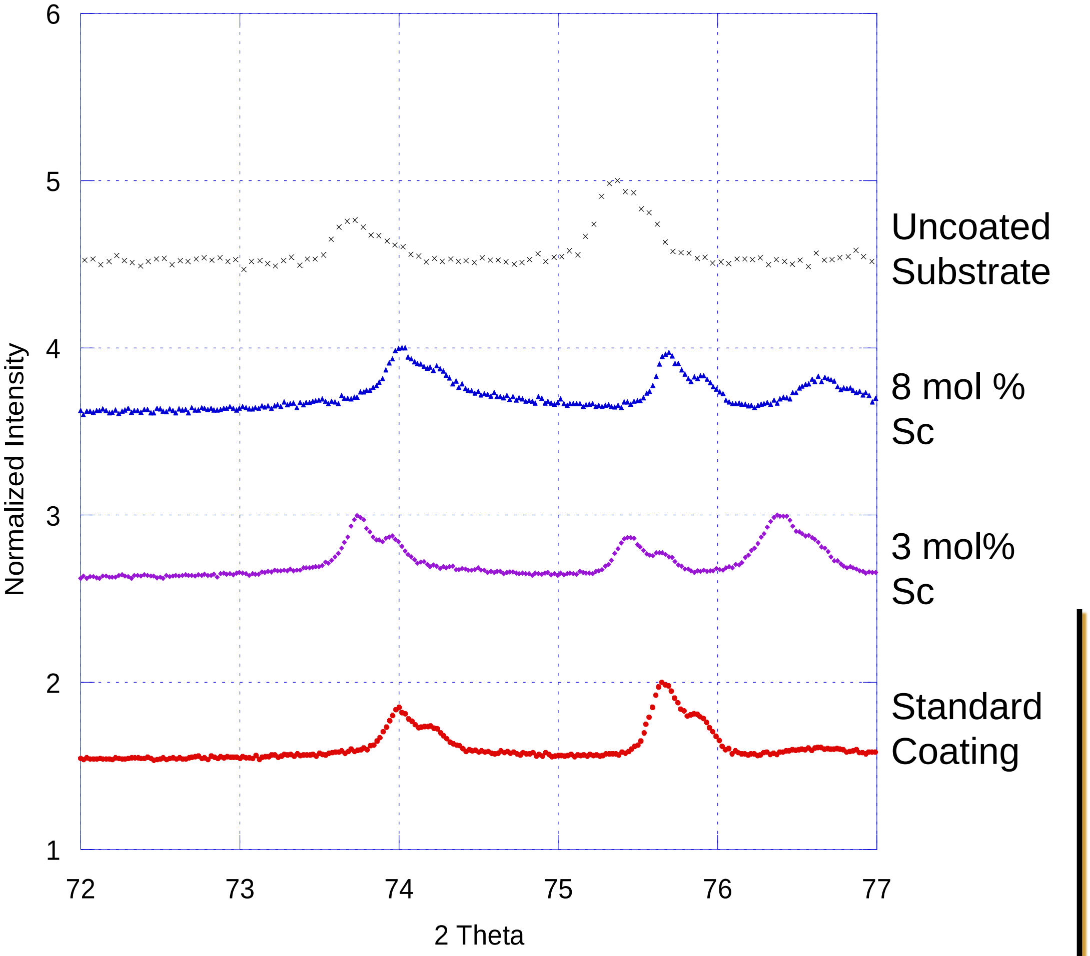
Extra Info: Suspensions Used



- Coulter Counter Measurement of powder feedstock used

Additional XRD Analysis of Sc Doping Effect

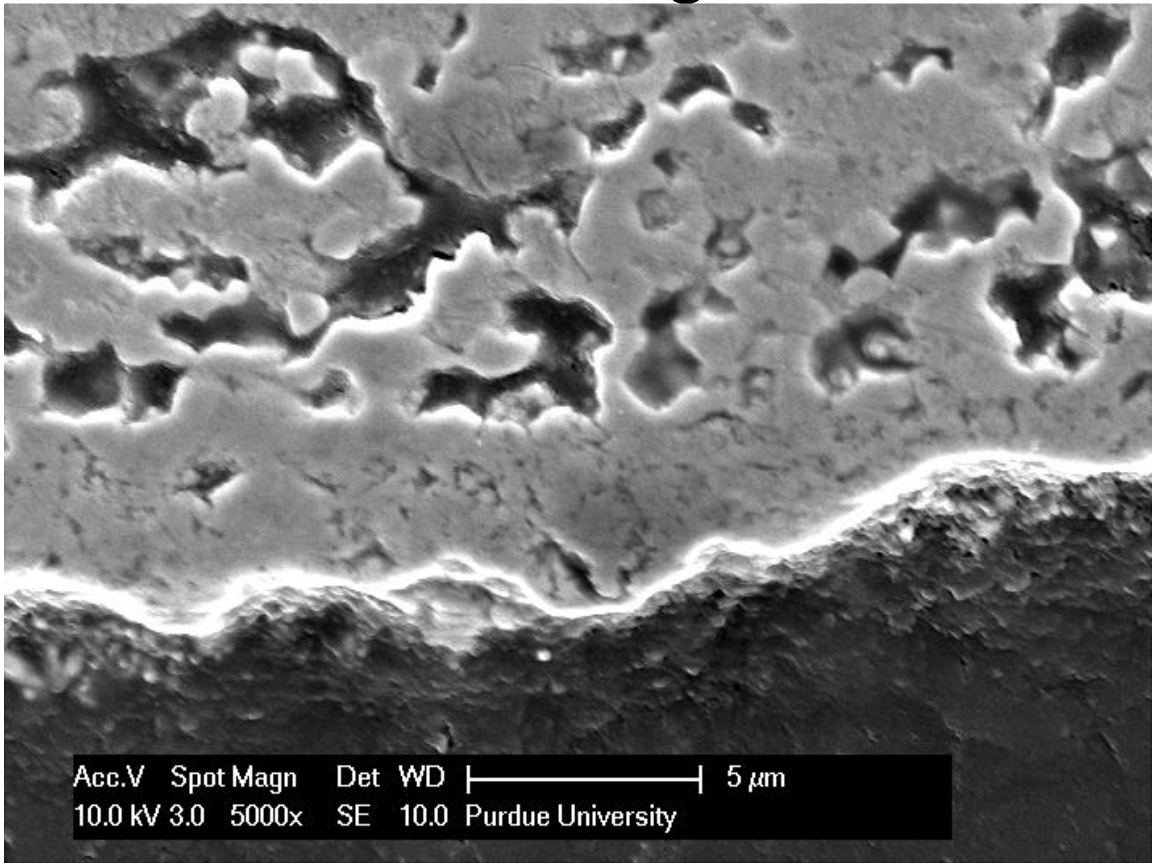
- XRD of 0.5 vol. % YSZ with varying scandium doping
  - Sc_2O_3 caused new peak at 2 theta of ~76.5˚
  - Some peak shifting in cubic ZrO_2 peaks



Coating Microstructure After Fuel Cell Testing

Anode

Electrolyte



0.5 vol% YSZ/7 min/109cm/Undoped – peak temp of 1200 ˚C for 2 hours

Review of Pertinent Research Findings

- May 2010 successful coatings
  - 0.25v% 8-YSZ 10 minutes
  - 1v% 8-YSZ 10 minutes
  - 0.5v% 8-YSZ 7 minutes
    - Un-doped
    - 3 mol% Sc
    - 8 mol% Sc
- Trice sabbatical coatings
  - 0.5v% 8-YSZ 5 minutes @ 46”
- Deposition rate ~(1.1 μm/min)*vol.%
- Coating thicknesses of 3 +/- 2 μm to 12 +/- 5 μm

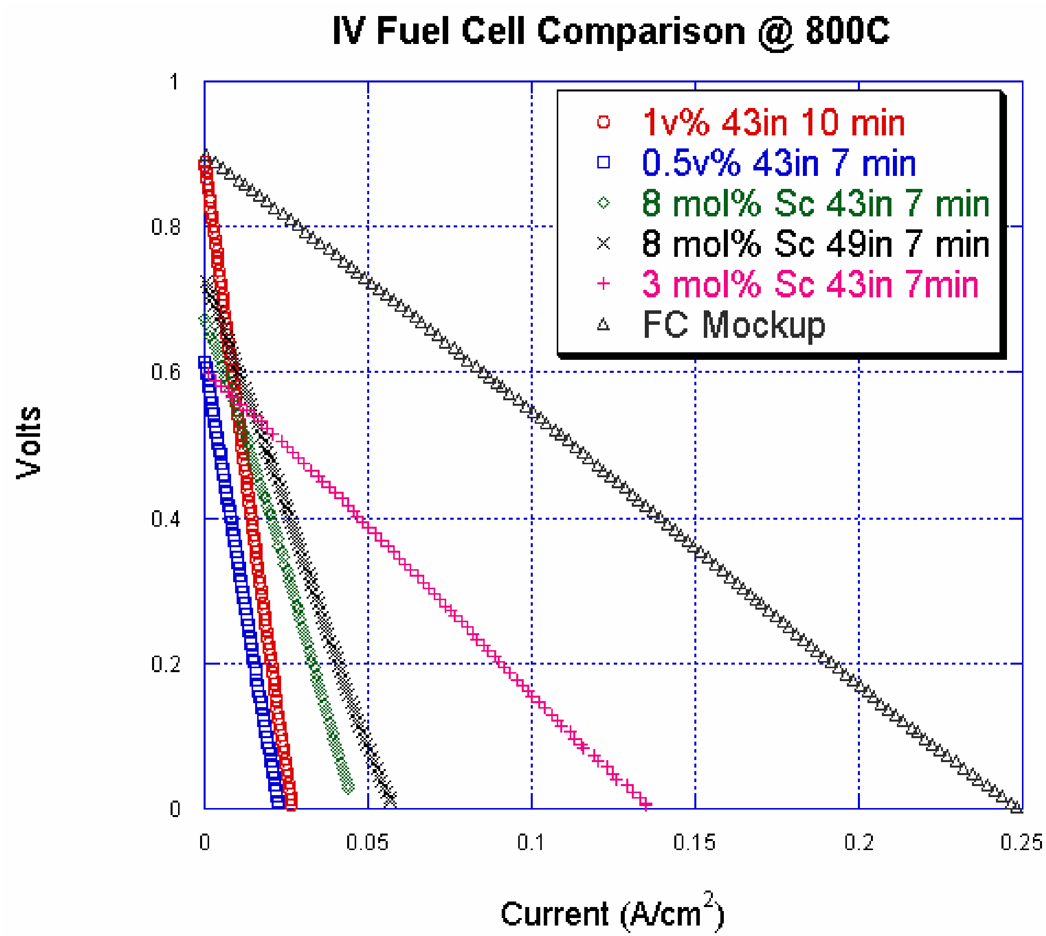
- Primary spray process issues
  - Overheating of substrate/holder
    - Limited gas mix (Helium cut)
    - Limited gun power (69 kW)
  - Clogging of spray nozzle
    - 230 μm diameter straight-hole
    - Mostly resolved, but we still have an upper limit on spray time (10 minutes @ 1vol%)
- Insufficient melting of particles at point of coating deposition
  - Previous stand-off distance was too long (43”-46”-49”)
  - Plasma enthalpy too low
    - Gun power: 69 kW
    - Plasma mix: 59 slm Ar/ 7 slm H_2
  - Solvent (Ethanol) absorbed too much of the plasma enthalpy

VLPPS/SPS Overall Process Variables

- Gun power
- Stand-off distance
- Powder loading
  - Material selection
  - Particle size & distribution
- Dopant loading
- Solvent
- Spray time
- Gas mix
- Substrate temperature
- Substrate
- Spray chamber pressure (~2.4 Torr)
- Pressure vessel back-pressure (60 psi)
- Spray nozzle (230 μm straight-hole)
- Injection positioning

- Primary focus of previous data sets
  - Gun Power (69 kW)
  - Stand-off distance
    - 43” – 46” – 49”
  - Powder loading
    - 0.25 vol%
    - 0.5 vol%
    - 1 vol%
  - Dopant loading
    - 3 mol% Sc
    - 5 mol% Sc
    - 8 mol% Sc
  - Spray time
    - 7 minutes
    - 10 minutes

Extra Information - Potentiodynamic Performance



Comparison of Plasma at 100 Torr and 1 Torr

Anode Substrate Manufacture

- Made from 10 laminated layers of 180 µm NiO/YSZ tape cast
  - ElectroScience part # 42421
- A 1 ¼ in. diameter arch punch is used to cut the discs out
- Layers are hot pressed together in a 1 ¼ in. die
  - Temperature: 70 ˚C
  - Pressure: 21 MPa
  - Time: 15 Minutes
- Substrates are then sintered
  - Ramp Rate: 5 ˚C/min
  - Hold Temperature: 1400 ˚C
  - Hold Time: 2 hours

Image of hot pressing die used

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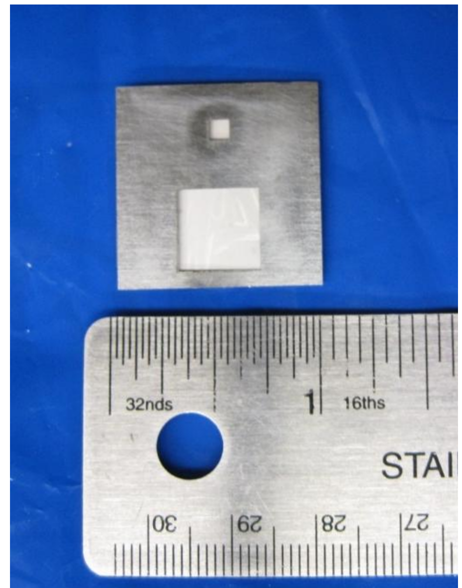
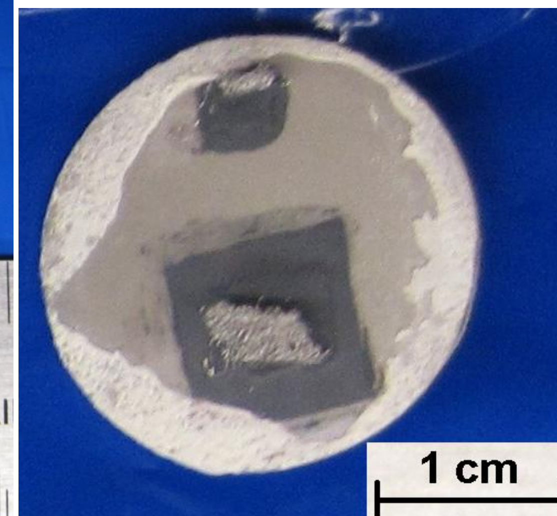
Cathode & Electrode Assembly

- **Cathode & Electrode**
  - **LSM/YSZ Paste**
  - **Platinum Mesh**
- **Anode Electrode**
  - **Platinum Paste**
  - **Platinum Mesh**
- **Curing**
  - **Heat Lamp for ~6 hours (until dry)**
  - **Cathode first, then Anode**
- **Heat Treatment**
  - **Metalizes the Pt paste**
  - **Ramp Rate: 5˚C/min**
  - **Hold Temperature: 1100˚C**
  - **Hold Time: 2 hours**





Images of the mask used to apply cathode/electrode pastes and the finished product. Note: separate masks are used for the LSM/YSZ and Pt pastes and the smaller mask is no longer used in testing as explained in next slide

Substrate Progression

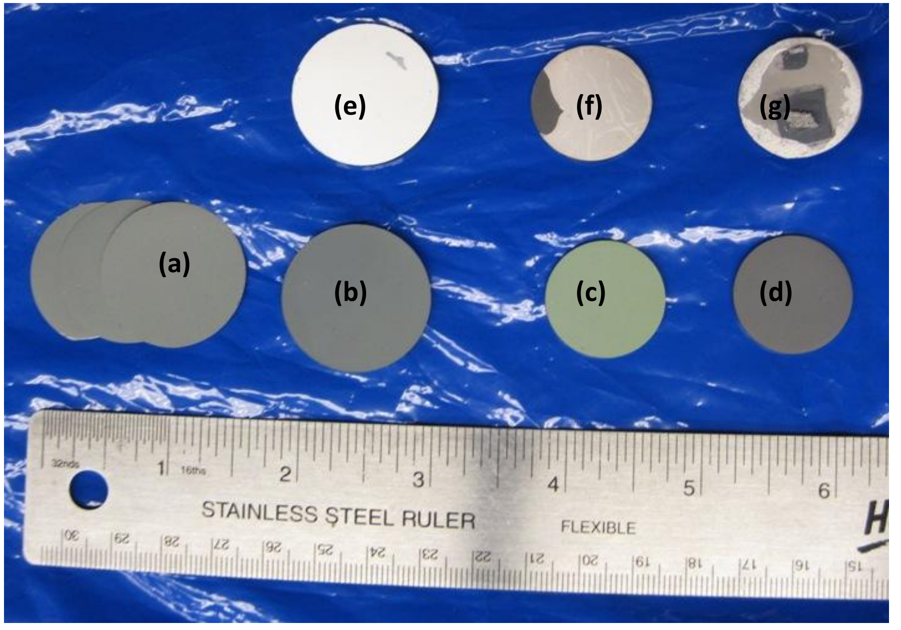
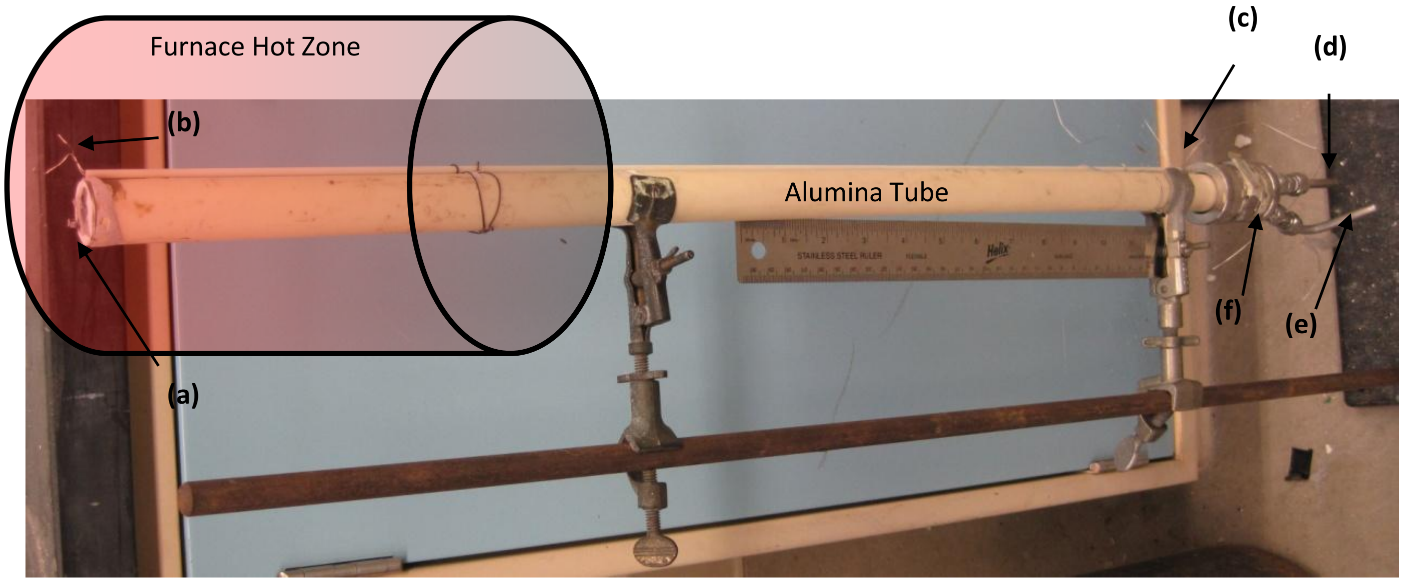


Image of (a) unlaminated sheets of NiO-YSZ, (b) hot-pressed laminated sheets of NiO-YSZ, (c) sintered laminated sheets of NiO-YSZ (in oxidized state), (d) sintered laminated sheets of NiO-YSZ (in reduced state), (e) an example of the initial material system used: NiO-YSZ with a YSZ electrolyte laminated sheet on top, (f) a sintered version of (e), in which the electrolyte delaminated, and (g) a complete fuel cell after testing, showing the cathode side (the white border is the bonding cement, the dark grey is the LSM-YSZ cathode material with platinum electrodes bonded to it, and the pearlescent area is exposed electrolyte)

Fuel Cell Testing



An image of the fuel cell testing rig outside of the furnace and fume hood, showing: (a) the cathode-side of the SOFC, (b) the cathode-side platinum electrode wires that attach to the fuel cell, (c) the cathode-side platinum wire measurement output connections, (d) the H2 gas input tube, (e) the exhaust gas tube (which feeds through two bubblers and out a fume hood), and (f) the anode-side platinum wire measurement output connections . This is the primary tool used to measure the effectiveness of SOFC's, through measurements of open circuit voltage, impedance of the electrolyte, and I-V (Current-Voltage) behavior.

Fuel Cell Test Rig Assembly

- Anode electrodes attached to FC rig electrode wires
- Cement applied on outer ring of alumina tube
  - Note: very quick drying, <30s before it congeals
- Anode wires gently pulled to lower fuel cell onto tube for a close fit
  - Note: do not try to pull the fuel cell tight, just get it to match up

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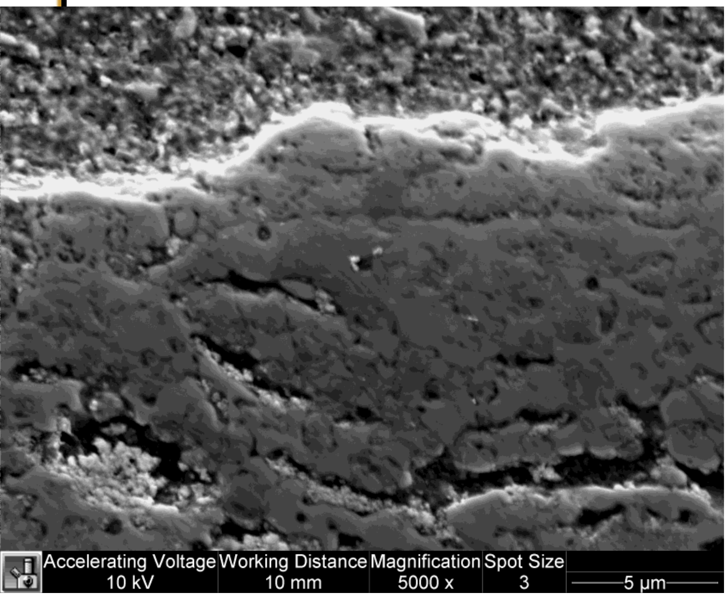
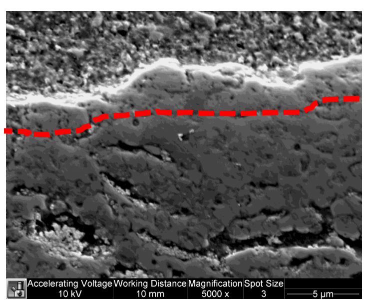
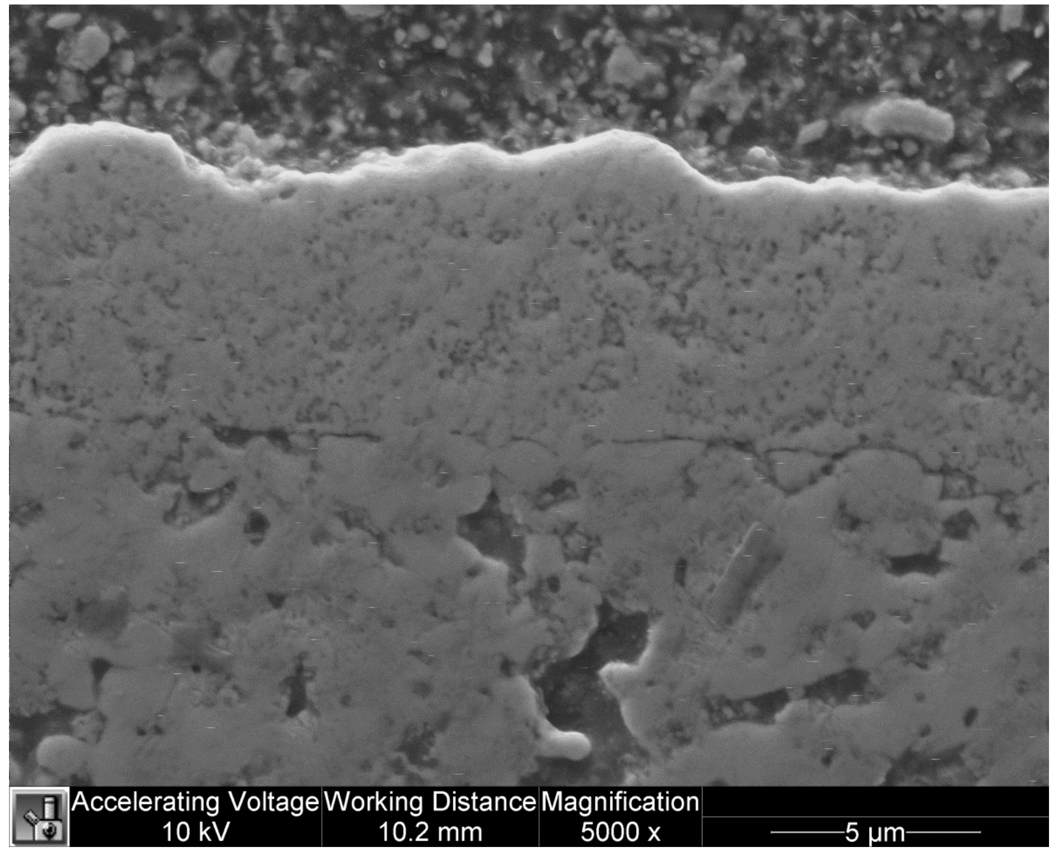
Overview of Fuel Cell Test Process

- 3°C/min to 123°C, hold 3 hours
- 3°C/min to 295°C, hold 3 hours
- 3°C/min to 402°C, hold 3 hours
  - Start hydrogen gas ~1 hour until end of hold to reduce the anode (15 psi supply, at ~40 on flow regulator (need conversion))
  - Start measuring OCV (continuous)
- 5°C/min to 600°C, hold 1 hour
  - I-V & Impedance Measurements taken
- 5°C/min to 800°C, hold 1 hour
  - I-V & Impedance Measurements taken
- 5°C/min to RT, end

0.5v% Vs. 1v% Undoped







- 0.5vol%/8-YSZ/7 min/43”
- 1vol%/8-YSZ/7 min/43”

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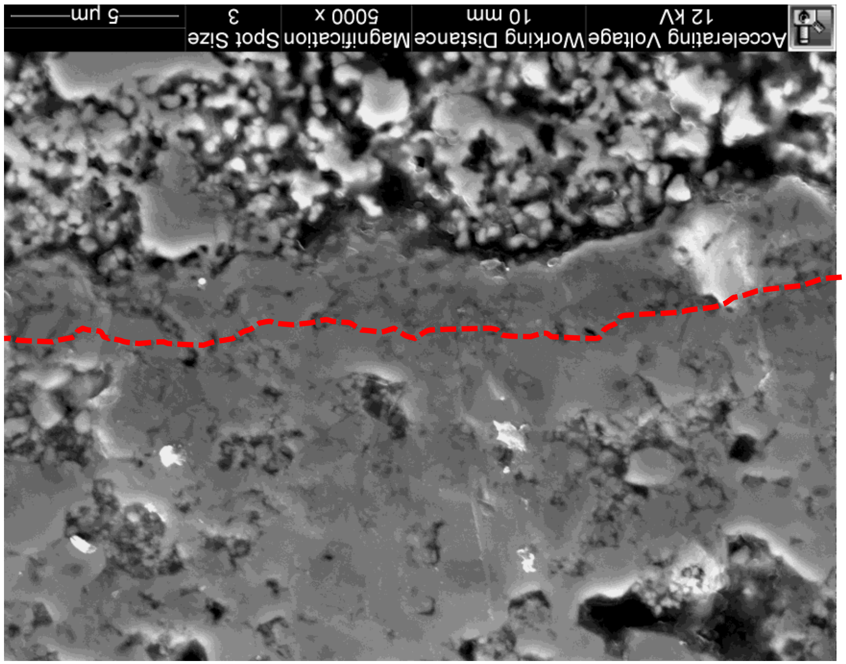
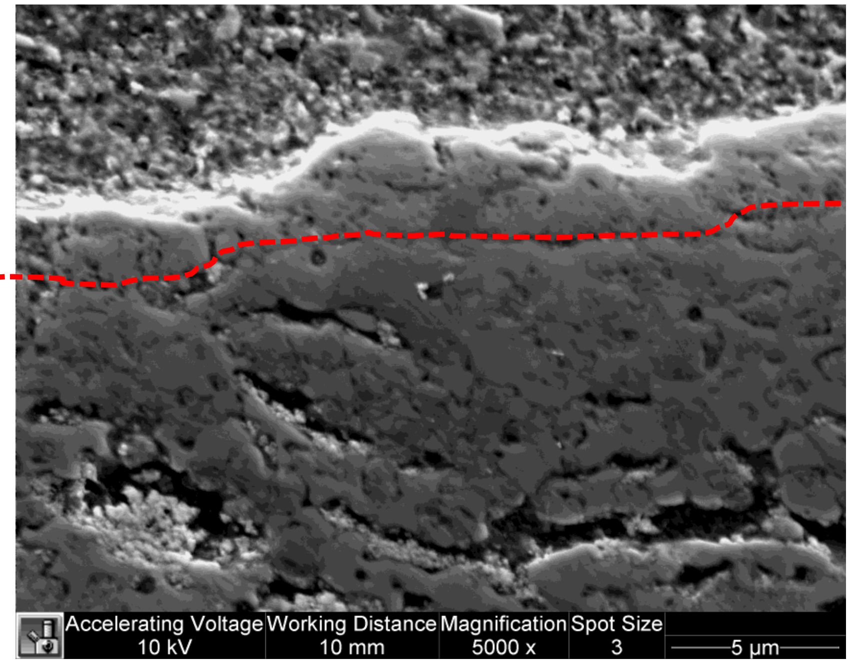
Effect of Powder Loading: 0.25v% Vs. 0.5v% Undoped



0.25vol%/8-YSZ/10 min/43”



0.5vol%/8-YSZ/7 min/43”

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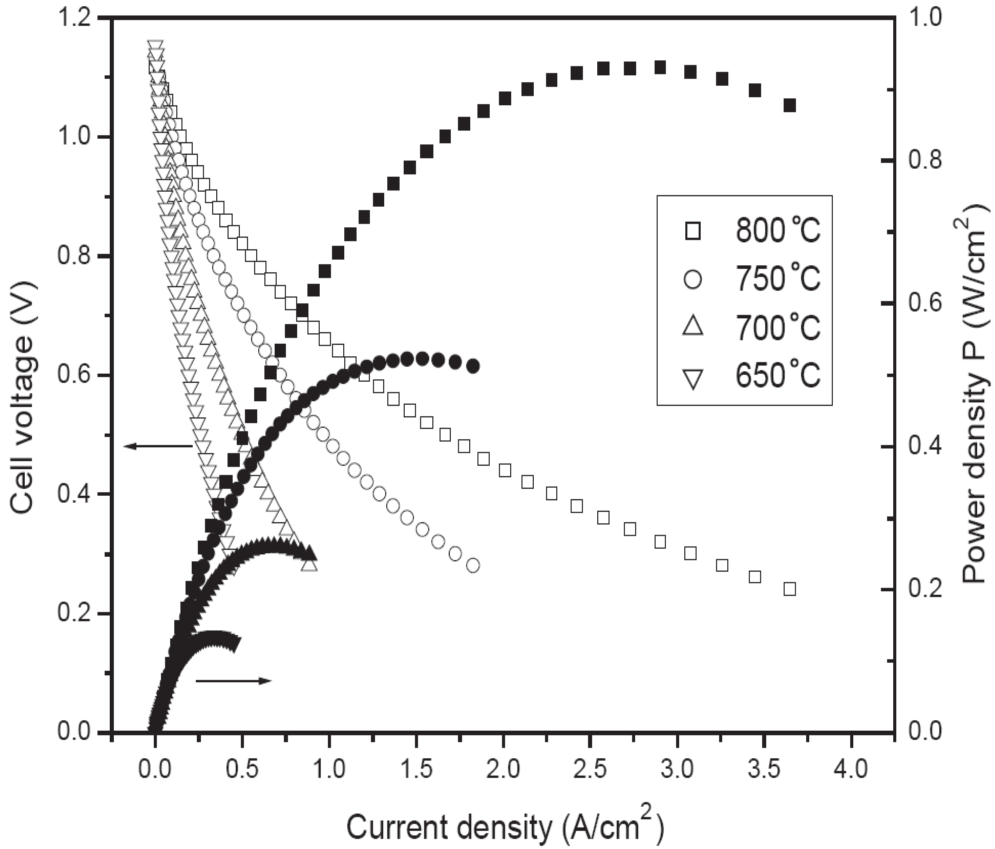
SOFC Performance Comparison



Coating	Power Density (W/cm^2)
0.5 vol% 8-YSZ/ 7min/125cm/ 8 mol% Sc	0.039
Standard Cell from Fuel Cell Materials, Inc	0.042
"Good" Fuel Cell[6]	0.9

0 0.05 0.1 0.15 0.2 0.25

Current (A/cm^2)

IV behavior for a 18 µm YSZ electrolyte coating showing the effect of temperature on power output

Y.J. Leng et al, International Journal of Hydrogen Energy 29 1025-1033 (2004) .

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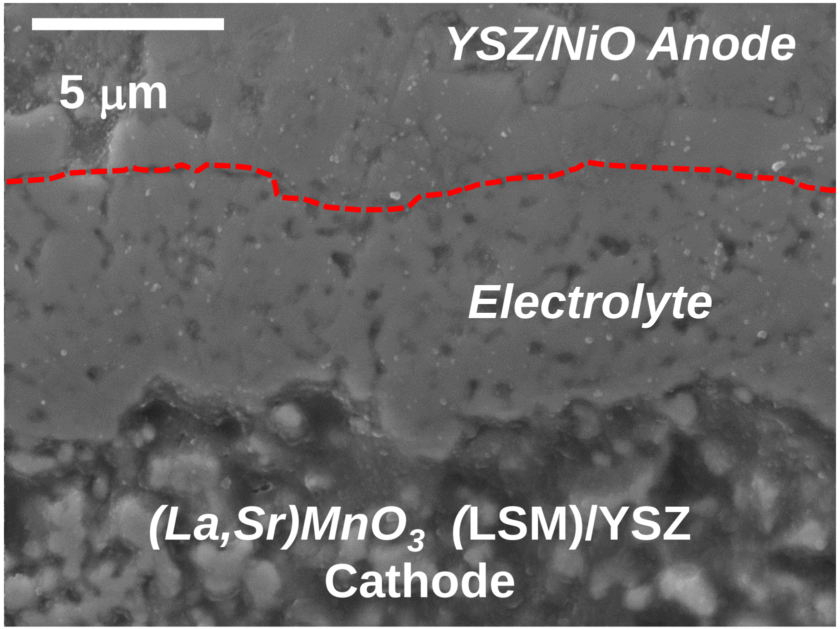
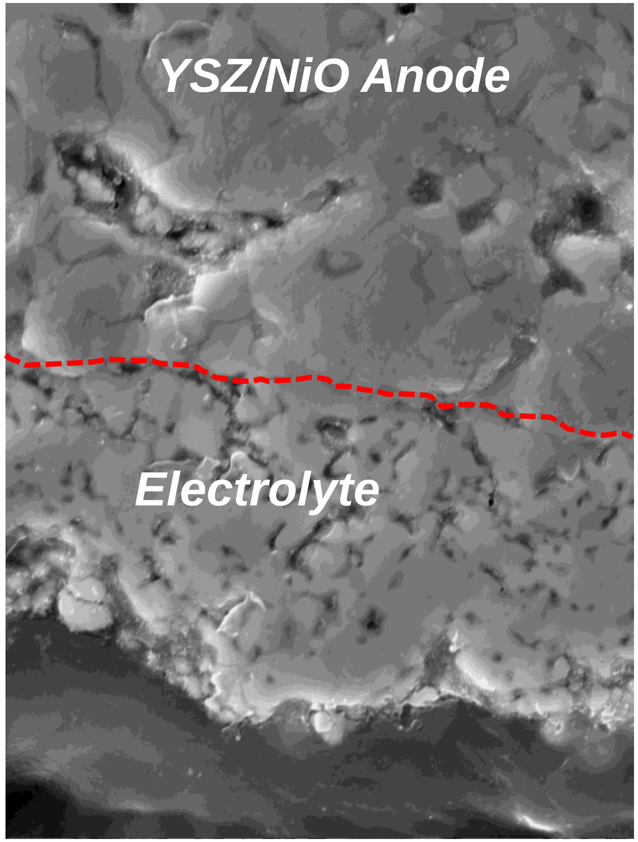
Effect of Standoff Distance on YSZ-Sc Electrolytes



0.5 vol%/8-YSZ/8mSc/7 min/109cm



0.5 vol%/8-YSZ/8mSc/7 min/125cm

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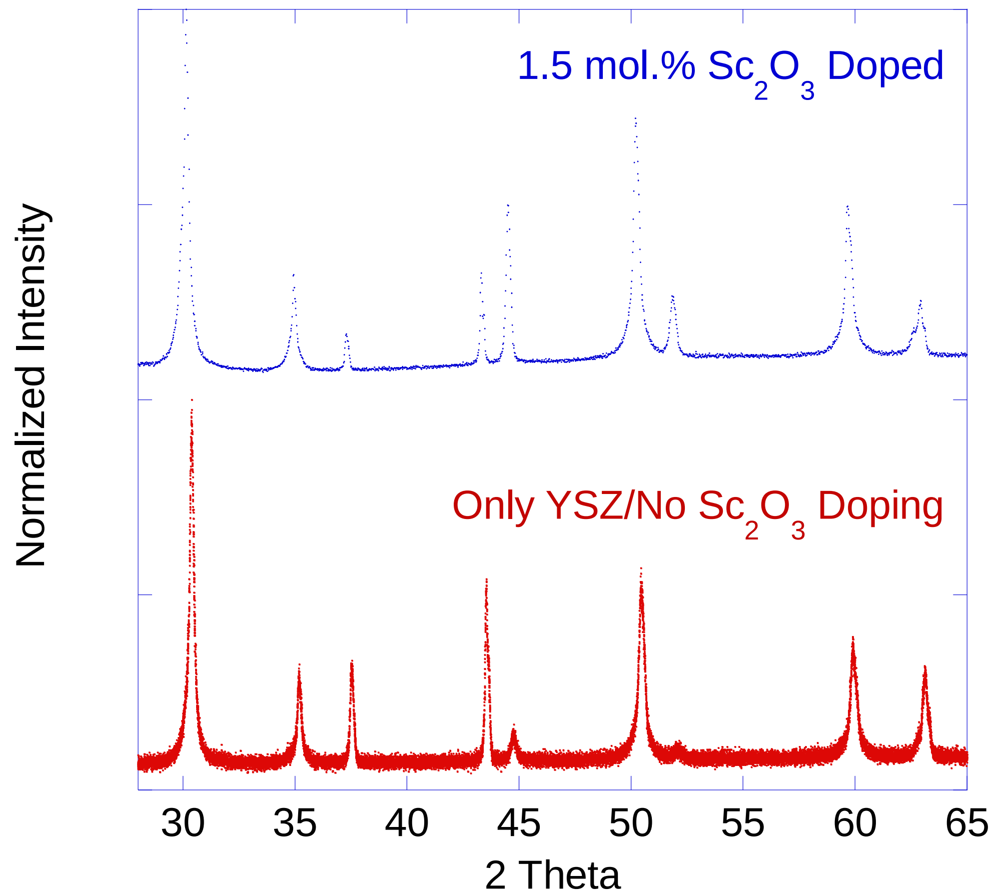
XRD Analysis of Sc^{3+} Doping Effect

- XRD of 0.5 vol. % YSZ with 1.5 mol.% of Sc^{3+} doping
  - No peaks associated with Sc_2O_3 phase suggesting Sc^{3+} is in solid solution with ZrO_2
  - Doped coatings have peaks shifted to lower 2 theta values as should be case for larger Sc^{3+} ion compared to Y^{3+}



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