Precursor Solution Additives Improve Desiccated $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ Infiltrated Solid Oxide Fuel Cell Cathode Performance

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Abstract

Here, the addition of the surfactant Triton X-100 or the chelating agent citric acid to Solid Oxide Fuel Cell (SOFC) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ (LSCF) precursor nitrate solutions is shown via scanning electron microscopy (SEM) and X-ray diffraction (XRD) to reduce average infiltrate nano-particle size and improve infiltrate phase purity. In addition, the desiccation of LSCF precursor solutions containing the aforementioned organic solution additives further reduces the average LSCF infiltrate nano-particle size and improves the low-temperature infiltrate phase purity. In particular, CaCl_2 -desiccation reduces the average size of Triton X-100 derived (TXD) LSCF particles fired at 700°C from 48 to 22 nm, and reduces the average size of citric acid derived LSCF particles fired at 700°C from 50 to 41 nm. Modeling and electrochemical impedance spectroscopy (EIS) tests indicate that particle size reductions alone are responsible for desiccation-induced cathode performance improvements such as CaCl_2 -desiccated TXD $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (LSCF-GDC) cathodes reaching a polarization resistance of $0.17 \, \Omega\text{cm}^2$

at 540°C, compared to 600°C for undesiccated TXD LSCF-GDC cathodes. This excellent low-temperature performance, combined with a low open-circuit 540°C degradation rate, suggests that the desiccation of organic-additive-containing infiltrate precursor solutions may be useful for the development of durable, high-power, low-temperature SOFCs.

Keywords: Electrode; Infiltration; Desiccation; Degradation; Stability

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1. Introduction

Solid Oxide Fuel Cells (SOFCs) are a promising green energy technology offering high chemical to electricity conversion efficiencies, the ability to both store and produce energy, and a possible path to transition from today's hydrocarbon-based economy to a CO₂-neutral economy running on hydrogen, solar fuels, or biofuels [1, 2]. Unfortunately, the poor low-temperature oxygen surface exchange and bulk transport properties of traditional, single-phase cathodes utilizing micro-sized La_{0.8}Sr_{0.2}MnO_{3-x} (LSM) particles have historically restricted SOFC operating temperatures to greater than ~750°C [3, 4].

One approach for realizing reduced SOFC operating temperatures has been to replace LSM with alternative mixed ionic electronic conducting (MIEC) compounds possessing 1) a low intrinsic oxygen surface exchange resistance (R_S) that facilitates MIEC oxygen exchange with the gas phase, 2) a high bulk oxygen vacancy conductivity (σ_b) that facilitates oxygen transport through the MIEC, and 3) a large characteristic thickness (L_C [R_S [5, 6]) that ensures a large percentage of the MIEC surface participates in the oxygen exchange reaction. This was first achieved by replacing B-site LSM cations with transition metal ions such as iron or cobalt (to produce lanthanum strontium iron oxide, lanthanum strontium cobalt oxide) and later by also replacing A-site LSM cations with rare or alkaline earth ions such as barium or samarium (to produce barium strontium cobalt iron oxide, samarium strontium cobalt iron oxide). Recently, the search for improved MIEC materials has extended beyond simple perovskite crystal structures to Ruddlesden-Popper rock salt-perovskite hybrids [7], layered double perovskites [8], and

other crystal structures. Unfortunately, despite these advances, the number of high-performance MIEC oxygen exchange materials has remained limited.

An alternative approach for realizing reduced SOFC operating temperatures has been to replace traditional, single-phase cathodes **which utilize** micro-sized $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-x}$ (LSM) particles, with microstructurally-tailored nano-micro-composite cathodes (NMCCs) consisting of MIEC nano-particles decorating necked, porous micro-sized ionic conducting (IC) scaffolds [9-11]. These MIEC-IC NMCCs have typically been produced by 1) dissolving multiple precursor nitrates in water, 2) infiltrating the resulting infiltrate precursor solutions into porous IC scaffolds, 3) gelling the infiltrated precursor solutions through the application of heat and/or uncontrolled solvent evaporation in air, and 4) thermally decomposing the resulting gels to form oxide MIEC nanoparticles.

Unfortunately, it has been difficult to control MIEC infiltrate particle sizes using this infiltration technique. For instance, the average diameters of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) infiltrate particles produced on doped ceria scaffolds have ranged from 40 nm to 100 nm for studies utilizing identical heating rates, firing conditions, and nominally identical compositions [12-14]. Similar average infiltrate particle size variations have also been observed for other infiltrate compositions such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSFC) utilizing identical heating rates, firing conditions, and nominally identical compositions [13, 15, 16]. However these identical heating rates, firing conditions, and nominally identical compositions are not the entire story, as some of the infiltrate precursor solutions used in these studies have contained the surfactant

Triton X-100, some have contained the chelating agent citric acid, and some have contained no organic precursor solution additives [12-16].

This suggests that organic precursor solution additives, and/or a sensitivity to certain processing parameters activated by these precursor solution additives, may be responsible for the observed variation in infiltrate particle size. This idea is further supported by recent studies showing that extended precursor solution drying [17], freeze-drying [18], and/or the chemical desiccation [19] of cobaltite precursor solutions containing either nonionic surfactants (such as Triton X-100, P123, etc) or chelating agents (citric acid, glycine, etc.) can be used to reduce infiltrate particle size and increase NMCC performance. The relationship between the presence of precursor solution additives, precursor gel water content, and infiltrate nano-particle size suggested by the results in references [17-19] is consistent with studies on other material systems showing that 1) the evaporation-induced self-assembly (EISA) of organic solution additives can be used to control the size, geometry, and patterned placement of oxide nano-particles generated from thermally decomposed gels [20, 21], and 2) that precursor gel water content dramatically alters the size of the oxide nano-particles resulting from the EISA process [22, 23].

In light of these possible relationships, the objective of the present work was to characterize how Triton X-100 precursor solution additions, citric acid precursor solution additions, and precursor solution desiccation interact to determine LSCF infiltrate particle size, 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. Materials and Methods

2.1 Cathode-Electrolyte-Cathode Symmetric Cell Production

Here, symmetrical (infiltrated cathode)-electrolyte-(infiltrated cathode) fabrication was initiated by first manufacturing GDC electrolyte supports. Each support was manufactured by heating 0.8 g of GDC powder previously pressed to 63 MPa in a 19 mm wide steel die to 1475°C at a ramp rate of 3°C per minute, holding each support at 1475°C for ~10 hours, and finally cooling each support to 25°C at a nominal ramp rate of 3°C per minute,. The resulting disks, which had relative densities >95%, were then sanded flat and parallel with SiC sandpaper to thicknesses ranging from 432 μm to 457 μm . According to manufacturer (Rhodia; Cranbury, NJ, USA) specifications, the original GDC ultra-high surface area powder used to produce these supports had an agglomerate d_{50} size of 240 nm, a specific surface area of 25.2 m^2g^{-1} , and an average particle size of ~32 nm.

Porous, well-necked GDC IC cathode scaffolds were then produced on either side of these dense electrolyte pellets. First, a portion of the aforementioned Rhodia GDC powder was coarsened at 800°C for 4 hours and then three-roll milled with V-737 electronic vehicle (Hereaus; West Conshohocken, PA, USA) to form a GDC ink with a 34% solids loading level. IC cathode scaffolds were then produced by screen printing three layers of GDC ink onto each side of each electrolyte pellet using a 80 mesh stainless steel screen with a circular 0.5 cm^2 open area. The samples were then heated at 3°C per minute, held at 400°C for 1 hour, heated to 600°C at 3°C per minute, held at

600°C for 1 hour, heated to 1100°C at 5°C per minute, held at 1100°C for 3 hours, and finally cooled to room temperature at a nominal ramp rate of 10°C per minute. Profilometry measurements using a Dektak 3 profilometer (Bruker, Tuscon, AZ, USA) were then used to determine the thickness of each cathode.

Pure nitrate derived (PND) LSCF precursor solutions, Triton X-100 derived (TXD) LSCF precursor solutions, or citric acid derived (CAD) LSCF precursor solutions were then infiltrated into these GDC scaffolds, possibly desiccated, and fired to coat the GDC scaffold surface with LSCF nanoparticles. Each precursor solution was prepared by dissolving 99.999% pure $\text{La}(\text{NO}_3)_3 \cdot 6.3 \text{ H}_2\text{O}$, 99.9965% pure $\text{Sr}(\text{NO}_3)_2$, 99.999% pure $\text{Co}(\text{NO}_3)_2 \cdot 5.67 \text{ H}_2\text{O}$ and 99.999% pure $\text{Fe}(\text{NO}_3)_3 \cdot 9.42 \text{ H}_2\text{O}$ (Alfa Aesar; Ward Hill, MA, USA) in 18.2 M 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, USA) with heating under nitrogen up to 850°C). For those solutions containing either 3 wt% (additive weight divided by nitrate weight) of Triton-X 100 or citric acid, the appropriate solution additive was pre-dissolved into the water before nitrate dissolution. A ratio of 0.75 moles of citric acid per mole of metal nitrates was used for the CAD LSCF precursor solutions, and the final solution pH was adjusted to 3 through the drop-wise addition of ammonium hydroxide. After infiltration into the top cathode, the precursor solutions were allowed to soak in for 5 minutes in air before being gelled in flowing 80°C air inside a drying oven for 10 minutes. The symmetrical cells were then flipped over and this process was repeated for the cathodes on the opposite side. Based in part on past literature desiccation

kinetic studies identifying the amount of time necessary to achieve complete desiccation [24], the undesiccated cells were immediately fired, the dry air cells were held in flowing 80°C air inside a drying oven for 1 hour before firing, the CaSO₄-desiccated cells were held in a room temperature CaSO₄-containing desiccator for 56 hours before firing, and the CaCl₂-desiccated cells were held in a room temperature desiccator for 8-10 hours before firing. CaSO₄ and CaCl₂ desiccation was performed inside sealed ~1 L glass desiccators (Wheaton, Millville, NJ, USA) by placing LSCF infiltrated cells on perforated metal shelves suspended ~25 mm above ~40 g of desiccant to produce a desiccant to LSCF precursor solution weight ratio of ~ 10,000:1. All cells were then heated to the target firing temperature at 10°C per minute, held at the target firing temperature for one hour, and then cooled to room temperature at a nominal cooling rate of 20°C per minute. This fabrication technique was repeated a total of 3 times for 1.5M solutions and 6 times for 0.5M solutions to achieve a desired LSCF loading level of 12 vol%.

Finally, (LSM) – Au current collectors were screen printed onto the surface of each NMCC in the same manner as previous studies [19].

2.2: Scanning Electron Microscopy Measurements

NMCC microstructure was evaluated using a Auriga Dual Column Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) (Carl Zeiss Microscopy GmbH; Jena, Germany) operated with a beam voltage of 20 kV, a 30 µm aperture, a 40 second scan speed, a 1.4 mm working distance, and magnifications between 100,000 and 300,000x.

SEM samples were prepared by fracturing symmetric cells in half, bonding the broken remnants to an aluminum vertical sample holder, and sputtering 2.0 nm of tungsten on the surface. All infiltrate particle size fracture surface measurements were performed at the electrolyte-cathode interface identified in Figure 1. Particle size measurements were conducted using the Heyne linear intercept method [25], three micrographs per sample, and at least 35 intercepts per micrograph.

2.3: X-ray Diffraction Measurements

MIEC infiltrate phase purity was evaluated using X-ray diffraction (XRD). XRD analyses were conducted at room temperature from 20° to 80° with a 0.040° step, a 1.00 second scan speed, and a copper filament using a Miniflex II (Rigaku Americas Corporation; The Woodlands, TX, USA) operated at 30kV and 15 mA. Due to overlap of the 33.0° LSCF and 33.0° GDC peak, the 47.3° LSCF peak and the 47.4° GDC peak, the 69.2° LSCF peak and the 69.3° GDC peak, and the 78.6° LSCF peak and the 78.9° GDC peak [26, 27], LSCF XRD analyses were conducted on precursor nitrate solutions fired outside a GDC scaffold on an alumina plate.

2.4 Williamson-Hall Particle Size Calculations

LSCF nano-particle sizes were calculated via the Williamson-Hall method [28] for LSCF powders fabricated outside the GDC scaffold. The full-width half-max (FWHM) values for the single-reflection LSCF peaks were located at $\sim 22.7^{\circ}$, $\sim 46.9^{\circ}$, and $\sim 58.4^{\circ}$. The Lorentzian profile shape function using a parabolic background was used to

determine the FWHM values using the JADE 9 computer program. The breadth (β) of each peak was calculated using the FWHM values. The linear intercept values from plots of $\beta\cos(\theta)$ vs. $4\sin(\theta)$ were then used to calculate the nano-particle size, where the intercept was placed into:

$$[1]$$

where D is the average nano-particle size in nm, K is shape factor (0.9 used in calculations) and λ is the x-ray wavelength (0.154 nm for Cu K_{α} x-rays).

2.5 Symmetric Cell Impedance Measurements

NMCC performance as a function of temperature was evaluated in static air under open-circuit conditions using electrochemical impedance spectroscopy (EIS). Specifically, two-point EIS measurements were taken every 50 degrees between 400 and 700°C using an IM6 impedance analyzer (Zahner Elektrik GmbH; Kronach, Germany). At each temperature, a 100 mV AC amplitude was used to collect impedance measurements between 100 kHz to 0.1 Hz. All samples were allowed to equilibrate for 60, 45, 35, 35, 30, 20, and 20 minutes at 400, 450, 500, 550, 600, 650, and 700°C, respectively, before EIS spectra were collected. Cathode polarization resistance (R_p) values were extracted by measuring the distance between x-axis intercepts on Nyquist plots that had been multiplied by the geometric cathode area (0.5 cm²) and divided by two (since each symmetric cell had two cathodes). Ohmic resistivity values for each cell were determined by combining the measured distance between the origin and the high

frequency x-intercept on a Nyquist plot , the 0.5 cm^2 geometric cathode area , and the measured electrolyte thicknesses using the definition of resistance:

[2]

2.6 NMCC Performance Modeling

NMCC performance was modeled using the Simple Infiltrated Polarization Loss Estimation (SIMPLE) Model [12, 13, 16]. As discussed fully in Ref. [13], the SIMPLE model accounts for NMCC resistances associated with oxygen exchange across the MIEC infiltrate surface and oxygen transport through a microstructurally idealized IC scaffold. As such, it predicts the lowest-possible NMCC , since additional sources of resistance (electronic transport losses through the MIEC infiltrate, IC tortuosity induced resistances, gas concentration polarization resistances, etc.) that would increase R_P are ignored. The model is “simple” in that it only relies on intrinsic materials properties and easily-measured microstructural properties. These materials properties include the intrinsic area specific resistance for oxygen surface exchange into the MIEC (R_S) and the bulk oxygen vacancy conductivity of the IC scaffold (σ_{IC}). These microstructural parameters include the IC scaffold surface area (A_{IC}), the MIEC infiltrate surface area (A_{MIEC}), the cathode thickness (δ), the IC scaffold column repeat unit width (W), and the scaffold porosity (ϵ). The model is also “simple” in that R_P is expressed in terms of an analytical expression:

[3]

where:

[4]

and:

[5]

that can be quickly solved within a spreadsheet or via an online calculator, as done on-demand for a variety of user-selected NMCC materials and geometries at <https://www.egr.msu.edu/nicholasgroup/simple.php>. Here, the SIMPLE model was used to combine the SEM-measured LSCF particle size, the LSCF loading level, and the cathode thickness with previous GDC IC scaffold porosity measurements [13], previous SEM GDC scaffold column width measurements [13], literature LSCF measurements [29], and literature GDC measurements [13] to produce NMCC R_p predictions. Calculations of the GDC surface area were made based on the cathode geometric area, the cathode thickness, the idealized SIMPLE model GDC scaffold geometry, and previous literature SEM measurements on the GDC scaffold width [12]. Lastly, calculations of the LSCF surface area were made based on the LSCF loading level, the cathode geometric area, the cathode thickness, the average LSCF infiltrate particle size, and the idealized SIMPLE model LSCF hemispherical shape. Representative calculations used to determine the GDC surface area, the LSCF surface area, and the SIMPLE model predicted R_p can be found in the Supplementary Materials.

3. Results and Discussion

Table 1 shows how the experiments were conducted so that only a single microstructural or processing variable (either desiccant type, firing temperature, solution additive, or solution molarity) was varied at a time. Efforts were made to ensure similar a cathode thickness across all the samples, with the average and standard deviation of the

cathode thickness values being equal to 34.4 μm and 2.7 μm , respectively. Similarly, the average and standard deviation of the root mean square (RMS) surface roughness values were 4.2 μm and 0.8 μm , respectively. In all cases, the number of infiltrations and the amount of infiltrate precursor solution was adjusted based on the cathode thickness and the solution molarity to keep the LSCF loading level constant at 12 vol% (infiltrate volume divided by total cathode volume). This was done because past SSC and LSCF infiltration studies have reported that the number of precursor solution infiltrations has little effect on infiltrate particle size, but the total amount of infiltrate is an important parameter in determining NMCC electrochemical performance [13, 30]. Interestingly, the similar average Table 1 particle sizes for the 0.5M PND LSCF compared to the 1.5M PND LSCF, and the 0.5M TXD LSCF compared to the 1.5M TXD LSCF, indicate that solution molarity did not impact average infiltrate particle size. This in agreement with past studies showing that the precursor solution molarity of cobaltite infiltrate solutions has no effect on infiltrate particle size [19, 30], but is in contrast to past studies showing that increased precursor solution molarity of manganate infiltrate solutions reduces infiltrate particle size [22].

3.1 The Effect of Precursor Solution Additives and Desiccation on Infiltrate Particle Size and Phase Purity

Figure 1 shows that for NMCCs fired at 700°C, increased desiccant strength resulted in smaller TXD LSCF and CAD LSCF infiltrate particles, but had no impact on the average particle size of PND LSCF infiltrate. In fact, while the 700°C PND LSCF

average particle size remained roughly constant at ~70 nm with desiccation, the 700°C TXD LSCF average particle size was reduced from ~48 to 22 nm, and the 700°C CAD LSCF average particle size was reduced from ~48 to 38 nm.

Figure 2 shows the LSCF particle size trends for PND, TXD, and CAD LSCF as a function of desiccant strength and firing temperature. In all cases, higher firing temperatures led to larger particle sizes, and particle size measurements before and after electrochemical testing showed identical particle sizes. Further, even without desiccation, TXD and CAD LSCF precursor solutions produced smaller average LSCF particle sizes than identically processed PND LSCF. As shown in Figure 2a, desiccation had no effect on the PND LSCF average particle size, regardless of the 600-800°C firing temperature. In contrast, as shown in Figure 2b and reported previously [19], increasing desiccant strength led to systematically smaller TXD LSCF average particle sizes at each 600-800°C firing temperature. As shown in Figure 2c, increasing amounts of desiccation led to systematically smaller CAD LSCF average particle sizes at 700 and 800°C firing temperatures, but had little effect on CAD LSCF fired at 600°C. In fact, CaCl_2 -desiccation reduced the average size of CAD LSCF particles fired at 700°C from 50 to 41 nm, and reduced the average size of TXD LSCF particles fired at 700°C from 48 to 22 nm. To the best of the author's knowledge, these 22 nm average diameter particles are the smallest LSCF infiltrate particles ever produced.

Figure 3a shows that significant amounts of impurity phases formed at all undesiccated PND LSCF firing temperatures between 80 and 800°C, and that perovskite-structured LSCF only became the dominant phase at firing temperatures at or above

700°C. This is unsurprising since undesiccated PND infiltrate cobaltite materials reported in the literature have exhibited similar levels of impurity phases [12, 31, 32]. Past studies have attributed the lack of phase purity to precursor solution metal nitrates precipitating out of solution at different times (due to their different solubility limits) during solvent evaporation [12, 22]. The disparate room temperature solubilities of lanthanum nitrate, strontium nitrate, iron nitrate, and cobalt nitrate (200, 80, 83, and 103 grams per 100 grams of water, respectively [33]) support this interpretation. Figure 3b shows that CaCl_2 precursor solution desiccation increased the percentage of impurity phases at all 80-800°C PND LSCF firing temperatures.

Figure 4a, when compared to Figure 3a, shows that Triton X-100 surfactant additions increased the phase purity of undesiccated LSCF fired at and above 600°C. Even though LSCF was the dominant phase after firing to 600-800°C, some secondary phases remained, as indicated by impurity phase peaks at $\sim 23^\circ$, 28° , 29.5° , 33° , and 44° . Figure 4b shows that CaCl_2 precursor solution desiccation improved the phase purity of TXD LSCF fired at 600°C, and (like the undesiccated TXD LSCF case) produced nearly phase pure LSCF at higher firing temperatures. The improved phase purity of TXD LSCF compared to PND LSCF is especially interesting because Triton X-100 precursor solution additions have been shown to improve the phase purity of infiltrated LSM [32] but not infiltrated SSC [12, 13, 31].

Figure 5a shows that perovskite-structured LSCF formed at all undesiccated LSCF firing temperatures at and above 600°C when citric acid was used as a precursor solution chelating agent. This result is somewhat expected since chelating agents such as

urea [13, 31] citric acid [12, 13, 34] and ethylene glycol [35-37], have been used in the past to produce phase pure infiltrated MIEC infiltrate. The improved phase purity of CAD LSCF over TXD LSCF may result from the fact that amphiphilic surfactants such as Triton X-100 only interact with dissolved solution cations over a portion of their length while chelating agents such as citric acid can deprotonate over their entire length (depending on the solution pH) and hence potentially bring disparate solution cations closer together. Figure 5b shows that CaCl_2 desiccation improved the phase purity of CAD LSCF fired at 400 and 500°C, and (like the undesiccated CAD LSCF case) gave phase pure LSCF at firing temperatures at and above 600°C.

The inability to form phase-pure LSCF below 600°C in Figures 3-5 suggests that LSCF diffusion within the LSCF nano-particles **did not occur to a meaningful extent below 600°C**. This, combined with a larger diffusion distances between physically distinct particles, suggests that nano-particle microstructural coarsening was not active below 600°C. Hence, it is likely that the 600°C Figure 2 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.

Unfortunately, the exact mechanisms by which Triton X-100 and citric acid precursor solution additions reduce undesiccated infiltrate particle size remain unclear. **While past studies have argued that Triton X-100 reduces infiltrate particle size by self-assembling during precursor solution solvent evaporation [38], other studies have argued 1) that self-assembly does not occur under typical infiltration fabrication conditions [39], and 2) that Triton X-100 instead acts through either improved wetting [39] and/or**

improved cation complexing [13, 32, 40]. Similarly, the beneficial effects of citric acid have been attributed to the material's chelating abilities [12, 41]. Clearly, additional studies beyond the scope of the present work are needed to definitively determine whether TXD or CAD LSCF precursor solutions self-assemble during infiltrated cathode fabrication. Even if TXD and CAD LSCF precursor solutions remain amorphous during processing and do not undergo self-assembly, one possible explanation for the observed particle size and phase purity behavior with desiccation is that desiccation further collapsed the Triton X-100 or citric acid polymer networks produced during solution drying, and in the process produced smaller metal nitrate pockets in the pre-fired gels. Consistent with the TXD 600°C LSCF particle size data (Figure 2b) and the TXD/CAD LSCF phase purity data (Figures 4 and 5), these smaller metal nitrate pockets would be expected to 1) decompose to form smaller 600°C LSCF particles, and 2) improve the TXD and CAD LSCF phase purity through reduced diffusion distances. Consistent with experimental data on LSCF nanoparticles intentionally doped with impurity phases [42], the observed 400-600°C LSCF phase purity may have imparted coarsening resistance to the LSCF infiltrate particles that allowed them to remain close to their 600°C Figure 2 particle sizes; even as they were exposed to higher firing temperatures. Under this mechanism, the lack of a polymer network in the PND LSCF precursor solutions would be expected to produce PND LSCF particle sizes that, as observed in Figure 2a, did not change size with desiccation. Similarly, under this mechanism the additional time introduced for unconstrained metal nitrate segregation during PND LSCF desiccation

would be expected to lead to reduced PND LSCF phase purity with desiccation, as observed in Figure 3.

3.2. The Effect of Precursor Solution Additives and Desiccation on NMCC Performance

Figure 6 shows representative impedance spectra for the TXD LSCF-GDC and CAD LSCF-GDC NMCCs. The PND LSCF-GDC NMCCs (not shown) displayed similar shapes to those in Figure 6. All the LSCF-GDC cathodes tested here had identical shapes using both a 50 and 100mV AC amplitude, indicating that the EIS scans represented open-circuit behavior. In addition, the observed impedance curve shapes were similar to those observed previously in the literature for infiltrated PND LSCF-GDC [13, 43, 44]. Unfortunately, an unsystematic characteristic frequency temperature dependence and a non-semi-circular shape to the Figure 6 EIS arcs indicated that multiple electrochemical processes contributed to each arc, and prevented the assignment of a specific physical process to each arc through equivalent circuit modelling and an accompanying activation energy analysis.

Figure 7 shows R_P plots for undesiccated and CaCl_2 -desiccated PND, TXD, and CAD LSCF-GDC cathodes. All the samples displayed a change in Arrhenius slope around $\sim 600^\circ\text{C}$. This is interpreted to result from a transition from a mainly LSCF surface exchange controlled regime below $\sim 600^\circ\text{C}$ to a mainly GDC bulk ionic conduction controlled regime above $\sim 600^\circ\text{C}$. This is supported by 1) the agreement of the literature-reported 1.1 eV 400-600°C LSCF R_S activation energy [29] with the 1.0 eV Figure 7 400-600°C activation energies, and 2) the agreement of the literature-reported 0.6-0.9 eV

600-700°C activation energy [13, 45-47] with the 0.59-0.60 eV Figure 7 600-700°C activation energies. Consistent with the particle sizes reported in Figure 2, the Figure 7 TXD LSCF-GDC cathodes performed the best, and the CAD-LSCF-GDC cathodes performed better than the PND LSCF-GDC cathodes. Specifically, the TXD LSCF-GDC cathodes reached the $0.1 \text{ } \Omega\text{cm}^2$ R_P commercialization target at 575°C instead of the >625°C needed for the other cathodes. This TXD LSCF-GDC performance is among the best low temperature infiltrated SOFC cathode performance ever observed [42, 48, 49].

Figure 7 also shows SIMPLE model comparisons made using the observed microstructure, literature GDC conductivity values [13], and literature R_S values [29]. Close agreement existed between the measured and SIMPLE modeled 400-600°C CAD LSCF-GDC R_P values (i.e. in the LSCF R_S controlled regime). However, the measured 400-600°C PND LSCF-GDC and TXD LSCF-GDC R_P values were consistently higher than the SIMPLE model predicted values. This suggests that PND and TXD LSCF impurity phases (Figures 3 and 4) may have raised the intrinsic LSCF R_S values above those seen in phase pure LSCF. As argued previously [13], the measured 600-700°C R_P values were likely higher than the SIMPLE modeled values because the idealized ionic conducting scaffold microstructure in the SIMPLE model failed to account for additional, tortuosity-induced resistances caused by the non-idealized geometry of the GDC scaffold. Previous 20%O₂:80%N₂ and 20%O₂:80%He TXD LSCF-GDC concentration polarization tests [19] indicated these 600-700°C discrepancies were not the result of poor gas transport through the cathode pores.

Consistent with the minimal, large, and moderate changes in the respective Figure 2 PND, TXD, and CAD LSCF particle sizes with desiccation, the PND LSCF-GDC, TXD LSCF-GDC, and CAD LSCF-GDC NMCCs respectively exhibited minimal, large, and moderate Figure 7 desiccation-induced R_P reductions, respectively. In fact, the similarity in magnitude of the SIMPLE model R_P changes predicted from the observed Figure 2 desiccation-induced particle size reductions, and the observed NMCC R_P changes shown in Figure 7 suggest that desiccation-induced reductions in particle size alone were responsible for the observed TXD LSCF-GDC and CAD LSCF-GDC performance increases. (As shown in Equations 3-5, smaller infiltrate particle sizes produce lower ratios that lead to reduced R_P values.) The constancy of the 700°C TXD and CAD LSCF phase purity with desiccation (Figures 4 and 5) indicate that the observed desiccation-induced R_P reductions were not caused by phase purity changes. In addition, the similar scaffold porosities and infiltrate loading levels across all the samples (Table 1), combined with identical 400-700°C TXD LSCF-GDC R_P behavior in both a 20%O₂:80%N₂ atmosphere and a 20%O₂:80%He atmosphere (reported previously) [19] suggest that changes in gas phase concentration polarization resistance caused by desiccation-induced changes in pore structure were not responsible for the observed desiccation-induced R_P reductions. Lastly, the fact that the ohmic offset resistivities for all the PND, TXD, and CAD LSCF-GDC cathodes agreed with what would be expected from a GDC electrolyte alone (not shown) indicated that electronic conduction losses in the infiltrated cathodes were not a significant portion of the open-circuit Figure 7 R_P values, and hence also

indicated that the observed TXD and CAD LSCF R_P improvements with desiccation were not the result of changes in NMCC electronic conduction losses.

Taken together, all this evidence suggests that desiccation-induced particle size reductions alone were responsible for the all the observed TXD LSCF-GDC and CAD LSCF-GDC R_P improvements.

3.3 The Effect of Precursor Solution Additives and Desiccation on NMCC Open-Circuit Stability

Figure 8a shows the 540°C open-circuit degradation behavior of a conventional undesiccated PND LSCF-GDC NMCC, a CaCl_2 -desiccated TXD LSCF-GDC NMCC, and a CaCl_2 -desiccated CAD LSCF-GDC NMCC (the initial R_P values in Figure 8a are identical to those in Figure 7) Consistent with some of the infiltrated LSCF aging reports in the literature [15, 42, 50], all the cathodes tested here experienced accelerated “break-in” degradation rates during the first 100 hours of operation and then established lower, more constant degradation rates. Linear fits to the “post-break-in” R_P data indicated that the undesiccated PND LSCF-GDC cathodes had a 100-500 hour degradation rate of 9.8% /khrs, the CaCl_2 -desiccated TXD LSCF-GDC cathodes had a 100-500 hour degradation rate of 1.7% /khrs, and the CaCl_2 -desiccated CAD LSCF-GDC cathodes had a 100-500 hour degradation rate of 3.3% /khrs. Although some literature studies have reported no long-term infiltrated cathode performance degradation [51-53] and some have reported performance improvements [48] during long-term operation, the single digit degradation

rates reported here are promising considering that long-term degradation rates in excess of 100% /khrs are common in the literature [15, 54].

Figure 8b shows SEM images of the CaCl_2 -desiccated TXD LSCF infiltrate before and after 500 hours of open circuit 540°C aging. Interestingly, no significant increase in the average LSCF infiltrate particle size was observed, suggesting that infiltrate particle coarsening was not an operable degradation mechanism at 540°C. The low 540°C LSCF diffusion rates this implies is consistent with the lack of LSCF phase purity below 600°C observed in Figures 3-5. The conclusion that LSCF infiltrate does not coarsen at 540°C is also supported by SIMPLE modeling which indicates that an average infiltrate particle of ~60 nm, (i.e. much larger than the Figure 8b particle sizes) would be needed to produce the observed 500 hr CaCl_2 -desiccated TXD LSCF R_p . This conclusion is also supported by literature studies which have demonstrated no 650°C LSCF infiltrate particle size growth over 600 hours [15], and the fact that the Figure 8a R_p aging trajectory cannot be fit by the time to the one fourth power law behavior theoretically predicted to result from infiltrate microstructural coarsening [15].

Figure 8c shows raw EIS curves at various times during aging of the CaCl_2 -desiccated TXD LSCF cell. As shown by comparing the 0 and 250 hour EIS spectra, the large R_p increase during the initial “break-in” period was accompanied by a large ohmic offset increase. As discussed in the literature, NMCC ohmic offset increases typically indicate a drop in either the ionic conductivity of the electrolyte or the electronic conductivity/connectivity of infiltrate network [13]. Consistent with the ionic conductivity of undoped and Co-doped GDC [55], this “break-in” degradation may have

been caused by Co migrating from the LSCF into the GDC scaffold (at least until the GDC scaffold reached its <1% Co solubility limit [56, 57]). However, additional work beyond the scope of this paper is needed to evaluate this hypothesis. As shown by comparing the 250 and 500 hour EIS spectra, the “post-break-in” R_p increase was not associated with a change in ohmic offset and only resulted from an increased resistance of the low-frequency portions of the EIS spectra likely to be associated with oxygen surface exchange [29, 49, 58, 59]. Although additional work is also needed here to identify the operational degradation mechanism, this “post-break-in” degradation may have been caused by Sr segregation to LSCF infiltrate surface (Sr surface segregation has been identified as the primary degradation mechanism in bulk LSCF [60, 61]).

4. Conclusions

Here, the addition of organic solution additives (either the surfactant Triton X-100 or the chelating agent citric acid) was shown to reduce the average LSCF infiltrate particle size and improve the LSCF infiltrate phase purity. In addition, desiccated LSCF precursor nitrate solutions with organic solution additives displayed smaller average LSCF particle sizes as the desiccant strength was increased. Conversely, desiccation showed no effect on PND LSCF average particle sizes. Desiccation was more effective in reducing TXD LSCF average particle sizes than CAD LSCF average particle sizes (with CaCl_2 -desiccation reducing the 700°C TXD LSCF particle size from 48 to 22 nm, in contrast to the 50 to 41 nm observed for CAD LSCF). Changes in LSCF infiltrate particle size alone (and not changes in LSCF infiltrate phase purity, gas concentration polarization

resistance, and/or infiltrate network electronic conductivity) were responsible for the R_P decreases observed with desiccation. Precursor solution molarity changes between 0.5 and 1.5M were found to have no impact on LSCF infiltrate particle size. Desiccation increased the already large fraction of PND LSCF impurity phases, but improved the intermediate temperature phase purity of TXD and CAD LSCF. The inability of LSCF particles fired below 600°C to achieve phase purity, the constant size of LSCF particles aged for 500 hours at 540°C, and long-term 540°C R_P aging trajectories inconsistent with degradation via infiltrate microstructural coarsening, all indicated that LSCF nanoparticle coarsening was not an active NMCC degradation mechanism below 600°C. Compared to CAD LSCF which was phase pure and had R_S values that matched well with literature thin film R_S values, PND LSCF and TXD LSCF exhibited R_S values slightly greater than literature thin film R_S values, presumably as a result of their higher impurity phase fractions. Even so, due to large, desiccation-induced particle size reductions, CaCl₂-desiccated TXD LSCF-GDC NMCCs achieved R_P values of 0.17 Ωcm^2 at 540°C, making them some of the best performing infiltrated SOFC cathodes ever produced [48, 49]. This excellent performance, combined with a low 540°C “post-break-in” open-circuit degradation rate of 1.7% /khr, suggests that the desiccation of infiltrate precursor solutions containing organic solution additives may be useful for the development of durable, high-power, low-temperature SOFCs.

5. Acknowledgements

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6. List of Symbols and Acronyms

A	Geometric Cathode Area
	MIEC Infiltrate Surface Area
	IC Scaffold Surface Area
AC	Alternating Current
CAD	Citric Acid Derived
D	Average Williamson-Hall Determined Nano-Particle Size
EIS	Electrochemical Impedance Spectroscopy
EISA	Evaporation-Induced Self-Assembly
FWHM	Full Width Half Max
GDC	$\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$
	Cathode Thickness
IC	Ionic Conductor
K	Williamson-Hall Particle Shape Factor
λ	X-Ray Wavelength

	Electrolyte Thickness
L_C	Characteristic Thickness
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$
LSFC	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-x}$
LSM	$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-x}$
MIEC	Mixed Ionic and Electronic Conductor
NMCC	Nano-Micro-Composite Cathode
	IC Scaffold Porosity
PND	Pure Nitrate Derived
	Symmetric Cell Ohmic Resistivity
	SIMPLE Model Repeat Unit Cell Width
	Symmetric Cell Ohmic Resistance (a.k.a. Ohmic Offset)
R_P	Cathode Polarization Resistance
R_S	Oxygen Surface Exchange Resistance
RMS	Root Mean Square
	Oxygen Vacancy Conductivity of the IC Scaffold
SEM	Scanning Electron Microscopy
SIMPLE	Simple Infiltrated Microstructure Polarization Loss Estimation
SOFC	Solid Oxide Fuel Cell
SSC	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$
TGA	Thermo-gravimetric analysis
TXD	Triton X-100 Derived

XRD X-ray diffraction

Table 1. LSCF-GDC NMCC Characteristics

Surfa ctant	Desicca nt Type	Firing Tempe rature (°C)	LSC F Load ing Leve l (%)	Numb er of LSCF Infiltr ations	LSC F Nitra te Solut ion Mola rity	Cath ode Thick ness (μm)	Scaff old RMS Surfa ce Rough ness (μm)	Volum e of Solutio n per Infiltrat ion (μL)	Cath ode Geo metri c Area (cm^2)	Cat hod e Porosit y (%)	Scaf fold Col umn Wid th (nm)	LSC F Dia mete r (nm)	Tota l LSC F Surfa ce Area (cm^2)	Tot al G D C Surfa ce Area (cm^2)	LSC F Surfa ce Area/ GDC Surfa ce Area (%)
PND	Undesic cated	700	12	3	1.5	35.7	4.00	2.78	0.5	32	120	65	198	148	134
PND	Undesic cated	700	12	3	1.5	36.3	4.05	2.82	0.5	32	120	65	202	151	134
PND	Undesic cated	700	12	6	0.5	35.4	3.50	4.13	0.5	32	120	62	206	147	140
PND	Undesic cated	700	12	6	0.5	36.4	3.41	4.25	0.5	32	120	62	212	151	140
PND	Dry Air	700	12	3	1.5	34.3	3.50	2.67	0.5	32	120	73	170	142	120
PND	Dry Air	700	12	3	1.5	35.2	3.90	2.74	0.5	32	120	73	174	146	120
PND	CaSO ₄	700	12	3	1.5	36.3	4.30	2.82	0.5	32	120	72	182	151	121
PND	CaSO ₄	700	12	3	1.5	36.0	4.42	2.80	0.5	32	120	72	180	149	121
PND	CaCl ₂	700	12	3	1.5	35.2	4.61	2.74	0.5	32	120	71	179	146	123
PND	CaCl ₂	700	12	3	1.5	35.7	4.04	2.78	0.5	32	120	71	182	148	123
PND	CaCl ₂	700	12	6	0.5	34.8	4.10	4.06	0.5	32	120	70	179	144	124
PND	CaCl ₂	700	12	6	0.5	35.8	3.95	4.18	0.5	32	120	70	185	148	125
CAD	Undesic cated	700	12	6	0.5	34.2	3.74	3.98	0.5	32	120	50	246	142	173
CAD	Undesic cated	700	12	6	0.5	34.5	3.54	4.02	0.5	32	120	50	249	143	174
CAD	Dry Air	700	12	6	0.5	26.7	3.84	3.11	0.5	32	120	43	224	111	202
CAD	Dry Air	700	12	6	0.5	31.8	4.678	3.70	0.5	32	120	43	266	132	202

CAD	CaSO ₄	700	12	6	0.5	27.7	4.62	3.23	0.5	32	120	42	237	11 5	207
CAD	CaSO ₄	700	12	6	0.5	29.5	4.35	3.44	0.5	32	120	42	253	12 2	207
CAD	CaCl ₂	700	12	6	0.5	32.1	3.50	3.74	0.5	32	120	41	282	13 3	212
CAD	CaCl ₂	700	12	6	0.5	34.1	3.55	3.97	0.5	32	120	41	300	14 1	213
TXD	Undesic cated	700	12	3	1.5	35.2	4.39	2.74	0.5	32	120	48	275	14 6	188
TXD	Undesic cated	700	12	3	1.5	36.1	4.05	2.81	0.5	32	120	48	282	15 0	188
TXD	Undesic cated	700	12	3	0.5	36.0	3.50	8.40	0.5	32	120	49	254	14 9	170
TXD	Undesic cated	700	12	9	0.5	36.3	3.41	2.82	0.5	32	120	51	256	15 1	170
TXD	Dry Air	700	12	3	1.5	32.1	4.11	2.50	0.5	32	120	30	385	13 3	289
TXD	Dry Air	700	12	3	1.5	35.8	3.91	2.78	0.5	32	120	30	429	14 8	290
TXD	CaSO ₄	700	12	3	1.5	34.9	3.67	2.71	0.5	32	120	25	503	14 5	347
TXD	CaSO ₄	700	12	3	1.5	36.7	4.64	2.85	0.5	32	120	25	529	15 2	348
TXD	CaCl ₂	700	12	3	1.5	36.6	4.28	2.84	0.5	32	120	22	599	15 2	394
TXD	CaCl ₂	700	12	3	1.5	36.2	4.36	2.81	0.5	32	120	22	592	15 0	395
TXD	CaCl ₂	700	12	3	0.5	35.2	4.30	8.20	0.5	32	120	23	551	14 6	377
TXD	CaCl ₂	700	12	9	0.5	36.6	4.21	2.85	0.5	32	120	23	575	15 2	378

Figure 1. Scanning electron micrographs of 1.50M PND LSCF (a-d), 1.50M TXD LSCF (e-h) and 0.50M CAD LSCF (i-l) NMCCs produced by firing at 700°C. NMCCs in each row were processed with identical desiccation conditions, with the desiccant strength increasing with each subsequent row [62, 63]. The scale bars are all 50 microns in width.

Figure 2. *The average particle size of (a) 1.50M PND LSCF, (b) 1.50M TXD LSC, and (c) 0.50M CAD LSCF measured from SEM micrographs (opaque bars with stripes increasing to the right) of infiltrated particles and Williamson Hall XRD measurements (translucent bars with stripes increasing to the left) on LSCF fired outside a GDC scaffold. At each temperature, desiccants are listed in order of increasing effectiveness when moving from left to right [24, 64]. Open symbols denote undesiccated cathodes, partitioned symbols denote dry air-desiccated cathodes, half-filled symbols denote CaSO_4 -desiccated cathodes, and completely filled samples denote CaCl_2 -desiccated cathodes. The error bars represent $\pm$ a standard deviation in the SEM-measured particle size distribution. Black horizontal lines represent the average particle size found across multiple samples. Unfortunately, a lack of isolated, well-defined LSCF XRD peaks in the 600 and 700°C PND LSCF peaks prevented Williamson-Hall particle size measurements on those cathodes.*

Figure 3. Powder X-Ray diffractograms of (a) undesiccated and (b) CaCl_2 -desiccated 1.5M PND LSCF fired outside a GDC scaffold at various temperatures. The JCPDS $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ peak reference comes from PDF #00-048-0124 [26].

Figure 4. Powder X-Ray diffractograms of (a) undesiccated and (b) CaCl_2 -desiccated 1.5M TXD LSCF fired outside a GDC scaffold at various temperatures. The JCPDS $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ peak reference comes from PDF #00-048-0124 [26].

Figure 5. Powder X-Ray diffractograms of (a) undesiccated and (b) CaCl_2 -desiccated 0.5M CAD LSCF fired outside a GDC scaffold at various temperatures. The JCPDS $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ peak reference comes from PDF #00-048-0124 [26].

Figure 6. EIS Nyquist plots of (a) TXD LSCF-GDC and (b) CAD LSCF-GDC NMCCs fired at 700°C after various precursor nitrate solution desiccation treatments. The outermost data was taken at 500°C, the nested data was taken at 600°C and the double nested data was taken at 700°C. Open symbols denote undesiccated cathodes, partitioned symbols denote dry air-desiccated cathodes, half-filled symbols denote CaSO_4 -desiccated cathodes, and completely filled samples denote CaCl_2 -desiccated cathodes. Desiccants are listed in order of increasing effectiveness from top to bottom [24, 64].

Figure 7. R_P Arrhenius plots for (a) PND LSCF-GDC, (b) TXD LSCF-GDC, and (c) CAD LSCF-GDC cathodes fired at 700 $^{\circ}\text{C}$. Open symbols denote undessicated cathodes and completely filled samples denote CaCl_2 -desiccated cathodes. The solid inclined lines are a guide to the eye linking the experimental data. The dashed inclined lines are

SIMPLE model predictions for the undesiccated (coarse dash) and CaCl_2 (fine dash) cathodes. The horizontal dashed line is the $0.1 \text{ } \Omega\text{cm}^2$ performance target.

Figure 8. a) Open-circuit 540°C R_P aging measurements for various 12 vol% LSCF-GDC cathodes produced with a 700°C LSCF firing temperature, b) scanning electron micrograph images of the CaCl_2 -desiccated TXD-LSCF infiltrate before and after 500 hours of 540°C, open-circuit aging, and c) impedance spectra of the CaCl_2 -desiccated TXD-LSCF cell at various points in the 540°C, open-circuit aging process.

References:

- [1] E.D. Wachsman, K.T. Lee, *Science*, 334 (2011) 935-939.
- [2] J.D. Nicholas, *ECS Interface*, 22 (2013) 49-54.
- [3] T. Tsai, S.A. Barnett, *Solid State Ionics*, 93 (1997) 207.
- [4] S. DeSouza, S.J. Visco, L.C. DeJonghe, *J. Electrochem. Soc.*, 144 (1997) L35-L37.
- [5] J. Fleig, H.R. Kim, J. Jamnik, J. Maier, *Fuel Cells*, 8 (2008) 330-337.
- [6] H.J.M. Bouwmeester, A.J. Burggraaf, *Dense Ceramic Membranes for Oxygen Separation*, in: P.J. Gellings, H.J.M. Bouwmeester (Eds.) *The CRC Handbook of Solid State Electrochemistry*, CRC Press, New York, 1997, pp. 481-554.
- [7] E. Boehm, J.M. Bassat, M.C. Steil, P. Dordor, F. Mauvy, J.C. Grenier, *Solid State Sci.*, 5 (2003) 973-981.
- [8] S. Sengodan, S. Choi, A. Jun, T.H. Shin, Y.-W. Ju, H.Y. Jeong, J. Shin, J.T.S. Irvine, G. Kim, *Nature Materials*, 14 (2015) 205-209.
- [9] J.M. Vohs, R.J. Gorte, *Adv. Mater.*, 21 (2009) 943-956.
- [10] S.P. Jiang, *Mat. Sci. Eng. A-Struct.*, 418 (2006) 199-210.
- [11] D. Ding, X. Li, S.Y. Lai, K. Gerdes, M. Liu, 7 (2014) 552-575.
- [12] J.D. Nicholas, S.A. Barnett, *J. Electrochem Soc.*, 157 (2010) B536-B541.
- [13] J.D. Nicholas, L. Wang, A.V. Call, S.A. Barnett, *Phys. Chem. Chem. Phys.*, 14 (2012) 15379-15392.
- [14] H. Zhang, F. Zhao, F.L. Chen, C.R. Xia, *Solid State Ionics*, 192 (2011) 591-594.
- [15] M. Shah, P.W. Voorhees, S.A. Barnett, *Solid State Ionics*, 187 (2011) 64-67.
- [16] M. Shah, J.D. Nicholas, S.A. Barnett, *Electrochem. Commun.*, 11 (2009) 2-5.
- [17] N.P. Bansal, B. Wise, *Ceram. Int.*, 38 (2012) 5535-5541.
- [18] Y. Chen, Y. Lin, Y. Zhang, S. Wang, D. Su, Z. Yang, M. Han, F. Chen, *Nano Energy*, 8 (2014) 25-33.
- [19] T.E. Burye, J.D. Nicholas, *J. Power Sources*, 276 (2015) 54-61.
- [20] C.J. Brinker, Y.F. Lu, A. Sellinger, H.Y. Fan, *Adv. Mater.*, 11 (1999) 579-+.
- [21] D. Grosso, C. Boissiere, B. Smarsly, T. Brezesinski, N. Pinna, P.A. Albouy, H. Amenitsch, M. Antonietti, C. Sanchez, *Nature Mater.*, 3 (2004) 787-792.
- [22] R. Chao, R. Munprom, R. Petrova, K. Gerdes, J.R. Kitchin, P.A. Salvador, *J. Am. Cer. Soc.*, 95 (2012) 2339-2346.
- [23] F. Cagnol, D. Grosso, G. Soler-Illia, E.L. Crepaldi, F. Babonneau, H. Amenitsch, C. Sanchez, *J. Mater. Chem.*, 13 (2003) 61-66.
- [24] D.R. Burfield, K.H. Lee, R.H. Smithers, *J. Org. Chem.*, 42 (1977) 3060-3065.
- [25] ASTM International, *Annual Book of ASTM Standards*, (2004) 1-26.
- [26] J.E. ten Elshof, J. Boeijsma, *Powder Diffr.*, 11 (1996) 28-30.
- [27] G. Brauer, H. Gradinger, *Z. Anorg. Allg. Chem.*, 276 (1954) 209-226.
- [28] V.D. Mote, Y. Purushotham, B.N. Dole, *J. Theor. Appl. Phys.*, 6 (2012) 6.
- [29] H. Xiong, B.K. Lai, A.C. Johnson, S. Ramanathan, *J. Power Sources*, 193 (2009) 589-592.
- [30] J.D. Nicholas, S.A. Barnett, *J. Electrochem. Soc.*, 157 (2010) B536-B541.
- [31] X.Y. Lou, Z. Liu, S.Z. Wang, Y.H. Xiu, C.P. Wong, M.L. Liu, *J. Power Sources*, 195 (2010) 419-424.

- [32] T.Z. Sholklapper, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, Fuel Cells, 8 (2008) 303-312.
- [33] W.H. Hayes, T.J. Bruno, D.R. Lide, in, CRC Press, Boca Raton, FL, 2015.
- [34] S. Lee, N. Miller, H. Abernathy, K. Gerdes, A. Manivannan, J. Electrochem Soc., 158 (2011) B735-B742.
- [35] H. Fan, M. Keane, N. Li, D. Tang, P. Singh, M.F. Han, Int. J. Hydrogen Energy, 39 (2014) 14071-14078.
- [36] X. Zhu, D. Ding, Y. Li, Z. Lü, W. Su, L. Zhen, Int. J. Hydrogen Energy, 38 (2013) 5375-5382.
- [37] A. Buyukaksoy, V. Petrovsky, F. Dogan, J. Electrochem Soc., 159 (2012) B666-B669.
- [38] R. Chao, J. Kitchin, K. Gerdes, E. Sabolsky, P. Salvador, 35 (2011) 2387-2399.
- [39] T. Klemenso, C. Chatzichristodoulou, J. Nielsen, F. Bozza, K. Thyden, R. Kiebach, S. Ramousse, Solid State Ionics, 224 (2012) 21-31.
- [40] D. Ding, X.X. Li, S.Y. Lai, K. Gerdes, M.L. Liu, Energ. Environ. Sci., 7 (2014) 552-575.
- [41] J.M. Serra, S. Uhlenbruck, W.A. Meulenberg, H.P. Buchkremer, D. Stöver, Top Catal, 40 (2006) 123-131.
- [42] T.E. Burye, J.D. Nicholas, J. Power Sources, 300 (2015) 402-412.
- [43] M. Shah, S.A. Barnett, Solid State Ionics, 179 (2008) 2059-2064.
- [44] Y.H. Liu, F.Z. Wang, B. Chi, J. Pu, L. Jian, S.P. Jiang, J. Alloy. Compd., 578 (2013) 37-43.
- [45] M. Mogensen, N.M. Sammes, G.A. Thompson, Solid State Ionics, 129 (2000) 63-94.
- [46] B.C.H. Steele, 129 (2000) 95-110.
- [47] J.W. Fergus, J. Power Sources, 162 (2006) 30-40.
- [48] F. Zhao, Z. Wang, M. Liu, L. Zhang, C. Xia, F. Chen, J. Power Sources, 185 (2008) 13-18.
- [49] Z.L. Zhan, D. Han, T.Z. Wu, X.F. Ye, S.R. Wang, T.L. Wen, S. Cho, S.A. Barnett, RSC Advances, 2 (2012) 4075-4078.
- [50] E.O. Zhao, Z. Iia, X.T. Liu, K.O. Gao, H. Huo, Y.P. Xiong, Ceram. Int., 40 (2014) 14891-14898.
- [51] A.J. Samson, P. Hjalmarsson, M. Søgaaard, J. Hjelm, N. Bonanos, J. Power Sources, 216 (2012) 124-130.
- [52] D. Ding, M.F. Liu, Z.B. Liu, X.X. Li, K. Blinn, X.B. Zhu, M.L. Liu, Adv. Energy Mater., 3 (2013) 1149-1154.
- [53] H.S. Song, S. Lee, S.H. Hyun, J. Kim, J. Moon, J. Power Sources, 187 (2009) 25-31.
- [54] X.Y. Lou, S.Z. Wang, Z. Liu, L. Yang, M.L. Liu, Solid State Ionics, 180 (2009) 1285-1289.
- [55] J.D. Nicholas, L.C. DeJonghe, Solid State Ionics, 178 (2007) 1187-1194.
- [56] J. Ranlov, F.W. Poulsen, M. Mogensen, 61 (1993) 277-279.

- [57] M. Chen, B. Hallstedt, A.N. Grundy, L.J. Gauckler, J. Am. Cer. Soc., 86 (2003) 1567-1570.
- [58] S.B. Adler, X.Y. Chen, J.R. Wilson, J. Catalysis, 245 (2007) 91-109.
- [59] F.S. Baumann, J. Fleig, H.-U. Habermeier, J. Maier, Solid State Sci., 177 (2006) 1071-1081.
- [60] D. Oh, D. Gostovic, E.D. Wachsman, J. Mater. Res., 27 (2012) 1992-1999.
- [61] Y. Yu, H. Luo, D. Cetin, X. Lin, K. Ludwig, U. Pal, S. Gopalan, S. Basu, 323 (2014) 71-77.
- [62] D.R. Burfield, K.H. Lee, R.H. Smithers, J. Org. Chem., 42 (1977) 3060-3065.
- [63] K. Pitzer, Y. Shi, J Solution Chem, 22 (1993) 99-105.
- [64] K.S. Pitzer, Y.W. Shi, J. Solution Chem., 22 (1993) 99-105.

Table 1. LSCF-GDC NMCC Characteristics

Figure 1. Scanning electron micrographs of 1.50M PND LSCF (a-d), 1.50M TXD LSCF (e-h) and 0.50M CAD LSCF (i-l) NMCCs produced by firing at 700°C. NMCCs in each row were processed with identical desiccation conditions, with the desiccant strength increasing with each subsequent row [40, 41]. The scale bars are all 50 microns in width.

Figure 2. The average particle size of (a) 1.50M PND LSCF, (b) 1.50M TXD LSC, and (c) 0.50M CAD LSCF measured from SEM micrographs (opaque bars with stripes increasing to the right) of infiltrated particles and Williamson Hall XRD measurements (translucent bars with stripes increasing to the left) on LSCF fired outside a GDC scaffold. At each temperature, desiccants are listed in order of increasing effectiveness when moving from left to right [16, 42]. Open symbols denote undesiccated cathodes, partitioned symbols denote dry air-desiccated cathodes, half-filled symbols denote CaSO_4 -desiccated cathodes, and completely filled samples denote CaCl_2 -desiccated cathodes. The error bars represent +/- a standard deviation in the SEM-measured particle size distribution. Black horizontal lines represent the average particle size found across multiple samples. Unfortunately, a lack of isolated, well-defined LSCF XRD peaks in the 600 and 700°C PND LSCF peaks prevented Williamson-Hall particle size measurements on those cathodes.

Figure 3. Powder X-Ray diffractograms of (a) undesiccated and (b) CaCl_2 -desiccated 1.5M PND LSCF fired outside a GDC scaffold at various temperatures. The JCPDS $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ peak reference comes from PDF #00-048-0124 [18].

Figure 4. Powder X-Ray diffractograms of (a) undesiccated and (b) CaCl_2 -desiccated 1.5M TXD LSCF fired outside a GDC scaffold at various temperatures. The JCPDS $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ peak reference comes from PDF #00-048-0124 [18].

Figure 5. Powder X-Ray diffractograms of (a) undesiccated and (b) CaCl_2 -desiccated 0.5M CAD LSCF fired outside a GDC scaffold at various temperatures. The JCPDS $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ peak reference comes from PDF #00-048-0124 [18].

Figure 6. EIS Nyquist plots of (a) TXD LSCF-GDC and (b) CAD LSCF-GDC NMCCs fired at 700°C after various precursor nitrate solution desiccation treatments. The outermost data was taken at 500°C, the nested data was taken at 600°C and the double nested data was taken at 700°C. Open symbols denote undesiccated cathodes, partitioned symbols denote dry air-desiccated cathodes, half-filled symbols denote CaSO_4 -desiccated cathodes, and completely filled samples denote CaCl_2 -desiccated cathodes. Desiccants are listed in order of increasing effectiveness from top to bottom [16, 42].

Figure 7. R_p Arrhenius plots for (a) PND LSCF-GDC, (b) TXD LSCF-GDC, and (c) CAD LSCF-GDC cathodes fired at 700°C. Open symbols denote undesiccated cathodes and completely filled samples denote CaCl_2 -desiccated cathodes. The solid inclined lines are a guide to the eye linking the experimental data. The dashed inclined lines are SIMPLE model predictions for the undesiccated (coarse dash) and CaCl_2 (fine dash) cathodes. The horizontal dashed line is the $0.1 \Omega\text{cm}^2$ performance target.

Figure 8. a) Open-circuit 540°C R_p aging measurements for various 12 vol% LSCF-GDC cathodes produced with a 700°C LSCF firing temperature, b) scanning electron micrograph images of the CaCl_2 -desiccated TXD-LSCF infiltrate before and after 500 hours of 540°C, open-circuit aging, and c) impedance spectra of the CaCl_2 -desiccated TXD-LSCF cell at various points in the 540°C, open-circuit aging process.

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

Precursor Solution Desiccated
 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$
Infiltrate