# Optimization of Mn-Co-O Spinel Spray Coatings for SOFC Applications Using The Design of Experiment Method

Jung Pyung Choi, Jeffry W. Stevenson, and Y.S. Matt Chou
Fuel Cell, P.O.Box 999, Pacific Northwest National Laboratory, WA 99352, USA

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## Introduction

Ferritic stainless steel interconnects are generally used in planar type SOFC stacks, due to their low-cost, chromia scale-forming behavior, and good thermal expansion match to other stack components. However, volatile Cr-containing species, which originate from the oxide scale, can poison the cathode material in the cells and subsequently cause power deterioration in the device. A conductive MnCoO spinel coating has been developed for preventing cathode poisoning and to provide low electrical resistance in SOFC stacks. It is essential that the spinel coating be sufficiently dense to block the Cr-containing species volatilization, so it is important to develop an optimized process for fabricating the coatings. This paper will summarize development of an ultrasonic spray coating method and optimization of the process using design of experiment methodology with Taguchi and ANOVA analysis. Using spray parameters obtained from the DOE optimization, dense spinel layers with about 2-micrometer thickness have been fabricated. The results of this work demonstrate the possibility of automated mass production of dense conductive spinel-coated interconnect materials.

## Objective

Prevent Chromia species evaporation and show conductivity in between 6mΩ*Cm$^2$ and 20mΩ*Cm$^2$ range during long term operation at high temperature. Dense thin layer coating.

## Design of Experiment

### Factors and Levels

| Factors | level1 | level2 | level3 | level4 |
|---|---|---|---|---|
| Viscosity | 37 cP | 17 cP | 9 cP | 5 cP |
| Coating speed | 40mm/sec | 60mm/sec | 80mm/sec | 100mm/sec |
| Head height | 15mm | 25mm | 35mm | 45mm |
| Ink feeding rate | 0.5ml/sec | 1ml/sec | 1.5ml/sec | 2ml/sec |
| Air flow rate | 30ml/sec | 40ml/sec | 50ml/sec | 60ml/sec |

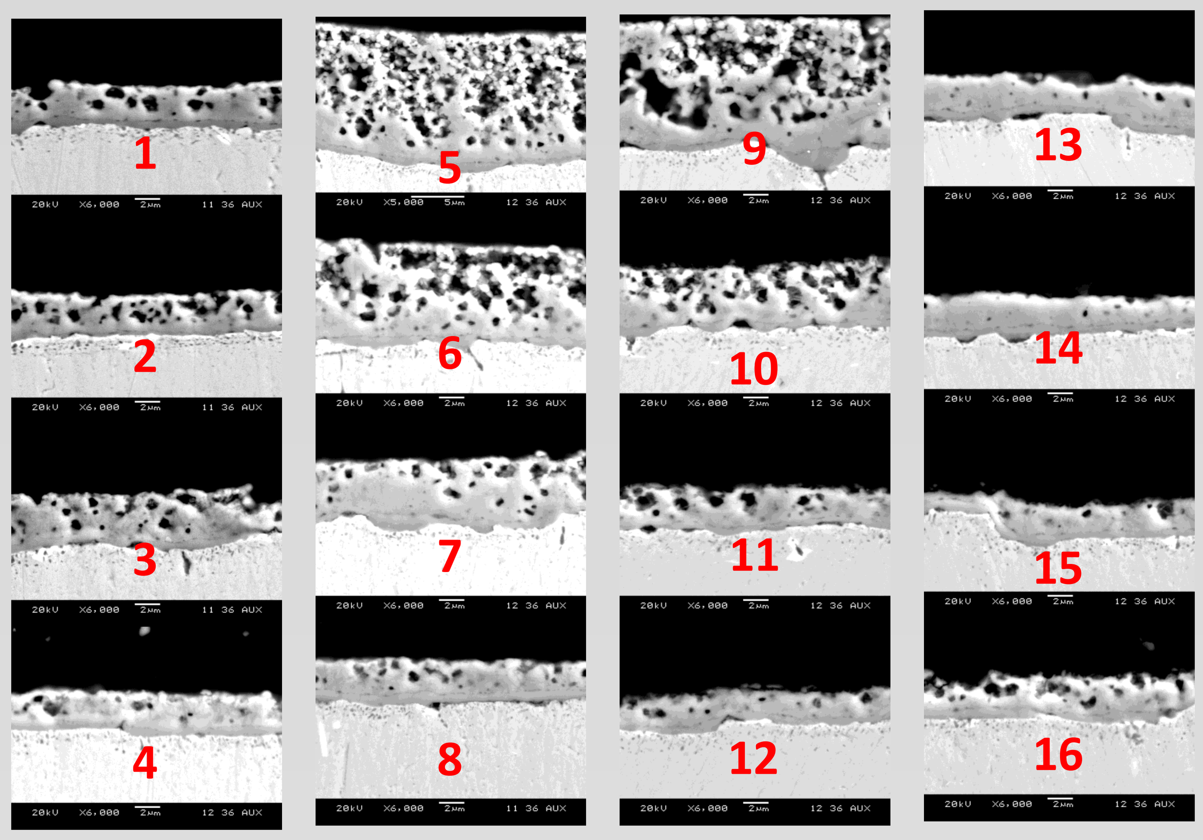
### Orthogonal Array

L'16

| Sample # | Viscosity | Coating speed | Head height | Ink feeding rate | Air flow rate |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 |
| 2 | 1 | 2 | 2 | 2 | 2 |
| 3 | 1 | 3 | 3 | 3 | 3 |
| 4 | 1 | 4 | 4 | 4 | 4 |
| 5 | 2 | 1 | 2 | 3 | 4 |
| 6 | 2 | 2 | 1 | 4 | 3 |
| 7 | 2 | 3 | 4 | 1 | 2 |
| 8 | 2 | 4 | 3 | 2 | 1 |
| 9 | 3 | 1 | 3 | 4 | 2 |
| 10 | 3 | 2 | 4 | 3 | 1 |
| 11 | 3 | 3 | 1 | 2 | 4 |
| 12 | 3 | 4 | 2 | 1 | 3 |
| 13 | 4 | 1 | 4 | 2 | 3 |
| 14 | 4 | 2 | 3 | 1 | 4 |
| 15 | 4 | 3 | 2 | 4 | 1 |
| 16 | 4 | 4 | 1 | 3 | 2 |

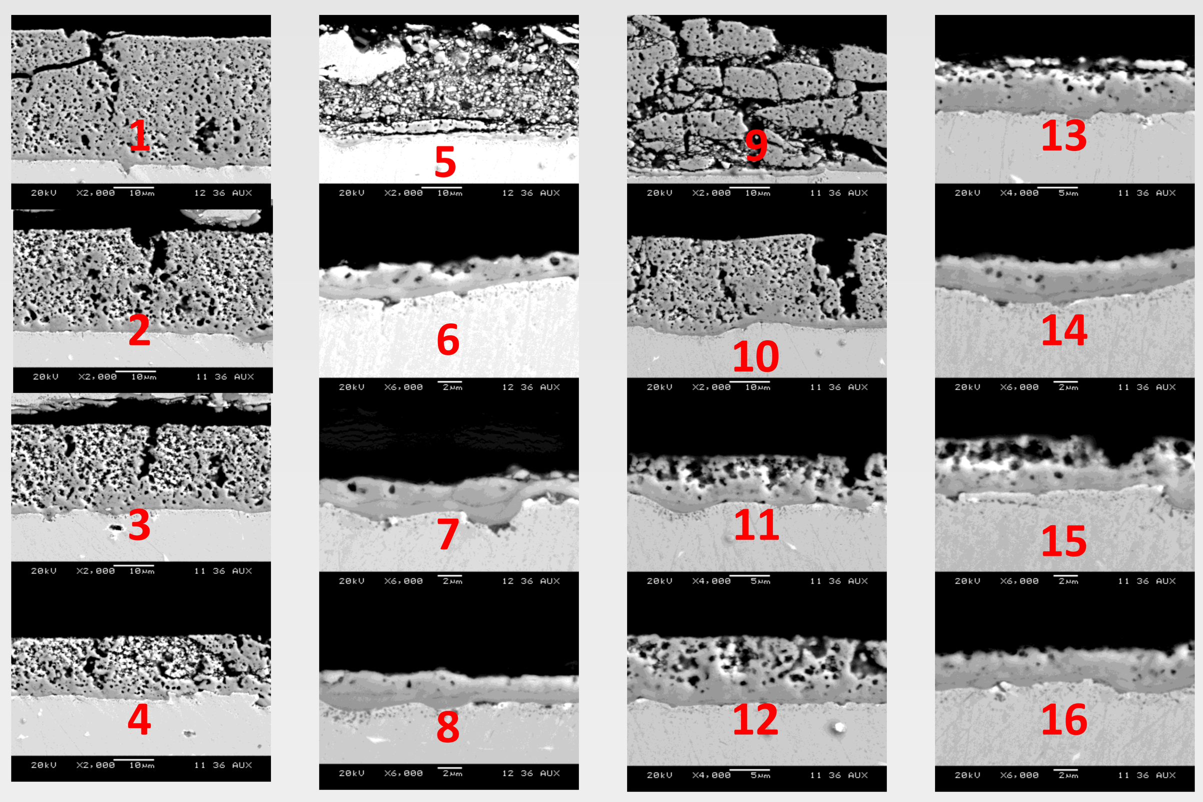
## Coating Result

### Wide Mode




| Sample # | Thickness (μm) | Used material (g) | Porosity area % |
|---|---|---|---|
| 1 | 3.11 | 0.17115 | 6.87 |
| 2 | 3.31 | 0.13265 | 18.80 |
| 3 | 3.92 | 0.098 | 12.90 |
| 4 | 3.48 | 0.0903 | 7.36 |
| 5 | 12.16 | 0.1593 | 17.95 |
| 6 | 8.03 | 0.1134 | 27.88 |
| 7 | 3.52 | 0.0912 | 7.73 |
| 8 | 2.96 | 0.0771 | 2.16 |
| 9 | 5.06 | 0.13225 | 28.33 |
| 10 | 4.23 | 0.094 | 20.96 |
| 11 | 2.85 | 0.076 | 13.62 |
| 12 | 4.08 | 0.05975 | 7.47 |
| 13 | 2.62 | 0.098 | 3.77 |
| 14 | 3.78 | 0.0756 | 2.13 |
| 15 | 2.43 | 0.0564 | 6.38 |
| 16 | 3.69 | 0.0518 | 16.25 |

### Narrow Mode




| Sample # | Thickness (μm) | Used material (g) | Porosity area % |
|---|---|---|---|
| 1 | 24.43 | 0.413 | 14.12 |
| 2 | 18.92 | 0.29085 | 16.78 |
| 3 | 13.69 | 0.2058 | 21.85 |
| 4 | 11.34 | 0.1827 | 29.35 |
| 5 | 33.68 | 0.3639 | 28.29 |
| 6 | 2.35 | 0.249 | 6.10 |
| 7 | 3.21 | 0.1914 | 4.25 |
| 8 | 2.39 | 0.1551 | 0.88 |
| 9 | 22.76 | 0.28075 | 22.98 |
| 10 | 17.78 | 0.20725 | 17.84 |
| 11 | 7.49 | 0.154 | 22.68 |
| 12 | 4.10 | 0.1305 | 24.24 |
| 13 | 6.29 | 0.2238 | 9.79 |
| 14 | 3.57 | 0.1654 | 2.98 |
| 15 | 6.16 | 0.1278 | 9.68 |
| 16 | 3.21 | 0.1008 | 0.21 |

## Calculation Result

### DoE : Governing equation

**1. Larger the Better**

$$S/N-ratio(\eta) = -10\log_{10}\left(\frac{1}{n}\right)\sum_{i=1}^{n}\frac{1}{y_{ij}^2}$$

**2. Larger the Better**

$$S/N-ratio(\eta) = -10\log_{10}\left(\frac{1}{n}\right)\sum_{i=1}^{n}y_{ij}^2$$

→ Normalized

**3. Nominal the Best**

$$S/N-ratio(\eta) = 10\log_{10}\left(\frac{\mu^2}{\sigma^2}\right)$$

$$\mu = \frac{y1+y2+y3+.....+yn}{n} \qquad \sigma^2 = \frac{\sum(yi-\bar{y})^2}{n-1}$$

**Grey relational coefficient**

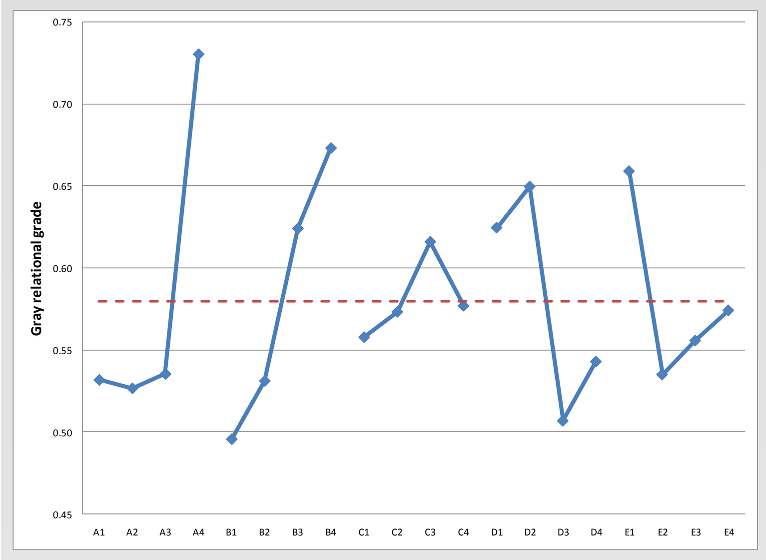
$$\gamma(y_0(k), y_i(k)) = \frac{\Delta\min + \xi\Delta\max}{\Delta_{0j}(k) + \xi\Delta\max}$$

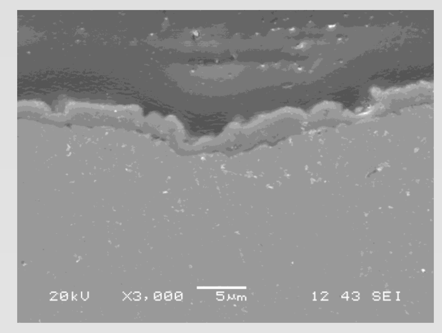
**Grey relational grade**

$$\overline{\gamma_j} = \frac{1}{k}\sum_{i=1}^{m}\gamma_{ij}$$

### Wide Mode

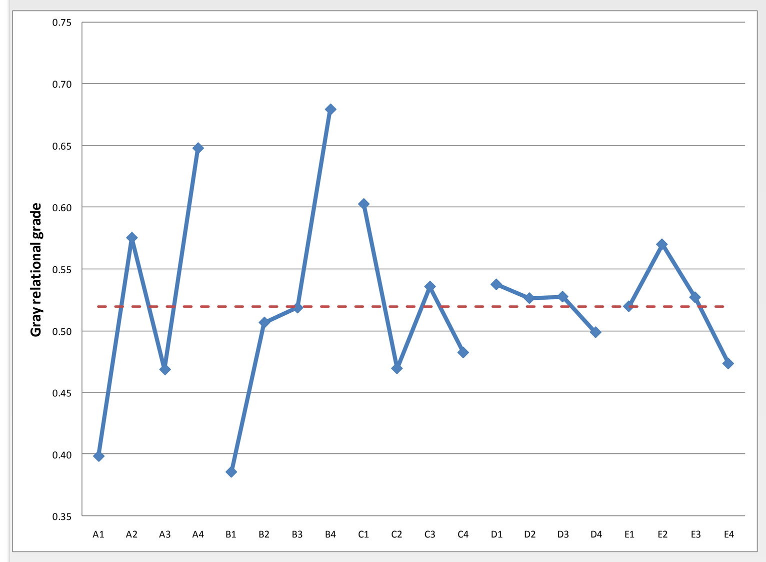
| symbol | Process Parameter | DOF | Correction Factor | sum of square | Mean square | F | Contribution percentage |
|---|---|---|---|---|---|---|---|
| A | Viscosity | 3 | 5.40 | 0.12 | 0.04 | 0.66 | 33.36 |
| B | Coating speed | 3 | | 0.08 | 0.03 | 0.45 | 22.56 |
| C | Head height | 3 | | 0.01 | 0.00 | 0.04 | 2.06 |
| D | Ink feeding rate | 3 | | 0.05 | 0.02 | 0.30 | 15.21 |
| E | Air flow rate | 3 | | 0.04 | 0.01 | 0.20 | 9.96 |
| Error | | 1 | | 0.06 | 0.06 | | 16.84 |
| Total | | 16 | | 0.36 | | | 100.00 |

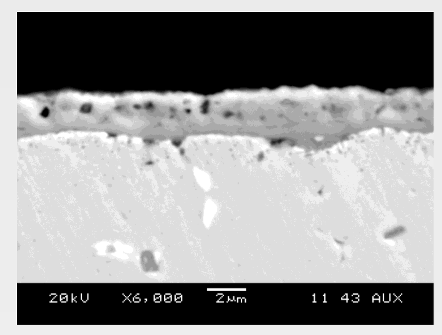


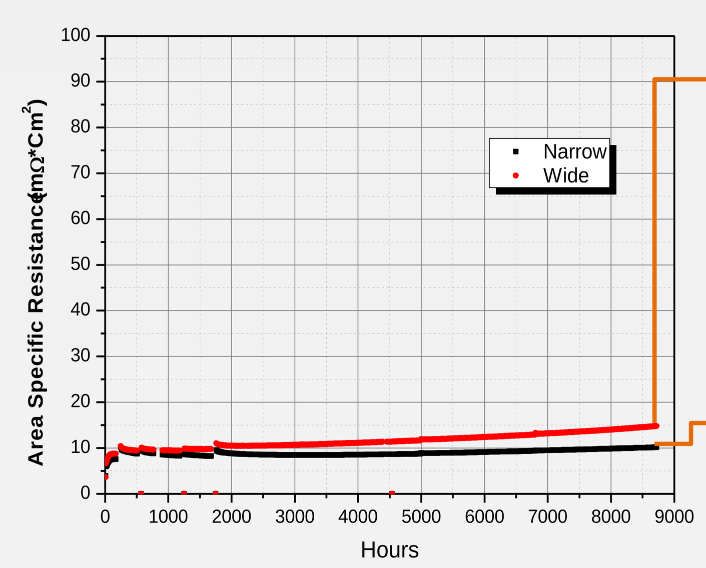
### Narrow Mode

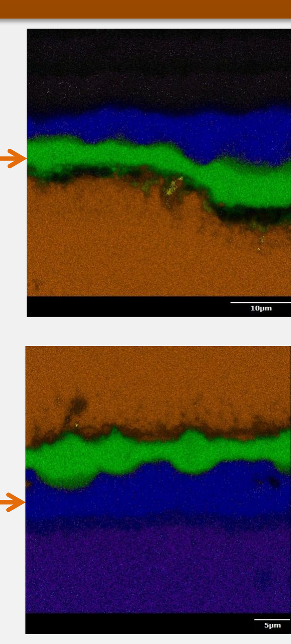
| symbol | Process Parameter | DOF | Correction Factor | sum of square | Mean square | F | Contribution percentage |
|---|---|---|---|---|---|---|---|
| A | Viscosity | 3 | 4.37 | 0.15 | 0.05 | -0.54 | 49.69 |
| B | Coating speed | 3 | | 0.18 | 0.06 | -0.64 | 58.84 |
| C | Head height | 3 | | 0.04 | 0.20 | -0.16 | 14.88 |
| D | Ink feeding rate | 3 | | 0.00 | 0.00 | -0.01 | 1.12 |
| E | Air flow rate | 3 | | 0.02 | 0.01 | -0.07 | 6.33 |
| Error | | 1 | | -0.09 | -0.09 | | -30.85 |
| Total | | 16 | | 0.30 | | | 100.00 |



## Conductivity Result

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For more information about the science you see here, please contact:
**Jung Pyung Choi**
Pacific Northwest National Laboratory
P.O. Box 999, K6-28
Richland, WA 99352
(509) 375-2120
jungpyung.choi@pnl.gov

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