Wet chemical synthesis and characterization of strontium-doped LaFeO$_3$ cathodes for an intermediate temperature solid oxide fuel cell application

A. Samson Nesaraj$^{a,*}$, S. Dheenadayalan$^{b}$, I. Arul Raj$^b$ and R. Pattabiraman$^b$

$^a$Department of Chemistry, Karunya University, Coimbatore, 641 114, India
$^b$Central Electrochemical Research Institute, Karaikudi, 630 006, India

Recently partially strontium substituted lanthanum ferrites, La$_{1-x}$Sr$_x$FeO$_3$ have been proposed as suitable alternative cathodes for intermediate temperature solid oxide fuel cells (ITSOFCs). In this study, La deficient - La$_{0.65}$Sr$_{0.30}$FeO$_3$ (LSF) perovskite oxide material was synthesized by a simple wet chemical route and systematically characterized by XRD, TGA-DTA, FTIR, particle size analysis and SEM. The sintering properties of the LSF circular components were studied and are reported. The electrical properties of the LSF specimens were studied by a four probe DC technique in air. From the electrical characterization studies, it was found that the conductivity values of the LSF specimens increased with an increase in temperature and reached a maximum value of 153.41 Scm$^{-1}$ at 769 K. Hence, this new type of material may be considered as a suitable alternative candidate cathode material for ITSOFC application.

Key words: Alternate cathode material, Synthesis, Characterization, ITSOFC.

Introduction

The global experiences gained in SOFC development have warranted a change from state-of-the-art cathode materials and also to look for operating them in the intermediate temperature range (973 to 1073 K) and termed as intermediate temperature solid oxide fuel cells (ITSOFC). However, the realization of a useful cell is dependent on whether materials problems arising from a high operating temperature can be solved. Manganese-based perovskite oxides such as La$_{1-x}$Sr$_x$MnO$_3$ (LSM) have been widely used as cathodes due to their stability at high temperatures and thermal expansion compatibility with yttria stabilized zirconia (YSZ). These manganite-based perovskites have a relatively good stability at high temperature; however during long annealing times, pyrochlores(La$_2$Zr$_2$O$_7$) are reported to form at the boundary between LSM and YSZ [1-3]. Better electrode materials that are less reactive with YSZ are required. Moreover, to reduce the operating temperature of the SOFCs, a search for new cathode materials is important. In our search for an alternate cathode material, we have investigated the properties of La$_{1-x}$Sr$_x$FeO$_3$ (LSF) in this study. Partially strontium substituted lanthanum ferrites, La$_{1-x}$Sr$_x$FeO$_3$, are known for their good electrical properties and electrocatalytic activities which are useful for application as a cathode material in a SOFC. Partially substituted LaFeO$_3$ is reported to have a high mixed conductivity and is hence a good candidate for a SOFC cathode. The capability for oxygen conduction has been attributed to a vacancy transport mechanism with reference to the data for La$_{1-x}$Sr$_x$FeO$_3$. On the other hand, partially Sr substituted LaFeO$_3$ has a relatively higher melting point, a lower thermal expansion coefficient and superior phase stability as compared to other alternative cathode materials[4]. It has been reported that unsubstituted LaFeO$_3$ contains high-spin Fe$^{3+}$ : t$_{2g}^3$e$_{g}^2$ localized electron configurations; it is an antiferromagnetic insulator with a Neel temperature $T_N = 750$ K. In the La$_{1-x}$Sr$_x$FeO$_3$ system, a thermally-activated hopping of small polarons between Fe ions appears to describe the transport properties. Also it has been found by soft X-ray absorption spectroscopy, that the initial substitution of Sr$^{2+}$ for La$^{3+}$ in La$_{1-x}$Sr$_x$FeO$_3$ oxidizes primarily the oxygen rather than the iron atoms of the FeO$_2$ array; the holes occupy molecular antibonding states of an FeO$_2$ complex in which the dominant component of the ground state is 3d$^1$L, where L denotes a ligand hole. However, as the Sr$^{2+}$-ion concentration increases, the spectral weight shifts to an increasing Fe-3d component in the hole ground state. The end member SrFeO$_3$ retains a high-spin configuration: the t$_{2g}$ manifold remains localized, but the single electron per Fe$^{3+}$ occupies a narrow electron band of d-orbital parentage having a large O-2p component [5].

Very little information is available regarding their chemical compatibility with solid electrolytes such as YSZ. A perovskite with 30 mol.% Sr on A-site La$_{0.70}$Sr$_{0.30}$FeO$_{3}$ with 8 mol.% YSZ at 1373 K formed lanthanum zirconate and a strontium zirconate phase [6-7]. Also, it has been found that La$_{0.80}$Sr$_{0.20}$FeO$_{3}$...
showed no reaction with YSZ [8]. Further, it is reported that La-deficient cathode materials show normally enhanced chemical inertsness in a reaction with YSZ, as has been demonstrated by systematic reactivity investigations on the La(Sr)MnO$_3$ (LSM) series [9]. In this study, the parent LaFeO$_3$ and partially Sr (30 mol.%) substituted La deficient - La$_{0.65}$Sr$_{0.30}$FeO$_{3-δ}$ perovskite oxide materials have been synthesized and studied. We propose La$_{0.65}$Sr$_{0.30}$FeO$_{3-δ}$ as a new cathode material for a SOFC at reduced temperatures with thin YSZ / ceria based electrolytes.

**Experimental**

**Combustion synthesis**

La$_{0.65}$Sr$_{0.30}$FeO$_{3-δ}$ was prepared by the combustion synthesis process using glycine as a fuel. The chemicals used in the preparative method were: La(NO$_3$)$_3$ (99.99%; CDH, India), Sr(NO$_3$)$_2$ (99.99%; CDH, India), Fe(NO$_3$)$_3$ (99.99%; CDH, India) and NH$_2$CH$_2$COOH (99.99%, CDH, India). The combustion synthesis process involves the combustion of a saturated aqueous solution containing stoichiometric quantities of the corresponding nitrates (oxidizers) and glycine (NH$_2$CH$_2$COOH) fuel. The appropriate quantities of the precursor salts (normally nitrates) were weighed accurately (Table 1), taken in a quartz crucible and dissolved in triple distilled water. The calculated amount of glycine (fuel & complexant) was added to the above solution with continuous stirring and homogenized well. The oxidizer: fuel ratio was calculated based on oxidizing (O) and fuel (F) valencies of the reactants keeping O/F = 1 as reported [10-11].

The aqueous redox solution containing metal nitrates and glycine when introduced into a muffle furnace preheated to 823 K, boils, froths, ignites and catches fire (temperature 1373 ± 100 K). At this higher temperature the metal nitrates decompose to metal oxides and oxides of nitrogen and hence act as an oxidizer for further combustion, which leads to a voluminous, foamy combustion residue in less than 5 minutes. The flame persisted for about 1 minute. The foam was then lightly ground in a silica basin with a porcelain pestle to obtain fine powders. The procedure is explained in the schematic (Fig. 1). When glycine is the fuel the following reaction takes place. 1 mole of glycine gives 5 moles of gases:

\[
2 \text{C}_2\text{H}_4\text{O}_2 + 9/2\text{O}_2 \rightarrow \text{N}_2 + 4 \text{CO}_2 + 5\text{H}_2\text{O} \quad (1)
\]

![Flow chart to prepare Ln$_{0.65}$Sr$_{0.30}$FeO$_{3-δ}$ cathode powder prepared by combustion synthesis.](image)

**Table 1.** Amount of precursor materials taken for combustion synthesis of La$_{0.65}$Sr$_{0.30}$FeO$_{3-δ}$

<table>
<thead>
<tr>
<th>Lat(NO$_3$)$_3$, Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$, Glycine</th>
<th>Yield</th>
<th>Wt. (g) after heat treatment</th>
<th>% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g)</td>
<td>(g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.07</td>
<td>3.17</td>
<td>20.2</td>
<td>40.00</td>
</tr>
<tr>
<td>11.91</td>
<td>10.85</td>
<td>8.90</td>
<td></td>
</tr>
</tbody>
</table>

The mechanism of the combustion reaction is quite complex. The parameters which influence the reaction include type of fuel, fuel-to-oxidizer ratio, use of excess oxidizer, ignition temperature, and water content of the precursor mixture. In general, a good fuel should react nonviolently, produce nontoxic gases, and act as a complexant for metal cations. Complexation increases the solubility of metal cations, thereby preventing preferential crystallization as the water in the precursor solution evaporates. However, the redox mixtures containing metal nitrates and glycine fuel undergo a smooth combustion reaction to yield the corresponding partially substituted perovskite oxides. The formation of La$_{0.65}$Sr$_{0.30}$FeO$_{3-δ}$ from combustion reaction can be represented by the following theoretical equation:

\[
0.65\text{La(NO}_3)_3 + 0.30\text{Sr(NO}_3)_2 + \text{Fe(NO}_3)_3 + 3.0885\text{NH}_2\text{CH}_2\text{COOH} \rightarrow \\
\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{2.775} + 6.177\text{CO}_2 + 4.3177\text{N}_2 + 7.7212\text{H}_2\text{O} \\
(18.216 mol of gases/mol La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-δ}
\]

Calcination of the as-synthesized samples was carried out in clean alumina crucibles at 1073 K for 6 h in air to remove the deposited carbon and the unreacted organic residues to get phase-pure compounds [12]. Calcination of the as-synthesized powder implies a very significant weight loss which is given in Table 1.

**Physical, thermal and electrical characterization**

The heat treated powder was characterized by a JEOL-8030 X-ray diffractometer with a 20 scan mode at an operating rate of 40 kV, 20 mA; the characteristic X-radiation was CuK$_α$ (Ni filter) possessing a wavelength, $λ = 1.5418$ Å. The lattice parameters were...
Wet chemical synthesis and characterization of strontium-doped \( \text{LaFeO}_3 \) cathodes for an intermediate temperature solid oxide... 

Calculated by a least square fitting method using DOS computer programming. The theoretical density of the powders were calculated from the obtained XRD data. The crystallite sizes of the powder were calculated by Scherrer’s formula. The thermogravimetry and differential thermal analysis of the powder was carried out in a STA 1500 simultaneous thermal analysis system. A Perkin-Elmer ‘Paragon 500’ FT-IR spectrometer was employed to record the IR spectra of the cathode powder in the range of 4000-400 cm\(^{-1}\). The particle size of the powder was measured using a Horiba laser scattering particle size analyzer (LA-910) using triple distilled water as the medium. The BET surface area of the powder was measured using a Quantasorb BET surface area analyser. Microstructures of sintered components were studied using a S-3000 H, Hitachi scanning electron microscope at an acceleration voltage of 20 kV.

The sintering behavior of the cathode components was studied in a Heraeus programmable rapid heating furnace (Model D6450 Hanu Type K-1710) between the temperatures of 1073 and 1673 K. The DC electrical conductivity was measured as a function of temperature on sintered rectangular specimens (length = \( \sim 2.25 \) cm, breadth = \( \sim 0.5 \) cm and thickness = \( \sim 0.5 \) cm) using a four-probe method. Silver wires (0.2 mm thick) were used as current and potential leads and the measurements were carried out in the temperature range 298-1173 K in air. Current and voltage were measured using calibrated multimeters. The temperature near the sample was measured using a calibrated CrAl thermocouple which was kept very close (0.5 mm) to the sample and the rate of heating was controlled by a temperature programmer. Computer software was used to control all the main instrumental functions for data acquisition and manipulation.

**XRD measurements**

X-ray powder diffraction of the heat treated \( \text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_3\delta \) is shown in Fig. 2 (a). In the pattern no other secondary phases were found. It has been reported that the structure of \( \text{LaFeO}_3 \) is orthorhombic at room temperature [13]. On the other hand, it has been found that partially substituting Sr for La will not change the structure of the parent perovskite, but the lattice parameters will change [5]. The XRD pattern of the \( \text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_3\delta \) is found to be in the orthorhombic cell geometry having four formula units per unit cell as indicated in the literature [5]. The XRD data obtained on \( \text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_3\delta \) is reported in Table 2. The ‘d’ values are close with the reported JCPDS data. The other parameters such as unit cell volume, theoretical density and crystallite size were also calculated for the oxide material. The data is given in Table 2.

**TGA/DTA measurements**

The prepared powder were subjected to TGA/DTA measurements at a heating rate of 10 K/minute in air from room temperature to 1173 K. These experiments aim to obtain information on the thermo-chemical properties of the synthesized material when it is introduced in air in an actual solid oxide fuel cell working condition. Fig. 2 (b) shows the TGA/DTA...
patterns obtained on the $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$ powder. In the TGA pattern, a gain of 2.5 wt.% at 373-383 K and a loss of 0.7 wt.% at 403-453 K were observed. From 453-873 K, a slight weight loss and gain were observed. On further heat treatment, an abrupt weight loss (2 wt.%) at 873 K followed by a continued loss until 1173 K. Generally, the TGA pattern revealed that the $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$ sample undergoes a stepwise weight gain/loss due to a stepwise absorption/desorption of oxygen from air. The loss of 0.8 wt.% observed at 1173 K means that the sample loses lattice oxygen upon heating from its structure, so that the oxygen stoichiometry $(3-\delta)$ decreased with an increase in the temperature. In the DTA curve, it is seen that there no distinct peaks are observed. But, the DTA curve showed a broad exothermic peak at around 593 K corresponding to a stepwise weight loss/weight gain (0.1-0.5 wt.%) from 453-873 K and this is attributed to a loss of oxygen atoms from the structure, resulting in the formation of oxygen vacancies. From the above TGA/DTA patterns of $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$, it is inferred that it may lose/absorb oxygen from the air when it is exposed to air up to a temperature of 873 K in an actual solid oxide fuel cell operating condition and finally at 1073-1173 K, it may lose oxygen atoms continuously from its structure which will lead to an increase in oxygen vacancies [14].

**FTIR measurements**

Fig. 2(c) shows the FTIR spectra obtained on calcined $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$ cathode powder. A strong peak appeared at 576.61 cm$^{-1}$ for $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$, accounted for by the asymmetrical stretching mode of the FeO$_6$ octahedra in the Fe based perovskite [15]. Also, the strong bands observed in-between 500-600 cm$^{-1}$ in the sample indicate the presence of metal-oxygen bonds in their structure [16]. The weak broad bands observed at 3400 in $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$ is attributed to...
to the presence of moisture in the sample [17].

**Particle characteristics**

The particle size distribution curve of the La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ powder is shown in Fig. 2(d). In the figure, the frequency percentage on the left-hand side of the plot corresponds to the average agglomerated size of the powders indicated by the line. The % on the right hand side of the plot corresponds to the particle distribution (histogram) indicated by the bars. From the particle characteristics data, the particle size of the powder is present in the range of 1.15 to 44.94 μm. Further, 44.04% of particles lie below 10 μm and 55.96% of particles are in between 10 to 45 μm in diameter. The mean particle diameter is found to be 12.55 μm. The BET surface area of the powder is found to be 2.382 μm. From this, it is drawn that combustion method can be used effectively to prepare micro / nano sized materials.

**Sintering studies**

The sintering studies in La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ pellet (dimension is 2 cm in diameter and 2 mm thickness) were carried out from 1073 to 1573 K. It can be noted that the initial green density for the specimen is found to be 3 g/cc. The sample has not shown any variation in density after sintering at 1073 K for 3 h. From 1173 K, the sintering effect started for the La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ sample and reached a maximum density of 4.4 g/cc at 1473 K. The % densification also gradually increased from 1173 K and reached a maximum value of 43.31% at 1473 K. Also, it was understood that the densification of the sample should be carried out slowly to beyond 1473 K to get a perfectly sintered specimen for further studies. The sintering curve obtained on La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ pellet is shown in Fig. 3 (a). The reduction in % densification beyond 1473 K is due to the formation of inhomogeneous solid particulates on the surface of the sample.

**SEM studies**

Fig. 3 (b) shows the microstructure of a La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ pellet sintered at 1473 K for 3 h. The La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ compact has shown a microstructure with small pores in the body after sintering at 1473 K. From the micrograph, it is noted that the surface of the pellet is rough. The grain sizes are found to be around 10 μm in diameter. From the microstructural studies, it was understood that the La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ cathode specimen may be sintered at a temperature lower than 1473 K to get a suitable porous specimen for application in an ITSOFC.

**Electrical conductivity measurements**

The electrical conductivity of a La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ cathode was measured by four probe d.c. technique after sintering the material at 1673 K for 5 h. Fig. 3 (c) shows the electrical conductivity of a La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ cathode with respect to temperature in air. From Fig. 3, it is evident that the electronic conductivity of La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ cathode at 297 K is found to be 2.07 Scm$^{-1}$. It can also be seen that the conductivity values of La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ increased with an increase in the temperature and reached a maximum value of 153.41 Scm$^{-1}$ at 769 K. Afterwards, from a temperature of 866 K, the conductivity of La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ decreased and showed a value of 116.44 Scm$^{-1}$ at 1169 K. It has been reported that the electrical conductivity in partially Sr substituted LaFeO$_3$ is generally believed to occur by the hopping of P-type small polarons [18] associated with the tetravalent state of iron cations. Fig. 3(d) shows an Arrhenius plot for the conductivity of La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ cathode in air. From the Fig. 3 (d), it is evident that at a low temperature, the plots are nearly linear, with the conductivity increasing with an increase in the temperature. This behavior is consistent with small polaron conduction (i.e., localized electronic carriers having a thermally-activated mobility). If the carrier concentration is constant, the Arrhenius plots of log $\sigma$ Vs 1000/T should be linear, as the small polaron mechanism follows the relation described in the equation below:

$$\sigma_T = C \exp \left(-\frac{E_A}{K_BT}\right)$$

(3)

At high temperatures, the plots show a significant negative deviation from linearity, due to a substantial decrease in conductivity with increasing temperature. The activation energy for the LSF specimen was calculated to be 0.1568 eV. From Fig. 3, it is evident that the concentration of charge carriers is not constant at high temperatures. When a divalent acceptor (e.g. Sr) is substituted for a trivalent ‘La’, electroneutrality requires that the effective negative charge of the ‘Sr’ cations be compensated by an increase in valence of some of the B-site cations (electronic compensation) and/or the formation of oxygen vacancies (ionic compensation):

$$[\text{Sr}^+\text{La}^3+] : [\text{B}^{4+}] + 2[\text{V}^{5+}]$$

(4)

In the above Kroger-Vink notation the brackets refer to the concentration of enclosed species expressed as a mole fraction “” represents unit negative charge with respect to the host lattice. “” represents unit positive charge with respect to the lattice and Vo refers to oxygen vacancies. Thus electronic conduction results in an increase in the average valence of the transition metal cations, while ionic compensation reduces the oxygen stoichiometry. At low temperatures, the charge compensation for La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ is primarily electronic with a substantial fraction of B-site cations being converted from the trivalent to the tetravalent state due to the presence of the acceptor cations. La$_{0.65}$Sr$_{0.30}$FeO$_{3.5}$ exhibits P-type (electron hole, h$^+$) conduction, i.e., electronic conduction occurs through the migration of electron holes (associated with the tetravalent cations, B$^3$) to adjacent trivalent cations. At high temperature, ionic compensation becomes significant as the oxygen...
content of the material decreases which is in line with the TGA results. The decrease in conductivity at high temperatures occurs in the same temperature region in which the loss of lattice oxygen occurs. Thus, this is related to a decrease in the concentration of electron holes as the concentration of oxygen vacancies in the material increases.

Conclusions

Combustion synthesis can be effectively utilized for the synthesis of alternate cathode materials such as $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$. The powder XRD data obtained on the powder is in good agreement with the JCPDS data. TGA/DTA measurements indicated the absorption-desorption of oxygen takes place in the sample. FTIR analysis confirmed the presence of metal-oxygen bonds in the sample. Particulate properties obtained on the powder suggest that the as-formed powders are porous. To obtain a perfectly sintered specimen, sintering has to be carried out slowly until 1500 K. The specimen exhibited very good electrical conductivity in air, hence, $\text{La}_{0.65}\text{Sr}_{0.30}\text{FeO}_{3-\delta}$ may be considered as a suitable alternate cathode material in intermediate temperature solid oxide fuel cells (ITSOFCs).

Acknowledgements

ASN thanks the Director, CECRI for extending all the facilities to carry out this research work. Also, he thanks the management of Karunya University for promoting high temperature fuel cell research activity on the University campus.

References