Research Progress in Mechanical and Manufacturing Engineering Vol. 2 No. 2 (2021) 955-963

RPMME

Homepage: http://publisher.uthm.edu.my/periodicals/index.php/rpmme
e-ISSN : 2773-4765

A Study Review Between Ss430 and Crofer 22 Apu Solid Oxide Fuel Cell (SOFC) Interconnect After Spinel Coating Produced by Electrophoretic Deposition

Arfizan Kaha[1], **Mohd. Azham Azmi**[1*]

[1]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja,
Batu Pahat, Johor, MALAYSIA

*Corresponding Author Designation

DOI: https://doi.org/10.30880/rpmme.2021.02.02.103
Received 30 July 2021; Accepted 30 Nov. 2021; Available online 25 December 2021

Abstract: The study of multiple review on interconnect spinel coating for solid oxide fuel cell (SOFC) based on stainless steel SS 430 and Crofer 22 APU has been considered in this study. The objectives for this research are to review the fabrication method of solid oxide fuel cell through stainless steel 430 (SS430) and Crofer 22 APU as interconnect material mainly via electrophoretic deposition technique (EPD) based on previous studies and to identify the influence of applied voltage and coating duration during the process of coating as well as to advise the appropriate voltage and coating duration for the required Area Specific Resistance (ASR) value and the coating thickness for the solid oxide fuel cell (SOFC) application. In order to understand the best possible in order to achieve the requirements for interconnect SOFC, a review on previous studies has been conducted. This process is followed by characterization of coated and oxidized SS430 substrate and Crofer 22 APU substrate. These review characterization include phase analysis, surface morphology analysis, elemental distribution analysis and performance of area specific resistance (ASR). The result for this experiment show that, ss430 substrate is most suitable compare to crofer 22 apu. To increase the EPD can be examined by adding parameters to the applied voltage and time deposition.

Keywords: SOFC, Spinel Coating, EPD, Interconnect, XRD, SEM, EDS, ASR

1. Introduction

For a wide variety of power generation applications, solid oxide fuel cell (SOFC) technology has been under development. The appeal of this technology is its effective and safe electricity generation from a variety of fuels. Both solid-state construction and high-temperature operation are the primary features of the SOFC, usually between 500 and 1000 °C. The development in SOFC's manufacturing

*Corresponding author: azham@uthm.edu.my

technology has made it possible to decrease to the intermediate temperature range of 600-800 °C without affecting output. As a result, some relatively inexpensive Cr2O3 forming alloys such as ferritic stainless steel 430 (SS430) may be used as interconnects to replace costly ceramics [1].

As interconnecting materials, only special metal alloys that meet interconnection requirements can be used in terms of SOFC operating temperature. There are some benefits to the use of stainless steel in fuel cells over ceramic materials. This is linked to their elevated thermal conductivity, high electrical conductivity and ease of processing. A major factor is also the price of steel, which is around an order of magnitude smaller than the price of ceramic materials. Also dense ceramic supporting layers need to be used for the development of SOFC when dense steels are used. The inclusion of porous steel, however, offers an incentive for the use of much thinner ceramic layers and thus contributes to further cost reductions. Porous steel has similar benefits to dense steel and can well act as a mechanical basis for SOFC [2].

Essentially, this research was conducted on the basis of these problems aimed at finding the best value of deposition time and applied voltage as the parameter in maximizing the EPD process through its impact on the rate of deposition on SOFC interconnects.

2. Methodology

This chapter explains about the methodologies to prepare (MnCO)3O4 coating and the analysis conducted to determine the performances for SOFC application. The analysis conducted for the performance are by using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-Ray Spectroscopy (EDS), Dilatometer and Electrochemical Impedance Spectroscopy (EIS). For this review, the methodology of SOFC application was start from the characterization of manganese cobalt $(MnCo)_3O_4$ powder. This process consists of 3 analyse which are phase analysis, surface morphology and elemental analysis.

2.1 Fabrication of Interconnect

The electrophoretic deposition (EPD) method for the coating technique was used for the production process. This process was used to produce solid oxide fuel cell interconnects of SS430 and Crofer 22 APU stainless steel. In addition, many criteria, such as the preparation of steel substrates, the preparation of aqueous suspension and the arrangement of the EPD procedure, need to be prepared before the EPD method is carried out. To obtain the best spinel coating on the steel substrate, the preparation must be done correctly as it is necessary.

2.2 Testing and Analysis

2.2.1 Phase Analysis by X-ray Diffraction

X-ray powder diffraction is a simple technique primarily for the identification of crystalline shape and degree of crystallinity of thin film and powder. The diffraction pattern allows the composition and texture of the film's phase, desired orientation and volume of crystallite, and life of film pressure to be established. All possible diffraction directions of the lattice should be obtained by scanning the sample through a spectrum of 2 different angles due to the random orientation of the thin films. It is hard to define the crystal structure for the high symmetry crystals. The angle between x-ray incident and x-ray diffraction is 2x [3]. The equipment used are X-ray Diffraction (XRD), Bruker D8 Advances, Germany. The equipment used are shown in Figure 1.

2.2.2 Surface Morphology and Elemental Distribution Analysis by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

The scanning electron microscope (SEM) is a type of electron microscope which images the sample surface by scanning with high-emitting electrons. The electrons interacting with the atoms of

the sample produce a signal providing details about the characterization of the sample's morphology. Energy Dispersive X-ray spectroscopy (EDS) is an analytical method used for the chemical characterization or elemental analysis of a sample. The most popular addition to the SEM is the EDS. Due to the EDS system's pulse counting function, it has the ability to detect the characteristic X-ray of all elements above F in the periodic table. The equipment used for this analysis is Scanning Electron Microscope (SEM), JSM-6380 LA, Japan. Figure 2 displays the equipment used to analyze surface morphology and elemental analysis, as the same equipment is used for both studies.

2.2.3 Measurement of Area Specific Resistance (ASR) by Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy measures the area specific resistance (ASR), otherwise known as the Electrochemical Impedance Spectroscopy (EIS). EIS is an electrochemical tool for calculating a system's impedance based on the frequency of the AC potential. The equipment used for this analysis is Electrochemical Impedance Spectroscopy (EIS), Autolab PGSTAT30, Netherland. The equipment used are shown in Figure 3.

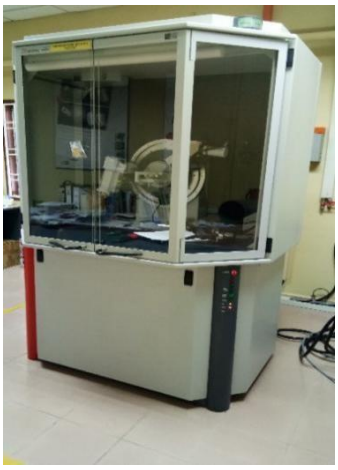

Figure 1: X-ray Diffraction (XRD), Bruker D8 Advances

Figure 2: Scanning Electron Microscope (SEM), JSM-6380 LA

Figure 3: Electrochemical Impedance Spectroscopy (EIS), Autolab PGSTAT30

3. Results and Discussion

3.1 Coated Substrate Characterization Review Analysis

3.1.1 Phase Review Analysis

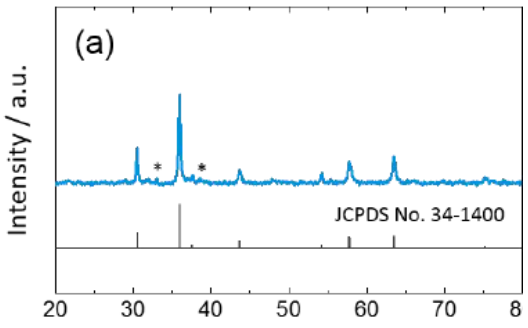

Figure 4: XRD pattern of Mn2CuO4 (Waluyo et. al., 2018)

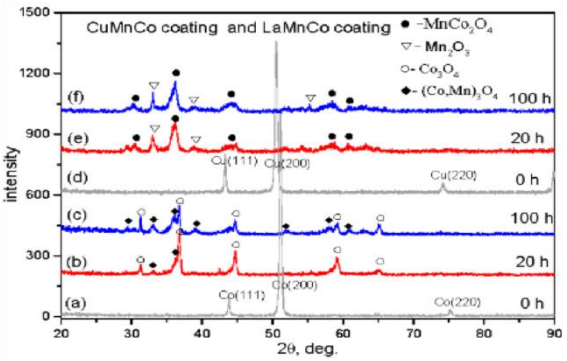

Figure 5: XRD pattern of Co-38Mn-2La and Co-33Mn-17Cu (Guo et al., 2018)

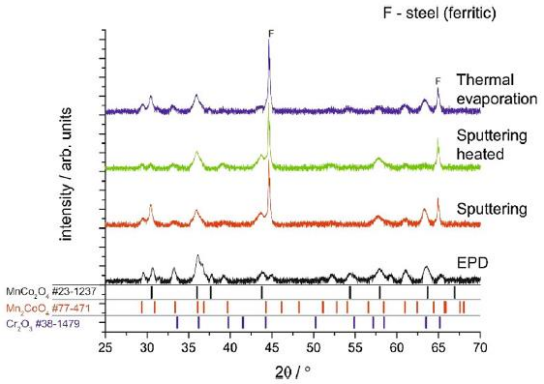

Figure 6: Electrochemical Impedance Spectroscopy (EIS), Autolab PGSTAT30

The first reference, by Waluyo et al., (2018), using Crofer 22 APU as the substrate and Mn2CuO4 as the coating material through a plasma spray without the requirement for post heat treatment. This author additionally utilised Rigaku Co.'s XRD D/MAX-3B for analytical testing. The pattern depicts the diffraction peaks associated with the cubic spinel phase of Mn2CuO4 with a space group of Fd-3m (JCPDS No. 34-1400) The XRD data of the interconnects tested for stability at 800°C in air revealed typical diffraction peaks for the spinel phase as well as Mn3O4 peaks [4]. This clearly shows that the spinel phase was recreated spontaneously during SOFC operations.

The second reference utilised SS430 as the substrate and coating materials Co-38Mn-2La and Co-33Mn17Cu. The XRD, D/MAX-3B, Rigaku Co., Tokyo, Japan, was used for the analysis. The deposition duration was 1.2 minutes and the voltage was 110 V. The XRD pattern for alloy coatings of Co-38Mn-2La and Co-33Mn-17Cu is shown in Figure 4.2. Figure 4.2 demonstrates that the alloy covering Co-38Mn-2La is basically a cubic Co structure, with peaks changing to low angles when compared to pure Co. Figure 4.2 shows the Cu characteristic peak of a Co-33Mn-17Cu alloy coating [5].

This author utilised Crofer 22 APU as the substrate and (MnCo)3O4 as the coating material for the third reference. All samples included (Mn,Co)3O4 spinel phase. The cubic MnCo2O4 and tetragonal Mn2CoO4 phases have both been discovered. Some peaks in the spectra of the EPD sample can be attributed to Cr2O3. Its summits, however, coincide with the spinel peaks. Furthermore, due to potential Cr, Mn diffusion, the peaks are somewhat displaced in relation to the reference locations. The main difference between the spectra of thin coatings and EPD coatings is the existence of a prominent alloy peak in the thin coatings, whereas this peak is very weak in the thicker EPD coating [6].

The bulk of the discovered phases, according to previous study, are of two types: cubic and tetragonal. When the settings are changed, the XRD pattern shows an increase in spinel intensity. This advancement suggests a better coating microstructure to minimise Cr poisoning from the SS430 and Crofer 22 APU substrates. As a result, the substrate is suitable for use in SOFC applications as a steel connection.

3.1.2 Surface Morphology Review Analysis

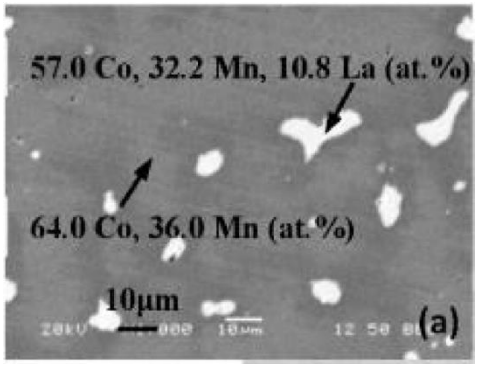

Figure 7: Surface Morphology of Co-38Mn-2La (Guo et al., 2018)

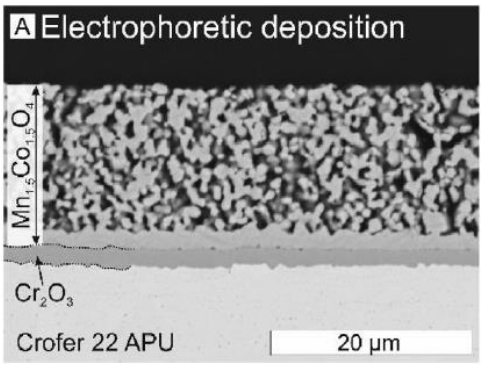

Figure 8: XRD pattern of Co-38Mn-2La and Co-33Mn-17Cu (Guo et al., 2018)

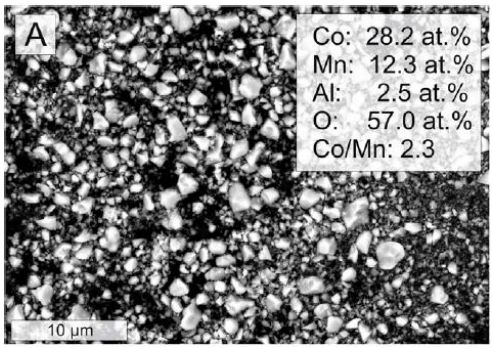

Figure 9: Electrochemical Impedance Spectroscopy (EIS), Autolab PGSTAT30

The first author utilised SS430 as the substrate, Co-38Mn-2La as the coating material, and Co-33Mn-17Cu as the coating material. The SEM, JSM-5800, JEOL, Tokyo, Japan, was used for the analysis. The deposition duration was 1.2 minutes and the voltage was 110 V. According to Figure 7, the alloy Co-38Mn-2La (electrode) is a two-phase structure composed of a solid co-based solution and a liquid La-rich solution (light phase). Continuous Co-38Mn-2La coating was produced on the surface of the substrate via metallurgical bonding, with an average coating thickness of around 30 m. Figure 7 depicts a Co-33Mn-17Cu alloy with a Co-rich phase and a Cu-rich phase [5].

Molin et al. (2017) utilised Crofer 22 APU as the substrate and (Mn,Co)3O4 as the coating material in their second reference. On the surface, the EPD coating seems porous, with well-connected granules of about 1m in size. The coatings cross sections analysis shows a 15 m Mn-Co layer with a more porous layer in the outer half. In the inner coating region, the thick layer is plainly apparent [6]. Figure 4.6 shows the typical presence of splashes and spattering particles on the top surface. There is also a continuous contact and a metallurgical connection between the coating and the substrate. There were also fine holes on the covering.

Following that, Bobruk et al. (2018) utilised Crofer 22 APU as the substrate and MnCO2O4 as the coating material. A symmetrical arrangement was used for the deposition, which was carried out at 60V for 1 minute. During heating and cooling, the ramping rates were always 120oC/h. The surface morphology of the covered substrate is seen in Figure 44. Minor densification is seen when sintered at

900°C, and the microstructure is comparable to that of "green" coatings. When sintered at 1000°C, some densification may be seen, but the covering remains porous with open holes. At 1100°C sintering, the coating densified considerably, although few fractures were detected at the chromia/spinel contact [7].

3.1.3 Elemental Distribution Review Analysis

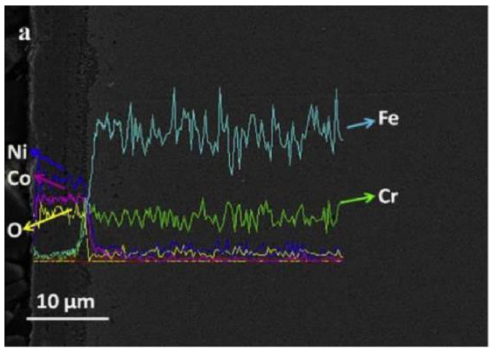

Figure 10: EDS line scan of Co-Ni-O SS430 (Cheng et al., 2017)

The substrate was Crofer 22 APU, and the coating material was Co-40Mn/Co, according to the original author [8]. The substrate samples were annealed after being sprayed with parameters 1, 7, and 9 to assess the restoration of the spinel structure. The samples were annealed at 800°C for 3 hours in normal atmosphere before being analysed for crystal structure. Mn, Fe, and Co elements were identified in the covered substrate.

Cheng et al. employed SS430 for the substrate and Co-Ni-O for the coating. EDS (X-Max, OXFORD, UK) machines were utilised, with a scanning voltage of 40kV. Figure 10 depicts Co, Ni, and O enrichment in the oxide layer. Fe and Cr are present in the substrate and decrease fast in the high O layer, which is dependent on the oxide thin higher Cr area at the interface of the oxide layer and the substrate. The Cr element diffuses outward from the steel substrate toward the surface [9].

The third reference utilised Crofer 22 APU as the substrate and MnCO2O4 as the electrophoretic deposition coating material. Element discovered Co, Mn, O, and Co when sintered at 900oC. Element discovered Co, Mn, O, and Co when sintered at 1000°C. Element discovered Co, Mn, O, Co, Cr when sintered at 1100°C. [7]. This suggests that the coated substrate can be used as a SOFC interconnect.

We can observe from the findings that a foreign element, Cr, was discovered in the EDS line. As a result, it is possible to deduce that the Cr element is present in the substrate itself. The findings from all of the references lead us to the conclusion that the purpose of protective coating is to aid in the reduction of the oxygen partial pressure at the coating or oxide contact. The existence of spinel components, however, may still be observed in the stratum.

3.2 Impedance Review Analysis

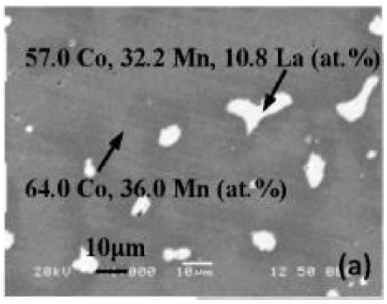

Figure 11: Surface Morphology of Co-38Mn-2La (Guo et al., 2018)

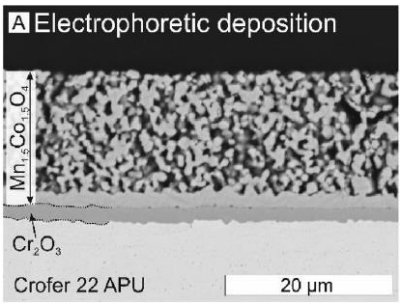

Figure 12: XRD pattern of Co-38Mn-2La and Co-33Mn-17Cu (Guo et al., 2018)

The first author utilised SS430 as the substrate and Cu/La doped Co-Mn coatings for the coating. The applied parameter was 5 V. The sample was heated to the desired temperature (500-8000 C). The ASR findings of Co-40Mn coating oxidised at 750° C for 100 h and 20 h (1 and 2), Co-38Mn-2La coating oxidised at 750° C for 100 h and 20 h (3 and 4), and Co-33Mn-17Cu coating oxidised at 7500 C for 100 h and 20 h are shown in Figure 4.27. (5 and 6). The ASR of a Co-40Mn oxide coating at 800° C is 79.2 m cm2 after 20 hours and 43.2 m cm2 after 100 hours. Obviously, the value decreases with oxidation time. The ASR of a Co-38Mn-2La oxide coating at 8000 C is 19.6 m**Ω** cm2 after 20 hours and 24 m**Ω** cm2 after 100 hours. The value progressively increases over time due to oxidation. ASR of Co-33Mn-17Cu oxide coating at 800° C is 7.5 m**Ω** cm^2 for 20 h and 41 m**Ω** cm^2 for 100 h, with the value rising with oxidation duration [5].

The following reference employed Crofer 22 APU as the substrate and CeO2-doped (Co-Mn)$_3O_4$ as the coating material. ASR tests on the basic Crofer 22 APU yielded an ASR of 24 m**Ω** cm^2. The obtained value for coating alloy (Co-Mn)$_3O_4$ is 13 m**Ω** cm^2. The ASR value obtained for the coated alloy CeO_2-doped (Co-Mn)$_3O_4$ is 8 m**Ω** cm^2. By comparing the three, the steady decline in ASR value demonstrates that the coated alloy CeO_2-doped (Co-Mn)$_3O_4$ provides importance as a protective coating by having the lowest ASR value [10].

According to Shen et al., (2019), the substrate was 430 FSS and the coating material was $MnxCo_3$-xO_4 with four distinct values of x. Figure 4.11 indicates that after 1000 hours of isothermal oxidation, the minimum ASR value of the $Mn_{1.2}Co_{1.8}O_4$ coating is 11.22m**Ω**cm^2. The ASR of the $Mn_{1.2}Co_{1.8}O_4$ coating was lowered by about 70% when compared to the bare matrix (35.02m**Ω**cm^2), demonstrating its high electrical conductivity [11].

As we can see from the preceding findings, the three interconnect investigations yielded encouraging ASR values. Thus, demonstrating that spinel coating, rather than uncoated substrate, can lower the value of ASR.

4. Conclusion

This paper reviews past research on the fabrication of SOFC stainless steel 430 (SS430) and Crofer 22 APU interconnect coatings. The primary goal of this research was to examine the best possible candidates for spinel coated interconnect based on SOFC SS430 and Crofer 22 APU substrate. EPD coating techniques are mainly used on SS430 and Crofer 22 APU steel interconnects in this investigation. Following the procedure, numerous analyses were performed to characterise the coated substrate and the oxidised coated substrate. These analyses include XRD phase analysis, SEM morphological analysis and EDS elemental analysis. The other goal was to discover the effect of voltage applied and deposition time length on coating thickness on area specific resistance (ASR) by reviewing prior studies. Based on the findings, it is possible to deduce that the parameters used create varying ASR values and coating thicknesses. The experiments done demonstrate that the goal of this

study was met when the ASR recorded had a relationship with the parameters. High voltage parameters result in a reduced ASR value, which provides high performance when used in SOFC interconnects. The most suitable substrate from this review is SS430 substrate because it can produce lower ASR compare to Crofer 22 APU.

Acknowledgement

The authors would like to thank the Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia for its support.

References

[1] Bianco, M., Tallgren, J., Hong, J. E., Yang, S., Himanen, O., Mikkola, J., & Steinberger-Wilckens, R. (2019). Ex-situ experimental benchmarking of solid oxide fuel cell metal interconnects. *Journal of Power Sources*, *437*, 226900.

[2] Puranen, J., Pihlatie, M., Lagerbom, J., Salminen, T., Laakso, J., Hyvärinen, L., ... & Vuoristo, P. (2014). Influence of powder composition and manufacturing method on electrical and chromium barrier properties of atmospheric plasma sprayed spinel coatings prepared from MnCo2O4 and Mn2CoO4+ Co powders on Crofer 22 APU interconnectors. *International Journal of Hydrogen Energy*, *39*(30), 17246-17257.

[3] Rabia, N. (2017). *Fabrication and characterization of nanostructured ceramic thin films for electrochemical studies/Rabia Naeem* (Doctoral dissertation, University of Malaya).

[4] Waluyo, N. S., Park, S. S., Song, R. H., Lee, S. B., Lim, T. H., Hong, J. E., ... & Lee, J. W. (2018). Protective coating based on manganese–copper oxide for solid oxide fuel cell interconnects: plasma spray coating and performance evaluation. *Ceramics International*, *44*(10), 11576-11581.

[5] Guo, P., Lai, Y., Shao, Y., Zhang, Y., Sun, H., & Wang, Y. (2018). Oxidation characteristics and electrical properties of doped Mn-Co spinel reaction layer for solid oxide fuel cell metal interconnects. *Coatings*, *8*(1).

[6] Molin, S., Sabato, A. G., Bindi, M., Leone, P., Cempura, G., Salvo, M., ... & Smeacetto, F. (2017). Microstructural and electrical characterization of Mn-Co spinel protective coatings for solid oxide cell interconnects. *Journal of the European Ceramic Society*, *37*(15), 4781-4791.

[7] Bobruk, M., Molin, S., Chen, M., Brylewski, T., & Hendriksen, P. V. (2018). Sintering of MnCo2O4 coatings prepared by electrophoretic deposition. *Materials Letters*, *213*, 394–398.

[8] Puranen, J. (2015). Protective Spinel Coatings for Solid Oxide Fuel Cell Interconnectors by Thermal Spray Processes: From Conventional Dry Powder to Novel Solution Precursor Thermal Spraying.

[9] Cheng, F., Cui, J., Wang, L., Li, S., & Sun, J. (2017). Performance of Co[sbnd]Ni[sbnd]O spinel oxide coating on AISI 430 stainless steel as interconnect for intermediate temperature solid oxide fuel cell. *International Journal of Hydrogen Energy*, *42*(17), 12477–12484.

[10] Zhu, J. H., M. J. Lewis, S. W. Du, and Y. T. Li. 2015. "CeO2-Doped (Co,Mn)3O4 Coatings for Protecting Solid Oxide Fuel Cell Interconnect Alloys." Pp. 179–84 in *Thin Solid Films*. Vol. 596. Elsevier B.V.

[11] Shen, Z., Rong, J., & Yu, X. (2019). MnxCo3-xO4 spinel coatings: Controlled synthesis and high temperature oxidation resistance behavior. *Ceramics International*.