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# "Fabrication of Intermediate SOFCs Via Plasma Spray"

## Sponsors

1. DOE SBIR Phase I: Contract No: DEFG0201ER83340
2. Siemens Westinghouse Power Corporation ("SWPC")

**Danny Xiao, Ph.D.**

**US Nanocorp®, Inc.**

**June 18, 2002**

# *Program Objectives*

**The program objectives are to demonstrate the feasibility of:**

- **Synthesizing a novel mixed ionic and electronic conductor ("MIEC") yttrium-doped strontium titanate anode material $Sr_{1-1.5x}Y_xTiO_3$ ("SYT")**
- **Plasma spray fab. SOFC testing cells using LSM cathode, LSGM electrolyte, and $Sr_{1-1.5x}Y_xTiO_3$ anode for intermediate temperature (500 - 800°C) appls.**

DOE SBIR Phase I

- **Plasma spray fab. SOFC cells using SWPC's cathode tubes, LSGM electrolyte, and LDC40 + Ni anode for intermediate temperature (500 - 800°C) appls.**

SWPC

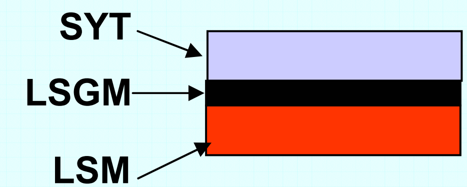
# *Fuel Cell Systems*

## System one: DOE Program:

Anode- Nano $Sr_{1-1.5x}Y_xTiO_3$

Electrolyte – $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$

Cathode – $La_{0.8}Sr_{0.2}MnO_3$



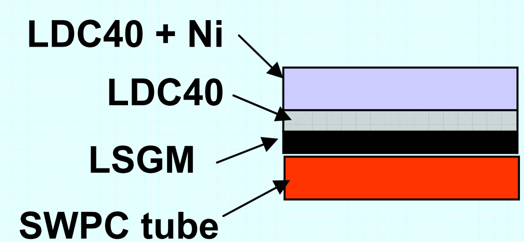

## System two: SWPC Program:

Anode- LDC40 + Ni

Interlayer LDC40

Electrolyte – $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$

Cathode – SWPC proprietary tubular substrate



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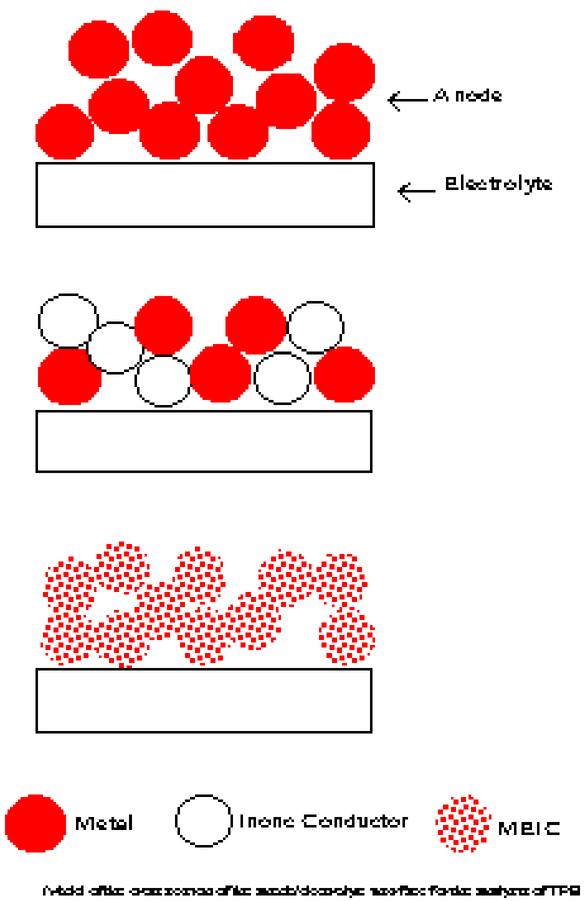
# *Nanostructured MIEC SYT Anode*




| Properties | Nickel – ceramic anode | US Nanocorp Nanostructured SYT |
|---|---|---|
| **Carbon deposition** | Yes | No |
| **Sulfur Poisoning** | Yes | No |
| **Available reaction sites** | Limited | Extended |
| **Operation temperatures** | 800 – 1000°C | 500 – 800°C |
| **Long term phase stability** | Not stable | Stable |
| **Particle size stability @ 500 – 800°C** | Yes | Yes |

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# *Synthesis of $Sr_{1-1.5x}Y_xTiO_3$ nanoparticles*

**(1). Prepare precursor solutions of Sr-, Y-, and Ti-containing salt solutions, and a reducing solution**

**(2). Reaction of the precursors at 60-100$^o$ C to form a preceramic gel-like powder**

**(3). Initial calcinations of the Sr-Y-Ti-O complex at 350$^o$C to form to form intermediate powder**

**(4). Calcination of the intermediate powder at 650$^o$C to form nanostructured $Sr_{1-1.5x}Y_xTiO_3$ anode material**

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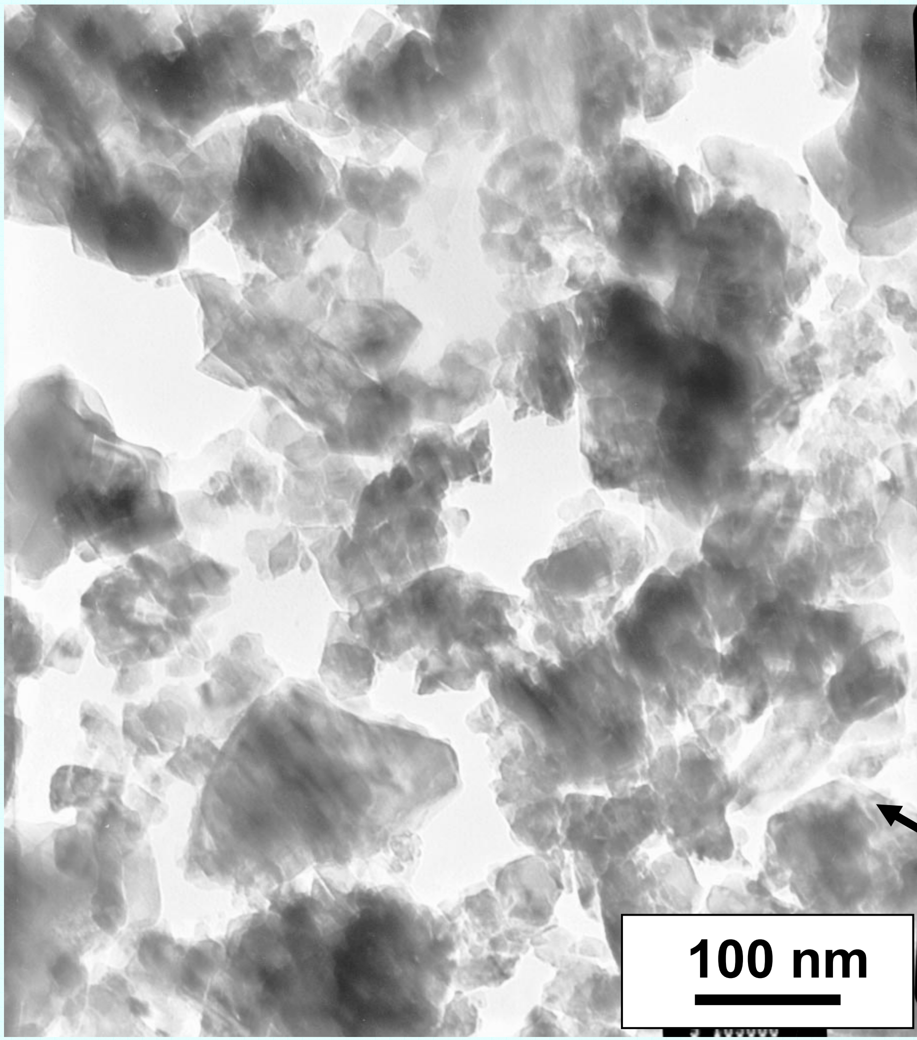


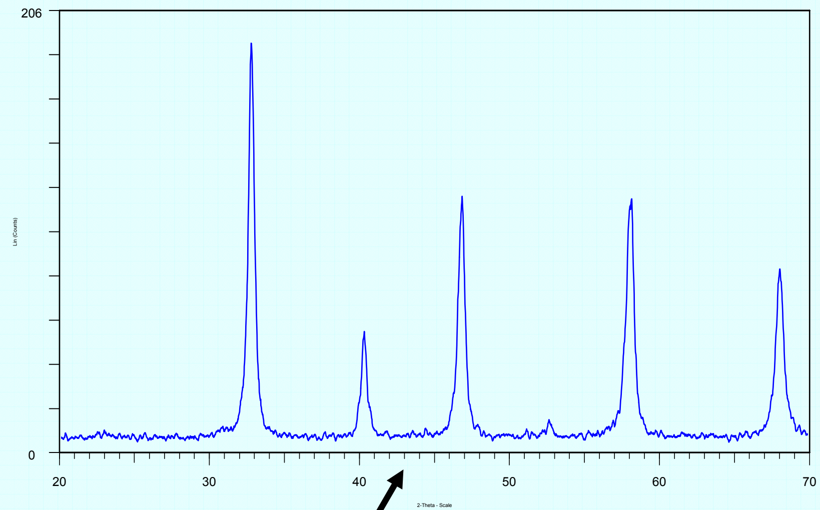


**XRD spectra of the synthetic SYT powders with average SYT grain size ~ 50 nm.**

**TEM micrographs showing the microstructures of SYT nanoparticles synthesized by wet chemical synthesis**

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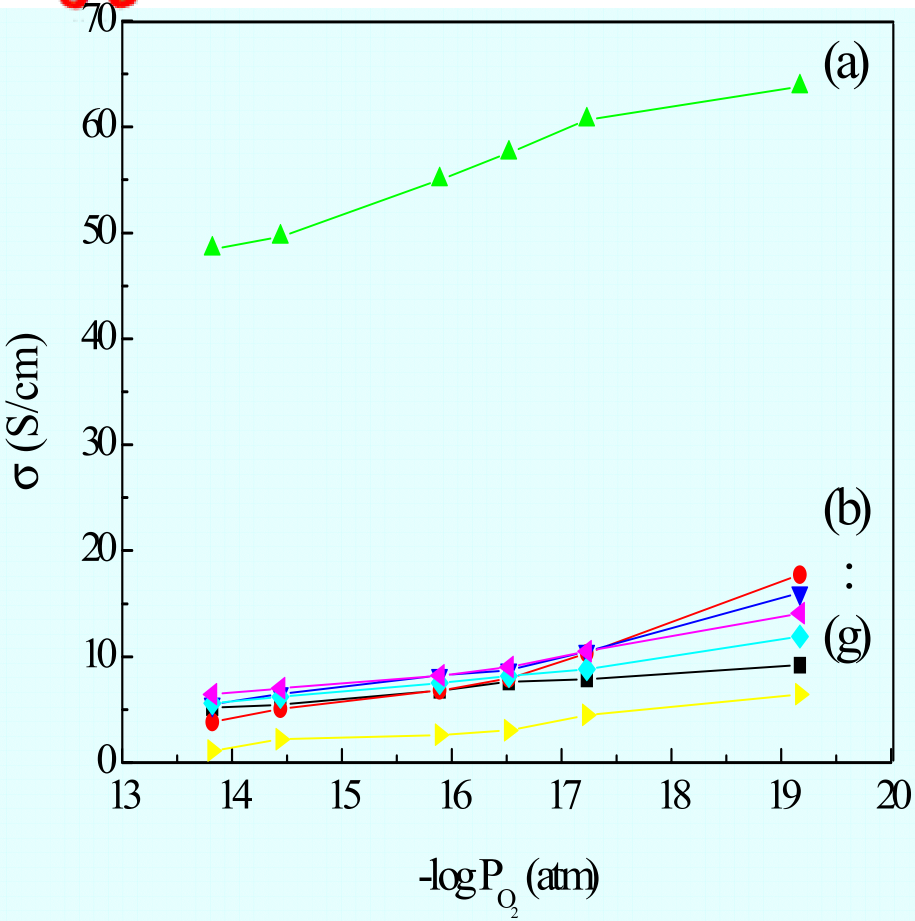
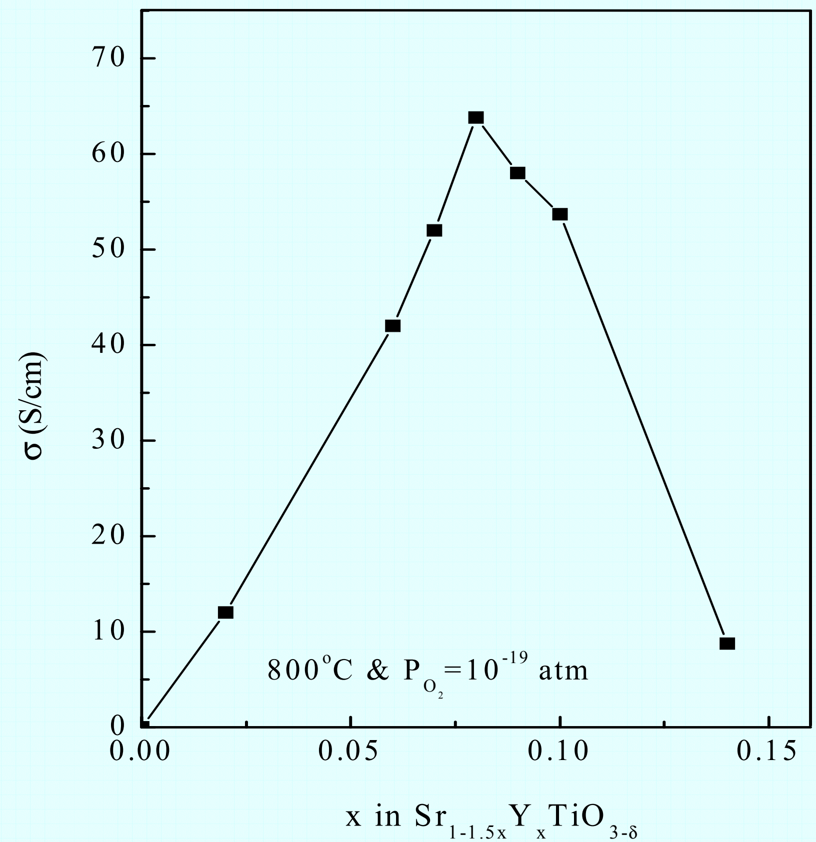
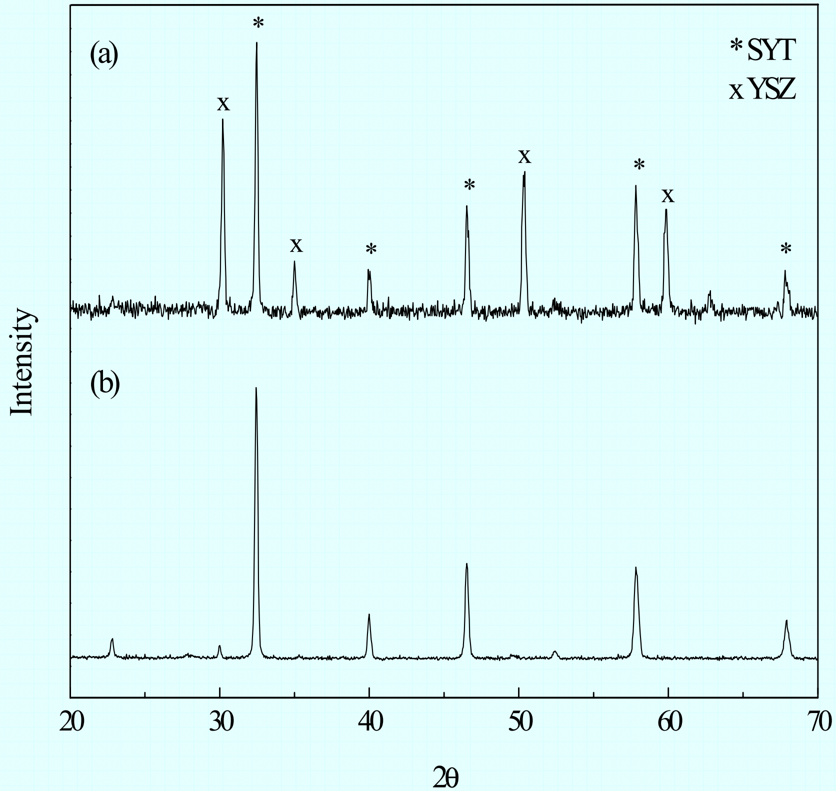



Electrical conductivity vs partial $O_2$ pressures at 800°C for donor doped SYT (a) $Sr_{0.88}Y_{0.08}TiO_{3-\delta}$, (b) $Sr_{0.25}La_{0.50}TiO_{3-\delta}$, (c) $Sr_{0.88}Yb_{0.08}TiO_{3-\delta}$, (d) $Sr_{0.88}Gd_{0.08}TiO_{3-\delta}$, (e) Sr0.88Sm0.08TiO3$_{-\delta}$, (f) $Sr_{0.85}La_{0.10}TiO_{3-\delta}$, (g) $Ca_{0.88}Y_{0.08}TiO_{3-\delta}$.

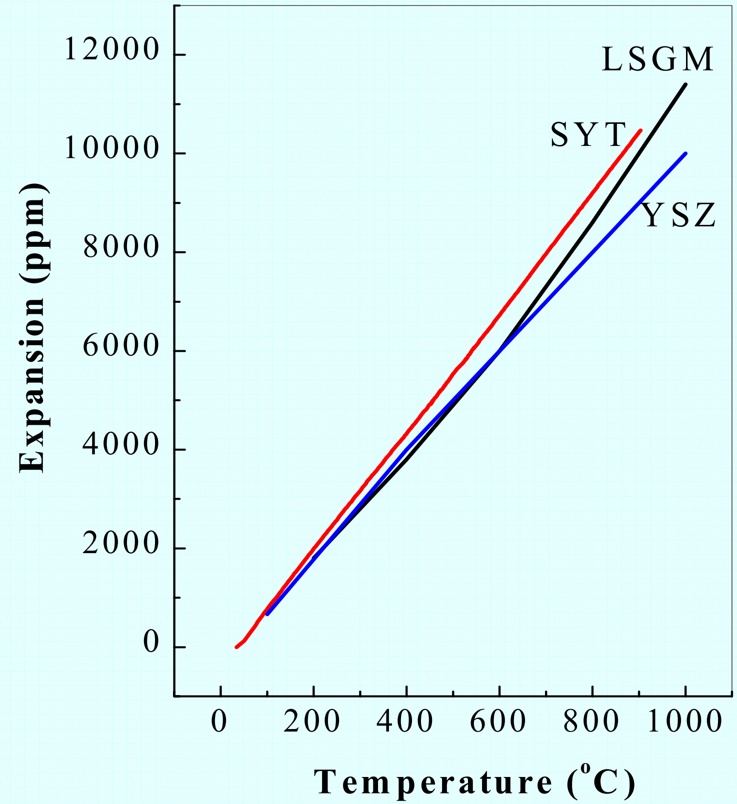



Conductivity as a function of Y-doping level at 800°C and oxygen partial pressure of $10^{-19}$ atm.

# Compatibility of SYT Nanoparticles




**XRD for the sintered mixtures (a) SYT + YSZ, (b) SYT + LSGM. No new phase has been detected**




Thermal expansion plots for SYT, LSGM, and YSZ

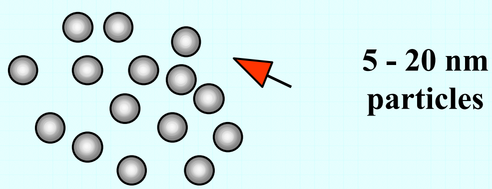
# *Problems of Nanopowders in Thermal Spray*

- **Cannot be fed into the existing industrial thermal spray systems**
- **Too low mass**
- **Inability to be carried in a moving gas stream**
- **Inability to be deposited onto a substrate to form a dense coating**

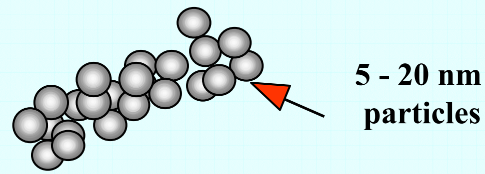
# Thermal Spray Feedstock Specifications

- Solid spherical particles, 15 to 100 mm
- Fully sintered solid agglomerates
- Flow freely in the existing thermal spray powder feeding
- Right porosity for anode application

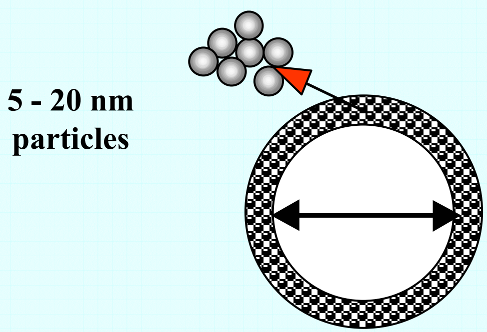
# Thermal Spray Feedstock Reconstitution



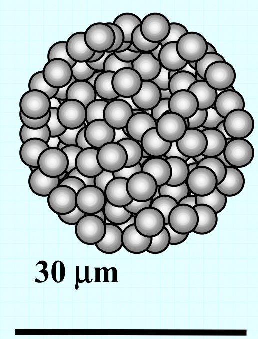

non-agglomerated




loosely agglomerated




hollow shell agglomerates




reconstituted sprayable form

# Thermal Spray Feedstock Reconstitution

- **Dispersion of SYT nanoparticles into a solvent**
- **Addition of surfactants and binders**
- **Reconstitution of the nanoparticle slurry into agglomerated micrometer sized particles**
- **Heat treatment to remove binder and nanoparticle sintering**
- **Agglomerated particle size classification**

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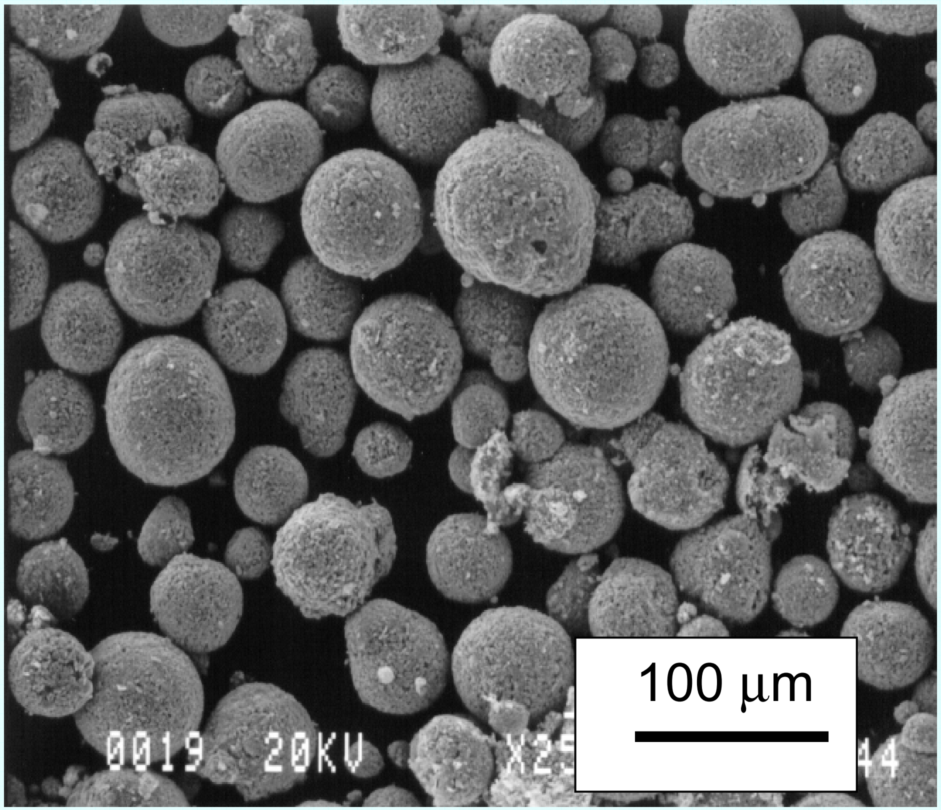
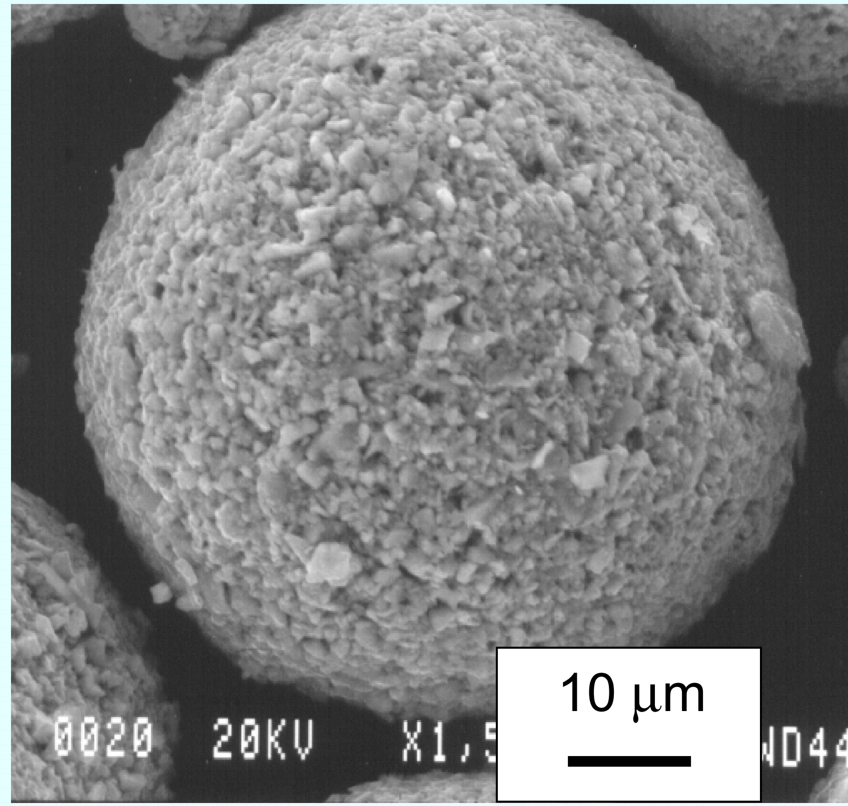
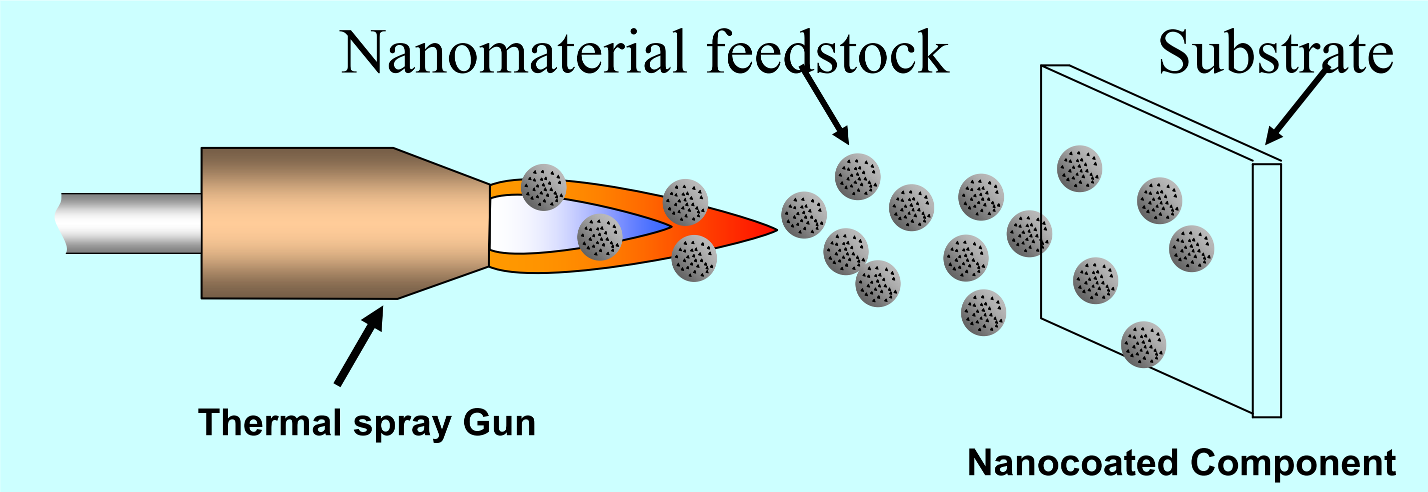
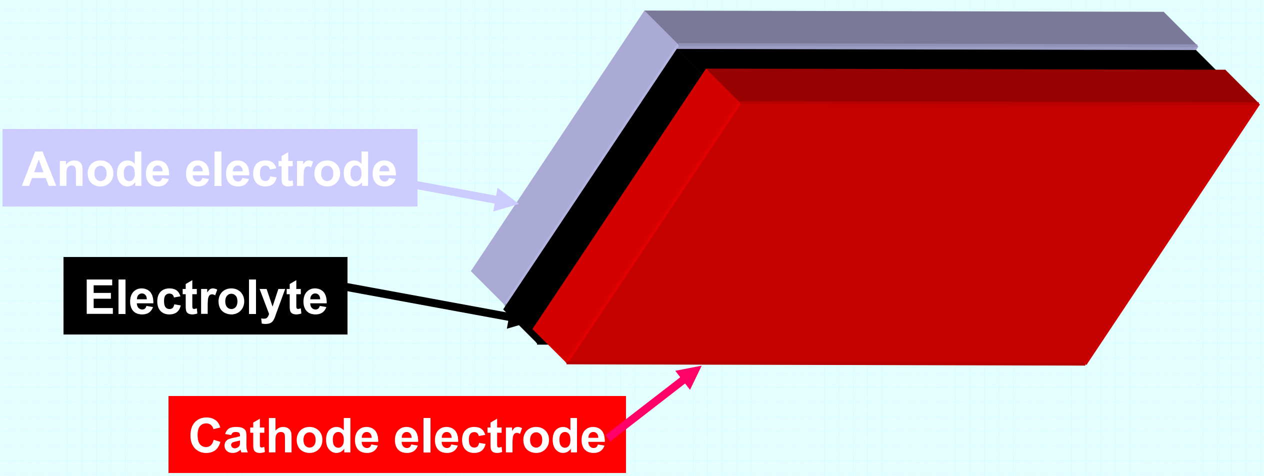



**SEM micrograph showing the reconstituted nanostructured SYT thermal spray feedstock**

# Thermal Spray Fab. Thermal Batteries



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# Advantages of T/S Fab. Vs. Other Fab of SOFC

- Rapid fabrication and sequential fabrication of cells
- Thickness of each material can be accurately controlled
- Robotic control / continuous operation
- Potential low cost production (automation)
- Graded & multilayer structures (porosity & composition)
- Excellent interfacial contact
- Nanostructured materials
- Large area and free geometry
- Unlimited substrates (room temperature)

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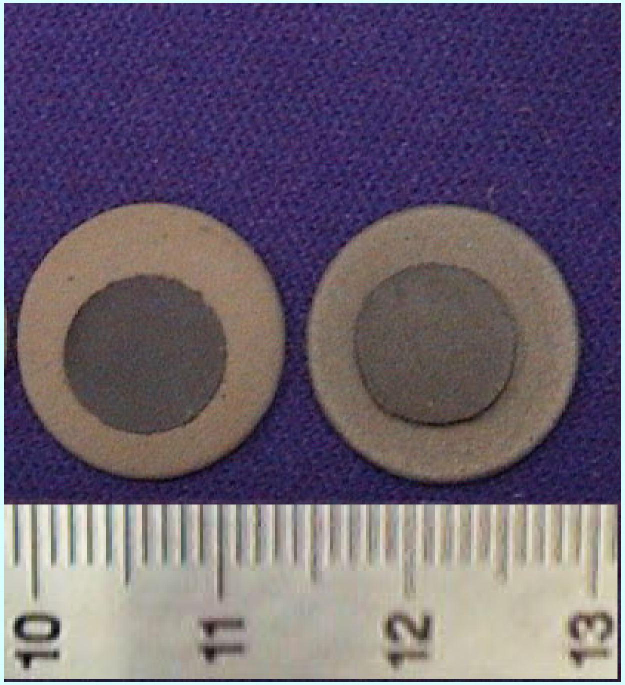


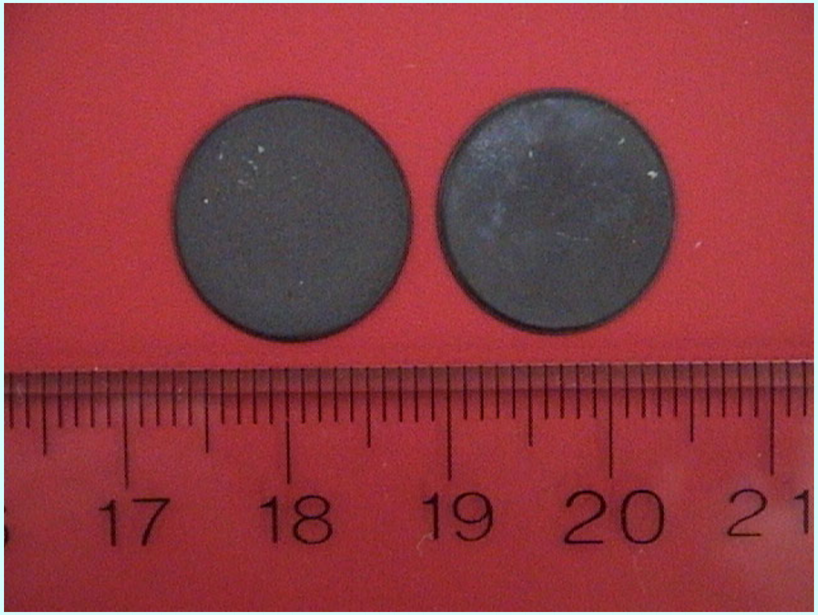


Photos of plasma sprayed free standing SOFC single cells porous consisting anode and cathode, and dense electrolyte

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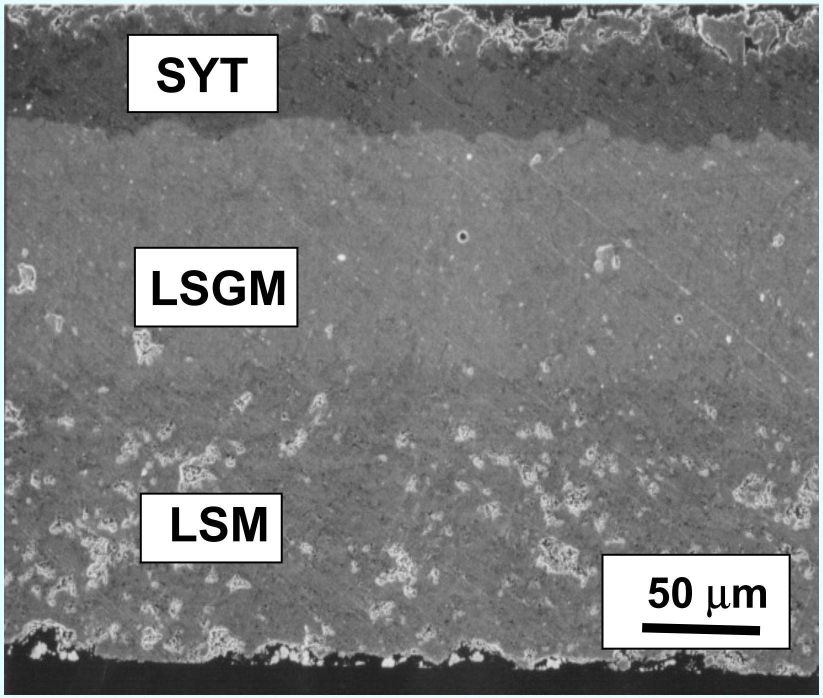
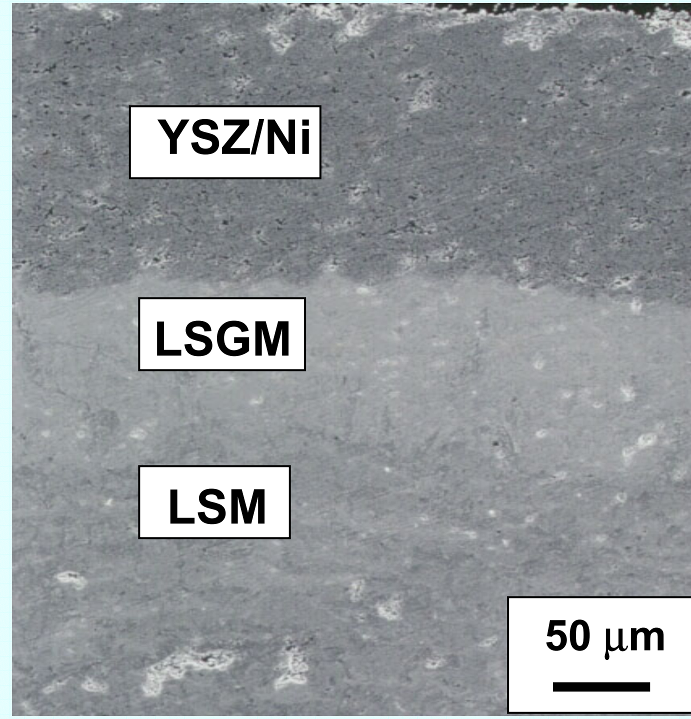
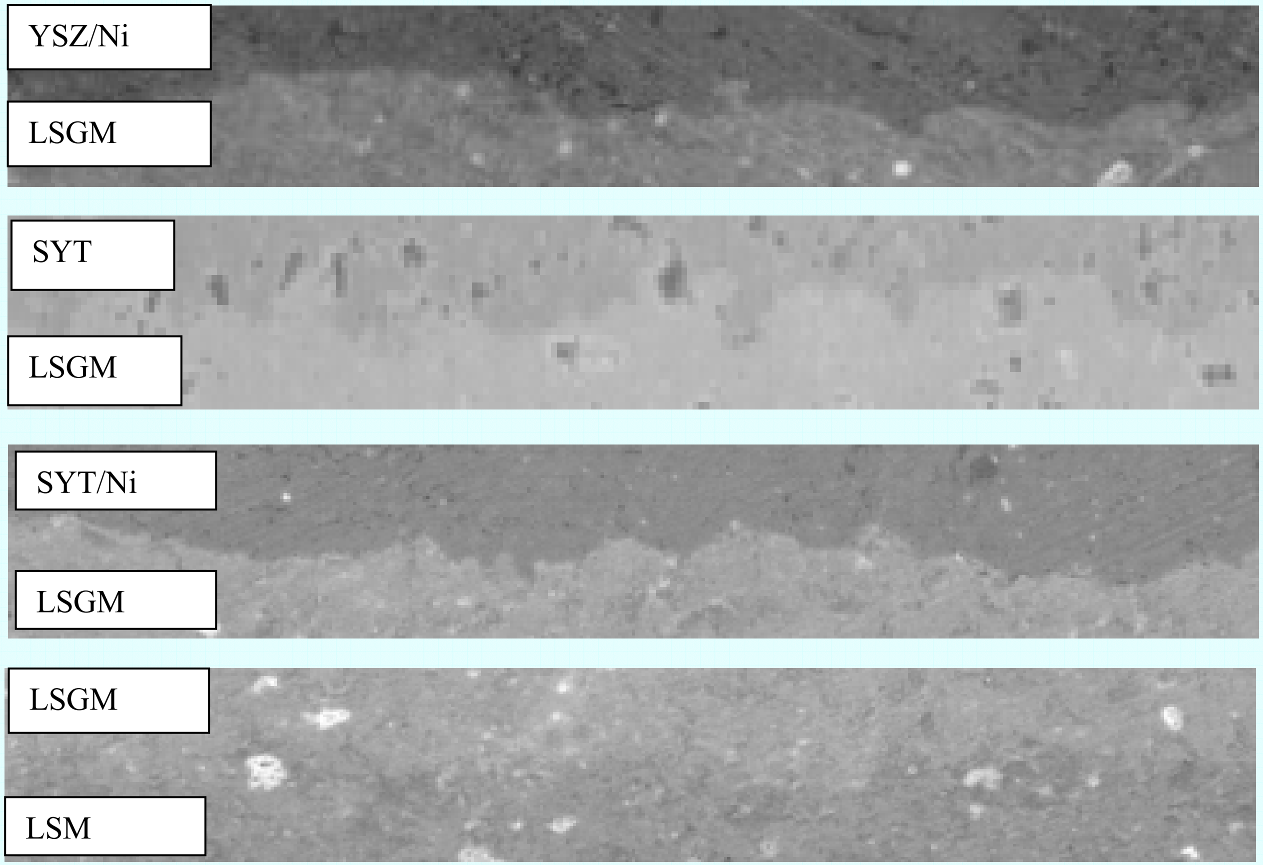



**SEM image for the thermal spray SYT– LSGM – LSM/LSGM layer**

**SEM image the thermal spray YSZ/Ni-LSGM-LSM/LSGM layer**




**SEM micrographs showing excellent interfacial bonding between anode/electrolyte, electrolyte/cathode using the plasma spray technique.**

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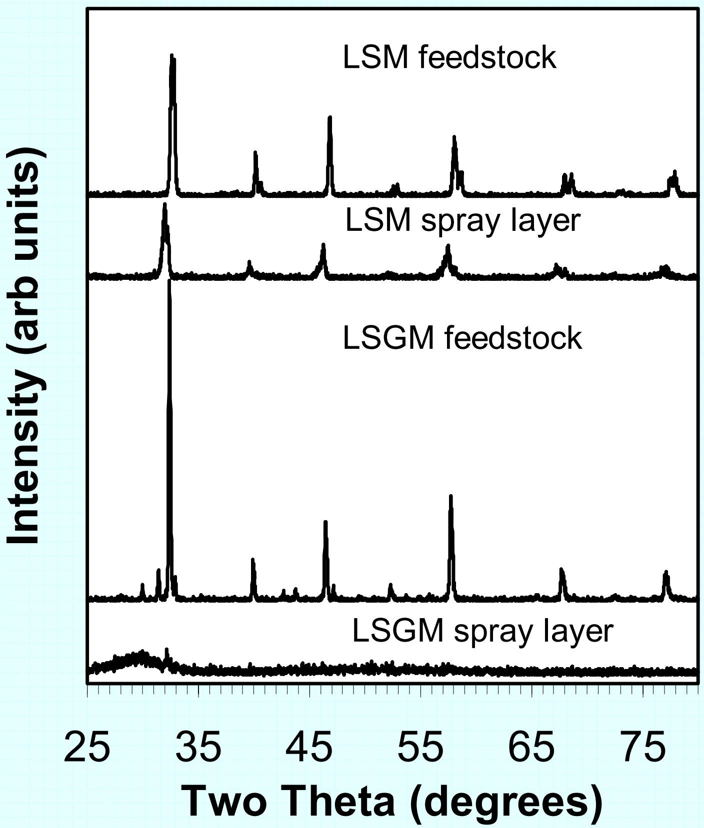
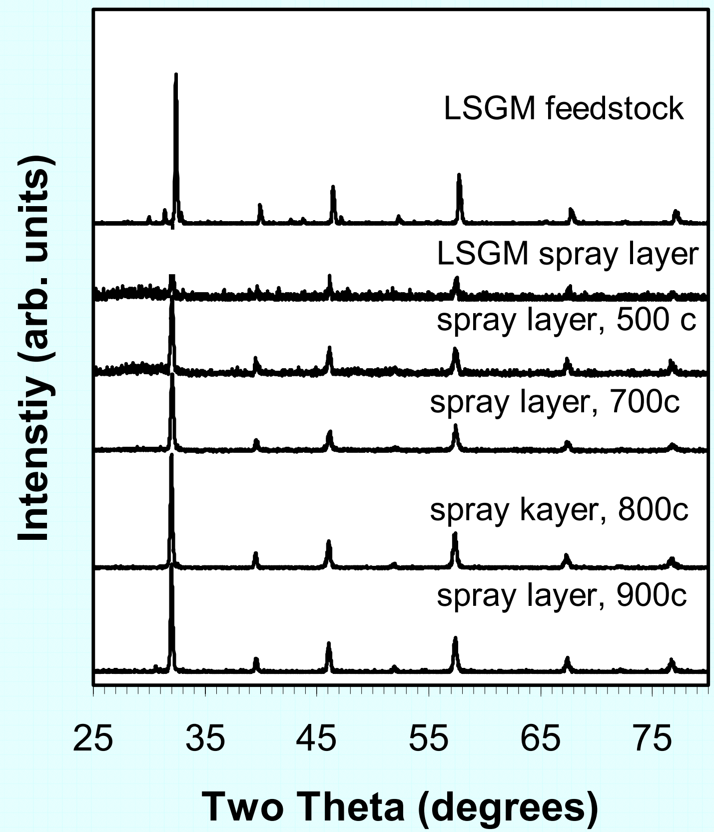
# XRD for Thermal Sprayed Materials

## Non – Annealed




XRD patterns for the feedstock and thermal spray layers of LSM and LSGM

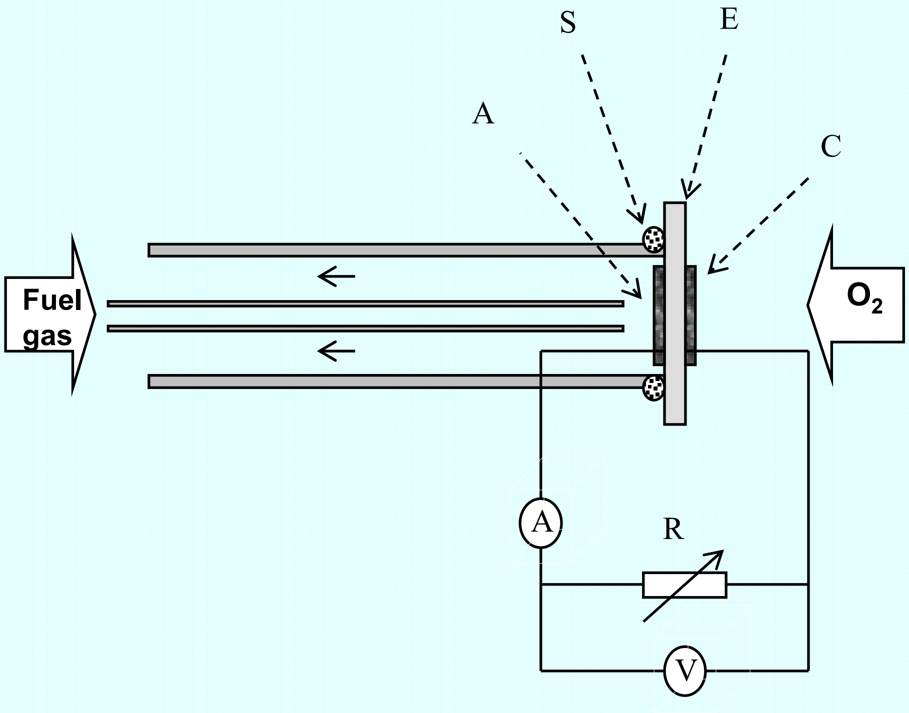
## Annealed




XRD Patterns showing thermal sprayed LSGM annealing at different temperatures

# Fuel Cell Performance Evaluation

Photo of the fuel cell evaluation system




Schematic setup

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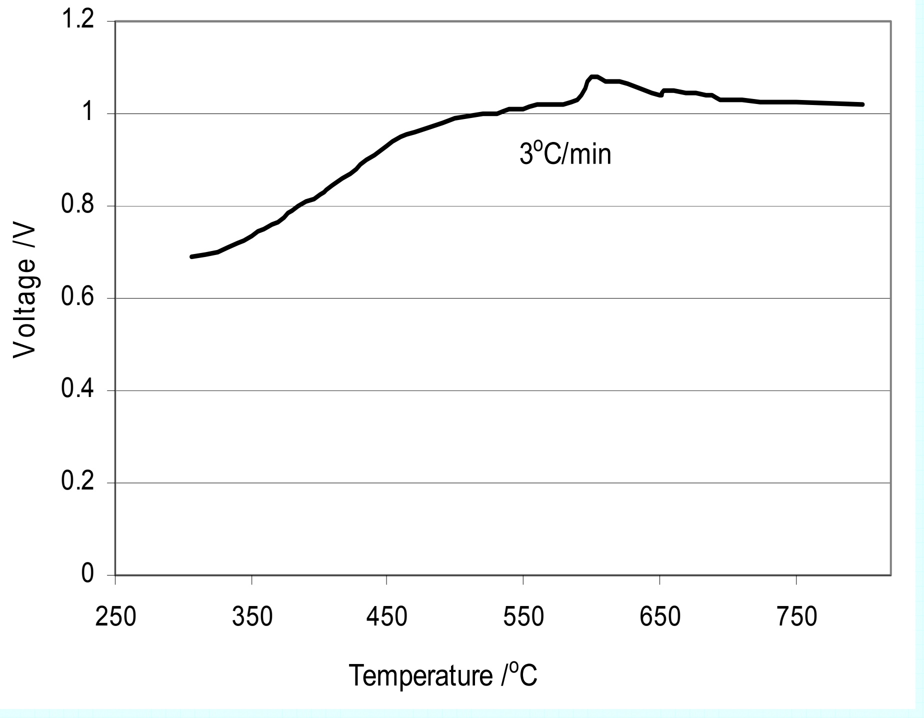
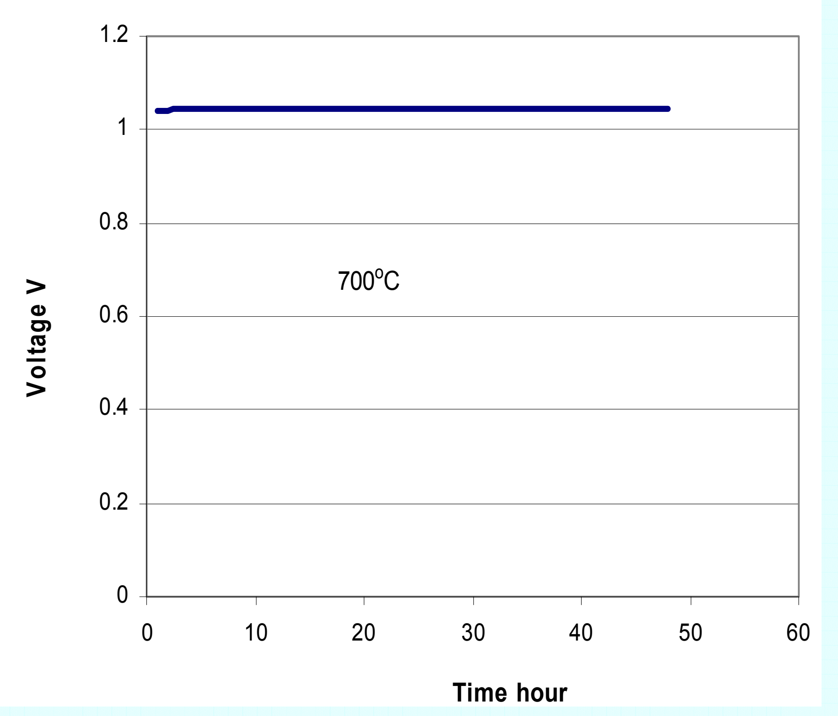
# Stability of Open-Circuit Voltage




Open-circuit voltage vs. temperature




Open circuit voltage vs time

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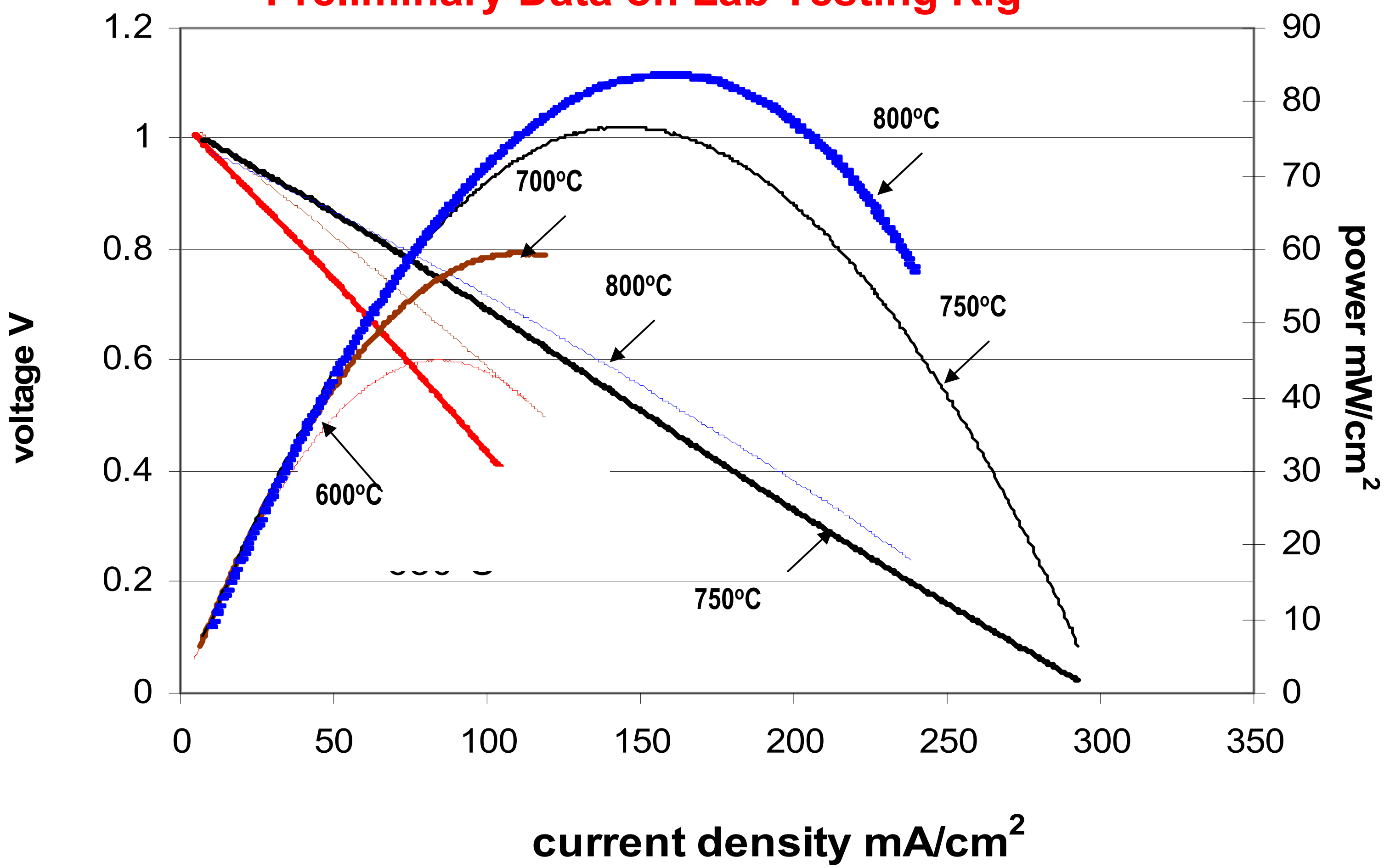
## Preliminary Data on Lab Testing Rig*




Voltage-power vs. current density

*Low values due to poor crystallinity of the electrolyte

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# Technical Issues Concern T/S LSGM SOFC

## *Mechanical strength:*

– Normally LSGM is weak. When it is deposited on a substrate, such as SWPC's tubular cathode design, this coating becomes more durable

## *Pinhole issue:*

– Studies indicated ~ 50 μm thickness of LSGM, pinholes are unavailable. Also SWPC's thermal sprayed YSZ has to be > 80 mm thick to avoid pinholes. From our preliminary results using lab scale cell, we have eliminated all pinholes using our plasma parameters for ~50 μm thickness.

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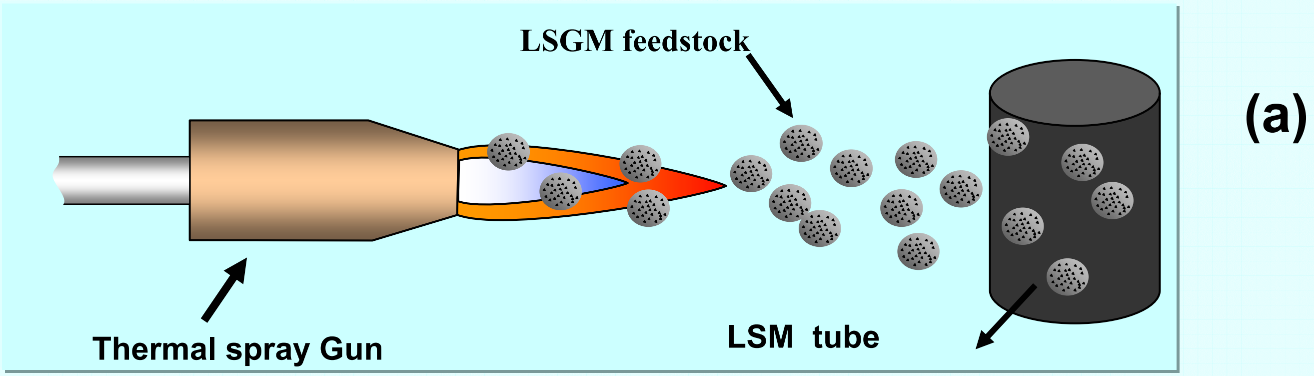
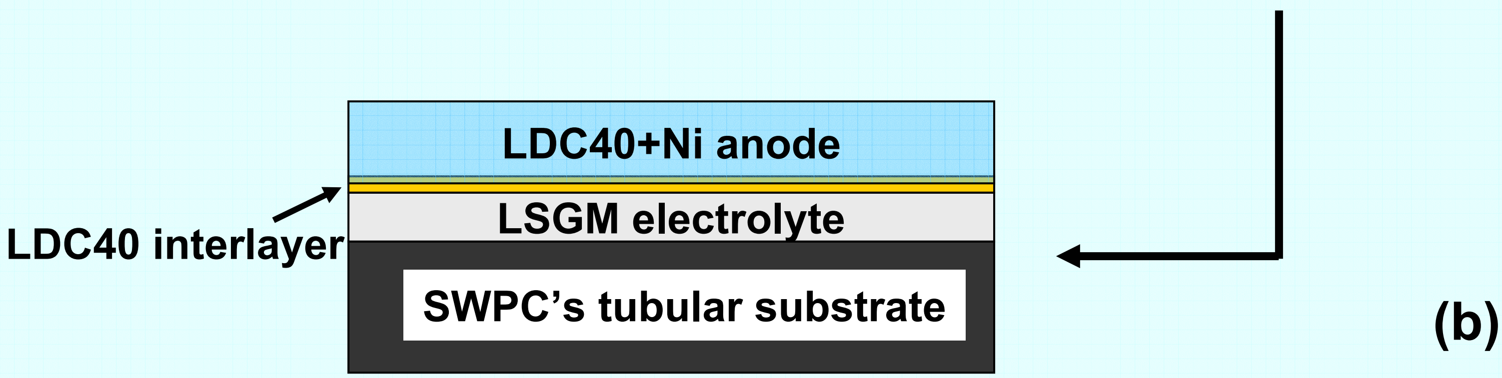
# Plasma Spraying LSGM SOFC using SWPC's Cathode Tubes



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# Thermal Spray Process Description

**Cathode:** SWPC's proprietary substrate

**Electrolyte:** LSGM powder or liquid

**Interlayer:** LDC powder or liquid spray

**Anode:** Nickel + LDC both via:
(1) plasma spray powder
(2) plasma spray liquid feedstock

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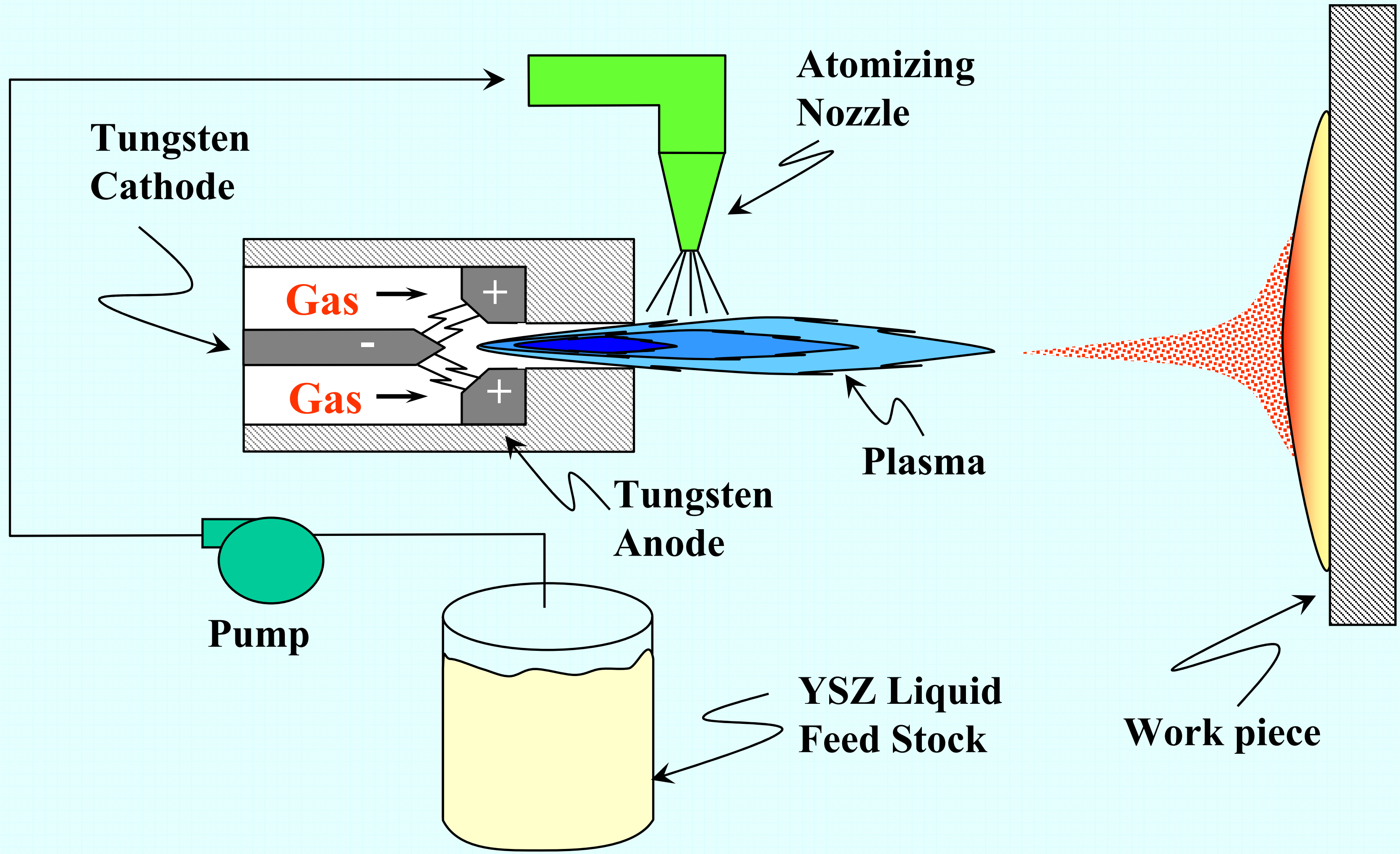
# Liquid Feedstock Plasma Spray



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# Advantages of Liquid Spray Anode

- Forming 3-D porosity structure, leading to high fuel gas permeability toward LSGM electrolyte
- Forming nanostructured anode, increase surface area of fuel – solid interaction
- Enable thin layer coating formation
- Higher thermal shock resistance

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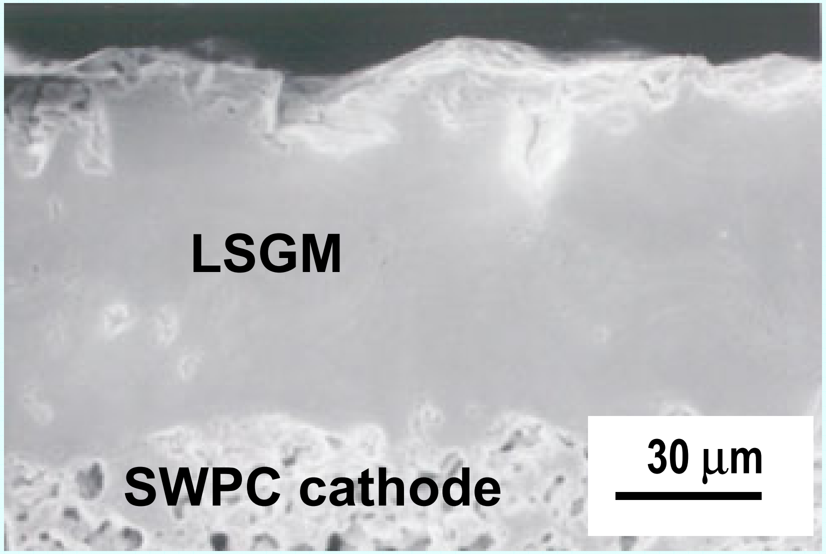


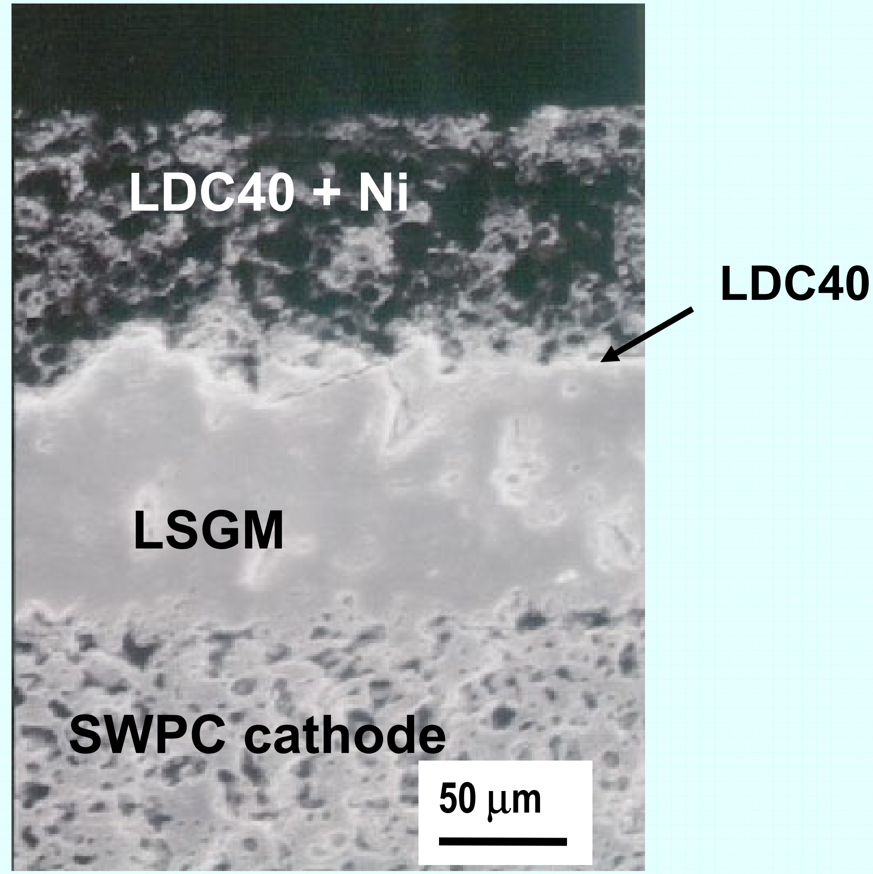


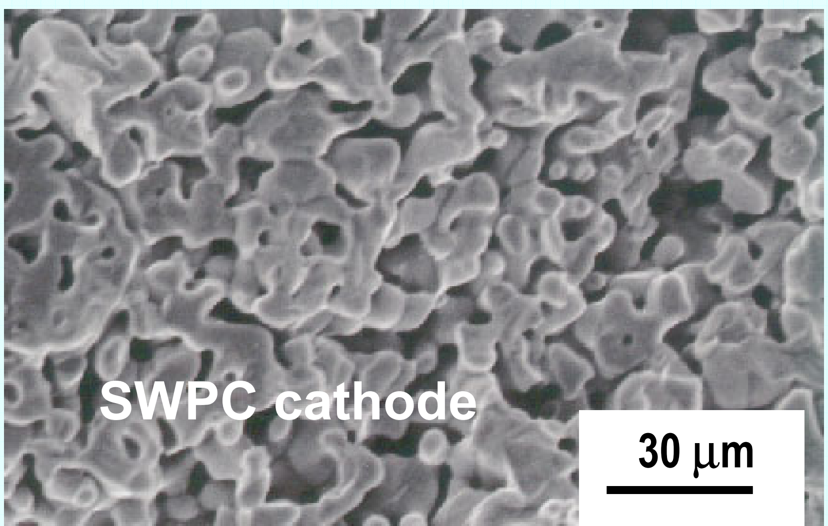

# Conclusions

1. Demonstrated the feasibility of synthesizing nanostructured SYT anode material using a wet chemical synthesis route and reconstitute into thermal spray feedstock
2. Demonstrated the feasibility of fabricating single SOFC units via sequential plasma spray technique, for porous SYT anode, dense LSGM electrolyte, and porous LSM

# Conclusions – continued

3. Demonstrated acceptable performance of the single SOFC using plasma spray technique

4. Demonstrated the feasibility of fabricating single SOFC units via sequential plasma spray technique, where the anode electrode is formed by a novel liquid feedstock technique

# Future Studies

1. Cell polarization vs. components
2. Crystallinity of thermal sprayed LSGM electrolyte
   - Post annealing temperature vs. crystallinity
   - Cell performance vs. crystallinity
3. Pinholes
   - Thickness of LSGM electrolytes
   - Plasma spray parameters
4. Anode conductivity
   - Ionic conductivity
   - Electronic conductivity