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Short communication

# High performance composite interconnect $La_{0.7}Ca_{0.3}CrO_3$/20 mol% $ReO_{1.5}$ doped $CeO_2$ (Re = Sm, Gd, Y) for solid oxide fuel cells

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**Abstract**

This paper reports and discusses composite interconnect materials that were modified from $La_{0.7}Ca_{0.3}CrO_{3-\delta}$ (LCC) by addition of Re doped $CeO_2$ (Re = Sm, Gd, Y) for improved conductivity at relative low temperatures. It is found that the addition of small amounts of RDC ($ReO_{1.5}$ doped $CeO_2$) into LCC dramatically increased the electrical conductivity. For the best system studied, LCC + 5 wt% SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$), LCC + 3 wt% GDC ($Gd_{0.2}Ce_{0.8}O_{1.9}$) and LCC + 3 wt% YDC ($Y_{0.2}Ce_{0.8}O_{1.9}$), the electrical conductivities reached 687.8, 124.6 and 104.8 S cm$^{-1}$ at 800 °C in air, respectively. The electrical conductivities of the specimens, LCC + 3 wt% SDC, LCC + 1 wt% GDC and LCC + 2 wt% YDC in $H_2$ at 800 °C were 7.1, 3.8 and 5.9 S cm$^{-1}$, respectively. With the increase of RDC content, the relative density increased, indicating that RDC served as an effective sintering aid in enhancing the sinterability of the powders. The average coefficient of thermal expansion (CTE) at 30–1000 °C in air increased with the increase of the RDC content. The oxygen permeation measurements indicated a negligible oxygen ionic conduction, indicating that the efficiency loss of a solid oxide fuel cell by permeation is negligible for the general cell design using LCC + RDC as interconnect. Therefore, the composite materials $La_{0.7}Ca_{0.3}CrO_3$/20 mol% $ReO_{1.5}$ doped $CeO_2$ are very promising interconnecting ceramics for solid oxide fuel cells (SOFCs).


*PACS:* Fuel cell (84.60 D)

*Keywords:* Doped ceria; Conductivity; Auto-ignition process; Interconnect; SOFC

## 1. Introduction

Solid oxide fuel cells (SOFCs) have been considered as power generation devices in the future as they have demonstrated high energy-conversion efficiency, high power density and extremely low pollution, in addition to flexibility in using hydrocarbon fuels. To raise the voltage output, multiple cells are electrically connected into series via interconnects. A major challenge in SOFC development is the interconnect material, which provides the conductive path for electrical current to pass between the electrodes and to the external circuit [1–3]. Obviously, the interconnect material must have a good electrical conductivity to minimize ohmic losses. The interconnect material is exposed to both oxidizing and reducing conditions. SOFCs operate at high temperatures, therefore the interconnect must have a coefficient of thermal expansion (CTE), which is close to those of the other cell components to minimize thermal stresses. Other requirements of the interconnect materials include adequate mechanical strength, low permeability to oxygen and hydrogen and reasonable thermal conductivity. In addition, cost-effective manufacture of fuel cells requires easy fabrication of the interconnect materials.

Lanthanum chromite ($LaCrO_3$) based perovskite materials have been widely studied as the ceramic interconnect for SOFCs owing to its thermal and chemical stability and high electrical conductivity at both reducing and oxidizing atmospheres [4,5]. Due to the strong dependence of electrical conductivity on the oxygen pressure, the electrical conductivity of the doped $LaCrO_3$ in reducing atmosphere like hydrogen is significantly lower than that in oxidizing atmosphere like air [6]. One disad-

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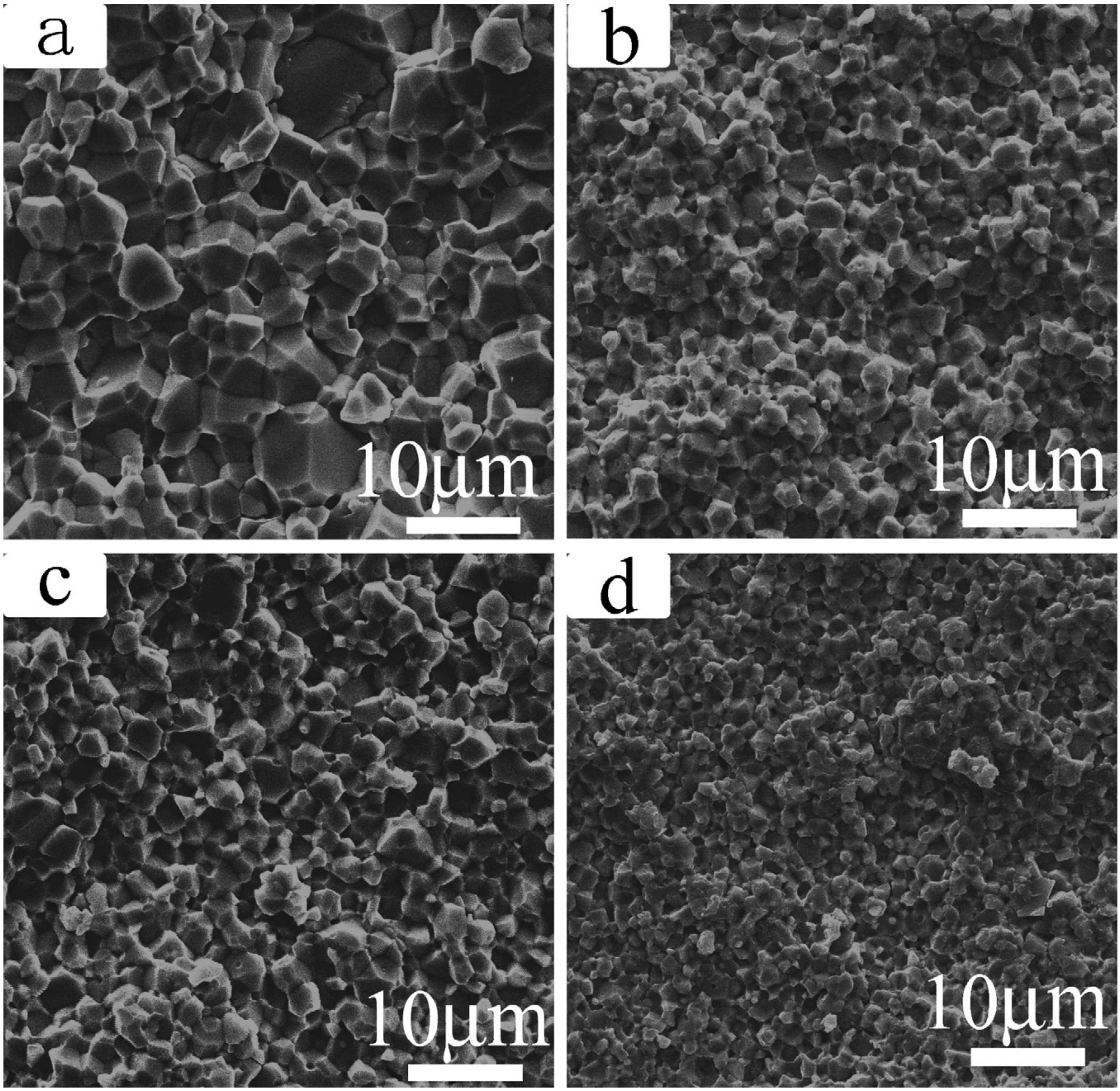


Fig. 1. SEM images of the samples sintered at 1400 °C for 4 h: Panel (a–d) LCC, LCC + 10 wt% SDC, LCC + 10 wt% GDC and LCC + 10 wt% YDC, respectively.

vantage for LSC (Sr-doped $LaCrO_3$) is that the LSC ceramic interconnects tend to be reduced in the reducing anode-side environment, causing size instability [7]. As such, a conductivity gradient across the doped $LaCrO_3$ is established when it is utilized as an interconnect in a SOFC, considering that it is subjected to fuel on one side and oxidant on the other. Fortunately, the overall conductivity of the doped $LaCrO_3$ is still sufficient for its use as long as the operating temperature is above 800 °C [2]. However, at temperatures below 800 °C, the electrical conductivity of doped $LaCrO_3$ is reported to experience substantial degradation [8]. This limitation renders it virtually useless for intermediate temperature 600–800 °C. This is also one of the reasons why the operating temperature of currently explored SOFC with use of LSC interconnects should be higher than 800 °C. SOFCs with metallic interconnects are operating at 650–800 °C. The work reported in this communication aimed to develop novel interconnect materials, which can significantly reduce the operating temperatures. This is a critical step toward making SOFCs affordable for a wide variety of applications. In this communication, we report our recent advance in preparation and properties of LCC ($La_{0.7}Ca_{0.3}CrO_3$) with an addition of the electrolyte RDC (Re doped $CeO_2$, Re = Sm, Gd, Y).

## 2. Experimental details

$La_{0.7}Ca_{0.3}CrO_{3-\delta}$ powders were synthesized by auto-ignition process [9]. The starting materials, calcium nitrate ($Ca(NO_3)_2\cdot4H_2O$) (AR), lanthanum oxide ($La_2O_3$) (AR) and

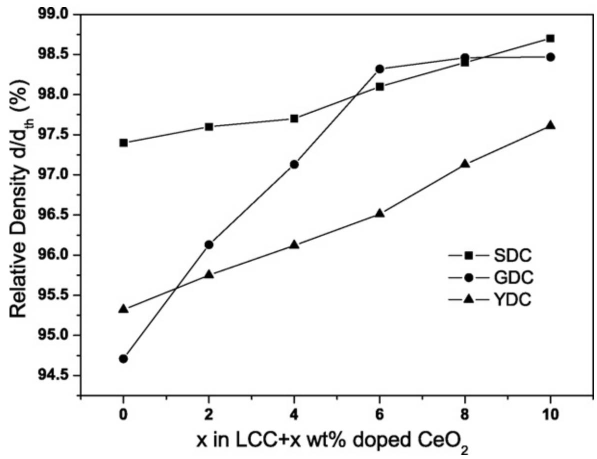


Fig. 2. Influence of RDC content on the relative density of different samples.

chromic nitrate ($Cr(NO_3)_3·6H_2O$) (AR), were dissolved in nitric acid. Citric acid was added as the complexing agent to the above solution. The amount of citric acid added was such that the ration of total number of moles of cations to that of citric acid was 1:3. The mixture was then heated to form a gel and the wet gel was further heated up to about 120 °C to remove the solvents. The dried gel was placed in an oven at 650 °C. The combustion reaction took place within a few seconds, forming the primary powder. The as-synthesized powders were calcined at 1000 °C for 2 h. In order to prepare 20 mol% $ReO_{1.5}$ doped $CeO_2$ powders by glycine-nitrate process (GNP) [10–12], stoichiometric amounts of $Ce(NO_3)_3·6H_2O$ (AR) and $Re(NO_3)_3·6H_2O$ (AR) (Re = Sm, Gd, Y) were dissolved in distilled water and 1.6 mol of glycine was added per mole of nitrate. After spontaneous ignition, the resulted pale-yellow ash was collected and calcined in air at 600 °C for 2 h to remove any carbon residue remained in the oxide powder and a well-crystalline structure was formed.

The fine powders with the composition of LCC + *x* wt% RDC (*x* = 0–6, 8 and 10) were ball-milled in ethanol medium overnight and dried subsequently. Small pellets and rectangular bar specimens were then produced by pressing at 360 Mpa and sintered in air at 1400 °C for 4 h. The heating rate was fixed at 1 °C $min^{-1}$ before 550 °C and 2 °C $min^{-1}$ between 550 and 1400 °C.

The particle size and fractured surface of the sintered specimens were observed by scanning electron microscopy (Hitachi

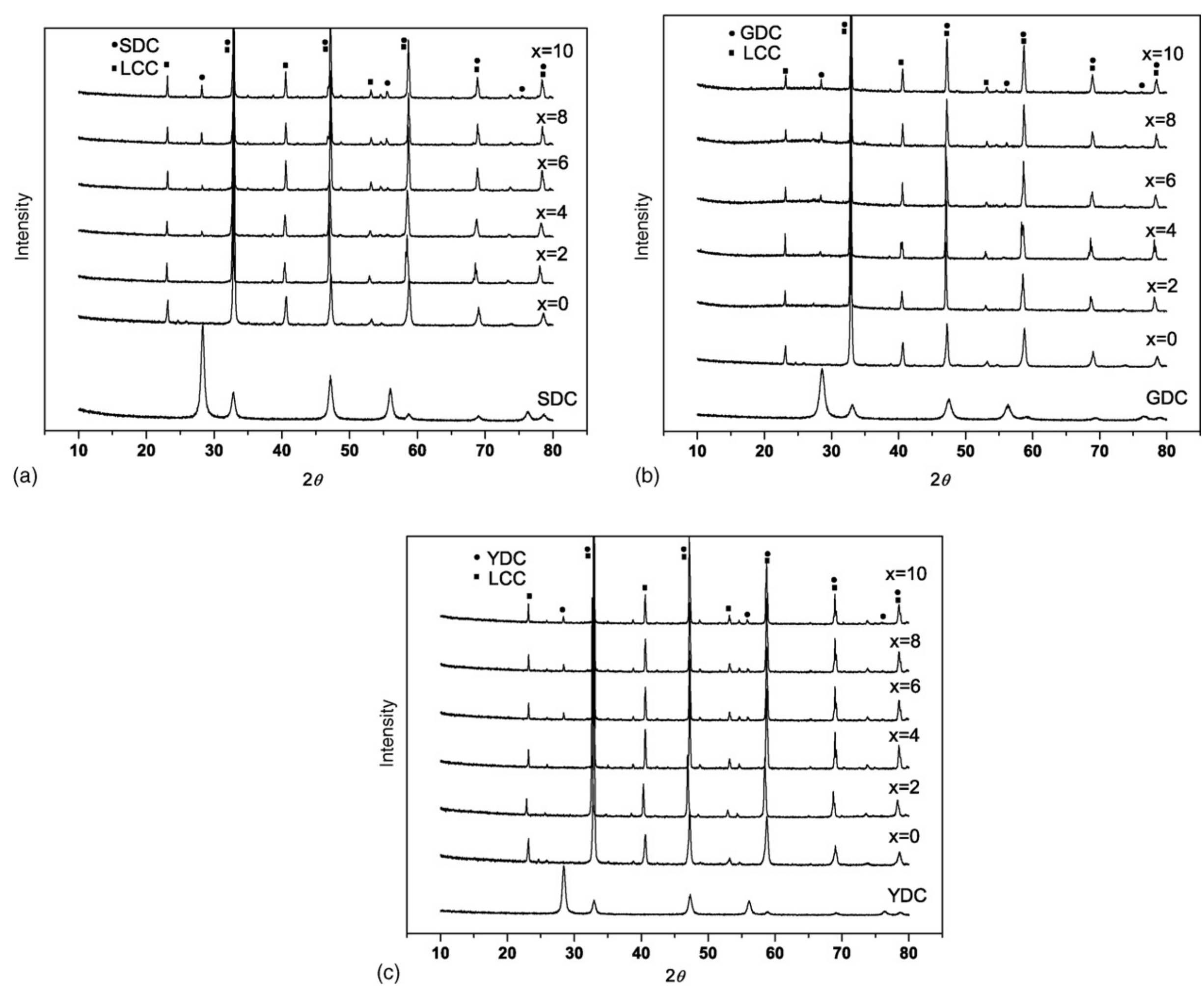


Fig. 3. X-ray patterns of material LCC + *x* wt% RDC and RDC (a) LCC + SDC, (b) LCC + GDC and (c) LCC + YDC.

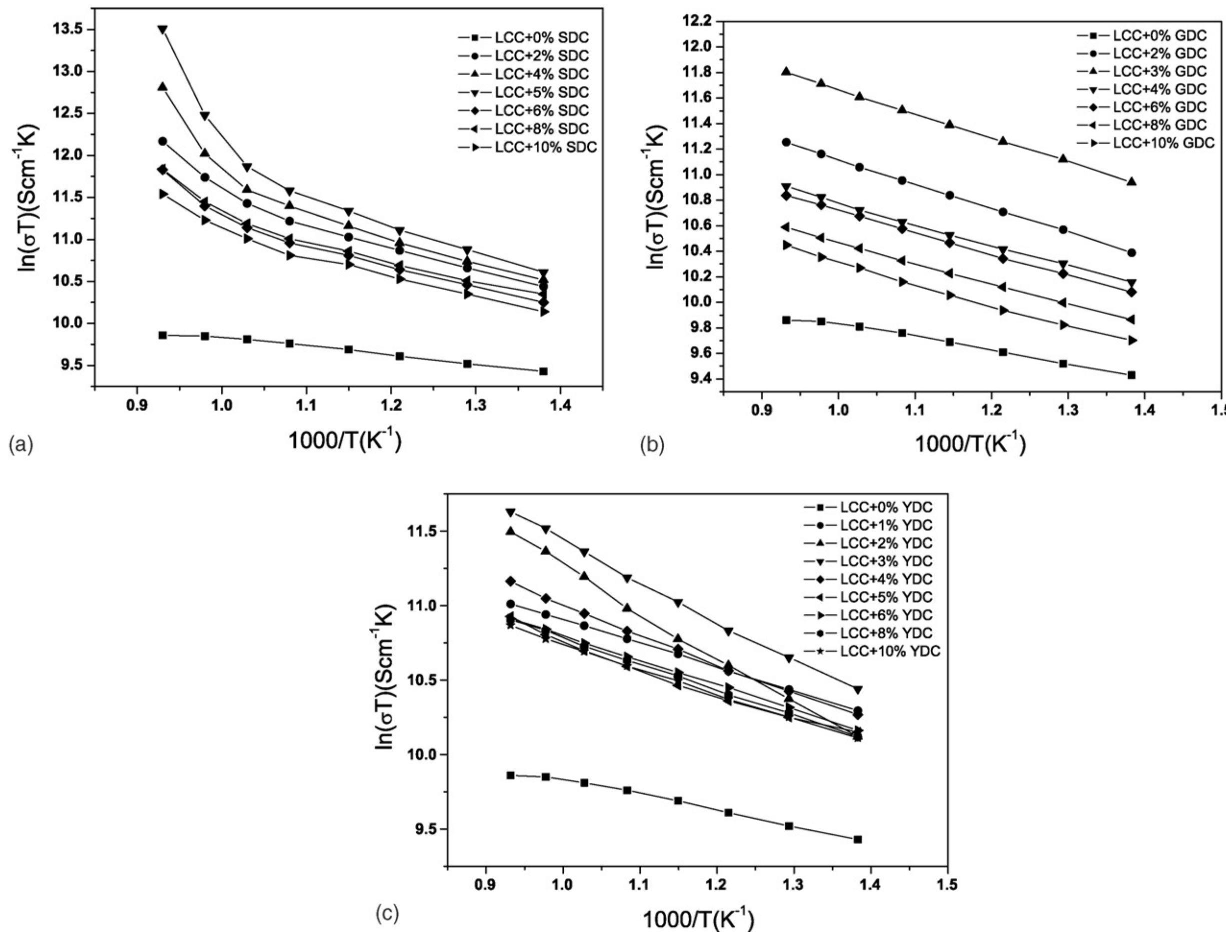


Fig. 4. Arrhenius plots of conductivities of the samples with different RDC contents in air (a) SDC, (b) GDC and (c) YDC.

X-650 and XT30 ESEM-TMP). Various phases of the sintered samples were identified by X-ray diffraction analysis on a Philips PW 1730 diffractometer using Cu Kα radiation. The electrical conductivity of the materials was studied from 450 to 800 °C using standard DC four-probe technique on a H.P. multimeter (Model 34401). Rectangular bar specimens were used for this purpose. The bulk density of all the sintered samples was measured by liquid displacement method using toluene. The thermal expansion was measured at 30–1000 °C on cylindrical rods of the sintered samples using a dilatometer (SHIMADZU50) at a heating rate of 5 °C min$^{-1}$. The oxygen penetration flux was measured by gas chromatography. The oxygen pressures on the two sides of pellets were $8.61 \times 10^{-4}$ and 0.25 atm, respectively. The thickness of pellet is 1.11 mm.

## 3. Results and discussion

### 3.1. SEM analysis and relative density measurements

The SEM images of the samples for the selected sintering conditions (Fig. 1) showed that dense materials were fabricated in air after sintering, suggesting that the present powders were sinterable. The average grain sizes were determined by direct observation. As shown in Fig. 1, the average grain sizes of the different samples ranged from 2 to 6 μm. Fig. 1(a) shows that the average grain size was 6 μm when the sample contained no RDC. The average grain sizes of other samples were smaller than that of the sample without RDC. The existence of RDC thus may restrain the growth of grains. The influence of RDC content on relative density of different LCC + RDC samples is shown in Fig. 2. With the increase of RDC content from 0 to 10 wt%, the relative density increased to a great extent. Therefore, RDC may serve as an effective sintering aid in enhancing the sinterability of the powders.

### 3.2. XRD phase structure analysis

The XRD patterns of LCC + *x* wt% RDC and RDC obtained after sintered at 1400 °C for 4 h are shown in Fig. 3. The XRD patterns of the RDC sample displayed all peaks associated with those of a pure fluorite structure. The LCC sample showed a pure perovskite phase with an orthorhombic symmetry. For other samples, LCC and RDC still remained their own phases after sintered at 1400 °C for 4 h when the RDC content ranged from 4 to 10 wt%. At lower RDC content, there was no evident RDC phase in the XRD. This may result from that the RDC dissolved into LCC structure and formed one phase with LCC. However, it is also possible that RDC still existed in the form of a pure fluorite structure since XRD commonly has a detection limit of ∼5%.

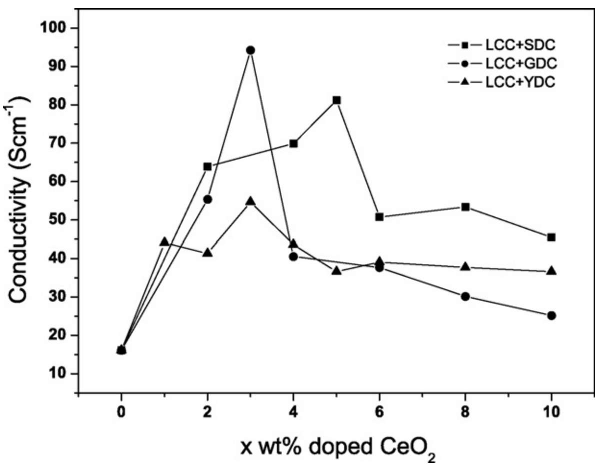


Fig. 5. Effect of RDC content on the conductivities of the samples in air at 550 °C.

### 3.3. Electrical conductivity

Fig. 4(a) shows Arrhenius plots of conductivities of the samples with different SDC contents in air. It can be seen that the electrical conductivities of the samples with a specific SDC content increased with increasing temperature and reached a maximum at 800 °C in the investigated range. At each specific temperature studied, the sample containing 5 wt% SDC showed the highest electrical conductivity and reached as high as 687.8 S cm$^{-1}$ at 800 °C under the experimental conditions, which is 38.7 times as high as that of the commonly used lanthanum chromite ($La_{0.7}Ca_{0.3}CrO_3$). It is also notable that even at 600 and 700 °C, the electrical conductivities reached 96.7 and 146.3 S cm$^{-1}$, respectively. In Fig. 4(b), the sample LCC + 3 wt% GDC showed the highest electrical conductivity of 124.6 S cm$^{-1}$ at 800 °C under the experimental conditions among all LCC + GDC specimens studied, which is about 5.5 times as high as that of the commonly used lanthanum chromite. In addition, at 600 and 700 °C, the electrical conductivities reached 101.1 and 112.8 S cm$^{-1}$, respectively. Arrhenius plots of conductivities of the samples with different YDC contents in air are shown in Fig. 4(c). In this material system, the sample, LCC + 3 wt% YDC, was found to have the maximal electrical conductivity of 104.8 S cm$^{-1}$ at 800 °C in air which is 5.9 times as high as that of the commonly used lanthanum chromite. At 600 and 700 °C, the electrical conductivities were 70.3 and 88.4 S cm$^{-1}$, respectively. Therefore, the addition of small amount of RDC into LCC can dramatically increase the electrical conductivity. As shown in Fig. 5, the most important in this experiment is that at 550 °C, the electrical conductivities of LCC + 5 wt% SDC, LCC + 3 wt% GDC and LCC + 3 wt% YDC in air were 81.2, 94.2 and 61.5 S cm$^{-1}$, respectively. Under

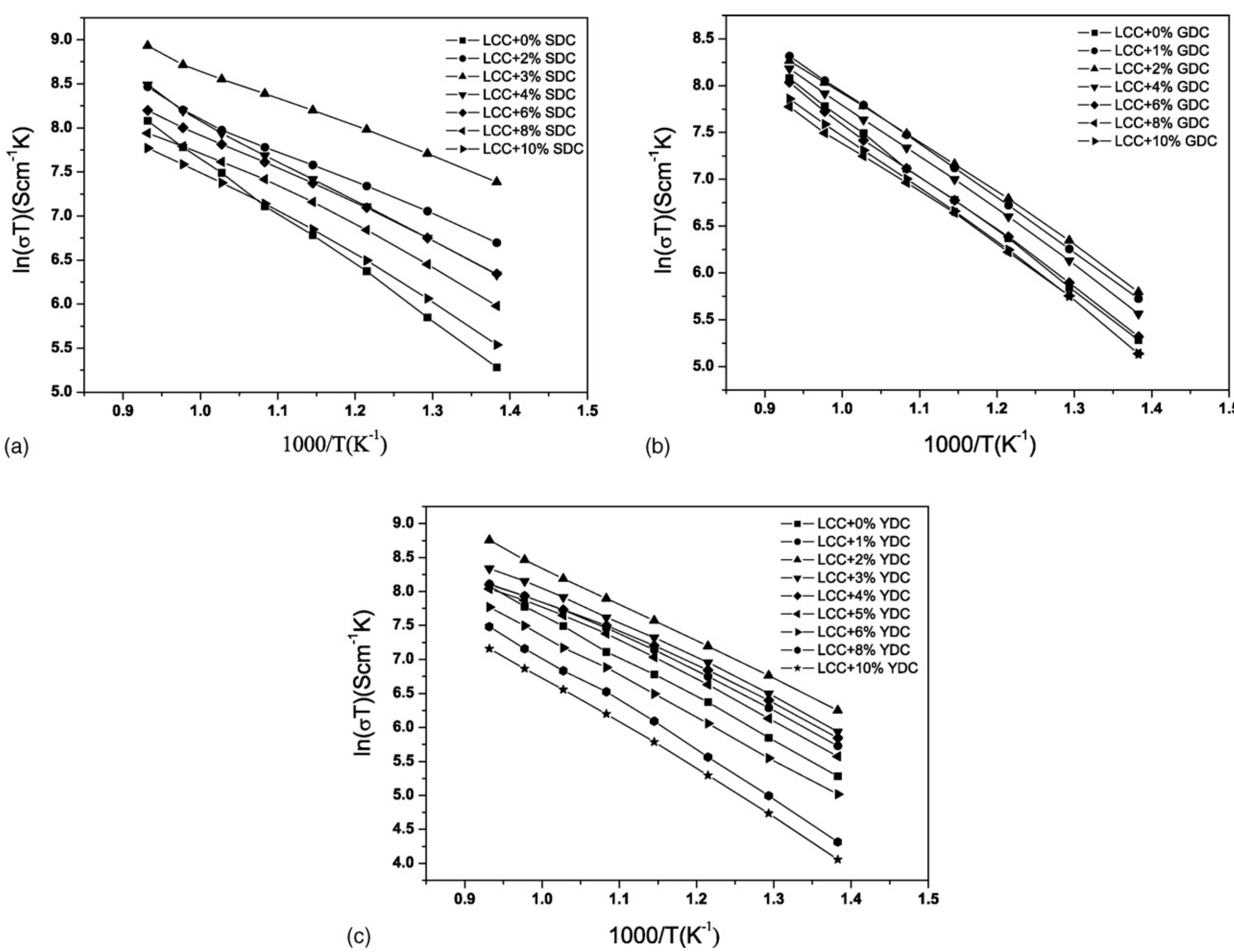


Fig. 6. Arrhenius plots of conductivities of the samples with different RDC contents in $H_2$ (a) SDC, (b) GDC and (c) YDC.

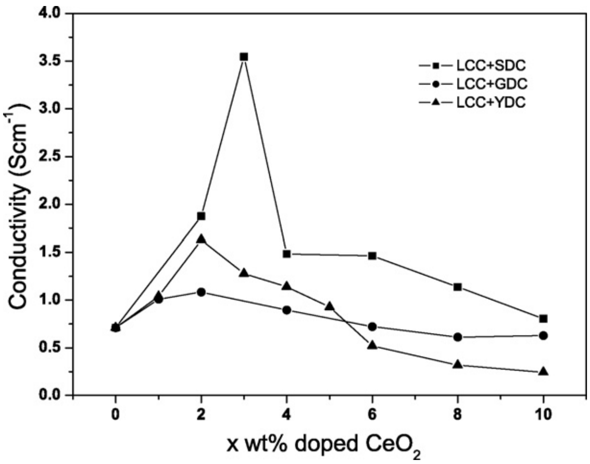


Fig. 7. Effect of RDC content on the conductivities of the samples in $H_2$ at 550 °C.

SOFC operating environments, the interconnect must exhibit excellent electrical conductivity preferably with nearly 100% electronic conduction. In an ideal situation, the ohmic loss due to the introduction of interconnect is noticeably small so that the power density of a stack does not show a profound drop as compared to that of an individual cell. Thus, reducing the ohmic resistances is an effective way to enhance the performance of low-temperature SOFCs. In our experiment, the addition of RDC enhanced the electrical conductivity of LCC, making it possible for LCC to be used as interconnect for intermediate-temperature or low-temperature SOFCs.

Due to the strong dependence of electrical conductivity on the oxygen partial pressure, the electrical conductivity of $La_{0.7}Ca_{0.3}CrO_3$ in reducing atmosphere such as hydrogen is significantly lower than that in oxidizing atmosphere such as air. Therefore, the electrical conductivities of LCC + RDC in $H_2$ were measured in our studies. Fig. 6(a) demonstrates Arrhenius plots of conductivities of the samples with different SDC contents in $H_2$. The sample of LCC + 3 wt% SDC shown the maximal electrical conductivity of 7.1 S cm$^{-1}$ at 800 °C when SDC content ranged from 1 to 10 wt%, which is nearly twice as high as that of the commonly used lanthanum chromite. At 600 and 700 °C, the electrical conductivities dropped to 1.5 and 2.5 S cm$^{-1}$, respectively. In Fig. 6(b), LCC + 1 wt% GDC showed the higher electrical conductivity of 3.8 S cm$^{-1}$ at 800 °C than the others, which is a little higher than that of the commonly used lanthanum chromite. 1.4 and 2.5 S cm$^{-1}$ were the electrical conductivities at 600 and 700 °C, respectively. Similarly, Arrhenius plots of conductivities of the samples with different YDC contents in $H_2$ in Fig. 6(c) shows that the electrical conductivity of LCC + 2 wt% YDC reached the highest of 5.9 S cm$^{-1}$ at 800 °C among the LCC + LCC samples. As such, the electrical conductivities reached the maximal values of 1.6 and 3.7 S cm$^{-1}$ at 600 and 700 °C, respectively. Therefore, the improvement of electrical conductivity in $H_2$ is not as remarkable as in air. However, the value of 1 S cm$^{-1}$ is a well-accepted minimal electrical conductivity for the application of interconnects in SOFC community [13]. Fig. 7 shows the effect of RDC content on the conductivity of the samples in pure $H_2$ at 550 °C, from which it can be concluded that LCC + 3 wt% SDC, LCC + 2 wt% GDC and LCC + 2 wt% YDC showed the maximal electrical conductivities of 3.6, 1.1 and 1.6 S cm$^{-1}$ in $H_2$, respectively. This makes it possible to operate SOFCs at temperatures about 550 °C. The significant reduction in operating temperature, therefore, will dramatically reduce the cost for both materials and fabrication. It will also provide greater system reliability, longer operational life and increased potential for mobile applications. Low-temperature SOFCs have great potential to be affordable for many applications, including residential and automotive applications.

### 3.4. *Concern about thermal expansion mismatch*

The interconnect material is exposed to both oxidizing and reducing conditions. SOFCs operate at high temperatures, and the interconnect must thus have a coefficient of thermal expansion (CTE) close to those of the other cell components to minimize thermal stresses. In Fig. 8, the thermal expansion of LCC was used as a control. The linear CTE of LCC is $11.12 \times 10^{-6}$ K$^{-1}$ in the temperature range of 30–1000 °C. With increasing RDC, the CTEs of the samples increased and reached the maximum when the RDC content is 10 wt%, suggesting a distinct effect of RDC on the sample's CTE. However, the CTEs of most samples are still close to those of other components of IT-SOFC, such as YSZ electrolyte, Sr-doped LaFeO3 cathode and Ni-SDC or Ni-YSZ anode when the RDC content ranged from 1 to 6 wt%. Therefore, it would be possible to minimize the thermal stress developed during stack start-up and shutdown.

### 3.5. *Oxygen penetration measurements*

High density is required for SOFC interconnect plates since they should act as a complete gas barrier between fuel and air. However, even if completely dense alkaline-earth-substituted lanthanum chromites are obtained, the partial reduction and oxygen vacancies at the reducing side may result in oxygen permeation. For our samples the oxygen penetration flux was examined using gas chromatography. The oxygen permeation

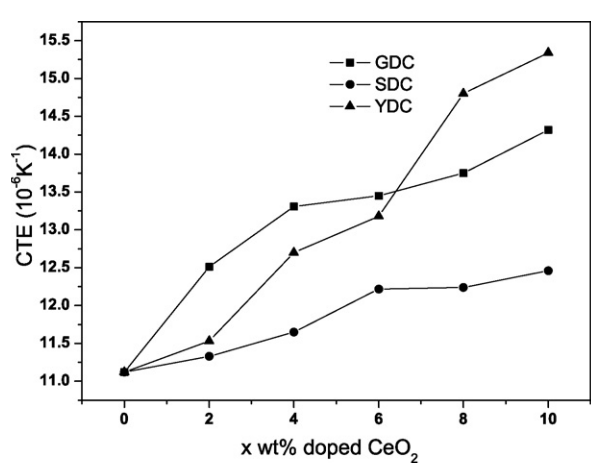


Fig. 8. Influence of RDC content on the CTE in the temperature range of 30–1000 °C in air.

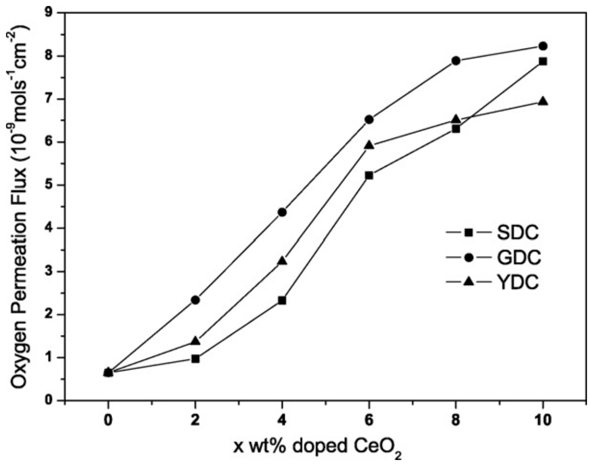


Fig. 9. Influence of RDC content in LCC + RDC on oxygen permeation flux at 800 °C.

flux values at 800 °C are shown in Fig. 9. It clearly shows that the oxygen permeation flux increased with the increase of RDC content, ranging from $6.51 \times 10^{-10}$ mol$^{-1}$ cm$^{-2}$ (of pure LCC) to the maximal value of $7.88 \times 10^{-9}$ mol$^{-1}$ cm$^{-2}$ (of LCC + 10 wt% GDC) at 800 °C. Therefore, the efficiency loss of SOFC by permeation is negligible for the general cell design using LCC + RDC as interconnect.

## 4. Conclusions

In the past two decades, many efforts have been devoted to the studies of the doped lanthanum chromites since it has been a predominant interconnect material for electrolyte-supported planar and tubular SOFCs. However, little research has been conducted on a composite of LCC and electrolyte. Here, we report LCC + RDC as the interconnect materials for SOFC. The addition of small amounts of RDC (20 mol% $ReO_{1.5}$ doped $CeO_2$, Re = Sm, Gd, Y) to LCC dramatically increased the electrical conductivity. For the best system, LCC + 5 wt% SDC, LCC + 3 wt% GDC and LCC + 3 wt% YDC, the electrical conductivities reached 687.8, 124.6 and 104.8 S cm$^{-1}$ at 800 °C in air, respectively. The electrical conductivities of the specimens, LCC + 3 wt% SDC, LCC + 1 wt% GDC and LCC + 2 wt% YDC in $H_2$ at 800 °C were 7.1, 3.8 and 5.9 S cm$^{-1}$, respectively. With the increase of RDC content, the relative density increased, indicating that RDC served as an effective sintering aid in enhancing the sinterability of the powders. The average coefficient of thermal expansion at 30–1000 °C in air increased with the increase of RDC content. The oxygen permeation measurements showed a negligible oxygen ionic conduction, indicating that it is still primarily an electronically conducting ceramic. This material system exhibited excellent electrical conductivity even at 550 °C, a very small oxygen permeation flux, a high relative density and thermal expansion that matched the other components. The addition of RDC making the electrical conductivity increase at low temperature, is an important to achieve a low ohmic polarization resistance, high power density and potentially lower operating temperature. Therefore, the LCC + RDC system could be a very promising interconnect material for lowering the operating temperature of solid oxide fuel cells.

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