Synthesis and characterization of LaCoO$_3$ based cathode and its chemical compatibility with CeO$_2$ based electrolytes for intermediate temperature solid oxide fuel cell (ITSOFC)

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The use of alternate cathode materials with improved performance and without any chemical reaction with adjoining electrolyte is required for a reduction in operating temperature of SOFC from 1273 K to about 1073 K (ITSOFC). Cobalt containing perovskite oxides such as LaCoO$_3$ tend to exhibit a higher ionic conductivity due to a greater concentration of oxygen vacancies than other perovskite oxides. 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. In this research work, fine powders of La$_{0.70}$Sr$_{0.30}$CoO$_{3-\delta}$ (LSC) cathode and Ce$_{0.90}$Gd$_{0.10}$O$_{2-\delta}$ (GDC) and Ce$_{0.80}$Sm$_{0.20}$O$_{2-\delta}$ (SDC) are synthesized by glycine nitrate combustion synthesis and systematically characterized by XRD and particle characteristics. The electrical properties of LSC cathode and GDC and SDC electrolytes are also studied. But, the crucial requirement for applicability of LSC cathode is its chemical compatibility in conjunction with the alternate solid electrolytes, GDC and SDC without any phase formation. The XRD studies showed no reaction products when the La$_{0.70}$Sr$_{0.30}$CoO$_{3-\delta}$ cathode is mixed and calcined with GDC and SDC electrolyte at 1573 K. Hence, the LSC cathode may be combined with CeO$_2$ based electrolytes in ITSOFC application.

Keywords: Solid oxide fuel cell, Perovskite oxide, Intermediate temperature

IPC Codes: C22B59/00, H01M8/00

Solid oxide fuel cells (SOFCs) have been attracting a great attention as a promising technique for electrical power generation because of potential for high-energy conversion efficiency (>70%) and low environmental pollution. In general, they must be operated at high temperature between 1173 to 1273 K because the Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) is used as the usual electrolyte material and has low ionic conductivity at operating temperatures lower than 1073 K. Such high operating temperatures of SOFC lead to some serious problems, such as, physical and chemical degradation of components. Therefore, it is desirable to develop SOFCs operating at intermediate temperatures below 1073 K. To reduce the operating temperature, two approaches are under active considerations as follows: one is development of suitable alternative to Sr doped LaMnO$_3$ (LSM) cathode and another is development of promising alternative to Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) electrolyte[1-3].

Doped lanthanum cobaltite La$_{0.70}$Sr$_{0.30}$CoO$_{3-\delta}$ is of great interest as potential cathode material for ITSOFCs[4-5]. Also, it is reported that doped ceria electrolytes such as Ce$_{0.90}$Gd$_{0.10}$O$_{2-\delta}$ and Ce$_{0.80}$Sm$_{0.20}$O$_{2-\delta}$ have shown greater oxide ion conductivities (>0.1 Scm^{-1}) in intermediate temperature range[6-7]. For using LSC ceramic as cathode in ITSOFC, it's interface stability with GDC/SDC electrolytes became a major concern. In this research work, LSC cathode and GDC/SDC electrolyte materials by glycine-nitrate combustion method in the form of fine powder have been synthesized. The physico-chemical properties of these powders are systematically evaluated. The chemical compatibility between the above cathode and ceria based electrolytes is also studied. The obtained results are discussed in order to qualify them as alternative components for ITSOFC application.
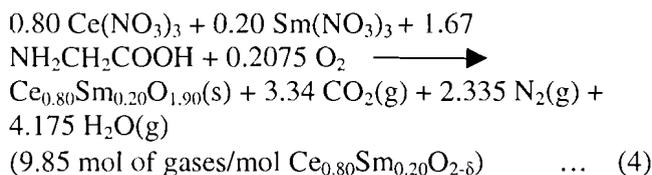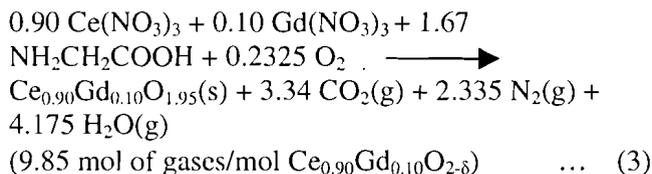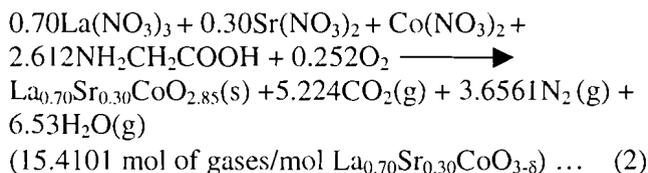
Experimental Procedure

Preparation of powders

La$_{0.70}$Sr$_{0.30}$CoO$_{3-\delta}$ cathode and Ce$_{0.90}$Gd$_{0.10}$O$_{2-\delta}$ / Ce$_{0.80}$Sm$_{0.20}$O$_{2-\delta}$ electrolyte powders were synthesized

by glycine-nitrate combustion method[8,9]. Stoichiometric amounts of corresponding metal nitrates were dissolved in distilled water along with appropriate quantity of glycine (fuel and complexant) in a quartz crucible. The resulting clear solution was introduced into a preheated muffle furnace maintained at 823 K. The mixture then froths, undergoes dehydration, ignites and burns to yield voluminous and foamy homogeneous fine ceramic powders. Thus, combustion reaction was completed with in a few seconds. When glycine is the fuel the following reaction (Eq. 1) takes place. 1 mole of glycine gives 5 moles of gases.

$$2\ C_2NH_5O_2 + 9/2\ O_2 \longrightarrow N_2(g) + 4CO_2(g) + 5H_2O(g) \quad \dots \quad (1)$$

The stoichiometric redox reaction between metal nitrates and glycine to produce substituted LaCoO₃/CeO₂ can be represented by the following theoretical equations (Eqs 2, 3 & 4):

$$0.70La(NO_3)_3 + 0.30Sr(NO_3)_2 + Co(NO_3)_2 + 2.612NH_2CH_2COOH + 0.2520_2 \longrightarrow$$
$$La_{0.70}Sr_{0.30}CoO_{2.85}(s) + 5.224CO_2(g) + 3.6561N_2(g) + 6.53H_2O(g)$$
(15.4101 mol of gases/mol $La_{0.70}Sr_{0.30}CoO_{3-\delta}$) ... (2)

$$0.90\ Ce(NO_3)_3 + 0.10\ Gd(NO_3)_3 + 1.67\ NH_2CH_2COOH + 0.2325\ O_2 \longrightarrow$$
$$Ce_{0.90}Gd_{0.10}O_{1.95}(s) + 3.34\ CO_2(g) + 2.335\ N_2(g) + 4.175\ H_2O(g)$$
(9.85 mol of gases/mol $Ce_{0.90}Gd_{0.10}O_{2-\delta}$)   ... (3)

$$0.80\ Ce(NO_3)_3 + 0.20\ Sm(NO_3)_3 + 1.67\ NH_2CH_2COOH + 0.2075\ O_2 \longrightarrow$$
$$Ce_{0.80}Sm_{0.20}O_{1.90}(s) + 3.34\ CO_2(g) + 2.335\ N_2(g) + 4.175\ H_2O(g)$$
(9.85 mol of gases/mol $Ce_{0.80}Sm_{0.20}O_{2-\delta}$)   ... (4)

Calcination of as-synthesized powders was carried out in alumina crucibles at 1073 K for 6 h in air to remove deposited carbon and unreacted organic residues and to get phase pure compounds[10].

Results and Discussion
Powder XRD studies
Sr doped LaCoO₃

The $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ cathode powder is crystallized to a single-phase perovskite (rhombohedral-hexagonal system) with no intermediate phases such

as La_2O_3, La_2CO_3 and CO_3O_4 which have been observed in other synthesis processes like acetate or nitrate processes[11]. The Fig. 1 shows the XRD pattern of the $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ powder. The unit cell parameters 'a' (= 5.4264) and 'c' (=13.2576) agree well with those reported (a = 5.4270 and c = 13.2180) in the JCPDS card No. 36-1393 (for $La_{0.60}Sr_{0.40}CoO_{3-\delta}$).

Doped Ceria

The obtained XRD patterns of both heat-treated $Ce_{0.90}Gd_{0.10}O_{2-\delta}/Ce_{0.80}Sm_{0.20}O_{2-\delta}$ powders had a cubic (f.c.) fluorite crystal structure. The observed XRD patterns of the doped ceria electrolytes are shown in Figs 2 to 3. All peaks in the XRD patterns are very sharp showing the crystalline nature of the heat-treated powders. The XRD patterns of the doped CeO₂ are matched with the data for CeO_2, which is indexed in JCPDS card No. 34-0394. No other peak corresponding to any impurity is observed in the XRD patterns of the doped ceria powders. Not much change
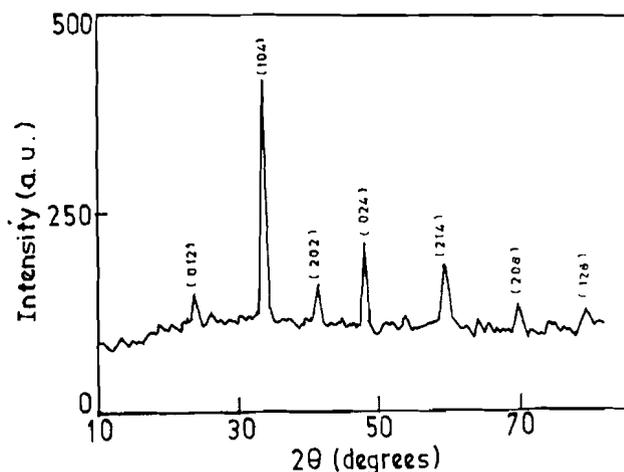

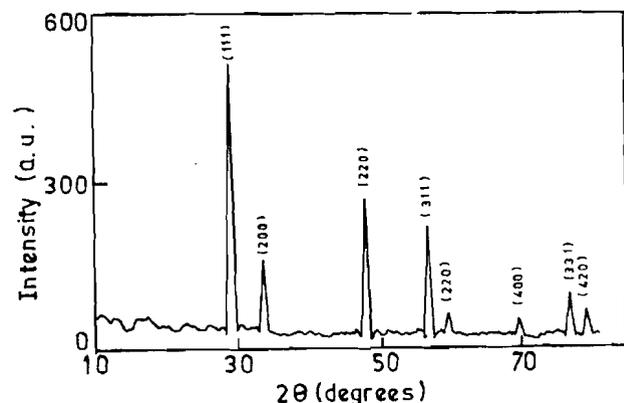Fig. 1-XRD pattern obtained on $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ powder

Fig. 2-XRD pattern obtained on $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ powder
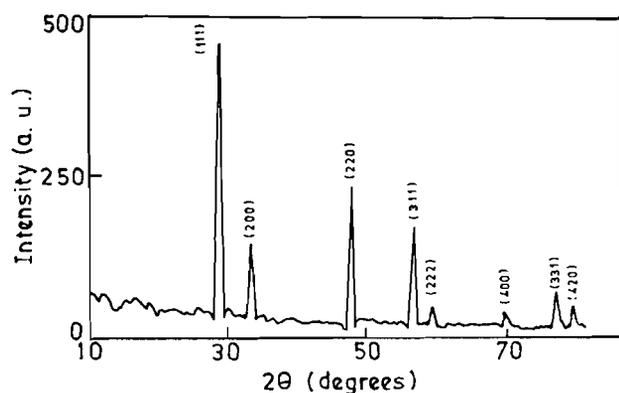
Fig. 3-XRD pattern obtained on $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ powder

in the lattice parameters (a = 5.39664 for GDC and a = 5.41839 for SDC) is observed.

Powder characteristics

The particle characteristics data obtained on $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ and $Ce_{0.90}Gd_{0.10}O_{2-\delta}/Ce_{0.80}Sm_{0.20}O_{2-\delta}$ electrolyte powders clearly indicate the fine quality of combustion-synthesized materials. The prepared cathode/electrolyte were subjected to particle size measurements using Horiba Laser Particle Size Analyzer (LA-910) with triple distilled water as medium. The obtained particulate properties are indicated in Table 1. The mean particle diameter represents the arithmetically averaged value of the frequency distribution. The BET surface area of the doped based electrolyte materials was measured using the nitrogen gas adsorption multipoint BET method assuming the cross sectional area of 16.2×10^{-20} m^2 for a nitrogen molecule using H$_2$ as a carrier gas at a temperature of 473 K with relative gas pressure range of 0.3. The bulk/tapped density[9] for these powders was also measured and reported. The increase in mean particle size of SDC is due to the formation of agglomerates after heat treatment. The particle size, density and surface area appear to depend mainly upon the number of moles of gaseous products liberated (Eqs 1, 2, 3 & 4) during combustion[8]. The escaping gases not only make the combustion residue fine but also help to dissipate the heat, thereby preventing the oxides from sintering and consequently, more porous oxides (with high surface area, lower density and particle size) are obtained.

Electrical conductivity studies

Sr doped LaCoO$_3$

The d.c. electrical conductivity for LSC cathode was measured on the sintered (at 1673 K for 5 h) rectangular specimens (Length = ~2.25 cm,

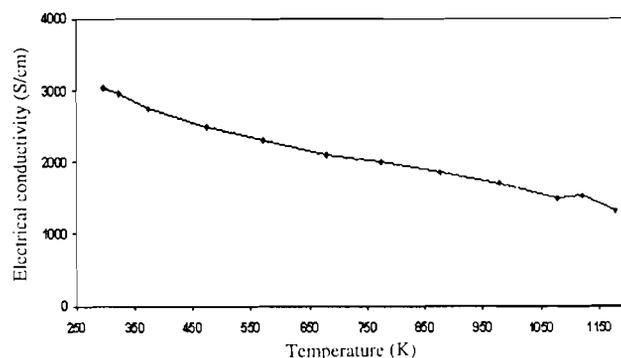Fig. 4-Electrical conductivity of $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ pellet measured in air

Table 1—Particulate properties obtained on alternative cathode / electrolyte powders

Sl. No.	Sample	Mean particle diameter (μm)	BET surface area (m^2/g)	Bulk density (g/cc)	Tap density (g/cc)
1	$La_{0.70}Sr_{0.30}CoO_{3-\delta}$	9.25	2.573	0.200	0.417
2	$Ce_{0.90}Gd_{0.10}O_{2-\delta}$ (GDC)	9.794	2.213	0.2160	0.4909
3	$Ce_{0.80}Sm_{0.20}O_{2-\delta}$ (SDC)	61.212	2.432	0.1820	0.4136

Breadth = ~0.5 cm and Thickness = ~0.5 cm) using a four-probe method between 297 – 1178 K. Fig. 4 shows the electrical conductivity of $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ measured in air as a function of temperature. From the Fig. 4, it is evident that the electrical conductivity of LSC decreases with temperature upto 1178 K (1324 Scm^{-1}). LSC has shown electrical conductivity of 3038 Scm^{-1} at 297 K (initial temperature). A similar behaviour of $La_{1-x}Sr_xCoO_{3-\delta}$ (where $\times \geq 0.3$) is also reported in literature[12]. This decrease in conductivity with increasing temperature suggests that the conductivity for LSC specimen is metallic at all temperatures. The electrical conductivity value ($\sigma \approx 10^2$ Scm^{-1}) at the operating temperature of SOFC is acceptable for the cathode[13]. From these results, it is drawn that LSC exhibits high electrical conductivity suitable for cathode in SOFC for intermediate temperature operation.

Doped Ceria

The electrical properties of sintered (at 1573 K for 3 h) circular GDC/SDC (diameter = 1 cm) components were studied by A.C. impedance spectroscopy in air. The A.C. impedance spectra of

GDC electrolyte specimen obtained at 773, 873 and 973 K is indicated in Figs 5(a), (b) and (c). From the plots, it is noted that as the temperature is increased, the time constants of the relaxations resulting from the individual polarizations are reduced and the arcs are shifted to higher frequencies as reported earlier[14]. The A.C. impedance spectra of SDC electrolyte specimen obtained at 773, 873 and 973 K is indicated in Figs 6(a), (b) and (c). From the impedance plots, the individual resistance R_i of the specimens can be converted to conductivity, σ_i using the Eq. (5)

$$\sigma_i = l \, / \, SR_i \qquad \qquad \text{... (5)}$$

where l is the sample thickness and S the electrode area of the sample surface. The calculated conductivity values are indicated in Table 2. From the Table 2, it is found that the conductivities of both the specimens (GDC/SDC) are in line with the reported data[14].

Chemical compatibility studies - Reaction experiments

In this research work, $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ is examined as alternative cathode material for ITSOFC application. The crucial requirement for its applicability is its chemical compatibility in conjunction with the alternate solid electrolytes, $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ (GDC) and $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ (SDC) without any new phase formation. Therefore, the

Table 2—Electrical conductivity data obtained on doped ceria electrolyte specimens

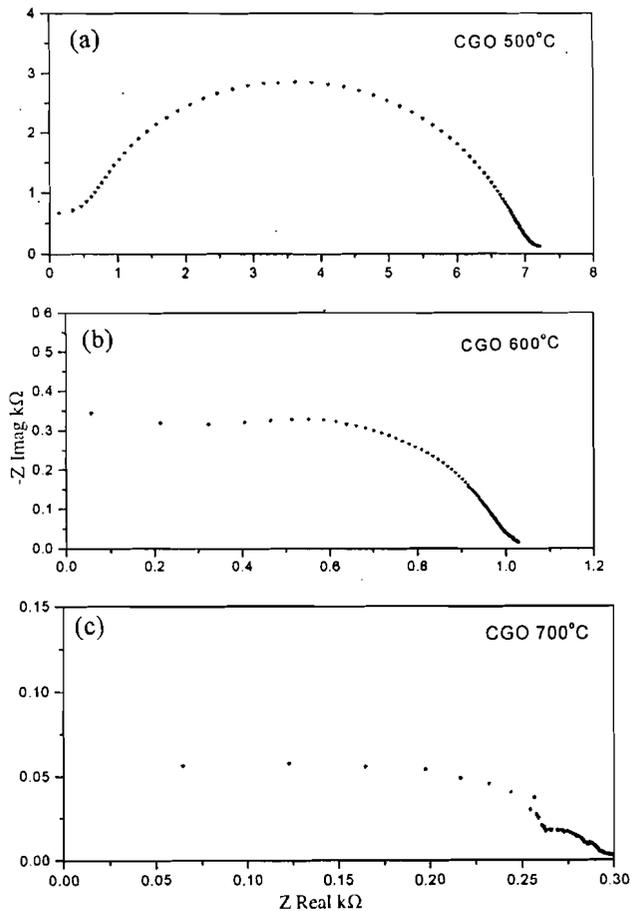| Sample	Temperature (K)	Electrical conductivity (S/cm)
$Ce_{0.90}Gd_{0.10}O_{2-\delta}$ (GDC)	773	0.000051015
	873	0.00035711
	973	0.001190
$Ce_{0.80}Sm_{0.20}O_{2-\delta}$ (SDC)	773	0.00006422
	873	0.0004816
	973	0.001605

Fig. 5-(a), (b) & (c) The A.C. impedance spectra of $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ electrolyte specimen obtained at 773, 873 and 973 K
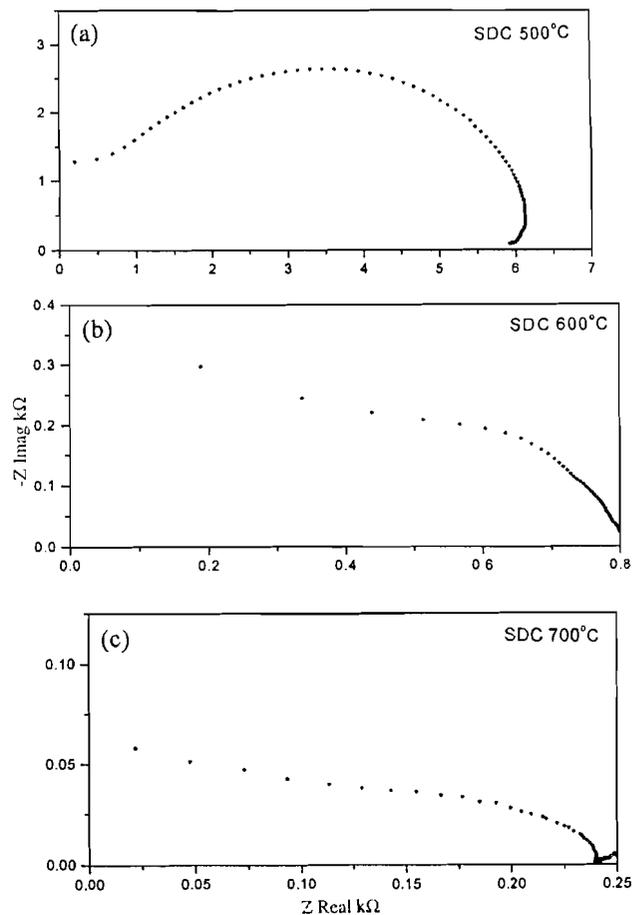

Fig. 6-(a), (b) & (c) The A.C. impedance spectra of $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ electrolyte specimen obtained at 773, 873 and 973 K

chemical compatibility between the above cathode and GDC and SDC based solid electrolytes is investigated.

The $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ cathode and $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ (GDC) and $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ (SDC) electrolyte powders were mixed individually in a 1:1 weight ratio, together in a pestle and mortar. Each powder (cathode + electrolyte) mixture was ground well, placed in a 20 mm diameter die, compacted with an uniaxial hydraulic pressing machine at a load of 156 Mpa. Each pellet was then annealed in air at 1573 K for 3 h. The temperature of 1573 K was selected for the chemical compatibility tests, because, although the operating temperature of the cell is substantially less, the steps involved in the fabrication of ceramic cathode/ electrolyte/ anode structures usually require processing up to at least 1473 K[15-16]. The calcined pellets were crushed into powder and the reaction products were identified by X-ray diffraction (XRD). Prior to XRD, the microstructures of annealed samples were investigated by scanning electron microscopy.

XRD studies

LSC + GDC

The comparison of X-ray diffraction data of the individual powder (LSC and GDC) and mixed powder (LSC + GDC) is shown in Table 3. It is reported that $La_{0.80}Sr_{0.20}CoO_{3-\delta}$ showed no reaction with GDC, whereas, it reacted with YSZ when annealed at 1473 K[17]. From the Table 3, it is noted that $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ when calcined with $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ at 1573 K for 3 h did not form new reaction products. Also, it is seen that the peaks observed at $2\theta = 33.0°$, $47.0°$, $58.7°$, $68.8°$ and $78.2°$ in the XRD pattern of LSC + GDC are assigned to both LSC and GDC

phases, since the d values of both the samples are similar. As there is no new reaction product detected, it is drawn that the chemical compatibility between Sr-doped $LaCoO_3$ and GDC solid electrolyte is good.

LSC + SDC

The comparison of X-ray diffraction data of the individual powder (LSC and SDC) and mixed powder (LSC + SDC) is shown in Table 4. It is reported that the YSZ electrolyte coated with SDC interlayer was used to protect the solid-state reaction with LSC cathode in SOFC[18]. From the table, it is noted that the $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ calcined with $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ at 1573 K for 3 h showed no reaction products. Also, it is seen that the peaks observed at $2\theta = 32.8°$, $46.9°$ and $59.0°$ are indexed to both LSC and SDC phases, since the d values of both the samples are same. As no reaction products could be detected, it is drawn that there is chemical compatibility between $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ cathode and $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ electrolyte.

SEM studies

LSC + GDC

Figure 7 shows the microstructure of a $La_{0.70}Sr_{0.30}CoO_{3-\delta}+Ce_{0.90}Gd_{0.10}O_{2-\delta}$ pellet after sintering at 1573 K for 3 h. It is seen that a well defined boundary between the two phases (LSC/GDC) exists. The GDC grains are found in between LSC grains in some places. The grain size of LSC is 50 μm. The grain size of GDC is 25 μm. The surface of the pellet is smooth.

LSC + SDC

Figure 8 shows the microstructure of a $La_{0.70}Sr_{0.30}CoO_{3-\delta}+Ce_{0.80}Sm_{0.20}O_{2-\delta}$ pellet after sintering at 1573 K for 3 h. It is noted that the surface is completely covered by LSC grains. LSC grains are

Table 3—Comparison of XRD data of individual powder with the XRD data of $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ + $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ powder mixture after annealing at 1573 K for 3 h

XRD data for LSC + GDC powder mixture				XRD data for LSC		XRD data for GDC	
Peak No.	2θ values	d values	Peak assigned for	2θ values	d values	2θ values	d values
1	28.200	3.162	GDC	--	--	28.800	3.097
2	33.000	2.712	LSC/GDC	33.400	2.681	33.300	2.688
3	47.000	1.932	LSC/GDC	47.800	1.901	47.700	1.905
4	55.800	1.646	GDC	--	--	56.600	1.625
5	58.700	1.572	LSC/GDC	59.200	1.559	59.300	1.557
6	68.800	1.363	LSC/GDC	69.400	1.353	69.600	1.350
7	76.100	1.250	GDC	--	--	76.900	1.239
8	78.200	1.221	LSC/GDC	79.500	1.205	79.300	1.207

Table 4—Comparison of XRD data of individual powder with the XRD data of $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ + $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ powder mixture after annealing at 1573 K for 3 h

| | XRD data for LSC + SDC powder mixture | | | XRD data for LSC | | XRD data for SDC 8020 | |
Peak No.	2θ values	d values	Peak assigned for	2θ values	d values	2θ values	d values
1	28.100	3.173	SDC	--	--	28.600	3.119
2	32.800	2.728	LSC / SDC	33.400	2.681	33.100	2.704
3	46.900	1.936	LSC / SDC	47.800	1.901	47.500	1.913
4	55.700	1.649	SDC	--	--	56.300	1.633
5	59.000	1.564	LSC / SDC	59.200	1.559	59.000	1.564
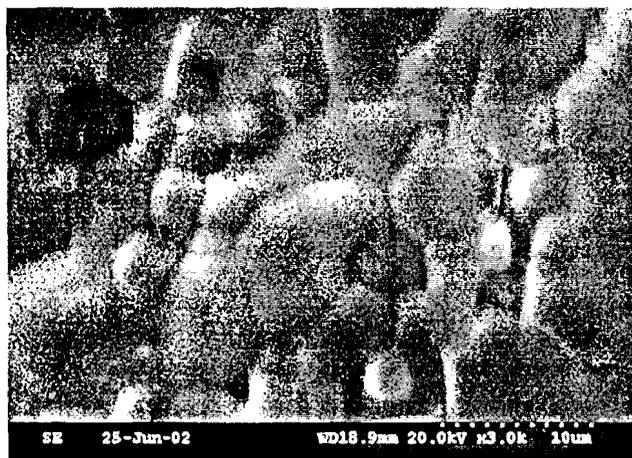
Fig. 7-SEM photograph obtained on $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ + $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ pellet after sintering at 1573 K for 3 h

Fig. 8-SEM photograph obtained on $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ + $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ pellet after sintering at 1573 K for 3 h

larger (100 μm). The SDC grains are seen in between the LSC grains. The grain size of SDC is smaller, (50 μm). The pore size is 10 μm. Also, it is seen that there exists well defined boundary between LSC and SDC grains. No new grains are observed.

Conclusion

The glycine nitrate combustion synthesis is a simple method to prepare ultrafine particles of cathode/electrolytes for SOFC application. The $La_{0.70}Sr_{0.30}CoO_{3-\delta}$ cathode showed no reaction products when mixed and calcined with $Ce_{0.90}Gd_{0.10}O_{2-\delta}$ and $Ce_{0.80}Sm_{0.20}O_{2-\delta}$ electrolyte. Hence, this LSC cathode is useful with doped ceria electrolytes in ITSOFC.

Acknowledgement

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