



Short communication

Solid oxide fuel cell with compositionally graded cathode functional layer deposited by pressure assisted dual-suspension spraying

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ABSTRACT

In this work, the benefit of compositionally grading a cathode functional layer (CFL) for solid oxide fuel cells (SOFCs) is explored. Cells are prepared wherein either a standard cathode functional layer (SCFL) or a linearly compositionally graded cathode functional layer (CGCFL) is placed between the cell electrolyte and cathode current collecting regions. The electrochemical performance of these cells is compared with a SOFC cell containing no CFL. All cells are fabricated using a pressurized dual-suspension spraying system. Electrolytes, cathode functional layer, and cathode current collecting materials are deposited on a powder compacted anode support. SEM and EDAX area maps are taken to study the resulting micro-structures and to verify that the desired CFL profiles are produced. The EDAX area map verifies that a compositionally graded CFL and a SCFL are obtained. The cells are analyzed using impedance spectroscopy to evaluate the electrochemical performances of each cell. The open circuit voltage (OCV) and peak power densities of all three cells are 1.04 V with 80 mW cm⁻², 1.12 V with 108 mW cm⁻², and 1.08 V with 193 mW cm⁻² at 850 °C for the SCFL cell, the cell without a CFL, and the compositionally graded CFL cell respectively. The results show that this approach is a viable means for producing SOFC functional layers with unique composition and interfacial properties.

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1. Introduction

Solid oxide fuel cells (SOFC) are a branch of fuel cells characterized by the use of a solid ceramic material as an electrolyte. Yttria stabilized zirconia (YSZ) is a common ceramic electrolyte choice and becomes ionically conductive at high temperatures ranging from 600 °C to 1000 °C [1]. It is well known that SOFC's are highly efficient at converting chemical energy into usable electrical energy. However, high operating temperatures limit the applications of SOFC and increase the cost to operate. Mogenson et al. [2] set out a list of important requirements for SOFC electrodes to make them more economically feasible. Two of these requirements were to lower the operating temperature and increase the power density. It has been shown that SOFC microstructure and processing techniques are factors in bringing down the operational temperature [3]. Processing of the cathode has shown to have an especially strong impact on SOFC performance. Cathode process-

ing parameters including layer thickness, composition, application methodology, and firing temperature are all factors impacting electrochemical performance [4]. Jorgensen et al. showed how lowering the sintering temperature of the cathode decreased the polarization resistance but would be counteracted by an increase in series resistance [5]. The polarization resistance on the cathode side of the SOFC has been shown to improve by the addition of a cathode functional layer (CFL) composed of the cathode and electrolyte material [6–8]. Specifically, the promotion of triple phase boundaries is critical to ensure effective oxygen reduction kinetics and high electronic conductivity [9]. Further polarization resistance reduction has been shown by compositionally grading the cathode with multiple discrete layers [10]. Computer modeling has also indicated that grading the CFL should increase the oxygen reduction rate [11]. The CFL helps in the matching of the coefficients of thermal expansion (CTE), provides an increase in reaction sites or triple phase boundaries (TPB) and prolongs the life of the fuel cell by decreasing the overall polarization resistance [12]. The composite layer can be applied using the methods of tape casting, dip coating, screen printing and ink jet printing, though these approaches do not readily permit the compositional grading of cell layers [13–16]. Grading of the CFL has been accomplished by screen printing three compositionally different CFLs onto the electrolyte. This type of grading results in an increased number of discrete CFL layers wherein the

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additional interfacial regions introduced can result in an increase in electrochemical series resistance [17]. Plasma spraying has been shown to be cost effective and efficient at depositing a graded composite layer using dual sources of feed stock [18–20]. Combustive CVD processes have achieved gradation in both composition and microstructure but this approach is difficult to scale up to levels required for low-cost manufacturing [21]. Pressure atomized spray is one approach for low-cost production and should allow the potential for greater control of cell porosity and composition [22,23].

2. Experimental

In this research, the pressure assisted atomization approach is modified to allow two homogenous ceramic containing inks to be proportionally combined to form a compositionally varying heterogeneous ink. Compositional grading of the CFL is accomplished by the use of a 6 wt% Sr-doped LaMnO₃ (LSM) and 22 wt% Y₂O₃-stabilized ZrO₂ (YSZ) solids loaded ink. These inks can be proportionally mixed in situ to vary the composition of the spray cone during deposition onto the substrate. In this research, a thin 15 μm electrolyte made of YSZ is initially deposited onto a bisque fired anode substrate and subsequently sintered. This is followed by the deposition of a 15 μm CFL and 10 μm LSM cathode layer. The standard cathode functional layer (SCFL) is sprayed down onto the electrolyte with a constant 50/50 vol% LSM/YSZ ink flow rate. The compositionally graded CFL (CGCFL) is sprayed down onto the electrolyte starting with a ratio of 50/50 vol% ink flow rate and ending in a ratio of 100/0 vol% ink flow rate. The objective of this effort is to quantify the relative benefits of a compositionally graded CFL, SCFL, and no cathode functional layer (NCFL) deposited by the novel pressurized dual suspension spraying system.

2.1. Fabrication of anode substrate

In this research the anode supported solid oxide fuel cell design was chosen. Structural anodes substrates were fabricated using traditional powder processing techniques. A base powder was prepared for the fabrication of the anode substrates with a combination of 55 wt% Nickel Oxide (Aldrich) and 45 wt% TZ-8Y (YSZ, Tosoh-Zirconia). The base powder was ball milled in ethanol for 24 h to ensure even distribution of both materials. The ethanol was decanted and the powder was allowed to dry. Carbon powder was added to the base powder as a pore-former (5 wt%). The combined powder was ball milled in a glass bottle for 24 h with 3 mm diameter zirconia balls and ethanol. The ethanol was decanted and the cermet was allowed to dry out. The dry cermet powder was placed into an oven at 800 °C for 1 h. The dried cermet was broken into clumps and sifted with a 50 mesh sieve. The powder was measured out in 2 g amounts and dry-pressed in a 1.25 in diameter die (4 metric tons). The green substrates were subsequently bisque fired in air at 900 °C for 1 h. No reduction in size occurred during the bisque firing.

2.2. Ink preparation

The inks used in this experiment were tailored to have low viscosity with moderate particle loading. The LSM ink was fabricated by mixing 2.5 g LSM, 0.393 g polyvinyl butyral, 0.393 g butyl benzyl phthalate, and 0.393 g polyalkylene glycol in 50 ml of ethanol and ball milled for 24 h. YSZ ink was fabricated by mixing 11.8 g Tosoh-Zirconia TZ-8Y, 0.393 g polyvinyl butyral, 0.393 g butyl benzyl phthalate, and 0.393 g polyalkylene glycol in 50 ml of ethanol and ball milled for 24 h.

2.3. Spraying system

Deposition of the cathode, electrolyte, and compositionally graded CFL was accomplished by spraying a pressure-assisted atomized mist onto a rotating anode substrate. The composition of materials in the atomized mist was controlled to allow each material to be deposited either separately or as a mixture. The composition of the deposition mist was controlled using a Harvard33 dual syringe pump having two independently computer controlled syringe pumps. The pumps provided the ink to a pneumatic spray deposition nozzle (Central Pneumatic). Lab-View was utilized to control the composition of the atomized mist in order to deposit the electrolyte, compositionally graded CFL and cathode. The algorithm that controlled the compositionally graded CFL follows Eq. (1) given by Deseure et al. [11].

$$\varepsilon_a = \frac{x}{L} \Delta \varepsilon_a + \frac{2\bar{\varepsilon}_a - \Delta \varepsilon_a}{2} \quad (1)$$

Eq. (1) gives the volume fraction of YSZ ε_a at thickness x while L is the total layer thickness, as determined by deposition time. The Lab-View program used the input factors of total deposition time and combined maximum flow rates to determine the percentage of flow to each syringe over the course of the deposition. As shown in Eq. (1), the distribution of the volume fraction of YSZ ink was programmed to follow a linear deposition.

2.4. Fabrication of SOFC unit cells

The substrates consisting of the anode and electrolyte were co-sintered. The samples were held for 3 h at 1400 °C to allow the electrolytes to densify. The sintering of the substrates resulted in a 20% reduction of volume. The electrolyte side of the sintered substrate was then masked, allowing only 1 cm² circle of area to be exposed. The CFL was deposited over the mask and allowed to dry at room temperature prior to the deposition of the cathode layer. Once the cathode was dry, the mask was removed from the SOFC and subsequently sintered in air. The cells were sintered using a ramp rate of 10 °C min⁻¹ up to 900 °C changing to 2 °C min⁻¹ up to 1200 °C. The cells were held at 1200 °C for 2 h. This was followed by a slow cool of 5 °C down to 900 °C and then cooled, unimpeded, to room temperature.

2.5. Cell preparation and testing

A 15 cm silver wire was formed into a W-shaped collector and attached to the cell using silver paint (Ted Pella inc. Leitsilber 200). The two leads coming off the W shaped silver wire were secured to the cell surface with ceramic glue (Aremco ultra temp 516). The process was repeated for both sides of the cell. Once the ceramic paste cured the cell leads were twisted onto 50 cm silver wires and the twisted connections were coated with silver paint for increased strength and conductivity. The cell was attached to an alumina tube of 2.54 cm diameter using ceramic glue and allowed to cure at room temperature for 4 h. The cell was placed in the test station at room temperature. Cell reduction was accomplished in 5% hydrogen and 95% argon at 650 °C for 24 h prior to testing (1 °C min⁻¹ ramp, 5 cc min⁻¹). Prior to testing, the cell was equilibrated for 2 h at 650 °C in pure hydrogen with a flow rate of 20 cc per minute. After allowing the cell to equilibrate, electrochemical impedance spectroscopy (EIS) was performed using an EG&G model 274 potentiostat. Each cell was tested over five temperatures: 650, 700, 750, 800, and 850 °C. The polarization curves were collected from 0.0 V to 1.0 V at 0.1 V per minute in order to allow for cell equilibrium between current collections. Nyquist plots were collected from 0.1 Ω to 100 kΩ at open circuit voltage. After each cell was tested they were examined in cross-section by SEM (JEOL 7401-

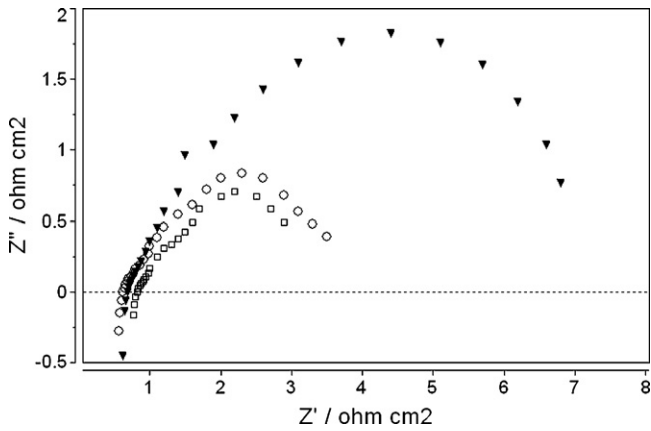


Fig. 1. Impedance spectra of SOFC unit cells at 850 °C with different CFL schemes (CGCFL: □; SCFL: ○; NCFL: ▼).

FE-SEM) and subsequently EDS area-mapped (Ametek EDAX unit operated by Genesis 5.1 software).

3. Results

It is well known that exchange current density or kinetic performance can be improved by increasing the number of possible reaction sites (i.e., increase the reaction interface roughness) per unit area. Increasing the functional surface area is typically done by the addition of a CFL between the electrolyte and cathode. In this research a SOFC with a compositionally graded CFL was compared to a cell with a SCFL and one with NCFL to quantify the relative benefit of a compositionally graded cathode functional layer deposited via the pressurized duel suspension spraying technique.

3.1. Electrochemical analysis of I–V and EIS

Electrochemical analysis was performed on each SOFC design to identify the relative cell performances. The EIS Nyquist plots in Fig. 1 show an example of the EIS results for each of the three disparate profiles at 850 °C and illustrate the origins of the proposed polarization and ohmic resistances. The Nyquist plot is subdivided into two regions that correlate to the ohmic, and polarization resistances. On the left side of the Nyquist plot is the high frequency intercept. The difference between this point and the imaginary-axis represents the inherent ohmic resistances of the system, and is referred to as the area-specific ohmic resistance (ASOR). The polarization resistance, causing polarization losses under operation, corresponds to the semicircles limited by the high frequency and low frequency intercept of the impedance spectrum with the real axis in the Nyquist plot. The NCFL cell has the largest polarization resistance. The compositionally graded CFL has the lowest polarization resistance, suggesting that it has improved electrochemical performance over the other two cells.

Table 1 gives the ASOR and polarization resistance as a function of temperature for all three cells. The ASOR of the cells decreased

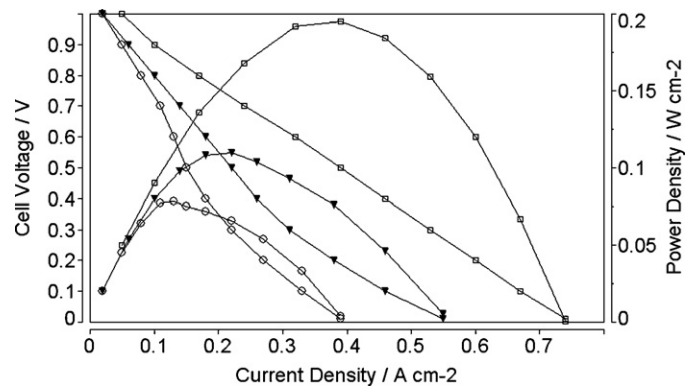


Fig. 2. I-V curves and current-power density curves of SOFC unit cells with different CFL schemes at 850 °C having open circuit voltage and peak power densities of 1.08V/193 mW cm⁻², 1.12V/108 mW cm⁻², and for the 1.04 V/80 mW cm⁻² CGCFL: □; NCFL: ▼; and SCFL: ○ respectively.

from 650 °C to 850 °C. At 650 °C the SCFL and CGCFL had larger ASOR than the NCFL but all three cells had comparable ASOR at 850 °C. The reduction in the ASOR of the cells is associated with an increase in conductivity of YSZ as the temperature increases. The EIS data suggests that the addition of a cathode functional layer adds to the ASOR during low temperature operation. The increased resistance due to the addition of the CFL is most likely a result of the portion of the layer that is below the percolation threshold. Despite the increase in the ASOR (due to the addition of a CFL) the overall polarization resistance appears to decrease even at low temperatures.

Fig. 2 shows I–V and power density curves of the SOFC cells with different CFL schemes at 850 °C. The SOFC with the compositionally graded CFL had the highest power density of 193 mW cm⁻². The decrease of resistance leading to the best performance is due to the fact that graded composition follows the divergence of current from the electronic percolating network to the ionic one while approaching the CFL/electrolyte interface. While the reaction takes place along the electrode thickness, the electronic current is converted progressively into ionic current; the change in composition reduces the polarization resistance of the cathode through the decrease of the current density in the dominating transport medium.

The SOFC with the SCFL had the lowest power density of 80 mW cm⁻². This is associated with the poor ionic/electronic conduction of the SCFL deposited in this research. Despite having been deposited with a 50/50 vol% ink flow rate, the actual powder loading of the inks resulted in close to a SCFL having a 21% volume fraction of LSM solids. According to Chen et al., using powders with approximately the same radius requires at a minimum, a 30% volume fraction of LSM to be above the percolation threshold of a LSM/YSZ composite [24]. Furthermore, when comparing the EIS and I–V graphs, it becomes apparent that an anomaly occurs in the data of the SCFL. The EIS data shows a lower polarization resistance in the SCFL when compared to the NCFL while the I–V graph shows the NCFL having a higher power density. This result requires further investigation.

Table 1

Contribution of charge transfer resistance (CTR) and area specific resistance (ASOR) as a function of temperature at OCV.

Temperature (°C)	NCFL		SCFL		CGCFL	
	CTR (Ω cm ⁻²)	ASOR (Ω cm ⁻²)	CTR (Ω cm ⁻²)	ASOR (Ω cm ⁻²)	CTR (Ω cm ⁻²)	ASOR (Ω cm ⁻²)
650	–	0.96	–	1.47	15.4	1.7
700	–	0.85	–	1.06	9	1.43
750	–	0.76	13	0.82	5.4	1.18
800	22	0.7	8	0.7	3.4	1.06
850	7	0.7	3.5	0.61	3.2	0.81

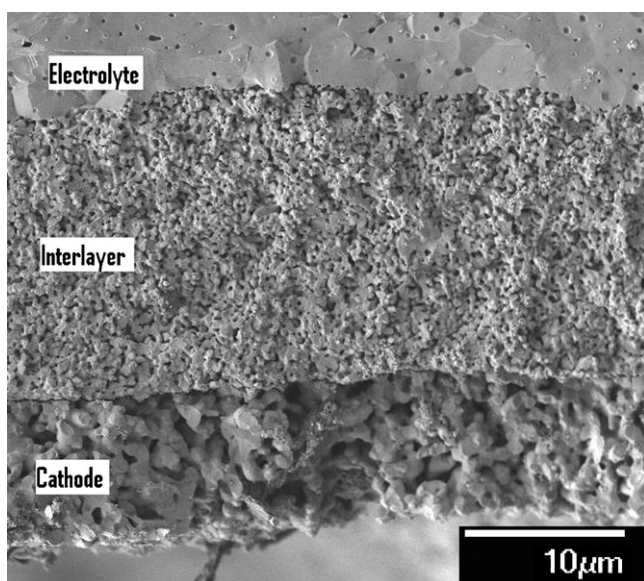


Fig. 3. SEM photograph of SCFL showing a discrete CFL and cathode.

Finally, it should be noted that the sprayed layers in this work were not optimized for overall cell performance, which is evident in the relatively high overall polarization losses and ohmic losses in comparison to state-of-the-art SOFC data. Along with the lack of optimization some of the processing steps used may have induced silicon contamination through ball milling and furnace materials which has been shown to limit electrochemical performance [25]. Furthermore the slight variations in the OCV could be the result of fuel crossover either via cracks in the electrolyte layer or the ceramic sealing.

3.2. Analysis of SEM images

Figs. 3 and 4 show the SCFL and compositionally graded CFL respectively, capturing the cross-sectional microstructure of the cathodes, CFL's, and electrolytes, as deposited by the pressurized dual-spraying system onto the anode substrates.

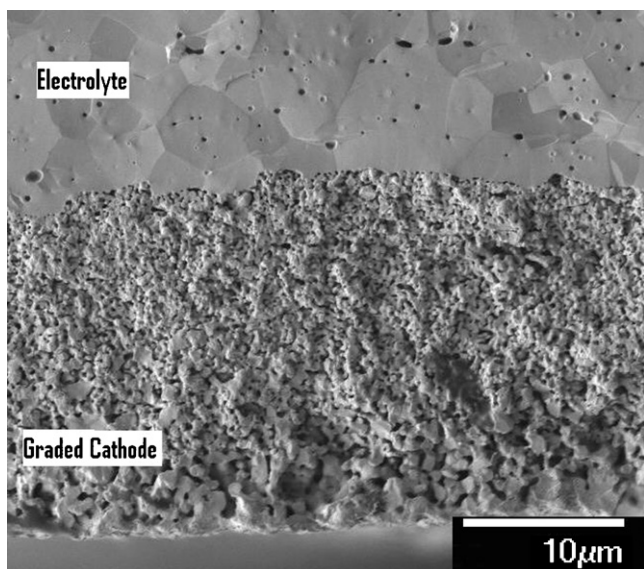


Fig. 4. SEM photograph of CGCFL showing compositional gradation of the CFL and cathode.

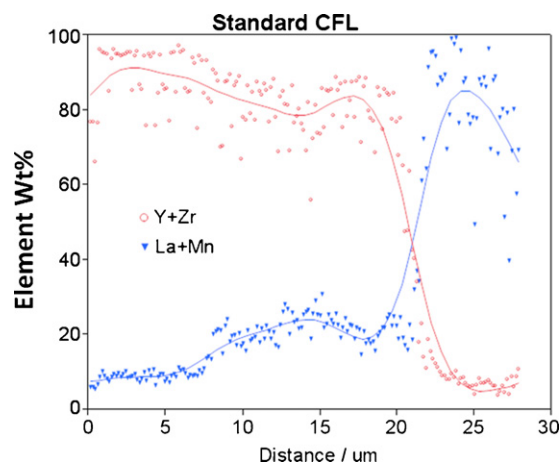


Fig. 5. X-ray count intensities profile plot showing Zirconium: ○ and Manganese: ▼ of SOFC cell having a SCFL. Each point is summed and normalized from an EDAX 256×200 ($38 \times 30 \mu\text{m}$) area map. The cathode is located at 0–5 μm , and the SCFL is located at 5–20 μm on the x-axis. The electrolyte is located beyond the 20 μm on the x-axis.

It can be seen in Fig. 3 that the SCFL has two discrete interfaces (electrolyte–CFL and CFL–cathode) while the compositionally graded CFL in Fig. 4 only has one discrete interface located at the electrolyte. The compositionally graded CFL's lack of a discernable interface between the cathode and the CFL implies that continuous gradation has occurred. As both samples were physically cleaved to expose the micro structure for SEM analysis, only the SCFL appears to have delaminated at the cathode and CFL interface. This was the case for multiple SCFL cells, and locating an intact cell displaying a cathode layer during microscopy was challenging. This was not the case for the compositionally graded CFL. The compositionally graded CFL's increased physical resilience to delamination may be a result of having a better interconnected micro structure at the graded interface.

3.3. Analysis of EDAX image plots

In order to attempt a limit quantification of the compositionally graded profile, energy dispersion spectroscopy analysis (EDS) area maps were made. The EDAX area maps were taken over a resolution of 256 (pixel width) by 200 (pixel depth) where one pixel represented a surface area of $0.014 \mu\text{m}^2$. The elemental weight percents of each pixel was recorded as a numerical value and summed along its respective row. The average elemental weight percent was plotted as a function of depth into the SOFC. Figs. 5 and 6 show EDS plots of the elemental weight percent of the SCFL and compositionally graded CFL, respectively, as a function of distance from the electrolyte to the cathode.

The composition plot of the SCFL cell shown in Fig. 5 indicates a slight increase in the La + Mn wt% at approximately 7 μm . This identifies the interface between the electrolyte and the SCFL. The plot shows the elemental wt% of La + Mn accounts for approximately 20 wt% of the SCFL. At approximately 22 μm there is a rapid increase in the La + Mn wt%. This indicates the interface between the SCFL and the cathode.

The composition plot in Fig. 6 of the compositionally graded CFL cell shows a trend of slightly increasing La + Mn wt% starting at approximately 10 μm . This trend continues until approximately 18 μm where there is a sharp knee in the plot. The knee indicates a complex phenomenon and may have occurred during the sintering process. The wt% distribution of the constituents in the compositionally graded CFL indicates the potential of linear deposition by this method. The EDS area mapping looks to be useful tool in future

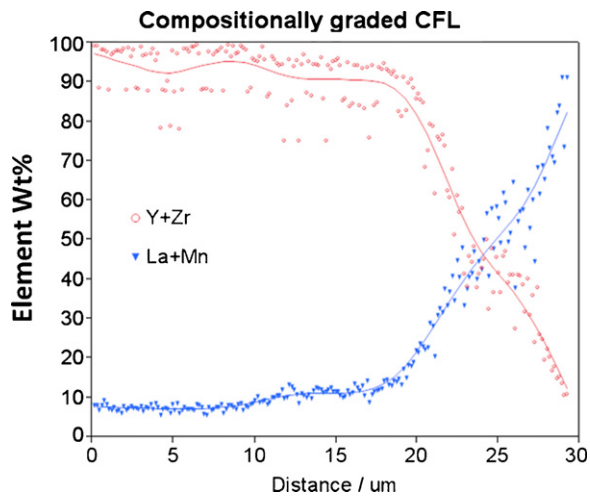


Fig. 6. X-ray count intensities profile plot showing Zirconium: ○ and Manganese: ▼ of SOFC cell having a CGCFL. Each point is summed and normalized from an EDAX 256×200 (38×30 μm) area map. The cathode is located at 0–5 μm, and the CGCFL at 5–20 μm on the x-axis. The electrolyte is located beyond 20 μm on the x-axis.

work to correlate cell performance with deposition concentration profiles as a function of CFL thickness.

4. Discussion

In this research, a compositionally graded CFL was fabricated based on the model proposed by Deseure et al. In this model, Deseure et al. sought to determine the effects of the volume fraction distribution of YSZ through compositionally graded CFL linearly with respect to thickness. The model predicted that charge transfer resistance is reduced due to enlarging the LSM-YSZ intimate contact cross-sectional area. In this research, Fig. 4 shows that a comparable linear distribution of YSZ occurred. The results of the impedance analysis verify that the compositionally graded CFL showed improvement over the other two cells, supporting the conclusions drawn by Deseure et al. Heart et al. [8] fabricated SOFCs with varying levels of graded cathode functional layers using screen printing. Three of the four cells that were fabricated by screen printing in Harts' research are comparable to the three cells fabricated in this study. Hart et al. concluded that overall polarization resistance decreased as the level of grading increased. In regard to polarization resistance, the results of this research were consistent with Hart's findings. It was also concluded that the 20/80% LSM/YSZ respectively, layer should be avoided due to poor electronic conductivity as it's below the percolation limit of LSM and effectively adds thickness to the electrode. In this research the LSM content for the SCFL was 21 vol% and may have contributed to the increased series resistance mentioned by Hart et al. As the number of layers of screen printing increases so does the cost and complexity of fabrication making it difficult to scale up. By implementing the novel pressurized dual suspension spraying system, complex fabrication of graded cathode functional layers can be reduced to a single deposition step while avoiding multiple interfaces.

5. Conclusion

Solid oxide fuel cells with NCFL, a compositionally graded CFL and a SCFL between the cathode and electrolyte were built using a pressurized dual suspension spraying system. The EIS data showed that the addition of the compositionally graded CFL or the SCFL increased the ASOR, but was overall effective at reducing the polarization resistance when compared to the NCFL cell. The IV data

indicates that the SCFL may have suffered from poor conductivity, possibly due to a lack of optimization i.e. ratio of YSZ to LSM. The compositionally graded CFL outperformed both of the other cells in power density. The SEM images of the compositionally graded CFL clearly showed the lack of a discreet interface between the cathode and CFL, possibly contributing to improved interfacial contact with the cathode. The data in this work supports previously reported evidence that continuously graded CFLs can improve SOFC performance. In addition, this paper demonstrates that an inexpensive and easily scalable deposition system can be used to produce a viable SOFC with a compositionally graded CFL.

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