Properties of a Ceria-Based \((\text{C}_6\text{S}_2\text{G}_2)\) Solid Oxide Electrolyte Sintered with Al\(_2\)O\(_3\) Additive

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Abstract:
Ceria-based Al\(_2\)O\(_3\) composite electrolytes were prepared using \((\text{CeO}_2)_{0.6}(\text{SmO}_1.5)_{0.2}(\text{GdO}_1.5)_{0.2} \ (\text{C}_6\text{S}_2\text{G}_2)\) and Al\(_2\)O\(_3\) powders, employing sol-gel and low temperature combustion synthesis methods (SGLCS). The influence of Al\(_2\)O\(_3\) content on the sintering behavior and electrical properties was studied. The results showed that electrical properties could be improved by adding 10wt% Al\(_2\)O\(_3\). The sintered density was up to 5.61g/cm\(^3\). Most measurements of open circuit voltage (OCV) ranged between 0.8 and 1.2V; an OCV value of 1.15V was obtained at 370\(^\circ\)C. The performance of intermediate-temperature solid oxide fuel cells (ITSOFCs) with a properly Al\(_2\)O\(_3\) doped electrolyte was better than when a pure ceria-based one was used. The highest power density was 200mWcm\(^{-2}\).

Keywords: Ceria-based Al\(_2\)O\(_3\) composite electrolytes; ITSOFC; Sintering behavior; Mechanical property; Microstructure; Electrical properties

1. Introduction
Solid oxide fuel cells (SOFCs) have attracted considerable research interest because of their many advantages as energy conversion devices. Most conventional SOFCs use yttria-stabilized zirconia (YSZ) as an electrolyte and operate at high temperatures around 1000\(^\circ\)C. A high operating temperature brings about such disadvantages as poor stability in the long-term and component manufacturing costs, etc. Thus, decrease of the operating temperature for SOFCs could lead to reducing the production cost and saving energy for holding cell working. One of the most promising methods to reduce the working temperature for SOFCs is to replace YSZ with other electrolytes possessing high oxide ion conductivity at low temperature. Ceria doped with a rare-earth oxide is a potential electrolyte for so called intermediate-temperature SOFCs because of their higher oxide ion conductivity at relatively lower temperatures than YSZ [1-9]. On the other hand, inorganic solid compounds, working as electrolytes with protons, can also make fuel cells operating at lower temperatures [10-12]. Some authors doped CeO\(_2\) with a NiAl solid phase and NaOH phase to produce a maximum output power of 716.2mWcm\(^{-2}\) at 590\(^\circ\)C [13].

Solid electrolyte cracking may occur during cell working because of their poor

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toughness and strength so the performance of SOFCs deteriorates. Miyayama et al. [14-17] found that this could be somewhat improved by doping YSZ with an appropriate amount of Al$_2$O$_3$. Furthermore, addition of a second phase such as Al$_2$O$_3$ and SiO$_2$ not only greatly improves the mechanical strength but enhances the conductivity of the materials [18-20].

The purpose of this paper is to study the effects of alumina on the performance of sintering and electrical properties of ceria-based electrolytes in the intermediate temperature (500°C) working range.

2. Experimental Procedures

2.1. Preparation of (CeO$_2$)$_{0.6}$(SmO$_{1.5}$)$_{0.2}$(GdO$_{1.5}$)$_{0.2}$ powder

(CeO$_2$)$_{0.6}$(SmO$_{1.5}$)$_{0.2}$(GdO$_{1.5}$)$_{0.2}$ powders, denoted as (CSG2), were synthesized by employing sol-gel and low temperature combustion synthesis methods (SGLCS). Cerium nitrate, samarium nitrate and gadolinium nitrate were used as starting materials. They were mixed together with a citric acid solution. The pH value (5.0-6.0) of the mixed solution was adjusted with an ammonia solution under continuous stirring at 70°C and a homogenous sol was formed. With the evaporation of water, a yellow sponge-like gel was obtained, and then the gel was placed in a 130°C drying oven, where the gel underwent a self-igniting reaction at 260°C and became a light yellow powder with an average particle size of 30nm.

2.2. Sample preparation

(C6S2G2 and Al$_2$O$_3$ (<4µm) powders were used as the starting materials. Al$_2$O$_3$ was doped into C6S2G2 in the amount of 0–20wt%, respectively. Each specimen was calcined at 600°C for 2h. After being cooled down to room temperature, the dried powders were ground for 30 min in an agate mortar, then pressed under a pressure of about 200 MPa into tablets of Φ13×1mm. These tablets were sintered at 1200°C for 10 h in open air.

2.3. Property measurements

The X-ray spectra were obtained by a X-ray diffractometer, model D/2500PC Rigaku (monochromated Cu Ka radiation λ=0.15418nm), in the Bragg angle range of 20≤2θ≤80. The crystallite size, D, of the calcined powders was estimated using the Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  (1)

Microstructures and phase analysis were examined by an electron microscope (SEM) (Model JSM-5310, Japan, equipped with EDS). Radial shrinkage of the tablet samples were measured by the conventional calculation formula $\left(\frac{d_2-d_1}{d_1}\right) \times 100\%$, where $d_1$ is the green compact diameter and $d_2$ the sintered compact diameter, respectively. The axial dimension variation of was negligible. The real density was measured by the Archimedes method.

2.4. Fabrication of SOFCs and performance measurements

Ceria-based tablets doped with Al$_2$O$_3$ and pure ceria-based materials were used as electrolyte components. Each tablet was attached to one end of an alumina tube using a glass phase material for sealing. Silver glue was pasted on the surface of the holders in contact with the cell tablet to seal the H$_2$ and air rooms of the device. Anodes and cathodes were then exposed, respectively, to dry H$_2$ and air to test the performances of the fuel cells; Hydrogen...
gas was fed into the tube as fuel while oxygen in the air was used as an oxidant. Both gases were allowed to flow with a rate of 45 mL min⁻¹ at a pressure of about 1.2 atm into the respective cell rooms and then came out from the other side of the tube. A series of open circuit voltage (OCV) and voltage/current values were measured properly by changing the resistance of the measurement circuit at a constant temperature. Common copper electricity wires were connected with the tubes to set up a measurement circuit and the output voltage and current were measured by a recording meter with an input resistance of 2000Ω. The current density of SOFCs was determined by an Ampere meter.

3. Results and Discussion

3.1. X-ray diffraction

Fig. 1 shows the X-ray spectra for some samples. It can be seen that the spectra of pure C₆S₂G₂, C₆S₂G₂-10wt% Al₂O₃ and C₆S₂G₂-15wt% Al₂O₃ are almost the same while pure Al₂O₃ (JCPDS: 43-1484 Corundum, syn. Aluminum oxide) and pure C₆S₂G₂ (JCPDS: 43-1002 Cerianite, syn. Cerium oxide) phases appeared independently in the spectrum of C₆S₂G₂-10wt% Al₂O₃ and C₆S₂G₂-15wt% Al₂O₃. That means that doping with Al₂O₃ does not change the structure of C₆S₂G₂, differing from the result that GdAlO₃ formed as the second phase [21].

Fig. 1 X-ray spectra of pure C₆S₂G₂, C₆S₂G₂-10wt% Al₂O₃ and 15wt% Al₂O₃.

The average grain sizes of the sample powders were calculated by the Scherrer formula are 20.5, 17 and 17.9nm, respectively. It can be seen that the sample with 10wt% Al₂O₃ has fine grains. There is no big difference reflected in the formation of a new phase or a new compound in C₆S₂G₂-Al₂O₃, except for some changes in the sintering behavior, grain size growth and microstructure.

3.2. Sintering behavior

The shrinkage ratio of sintered samples of C₆S₂G₂-Al₂O₃ is shown in Fig. 2. The addition of Al₂O₃ to C₆S₂G₂ affects the sintering behavior. The shrinkage ratio of C₆S₂G₂ with a small amount of Al₂O₃ is higher than that of pure ceria-based materials. However, the shrinkage ratio of samples doped with too much Al₂O₃ decreased. The maximum of the shrinkage ratio for the doped materials is 10wt% Al₂O₃.
The variation in sintered densities $\rho_s$ and porosity parameter $\theta$ for the sintered $\text{Ce}_x\text{Sr}_{2}\text{G}_2\text{Al}_2\text{O}_3$ is shown in Tab. I, indicating the effect of the $\text{Al}_2\text{O}_3$ content on densification. It is obvious that the maximum of sintered densities $\rho_s$ is 5.61 g/cm$^3$ and accordingly, the porosity parameter $\theta$ is 22.2% for 10wt% $\text{Al}_2\text{O}_3$ content. A higher shrinkage ratio means better sintering density. Higher sintered density usually produces better mechanical properties.

![Fig.2](image_url) Dependence of the sample shrinkage ratio on the composition of alumina in $\text{Ce}_x\text{Sr}_{2}\text{G}_2\text{Al}_2\text{O}_3$.

The sintering density of samples doped with too much $\text{Al}_2\text{O}_3$ is lower. It can be concluded that the sintering behavior of ceria-based materials can be improved by doping with a right amount of $\text{Al}_2\text{O}_3$.

### 3.3. SEM analysis

SEM micrographs together with elemental images for both pure and doped $\text{Ce}_x\text{Sr}_2\text{G}_2$ materials with 10wt% and 15wt% $\text{Al}_2\text{O}_3$ sintered at 1200°C are shown in Fig.3. Clear boundaries between grains and even a variety of cracks along the boundaries can be seen in pure $\text{Ce}_x\text{Sr}_2\text{G}_2$ in Fig.3. That will not improve properties. When 10wt% $\text{Al}_2\text{O}_3$ was used to dope the materials, $\text{Al}_2\text{O}_3$ particles are well-proportionally distributed (see Fig.3 (b)), some cracks disappear and pores become smaller. When the $\text{Al}_2\text{O}_3$ content is increased to 15wt%, congregation of $\text{Al}_2\text{O}_3$ particles occurs in the some pores and the boundaries tend to merge and become blurred. (See Fig.3 (c). The reason for this is attributed to the fine ($\text{Ce}_x\text{Sr}_2\text{G}_2$) powders size. $\text{Al}_2\text{O}_3$ solubility in $\text{Ce}_x\text{Sr}_2\text{G}_2$ must be rather small. This is consistent with the

### Tab. I Sintered density and porosity of samples with different compositions of alumina

<table>
<thead>
<tr>
<th>Composition of alumina (wt %)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered density (g/cm$^3$)</td>
<td>5.32</td>
<td>5.39</td>
<td>5.61</td>
<td>5.52</td>
<td>5.44</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>26.3</td>
<td>25.3</td>
<td>22.2</td>
<td>23.5</td>
<td>24.7</td>
</tr>
</tbody>
</table>
results of X-ray diffraction. It is presumed that the electrical properties could be improved by
the increased density.

Fig. 3 SEM micrographs with elemental images of (a) pure C$_6$S$_2$G$_2$, (b) C$_6$S$_2$G$_2$-10wt%Al$_2$O$_3$
and (c) C$_6$S$_2$G$_2$-15wt% Al$_2$O$_3$. 
3.4. SOFC performance

$C_6S_2G_2-10wt\%Al_2O_3$ materials were used as composite electrolytes to make SOFCs. The OCV (open circuit voltage) – temperature curve of the SOFC is shown in Fig.4. OCV first increases and then decreases with increasing temperature, and finally stabilizes at 500°C. OCVs range from 0.8 to 1.2 V, and the maximum measured value is 1.15 V at 370°C, significantly higher than for the pure $C_6S_2G_2$ electrolyte (1.065 V).

Fig. 5 shows current-voltage variations with corresponding power densities of pure $C_6S_2G_2$, $C_6S_2G_2-10wt\% Al_2O_3$ and $C_6S_2G_2-15wt\% Al_2O_3$ composite electrolytes at 500°C. It reached about 0.84 V for the pure $C_6S_2G_2$ specimen, 0.883 V for the $C_6S_2G_2-10wt\% Al_2O_3$ sample and 0.83 V for the $C_6S_2G_2-15wt\% Al_2O_3$ sample. According to Fig.5, the highest power density mean values are 187.5, 200 and 119 mW cm$^{-2}$, respectively. It is better than the values obtained for GDC-based ($Ce_{0.8}Gd_{0.2}O_{1.9}$) SOFCs exhibiting a power density of 140 mW cm$^{-2}$ at 500°C [22]. Corresponding current densities for the highest power density are 375 mA cm$^{-2}$, 400 mA cm$^{-2}$ and 225 mA cm$^{-2}$, respectively.

![Fig. 4](image4.png)

**Fig. 4** OVC-temperature relation of a SOFC using $C_6S_2G_2-10wt\% Al_2O_3$ as an electrolyte.

As shown in Fig.5, advantages of the composite electrolyte $C_6S_2G_2-10wt\% Al_2O_3$ are obvious, resulting from better sintering behavior and finer grain size.

![Fig. 5](image5.png)

**Fig. 5** Typical voltage-current and power performance relations of SOFCs using pure $C_6S_2G_2$, $C_6S_2G_2-10wt\% Al_2O_3$ and $C_6S_2G_2-15wt\% Al_2O_3$ as electrolytes.
Thus, it has been shown that SOFC performance in power production can be improved by doping \( \text{C}_6\text{S}_2\text{G}_2 \) with a proper amount of alumina.

4. Conclusions

The properties of the \( \text{C}_6\text{S}_2\text{G}_2 \) composite electrolytes doped with \( \text{Al}_2\text{O}_3 \) were studied. The sintering behavior and electrical properties can be improved significantly by doping \( \text{Al}_2\text{O}_3 \) into pure \( \text{C}_6\text{S}_2\text{G}_2 \). The maximum of sintered density of \( \text{C}_6\text{S}_2\text{G}_2\)-10wt\%\text{Al}_2\text{O}_3 \) is 5.61g/cm\(^3\) and the porosity parameter is 22.2%. Among all the specimens measured in the experiment, \( \text{C}_6\text{S}_2\text{G}_2\)-10wt\%\text{Al}_2\text{O}_3 \) possessed the highest performance (power density=200mWcm\(^{-2}\)) working in ITSOFC as an electrolyte.

6. References


**Садржај**: Композитни електролити на бази церијума са додатком \( \text{Al}_2\text{O}_3 \) су припремљени од прахова \((\text{CeO}_2)_{0.6}(\text{SmO}_1)_{0.2}(\text{GdO}_1)_{0.2}(\text{C}_6\text{S}_2\text{G}_2)\) и \( \text{Al}_2\text{O}_3 \) коришћењем сол-гел методе и нискотемпературне синтезе сагоревањем. Проучен је утицај садржаја \( \text{Al}_2\text{O}_3 \) на синтеровање и електрична својства. Резултати су показали да се електрична својства могу побољшати додавањем 10wt% \( \text{Al}_2\text{O}_3 \). Добијена синтерована густина узорака је била до 5.61g/cm\(^3\). Већина мерења напона у отвореном колу је била у опсегу од 0,8 до 1,2 V. Вредност од 1,15 V је добијена на 370°C. Перформансне чврстих горивних оксидних ћелија за средње температуре са правилно допираним \( \text{Al}_2\text{O}_3 \) електролитом су биле боље него када је коришћен само онај заснован на церијуму.
Највећа добијена густина снаге је била 200 mWcm⁻².

Кључне речи: Церијум композитни електролит, ITSOFC, синтеровање, механичка својства, микроструктура, електрична својства.