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ORIGINAL PAPER

Thin film YSZ coatings on functionally graded freeze cast NiO/YSZ SOFC anode supports

**Paul Gannon · Stephen Sofie · Max Deibert ·
Richard Smith · Vladimir Gorokhovsky**

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Abstract Intermediate temperature (600–800 °C) solid oxide fuel cell (SOFC) technology is often limited by inadequate gas transport in electrodes, and high ion transport resistance electrolytes. In this study, large area filtered arc deposition (LAFAD) and hybrid filtered arc-assisted e-beam physical vapor deposition (FA-EBPVD) technologies, in combination with freeze-tape-casting, were used to fabricate SOFC anode/electrolyte bi-layers with functionally graded porous anode microstructures and thin film electrolytes favorable for both gas transport and low resistance. Traditionally-processed NiO/YSZ in addition to freeze-tape-cast NiO/YSZ anode substrates were fabricated and subsequently coated with thin film (<1–20 μm) YSZ via LAFAD and FA-EBPVD. LAFAD was found to be effective in applying thin (∼1 μm) dense YSZ films on porous substrates at ∼400 °C. FA-EBPVD produced relatively thick (∼10–20 μm) dense YSZ coatings on porous substrates, with columnar morphology and nano-metrical grain size. A ∼10 μm FA-EBPVD YSZ coating was observed to bridge NiO/YSZ surface pores of ∼10 μm, which typically requires pre-filling prior to conventional thin film coating processes. Coated substrates exhibited negligible curvature, yielding flat anode/electrode bi-layers up to 2.5 cm in diameter. These results are presented with conderations for future SOFC development discussed.

Keywords SOFC · PVD · YSZ · Thin film electrolytes · Freeze-tape-casting

1 Introduction

Decreasing Ohmic losses and concentration polarization are focus areas for high current density intermediate temperatures (650–800 °C) anode-supported SOFC technology. Substantial research activity has been directed to understand the extent of these contributions to SOFC performance [1, 2]. Desirable performance is achieved only with thin (∼10–30 μm) robust yittria-stabilized zirconia (YSZ) electrolytes, yielding an area specific resistance (ASR) of <0.3 Ω cm^2 [3]. Further, conventional tape-cast NiO/YSZ anode microstructures often suffer from concentration polarization, a condition where fuel demand exceeds supply. The onset of concentration polarization in thick SOFC anodes has been shown to range from 0.25 to >2 A cm^{-2}, dependent upon the fuel and diluent gas concentrations [4]. This limitation has been attributed in part to the high tortuosity of gas diffusion pathways within these porous ceramics and the relatively thick cross section required for cell structural support [4].

Traditional electrolyte fabrication processes for SOFCs include: aerosol spray; screen printing; and, tape casting. While these powder ceramic processes are effective and economical for application of film thicknesses greater than ∼10 μm, fabrication of films <10 μm using these

P. Gannon (✉) · M. Deibert
Department of Chemical and Biological Engineering,
Montana State University, 306 Cobleigh Hall, Bozeman,
MT 59717-3920, USA
e-mail: pgannon@coe.montana.edu

S. Sofie
Department of Mechanical Engineering, Montana State
University, Bozeman, MT, USA

R. Smith
Department of Physics, Montana State University,
Bozeman, MT, USA

V. Gorokhovsky
Arcomac Surface Engineering, LLC, Bozeman, MT, USA

processes often yields pinholes and other defects which can result in non-hermetic sealing between the air/fuel (cathode/anode) electrode compartments [5]. Defects are common in powder processed coatings due to large particle sizes (e.g., 1 μm particles would span approximately 1/10th of the electrolyte thickness), which requires extremely homogeneous suspensions/pastes for uniform thin film electrolytes, especially in large area applications.

While electrolyte supported cell (ESC) technology has an established open circuit voltage (OCV) greater than 1.1 V, anode supported cell (ASC) technology often yield lower OCVs [6–8]. This unfortunate phenomenon is often attributed to defects within the YSZ electrolyte, and not leak current as with some ceria-based electrolytes [9]. These features illustrate the inherent weakness of traditional ceramic processes for SOFC fabrication.

The structural integrity of ASC technology is afforded entirely by the relatively thick (e.g., 0.25–1 mm) anode, which is usually joined by a thin (~10–30 μm) electrolyte. Anode microstructure design is complicated by the necessity for sufficient porosity to adequately deliver fuel gases (e.g., CH_4, H_2, CO) and remove bi-product gases (e.g., H_2O, CO_2). Finding the proper balance between mechanical properties and gas transport is non-trivial as it involves optimization in each stage of SOFC fabrication; materials processing, cell operation, as well as interconnection and sealing within stacks. Traditional Ni/YSZ anodes are fabricated by tape casting utilizing YSZ and NiO powder as precursors [10]. While Ni metal melts at 1455 °C, NiO melts at ~1984 °C, and is non-reactive with YSZ in sintering processes which can reach 1500 °C. Upon sintering, the NiO/YSZ anode is highly dense; however, during initial cell start-up, exposure to H_2 reduces NiO to Ni, yielding the desired porous Ni/YSZ anode. Starting compositions of 34 wt% YSZ and 66 wt% NiO can be utilized to yield 50 vol% YSZ and 50 vol% Ni after reduction, which generates an approximately 35% porosity to form an interconnected (percolating) porous network. Porosity can be further increased by the addition of thermal fugitives (e.g., carbon, polymers, graphite, etc. of varying morphologies) to the tape cast premix to improve the gas transport characteristics, but at the cost of mechanical strength [11, 12].

The combination of traditional ceramic processes to fabricate the critical anode/electrolyte bi-layer results in two additional engineering challenges associated with anode surface condition as well as the asymmetry of the ASC geometry. ASCs are fabricated using either co-sintering or post-sintering approaches. In the co-sintering approach (single step process) the electrolyte is applied to the green anode prior to sintering, and in the post-sintering approach (two-step process) the electrolyte is applied to the pre-sintered anode and then they are sintered together. Regardless of the approach, traditional tape cast anodes (without pore formers) exhibit smooth, dense surfaces ideal for powder/liquid based coating systems. Deviations from traditional anode processes to improve gas transport characteristics, however, can yield less than ideal for non-uniform and defect laden surfaces. Furthermore, a thick NiO/YSZ anode (250–1000 μm) and thin YSZ electrode (5–20 μm) have different coefficients of thermal expansion (CTE) as well as differing shrinkage rates. Often, cell curvature, or camber is the result of these thermally induced mechanical stresses at the anode/electrolyte interface. While advanced processing methods and presintering steps can yield an overall shrinkage match, the 12.5 ppm/°C CTE of the anode (NiO state), compared to the 10.8 ppm/°C CTE of the electrolyte often results in convex curvature of the electrolyte surface, as depicted in Fig. 1. This cell curvature, found even in commercially-processed SOFCs, can generate substantial stack construction and stability difficulties [13].

Recent development of the freeze-tape-casting process has shown the ability to engineer large area, thick film (0.2–1 mm), functionally graded columnar pore structures highly conducive to gas transport [14]. This novel ceramic powder tape casting process inherently creates macro pores, which is greater than the thickness of the desired electrolyte coating, in both the green and sintered anode substrates. This dramatically increases the difficulty of applying effective ultra thin, pinhole free electrolytes. To

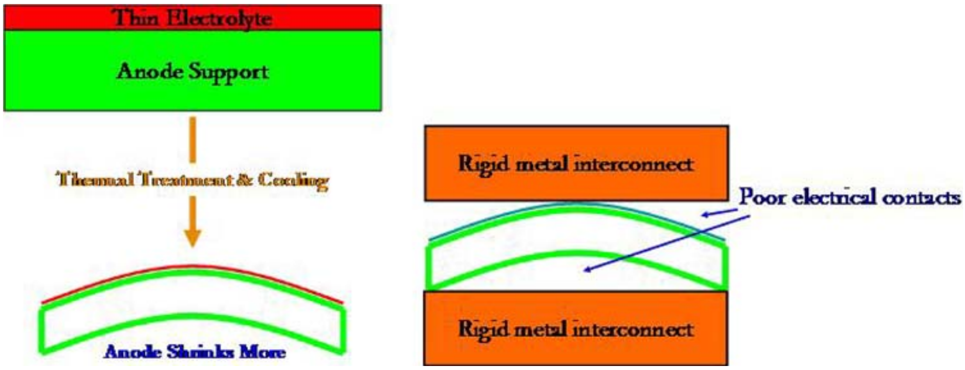

Fig. 1 The formation of cell camber is SOFC fabrication as well as the effects of cell camber in stack assembly and operation

overcome these limitations, conventional EB-PVD has been investigated to deposit thin film YSZ SOFC electrolytes on NiO/YSZ substrates [15]. Others are using filtered arc deposition to create thin-film, nano-structured YSZ coatings [16]. The hybridization of these PVD techniques is realized in FA-EBPVD, which may provide distinct advantages over either technique alone. The combination of advanced (LAFAD) and hybrid (FA-EBPVD) PVD techniques with freeze-tape-cast technology shows promise to substantially improve the fabrication and performance of both the anode and electrolyte for state-of-the-art SOFCs. Therefore, the objective of this study is to investigate the application of LAFAD and FA-EBPVD YSZ coatings on freeze-tape-cast NiO/YSZ anode substrates. The effects of anode porosity and YSZ coating characteristics have been analyzed by electron microscopy to assist in ascertaining the effectiveness of this proposed bi-layer system.

2 Experimental

Freeze-tape-casting was performed with NiO (Alfa Aesar) and 8YSZ (TZ8YS, Tosoh) powders used as received. The NiO/YSZ tapes were prepared with 34 wt% YSZ and 66 wt% NiO powder pre-mix. The slurries were homogenized in aqueous suspension by ball milling at 30 vol% solids loading and frozen on a −30 °C bed to generate the graded pore morphology. The freeze-tape-casting processes were performed in a manner identical to that described in the literature [14]. The approximately 1 mm thick frozen tapes were freeze dried to remove the water and cut into 1.0 and 2.5 cm circular substrates for sintering. Additionally, NiO/YSZ powders of the same weight ratios were uni-axially pressed to a thickness of 1 mm in a 3.175 cm diameter stainless steel die at 75 MPa for comparative study. The tapes and discs were sintered at 1450 °C for 2 h to achieve flat substrates for coating.

LAFAD and FA-EBPVD processes were carried out by Arcomac Surface Engineering, using equipment described elsewhere [17, 18]. For LAFAD processes, NiO/YSZ anode substrates (2.5 cm dia) were fixed on stainless steel plates and placed on a rotating substrate carousel in front of the dual LAFAD sources, which were equipped with Zr-Y (82–18 wt%) alloy targets. In a highly-ionized Ar/O_2 gas atmosphere, Zr and Y ions were deposited from LAFAD sources onto the NiO/YSZ substrates at ~400 °C. For FA-EBPVD processes, NiO/YSZ anode substrates were positioned stationary ~3″ above a 6 kW electron beam hearth containing a dense 8 mol% YSZ pellet (Praxair Specialty Ceramics). Filtered arc plasma (from the LAFAD source) ionized the YSZ vapor (from EBPVD), which condensed onto the porous NiO/YSZ anode substrates to form dense, 10–20 μm YSZ films with columnar morphology and nanometrical grain size. Further LAFAD and FA-EBPVD process details will be presented in an upcoming manuscript [19].

Surface and cross sectional scanning electron microscopy (SEM) of coated samples was conducted using a Zeiss VP55 Supra, equipped with an energy dispersive X-ray spectrometer (EDS). Fractured cross sections were prepared manually and polished cross sections were prepared using a precision polishing system (Allied High Tech). Presented and discussed here are YSZ coating thickness, uniformity, and coverage on porous NiO/YSZ, along with considerations for future development.

3 Results

Baseline evaluation of the coating process was performed on uniaxially pressed NiO/YSZ pellets. Figure 2 show the SEM images of fractured cross sections of LAFAD YSZ coatings on these traditionally fabricated porous NiO/YSZ anode substrates. The ~1 μm YSZ coating shows a clean, coherent coating which substantially cover the surface pores. The effect of pore-filling is illustrated in Fig. 3, in which the LAFAD YSZ coating is shown to penetrate down to ~10 μm below the surface.

The characteristics of freeze-tape-cast NiO/YSZ substrates are shown in Fig. 4, where the engineered columnar porosity is evident. The thin (significantly discontinuous) YSZ layer is visible at the top of the image. Figure 5 presents more magnified polish cross section SEM images of this sample. The ~10 μm coating was not continuous, but did bridge ~10 μm surface pores.

The low tortuosity (linear porosity) of the freeze-tape-cast substrates is further illustrated in Fig. 6 by the extensive penetration of a LAFAD YSZ coating ~50 μm into the structure. As substrate surfaces are covered with a

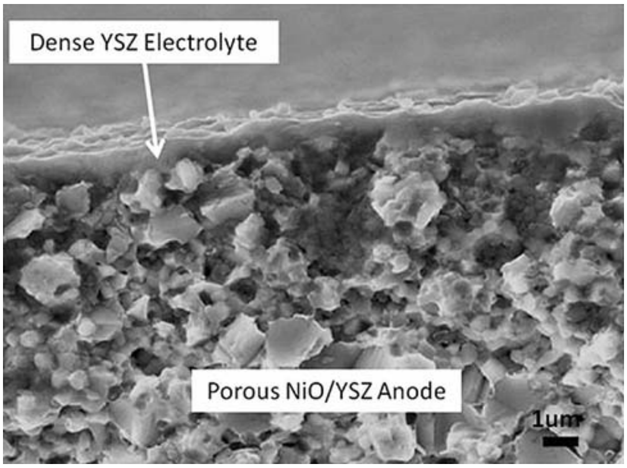

Fig. 2 SEM fractured cross section images of ~1 μm LAFAD YSZ coating on traditional porous NiO/YSZ (bar = 1 μm)

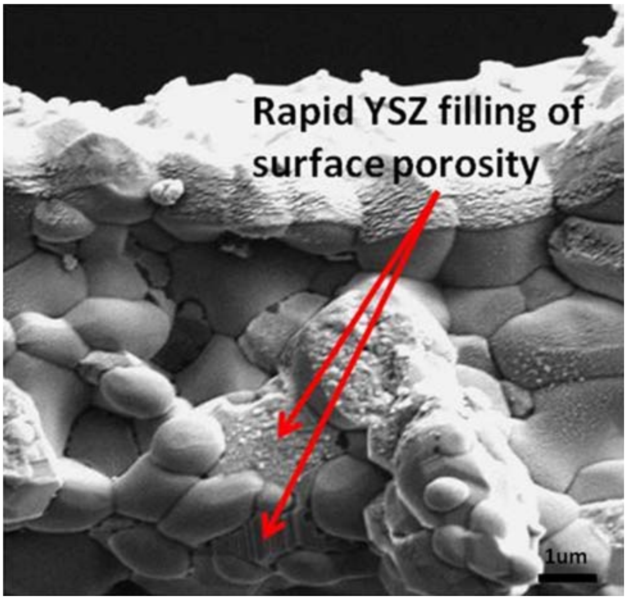

Fig. 3 The filling of surface porosity (i.e. pore bridging) evidenced in the LAFAD YSZ coating on porous NiO/YSZ (bar = 1 μm)

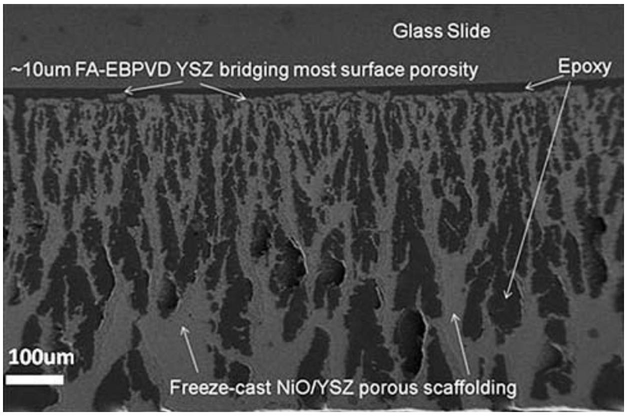

Fig. 4 SEM fractured cross section images of $\sim$10 μm FA-EBPVD YSZ coating on freeze-tape-cast porous NiO/YSZ (white bar = 100 μm)

thin YSZ film, pores do not become bridged, and a continuous electrolyte is not formed.

Figure 7 presents SEM surface images of FA-EBPVD YSZ on a Ni-based alloy before and after 36 h of thermal cycling in air from 500–1100 °C. The nano-structured YSZ (~ -20 nm surface crystallites) did not change significantly during the thermal cycling exposure.

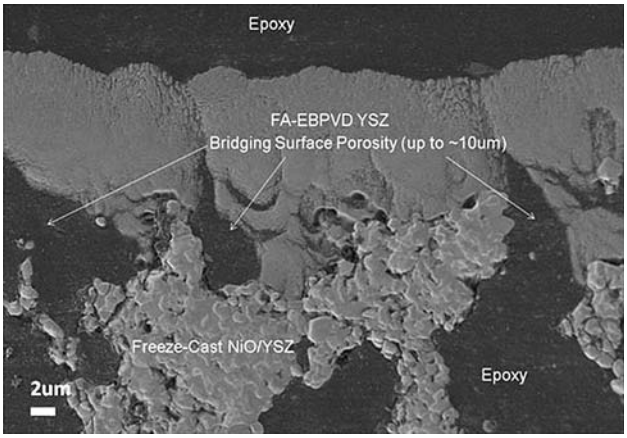

Fig. 5 The filling of surface porosity (i.e. pore bridging) evidenced in the FA-EBPVD YSZ coating on freeze-tape-cast porous NiO/YSZ (bar = 2 μm)

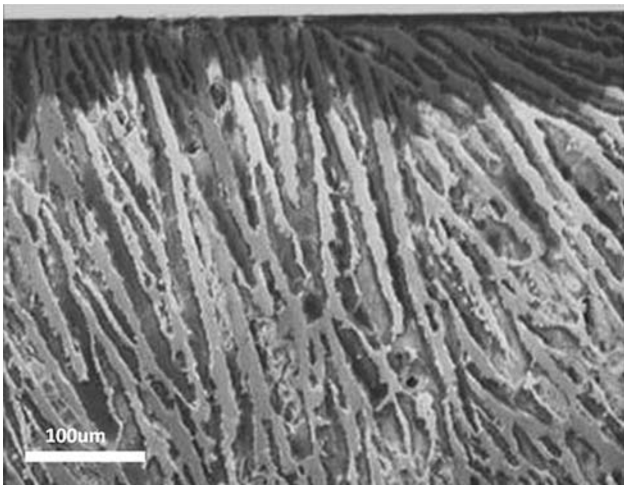

Fig. 6 The penetration of LAFAD YSZ coating material on freeze-tape cast NiO/YSZ. (bar = 100 μm)

4 Discussion

Traditionally-processed NiO/YSZ was initially coated with the LAFAD process to demonstrate PVD technology in a manner more consistent with state-of-the-art ASCs, utilizing a low porosity support structure. The LAFAD YSZ coating shown in Fig. 2 has a very uniform thickness across the imaged specimen surface. The upper surface of the LAFAD YSZ shows substantial surface roughness due to the high deposition rates, however, this may be advantageous for subsequent cathode application processes by means of electrolyte texturing. The coating appears to have penetrated surface pores to a considerable distance, as shown in Fig. 3. The depth of the pore-filling substantially exceeds the thickness of the coating, illustrating the ease by which highly textured/rough electrolytes can be fabricated. Figure 3 also shows, however, that the electrolyte is a semi-continuous $\sim$1 μm YSZ layer on the porous NiO/YSZ anode substrate. While the layer did not completely bridge all of the substrate surface porosity, it is anticipated that with process modifications, LAFAD technology is capable of depositing continuous defect-free YSZ layers on porous NiO/YSZ substrates.

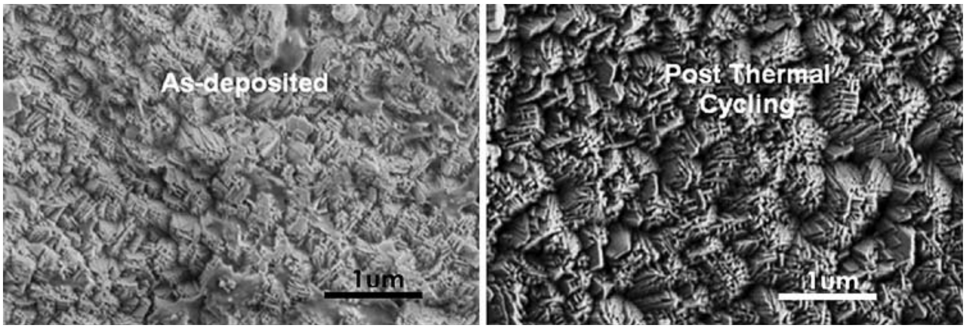

Fig. 7 SEM surface images of FA-EBPVD YSZ on Ni-based alloy before (left) and after (right) thermal cycling exposures (12, 3 h cycles from 500–1100 °C in air)

While thin film coatings are potentially useful in their own right to enhance the performance of ASC technologies, combination of ultra thin films on functionally graded anodes bears the greatest potential for substantial performance improvements. The freeze-tape-casting system generates a continuous pore size gradient from approximately 50–100 μm down to 3–10 μm, as shown in Fig. 4. The large pore side is intended to enhance fuel delivery while the small pore side provides the fine microstructure needed to expand the triple phase boundary (TPB) region at the anode/electrolyte interface. The extent of open, linear porosity (tortuosity ~1) typically necessitates preliminary pore-filling prior to electrolyte application. However, the FA-EBPVD YSZ coating was directly applied to the small pore side of the freeze-tape-cast NiO/YSZ anode without previous pore-filling. This feature is attributed to high deposition rates (~10–100× higher than LAFAD) and the highly-activated deposition vapor, which condenses rapidly and bridges surface porosity. Most surface porosity was effectively bridged by the FA-EBPVD YSZ coating; however, ~10% of the surface pores remain uncovered, thereby requiring additional optimization.

The high porosity of the freeze-tape-cast NiO/YSZ (~60%) can be susceptible to curvature effects from traditional coating and subsequent high temperature sintering processes. The relatively low temperature FA-EBPVD process (~400 °C) results in substantially dense YSZ films without required thermal treatment, thus alleviating the generation of cell camber as indicated in Fig. 1. The pore-bridging effect of the FA-EBPVD coating is shown in Fig. 5 where the approximately 10 μm pores were effectively bridged without altering the gas diffusion pathways. The surface pore size of the freeze-tape-cast NiO/YSZ varied, but was significantly larger than the thickness of the LAFAD YSZ coating. While very large pores (>10 μm) will be almost impossible to bridge with ultra thin PVD films, the coating system can also be employed to pre-coat porous anode surfaces prior to conventional electrolyte application to mechanically anchor the YSZ electrode and increase the TBP region and associated electrochemical performance. Figure 6 shows the ~100 μm penetration of LAFAD YSZ into the freeze-tape-cast substrate. Through multiple deposition iterations, compositionally-graded electrolyte layers may be successively applied to grow the electrolyte from within the porous anode. Alternatively, LAFAD could be used as a process prior to FA-EBPVD for YSZ electrolytes on porous anode supports.

The nanostructured FA-EBPVD YSZ surface stability evidenced in Fig. 7 displays another potential advantage of ionized PVD electrolyte fabrication. Nano-crystalline YSZ has been observed to have increased ionic conductivity via increase grain boundary area as compared with bulk YSZ [20, 21]. The stability of this nano-cystalline structure during thermal cycling to 1100 °C in air provides encouraging evidence for its durable application as an SOFC electrolyte. It is likely these ionized PVD techniques would similarly result in nano-structured proton-conducting electrolytes, which may offer substantial performance and mechanical properties improvements compared to conventional electrolyte fabrication.

Additional benefits of electrolyte texturing further expands the potential of merging freeze-tape-cast and ionized PVD technologies. Traditional texturing processes increase net thickness of the electrolyte, thus increasing surface area and interface integrity, but ultimately increasing Ohmic resistance through a thick electrolyte. The FA-EBPVD system provides the means to maintain a very thin electrolyte while simultaneously achieving texture. Further, the freeze-tape-cast NiO/YSZ anode columnar pore morphology and resultant capillary forces may also promote extension of the TPB region. This is shown schematically in Fig. 8 where traditionally, a planar interface between the electrolyte and anode is achieved. However, the surface morphology of freeze-tape-cast anodes permits significant electrolyte coating penetration, thus extending the critical TPB region, while also minimizing anode/electrolyte degradation induced by delamination.

These tape-casting and PVD technologies are not limited to NiO/YSZ materials, making them promising candidates for fabrication of ceria-based and other proton-conducting SOFC (p-SOFC) systems. To assess the economic feasibility of these technologies for SOFC and/or p-SOFC applications, in-depth productivity and cost analysis of potential industrial-scale systems are warranted.

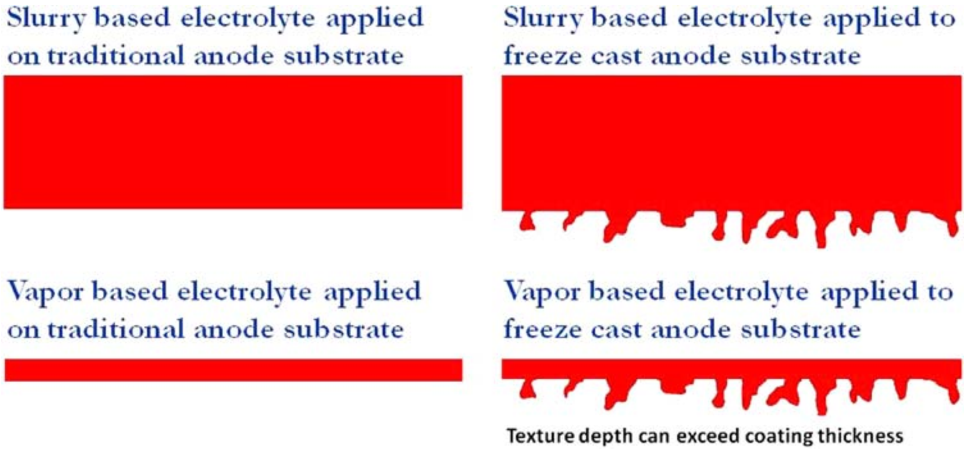

Fig. 8 Conceptual comparison of slurry vs. vapor coating techniques on traditional and freeze cast substrates

5 Conclusions

NiO/YSZ freeze-tape cast anode substrates were fabricated with functionally graded porosity and subsequently coated with thin film (<1–20 μm) YSZ via LAFAD and FA-EB-PVD. LAFAD was found to be effective in applying thin (∼1 μm) dense YSZ films on traditional porous substrates at ∼400 °C. FA-EBPVD produced relatively thick (∼10 μm) dense YSZ coatings on porous substrates, with columnar morphology and nano-metrical grain size. Although both LAFAD and FA-EBPVD produced dense YSZ coatings on porous substrates, further optimization is required to realize uniform and complete coverage of substrate surface pores. These PVD technologies, combined with freeze-tape-casting show promise for fabricating SOFC anode/electrolyte bi-layers with highly favorable microstructures for improved performance. Future work will include coating optimization for SOFC fabrication and Nernst potential measurements to ascertain coating integrity. Further, electrochemical testing will be performed utilizing traditional screen printed cathodes to determine the operational benefits and durability of these engineered SOFC and/or p-SOFC microstructures.

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