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Dispersion, connectivity and tortuosity of hierarchical porosity composite SOFC cathodes prepared by freeze-casting

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Abstract

Aqueous co-dispersions of Lanthanum Strontium Manganite (LSM) and Yttria-Stabilized Zirconia (YSZ) were freeze-cast and partially sintered, resulting in anisotropic, hierarchically porous composites for potential applications as solid oxide fuel cell (SOFC) cathodes. The uniform phase dispersion was validated using SEM–EDS and FIB-SEM tomography. Using reconstructed 3D images of samples sintered at 1200 and 1300 °C, the effect of sintering on phase connectivity, triple phase boundary (TPB) density and phase tortuosity was explored. The higher sintering temperature resulted in lower TPB density and, less open pore volume but decreased tortuosity for both the LSM and YSZ due to densification of the structure at high temperatures. Due to the unique double-sided morphology of the freeze-cast walls and the benefits gained from less tortuous percolation paths, a decrease in TPB density and open porosity from elevated sintering temperatures may not degrade the electrochemical performance as much as it would for a standard isotropic microstructure.

Keywords: SOFC; Hierarchical porosity; 3D microstructure; TPB; Freeze-casting

1. Introduction

Solid oxide fuel cells (SOFC) are electrochemical devices used to efficiently convert chemical energy from a fuel (e.g. H_2) into electrical energy. An SOFC typically is comprised of a dense electrolyte and two porous composite electrodes. Electrochemical reactions take place within the composite electrodes at the so-called triple phase boundary (TPB) where the gas (porous phase), ionic conductor and electronic conductor meet. To function, the porous phase must be connected to a gas inlet, the ionic conductor should be connected to the electrolyte and the electron conductor should connect with the current collector and external circuit. A high operating temperature (typically between 600 and 1000 °C) is needed to ensure adequate ionic conductivity within the ion-conducting material, usually Yttria-Stabilized Zirconia (YSZ). The most common materials used for the electron conductor are Strontium-Doped Lanthanum Manganite (LSM) for the cathode and nickel metal for the anode.

Powder processing techniques such as tape-casting or screen-printing followed by partial sintering are commonly used methods for obtaining SOFC electrodes which maintain sufficient porosity for gas access.[1] The microstructure of the electrodes plays a crucial role in the performance of the SOFC, and its optimization is a complex process due to the following functional requirements: (1) ensure high electronic and ionic conductivity, (2) maximize total TPB density and (3) maximize gas access to the TPBs by maintaining adequate open porosity. In addition, handling and thermal loading require that the electrodes maintain a minimum amount of strength and toughness.

It is worth noting that some of these requirements are contradictory; for example, gas access can be easily improved by increasing porosity but this results in a decrease in conductivity and strength. The development of new microstructures and their careful characterization combined with modeling approaches

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is a promising way of obtaining tailored microstructures with an optimal compromise between the various electrode properties. In this respect, anisotropic structures offer an interesting alternative to isotropic ones. Indeed, some of the requirements mentioned above are actually directional, namely conductivity, gas access and to a certain extent mechanical properties. The freeze-casting process in particular can be used to obtain a microstructure with aligned pore channels to improve gas penetration and aligned walls to provide enhanced mechanical properties. This process takes advantage of the highly directional growth of ice crystals within a ceramic slurry followed by removal of the ice crystals by sublimation to controllably template a directionally porous ceramic.[2,3] The green body can then be partially sintered to obtain a hierarchical structure with aligned macro-pores (~10–20 μm) that alternate with microporous ceramic walls. In the previous few years, freeze-casted composite anodes have been produced by several research groups,[4–6] but only recently, the successful processing of freeze-cast LSM–YSZ cathode materials has been reported.[7]

Within the context of freeze-cast processing as a means of microstructure tailoring, studying the influence of processing parameters on the microstructure of the ceramic walls is essential. Indeed, the electrochemical performance of a freeze-cast electrode is highly dependent on the microstructure of its walls, which is controlled by the sintering temperature, freezing conditions and initial slurry characteristics (composition, particle size, dispersion, etc.).[2] In particular, an essential requirement to obtain a functioning composite electrode is the percolation of both the ionic and electronic conducting materials. This requirement can be met using a properly dispersed composite suspension. If both the ionic and electronic conductors have the same particle size and conductivity, the ideal volume ratio for maximum electrochemical performance would be 50:50. Since however, the conductivity of YSZ is over 100 times slower than that of LSM, a 40:60 volume ratio of LSM:YSZ has been shown to increase performance by decreasing ohmic losses while still maintaining percolation of both the electron- and ion-conducting networks.[8,9]

The microstructures of these directionally porous, hierarchical ceramics has been investigated using Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) tomography, which is based on the serial sectioning by FIB and SEM imaging of a sample followed by reconstruction of the SEM micrographs into a 3D image. This powerful technique allows the quantitative 3D examination of electrode microstructures and has been used to study the influence on electrode performance of electrode composition,[10,11] sintering temperature[12] and particle size.[13]

The objective of the present study is to develop a co-dispersion procedure for LSM and YSZ to make a slurry that can be freeze-cast, validate the phase dispersion, characterize the structure of freeze-cast SOFC cathode material, and to analyze the effect of sintering temperature on the microstructure of the microporous walls. First, the spatial dispersion and phase composition of the LSM and YSZ phases are investigated using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffractometry (XRD). Then FIB-SEM tomography is used to investigate the microstructure at the scale of a single wall (~15 μm) from two LSM–YSZ freeze-casts sintered at two different temperatures (1200 and 1300 °C). These temperatures were chosen as they gave significantly different micro-pore morphologies while still maintaining adequate strength and residual porosity for use as an SOFC cathode. FIB-SEM characterization was used to confirm the proper spatial repartition of LSM and YSZ grains and to analyze the effect of the sintering temperature on the connectivity of the LSM, YSZ and pore phases within the walls of a freeze-cast SOFC cathode. FIB-SEM characterization also allows the density of TPBs as well as the tortuosity factors for all three phase networks (LSM, YSZ and pores) to be calculated in various directions.

2. Experimental procedure

2.1. Preliminary aqueous co-dispersion studies

Initial attempts at slurry dispersion and freeze-casting were based on previously successful methods for co-dispersing SOFC anode materials.[14] The LSM and YSZ powders were first ball-milled dry to form a homogenous powder. This mixture was slowly added into deionized (DI) water containing an ammonium polymethacrylate dispersant (Darvan C-N, R.T. Vanderbilt Co., Norwalk, CT) until approximately 25 vol.% solids was reached. The pH was not controlled during these initial attempts. The slurries produced using this method were highly viscous and impossible to freeze-cast no matter the level of dispersant used.

More advanced, methods for the co-dispersion of two materials typically rely on exploiting the isoelectric points of the individual materials.[15] These methods alone proved inadequate however and the suspensions which were initially created were unstable and resulted in the immediate segregation of LSM from YSZ. Indeed, over a broad range of experimental parameters (18–25 vol.% solids, 1.5–5 wt.% dispersant, 3–5 wt.% binder, pH = 6–10), freeze-casting resulted in the formation of spherical YSZ agglomerates, which sintered into dense spheres 10–50 μm in size, which would embed themselves within the larger freeze-cast matrix (Fig. 1). EDS spectra showed that these spheres were composed almost exclusively of YSZ. The spheres reduced the active volume fraction of YSZ within the freeze-cast matrix inhibiting the percolation of the ion-conducting phase.

Three steps were required to produce a stable, aqueous co-dispersion. First, YSZ must be fully dispersed on its own, prior to the addition of the LSM, thereby allowing full coverage of the dispersant on the YSZ particles. Second, the pH of the solution during co-dispersion must be carefully controlled. Acidic pH values can potentially lead to the leaching of Yttrium ions out of solution while values too close to the isoelectric points of the materials (6 and 8 for LSM and YSZ, respectively) will result in particle sedimentation.[16–18] For these reasons, the pH of the slurry was kept between 7 and 8. At this pH, the two particles are oppositely charged and coagulate without segregation. Lastly, the viscosity of the slurry must remain high enough to partially coagulate the suspension, hindering the majority of particle segregation, while at the same time be low enough to still allow the slurry to be easily freeze-cast.[7] The high