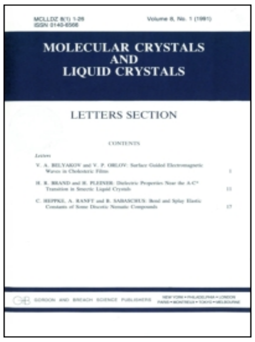
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Addition effects of bismuth oxide on Samaria-doped ceria based lithium carbonate composite electrolytes for intermediate temperature-solid oxide fuel cells

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ABSTRACT

The effect of amounts (3, 5, 10, 20 wt%) of Bi_2O_3 on the sintering characteristics and porosity of Samaria-doped Ceria (SDC) based Lithium carbonate has been evaluated. The density had a maximum as high as 98.5% of theoretical density at 800°C with only 1wt%Li_2CO_3 and 3 wt%Bi_2O_3. The composite electrolytes showed high ion conductivity at evaluated temperatures. Composition and calcination temperature were found to affect the morphology and conductivity of the composite electrolytes greatly. The total conductivity closed to 3 orders of magnitude greater than pure SDC at operating temperature of 900°C and 3.5 orders of magnitude greater than pure SDC at operating temperature of 600°C. Especially, the best sample containing 3 wt% Bi_2O_3 sintered at 800°C for 2 h which had an ionic electrical conductivity of 0.17S cm^{-1}. According to fuel cell performance, these composite electrolytes are chemically stable, which is an attractive prospect in intermediate temperature solid oxide fuel cell applications.

KEYWORDS
Intermediate temperature-Solid Oxide Fuel Cells (IT-SOFCs); Samaria-doped Ceria (SDC); ionic electrical conductivity

1. Introduction

A solid oxide fuel cell (SOFC) is an energy conversion device using oxide ceramics as electrolytes and electrodes and operating at high temperature (700–1000°C). It is highly efficient and has fuel flexibility due to the high operating temperature [1]. However, high temperature operation has serious negative impacts on the chemical stability, durability, and long-term reliability. Therefore, SOFCs that operate at temperatures below 700°C have received much attention in recent years because they may dramatically contribute to the reduction in the cost of SOFC technology, in which inexpensive materials can be used in cell construction and novel fabrication techniques can be applied to the stack and system integrations due to the low operating temperature [2–4]. In addition, SOFCs have greater potential for use as a portable power source if their operating temperature is reduced [5–9]. However, the performance of low-temperature SOFCs is typically unsatisfactory because the catalytic activity of the electrode and the ionic conductivity of the electrolyte decrease exponentially with temperature. The resistance induced by the reduced catalytic activity of the cathode is of particular concern because it is the major contribution to the total resistance of the cell [8]. It is, therefore, vital to

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develop new electrolyte materials that can provide high ion conductivities at low temperature for advanced IT-SOFCs.

As an alternative material, Scandia stabilized zirconia (ScSZ) has been reported to have much higher ionic conductivity (12 S/m at 800°C) [10], but the existing cubic-rhombohedral transformation at low-temperature (≈ 600°C) makes it unfavourable for use as an electrolyte. As another possible electrolyte candidate, attention has been drawn to the ceramic material Ceria. CeO_2-based materials have been widely studied as catalyst supports and promoters for heterogeneous catalytic reactions. On the other hand, they are an upcoming alternative solid electrolyte to yttria-stabilized zirconia (YSZ) in SOFC applications [11–13]. CeO_2-based materials have higher ionic conductivity and lower interfacial losses than YSZ, and can also operate at lower temperatures (600–700°C). However, such powders were usually fired to only 95% dense at fairly high temperatures (≥1500°C), which implies a high energy cost precluding, thus, the possibility of cofiring this electrolyte with other SOFC components due to the solid-state reaction and interdiffusion between them at those sintering temperatures. At the operating conditions of the IT-SOFCs, a limit in both the temperature and oxygen-partial pressure still restricts its use. However, several experiments have shown that doped-ceria can work as an oxide ion conductor electrolyte at temperatures well-below 700°C and oxygen partial pressure $\geq 10^{-5}$ atm. Above those limits an oxygen loss can occur with the reduction of Ce^{4+} to Ce^{3+}, and the corresponding appearance of electronic conduction along with the oxide-ion conduction [14].

$Ce_{0.8}Sm_{0.2}O_{1.9}$ dense ceramic membranes are needed for electrolytes but it is well known, as mentioned before, that ceria-based materials are very difficult to densify below 1500°C by the conventional ceramic techniques when using mixed oxides as raw materials. Then the use of non-conventional methods or, as another alternative, using sintering aids to reduce the sintering temperature become necessaries. In this study I report, at my best knowledge for the first time, the preparation of dense (≥97% of theoretical density) $Ce_{0.8}Sm_{0.2}O_{1.9}$ materials at 800°C for 2 h, starting from a commercial powders by using lithium carbonate and bismuth oxide as sintering aids. Bi_2O_3 has been chosen as sintering aid because of its low melting point (≈890°C), which could help during the sintering process by forming a liquid phase [15]. The effect of Bi_2O_3 and Li_2CO_3 additions on the microstructure as well as on the electrical conductivity and performance of these dense ceramics will also be reported.

2. Experimental

The commercial SDC powder was used as starting raw material. The dopant-1wt%Li_2CO_3 was added to a SDC powder/ethanol suspension by ball milling for 1 day. After drying at 80°C for 1 day, the powder was calcined at 700°C for 2 hours and taken out from furnace directly for cooling, then grinding thoroughly to obtain eutectic powder SDC-1wt%Li_2CO_3 (SDCL).

SDCL powder/ethanol suspension was added the dopant (3, 5, 10, 20 wt%) Bi_2O_3 by ball milling for 1 day. After drying at 80°C for 1 day, the powder was calcined at 700°C for 2 hours and taken out from furnace directly for cooling, then grinding thoroughly to obtain eutectic powder SDCL/Bi_2O_3.

The calcined composite electrolyte powder was cold pressed at 2000Lb into cylindrical pellets 7 mm diameter and 1 mm thick using a uniaxial die-press. The green pellets were then sintered at 800, 900, 1000°C for 2 h. The porosity of the samples after sintering was measured by the Archimedes method.

In order to study the possible influence of the Li_2CO_3 and Bi_2O_3 additive on the crystalline structure of the prepared samples, these were heat-treated at 800–1000°C for 2 h, and then

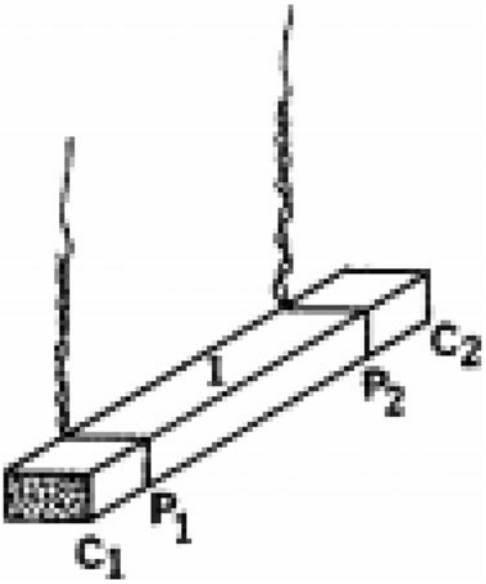


Figure 1. A schematic of the ceramic specimen: C_1 and C_2: current probes. P_1 and P_2: potential probes.

characterized by X-ray diffraction (XRD). The microstructure of the sintered samples was examined by scanning electron microscope (SEM).

For conductivity measurements, the sample with porosity less than 5% was chosen to investigate. Sintered specimens usually 30 mm long and in the form of rectangular bars with cross-sectional area of 0.2–0.25 cm^2 were used. Potential probes were constructed by cutting a 0.3 mm wide groove around the specimen (approximately 10 mm from each end). Current probes were usually constructed by applying a thick layer of platinum paste to each end of the specimen bar. A schematic of the cell assembly was shown in Figure 1. The conductivity measurement was tested under air condition.

For cell fabrication and schematic reactor, anode-supported cells were prepared to investigate the cell performance of modified electrolyte. The anode comprised NiO (70wt%) and commercial powder SDC (30wt%), cathode material was $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and SDCL/Bi_2O_3 was electrolyte material. Figure 2 presents a schematic representation of the experimental apparatus used for testing the button-type SOFCs. A button cell was mounted between two alumina tubes and sealed with Pyres glass on the dense electrolyte of the cathode size. A perforated Pt plate (area of 1cm^2) and a wire (thickness of 0.5 mm) were used as a current collector, which was spring-loaded a both electrodes. H_2 was used as the anode gas; O_2 was the cathode gas. The flow rate was 200 $mLmin^{-1}$ for both electrodes; the cell was tested at 600–800°C.

3. Results and discussion

3.1. Sintering behavior

Figure 3 shows the effect of SDCL/Bi_2O_3 addition on the sintering behavior of SDC ceramics as a function of temperature for a holding time of 2 h. The density had a maximum as high as 98.5% of theoretical density at 800°C with only SDCL-3wt%Bi_2O_3 but at a higher doping

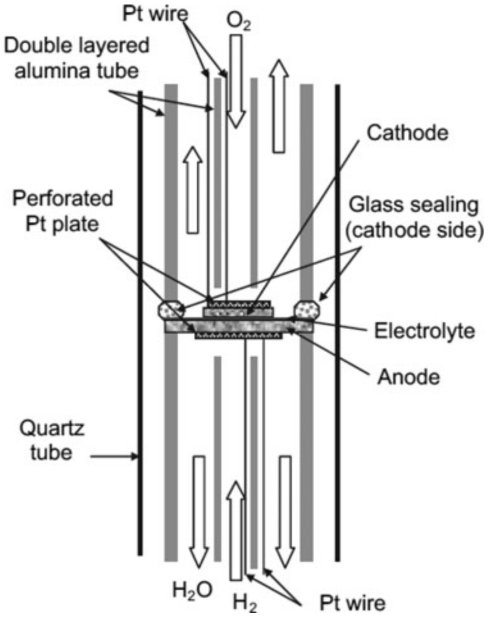


Figure 2. Experimental schematic diagram.

level of 5wt% to 20wt%, the porosity increased dramatically for higher sintering temperatures. Given that the density at 800°C was of the order of 98.5%, it can be stated that sintering was complete in a temperature range as short as 600°C when Li_2CO_3 and Bi_2O_3 were used as sintering aids for SDC ceramics. This sintering temperature can be considered as very competitive for a co-sintering process for the assembly of the different SOFC components. Due to the lowest porosity of the SDCL-3wt%Bi_2O_3 composite electrolyte (around 2%), this composition will be chosen to study other properties.

3.2. X-ray diffraction study

X-ray diffraction patterns of SDC/1wt%Li_2CO_3 with 3, 5, 10 and 20 wt.% Bi_2O_3 added after heat treatment at 800°C. From the above diagram, with the ratio from 5 to 20wt%, there were

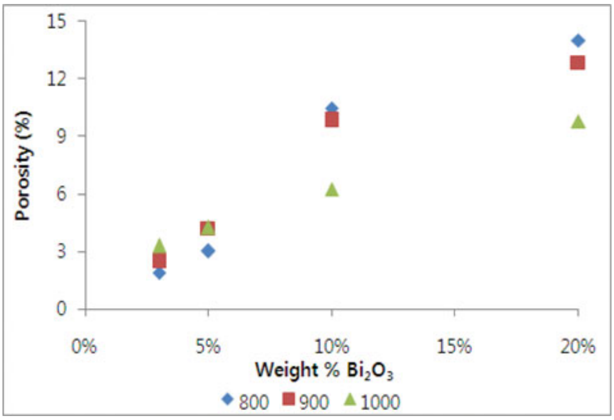


Figure 3. Experimental data for porosity versus Bi_2O_3 weight fraction at variety of temperature for SDCL-Bi_2O_3 system.

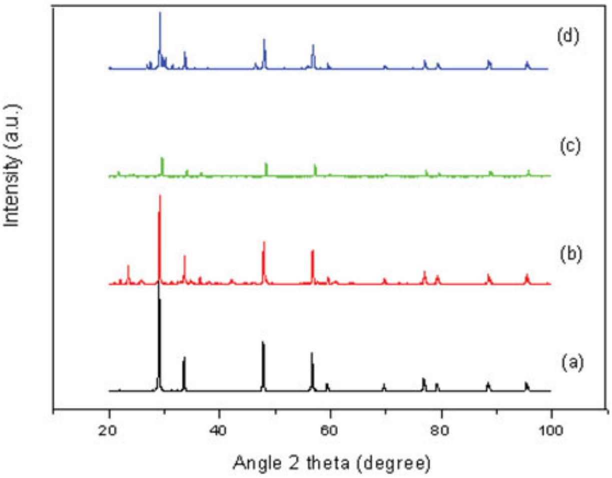
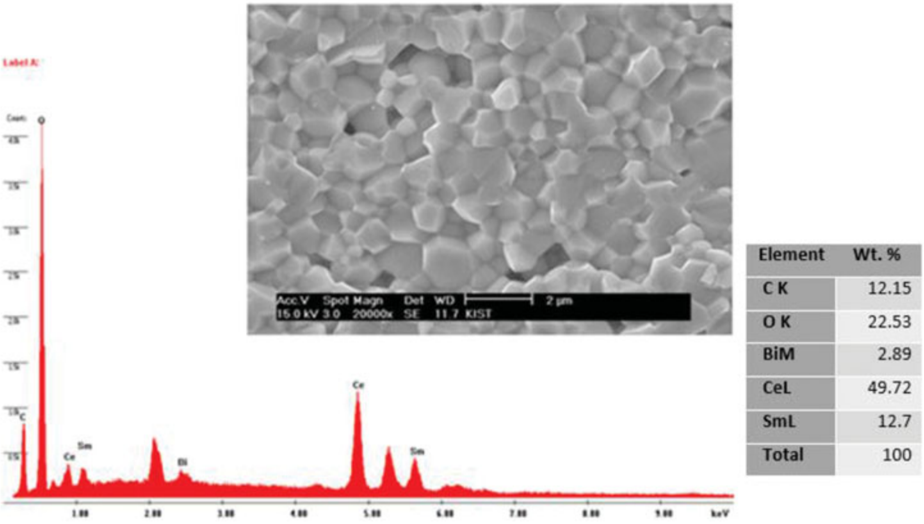


Figure 4. XRD patterns for SDCL-Bi_2O_3 composites with content of (a) 3, (b) 5, (c) 10, (d) 20 wt% after sintering at 800°C.

some secondary phases such as δBi_2O_3–Sm_2O_3. However, with 3wt% dopant of Bi_2O_3 onto SDCL, no free Bi_2O_3 or secondary peaks phase was detected. If some secondary phase was formed the amount was too small to be detected by X-ray diffraction. The XRD peaks due to the fluorite solid solution of the SDC sample were slightly shifted to smaller angles with increasing Bi_2O_3 content, as shown in Figure 4.

3.3. Microstructural behavior

Figure 5 shows the scanning electron micrographs of the polished and thermally etched surface and cross-section of SDCL-3wt%Bi_2O_3 composite electrolyte pellet sintered at 800°C. From SEM images, it can be seen that this kind of composite presented a very dense



Element	Wt. %
C K	12.15
O K	22.53
BiM	2.89
CeL	49.72
SmL	12.7
Total	100

Figure 5. SEM images of cross section and EDX data of SDCL-3wt%Bi_2O_3 composite electrolyte pellet sintered at 800°C.

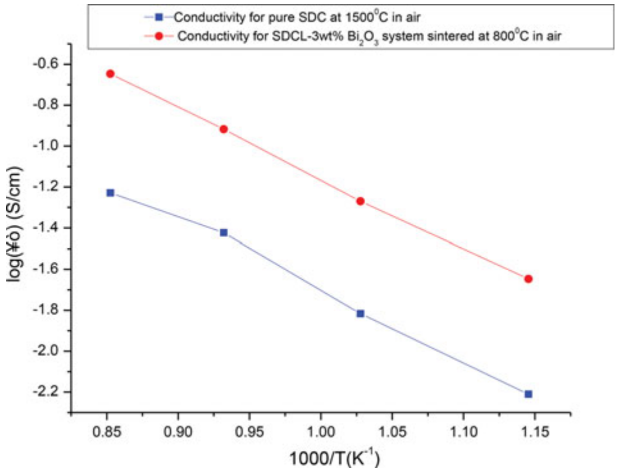


Figure 6. Arrhenius plots of log σ versus 1/T for system of SDCL-3wt%Bi_2O_3 sintered at 800°C and pure SDC sintered at 1500°C.

microstructure. The influence of Bi_2O_3 additions on porosity during sintering of SDC electrolyte was an important factor, besides a high density, to define its performances when this was used in a SOFC device.

3.4. Electrical properties

Figure 6 depicts the Arrhenius plots of log σ against 1/T corresponding to the total conductivity of un-doped and Li_2CO_3 and Bi_2O_3 co-doped sample, sintered at 1500°C for un-doped and 800°C for co-doped sample. It can be seen that in doping sample, the total conductivity mechanism closed to 3 orders of magnitude greater than pure SDC at operating temperature of 900°C and 3.5 orders of magnitude greater than pure SDC at operating temperature of 600°C. Thus, it can be possible to assert that the Li_2CO_3 and Bi_2O_3 co-doping was not detrimental to the electrical behavior of the SDC ceramic, but increased the total conductivity with doping.

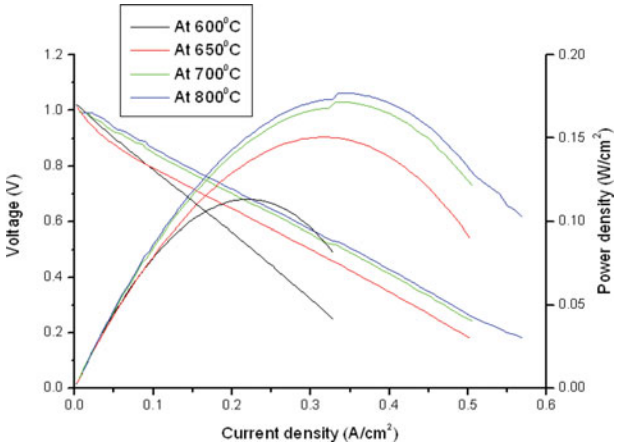


Figure 7. Performance of the fuel cell based on SDCL-3wt%Bi_2O_3 using H_2 and O_2.

3.5. Cell performance

Figure 7 exhibits the current-voltage characteristics and corresponding power densities for a single cell based on the SDCL-3wt%Bi_2O_3 composite electrolyte at various temperatures. The maximum power densities (P_{max}) of 110, 150, 165 and 175 mW cm^{-2} have been achieved for the fuel cell at 600, 650, 700 and 800°C, respectively. The mechanism of the better performance can be ascribed to enhanced ionic conductivity of Li_2CO_3 and Bi_2O_3 addition.

4. Conclusion

New electrolyte materials based on the SDC-low melting point oxide composites were developed and applied for ITSOFC. Additions of 1wt%Li_2CO_3 and 3 wt%Bi_2O_3 onto commercial SDC promoted densification rate and theoretically dense bodies after sintering at 800°C for 2 h. The fuel cell based on SDC-Li_2CO_3-Bi_2O_3 composites electrolyte has demonstrated excellent performance at the intermediate-temperature region. Compared with pure SDC electrolyte, the SDC-Li_2CO_3-Bi_2O_3 composite is a more promising electrolyte material for the development of cost-effective and marketable fuel cell technology.

References

[1] Steele1, Brian C. H., & Heinzel, Angelika. (2001). *Nature*. *414*, 345.
[2] Wachsman, Eric D., & Lee, Kang Taek. (2011). *Science*, *334*, 935.
[3] Myunga, Doo-Hwan, Hong, Jongill, Yoon, Kyungjoong, Kim, Byung-Kook, Lee, Hae-Weon, Lee, Jong-Ho, & Son, Ji-Won. (2012). *J. Power Sources*, *206*, 91.
[4] Oh, Eun-Ok, Whang, Chin-Myung, Lee, Yu-Ri, Park, Sun-Young, Prasad, Dasari Hari, Yoon, Kyung Joong, Son, Ji-Won, Lee, Jong-Ho, & Lee, Hae-Weon. (2012). *Adv. Mater*. *24*, 3373.
[5] Kwon, Chang-Woo, Son, Ji-Won, Lee, Jong-Ho, Kim, Hyun-Mi, Lee, Hae-Weon, & Kim, Ki-Bum. (2011). *Adv. Funct. Mater.*, *21*, 1154.
[6] Schlupp, Meike V. F., Martynczuk, Julia, Prestat, Michel, & Gauckler, Ludwig J.. (2013). *Adv. Energy Mater.*, *3*, 375.
[7] Scherrer, Barbara, Martynczuk, Julia, Galinski, Henning, Grolig, Jan G., Binder, Selmar, Bieberle-Hütter, Anja, Rupp, Jennifer L. M., Prestat, Michel, & Gauckler, Ludwig J.. (2013). *Adv. Funct. Mater.*, *23*, 1957.
[8] Peters, Christoph, Weber, André, & Ivers-Tiffée, Ellen. (2008). *J. Electrochem. Soc.*, *155*, B730.
[9] Evans, Anna, Bieberle-Hütter, Anja, Rupp, Jennifer L.M., & Gauckler, Ludwig J.. (2009). *J. Power Sources*. *194*, 119.
[10] Zhu, Bin, Liu, Xiangrong, Zhou, Peng, Zhu, Zhigang, Zhu, Wen, & Zhou, Shaofeng. (2001). *J. Mater. Sci. Lett.*, *20*, 591.
[11] Zhu, Bin, Liu, Xiangrong, Zhou, Peng, Yang, Xiaotian, Zhu, Zhigang, & Zhu, Wen. (2001). *Electrochem. Commun*. *3*, 566.
[12] Zhu, Bin, Yang, XT, Xu, J, Zhu, ZG, Ji, SJ, Sun, MT, & Sun, JC. (2003). *J. Power Sources*. *118*, 47.
[13] Zhu, Bin, Liu, Xiangrong, Sun, Mingtao, Ji, Shijun, & Sun, Juncai. (2003). *Solid State Sci.*, *5*, 1127.
[14] Bhoga, S.S., & Singh, K.. (1998). *Solid State Ionics*, *111*, 85.
[15] Brett, Daniel J. L., Atkinson, Alan, Brandon, Nigel P., & Skinnerd, Stephen J.. (200). *Chem. Soc. Rev*. *37*, 1568.