# CHAPTER-1

# INTRODUCTION

## 1.1 Energy Crisis and Global Warming

Energy is the life blood of our society that drives the world. Currently whole world is facing the energy crisis due to continuous depletion of fossil fuels, interrupted supply and fluctuating price this in turn resulting the huge gap between the global fuel demand and supply. As per report by International energy agency, (Figure 1.1)[1] shows that demand has already been increasing continually and also projecting a very strong growth in demand of fuels in coming years.

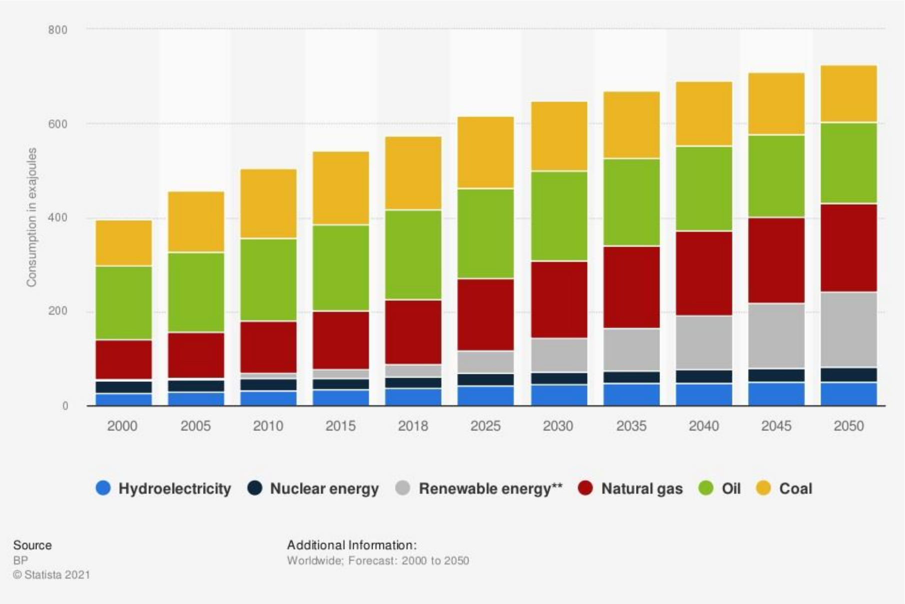

Figure 1.1. Energy Consumption World Wide 2000 to 2018, with a forecast till 2050* (in extra joules) (source: International Energy agency) [1]

Consumption of fossil fuels resulting huge carbon emission creating greenhouse emission. Energy security, high oil prices, climate change & growing greenhouse gases emission are most critical challenges faced by our global economy. To fulfil our electricity requirement, we are mainly dependent on the thermal power (Figure 1.2). Renewable energy sources such as wind farms, nuclear power and solar energy based technologies can serve as alternative for generation of clean energy with lower carbon emission per gigawatt-hour (GWh) compared to conventional coal-fired plants. .

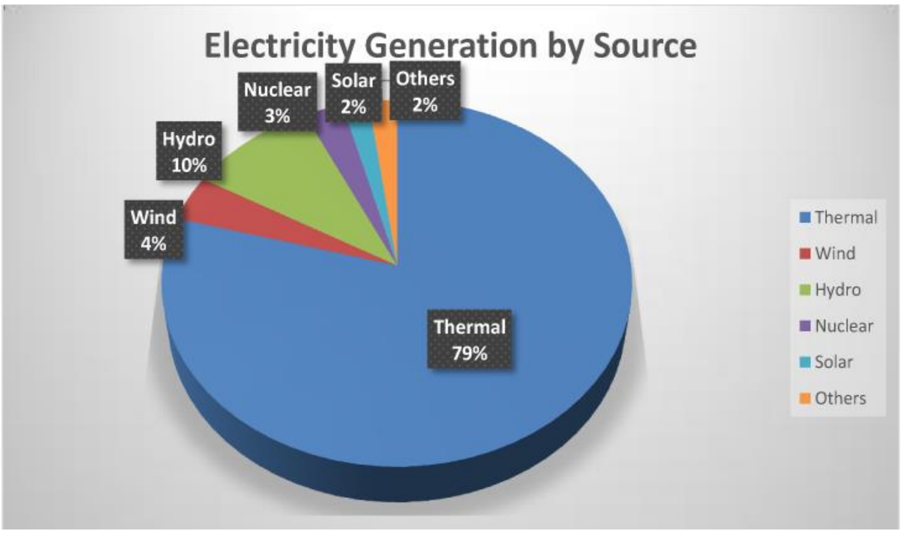

Figure 1.2. Electricity Generation by Source ( Ref: Central Electricity Authority, Ministry of Power, GOI)

The major roadblock for renewable energy to become large-scale uptake is due to the unreliable nature of generation. For example, the energy generation using wind mills highly depends on wind blows which is more often discontinuous in power generation, thus fluctuation occurs. This change in power generation at different time of day makes it difficult to do grid balancing which is must and should be carried out online. This is one of the major causes due to which majority of renewable energy sources are limited in use and are not able to become large portion of power generation. It has been estimated that once renewables reach 30% of the total grid capacity the stability of the system will be compromised without large-scale capacity for energy storage. To fulfil the demand of the fuel supply and to deal with environmental issues, clean energy (renewable) sources has been introduced such as hydrogen, CNG, that don't pollute environment if generated from green sources such as biomass & residual organic waste. As an energy converting device, fuel cell is considered as highly efficient, energy production unit in comparison with available non-renewable energy resource systems. Fuel Cells harness the chemical energy of fuel (hydrogen) to generate electricity (electric energy).[2,3] As per conventional power generation systems there are too many steps involved that results a less efficient systems. On contrary, as we can see in Figure.1.3, fuel cells are more efficient because of direct conversion of energies (single step).

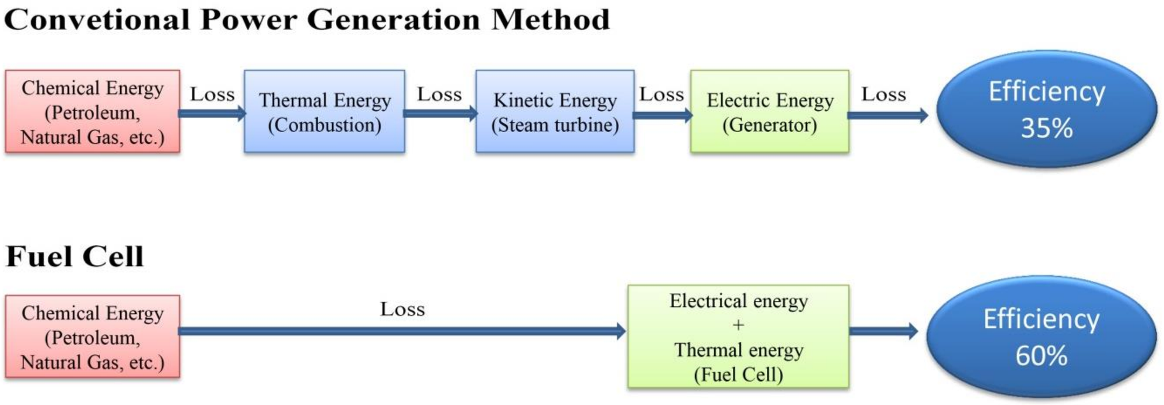

Figure 1.3. Comparison of efficiencies of conventional power generation & fuel cells.

## 1.2 Historical background

Development of fuel cell was recorded since 1838 when it was discovered by William Grove and as “Grove cell” or “wet cell battery” or gas battery.[3-7] This cell works on the principle of reversing the electrolysis of water. Since then, fuel cell is explained as an electrochemical device that converts the chemical energy of fuels into electricity and heat. A series of development thereafter led the foundation of realisation of the fuel cell & its components. F. W. Ostwald has identified & establishes the first generation of structured fuel cell.[2,5-7] In 1896, William W. Jacques develops the first fuel cell with practical application [5] & 1900 nernst used $ZrO_2$ as solid electrolyte and led the foundation of development of SOFCs.[8-10] Early in 1800, Davy found that dried Solid alkali compounds were non-conductors but became electrically conducting through just a little moisture.[11] Later, Faraday established basic terminology of electrochemistry and the term electrolyte in 1834.[12-13] Followed by Gauguin discovered solid electrolyte gas cell.[14]

Towards the end of 19th century the term solid electrolyte was in use and many facts of ionic conductivity were investigated in solids. In 1905 Haber filed the first Patent an fuel cell with solid electrolyte, leading development in this era was of different type of solid electrolyte based gas fuel cell.[15-18] In 1921, Baur has first develop molten carbonate fuel cell[19] and followed by series of development on alkaline electrolyte fuel cells by Bacon.

A technological interest in Solid ion conductors was first arose in connection with the development of electric lighting devices. Inspired by Nernst study, Reynolds presented his thesis in 1902 with considerable achievements.[20] Thesis concerned the conductivity in the range 800-1400°C of numerous binary and ternary systems, among others, formed by $ZrO_2$ with the oxides of the elements La, Ce, Nd, Sm, Ho, Er, Yb, Y, Sc, Mg, Ca, Th, and U, including investigations on the role of composition, concentration, direction of temperature alteration (hysteresis) and other phenomena. [20] It was not until 1943 that Wagner (in memoriam Walther Nernst) recognised the existence of vacancies in the anions sub lattice of mixed oxide solid solutions and thus explained the conduction mechanism of the Nernst glowers.[21] We now know that Nernst glowers are oxide ion conductors and the platinum contacts behaved as air electrodes.[6-7] It follows that Nernst lamps were the first commercially produced solid electrolyte gas cells. Since 1950s, work on fuel cell domain has expanded widely in terms of various components of materials, cathode, anode and electrolyte. The research of various types of electrolyte material leads to development of different type of fuel cells as proton exchange membrane fuel cells, phosphoric acid fuel cells, direct methanol fuel cells, molten carbonate fuel cells and solid oxide fuel cells.[22-30]

## 1.3 Type of fuel cells

Fuel cells are basically classified by their electrolyte materials used. Different types of fuel cell have different operating temperatures and conditions which lead to uses in different applications. Here, I listed common type of fuel cells.

### 1.3.1 Alkaline Fuel Cells (AFCs)

40% aqueous potassium hydroxide is generally used as electrolyte in alkaline fuel cell. Negative ions ($OH^-$) passes through the electrolyte to reach the anode where it combines with hydrogen to generate $H_2O$ and electrons. Alkaline fuel cells (AFCs), also known as Bacon Fuel Cell, were the first fuel cell technology which was widely used to produce electricity and water in US space program for the onboard spacecraft members. A solution of potassium hydroxide in water is used as the electrolyte and non-precious metal as a catalysis agent at the anode and cathode. AFCs operating temperature ranges between 100ºC and 250ºC (212ºF and 482ºF). However, with recent development in technologies, AFC are developed to operate at lower temperatures of range 23ºC to 70ºC (74ºF to 158ºF). The rate at which the chemical reaction takes place in an AFC makes it a high performance fuel cell. The major drawback of AFCs is that it is easily poisoned by carbon dioxide ($CO_2$) and further the electrolyte is highly corrosive. The performance of AFCs is even affected by presence of $CO_2$ in air and thus requires purifying of both hydrogen and oxygen to be used in the cell. $CO_2$ combines with KOH to form potassium carbonate which increases the resistance. To get rid of this, purification is done which is a costly process. Along with increasing the resistance of the cell, $CO_2$ also decreases the lifetime of the cell, the amount of time before it must be replaced, further adding to cost. In context to space application or underwater application, the cost is not that much of importance but AFCs to come in main stream of power generation, it must be cost effective. AFC stacks have been found to maintain sufficiently stable operation for more than 8,000 operating hours.[24-25]

Anode Reaction: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

Cathode Reaction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

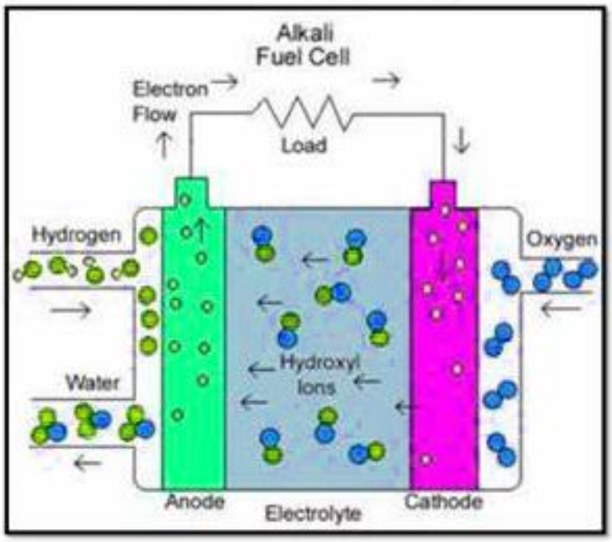

Fig 1.5: Alkaline fuel cell

### 1.3.2 Phosphoric Acid Fuel Cells (PAFCs)

Anode and the cathode of a PAFC are made of a finely dispersed platinum catalyst on carbon and a silicon carbide structure is used to hold the phosphoric acid electrolyte. In PAFCs, protons generated at anode passes through the electrolyte to the cathode to combine with oxygen and electrons giving water and heat as by product. PAFCs are the most commercially used fuel cell and is used to provide power to many commercial places. PAFCs uses liquid phosphoric acid as an electrolyte- the acid is placed in a Teflon-bonded silicon carbide matrix and carbon based porous electrodes containing platinum as catalysis agent is used. PAFCs is considered as the "first generation" of modern fuel cells. PAFCs are generally used for stationary power generation, but it can be also used to power large vehicles such as city buses. Unlikely AFCs, PAFCs are more tolerant of impurities and have little effect of surrounding $CO_2$ on performance. PAFCs can have efficiency of up to 85% when used for the co-generation of electricity and heat, but the efficiency drops considerably when used for generation of electricity in standalone mode (37 to 42 percent). Given the same weight and volume, PAFCs are less efficient compared to other fuel cells.[24-27] Due to this, PAFCs are generally large is size heavy in weight making it expensive too. Like PEM fuel cells, PAFCs require an expensive platinum catalyst, which raises the cost of the fuel cell.

Anode Reaction: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode Reaction: $1/2O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

### 1.3.3 Proton Exchange Membrane Fuel Cells (PEMFCs)

In PEM fuel cells, protons generated at anode passes through the electrolyte to reach the cathode where it combines with oxygen and electrons, producing water and heat. PEMFCs uses a polymeric proton conducting membrane as the electrolyte, with platinum electrodes. PEMFCs cells operate at relatively low temperatures compared to other fuel cells. PEMFCs are the best candidates for general purpose used of fuel cell such as in cars, for buildings and smaller applications. PEMFCs, also called proton exchange membrane fuel cells that can deliver high power density and had benefits like light weight and low volume, compared to other fuel cells. Similar to PAFCs, PEMFCs also used porous carbon electrodes containing platinum as catalyst. It used a solid polymer as electrolyte. They uses hydrogen, oxygen from the air, and water to operate and thus do not require corrosive fluids as required in other fuel cells. PEMFCs are fuelled with pure hydrogen stored in tank or from onboard reformers. PEMFCs operate at relatively low temperatures, around 80°C (176°F). This low operating temperature helps it to start fast as the warm-up time required is reduced considerably resulting a less wear and thus increases the durability of the cell. However, PEMFCs requires noble metal catalyst, commonly used platinum, to separate out hydrogen into electron and protons that considerable increases the cost of the system. The platinum catalyst used in PEMFCs are extremely sensitive to CO poisoning thus an additional reactor is required to reduce the CO in fuel gas if the hydrogen is derived from hydrocarbon fuel which in turn increases the cost of the system. Different research groups are exploring platinum/ruthenium catalyst which is more resistant to CO. The PEMFCs has a polymer membrane electrolyte which is used to conduct the protons from anode to cathode. Nafion, a perfluorosulfonic acid polymer, is found to be the best performing electrolyte till date and was first used by DuPont (USA) in the 1970s. Nafion have an operational lifetime of 104 – 105 hours in PEMFCs operating at a temperature range of 50-80°C. PEMFCs generally have an efficiency of 40-50%. High power density and low operating temperature are due to low temperature of operation for PEMFCs that makes it applicable for wide range of applications. Major drawback for PEMFCs includes use of high cost platinum catalyst and high sensitivity of system to CO and $H_2S$ that require use of ultra-purified hydrogen as a gas feed at anode.[24-28]

Anode Reaction: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode Reaction: $1/2O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

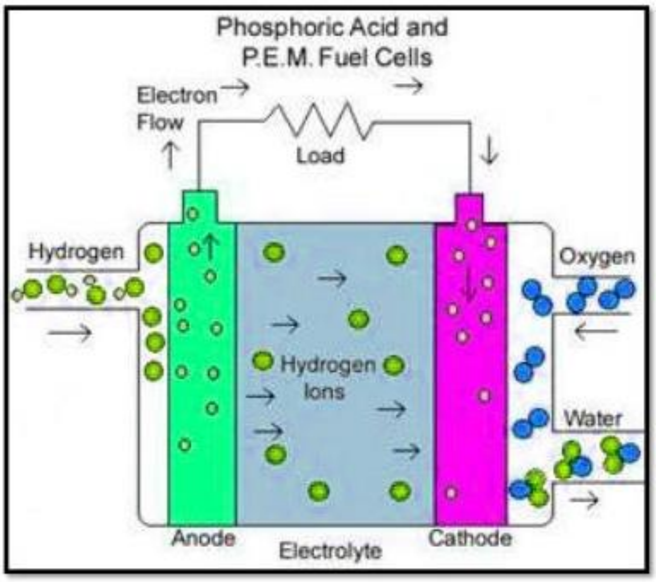

Figure 1.6. Phosphoric Acid & PEM fuel cell

### 1.3.4 Molten Carbonate Fuel Cells (MCFCs)

In this kind of fuel cells, a molten carbonate salt is used as the electrolyte. Fuel such as coal-derived fuel gases, methane or natural gas can also be used in MCFCs. Up to 60% efficiency can be achieved. In MCFCs, $CO_3^{2-}$(carbonate ions) travels through the electrolyte to the anode where it reacts with hydrogen to produce water and $CO_2$. Molten carbonate fuel cells are currently being used in natural gas and coal-based power plants for various application such as electrical utility, industrial, and military applications. MCFCs operates at high-temperature and thus is high temperature fuel cells. It uses an electrolyte composed of a molten carbonate salt mixture which is suspended in a porous ceramic lithium aluminium oxide ($LiAlO_2$) matrix which is inert to chemical reactions. MCFCs operates at very high temperature range (~650$^oC$ and above) making it suitable for use of non-precious metal as catalysts at the anode and cathode terminals which in turn reduces cost. Unlike AFCs, PAFCs, and PEMFCs, MCFCs don't require any external reformer to convert more energy-dense fuels to hydrogen. As MCFCs operates at high temperature, the fuel is converted to hydrogen within the fuel cell itself. This process is called internal reforming, which further reduces the cost. However even though MCFCs are known to be more resistant to impurities compared to other fuel cell types, researchers are looking for ways to make MCFCs resistant enough to impurities from coal, such as sulphur and particulates. The major drawback of MCFCs is durability due to high temperature operation and evaporation or degradation of molten carbonate salt electrolyte. Researchers are trying to explore corrosion-resistant materials for components as well as fuel cell designs which is expected to increase the cell life without decreasing performance.[24,27, 29]

Anode Reaction: $CO_3^{2-} + H_2 \rightarrow H_2O + CO_2 + 2e^-$

Cathode Reaction: $CO_2 + ½O_2 + 2e^- \rightarrow CO_3^{2-}$

Overall Cell Reaction: $H_2 + ½O_2 \rightarrow H_2O$

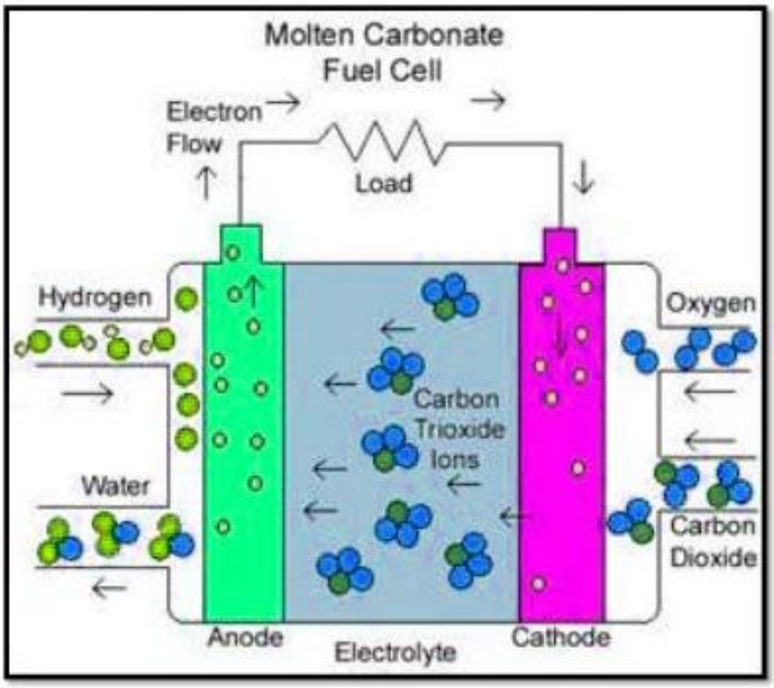

Fig 1.7: Molten carbonate fuel cell

### 1.3.5 Solid Oxide Fuel Cells (SOFCs)

SOFCs uses a solid ceramic electrolyte, such as zirconium dioxide stabilised with yttrium oxide, in place of a liquid electrolyte generally used in fuel cells and operate at high temperature range of 800 to 1000°C. In SOFCs, oxide-ions ($O^{2-}$) passes through the electrolyte to the anode where they combine with hydrogen to generate water and electrons. Efficiency of around 60% is achieved for SOFCs and application area includes electricity and heat generation in industries and also as secondary power source in vehicles. The Plate like configuration of SOFC is easy to fabricate, however there is some issue of interconnects and efficiency losses in the planar geometry of SOFCs. [2-3, 24, 30-31] Reactions involve in SOFCs :

Anode Reaction: $2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$

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

Overall Cell Reaction: $2H_2 + O_2 \rightarrow 2H_2O$

Just like MCFCs, high temperature operation of the system eliminates the requirement of precious-metal catalyst, again reducing the cost of the SOFCs. Solid oxide-ion electrolyte generally not poisoned by carbon monoxide (CO), but the Ni-based anode utilised in SOFC suffer with Ni-poisoning or coking due to CO or other hydrocarbon present as impurity in hydrogen. Different groups are working on the potential for developing lower temperature SOFCs operating at or below 800ºC which will increase the durability of the cell and thus the cost. Conventionally, the electrolyte used were oxide-ion conductor  and required operating temperatures between 800-1000°C.[32,33] Recently proton conducting solid materials came and are under investigation by different research groups to be used as ceramic fuel cells and it is anticipated that this might lower the operating temperature in range of 500-600°C. The high temperature operation eliminates the need for the use of platinum in the electrodes.[34] Also, the heat can be recycled in combined heat and power systems. It was first demonstrated by Siemens Westinghouse on a 220KW system. 70% electrical efficiency was achieved for SOFCs running on natural gas.[35] As SOFCs are high temperature operating system, fuels such as hydrocarbons and hydrogen gas can also be used. Major drawbacks include poor sealing of the cells for prolonged time period due to high temperature. Also, chemical reactions between the electrolyte and electrode materials are another drawback of such systems.

A comparison of SOFCs with other type of fuel cells configuration avails is presented in table 1.1. From table 1.1, we can see SOFC offer multiple fuel flexibility and usage of non-precious metal as catalyst and electrodes. That is why, the world is moving towards SOFC implications and establishments.

| Type of cells | Electrolyte | Operating Temperature | Fuel Supply | Efficiency |
|---|---|---|---|---|
| Alkaline Fuel Cells | KOH | 100°C - 250°C | Pure Hydrogen | 35-42% |
| Polymer Electrolyte Membrane | Proton Conducting Polymer | 50°C-80°C | Pure Hydrogen | 40-50% |
| Phosphoric Acid Fuel Cells | Phosphoric Acid | 160°C - 220°C | Hydrogen | 37-42% |
| Molten Carbonate Fuel Cells | Molten carbonate salt | 650°C & above | Methane, natural gas, hydrogen | 50-60% |
| Solid Oxide Fuel Cells | Oxide-ion electrolyte | 800°C - 1000°C | Methane, natural gas, hydrogen | 60-70% |

Table 1.1. Comparison of different types of fuel cells

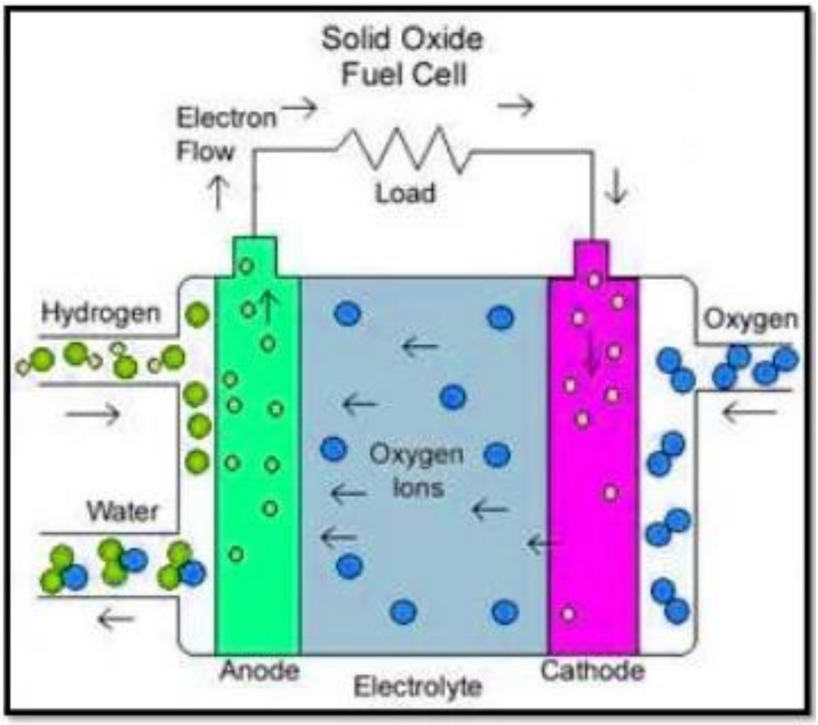

Figure 1.8 Solid Oxide Fuel Cell

## 1.4 SOFC Design

Stacks or array of fuel cells are generally used to increase the power output large enough for use in devices. Fuel cell array can be either supported or un-supported- in supported system, additional layer of substrate is added between the cells to add mechanical strength while in unsupported system, either of cathode or anode is used to support the system and provide mechanical strength to the system. SOFCs can be designed in tubular manner or in flat cell stack manner. The designs are formulated to obtain efficient gas flow and stacking capabilities.[36]

Figure 1.9 shows the tubular configuration of SOFCs which is more efficient for sealing as the electrolyte seals most of the cell. On the other hand, planar or flat cell design requires sealing at each level and an interconnect material is then used to link the cathode to the outer of the cell as shown in figure 1.10. In a planar/flat fuel cell stack, the interconnect also serves as a gas flow guide to both the cathode of one cell and the anode of another with the gases applied perpendicular to each other in order to reduce the number of parts required. The planar design of SOFCs is more efficient. The major drawback of flat or planar stack is finding suitable sealants or interconnecting materials for high temperature application.[37]

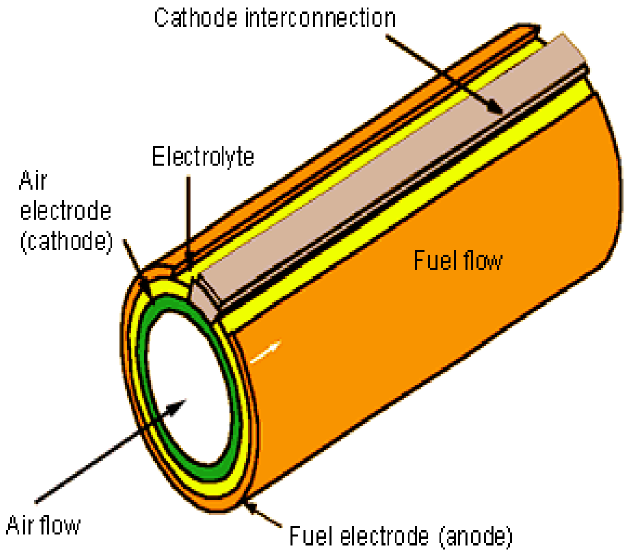

Figure 1.9 Tubular design of SOFC [93]

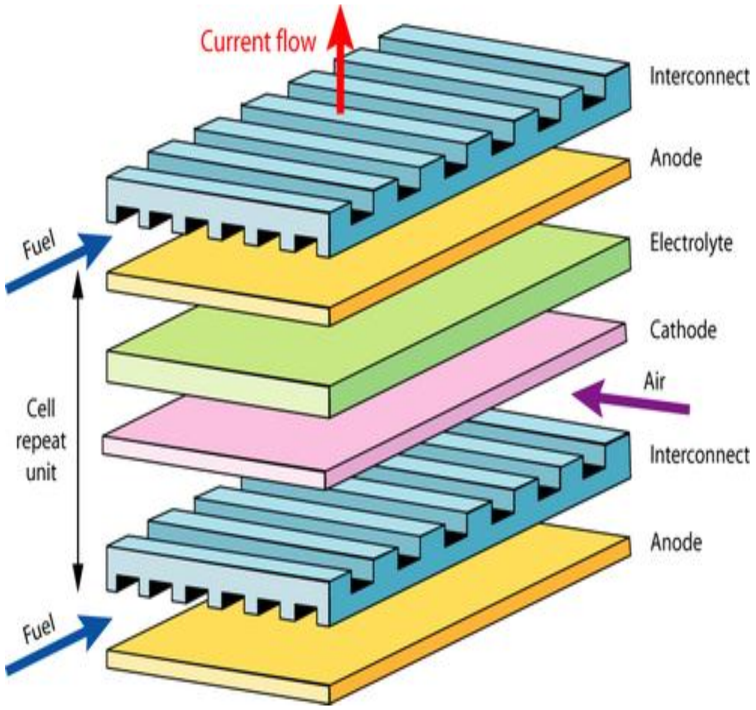

Figure 1.10 Planar design of SOFC [94]

## 1.5 Key challenges in SOFCs

Over the past few decades, the solid oxide fuel cell (SOFC) has emerged as a highly efficient alternative method of energy production. There is immense interest in developing SOFC due to multi fuel flexibility and high efficiency (~70%) with regeneration.[38-41] Further multiple fuel flexibility makes SOFC more amicable toward CNG and impure hydrogen, making it suitable for electricity production using the exhaust from bio/agro-waste reactors/digesters. However, the commercialization of SOFC technology is limited due to its high operating temperature of over 800°C.[42-43] The high operating temperature also limits the choice of materials and causes the rapid degradation rate of the system components. Over the years, the high research focus is on lowering the operating temperature of SOFC to reduce the system cost, improve the long- term stability, and shorten the start-up time. The electrolyte of an SOFC blocks electron transport inside the cell while transporting oxide-ions from the cathode, where $O_2$ is reduced to $2O^{2-}$, to the anode where a $H_2$ or a hydrocarbon fuel is oxidized; the power output of the cell depends on the oxide-ion conductivity of the electrolyte as well as the catalytic activities of the two electrodes.[44-47] Fast oxide-ion conductors play a significant role in determining the performance and in bringing down the operating temperature of a solid oxide fuel cell. Several oxide-ion conductor systems have been identified so far, such as $Y_2O_3$-stabilized $ZrO_2$[48-49] $Gd_2O_3$-doped $CeO_2$[50-51] and Sr and Mg-doped $LaGaO_3$.[52-53] However, it seems to be a very difficult task to achieve low temperature SOFCs at a commercial scale using these electrolytes.[54–57]

Rigorous research is going on the materials with potential applications in electrolytes of SOFCs across the world. All the materials must fulfil certain conditions to be used in SOFC systems; such as, the thermal expansion coefficients (TECs) for all the materials used within a single cell must be close to each other in value, otherwise heating will cause different layers to expand differently and cause cracking. In addition, physical stability & chemical compatibility with other components at the high operating temperatures is required. The aim for this thesis is to expand the knowledge and understanding of oxide-ion electrolyte materials alongside the development of newer oxide-ion electrolyte materials, and establish a design principle to develop a superior oxide-ion electrolyte. Most of the oxide-ion vacant existing oxide-ion conductors exist in either fluorite or perovskite structure.[58-59] However, interstitial-based apatite type structures are also known to have superior oxide-ion conductivity. The highest oxide-ion conductivity in the perovskite structure was found in Sr- & Mg-doped $LaGaO_3$.[52-53] At 800°C, the maximum conductivity was recorded as 0.14 S/cm for $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$.

A review of oxide-ion electrolyte developed till now is presented below:

## 1.6 Fluorite electrolytes

Most of the oxide-ion conducting SOFC electrolytes like yttria stabilised zirconia (YSZ), gadolinia stabilised ceria (CGO) and bismuth oxide have a fluorite structure with a chemical formula $AO_2$ where A is a $M^{4+}$ ion. The $M^{4+}$ cations (red colour atoms in Figure 1.11) occupy the face centre positions in the structure and vertices are occupied by the anions in the eight tetrahedral sites surrounding cations.

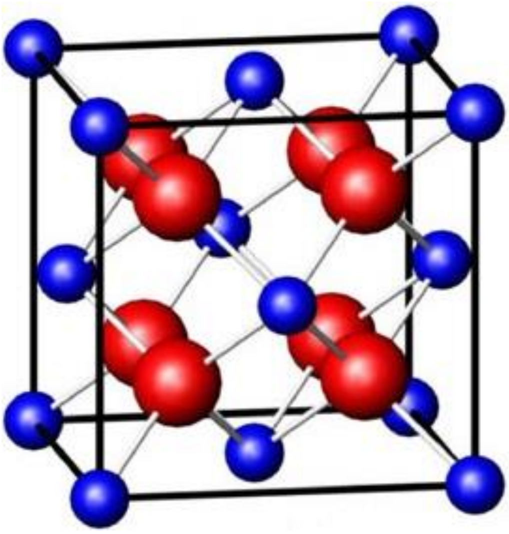

Fig 1.11 Fluorite structure

### 1.6.1 Stablized $ZrO_2$

Electrolyte materials based on zirconia ($ZrO_2$) are the most popular SOFC electrolyte material and were first to be used in a fuel cell by Nerst in 1899.[9] Pure zirconia does not have a cubic fluorite structure at room temperature and is a poor ionic conductor, the cubic fluorite structure is only present above 2300°C. The stabilization of fluorite structure at room temperature is possible by doping with trivalent rare earth metals or divalent alkaline earth metals this doping also introduces oxygen vacancies in the structure, which improves oxide-ion conductivity. One of the most common SOFC electrolyte material is yttria stabilised zirconia (YSZ)[48] which exhibits good oxide-ion conductivity at high temperatures when $ZrO_2$ doped with 8 mol% $Y_2O_3$. Recent studies show that doping of trivalent ions (rare earth metals) are more effective than divalent ions (alkali metals) doping, mainly because of the higher defect association tendency and the lower thermodynamic stability of the cubic fluorite. For trivalent ions, the order of doping effect on oxygen ion conductivity is mainly $Eu < Gd < Dy < Y < Er < Yb < Sc$. Among them, $Sc_2O_3$ stabilized $ZrO_2$ (ScSZ) shows the highest ionic conductivity, reaching as great as 0.003 S $cm^{-1}$ at 500 °C. Also the use of better electrodes, the SOFC with the thin-film ScSZ electrolyte has shown high power output at intermediate temperature.[60-62] Unfortunately, scarcity of scandium-rich minerals limits their use, also the separation and extraction process of scandium is very difficult, which makes scandium and its compounds expensive and imperfect for large-scale applications. $Sc_2O_3$, $Er_2O_3$ and $Yb_2O_3$ are much cheaper alternative and the ionic conductivities of $ZrO_2$ stabilized with these materials are significantly good. Therefore, Sc- or Yb-stabilized zirconia are more promising for low temperature SOFC application. However, there is very limited choice for the cathode materials in case of IT-SOFCs with stabilized $ZrO_2$ electrolytes. It was shown that cathodes containing Ba, La and other elements shows high reactivity with YSZ, which causes a substantial increase in both ohmic resistance and electrode polarization resistance, as well as poor long-term stability of the cells.[63] A buffer layer may be applied in case a direct contact between YSZ electrolyte and the cathode. It must have a high chemical inertness towards both the electrolyte and the cathode and high oxygen-ionic conductivity.[64-65]

### 1.6.2 Doped Ceria

In contrast to $ZrO_2$ which is of multiphase nature, $CeO_2$ sustain its cubic flourite structure from room temperature till melting point. To enhance oxide-ion conductivity, partial substitution of trivalent cations for e.g. namely $Gd^{3+}$, $Sm^{3+}$, $Y^{3+}$, $La^{3+}$ or $Ca^{2+}$ in place of $Ce^{4+}$ has been investigated vastly, leading to the causation of more oxygen vacancies that are the carriers of oxygen ions. It has been manifested from the studies that the closer is the ion radius of the dopant cation to $Ce^{4+}$, the higher is the expected oxygen ion conductivity.[50-51] For $CeO_2$ with trivalent dopants, the value of critical ionic radius ($r_c$) is 1.038 Å. Amongst these doped $CeO_2$ oxides, $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) have the highest ionic conductivity and are used in IT-SOFCs. A large concern in the use of a doped ceria electrolyte is the partial electronic conductivity at elevated temperature and reduced atmosphere, that is related to the reduction of $Ce^{4+}$ to $Ce^{3+}$.[66-68] Such partial electronic conductivity prompts a decrease in the open circuit voltage (OCV) and reduces overall Faradaic efficiency of the IT-SOFCs. To be specific, for a thin-film electrolyte, such internal shorted current becomes more apparent. For example, Zhang et al. investigated the internal shorting of a thin-film SDC electrolyte cell. At 600 °C, the respective OCV values were 0.84 V, 0.87 V, and 0.91 V for a cell with an electrolyte thickness of 10μm, 20μm, and 400μm. Thus, it is generally contemplated that the doped ceria thin-film electrolyte is suited for operation at a temperature of 600 °C or lower. Hence, IT-SOFCs based on a doped ceria thin-film electrolyte are generally operated at the temperature range of 450–600 °C .[69-70]

### 1.6.3 $Bi_2O_3$-based electrolyte

Ceria based electrolytes were now point of attraction in IT-SOFCs. However, $Bi_2O_3$-based conductors were investigated to develop low temperature oxide-ion conductors. The low thermal stability and high reducibility of $Bi_2O_3$-based electrolytes in hydrogen atmosphere led to the omission of Bi2O3-based electrolytes for practical application of SOFCs. It has three distinct crystal structure i.e. monoclinic ($\alpha$-$Bi_2O_3$), tetragonal ($\beta$-$Bi_2O_3$) and cubic ($\delta$-$Bi_2O_3$). Among these structures, $\delta$-$Bi_2O_3$ is stable from 730 to 804 °C, and possesses a defective fluorite structure in which two of the tetrahedral sites are unoccupied.[71-72] At room temperature, some dopants like $Y^{3+}$, $Pr^{3+}$ and $Er^{3+}$, can stabilize the cubic structure of $\delta$-$Bi_2O_3$. A few among them have shown higher oxygen ion conductivity than doped ceria but one of the major limitations is its poor chemical stability. It is comfortably reduced to Bi metal under reducing media. Also because of $Bi_2O_3$ has low melting point and easy volatilization at high temperature, electrolyte rarely become densified and show poor mechanical strength. Other bismuth oxide based electrolyte. [73-77]

$\gamma$-$Bi_4V_2O_{11}$ series oxides, also show favourable oxygen-ion conductivity at reduced temperature but same reduction problem exists. Due to this poor chemical stability of $Bi_2O_3$ based oxides under reducing atmosphere, concept of dual-layer electrolyte was proposed, which takes advantage of better oxide-ion conductivity of Bi-based oxides.[64-66] Also a new family of oxygen anionic conductors, exhibiting high performances at low temperature, has been derived from $Bi_4V_2O_{11}$ by partial substitution of vanadium by other metallic ions (BIMEVOX).[78] & with the copper substituent (BICUVOX) which also show better conductivity along with stability. [78]

## 1.7 Perovskite electrolytes

The perovskite structure is frequently adopted by materials with the general formula $ABX_3$, where A and B are cations and X is an anion which can bond to both (often O). The A cation is larger than the B cation; an ideal cubic perovskite is shown in Figure 1.12. Typically, structures ($ABX_3$) consist of large-sized 12-coordinated cations at the A-site and small-sized 6-coordinated cations at the B-site.[38]

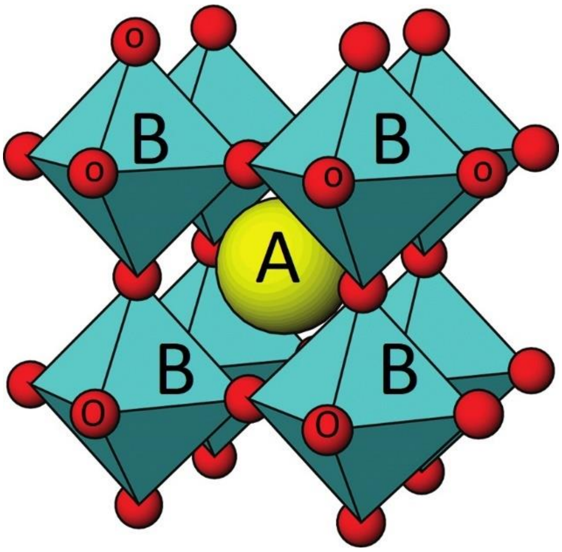

Figure 1.12 Pervoskite Structure

The perovskite structure can be hexagonal, cubic or orthorhombic / rhombohedral; to determine which will be formed, and whether a perovskite is possible, a Goldschmidt tolerance factor is used. The Goldschmidt tolerance factor (t) is calculated from the formula

$$t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}} \qquad \text{Eq (1.1)}$$

where $r_A$ and $r_B$ are the ionic radius of the A and B site cations respectively, and $r_X$ is the ionic radius of the anion. The tolerance factor assesses whether the A site cation can fit within the cavities in the $BX_3$ framework. Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate

($KNbO_3$), Barium Zirconate ($BaZrO_3$) etc. have a cubic perovskite type structure (in the paraelectric state) with chemical formula $ABO_3$. As conventionally drawn, A-site cations occupy the corners of a cube, while B-site cations sit at the body centre. Three oxygen atoms per unit cell rest on the faces. The lattice constant of these perovskite is always close to the 4 Å due to rigidity of the oxygen octahedral network and the well-defined oxygen ionic radius of 1.35 Å. A practical advantage of the perovskites structure is that many different cations can be substituted on both the A and B sites without drastically changing the overall structure. Complete solid solutions are easily formed between many cations, often across the entire range of composition

### 1.7.1 $LaGaO_3$ based electrolyte

Many perovskite oxides show mixed oxygen ion and electronic conductivity and they have been extensively used as electrode materials in SOFCs, especially as cathode materials. Some perovskite-type or related materials, like $LnBO_3$ (B = Al, In, Sc, Y) perovskites, doped $LaGaO_3$ perovskites[52-53]. Among these oxides, $LaGaO_3$- based perovskite oxides were most intensely investigated as electrolytes for IT-SOFCs.[52-53] If the A site of $LaGaO_3$ is doped with divalent alkaline earth metal ions, like $Sr^{2+}$, $Ba^{2+}$, and $Ca^{2+}$, oxygen vacancies will be generated. Research shows that the partial substitution of $La^{3+}$ with $Sr^{2+}$, which has the closet ionic radius to $La^{3+}$, results in the highest oxygen-ion conductivity. Theoretically, as the amount of A-site doping increases, the number of oxygen vacancies should increase and thus the oxygen-ion conductivity increases. However, in practice, the amount of $Sr^{2+}$ doping in the A site is limited. For example, if the doping amount of $Sr^{2+}$ is higher than 10%, in addition to the main perovskite phase, $SrGaO_3$ or $La_4SrO_7$ impurity phases are also found, which negatively affects the oxygen ion conduction. Doping the B site of $LaGaO_3$ with divalent ions will also encourage oxygen vacancies. After doping $Mg^{2+}$ into the B site, additional oxygen vacancies will be created, and the ionic conductivity improves rapidly. doping of $Ga^{3+}$ with $Mg^{2+}$ also increases the doping limit of $La^{2+}$ at the A site, which may be caused by the larger crystal lattice. Ishihara et al. found that $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) has the best oxygen ion conductivity among the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (x = 0.10–0.20, y = 0.15–0.20) series oxide electrolytes. It has higher oxygen ion conductivity than stabilized $ZrO_2$ and is comparable to doped $CeO_2$ at intermediate temperatures.[81-82] Pelosato et al. prepared LSGM via a co-precipitation route in aqueous medium, and the sintered sample had a relative density of 98% and a total conductivity of $1.13 \times 10^{-2}$ S $cm^{-1}$ at 600°C.[83] In spite of its high conductivity, the LSGM electrolyte has been used less in IT-SOFCs than doped ceria. This is due to several challenges for IT-SOFCs based on an LSGM electrolyte. Firstly, LSGM is very difficult to densify. Secondly, very often, an impurity phase could be formed during the synthesis of LSGM perovskite, which inevitably reduces the apparent conductivity. Thirdly, LSGM easily reacts with Ni-based anode and forms a low conductivity phase at the interface. To avoid a reaction between the anode and the LSGM electrolyte, a perovskite oxide or a low temperature-sintered Ni-based anode is a good choice.[84-85]

### 1.7.2 NBT based electrolyte

In 2013, Sinclair and group introduced $Na_{0.5}Bi_{0.5}TiO_3$, a ferroelectric pervoskite as an oxide-ion conductor. NBT is a very well know lead-free piezoelectric material, possess high leakage conductivity. This high leakage is to be claimed as beneficial for the oxide-ion conduction due to Bi-deficiency and induced oxygen vacancies. One major drawback of NBT as a piezoelectric/dielectric material is its high electrical conductivity which leads to high and unacceptable dielectric loss and leakage currents at elevated temperatures. To solve this problem improved understanding of the electrical conductivity and the conduction mechanisms of NBT is essential.[86-87] Hiruma et al.[88] and Sung et al.[89-90] have shown that the electrical properties of NBT are highly sensitive to A-site cation non-stoichiometry and that small deviations in nominal A-site cation stoichiometry can result in more than 3 orders of magnitude difference in the room temperature dc resistivity. Although it is widely accepted that the mobility of oxygen vacancies plays an important role and that $Bi_2O_3$ loss during ceramic processing is a likely source of the oxygen vacancies, the origin of the dramatic dependence of electrical conductivity with such small variations in the nominal starting compositions, as well as the conduction mechanisms of NBT, remain challenging issues.[91] The electrical conduction mechanisms in NBT and revealed the significant change in the electrical conductivity induced by small variations of Na or Bi non stoichiometry being related to a switch between oxide-ion and electronic conduction. The nominally stoichiometric NBT ($Na_{0.5}Bi_{0.5}TiO_3$), presents high conductivity with an oxide-ion transport number as 0.9 at 600–800$^{o}$C, suggesting that the electrical conduction is dominated by oxide-ions. The predominance of oxide-ion conduction (as opposed to sodium ion or electronic conduction) in NB0.50T has been further confirmed by O tracer diffusion measurements.[87,92]

### 1.7.3 Other Electrolyte

In addition to the above-mentioned oxide electrolytes, $La_2Mo_2O_9$ have shown high and pure oxygen ion conductivity at intermediate temperatures, making them suitable for use as electrolyte materials for IT-SOFCs. [67] A series of oxide compounds with a 2D layered structure, firstly reported by Goodenough et el., also show favorable oxygen ion conductivity at intermediate temperatures, which can be used as electrolytes for ITSOFCs.[96-99] These oxides have the structural formula of $Sr_{1-x}A_xSi_{1-y}Ge_yO_{3-0.5(x+y)}$ (A = Na or K). Research has shown that K-doped samples in this system were subsequently highly hygroscopic at room temperature, while Na-doping, with the large range of solubility of Na ions on the Sr site, proved to be highly effective in introducing pure oxygen ion conduction into the system[98]. The best oxide ion conductivity of the $Sr_{1-x}A_xSi_{1-y}Ge_yO_{3-0.5(x+y)}$ (A = Na or K) series was found in the composition $Sr_{0.55}Na_{0.45}SiO_{2.755}$ (SNS). At 500 °C, the measured oxide ion conductivity reached>$10^{-2}$ S cm−1 [96]. It is worth noting that the oxygen ion conduction activation energy of

SNS is only 0.3 eV, which is much lower than that of traditional oxygen ion conductors based on oxygen vacancies.

Oxide-ion conductors with hexagonal perovskite related structures are rare. Recently, Yashima M. et.al report oxide-ion conductors based on a hexagonal perovskite-related oxide $Ba_7Nb_4MoO_{20}$. $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ shows a wide stability range and predominantly oxide-ion conduction in an oxygen partial pressure range from $2 \times 10^{-26}$ to 1 atm at 600 °C. Surprisingly, bulk conductivity of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$, $5.8 \times 10^{-4}$ S $cm^{-1}$, is remarkably high at 310 °C, and higher than $Bi_2O_3$-based and zirconia-based materials. The high conductivity of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ is attributable to the interstitial-O5 oxygen site, providing two-dimensional oxide-ion O1−O5 interstitialcy diffusion through lattice-O1 and interstitial-O5 sites in the oxygen-deficient layer, and low activation energy for oxide-ion conductivity. [100]

## 1.8 Scope of thesis

Keeping all these positive and drawbacks of above electrolytes, similar structures based on similar properties have been explored. We have tried different substitutions in pervoskite structure based $KTaO_3$, $BaZrO_3$ & $SrTiO_3$ and also in cubic fluorite $ZrO_2$. Similar to NBT, dielectric leakage or Relaxor-like characteristics of ferroelectrics or high k dielectric materials reveal as a strong temperature and frequency dependence in the maximum of both real and imaginary part of dielectric permittivity. However, relaxors not only show particular and intriguing behaviours in the dielectric response, also show promising activity in fast-ion conduction to be applied as an oxide-ion conductor for the application in solid oxide fuel cells (SOFCs), the relaxor nature of high k dielectricity and higher polarizability of our doped ion in parent structure seems to play a directive role in providing superior oxide-ion transport throughout the lattice at temperature close to dielectric relaxation temperatures. In this thesis, we have envisaged that high polarizability of doped ion couple with high k dielectric relaxation (high dielectric leakage) can generate superior oxide-ion conduction near $T_m$ (The temperature of the maximum dielectric permittivity). To develop the proof of concept, we attempted the suitable doping of $Ti^{4+}$ & $Ge^{4+}$ ions into $KTaO_3$ lattice, $Bi^{3+}$ and $Gd^{3+}$ ions into $ZrO_2$ lattice, K & Ga ions into $BaZrO_3$ & $SrTiO_3$ lattice, to stabilize cubic phase. This dissertation covers a series of work to support the conclusion of the thesis and design of novel strategy to develop superior oxide-ion electrolyte in the intermediate temperature range.