CHAPTER 2

LITERATURE SURVEY

2.1 GENERAL

Even though the technology for electrochemical power plants exists since 1839, the fuel cells have gained popular recognition as an economically and technically viable power source only recently. Fuel cells have been considered as a prime candidate for 'green' energy production which is clean, quiet, and efficient. Regardless of their relatively new arrival, fuel cells have already found their way into early commercial testing in stationary applications and prototype testing in mobile and portable applications.

Depending upon the fuel cell type the primary fuels which can be directly utilized today within fuel cell stacks are hydrogen, carbon monoxide, methanol, and dilute light hydrocarbons. The discussions regarding the different types of fuels that can be used for fuel cells are made in this chapter.

There are many types of fuel cells; they all consist of an anode, a cathode and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. As the main difference among fuel cell types is also based on the electrolyte, fuel cells are classified by the type of electrolyte they use. As discussions regarding Solid Oxide Fuel Cells were made in the previous chapter, only other types of fuel cells are discussed in detail in this chapter.
Electrolyte is the primary component of importance for fuel cell and the electrolyte material plays a vital part in characterizing the type of fuel cell. In this research as only SOFC is being concentrated the electrolyte materials so far in use and undergoing research based on SOFC are discussed in this chapter.

Further the methods used to synthesize the electrolyte materials are also discussed along with the characterization techniques and the instrumentation procedures adopted to compare the ionic conductivity of material so as to find out the suitability to be used as an electrolyte in SOFC.

Hence to consolidate, this chapter formally makes about the literature survey and brief discussions based on the following

1. Fuel Flexibility
2. Types of fuel cells
3. Electrolytes for SOFC
4. Powder Synthesis and Characterization

2.2 FUEL FLEXIBILITY

Development in the design of fuel cells must be more focused to make use of widely available fossil fuels, handle varying fuel composition, and operate without harmful impact to the environment. In order to capture the market opportunities for fuel cells it is essential to run fuel cells on renewable and waste fuels.

The primary fuel used in a fuel cell is hydrogen, which can be obtained from natural gas, gasoline, coal-gas, methanol, propane and other fuels containing hydrocarbons. Increasing the fuel flexibility of fuel cells implies that power generation can be assured even when a primary fuel source
is unavailable. This will increase the initial market opportunities for fuel cells and enhance market penetration. Some of the fuels used for fuel cells have been discussed in detail in the following pages.

Currently, the most economically viable fuel source for utility generation of electricity using fuel cells is natural gas. This is due to the fact that the nation’s power supply relies heavily on natural gas production of electricity using gas turbines. In the future, hydrogen would be the ideal fuel source, as the chemical reactions within the fuel cell would be minimal, as there would be no need for fuel reformers and by-products would be heat and water. This section focuses on natural gas and other fuel types, including hydrogen, methanol and liquid propane.

2.2.1 Natural Gas

India had 53 trillion cubic feet (Tcf) of proven natural gas reserves at the end of 2015. The total gas production in India was about 1.1 tcf in 2014. Almost 70% of India’s natural gas reserves are found in the Bombay High basin and in Gujarat. Offshore gas reserves are also located in Andhra Pradesh coast (Krishna Godavari Basin) and Tamil Nadu coast (Cauvery Basin). Onshore reserves are located in Gujarat and the North Eastern states (Assam and Tripura).

Natural gas will most likely be the fuel of choice for fuel cells until hydrogen is readily available and cost-competitive. The natural gas deliveries to electric utility customers also fluctuate with the change in seasons. Natural gas deliveries peak in the summer months, due to power generation using gas turbines. Overall, the natural gas demand for power generation is increasing. The increase of natural gas consumption in the utility sector is the fastest increasing use for natural gas.
Natural gas is consumed at a rate nearly equal to production, with an excess of around 10% of annual consumption. Natural gas storage for utility consumption is stored in relatively small amounts onsite in large storage tanks. Bulk storage uses three mediums: depleted natural gas or oil fields, aquifers and salt caverns. Depleted natural gas or oil fields store most of the nation’s natural gas. These sites use existing facilities, including access to the pipeline system, to store gas in underground storage sites. Aquifers, used mostly in the Midwest, store gas in converted water aquifers. Salt caverns are more costly than depleted natural gas or oil fields, but it is easier to monitor amounts of gas.

2.2.2 Coal Gas

Today, the establishment of new power plants in India is strongly dependent on the import of highly volatile fossil fuels. Sustainable renewable energy is becoming an important link in industrialization and development. India is finding ways past energy related growth obstacles through versatile and efficient utilization of its abundant renewable energy resources.

Energy security and environmental considerations are the two big challenges the world is facing today. India is not exceptional to these challenges but the difference is that our developmental goals are more pressing compared to the global environmental considerations and the fact that our dependence on coal in meeting our energy requirements would continue in near future also makes it further challenging.

The total installed electricity capacity in India at the end of October 2016 is 307.28 GW, of which 60.7% is coal based. Coal will continue to dominate the additional capacity to be created in the next two
decades. India needs to master the coal-gasification technology so as to boost both energy efficiency and attendant security.

Coal gas is a hybrid of natural gas and hydrogen made by the destructive distillation (gasification) of bituminous coal. The chief components are methane (20% to 30%) and hydrogen (about 50%). Use of this gas has declined to virtually nil in favour of Natural Gas. Coal-bed gas reservoirs provide unconventional storage of methane by storing it in micro pores and bedding planes, as well as free gas within natural fractures or cleats. These reservoirs act both as the source rock and storage reservoir for methane gas. Coal-bed methane is peculiar in that methane and carbon dioxide are predominantly stored in a molecular adsorbed phase within micro pores of the coal.

The ability of the coal-bed reservoir to store methane is dependant upon numerous factors: reservoir pressure, composition and rank of the coal, micro pore structure and its surface properties, the molecular properties of the adsorbed gas constituents, and reservoir temperature.

Coal-beds are an attractive prospect for development because of their ability to retain a higher amount of gas at shallow depths in comparison to conventional reservoirs at comparable depths and reservoir pressures. Coal-Bed Methane (CBM) wells are drilled with techniques similar to those utilized for drilling conventional wells, but completion practices and the method of reservoir evaluation are different. It requires that the production casing of all coal-bed methane wells be cemented from producing horizon to surface by grout circulation methods. The intent of requiring this extensive primary cementing is to minimize or preclude inter-zonal flow of fluids between producing horizons and aquifers within the casing annulus.
Today, coal-bed gas wells are usually completed for production in one of two different manners. By altering the velocity of the gas escaping from the coal reservoir, the so-called “cavitations method” creates a cavity in the targeted coal seams, effectively enlarging the original well bore. The increased well-bore volume promotes linking the well bore with the natural fracture system of the coal-beds.

The second method involves conventional completion techniques in which individual or multiple coals are hydraulically fractured by pumping water or other fracture inducing fluids and fracture-sustaining material under high pressure through pipe perforations into the coal-beds. Since methane gas is stored (adsorbed) on micro pores of the coal, and storage is a function of pressure (the higher the pressure the greater the storage potential), production of coal gas is dependent upon reduction of pressure within the coal-beds.

Methane can be produced from the coal-beds by reducing overall reservoir pressure or by reducing the partial pressure of the methane alone, while sustaining reservoir pressure. Pressure reduction frees the methane molecules from the coal and allows gas to migrate through permeable strata, cleats and fractures to an area of lower pressure, ideally into the well bores that created the pressure reduction.

In near surface coal outcrops, hydrostatic pressure reduction may allow locally desorbed coal gas to migrate entrained with groundwater or rise vertically to the surface.

Mined coal is burned to produce electricity and flue gas. The carbon dioxide is captured from the flue gas (comprised mainly of CO₂ and N₂) and injected into deep coal beds. Once there, the coal adsorbs the CO₂
releasing methane from the coal. The methane gas (CH$_4$) is produced and is reformed in H$_2$ and CO$_2$.

The H$_2$ can be used to fuel the next generation fuel cell and pure carbon dioxide is injected back into the coal bed.

**2.2.3 Hydrogen**

At the end of last century Knowledge and Natural Gas were assigned as hallmark of 21st Century, but now we have realized in the first few years of this century that the Natural Gas alone will not be able to help us reduce our movement for containing and reducing the CO$_2$ emission. In the process of decarburizing our sources of energy, the scientists world over have accelerated the innovations on finding sustainable alternate sources of energy, and we believe that the research is narrowing down to “zero carbon fuel Hydrogen”, which only has the potential to fulfil the need to be a clean, reliable and sustainable energy carrier, satisfying the need of both the hearth and the wheel.

Scientists, in the olden days were unknowingly producing Hydrogen in their labs. Robert Boyle produced Hydrogen gas as early as 1671 in an experiment with iron and acids. However, it took almost a century before it was finally recognized as a distinct element by Henry Cavendish in 1766.

The Hydrogen molecule is a simple combination of an electron and a proton. It is perhaps the simplest element known to man and is virtually the basic building block of the universe. It is the fuel which is burnt by the stars. The process, known as ‘fusion’ is being tapped into to solve the earth’s impending energy crisis.
Hydrogen is an element that is abundant and pervades the universe. The sun’s supply of Hydrogen is expected to last another 5 billion years. The importance of the gas is amazing. Its range of uses includes edible fats & oils on one hand and superconductors & rocket fuel for space ships, on the other.

When astronauts travel to outer space, their ship is propelled by Hydrogen fuel in its liquid form, even as Hydrogen batteries, known as fuel cells, power the electrical systems in the ship. So clean is this fuel that its only by-product is water which quenches the thirst of space travellers.

Hydrogen is omnipresent and is pure to the core. It has tremendous energy content within it. It forms the basis of life on the planet with its combination with another vital gas – oxygen, to form water. It is this that we see at all times. This energy makes plants grow; it is the cause of the movement of air and rain. It is this energy that is stored in fossil as chemical energy.

The formation of Hydrogen Association of India is expected to provide further drive to the hydrogen research activities in the country. HAI provides a common platform for sharing experiences regarding the latest technological trends in generation, usage and safety issues related to application of hydrogen as automotive fuel & other purposes, with national and overseas experts. HAI shall provide excellent networking opportunities for one & all who want to contribute for the cause of Hydrogen Economy for a new world order

Currently there is an insufficient hydrogen infrastructure to support hydrogen fuel cells for utility generation. This is due to the fact that there is no hydrogen pipeline system. The National Hydrogen Energy Roadmap is the second step in the U.S. Department of Energy's National Hydrogen Vision
and Roadmap. It describes the need for a collaborative effort to migrate towards a hydrogen energy future. Until a hydrogen transport system can make hydrogen readily available to utilities, fuel cells will most likely be powered by natural gas.

Hydrogen for use in industrial applications is derived from several sources. Methods of hydrogen production are out of the scope of this report. Hydrogen is considered an alternative fuel source, and its primary uses are for hydrogen fuel cell cars. Current availability of hydrogen for fuel cell generation of electricity is meagre, and adequate supply for this purpose would most likely be a by-product of industrial processes.

Current hydrogen storage methods include compressed gas, liquid hydrogen, metal hydride and carbon based systems. Other potential storage techniques include storage of hydrogen in the actual pipelines used to transport the fuel. Metal hydride storage involves storing hydrogen atoms within a metal lattice structure. Carbon based systems store hydrogen within microscopic carbon structures. The most economic storage techniques for smaller amounts are short-term compressed gas and short-term metal hydride. For large amounts, long-term liquid hydrogen is the most economical.

2.2.4 Methanol

Methanol is an organic chemical and forms an important part of the Indian petrochemical industry. Being an organic chemical, methanol contains as its main constituents oxygen, hydrogen, and carbon. Methanol is manufactured from natural gas that has methane content. The market of methanol in India is expected to be around 435 crore.
In the last few years, the methanol industry has faced a slow down as a result of which the domestic supply have been more than the demand. Around 15% of the total methanol is imported.

Methanol is a colourless volatile liquid with a faintly sweet pungent odour similar to ethyl alcohol. The substance is fully soluble in water. Vapours of methanol are slightly heavier than air and may travel some distance to a source of ignition and flash back. Accumulations of vapours in confined spaces such as buildings or sewers may explode if ignited. There is potential for containers of liquid to rupture violently if exposed to fire or excessive heat for sufficient time duration. Methanol is listed as a “Poison-Class B”. It is harmful if swallowed or absorbed through the skin.

Excessive heating and/or incomplete combustion will generate carbon monoxide, formaldehyde, and possibly unburned methanol.

Listed below are the incompatibilities of methanol.

a. It has an explosive reaction with chloroform + sodium meth oxide and diethyl zinc.

b. It has a violent reaction with alkyl aluminum salts, acetyl bromide, chloroform + sodium hydroxide, cyanuric chloride, nitric acid, etc.

c. Incompatible with beryllium dihydride, metals (potassium, magnesium, etc.), oxidants (barium, perchlorate, bromine, chlorine, etc.), etc.

d. Dangerous; can react vigorously with oxidizing materials.

Most retail fuelling stations use underground tanks because they allow for greater commercial use of the available land. Aboveground tanks
are common for fleet refuelling facilities and may also be used in rural applications where land use is not an issue. Underground tanks are available in sizes from 500 to 50,000 gallons, while aboveground tanks are available in the range of 250 to 12,000 gallons.

Acceptable tank materials for containing methanol include carbon steel, fibreglass, and stainless steel. Due to cost, stainless steel tanks are rare. Carbon steel tanks used underground must be protected against corrosion, usually by a fibreglass coating. The crown of a buried tank must have a minimum covering of 36 inches of fill material or 30 inches of fill material with an 8-inch reinforced concrete slab. Fill material for fibreglass and fibreglass-over-steel composite tanks should be pea gravel; sand may be used for all steel tanks. Anti flotation tie-downs may be required if the local water table is high enough to interfere with the tank. Aboveground tanks are exposed to the elements and must be protected by coating with materials that are not degraded by the sun’s ultraviolet radiation. Aboveground tanks require protective barriers to prevent impact with vehicles using the fuelling facility. Since burning materials can come into contact with the exterior of an aboveground tank, and possibly result in detonation of the contained fuel, aboveground tanks are often covered with a fire-protective material such as concrete.

Methanol industry in India have been facing decline in the last few years. For it to grow the government of India and the Indian petrochemical industry will have to make a combined effort. And only then the industry of methanol will be able to rise.
2.2.5 LPG (Propane)

Propane, the most common Liquefied Petroleum Gas (LPG), is one of the nation's most versatile sources of energy and supplies about 4 percent of our total energy needs. Propane exists as a liquid and a gas. At atmospheric pressure and temperatures above -44 F, it is a non-toxic, colourless and odourless gas. Just as with natural gas, an identifying odour is added so it can be readily detected. When contained in an approved cylinder or tank, propane exists as a liquid and vapour. The vapour is released from the container as a clean-burning fuel gas. Propane is 270 times more compact as a liquid than as a gas, making it economical to store and transport as a liquid. Approximately equal amounts of propane come from the refining of crude oil and from natural gas processing. Thus, propane is a readily available, secure energy source whose environmental benefits are widely recognized. Propane is an approved, alternative clean fuel listed in the 1990 Clean Air Act, as well as the National Energy Policy Act of 1992.

As the demand for propane grew, a vast transportation network was created. After crude oil and petroleum gases are extracted from the earth, they are shipped to an oil refinery or natural gas processing plant, respectively, where propane is one of many products that can be separated from the raw hydrocarbon stream. From the refinery or processing plant, propane is shipped in two stages. First, to an intermediate terminal and from there to the local propane supplier for delivery to the end user. All propane is transported under pressure in its more compact liquid form; 75 percent is transported by a pipeline-truck combination. Two types of trucks are used for propane transportation: a highway transport (which typically carries 7,000 to 12,000 gallons) and a smaller bulk delivery truck, called a "bobtail" (which carries 1,000 to 5,000 gallons). Both types of trucks are constructed of high-strength steel.
Retail propane storage facilities are known in the propane industry as "bulk plants." Bulk propane storage tanks are constructed of steel in accordance with the Boiler and Pressure Vessel Code, Section VIII of the American Society of Mechanical Engineers (ASME) and the requirements of state and municipal authorities. The tanks are equipped and located as set forth in NFPA 58, "Liquefied Petroleum Gas Code." Each storage tank, depending on size, is set a specific distance away from other tanks, buildings, and property lines. Bulk storage tanks are always installed on a firm foundation and are protected by an enclosure to prevent trespassing and tampering. Tanks are painted light, reflective colours for both safety and appearance.

2.3 TYPES OF FUEL CELL

Fuel cell types are generally characterized by electrolyte material and the type of fuel used. The electrolyte is the substance between the positive and negative terminals, serving as the bridge for the ion exchange that generates electrical current. While many types of fuel cells exist, there are six principle kinds in various stages of commercial availability, or undergoing research, development and demonstration. These six fuel cell types are significantly different from each other in many aspects; however, the main distinguishing feature is the electrolyte material.

They are:

1. Alkaline Fuel Cell (AFC)
2. Molten Carbonate Fuel Cell (MCFC)
3. Phosphoric Acid Fuel Cell (PAFC)
4. Proton Exchange Membrane Fuel Cell (PEMFC)
5. Solid Oxide Fuel Cell (SOFC)
6. Direct Methanol Fuel Cell (DMFC)
Figure 2.1 illustrates the scheme of basic principle of different kinds of fuel cells. These types are chosen because of their electric efficiency, which can be increased when used as a combined heat and power (CHP) unit, as well as having the greatest power output per volume of the cell. When a fuel cell is used as a CHP unit, efficiency of the system can reach in excess of 70% with a maximum value of around 80%.

By far Solid Oxide Fuel Cell attracts much research interest throughout the world for its potential market competitiveness, including highest efficiency, fuel-flexibility, low price, and long life expectancy (McIntosh & Gorte 2004, Lu et al. 2002, Steele 2000, Mogensen & Kammer 2003). As SOFC was discussed in detail in the previous chapter other types of fuel cells are discussed in detail in this chapter.
Table 2.1 Fuel cell types and characteristics
(Source:http://seniord.ee.iastate.edu/may0316/Client%20Final.pdf)

<table>
<thead>
<tr>
<th></th>
<th>Phosphoric Acid Fuel Cells</th>
<th>Molten Carbonate Fuel Cell</th>
<th>Solid Oxide Fuel Cell</th>
<th>Proton Exchange Membrane Fuel Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Abbreviation</strong></td>
<td>PAFC</td>
<td>MCFC</td>
<td>SOFC</td>
<td>PEMFC</td>
</tr>
<tr>
<td><strong>Operating Temperature</strong></td>
<td>205°C</td>
<td>650°C</td>
<td>1000°C</td>
<td>80°C</td>
</tr>
<tr>
<td><strong>Electric Efficiency</strong></td>
<td>40%</td>
<td>60%</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td><strong>Cogen Efficiency</strong></td>
<td>80%</td>
<td>85%</td>
<td>80%</td>
<td>70%</td>
</tr>
<tr>
<td><strong>Co-generation</strong></td>
<td>Hot water</td>
<td>Hot water, LP/HP steam</td>
<td>Hot water, LP/HP steam</td>
<td>80°C water</td>
</tr>
<tr>
<td><strong>Size Range</strong></td>
<td>250 kW-1MW</td>
<td>10 kW-2MW</td>
<td>25-200 kW</td>
<td>50-250 kW</td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
<td>Natural gas, hydrogen, landfill gas, digester gas, propane</td>
<td>Natural gas, hydrogen</td>
<td>Natural gas, hydrogen, landfill gas, fuel oil</td>
<td>Natural gas, hydrogen, propane, diesel</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Phosphoric acid</td>
<td>Lithium-potassium carbonate salt</td>
<td>Solid ceramic zirconia</td>
<td>Polyperflouro-sulfonic acid</td>
</tr>
<tr>
<td><strong>Environment</strong></td>
<td>Nearly zero emissions</td>
<td>Nearly zero emissions</td>
<td>Nearly zero emissions</td>
<td>Nearly zero emissions</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>Platinum</td>
<td>Nickel</td>
<td>Platinum</td>
<td>Platinum</td>
</tr>
</tbody>
</table>

2.3.1 Proton Exchange Membrane Fuel Cell (PEMFC)

PEMFCs use a polymer membrane, perfluorosulfonic acid, as the electrolyte, and due to the acidic nature of the electrolyte, the ions transported
are hydrogen ions (H⁺). In that manner the fuel that is supplied to the system is hydrogen and oxygen or air as the oxidant.

A PEMFC is the only low temperature fuel cell that is being considered for the power generation application. The operating temperature of PEMFC is 80°C using acidic electrolyte. Therefore, noble metals are required for the catalyst layer.

The cathode is the most essential electrode because catalytic reduction of oxygen is more difficult than catalytic oxidation of hydrogen. The high activity of the catalyst has the disadvantage of the great affinity for carbon monoxide and sulphur products.

These molecules strongly bind to the catalyst and inhibit hydrogen or oxygen from reaching it. Although poisoning from carbon monoxide can be prevented, this is cost ineffective since it requires individual treatment of each cell. For the operation of PEMFCs the polymer membrane needs to be kept humid, since the conduction of ions in polymer membranes requires humidity. Therefore the membrane should not be dry because there will not be enough acid ions to carry the protons, but it should not be too wet because the pores of the diffusion layer will be locked and the reactant gases will not be able to reach the catalyst.

The advantages of a PEMFC are, no possibility of electrolyte leakage, lack of corrosion of electrodes, and the electrolyte has a resistance to gas crossover.

The power density of a typical PEMFC is equal to 6.4 kW/m². Ballard Power Systems, using a special membrane, have achieved a power density of 21.5 kW/m² for a PEMFC. Since this type of fuel cell operates at
such a low temperature, the fuel required for the cell to function needs to be extremely pure.

Another disadvantage of the PEMFC is the fact that it has such a large output of H₂O. In an environment where the temperature drops below 0°C, the fuel cell would stop operating, or would have to be in a heated enclosure during the winter months. A PEMFC can have a power capacity between 5 and 250 kW. They can also be used in a CHP application, which
will increase the efficiency from 40%, up to 75%. Figure 2.2 shows a complete PEMFC with chemical reaction and electrical circuit.

2.3.2 Alkaline Fuel Cell (AFC)

![Alkaline Fuel Cell Diagram](http://www.fuelcellmarkets.com/fuel_cell_markets/alkaline_fuel_cells_afc/4,1,1,2506.html)

**Figure 2.3 Alkaline fuel cell**

The electrolyte in AFCs is an aqueous solution of potassium hydroxide (KOH). The ions carried by the alkaline electrolyte are OH\(^-\) forming water at the anode electrode. AFCs exhibit high efficiency due to the fast kinetics allowed by the KOH electrolyte, since the oxygen reaction is much easier than the oxygen reduction in acidic fuel cells.
The fast kinetics of AFCs allows the use of less expensive catalyst than platinum, such as silver or nickel. AFCs operate over a wide range of temperature from 80-230°C and pressure from 2.2-45 atm. Although poisoning is also a problem in AFCs, since the hydroxide electrolyte has great affinity for carbon dioxide forming carbonate ions.

2.3.3 Phosphoric Acid Fuel Cell (PAFC)

PAFCs use phosphoric acid (H₃PO₄) as electrolyte in a liquid form which unlike other acids does not require water to conduct; therefore they can operate at a higher temperature. The electrolyte is acidic and conducts hydrogen ions. PAFCs operate above 420°C which is the freezing point of H₃PO₄. Besides the low operating temperature of the stack, another advantage of PAFCs is the low cost of the electrolyte. However, the slow kinetics of the electrolyte requires expensive catalyst.

Its electrical efficiency is around 40% and this increases to 80% if used in a co-generation cycle. Phosphoric acid fuel cells can use a wide variety of fuel, particularly, impure hydrogen. Hydrogen with a carbon monoxide (CO) concentration of 1% can be used, which would typically be greater than other types of fuel cells that have a lower operating temperature. Phosphoric acid fuel cells are typically around 250 KW in size, with the largest being 11MW.

The advantages of a PAFC are based on the fact that they operate at a temperature of 220°C. Since the temperature is so high, it improves the kinetics of the chemical reaction, which in turn produces more power. They can also withstand 1% CO impurity in the fuel stream. A PAFC is versatile enough to use either liquid cooling or gas cooling, depending on what is
available. Unlike a fuel cell that operates at a cooler temperature, this type of fuel cell can extract some steam from the process, instead of just warm water.

![Phosphoric acid fuel cell](http://www.greenoptimistic.com/phosphoric-acid-fuel-cells-20120423/)

**Figure 2.4 Phosphoric acid fuel cell**

The advantages also include the requirement of an external reformer and platinum as a catalyst. Because of the operating temperature the internal environment is very corrosive. It is even worse when there is an open circuit type state. Special procedures need to be followed because of the temperature, and the supports that hold the catalyst requires special thermal treatment to withstand corrosion. If there are impurities in the fuel stream such as sulphur compounds, ammonia or large amounts of CO, the anodes will suffer poisoning and will decrease the power output. The PAFC also has a long-term performance degradation, which will decrease the output voltage anywhere from 2 to 5mV per 1000 hours. Figure 2.4 illustrates a PAFC in a CHP application.
2.3.4 Molten Carbonate Fuel Cell (MCFC)

MCFCs use lithium-potassium carbonate or lithium sodium carbonate salt as an electrolyte in order to conduct ions. The conducted ions are carbonate ions ($\text{CO}_3^{2-}$) and the reaction mechanism is as follows

Anode: \[ \text{H}_2 + \text{CO}_3^{-2} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \]

Cathode: \[ \frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{-2} \]

(Source:http://mypages.iit.edu/~smart/garrear/fuelcells.htm)

Figure 2.5 Molten carbonate fuel cell

The operating temperature of MCFCs is from 500-800°C and CO$_2$ should be supplied at the cathode. MCFCs offer the advantage of low cost catalyst due to fast kinetics of the electrolyte, and the low sensitivity to
poisoning. Although they need complex fuel cell system due to CO$_2$ cycling, additionally the electrolyte is very sensitive to corrosion. The higher operating temperature has the advantages such as higher efficiency and ability to economically produce steam as a by-product. Electrical efficiency is around 60%, but when operated with co-generation the overall efficiency is around 85%.

Unlike the phosphoric acid fuel cell, the MCFC doesn’t suffer from anode poisoning because of the temperature. Also, they can function on natural gas, CO, or other hydrocarbons as fuel. Molten carbonate fuel cells do not need external fuel processors and can use a wide variety of fuels. Using an internal reformer rather than external one the fuel cell creates a gas rich in nitrogen by combining natural gas with steam. Another advantage of this type of fuel cell is that it uses nickel as a catalyst rather than platinum. Although the MCFC has some advantages over other fuel cells, corrosion is a major problem in this type of unit, and requires the use of expensive materials and protective layers. The MCFC needs another source of carbon dioxide (CO$_2$) and the extra source could introduce contaminants into the fuel stream that could harm the cathode. Chemical reactions for MCFCs are shown in Figure 2.5.

2.3.5 Direct Methanol Fuel Cell (DMFC)

DMFCs use trifluoromethane sulfonic acid or a PEM as electrolyte. Instead of using H$_2$ or other fuel they use methanol which is directly supplied to the cell. The major advantage of methanol is that it is liquid and therefore easy to store and distribute. DMFCs operate at 50-100$^\circ$C and exhibit lower efficiency than the other fuel cell systems. The preparation of electrolyte materials for SOFCs and the characterization techniques are discussed in the following headings.
2.4 NANO-TECHNOLOGY IN POWDER PREPARATION

Nanotechnology, a broad and interdisciplinary field involving solid state physics and chemistry, solid state ionics, materials engineering, medical science, biotechnology, etc., is considered to be one of the most important future technologies (Wilson et al. 2002). Nanotechnology makes it possible to design and create new materials with improved properties by manipulating matter at the nanometer scale, which in turn will profoundly impact our economy, our environment, and our society.

Nanostructured materials have a significant fraction of grain boundaries and a large surface–to-volume ratio, which exhibit unique properties arising from their size or shape in nanoscale region, e.g. “quantum
“size effect”, where the electronic properties of solids are altered due to confinement of charge carriers (Gogotsi 2006).

The improvement of ionic conductivity in the nanostructured solid conductors, known as “nanoionics”, (Maier 2005, Despotuli & Nikolaichik 1993) recently became one of the hottest fields, since they can be used in advanced energy conversion and storage devices, (Arico et al. 2005) such as solid oxide fuel cell (Maier 2005, Ruiz-Trejo et al. 2007, Knoner 2003).

Nanotechnology deals with the synthesis, characterization, exploration, and exploitation of nanostructured materials. These materials are characterized by at least one dimension in the nanometer (1 nm = 10^{-9} m) range.

Hence, the synthesis methods of nano materials and the characterization techniques adopted to study the ionic conductive behaviour of the nanostructured materials are discussed in detail.

Nanostructures include nanocrystals, nanowires, quantum dots, clusters, and nanotubes, while collections of nanostructures involve arrays, assemblies, and superlattices of the individual nanostructures (Rao et al. 2004). Nanoparticles possess large surface areas and essentially no inner mass, that is, their surface-to-mass ratio is extremely high. Therefore, the physical and chemical properties of nanomaterials can differ significantly from those of the bulk materials of the same composition. The uniqueness of the structural characteristics, energetics, dynamics and chemistry of nanostructures is the foundation of nanoscience.

Nanoscale materials and devices can be fabricated using either “bottom-up” or “top-down” fabrication approaches. In bottom-up methods,
nanomaterials or structures are fabricated from buildup of atoms or molecules in a controlled manner that is regulated by thermodynamic means such as self-assembly (Whitesides et al. 2002). While top-down fabrication technologies include photolithography, dip-pen lithography, nanomolding and nanofluidics, etc., (Chung et al. 2005). Size effects are an essential aspect of nanomaterials (Nakada et al. 1996, Jun et al. 2005). Size effects are of two types: one is concerned with specific size effects (e.g., magic numbers of atoms in metal clusters, quantum mechanical effects at small sizes) and the other with size-scaling applicable to relatively larger nanostructures (Gogotsi 2006). One example is the “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size due to the confinement of the movement of electrons (Wang & Herron 1991, Ekimov et al. 1985). Shapes of nanoparticles also play a role in determining properties (Jana 2004), such as reactivity and electronic spectra.

Nanotechnology has an extremely broad range of potential applications from nanoscale electronics and optics, to nanobiological systems and nanomedicine, to new materials, and therefore it requires formation of and contribution from multidisciplinary teams of chemists, materials scientists, physicists, engineers, molecular biologists, pharmacologists and others to work together on (i) synthesis and processing of nanomaterials and nanostructures, (ii) understanding the physical properties related to the nanometer scale, (iii) design and fabrication of nano-devices or devices with nanomaterials as building blocks, and (iv) design and construction of novel tools for characterization of nanostructures and nanomaterials (Cao 2004).

2.5 POWDER PREPARATION METHODS

The need for nano materials for different applications and with different properties has led to the development of a significant variety of
methods for preparing them. Therefore the method that should be chosen each time depends not only on the composition of the material but also on the form it is required for its proposed use. Emphasis will be placed on the solid state powder preparation method, sol-gel, co-precipitation and complexation which are the most common methods adopted due to their cost effectiveness and simplicity.

2.5.1 The Solid-State Method or Ceramic Method

The simplest and most common method is the ceramic method, used both in industry and in the laboratory. In the ceramic method the heating of two non-volatile solids takes place in order to form the desired product. The first high temperature superconductors were obtained using this method.

The ceramic method encounters several disadvantages, as high temperature is required (500-2000°C) for high input of energy and may sometimes cause unstable phase or compound. Diffusion of ions is not very fast, and this is because even by increasing the temperature in order the reaction to occur faster and diffusion of ions to take place, there is a plateau of temperature that could be reached, which is as rule of thumb, the two third of the melting temperature of the solids. Apart from ion diffusion problems, even by grinding the materials carefully the particle size would only be reduced to around 0.1 μm which is still not enough.

The mathematical description of the solid-state preparation method can be given by simplifying the shape of the solid particles to spherical (Louis Winnubst 2007). The Carter relation (Equation 2.1) describes the time \( t \) of the reaction of volume fraction \( x \) of reactant A with radius \( r \).

\[
[1 + (z - 1)]^{2/3} + (z - 1)(1 - x)^{2/3} = z + 2(1 - z) \left( \frac{Kt}{r^2} \right) \quad (2.1)
\]
Where \( z \) is the ratio of volume formed to volume consumed, and \( K \) is the apparent rate constant. The effect of temperature is expressed from an Arrhenius relation (Equation 2.2). \( K_0 \) is the pre-exponential factor that depends on the diffusion path length, and \( Q \) is the apparent activation energy for diffusion. However, even though the reaction is a function of diffusion and temperature, the temperature has greater influence on the rate constant \( K_0 \).

\[
K = K_0 \exp\left(-\frac{Q}{RT}\right) \tag{2.2}
\]

Regarding the procedure, the method is rather simple. Firstly the grinding of the materials takes place, where a homogenous mixture should be formed with small particle size of the grains, and then they are placed in a furnace to the desired temperature for several hours until the desired product is obtained. It is quite common that the reaction mixture is often removed during the heating process and reground in order to bring the “fresh” surfaces in contact and to speed up the reaction. Although homogeneity of the product is harder to achieve, as the reaction proceeds, a layer of the ternary oxide is produced at the interface of the two crystals and the ions have to diffuse through this before they react. Therefore the mixture has to be reground and reheated until the desirable phase is reached.

### 2.5.2 The Co-Precipitation Method

In order to overcome some of the disadvantages of the ceramic method new methods were encouraged. The new techniques pioneered in order to bring the components of the reaction into more intimate contact or into contact at an atomic level and to reduce the diffusion path and hence, the reaction could take place in lower temperatures.
Co-precipitation is used in order to obtain the starting materials, where a stoichiometric mixture of soluble salts of the metal ions is dissolved and then precipitated as hydroxides, citrates, oxalates or formates. Then this mixture is filtered, dried and then heated to give the desired product (Lesley & Elaine 2005).

2.5.3 Complexation

In the complexation method the immobilization of the precursor solution is achieved by the formation of a viscous matrix in which the precursor is either dispersed or forms a polymeric network. The important step during complexation is the fast dehydration at low temperature and pressure starting from a solution of cations and complexing agent. The final powder is obtained by the pyrolysis of the viscous solution. The advantages of this method are versatility in the choice of materials, the good homogeneity and sinter reactivity of the resulting powders, and the ease to perform this method on lab scale.

2.5.4 The Sol-Gel Method

In sol-gel method colloidal particles dispersed in a suspension (a sol) undergo a further reaction, which causes the colloidal particles to join together in a continuous network called a gel. The gel is dried, calcined, and powder milled (Louis Winnubst 2007). The main advantage in sol-gel process is, the reactants never precipitate (Lesley & Elaine 2005).

Initially the “sol” is prepared, which is basically a concentrated solution or colloidal suspension of the reactants and finally is concentrated to form the “gel” which is then heated to form the product. The sol preparation can be either the dispersal of an insoluble solid or the addition of a precursor which reacts with the solvent to form a colloidal product. Then the sol is
either treated or simply left to form the gel overtime by dehydrating and/or polymerizing and finally the gel is heated in order to obtain the final product. The final step of heating is of great importance because it removes the solvent, it decomposes anions, it allows rearrangement of the structure of the solid and it allows crystallization to occur. Also sol-gel process overcomes the disadvantages of the ceramic method which are the reaction time from days to hours and decrease in temperature of few hundred degrees.

2.6 INSTRUMENTATION

2.6.1 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Figure 2.7 shows the X-ray Diffraction Analyser used in the research at PSG Institute of Advanced Studies, Coimbatore, Tamilnadu, India.

X-rays are a form of electromagnetic radiation that has high energies and short wavelengths in the order of the atomic spacing of solids (William & Callister 2007). When an x-ray beam with wavelength $\lambda$ impinges on a solid material at an angle $\theta$, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beams path.
Figure 2.7  X-ray Diffraction Analyser

Diffraction will occur when the distance travelled by the rays reflected from successive planes differs by a complete number \( n \) of wave lengths known as constructive interference.

(Source:https://tap.iop.org/atomss/xray/530/page_47297.html)

Figure 2.8  Diffraction of X-rays by planes of atoms

By varying the angle \( \theta \), the Bragg's Law (Equation 2.3) conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation
produces a pattern, which is characteristic of the sample (http://www.panalytical.com).

\[ n\lambda = 2d_{hkl} \sin \theta \]  

(2.3)

If Bragg’s law is not satisfied, then the interference will not be constructive in nature so as to yield a very low-intensity diffraction beam. The magnitude of the distance, \( d_{hkl} \), between two adjacent and parallel planes of atoms is a function of the Miller indices (h, k, l) as well as the lattice parameters (a, b, c). For example, for crystal structure that has cubic symmetry \( d_{hkl} \) is given by Equation 2.4

\[ d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \]  

(2.4)

### 2.6.2 Scanning Electron Microscopy (SEM)

Electron microscopy is used to study the structure, morphology, defects and to determine the distribution of elements. A conventional microscope uses visible radiation (400-700 nm) and so cannot resolve images of objects, which are smaller than half the wavelength of light. On the contrary, electron microscopes allow resolution down to 0.1 nm (Lesley & Elaine 2005).

The electron beam is produced by heating a tungsten filament, and focused by magnetic fields in a high vacuum. In SEM, the electrons are rastered across the surface of the sample. Electrons reflected by the surface of the sample and emitted secondary electrons are detected to give a map of the surface topography of the sample.
Figure 2.9 shows the Scanning Electron Microscope used for the research at Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India.

2.6.3 Laser Diffraction

Laser diffraction is one of the simplest methods to determine the particle size distribution. For particles larger than the wavelength of light, the light scatters from the edge of the particle at an angle which is dependent on the size of the particle. Larger particles scatter light at relatively smaller angles than light scattered from smaller particles. From observing the intensity of light scattered at different angles, the relative amounts of different size particles can be determined.

2.6.4 Energy-Dispersive X-ray Spectroscopy (EDS)

Energy-dispersive X-ray Spectroscopy (EDS, EDX, or XEDS), sometimes called Energy Dispersive X-Ray Analysis (EDXA) or Energy
Dispersive X-Ray Microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample at Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

2.6.5 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a method of characterizing the electrical properties of materials and their interfaces with electronically conducting electrodes.
Figure 2.10 Electrochemical Impedance Spectroscopy

The evaluation of the electrochemical behaviour of electrolyte and/or electrode materials is done by applying voltage to the electrodes and the response is observed. It is assumed that the properties of the electrode-material system are time-invariant and EIS is used to determine these properties at Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India. There are three different types of electrical stimuli, which are used in EIS. First, in transient measurements a step function of voltage is applied at t=0 to the system and the resulting time-varying current i (t) measured. A second technique that is used is to apply a signal v (t) composed of a random (white) noise to the interface and measure the resulting current. The third technique is to measure the impedance by applying a single frequency voltage or current to the interface and measuring the phase shift and amplitude, or real and imaginary parts, of the resulting current at that frequency. Among the above three methods the third method was adopted in this research.

EIS studies the intrinsic properties that influence the conductivity of an electrode-material system. There are two categories of parameters that can be derived from an EIS spectrum. The first category is the parameters that are related only to the material itself such as, conductivity and dielectric
constant. The second class of parameter is the one which is related with the electrode material interface, such as absorption-reaction rate constants and diffusion coefficient of neutral species in the electrode itself.

The EIS technique in general involves the measurement of current through a solid electrolyte cell when a sinusoidal voltage of low amplitude is applied (Jiang et al. 1997). Also for a linear system, the magnitude of the response is directly related to the electrical stimulus for any given frequency. Hence, in a linear system, the applied potential is given by:

$$E(t) = \Delta E \exp(j\omega t) \quad (2.5)$$

The current output of the system is also sinusoidal and has the same angular frequency $\omega$, but differences in amplitude and phase from the voltage signal may occur depending on the elements in the circuit and can be represented by:

$$I(t) = \Delta I \exp(j\omega t + \phi) \quad (2.6)$$

Where, $\phi$ is the phase angle, $\Delta E$ is the amplitude of the voltage and $\Delta I$ the amplitude of the current signal. For a pure resistor, the phase shift is zero.

Since Ohm's law holds true in the time or the frequency domain, the impedance of a circuit consisting of resistors, capacitors and/or inductors is the ratio of the voltage signal divided by the current flowing through the circuit.

The impedance of the circuit $Z(\omega)$ at any frequency $\omega$ can be represented in both polar and Cartesian form and has both the magnitude $Z$ and the phase angle $\phi$. 
$Z(\omega) = \frac{E(t)}{I(t)} = Z \exp(-j\omega) = Z \cos \phi - jZ \sin \phi = Z' - jZ''$ \hspace{1cm} (2.7)

Where, \( j \) is a complex number with value of \(-1\), \( Z' \) and \( Z'' \) are real and imaginary parts of the impedance.

In this work, EIS analyses were performed in air, using a computerized HIOKI 3532 analyser. The measured frequency range covers from 50Hz to 5MHz. The temperature is manually controlled at 500\(^\circ\)C.

In the previous chapters discussions regarding the existing systems and areas of research were made and in the on coming chapter’s the investigations, results and discussions regarding the research work carried out based on singly doped and co-doped ceria electrolyte material is discussed in detail.

2.7 ELECTROLYTE MATERIALS FOR SOFC

The basic components of a ceramic fuel cell stack are electrolyte, anode, cathode and interconnect. Among them the electrolyte material plays a vital part in characterizing the type of fuel cell.

The materials for different cell components are to be selected based on the following criteria:

- Suitable electrical conductivity is required for different cell components to perform their intended cell functions,

- Adequate chemical and structural stability at high temperatures are required during cell fabrication as well as during cell operation,
• There should be thermal expansion matching among different cell components.

As the materials used for the above components were discussed in detail in the previous chapter, the materials used for electrolyte in SOFCs alone are discussed in this chapter.

SOFC power systems are not yet cost effective to merit large scale deployment in the power generation industry. Among the approaches currently being investigated to decrease the cost of SOFCs, improving power density while decreasing operating temperature is perhaps the most promising option.

However, decreasing operating temperature has the effect of increasing all types of performance losses in the cell. Thus the simultaneous goals of improving power density while lowering the operating temperature are at odds with each other. Therefore, the focus of recent research is aimed at development of more conductive electrolyte materials that can efficiently operate at lower temperatures (500°C).

The main focus of investigation has been the optimization of SOFC cell performance at a relatively low (<600°C) operation temperature to enable the use of less-costly materials for system components. The optimization has been carried out to reduce internal resistances of SOFC by two methods:

1. The reduction of electrolyte layer thicknesses to 5-10μm and

2. The use of electrolyte materials with high ionic and electrical conductivities.
2.7.1 Selection of Electrolyte Material

Solid oxide fuel cells are based on the concept of an oxygen ion-conducting electrolyte through which the oxide ions (O$_2^-$) migrate from the air electrode (cathode) side to the fuel electrode (anode) side where they react with the fuel (H$_2$, CO, etc.) to generate an electrical voltage.

For optimum cell performance, the electrolyte must be free from porosity to avoid gas permeation from one side to the other. It should also be uniformly thin to minimize ohmic loss, and it should have high oxygen ion conductivity with transport number for oxygen ions close to unit and a transport number for electrons as close to zero as possible.

Singhal & Kendall 2003 stated that the electrolyte is the component of the fuel cell responsible for conducting ions between the electrodes, for the separation of the reacting gases and for the internal electronic conduction blocking, forcing the electrons to flow through the external circuit. Without significant ion conduction, no current would pass through the cell and only a potential difference would be detected. Fergus et al. 2009, Singhal & Kendall 2003 found that for satisfactory performance, the electrolyte must meet some requirements that limit the choice of the material. These include:

1. An oxide-ion conductivity greater than $10^{-2}$ S.cm$^{-1}$ at the operating temperature

2. Negligible electronic conduction, which means an electronic transport number close to zero

3. High density to promote gas impermeability
(4) Thermodynamic stability over a wide range of temperature and oxygen partial pressure

(5) TEC compatible with that of the electrodes and other cell materials from ambient temperature to cell operating temperature

(6) Suitable mechanical properties, with fracture resistance greater than 400 MPa at room temperature

(7) Negligible chemical interaction with electrode materials under operation and fabrication conditions to avoid formation of blocking interface phases

(8) Ability to be elaborated as thin layers (less than 30 μm)

(9) Low cost of starting materials and fabrication.

Faro et al. 2009 & Fergus et al. 2009 investigated that Zirconium based ceramic materials have been the most developed electrolytes for high temperature use. At room temperature, pure zirconium is monoclinic. At 1170°C, it undergoes a phase transition to a tetragonal structure with a large volume change. Above 2370°C, pure zirconium is transformed into the cubic fluorite structure. The cubic phase still remains up to the melting point at 2680 °C. To stabilize the cubic fluorite structure from room temperature up to its melting point doping zirconium with aliovalent ions is a common practice. The doping process increases the oxygen vacancy concentration, and consequently improves the ionic conductivity. The main dopants of zirconium are CaO, MgO, Y₂O₃, Sc₂O₅, Sm₂O₃ and Yb₂O₅. They exhibit high solubility in the zirconia fluorite structure. Among these, the most frequently used is Y₂O₃ followed by Sc₂O₃.
Tarancon 2009 investigated that addition of 8 mol% of yttria i.e. \((\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}\) (8YSZ) has the highest oxide ion conductivity. \((\text{Y}_2\text{O}_3)_{0.08} \text{(ZrO}_2)_{0.92}\) is widely employed as an electrolyte material in high temperature SOFCs because of its sufficient ionic conductivity and stability in both oxidizing and reducing environments. Beyond that, its components are abundant, inexpensive and it is easy to produce. SOFCs with yttria-stabilized zirconia (YSZ) electrolyte require high operation temperature (800-1000°C), which hinders their broad commercialization due to associated high cost and technological complications. Therefore, there is a broad interest in reducing the operating temperature of SOFCs. The key for development of Intermediate-temperature SOFCs (IT-SOFCs) is to explore new electrolyte materials with high ionic conductivity at such low temperature (400-600°C).

Kharton et al. 2004 investigated that Scandia doped zirconia (ScSZ) has higher ionic conductivity. This material exhibit ionic conductivity that is 3-5 times higher than YSZ material, enhancing device performance at operating temperatures below 700°C and enabling thicker electrolyte layers. ScSZ compositions with 8-12 mol % Scandia have the highest oxide ion conductivities among all the zirconium oxides. ScSZ with 9.0% (by mole) \(\text{Sc}_2\text{O}_3\) (9ScSZ) has the conductivity of 0.34 S.cm\(^{-1}\) at 1000°C. However, at high temperature, ScSZ suffers thermal aging, reducing its conductivity. Its high ionic conductivity might enable the use of ScSZ at intermediate temperatures, in which there is no significant degradation. The main limiting factors in this case are the purity and availability of scandium oxide.

2.7.2 Doped Ceria Electrolyte

Ceria (CeO\(_2\)) is a material of exceptional technological importance due to its unique and versatile properties, which include high mechanical strength, oxygen ion conductivity and oxygen storage capacity and as the
basic component of materials for solid oxide fuel cells. Ceria is a rare earth metal oxide and is extensively used due to its oxygen storage capacity, electronic conductivity and oxygen deficiency. It is one of the most promising electrolyte materials for SOFC.

Pure CeO$_2$ has low thermal resistance and low textural stability, which are not high enough to meet the requirements of high-temperature applications. Hence pure ceria is generally not preferred. Moreover the catalytic efficiency may also be reduced at elevated temperatures because of sintering and loss of surface area. This loss in surface area may be attributed to changes in the pore structure and to crystallite growth. Hence it is very much important to improve its textural stability. To eliminate this drawback doped ceria is used which possess high ionic-electronic conductivity even at relatively low temperatures. The host lattice of ceria is compatible with a wide range of rare-earth ion substitutions. Table 2.2 shows the list of rare-earth elements which can be doped with ceria.

**Table 2.2 List of rare-earth elements with their properties**

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic number</th>
<th>Atomic weight</th>
<th>Density (g/cm$^3$)</th>
<th>Melting point (°C)</th>
<th>Vicker’s hardness, (10 kg load, kg/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium</td>
<td>Sc</td>
<td>21</td>
<td>44.95</td>
<td>2.989</td>
<td>1541</td>
<td>85</td>
</tr>
<tr>
<td>Yttrium</td>
<td>Y</td>
<td>39</td>
<td>88.90</td>
<td>4.469</td>
<td>1522</td>
<td>38</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>La</td>
<td>57</td>
<td>138.90</td>
<td>6.146</td>
<td>918</td>
<td>37</td>
</tr>
<tr>
<td>Cerium</td>
<td>Ce</td>
<td>58</td>
<td>140.11</td>
<td>8.160</td>
<td>789</td>
<td>24</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>Pr</td>
<td>59</td>
<td>140.90</td>
<td>6.773</td>
<td>931</td>
<td>37</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Nd</td>
<td>60</td>
<td>144.24</td>
<td>7.008</td>
<td>1021</td>
<td>35</td>
</tr>
<tr>
<td>Element</td>
<td>Symbol</td>
<td>Atomic Number</td>
<td>Atomic Mass</td>
<td>Atomic Radius</td>
<td>Conductivity</td>
<td>Melting Point</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>---------------</td>
<td>-------------</td>
<td>---------------</td>
<td>--------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Promethium</td>
<td>Pm</td>
<td>61</td>
<td>145.00</td>
<td>7.262</td>
<td>1042</td>
<td>-</td>
</tr>
<tr>
<td>Samarium</td>
<td>Sm</td>
<td>62</td>
<td>150.36</td>
<td>7.520</td>
<td>1074</td>
<td>45</td>
</tr>
<tr>
<td>Europium</td>
<td>Eu</td>
<td>63</td>
<td>151.96</td>
<td>5.244</td>
<td>822</td>
<td>17</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>Gd</td>
<td>64</td>
<td>157.25</td>
<td>7.901</td>
<td>1313</td>
<td>57</td>
</tr>
<tr>
<td>Terbium</td>
<td>Tb</td>
<td>65</td>
<td>158.92</td>
<td>8.230</td>
<td>1356</td>
<td>46</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td>66</td>
<td>162.50</td>
<td>8.551</td>
<td>1412</td>
<td>42</td>
</tr>
<tr>
<td>Holmium</td>
<td>Ho</td>
<td>67</td>
<td>164.93</td>
<td>8.795</td>
<td>1474</td>
<td>42</td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td>68</td>
<td>167.26</td>
<td>9.066</td>
<td>1529</td>
<td>44</td>
</tr>
<tr>
<td>Thulium</td>
<td>Tm</td>
<td>69</td>
<td>168.93</td>
<td>9.321</td>
<td>1545</td>
<td>48</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>Yb</td>
<td>70</td>
<td>173.70</td>
<td>6.966</td>
<td>819</td>
<td>21</td>
</tr>
<tr>
<td>Lutetium</td>
<td>Lu</td>
<td>71</td>
<td>174.97</td>
<td>9.841</td>
<td>1663</td>
<td>77</td>
</tr>
</tbody>
</table>

Doped CeO₂ and doped LaGaO₃ have shown promise for the replacement of YSZ in intermediate temperature SOFCs (600-800°C) (IT-SOFC) due to their higher conductivity.

Faro et al. 2009 found that when compared to stabilized zirconia, doped ceria presents ionic conductivities approximately one order of magnitude greater, for similar temperature conditions. This is due to the larger ionic radius of Ce⁴⁺ (0.87 Å) as compared to Zr⁴⁺ (0.72 Å) producing a more open structure through which oxide ions can easily conduct.

Fergus et al. 2009 investigated that unlike zirconia, ceria naturally presents a fluorite structure at room temperature up to its melting point at 2400°C.
Mogensen et al. 2000 found out that pure ceria is not a good oxygen ion conductor, but its conductivity can be increased significantly by substituting Ce$^{4+}$ with divalent alkaline earth or trivalent rare earth ions. So, in its case the only function of the doping is an increase of the ionic conductivity through the formation of vacancies.

Mingfei Liu et al. 2012 have demonstrated an efficient IT-SOFC structure based on doped ceria electrolytes. NiO-BZCYYb has been successfully employed as the anode for SDC based electrolyte to effectively block the electronic conductivity while maintaining the high performance. Single cells with LSCF cathode achieved high power densities of 0.86, 0.64, and 0.36 mWcm$^2$ at 750, 650, and 550°C, respectively. EDX analysis suggests that there is some inter-diffusion between BZCYYb and SDC near the interface, leading to the formation of a new phase that suppresses the internal shorting of the SDC electrolyte and enhances the open circuit voltage. Furthermore, the cell shows stable operation when wet H$_2$ and methane were used as the fuel at 750°C, indicating that the anode has good coking tolerance. The results suggest that the new cell configuration, LSCF / SDC / Ni-BZCYYb, is very promising for practical applications.

Dudek & Molenda 2006 investigated Pure ceria and ceria-yttria solid solution powders with formula Ce$_{1-x}$Y$_x$O$_2$, where $0 < x < 0.30$ prepared by the co-precipitation-calcination method. The samples were sintered at 1250–1600°C for 2 hours. The XRD method was used to determine cell parameters of the samples. Their electrical properties were investigated by ac impedance spectroscopy in the temperature range of 100–700°C in air. They found that the electrical conductivity, fracture toughness, and flexural strength of the samples increased with yttria concentration and reached a maximum for
The obtained material seems to be a promising solid electrolyte for IT-SOFC.

Steele 2000 stated that among the ceria dopants $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composition is promising for IT-SOFC applications because of its high ionic conductivity at 500°C.

Mamoune et al. 2012 prepared Gadolinium-doped ceria-based electrolyte (at 20% dopant cation) for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). The fine powder has been synthesized by a simple and fast freeze drying method at relatively low temperature. The XRD results showed that the powder has a single phase with cubic fluorite structure. The SEM results exhibited that electrolyte pellets sintered at 1100 °C was dense, and the relative density of pellet was over 96%. Impedance spectra analysis of this electrolyte has been performed at 200–850°C. The results displayed that $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2.8}$ appeared higher conductivity at the temperature range of 550–700°C.

Badwal 2001 investigated oxygen conductors with perovskite cubic structure based on lanthanum gallate (LaGaO$_3$). In these ceramics, La can be partially replaced by Sr, Ca, Ba, Sm and Nd, while Ga may also be partially replaced by Mg, In, Al or Zn, as in $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ (LSGM). Compositions containing Sr and Mg substitutions respectively for La (between 10 and 20%) and Ga (between 10 and 20%) showed high ionic conductivities in both oxidizing and reducing atmosphere. It reaches about 0.17 S.cm$^{-1}$ at 800°C. The most commonly used composition for the LSGM electrolyte in SOFCs is $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_2$. Their TEC are comparable to the other usual cell components. Strontium and magnesium doped lanthanum gallate (LSGM) was discovered more recently and has an ionic conductivity similar to that of doped ceria and it has higher oxygen-ion conductivity than
conventional YSZ between 600-800°C and negligible electronic conductivity. While it is not reducible like ceria, the fact that it is a stoichiometric compound implies that the composition must be precise. LSGM is substantially more expensive than ceria based electrolytes, and it has also proved difficult to prepare pure single phase electrolytes of LSGM. Besides, challenges of matching the thermal expansion coefficients, mechanical strength, and chemical compatibilities need further development.

Kharton et al. 2004 found out that these ceramics are unstable under reducing atmospheres and Ga losses are observed, resulting in the formation of new phases. These facts decrease the use of doped lanthanum gallate as SOFC electrolyte.

Wachsman et al. 1997 investigated that Bismuth oxide based materials, such as yttria and erbia- stabilized bismuth oxides, showed highest conductivities. For example, at 500°C, the resistance of erbia-stabilized bismuth oxides is reported to be 0.037 Ω.cm², 2 orders of magnitude lower than 1.259 Ω.cm² for YSZ at the same temperature. The high oxygen mobility is a result of weak metal- oxygen bonds and thus Bi₂O₃-based materials have lower stability under reduced partial pressure of oxygen at the anode side, resulting in the decomposition to metallic Bi. However, the cell stability can be substantially improved by using functionally graded ceria/bismuth oxide bi-layered structure. A high power density of 2 W.cm⁻² at 650°C was reported on an anode-supported cell with ceria/bismuth oxide bi-layered structured electrolyte.

Feng-Yun Wang et al. 2004 investigated the ionic conductivity of Co-doped Ce₁₋ₐGdₐ₋₀.5ySm₂₀.5a, wherein a = 0.15 or 0.2, 0≤y≤a, prepared for intermediate temperature solid oxide fuel cells (IT-SOFCs). Their structures and ionic conductivities were characterized by X-ray diffraction and AC
impedance spectroscopy. All the electrolytes were found to be ceria based solid solutions of fluorite type structures. However, co-doping effect was observed more apparent for the electrolytes with $a = 0.15$ than for those with $a = 0.2$. In comparison to the singly doped ceria, the co-doped ceria of $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{Y}_{0.15}\text{Sm}_{0.15}\text{O}_{1.925}$, wherein $0.05 \leq y \leq 0.1$, showed much higher ionic conductivity at 773–973 K. These co-doped ceria are more ideal electrolyte materials of IT-SOFCs.

Feng-Yun Wang et al. 2004 also investigated Gd and Mg co-doped ceria electrolyte $\text{Ce}_{0.85}\text{Gd}_{0.1}\text{Mg}_{0.05}\text{O}_{1.9}$ (CGM) prepared by sol–gel method. Its conductivity behaviour was studied and compared with those of singly doped ceria electrolytes $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_{1.9}$ (CM10) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO). By using CGM as the electrolyte, a fuel cell was fabricated with a Ni/CGM anode and a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3}$ (LSCF)/CGM composite cathode. Its performance was compared with that of CGO based fuel cells. Both the CM10 and CGM electrolytes were ceria based solid solutions. The dopant $\text{Mg}^{2+}$ might be situated in the interstitials of the crystal lattice of $\text{CeO}_2$. The co-doped CGM showed a higher conductivity in air at 773–973 K in comparison to that of CGO and CMO. The CGM based fuel cell also showed higher open circuit voltage (OCV) and higher maximum power density (MPD) than the CGO based cell at 773–973 K. The MPD of the fuel cells were improved further by using composite cathode of LSCF/CGO (or CGM). With Ni/CGM anode and LSCF/CGM cathode, the MPD of the CGM based fuel cell at 873 K reached 202.5 mW cm$^{-2}$.

Dudek et al. 2008 fabricated nano powders of pure $\text{CeO}_2$ and singly or co-doped ceria materials in the $\text{CeO}_2$–$\text{Sm}_2\text{O}_3$–$\text{Y}_2\text{O}_3$ or $\text{CeO}_2$–$\text{Gd}_2\text{O}_3$–$\text{Sm}_2\text{O}_3$ systems using Co-precipitation method and hydrothermal synthesis. All sintered powders and samples were found to be pure $\text{CeO}_2$ and
ceria-based solid solution of fluorite type structure. The surface areas of CeO$_2$-based nano powders were measured by the one-point BET method. The morphologies of powders were observed by means of transmission electron microscopy. Particle sizes of ceria powders synthesised by the hydrothermal method ranged from 9 to 15 nm, the particle sizes of powders calcined at 800°C ranged from 13 to 26 nm. The TEM observations indicated that all CeO$_2$-based powders consisted of isometric in shape and agglomerated particles. Scanning electron microscope was used to observe the microstructure of the sintered samples. Electrical conductivity was studied by the a.c. impedance spectroscopy in the temperature range 200–700°C. The oxygen transference number was determined from EMF measurements of oxide galvanic cells. It was found that co-doped ceria materials such as Ce$_{0.8}$Sm$_{0.1}$Y$_{0.1}$O$_2$ or Ce$_{0.85}$Gd$_{0.1}$Sm$_{0.05}$O$_2$ seem to be more suitable solid electrolytes than singly-doped ceria Ce$_{1-x}$M$_x$O$_2$ (M – Sm, Gd, Y, X = 0.15 or 0.20) for electrochemical devices working in the temperature range 600–700°C.

Montalvo-Lozano et al. 2012 prepared electrolytes of co-doped ceria with nominal compositions of Ce$_{0.9}$Y$_{0.1-x}$M$_x$O$_{2-\delta}$ (X=0, 0.05) and Ce$_{0.85}$Y$_{0.15-x}$M$_x$O$_{2-\delta}$ (X = 0, 0.05, 0.1) (M = Ca, Mg) by mechanical milling. The X-ray diffraction patterns of all the synthesized samples confirm the cubic fluorite structure after 1 h milling and sinterization. Increasing sintering temperature helps in obtaining dense materials with better electrical properties. The dense microstructure with a wider grain size distribution was achieved after sintering at 1500°C. Co-doping was found to enhance effectively the conductivity of the samples. In comparison to singly doped ceria, co-doping with appropriate ratio of Y$^{3+}$ and Ca$^{2+}$ or Mg$^{2+}$ showed higher conductivities and lower activation energies. The effect of co-doping on the electrical properties of grain boundary was more apparent than that of the
bulk. The bulk and grain boundary conductivity increases as the dopant concentration increases and the composition $\text{Ce}_{0.85}\text{Y}_{0.05}\text{Ca}_{0.1}\text{O}_{1.875}$ exhibits the highest total conductivity out of all studied samples. It implies that co-doping with optimal ratio of yttria and magnesia or calcia can further improve the electrical performance of ceria-based electrolytes.

Nandini Jaiswal et al. 2014 prepared Co-doped samples of $\text{Ce}_{0.95-x}\text{Ca}_{0.05}\text{Sr}_x\text{O}_{1.95-x}$, where $(X=0.00, 0.01, 0.02, \text{ and } 0.03)$, by auto-combustion method and characterized to explore their use as a solid electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs). Crystal structure, microstructure, and ionic conductivity have been characterized by X-ray diffraction, scanning electron microscopy, and impedance spectroscopy, respectively. All the compositions have been found to be single phase. Results showed that the samples co-doped with Ca and Sr exhibited higher ionic conductivity than the samples singly doped with Ca in the intermediate temperature range. $\text{Ce}_{0.93}\text{Ca}_{0.05}\text{Sr}_{0.02}\text{O}_{2-\delta}$ exhibited maximum conductivity among all the compositions. This may be a potential candidate as a solid electrolyte for IT-SOFCs.

Arie Hardian et al. 2014 synthesized and characterized several co-doped ceria $\text{Ce}_{1-x-y}\text{Gd}_x\text{M}_y\text{O}_{2-\gamma}$, $M = \text{Er, Dy, or Nd}$ and $0.0 \leq x, y \leq 0.1$. Solid state method was used due to it is a simple and suitable method for pilot scale. For the same total dopant concentration, the correlation between cation mean radii and the lattice parameter followed the Vegard’s rule. The activation energies of co-doped ceria were lower than 1 eV and most of co-doped ceria showed conductivities higher than $10^{-2}$ S.cm$^{-1}$ at intermediate temperature range (500-800°C). Hence, co-doped ceria is believed as the promising candidate for IT-SOFC electrolyte. Co-doped strategy can increase the conductivity of single doped ceria at lower operating temperature.
Ramesh et al. 2011 investigated doped and co-doped ceria electrolyte materials for solid oxide fuel cells. Ce$_{0.9}$Sm$_{1-x}$Sr$_x$O$_2$ ($x=0–0.09$) compositions were synthesized through sol-gel method. Dense Ce$_{0.9}$Sm$_{1-x}$Sr$_x$O$_2$ ceramics were obtained through sintering the pellets at 1300°C for 8 h. XRD measurements indicated that all synthesized materials crystallized in cubic fluorite-type structure. Average crystallite sizes of the samples were in the range 21–27 nm. The relative density of Ce$_{0.9}$Sm$_{1-x}$Sr$_x$O$_2$ samples was over 94% of the theoretical density. The lattice parameter increased linearly with increasing Sr concentration in Ce$_{0.9}$Sm$_{1-x}$Sr$_x$O$_2$ following Vegard's rule. Surface morphology was analyzed using SEM. It was observed that the thermal expansion increased linearly with increasing temperature. The two-probe a.c. impedance spectroscopy was used to study the grain, grain boundary and total ionic conductivity of doped and co-doped ceria in the temperature range 250°C–500°C. The Ce$_{0.9}$Sm$_{0.07}$Sr$_{0.03}$O$_2$ composition showed higher grain ionic conductivity and minimum activation energy at 500°C.

Yifeng Zheng et al. 2011 studied the effect of Sr addition (0–10 mol%) on the densification, crystal structure, ionic conductivity, thermal expansion, and flexural strength of Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (SDC) . Sr addition promotes densification and reduces sintering temperature by ~100°C. X-ray diffraction analysis showed that all the samples exhibit a fluorite structure. Impedance spectroscopy measurements indicated that SDC incorporated with an appropriate ratio of Sr (4–10 mol%) has higher ionic conductivity and lower activation energy compared with those of SDC. As the added amount of Sr increased by up to 6 mol% (0.94SDC-0.06Sr), the sample attained the highest ionic conductivity, about 30% higher than that of SDC at 700°C. Moreover, flexural strength increased with Sr content, with the addition of 10 mol% Sr increasing the flexural strength of SDC from 97 to 160 MPa. In
addition, thermal expansion was linear for all the samples. The addition of Sr does not appreciably change thermal expansion coefficient.

Shobit Omar et al. 2012 evaluated the oxide ionic conductivity of $\text{Sc}_{0.18}\text{Zr}_{0.82}\text{O}_{1.91}$ doped with 0.5 mol% of both $\text{Yb}_2\text{O}_3$ and $\text{In}_2\text{O}_3$ at various temperatures in air. Among various co-doped compositions, $\text{In}_{0.02}\text{Sc}_{0.18}\text{Zr}_{0.80}\text{O}_{1.90}$ exhibited the highest grain ionic conductivity followed by $\text{Yb}_{0.02}\text{Sc}_{0.18}\text{Zr}_{0.80}\text{O}_{1.90}$ at 500°C. However, it also possesses phase transformation from c- to β-phase at 475°C on cooling. In the work, an attempt was made to completely stabilize the c-phase in $\text{In}_{0.02}\text{Sc}_{0.18}\text{Zr}_{0.80}\text{O}_{1.90}$ by substituting 0.5 mol% of $\text{In}_2\text{O}_3$ with $\text{Yb}_2\text{O}_3$, which enhanced the ionic conductivity in co-doped compositions.

Rizwan Raza et al. 2014 synthesized a nanocomposite Zr/Sm co-doped ceria electrolyte coated with $\text{K}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ by co-precipitation method. The electrochemical study of the two-phase nanocomposite electrolytes with carbonate coated on the doped ceria showed high oxygen ion mobility at low temperatures (300–600°C). The interface between the two constituent phases was studied by electrochemical impedance spectroscopy. Ionic conductivities were also measured with electrochemical impedance spectroscopy. The morphology and structure of composite electrolyte were characterized using field-emission scanning electron microscopy and X-ray diffraction. The fuel cell power density was 700mWcm$^{-2}$, and an open-circuit voltage of 1.00V was achieved at low temperatures (400–550°C). This co-doped approach with a second phase provided a good indication regarding overcoming the challenges of solid oxide fuel cell technology.

Arabaci Aliye et al. 2014 synthesized $\text{Ce}_{0.9-x}\text{Gd}_{0.1}\text{Er}_x\text{O}_{1.9-x/2}$ ($0 \leq x \leq 0.1$) (EGDC) powders with a fast and facile cellulose-templating method and the powders were characterized by X-ray diffraction, scanning
electron microscopy, and energy-dispersive X-ray spectroscopy. The samples were calcined at a relatively low calcination temperature of 773 K (500 °C). The sintering behavior of the calcined EGDC powders was also investigated at 1673 K (1400 °C) for 6 hours. Calcined $\text{Ce}_{0.9-x}\text{Gd}_{0.1}\text{Er}_x\text{O}_{1.9-\frac{x}{2}}$ (0 ≤ x ≤ 0.1) powders and sintered $\text{Ce}_{0.9-x}\text{Gd}_{0.1}\text{Er}_x\text{O}_{1.9-\frac{x}{2}}$ (0 ≤ x ≤ 0.1) pellets were crystallized in the cubic fluorite structure. It was found that the relative densities of the sintered EGDC pellets were over 95 pct for all the Er contents studied. Moreover, the effect of Er content on the ionic conductivity of the gadolinium-doped ceria (GDC, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.90}$) was investigated. The highest ionic conductivity value was found to be $3.57 \times 10^{-2}$ S cm$^{-1}$ at 1073 K (800 °C) for the sintered $\text{Ce}_{0.82}\text{Gd}_{0.1}\text{Er}_{0.08}\text{O}_{1.91}$ at 1673 K (1400 °C) for 6 hours.

Dapcevic et al. 2015 investigated and studied the possibility to stabilize δ-Bi$_2$O$_3$-type polymorph with high ionic conductivity by doping with Tm$_2$O$_3$. Five microcrystalline samples were synthesized at 750 °C from α-Bi$_2$O$_3$ and Tm$_2$O$_3$ mixtures with compositions (Bi$_{1-x}$Tm$_x$)$_2$O$_3$, where $x = 0.04, 0.08, 0.11, 0.14$ and $0.20$. The XRD, SEM, HRTEM and SAED results showed that the targeted δ-Bi$_2$O$_3$-type single-phase (space group $Fm\bar{3}m$ Fm$\bar{3}$m) was formed for $0.11 \leq x \leq 0.20$. The unit cell parameter of δ-Bi$_2$O$_3$-type phase decreased with increase in Tm content. According to DTA, no phase transitions were observed in the sample with $x = 0.20$, indicating that the obtained δ-Bi$_2$O$_3$-type phase is structurally stable from room temperature to 985 °C. Based on EIS, (Bi$_{0.80}$Tm$_{0.20}$)$_2$O$_3$ exhibits high conductivity (0.117 S cm$^{-1}$ at 550 °C) with activation energies: 0.38(4) eV above 550 °C and 1.27(2) eV below 550 °C, due to the change in charge carrier mobility. The effect of thermal aging was investigated and discussed.
Abhinav Rai 2014 evaluated the effect of varying co-doping ratios on the grain and grain boundary conductivity is in the Sm$_{x}$Nd$_{0.15-x}$Ce$_{0.85}$O$_{2-δ}$ system. A slight decline in the grain conductivity was found on replacing Sm$^{3+}$ with Nd$^{3+}$ in Sm$_{x}$Nd$_{0.15-x}$Ce$_{0.85}$O$_{2-δ}$. Nevertheless, the activation energy values for grain conductivity were comparable for all the compositions. The specific grain boundary conductivity calculated at lower temperatures, were found to be nearly 3 orders of magnitude smaller than the grain conductivity. Further, a wide variation in specific grain boundary conductivity data was observed across various tested compositions, with Sm$_{0.10}$Nd$_{0.05}$Ce$_{0.85}$O$_{2-δ}$ exhibiting the highest conductivity. The high specific grain boundary conductivity contributes towards high total conductivity in this composition.

Nandini Jaiswal et al. 2015 prepared a series of ceria-based nanocomposites consisting of lanthanum and strontium co-doped ceria with composition Ce$_{0.89}$La$_{0.07}$Sr$_{0.04}$O$_{1.925}$ (CL7S4). Eutectic mixture of carbonates Li$_2$CO$_3$-Na$_2$CO$_3$ (LNCO) was also prepared by mixing nanosize powders of CL7S4 and LNCO. Samples were characterized using differential thermal analysis, X-ray diffraction, scanning electron microscopy combined with energy-dispersive spectroscopy, thermal expansion, and impedance spectroscopy. A sharp increase in ionic conductivity was observed in all the composite specimens corresponding to superionic transition. Sample containing 35 wt% of carbonate showed the maximum conductivity ($2.56 \times 10^{-1}$ S/cm at 500°C) with activation energy of conduction, $E_a$ 0.23 eV.

Samuel Taub et al. 2015 examined the effects of transition metal oxide dopants (Co and Cr) on the electrical conductivity of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO). Co is an effective sintering aid for CGO whereas Cr inhibits densification. After sintering both transition metals were found segregated at grain boundaries and as second phase precipitates at triple grain junctions.
Co addition has negligible effect on bulk conductivity, but increased the grain boundary intrinsic conductivity, whereas Cr addition in the range 0.01–4% also has negligible effect on bulk conductivity, but decreases the grain boundary intrinsic conductivity even at very low concentrations. For both Co and Cr these changes in conductivity are ionic and electronic conductivity remains negligible. The changes can be accounted for by changes to the boundary core charge (electrical potential) and surrounding space charge regions induced by the Co and Cr. Both Co and Cr increased the electronic conductivity mainly due to electron hopping along the network of transition metal ions segregated in the boundary cores.

Based on the above discussed research reviews showing that co-doped ceria electrolytes could improve the ionic conductivity of a SOFC than singly doped ceria, the present research is focusing on the development of co-doped ceria electrolyte used in SOFC. As low temperature operations are not suitable for singly doped ceria due to higher electrical resistance, structural modifications of ceria-based solutions has to be made by co-doping of the elements to increase the oxide ionic conductivity of ceria–based electrolytes in the intermediate temperature range of 500-600°C. Ceria co-doped with Lanthanides and other divalent or trivalent elements depending on chemical composition have generally improved ionic conductivities.

2.8 EXPECTED LIFE OF FUEL CELL

There is a wide variety in expected lives depending on the fuel cell manufacturer and type of fuel cell technology. A survey of fuel cell manufacturers and developers was conducted. Most of the survey participants believe the fuel cell stacks will last longer than three years, with few participants expecting fuel cell stacks to last more than five years. The whole fuel cell system has an expected lifetime of 20 years.
2.8.1 Fuel Cell Economics

Fuel cell system life expectancy is projected to be 20 years with fuel cell stack replacement every five years. Fuel cell stacks for stationary applications have 40000-hour design criteria based on full load cell operation. This constitutes the only major maintenance item expected at this time. Remaining maintenance items include routine evolutions for the ancillary system equipment fans, pumps, filters, controls, and samples.

Fuel cells for buildings require selection of an operating strategy, coordination with the local utility systems, and evaluation of the economic value of the system. A preliminary indication of potential consists of a simple calculation of the cost of the electricity from the fuel cell compared to the utility. However, a more accurate estimate of savings can be calculated based on an hour-by-hour model (ASHRAE 2002).

Currently, residential and commercial applications are around $2000/kWe and as low as $500/kWe. The current goal is set at $1500/kWe for the initial project cost. Fuel cells for stationary applications require selection of an operating strategy, coordination with the local utility systems, and evaluation of the economic value of the system. A preliminary indication of potential begins with the Cost of Electricity (COE) from the fuel cell compared to the utility. However, a more accurate estimate of savings can be calculated based on an hourly model (ASHRAE 2002).