Large Scale, Homogeneous SOFC Cathode Infiltration by Single Step, Ultrasonic Spraying Process

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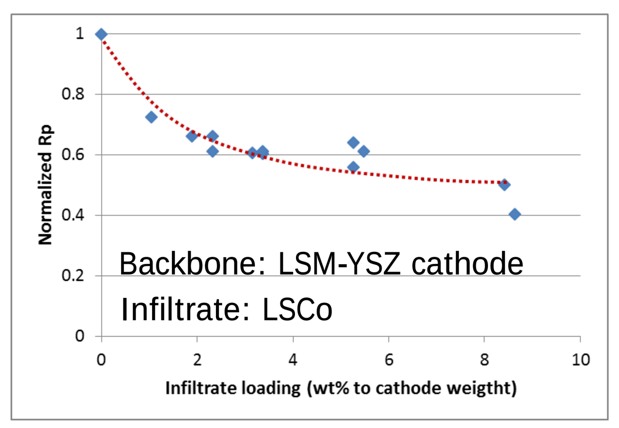
Large scale, Homogeneous Infiltration

Limitations of conventional manual infiltration process in applications for large scale, commercial manufacturing process:

- ❑ **Inhomogeneity:** Conventional manual process is unable to control spatial homogeneity of catalyst distribution and inefficient in terms of cost and manufacturing time.
- ❑ **Multiple steps:** It requires multiple infiltration (> 4 times) and heating cycles to 850C to deposit a sufficient amount of electrocatalyst at the cathode active layer while preventing agglomeration at the cathode surface.

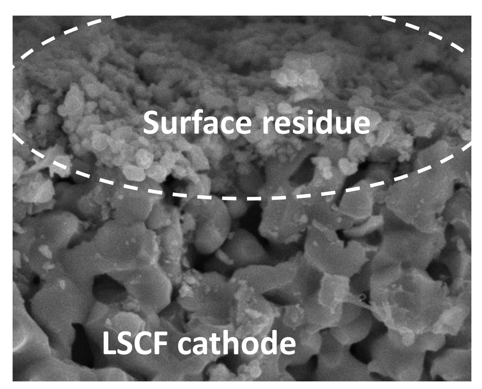
Motivation: Minimum number of processing steps are required for industry's commercialization application. The goal of this research is to develop a single step infiltration process to introduce required amount of electrocatalyst to large scale SOFC cathode, thereby greatly reduce the overall time and cost.

Single-step Infiltration

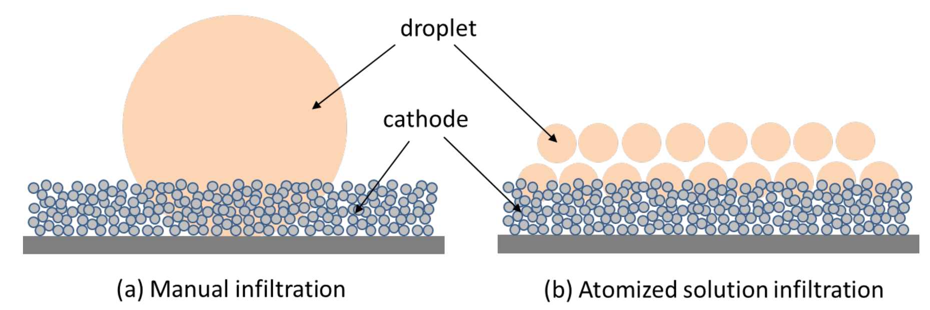


Threshold infiltrate mass: Polarization resistance decreases with infiltrate loading, and a minimum threshold infiltrate mass is required for "full" activation. The threshold amount of infiltrated electrocatalyst is **6-8 wt%** of a baseline cathode.

Single step infiltration means an infiltration process that does not require interspersed heat-treatment before infiltrating the full threshold mass of catalyst materials in the porous electrode.



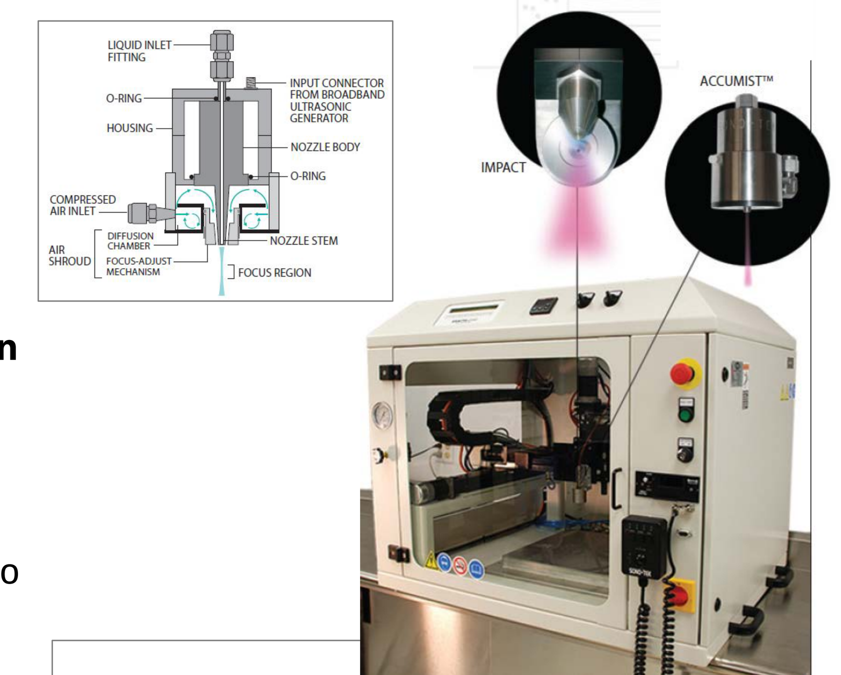
2 Solution Atomizing and Spraying Process



- ❑ Schematic diagram comparing conventional manual infiltration with atomized solution infiltration.
- ❑ **Homogeneous distribution of smaller droplets** are expected to enhance penetration rate and to prevent local build up of residue.

Features of Spraying Infiltration

- ❑ **Uniform distribution of droplets and translating to homogeneous distribution** by continuous ultrasonic vibrations along the length of the nozzle create
- ❑ **Spatial homogeneity and controllability of catalyst distribution** that are essential to minimize performance degradation caused by uneven temperature and overpotential profile over the electrode.
- ❑ **Continuous manufacturing process** to generate a high volume of infiltrated SOFC using an automated mechanism.
- ❑ Variables:
  - **Frequency:** Higher frequencies produce a smaller droplet
  - **Translation velocity:** Solution mass per unit area



Spray coater
- Sono-Tek® ultrasonic spray nozzle
- Frequency: 120 kHz
- Median droplet size ~ 17 μm

Result: Weight gain by single step infiltration

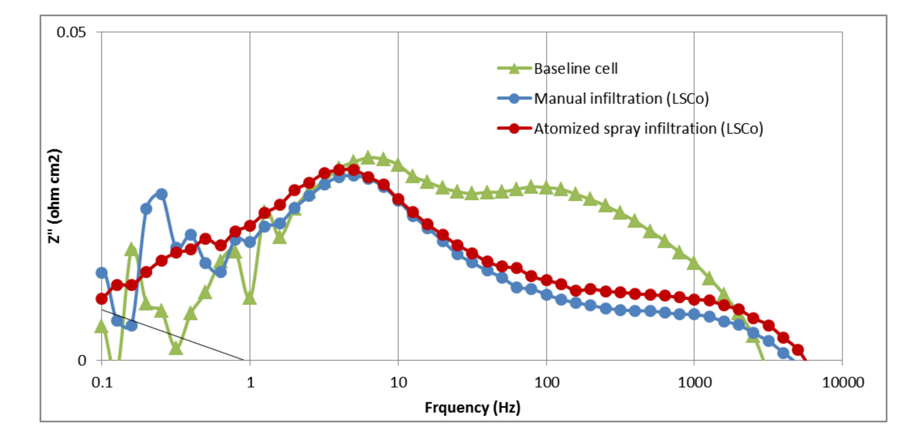
❑ Weight increase after single step infiltration with electrocatalyst either LSCo or PSCo.

Catalyst	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10	Average (wt%)
$La_{0.6}Sr_{0.4}CoO_3$ (LSCo)	8.75	8.65	8.81	8.86	8.73	9.10	8.83	9.00	8.85	9.00	**8.86**
$Pr_{0.6}Sr_{0.4}CoO_3$ (PSCo)	9.57	9.35	9.54	9.51	9.68	9.57	9.86	9.54	9.82	9.73	**9.62**

- The required amount for cathode activation (6-8 wt% of cathode) was obtained by single step spraying infiltration

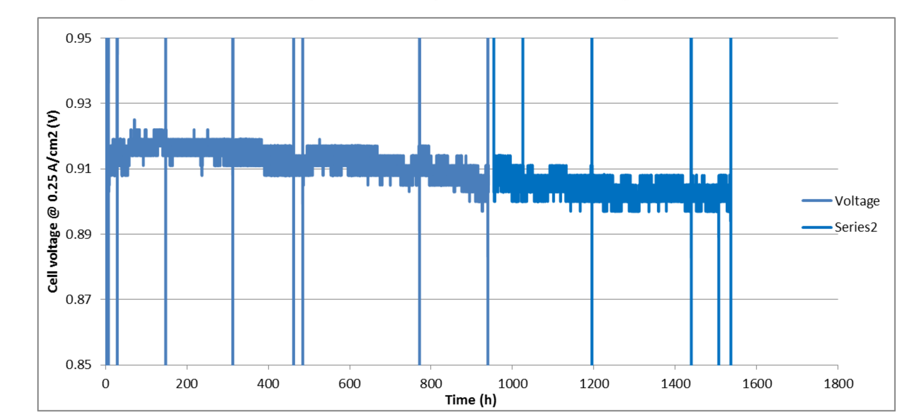
Result: Cell Performance

❑ Comparison of impedance spectra (Bode plot)



- ❑ Backbone: LSCF / LSCF-SDC functional layer
- ❑ Infiltrate: **LSCo**
- ❑ Operating Conditions:
  - 750°C, 0.75 A/cm² or 0.25 A/cm²
- ❑ Cathode performance of the cell prepared by the invention is virtually indistinguishable with that of the cell prepared by manual infiltration.

❑ Long-term test (1,600 h): Cell voltage vs. time



- ❑ Backbone: LSCF / LSCF-SDC functional layer
- ❑ Infiltrate: **PSCo**
- ❑ Operating Conditions:
  - 750°C, 0.25 A/cm²
- ❑ Cell voltage degradation rate: 0.91%/1000h

1 Chemical Approach

The following items comprise the essential components of the present research.

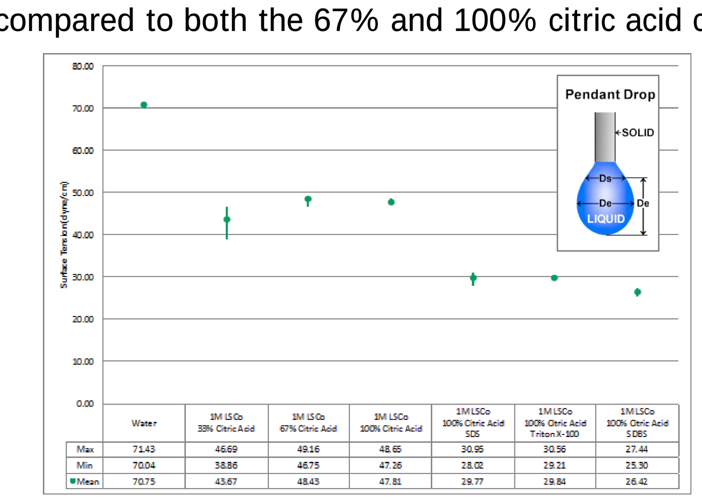
Surfactant
- Reduce surface tension and improve wettability
- CMC (Critical micelle concentration): Surfactant concentration above which additional surfactant generates micelles instead of solvating the solute.
  - **Triton X-100 (Octylphenol ethoxylate): 0.23 mM**
  - SDBS (Sodium dodecyl benzene sulfonate): 1.6 mM
  - SDS (Sodium dodecyl sulfate): 8.0 mM

Chelating Agent
- Complex with metal ions and assist with forming correct catalyst phase upon calcination
- Molar fraction of the chelating agent (**citric acid** in this study) affects concentration and viscosity of solution, and ultimately residual infiltrate mass after calcination.

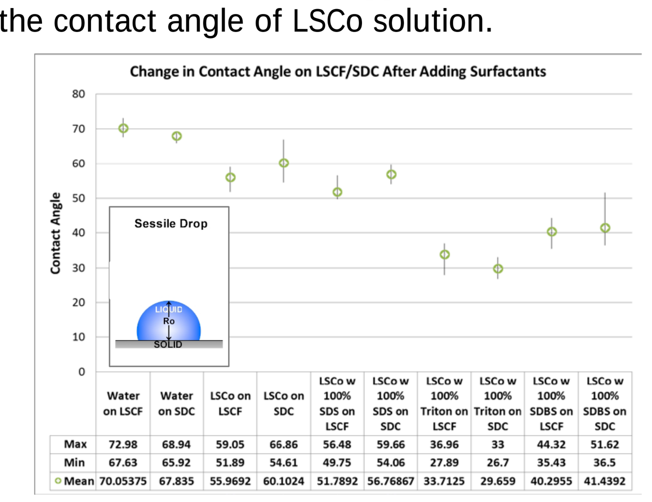
Concentration
- Determine (1) residual amount of electrocatalyst after calcination, which directly correlated with the number of infiltration-calcination step
- Determine (2) degree of solution penetration into porous electrode by affecting solution viscosity
- **1 M solution** was selected. (cf. saturation concentration = 1.5 M)

Pretreatment (surface energy control)
- Chemical method: Surface treatment with polar or non-polar solution
- Thermal method: Heat-treatment at mild temperatures
- Plasma method

❑ **Effects of chelating agent and surfactant on surface tension:**
- Lower surface tension resulted when adding the surfactants to the infiltrate solution.
- 33% citric acid resulted in lower surface tension as compared to both the 67% and 100% citric acid cases.



❑ **Contact angle measurement:**
- Goniometer contact angle for different solutions in contact with cathode backbone materials, LSCF or SDC.
- Triton X-100 shows the biggest effect in lowering the contact angle of LSCo solution.



❑ **Relationship of Concentration and Number of infiltration step**

Concentration (mol/L)	# of step to fully cover backbone cathode	Features
0.25	5.2	Homogeneous distribution Time-consuming
0.5	2.6	
1.0	**1.3**	Reduce infiltration steps Viscous solution
1.3	1.0	

Temperature effect
- Solution heating (claimed in US Patent App. 20080193803): Negative effect by forming highly viscous solution that cannot penetrate porous cathode
- Substrate heating: Effective in lowering surface energy of substrate, but simultaneously accelerate solvent evaporation rate

Result: Productivity/Cost

- ❑ Productivity: 6,000 cells/year (24 cells/year) for 100 cm² SOFC
  2,000 cells/year (8 cells/day) for 400 cm² SOFC
- ❑ Cost (material): \$0.46/100cm² for LSCo, \$1.20/100cm² for PSCo

Summary & Conclusion

- ❑ **A commercially applicable cathode engineering technique** that provides improved electrocatalytic activity and performance stability of SOFC cathode has been developed.
- ❑ The developed technique includes the addition of critical threshold mass (6 – 8 wt% of cathode) of electrocatalyst required for "full" activation of cathode into a porous baseline cathode **by a single step process.**
- ❑ The industrially feasible single step process was realized **by controlling infiltration solution chemistry and catalyst phase formation** through solution composition of metal salts, chelating agent, surfactant, etc.
- ❑ In addition to chemistry control, **the solution atomizing technique** with an ultrasonic spraying system facilitates uniform distribution of infiltrated electrocatalyst over the entire large scale cathode by generating soft, highly focused beam of fine spray drops.
- ❑ The button cells prepared by the single-step infiltration showed similar performance compared to the ones prepared by manual infiltration, implying that the technique can be applied to larger scale cells without sacrificing performance.

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