CHAPTER - II
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2. CURRENT STATE OF THE ART AND THE SCOPE OF THE PRESENT WORK

This research work is concerned with the preparation and characterisation of new alternate cathode and electrolyte materials for intermediate temperature solid oxide fuel cell (ITSOFC) application. A brief description about the recent literature on the materials is presented in this section.

2.1 Survey of materials selection of cathodes

The main function of the cathode is to provide reaction sites for the electrochemical reduction of the oxidant. Thus, the cathode material must be stable in the oxidant oxidizing environment and have sufficient electronic conductivity and catalytic activity for the oxidant gas reaction at the operating conditions. Since the SOFC operates at high temperatures (873 to 1273 K), the cathode must be chemically and thermally compatible with other cell components, from room temperature to the operating temperature and also at even higher temperature at which the fuel cell components are fabricated. The key requirements for the cathode in the SOFCs are stated below.

1) The cathode must be chemically, morphologically, and dimensionally stable in the oxidant environment. The cathode material must not undergo disruptive phase transformation involving large changes in molar volume between room temperature and fabrication temperature. The cathode must maintain its desired microstructure in long-term operation; significant micro structural changes can cause degradation in cell performance.

2) The cathode must possess sufficient electronic conductivity to support electron flow in the oxidizing environment at the operating temperature. In general, maximum possible cathode conductivity is desirable to minimize ohmic losses.

3) The cathode must be chemically compatible with other components, not only at the operating temperature, but also at the much higher temperature at which the fuel cell ceramic structure is fabricated. Chemical interaction or chemical interdiffusion between the cathode and adjoining components must be limited in order to minimize unacceptable occurrences such as second phase formation, change in thermal expansion and introduction of electronic conductivity in the electrolyte.
4) The thermal expansion of the cathode must match (from room temperature to operation and fabrication temperatures) that of other cell components to avoid cracking and delamination during fabrication and operation, including thermal cycling.

5) The cathode must have sufficient porosity to allow gas transport to the reaction sites. The lower limit on porosity is set by mass transport considerations. The upper limit is based on consideration of mechanical strength of the component.

6) The cathode must have sufficient catalytic activity for the electrochemical reduction of the oxidant.

In addition to these requirements, other desirable properties for the SOFC cathode are high strength and toughness, fabricability, and low cost. At present, doped lanthanum manganite (LaMnO$_3$) is most commonly used[1].

2.1.1 Manganite based cathode materials

Sr - doped LaMnO$_3$ (LSM) has been extensively used as cathode material in the SOFC. This selection has been based primarily on three factors: high electrical conductivity in oxidizing atmospheres, adequate compatibility with Y$_2$O$_3$ - stabilized ZrO$_2$ (YSZ) electrolyte, and acceptable thermal expansion match with other cell components. Other properties of LaMnO$_3$ are tailored to meet the requirements for SOFC application.

LaMnO$_3$ belongs to the class of perovskite oxides of the general formula ABO$_3$. The cubic perovskite structure comprises three interpenetrating three dimensional networks: two consisting of the separate A and B cations and the third of corner-sharing $O_6$ octahedra. The LaMnO$_3$ melts at about 2153 K. Undoped stoichiometric LaMnO$_3$ is orthorhombic at room temperature and shows an orthorhombic/rhombohedral crystallographic transformation at about 873 K. At the SOFC operating temperature, LaMnO$_3$ is stable in oxidizing atmospheres but decomposes under highly reducing conditions. LaMnO$_3$ has intrinsic p-type conductivity due to the formation of cation vacancies. The material has an electrical conductivity of 0.1Scm$^{-1}$ at 973 K. The electrical conductivity of LaMnO$_3$ has been enhanced for SOFC applications by substituting a lower valence cation on either the A or B sites. The thermal expansion coefficient of undoped LaMnO$_3$ (La$_{0.99}$MnO$_3$) from 298 K to 1373 K is $11.2+0.3\times10^{-6}$ cm/cm.K. Lanthanum deficiency and oxygen nonstoichiometry appear to lower the thermal expansion of the material. Strontium
doping increases the thermal expansion coefficient of LaMnO$_3$, and the coefficient increases with increasing strontium dopant content. LaMnO$_3$ can be sintered to full density at temperatures above 1523 K in air. Because the material can be easily densified under normal firing conditions, starting powders and processing procedures are tailored to reduce the sinterability of LaMnO$_3$ to produce a porous cathode structure for SOFC application.

Masashi Mori et al. have investigated the properties of (La, Sr)$_{1.2}$(Mn$_{1.5}$Cr$_{0.5}$)$_3$O$_{3.8}$ (0<y<0.2) system as a new air electrode material of SOFC having chemical and morphological stabilities. Electrical conductivities of the sintered samples were 61.9 S cm$^{-1}$ and 47.3 S cm$^{-1}$ at 1273 K in air for Lao.92Sr0.08MnO$_3$-5 and (Lao.92Sr0.08)(Mn0.88Cr0.12)O$_3$-5 respectively[2]. Junichiro Mizusaki et al. have showed that the properties of SOFC air electrode can be improved by the (1-x) La$_{0.60}$Ca$_{0.40}$MnO$_{3.5-x}$-YSZ composite instead of La$_{0.60}$Ca$_{0.40}$MnO$_3$. When the composite of x<0.2 was prepared from fine sub-micron powders of La$_{0.60}$Ca$_{0.40}$MnO$_3$ and YSZ[3]. Tai and Lessing have fabricated porous electrodes from Sr-doped lanthanum manganite for a planar SOFC by the plasma spray technique. Spherical carbon particles were utilized as an effective pore former. The most porous coating made in this study had a porosity of about 40%, which was sprayed from LSM with a broad particle size distribution (53 to 180 µm) plus 15 wt.% solid carbospheres[4].

Christiansen and Gordes have developed a simple continuous drip pyrolysis process to synthesize La$_{0.85}$Sr$_{0.15}$MnO$_3$. Powder using mixtures of nitrate and acetate salt solutions. Colloidal dispersions of powder having controlled agglomerate size in non-aqueous media were optimized for tape casting. Highly porous La$_{0.85}$Sr$_{0.15}$MnO$_3$ plates were obtained after sintering at 1473 K - 1623 K with a linear shrinkage of up to 22%[5]. Roosmalen et al. have found that the La$_{1-x}$Sr$_x$MnO$_{3.5}$ powder synthesized via citrate process showed a higher sinter rate than the co-precipitate powder. Electrical conductivities for 100% density at 1223 K were found to be (115, 175, 265, 300) ± 5 S cm$^{-1}$ for La$_{1-x}$Sr$_x$MnO$_{3.5}$ with 0, 15, 30 and 50 at. wt.% of strontium, respectively[6]. Wen et al. have synthesized the ternary oxide system, Ln$_{1-x}$Sr$_x$MnO$_3$ (Ln=Pr, Nd, Sm, Gd, Yb and Y, with x<0.5), by means of solid state reaction at 1673 K. It was found that the conductivities of (Pr,Nd,Sm)$_{1-x}$Sr$_x$MnO$_{3.5}$ were approximately one order of magnitude higher than La$_{1-x}$Sr$_x$MnO$_{3.5}$ at high temperatures[7].
Syskakis et al. have synthesized the perovskite powders of the type \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) (0≤x≤0.4) by hot petroleum drying, by the sol-gel process, solid state reaction and spray drying. Increase in the Sr-content, x has been observed to depress the shrinkage of green bodies during sintering, thus leading to lower final density. The DC electrical conductivity at 300 K measured on sintered bodies at above 1373 K increased considerably with x, showing a maximum at x = 3 and \( T_s \geq 1570 \text{ K} \)[8].

Kautschke et al. have synthesized the perovskite based materials of the formula \( \text{La}_{1-y-x}\text{Mn}_{1-y}\text{Co}_y\text{O}_3 \), y = 0, 0.05; 0≤x≤0.4; 0≤y≤0.2, using spray-drying and treated under oxygen partial pressures extending up to \( 10^{12} \text{ bar} \) at 1273 K as new cathode material for SOFC. The lattice parameters and unit cell volume variation observed were interpreted in terms of the reduction of the average valence state of the B-site cation(s) in the perovskite lattice. However, for Co-containing specimens the appearance of a cubic phase at \( P_{O_2} \leq 10^{10} \text{ bar} \) was in apparent disagreement with expectations based on simple tolerance factor arguments[9].

Teske et al. have investigated the oxidation-reduction behaviour of Sr-doped \( \text{La}(\text{Mn,Co})\text{O}_3 \), especially the reaction \( \text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3 = \text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3 + 8\text{O}_2 \) by a solid electrolyte based coulometric (SEC) technique in a carrier gas mode. Direct coupling of SEC and electrical conductivity measurements has given further information about the relation between oxygen deficiency and conductivity. Pt contact enhances the rate of oxygen exchange up to ten times[10].

Syskakis et al. have studied the La deficient materials of the formula \( \text{La}_{y-x}\text{Sr}_x\text{MnO}_3 \) perovskites for \( y=0.95 \) and 0≤x≤0.4, showing crystal structure as single phase stoichiometric compounds. These materials were semiconductors at low Sr-content and exhibited metallic-like conduction for x≥0.2 and y<1. This observation indicated the importance of oxygen content for the electrical behaviour of this type of materials[11].

Tai et al. have synthesized fine powder of cathode materials with composition \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) (x=0 - 0.6) by buffer solution method. The \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) display three lattice types at room temperature: orthorhombic (0≤x≤0.15), hexagonal (0.15≤x≤0.45) and cubic (x≥0.45). The electrical conductivity of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) was influenced remarkably by the content of Sr, the peak value of \( 200 \text{ Scm}^{-1} \) was located at x=0.5 (at 1273 K in air)[12].

Chakroborty et al. have synthesized the fine powders of Sr-substituted \( \text{LaMnO}_3 \) at relatively low temperatures by auto-ignition of citrate-acetate-nitrate gels. The ignition temperature and the enthalpy change during the combustion varied with Sr
content leading to a variation of average particle size in the range of 0.3 to 3 μm. As- 
ignited powders, particularly with less Sr substitution, are amorphous in nature. 
However, the crystallographic phase became either pseudocubic or rhombohedral or 
orthorhombic depending on the calcination temperature as well as the extent of 
substitution[13]. Chakroborty and Maiti have found that addition of 10 wt.% Bi₂O₃ as 
sintering aid on La₁ₓSrₓMnO₃₋₅ powder lowered the sintering temperature by 
around 573 K. Bi₂O₃ addition did not affect significantly the physical properties like 
electrical conductivity and thermal expansion of the material[14]. Serge Bilger et.al have 
synthesized Sr-doped LaMnO₃ powders using a peroxide acetate salt based 
solution. The amorphous dried gel powder decomposed in a single step at low 
temperature(543 K) to form a homogeneous fine crystallized oxy-carbonate phase. 
After a gradual loss of remaining organic content through a diffusion process based 
on temperature, the early stage of crystallization, controlled by nucleation of large 
number of small particles, began at a temperature of around 903 K. The perovskite 
phase was formed very rapidly at temperatures above 973 K[15].

Erik and Finn determined the thermoelectric power and electrical conductivity 
of pure and 5, 10 and 20 mol.% Sr doped LaMnO₃ as a function of temperature in air 
and of P₀₂ at 1273 K. At high temperatures the thermoelectric power was negative. 
La₁ₓSrₓMnO₃₋₅ was independent of doping and it may be regarded as intrinsic 
conductor at 1273 K. This can be explained if it was assumed that Mn³⁺ 
disproportionates into Mn²⁺ and Mn⁴⁺. In reducing atmospheres the thermoelectric 
power was found to be only slightly dependent on P₀₂, which also might be explained 
by the disproportionation reaction[16]. Tsai and Barnett have studied the performance 
of SOFC with two phase mixtures of La₁ₓSrₓMnO₃₋₅ and YSZ cathode. Addition of 
40-60 vol.% YSZ to La₁ₓSrₓMnO₃₋₅ increased the resistivity by ≈ 10 times, but the 
resistivity was still low for effective current collection. A powder processing method 
employing freeze drying provided lower cathode interfacial resistance and higher 
SOFC power densities than drying at elevated temperatures. The addition of YSZ to 
La₁ₓSrₓMnO₃₋₅ allowed one to tend the range of SOFC operation down to 973 – 1073 
K, where the maximum power density ranged from 250 to 470 mW/cm², respectively, 
in humidified H₂ and air[17].

Michibata et.al have studied the preparation process of a thin film zirconia fuel 
cell by means of vacuum evaporation technique. The thin film cell was composed of a
partially stabilized zirconia (PSZ) thin film, porous nickel anode and thin film oxide cathode. It was found that LaMnO₃ was superior to LaCoO₃ for the cathode of PSZ thin film cells[18]. Choy et.al have fabricated thick films of La₃-xSrₓMnO₃₋₈ by flame assisted, vapour deposition method, a simple and cost-effective technique than the conventional techniques. The interfacial resistive loss measured was better than those of a slurry technique[19]. Basu et.al have deposited thick films of La₃-xSrₓMnO₃₋₈ on impervious YSZ electrolyte by the screen printing technique. Application of three consecutive layers (with intermediate firing) produces films of approximately 60 μm thick. An optimum sintering temperature for three or more coatings (depending on required thickness) was 1523 – 1573 K[20]. Akira Endo et.al have studied the electrochemical characteristics of three types of La₃-xSrₓCoO₃₋₈ and La₃-xSrₓMnO₃₋₈ electrodes, (dense, porous and porous/dense double layer). The dense layers of La₃-xSrₓCoO₃₋₈ and La₃-xSrₓMnO₃₋₈ were prepared by a laser ablation method and the porous layers were prepared by a tape-casting method. Electrochemical measurements (ac impedance and dc polarization measurements) revealed that surface area was an important factor for the reaction rate on the La₃-xSrₓCoO₃₋₈ electrode, while the electrode/electrolyte boundary structure was important on the La₃-xSrₓMnO₃₋₈ electrode [21]. Eming et.al have investigated the effects of highly dispersed (≤0.1 mg/cm²) noble metal catalysts (e.g. Pd, Pt, Ir and Ru) on the electrochemical performance of screen printed Laₐ.₈₄Srₐ.₁₆MnO₃₋₈ cathodes using potentiodynamic current-potential measurements and impedance spectroscopy. At typical operating conditions (e.g. T=1273 K, η=-0.1 V), the current density in presence of palladium was increased by about one order of magnitude as compared to the current density obtained with pure Laₐ.₈₄Srₐ.₁₆MnO₃₋₈ cathodes[22].

D'Souza and Sammes have studied the mechanical properties of La₃-xSrₓMnO₃₋₈. While in operation, the cathode can be subjected to significant stresses, because of thermal expansion mismatch between the adjoining components. The mechanical behaviour of Laₐ.₈₇Srₐ.₁₂₃MnO₃₋₈ has been studied using three-point bend strength measurements at ambient, 673 K, 1073 K and 1273 K. The results showed that phase transformations have an important role in the mechanical-strength behaviour[23]. Mori et.al have investigated the thermal expansion behaviour and mechanism of A-site deficient manganite perovskites, La₃-xMnO₃(0<x<0.1) and alkaline earth metal (AE)-doped lanthanum manganite perovskites,
La$_{1-x}$AE$_x$MnO$_{3.6}$ (AE=Ca and Sr, 0≤x≤0.4), under oxidizing atmospheres. AE doping to LaMnO$_3$ controlled their TECs, and the perovskites with approximately 20 mol.% AE dopant showed excellent compatibility of thermal expansion with the YSZ electrolyte, although they shrank during thermal cycling. Since no shrinkage was observed during thermal cycling, the La$_{0.60}$AE$_{0.40}$MnO$_{3.6}$ perovskites were the best candidates to use as cell components[24]. Choi et.al have found that the microstructure of La$_{0.90}$Sr$_{0.10}$MnO$_{3.6}$ electrodes was controlled by varying the particle size of the starting powders while keeping the other variables fixed. The cathodic activity was monitored by estimating the charge transfer resistance values with half-cell operations, and the results were correlated to the micro-structural change[25]. Recently, Jørgensen and Mogensen have studied the La$_{1-x}$Sr$_x$MnO$_{3.6}$/YSZ composite electrodes by impedance spectroscopy. They found that at least five processes affect the impedance. Going from high to low frequency, these processes are, (i), (ii) two geometry-related contributions interpreted as transport across La$_{1-x}$Sr$_x$MnO$_{3.6}$/YSZ interfaces and through the YSZ of the composite, (iii) a process reflecting competitive reaction steps such as bond breaking and surface diffusion, (iv) gas diffusion in a stagnant gas layer above the electrode structure, and (v) an activation process (inductive) presumably located at the triple phase boundary of electrode, electrolyte, and gas phase[26].

2.1.1.1 Reaction between manganite based cathode and YSZ electrolyte

Interfaces between electrolyte and electrode can be regarded as “cross road” of electrical current, heat flow and flow of chemicals. The steady state operation of SOFCs will require many kinds of stability such as mechanical, morphological, chemical and electrical. Among them, the chemical stability is required to prevent possible degradation due to chemical reactions or interdiffusion; precipitation or new phases or change in composition due to diffusion may affect the electrical conductivity, gas permeability and the electrochemical properties. The high fabrication and operation temperature of the SOFC raise concerns regarding the chemical compatibility of the manganite cathode with other cell components, especially the YSZ electrolyte. The recent literature obtained on the chemical interaction between manganite based cathode and zirconia based electrolyte is summarised below.

Kawada et.al have estimated the reactivity of LaMnO$_3$ and YSZ by
thermodynamic calculations, and reported that the non-stoichiometry at La site in LaMnO$_3$ played an important role on the reaction. Diffusion of Mn into YSZ lead to increase of La activity at the interface and promoted the reaction. Electrical conductivity of YSZ decreased when Mn dissolved in the cubic phase of YSZ. Oxidation state of the dissolving Mn varied with partial pressure of oxygen and affected the electrical properties of YSZ. Shen et.al have studied the reaction between La$_{0.9}$MnO$_3$ and YSZ[27]. They found the thermal reactivities of the couples of La$_{0.9}$MnO$_3$ and YSZ decreased with increase in the yttria content in YSZ at temperature range 1523 - 1673 K. The activation energy for the reaction decreased with the increasing of the yttria content in YSZ. The rate determining step for the reaction was assumed to be the diffusion of Mn$^{3+}$ in YSZ[28]. Taimatsu et. al have studied the reactions between 8 mol.% YSZ and La$_{1-x}$Ca$_x$MnO$_{3-δ}$($x=0 - 0.2$) as a cathode for SOFC. La$_2$Zr$_2$O$_7$ phases formed at the interface between YSZ and LaMnO$_3$ at 1773 K and liquid phases formed at grain boundaries in YSZ at 1723 K. Below 1698 K, manganese mainly diffused into YSZ along grain boundaries, while yttrium and zirconium did not migrate into La$_{1-x}$Ca$_x$MnO$_{3-δ}$. The results obtained suggested that the reaction proceeded due to the migration of cations, chiefly manganese ions, in La$_{1-x}$Ca$_x$MnO$_{3-δ}$ into YSZ together with oxygen ion[29].

Stochniol et.al have found that the formation of La$_2$Zr$_2$O$_7$ and SrZrO$_3$ was least with perovskite having Sr content of $x = 0.3$. The inertness of the cathode material could be improved further by choosing the substoichiometric composition La$_{0.65}$Sr$_{0.35}$MnO$_{3-δ}$. An increased Sr content lead to a decreased formation of La$_2$Zr$_2$O$_7$ but also to an increased diffusion of Mn oxide into the electrolyte material. A high Sr content ($x = 0.4$) revealed both aspects: the formation of La- and Mn- enriched SrZrO$_3$ layer at the reaction interface, as well as a diffusion of Mn oxide into YSZ[30-31]. Wiik et.al have found that the secondary phases of La$_2$Zr$_2$O$_7$ and SrZrO$_3$ were formed from the reaction between YSZ and La$_{1-x}$Sr$_x$MnO$_{3-δ}$ at low and high content of Sr respectively in La$_{1-x}$Sr$_x$MnO$_{3-δ}$. However, at 30 mol.% Sr in La$_{1-x}$Sr$_x$MnO$_{3-δ}$ only minor amounts of secondary phases were observed[32].

The addition of 40% by weight of YSZ to LSM improved its performance due to the better adhesion to the base electrolyte and to the increase of the triple phase boundary length. The extent of the Mn dissolution depended on the content of YSZ in the cathode layer. Therefore, in order to prevent the formation of zirconates it was
necessary to balance the amount of excess Mn for each given LSM/YSZ ratio[33]. In the case of Ln1-xSr1_xMnO3-δ (Ln = La, Pr, Nd, Sm and Gd), the formation of the pyrochlore, Ln2Zr2O7, was suppressed for the perovskites having lanthanoids smaller in size than La, especially for the Pr1-xSr1_xMnO3-δ and Nd1-xSr1_xMnO3-δ systems. The Ln1-xAxCoO3-δ systems with smaller lanthanoid ions were also effective in suppressing the reaction with YSZ. However, the Ln1-xAxCoO3-δ systems, which are promising cathode materials for ITSOFC, have higher thermal expansion rates than YSZ. The formation of a solid solution with Mn in the B-site of the perovskite such as Gd1-xAxMn1-xCoO3-δ (A = Sr and Ca) brought reasonable thermal expansion rates, compatible with YSZ and high oxygen reduction catalytic activity[34]. From the view point of the electrode activity, high electrical conductivity, low reactivity and good compatibility with YSZ, Pr0.70Sr0.30MnO3-δ and Nd0.70Sr0.30MnO3-δ were considered to be most suitable electrode materials for the co-firing process[35].

The chemical compatibility of Nd1-xSr1_xMnO3-δ (x = 0.4, 0.5) with Ce0.90Gd0.10O2-δ (CGO) electrolyte was excellent, since no reaction products were detected after 120 h of sintering equimolar powder mixtures of these compounds at 1573 K. In addition, the TEC values of the perovskite compositions with 40 and 50 mol.% Sr were compatible with that of Ce0.90Gd0.10O2-δ electrolyte, and therefore these compositions could be considered as candidate intermediate temperature cathode materials[36]. Yoon et.al have synthesized Gd1-xSr1_xMnO3-δ (0 ≤ x ≤ 0.6) as the cathode materials for SOFC using citrate process. The thermal expansion coefficient showed a normal behavior for x ≤ 0.3 and increased with increasing Sr contents. When heated at 1573 K for 48 h, Gd1-xSr1_xMnO3-δ reacted with 8 mol.% YSZ to produce SrZrO3, but did not react at all with Ce0.80Gd0.20O2-δ electrolyte[37-38].

2.1.2 Cobaltite based cathode materials

Doped lanthanum cobaltite (LaCoO3) was another perovskite of interest as SOFC cathode material. The material belonged to the same class of oxide compounds as LaMnO3. LaCoO3 was rhombohedral from room temperature to 1273 K. The rhombohedral structure transforms into a cubic phase; the transformation temperature depends on dopant content. LaCoO3 has no oxygen excess but showed a large oxygen deficiency at high temperatures, especially when doped with lower-valence cation such as strontium.

LaCoO3 was stable in oxidizing atmospheres but decomposes in reducing
environments. The material was less resistant toward reduction, when compared with LaMnO$_3$. Doping reduced the stability of LaCoO$_3$, and the critical oxygen partial pressure shifted to higher values with increasing dopant content. LaCoO$_3$ has been shown to have intrinsic p-type conductivity, and the electrical conductivity can be enhanced by substituting a lower-valence ion on the lanthanum site. Sr and Ca are the most commonly used dopants for LaCoO$_3$. The conductivity of doped LaCoO$_3$ increased with increasing dopant level and exhibited a maximum at 40 mol.% for Sr and 30 mol.% for Ca. Undoped LaCoO$_3$ showed a semiconducting-metallic conduction transition at about 1073 K in an oxygen atmosphere. The average thermal expansion coefficient of LaCoO$_3$ was about 22 to 24 x $10^{-6}$ cm/cm.K. In general, the thermal expansion coefficient of LaCoO$_3$ (even with doping) was significantly higher than that of YSZ electrolyte.

Ohano et.al have studied the thermal expansion, electrical conductivities and structure transitions of the perovskite-type compounds based on LaCoO$_3$ in the temperature range RT (room temperature) ~ 1373 K in air. They have described a series of compositions made by substitution of the La$^{3+}$ cation by the divalent cations Ca$^{2+}$ and Sr$^{3+}$. In the case of Sr substituted compound, the electrical properties were metallic in all the temperature range when $x$ became larger than 0.3. The La$_{1-x}$Ca$_x$CoO$_{3-\delta}$ was more stable than the La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ with regard to the thermal expansion[39]. Yamamoto et.al have studied the polarization and electrical conductivity at 1073 K in open air using the perovskite oxides La$_{1-x}$Sr$_x$MO$_{3-\delta}$ (M = Cr, Mn, Fe, Co) sputtered on YSZ electrolyte. The lowest cathodic overpotential and the highest conductivity were obtained for the LaCoO$_3$ electrode at 1073 K. LaCoO$_3$ and La$_{0.7}$Sr$_{0.3}$CoO$_{3-\delta}$ reacted with the YSZ electrolyte to form La$_2$Zr$_2$O$_7$ and Sr$_2$ZrO$_4$, respectively at 1273 K. With La$_{0.7}$Sr$_{0.3}$MO$_{3-\delta}$ (M=Cr, Mn, Fe), no reaction product between the electrodes and the electrolyte was observed at 1073 K and Sr$_2$ZrO$_4$ was observed at 1373 K. Of the perovskite type oxides examined, La$_{0.7}$Sr$_{0.3}$MnO$_{3-\delta}$ was the most adaptable electrode material at 1073 K, because of the chemical stability with YSZ, high electric conductivity and the good catalytic activity for oxygen reduction[40].

Ivers-Tiffe et.al investigated two solid solution systems La$_{1-u}$Sr$_u$Mn$_{1-x}$Co$_x$O$_{3-\delta}$ (with $u = 0.2$ and 0.5, and $0 \leq x \leq 1$) with respect to their material properties in SOFCs at low operating temperatures ($\approx 1073$ K). They confirmed an increase of electrical
conductivity and of thermal expansion coefficients in these solid solution systems with increasing Co content. The Mn rich compounds behaved like a semiconductor, and the Co rich compounds exhibited metallic behaviour. At higher Co contents (≤0.5) interfacial reactions which usually destroy the cells, i.e., the formation of La$_2$Zr$_2$O$_7$ and SrZrO$_3$. The application of Co-containing cathodes therefore seemed to be quite reasonable, especially with ITSOFC[41]. Syskakis et al. have synthesized the Sr-and/or Co-doped LaMnO$_3$ perovskite materials with various cation stoichiometries (A/B ratios) by spray drying process. Equimolar mixtures of La$_{y-x}$Sr$_x$Mn$_{1-y}$Co$_y$O$_{3.5}$ (y=1, 0.95, 0.9; 0.0≤x≤0.4; 0.0≤u≤0.2) and YSZ after annealing at 1473 and 1673 K indicated a strong dependence of the chemical interaction on the composition of the perovskite and on temperature. La-deficiency lead to slower reaction rates. The materials with y=0.95, u=0, and 0.2≤x≤0.4 did not form La$_2$Zr$_2$O$_7$ or SrZrO$_3$ in reaction with YSZ at 1473 K (400 h), while La$_{0.65}$Sr$_{0.35}$Mn$_{0.3}$O$_{3.5}$ resisted the formation of zirconates even at 1673 K (200 h). Although Co-doping enhanced the reactivity, the perovskite La$_{0.79}$Sr$_{0.2}$Mn$_{0.9}$Co$_{0.1}$O$_{3.5}$ also did not form zirconates with YSZ at 1673 K (20 h). The electrical conductivity and thermal expansion of the same materials confirmed the applicability of La$_{0.95-x}$Sr$_x$Mn$_{1-y}$Co$_y$O$_{3.5}$ perovskites with an A-cation deficiency for the cathode of SOFC compared to their stoichiometric counterparts [42].

Routbort et al. have measured the tracer diffusion of $^{18}$O in dense, polycrystalline La$_{1-x}$Sr$_x$CoO$_{3.5}$ for x=0.1 in the temperature range 673 to 873 K and at 773 K for x=0.2 at an oxygen partial pressure of 1x10$^5$ Pa. La$_{0.80}$Sr$_{0.20}$CoO$_{3.5}$ exhibited a higher diffusivity at 773 K than did La$_{0.90}$Sr$_{0.10}$CoO$_{3.5}$[43]. Takeda et al. have studied the electrical conductivity, cathodic polarization and reactivity between Gd$_{1-x}$Sr$_x$CoO$_{3.5}$ and YSZ (8 mol.% Y$_2$O$_3$ doped ZrO$_2$). Although the cathodic activity was excellent and similar to the La$_{1-x}$Sr$_x$CoO$_{3.5}$ system, the formation SrZrO$_3$ at the interface between Gd$_{1-x}$Sr$_x$CoO$_{3.5}$ and YSZ was observed at higher temperature, which caused the deterioration of the cathodic activity. However, the GdCoO$_3$, being different from LaCoO$_3$, yielded no reaction product with YSZ at high temperature and showed no deterioration in the cathodic activity for the electrode even when sintered at 1273 K[44]. Tu et al. have examined the perovskite-type oxides of Ln$_{1-x}$Sr$_x$CoO$_{3.5}$ (Ln = Sm, Dy) for the cathodes of SOFC. The formation of solid solutions in
conductivity and of thermal expansion coefficients in these solid solution systems with increasing Co content. The Mn rich compounds behaved like a semiconductor, and the Co rich compounds exhibited metallic behaviour. At higher Co contents (≤0.5) interfacial reactions which usually destroy the cells, i.e., the formation of La₂Zr₂O₇ and SrZrO₃. The application of Co-containing cathodes therefore seemed to be quite reasonable, especially with ITSOFC\[41\]. Syskakis et.al have synthesized the Sr-and/or Co-doped LaMnO₃ perovskite materials with various cation stoichiometries (A/B ratios) by spray drying process. Equimolar mixtures of La₄₋ₓSrₓMn₁₋ₜCoₜO₃₋ₜ \((y=1, 0.95, 0.9; 0≤x≤0.4; 0≤t≤0.2)\) and YSZ after annealing at 1473 and 1673 K indicated a strong dependence of the chemical interaction on the composition of the perovskite and on temperature. La-deficiency lead to slower reaction rates. The materials with \(y=0.95, t=0,\) and \(0.2≤x≤0.4\) did not form La₂Zr₂O₇ or SrZrO₃ in reaction with YSZ at 1473 K (400 h), while La₀.₆₅Sr₀.₃₀MnO₃₋₅ resisted the formation of zirconates even at 1673 K (200 h). Although Co-doping enhanced the reactivity, the perovskite La₀.₇₀Sr₀.₁₆Mn₀.₉₀Co₀.₁₀O₃₋₅ also did not form zirconates with YSZ at 1673 K (20 h). The electrical conductivity and thermal expansion of the same materials confirmed the applicability of La₀.₉₅Sr₁₋ₜMn₁₋ₜCoₜO₃₋₅ perovskites with an A-cation deficiency for the cathode of SOFC compared to their stoichiometric counterparts \[42\].

Routbort et.al have measured the tracer diffusion of \(^{18}O\) in dense, polycrystalline La₁₋ₓSrₓCoO₃₋₅ for \(x=0.1\) in the temperature range 673 to 873 K and at 773 K for \(x=0.2\) at an oxygen partial pressure of \(1×10^5\) Pa. La₀.₈₆Sr₀.₂₄CoO₃₋₅ exhibited a higher diffusivity at 773 K than did La₀.₉₀Sr₀.₁₀CoO₃₋₅\[43\]. Takeda et.al have studied the electrical conductivity, cathodic polarization and reactivity between Gd₁₋ₓSrₓCoO₃₋₅ and YSZ (8 mol.% Y₂O₃ doped ZrO₂). Although the cathodic activity was excellent and similar to the La₁₋ₓSrₓCoO₃₋₅ system, the formation SrZrO₃ at the interface between Gd₁₋ₓSrₓCoO₃₋₅ and YSZ was observed at higher temperature, which caused the deterioration of the cathodic activity. However, the GdCoO₃, being different from LaCoO₃, yielded no reaction product with YSZ at high temperature and showed no deterioration in the cathodic activity for the electrode even when sintered at 1273 K\[44\]. Tu et.al have examined the perovskite-type oxides of Ln₁₋ₓSrₓCoO₃₋₅ (Ln = Sm, Dy) for the cathodes of SOFC. The formation of solid solutions in
Dy₁₋ₓSrₓCoO₃₋₅ was limited, compared with that in Sm₁₋ₓSrₓCoO₃₋₅. The highest conductivity of around 500 Scm⁻¹ at 1273 K was found in Sm₀.₇₀Sr₀.₃₀CoO₃₋₅. The Sr-doped oxides were more reactive with YSZ at higher temperatures and produced SrZrO₃. SmCoO₃ showed good chemical compatibility with YSZ, and no degradation of the electrode performance at higher temperatures. Ln₁₋ₓSrₓCoO₃₋₅ (Ln = Sm, Dy) exhibited the higher thermal expansion, as compared to YSZ[45].

Morin et.al studied the phase stability of La₀.₅₀Sr₀.₅₀CoO₃₋₅. Control of the actual cation ratios was the most important parameter in the course of single-phase materials preparation. More specifically, the stability field of La₀.₅₀Sr₀.₅₀CoO₃₋₅ was very narrow in regard to the A/B ratio. It has been estimated to be within 0.997<A/B<1.003. Thus, secondary phase formation was expected to occur readily whenever there was an insufficient control on the respective accuracies of the various cationic ratios. A strontium-substituted lanthanum-rich phase of the La₂CoO₄-type was formed on the A side and a complex Co-rich oxide phase on the B side. Of course, the presence of these secondary phases played a major role in regard to the determination of various properties of La₀.₅₀Sr₀.₅₀CoO₃₋₅ and to the sintering ability of these ceramics[46]. Huang et.al have found that the compositions La₀.₈₀Sr₀.₂₀Co₀.₈₀Ni₀.₂₀O₃₋₅ and La₀.₇₀Sr₀.₃₀Fe₀.₈₀Ni₀.₂₀O₃₋₅ have a TEC better matched to that of electrolyte than TEC of La₁₋ₓSrₓCoO₃₋₅, and the electrodes showed a comparable electrode resistance at an operating temperature T₂< 973 K. In contrast to the conventional La₁₋ₓSrₓMnO₃₋₅ cathode, these materials have lost oxygen reversibility at T> 873 K, which made them mixed electronic/oxide-ion conductors with good catalytic activity for oxygen reduction. The La₀.₈₀Sr₀.₂₀Co₀.₈₀Ni₀.₂₀O₃₋₅ and La₀.₇₀Sr₀.₃₀Fe₀.₈₀Ni₀.₂₀O₃₋₅ systems thus offered attractive alternatives to the conventional cathode materials now employed in SOFCs[47].

Uchida et.al have used a samaria-doped ceria(SDC) interlayer to avoid unfavorable solid-state reactions when using La₁₋ₓSrₓCoO₃₋₅ as a cathode on YSZ electrolyte. A porous La₁₋ₓSrₓCoO₃₋₅ prepared on a thin and dense SDC interlayer exhibited very high performance even at 1073 K. The performance was enhanced further by dispersing a small amount of nanometer-sized Pt catalysts on the La₁₋ₓSrₓCoO₃₋₅ surface. The current density on the Pt-La₁₋ₓSrₓCoO₃₋₅ cathode at an overpotential of −0.05 V was 0.6 A/cm² at 1073 K in O₂[48]. Kleveland et.al have investigated the densification / sintering of submicron powders of La₁₋ₓMₓCoO₃₋₅
(M= Ca, Sr; x = 0, 0.2) prepared by glycine-nitrate combustion method. They found that the sintering temperature was observed to decrease with Ca or Sr substitution. Dense materials with grain size in the order of 3-5\(\mu\)m have been obtained at 1473 K for near stoichiometric powders. Presence of secondary phases may lead to cracking of the material and decline the functional properties[49-50]. Koyama et.al have investigated the cathodic reaction mechanism of a SOFC for an electrode-electrolyte system of \(\text{La}_{0.60}\text{Ba}_{0.40}\text{CoO}_{3}\) and BaCeO\(_3\) under O\(^2-\) conducting and H\(^+\)/O\(^2-\) mixed ionic conducting conditions. They found that with BaCeO\(_3\) electrolyte, \(\text{La}_{0.60}\text{Ba}_{0.40}\text{CoO}_{3}\) shows not only good chemical compatibility but also has electrode characteristics comparable to those of rare-metal electrodes[51].

Horita et.al investigated the chemical reactivity of \(\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_{3}\) cathode with \(\text{La}_{0.60}\text{Sr}_{0.40}\text{Ga}_{0.20}\text{Mg}_{0.20}\text{O}_{3}\) electrolyte. The lattice parameter of LaGaO\(_3\) decreased due to the reaction with \(\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_{3}\). The long term stability was investigated at the porous \(\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_{3}\) cathode/LaGaO\(_3\) electrolyte interface under cathodic polarization at 1073 K. A AC impedance measurements distinguished the electrolyte and electrode reaction resistance under cathodic polarization. The electrolyte resistance of LaGaO\(_3\) decreased with an operation time under cathodically polarized conditions, while the interface resistance increased. No distinct reaction layer was observed at the interface of porous \(\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_{3}\)/LaGaO\(_3\) electrolyte after long-term operation test (700 h). Small amounts Co were observed in LaGaO\(_3\) electrolyte at the range of 1-2 \(\mu\)m from the interface. An applied voltage in a cathodic direction affected the \(\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_{3}\) porous/ LaGaO\(_3\) electrolyte interface nature[52]. Petrov and Kofstad have studied the crystal structure and electrical properties of \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3}\) with different strontium contents(0.1<\(x<0.7\)) as a function of temperature at P\(_{O_2}\) = 0.21 atm(air). The solid oxide solutions were rhombohedral at reduced temperatures and low values of \(x\); at room temperature the transition taken place for \(x=0.55\). The electrical conductivity reached a maximum at \(x \sim 0.4\). Under these conditions the electrical conductivity was approximately 3000 Scm\(^{-1}\) and decreased slowly with increasing temperature[53].

Yamamoto et.al have studied the electrical conductivity of the sintered samples \(\text{Gd}_{1-x}\text{A}_x\text{MnO}_{3}\) and \(\text{Gd}_{1-x}\text{A}_x\text{CoO}_{3}\) (A=Ca, Sr) as a function of \(x\) in the temperature range 303 to 1273 K. The highest conductivity of 400 Scm\(^{-1}\) at 1273 K was found in \(\text{Gd}_{0.90}\text{Sr}_{0.10}\text{CoO}_{3}\). The Sr doped GdCoO\(_3\) was more reactive with YSZ
and produced SrZrO$_3$ at 1123 K after 94 h. On the other hand, no reaction product between GdCoO$_3$ and YSZ was observed at 1273 K for 96 h[54]. Kharton et al. have studied the electrical conductivity of Ln$_{1-x}$Sr$_x$CoO$_{3+d}$ (Ln=Pr, Nd, Sm, Gd; x = 0-0.5). It was found that ionic conductivity of cobaltites decreases in the La>Pr>Nd sequence[55].

2.1.3 YFeO$_3$ based cathode materials

Fu et al. have investigated a new cathode, Y$_{1-x}$Ca$_x$FeO$_{3-d}$ (0 ≤ x ≤ 1) for SOFCs. This system was chosen on the basis of its material commonality with YSZ, potential mixed conductivity, high phase stability at low partial pressures of oxygen and considerations of interfacial stability. Within this system the best composition for cathode applications would be Y$_{0.90}$Ca$_{0.10}$FeO$_{3-d}$, which exhibited a thermal expansion coefficient of 11 cm/cm-K and a p-type, DC conductivity of 1.7 Scm$^{-1}$ at 1273 K. The conductivity was still lower than La$_{1-x}$Sr$_x$MnO$_3$ by a factor of 4 to 5, but the improvement to the cell performance from being a mixed conductor may compensate for this limitation[56]. Kim and Yoo have determined the electrical conductivity, ionic conductivity and thermopower as functions of temperature (1173 ≤ T/K ≤ 1373) and oxygen partial pressure (10-16 ≤ P$_{O_2}$/atm ≤ 1) on the cathode Y$_{0.90}$Ca$_{0.10}$FeO$_{3-d}$. The majority ionic carriers have been found to be oxygen ions via electro-transport experiments. The ionic transference number taken a value in a range of 10$^{-4}$ to 10$^{-2}$ depending on oxygen partial pressure at 1173–1373 K. The activation energy of ionic conduction is 1.6 eV. The ionic conductivity, which was in the range of 10$^{-3}$ to 10$^{-1}$ Scm$^{-1}$ at 1373 K, tend to increase with increasing P$_{O_2}$ in oxidizing atmospheres and with decreasing P$_{O_2}$ in reducing atmospheres[57-58].

Lee et al. have studied the high temperature phase stability and cathodic activity of Y$_{0.80}$Ca$_{0.20}$Co$_{1-x}$Fe$_x$O$_{3-d}$ (x = 0.1–0.7) cathode. Among those samples of x = 0.1–0.7, the Y$_{0.80}$Ca$_{0.20}$Co$_{0.70}$Fe$_{0.30}$O$_{3-d}$ showed the best cathodic activity which was superior to La$_{0.90}$Sr$_{0.10}$MnO$_3$. The thermal expansion coefficient of this material (10.5 × 10$^{-6}$ cm/cm-K at 298 – 1273 K) was very close to that of 8 mol.% YSZ (10.8 x 10$^{-6}$ cm/cm-K). As a result of interfacial reaction between Y$_{0.80}$Ca$_{0.20}$Co$_{0.70}$Fe$_{0.30}$O$_{3-d}$ and YSZ electrolyte, a spinel type oxide was produced. But the interfacial product formation proceeded mainly during the electrode adhesion period (1473 K) whereas its growth during the cell operation (1173–1273 K) was negligible[59]. Cao et al. have studied the substitution of Mn for Iron on the structure and electrical properties of
YFeO₃. The solubility of Mn in YFe₁₋ₓMnₓO₃₋₈ reached y = 0.4. Among these compositions, YFe₀.₆₀Mn₀.₄₀O₃₋₈ has the highest conductivity with σ = 2.16 S cm⁻¹ (1273 K in air), which was >1 order of magnitude higher than that of yttrium ferrite, YFeO₃ (σ = 0.10 S cm⁻¹, 1273 K). They have attempted to improve the conductivity of YFeO₃ by substituting Mn for Iron. However, the result was opposite to the expectation. The substitution of Ca for Y in YFe₁₋ₓMnₓO₃₋₈ resulted only in a small increase of conductivity that was much lower than that of Y₀.₉ₒCa₀.₁ₒFeO₃₋₈ [60].

2.1.4 La₁₋ₓSrₓCo₁₋ₙFeₙO₃₋₈ based cathode materials

In recent years, perovskite-type oxides with compositions of La₁₋ₓAₓCo₁₋ₙFeₙO₃₋₈ (A=Ca, Sr and Ba) have been extensively studied. The substitution of A-site cations by a lower valence cation formed oxygen vacancies and caused a change of valence state in B-site cations to maintain charge neutrality. The concentration of oxygen vacancies can also be tailored by substituting ions of similar sizes but lower valences at B sites. As a result, the materials can exhibit not only high ionic conductivity because of the high concentration of oxygen vacancies but also a high electronic conductivity because of mixed-valence states.

Teraoka et al. measured the ionic (σᵢ) and electronic (σₑ) conductivity of mixed conducting La₁₋ₓSrₓCo₁₋ₙFeₙO₃₋₈ materials. At 1073 K, for instance, σᵢ ranged in the order of 1-10² S cm⁻¹ while σₑ was around 10² S cm⁻¹, indicating that the present oxides were good mixed conductors with ionic transport number 10⁻² - 10⁻⁴. σᵢ increased as contents of Sr and Co increased though Sr content was more influential [61]. Tai et al. have studied the several compositions of La₁₋ₓSrₓCo₁₋ₙFeₙO₃₋₈ for their possible use as cathode in ITSOFC. Results suggested that La₁₋ₓSrₓCo₀.₂ₒFe₀.₈ₒO₃₋₈, with x=0.2-0.4, were potential cathode compositions for SOFCs operating between 873-1073 K. These compositions were single phase and stable throughout a wide range of temperature. Peak conductivity values of 200-330 S cm⁻¹ at temperatures of 1073 and 873 K were observed in air for x=0.2-0.4, respectively. The peak conductivity increased and shifted to lower temperature as the Sr content increased [62]. Chen et al. have made dense, smooth and fine-grained La₀.₆ₒSr₀.₄ₒCo₀.₂ₒFe₀.₈ₒO₃₋₈ cathode films on (ZrO₂)₀.₈₄(YO₁.₅)₀.₁₆(YSZ) and (CeO₂)₀.₈₀(SmO₁.₅)₀.₂₀ (SDC) substrates by a spin-coating technique and subsequent heat treatment at temperatures as low as 873 K. These dense films showed very low interfacial resistance, at temperatures up to 1073 K, as compared to either La₁₋ₓSrₓMnO₃₋₈ or Pt. These results
suggested that $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3.5}$ may be a good candidate for ITSOFC. However, the interaction between $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3.5}$ and YSZ, defined a temperature limit of less than 1073 K for this electrode on YSZ. No reaction were detected between $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3.5}$ and SDC up to 1473 K, so this combination can be used upto 1473 K\cite{63}.

Anderson et.al have determined that all compositions in the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3.5}$ (x=0.2, 0.4) system had a perovskite-type structure. Both the thermal expansion coefficient and the p-type electrical conductivity increased with Co content. Oxygen vacancies formed in these oxides at high temperatures resulted in a lattice expansion and a reduction in the concentration of electronic charge carriers. As a result maxima in the electrical conductivity ranging from 200-330 Scm$^{-1}$ were observed for compositions with x=0.2-0.4 and Fe=0.8 in the temperature range of 873-1073 K, in air\cite{64}. Tai et.al have studied the crystal structure, thermal expansion, thermo-gravimetry and electrical conductivity of compositions in the system $\text{La}_{0.80}\text{Sr}_{0.20}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3.5}$ with 0$\leq$y$\leq$1 as a function of Co/Fe ratio and temperature in air. The electrical conduction mechanism was attributed to the adiabatic-hopping of p-type small polarons. At high temperatures, oxygen deficiency caused lattice expansion and a reduction in electrical conductivity\cite{65}. The same group studied the crystal structure, thermal expansion, thermo-gravimetry and electrical conductivity of compositions in the system $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3.5}$ with 0$\leq$x$\leq$0.6 as function of temperature and Sr content, in air. The solubility of Sr in the sintered perovskite-type oxide(ABO$_3$) was limited to x$\leq$0.4. The observed p-type electrical conduction appeared to occur via a small-polaron hopping mechanism. The thermally-induced oxygen loss caused a lattice expansion plus decrease in both the carrier concentration and the carrier mobility\cite{66}.

Waller et.al have synthesized $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3.5}$ with perovskite structure using citrate and glycine complexation method. Low temperature calcination of the precursor phases led to the formation of cubic perovskites, which on high temperature calcination form rhombohedrally distorted perovskites. They demonstrated that the $\text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3.5}$ perovskites remained stable with a high degree of cation deficiency on the A-site and that for 0.2$\leq$x$\leq$0.25 the symmetry of the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3.5}$ changed from rhombohedral, as observed in more Sr-rich $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3.5}$, to cubic\cite{67}. Tu et.al have prepared the perovskite type oxides
of \( \text{Ln}_{0.40}\text{Sr}_{0.60}\text{Co}_{0.80}\text{Fe}_{0.20}\text{O}_{3-\delta} \) (\( \text{Ln} = \text{La, Pr, Nd, Sm, Gd} \)) by the solid state reaction. The electrical conductivity of the sintered samples showed semiconductor-like behaviour at low temperature and metallic behaviour at a high temperature. \( \text{Nd}_{0.40}\text{Sr}_{0.60}\text{Co}_{0.80}\text{Fe}_{0.20}\text{O}_{3-\delta} \) exhibited the highest conductivity in the temperature range 298 – 1273 K. The conductivity values of all the compositions, which were higher than 100 Scm\(^{-1}\) above 873 K, were acceptable as a cathode in SOFC. The perovskite oxides reacted with 8 mol.% YSZ to produce \( \text{SrZrO}_3 \) at 1173 K and no reaction product was observed at 1073 K. The cathodic polarization of these oxide electrodes sputtered on the 8 YSZ tablet was studied at 873 – 1073 K in air. \( \text{Nd}_{0.40}\text{Sr}_{0.60}\text{Co}_{0.80}\text{Fe}_{0.20}\text{O}_{3-\delta} \) showed the best catalytic activity for oxygen reduction at the intermediate temperature (873 – 1073 K)\cite{68}. Chou et.al examined the room-temperature mechanical properties of a mixed-conducting perovskite \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Co}_{0.80}\text{Fe}_{0.20}\text{O}_{3-\delta} \) synthesized by glycine nitrate combustion method. The Young’s and shear modulus slightly increased with increasing strontium content. Young’s modulus of 151-188 Gpa and shear modulus of 57-75 Gpa were measured. Biaxial flexure strength of \( \sim 160 \) Mpa was measured for lower Sr content batches. Strength greatly decreased to \( \sim 40 \) Mpa at higher Sr concentrations \((x = 0.6 – 0.8)\) because of the formation of extensive cracking. Indentation toughness showed a higher value \((\sim 1.5 \text{ Mpa.m}^{1/2})\) for Sr \((x=0.2)\) content and a lower value \((\sim 1.1 \text{ Mpa.m}^{1/2})\) for the other batches \((x=0.4-0.8)\). Current results shown that LSCF materials with lower Sr content have acceptable mechanical properties to be used as potential cathodes for ITSOFCs\cite{69}. Sahibzada et.al have studied the AC impedance spectroscopy for the Pd added porous \( \text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-\delta} \) cathode supported on \( \text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-\delta} \) electrolyte. The optimum Pd loading resulted in 3-4 times lower cathodic impedance in the temperature range 673 – 1023 K. The overall cell resistance for unit SOFC was found to decrease by 15% at 923 K and 40% at 823 K when Pd was added to the \( \text{La}_{0.60}\text{Sr}_{0.40}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-\delta} \) cathode. This suggested that the SOFC became more limited by the performance of the cathode at lower temperature and hence the greater effect of Pd promotion\cite{70}. Mantzavinos et.al have investigated the effect of temperature, ambient oxygen partial pressure and composition on the extent of oxygen deficiency for \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \) based perovskites electrochemically by means of solid electrolyte coulometry. They found that the degree of oxygen non-
stoichiometry(δ) increased with increasing temperature, decreasing oxygen partial pressure and increasing Sr or Co content. Transient re-equilibrium experiments were also performed in an attempt to investigate the oxygen transport characteristics of the perovskite under various operating conditions. These experiments have shown that the time needed for re-equilibration increases with increasing oxygen deficiency[71].

2.1.5 Other new type of cathode materials

A number of new cathode materials have been proposed for SOFC application. The advantages and problems associated with this new type of cathode materials are summarized below from recent literature.

Tikhonova et.al have studied the structural, thermal, electrical and electrochemical properties of the electrode materials $\text{La}_{0.60}\text{Sr}_{0.40}\text{Mn}_{1-x}(\text{Co},\text{Ni})_x\text{O}_3.5$, where $x = 0-0.05$. The manganite conductivity raised at room temperature from 250 to 700 Scm$^{-1}$ at $x = 0$ and $x = 0.02$, respectively. At 300-1100 K, all samples have metallic conduction; samples with $x = 0.02$ have the maximum conductivity. The coefficient of linear thermal expansion was virtually independent of the doping and varied in the region $(13.9-14.6) \times 10^{-6}$ K$^{-1}$. Introducing additives of transition metals in $\text{La}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$ reduced the polarization resistance of the gas-electrode-solid electrolyte interface[72]. Chiba et.al have found that the $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3.5$ satisfied the important requirements for a cathode, if $x$ in this system was around 0.4. This system had its highest electronic conductivity of 580 Scm$^{-1}$ at 1073 K, when $x$ in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3.5$. This value was more than three times higher than that of $\text{La}_{0.80}\text{Sr}_{0.20}\text{MnO}_3$ (180 Scm$^{-1}$). The average thermal expansion coefficient of $\text{LaNi}_{0.60}\text{Fe}_{0.40}\text{O}_3.8$ from 303 to 1273 K was relatively low ($11.4 \times 10^{-6}$ K$^{-1}$) and closer to the 8 mol.% YSZ value ($10.0 \times 10^{-6}$ K$^{-1}$) than $\text{La}_{0.80}\text{Sr}_{0.20}\text{MnO}_3.8$ ($12.0 \times 10^{-6}$ K$^{-1}$)[73]. Kindermann et.al have investigated the physicochemical compatibilities of the series of $\text{LaFe}_3$ based perovskites such as, $\text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{M}_{0.20}\text{O}_3.5$ and $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.90}\text{Fe}_{0.80}\text{M}_{0.20}\text{O}_3.5$ ($M = \text{Cr, Mn, Co, Ni}$) with the solid electrolyte 8 mol.% YSZ. They found that the chemical reactions between YSZ and the perovskites $(\text{La}_{0.60}\text{Sr}_{0.40})_{1-z}\text{Fe}_{0.80}\text{M}_{0.20}\text{O}_3.5$ ($z = 1, 0.9, M = \text{Cr, Mn, Co, Ni}$) led to the development of $\text{La-Sr-Fe-M-O}$ base perovskites with high chemical compatibility with YSZ[74].

Hole et.al have evaluated the perovskites with nominal compositions $(\text{La}_{0.80}\text{Sr}_{0.20})(\text{Fe}_{1-x}\text{Al}_x)\text{O}_3.5$ and $(\text{La}_{0.80}\text{Sr}_{0.20})(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3.5$ ($x$ from 0 to
0.94) as possible SOFC cathodes. As compared with pure perovskites, doping with Sr and Al decreased and increased their specific resistivity respectively. The reaction rate between perovskite materials and YSZ at high temperatures was higher for lanthanum manganites than for lanthanum ferrites, and the partial exchange of cations on ‘B’ sites with Al decreased the reaction rate[75]. Moure et al have found that the YMnO₃ based perovskite, with formula (Y₀.₇₀Ca₀.₃₀)MnO₃₋₈ was chemically compatible with the fluorite type compound CeO₂-Y₂O₃-CaO, and no reaction products have been observed after heat treatments of more than 50 h at 1623 K. The electrical conductivity of the perovskite at 1073 K was high enough for an adequate yield of a cell for intermediate temperatures(IT) made using ceria-yttria electrolyte[76]. Priestnall et al have investigated the new cathode material La₁₋₅Sr₀.₅CuO₄. Bulk electronic conductivity in air has been measured to be around 10⁻² Scm⁻¹, of the same order as other cathode materials. This new cathode material was highly compatible with a YSZ electrolyte substrate and offer a promising cathode[77]. Sasaki et al have investigated the system In₂O₃-ZrO₂ as a cathode material for SOFCs. The two-phase materials consisting of cubic ZrO₂ + bcc In₂O₃ at 70 mol.% InO₁.₅ had almost the same thermal expansion coefficient to that of the electrolyte ZrO₂-Y₂O₃. They found that the ZrO₂ –doped In₂O₃ was a chemically compatible cathode material with ZrO₂ based electrolytes. The In₂O₃-ZrO₂ cathode has a comparable I-V characteristic to other metal and manganite cathode materials[78].

Chiba and Ishii have studied the characteristics of Pr₀.₈₀Sr₀.₂₀Mn₁₋ₓCoₓO₃₋₄ as a cathode material for ITSOFC. When the value of x was less than 0.2, the TEC was very close to that of YSZ. The electrical conductivity of the Pr₀.₈₀Sr₀.₂₀Mn₁₋ₓCoₓO₃₋₄ system decreased gradually as x was increased and exhibited a jump at 0.5. This was the critical point separating semiconductor-like and metallic regions of composition [79]. Erning et al studied the effects of highly dispersed (≤ 0.1 mg/cm²) catalysts (e.g. Pd, Pt, Ir and Ru) on the electrochemical performance of screen printed La₀.₈₄Sr₀.₁₆MnO₃₋₄ cathode. At typical operating conditions (e.g. T = 1273 K, η=-0.1 V), the current density in presence of palladium was increased by about one order of magnitude as compared to the current density obtained with pure La₀.₈₄Sr₀.₁₆MnO₃₋₄ cathodes. At the same time, the apparent activation energy of the oxygen reduction reaction decreased from ≈ 2 eV (without catalyst) to ≈ 1 eV (with Pd)[80]. Takeda et al have studied the ruthenium pyrochlores, A₂Ru₂O₇₋₄ (A=Pb, Bi) and ruthenium
perovskites, ARuO₃ (A= Cu, Sr) as new electrode materials for SOFC. The pyrochlores showed low cathodic overpotential even at 1073 K, metallic behaviour with high electrical conductivity, and no reaction with YSZ at 1173 K. The thermal expansion coefficient of the bismuth pyrochlore was compatible to 8 mol.% YSZ. The pyrochlores were very attractive for application as cathode materials in a SOFC with low operating temperature[81].

2.2 Survey and selection of electrolyte materials

The main function of the SOFC electrolyte is to conduct ions between the anode and cathode. The electrolyte carries the ions produced at one electrode to the other electrode to balance the charge of the electron flow and complete the electrical circuit in the fuel cell. The conducting ions must be or contain one of the elements present in the fuel and/or oxidant. The electrolyte also separates the fuel from the oxidant in the fuel cell.

2.2.1 The basic requirements of an ideal SOFC electrolyte

The oxide ion conducting solid electrolyte is the main material, which needs to work without any detrimental phase changes across the cathode-electrolyte interface in SOFC. Under the SOFC operation conditions the electrolyte will normally be subjected to a wide oxygen potential difference owing to the presence of H₂, CO, CO₂, CH₄(fuel) and O₂(oxidant) in the respective compartments. Very high oxide ion conductivity, preferably higher than 0.1 S cm⁻¹ is necessary so that the internal resistance loss per cell is well below 100 mV. When the conductivity value is lower than 0.1 S cm⁻¹, the electrolyte must be fabricated in the form of very thin film that must normally be supported by a porous substrate. The electronic conductivity of the electrolyte material must be very low, or else, this will cause the loss in energy due to internal short-circuiting.

The electrolyte material is expected to have very high crystallographic and thermo-chemical stability under the component fabrication and the cell operation conditions, which normally involve long time annealing procedures. Normally the electrolyte surface is in close contact with the cathode and the anode substrates that are bathing in the respective gas atmospheres. If, the thermal compatibility between the functional components is not stable, this will result in atomic interdiffusion across the interface. This ends in phase transformation with large volume changes causing break down in the temperature cycling under the oxygen potential gradient. So, the
Electrolyte must be chemically compatible with the other cell components, not only at the operating temperature, but also at the much higher temperature at which the fuel cell ceramic structure is fabricated. The thermal expansion of the electrolyte must match (from room temperature to operation and fabrication temperatures) that of other cell components to avoid cracking and delamination during fabrication and operation, including thermal cycling. Further, the electrolyte must be dense (or contain no connected porosity) to prevent gas cross leakage. The electrolyte material must be impervious to both oxidant (oxygen) and fuel (hydrogen) gases between room temperature and operating temperature. In addition to these requirements, other desirable properties for the SOFC electrolyte are high strength and toughness, fabricability and low cost.

2.2.2 Stabilized zirconia electrolytes

Pure ZrO₂ does not serve as a good electrolyte because its ionic conductivity is too low, and it has disruptive phase transformations on heating and cooling. Doping ZrO₂ with certain divalent or trivalent oxide can stabilize the cubic fluorite phase and, at the same time, increase its oxygen vacancy concentration. This enhances the ionic conductivity and extends the oxygen partial pressure range of ionic conduction, making stabilized ZrO₂ suitable for use as electrolyte in SOFC. In general, fully stabilized ZrO₂ is preferred as SOFC electrolyte in order to realize maximum conductivity. The use of fully stabilized ZrO₂ also avoids the problems of phase transformation and conductivity deterioration associated with the partially stabilized materials during cell operation. The ionic conductivity of stabilized ZrO₂ obviously depends on dopant and dopant concentration.

Yttria stabilized zirconia exhibits ionic conductivity higher than 0.1 S cm⁻¹ at 1273 K and the electronic conductivity is less than 10⁻⁴ S cm⁻¹ in the entire oxygen potential range used for the SOFC operation. The maximum conductivity is observed at about 10 mol.% yttria substitution. The YSZ electrolyte is generally fabricated as a polycrystalline dense film. Of the various techniques employed to make thin YSZ electrolyte layers, the particulate approach involves compaction of YSZ powder in to the desired shape, and densification at elevated temperature. Examples of the particulate approach are tape casting and tape calendaring. The deposition approach involves the formation of thin layer of YSZ on a support by a chemical or physical process. Examples of the deposition approach are electrochemical vapour deposition
(EVD) and plasma spraying. But, ZrO₂ reacts with LaMnO₃ to form insulating phases such as La₂Zr₂O₇ at the interface at very high temperatures. The thermal expansion coefficient of undoped ZrO₂ single crystals is about 8.12 x 10⁻⁵/K in the temperature range of 393 to 1453 K[82].

Rajiv Dayal et.al have prepared zirconia and yttria stabilized zirconia powders by sol-gel synthesis. Addition of yttria increased the thermal stability of the tetragonal phase, while the crystallite size for the transformation remained unchanged[83]. Noguchi et.al have measured the tensile strength of YSZ polycrystals (YSZ-P) by a newly developed tensile testing method with a rectangular bar. The tensile strength of YSZ-P was lower than that of the three-point bend strength, and the shape of the tensile strength distribution was quite different from that of the three-point bend strength distribution[84]. Chartier et.al have investigated the effect of the processing route on both the sintering and mechanical properties of a stabilized zirconia. They have found that the tape cast materials exhibit an enhanced densification and grain growth, and improved mechanical properties compared to pressed ones[85]. Ishizaki et.al have studied the effect of alumina additions to YSZ(AAZ). The electrical resistivity of YSZ was increased by alumina addition. The V-I characteristics have shown that the fuel cell performance using AAZ depended mainly on the electrical resistance of AAZ electrolyte and electrodes. Therefore, alumina addition to YSZ had no effect on the fuel cell performance, except increasing the electrical resistance of AAZ electrolyte. Also, alumina addition to YSZ improved the mechanical strength[86]. Ikuma have determined the oxygen tracer diffusion coefficient in yttria – tetragonal zirconia polycrystals (Y-TZP, 2.75 mol.% Y₂O₃ in ZrO₂) using microbalance and quadrupole mass spectrometer over the temperature range: 923 – 1473 K. They found that the transport number of oxygen ion Y-TZP was close to unity[87].

Pal and Singhal have studied the growth of YSZ electrolyte films by the electrochemical vapour deposition (EVD) process and found to be parabolic with time. The rate controlling step in the EVD process was identified to be the electronic transport (diffusion of electrons) through the electrolyte film. Finally it was demonstrated that the electrochemical transport that occurs during EVD was similar to the phenomena of oxygen semi-permeability wherein electrons migrated from the low oxygen partial pressure side to the high oxygen partial pressure side and oxygen
ions migrated in the reverse direction maintaining electro-neutrality[88]. Ishihara has prepared the YSZ films by electrophoretic deposition (EPD) method. Dense YSZ films with uniform thickness can be readily prepared with EPD method by using acetyl acetone as a solvent. The open circuit voltages of SOFC, for which the YSZ films were obtained by the EPD method, increased with increasing number of deposition and calcination steps and attained a theoretical open circuit voltage value above 5 repetitions. When the planar SOFC was fabricated by using La_{0.60}Sr_{0.40}MnO_3 as cathode and electroless plated Pt as an anode, the open circuit voltage and the maximum power density attained were 1.03 V and 1.84 W/cm^2, respectively[89-90]. Chen et al. have prepared a dense, homogeneous and crack-free thin films (0.2 – 2 μm in thickness) of (ZrO_2)_{0.84}(YO_{1.5})_{0.16}(YSZ) on dense or porous substrates at temperature not exceeding 873 K using a solution – deposition technique. To obtain continuous substrates, higher viscosity of the precursor and multiple depositions were needed. Fine-grain(200Å) crack-free films of cubic YSZ were obtained at temperature not exceeding 873 K. The deposited films were be considered for electrolyte application for ITSOFCs[91].

Steele has reviewed the oxygen transport and exchange in oxide ceramics for SOFC. It was the relative magnitude of oxygen ion vacancy and electronic charge carrier concentrations and mobilities which determined whether oxide materials can function at effective electrolyte or electrode components. Oxygen ion vacancies were also involved in the cathodic reduction of oxygen and influenced the magnitude of the exchange current density which can be measured by isotopic oxygen exchange measurements[92]. Shukla and Gopalakrishnan have summarized the various type of oxygen-ion electrolytes and outlined the strategy for the identification and synthesis of improved materials[93].

Ishii and Chiba have examined the performance of SOFC using cubic stabilized zirconia in ZrO_2-Sc_2O_3-Al_2O_3 system as an electrolyte. The maximum power density obtained was 0.63 W/cm^2 at 1073 K and 1.0W/cm^2 at 1153 K using a thin plate electrolyte (thickness: 0.2mm). The current-voltage performance of the fuel cell suggested that this electrolyte was promising for low temperature operation in the 1073 – 1173 K[94]. Soho and Morinaga have fabricated the YSZ ceramic plates by extrusion which exhibited suitable performance as the electrolytes in planar SOFC. They obtained the YSZ film with dense and thickness under 100 μm. By this method
of fabrication, they reduced the production costs\[95\].

Uchida et al. have studied the polarization behaviour of porous platinum and \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) cathodes with zirconia electrolytes with various ionic conductivities (\( \sigma_{\text{ion}} \)). The exchange current density, \( j_0 \), on Pt cathode was not influenced by the \( \sigma_{\text{ion}} \) at 1173 and 1273 K, whereas \( j_0 \) increased proportionally to \( \sigma_{\text{ion}} \) at lower temperature of 1073 K. They found that the cathodic performance was controlled by the transport of \( \text{O}^2^- \) at the interface when the surface reaction rate was sufficiently high\[96\]. Du et al. have developed a procedure to prepare thin (wall thickness 0.25 – 0.35 mm) tubes, as tubular electrolytes for SOFCs from YSZ by way of extrusion with either water-based additives, or organic additives. With the water based additive system, the degree of success in producing tubes with defined shapes was higher than that of the organic system\[97\].

Basu et al. have used high-quality fragitive pyrolytic carbon (PyC) film as an interlayer material in fabricating SOFCs by electrophoretic deposition. For the preparation of zirconia electrolytes on \( \text{LaMnO}_3 \) cathodes, it was shown that an ordered and uniformed carbon interlayer was required. A high-quality (gastight, continuous, crack-free and well adherent with the porous substrate) zirconia electrolyte film on doped – \( \text{LaMnO}_3 \) was obtained when the substrate tubes were coated with PyC within the temperature range 998 – 1048 K. Tube and film cracking occurred when the carbon interlayer was deposited under conditions corresponding to disordered carbon (higher temperature; residence time > 14 s). This technique of PyC formation showed promise for replacing sputter-coating technique used previously to make fragitive carbon interlayers for electrophoretically deposited zirconia electrolytes in SOFCs\[98\].

Basu et al. have demonstrated the electrophoretic deposition method via simple suspension chemistry (8 mol.% YSZ particles in acetic acid) to obtain thin (10-50 \( \mu \text{m} \)) zirconia electrolyte films on porous air-electrode-supported (AES) SOFC cathode doped \( \text{LaMnO}_3 \) tubes. This process yielded films of similar quality to those from conventional approaches (such as electrochemical vapor deposition), but at potentially much less expense\[99\].

2.2.3. \( \text{LaGaO}_3 \) based electrolyte materials

2.2.3.1 Preparation and characterization of \( \text{LaGaO}_3 \) based electrolyte materials

It is reported that partially substituted lanthanum gallate based perovskite
oxides exhibit high oxide ion conductivity at relatively lower temperature (<1073 K), which is comparable with that of YSZ at 1273 K over a broad range of oxygen partial pressure values in SOFC[100]. These LaGaO$_3$ based powders prepared by glycine nitrate combustion synthesis in different compositions partially substituted with 10 – 20 mol.% Sr or Ba in the ‘A’ site and 15 – 20 mol.% Mg on the ‘B’ site of the perovskite structure exhibited higher conductivity than YSZ. The superior electrical and chemical properties make it a candidate for use as the solid electrolyte in ITSOFC [101]. The increased conductivity in the gallates was attributed to both the greater oxygen ion mobility and a greater concentration of oxygen ion vacancies relative to YSZ[102]. This LaGaO$_3$ based oxide partially substituted with Sr for La and Mg for Ga sites (LSGM) exhibits the high oxide ion conductivity stable over wide oxygen partial pressure range.

Drennan et.al have prepared the La$_{0.90}$Sr$_{0.10}$Ga$_{0.80}$Mg$_{0.20}$O$_{3-\delta}$ perovskite oxide by solid state reaction and measured the conductivity at 1073 K as 0.12 Scm$^{-1}$[103]. At 1273 K, the ionic conductivity of La$_{0.90}$Sr$_{0.10}$Ga$_{0.80}$Mg$_{0.20}$O$_{3-\delta}$ was higher by a factor of two compared to ZrO$_2$ doped with 8 mol.% Y$_2$O$_3$. However, it was similar to that of ZrO$_2$ doped with 9 mol.% Sc$_2$O$_3$. Huang et. al have synthesized Sr- and Mg- doped LaGaO$_3$ powders from a acetate salt solution (Sol gel synthesis)[104]. The impedance spectra on a 93% dense sample exhibited no grain – boundary contribution and an ac conductivity of 0.11 Scm$^{-1}$ at 1073 K. The powder X-ray diffraction data showed that the crystallization of a perovskite phase was initiated at a calcining temperature at 873 K. The formation of single phase LSGM phase cubic form was completed only by 1573 K, with internal sintering occurring at 1623 K.

Maffei et.al have reported a simple nitrate synthesis route for LaGaO$_3$ based electrolyte. This new nitrate process yielded material that is phase pure without the need of any complicated or elaborate processing steps and can thus be easily scaled up. A NiO – CeO$_2$ anode performed well with both La$_{0.60}$Ca$_{0.40}$Fe$_{0.80}$Co$_{0.20}$O$_{3-\delta}$ perovskite and La$_{0.60}$Sr$_{0.40}$CoO$_{3-\delta}$ perovskite cathodes. The La$_{0.60}$Ca$_{0.40}$Fe$_{0.80}$Co$_{0.20}$O$_{3-\delta}$ performance was slightly inferior to the La$_{0.60}$Sr$_{0.40}$CoO$_{3-\delta}$ cathode. Nevertheless, it performed well and can be considered a viable cathode material for LSGM based fuel cells[105]. Thangadurai et.al. have shown that isovalent substitution of Mn(II) for Mg (II) in the most promising oxide ion conductor La$_{0.90}$Sr$_{0.10}$Ga$_{0.80}$Mg$_{0.20}$O$_{3-\delta}$ yielding a new oxide ion conductor (La$_{0.90}$Sr$_{0.10}$Ga$_{0.80}$Mn$_{0.20}$O$_{3-\delta}$) exhibiting a conductivity
(σ=4.6x10^{-2} Scm^{-1} at 1073 K) that is comparable to the conductivity of Mg (II) analogue. The Mn(II) oxide has a lower activation energy for conduction (E_a = 0.47 eV) than the Mg (II) oxide[106].

Similarly, Litty Sebastian et.al have reported the preparation of LaGaO_3 based perovskite oxide of the general formula La_{0.90}Sr_{0.10}Ga_{0.80}M_{0.20}O_3 (for M= Mn, Co, Ni, Ca and Zn)[107]. All these oxides exhibited high electrical conductivity (σ~10^{-2} Scm^{-1} at 1073 K) comparable to that of the best perovskite oxide ion conductor La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3 (σ ~ 8x10^{-2} Scm^{-1} at 1073 K). While M= Mn, Co, Ni, Cu members appeared to be mixed conductors with a variable electronic contribution to the conductivity, especially at high oxygen partial pressure (P_{O_2} ≥1 atm) arising from mixed – valency of the transition metals, the M= Zn (II) phase was a pure oxide ion conductor exhibiting conductivity (σ ~ 1.5x10^{-2} Scm^{-1} at 1073 K) that is slightly lower than that of LSGM. The lower conductivity of the M= Zn (II) derivative was ascribed to the preference of Zn(II) for tetrahedral oxygen coordination.

Audinot et.al have synthesized LaGa_{1-x}Ni_{x}O_3 (x ≤0.50). The chemical analysis of these materials have shown that both the oxygen non-stoichiometry(δ) and the electron carrier concentration increased with the substitution of nickel for gallium [108]. While LaGaO_3 is an insulator, the Ni-doped phases were semi-conducting and behave as a metal for the highest nickel contents. The dilatometric features versus temperature showed that these materials were mechanically compatible with the electrolyte La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3. In addition, their chemical composition did not change at high temperature. All these characteristics make Ni-doped LaGaO_3 based materials as good candidates for cathodes of SOFCs.

Ishihara et.al developed a new solid electrolyte (La_{0.90}Nd_{0.10})_{0.80}Sr_{0.20}Ga_{0.80}Mg_{0.20}O_3 which exhibited pure oxide ion conduction over the oxygen partial pressures from 1 to 10^{-21} atmosphere and the electrical conductivity attained the value of log (conductivity) Scm^{-1} = -0.5 at 1223 K[109]. These researchers have also prepared other rare earth based doped lanthanum gallates for SOFC application[110]. Recently, it was reported that PrGaO_3 doped with Sr and Mg for the Pr and the Ga sites, respectively, exhibited the high oxide ion conductivity, which was comparable to that of Sr and Mg substituted LaGaO_3. The highest oxide ion conductivity at temperatures higher than 1073 K was obtained for the
composition of $Pr_{0.91}Sr_{0.07}Ga_{0.85}Mg_{0.15}O_3$ [111].

2.2.3.2 Physico-chemical characterization of LaGaO$_3$ based electrolyte materials

Due to high ionic conductivity values, the LaGaO$_3$ based materials are effectively used and chosen as alternative electrolytes for ITSOFC systems. Yamaji et al. have measured the electron and hole conductivity of La$_{0.90}$Sr$_{0.10}$Ga$_{0.80}$Mg$_{0.20}$O$_{3.6}$ by ion blocking method [112]. They found that in a region of $Po_2 > 10^{-5}$ atm., the hole conduction is dominant and proportional to $Po_2^{1/2}$. The transference number of hole is 0.012 at 1273 K at $Po_2 = 0.21$ atm. and it decreased with decreasing temperature. The optimum thickness was calculated from oxygen permeability and joule loss and was found to decrease with decreasing temperature. It is 10 $\mu$m at 873 K under current flow of 0.5 Acm$^{-1}$. Decrease in temperature made the transference number of holes small. Recently, Anderson et al. have reported the ionic and electronic conduction in La$_{0.95}$Sr$_{0.05}$Ga$_{0.93}$, La$_{0.93}$Sr$_{0.05}$AlO$_{3.6}$, Y$_{0.93}$Sr$_{0.05}$AlO$_{3.6}$ as a function of oxygen partial pressure ($Po_2$ - ranging from air to $10^{15}$ Pa) and temperature ranges between 1073 – 1273 K [113]. La$_{0.95}$Sr$_{0.05}$Ga$_{0.4}$ samples had the highest ionic conductivity with only a minor p-type contribution in air and an ionic domain extending to high $Po_2$ levels. They have shown that these materials were stable with large $Po_2$ domains and exhibited negligible n-type conductivity even under reducing conditions typical of fuel rich atmospheres.

Huang and Petric have investigated the solid solution range and conductivity of Sr and Mg-doped LaGaO$_3$ perovskites [114]. The solid solution range can be extended by balancing the oxygen vacancies created by doping Sr and Mg ion at A and B sites, respectively. Dopants on both sides enhanced the oxygen ion conductivity, but the oxygen vacancies originating from doping Sr for La had resulted in lower activation energy. They have shown that La$_{0.90}$Sr$_{0.20}$Ga$_{0.90}$Mg$_{0.10}$O$_{3.6}$ exhibited the highest conductivity at temperature below 973 K (7.14 X $10^{-2}$ Scm$^{-1}$ at 973 K, 2.92 X $10^{-2}$Scm$^{-1}$ at 873 K), while La$_{0.80}$Sr$_{0.20}$Ga$_{0.85}$Mg$_{0.15}$O$_{3.6}$ had the highest value at temperatures above 973 K (0.14 Scm$^{-1}$ at 1073 K. Gharbage et al. have carried out the high temperature electrochemical permeability measurements with La$_{0.90}$Sr$_{0.10}$Ga$_{1-x}$Fe$_x$O$_{3.6}$ [115]. They confirmed that Fe plays an important role in determining the p-type conductivity of this family of materials. The increase in p-type conductivity with Fe was explained by the formation of Fe$^{4+}$ ions under oxidizing conditions. This is in tune with a small polaron type conduction mechanism.
activation energy for p-type conductivity was found to be in the range 0.9 – 1 eV,
lower than that usually observed for alternative electrolytes based in zirconia or ceria.
Wolfenstein et al. have measured the creep behaviour of $La_{0.80}Sr_{0.20}Ga_{0.85}Mg_{0.15}O_3.5$
over the temperature range 1473 to 1573 K in air[116]. A comparison of the
activation energies determined by ionic conductivity, oxygen tracer diffusion and
theoretical predictions revealed that the creep rate of $La_{0.80}Sr_{0.20}Ga_{0.85}Mg_{0.15}O_3.5$ was
controlled by cation lattice diffusion. Similarly, Wolfenstein had experimentally
measured and compared the intrinsic resistance of cubic zirconia with
$La_{0.80}Sr_{0.20}Ga_{0.85}Mg_{0.15}O_3.5[117]$. The results revealed that the intrinsic creep
resistance of cubic zirconia was much higher than that of doped lanthanum gallate
($La_{0.80}Sr_{0.20}Ga_{0.85}Mg_{0.15}O_3.5$) over the entire temperature range. This is most likely a
result of the difference in the complexity of crystal structure. Goodenough et al. found
out that $La_{0.80}Sr_{0.20}Ga_{0.85}Mg_{0.17}O_3.5$ exhibited stable conductivity of 0.166 and 0.079
Scm$^{-1}$ at 1073 K and 973 K respectively and concluded that it is purely an oxide ion
conducting phase and it is the most promising candidate for thick membrane
electrolytes (>100 μm) for ITOSFC[118]. Hrovat et al. have studied the subsolidus
equilibria in air in the $La_2O_3 - Ga_2O_3 - NiO$ system at 1573 K with the aim of
obtaining information on possible interactions between a $LaGaO_3$ based solid
electrolyte and NiO during preparation of the anode in SOFC[119]. The results
indicated that NiO had not undergone any reaction with “pure” $LaGaO_3$. Huang et al.
have studied the chemical reactions between two cathode materials,
$La_{0.84}Sr_{0.16}MnO_3.6$, $La_{0.50}Sr_{0.50}CoO_3.6$, and the electrolyte $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3.6$
[120]. Significant interdiffusion of Co into
$La_{1.1}Sr_{1}Ga_{1.2}Mg_{0.3}O_3.8$ and Ga into $La_{1.1}Sr_{1}CoO_3.8$ were found at the interface even at
relatively low fabrication temperatures. In contrast, only small interdiffusion of Mn
into $La_{1.1}Sr_{1}Ga_{1.2}Mg_{0.3}O_3.8$ and Ga into $La_{1.1}Sr_{1}MnO_3.8$ were detected at the
$La_{1.1}Sr_{1}MnO_3.8 / La_{1.1}Sr_{1}Ga_{1.2}Mg_{0.3}O_3.8$ interface, though it was fired at 1743 K for
36 h. Considering both the small interdiffusion reactions between $La_{1.1}Sr_{1}MnO_3.8$ and
$La_{1.1}Sr_{1}Ga_{1.2}Mg_{0.3}O_3.8$ and their similar thermal expansion coefficients,
$La_{1.1}Sr_{1}MnO_3.8$ could be an appropriate cathode material for $La_{1.1}Sr_{1}Ga_{1.2}Mg_{0.3}O_3.8$
based fuel cells. Slater et al. have studied the actual structure of
$La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3.6$ based solid electrolyte by using high resolution powder
neutron diffraction technique[121]. It was shown that the room temperature structure of the new fast ion conducting solid electrolyte $\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3.3}$ is monoclinic, rather than orthorhombic, as for the undoped parent phase $\text{LaGaO}_3$.

**2.2.3.3 Performance characteristics of $\text{LaGaO}_3$ based ITSOFCs**

The ITSOFCs with new alternate solid electrolytes (having high oxide ion conductivity) were studied for power generation applications with high energy conversion efficiency. Feng et al. have constructed the SOFC with doped lanthanum gallate electrolyte material and tested from 873 to 1073 K[122]. Both ceria and the lanthanum gallate electrolyte material were mixed with NiO powder respectively to form composite anodes. Doped lanthanum cobaltite was used exclusivity as the cathode material. Power density realized was 0.336 W/cm$^2$, which was 70% of theoretical value 0.517 W/cm$^2$ (thickness - 395 μm, electrolyte conductivity - 0.07 S/cm$^{-1}$ & OCV = 1.08V) using Ni/LSGM anode. Huang et al. have studied the electrode performance of a single SOFC using a 500 μm thick $\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3.3}$ electrolyte membrane[123]. Comparison of $\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ and $\text{La}_{0.90}\text{Sr}_{0.10}\text{MnO}_3$ as cathodes showed $\text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$ gave an exchange current density two orders of magnitude higher than that of $\text{La}_{0.90}\text{Sr}_{0.10}\text{MnO}_3$. Comparison of CeO$_2$/Ni and LSGM/Ni anodes showed a degradation of the latter with time. The anode – electrolyte interface and the reactivity of NiO and LSGM suggest better anode performance can be obtained with a buffer layer that prevents formation of $\text{LaNiO}_3$. The cell performance showed that, with a proper choice of electrode materials and LSGM as the electrolyte, a SOFC operating at temperatures $973 \text{ K} < T_{op} < 1073 \text{ K}$ is a realistic goal.

Ishihara has assembled and tested SOFC consisting of $\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.20}\text{Mg}_{0.20}\text{O}_3$, Ni and $\text{La}_{0.90}\text{Sr}_{0.10}\text{CoO}_3$ as the electrolyte, anode and cathode respectively[124]. The maximum power density was as high as 1.01 W/cm$^2$ at 1273 K despite the low thickness (0.5mm) of the electrolyte plate. The attained maximum power density of cells with $\text{LaGaO}_3$ based electrolyte was three times larger than that of YSZ at 1273 K, an order of magnitude larger than that at 973 K. High power density of SOFC at low temperature seems to be due to the high oxide ion conductivity of $\text{LaGaO}_3$ based perovskite and the high electrocatalytic activity of $\text{La}_{0.90}\text{Sr}_{0.10}\text{CoO}_3$ cathode for the dissociation of oxygen molecules to oxide ions. Ishihara et al. have found that the Ni and doped SmCoO$_3$ ($\text{Sm}_{0.60}\text{Sr}_{0.40}\text{CoO}_3$) were
suitable as anode and cathode respectively for SOFC with La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3.5 electrolyte[125]. The maximum power density of SOFC, with these materials, attained a value as high as 1.3 W/cm^2 at 1273 K, despite 0.5mm thickness of electrolyte. Moreover, the power density of the cell was still high, 0.44 W/cm^2 at 1073 K. This power density is about 9 times higher than that of SOFCs where YSZ is used as electrolyte under the same conditions. Yamaji et.al have studied the compatibility of La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3.5[126]. They reported La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3.5 reacted with other components such as alumina tubes or pyrex glass sealant in test cell. It was reported that a significant depletion of B-site ions, especially Ga ion, from the surface outside the effective electrode area in La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_3.5 occurred and the surface morphology was changed from dense to porous.

The reaction of NiO with LSGM (La_{0.80}Sr_{0.20}Ga_{0.83}Mg_{0.17}O_3.5) was prevented by using an interlayer Sm – CeO_2 in between the anode and the electrolyte[127]. It prevented the formation of LaNiO_3. The peak power density of the inter-layered cell was 100mW higher than that of the standard cell without the interlayer. This improvement is due to the significant reduction in the anode over-potential; the over potential of the cathode La_{0.60}Sr_{0.40}CoO_3 remained unchanged. The power density obtained was 550mW/cm^2 at 1073 K. Recently, Goodenough et.al have studied the chemical reactions between the superior perovskite oxide ion conductor Sr- and Mg-doped LaGaO_3(LSGM), CeO_2 and NiO by powder X-ray diffraction[128]. The results showed that an extensive reactivity occurs as a result of La migration driven by a gradient of La chemical activity. La migration across the LSGM/electrode interfaces in a fuel cell leads to the formation of resistive phases at the interface, either LaSrGa_3O_7 or LaSrGaO_4. Use of 40 mol.% La_2O_3 doped CeO_2 as an interlayer between anode and electrolyte as well as in the NiO-containing anode prevents all reactions found. Consequently, the air-H_2 cell maximum power density was increased to nearly 900 mW/cm^2 at 1073 K with a 600 μm thick LSGM electrolyte. No sign of degradation was observed at 1073 K over 2 weeks for an inter-layered cell under a loading current density of 250 mA/cm^2. Yamada et.al have reported increased power density of SOFC by doping small amount of Co to LaGaO_3 electrolyte[129]. Increasing the amount of doped Co monotonically enhanced the hole conduction resulting in a decrease in the OCV and an increase in the amount of leaked oxygen
which results in diminished electric power. Consequently, it became clear that the optimized composition for this electrolyte was \( \text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3.8} \), considering the power density and the amount of oxygen leakage. Although the thickness of electrolyte with the above composition was 0.5mm, a maximum power density obtained was 242 mW/cm\(^2\) at 1073 K. Yamaji et al. have investigated the chemical stability of \( \text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3.4} \) as an SOFC electrolyte in humidified hydrogen at 1273 K[130]. After annealing at 1273 K, significant changes were observed in the surface morphology of the electrolyte, and \( \text{La(OH)}_3 \), \( \text{LaSrGaO}_4 \) and some unknown phases were formed, which was interpreted as a result of the vaporization of Ga as \( \text{Ga}_2\text{O} \). After annealing at 1073 K, changes in the morphology were small, but slight amount of Ga depletion was observed. The existence of Pt, which was commonly used as a test electrode to investigate the electrolyte property, increased the rate of the Ga depletion. It was considered that Pt and Ga react and form Pt-Ga alloys if enough amounts of Pt contacts with Ga-contained oxide in reducing atmosphere. To realize the SOFC using \( \text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3.4} \) more efforts are required to decrease the vaporization of the Ga component by adding some other dopants in LSGM, so that one can decrease the operating temperature of SOFC.

Yaremchenko et al. have studied the performance of lanthanum gallate based electrolyte materials with the addition of Co content[131]. The \( \text{LaGa}_{1-x-y}\text{Co}_x\text{Mg}_y\text{O}_{3.8} \) solid solutions with rhombohedrally distorted perovskite structure were ascertained to form in the concentration range of \( 0 \leq y \leq 0.10 \) at \( x = 0.60 \) and \( 0 \leq y \leq 0.20 \) at \( x = 0.35 - 0.40 \). Increasing cobalt content has resulted in an increase in electrical conductivity and thermal expansion of the perovskites. The thermal expansion coefficients of the \( \text{LaGa}_{1-x-y}\text{Co}_x\text{Mg}_y\text{O}_{3.8} \) ceramics were calculated from the dilatometric data to vary in the range of \( 12.4 - 19.8 \times 10^{-6} \, \text{K}^{-1} \) at 300 - 1100 K. Doping \( \text{La(Ga,Co)}\text{O}_{3.8} \) solid solution with Mg has led to increasing oxygen nonstoichiometry, electronic and oxygen ionic conductivity.

Ishihara et al. have found that doping small amount of Fe is effective for improving the oxide ion conductivity in \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3.8} \)[132]. Power density of the SOFC was also increased by doping Fe in LSGM electrolyte due to the increased oxide ion conductivity. The maximum power density close to 700 mW/cm\(^2\) was reported at 1073 K on the cell employing 0.5mm thick \( \text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.80}\text{Mg}_{0.15}\text{Fe}_{0.05}\text{O}_{3.8} \) electrolyte and \( \text{O}_2 \) as oxidant. Ishihara et al.
have also reported the power generation characteristics of SOFC with La$_{0.80}$Sr$_{0.20}$Ga$_{0.80}$Mg$_{0.15}$Co$_{0.05}$O$_{3.5}$ electrolyte[133]. The maximum power density obtained was 1.53 and 0.50 W/cm$^2$ at 1073 and 873 K respectively, when the thickness of electrolyte was 0.18mm. Maric et al have studied the electrode performance using La$_{0.90}$Sr$_{0.10}$Ga$_{0.80}$Mg$_{0.20}$O$_{3.5}$ electrolyte, La$_{0.60}$Sr$_{0.40}$CoO$_{3.6}$ cathode and samaria doped ceria (CeO$_2$)(SmO$_{1.5}$)$_{0.20}$–Ni cermet anode materials[134]. The maximum power density of the cell was 425 mW/cm$^2$ at 1073 K. Ishihara et al have reported the power generation characteristics of cells employing various materials as anodes and cathodes [135]. They have found that the maximum power density of cells increased in the following order, Pt<La$_{0.75}$Sr$_{0.25}$CrO$_{3.4}$<(La$_{0.60}$Sr$_{0.40}$Co$_{0.30}$)$_{0.90}$MnO$_{2.6}$<La$_{0.60}$Sr$_{0.40}$FeO$_{3.5}$<La$_{0.60}$Sr$_{0.40}$CoO$_{3.5}$ for the cathode, and Ru<Pt<Co<Ni for the anode. Also, they have reported that the maximum power density of the SOFC, which consisted of Ni anode and Sm$_{0.60}$Sr$_{0.40}$CoO$_{3.5}$ cathode attained the values 0.44 and 0.14 W/cm$^2$ respectively at 1073 K and 973 K. Due to its very good performance characteristics, the commercialization of LaGaO$_3$ based ITSOFC at intermediate temperature range seems to be a realistic goal. Also, these results indicate the possibility of using ITSOFC for stationary power generation applications in the future.

2.2.4 Partially rare earth substituted ceria based alternate solid electrolytes

2.2.4.1 Physical and electrical properties of ceria based electrolytes

The undoped CeO$_2$ has n-type electrical conduction, and the conduction takes place by a small polaron hopping mechanism. Pure CeO$_2$ has negligible ionic conductivity. CeO$_2$ doped with divalent or trivalent oxides shows relatively high oxygen-ion conductivity at elevated temperatures. Doped CeO$_2$, however, has the tendency to undergo reduction (Ce$^{4+}$ ion to Ce$^{3+}$ ion) at low oxygen partial pressures (with the consequent introduction of electronic defects). This reduction restricts the range of oxygen partial pressure over which the ionic transference number remains close to unity. Thus, at 1073 K the oxygen partial pressure range for predominant ionic conduction in CeO$_2$ limited to about 10$^{-12}$ atm (10$^{-7}$ Pa). The increase in electronic conductivity due to the formation of Ce$^{3+}$, severely restricts the ionic domain of CeO$_2$ based electrolytes so that they cannot be used at high temperatures (> 973 K). In view of the tendency of CeO$_2$ be reduced in a reducing environment, doped CeO$_2$ has been considered for use as SOFC electrolyte, especially at reduced
temperature, because of its high ionic conductivity. Compared to stabilized ZrO₂, doped CeO₂ shows a higher conductivity and a lower conduction activation energy [136].

Chiodelli et al. have found that ZrO₂:CeO₂ materials with high ceria (>50 mol.%) content exhibited a mixed conduction at the SOFC operation temperature, even in air. At lower oxygen partial pressure the electronic component of the conductivity was further increased [137]. Christiansen et al. have measured the oxygen stoichiometry of CeO₂ and Ce₁₋ₓGdₓO₂₋ₓ/₂ (y=0.05, 0.18, 0.4) by a combination of cyclic voltammetry and coulometric titration. The electrochemical cell employed was an oxygen pumping cell, in which the oxide is equilibrated with the atmosphere corresponding to the potential imposed. The maximal number of vacancies introduced by Gd-doping or by reduced oxygen partial pressure was found to be 0.25 vacancy/mol, corresponding to an average cation oxidation number of +3.5 [138]. Steele et al. have measured the ionic and electronic conductivities of Ce(Gd)O₂₋ₓ (CGO) compositions as a function of temperature, oxygen partial pressure and microstructure. The conductivity of co-precipitated Ce₀.₉₀Gd₀.₁₀O₂₋₆ approached the value of 10⁻² Scm⁻¹ at 773 K. Single planar cells were tested incorporating Ce₀.₉₀Gd₀.₁₀O₂₋₆ electrolytes (fabricated by tape casting procedure) coated with Ni-ZrO₂ anodes and La₀.₆₀Sr₀.₄₀Co₀.₂₀Fe₀.₈₀O₃₋₆ cathodes. The excellent performance was recorded with power densities as high as 0.35 W/cm² at 983 K [139].

Sammes and Cai have studied the effect of YSZ additions on (CeO₂)₀.₈₀(GdO₁.₅)₂ materials. They found that between 1 and 5 mol.% 8YSZ and 3YSZ, the ionic conductivity was very similar to CGO with no YSZ additions. However, the ionic domain increased from P₀₂ = 10⁻¹⁵ to 10⁻¹⁷ atm. showing greater stability of the system containing YSZ [140]. Hong et al. have fabricated the polycrystalline ceria doped with several rare-earth oxides (Dy₂O₃, Er₂O₃, Gd₂O₃, Ho₂O₃, La₂O₃, Nd₂O₃, Sm₂O₃ and Yb₂O₃) at various concentrations. They have studied the effect of dopant type and concentration on grain boundary conductivity. They found that the conductivity of doped ceria was found to be a function of both the composition and grain size. The activation energy for conduction through the grains was lower than that for transport across the grain boundaries [141].

Higashi et al. have studied the sintering behaviour rare-earth-doped ceria (Ce₀.₈₀R₀.₂₀O₂₋₆ where R = Yb, Y, Gd, Sm, Nd and La) powder prepared by oxalate
co-precipitation method. The lattice parameter of oxide powders increased linearly with increasing ionic radii of doped rare earth. The grain size of rare-earth-doped ceria after sintering at 1873 K was larger in the samples with larger rare-earth element [142]. Tsoga et al. have synthesized the readily sinterable (at 1523 K) fine crystalline gadolinia doped ceria (CGO) - powder by co-precipitation process. They have also studied the fabrication and characterization of solid solution phases with a graded composition (CGO)x(YSZ)1-x, to be used as an interlayer between YSZ and CGO, in order to avoid delamination. They found that (CGO)x(YSZ)1-x powder prepared by the glycine combustion method required higher sintering temperature (1773 K) to densify and showed significantly lower ionic conductivity than YSZ and CGO. It was attributed to the large lattice deformation and scattering of oxygen ions [143]. Torrens et al. have studied the physical and electrical properties of (CeO2)0.80(GdO1.5)0.20 using powder prepared by co-precipitation reaction and solid state reaction. Co-precipitation technique produced sintered density greater than 98% of the theoretical, when the green body was sintered at 1923 K. It should be noted that even at 1973 K, the samples fabricated from the powder that had been synthesized using the solid state method only reached 85% theoretical density. The ionic conductivity varied between $4.5 \times 10^{-2}$ Scm$^{-1}$ for the powder prepared by solid state techniques to $3.2 \times 10^{-2}$ Scm$^{-1}$ at 1073 K for powder prepared by co-precipitation [144].

Mehta et al. have deposited a thin coat of YSZ over ceria by sputtering and by EVD using CeCl3 as the source of cerium over a range of temperature between 1323 to 1573 K. Thermal treatment at ~1773 K was effective in improving the quality of the film by crack healing. The OCV of cells with YSZ coated disc was consistently higher than those with uncoated discs showing the effectiveness of the film in suppressing the electronic current. When the YSZ-coated side was exposed to oxygen, however, electronic transference number of the film could be kept to a minimum ensuring higher OCV [145]. Van Berkel et al. have developed self-supported electrolytes and electrode supported electrolytes of zirconia and ceria by means of tape casting. It has been shown that SOFCs with self supported electrolytes of thickness 130 μm, utilizing optimized electrodes (Ni/YSZ cermet anode, La0.85Sr0.15MnO3-δ / La0.60Sr0.40Fe0.80Co0.20O3-δ cathodes) could be used in SOFC system in the temperature range of 923 to 1073 K [146].
Van herle et.al have studied the fabrication and sintering behaviour of yttria doped ceria powder. The conductivity values of 0.037 and 0.078 Scm\(^{-1}\) at 973 and 1073 K respectively, were measured for the 20 YDC tape which approached the value of gadolinium-and samarium-doped ceria. The grain boundary resistivity contribution vanished at temperature below 773 K, the projected operation condition for ceria-based cells (973–1073 K). An attractively low activation energy of 0.68 eV was observed in the high-temperature portion of interest\[147\]. Sintering of samaria doped ceria (SDC) was significantly promoted by adding a small amount of gallia. Yoshida et.al found that SDC with 1% of gallia added, sintered at 1723 K, and showed almost the same properties as SDC sintered at 1973 K. Measurements showed that the addition of gallia could reduce the sintering temperature by 423 K without deteriorating the properties of SDC as an electrolyte for SOFCs\[148\].

Hatchwell et.al have studied the chemical compatibility of chromium based interconnect related materials with gadolinia-doped cerium oxide electrolyte. They found that phase pure La\(_{0.80}\)Sr\(_{0.20}\)CrO\(_3\)-\(_3.5\) did not react with CGO even at temperature (at 1873 K for 10 h) well above co-sintering temperature\[149\]. Hrovat et.al studied the sub-solidus equilibria in air in the NiO-CeO\(_2\) and La\(_2\)O\(_3\)-CeO\(_2\)-Fe\(_2\)O\(_3\) systems at 1473 K. Their aim was to investigate the possible interactions between ceria-based solid electrolyte and LaFeO\(_3\) – based cathode or nickel oxide and ceria during sintering of anode material. In NiO-CeO\(_2\) and Fe\(_2\)O\(_3\)-CeO\(_2\) systems, no binary compound and no solid solubility were detected. In the La\(_2\)O\(_3\)-CeO\(_2\)-Fe\(_2\)O\(_3\) system no ternary compound was found. There was no solubility of CeO\(_2\) in LaFeO\(_3\). The results obtained in both systems (i.e., NiO-CeO\(_2\) and La\(_2\)O\(_3\)-CeO\(_2\)-Fe\(_2\)O\(_3\)), indicated that a ceria-based solid electrolyte in SOFC would not react with either NiO on the anode side or LaFeO\(_3\)-based materials on the cathode side\[150\]. Similarly, they studied the subsolidus phase equilibria in the La\(_2\)O\(_3\)-CeO\(_2\)-Co\(_2\)O\(_3\) system in air at 1473 K with the aim to obtain information on possible interactions between LaCoO\(_3\)-based cathode and CeO\(_2\)-based solid electrolyte in SOFC. No ternary compound was found. The results obtained indicated that LaCoO\(_3\) from La(Fe,Co)O\(_3\)-based cathode material did not react with CeO\(_2\)-based solid electrolyte in SOFC\[151\].

Tsoga et.al have found that when a gadolinia-doped-ceria layer was used to protect YSZ against interaction with Co-containing cathodes, the undesirable solid state reaction at the YSZ-CGO interface can be efficiently suppressed when a thin
(≤1μm thick) interlayer with nominal composition of Ce_{0.43}Zr_{0.43}Gd_{0.10}Y_{0.04}O_{2-δ} was incorporated at the interface[152]. Gu et al. have investigated the effect of sintering temperature on the sinterability and electrical conductivity of the Ce_{0.80}Y_{0.20}O_{2-δ} (YDC) electrolyte[153]. YDC powder calcined at temperatures 773 – 1023 K became highly dense (over 98% theoretical density) when sintered at 1773 K, while the YDC powder calcined at 1273 K reached only 93% relative density. The electrical measurements shown that YDC calcined at 1023 K exhibited a higher electrical conductivity, approximately 4 Scm^{-1} at 1023 K in air. Nakagawa et al. have measured the catalytic activity of Ni-YSZ-CeO_{2} anode layer of an internal reforming (IR)-SOFC for the steam reforming of methane. The catalytic activity of the Ni-YSZ-CeO_{2} anode was higher than that of the Ni-YSZ at low temperature as long as the reaction gas contained some hydrogen. They found that a gradual deterioration in the catalytic activity of the anode was observed at low PH_{2} and high PH_{2}O atmosphere, and also at high current densities. This is caused by the oxidation of Ni surface by steam with high PH_{2}O in the reaction gas and that produced via electrochemical oxidation[154].

Zhan et al. have studied the AC impedance of samaria-doped ceria electrolyte CeO_{2-x}(SmO_{1.5})_{x}(0.10 ≤ x ≤ 0.40) in air. The maximum lattice conductivity observed at 873 K was 2 Scm^{-1} for Ce_{0.90}Sm_{0.10}O_{2-δ}. With an increase in samarium concentration, the grain interior conductivity decreased gradually, but the grain boundary conductivity increased dramatically[155]. Arachi et al. have studied the effects on the electrical conductivity and the crystalline structure of the addition of HfO_{2}, CeO_{2} and Ga_{2}O_{3} to ZrO_{2} with 11 mol.% Sc_{2}O_{3}(11ScSZ). They have shown that the cubic phase was stabilized at room temperature by the addition of about 6 mol.% of CeO_{2} and 2 mol.% Ga_{2}O_{3} to 11 ScSZ. No such effect was observed by addition of HfO_{2}. They found that the electrical conductivity of 11 ScSZ decreased by the addition of HfO_{2}, CeO_{2} and Ga_{2}O_{3}[156]. Jurado et al. have synthesized the reactive ceria based solid electrolytes by combustion technique using urea as fuel. The presence of small amounts of titania (1 mol.%) and alumina (1 mol.%) in CeO_{2}0.92(Gd_{2}O_{3})_{0.08} was beneficial, since it produced a significant reduction of the grain boundary resistance. Similarly, they found that the reactivity of the ceria electrolyte against lanthanum-NiO perovskites at high temperature(1748 K), enhanced both the LaNiO_{3-δ} decomposition and the diffusion of Ni and La ions [157].
2.2.4.2 Performance characteristics of ceria based ITSOFCs

The performance of ITSOFCs was studied by several research groups with rare earth doped ceria solid electrolytes. Milliken et al. have demonstrated the 20% samaria-doped ceria SOFC-single cells with power densities of >250 mW/cm² at 973 K and stable performance for 15,000 h[158]. The optimized and screen printed \( \text{La}_{0.60}\text{Sr}_{0.40}\text{CoO}_{3\delta} \) cathode and Ni/CeO₂ cermet anode were used in the single cell testing. Stainless steel 446 had a thermal expansion match to the ceria and was used extensively as a cell holder in single-cell tests. Godickemeier et al. have fabricated dense electrolyte membranes with a thickness of 200 μm by tape casting[159]. The current-voltage characteristics were obtained for single cell with Ce₀.₈₀Sm₀.₂₀O₂₋₅ electrolyte, Ni-ceria cermet anode and \( \text{La}_{0.80}\text{Sr}_{0.16}\text{CoO}_{3\delta} \) cathode. The maximum output was found to be 350 mW/cm² at 1023 K and 225 mW/cm² at 973 K. The open circuit voltage was 0.82 V and 973 K and 0.785 V at 1023 K.

The deposition of an anchoring layer of YSZ particles was used to obtain sufficient adhesion between porous Ce₀.₆₀Gd₀.₄₀O₂₋₅ anode and YSZ electrolyte without detrimental reaction. Single SOFC comprising the Ce₀.₆₀Gd₀.₄₀O₂₋₅ anode, a composite La₁₋ₓSrₓMnO₃₋₅ cathode and the YSZ electrolyte was assembled and tested in \( \text{H}_2/\text{H}_2\text{O} \) and \( \text{CH}_₄/\text{H}_2\text{O} \) atmospheres vs. air in the temperature range 1073 – 1288 K. An area specific internal resistance of 0.39 \( \Omega \text{cm}^² \) at 0.71 V and 470 mW/cm² was obtained at 1273 K[160]. Livermore et al. have studied the methane reforming and carbon deposition characteristics of two nickel/ceria-gadolinia cermet anodes over the temperature range 823–1073 K, for use in intermediate temperature CGO based SOFCs. Planar CGO-based SOFCs with a 280 μm thick CGO electrolyte, prepared by viscous plastics processing, a screen printed two-layer \( \text{La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3\delta} / 30 \text{ mol.\% ceria-gadolinia and La}_{0.60}\text{Sr}_{0.40}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3\delta} \) cathode and screen printed Praxair 85 mol.% Ni/CGO anode, gave a maximum power density of 90 mW/cm² at a cell temperature of 873 K. The assembled cell gave excellent durability over 100 h operation and temperature cycling with less than 2 % loss of power[161]. Ohara et al. have investigated the influence of Ni content in Ni – SDC( Ce₀.₈₀Sm₀.₂₀O₂₋₅) cermet on the electrode performance in order to come out with the most suitable microstructures. It was found that anodic polarization was strongly influenced by the Ni content in Ni-SDC cermets. The best results were obtained for anode cermets
with Ni content of around 50 vol.%, anodic polarization was about 30 mV at a current density of 300 mA/cm². This Ni-SDC anode have shown good stability as well as high performance[162].

Uchida et.al have developed and used a samaria-doped ceria interlayer to avoid unfavourable solid-state reaction when using La(Sr)CoO₃ as a cathode on yttria-stabilized zirconia electrolyte[163]. They have prepared a porous La(Sr)CoO₃ cathode on a thin dense SDC interlayer which exhibited very high performance even at 1073 K. The performance was enhanced further by dispersing a small amount of nanometer-sized Pt catalysts on the La(Sr)CoO₃ surface. The current density on the Pt-LSC cathode at an overpotential of -0.05 V was 0.6 A/cm² at 1073 K in O₂. Inagaki et.al have demonstrated ITSOFC with 0.5 mm thick La₀₆Sr₀₄Co₀₂₀₀₃-δ electrolyte, La₀₆Sr₀₄Co₀₂₀₃-δ cathode and Ni-(CeO₂)₀.₆₀(SmO₁₅)₀.₀₂ cermet anode. The cell showed an excellent initial performance and maximum power density (0.47 W/cm²) at 1073 K. They found that the calcination of La₀₆Sr₀₄Co₀₂₀₃-δ powder could be possible way to suppress interdiffusion at the interface[164].

Huijsmans et.al have demonstrated the 5x5 cm² ITSOFCs with 115 μm thick 10 CGO electrolytes, La₀₆Sr₀₄Fe₀₂₀₀₃-δ cathodes, conventional type anode and with ferritic steel separator plate. The cells delivered maximum power densities in excess of 200 mW/cm² at temperature 873 K. Operating such cells at 973 K resulted in maximum power densities of around 500 mW/cm²[165]. Lane et.al have shown that the AC impedance spectroscopy confirmed the interfacial polarisation at the electrode/electrolyte interface between La₀₆Ca₀₄Fe₀₂₀₀₃-δ and Ce₀₉Sm₀₁₀O₂-δ was low compared to similar materials on YSZ electrolyte. Electrical conductivity of La₀₆Ca₀₄Fe₀₂₀₀₃-δ was less than that of materials containing a greater proportion of cobalt but was greater than similar manganite perovskites and was well within the limits defined for useful SOFC operation[166]. Hibino et.al have studied the performance of single-chamber ITSOFC using Ce₀₉Sm₀₁₀O₂-δ solid electrolyte, 10 wt.% SDC containing Ni anode and Sm₀₅Sr₀₅Co₀₂₀₃-δ cathode at temperature below 773 K. EMF of ~900 mV was generated from the cell in a flowing mixture of ethane or propane and air, where the solid electrolyte functioned as a pure ionic conductor. The electrode-reaction resistance was negligibly small when compared with the total internal resistance of the cell. The resulting peak power
density reached 403 and 101 mW/cm² at 773 and 623 K respectively[167].

Rajiv Doshi et.al have shown that doped ceria was a feasible electrolyte for operation at 773 K with fuels such as liquid methanol or hydrogen-containing gases. Cathodes made from La₀.₆₀Sro.₄₀Fe₀.₈₀Co₀.₂₀O₃₋₈ have inherently high performance, but the microstructure must be stabilized to achieve a stable area of contact at the electrode/electrolyte interface. Using the ITSOFC technology, a potentially simple propulsion system can be realized if the 773 K SOFC was operated directly on methanol or coupled to a partial oxidation reformer (POX) for heavier hydrocarbon fuels such gasoline[168]. Hibino et.al have studied the single chamber ITSOFC between 623 and 1173 K in flowing mixtures of methane, ethane, propane or liquefied petroleum gas and air with a fuel/air volume ratio of one, where their oxidation proceeded safely without explosion. Among all tested electrode materials, Ni₀.₈₀Ce₀.₂₀Sm₀.₂₀O₂₋₈ cermet and Sm₀.₅₀Sr₀.₅₀CoO₃₋₈ oxide functioned best as the anode and cathode, respectively, in various gas mixtures. A cell constructed from a La₀.₉₀Sr₀.₁₀Ga₀.₈₀Mgo.₂₀O₃₋₈ electrolyte with the two electrodes generated >900 mV in a methane-air mixture between 873 and 1073 K and in ethane-air mixture between 723 and 923 K. The peak power density at 723 K increased from 34 to 101 mW/cm² [169].

Zhu has found that methanol and ethanol can be employed in ITSOFC technology for the electrical (hybrid) vehicles. ITSOFCs were tested with composite Ce₀.₉₀Gd₀.₁₀O₂₋₈ − NiO anode, Ce₀.₉₀Gd₀.₁₀O₂₋₄ electrolyte and the composite Ce₀.₉₀Gd₀.₁₀O₂₋₄ − La₀.₆₀Sr₀.₄₀Co₀.₈₀Fe₀.₂₀O₃₋₈ cathode. The ITSOFCs using these new composite ceramic electrolytes were operated between 300 and 1500 mA/cm² (200−700 mW/cm²) continuously between 673 and 873 K. Without any efforts in developing new catalysts for the liquid fuels and using just the same electrodes for the regular ITSOFCs, the fuel cell devices showed around the OCV 0.95 V for the 2 M methanol, 0.91 V for the 1 M ethanol and 0.787 V for the 1 M acetone at 873 K. Using directly these liquid fuels, the ITSOFCs were operated under 300 – 450 mA/cm² (180-280 mW/cm² at 873 K with a peak power density around 330 and 300 mW/cm²) for the methanol and ethanol fuels utilized cells[170]

2.2.5 Performance characteristics of ITSOFCs with other alternate solid electrolytes

Several alternate perovskite solid electrolytes other than doped LaGaO₃ and
doped CeO$_2$ were also proposed for ITSOFC application. Cook et al. have synthesized a new perovskite solid electrolyte, BaTb$_{0.90}$In$_{0.10}$O$_{3.6}$ and tested the ITSOFC with the configuration (H$_2$, 3%H$_2$O / Ni anode / BaTb$_{0.90}$In$_{0.10}$O$_{3.6}$ electrolyte / La$_{0.90}$Sr$_{0.10}$MnO$_{3.6}$ cathode / O$_2$). The open circuit potential measured for this cell at 873 K was 1.007 V[171]. The current density of 120mA/cm$^2$ at a cell voltage of 0.6 V could be achieved at this temperature. Under OCP conditions the fuel cell was stable >3 days; however, under load it began to show some evidence of instability as manifested by a lowering in this operating potential. Sammells have studied the fundamentals of solid-state crystallographic parameters which permit high ionic conductivities to be achieved in perovskite solid electrolytes at intermediate temperatures (873 K). He found that activation energy for ionic conduction is influenced by: (1) the average perovskite metal-oxygen energy and associated enthalpy of formation 2) the lattice free volume, obtained by subtracting the ionic volumes of lattice constituents in the unit cell from the overall unit cell volume, 3) the parameter $r_{critical}$ ($r_c$) which corresponds to the radius of the opening between the two A site cations and one B site cation through which the mobile anion must pass, and 4) the lattice polarizability. He also determined that the operation of fuel cells in this intermediate temperature range also required insight into the rational selection of electrocatalytic site for promoting the oxygen reduction reaction at low over potentials[172-173].

Cook et al. incorporated the perovskite solid electrolyte, BaTb$_{0.90}$Gd$_{0.10}$O$_{3.8}$ into fuel cell possessing the general configuration (H$_2$, 3%H$_2$O / Pd anode/ BaTb$_{0.90}$Gd$_{0.10}$O$_{3.8}$ electrolyte/ La$_{0.90}$Sr$_{0.10}$CoO$_{3.8}$ cathode/ 3%H$_2$O, O$_2$) and studied the performance[174]. They found that ionic conductivity was found to progressively increase by 30% upon passage of current through cell for over a day, with values up to 8.7 x 10$^{-2}$ S/cm$^{-1}$ being found at 823 K. They suggested that this solid electrolyte to be predominantly a proton conductor at intermediate temperatures. Wang and Barnett have described a new approach for lowering the air-electrode interfacial resistance in ITSOFC. Thin interfacial layer (thickness-50nm) of (Y$_2$O$_3$)$_{0.25}$(Bi$_2$O$_3$)$_{0.75}$ interposed between La$_{0.70}$Sr$_{0.30}$CoO$_{3.8}$ electrode and (Y$_2$O$_3$)$_{0.10}$(ZrO$_2$)$_{0.90}$ electrolyte yielded the interfacial resistance ($r_i$) = 0.4 $\Omega$.cm$^2$ at 1023 K[175]. Ishihara et al. have studied the cathodic overpotentials of Ln$_{0.60}$Sr$_{0.40}$MnO$_{3.6}$ (Ln is La, Pr, Nd, Sm, Gd, Yb and Y) for new cathodes in SOFCs with low overpotentials in a relatively-low temperature
The same power density of SOFCs with the La$_{0.60}$Sr$_{0.40}$MnO$_{3-δ}$ cathodes at 1073 K could be attained at 973 K in the cells with Pr$_{0.60}$Sr$_{0.40}$MnO$_{3-δ}$ cathode. Moreover, the thermal property of Pr$_{0.60}$Sr$_{0.40}$MnO$_{3-δ}$ cathode was more in match with that of YSZ solid electrolyte compared with that of Sr-doped LaMnO$_3$.

Zhu and Mellander have studied the ITSOFC electrolyte based on oxyacid salts which were salt-alumina composites, where both cations and protons were mobile[178]. The ITSOFCs using materials based on nitrate salts (RbNO$_3$-Al$_2$O$_3$) as electrolytes were successful, the best fuel cell performance was a current density of 300 mA/cm$^2$ at 0.75 V. Fung et.al have fabricated YSZ/Ni-zirconia electrolyte/electrode discs of ~2.5 cm in diameter by a single step dip-coating process followed by sintering for lower temperature SOFC. Single cell tests were conducted with LSM as the cathode with pure O$_2$, 80% O$_2$-20% N$_2$ and air (~21% O$_2$) as oxidants. The power density of 0.55 watts/cm$^2$ at 0.7 volts was measured in air at 1073 K[179].

Rim et.al have studied 8 mol.% ytterbia stabilized zirconia (YbSZ) as an electrolyte material for ITSOFC application and the electrical conductivity at 1063 K was 1.54 x 10$^{-1}$ S/cm$^{-1}$. The power density of unit cell using Pr$_{0.70}$Sr$_{0.30}$MnO$_{3-δ}$ cathode, YbSZ electrolyte and Ni-ZrO$_2$ anode was higher than that using La$_{0.90}$Sr$_{0.10}$MnO$_{3-δ}$ cathode, YSZ electrolyte and Ni-ZrO$_2$ anode at 1173 K[180]. Tsai and Barnett have studied the effect of cathode composition, processing and structure on the performance of ITSOFC with two phase mixtures of La$_{1-x}$Sr$_x$MnO$_{3-δ}$ and YSZ cathode. YSZ electrolyte (<10μm thick) and Ni-YSZ anodes with Y – doped CeO$_2$ interfacial layers[181]. The cathode overpotential was the primary factor limiting cell power densities. Increasing the YSZ volume fraction in LSM-YSZ cathodes from 0 to 60% reduced the low-current area-specific resistance of the cells (in air and humidified hydrogen) from ~3.3 to 0.7 Ω cm$^2$ at 1023 K. The maximum power measured in humidified H$_2$ and air ranged form ~110mW/cm$^2$ at 1073 K.

Honegger et.al have studied the thin film SOFC for intermediate temperature operation. They have deposited YSZ as 4 μm thick films by closed loop unbalanced reactive magnetron sputtering from a ZrY-alloy target in O$_2$-Ar plasmas onto microporous NiO/YSZ substrates. Cells with 4.2 cm$^2$ active area using stainless steel current collectors showed maximum power densities of 1.0 W/cm$^2$ at 998 K but considerable degradation within 500 h operation. The degradation was reduced by the addition of a 1 μm thick CeO$_2$ 10 mol.% Y$_2$O$_3$ solid solution (YDC) layer on top of
the YSZ thin film electrolyte. Cells with the bilayer electrolyte were operated over 1800 h with tolerable degradation[182].

Choy et al. have demonstrated the technical viability of the both electrostatic assisted vapour deposition (EAVD) and flame assisted vapour deposition (FAVD) methods in the fabrication of ITSOFC components. They also demonstrated the potential of EAVD to manufacture PEN (positive electrode/electrolyte/negative electrode) cell of LSM/YSZ/Ni-YSZ cost effectively. The interfacial resistance can be improved with an interlayer of electrolytes, \((Y_2O_3)_{0.15}(CeO_2)_{0.85}\) and \(Ce_{0.80}Gd_{0.20}O_2\). These interlayers allowed the use of \(La_{0.80}Sr_{0.20}CoO_3\) cathode with YSZ electrolyte instead of the conventional \(La_{0.82}Sr_{0.18}MnO_3\), which has lowered the interfacial resistance two-fold[183]. Kim et al. have fabricated the anode supported SOFCs with YSZ electrolyte, LSM+YSZ cathode and Ni+YSZ anode and their performance was evaluated between 923 and 1073 K with humidified hydrogen as the fuel and air as the oxidant. Maximum power densities measured were ~1.8 W/cm² at 1073 K and ~0.82 W/cm² at 923 K. The area specific resistance of the cell (ohmic part), varied between ~0.18 \(\Omega\) cm² at 923 K and ~0.07 \(\Omega\) cm² at 1073 K with an activation energy of ~65 kJ/mol[184].

Zhu has studied the operation of cells using \(MF_x\) (\(M = Na, Ca, Ba, La, x=1-3\)) based electrolytes. The LiNiO₂ anode-supported cell has shown the best performance, 200 mA/cm² at 0.4 V could be reached based on bulk materials[185]. Tao et al. have studied the electrode materials for intermediate temperature proton-conducting fuel cells. The performance of cells using the alternate electrode materials with LiNaSO₄ – Al₂O₃ as the electrolyte indicated that Ni-Al alloy, Ni-Al₂O₃ catalyst and Ni-YSZ cermet were potential candidates for anode materials and that LiNiO₂, LiCoO₂, Ag-SnO₂ and \(La_{0.80}Sr_{0.20}MnO_3\) were good candidates for cathode materials. Among the tested electrode materials, for the same electrolyte the LiNiO₂/Ni-Al₂O₃ anode and cathode pair gave the best cell performance[186]. Recently, Ishihara et al. have studied the performance of SOFC at 973 K with the screen printed NiO-Ce₀.₈₀Sm₀.₂₀O₂.₅ anode, screen printed Sm₀.₅₀Sr₀.₅₀CoO₃.₅ cathode and \(La_{0.80}Sr_{0.20}Mg₀.₈₀Co₀.₀₅O₃.₅\) electrolyte with the cell size as large as 154 mm in diameter. The obtained cell attained an output power of 31 W with an effective electrode area of 177 cm². Also, they have examined the internal CH₄ reforming and the cell output performance using methane [steam/carbon ratio; S/C = 2] was about
93% of the power density of the cell using hydrogen[187]. Very recently, Liu et.al have fabricated the electrolyte films of samaria doped ceria (SDC, Sm$_{0.26}$Ce$_{0.80}$O$_{2.6}$) on to porous NiO-SDC substrates by a screen printing technique. A cathode layer, consisting of Sm$_{0.50}$Sr$_{0.50}$CoO$_{3}$, and 10 wt.% SDC, is subsequently screen printed on the electrolyte to form a single cell, which is tested at temperatures from 673 to 873 K. When humidified (3% H$_2$O) hydrogen or methane is used as fuel and sustaining air as oxidant, the maximum power densities are 188 (or 78) and 397 (or 304) mW/cm$^2$ at 773 and 873 K respectively. Impedance analysis indicates that the performances of the SOFCs below 723 K are determined primarily by the interfacial resistance, implying that the development of catalytically active electrode materials is critical to be successful development of high performance SOFCs to be operated at temperatures below 873 K[188].

2.3 Objectives and scope of the present work

2.3.1 Specific objectives of the research work

The materials, design and operating temperature of solid oxide fuel cells have evolved together over several decades of research. Current SOFC designs generally have an operating temperature of 1273 K. This temperature results from the need to minimise the ohmic loss through YSZ electrolyte and the need for high reaction rates at the electrodes (especially at the air cathode).

The choice of operating temperature has had a profound influence on the selection of the materials. The materials must have the proper stability (chemical, phase, morphological and dimensional), both, alone and together, between room temperature and the fabrication temperature. The requirement for stability at 1273 K places severe constraints on the choice of the materials, and most importantly precludes the use of metals in the fuel cell stack, resulting in all ceramic stack.

The high operating temperature creates a number of other problems like maintaining gas tight seals, voltage degradation caused by electrode sintering, interfacial diffusion, volatilisation and segregation of trace components, mechanical stresses arising from differential thermal expansion, high temperatures during manufacturing and difficulties in producing large fuel cell structures. Although all these problems have been solved by appropriate selection of materials and fabrication techniques, the result is that the capital cost of current cell designs is too high for SOFCs to be commercially attractive.
Research efforts are now a days focussed towards reducing the operating temperature of SOFC from 1273 to about 1073 K by going in for an appropriate choice of new materials from ceramics and in evolving suitable fabrication techniques. The present work is one such effort to select the suitable alternate cathode and electrolyte materials based on perovskites of ABO₃ type with specific properties as the cell components to be used for intermediate temperature solid oxide fuel cell (ITSOFC) operating below 1073 K.

2.3.2 Scope of the research work

The generation of electricity in SOFC is based on the flow of oxide ions from cathode (which is exposed to air) to the anode (which is exposed to hydrogen rich fuel). The electrolyte plays the main role in facilitating the transfer of oxide ions while blocking the flow of electrons between the electrodes. The scope this work is to come out with a new cathode of high electronic conductivity and a new electrolyte with good oxide ion conductivity at intermediate temperature range (873 to 1073 K). This class of materials offers scope to experiment the trick of partially substituting the cationic sites with very reactive and proven variable valent transition metal ions towards realizing practically workable oxide ion conducting electrolyte and electronically conducting cathode and anode from same class of materials. Technical programme of this research work is given below.

1. The cathode materials such as, La₁ₓSrₓFeO₃₋₅, La₁ₓSrₓCoO₃₋₅, La₁ₓSrₓNiO₃₋₅, Y₁₋ₓCaₓFeO₃₋₅, La₁₋ₓSrₓFeₓCoyO₁₋₅₋₅ and state of the art La₁₋ₓSrₓMnO₃₋₅ have to be synthesized in the form of fine powder and their physical and electrical characterization have to be made. The prepared cathode powders have to be fabricated in the form of circular components and the fine details of their sintering behaviour at different annealing temperature have to be brought out.

2. The LaGaO₃ based electrolyte materials are being studied to reduce the operating temperature of SOFCs. Several compositions of LaGaO₃ based materials partially substituted with ‘Sr’ on A site and ‘Mg’ on the B site have to be synthesized and their physical and electrical characterization have to be studied in order to select a suitable composition as an electrolyte material. The fine details of their sintering behaviour have also to be brought out.

3. The ceria based solid electrolytes like Ce₁ₓGdₓO₂₋₅ (where x = 0, 0.05, 0.10, 0.15 & 0.20) and Ce₁ₓSmₓO₂₋₅ (where x = 0, 0.05, 0.10, 0.15 & 0.20) have to
be synthesized and their physical and electrical properties have to be examined for ITSOFC application. The sintering behaviour of the doped ceria based electrolytes have to be understood.

4. The compositions for making thin flat sheets of ITSOFC components using tape casting technique have to be optimised by trials of experiments.

5. The temperature effect on sintering of these ceramic components, densification factor and % shrinkage have to be analyzed.

6. The sintering program for sintering the electrolytes has to be optimized in order to densify them close to the theoretical density.

7. Evaluation of chemical compatibility between the alternate cathode and electrolyte materials leading to the formation of thermo-chemical products owing to the diffusion of cations.

8. Based on the results obtained on sintering and chemical reactivity experiments, the best cathode-electrolyte combination with similar shrinkage/densification characteristics have to be found out for ITSOFC application.

This research will enable us to eliminate the reported problems involving the formation of insulating compounds while they are in operation together in ITSOFC. Moreover, the thermal expansion / shrinkage characteristic mismatch among the components can be brought down to a minimum as the materials chosen are from same class with very similar solid-state chemistry.
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