Journal of Power Sources 300 (2015) 402–412

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Nano-ceria pre-infiltration improves $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-x}$ infiltrated Solid Oxide Fuel Cell cathode performance

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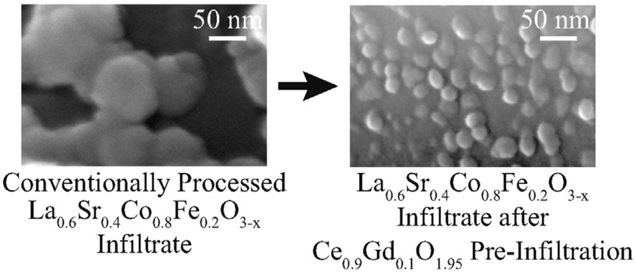
HIGHLIGHTS

- Ceria pre-infiltration reduces infiltrated lanthanum strontium cobalt ferrite size.
- Organic solution additives also reduce lanthanum strontium cobalt ferrite size.
- Ceria pre-infiltrated cathodes with 21 nm sized infiltrate achieve 0.1 Ωcm^2 at 540 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form
24 August 2015
Accepted 21 September 2015
Available online 3 October 2015

Keywords:
Solid oxide fuel cell
Infiltration
Composite
Nano-particle
Degradation
Stability

ABSTRACT

Here, scanning electron microscopy, X-ray diffraction, and thermo-gravimetric analysis experiments show that the pre-infiltration of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) nano-particles reduces the average size of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-x}$ (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 Ωcm^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.

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

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http://dx.doi.org/10.1016/j.jpowsour.2015.09.080
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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 ~0.1 Ω cm^2 at temperatures as low as 575 °C [6]. In these NMCCs, the SOFC cathode reaction:

$$2e'_{(xl)} + \frac{1}{2}O_{2(g)} + V_{O\,(xl)}^{\bullet\bullet} \rightarrow O_{O\,(xl)}^{x} \qquad (1$$

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 Eq. (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 Eq. (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 Eq. (1) reactant) [8]. A high MIEC oxygen surface exchange chemical rate coefficient (k_{chem}) that catalyzes Eq. (1) [9], a high MIEC characteristic thickness ($L_C = D/k$) that ensures Eq. (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 Eq. (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 $Sm_{0.5}Sr_{0.5}CoO_{3-x}$ (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 $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [11] and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [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 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 precursor 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 $La_{0.4}Sr_{0.6}TiO_3$ [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 $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{1.95}$ (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} agglomerate size of 240 nm, a specific surface area of 25.2 m^2/g, and a specific surface area predicted 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 h, 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, ~20 g of Rhodia GDC powder was coarsened at 800 °C for 4 h 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 wt % solids loading. Three layers of GDC ink were screen printed onto both sides of the dense GDC