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A novel route for manufacturing asymmetric BSCF-based perovskite structures by a combined tape and freeze casting method

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ABSTRACT

In this work, we present an innovative route for the preparation of asymmetric structures by combining the tape and freeze casting methods A perovskite oxide ceramic based on BSCF ($Ba_{0.5}S_{0.5}Co_{0.8}Fe_{0.2}O_{3\text{-}\delta}$) was chosen as the mother material. BSCF freeze cast substrates showed highly ordered and interconnected pores networks with open porosity from 66% to 79%. The top layer for the tape cast was altered by doping BSCF with Zr, thus forming a slightly different compound BSCFZ. The BSCFZ slurries containing 1.0 wt% dispersant and pH >6 were characterised by pseudoplastic behaviour, ideal for the preparation of tape cast layers. Coupling the BSCF freeze cast substrate with the BCSFZ tape cast green top layer to make asymmetric structures was achieved by the pre-sintering of the substrate between 900 and 1050 °C. This allowed for the densification and coupling of the BSCFZ top layer, resulting in suitable adhesion with no cracks or delamination. Higher pre-sintering temperatures than 1050 °C limited the densification of the BSCFZ top layer as the coefficient of expansion between the substrate and top layer did not match, leading to the formation of surfaces with high porosity.

1. Introduction

Ceramic asymmetric structures are very desirable in many industrial applications. One clear example is ceramic membranes, where a top thin layer is generally deposited on porous asymmetric ceramic substrates [1]. There are several advantages for this type of asymmetric configuration. First, top layers are generally very thin ($<100\ \mu m$) and since the mass transport is inversely proportional to thickness, the membrane flux can be improved. However, top thin ceramic layers are mechanically weak, and break quite easily. Hence, the second reason for ceramic asymmetric structures is that the porous substrate provides the mechanical strength to increase the robustness of membranes [2].

Conventionally asymmetric structures were prepared by stacking particles with different sizes [3]. In this configuration, there is a gradient of particle sizes where the porous substrate is mainly composed of larger particles, followed by interlayers which contain smaller particles, and finally the top thin layer. The interlayers have a special function as they smooth the porous substrate surface for the coating of the top thin layers, thus reducing the probability of thin film defects [4]. However, interlayers tend to increase the number of manufacturing steps and likewise the cost of the final membrane. There are ample examples of using ceramic asymmetric structures in the membrane field, where the majority of the porous substrates are alpha-alumina [5–7]. The interlayers are generally composed of small gamma-alumina particles [8], whilst a variety of ceramic derived materials have been used as top thin layers including metal oxide silica [9,10], titania [11–13] and zirconia [14,15].

Perovskite oxides are ceramic materials which are of great interest for many applications such as membranes for oxygen separation from air [16–18] and catalysis [19,20]. However, many perovskite compounds undergo phase changes at high temperatures, and their thermal expansion coefficients change subtly particularly BSCF ($Ba_{0.5}S_{0.5}Co_{0.8}Fe_{0.2}O_{3\text{-}\delta}$) above 500 °C [21]. As a result, coating perovskites on traditional alpha-alumina asymmetric porous substrate

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has been challenging, cracking the perovskite layers and rendering the membranes ineffective. To tackle this problem, Baumann, Meulenberg and co-workers [22] pioneered high performance BSCF perovskite asymmetric membrane. Their successful approach was contrary to the traditional method of preparation of asymmetric structures, as the BSCF dense film was initially prepared by tape casting, and then a porous substrate was used to coat the top of the dense film. As both the top layer and the porous substrate were of the same material, the coefficient of thermal expansion matched across the whole asymmetric structure. Recently, asymmetric BSCF structures were prepared in a single production step, by pressing perovskite layers containing pore forming agents such as graphite [23], activated carbon [24], carbon fibre [25], amorphous malic precursor [26], corn starch [27] and surfactants [28], together with a dense perovskite thin top layer. Upon sintering in air, the pore forming agents were burnt off, resulting in cavities and the formation of a porous substrate whilst the top layer remained dense. However, this latest approach resulted in an undesirable reduction of the pores on the external surface of the substrate [24] whilst pore size control proved to be difficult.

A more attractive method to control the pore size of ceramic substrates is the freeze casting technique. In this method, the solvent present in ceramic slurries is frozen, and the ceramic particles are trapped between the growing solvent crystals [29–33]. Subsequent to sublimation, the particles are still connected. Upon sintering, this process leads to the formation of highly interconnected pore networks. Serra's group reported the preparation of perovskite freeze cast structures with aligned pore structure [34,35]. The same group used screen printing to prepare LSCF top layers on LSCF freeze cast porous substrates resulting in improved performance of membranes against those prepared by conventional methods. Again, the same LSCF material was used for both top layer and freeze cast porous substrates, whilst using different perovskite materials has yet to be reported. The partial substitution of compounds in the perovskite structure has been extensively used to improve the performance of perovskites, including doping with Cu [36], Zr [37–39], Y [40] and Bi [41]. Therefore, coupling doped or partially substituted perovskites top layers on freeze cast porous substrates may be desirable, though the ceramic processing and sintering of using slightly different materials warrants further understanding.

Therefore, this work investigates a novel route for obtaining asymmetric perovskite structures by a combined tape and freeze casting method. We chose BSCF as the mother material for the freeze cast porous substrate and a modified BSCF doped with Zr for the top layer to form asymmetric structures with slight different materials. This work also investigates the effect of the pre-sintering temperature on open porosity and shrinkage of the freeze-cast porous substrate and their subsequent effect by co-sintering the top layer together. The rheological properties of the Zr doped BSCF with dispersant are fully studied to determine the best parameters for the preparation of tape casting layers.

2. Materials and methods

2.1. Preparation of freeze cast substrate

A commercial grade BSCF powder purchased from Treibacher AG (> 99.8 wt%, Austria) was used as received (mean particle size of ~2.7 μm). This powder was dispersed in deionised water and citric acid (Aldrich/≥99.5 wt%). The final BSCF: water: citric acid ratio was 50.0: 49.0: 1.0 wt%. The slurry was then maintained under stirring for 16 h, and under sonication for further 10 min. Then the slurry was poured into cylindrical moulds (16 mm in diameter, 25 mm long) positioned on a copper holder. The unidirectional freezing of the solution was carried out by partially submerging the copper holder in liquid nitrogen. Subsequently, the samples were freeze dried for 48 h at −50 °C and 2.7×10^{-4} bar (Liotop L101 freeze-drier). The green bodies were heat treated at 900, 1050 or 1100 °C in air at a ramping rate of 2 °C min^{-1}. The dwell time at the target temperature was kept constant at 1 h. The heat treated samples were then cut in the direction perpendicular to the freezing direction with a low speed diamond saw. The as-prepared substrate dimensions were 13–15 mm in diameter and 2 mm in height. After the cutting step, the substrates were washed with acetone and dried in hot air.

2.2. Preparation of tape cast top layers

The tape cast top layers were synthesized using a zirconium-doped BSCF powder. This powder was prepared via and ethylenediamine-tetra-acetic acid (EDTA) citrate method. Briefly, nitrates of barium, strontium, cobalt, iron (~98 wt%, Vetec) and zirconium (~98 wt%, Inlab) were dispersed in a previously prepared solution of EDTA (> 99 wt%, Vetec), distilled water, ammonia and citric acid (> 99 wt%, Vetec). The molar ratio of metal ions: citric acid: EDTA was kept constant at 1: 2: 1.1. The as-obtained solution was kept under stirring at 100 °C for 3 h. Ammonium hydroxide was added to adjust the pH to 5. After stirring, a gel was obtained, which was subsequently dried at 200 °C for 8 h, and then calcined at 900 °C for 8 h. Both the drying and calcination steps were performed in air. The as-prepared powders were milled in a planetary ball mill (Retsch PM100) at 400 rpm for 1 h using agate beads. The obtained powders exhibited a mean particle size of ~1.1 μm.

The BSCFZ powder was then mixed with distilled water and a dispersant (Dolapix CE 64, Zschimmer-Schwarz) and further ball milled at 160 rpm for 4 h. In a second milling step, an acrylic binder (Mowilith LDM 6138, Clariant) was added to the solution which was ball milled for further 30 min. The concentration of BSCFZ powder was set at 15 and 25 vol% of the total slurry, while the amount of dispersant and binder were calculated in relation to solids loading of 1 and 20 wt%, respectively. Small amounts (0.5 wt% of solids loading) of an antifoamer (Antifoam A, Sigma Aldrich) and a surfactant (Cocoamide) were also added in the second step of milling to help removing air bubbles of the slurry and to make easier the releasing of the cast tape after drying, respectively.

Tape casting was carried out at room temperature using a tape caster machine (CC-1200, Richard E. Mistler, Inc.) on a moving polyethylene terephthalate carrier film coated with a fine silicon layer (Mylar, G10JRM, Richard E. Mistler, Inc.). The casting speed was kept constant at 6 cm min^{-1} and the gap between the blade and the carrier was adjusted manually to 240 μm. The pre-sintered porous substrates were deposited on the cast slurry, around 30 min after casting. The as-prepared asymmetric membranes were dried in air at room temperature for 24 h and then cut and removed from Mylar for co-sintering stage. Subsequently, the asymmetric ceramics were thermally treated in air up to 500 °C at a ramping rate of 1 °C min^{-1} with a dwell time of 1 h for debinding. Co-sintering was subsequently applied up to 1050 °C with a ramping rate of 5 °C min^{-1} and a dwell time of 8 h.

2.3. Characterization

The freeze cast BSCF substrates were examined by scanning electron microscopy (SEM, Aspex Explorer) and X-ray microtomography (μCT, Skyscan 1172 high-resolution micro system). The SEM samples were not sputtered before those analyses. μCT was performed using an X-ray voltage of 100 kV and a 0.5 mm thick aluminium filter. A CCD camera with 2000 × 1048 pixels was applied to record the transmission of the X-ray beam across the samples. Three-frame averaging and a step size of 0.30° were used, covering a view of 180°. The porosity of the freeze cast substrates was

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