Stannate-Based Ceramic Oxide as Anode Materials for Oxide-Ion Conducting Low-Temperature Solid Oxide Fuel Cells

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Lanthanum-doped barium stannate, $\text{Ba}_{0.98}\text{La}_{0.02}\text{SnO}_3$ (LBS) ceramic oxide was developed as an alternative redox stable anode material for oxide-ion conducting, low-temperature solid oxide fuel cells (350–650°C). LBS with ZnO as a sintering aid exhibited a high electronic conductivity of 216 S/cm at 650°C under reducing gas conditions. A flexural strength of ~66 MPa at 550°C was obtained for ZnO-doped LBS; further investigation revealed that it can withstand 10 reduction-oxidation and thermal cycles. The performance of ZnO-doped LBS as an anode was determined with a GDC based electrolyte-supported SOFC. The catalytic activity for hydrogen oxidation and oxide conductivity was introduced by infiltration of Ni-GDC precursor. The maximum power densities of 0.28 W/cm² (at 0.6 A/cm²) and 0.17 W/cm² (at 0.36 A/cm²) was achieved at 650 and 600°C, respectively, in humidified hydrogen as fuel for 2 wt% ZnO-doped LBS.

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Solid oxide fuel cells (SOFCs) are highly efficient, electrochemical energy conversion devices that utilize a range of fuels such as hydrogen, natural gas, gasoline, diesel or biofuel with air as oxidant.¹ Development of efficient SOFCs at a lower cost is essential for commercialization.² Problems associated with conventional high temperature operating SOFCs ($\geq 800^\circ\text{C}$), such as degradation of stack materials, slow startup time and thermal cycling instability can be improved by lowering the operating temperature. As such, extensive efforts are underway to develop low operating temperature solid oxide fuel cells (LT-SOFCs, 350–650°C).^{3,4} LT-SOFCs can satisfy the power requirement in the ranges between 0.01–100 kW for a variety of applications such as residential (e.g., powering households), transportation (e.g., range extender for plug-in-vehicles) and military and portable needs (e.g., remote access, charger for laptops/cell phones).³ Moreover, LT-SOFCs enable the use of nanostructured electrodes to obtain high performance without compromising long-term stability. In addition, lower temperature enables the use of low-cost compressive gasket seals and inexpensive materials e.g., steel interconnects.^{4,5}

Ni-GDC based metal-ceramic composite (cermet) is a commonly used anode for LT-SOFCs and a high performance of 2 W/cm² at 650°C in H₂ was achieved using Ni-GDC cermet anode.³ However, they impose challenges for fuel cell developers. For example, Ni/NiO volumetric changes upon reduction-oxidation cycles are irreversible.⁶ Ni-GDC based cermet is prone to carbon deposition and sulfur poisoning in the hydrocarbon-based fuels, albeit with greater tolerance than Ni-YSZ anodes.⁷ Carbon deposition can be prevented by internal steam reforming of CH₄; however considerable dilution (steam content $\geq 50\%$) of fuel is needed, which affects the cell voltage.⁴ Further, Ni-GDC based cermet anodes are weak under the anode operating conditions due to the reduction of NiO (Ni^{2+/0}) and ceria (Ce^{4+/3+}).⁶ Porosity induced by pore-formers further weakens the cermet anode support. Moreover, coarsening of Ni under long-time operation impacts the reliability of LT-SOFC made using Ni-GDC cermet as an anode.

In order to develop reliable, cost effective LT-SOFC technology, identification of alternative anode materials is critical. Alternative anode materials should meet certain characteristics to function as an efficient SOFC anode. The major requirements include high electrical conductivity, high catalytic activity for oxidation of fuels, O²⁻ conductivity to enlarge the triple phase boundaries (TPB), high mechanical strength, sufficient porosity, thermal compatibility with electrolyte and exceptional reduction-oxidation (redox), thermal, and chemical stability. Perovskite-type oxides exhibit characteristics that

are required for an efficient fuel electrode for LT-SOFCs, broadly classified by two types of ceramic oxides. The first one is mixed oxide-ion/electronic conductors (MIEC) such as chromates (e.g., $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$)^{8–10} or molybdates (e.g., $\text{Sr}_2\text{MgMoO}_6$).^{11,12} MIEC type perovskite oxides are usually redox stable and are catalytically active at high temperatures. The second one is mostly electronic conducting (EC) ceramic oxides such as titanates (e.g., $\text{SrTi}_{0.75}\text{Nb}_{0.25}\text{O}_3$).^{13–15} These materials possess excellent redox stability, however, they lack catalytic activity and oxide conductivity, which are usually incorporated by infiltration of catalysts. Nevertheless, both MIEC and EC, ceramic oxides require high temperature ($>900^\circ\text{C}$) pre-reduction to achieve high electronic conductivity.

BaSnO₃ substituted on the Ba and/or Sn-site with trivalent cations (such as Fe, Sc, In, Y, Gd, Sm, Nd and La) are mixed proton and electronic conductors.^{16,17} These materials have been extensively investigated for their application as photocatalyst,¹⁸ thermoelectric,¹⁹ capacitors,²⁰ protonic conductors¹⁶ and sensors.²¹ In particular, La₂O₃-doped BaSnO₃ is an n-type semiconductor with interesting electrical properties.²² Under low pO₂ conditions, the electrical conductivity of La-doped BaSnO₃ is mainly achieved by substitution of Ba²⁺ by La³⁺, which leads to a reduction of Sn⁴⁺ to Sn²⁺ and electron donation. The ionic radius of La³⁺ (1.36 Å) is smaller than Ba²⁺ (1.61 Å) in 12-fold coordination, as such lattice constant slightly increases with 2% La-doped BaSnO₃ when compared to undoped BaSnO₃.^{23,24} Hadjarab et al. proposed that the partial reduction of Sn⁴⁺ (0.69 Å) to Sn²⁺ (1.12 Å) in the octahedral site induced by La-doping could increase the lattice constant.²⁵

Until now no studies have been reported on utilizing this material as anode for oxide-ion conducting SOFCs. In this work, we investigated the applicability of LBS as novel alternative anode material for oxide-ion conducting LT-SOFCs. The sinterability of the material was greatly improved by adding ZnO as a sintering aid. The material was characterized considering the LT-SOFC anode requirements, such as electrical conductivity, mechanical strength, redox, chemical and thermal stability at temperatures $\leq 650^\circ\text{C}$. ZnO-doped LBS shows high electronic conductivity, excellent redox and thermal stability in LT-SOFC anode operating conditions. Compatibility of ZnO-doped LBS with GDC electrolyte was also investigated. GDC-based electrolyte-supported SOFCs were successfully fabricated and the electrochemical performance of ZnO-doped LBS was evaluated.

Experimental

Sample preparation.—The solid-state synthesis was used to prepare LBS. Stoichiometric amounts of barium carbonate (BaCO₃, Alfa Aesar), tin oxide (SnO₂, Alfa Aesar), lanthanum oxide (La₂O₃, Alfa Aesar) were ball-milled for 24 h in ethanol. Subsequently, ethanol was

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evaporated and the resulting oxides were heat-treated at 1300°C for 6 h to form the $\text{Ba}_{0.98}\text{La}_{0.02}\text{SnO}_3$ cubic perovskite-type oxide.

Zinc oxide (ZnO, J.T. Baker) was used as a sintering aid for LBS in the weight percent of 1, 2 and 3. The already prepared LBS powder was mixed with the three concentrations of ZnO for 12 h in ethanol separately. Ethanol was then dried and the resulted powder samples were collected and calcined at 1200°C for 6 h.

Sample characterizations.—The crystal structure of the resulting ceramic oxide was determined using a Bruker D8 powder X-ray diffractometer with Cu K-alpha radiation. The XRD patterns were analyzed using TOPAS software to extract the lattice parameter. The LBS peaks were indexed for cubic symmetry having a space group $pm\bar{3}m$ using Le Bail fitting procedure. The relative crystallite sizes of the powders from XRD data were determined using the same procedure.

DC electrical conductivity measurements were performed on ZnO-doped LBS (Zn-LBS) rectangular bars. The bar samples were prepared by ballmilling Zn-LBS powder ($3/4^{\text{th}}$ of the 100 ml bottle was filled with $\phi 10$ zirconia balls) over a period of 15 h in ethanol, followed by evaporation of ethanol and powder compaction. The compacted pellets were sintered at 1550°C for 6 h in air. The porosity of the sintered samples determined using Archimedes principle (buoyancy method) using Mettler Toledo's Density Kit. Samples with 0, 1, 2 and 3 wt% Zn-LBS had a porosity of 50.4, 19.0, 9.1 and 6.7%, respectively. Silver wires and silver paste was used as the I-V probe and current collector, respectively and attached to a Keithley 2400 source meter. The measurements were made using an in-house reactor capable of operating under controlled oxygen partial pressures. For electrical conductivity measurement, in the range of 350–650°C, the samples were heated up in N_2 and changed to 10% H_2 /3% H_2O /87% N_2 gas conditions. This gas composition was used considering the safety issues of using pure/humidified H_2 in our in-house reactor. The samples were allowed to stabilize in reducing gas conditions at 650°C over a period of 12 h and measurements were made at 50°C intervals. At each temperatures the samples was allowed to stabilize for 30 minutes.

The flexural strength of Zn-LBS was determined using a three-point bend test. A Tinius Olsen H25K-T benchtop Universal Testing Machine (UTM) was used to determine the strength at room temperature, 400, 550 and 650°C in air. The samples for mechanical testing were prepared by compaction of Zn-LBS powder using a rectangular die. Each rectangular pellet was compacted separately to dimensions of length 2.5 cm and width 1 cm and sintered at 1550°C in air. Rectangular bars of the material were placed on support rods with a fixed spacing. A point load was then applied at a constant strain rate until failure. The maximum force experienced by the bar was recorded and the corresponding flexural stress calculated using Eq. 1.

$$\text{Flexural strength, } \sigma = \frac{3FL}{2bd^2} \quad [1]$$

Where, F is the applied force in Newtons. L, d, and b are length, thickness and width respectively. 5 samples were tested at each temperature to maintain accuracy in results.

For the preparation of electrolyte-supported cells, a $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2.8}$ (GDC, Fuel Cell Materials) tape casting slurry was prepared following standard procedures. The raw tapes were heat-treated stepwise to a maximum temperature of 1450°C for 4h to obtain a thick GDC support. GDC sintered tapes having thicknesses in the range of 140–230 μm were used in this study. Already prepared Zn-LBS and 20 wt% poly (methyl methacrylate) (10 μm , PMMA-Soken) pore former were mixed with commercial ink making vehicle (ESL ElectroScience, type 441) to make an ink of screen printing consistency. The half-cells were prepared by depositing Zn-LBS ink on the GDC electrolyte by doctor-blade coating. The resulting half-cells were sintered at 1200°C for 4 h to bond Zn-LBS ($\sim 60 \mu\text{m}$) to the GDC substrate. The half-cell was then deposited with LSCF-GDC ($\sim 20 \mu\text{m}$) cathode on the other side and sintered at 1100°C for 2h. The SOFC active area was 0.50 cm^2 and gold wires and silver paste were used as leads and current collector on the anode and cathode. Catalytic activity for H_2 oxidation and oxide-ion conductivity in the anode was introduced by

NiO-GDC infiltration. 0.75M of NiO-GDC ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2.8}$) precursor was prepared by dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in water. The NiO-GDC contains 10 wt% of Ni relative to GDC. Few drops of prepared solution were infiltrated into the porous Zn-LBS scaffold and placed in the vacuum chamber for 5 minutes. Between each successive infiltration step, the sample was heat-treated at 450°C for an hour to decompose the nitrate salts. The loading of NiO-GDC was determined by measuring the weight gain after final heat-treatment step and compared to the initial weight of the sample. NiO-GDC loading after 9 infiltrations was estimated to be 5.30, 3.34, 3.84 wt% for 1%, 2% and 3% Zn-LBS samples, respectively. It is to be noted that the number of infiltrations was kept constant for all samples and as a result 1% Zn-LBS showed higher weight gain due the higher LBS layer porosity.

Current-voltage (I-V) characteristics and power density of the SOFCs was determined using a ParStat 2273/Solartron 1470E. The electrochemical impedance spectroscopy (EIS) response of the SOFCs under investigation were obtained using ParStat 2273/ Solartron 1425 frequency response analyzer. The SOFC was loaded in the fuel cell testing fixture to determine the electrochemical performance including I-V and impedance spectra. Commercial two-part sealant (ceramabond-517, Aremco) was used as seal between anode and cathode side. The anode and cathode side of the fixture was flown with 100ml/min of humidified H_2 and air, respectively. Impedance spectra were measured in 2-point probe method over a frequency ranges from 100 mHz to 100 kHz under open-circuit voltage (OCV) conditions. The impedance spectra were obtained for the full cell which includes the contribution from cathode, electrolyte and anode. The impedance spectra were fitted with an equivalent circuit model using the code ZsimpWin with a complex non-linear squares fitting routine (CNLS).

Scanning electron microscopy (SEM) of the post-tested SOFCs was performed using a Hitachi SU-70 with field emission gun equipped with a Bruker XFlash silicon drift EDS detector. Change in weight during solid-state synthesis was determined using thermogravimetric analysis (TGA) analytical instrument, TA SDT Q600. The sample was heated at a ramp rate of 5°C/min to 1000°C in the presence of air flow (100 ml/min).

Results and Discussion

TGA of LBS precursor (a mixture of $\text{BaCO}_3/\text{SnO}_2/\text{La}_2\text{O}_3$) is shown in Figure 1a. TGA reveals an initial weight loss of 2.5% in the temperature ranges of 21–200°C attributed to the evaporation of H_2O (region 1). At temperature >200°C (region 2), the departure of residual H_2O and sublimation of carbonates begins and the weight loss is gradual until 800°C, beyond which, a rapid weight loss occurred implying a complete removal of carbonate and onset of BaSnO_3 perovskite formation. No change in weight loss at temperature >960°C was observed indicating formation of LBS single phase (region 3). Shown in Figure 1b are the XRD pattern of LBS precursor at 25°C and calcined samples at 500 and 1000°C. XRD pattern of LBS precursor calcined at 500°C showed BaCO_3 reflection; however, the intensity of these reflections are less compared to XRD pattern of as-mixed powders at 25°C indicating a slight loss of carbonates. The XRD pattern of LBS powder calcined at 1000°C showed a cubic phase consistent with TGA measurements.

One of the main issues with LBS based ceramic oxides is their poor sintering characteristics. For example, BaSnO_3 based perovskite oxide showed only a maximum density of 80% even at a high sintering temperature of 1600°C. Y. Wang et al studied the effect of using ZnO as additive in $\text{BaSn}_{0.75}\text{Y}_{0.25}\text{O}_3$ based proton-conducting ceramic oxide.¹⁷ Their investigation revealed that addition of 3.25 wt% ZnO reduced the sintering temperature down to 1300°C. Shown in Figure 2a are the XRD patterns of LBS with varying amount of ZnO additive from 0 to 3 wt%. No appearance of secondary phases or segregation of ZnO occurred up to 3 wt% loading of ZnO. Figure 2b shows the lattice parameters of the Zn-LBS from 0–3 wt%. Although there is no chemical reaction between ZnO and LBS, the lattice parameter shrunk slightly due to addition of ZnO indicating the possibility of

Figure 1. (a) Thermogravimetric analysis of $\text{BaCO}_3/\text{SnO}_2/\text{La}_2\text{O}_3$ mixture in air and (b) XRD patterns of the $\text{BaCO}_3/\text{SnO}_2/\text{La}_2\text{O}_3$ mixture at 25, 500 and 1000°C in air.

ZnO dissolution in the lattice of LBS. However, the difference in lattice parameter of pristine LBS (4.116 Å) is comparable to 3 wt%. ZnO doped sample (4.115 Å) when considering the experimental error. Further, the crystallite size extracted from XRD data increased from 168 nm to 400 nm with 3 wt.% ZnO addition. Shown in Figure 2c is the shrinkage behavior of pristine and Zn-LBS ceramic oxide measured using the geometrical changes. A ~15% shrinkage is obtained for all ZnO concentrations investigated. These results convincingly illustrate that even 1 wt. % of ZnO acts as a sintering aid for LBS.

One of the main requirements of alternative anode development is high electrical conductivity. Most of the ceramic oxides, when pre-reduced at a low temperature of 650°C have shown low electrical conductivity. For instance, an in-house measurement of $\text{SrTi}_{0.75}\text{Nb}_{0.25}\text{O}_3$ ceramic oxide showed a low conductivity of 1.8 S/cm at 650°C in 10% H_2/N_2 . However, an electrical conductivity of >10 S/cm is required to obtain efficient LT-SOFCs. Figure 3 shows the electrical conductivity of LBS with and without the addition of ZnO measured in 10% $\text{H}_2/3\text{H}_2\text{O}/\text{N}_2$. Base LBS without ZnO doping showed a comparatively low conductivity of 23 S/cm at 650°C, mainly due to its high porosity (~50.4%) and poor shrinkage behavior. However, samples with gradual addition of ZnO from 1 to 3 wt% show a dramatic enhancement in conductivity. The conductivity of the samples is in the order 3 wt% (210 S/cm) > 2 wt% (123 S/cm) > 1 wt% (78 S/cm) at 650°C and the trend follows at all temperatures. The conductivity of the samples depends on the porosity i.e., the denser sample the better the conductivity. In addition, the enhanced conductivity in all Zn-LBS samples compared to the pristine LBS could be due to the enrichment of Zn at the grain boundaries. It is expected that the un-reacted ZnO sublimed due to high sintering temperature. The conductivity values at lower temperatures are higher than 650°C due to metallic-type conduction behavior of Zn-LBS.

Anode materials must withstand redox cycles due to fuel starvation conditions during practical operation of SOFC stacks. Redox stability was determined by alternating between 10% $\text{H}_2/3\text{H}_2\text{O}/\text{N}_2$ and air at

Figure 2. (a) XRD patterns of LBS with 0, 1, 2 and 3 wt% ZnO. (b) Lattice parameters of LBS with 0, 1, 2 and 3 wt% ZnO additions. (c) Volumetric shrinkage of LBS with the addition of 0, 1, 2 and 3 wt% ZnO sintered at 1550°C for 6 h.

650°C over a period of 200 h with a 3 wt% Zn-LBS sample as shown in Figure 4a. No change in conductivity at each gas composition was observed up to 10 redox cycles indicating an excellent redox stability of LBS anode. The conductivity value at 650°C under reducing gases is higher than the value reported in Figure 3, because the sample was left in reducing conditions for about 450 h before the redox cycling experiment.

In addition, the anode support should not propagate cracks that lead to mechanical failure during heating/cooling cycles. Thermal stability

Figure 3. DC electrical conductivity measurement of LBS with 0, 1, 2 and 3 wt% ZnO sintered at 1550°C for 6 h and the measurements were made in 10% $\text{H}_2/\text{N}_2/3\text{H}_2\text{O}$.

Figure 4. (a) Redox stability of 3 wt% Zn-LBS. (b) Thermal stability of 3 wt% Zn-LBS cycled between 350 and 650°C, (c) Flexural strength of 3 wt% Zn-LBS samples as a function of porosity in the ranges between 5.2–7.3% at different temperatures and (d) XRD patterns of LBS/GDC composite. The solid squares are GDC and solid circles represent 3 wt% Zn-LBS peaks.

was determined in reducing gas conditions by cycling the sample between 650 and 350°C for 10 cycles at a high ramp rate of 10°C/min as shown in Figure 4b. The investigation revealed that 3 wt% Zn-LBS retained its conductivity (216 and 280 S/m at 650 and 350°C, respectively) after several heating/cooling cycles demonstrating good thermal stability and indicating no crack formation during cycling.

The anodes are the principle structural component in an anode-supported SOFC and must have sufficient mechanical strength. Zn-LBS samples were used to determine the flexural strength using a three point bend test and results are shown in Figure 4c. Tests were carried out at room temperature and various elevated temperatures (450, 550 and 650°C). 3 wt% Zn-LBS showed very little variation in strength across the 5.2–7.3% porosity range. The variation in porosity (~2%) between samples arises due to the temperature gradient in the furnace. Samples tested at elevated temperatures were more resilient to fracture than those tested at room temperature. For example, a flexural strength of ~66 MPa was obtained at 550°C as compared to ~54 MPa at room temperature for 3wt.% Zn-LBS having the same porosity of ~7.3%.

Flexural strength of Zn-LBS is 29% lower than GDC (~87MPa) at 25°C as shown in Figure 4c. However, it must be noted that under reducing gas conditions ceria undergoes crystal lattice expansion leading to poor mechanical properties.²⁶

Lack of reactivity between GDC and Zn-LBS is essential to fabricate a successful SOFC. Figure 4d shows the XRD patterns for LBS, GDC, and 3wt. % Zn-LBS/GDC composite sintered at 1150 to 1250°C. No formation of secondary phase is seen for the sample fired at 1150°C, however, secondary phase starts to appear ($2\theta = 29.60$) for the sample fired at 1250°C for 6 h, which could put an upper limit on electrolyte sintering temperature.

The electrode/electrolyte interface and the microstructure of the Zn-LBS anodes were examined. Figures 5a–5i shows SEM micrographs of post-tested 1%, 2%, and 3 wt% Zn-LBS/GDC based

SOFCs. Figures 5a, 5d, and 5g illustrates the cross section of electrode/electrolyte interfaces for 1, 2, and 3 wt% Zn-LBS samples, respectively. As seen from the images, GDC electrolytes are fully dense and well-bonded with the LBS electrodes. The micrographs of the LBS anodes with higher magnifications are shown in Figures 5b, 5e, and 5h. The images show that 1 wt% Zn-LBS has higher porosity and finer microstructure (c.f. Figure 5b) than 2 and 3 wt% Zn-doped LBS that are shown in Figures 5e and 5h, respectively.

SOFC performance can be improved by the decoration of electron conducting scaffold with nanoparticles of Ni and GDC, wherein, Ni assists H₂ oxidation and GDC facilitates the extension of triple phase boundaries.^{13–15} The images in Figures 5c, 5f and 5i revealed the nano-morphology of Ni-GDC that was infiltrated into the porous LBS scaffolds. Ni-GDC particles finely decorated on the surface of LBS. The elements were confirmed using EDS analysis.

EDS line scan analysis was performed at the interface of the porous Zn-LBS anode and the GDC electrolyte as shown in Figure 6. The elemental distribution across the interface of Zn-LBS/GDC was collected over a 35 μm length. The anode region shows the high intensity of Ba and Sn. The appearance of Ce signal in anode region is due to the Ni-GDC that was infiltrated on the surface of Zn-LBS. Further, it is to be noted that the intensity of Zn, Ni and La are significantly less because of their lower quantities in the anode region. In the GDC electrolyte region; the intensity of Ce and Gd were much higher compared to rest of the elements. EDS analysis has the detection limit of <1%, thus further investigation is required for accurate quantification of elemental crossover between electrode and electrolyte.

Preliminary fuel cell performance in humidified H₂ as fuel and air as oxidant was obtained with Zn-LBS anodes on GDC based electrolyte-supported SOFCs. Electrolyte-supported cells were used because they were easier to make with the new anode material as compared to anode-supported cells. Typical I-V and power density plots at 550, 600 and 650°C, for 1%, 2%, and 3% Zn-LBS are shown in

Figure 5. (a-i) is the SEM images of post-tested LBS based electrolyte-supported SOFCs. (a) electrode/electrolyte cross section of 1 wt% Zn-LBS. (b) Morphology of 1 wt% Zn-LBS scaffold. (c) Decoration of Ni-GDC nanoparticles on the surface of 1 wt% Zn-LBS scaffold. (d) electrode/electrolyte cross section of 2 wt% Zn-LBS. (e) Morphology of 2 wt% Zn-LBS scaffold. (f) Decoration of Ni-GDC nanoparticles on the surface of 2 wt% Zn-LBS scaffold. (g) electrode/electrolyte cross section of 3 wt% Zn-LBS. (h) Decoration of Ni-GDC nanoparticles on the surface of 3 wt% Zn-LBS scaffold and (i) Decoration of Ni-GDC nanoparticles on the surface of 3 wt% Zn-LBS scaffold.

Figures 7a, 7b, and 7c, respectively. In Figures 7a–7c, the area specific resistance (ASR) decreases with increase in temperature due to faster electrode kinetics and higher oxide-ion conductivity. However, the open circuit value (OCV) decreases with increasing temperature due to the increase in electronic transference number of GDC. Highest power densities of 0.28 W/cm^2 (at 0.6 A/cm^2 , OCV: 0.89 V) and 0.17 W/cm^2 (at 0.36 A/cm^2 , OCV: 0.93 V) were achieved at 650 and 600°C , respectively for 2 wt% Zn-LBS (shown in Figure 7b). The ASR of 1% Zn-LBS is higher than 2% Zn-LBS, and the ASR of 2% Zn-LBS is comparable to 3% Zn-LBS. These arise from the GDC thickness

variation between samples. GDC thickness of 230, 140 and $150 \mu\text{m}$ were used for 1% Zn-LBS, 2% Zn-LBS and 3% Zn-LBS, respectively.

Figures 8a–8c are the EIS measurements of 1, 2 and 3 wt% Zn-LBS at 650 , 600 and 550°C . The impedance spectra were measured on the electrolyte supported full cells infiltrated with Ni-GDC on the anode side. The impedance spectra in all samples showed similar features. An equivalent circuit $\{LR_0(R_1Q_1)(R_2Q_2)\}$, containing inductance (L), the electrolyte series resistance, R_0 in series with elements (R_1Q_1) and (R_2Q_2) was used to model the spectra. R_1 and Q_1 were parallel to each other and the same applies to R_2 and Q_2 . The constant phase elements Q_1 and Q_2 were used in the place of pure capacitor considering the distributed catalytic activity of the porous microstructure. The impedance value of $Q_1 (= Q_2)$ is given by the relation $1/Y_0 n(j\omega)$, where, Y_0 is the a constant, ω is the angular frequency and n is the frequency power. The inductive component at very high frequencies arises from the measurement leads and is not shown in the plots. It is impossible to distinguish the anode and cathode ASR without reference electrode. Further, the time constants occurring in various electrode processes are overlapped in the spectra. A high frequency arc (R_1) is attributed to the cathode and anode charge transfer polarizations caused by the transportation of charged species at the interfaces of electrodes/electrolyte. The species include electrons, oxide ions and potentially protons in the anode. A low frequency arc (R_2) is attributed to the mass transfer limitation in electrodes caused by diffusion of adsorbed species on the surface of electrodes and gas diffusion limitations. In particular, the inductive loops (in the positive axis) at the very low frequencies originate from the coupling of mass transfer and surface reactions (e.g. absorption of moisture on anode surface). The inductive loops were removed during the fitting procedure for simplification.

The ohmic ASR of the electrode and electrolytes for SOFCs under investigation were subtracted from the impedance spectra and are shown in Figure 8d. At 650°C , the ohmic ASR of 0.43, 0.35 and

Figure 6. EDS analysis of 3wt.% Zn-LBS deposited on GDC which was fired at 1200°C for 6 h in air.

Figure 7. I-V and power density characterizations on GDC based electrolyte-supported cells. (a) 1 wt% Zn-LBS infiltrated with Ni-GDC loading of 5.3 wt% (b) 2 wt% Zn-LBS infiltrated with Ni-GDC loading of 3.34 wt% and (c) 3 wt% Zn-LBS infiltrated with Ni-GDC loading of 3.84%. The amount of Ni-GDC loading varies depending on the porosity of the anodes.

0.65 $\Omega \text{ cm}^2$ was obtained for 1, 2 and 3 wt% Zn-LBS. Variation in ohmic ASR between the samples are mainly from the GDC thicknesses. The calculated ohmic ASR of 230 μm -thick-GDC is 0.85 $\Omega \text{ cm}^2$ at 650°C corresponding to its bulk conductivity of 0.027 S/cm at 650°C measured in air.²⁷ However, the experimentally obtained ohmic ASR is $\sim 23\%$ lower than the calculated value. A similar ohmic behavior can be deduced from the data reported by B.D. Madsen et al. for a $\sim 300 \mu\text{m}$ GDC based electrolyte-supported SOFC with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.98}\text{V}_{0.02}\text{O}_{3-\delta}$ as anode and LSCF-GDC cathode.²⁸ The experimental ohmic ASR was $\sim 10\%$ lower than the calculated value. As such, this can be attributed to the reduction of Ce^{4+} to Ce^{3+} over the anode portion of the electrolyte that had been exposed to reducing gas conditions. Secondly, the grain boundary resistance of GDC electrolyte could overlap with the non-ohmic ASR; however, respective time constants are difficult to resolve at temperature $> 500^\circ\text{C}$.²⁷ Further, diffusion of elements from the electrode could decrease the ohmic ASR; however they have no detrimental effects on the OCV in our study. The ohmic ASR contribution of electrodes is much lower ($< 0.00003 \Omega \text{ cm}^2$) considering their thickness and high conductivity.

Non-ohmic ASR ($R_1 + R_2$) i.e., charge-transfer and concentration polarization measured at different temperatures are shown in Figure 8e. 1 wt% Zn-LBS showed lowest non-ohmic ASR of 0.16 $\Omega \text{ cm}^2$, while 2 and 3 wt% showed 0.18 and 0.19 $\Omega \text{ cm}^2$, respectively at 650°C, and this trend continues down to 550°C. In a previous study reported by Hussain et al. a non-ohmic ASR of 0.21 $\Omega \text{ cm}^2$ at 650°C was obtained on Nb-doped SrTiO_3 ceramic anode infiltrated with Ni-GDC.^{13–15} This value was determined using symmetrical cell made of Nb-doped SrTiO_3 scaffold deposited on either side of YSZ. In the present study the total non-ohmic ASR for 3 wt% Zn-LBS (0.19 $\Omega \text{ cm}^2$) is comparatively low considering the contribution from anode

and cathode altogether. Further, the variation in non-ohmic ASR between the samples in the present study depends on the loading of Ni-GDC. The higher the Ni-GDC loading the lower is the non-ohmic ASR, i.e., the loading of Ni-GDC was in the order 1 wt% $>$ 2 wt% $>$ 3 wt. % Zn-LBS. The number of infiltrations of Ni-GDC was fixed and the amount of loading obtained increased based on anode porosity and microstructure. Additionally, under low PO_2 in the temperature range 400–650°C, LBS is a mixed electronic and proton-conducting ceramic oxide.²⁹ However, non-ohmic ASR of pristine 3 wt% Zn-LBS tested using electrolyte-supported SOFC showed high values of 6.34, 11.51 and 35.93 $\Omega \text{ cm}^2$ at 650, 600 and 550°C, respectively, measured under humidified H_2 . These high values indicate that pristine LBS can only be an electronic conducting scaffold similar to that of Nb-doped SrTiO_3 ^{13–15} and has insufficient catalytic activity and oxide ion conductivity to function as stand-alone anode material. Furthermore, with regard to electronic conduction it should be noted that SnO_2 is readily reduced to the metallic state in the presence of reducing gasses such as H_2 under SOFC operating conditions which would reduce the ohmic ASR. However, the reducibility of LBS is expected to be less due to the stabilizing effect of the perovskite structure.

Conclusions

Electrical and physio-chemical properties of $\text{Ba}_{0.98}\text{La}_{0.02}\text{SnO}_3$ were investigated considering the applicability of this material as a fuel electrode in LT-SOFCs. The addition of ZnO as sintering aid greatly improved the sinterability and the electrical properties of LBS. 3 wt% Zn-LBS showed a high conductivity of 216 and 280 S/cm at 650 and 350°C, respectively in H_2 -containing gas. Zn-LBS has shown excellent redox and thermal stability appropriate for LT-SOFCs. The

Figure 8. Impedance spectra measured for 1–3 wt% of Zn-LBS measured at (a) 650°C, (b) 600°C, (c) 550°C, (d) Ohmic ASR Vs. temperature for the three concentrations of Zn-LBS and (e) Non-ohmic ASR vs. temperature for the three concentrations of Zn-LBS.

flexural strength at 550°C was higher than the room temperature measured value of 54 MPa. The fuel cell prepared using Zn-LBS (with Ni-GDC infiltration) as an anode and LSCF-GDC as a cathode has shown a peak power density of 280 mW/cm² at 650°C in H₂ as fuel and air as the oxidant. The SOFC performance was limited by ohmic ASR arising from the thick electrolyte. The non-ohmic electrodes/electrolyte interfacial resistance of 1wt. % Zn-LBS was lower than the 2 and 3 wt% due to a higher loading of Ni-GDC resulting from finer microstructure and higher porosity. Our study also indicates that pristine Zn-LBS cannot be a stand-alone ceramic anode material and can function only as an electron conducting scaffold similar to that Nb-doped SrTiO₃ reported in literature.

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