COMPARISON OF MECHANICAL AND THERMAL PROPERTIES OF THE TUBULAR LSGM, CGO, AND YSZ ELECTROLYTES

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ABSTRACT

Thermal properties and mechanical strength of ceramic fuel cell components are critical for allowing rapid-start up of a solid oxide fuel cell system, and operational stability at high temperatures. Tubular electrolytes were prepared using a plastic extrusion technique, from a dough that contains the electrolyte powders and additives. Strontium- and magnesium-doped lanthanum gallate (LSGM), gadolinium-doped ceria (CGO), and 8 mol% yttria-stabilized zirconia (YSZ) were studied. Thermal expansion coefficients and thermal shock resistance of the extruded tubular LSGM, CGO, and YSZ electrolytes were investigated and compared. Three point bending strength of these three extruded electrolyte materials were tested at room temperature, 600°C, 800°C, and 1000°C in air, and the results are discussed.

Keywords: modulus of rupture, thermal expansion coefficient, thermal shock resistant, electrolyte, solid oxide fuel cell.

INTRODUCTION

Since the first ceramic fuel cell was demonstrated by Baur and Preis (1) in 1937, zirconia based materials have been used as the most reliable electrolyte materials because of their high oxide-ion conductivity and low electronic conductivity, chemical stability and thermal performance. In recent years, great efforts have been made by researchers to identify new electrolyte materials in order to reduce the operating temperature of the solid oxide fuel cell (SOFC) from 900-1000°C (zirconia electrolyte) to 600-800°C. Gadolinia-doped ceria (CGO) materials have been studied as an alternative for 8 mol% yttria stabilized zirconia (YSZ) due to their higher oxide-ion conductivity than YSZ at comparative temperatures. However, at low oxygen partial pressures, P02<10^-12 atm or high temperature (greater than 800°C) for example, CGO shows undesirable electronic conduction (2). Sr- and Mg-doped LaGaO3 (LSGM) materials have been considered as an alternative to YSZ for use as an electrolyte in SOFCs, especially at intermediate temperatures, because these materials were found to have high oxide-ion conductivities in a wide range of oxygen partial pressures (3).

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Mechanical strength is one of the essential requirements for an electrolyte self-supported tubular SOFC. It requires a minimum strength to allow handling during the single cell and fuel cell stack fabrication. To successfully fabricate a multiple layer ceramic SOFC, it is desirable that the thermal expansion coefficients (TECs) of the SOFC components (anode, cathode, electrolyte, and current collector) match each other to avoid cracking during heating and cooling over the operating temperature range. Studying the TECs of electrolytes in the electrolyte supported tubular SOFCs is also essential for the system design and materials selection. Thermal shock resistance is another concern for building a rapid heating ceramic system. The materials should withstand thermal cycling from room temperature to operation temperature (600-900°C) with a high heating and cooling rate (250-500°C/min). Furthermore, for the tubular SOFCs, the temperature gradients along the tubes during operation conditions can be large and therefore create large stresses depending on the stack design. Kendall and Prica reported their work on the mechanical and thermal properties of small YSZ tubes a few years ago (4, 5).

The objective of this study was to determine and compare the mechanical strength, thermal expansion and thermal shock resistance of the commonly studied electrolytes LSGM, CGO, and YSZ. The results, obtained from directly measuring the extruded electrolytes, will guide the optimisation of the electrolyte and electrode materials selection to electrically and thermally meet the essential requirements of electrolyte supported tubular SOFCs.

**EXPERIMENTAL**

The compositions of the materials studied were La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ (LSGM), Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ (CGO), and 8 mole% yttria stabilized zirconia (YSZ). Specimens were either tubular electrolytes or rods extruded and sintered using the technique described elsewhere (6, 7). The dimensions of the specimens were for tubes: outside diameter 3.0±0.2 mm, length 25±0.5 mm, wall thickness 0.3±0.05 mm; for rods: diameter 2.0±0.2 mm, length 25±0.5 mm. The relative densities of the samples used in this study were greater than 97%.

Three point bending strength test was carried out using an INSTRON-4204 test machine with a span of 8.34 mm at a crosshead speed of 0.2 mm/min. High temperature strength was measured, using a tubular furnace attachment to the INSTRON-4204, after a dwell of one hour at 600°C, 800°C, and 1000°C in air. At least 10 samples were measured at each temperature.

Linear thermal expansion measurements were performed in air using a push-rod type differential dilatometer (Harrop HT) in the temperature range of 25°C to 1000°C, with the heating and cooling rate of 5°C/min. The reference used for the measurements was a quartz rod. The average thermal expansion coefficients ($\alpha$) can be calculated using equation [1], the initial sample length ($L_0$), and sample length change ($\Delta L$) over the temperature range ($\Delta T$) recorded from the measurements.

$$\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T}$$

[1]
Thermal shock resistances of the electrolytes were estimated using a Tetlow furnace. The samples were first heated up to 800°C in the furnace and dwelled at 800°C for 30 minutes, and then quenched in air or water. For air quench, the samples were taken out of the furnace and allowed to cool for 30 minutes from 800°C to 50°C. For the water quench, the samples were cooled from 800°C to 50°C in 0.5 minutes. The quenched samples were placed back into the furnace and heated up to 800°C for the next quench cycle. The temperature profile of the samples and the furnace during the thermal shock resistance test are illustrated in Fig. 1. The experimental set-up, and the samples before and after thermal quench test are shown in Fig. 2.

![Temperature profile](image)

**Fig. 1.** Illustration of the temperatures the samples and the furnace underwent during thermal shock resistance test.

![Test set-up and samples](image)

**Fig. 2.** Photographs of thermal shock test set-up and samples. (a) samples before test; (b) thermal shock test set-up; (c) samples after thermal shock test (20 cycles air quench and 1 cycle water quench from 800°C).
Mechanical Strength of LSGM, CGO and YSZ Electrolyte Materials

Fig. 3 shows a comparison of the modulus of rupture (MOR) of the extruded electrolyte materials (rods) tested at room temperature and high temperature in air. In general, for all of the three electrolytes (LSGM, CGO, YSZ), the mechanical strength decreases with an increase in temperature. The MOR of LSGM electrolyte is smaller than that of CGO and YSZ at the same temperature. At temperatures higher than 800°C, the MOR of LSGM and CGO decreased rapidly, while the MOR of YSZ at 1000°C is greater than that at medium temperatures (600°C and 800°C). The latter trend for YSZ was also observed by Minh (8) and Mori (9), however, the reason is currently under investigation.

Fig. 3, Modulus of rupture of the extruded LSGM, CGO, and YSZ electrolyte materials, tested at room temperature and high temperature.
Fig. 4. Comparison of linear thermal expansion of the tubular electrolytes extruded from LSGM (La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.85}), CGO (Ce_{0.8}Gd_{0.2}O_{1.9}), and YSZ (8 mol% yttria stabilised zirconia) materials.

Fig. 5. Comparison of thermal expansion coefficients of the tubular electrolytes extruded from LSGM (La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.85}), CGO (Ce_{0.8}Gd_{0.2}O_{1.9}), and YSZ (8 mol% yttria stabilised zirconia) materials.
Thermal Expansion Coefficient

Fig. 4 shows a comparison of the linear thermal expansion of the electrolytes extruded from LSGM, CGO, and YSZ materials. It can be seen that the linear thermal expansion of these materials increased in the order of YSZ<LSGM<CGO over the test temperature range (25-1000°C). TECs of these materials, calculated using equation [1], are shown in Fig. 5. The average TECs of LSGM are $10.45 \times 10^{-6}/°C$, $11.01 \times 10^{-6}/°C$, $11.58 \times 10^{-6}/°C$, at $25°C$ to $600°C$, $800°C$, and $1000°C$, respectively, which are 5-10 % greater than YSZ, however 5-10 % smaller than CGO in the same temperature range. TECs of Sr- and Mg-doped lanthanum gallate materials reported in the literature were between $10.5-11.6 \times 10^{-6}/°C$ (room temperature-1000°C) (9), which are in good agreement with the present study. However, the phase transition from orthorhombic to rhombohedral for LSGM at 681°C reported by Hayashi et al. (10) was not detected from the TEC measurement. Matching the thermal expansion coefficient in the SOFC components is critical, as a small difference in the thermal expansion coefficient of the cell components (electrolyte, anode, cathode, and current collector) can produce large thermal stresses during single cell fabrication and fuel cell stack operation.

Thermal Shock Resistance

Thermal shock is a stress induced in a material due to the temperature differences between the surface and the interior, or between different regions of the component. Rapid cooling of the dense electrolytes is more likely to cause thermal shock issues than heating, since the induced surface stresses are tensile. Thermal shock resistance of the electrolytes depends not only on the magnitude of the temperature differences, but also on the mechanical and thermal properties of the materials, and the dimensions of the components. For example, the electrolyte with higher fracture strength and higher thermal conductivity, as well as lower elastic modulus and lower thermal expansion coefficients, will have better thermal shock resistance. The thermal shock test results of this study were summarised in Table 1. Tubes and rods of the three different electrolytes showed excellent thermal shock resistance and withstood 20 air-quenched cycles from $800°C$ without visible cracks and delamination. The thermal shock treatment was made severer by introducing a water quench step. After 1 water quench cycle, as shown in Fig 1(c), all the tube samples were broken and the rod samples remained unbroken. This is due to the fact that the tube samples underwent a double-side quenching, whereby the heat transported to the cooling medium (water) from the outside surface and inside surface of the tube samples was greater than that from the outside surface of the rod samples. Further water quench showed the thermal shock resistance of the rod samples increased in the order of LSGM<CGO<YSZ. In comparison to YSZ, LSGM has a smaller mechanical strength and larger thermal expansion coefficient and thus can produce a bigger thermal stress. This stress can be high enough to cause failure of the component if it is greater than the tensile strength of the material. In addition, the mechanical strength of the samples decreased drastically after a thermal quench because of microcrack formation in the dense ceramics. Mori et al. (9) measured the quenching temperature dependence of the bending strength of YSZ, and showed that the MOR decreased from 250 MPa to 100 MPa after water quenching from $150°C$. Therefore, thermal shock is an important factor to be considered for selecting materials, designs and operating a SOFC system, especially for thermal cycling considerations.
Table 1. Thermal shock test cycles – air quench and then water quench from 800°C.

| Samples | Air quench cycles | Water quench cycles |
|---------|-------------------|---------------------|
|         | From 1 to 20      | 1 2 3 4 5 6 7 8 9 10 |
| Tubes   |                    |                     |
| LSGM-1  | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -2      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -3      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -4      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -5      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -6      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -7      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -8      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| CGO-1   | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -2      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -3      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| YSZ-1   | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -2      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -3      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -4      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -5      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -6      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| Rods    |                    |                     |
| LSGM-1  | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -2      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -3      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| CGO-1   | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -2      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -3      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| YSZ-1   | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -2      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -3      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -4      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -5      | 1 2 3 4 5 6 7 8 9 10 | Broken |
| -6      | 1 2 3 4 5 6 7 8 9 10 | Broken |

⇒ No visible cracks or delamination.
CONCLUSIONS

The three point bending strength, thermal expansion coefficient, and thermal shock resistance of the electrolytes (small scale tubes and rods) extruded from \(\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{2.8}\) (LSGM), \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\) (CGO), and 8 mol% yttria stabilized zirconia (YSZ) materials were investigated and compared. The modulus of rupture of LSGM are 287 MPa, 195 MPa, 184 MPa and 147 MPa at room temperature, 600°C, 800°C, and 1000°C, respectively, which are smaller than CGO and YSZ at the same temperature. Thermal expansion coefficients of the three electrolyte materials increased in the order of YSZ<LSGM<CGO. The average thermal expansion coefficients between room temperature and 800°C were 10.18×10^{-6}°C, 11.01×10^{-6}°C, 12.04×10^{-6}°C, for YSZ, LSGM, and CGO, respectively. All the three electrolyte tubes and rods showed excellent thermal shock resistance and withstood 20 air-quenched cycles from 800°C without visible cracks and delamination. Further water quench showed the thermal shock resistance of the rod samples increased in the order of LSGM<CGO<YSZ.

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