Nano-Ceria Pre-Infiltration Improves $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ Infiltrated Solid Oxide Fuel Cell Cathode Performance

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Abstract

Here, scanning electron microscopy, X-ray diffraction, and thermo-gravimetric analysis experiments show that the pre-infiltration of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) nano-particles reduces the average size of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ (LSCF) produced from the subsequent infiltration of precursor nitrate solutions containing the surfactant Triton X-100 or the chelating agent citric acid. In contrast, GDC pre-infiltration has no effect on the average size of LSCF particles produced from precursor solutions containing only lanthanum, strontium, cobalt, and iron nitrate. Consistent with the observed particle size trends, electrochemical impedance spectroscopy measurements show that GDC pre-infiltration improves the performance of Triton X-100 Derived (TXD) LSCF-GDC cathodes and Citric Acid Derived (CAD) LSCF-GDC cathodes, but has no effect on the performance of Pure Nitrate Derived (PND) LSCF-GDC cathodes. In particular, TXD LSCF-GDC cathodes with more than ~5 vol% of GDC pre-infiltration display average LSCF particle sizes of 21 nm and open-circuit polarization resistance values of $0.10 \text{ } \Omega\text{cm}^2$ at 540°C , compared to 48 nm and 640°C without GDC pre-infiltration. Results suggest that this

100°C reduction in cathode operating temperature is caused solely by LSCF particle size reductions. 7.4 vol% GDC pre-infiltrated TXD LSCF-GDC cathodes also display lower 540°C degradation rates than conventionally infiltrated PND LSCF-GDC cathodes.

Keywords: Solid Oxide Fuel Cell; Infiltration; Composite; Nano-particle; Degradation; Stability

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1. Introduction

Over the past decade many researchers have used the infiltration method to produce nano-particle-enabled Solid Oxide Fuel Cell (SOFC) cathodes with high-performance at low SOFC operating temperatures [1-3]. Of these, cathodes with mixed ionic electronic conducting (MIEC) nano-catalyst infiltrate particles atop porous ionic conducting (IC) scaffolds have displayed some of the best performance [4-6]. In particular, lanthanum strontium cobalt iron oxide-gadolinium doped ceria (LSCF-GDC) nano-micro-composite cathodes (NMCCs) have achieved polarization resistance (R_p) values of $\sim 0.1 \Omega\text{cm}^2$ at temperatures as low as 575°C [6]. In these NMCCs, the SOFC cathode reaction:

is facilitated by a high MIEC electronic conductivity that promotes electron (e') transport from the current collectors to the MIEC infiltrate surfaces (providing the first Eqn. 1 reactant) [7], an open porosity that promotes oxygen gas ($O_{2(g)}$) transport from the atmosphere to the MIEC infiltrate surface (providing the second Eqn. 1 reactant) [1-3], and a high IC scaffold oxygen ion conductivity that promotes oxygen vacancy ($V_O^{\bullet\bullet}$) transport from the electrolyte to the MIEC infiltrate surface (providing the third Eqn. 1 reactant) [8]. A high MIEC oxygen surface exchange chemical rate coefficient (k_{chem}) that catalyzes Eqn. 1 [9], a high **MIEC** characteristic thickness ($L_C = D/k$) that ensures Eqn. 1 occurs over the entire **surface of individual** MIEC infiltrate **particles** [10], and a nano-sized MIEC infiltrate that provides a large surface area for Eqn. 1, also contribute to good infiltrated cathode performance.

Unfortunately, it has been difficult to control average infiltrate particle size using the conventional infiltration approach of 1) dissolving MIEC precursor nitrates in water, 2)

infiltrating the MIEC precursor nitrate solutions into porous IC scaffolds, and 3) thermally decomposing gelled infiltrate solutions to form oxide MIEC nanoparticles. For instance, the average size of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ (SSC) infiltrate within doped ceria scaffolds have ranged from 40 nm to 100 nm for studies utilizing identical heating rates, firing temperatures, firing times, and nominally identical infiltrate compositions [11-13]. Similar average particle size variability has been observed for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [11] and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ [14, 15] infiltrate processed under identical heating rates, firing temperatures, firing times, and nominally identical infiltrate compositions. Despite these similar processing conditions, one potentially significant difference between these studies is that some have utilized the amphiphilic surfactant Triton X-100, some have utilized the chelating agent citric acid, and some have not utilized any organic precursor solution additions whatsoever.

Organic precursor solution additives have a long history of impacting the phase purity and/or size of multi-cation oxide particles produced from the thermal decomposition of precursor solutions. One common method for the production of high phase purity multi-cation oxide SOFC materials is the use of chelating agents via the Pechini method [16-18]. In this modified sol-gel process, chelating agents such as citric acid or ethylenediaminetetraacetic acid (EDTA) deprotonate, in the process complexing with solution cations. In the traditional Pechini process, the solution is then converted into a gel through a chelate polyesterification reaction when heated with a polyhydroxy alcohol (commonly ethylene glycol) before being fired at high temperature to produce a multi-cation oxide. Alternatively, many studies aimed at producing NMCCs have utilized a simplified Pechini method which eliminates the polyhydroxy alcohol and relies upon

solvent removal alone to gel the solution [19-23]. Despite the success of these Pechini-based methods in improving oxide phase purity, it is generally acknowledged [24] that it is difficult to control the size and shape of the resulting oxide particles.

Another method for the production of high phase purity multi-cation SOFC materials is through the use of precursor solution surfactants. With the correct combinations of surfactant, polar solvent, and nonpolar solvent, SOFC precursor solutions have been shown to self-assemble into polymer mesostructures (such as micelles) that prevent cation segregation, improve phase purity, and reduce the size of the multi-cation oxides formed through the addition of precipitating agents [25-27]. Unfortunately, the difficulty in mixing self-assembling precursor solutions with precipitating agent solutions inside porous scaffolds has prevented this traditional approach from being utilized in the production of NMCCs. Instead, many NMCCs studies have relied upon solvent removal to convert surfactant-containing precursor solutions into gels that are then fired to produce high phase purity multi-cation oxides [11, 28, 29]. However, the exact role of surfactants play during infiltration, gelation, and firing remains debatable. Evaporation-induced self-assembly (EISA) of surfactant-laden gels has been observed in TiO_2 gels [30, 31] and this mechanism has been claimed to contribute to the formation of nano-sized, high-phase-purity SOFC particles [32, 33]. However, other studies have argued that surfactant self-assembly does not occur during typical NMCC fabrication [34] and instead have argued that surfactants act by reducing solution wetting angles [34] or promoting cation intermixing through surfactant-cation complexing [3, 11, 35]. Regardless of the exact mechanism, surfactant precursor solution additions have been

shown to both increase the phase purity and reduce the size of the oxide infiltrate particles formed during NMCC fabrication [6, 13, 35].

In addition to organic solution additives, other processing variables have also been shown to alter the infiltrate particle size and/or phase purity of some infiltrate compositions. For instance, in LSCF infiltrated cathodes, faster heating rates have been found to reduce infiltrate particle size [5], and precursor solution desiccation has been found to both reduce infiltrate particle size and improve phase purity [6, 36]. Further, recent reports on SSC [4] and $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ [37] infiltrated electrodes suggest that doped ceria pre-infiltration also reduces infiltrate particle size.

In light of these past studies, the objective of present work was to characterize how nano-GDC pre-infiltration, Triton X-100 precursor solution additions, and citric acid precursor solution additions interact to determine the LSCF infiltrate particle size, the LSCF infiltrate phase purity, and the open-circuit performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (LSCF-GDC) NMCCs over time.

2. Experimental Methods:

2.1 Fabrication Methods

Cathode-supporting electrolytes were prepared in the following manner. First, 0.8 g of GDC powder was pressed to 63 MPa in a 0.75 inch steel die. This GDC powder (Rhodia; Cranbury, NJ) had a d_{50} size of 240 nm, a specific surface area of 25.2 m²/g, and an average particle size of ~32 nm. These porous pellets were then heated to 1475°C at 3°C/min, held at 1475°C for ~10 hours, and then returned back to ambient temperature at a nominal cooling rate of 3°C/min to produce electrolyte pellets with relative densities

>95%. These pellets were then sanded flat and parallel with thicknesses ranging from 430 to 480 μm using 240 grit SiC sandpaper.

Porous, well-connected GDC IC cathodes scaffolds were then screen printed on both sides of these dense GDC electrolyte pellets. To achieve this, ~20g of Rhodia GDC powder was coarsened at 800°C for 4 hours prior to being mixed with a V-737 electronic vehicle (Heraeus Circuit Materials Division; West Conshohocken, PA) to form a GDC ink with a 34% solids loading. Three layers of GDC ink were screen printed onto both sides of the dense GDC electrolyte pellets using a patterned 80 mesh stainless steel screen with a circular 0.5 cm^2 open area. After each layer deposition, the screen-printed ink was allowed to flow for 5 minutes before electronic vehicle solvent extraction in a 120°C oven. The scaffolds were then air-heated to 400°C at 3°C/min, held at 400°C for one hour, heated to 600°C at 3°C/min, held at 600°C for one hour, heated to 1050°C at 5°C/min, held at 1050°C for 3 hours, and then returned to room temperature at a nominal cooling rate of 10°C/min. Sintered IC scaffold thickness and roughness measurements were then performed with a Dektak 3 profilometer (Bruker; Tucson, AZ).

GDC precursor solutions were then infiltrated into the sintered GDC scaffolds, gelled, and fired to coat the GDC scaffold surface with nano-GDC particles. The GDC precursor solutions were prepared by dissolving 99.99% pure $\text{Ce}(\text{NO}_3)_3 \cdot 6.0 \text{ H}_2\text{O}$ and 99.99 % pure $\text{Gd}(\text{NO}_3)_3 \cdot 4.0 \text{ H}_2\text{O}$ (Alfa Aesar; Ward Hill, MA) in distilled water containing 3 wt% (weight Triton X-100/weight nitrate) of pre-dissolved Triton-X 100. (These precise nitrate water of hydration contents were determined prior to nitrate weighing by measuring the mass loss that occurred inside a Q500 thermogravimetric analyzer (TA Instruments; New Castle, DE) with heating under nitrogen up to 850°C.)

The GDC precursor solutions were then pipetted into the porous GDC cathode scaffolds, allowed to soak into the scaffold for 5 minutes, and gelled in an 80°C drying oven for 10 min. The GDC infiltrated GDC scaffolds were then heated to 700°C at 10°C/min, held at 700°C for one hour, and then returned to room temperature at a nominal cooling rate of 20°C/min. Since past infiltration studies have reported that the number of precursor solution infiltrations does not affect infiltrate particle size [11, 13], in some cases, this infiltrate-gel-fire process was repeated a second time to achieve the desired nano-GDC loading level.

Following GDC pre-infiltration, either pure nitrate LSCF precursor solutions, Triton X-100 containing LSCF nitrate precursor solutions, or citric acid containing LSCF nitrate precursor solutions were infiltrated into GDC scaffolds, gelled, and fired. Each LSCF precursor solution was prepared by dissolving 99.999% pure $\text{La}(\text{NO}_3)_3 \cdot 6.84 \text{ H}_2\text{O}$, 99.9965% pure $\text{Sr}(\text{NO}_3)_2$, 99.999% pure $\text{Co}(\text{NO}_3)_2 \cdot 5.9 \text{ H}_2\text{O}$ and 99.999% pure $\text{Fe}(\text{NO}_3)_3 \cdot 9.84 \text{ H}_2\text{O}$ (Alfa Aesar; Ward Hill, MA) in 18.2 M Ω water. (These precise nitrate water of hydration contents were determined prior to nitrate weighing by measuring the mass loss that occurred inside a Q500 thermogravimetric analyzer (TA Instruments; New Castle, DE) with heating under nitrogen up to 850°C.) No organic additives were introduced to the pure nitrate derived (PND) LSCF precursor solutions. In contrast, 3 wt % (weight Triton X-100/weight nitrate) of Triton X-100 (Sigma Aldrich; St. Louis, MO) was added to the Triton X-100 derived (TXD) LSCF precursor solutions, and 0.75 moles of citric acid (Sigma Aldrich; St. Louis, MO) per mole of metal nitrates was added to the citric acid derived (CAD) LSCF precursor solutions. For the CAD LSCF precursor solutions, ammonium hydroxide was added to raise the final solution pH

to 3. The LSCF precursor solutions were then pipetted into the GDC pre-infiltrated scaffolds, allowed to soak into the scaffold for 5 minutes, and gelled in an 80°C drying oven for 10 min, before firing. The LSCF-GDC cathodes were then heated to 700°C at 10°C/min, held at 700°C for one hour, and cooled to room temperature at a nominal cooling rate of 20°C/min. Depending upon the cathode thickness, this infiltrate-gel-fire process was repeated up to three times for the 1.5 M solutions and up to seven times for the 0.5 M solutions to achieve a LSCF loading level of 12.0 vol% (infiltrate volume divided by total cathode volume).

Lastly, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$ (LSM) –Au current collectors atop each cathode were prepared in the manner as described previously [6, 36].

2.2 Characterization Methods

Infiltrated cathode microstructure was evaluated using a Auriga Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) (Carl Zeiss Microscopy GmbH; Jena, Germany) operated with a 30 μm aperture, a 40 second scan speed, a 1.4 mm working distance, and 20 kV beam voltage. Infiltrate particles were measured at the electrolyte-cathode interface from symmetric cell fracture surfaces using the Heyne linear intercept method [38], at least three micrographs per sample, and at least 35 intercepts per micrograph.

Infiltrate phase purity was evaluated by performing X-ray diffraction (XRD) analyses from $20^\circ \leq 2\theta \leq 80^\circ$ with a 1.00 second scan speed, a 0.040° step, and a copper filament using a Miniflex II (Rigaku Americas Corporation; The Woodlands, TX, USA) operated at 30kV and 15 mA. XRD-determined LSCF nano-particle sizes were

calculated using the Williamson-Hall method [39] and previously described XRD peak fitting procedures [6]. Due to LSCF XRD signal overlap with the GDC scaffold [40, 41], samples for LSCF-only XRD measurements were made outside a GDC scaffold by gelling and firing solutions on an alumina plate. For GDC pre-infiltrated LSCF XRD measurements, GDC infiltrate solutions were gelled and fired on an alumina plate before LSCF solution was infiltrated into the nano-GDC, gelled and fired. High and low Williamson-Hall particle size error bars were calculated from the 0.03 degree two-theta full width half-max variation measured using the JADE computer program (Materials Data, Inc.; Livermore, CA) by inputting the high and low full width half max two theta values, respectively, into the Williamson-Hall analysis.

Infiltrated cathode polarization resistance was evaluated by performing two-point, open-circuit Electrochemical Impedance Spectroscopy (EIS) measurements in ambient air every 50°C between 400 and 700°C using an IM6 impedance analyzer (Zahner Elektrik GmbH; Kronach, Germany). Impedance measurements were performed from 0.1 to 100 kHz after 30-90 minutes of thermal equilibration at each temperature. Individual cathode polarization resistance (R_p) values were determined by multiplying the EIS-measured Nyquist plot x-axis intercept separation by the 0.5 cm² geometric cathode area and dividing by two to account for the fact that each symmetric cell contained two cathodes. As done previously [6, 36], Simple Infiltrated Polarization Loss Estimation (SIMPLE) Model [11, 13, 14] R_p predictions were made using the SEM-measured average LSCF particle sizes, the cathode thickness, the LSCF loading level, the GDC scaffold porosity [11], the GDC scaffold column width [11], literature LSCF R_s measurements [42], and literature GDC $\sigma_{V_{O,Sc}}$ measurements [11].

As done previously [11], symmetric cell Ohmic resistivity (ρ_{ohmic}) values were determined by multiplying the high frequency Nyquist plot x-intercept resistance by the 0.5 cm^2 geometric cathode area, and dividing by the electrolyte thicknesses.

Lastly, the thermal decomposition behavior of LSCF precursor solutions infiltrated into GDC pre-infiltrated scaffolds was evaluated in air using a $10^\circ\text{C}/\text{min}$ heating rate and a Q500 thermogravimetric analyzer (TGA) (TA Instruments; New Castle, DE, USA) with a 0.01 mg mass resolution.

3. Results and Discussion

3.1 The Effect of GDC pre-infiltration on LSCF Infiltrate

Figure 1 shows schematic and representative SEM micrograph images at various stages in the cathode fabrication process. Figure 1a shows that a smooth GDC electrolyte surface existed before infiltration, Figure 1b shows that GDC pre-infiltration and firing produced hemispherical GDC nano-particles with an average size of $25 \pm 7 \text{ nm}$, and Figure 1c shows that GDC pre-infiltration followed by LSCF infiltration and 700°C firing lead to an assemblage of GDC and LSCF hemi-spherical particles with an average size of $21 \pm 4 \text{ nm}$ (the $\pm$ values are $\pm$ a SEM-measured average particle size standard deviation). All the SEM images in this work were collected at the electrode-electrolyte interface, indicating that the infiltrate solution had no problems wetting the cathode and depositing nano-particles evenly throughout the cathode.

Table 1 shows that the experiments were conducted so that only a single microstructural or processing variable (either firing temperature, desiccant type, solution molarity or solution additive) was varied at once. The similarity of the Table 1 0.5 M and

1.5 M PND LSCF average particle sizes, as well as the similarity of the Table 1 0.5 M and 1.5 M TXD LSCF average particle sizes indicate that, consistent with previous infiltrated LSCF reports [6], solution molarity and the number of infiltrations have no effect on average LSCF particle size.

Figure 2 shows SEM images of LSCF infiltrated cathodes as a function of nano-GDC pre-infiltration loading level. For both 700°C-fired TXD and CAD LSCF, more than ~5.0 vol% of GDC pre-infiltration significantly reduced the average LSCF particle size. In contrast, 700°C-fired PND LSCF retained roughly the same average LSCF particle size across all nano-GDC loading levels.

Figure 3 shows average infiltrate particle size trends as a function of solution additive, GDC pre-infiltration loading level, and LSCF firing temperature. The Williamson-Hall-measured average particle sizes reflect just the LSCF particle sizes, while the SEM-measured particle sizes reflect contributions from both nano-GDC and LSCF particles. Figure 3 shows that regardless of the GDC pre-infiltration loading level or the precursor solution additive chemistry, higher LSCF firing temperatures typically led to larger average LSCF particle sizes. Figure 3 also shows that GDC pre-infiltration had no effect on the average particle size of 600°C-fired LSCF, regardless of the LSCF precursor solution additive. Further, Figure 3a shows that GDC pre-infiltration had no effect on the 700 or 800°C-fired PND LSCF average particle size, regardless of the GDC pre-infiltration loading level. In contrast, Figures 3b and 3c show that GDC pre-infiltration (especially more than ~5.0 vol%) significantly reduced the average particle size of TXD LSCF and CAD LSCF fired at 700 and 800°C. This behavior suggests that LSCF firing temperatures of at least ~700°C and infiltrate solution organic solution

additives (and/or the high LSCF phase purity they produce) are required for nano-ceria pre-infiltration to reduce average infiltrate particle sizes. Although this is the first time this relationship has been explicitly identified, this result is consistent with the fact that all previous literature studies utilizing ceria pre-infiltration to reduce infiltrate size have employed organic precursor solution additives and infiltrate firing temperatures $>700^{\circ}\text{C}$ (Specifically, the $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ of Ref. [4] was made using citric acid and a 700°C firing temperature [43], while the $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ of Ref. [37] was made using triethanolamine and a 900°C firing temperature).

Figure 4 shows XRD scans for PND, TXD and CAD LSCF solutions fired at various temperatures with 0.0 and 7.4 vol% of GDC pre-infiltration. Regardless of the precursor solution additive chemistry, temperatures of at least 600°C were required for highly-crystalline, perovskite-structured LSCF to form. This is clearly shown by multiple LSCF perovskite XRD peaks in the 0.0 vol% nano-GDC XRD scans, but is only indicated by the 58.7° LSCF (300) and 78.8° LSCF (128) peaks in the 7.4 vol% GDC pre-infiltrated XRD scans due to significant LSCF and GDC XRD peak overlap [40, 41]. This inability to form the equilibrium perovskite phase below 600°C indicates that sub- 600°C LSCF diffusion within the LSCF nano-particles was limited. Therefore, given the larger diffusion distances involved in mass transport between separate particles, nano-particle coarsening was not active below 600°C . This suggests that the 600°C Figure 3 LSCF particle sizes were close (if not equal) to the originally deposited LSCF particle sizes and that organic solution additives acted by reducing the originally deposited LSCF particle sizes.

Figure 5 shows TGA data for PND, TXD, and CAD LSC-GDC cathodes as a function of temperature and GDC pre-infiltration loading level. Figure 5a shows that while the pre-infiltration of nano-GDC eliminated or spread out some of the distinct PND LSCF mass loss events, PND LSCF mass loss continued (presumably through precursor nitrate decomposition) all the way up to 850°C, regardless of the nano-GDC loading level. In contrast, Figures 5b and 5c show that TXD and CAD LSCF with at least 6.4 vol% of GDC pre-infiltration encountered no mass loss above ~400°C. This behavior is consistent with the reduced Figure 4 TXD and CAD LSCF perovskite formation temperatures, compared to PND LSCF.

One possible explanation for the observed particle size behavior is that nano-GDC reduced LSCF particle sizes by facilitating the formation of coarsening-resistant phase-pure LSCF. Consistent with the reduced coarsening rates observed for phase pure LSCF compared to intentionally contaminated LSCF in Supplementary Materials Figure 1, 0.0 vol% GDC pre-infiltrated TXD and CAD LSCF displayed higher Figure 4 LSCF phase purity and lower Figure 3 700 and 800°C particle sizes than 0.0 vol% GDC pre-infiltrated PND LSCF, suggesting that infiltrate coarsening was a determinant of nanoparticle size. Further, the nearly identical GDC and LSCF particle sizes under all firing conditions (as indicated by the similar SEM measured and LSCF XRD determined particle sizes) suggests that the LSCF coarsening rate may be controlled by the GDC coarsening rate. The fact that the Figure 3 600°C particle sizes remained constant as the nano-GDC pre-infiltrate loading levels were increased suggests that nano-GDC did not reduce the “as-deposited” infiltrate particle size by inducing organic precursor solution self-assembly or by further collapsing an amorphous, gelation-induced polymer network.

As suggested in the literature, the smaller size of the 600°C CAD and TXD LSCF particle sizes compared to the 600°C PND LSCF particle sizes may be caused by mechanisms such as precursor solution additive induced wetting improvements [34], increased solution cation complexing [3, 11, 35], and/or evaporation-induced self-assembly [32].”

3.2 The Effect of GDC pre-infiltration on LSCF Infiltrated Cathode Performance

Figure 6 shows representative electrochemical impedance spectra for the TXD LSCF-GDC and CAD LSCF-GDC cathodes as a function of testing temperature and nano-GDC pre-infiltration loading level. PND LSCF-GDC cathodes (not shown) displayed similar EIS shapes. EIS measurements taken using both 50 mV and 100 mV AC amplitudes produced identical spectra, indicating that the EIS results represented open-circuit behavior. All the impedance curves had shapes similar to those for LSCF-infiltrated GDC cathodes already published in the literature [6, 11, 44, 45]. Previous literature studies on similarly infiltrated cathodes [4] and LSCF model electrodes [46, 47] have assigned the high frequency EIS arc to the charge-transfer reaction at the LSCF-GDC interface and the low frequency EIS arc to oxygen surface exchange at the LSCF-air interface. Unfortunately, the non-semi-circular shape of the Figure 6 arcs and an unsystematic characteristic frequency temperature dependence indicated that multiple electrochemical processes contributed to each arc, and prevented equivalent circuit modelling and an accompanying activation energy analysis from being used to assign specific physical processes to each arc.

Figure 7 shows the polarization resistance of PND, TXD, and CAD LSCF-GDC cathodes (derived from EIS data like that in Figure 6) as a function of testing temperature and GDC pre-infiltration loading level. Consistent with the constant PND average LSCF particle size with GDC pre-infiltration in Figure 3, Figure 7a shows that PND LSCF-GDC cathode performance was not impacted by GDC pre-infiltration. In contrast (and consistent with the Figure 3 particle sizes), Figures 7b and 7c show that 7.4 vol% of GDC pre-infiltration dramatically improved the TXD LSCF-GDC and CAD LSCF-GDC performance. In fact, the TXD LSCF-GDC cathodes reached a $0.1 \text{ } \Omega\text{cm}^2$ commercialization target at 540°C , making them one of the best performing (if not the best) infiltrated SOFC cathodes ever produced, [as shown in Supplementary Materials Figure 2 \[1, 2, 4, 5, 13, 29, 48-54\]](#).

Figure 7 also shows SIMPLE model fits to the measured R_p data. In light of the microstructural approximations inherent in the SIMPLE model, the absolute magnitudes of the SIMPLE model predictions are surprisingly close to the measured values. More importantly, the magnitude of the SIMPLE model predicted R_p differences for the 0.0 and 7.4 vol% GDC pre-infiltrated cells were similar to the observed R_p differences. This good agreement and the fact that the only difference between the 0.0 and 7.4 vol% GDC pre-infiltrated cathode SIMPLE model predictions were the LSCF particle size differences suggests that LSCF particle size changes alone were responsible for the observed performance improvements with GDC pre-infiltration. The observed R_p improvements with GDC pre-infiltration were not the result of reduced electronic transport losses since all the EIS measured Ohmic offset resistivities (not shown) were equal to that of the GDC electrolyte (as has been the case for all the 12.0 vol% infiltrated

LSCF-GDC cathodes reported previously in the literature [6, 11, 36]). In addition, The observed R_p improvements with GDC pre-infiltration on the >21% porous LSCF-GDC cathodes studied here were not the result of changes in gas concentration polarization since previous 20% O₂:80% N₂ and 20% O₂:80% He R_p measurements on 20% porous infiltrated LSCF-GDC cathodes [6] indicated the absence of gas concentration losses.

Figure 7 also shows that all the cathodes displayed a change in Arrhenius plot slope as the R_p transitioned from a mainly LSCF surface exchange controlled regime at low temperatures to a mainly GDC bulk ionic conduction controlled regime at high temperatures. This interpretation is supported by the agreement of the literature-reported 1.1 eV 400-600°C LSCF R_s activation energy [42] with the 1.0 eV Figure 7 400-600°C activation energies, and the agreement of the literature-reported 0.6-0.9 eV 600-700°C $\sigma_{V_{O,Sc}}^{\bullet\bullet}$ activation energy [8, 11, 55, 56] with the 0.59-0.60 eV Figure 7 600-700°C activation energies.

Figure 8 shows the long term, open-circuit 540°C degradation behavior of a conventional PND LSCF-GDC cathode, a 7.4 vol% GDC pre-infiltrated TXD LSCF-GDC cathode, and a 7.4 vol% GDC pre-infiltrated CAD LSCF-GDC cathode. While the initial Figure 8 R_p values agreed with those in Figure 7, each cathode experienced accelerated “break-in” degradation rates during the first 100 hours of operation before exhibiting lower, more constant, degradation rates. Although LSCF-GDC cathodes do not always age in this manner, “break-in” behavior commonly occurs in LSCF-GDC cathodes described in the literature [6, 57]. Linear fits to the “post-break-in” Figure 8 R_p data indicated that the conventional PND LSCF-GDC cathode had a 100-500 hour degradation rate of 9.8%/khrrs, the 7.4 vol% GDC pre-infiltrated TXD LSCF-GDC

cathode had a 100-500 hour degradation rate of 6.3% /khrs, and the 7.4 vol% GDC pre-infiltrated CAD LSCF-GDC cathode had a 100-500 hour degradation rate of 12.0% /khrs. Due to its lower degradation rate, the 7.4 vol% GDC pre-infiltrated TXD LSCF-GDC cathode was tested to longer times and yielded linear 500-1000 hr degradation rates of 2.1% /khrs. Although some studies have reported no long-term infiltrated cathode performance degradation [58-60] or even performance improvements with time [5], the single digit degradation rates reported here are promising considering that some literature cathodes have exhibited degradation rates in excess of 100% /khrs under some conditions [15, 61]. Further, since the 7.4 vol% GDC pre-infiltrated TXD LSCF-GDC degradation rate slows with time **over the first 1,000 hrs, continued slowing of the degradation over the next 39,000 hours** could allow the lifetime-averaged degradation rate for this kind of cathode to meet the **average** 0.2% /khr over a 40,000 hour lifetime cathode degradation target set by the U.S. Department of Energy Solid Oxide Fuel Cell Program [62]. However, additional studies utilizing longer testing times, bias/current, and/or degradation prevention mechanism are needed to fully evaluate the suitability of ceria pre-infiltrated cathodes for SOFC applications.

Figure 8b shows that LSCF particle size coarsening was not an active degradation mechanism during the 540°C aging of the 7.4 vol% GDC pre-infiltrated TXD LSF-GDC cathode. Instead, Figure 8c shows that most of the 7.4 vol% GDC pre-infiltrated TXD LSF-GDC cathode performance degradation resulted from an increase in Ohmic losses (indicated by the shift in the high frequency intercept to higher Z' values with time) and an increase in the LSCF-GDC interfacial resistance (indicated by the high frequency impedance arc [4, 46, 47]). The lack of 540°C LSCF infiltrate particle size coarsening

supports the previously mentioned hypothesis that the LSCF particles did not significantly coarsen below $\sim 600^{\circ}\text{C}$ during cathode fabrication. Further, the observed R_p aging trajectory is also inconsistent with the time to the one fourth power law behavior theoretically predicted to results from infiltrate coarsening [15]. Lastly, this nano-particle size stability is consistent with literature studies showing a lack of infiltrate coarsening at low homologous temperature for LSM infiltrate on a yttria stabilized zirconia scaffold aged for 130 hours at 800°C [63], LSM infiltrate on a scandia stabilized zirconia scaffold aged for 500 hours at 650°C [64], lanthanum strontium cobaltite infiltrate on a GDC scaffold aged for 1500 hours at 700°C [58], and LSCF infiltrate on a ceria scaffold aged for 600 hours at 650°C [15].

4.0 Conclusions

Here, the addition of precursor solution additions and the pre-infiltration of doped ceria nano-particles improved the performance of LSCF-GDC cathodes. Specifically, 7.4 vol% GDC pre-infiltrated TXD LSF-GDC and 7.4 vol% GDC pre-infiltrated CAD LSCF cathodes displayed $0.1\ \Omega\text{cm}^2$ R_p values at 540°C and 625°C , respectively, instead of the 640°C required for identical PND LSCF-GDC cathodes made without GDC pre-infiltration. These performance improvements were shown to be caused exclusively by reductions in the LSCF infiltrate particle size. The surfactant Triton X-100 and the chelating agent citric acid were shown to reduce the 600°C LSCF particle sizes from ~ 60 to ~ 20 nm, while GDC pre-infiltration was shown to catalyze precursor nitrate decomposition and limit the coarsening of perovskite structured LSCF above 600°C . In fact, no infiltrate coarsening was observed over 1000 hours of 540°C aging for a 7.4 vol%

GDC pre-infiltrated TXD LSF-GDC cathode. The superior low-temperature performance and improved long-term stability of the 7.4 vol% GDC pre-infiltrated TXD LSF-GDC cathodes (especially compared to conventionally processed PND LSCF-GDC cells) suggests that ceria pre-infiltration may be useful for the development of durable, high-power, low-temperature SOFCs.

5.0 Acknowledgements

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6.0 List of Symbols and Abbreviations

AC	Alternating Current
CAD	Citric Acid Derived
<i>D</i>	Diffusion Coefficient
EDTA	Ethylenediaminetetraacetic Acid
EIS	Electrochemical impedance spectroscopy
<i>e'</i>	Electron
FIB-SEM	Focused Ion Beam-Scanning Electron Microscope
GDC	Gd _{0.1} Ce _{0.9} O _{1.95}
IC	Ionic Conductor

k	Surface Exchange Coefficient
k_{chem}	Oxygen Surface Exchange Chemical Rate Coefficient
L_C	Characteristic Thickness
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
LSM	$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$
MIEC	Mixed Ionic and Electronic Conductor
NMCC	Nano-sized MIEC/Micro-sized IC Composite Cathodes
$\text{O}_{2(g)}$	Molecular Oxygen Gas
$\text{O}_{(xl)}^x$	Oxygen on a Lattice Oxygen Site
PND	Pure Nitrate Derived
R_p	Cathode Polarization Resistance
R_s	Oxygen Surface Exchange Resistance
ρ_{ohmic}	Symmetric Cell Ohmic Resistivity
SEM	Scanning Electron Microscopy
SIMPLE	Simple Infiltrated Microstructure Polarization Loss Estimation
SOFC	Solid Oxide Fuel Cell
SSC	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$
$\sigma_{V_{O,Sc}^{\bullet\bullet}}$	Oxygen Vacancy Conductivity of the IC Scaffold Material
TGA	Thermo-gravimetric analysis
TXD	Triton X-100 Derived
$V_{(xl)}^{\bullet\bullet}$	Lattice Oxygen Vacancy
XRD	X-ray diffraction

Table 1. LSCF|GDC Cathode Characteristics

Precursor Solution Additive	GDC Loading (%)	Firing Temperature (°C)	LSCF Loading Level (%)	Number of GDC Infiltrations	Number of LSCF Infiltrations	GDC/LSCF Nitrate Solution Molarity	Cathode Thickness (μm)	Scaffold RMS Surface Roughness (μm)	Volume of Solution per Infiltration (μL)	Cathode Geometric Area (cm ²)	Cathode Porosity (%)	Scaffold Column Width (nm)	LSCF&GDC Diameter (nm)	Total LSCF Surface Area (cm ²)	Total GDC Surface Area (cm ²)	LSCF Surface Area/GDC Surface Area (%)
PND	0.0	700	12.0	0	2	1.5/1.5	35.2	3.42	4.10	0.5	41	120	66	192	146	132
PND	0.0	700	12.0	0	2	1.5/1.5	36.1	3.85	4.21	0.5	41	120	66	197	150	132
PND	0.0	700	12.0	0	6	1.5/0.5	35.5	4.01	4.14	0.5	41	120	62	206	147	140
PND	0.0	700	12.0	0	6	1.5/0.5	36.7	3.85	4.28	0.5	41	120	62	213	152	140
PND	5.0	700	12.0	2	2	1.5/1.5	34.2	4.10	3.99	0.5	41	120	72	171	142	121
PND	5.0	700	12.0	2	2	1.5/1.5	34.8	4.30	4.06	0.5	41	120	72	174	144	121
PND	6.4	700	12.0	2	2	1.5/1.5	35.5	3.95	4.14	0.5	41	120	77	166	147	113
PND	6.4	700	12.0	2	2	1.5/1.5	34.9	3.81	4.07	0.5	41	120	77	163	145	113
PND	7.4	700	12.0	2	2	1.5/1.5	36.7	3.75	4.28	0.5	41	120	77	172	152	113
PND	7.4	700	12.0	2	2	1.5/1.5	36.1	4.15	4.21	0.5	41	120	77	169	150	113
PND	7.4	700	12.0	2	6	1.5/0.5	36.5	4.05	4.26	0.5	41	120	70	188	151	124
PND	7.4	700	12.0	2	6	1.5/0.5	36.2	3.95	4.22	0.5	41	120	70	186	150	124
TXD	0.0	700	12.0	0	2	1.5/1.5	35.2	4.39	4.10	0.5	41	120	48	264	146	181
TXD	0.0	700	12.0	0	2	1.5/1.5	36.1	4.05	4.22	0.5	41	120	48	271	150	181
TXD	0.0	700	12.0	0	2	1.5/0.5	36.0	3.50	12.60	0.5	41	120	49	265	149	178
TXD	0.0	700	12.0	0	9	1.5/0.5	36.3	3.41	2.83	0.5	41	120	51	257	151	171
TXD	5.0	700	12.0	2	2	1.5/1.5	35.8	4.43	4.17	0.5	41	120	42	307	148	207
TXD	5.0	700	12.0	2	2	1.5/1.5	35.6	4.27	4.17	0.5	41	120	42	307	148	207
TXD	6.4	700	12.0	2	2	1.5/1.5	34.8	5.30	4.06	0.5	41	120	22	507	144	352
TXD	6.4	700	12.0	2	2	1.5/1.5	36.4	5.78	4.24	0.5	41	120	22	595	151	394
TXD	7.4	700	12.0	2	2	1.5/1.5	34.6	5.41	3.86	0.5	41	120	21	568	143	397
TXD	7.4	700	12.0	2	2	1.5/1.5	35.1	6.00	3.92	0.5	41	120	21	577	146	395
TXD	7.4	700	12.0	2	2	1.5/0.5	36.1	4.23	12.62	0.5	41	120	23	566	150	377
TXD	7.4	700	12.0	2	9	1.5/0.5	35.4	4.30	2.75	0.5	41	120	23	554	147	377
CAD	0.0	700	12.0	0	7	1.5/0.5	34.2	3.74	3.42	0.5	41	120	50	247	142	174
CAD	0.0	700	12.0	0	7	1.5/0.5	34.5	3.46	3.46	0.5	41	120	50	250	143	175
CAD	5.0	700	12.0	2	7	1.5/0.5	32.6	4.96	3.26	0.5	41	120	43	273	135	202
CAD	5.0	700	12.0	2	7	1.5/0.5	37.9	5.34	3.78	0.5	41	120	43	317	157	202
CAD	6.4	700	12.0	2	7	1.5/0.5	32.9	4.50	3.29	0.5	41	120	27	439	136	323
CAD	6.4	700	12.0	2	7	1.5/0.5	34.3	4.78	3.43	0.5	41	120	27	458	142	323
CAD	7.4	700	12.0	2	7	1.5/0.5	34.8	3.50	3.48	0.5	41	120	27	465	144	323
CAD	7.4	700	12.0	2	7	1.5/0.5	36.0	3.99	3.60	0.5	41	120	27	481	149	323

Figure 1. Schematics (left) and scanning electron micrographs (right) of (a) a GDC scaffold, (b) a GDC scaffold pre-infiltrated with 7.4 vol% of nano-GDC, and (c) a GDC scaffold pre-infiltrated with 7.4 vol% of nano-GDC and 12.0 vol% of TXD LSCF. Scale bars indicate a length of 50 nm. Black in the schematics denotes GDC while orange denotes LSCF.

Figure 2. Scanning electron micrographs of 700°C fired (a-d) 1.50 M PND LSCF, (e-h) 1.50 M TXD LSCF, and (i-l) 0.50 M CAD LSCF-GDC cathodes with (a, e, i) no GDC pre-infiltration, (b, f, j) 5.0 vol% of GDC pre-infiltration, (c, g, k) 6.4 vol% of GDC pre-infiltration, and (d, h, l) 7.4 vol% of GDC pre-infiltration. Scale bars indicate a length of 50 nm.

Figure 3. *The average size of (a) 1.50 M PND LSCF, (b) 1.50 M TXD LSCF, and (c) 0.50 M CAD LSCF infiltrate particles as a function of LSCF firing temperature and GDC pre-infiltration loading level. Opaque bars with stripes increasing to the right denote average particle sizes obtained from SEM measurements, while translucent bars with stripes increasing to the left denote average particle sizes obtained from infiltrated LSCF Williamson Hall XRD measurements. The ceria pre-infiltration loading level increases from 0 to 5.0 to 6.4 to 7.4 vol% with increasing symbol stroke width. Black horizontal lines represent the average particle size found across multiple samples. A lack of LSCF phase purity prevented reliable Williamson-Hall LSCF particle size measurements for the 600 and 700°C PND LSCF samples. Error bars are +/- a standard deviation of the SEM-measured average particle size.*

Figure 4. XRD spectra for 1.5 M PND LSCF (*left*), 1.5M TXD LSCF (*middle*), and 0.5M CAD LSCF (*right*) precursor gels decomposed at various temperatures with 0 and 7.4 vol% of GDC pre-infiltration. The LSCF vol% was held constant at 12.0 vol % in all cases. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ reference spectrum came from JCPDS # 00-048-0124 [40] and the $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ reference spectrum came from JCPDS 01-075-0161)[41].

Figure 5. Thermogravimetric derivative mass loss plots collected in air for (a) 1.5 M PND LSCF, (b) 1.5 M TXD LSCF, and (c) 0.5M TXD LSCF precursor solutions infiltrated into GDC scaffolds containing various volume percents of GDC pre-infiltration.

Figure 6. *EIS Nyquist plots of ceria pre-infiltrated 12.0 vol% (a) 1.50 M TXD LSCF and (b) 0.50 M CAD LSCF GDC cathodes produced with a 700°C LSCF firing temperature. The outermost EIS spectra were taken at 500°C, the nested EIS spectra were taken at 600°C and the double nested EIS spectra were taken at 700°C. The observed differences in Ohmic offset were due to electrolyte thickness variations between cells.*

Figure 7. The performance of 12.0 vol% (a) 1.5M PND LSCF, (b) 1.5 M TXD LSCF, and (c) 0.5M CAD LSCF GDC cathodes produced with a 700°C LSCF firing temperature. The symbols with thin and thick stroke widths represent cathodes with 0.0

and 7.4 vol% GDC pre-infiltration loading level, respectively. The solid inclined lines are a guide to the eye linking the experimental data. The dashed inclined lines are SIMPLE model predictions for the 0.0 vol% nano-GDC (coarse dash) and 7.4 vol% GDC pre-infiltrated (fine dash) cathodes.

Figure 8. a) Open-circuit 540°C R_p aging measurements for various 12.0 vol% LSCF-GDC cathodes produced with a 700°C LSCF firing temperature, b) scanning electron micrograph images of the 7.4 vol% GDC pre-infiltrated TXD-LSCF infiltrate before and after 1000 hours of 540°C, open-circuit aging, and c) impedance spectra of the 7.4 vol% GDC pre-infiltrated TXD-LSCF cell at various points in the 540°C, open-circuit aging process.

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Conventionally Processed
 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$
Infiltrate

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$
Infiltrate after
 $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ Pre-Infiltration