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La$_{0.65}$Sr$_{0.35}$CoO$_{3-\delta}$ (LSC 6535) as a Cathode Material - A Study on Chemical Reactivity of LSC with Y$_2$Zr$_2$O$_7$ Pyrochlore Based Electrolyte for ITSOFC

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Abstract. A reduction in the operating temperature in SOFC can decrease materials degradation for long term operation. The efficiency of energy conversion and durability of performance mainly depend on the electro catalytic activity of the cathode and its thermo-chemical compatibility with the oxide ion conducting solid electrolyte. In this work, La$_{0.65}$Sr$_{0.35}$CoO$_{3-\delta}$ (LSC 6535), a mixed conducting stable perovskite oxide prepared by glycine nitrate route is systematically characterized. Circular pellets were fabricated and subjected to sintering at different temperatures ranging from 1073-1773 K, the sintering behaviour of LSC and LSC-YZ composite were investigated to obtain information on the densification, shrinkage in volume after heat treatment. The thermo-chemical compatibility of this cathode material with YZ is also brought out. Complex impedance spectroscopy was used for determining the conductivity and electrical behaviour. The component diffusion coefficient and mobility of ions were calculated from conductivity values. A brief discussion is made on its suitability for application as electro catalytic materials under ITSOFC operating conditions.

1. Introduction

Co-containing perovskite oxides such as LaCoO$_3$ are of interest for numerous applications, including SOFCs, oxygen separation membranes, catalyst laser and sensors [1-7]. This is due to excellent transport and electroanalytical properties of cobaltite, high electronic conductivity, significant oxygen ion mobility and appilicable electrochemical and catalytic activity in reactions involving oxygen. Appropriate A-site and B-Site doping of ABO$_3$ perovskite makes it possible to optimize these properties to a considerable extent. Lanthanum cobaltite has a rhombohedrally distorted perovskite structure and moderate oxygen deficiency at elevated temperatures, which increases with increasing reducing oxygen partial pressures [8-10]. The electronic conduction in LaCoO$_3$ occurs by transfer of charge carries via Co-O-Co bonds and exceeds ionic conductivity more than 1000 times [10-13]. The use of alternate electrode materials with improved performance is required for a reduction in the operating temperature of SOFC. The mixed ionic and electronic conducting cathode of the La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ systems has shown the lowest cathodic overpotential for an SOFC air electrode. Thus the system is the most promising candidate for the cathode in a reduced temperature SOFC. The crucial requirement for their applicability in ITSOFC is their compatibility inconjuction with the alternate solid electrolytes without any phase formation. The present work mainly deals with the properties and suitability of La$_{0.65}$Sr$_{0.35}$CoO$_{x-\delta}$ (LSC 6535) perovskite based cathodes for reduced temperature Solid Oxide Fuel Cells and also studies on chemical reactivity of this cathode with Y$_2$Zr$_2$O$_7$ (YZ) pyrochlore electrolyte.

2. Experimental Aspects

The desired compositions of LSC and YZ were prepared from nitrate solutions using the glycine nitrate combustion synthesis technique, described elsewhere

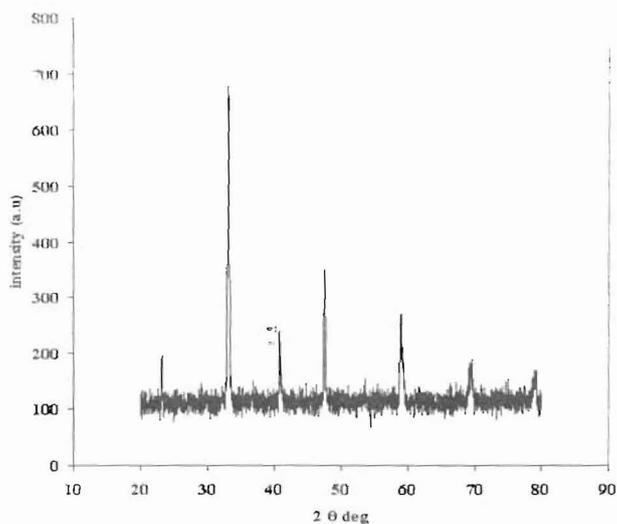*Corresponding author: rpraman@rediffmail.com (R. Pattabiraman)

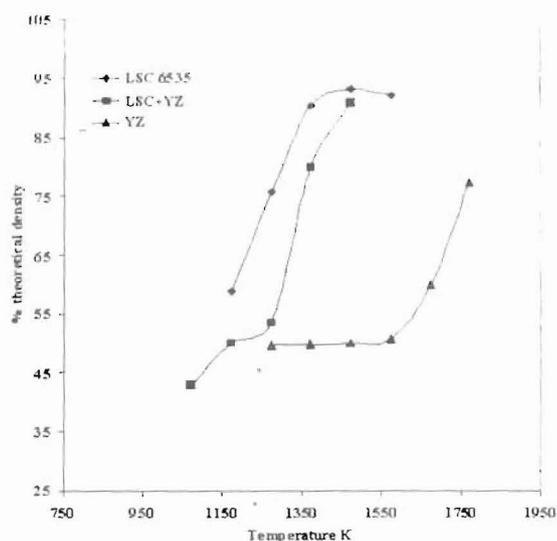Fig 1. XRD pattern of LSC 6535 cathode powders.

Fig. 3. The effect of temperature on theoretical density of LSC 6535, YZ and LSC-YZ composite.
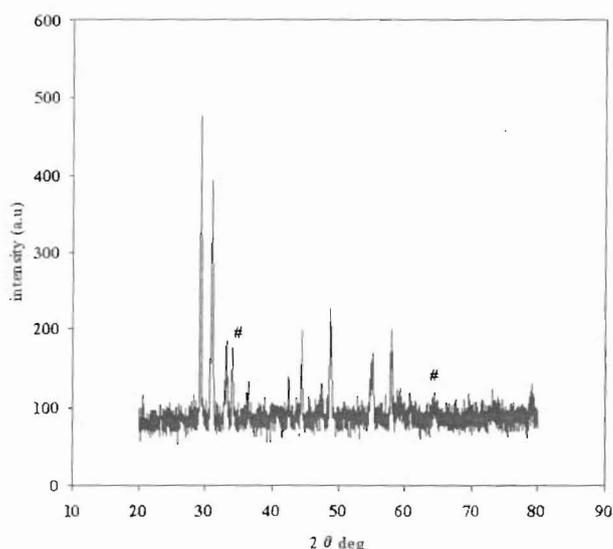

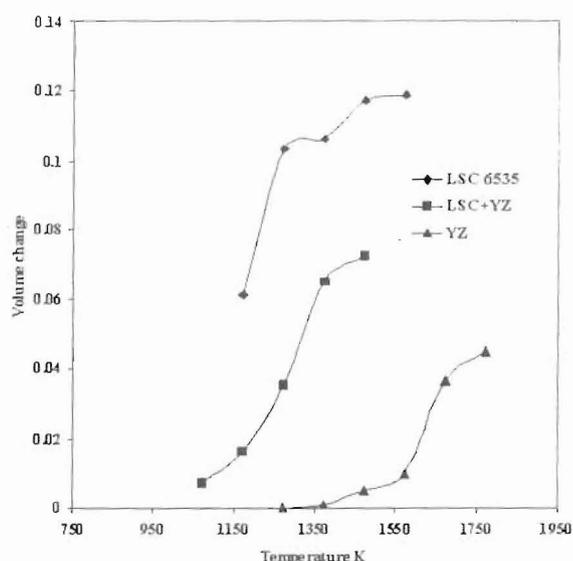Fig. 2. XRD pattern of LSC 6535-YZ composite powders.

Fig. 4. The effect of temperature on volume change of LSC 6535, YZ and LSC-YZ composite.

diameter requires higher temperature for sintering and higher particle diameter requires lower temperature for sintering.

3.2. Sintering Studies. The synthesized materials were uni-axially pressed into circular components at an axial stress of 156 Mpa by taking the powders in a die using hydraulic pressing machine for 2 minutes duration. The circular components were subjected to annealing at different temperatures ranging from 1073 to 1773 K in a computer controlled programmable furnace at a heating and cooling rate of 20 °C/min for 3 hrs. prior to

annealing and after annealing the shrinkage in volume and densification factor were calculated to assess the powder compaction and sintering behavior. The sintering behaviour of LSC was investigated in detail as a function of the sintering temperature. The percentage of theoretical density values of LSC were calculated from sintering data. The maximum percentage of theoretical density was found to be 93% at 1473 K. The effect of temperature on percentage of theoretical density is shown in Fig. 3. It shows that there is as sharp increase in the percentage of theoretical density as function of temperature from 1173
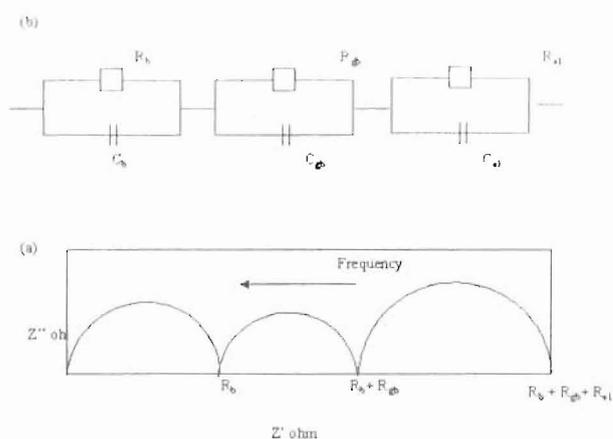
Fig. 5. An idealized equivalent circuit (b) and its corresponding impedance plot (a). C_b, R_b and C_{gb}, R_{gb} and C_d, R_d represents resistance and capacitance for bulk, grain boundary and electrode process, respectively.

Fig. 6. The effect of temperature on conductivity values of LSC 6535 cathode.

to 1473 K in LSC 6535. In the case of YZ, there is no marked difference in percentage of theoretical density at the temperature range from 1173 to 1573 K. The percentage of theoretical density values increases gradually as a function of temperature upto 1773 K. The maximum of percentage of theoretical density at 1773 K is about 77%. The percentage of theoretical density values of LSC-YZ composite powder gradually starts to increase as function of temperature from 1073 to 1273 K, then it raises sharply from 1273 to 1473 K. From Fig. 3, it is clear that the percentage of theoretical density values of YZ shifts right side of the graph to left side when LSC mixed with YZ. It is also confirmed by XRD experiment.

The volume changes in specimen of LSC, YZ and LSC-YZ powders are plotted as function of temperature, as shown in Fig. 4. The volume change increases with increasing temperature. There is no volume change even at 1273 K for YZ pyrochlore based electrolyte. While mixing LSC with YZ, the volume change starts at 1073 K. thus the volume change of LSC-YZ composite also shifts to low temperature region when compared to LSC and YZ.

3.3. *Conductivity Measurements.* The bulk conductivity of LSC, YZ and LSC-YZ composite powders were measured by a two probe ac impedance technique. The bulk conductivity has been measured in the range of temperature 773-1073 K. In general, the ac impedance of an ionic conductor measured by a two probe method contains contribution from the bulk, grain boundaries and
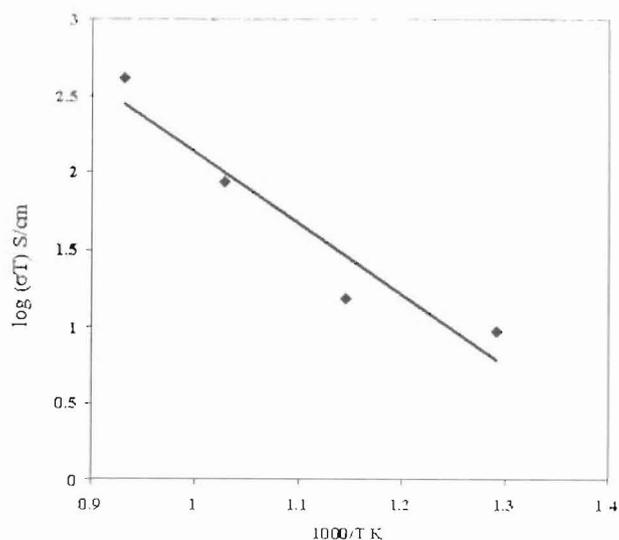
electrode/electrolyte interface, which can be reflected in a complex plane by three successive arc, as shown in Fig. 5a. The frequency increases from the right to the left across the plot. The arc at the high frequency end of spectrum represents the bulk resistivity; the arc at the middle is a consequence of the grain boundary effects; the low frequency arc is assigned to the electrode response. An idealized equivalent circuit for the ceramic oxides corresponding to the impedance plot is shown in Fig. 5b. In a practical case, however, not all these arcs can be observed, depending on the nature of the samples and testing conditions.

The effect of temperature on conductivity of LSC is shown in Fig. 6. It shows that the conductivity value increases with increasing temperature. The energy of activation for LSC 6535, YZ and LSC-YZ composite pellets (which were sintered at 1473 K, 1773 K and 1473 K) are 88.538, 16.532 and 47.483 kJ, respectively. It implies that the conductivity value of YZ increased by mixing LSC cathode powder to YZ. As a result, the higher energy of activation to be responsible for the higher conductivity.

Figure 7 shows that the conductivity value of LSC-YZ composite pellets which were sintered at different temperature ranging from 1073 to1473 K, 3 hrs is plotted as function of temperature. It gives the straight line for all temperatures. The energy of activation were calculated from the Arrhenius plot, which is plotted as function of sintering temperature, as shown in Fig. 8. It is clear that
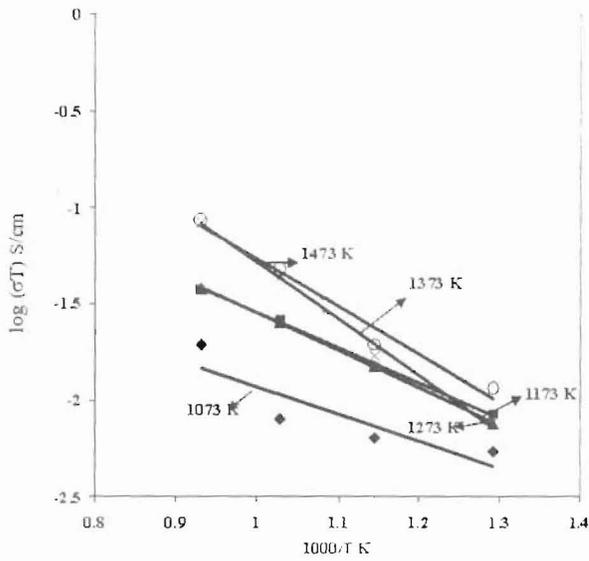
Fig. 7. The effect of temperature on conductivity values of LSC-YZ composite (which were sintered at different temperatures).
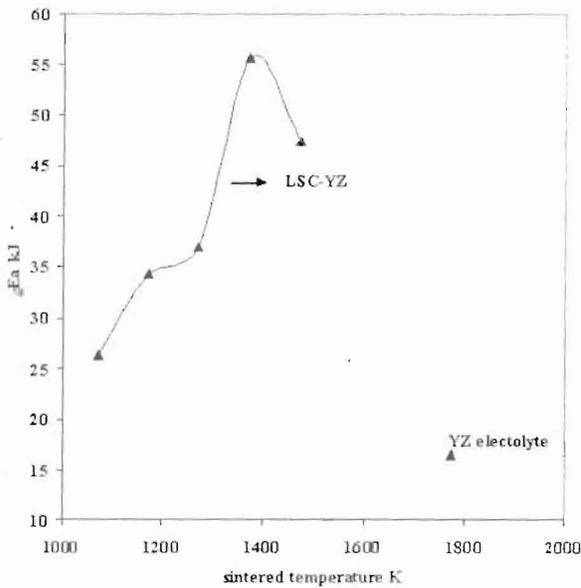

Fig. 9. The effect of temperature on component diffusion coefficient and mobility of ions of LSC 6535 cathode.

Fig. 8. The influence of sintered temperature on energy of activation of LSC-YZ composite and YZ.

Fig. 10. The effect of temperature on component diffusion coefficient and mobility of ions of LSC-YZ composite.

the energy of activation increases with increasing the sintered temperature. It means that the conductivity value of LSC-YZ composite increases with increasing sintering temperature. In other words, the mixing of LSC to YZ increases the conductivity value of LSC-YZ composite materials with respect to temperatures.

Component diffusion coefficient and Mobility of ions of those materials were calculated from conductivity
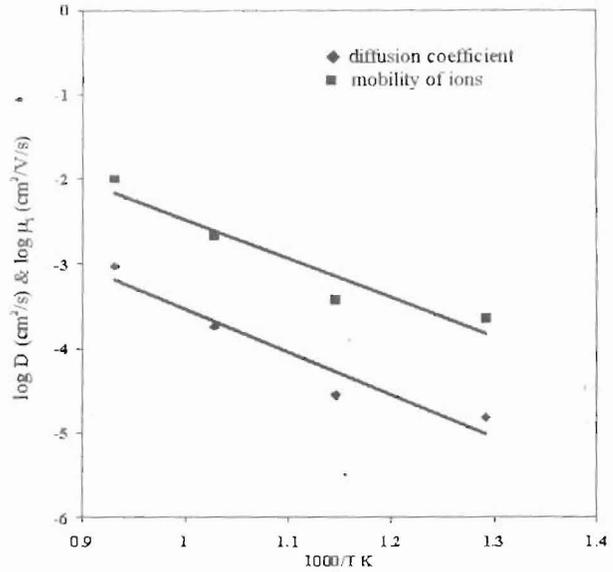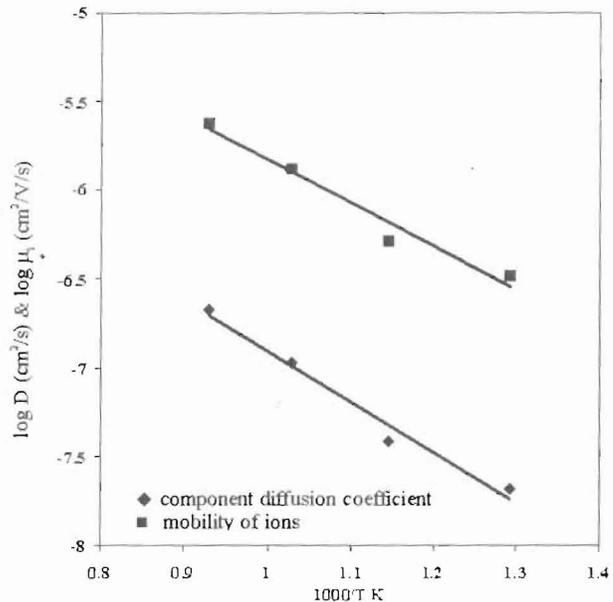
values of LSC, YZ and LSC-YZ composite. The component diffusion coefficient D_{comp} is for diffusion under some gradient which acts as driving force for migration a specified component. Migration of ions in solid electrolyte under electric field is an example of this diffusion. The equation for the mobility of ions is given as follows,

$$\mu_i = \sigma / N q.$$

Table 2. The Dcomp and μ_i of LSC and LSC-YZ composite powders.

Materials	Temperature K	D_{comp} cm^2/s	μ_i cm^2/V/s
LSC 6535 (sintered at 1473 K)	773	1.493×10^{-5}	2.242×10^{-3}
	873	2.796×10^{-5}	3.718×10^{-4}
	973	1.8041×10^{-4}	21.524×10^{-4}
	1073	9.267×10^{-4}	100.259×10^{-4}
E$_a$ kJ		96.055	88.505
LSC-YZ composite (sintered at 1473 K)	Temperature K	D_{comp} cm^2/s	μ_i cm^2/V/s
	773	2.0733×10^{-8}	3.1137×10^{-7}
	873	3.9025×10^{-5}	5.189×10^{-7}
	973	10.8135×10^{-8}	12.936×10^{-7}
	1073	21.5840×10^{-8}	23.3515×10^{-7}
E$_a$ kJ		54.99	46.143

The concept of D_{comp} is very important for the solid electrolyte, since it is intimately related to conductivity, σ with the Nernst-Einstein equation, given as,

$$\sigma = Z^2 e n D_{comp}/KT.$$

The values of D_{comp} for mobile ions in good solid electrolytes can be higher than 1×10^{-8} cm^2/s [21]. But we found that the obtained component diffusion coefficient was 2.158×10^{-7} cm^2/s. So that it can be used as solid electrolyte.

The D_{comp} and μ_i of LSC and LSC-YZ composite are given in Table 2. The effect of temperature on component diffusion coefficient and mobility of ions of LSC and LSC-YZ composite are shown in Figs. 9 & 10, respectively. It was found that the obtained graphs are similar when compared to conductivity plots of LSC and LSC-YZ. It reveals that the lower conductivity value is due to the lower D_{comp} and μ_i values. Thus, the higher mobility of ions and the component diffusion coefficient seem to be responsible for the higher conductivity values in LSC and LSC-YZ composite.

size of LSC-YZ composite is high when compared to LSC and YZ and the crystallite size of YZ in LSC-YZ composite is also increased. It implies that the LSC-YZ composite requires a low temperature for densification compared to YZ. The electrical conductivity of LSC and LSC-YZ composite were investigated. The conductivity is increased one order (compared to YZ). The thermal behaviour of LSC and LSC-YZ composite are brought out from the steady state sintering experiments to draw useful information on the inter-dependence of % shrinkage in volume and the % theoretical density. The component diffusion coefficients and mobility of ions are calculated from conductivity values. D_{comp} and μ_i are found in the range of 10^{-7} cm^2/s and 10^{-6} cm^2/V/s at 1073 K for LSC-YZ composite respectively. The values of D_{comp} for mobile ions in good electrolytes can be higher than 1×10^{-8} cm^2/s, but we found the calculated D_{comp} is higher than reported. Thus the LSC-YZ composite found to be a suitable electrolyte for ITSOFC.

4. Conclusion
The LSC 6535 perovskite based cathode powder was prepared through combustion method. The chemical reactivity of LSC and YZ powders were investigated. The lattice parameter of YZ in LSC-YZ composite is increased while mixing of LSC with YZ. The crystallite

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