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High performance ceria-bismuth bilayer electrolyte low temperature solid oxide fuel cells (LT-SOFCs) fabricated by combining co-pressing with drop-coating

Jie Hou, Lei Bi, Jing Qian, Zhiwen Zhu, Junyu Zhang and Wei Liu

The Sm_{0.97}Nd_{0.03}Ce_{0.5}O_{2-δ}-Er_{0.4}Bi_{1.6}O_{3} bilayer structure film, which showed an encouraging performance in LT-SOFCs, was successfully fabricated by a simple low cost technique combining one-step co-pressing with drop-coating.

The major challenge for solid oxide fuel cells (SOFCs) commercialization is to lower its operating temperature to low temperatures (LTs, ≤650 °C) while still maintaining a desirable cell performance. The LT operation (450-650 °C) can potentially provide a better stability and lower costs due to reduced thermal and chemical stresses and an increased range of material choices, as well as reduced energy consumption and faster start-up times for portable applications. Highly conductive electrolyte materials play one of the most important roles in lowering the operating temperature. Isovalent cation stabilized bismuth oxides (SBO) are particularly attractive because of their superior ionic conductivity at LTs, which is about 1-2 orders of magnitude higher than those of zirconia-based electrolytes. However, bismuth-based materials could decompose to metallic bismuth in the presence of the reducing gas such as H_{2} or CH_{4}. Therefore, they could not be used at the fuel side which makes it a poor choice by itself as an electrolyte for SOFCs. In contrast, the bismuth-based materials can be exposed to the air side since it is intended to be a pure oxide ionic conductor and thermodynamically stable under oxygen partial pressure down to 10^{-15} atm. To date, many works were focused on the ceria-based electrolytes to lower the operating temperature. Virkar et al. have pioneered proposed a two-layer fuel cell electrolyte structure with YSZ used as a blocking layer to prevent ceria reduction, whereafter Wachsmann et al. developed the ceria/bismuth oxide bilayer electrolyte consisting of an SBO layer on the oxidizing side and a doped ceria (DCO) layer on the reducing side to improve the thermodynamic stability of the bismuth oxide layer, by shielding it from very low P_{O2}. Several studies have demonstrated that the electrochemical properties of ceria-based SOFCs can be effectively improved using the ceria/bismuth oxide bilayer electrolyte structure. Though various fabrication methods were employed for ceria-bismuth bilayer electrolyte cells, such as spin coating, DC (Direct Current) magnetron sputtering, pulsed laser deposition (PLD) and so on, most of which required advanced small-scale techniques and the operating temperature was relative high above 550 °C. Therefore, the low cost fabrication of SBO electrolyte film fuel cells with reasonable performance at LT down to 450 °C still remains a challenge. Furthermore, limited compatible cathodes for the ceria-bismuth bilayer electrolyte cells were developed, though Ahn et al. exploited the cathode Er_{0.4}Bi_{1.6}O_{3}-Bi_{2}Ru_{2}O_{7} (ESB-BRO7) for GDC/ESB bilayer electrolyte and achieved very high electrochemical performance, which contains the noble metallic element Ru. Then seeking new low cost cathode materials for ceria-bismuth bilayer electrolyte is imperative.

Here a simple low cost fabrication technique combining one-step co-pressing with drop-coating was developed for the anode-DCO-SBO bilayer electrolyte half cells. The ESB and Sm_{0.97}Nd_{0.03}Ce_{0.5}O_{2-δ} (SNDc) were chosen as the SBO and DCO electrolyte, respectively. Hence, encouraging electrochemical performances at LTs with a novel composite cathode ESB-La_{0.74}Bi_{0.26}Sr_{0.16}MnO_{3.δ} (ESB-LBSM) were achieved and produced the maximum power density (MPD) output of 130 mW cm^{-2} at 450 °C that is the largest power output for this type of SOFCs.

Figure 1 shows the XRD patterns of SNDc, ESB, LBSM and the dry-mixed composite powder ESB-LBSM fired at 700, 650, 850 and 750 °C for 3h, respectively. Indexing of these patterns clearly reveals that ESB possesses the same cubic symmetry of space group Pm-3m with SNDc which has the pure phase with cubic fluorite structure. It also suggests that no obvious reactions occurred between the fluorite structure ESB and the perovskite structure LBSM after heat treatment at 750 °C and this temperature is applied for the composite cathode firing in this study.

Seen from Figure 2(a), the SNDc electrolyte is totally dense and the grain size ranges from around 1 to 2 μm which has the ability to...
block ESB electrolyte layer from the exposure to the reducing atmosphere. As SNDC is a good ionic conductor electrolyte material, the dense film is beneficial for blocking the gas and allowing the transport of oxygen ions. It can also be clearly observed from Figure 2.(b) that dense ESB electrolyte by drop-coating was obtained at the very low sintering temperature 800 °C. The ESB electrolyte layer is also sufficiently dense to block the electronic flux from SNDC in reducing atmospheres. Figure 2.(c) shows the morphology of the interface between ESB and SNDC electrolyte of the tested cell. Though the cell has suffered a heating and subsequent cooling process during testing, the ESB electrolyte layer still bonds to the SNDC membrane tightly. This firm adhesion confirms that the SNDC film shows a good thermal matching with the ESB electrolyte that is consistent with Wachsman’s conclusion,6, 7, 10 which is an important consideration in the design of the DCO-SBO bilayer electrolyte for high performance low temperature SOFCs (HPLT-SOFCs). Shown in Figure 2.(d) is the cross-sectional view of the four-layer single cell, both anode and cathode well adheres on both side of the SNDC-ESB bilayer structure without any sign of cracking or delamination. Apart from blocking gas leakage during operation, the high-quality SNDC|ESB bilayer electrolyte film definitely ensures fast oxygen ions transport through the electrolyte and thereby decrease internal resistance of the single cell. Interestingly, SNDC could prevent the reduction of ESB by the reducing gas while ESB could hold back electronic current from SNDC in reducing atmospheres, which state clearly that the two electrolyte films could protect each other. Notably, the well-designed configuration is quite in favor of mass and charge transfer in the cell and thus the cell is expected to attain good electrochemical performance.

In order to evaluate SNDC|ESB bilayer film for HPLT-SOFCs, button cells using NiO-SNDC as anode and SNDC|ESB bilayer film as electrolyte with ESB-LBSM cathode were fabricated and measured under conventional conditions (humidified hydrogen as the fuel gas; static air as the oxidant). The typical I-V and power density curves for the single cell NiO-SNDC|SNDC|ESB|ESB-LBSM fired at 700, 650, 850 and 750 °C for 3h, respectively.

Figure 2. Cross-section SEM images of (a) SNDC and (b) ESB electrolyte layer, the interface between ESB and SNDC electrolyte layer, and (d) the single cell with bilayer electrolyte SNDC|ESB after testing.

In order to evaluate SNDC|ESB bilayer film for HPLT-SOFCs, button cells using NiO-SNDC as anode and SNDC|ESB bilayer film as electrolyte with ESB-LBSM cathode was fabricated and measured under conventional conditions (humidified hydrogen as the fuel gas; static air as the oxidant). The typical I-V and power density curves for the single cell NiO-SNDC|SNDC|ESB|ESB-LBSM fired at 450-650 °C are shown in Figure 3. The open-circuit voltages (OCVs) after anode reduction are 0.80, 0.855, 0.902, 0.943 and 0.97V, corresponding to the MPDs are 980, 788, 515, 292 and 130 mW cm⁻² at 650, 600, 550, 500 and 450 °C, respectively. The OCV values are higher than most of the previously reported similar single cells, including 10GDC|5ESB (0.78 V at 650 °C),6 10GDC|4ESB (0.77 V at 650 °C)18 and SDC|YSB (0.887 V at 500 °C).17 Moreover, the current results show higher MPDs than many ceria-bismuth bilayer electrolyte reports, such as SDC|YSB (571 mW cm⁻² at 600 °C),17 SDC|YSB (381 mW cm⁻² at 650 °C),2 GDC|ESB (588 mW cm⁻² at 650 °C),2 GDC|ESB (667 mW cm⁻² at 600 °C).23 Some studies show higher OCV values with lower MPDs, while some display higher MPDs accompanied with lower OCVs. Considering the relatively low cost and facile fabrication technique used, the electrochemical performance in this work has its particular advantages. Although Ahn et al18 reported it that the GDC|ESB bilayer electrolyte cell...
achieved the MPD of 1.95 W cm$^2$ at 650 °C, it has no low temperature performance down to 450 °C given, and many other works report the cell performance at similar conditions.\textsuperscript{1,3,6} Noticeably, the SNDC|ESB bilayer structure cell in this assignment has the largest power output below 550 °C compared with the electrolytes reported in literature as summarized in Table 1, such as LBSM measured at 450-650 °C.\textsuperscript{6} This study has made a significant progress for LT operation in SOFCs down to 450 °C.

![Figure 3. I-V and I-P curves of the single cell NiO-SNDC|SNDC|ESB|ESB-LBSM measured at 450-650 °C.](image)

Table 1. Comparison of the fuel cell performance of anode-supported cells using DCO-SBO bilayer electrolyte films reported in the literature and in the present study.

<table>
<thead>
<tr>
<th>Year\textsuperscript{[reference]}</th>
<th>DCO thickness and fabrication</th>
<th>SBO thickness and fabrication</th>
<th>Cathode</th>
<th>MPD (mW cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006\textsuperscript{30}</td>
<td>GDC(84µm) co-pressing</td>
<td>YSB\textsuperscript{4}(16µm) screen-printing</td>
<td>Pt</td>
<td>260</td>
</tr>
<tr>
<td>2009\textsuperscript{18}</td>
<td>GDC(10µm) spray-coating</td>
<td>ESB(4µm) PLD</td>
<td>ESB-BRO</td>
<td>- 1.95 × 10\textsuperscript{1}</td>
</tr>
<tr>
<td>2010\textsuperscript{1}</td>
<td>GDC(50µm) co-pressing</td>
<td>ESB(20µm) screen-printing</td>
<td>ESB-BRO</td>
<td>- 588</td>
</tr>
<tr>
<td>2010\textsuperscript{1}</td>
<td>GDC(20µm) spray-coating</td>
<td>ESB, drop-coating</td>
<td>ESB-BRO</td>
<td>- 614</td>
</tr>
<tr>
<td>2010\textsuperscript{1}</td>
<td>GDC(10µm) spray-coating</td>
<td>ESB, PLD</td>
<td>ESB-BRO</td>
<td>- 1.45 × 10\textsuperscript{1}</td>
</tr>
<tr>
<td>2011\textsuperscript{17}</td>
<td>SDC(26µm) co-pressing</td>
<td>YSB(6µm) DC magnetron sputtering</td>
<td>YSB-La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}</td>
<td>- 381 266 153</td>
</tr>
<tr>
<td>2012\textsuperscript{2}</td>
<td>SDC(26µm) co-pressing</td>
<td>YSB(6µm) DC magnetron sputtering</td>
<td>YSB-Ag</td>
<td>- 571 380 223</td>
</tr>
<tr>
<td>2012\textsuperscript{23}</td>
<td>GDC(10µm) spin-coating</td>
<td>ESB(5µm) drop-coating</td>
<td>ESB-BRO</td>
<td>- 1.47 × 10\textsuperscript{1}</td>
</tr>
<tr>
<td>2012\textsuperscript{23}</td>
<td>GDC(24µm) spin-coating</td>
<td>ESB(2µm) spin-coating</td>
<td>ESB-La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}</td>
<td>- 1013 667 343 185 88</td>
</tr>
<tr>
<td>This work</td>
<td>SNDC(20µm) co-pressing</td>
<td>ESB(20µm) drop-coating</td>
<td>ESB-LBSM</td>
<td>- 980 788 515 292 130</td>
</tr>
</tbody>
</table>

\textsuperscript{25} Y\textsubscript{0.23}Bi\textsubscript{0.77}O\textsubscript{1.5} (YSB)

Typical electrochemical impedance spectra (EIS) at 450-650 °C with SNDC|ESB bilayer electrolyte cell was measured under open-circuit conditions to provide an insight understanding of how SNDC|ESB bilayer film and ESB-LBSM cathode work, as shown in Figure 4.(a). In the EIS plots, the high-frequency intercept corresponds to the ohmic resistance ($R_\text{o}$) of the cell which is mainly contributed by the electrolyte resistance, and the difference between the high frequency and the low frequency intercept with the real axis represents the interfacial polarization resistance ($R_\text{p}$) of the cell. Figure 4.(b) shows the values of $R_\text{o}$, $R_\text{p}$, and the total resistances $(R_\text{t} = R_\text{o} + R_\text{p})$ of the bilayer film cell estimated from the impedance spectra. The SNDC|ESB bilayer electrolyte cell has low $R_\text{p}$ values of $0.139, 0.169, 0.225, 0.326, 0.506 \Omega$ cm$^2$2 and the $R_\text{p}$ of 0.038, 0.081, 0.216, 0.754 and 2.494 Ω cm$^2$ at 650, 600, 550, 500 and 450 °C, respectively. It is clear that the corresponding electrochemical reactions are thermally activated processes for all resistances decrease with increasing temperature. The $R_\text{t}$ of the cell decrease from 2.494 to 0.038 Ω cm$^2$ with increasing temperature from 450 to 650 °C, while the $R_\text{p}$ only decreases from 0.506 to 0.139 Ω cm$^2$ under the same conditions. Meanwhile, the ratio of $R_\text{p}/R_\text{o}$ are 21.35%, 32.50%, 49.00%, 69.83% and 83.14% at 650, 600, 550, 500 and 450 °C, respectively. Obviously, at temperatures higher than 550 °C, $R_\text{p}$ dominates the total resistance, indicating it should be more important to decrease $R_\text{p}$ further improve the cell performance. Noticeably, the cell $R_\text{p}$ governs the downward trend of $R_\text{t}$ and plays a major role in determining the $R_\text{t}$ of the cell below 500 °C. Therefore, at lower temperatures, more attention should be paid to decrease the $R_\text{p}$ and to explore electrodes with high activity to decrease the $R_\text{o}$ and...
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Conclusions

In summary, a simple low cost fabrication technique was developed for anode-supported DCO-SBO bilayer configuration and a novel low cost composite cathode material ESB-LBSM was successfully applied for ceria-bismuth oxide bilayer electrolyte cell. The SNDC|ESB bilayer structure film showed the largest fuel cell performance ever reported for ceria-bismuth bilayer electrolytes at LT operation below 550 °C, to the best of our knowledge, suggesting that the facile fabrication technique provided an effective and interesting way to fabricate DCO-SBO bilayer electrolyte films with encouraging performance at LTs and could be beneficial to the application of SBO materials for HPLT-SOFCs.

Experimental Section
SNDC, ESB and LBSM powders were synthesized via a citric acid-nitrate gel combustion process. The raw materials for synthesis of SNDC powders were Sm$_2$O$_3$ (99.9%, 3N, Sinopharm Chemical Reagent Co., Ltd (SCR)), Nd$_2$O$_3$ (99.9%, 3N, SCR) and Ce(No$_3$)$_3$•6H$_2$O (AR, ≥99.0%, SCR). Er$_2$O$_3$ (99.9%, 3N, SCR), Bi(No$_3$)$_3$•5H$_2$O (AR, ≥ 99.0%, SCR) and La$_2$O$_3$ (99.9%, 3N, SCR), Bi(No$_3$)$_3$•5H$_2$O, Sr(No$_3$)$_2$ (AR, ≥99.5%, SCR), MnCO$_3$ (CP, 44.0-48.0%Mn, SCR) served as the raw materials for ESB and LBSM powders, respectively. After the combustion, the as-prepared ash-like powders were calcined at 700, 650 and 850 °C for 3 h in air to obtain SNDC, ESB and LBSM powders, respectively. The NiO-SNDC composite powders with a weight ratio of 6:4 for the anode substrates were mixed NiO with SNDC powders and 20 wt.% starch was added as the pore former. The anode supported half cell with monolayer SNDC electrolyte was fabricated by a co-pressing method and then co-fired at 1400 °C for 5 h to obtain NiO-SNDC|SNDC half cell. The thickness of the monolayer SNDC film was controlled by varying the amounts of the powders used. The ESB electrolyte film was fabricated by a drop-coating process on SNDC substrate followed by co-firing at 800 °C for 10 h in air. The ESB powders were firstly dispersed in ethanol with polyvinyl butyral (PVB, binder, 4%) and triethanolamine (TEA, dispersant, 6%), and then ball milled for 24 h to obtain the ESB electrolyte suspension. The ESB suspension was deposited onto SNDC substrate by a transferpettor. The electrolyte film thickness can be controlled by varying the suspension volume during coating. For full cell preparation, ESB powder was mixed with LBSM in weight ratio 1:1 thoroughly together with a 10 wt.% ethylcellulose-terpineol binder to prepare the composite cathode slurry ESB-LBSM. The slurry was then painted onto dense ESB electrolyte membrane and fired at 750 °C for 3 h in air to form porous cathode layer. Ag paste was applied to the cathode as a current collector and Ag wire was employed as the conducting wire. The effective area of the cathode layer in single cell was 0.237 cm$^2$ while the cell diameter and the anode area were 12.00 mm and 1.131 cm$^2$, respectively. Phase compositions of all the powders were identified by an X-ray diffractometer (Rigaku TTR-III) using CuKa radiation. The microstructures of the cell components were investigated by a scanning electron microscopy (SEM, JEOL JSM-6700F). The SNDC-ESB bilayer structure cell was tested in a home-made cell testing system at 450-650 °C. Humidified hydrogen (~3% H$_2$O) at a flow rate of 30 ml min$^{-1}$ and ambient air were used as the fuel and the oxidant, respectively. The water vapor pressure about 0.03 atm was achieved by bubbling H$_2$ through water at about 25 °C. I-V plots of the cells were collected with a DC Electronic Load (ITech Electronics model IT8511) based on a two-probe configuration. The EIS were measured under open circuit conditions using an impedance analyzer (CHI604E, Shanghai Chenhua)(0.1-100 kHz, 5 mV as AC amplitude). $R_p$ of the cells under open circuit conditions were determined from the impedance spectra.

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**Notes and references**

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The LT high performance SNDC-ESB bilayer structure cell was successfully fabricated by combining one-step co-pressing with drop-coating.