Chapter 2

Literature survey

Integration of power devices in LTCC is an interesting part of research. This enables a possibility of system on chip technology. A continue power supply will ensure long life operation of packages. This chapter provide brief introduction about LTCC materials and processes. The next part of chapter provides details about fuel cells, SOFCs technology and a brief materials survey for electrode, electrolyte, interconnects and sealing materials used in SOFC.

2.1 LTCC Materials and Process

There exist a few crucial aspects that have made LTCC attractive. First, due to innovation in glass-ceramic sintering that brought the sintering temperature below 900°C and allowed use of Ag and Au as conductors and enabled use of typical thick film materials (1). Second, in spite of the glass content, the dielectric losses could be under control, opening up a multilayer circuit option for microwave circuits, and third, is its layer-by-layer fabrication process that provides high flexibility for fabricating 3D structures. LTCC has very wide range of applications in microwave devices as it has very useful dielectric properties of low dielectric constant and losses. This property enables its use in microwave antenna, transmitter, receivers, and related circuit applications (2). It has stable frequency and temperature properties, better thermal conductivity compared with conventional substrates like FR4, and its packages are reliable due to its CTE matching to Si and GaAs. LTCC packages or circuits can handle thermal, mechanical, microfluidic and electrical signals simultaneously. These packages or
circuits can operate even at 600°C and can themselves integrate heater and temperature sensors (3). Further, LTCC materials are chemically stable, are themselves hermetic and can create hermetic cavities. Due to these factors, this technology is well suited for highly reliable mechanical and electrical interposer functionality to PCBs (3), Micro Electro Mechanical Systems (MEMS) and other sensor packaging and high temperature devices (4) (5). Clearly, LTCC technology has tremendous potential to become a low volume high performance and high volume low cost technology for integrated systems.

2.1.1 LTCC Materials:

Low Temperature Co-fired Ceramics (LTCC) materials are composed of ceramic materials systems in which glasses or low melting point fluxes are added to enhance sintering at lower firing temperatures (6). Based on volume content of glass added in ceramics, the LTCC materials are classified in three classes viz. Glass-Ceramics (GC), Glass-Ceramics Composites (GCC), Glass bonded Ceramics (GBC). The GC materials have $\geq 50-80$ vol % re-crystallizing glass. The commercially available ‘Ferro A6’ LTCC tapes belong to this category (7). The GCC materials contain 20-50 vol % glasses in which glasses played very important role in the sintering process and have dominant effect on electrical, mechanical and thermal properties. These glasses also re-crystallize after sintering. ‘DuPont 951’ and ‘Heraeus CT 700’ LTCC materials belong to this class in which dielectric constant of tapes found in between 5 to 30 (8). GBC is relatively new class of LTCC materials in which up to 10 vol% glasses are added, it has very high dielectric constants $\geq 20$. Recently, various kinds of glass-free materials and Ultra-LTCC (ULCC) are also under active research and development (9), (10). However, LTCC tapes with these materials are not yet produced commercially. For this reason, the present review does not cover these materials. Table 2.1 compares the technical data of some important LTCC tapes available in the market.
<table>
<thead>
<tr>
<th>Property</th>
<th>DuPont 951</th>
<th>DuPont 943</th>
<th>Ferro A6M</th>
<th>ESL 41010</th>
<th>Heraeus CT 2000</th>
<th>Heraeus HL 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>7.85</td>
<td>7.5</td>
<td>5.9</td>
<td>7.3</td>
<td>9.1</td>
<td>7.3</td>
</tr>
<tr>
<td>Dissipation factor (tan δ)</td>
<td>0.0045</td>
<td>0.001</td>
<td>0.002</td>
<td>0.004</td>
<td>0.002</td>
<td>0.0026</td>
</tr>
<tr>
<td>Breakdown voltage (V/25µm)</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;1500</td>
<td>&gt;1000</td>
<td>&gt;800</td>
</tr>
<tr>
<td>Insulation</td>
<td>&gt;10¹²</td>
<td>&gt;10¹²</td>
<td>&gt;10¹²</td>
<td>&gt;10¹²</td>
<td>&gt;10¹³</td>
<td>&gt;10¹³</td>
</tr>
<tr>
<td>CTE (ppm/K)</td>
<td>5.8</td>
<td>4.5</td>
<td>7.0</td>
<td>7.0</td>
<td>5.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Thermal cond. (W/m.K)</td>
<td>3</td>
<td>4.4</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Density</td>
<td>3.1</td>
<td>3.2</td>
<td>2.4</td>
<td>2.3</td>
<td>2.45</td>
<td>2.45</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>320</td>
<td>230</td>
<td>&gt;170</td>
<td>310</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>152</td>
<td>92</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness of green tapes (µm)</td>
<td>50,112,</td>
<td>125</td>
<td>125,</td>
<td>125</td>
<td>98, 127, 131</td>
<td>25, 50,</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
<td>250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fired thickness (µm)</td>
<td>42, 95,</td>
<td>112</td>
<td>92, 185</td>
<td>105</td>
<td>77, 102, 94</td>
<td>20, 40,</td>
</tr>
<tr>
<td></td>
<td>212</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shrinkage x-y (%)</td>
<td>12.7±0.3</td>
<td>9.5±0.3</td>
<td>14.7±0.2</td>
<td>13±0.3</td>
<td>10.6±0.3</td>
<td>0.16-0.24</td>
</tr>
<tr>
<td>Shrinkage z (%)</td>
<td>15.0±0.5</td>
<td>10.3±0.3</td>
<td>27±0.5</td>
<td>16±1</td>
<td>16.0±1.5</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 2.1: Physical properties of commercially available LTCC tapes (1)

DuPont 951 contains $\text{Al}_2\text{O}_3$ and mixture of crystallizing glasses such as $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (1), $\text{CaO-}\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3$, which form anorthite
phase with $\text{Al}_2\text{O}_3$ (11). The Fluoride based silica glass ceramics such as $\text{CaF}_2\cdot\text{AlF}_3\cdot\text{SiO}_2$, $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2$ are some of the recently reported new LTCC materials (6). These are low temperature melting glasses with low permittivity and firing temperature of LTCC below 950°C.

To prepare the LTCC tapes, the glasses are first milled together with Alumina or other suitable crystalline material to form the raw material of LTCC. This glass ceramic composite is added with inorganic constituent known as fillers, such as, $\text{BaTiO}_3$, $\text{CaTiO}_3$, $\text{SrTiO}_3$, $\text{MgCaTiO}_3$, $\text{CaZrO}_3$. Along with these crystallizing glasses containing $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{CaO}$, $\text{MgO}$ and $\text{SrO}$ alkali and alkaline glasses are added to provide viscosity control for appropriate flow and densification of the tape at firing temperature. This mixture of ceramics, crystallizing glasses and inorganic fillers dispersed in organic binder made up of polymers, plasticizers, release agents and stabilizing agents and solvents to prepare slurry which is used to tape cast green ceramic tapes by doctor blade tape casting method. This tape is a flexible sheet supported by polymeric sheet called as Mylar. The organic binders added in slurry provide strength and toughness of the tapes, whereas dispersant avoid agglomeration of tiny glass and ceramic particles in the prepared slurry. The co-firing conductor paste and passive components are applied on each layer of LTCC tapes by screen printing technique. Hence these components are available in form of screen printable paste. The conductor pastes consist of metals, such as, Silver (Ag), Gold (Au), Palladium (Pd), Platinum (Pt), Aluminum (Al), Nickel (Ni) and Copper (Cu). These metals along with glass frit are dispersed in organic solvent to form a screen printable paste with appropriate viscosity and thixotropy. Glass frit in paste facilitates adhesion of paste on LTCC surface after firing. Organic binders played a role of carrier of glass-metal compound to spread over screen in appropriate width and thickness. The co-firable pastes must exhibit physical and chemical
compatibility with LTCC and achieve shrinkage and its density during firing process simultaneously with tape. Any mismatching of shrinkage and densification process during firing results in cracks, deformations, warpage or chamber in LTCC structure (12).

The LTCC products are sometimes targeted towards specific applications. Since the microwave circuits are the major applications for LTCC, many manufacturers have only such tapes on their product list. In comparison, DuPont is having two different products, viz. for general purpose applications (including microwave at lower microwave frequencies) and a special product line for better microwave results at much higher frequencies. It is seen from the published catalogs and other available information, that DuPont has one of the widest set of products that cover most of the LTCC applications. For example, DuPont offers a set of brazing pastes for the general purpose tapes, which are not available with all the manufacturers. Further, having both, Ag or Au systems as well as the mixed system for conductors provides flexibility. DuPont also provides a wide range of products for lithography and other related processes. Clearly, DuPont enjoys preeminence in this field. While it is true that some materials of the competitor’s are reported to have better properties in certain respects, it is perceived that it is always better to start with standard product when one is starting afresh. For these reasons, we have selected DuPont 951 series general purpose tapes for compatibility tests and for the fabrication of packages. These aspects of the work are discussed further in this Thesis.

2.1.2 LTCC Process Flow:

LTCC process is, in essence, a multilayer ceramic process, circuit fabrication process. Therefore, the fabrication of the circuit or package is required to be considered layer by layer. Thus, the metallic interconnects run over each layer and connect to the top or bottom layer through via. Planar or 3D integration of passives is also possible,
and its fabrication is also taken up layer wise. The fabrication process starts from, again the layer wise design of the package / circuit as per the user requirements. Initially a 3D design of package is prepared. This design is then separated into the layer wise design and an array of this layer-wise design is created to accommodate several circuits / packages in the given tile area. These layer wise designs are then separated further into screen-printing, via punching and via filling designs. The screen printing design is used for preparing screens, while via filling designs are used to prepare stencils. The screens and stencils are fabricated by a vendor to the required specifications. The via punching design is transferred to the via puncher directly. The circuit / package is now ready for fabrication.

The fabrication process starts from pre-baking of green tapes at 80°C for 10 minutes or at room temperature for 24 hrs. The tapes are then used to punch via using programmable via punching machine. The via puncher has three different types of punching heads \textit{viz.} 200µm round punching required for interconnection, 3mm round punches mainly used for layer by layer alignment and the 2mm square punch for making cavities. These punched tapes are then forwarded for via filling and screen printing of the on-layer conductor and other material (such as resistor) patterns, using SS stencils and screens respectively. After drying these tapes are sent for stacking where these tapes are aligned and pressed gently to adhere to each other. The supporting Mylar sheet is removed at this stage. The pressing is carried out at a few MPa pressure and plate temperature of around 50°C. This stack is then cut to 4”×4” size, which is the circuit area. This is followed by lamination in isostatic laminator, using hydraulic pressure of about 20-25MPa and temperature of about at 60-90°C. This process ensures much closer interface between individual layers, which eventually helps in avoiding de-lamination after firing. This laminated stack is then cut to singulate individual circuits / packages using hot carbide blade cutter where the
The LTCC fabrication process flow for the fabrication of circuits or package is presented in Figure 2.1.
It may be noted that several processes are necessary to undertake even after co-firing. These include, brazing of pins and/or seal-rings, Ball Grid Array (BGA) preparation, Bare chip attachment and wire bonding, attachment of surface mount components, hermetic sealing through several possible sealing and welding processes, etc. Obviously, the requirements of the final product preeminently decide the required post-fire processes. Further, the sequence of these processes is usually decided by the thermal budget and flexibility offered by each process. Figure 2.2 provides a typical post-fire process flow chart.

**Surface Mount Technology (SMT)**
The following Section presents Literature Review of Solid Oxide Fuel Cells (SOFC).

### 2.2 SOFC construction and operation:

Fuel cells (FC) development has very long history. Fuel cells were invented in the 19th century, around 1838. Following are the year wise important milestones in fuel cell research (13):

- 1838-Christian Friedrich Schonbein discovered principle of the FC
- 1839-William grove demonstrated operation of first FC- gas battery
- 1932-First alkali fuel cell developed by Francis Bacon
- 1959- First alkali cell of 5kW power output demonstrated by Bacon
- 1960- NASA started FC program, FC launched on Gemini and Apollo satellite
- 1960-1970- Other FCs are discovered
1970- Used commercially in stationary power production

1990- Considered seriously for Terrestrial applications

Today, FCs are attracting interest as non-conventional power sources due to its high fuel efficiency, low emission of toxic gasses (no pollution in case Hydrogen fuel), low operating and maintenance cost, free of mechanical vibrations and silent operation, fitting well in pollutant emission standards set by National Emission Standards for Hazardous Air Pollutants (NESHAPS). Such enormous advantages of fuel cells provide enough motivation for its applications in large scale energy generation. Fuel cells are used in stationary power generation, in hybrid propulsion, compact power systems, distributed power systems, microturbine combined cycles and naval power systems (14).

A basic fuel cell operation is shown in Figure 2.2. Fuel cells consist of anode, cathode and electrolyte separated by triple phase boundary (TPB). TPB is interface between electrode and electrolyte where actual electrochemical reactions take place and ion conducting phase, electron conducting phase, and gas phase are present during cell operation.

![Figure 2.3: Schematic showing of basic fuel cell operation](image-url)
Solid Oxide Fuel Cell (SOFC) is a high temperature fuel cell which is presently operated at 1000°C temperature. This fuel cell consists of oxide ceramics electrolyte through which oxygen/proton ions hopping take place by blocking electronic current. SOFC is most efficient and versatile fuel cell in the family. It can generate highest power of the order of 1000kW with fuel efficiency 60-70% and if utilized heat produced during operations overall efficiency goes above 90%. Following are the advantages of SOFC:

**Advantages of SOFC:**

- High efficiency- fuel efficiency of the order of 60-70%
- Fuel flexibility- Can operate on fuels other than Hydrogen, such as various hydrocarbons, alcohols, ammonia
- Low pollutant emission- almost zero pollution in case of Hydrogen fuel, very less in case of hydrocarbons and alcohol fuels, zero emission of SOx, NOx gases
- Non precious metal catalyst- Platinum can be replaced by other catalysts
- Solid electrolyte- ensures stable and long life performance due to chemical and structural stability
- Moderate power density (230-350mW/cm²)
- Simplified fuel reforming requirements
- Modular and compact

However, following technological limitations becomes obstacle in its commercialization.

**Limitations of SOFC:**

- High operating temperature (800-1000°C)
- High temperature sealing and interconnects issues- expensive alloys are required for housing of cell and for current collection conductors
- Relatively expensive components and fabrication process
High operating temperature of SOFC has limited their applications to stationary power generation. Thus, in order to make use of the advantages of SOFC, selection and further research in materials and fabrication process has become a necessity. Lowering of the operating temperature at least to 600-800°C range may allow automotive and even portable device applications (15), and resolve the sealing and interconnects issues (16). This would also increase the cell lifetime by limiting degradation of the fuel cell components (17).

Before any attempt is made to undertake research towards reducing the operating temperatures through improved materials, one must take into account the present status of various materials used in SOFCs. The following sub-Sections review the present status of anode, electrolyte and cathode materials used in the present day SOFCs.

2.2.1 Anode Materials:

Anode plays an important role in oxidation of fuel. Following is the half-reaction that taken place at anode when hydrogen fuel is used:

\[ H_2 \rightarrow 2H^+ + 2e^- \]

Clearly, anode materials are required to provide good catalytic action, optimum porosity and mixed ionic and electronic conductivity. A catalytic activity generates ions and electrons at a specific rate. Porous anode helps to increase the area under triple phase boundary (TPB), which increases reactivity of anode with fuel (18).

Platinum is a well known anode material for hydrogen fuel. However, its high cost limits its use in SOFCs. Ni or NiO doped Yttrium Stabilized Zirconia (YSZ) cermets are known as SOFC anodes (19). However, it shows degradation in performance due to carbon deposition (carbon clogging) when used for hydrocarbon fuels. Materials such as, CuO and Ce\(_{0.6}\)Zr\(_{0.4}\)O\(_2\) have been used as anode for hydrocarbon fuels (20). Ceramic materials are more favorable as anode compared to metals as they have mixed ionic and electronic conductivity (MIEC), redox stability and they can be prepared in fine microstructures (21). Hence,
composites of metals/oxide or oxide/oxide are used as anode. Hirabayashi *et al.* have reported \((\text{Bi}_2\text{O}_3)_{0.82}(\text{Ta}_2\text{O}_5)_{0.18}\) as an anode for GDC electrolyte in intermediate temperature range (22). Bin Zhu *et al.* have reported active carbon and vapor grown carbon fiber added in CuO:SDC as anode at lower (<700°C) operating temperature (23). Anode materials reported frequently in the literature together with the information about their phase, operating temperature, properties, advantages and limitations are listed in Table 2.3.

Note that, remarks denoted by (▲) present advantages and (▼) symbol indicates limitations of the given anode materials.
<table>
<thead>
<tr>
<th>Sr No</th>
<th>Anode material</th>
<th>Crystal Structure</th>
<th>Preparation method</th>
<th>Operating temp.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-YSZ</td>
<td>Perovksite</td>
<td>Solid state reaction</td>
<td>800-1000°C</td>
<td>▲ Good electronic conductor, Very good catalyst at SOFC operating temperature, ▼ Shows carbon clogging when used for hydrocarbon fuels <em>i.e.</em> susceptibility to carbon formation sulfur poisoning, mechanical instability caused by redox cycling, Performance depends on anode architecture &amp; GDC concentration</td>
</tr>
<tr>
<td>2</td>
<td>NiO-Ce$<em>{0.9}$Gd$</em>{0.1}$O$_{1.95}$ (Nickel oxide doped GDC)</td>
<td>Perovskite</td>
<td>hydroxide co-precipitation method</td>
<td>500-700°C</td>
<td>▲ Strongest resistance to COx formation, higher activity of the oxide surface, Performance and stability depends on ZrO$_2$ doping, mixed conductivity $3.87 \times 10^{-2}$ S.cm$^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>Ce$<em>{0.2}$Zr$</em>{0.8}$O$_2$ Ni/CeZrO$_2$</td>
<td>Perovskite</td>
<td>citrate-nitrate combustion route</td>
<td>NA</td>
<td>▲ Good electronic conductivity ($190$ S cm$^{-1}$) at 900°C high catalytic activity for oxygen oxidation, chemical and thermal compatibility with YSZ, ▼ polarization in an oxidizing environment cause deactivation</td>
</tr>
<tr>
<td>4</td>
<td>Lanthanum strontium magnatate (LSM)/YSZ</td>
<td>NA</td>
<td>glycine-nitrate combustion process</td>
<td>600–800°C</td>
<td>▲ Used for both anode cathode &amp; applicable for reversible SOFC, Good redox stability, high power density, acceptable COx and sulphur tolerance</td>
</tr>
<tr>
<td>5</td>
<td>(La$<em>{0.75}$Sr$</em>{0.25}$)Cr$<em>{0.5}$ Mn$</em>{0.5}$O$_3$(LSCM) (LSCM/YSZ)</td>
<td>Rhombohedral Perovskite</td>
<td>Combustion synthesis technique</td>
<td>700-900°C</td>
<td>▲ Used for both anode cathode &amp; applicable for reversible SOFC, Good redox stability, high power density, acceptable COx and sulphur tolerance</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anode Material</th>
<th>Phase</th>
<th>Synthesis Method</th>
<th>Operating Temperature</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$<em>2$Fe$</em>{1.5}$Mo$<em>{0.5}$O$</em>{6-δ}$ - Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{1.9}$ Composite Anodes</td>
<td>Mixed perovskite</td>
<td>Mixed perovskite</td>
<td>500-1000°C</td>
<td>▲ Oxidation tolerant anode high ionic conductivity and electro-catalytic activity</td>
<td>▼ not stable at the very low oxygen partial pressure</td>
</tr>
<tr>
<td>Cu–YSZ</td>
<td>NA</td>
<td>Duel tape casting</td>
<td>700-800°C</td>
<td>▲ Stable in hydrocarbon environments, Cu to allow for direct oxidation, higher electronic conductivity,</td>
<td>▼ exhibited low performance for direct oxidation, poor catalyst for C–C bond</td>
</tr>
<tr>
<td>Ni$<em>{0.6}$Cu$</em>{0.4}$Zn$_x$</td>
<td>Mixed FCC and perovskite</td>
<td>EDTA-citrate sol-gel process</td>
<td>400–600°C</td>
<td>▲ Catalytically active anodes, hydrocarbon reforming reaction, kinetically suppress carbon formation, good stability</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{0.2}$Zn$</em>{0.8}$</td>
<td>perovskite</td>
<td>solid-state reaction</td>
<td>400–600°C</td>
<td>▲ Resistance for carbon deposition, prevent catalyst deactivation, high-catalyst activity,</td>
<td></td>
</tr>
<tr>
<td>C-MO-SDC M= Cu, Ni, Co</td>
<td>Mixed orthorhombic perovskite</td>
<td>Citrate/nitrate combustion technique</td>
<td>400–600°C</td>
<td>▲ CuO with n-type conductivity and NiO, CoO with p-type conductivity, good catalytic activities for H$_2$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3: List of Anode material reported in literature showing their phase, synthesis method, operating temperature, advantages and limitations.
Table 2.3 lists all known anode materials to the best of our knowledge. It is observed from Table that Ni/NiO and NiO doped YSZ/GDC are most frequently used anode materials in high temperature SOFCs. However, Ni/NiO based anodes have carbon clogging issues when it is used for organic fuels. Also, catalytic activity of these electrodes reduces with temperature. It is seen from literature that Cu/CuO based anode materials are showing good catalytic activity and very good electronic conductivity. These anodes are also used in intermediate and low temperature SOFCs. Hence, Copper based anode materials are selected as anode materials for this work. Recently, some of the metal anode materials are reported viz. $\text{Ni}_{0.6}\text{Cu}_{0.4-x}\text{Zn}_x$, $\text{Cu}_{0.2}\text{Zn}_{0.8}$ and C-MO-SDC (M=Cu, Ni, Co) are the recently reported as anode for Low temperature solid oxide fuel cells. $\text{Ni}_{0.6}\text{Cu}_{0.4-x}\text{Zn}_x$ and C-MO-SDC (M=Cu, Ni, Co) are used for SDC-Carbonate anode materials, these anodes are recently reported and details were not available. $\text{Cu}_{0.2}\text{Zn}_{0.8}$ show promising catalytic activity for Methanol fuel (38). In some of the catalytic applications elsewhere $\text{Cu}_{0.8}\text{Zn}_{0.2}\text{O}_{3.5}$ (CuZnO) reported having good catalytic activity as oxidative steam-reforming of methanol to produce $\text{H}_2$ at temperature above 200-300°C (39). $\text{Cu}_{0.2}\text{Zn}_{0.8}\text{O}_3$ crystallized in perovskite crystal structure in which Cu incorporated. Hence, CuZnO based anode was selected as anode for methanol fuel in this study.

### 2.2.2 Electrolyte Materials:

Electrolytes in SOFC are highly dense oxides that allow diffusion of oxygen or proton ions, while blocking electron flow through it. Electrolyte materials should be highly dense (39), must have higher ionic conductivity, lower electronic diffusion, must possess appropriate vacancies for ionic conduction (40) (41).

YSZ is presently used as electrolyte commercially for SOFCs that shows oxygen ion conductivity of the order of 0.1S.cm$^{-1}$ at 1000°C (42). According to literature, 8 mole% $\text{Y}_2\text{O}_3$ doped in $\text{ZrO}_2$ (8YSZ) shows
comparable ionic conductivity in intermediate range of operating temperature (600–800°C) (43). LaGaO$_3$ becomes good ionic conductor when doped with Strontium (Sr) and Magnesium (Mg). Strontium and Manganese doped Lanthanum Gallate (LSGM) materials have good oxygen ion conductivity in the intermediate temperature range (44) (45). The CeO$_2$ based materials doped by Samarium (Sm) or Gadolinium (Gd) are good oxygen ion conductor in temperature range of 600–800°C (46). According to recent reports, carbonate salts, such as, Li$_2$CO$_3$ mixed with K$_2$CO$_3$/Na$_2$CO$_3$ (47) (48) and BaCO$_3$ mixed with SrCO$_3$ (49) show promising ionic conductivity of 0.1S.cm$^{-1}$ at temperature around 550°C (50). However, these composite electrolytes become electronically conducting at temperature above 550°C. SOFC are also reported with proton conducting oxides used as electrolyte (51). Barium Zirconate and Barium Cerate are the best known proton ion conducting oxides reported in literature. Nd–BaCeO, Gd–BaCeO, Y doped BaZrO, Yb doped BaCeO have good proton ion conductivity 450°C (52). Proton ion conductors are promising alternative for oxygen ion conducting materials in LT SOFC. These include zirconia and ceria based oxides, lanthanum gallates, and bismuth oxides based materials (53).

There are several ceramic electrolytes with various dopants and preparation method reported in the literature. Table 2.4 presents a detailed comparison of the reported materials with respect to their preparation method, working temperature, ionic conductivity and various other relevant issues.
<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Electrolyte material (Crystal Structure)</th>
<th>Preparation methods</th>
<th>Operating temp (°C)</th>
<th>Ionic conductivity (S.cm⁻¹)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yttrium Stabilized Zirconia / 8 mol% Yttria-stabilized Zirconia (cubic fluorite structure)</td>
<td>atmospheric plasma spraying (APS)</td>
<td>600–1000</td>
<td>0.034</td>
<td>▲Thermal stability, high ionic conductivity and good thermal expansion compatibility with the electrodes materials ▼High operating temperature, require higher sintering temperature</td>
<td>(54), (55), (56), (57)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>spray pyrolysis</td>
<td>600–800</td>
<td>NA</td>
<td>▼</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>injection molding</td>
<td>900</td>
<td>0.10</td>
<td>▲</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8 mol% scandia (8ScSZ) ((ZrO₂)₁₋ₓ(Sc₂O₃)ₓ) (Mixed cubic tetragonal phases)</td>
<td>glycine nitrate process (GNP)</td>
<td>800</td>
<td>0.15</td>
<td>▲ Higher ionic conductivity than YSZ, lower operation temperature, ▼lack in compositional uniformity, phase instability</td>
<td>(58), (59), (60)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>co-precipitation</td>
<td>1000</td>
<td>0.34</td>
<td>▲</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pechini methods</td>
<td>800</td>
<td>0.112</td>
<td>▲</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ultrasonic spray pyrolysis</td>
<td>800</td>
<td>0.091</td>
<td>▲</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Gadolinium doped Ceria</td>
<td>co-precipitation</td>
<td>750</td>
<td>5.9x10⁻²</td>
<td>▲ High ionic conductivity compared to other electrolyte, lower electrolyte</td>
<td>(61), (62),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>3x10⁻²</td>
<td>▲</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$) (Gd$_x$Ce$_{1-x}$O$_{2-\delta}$) (cubic fluorite structure)

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>sol-gel</td>
<td>491</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>hydrothermal treatment</td>
<td>600</td>
<td>$7.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>IR-Assisted Sol-Gel Synthesis</td>
<td>1000</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>pulsed laser deposition (PLD)</td>
<td>700</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>glycine nitrate process (GNP), PVP assisted</td>
<td>600</td>
<td>$2.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>sol gel</td>
<td></td>
<td>$1.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>freeze drying method</td>
<td>650</td>
<td>$3.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>mixed oxide technique</td>
<td>700</td>
<td>$2.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>distillation techniques</td>
<td>600</td>
<td>$0.5 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

sintering temperature, compatibility with more active electrodes

▼ reduction in Ce$^{4+}$ to Ce$^{3+}$ at higher temperature, and reducing atmosphere, segregation of impurities such as Si or Ca at the grain boundaries

▲ high ionic conductivity compared to other electrolyte, lower electrolyte
| (Sm<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub>) | sol–gel process | 800 | 8.2×10<sup>-2</sup> | sintering temperature, compatibility with more active electrodes, carbonate composite salt based electrolyte can synthesis
| (Sm<sub>x</sub>Ce<sub>1-x</sub>O<sub>2.6</sub>) ( cubic fluorite structure) | urea–combustion technique | 800 | 9.0×10<sup>-2</sup> | ▼ reduction in Ce<sup>4+</sup> to Ce<sup>3+</sup> at higher temperature, and reducing atmosphere, segregation of impurities such as Si or Ca at the grain boundaries
| | PVA assisted combustion synthesis method | 800 | 9.0×10<sup>-2</sup> |

| acrylamide polymerization process | 600 | 1.9×10<sup>-2</sup> |

| oxalate coprecipitation route | 600 | 2.1×10<sup>-2</sup> |

| carbonate coprecipitation | 600 | 2.2×10<sup>-2</sup> |

| Glycine–nitrate combustion synthesis routes | 650 | 1.5×10<sup>-2</sup> |

<p>| 5 Ce&lt;sub&gt;0.8&lt;/sub&gt;Pr&lt;sub&gt;0.2&lt;/sub&gt;O&lt;sub&gt;2.6&lt;/sub&gt; ( cubic fluorite) | co-precipitation | 900 | 2×10&lt;sup&gt;-2&lt;/sup&gt; | ▼Electronic conductivity increasing the dopant level of Pr, high and non | (73), (74), (75), (76), (77) |</p>
<table>
<thead>
<tr>
<th>Structure</th>
<th>Wet chemical decomposition</th>
<th>Temperature</th>
<th>I.C. (×10⁻²)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 La&lt;sub&gt;0.8&lt;/sub&gt;Sr&lt;sub&gt;0.2&lt;/sub&gt;Ga&lt;sub&gt;0.8&lt;/sub&gt;Mg&lt;sub&gt;0.2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; (Mixed cubic perovskite phase)</td>
<td>900</td>
<td>1.5×10⁻²</td>
<td>Linear thermal expansion behavior high chemical expansion on reduction (78)</td>
<td></td>
</tr>
<tr>
<td>7 La&lt;sub&gt;1+,x&lt;/sub&gt;Sr&lt;sub&gt;1–x&lt;/sub&gt;Ga&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;7–δ&lt;/sub&gt; (tetragonal structure of melilite-type)</td>
<td>950</td>
<td>0.1</td>
<td>▲ Moderate ionic conductivity, stable phase, suggest proton conduction in humid atm., ▼ oxygen transference numbers depends on composition, temperature, and oxygen partial pressure (80)</td>
<td></td>
</tr>
<tr>
<td>8 Bi&lt;sub&gt;0.80&lt;/sub&gt;V&lt;sub&gt;0.20&lt;/sub&gt;O&lt;sub&gt;1.70&lt;/sub&gt; (trigonal)</td>
<td>600</td>
<td>9.0×10⁻⁴</td>
<td>▲ Lower calcination, sintering and operating temperature electrolyte, ▼ Unstable phase, lower ionic conductivity than δ-Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; phase (81)</td>
<td></td>
</tr>
<tr>
<td>9 (Dy&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;x&lt;/sub&gt;–(WO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;y&lt;/sub&gt;–(Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;1–x–y&lt;/sub&gt; (fluorite structure)</td>
<td>700</td>
<td>0.569</td>
<td>▲ Good stability, least conductivity decay, ▼ unrevealed effect of double doping on conductivity (82)</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Material</td>
<td>Reaction Type</td>
<td>Temperature</td>
<td>Conductivity</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>---------------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
</tbody>
</table>
| 10  | Bi$_{1.9}$M$_{0.1}$O$_{3-x}$ (M=Sb, Ta) (mixed tetragonal and cubic) | solid-state reactions | 300 | $\sim 10^{-4}$ for Sb, $\sim 10^{-6}$ for Ta | ▲ Provide structural stability to Bi$_2$O$_3$  
▼ Low ionic conductivity, increases grain boundary impedance |
| 11  | SDC/Na$_2$CO$_3$ composite (NA) | Solid state reactions | 300 | 0.1 | ▲ long time fuel cell performance and durability, notable thermal stability, ▼ volatilization or decomposition chances, very low synthesis temp$^1$ |
|     | Samaria-doped ceria/ sodium-lithium-carbonate (SDCLN) (NA) | Carbonate co-precipitation process followed by solid state addition of carbonate salt | 550 | 0.153 0.017 | ▲ higher conductivity, control partial reduction of Ce$^{4+}$ to Ce$^{3+}$, improved mechanical properties, negligible electronic conductivity, multi-paramaters effect, coexisting blocking and non-blocking mobile ions |

**Proton ion conductors**

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Reaction Method</th>
<th>Temperature</th>
<th>Conductivity</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>BaZr$<em>{1-x}$Y$<em>x$O$</em>{2.95}$ (BZY) BaZr$</em>{1-x}$Ce$<em>x$O$</em>{2.95}$ (BZC)</td>
<td>solid-state method</td>
<td>600</td>
<td>0.01</td>
<td>▲ high chemical -mechanical stability and high proton</td>
</tr>
</tbody>
</table>

---

$^1$ For work present in this Thesis
<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature</th>
<th>Conductivity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pechini method</td>
<td>700</td>
<td>NA</td>
<td>conductivity, high grain-interior conductivity, chemical stability under CO\textsubscript{2} and humid atm. ▼ low sintering properties and high specific grain boundary resistance</td>
</tr>
<tr>
<td>Pulsed laser deposition (PLD)</td>
<td>700</td>
<td>$2.7 \times 10^{-2}$</td>
<td>▲ ZnO doping effectively enhance the sintering by enhancing densification, uniform grain growth ▼ TEC mismatch, lowering electrical conductivity, elemental migration electrodes</td>
</tr>
<tr>
<td>Low temp. pressing</td>
<td>500</td>
<td>$2 \times 10^{-3}$</td>
<td>▲ low-cost membrane fabrication, better sintering activity and higher electrical conductivity</td>
</tr>
<tr>
<td>Carbonate route</td>
<td>400</td>
<td>$2.5 \times 10^{-3}$</td>
<td>▲ chemical and thermal stability, ▼ low and dependent conductivity on the atmosphere at high temperature, Higher sintering temperature,</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature</th>
<th>Conductivity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>{0.97}$Zr$</em>{0.77}$Y$<em>{0.19}$Zn$</em>{0.04}$O$_{3-\delta}$ (tetragonal structure or perovskite)</td>
<td>600</td>
<td>$1 \times 10^{-3}$</td>
<td>▲ ZnO doping effectively enhance the sintering by enhancing densification, uniform grain growth ▼ TEC mismatch, lowering electrical conductivity, elemental migration electrodes</td>
</tr>
<tr>
<td>BaZr$<em>{0.1}$Ce$</em>{0.7}$Y$<em>{0.2}$O$</em>{3-\delta}$ (BZCY7) (perovskite)</td>
<td>500</td>
<td>$5 \times 10^{-3}$</td>
<td>▲ low-cost membrane fabrication, better sintering activity and higher electrical conductivity</td>
</tr>
<tr>
<td>BaZr$<em>{0.1}$Ce$</em>{0.7}$Y$<em>{0.1}$Yb$</em>{0.1}$O$_{3-\delta}$ (BZCYYbO) (perovskite)</td>
<td>500</td>
<td>$1.3 \times 10^{-2}$</td>
<td>▲ chemical and thermal stability, ▼ low and dependent conductivity on the atmosphere at high temperature, Higher sintering temperature,</td>
</tr>
<tr>
<td>No.</td>
<td>Formula</td>
<td>Phase</td>
<td>Synthesis Method</td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>-------</td>
<td>------------------</td>
</tr>
<tr>
<td>16</td>
<td>BaZr$<em>{0.5}$Yb$</em>{0.25}$In$<em>{0.25}$O$<em>3$-δ (BZYI) BaZr$</em>{0.4}$Ce$</em>{0.4}$In$_{0.2}$O$_3$ (BZCI) (cubic)</td>
<td>wet chemical route</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>solid-state reaction</td>
<td>600</td>
</tr>
<tr>
<td>17</td>
<td>BaCe$<em>{0.9}$M$</em>{0.1}$O$<em>3$-δ (M=Y, Gd, Sm, Eu) BaCe$</em>{0.8}$Gd$<em>{0.15}$Pr$</em>{0.05}$O$_3$ (orthorhombic)</td>
<td>Solid state reaction</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>Electrophoretic deposition</td>
<td>650</td>
<td>1x10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>Solid state reaction</td>
<td>400</td>
<td>8.2x10$^{-3}$</td>
</tr>
<tr>
<td>18</td>
<td>La$<em>{0.9}$Sr$</em>{0.1}$Sc$<em>{0.9}$Mg$</em>{0.1}$O$_3$ (orthorhombic)</td>
<td>glycine–nitrate process and by solid state reaction</td>
<td>600</td>
</tr>
<tr>
<td>19</td>
<td>Sn$<em>{0.9}$In$</em>{0.1}$P$_2$O$_7$ (cubic structure with SnO$_6$ octahedral)</td>
<td>solid state reaction</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 2.4: List of Electrolyte materials reported in literature with their phase, synthesis method, operating temperature, ionic conductivity and remarks
Table 2.4 lists all known oxygen and proton ion conductors used or reported for SOFC application. It is clearly seen that very limited materials families available for the electrolyte materials Zirconia, Ceria and Bi$_2$O$_3$ based electrolyte materials are reported to have good oxygen ion conductivities. Zirconia based electrolytes are mechanically and chemically stable, however, these electrolyte required very high sintering temperature and ionic conductivity is low below 600°C. Bi$_2$O$_3$ based electrolyte materials shows promising conductivity properties in low operating temperature. These materials required very low sintering temperature. The phase stability and phase purity, hence, not suitable for long term SOFC operation. These are important issues in Bi$_2$O$_3$ based electrolytes. Doped Ceria is promising ionic conductor at intermediate operating temperature. It has issues regarding chemical stability in reducing environment. Sm/Gd Doped Ceria is good candidate as electrolyte for low operating temperature SOFCs due to their promising ionic conductivity in this temperature range. Samarium doped Ceria with alkali carbonate reported to have better ionic conductivity, however, these carbonate salt-SDC electrolyte has very low melting points and high temperature firing of these materials may cause evaporation of carbonates. Chapter 3 presents more details about the crystal structure, conduction mechanisms and other properties of these materials. In case of proton ion conductors also, very limited materials systems are available, BaZrO$_3$, BaCeO$_3$ and SrZrO$_3$ are three basic materials available doping of Yttrium (Y), Ytterbium (Yb), Samarium (Sm), and Gadolinium (Gd) etc trivalent atoms creates acceptor type proton ion conductivity. Similar to oxygen ion conducting electrolyte materials, ZrO$_2$ based electrolyte required high calcination temperature; on the other hand, CeO$_2$ based electrolytes shows promising ionic conductivity and has lower sintering temperature. There are recently reported proton ion conducting electrolyte viz.
La$_{0.9}$Sr$_{0.1}$Sc$_{0.9}$Mg$_{0.1}$O$_3$ and Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ showing promising ionic conductivity. This work studied both BaZrO$_3$ and BaCeO$_3$ materials as proton ion conductors and efforts were taken to reducing their sintering and calcination temperature using nanocrystalline materials synthesis method. Details about the crystal structure, conduction mechanisms and other properties of these materials presented in Chapter 4.

2.2.3 Cathode Materials:

Cathode plays important role in reducing air or oxygen. Following half reaction taken place at cathode

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

Again, just as anode material, cathode also must have mixed ionic and electronic conductivity and appropriate porosity (102). Power density and performance of SOFC depends on supply of oxygen ions to the electrolyte.

Lanthanum Strontium Magnetite (LSM), Lanthanum Strontium Cobalt Magnetite (LSCM) (103), Lanthanum Strontium Cobalt Ferrite (LSCF) (104) are reported to be high operating temperature cathodes for SOFC. ZrO$_2$-In$_2$O$_3$ (102), Pb$_2$Ru$_2$O$_{6.5}$ (105), K$_2$NiF$_4$ (106) also reported as cathodes for SOFC. Strontium and Iron doped Barium cobaltite (BSCF) (107) and Strontium and Samarium doped Cobalt oxides (SSC) (108) are reported as cathode for LT SOFC (400-600°C) in recently published literature. These materials shows better catalytic properties and mixed ionic conductivity at reducing atmosphere. LSM:YSZ (109), SSC:LSGM (110), BSCF:SDC (111), LSCF:GDC (112) are some composite cathode materials having Temperature Co-efficient of Expansion (TCE) values matching with respective electrolytes. Effort in direction of improved catalytic activity of cathode at lower operating temperature will be beneficial for reducing operating temperature of SOFC.
Table 2.5 presents detailed comparison of the reported cathode materials.
<table>
<thead>
<tr>
<th>Sr No</th>
<th>Cathode material</th>
<th>Crystal Structure</th>
<th>Preparation method</th>
<th>Operating temp (°C)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>La$<em>{0.85}$Sr$</em>{0.15}$MnO$_3$-$\delta$ (LSM)-YSZ</td>
<td>perovskite</td>
<td>single-step infiltration method</td>
<td>700</td>
<td>▲ Oxygen reduction reaction, most commonly used, similar TCE with YSZ, as cathode for (Er$_2$O$<em>3$)$</em>{0.2}$(Bi$_2$O$<em>3$)$</em>{0.8}$ (ESB) phase, highly desirable, oxygen reduction decreases ▼ dramatically, Chromium Poisoning</td>
<td>(113), (114), (115), (116), (117), (118), (119), (120), (121)</td>
</tr>
<tr>
<td></td>
<td>La$<em>{0.85}$Sr$</em>{0.15}$MnO$_3$-$\delta$ (LSM)-GDC</td>
<td></td>
<td>Solid oxide reaction method</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sequential electro-deposition</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>axial air plasma spraying</td>
<td>650 to 900</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sol-gel route</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>La$_{1-x}$Sr$<em>x$FeO$</em>{3-\delta}$ (LSF)</td>
<td>perovskite</td>
<td>Air Plasma Spray infiltration</td>
<td>800</td>
<td>▲ Electronic conductivity is p-type, high electronic conductivities, mixed electronic and ionic conductors</td>
<td>(122), (123)</td>
</tr>
<tr>
<td>3</td>
<td>La$<em>{0.6}$Sr$</em>{0.4}$CoO$_{3-\delta}$ (LSC)</td>
<td>perovskite</td>
<td>NA</td>
<td>NA</td>
<td>▲ Good mixed conductivity, promising cathodic performance, ▼ rapidly degrade due to interfacial reaction with YSZ electrolyte, results in the formation of SrZrO$_3$ and La$_2$Zr$_2$O$_7$, high TCE</td>
<td>(124), (125)</td>
</tr>
<tr>
<td></td>
<td>Formula</td>
<td>Phase</td>
<td>Preparation Method</td>
<td>Reaction Temperature</td>
<td>Properties</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---------------</td>
<td>-----------</td>
<td>---------------------------------------------</td>
<td>-----------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>La$_{1-x}$Sr$<em>x$Co$</em>{1-y}$Fe$_y$O$_3$ (LSCF)</td>
<td>perovskite</td>
<td>solid-state reaction</td>
<td>1000</td>
<td>▲ Better performance than LSM-YSZ, excellent properties for mixed conduction below 800°C, ▼ Chemically incompatible with YSZ, strong increase in the polarization resistance at 750°C, large mismatch in the CTE compared to common electrolytes, abrupt chemical expansion, phase decomposition for larger Co content (114), (121), (126)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hexagonal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ba$_{1-x}$Sr$<em>x$Co$</em>{1-y}$Fe$<em>y$O$</em>{3-d}$ (BSCF)</td>
<td>perovskite</td>
<td>sol-gel thermolysis method, solid-state reaction method, Pechini and Citrate-EDTA Complexing Methods</td>
<td>600-800</td>
<td>▲ Excellent properties for ionic, electronic conduction below 800°C due to high oxygen vacancy and high rate of oxygen diffusion, best candidate for cobaltate salt based electrolyte, ▼ Performance highly dependent on desired stoichiometric composition, chromium deposition on surface (127), (114), (128), (129), (130), (131), (125)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Sm$<em>{0.5}$Sr$</em>{0.5}$CoO$_3$ (SSC)</td>
<td>perovskite</td>
<td>Co-precipitation method, pulsed laser deposition</td>
<td>600-800</td>
<td>▲ High activity for oxygen reduction, better cathodic performance, excellent mixed conductivity, cost-effective wet ceramic process for interlayer, low polarization resistances (110), (132), (133), (134), (135)</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Material Description</td>
<td>Synthesis Method</td>
<td>Operating Temperature</td>
<td>Remark(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------------------</td>
<td>------------------</td>
<td>-----------------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>LaNi$_{1-x}$Fe$_x$O$<em>3$ La$<em>2$NiO$</em>{4+δ}$ La$</em>{2-x}$Sr$_x$NiO$_4$</td>
<td>Ruddlesden–Popper sol–gel route</td>
<td>800</td>
<td>▲ lowest observed ASR of 0.11 Ω cm$^2$ high ionic conductivity and high electrocatalytic activity, oxygen tracer diffusion coefficient of LSM / LSCF, ▼ Required GDC interlayer for YSZ electrolyte increases another process (136), (131)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>La$<em>{0.5}$Ba$</em>{0.5}$CoO$_{3-δ}$</td>
<td>perovskite solid-state route</td>
<td>650–775</td>
<td>▲ 1.2x10$^{-3}$ S cm$^{-1}$ at 650°, metal–insulator transition and unique magnetic behavior, chemically stable system, stable phase and exhibits the highest electronic conductivity ▼ possibility of carbonate formation at high temperatures when exposed to CO$_2$, (124)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Y$_2$Ru$_2$O$_7$ &amp; Y$_2$xPr$_x$Ru$_2$O$_7$ Pb$_2$Ru$<em>2$O$</em>{6.5}$</td>
<td>pyrochlore co-precipitation method</td>
<td>250-800</td>
<td>▲ significant decrease of electrodes impedance, best cathode for (Er$_2$O$<em>3$)$</em>{0.2}$(Bi$_2$O$<em>3$)$</em>{0.8}$, good electronic conductivity (137),</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>direct condensation method</td>
<td>300-600</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5: List of cathode materials reported in literature for solid oxide fuel cells along with their crystal structure, synthesis method, operating temperature and remarks covering important issues
Table 2.5 presents list of cathode materials used in SOFC. In cathode materials also, it is seen that limited materials systems were studied. Lanthanum Oxide based materials shows promising catalytic activity for Oxygen as well as Air, promising mixed electronic and ionic conductivity, however, these materials catalytic activity lowered dramatically at temperature < 600°C. There are novel oxide materials reported at lower temperature catalytic operation BSCF and SSC listed in above Table shows very good catalytic activity and mixed ionic conductivity at lower operating temperature of SOFC. These oxides show mechanical and structural compatibility with doped Ceria electrolyte materials. Also SSC is reported as promising cathode for BaZrO$_3$ and BaCeO$_3$ based proton ion conductor. Recently, catalytically more active oxides based on Ruthenium oxide reported. These materials crystallize in pyrocre and are good candidate as cathode for their mixed ionic conductivity and good candidate as cathode for Bi$_2$O$_3$ based electrolyte materials. Considering the oxygen and proton ion conducting electrolytes used in this work, Samarium and Strontium doped Cobaltite (SSC) was selected as cathode in this work.

### 2.2.4 Interconnects and Sealants:

Interconnectors are necessary in SOFC for collection of current. In stacked fuel cells interconnects collect current from the individual stacks. These materials should be good electronic conductors at high temperature (138). Apart from conductivity, these materials should have good mechanical, chemical, physical and structural stability as they are operated at different temperature and pressure condition at anode and cathode ends. Interconnects must have excellent immunity to the direct combination of oxygen and hydrogen during fuel operation (139). These materials must be chemically inactive and their TCE values must match with electrode and electrolyte materials (140).
Presently, limited interconnect materials are available, such as, Platinum (Pt), Gold (Au), Silver (Ag) are known interconnects in SOFC. However, due to high cost these materials are not a proper choice for such application. P-type conducting, doped LaCrO$_3$ materials are reported in literature, having general formula La$_{1-x}$Sr$_x$Cr$_{1-y}$ (Mn/Co/Ni)$_y$O$_{3.5}$ (141). Other metallic alternatives, such as, Chromium (Cr), Nickel (Ni) and Iron (Fe) metallic alloys reported as interconnections shows better electronic conductivity than ceramics at high operating temperature (139). Presently commercial SOFCs use Crofer, a Chromium alloy, as interconnects.

Sealants prevent mixing of fuel and oxidant during SOFC operation. Materials used as sealant must be electrically insulating, chemically compatible with SOFC components, thermally stable and durable in the harsh dual operating environment (oxidizing as well as wet reducing atmospheres). Sealing must survive thermal cycling as well as long-term operation at higher temperature (141) (142) (143).

According to literature, metals (144), ceramics (145), glasses (146), composites (146), and glass ceramic (147) materials are used as sealants in SOFC. Glasses, such as, soda lime silica were used as glass sealants as they are easy to synthesize and simple to apply. These glasses have very high melting point and good adherence, can bear mechanical stress during SOFC operation (148). However, cracking may occur in glasses because of tensile stresses due to thermal cycling. Glasses react with ceramic cathodes due to reducing atmosphere (149). Glass-ceramics are reported to have good strength at SOFC operating temperature, oxides like BaO, MgO, SrO, La$_2$O$_3$, B$_2$O$_3$, Al$_2$O$_3$, SiO$_2$ are used in sealing applications (150) (151). Glass-ceramics materials are refractory and capable for long term life and have tunable TCE values; but on the other hand have lower physical and chemical stability [50]. High temperature metal sealing, such as, Pt, Au paste were used to
avoid corrosion and reaction with SOFC electrode and electrolyte. However, these elements are too costly to use in such applications. Presently, CaO-Al₂O₃-BaO-SiO₂-B₂O₃ glass is used as sealant in SOFCs operating at temperatures 600-900°C (153). Incidentally most of the constituents of this glass are present in LTCC tapes in glass form as we seen earlier.

The above discussion concludes that, there are limited options for sealing and interconnects at higher operating temperature. These issues can be resolved if the operating temperature of SOFC is reduced. Clearly, there is ample scope for research in SOFC materials and process technology.

### 2.3 Introduction to Materials Characterization techniques:

This section of chapter briefly introduces the characterization techniques used in this work. The synthesized materials were characterized to analyze their elemental, structural, morphological properties. Several materials characterization techniques provide signature information regarding the obtained phases, purity and structural deformations during synthesis of the materials such as X-ray diffraction (XRD) and Raman spectroscopy. Material characterization techniques using Transmission Electron Microscopy (TEM) helped in determining the particle size, shape and also phase with crystal structure with help of Secondary Augur Electron Diffraction (SAED) pattern. Scanning Electron Microscopy (SEM) images give basic information regarding microstructure of the powder or pellets to determine grain size, grain boundary, pore size distribution. Along with these material characterizations, some electrical characterizations were used to find out electrical properties such as resistivity, conductivity, ionic conductivity, ionic transference number determination etc. Impedance analysis by Frequency response is one of the best methods.
to find out ionic conductivity and electrical equivalent circuit of bulk and grain boundaries. DC impedance measurement provides information about leakage currents and type of conducting charges. These measurements are important in fuel cell applications.

2.3.1 X-Ray Diffraction (XRD)

The X-ray diffraction is wave interference technique, in which two coherent X-ray beams produce interference patterns due to their diffraction at the edge of atomic planes in crystal structure. The basic formula relating the distance between atomic planes, diffraction angle and wavelength of the X-Ray is given by Bragg's law as follows,

$$2dsin\theta = n\lambda$$

where, $d$ is inter atomic plane distance,
$\theta$ is diffraction angle and
$\lambda$ is X-ray wavelength

This is basic characterization technique useful to measure average spacing between layers or rows of atoms, determine the orientation of single crystal or grain, identifies the crystal structure of materials as each crystal structure has signature orientation and hence peak positions. This study also facilitates size, shape, and internal stress of small crystalline regions. The samples in the form of powder, thin film and pellets can be used for this characterization and the obtained data in terms of pattern having peaks at specific 2$\theta$ values has to match with standard data card provided by Joint Committee on Powder Diffraction Standards, JCPDS (1969) which was later replaced by International Centre for Diffraction Data, ICDF (1978). There are thousands of data card available for inorganic materials. These cards consist of information regarding standard card number, chemical formula, chemical name, data of diffraction method used, crystallographic data and diffraction data. The obtained pattern has to
be match with one of the JCPDS data card in all respect to confirm its crystal structure and structural parameter such as lattice constant (a, b, c), lattice angles (α, β, γ) and Miller indices (h, k, l). This characterization confirms formation of phase, purity and density of the powder characterized. There are significances of peak shape available in XRD depending on peak position, peak width and peak intensity. The matching of peak position with JCPDS card concludes that obtained powders are strain free, a shift towards low 2θ values implies uniform strain and broadening of peaks at same peak position signifies non uniform strain usually observed in nano crystalline materials. The XRD is a non destructive technique to find structural properties such as strain, grain size, phase formation. It is a fast, easy characterization technique in which no specific sample preparation is required, has very high d spacing accuracy, easy to differentiate between single crystal, polycrystalline and amorphous material (152). However, this characterization technique gives limited information on structural and compositional details in case of amorphous materials such as glasses. All the samples used in this study were in the powder form and X-ray diffraction was carried out using XRD: PANanalytical PW3040/60 X’pert PRO diffractometer in the range of 5 to 100° rotation of the sample at scan rate of 2°/min using Cu ka X-ray wavelength of 1.5405Å.

2.3.2 Raman analysis

Raman spectroscopy is vibrational spectroscopy based on inelastic scattering of monochromatic excitation source. The spectral lines have energy range from 50 to 4000cm\(^{-1}\). It is a fingerprint technology for materials detection on the basis of peaks observed at different energy scale. This is almost similar technique to XRD except that in Raman analysis interaction of visible light with molecules is
considered. The phenomenon based on infrared or visible light absorption associated with same type of quantized vibrational states. The Raman scattering occurs when monochromatic light is scattered by molecule and scattered radiation has been modulated by the characteristic frequencies of the molecule. Unlike Rayleigh scattering where oscillations dipole is induced by EM radiation which reradiated at same frequency. Raman analysis has an additional advantage over infrared technique that obstruction due to water molecule does not affect Raman spectroscopy. The Raman process is elastic scattering process in which electron either loose energy or in some cases gain energy. The first case is known as Stokes process and the later is anti stokes. For Raman spectroscopy, the molecule is required to be Raman active i.e. it must have polarizability of the bond so that it absorbs energy and bond gets deform. If such deformation is not present in molecule, it is said to be Raman inactive. The molecular interaction of photon with molecule is depends on polarizability of molecule. The intensity of peak is directly proportional to concentration of Raman active species in the sample. Raman analysis of the powders was done in this work to identify phases, phonon interactions, vacancies and glass ceramic interactions. The Raman spectrometer used in this work was BRUKER RFS 27: Stand alone FT-Raman Spectrometer, in the scan range 100-800nm using Nd:YAG LASER of 1064nm wavelength.

2.3.3 Transmission Electron Microscopy (TEM)

The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons
are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of 0.025Å. The resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2 Å.

Materials for TEM must be specially prepared to thicknesses which allow electrons to transmit through the sample. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms. Magnifications of 350,000 times can be routinely obtained for many materials, whilst in special circumstances; atoms can be imaged at magnifications greater than 15 million times. In the present study, TEM (PHILIPS Model: CM200) was used at different magnifications and accelerating voltage of 100-200keV to confirm crystallite size and particle size, inter plane diffraction pattern to obtain ‘d’ values. TEM also used to find distortion in lattice plane in some cases where glass-ceramic interaction present in the lattice.

### 2.3.4 Scanning Electron Microscope

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that are obtained from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from
20X to approximately 30,000X, spatial resolution of 50 to 100 nm). In present study SEM (Philips X-30) is used to observe the microstructure of the powders synthesized by combustion method and Field Effect Gun-Scanning Electron Microscope (FEG-SEM: The Quanta 200 FEG) was used to observe grain structure of sintered pellets. The microstructure was observed at different magnifications from 12000-10^5X using different accelerating voltages.

### 2.4 Introduction to Electrical characterization

The electrical characterization of the samples is necessary to find their electrical properties. Resistivity, ionic transference number, ionic conductivity are some properties of materials required for certain applications. The ionic conductivity is an essential property for electrolytes used in solid oxide fuel cells. The ionic conductivity must be close to 0.1S.cm⁻¹, which is a benchmark set by YSZ electrolyte at1000°C. Impedance analysis is a tool to analyze conduction mechanism and measure ionic conductivity of the material. This tool is used to find equivalent electronic circuit that fitted conduction mechanism for given electrolyte. The impedance analysis is briefly explained in following section.

#### 2.4.1 Introduction to Impedance analysis

Impedance spectroscopy (IS) is an electrochemical technique to measure and analyze the response from electrode and electrolyte and their interface by applying small alternating voltage. The frequency perturbation is applied over wide range to analyze all responses. This method is useful to determine number of parameters related to electrochemical kinetics, electric and dielectric properties of materials. The complex impedance is presented as follows;
\[ Z(t) = \frac{U(t)}{I(t)} \]

where, \( U(t) \) is sinusoidal alternating signal = \( U_0 \sin(\omega t) \)

\( I(t) \) is time dependent current = \( I_0 \sin(\omega t + \theta) \)

The frequency domain of the \( Z(\omega) \) consists of two parts viz. real and imaginary part of impedance presented by following equation,

\[ Z(\omega) = Z'(\omega) + Z''(\omega) \]

Here, \( Z'(\omega) \) is pure resistance while imaginary impedance given by

\[ Z''(\omega) = \frac{1}{j\omega C} \]

Three different regions of \( \omega \) gives impedance/ resistance values for different regions of samples as follows

When, \( \omega \to 0 \)

\[ Z(\omega \to 0) = 2R_E + R_B \]

\[ Z(\omega \to \infty) = 0 \]

\[ Z(\omega_E \leq \omega \leq \omega_B) = R_B \]

The capacitance of the any circuit is given by following formula;

\[ C = \varepsilon'(\omega) \varepsilon_0 \frac{A}{d} \]

where, \( \varepsilon_0 \) = permittivity of free space

\( \varepsilon''(\omega) \) = frequency dependence permittivity of dielectric materials

\( A \) = area of plates and \( d \) = distance between two plates

The dielectric shows energy transfer to heat due to dipole rearrangement and leakage current. These dipole movements are frequency dependent. The frequency range in IS ranging from \( 10^{-3} \) to \( 10^{16} \) Hz, in which one can find polarization of electrons, atoms, dipoles
and interface in descending order of frequencies. Frequency range for commercial impedance analyzer for ionic conductivity measurement applications required below 1Hz. This frequency is sufficient to find corrosions in liquid, diffusions in solid materials and liquid solutions. Figure 2.4 presents the schematic of solid electrolyte sandwiched in two electrodes and its representative Nyquist plot with equivalent circuit.
Figure 2.4 shows that, each RC circuit representing part of electrochemical cell, the half circle at high frequency and first RC circuit in equivalent circuit represents grain contribution, second half circle and RC combination represents grain boundary contribution and third vertical line presents capacitance between sample and electrode. The time constant of RC circuit is given by,

$$\tau = RC$$

The half circles shown in figure are ideal cases, however in practice these half circles may be depressed and their centers may go below $Z'$ axis. These conditions occurred due to non ideal capacitor behavior, surface roughness of electrode, presence of more than one polarization mechanism or heterogeneous corrosion product layers. The ionic conductivity measured from impedance spectra by fitting of equivalent circuit and getting values of real impedance of each half circle using following formula,

$$\sigma = \frac{d}{AR}$$

where $d= \text{thickness of sample and}$

$A= \text{cross sectional area of sample}$
This study further extends to find temperature dependence of conductivity by plotting Arrhenius plot of $(\sigma T)$ verses $(1000/T)$ plot. Diffusivity of ions can be calculated from ionic conductivity according to Nerst-Einstein equation. The impedance measurements were carried out using Autolab PGSTAT100 Potentiostat/Galvanostat with a frequency perturbation between 1Hz to 1MHz and in temperature range of 500-700°C using laboratory made set up of a furnace with quartz chamber having Platinum electrodes and Platinum wire. Schematic of jig developed and set up is shown in Figure 2.5.

This set up consists of two stainless steel rods in a quartz tube. A sample is sandwiched between two electrodes platinum disk and platinum wire was used to make contact with Platinum disks to take contacts out of furnace. Following are specifications of the furnace;

Specifications: Max operating temp.: 1000°C
Ramp rate: 1-20°C/min
Temperature accuracy: 0.1°C
Sample size: Max diameter = 9.5mm, max. Thickness=1.2mm
Voltage rating: 240Volts at 50/60Hz
2.4.2 Ionic transference number determination

The ionic transference number gives information about ratio of electronic and ionic current flowing through ionic conductors. This number must be as high as possible and close to 1 for electrolyte in solid oxide fuel cells. The ionic transference number is measured by applying a small DC voltage across the pellet. Initially, small current flow through the circuit which is leakage current due to polarization. The current decays after some time if no electron transfer is taking place through pellet. This current is stabilized current and it should be almost negligible compared to initial current. The ionic transference number is calculated using following formula;

\[
\text{Ionic trans. number} = \frac{I_0 - I_s}{I_0}
\]

where, \( I_0 \) = initial current flowing through circuit

\( I_s \) = saturated current flowing through circuit after some time
Hence, this technique confirms ionic conduction through electrolyte with no internal shorting of electrodes. In this study, set up shown in Figure 2.4 was used for this measurement. A constant voltage source Keithly 2200-20-5 DC power supply was used as voltage source and current was measured using Keithly 2010 multimeter.

This chapter presents brief information regarding LTCC materials and process. The LTCC materials consist of ceramics, oxide glasses, organic/inorganic binders etc. These additives help lowering firing temperature of LTCC. On the contrary materials survey about SOFC materials shows all electrode and electrolyte materials are ceramics having firing temperature above 1000°C. Being a glass ceramic material other properties of LTCC are different from SOFC materials. Present status of these two technologies shows that their physical and chemical properties are quite different from each other. For integration of SOFC in LTCC, major challenge is to make their materials compatible with each other. Present work is motivated with this issue of materials compatibility.

Subsequent four chapters focus on the synthesis and characterization of SOFC materials and study of their compatibility with LTCC.

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