

Introduction & Literature Survey

1.1 General Introduction

The rapid depletion of fossil energy resources (coal, oil and natural gas etc.) is causing pressing need for the efficient utilization of green energy for human activities and fast economic growth. Moreover, it has been recognized that the consideration of fossil energy resources as a long term energy solution has adversely affected the environment due to emission of greenhouse and other harmful gases [Höök et al., 2013]. However, the emergent concerns over limited stock of conventional energy sources, consequent constant emission of global warming gases, unbalanced price and supply have caused in a progressive interest towards the development of unconventional renewable energy technologies with high efficiency and less environmental detrimentation. In this energetic perspective, hydroelectric, wind power, solar power, wave power, geothermal and bio-energy technologies are being considered and executed as alternative approaches for electricity generation as well as combustion-free renewable energy technology. The foremost advantages of these alternative energy sources are eco-friendly cleanliness, sustainability, better energy security and reliability of supply. Figure 1.1 depicts a comparative study chart of the world wide consumption of energy from various sources. As per this study, 83% energy consumption of the whole world is accounted by fossil fuel until 2011 and is expected to be 78% by 2040, with oil dominating for 37% of the total, owing to more induction of renewable energy resources [Abdalla et al., 2018]. However, a main shortcoming in the extensive uptake of numerous practices for generation of renewable energy is the unpredictable nature of their production. These alternative energy sources are prone to irregular weather variations, being seasonal, high price and less efficiency. Additionally, it is tough to handle many of these renewable sources for transportation applications, which is now one of the main causes of air pollution. While electrochemical devices, such as

capacitors and batteries, can be used to store energy and then fulfill the demand of world power consumption, however, the utilization of these devices as an option for transportation sector are not easy due to small driving range, large profiles, safety, and disposal issues. Until the majority of world energy demand can be met by these alternative energy resources, there is an urgent necessity for long lasting and cheap energy generation technique having high efficiency, low pollutants emission, easy incorporation with the renewable sources, that can operate easily with present infrastructure of fuel distribution [Chalk et al., 2000; Smith et al., 2000]. One of the promising technologies in future would be Fuel cells (FCs) which can easily achieve the above mentioned requirements of electricity generation. The electricity generation via utilization of FCs can mitigate numerous adverse effects of energy generation, owing to their cleanliness, combustion-free operation, integrally high conversion efficiency and environmental friendly nature.

Nowadays, Solid oxide fuel cells (SOFCs) are receiving attention above other kinds of fuel cells owing to their high energy conversion efficiency, better performance and fuel adaptability at high operation temperatures. Even with these many advantages, there are some challenges of high production cost and high operating temperature. Moreover, the performance and efficiency of this technology is influenced by the properties and materials used for the cell constituents, i.e., cathode, anode, and electrolyte [Suntivich et al., 2011].

Therefore, this thesis is focused on the development of the suitable materials for SOFC electrolytes and electrode cell components, at a scale of nano-meter range, which may lead to enhanced performance of SOFCs at low working temperatures. In this chapter, a brief overview of the background information on SOFCs is presented, that shall be helpful in understanding the motivation behind SOFCs research. This chapter

also underlines the kind of improvement in cell component materials still needed for large scale-up production of SOFCs. Then, an introduction of characteristics and main properties of generally used cell components in SOFC applications is presented. Afterward, a literature review of functional solid electrolytes together with all aspect of insights into the current progress concerning doped/codoped ceria based ceramic electrolytes, highlighting oxide ion conductivity is thoroughly described.

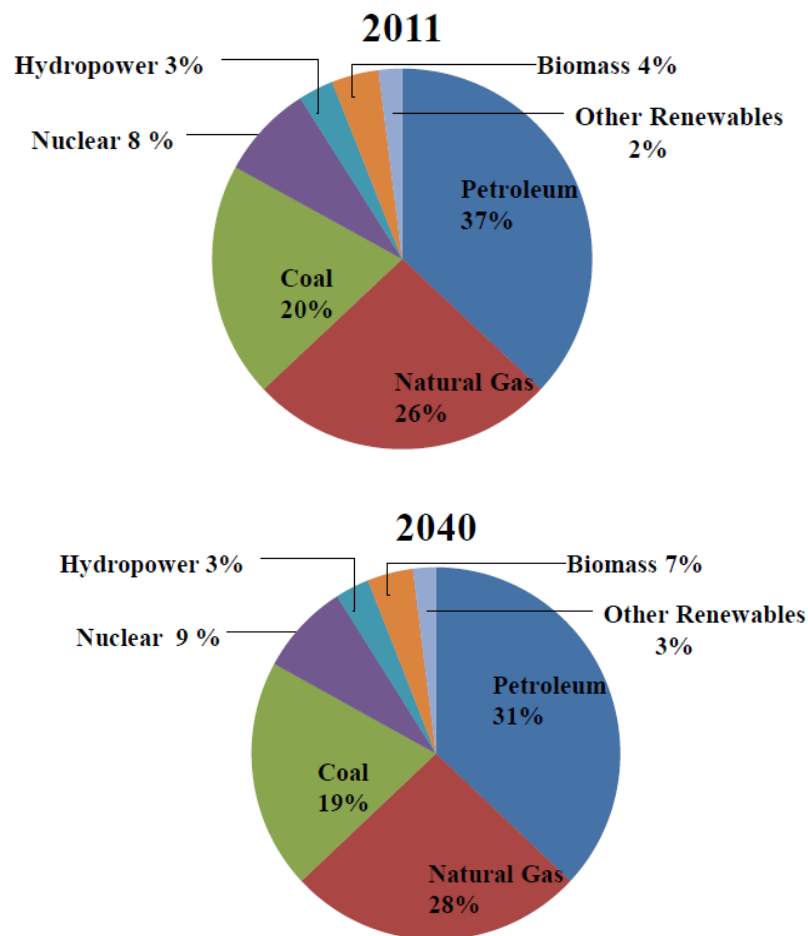


Figure 1.1 A comparison of energy consumption from various sources worldwide [Abdalla et al., 2018]

1.2 Fuel Cells

A fuel cell stands as a promising green energy conversion device generating electricity directly by transforming chemical energy of applied fuel to electrical energy

through efficient electrochemical reactions between a fuel such as H₂ with O₂ usually taken from air. Accordingly, electrochemical oxidation of H₂ can be attained with high conversion efficiency and low environmental impact. However, unlike battery, it can work for as long time as fuel is supplied and does not need recharging by external power sources. Moreover, Fuel cells provide much higher conversion efficiencies than conventional sources of green energy power, for example hydropower, wind energy and solar energy which are often disapproved due to the intermittent property of unsatisfactory supply security. Therefore, Fuel cells are drawing particular attention in recent year as a well-thought reliable energy conversion technology due to their environment friendly, extensive fuel flexibility, high conversion efficiency, a good potential to supply energy in stationary and portable energy applications.

1.3 History of Fuel Cells

The idea of fuel cell was identified by Humphry Davy in the nineteenth century, who demonstrated it as the reverse process of water electrolysis. Sir William Robert Grove generally recognized for developing the fuel cells in 1839, evidenced that the electrochemical reaction between H₂ and O₂ can produce electric current in a sulphuric acid electrolyte using platinum electrodes [Möbius et al., 2003; Ghosh et al., 2011]. First time, Charles Langer and Ludwig Mond used the term of fuel cells. They generated 6 Amp/ft² at voltage of 0.73 V experimentally by using hydrogen fuel cell. Furthermore, an inventor of physical chemistry, Friedrich Wilhelm Ostwald (1853-1932) derived the correlation among the various components of the fuel cell containing the electrodes (cathode and anode), electrolyte, reducing and oxidizing agents (cations and anions). At the same time, Francis Thomas Bacon (1904–1992) did extensive improvements through high-pressure fuel cells having an efficient electrode of nickel gauze that worked at pressure up to 3000 psi in the cells., The International Fuel Cells

(IFC) in Connecticut, USA established a power plant of fuel cell used for the Apollo space craft in the former time of 1960s. IFC had settled extra powerful unit of alkaline fuel cell designed for space shuttle Orbits of NASA in the time of 1970s [Cook et al., 2002; Singhal et al., 2000].

1.4 Type of Fuel Cells

There are numerous kinds of fuel cells which are categorized according to the requirement of specific materials such as chemical characteristics of electrolytes used that defines the nature of the electrochemical reactions that happen within the cell, fuels and working temperature range. According to this classification, different types of fuel cell as per their characteristics are listed in Table 1.1.

Table 1.1 Different fuel cell types and their characteristics [Jaiswal et al., 2019].

| Type of Fuel Cells | Operating temperature (°C) | Electrolyte | Electrical efficiency | Advantages | Applications |
|---|----------------------------|---|-----------------------|---|--|
| Alkaline fuel cells | <100 | Aqueous solution of Sodium hydroxide and potassium hydroxide | 60 | Low cost, Low working temperature, fast reaction at cathode in alkaline media | Portable electronic devices, Space, Backup power, stationary, Transportation military |
| Polymer electrolyte membrane fuel cells | 70-110 | Nafion polymer membrane | 35-60 | Low working temperature, rapid power up, Used solid electrolyte exhibit less corrosion | Portable power, Backup power stationary, Distributed generation Transportation |
| Molten carbonate fuel cells | ~650 | Molten, Sodium, Potassium Lithium and/or Carbonates | 40-45 | Fuel flexibility high efficiency, variation in catalysts | Electric utility, Distributed power generation |
| Phosphoric acid fuel cells | 150-200 | Phosphoric acid soaked in porous matrix | 40 | High operation temperature enables Combined Heat and Power (CHP), enhanced tolerance to fuels | Transportation Stationary power generator |
| Solid oxide fuel cells | 500-800 | Ytria stabilized zirconia, Sm/Gd doped ceria, Bismuth oxide Lanthanum gallate | 60-80 | High temperature, high efficiency, fuel flexibility, modularity, suitable for CHP | Auxiliary power in stationary power generation to vehicle, Electric utility Distributed power generation |

1.4.1 Alkaline Fuel Cells (AFCs)

They are created around an electrolyte composed of strongly alkaline, usually liquid form of sodium or potassium hydroxide with high concentration and inert porous solid structure support. The working temperature range is at about 60-90°C. As longest-proven fuel cells amongst the other technology, this was mostly employed for Apollo series of space missions investigated by NASA. This fuel cell possesses common working principle as at the cathode side, oxygen and water react to release hydroxide in presence of electrons, drawn from external circuit. At the anode side, the hydroxide ions move over the electrolyte material and combine with hydrogen ions to form water, liberating electrons that can travel through the outer circuit in the direction of cathode. The cause which inhibits the AFCs to develop the foremost fuel cell technology is the formation of CO₂ as a result of the high reactivity of hydroxide ions with carbon even the least amount of CO₂ can significantly decline the efficiency of cell. This infers that the fuel used in cell must be pure form of H₂ and O₂ which is not difficult inside an atmosphere such as space on the other hand it develops an excessive burden inside the environment of earth [Hirschenhofer et al., 1996; Giorgi et al., 2013].

1.4.2 Polymer Electrolyte Membrane Fuel Cells (PEMFCs)

The working temperature is little higher than AFC (80-110°C). A proton conductor containing water-based acidic polymer membrane is used as electrolyte. At the anode side in the cell, hydrogen splits into protons, which move via the membrane of electrolyte, and electrons, which travel through outside external circuit towards the cathode side. At this point, the electrons and protons combine with oxygen ions to create water as one byproduct. The materials used for this cell are expensive that has directed much research on their replacements, to make these cells more commercially

worthwhile. Furthermore, the metal required to catalyze the oxidation of fuel at the anode can experience poisoning as of Carbon mono-oxide, which can be existent in reformed hydrogen employed by way of fuel. The low operation temperature requirement permits PEMFCs to do on-off operation promptly, developing them extremely suitable to mobile applications. Still, it also refers that they usually are inappropriate for combined applications in both power and heat as the heat yield is excessively low [Hirschenhofer et al., 1996; Giorgi et al., 2013].

1.4.3 Molten Carbonate Fuel Cells (MCFCs)

MCFCs work at the temperatures above 500°C, permitting less expensive metals to perform as catalysts so that it is low cost. The material of electrolyte is composed of a mixture of molten salt that transports CO_3^{2-} ions, inside a porous inert solid support. At the cathode side, CO_2 must be present so as to produce the CO_3^{2-} ions, and it is frequently achieved via reprocessing the exhaust gas to raise the partial pressure of CO_2 . It can work on a variety of fuels, containing specific that are contagious to other type of fuel cells, for example carbon monoxide. If applying on hydrocarbons then reforming of internal system can take place, permitting the system to operate them reliably. The flexibility of fuel allows the system a significant benefit among other earlier discussed fuel cells; as MCFCs could operate on extensively accessible fuels avoiding necessity for variation of infrastructure. Still, the high working temperatures as well as unsafe electrolyte materials employed, do have their shortcomings. In view of this, the cell durability is compromised because of the corrosion of constituents in the tough chemical circumstances. The important present research work is thus focused on materials that can survive this situation whereas retaining extraordinary levels of energy conversion efficiency. Moreover, due to the high working temperatures, a rapid start and stop cycle is challenging to attain, rendering MCFCs incompatible in various

applications needing alternating or temporary power [Hirschenhofer et al., 1996; Giorgi et al., 2013].

1.4.4 Phosphoric Acid Fuel Cells (PAFCs)

Fuel cells developed with an electrolyte based on high concentration of phosphoric acid, have considerably high tolerance to impurities as compared to both AFCs and PEMFCs. At high concentrations, phosphoric acid forms pyrophosphoric acid that freezes at room temperature, due to this the elevated working temperatures range of (150 - 200 °C) are generally sustained for the cell life time, creating them preferably suitable for uninterrupted continuous load or electric power supply uses. They are also appropriate for use in automobiles. Operation reaction within cell is very comparable to those in PEMFCs, and the electrolyte possess a structure more alike to AFCs, having a conducting medium of liquid that is supported via a porous structured solid. Nevertheless, in the same way to AFCs, the harmful electrolyte materials as well as constant working requirements create difficulty in maintenance and the electrodes, usually platinum containing, again drives the price up [Hirschenhofer et al., 1996; Giorgi et al., 2013].

1.4.5 Solid Oxide fuel cells (SOFCs)

Solid oxide fuel cells (SOFCs), also recognized as ceramic FCs have better conversion efficiency up to 60-80% for practical applications, durability, low environmental impact, fuel flexibility at high working temperature. In principle, SOFCs shows exclusive properties among other kind of fuel cells, such as multi-fuel choice (for example H₂, hydrocarbon fuel, CO, syngas, gasoline, etc.). Additionally, the high operational temperature originates sufficient charge conduction, fast fuel oxidation kinetics and electrochemical reaction rates at electrodes. Furthermore, the all-solid

structure of ceramic oxides inhibits the risk of erosion, occurring among other kinds of fuel cells, which also assists the assembly of SOFC modules/stacks. Owing to ability of high conversion efficiency in reverse mode operation, SOFCs can also convert chemical energy to electrical energy in reverse mode, indicating their potential as a replacement for present energy storage systems (battery, capacitor) via exchanging excess renewable electrical energy to fuels in electrolysis mode. These factors, along with fuel flexibility, extensive potential application fields (for example, portable, stationary, transport, domestic stationary, industrial, and auxiliary power units), and combustion-free operation, render SOFCs the most promising candidate for long lasting energy conversion and storage technology. Further, SOFCs are classified in three kinds on the basis of cell operating temperature. Firstly, high temperatures SOFCs (HT-SOFCs) were developed that worked at high temperatures in the range of 900°C-1000°C. The high operating temperature is required to ensure adequate electro catalytic activity, especially for electrolytes, having ionic conductivity. On the one hand, the high working temperature improves the reaction rates and charge conduction, on the other hand it possess critical hurdles for practical applications such as high material cost, material degradation and other challenges for material compatibility, Therefore, to reduce the operating temperature, after so many efforts, intermediate temperature SOFCs (IT-SOFCs) were developed, that can work at temperature range from 650°C to 800°C. Moreover, nanostructured materials are currently well preferred, particularly at low temperatures, having operating temperature range up to 650°C. These are easy to operate, reduce the cell fabrication cost by using the lower-cost materials and have long term durability. Among growing fields of research, low temperature LT-SOFCs with high conversion efficiency are the need of the era [Hirschenhofer et al., 1996; Giorgi et al., 2013].

1.5 Working principle of SOFCs

Solid oxide fuel cells contain mainly three components: anode (oxidation of fuel), cathode (reduction of fuel), separated by highly dense electrolyte, that provide pathway for ions transport. The main reaction kinetics is established on the oxide ion (O^{2-}), originating from air introduced at the cathode side that split it to oxygen ions (oxygen reduction reaction) (ORR), and electrons (e^-). At cathode, forming oxide (O^{2-}) ions migrate via the dense solid electrolyte to get consumed with fuel gas such as hydrogen (H_2) molecules to form water and liberating electrons that is transferred to the surface of anode. These liberated electrons transport to cathode through the outer (load) circuit [Yokokawa et al., 2008; Goodenough et al., 2014; Stambouli et al., 2002; Orera et al., 2014]. The working principle for a SOFC is demonstrated in Figure 1.2.

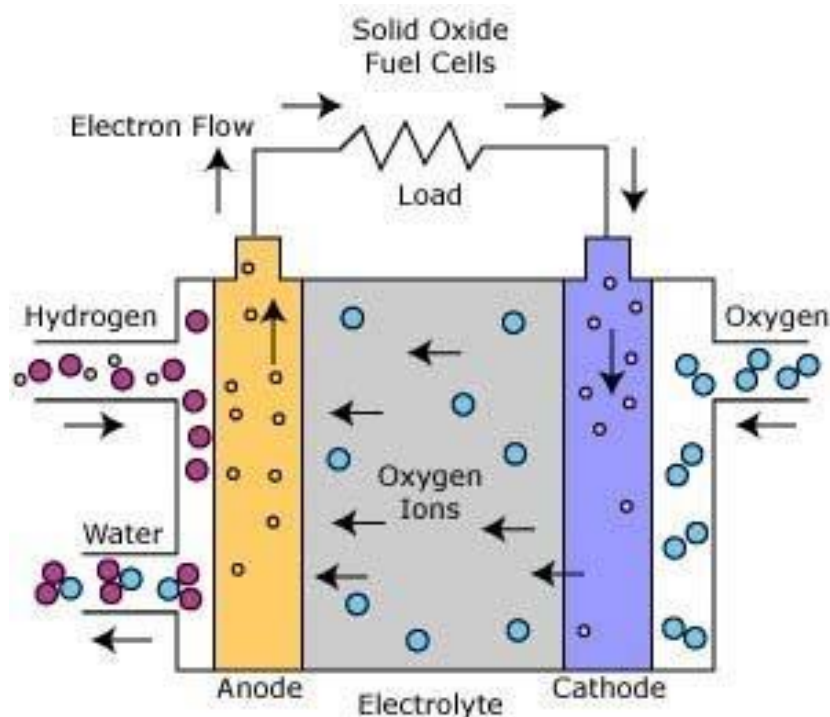


Figure 1.2 Schematic demonstration of operating principle of SOFCs [Pihlatie et al., 2010].

1.6 Investigation of SOFCs Material Components

Development of key components of the cell (cathode, anode, electrolyte) need in-depth understanding in materials science to obtain desired materials having exceptional properties such as desired electrical conductivity, electro catalytic activity, thermal stability and chemical compatibility. In order to get excellent performance of SOFC devices, there are necessities of more investigations for versatile materials and their combinations to accomplish the materials requirements of SOFCs. Moreover, the development of SOFCs devices for practical deployment are associated to the great technological challenges in energy material research, for example; material selection challenges in terms of cost, operating temperature and fabrication procedure. In the upcoming sections, we will concisely review the characteristics and main properties of generally used cell components in SOFCs applications.

1.7 Cathode Materials

The cathode material for SOFCs devices is exposed to oxygen usually air where oxygen reduction reaction occurs. The significance of cathode can be understood by the cell operation condition i.e. easy transportation of oxygen ion through itself to the cathode/electrolyte interface, as well as, working as charge carrier medium for electrons from external output circuits to cathode. A suitable cathode material needs some distinct properties, for example, high porosity to diffuse oxide ions, high mixed ionic electronic conductivity (MIECs) ($> 100 \text{ S/cm}$ at 600°C), thermal and mechanical compatibility (thermal expansion coefficients) matching well with the other cell components (electrolytes, interconnects), high temperature stability in reducing atmosphere, and high catalytic activity rate towards reduction reaction of oxygen, as illustrated Figure1.3.

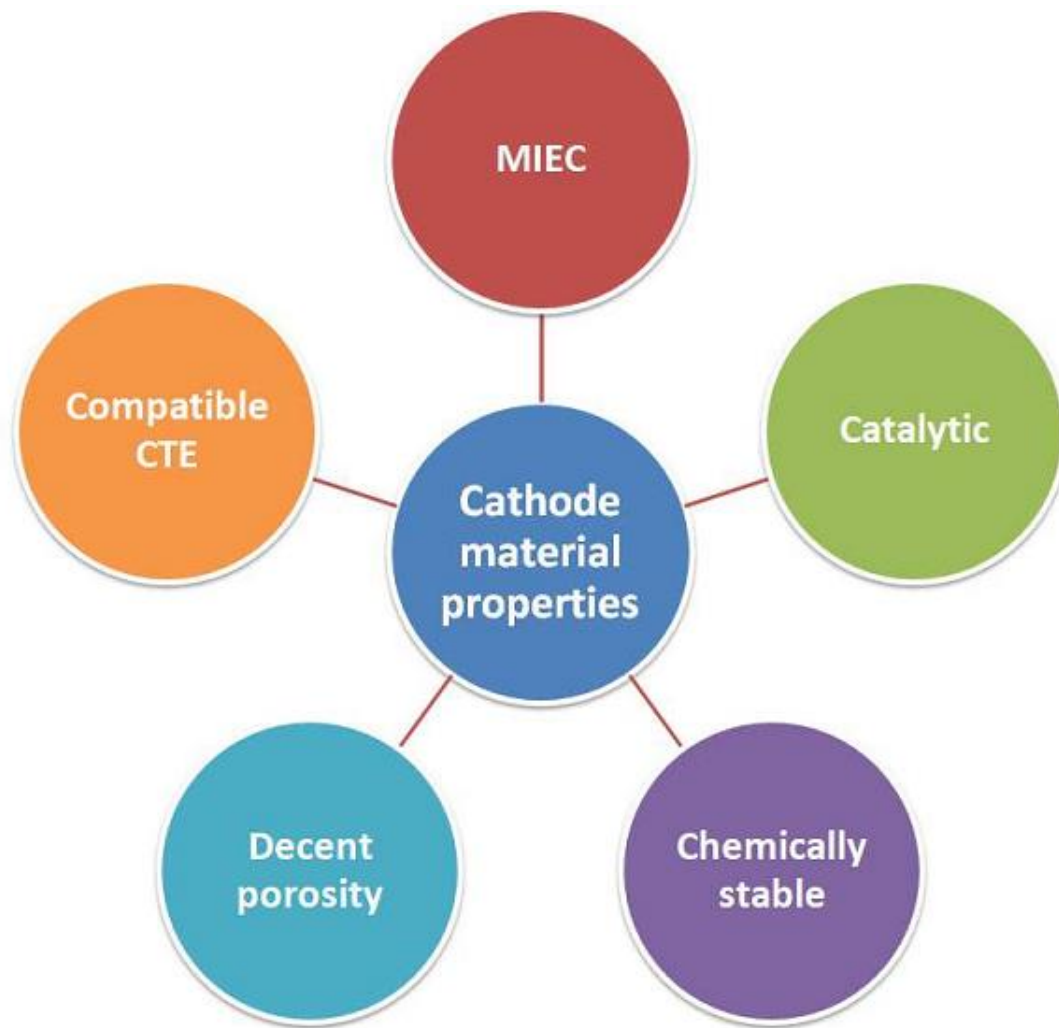


Figure 1.3 Properties of cathode materials for SOFCs application [Kaur et al., 2019].

1.7.1 Perovskite Cathode Materials

Perovskite-structure oxides using common formula ABO_3 are generally employed as SOFCs component material such as cathode and anode. Figure 1.4 represents schematic perovskite crystal structure containing positively charged A and B cations having an overall valence charge of +6. The cations at A site (such as, La, Ca, Sr, Pb, etc.) have bigger size, lower valences, and coordinated with twelve oxide anions. The cations at B site (such as, Cr, Ti, Fe, Ni, Zr, Co, etc.) reside in a very smaller space of lattice and are coordinated with six oxide anions [Singhal & Kendall, 2003; Sun et al., 2010].

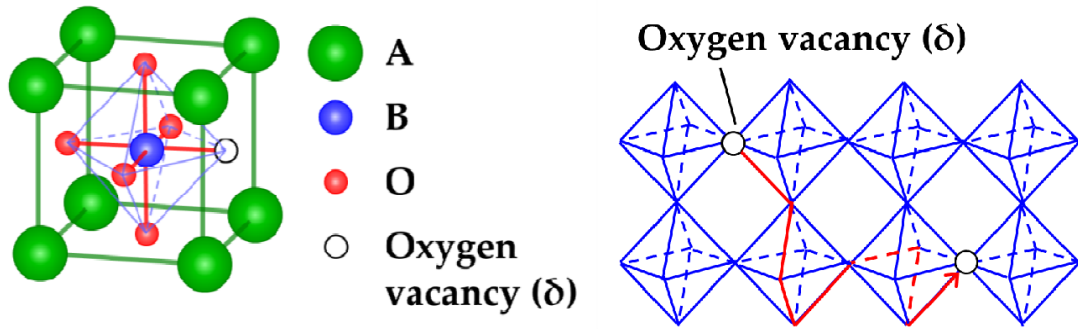


Figure 1.4 Representation of ABO_3 perovskite, lattice structure oxide adapted [De Larramendi et al., 2016].

For high operating temperature solid oxide fuel cells, the most commonly used cathode material is strontium doped lanthanum manganite $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM), perovskite, which exhibits very high electronic conductivity under atmospheric conditions. Unfortunately LSM shows a limited performance and insufficient polarization value is obtained at elevated temperature, for best performing configuration with Yttrium oxide stabilized zirconia (YSZ), a common electrolyte material. To address these concern new cathode materials has to be explored. The cubic-type perovskite systems, such as alkaline earth (Sr, Ca, Ba), transition metal oxides, with (Fe, Co, Cu) and/or lanthanide (Ln = La, Pr, Nd, etc.) dopants, have been studied extensively as listed in Table 1.2. The new promising cathode materials for SOFCs to be developed should have operating temperature in the intermediate temperature range. Various doped perovskites have been investigated in recent years for cathode applications, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $Sr_{0.9}Ce_{0.1}Fe_{0.8}Ni_{0.2}O_3$, $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $La_{0.6}Sr_{0.4}FeO_3$, $Sm_{0.5}Sr_{0.5}CoO_3$, $Pr_{0.5}Sr_{0.5}FeO_{3-\delta}$, $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF), $Pr_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Pr_{0.8}Sr_{0.3}Co_{0.2}Fe_{0.8}O_3$, $Sr_{0.8}Ce_{0.1}Fe_{0.7}Co_{0.3}O_{3-\delta}$, $Pr_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$, $Pr_{0.7}Sr_{0.3}Co_{0.2}Mn_{0.8}O_{3-\delta}$, $Pr_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Pr_{0.7}Sr_{0.3}Co_{0.9}Cu_{0.1}O_{3-\delta}$, $Pr_{0.8}Sr_{0.2}FeO_{3-\delta}$, $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, etc.,

with the objective to get high electronic and ionic conductivities, and thermal expansion coefficient (TEC) comparable to that of the commonly used electrolytes and excellent catalytic property at intermediate temperatures [Sun et al., 2010].

Table 1.2 Various Perovskite based cathode materials [Sun et al., 2010]

| Composition | TEC $\times 10^{-6} \text{K}^{-1}$ | T($^{\circ}\text{C}$) | σ_e (S cm^{-1}) |
|--|------------------------------------|-------------------------|----------------------------------|
| La _{0.7} Sr _{0.3} MnO ₃ | 11.7 | 800 | 240 |
| Pr _{0.6} Sr _{0.4} MnO ₃ | 12 | 950 | 220 |
| La _{0.6} Sr _{0.4} CoO ₃ | 20.5 | 800 | 1600 |
| La _{0.8} Sr _{0.2} CoO ₃ | 19.1 | 800 | 1220 |
| La _{0.5} Sr _{0.5} FeO ₃ | – | 550 | 352 |
| La _{0.5} Sr _{0.5} FeO ₃ | – | 800 | 369 |
| La _{0.6} Sr _{0.4} FeO ₃ | 16.3 | 800 | 129 |
| Pr _{0.8} Sr _{0.2} FeO ₃ | 12.1 | 800 | 78 |
| Pr _{0.5} Sr _{0.2} FeO ₃ | 13.2 | 550 | 300 |
| La _{0.7} Sr _{0.3} Fe _{0.8} Ni _{0.2} O ₃ | 13.7 | 750 | 290 |
| La _{0.8} Sr _{0.2} Co _{0.2} Ni _{0.8} O ₃ | 15.4 | 600 | 125 |
| La _{0.8} Sr _{0.2} Co _{0.2} Fe _{0.8} O ₃ | 20.1 | 600 | 1050 |
| La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O ₃ | 21.4 | 800 | 269 |
| La _{0.8} Sr _{0.2} Co _{0.2} Mn _{0.2} O ₃ | 18.1 | 500 | 1400 |
| Sr _{0.9} Ce _{0.1} Fe _{0.8} Ni _{0.2} O ₃ | 18.9 | 800 | 87 |
| La _{0.2} Sr _{0.8} Co _{0.2} Fe _{0.8} O ₃ | 19.3 | 800 | 1000 |
| Pr _{0.7} Sr _{0.3} Co _{0.2} Fe _{0.8} O ₃ | 11.1 | 800 | 200 |
| Pr _{0.7} Sr _{0.3} Co _{0.9} Fe _{0.1} O ₃ | – | 700 | 1236 |
| Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O ₃ | 20 | 500 | 30 |
| LaNi _{0.6} Fe _{0.4} O ₃ | 11.4 | 800 | 580 |
| Sm _{0.5} Sr _{0.5} CoO ₃ | 20.5 | 700-900 | >1000 |

1.7.2 Cobalt free Cathode Materials

The two most important factors that strongly decide the performance of cathode materials are crystal structure and concentrations of oxygen vacancies. The common observation is that the lattice having higher structural symmetry and higher

concentration of oxygen vacancies exhibit more rapid oxide ions bulk diffusion and association/dissociation through surface reaction, as reported in some cobalt-free and cobalt based mixed ion electronic conductor (MIECs) perovskite oxides [Efimov et al., 2010; Chen et al., 2011; Wang et al., 2009; Zhou et al., 2013]. Among the several types of MIECs, the series of Co-containing perovskite oxides is one of most attentive research topic as cathode materials for SOFCs application, for example $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) [Baqué et al., 2017] $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) [He et al., 2016; Xu et al., 2016] and $\text{LnBaCo}_2\text{O}_{5+\delta}$ (LnBCO, Ln = La, Pr, Nd, Sm, Gd) [Kim et al., 2015; Joung et al., 2013]. Cobalt-containing perovskite structured cathode materials exhibit maximum essential properties for SOFCs application. The MIECs oxides having cobalt offer adequate electrocatalytic properties because of their good capability to provide passage to the ions and electrons in the similar time. Nevertheless, in most cases, the cobalt-based materials have typically higher value of thermal expansion coefficients (TECs) as compared to the other components of SOFCs. The debonding/cracking at the electrode and electrolyte interface is caused by higher value of TEC of the cobalt-based materials, due to TEC mismatch between cathode and electrolyte throughout thermal cycling under working condition of SOFC. Likewise, mismatch of TEC results thermal stresses at the electrode-electrolyte interface that affects the long-term durability and working performance of the SOFC device. Furthermore, cobalt based cathode materials are expensive than other materials [Senaris-Rodriguez et al., 1995; Choi et al., 2013]. Besides the price, the practical application of cobalt-containing materials is detrimental due to poor chemical stability in reducing atmosphere, significant modification in unite cell volume related with the spin state transition and changed oxidation state of cobalt cations upon reduction, and chemical reactivity with zirconia-containing electrolyte materials. Thus, the

development of cobalt-free MIEC perovskite-structure cathode having outstanding electrochemical properties and operating under 800°C is one of the current hot research topics. Studies are being done to examine the effect of various metals incorporation at both A and B-sites of perovskite oxides (ABO_3) based materials. For example, $SrFeO_3$ perovskite oxide doped with Cr, Nb, Ti, W, Zr, V and Mo group of cations were investigated as cathode materials for SOFCs applications [Zhou et al., 2014; Falcón et al., 2002; Fernández-Ropero et al., 2014]. These studies reveal that $SrFeO_3$ doped with transition metal oxides having higher valence state substitution at A-site (e.g., $(Bi,Sr)FeO_{3-\delta}$) and $(La,Sr)FeO_{3-\delta}$) or B-site (e.g., $Sr(Ti,Fe)O_{3-\delta}$) and $Sr(Nb,Fe)O_{3-\delta}$) are appropriate for both cathode as well as anode materials for symmetrical SOFCs [Simner et al., 2003; Niu et al., 2010; Niu et al., 2011; Wedig et al., 2011].

Perovskite oxide $SrFeO_{3-\delta}$ is a remarkable MIECs perovskite structured cathode material that can be potentially employed in many electrochemical applications for instance oxygen sensors, SOFCs and oxygen permeation membranes. It is also a model system whose lattice structure and electrical behaviour are considerably associated to the ordering of oxygen vacancies [Yoo et al., 2005]. In this system, Fe-cations with mixed valence states ranging from +4 to +3, corresponding to an extensive range of oxygen nonstoichiometry (from 0 to 0.5) leads to change in structure from cubic to orthorhombic brownmillerite type having oxygen vacancies of long range ordering. Nevertheless, the nature of creation of oxygen vacancies ordering is not promising for cathode uses as it obstructs transfer of oxygen, whereas the oxygen deficiency additionally causes in a reduction in both charge mobility and amount of hole charge carriers [Vashuk et al., 2000; Patrakeeve et al., 2011; Niu et al., 2010]. Thus, doping in $SrFeO_{3-\delta}$ system is essential for developing suitable compositions for various applications. Numerous cathode materials used in SOFCs application can be designed

from $\text{SrFeO}_{3-\delta}$ via substitution with different cations [Simner et al., 2002; Liu et al., 2003]. A development toward emerging cobalt-free MIEC oxide electrodes for SOFCs working at intermediate temperature range (IT-SOFCs) provide the significant expenditure cut, thermal compatibility and stability (among the cell components) advantages acquired by eliminating cobalt. Although the electrochemical properties of the resultant cathode materials is improved, dropping performance of these cathodes is seen at lower working temperatures ($<650^\circ\text{C}$), as compared to the cobalt-containing cathode materials.

In recent times, Mo-substituted $\text{SrFeO}_{3-\delta}$ has grown into a subject of demanding investigations. Doping of Mo ions can intensely affect the oxidation state of iron as Molybdenum ions have higher oxidation state than iron ions and the immediate creation of oxygen defects in the perovskite, which influence the electrocatalytic activity as well as electronic behavior [Zhang et al., 2010; Xiao et al., 2010]. Thus, Mo ions substituted $\text{SrFeO}_{3-\delta}$ exhibits moderately altered properties for varying doping concentrations of Mo ions. At higher level of Mo content with perovskite phase of $\text{SrFe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($0.25 < x < 0.6$) having B site ordering of Fe and Mo has been achieved, in reducing environments that revealed better activity as an anode material for SOFCs application. More remarkably, in low Mo-doping series also the Mo-substituted $\text{SrFeO}_{3-\delta}$ exhibits good structural stability in broad range partial pressures of oxygen. The $\text{SrFe}_{0.75}\text{Mo}_{0.25}\text{O}_{3-\delta}$ has been established as a redox stable electrode material for SOFCs application. These observations promote greater interest in examining Mo-substituted $\text{SrFeO}_{3-\delta}$ perovskite oxides as a promising cathode materials [Markov et al., 2008; Savinskaya et al., 2011; Liu et al., 2010; Xiao et al., 2011]. In order to further investigate the effect of higher valence state at B-site cation, W doped $\text{SrFeO}_{3-\delta}$ perovskites have been systematically studied for sinterability, conductivity, thermal

expansion behavior, and oxygen catalytic activity to develop potential SOFC cathode materials. It has been suggested and experimentally confirmed that co-doping on both A and B sites of SrFeO₃ perovskite can cause synergistic effects in relation to structural, thermal and electrochemical properties. In view of this, at B-site, Ta and W co-doped SrTa_{0.1}W_{0.1}Fe_{0.8}O_{3-δ} perovskite was synthesized and its structural, thermal, conductivity and electrochemical properties were comparatively investigated with SrTa_{0.2}Fe_{0.8}O_{3-δ} and SrW_{0.2}Fe_{0.8}O_{3-δ} perovskite oxides having single doped Ta and W, respectively. The acquired results reveal that co-doped SrTa_{0.1}W_{0.1}Fe_{0.8}O_{3-δ} can be a potential cathode candidate for SOFCs [Yao et al., 2019]. In addition, some other new groups of perovskite-structured type oxides are being investigated as promising IT-SOFC cathodes, as described in forthcoming sections.

1.7.3 Layered Double Perovskites

The lanthanide (Ln)-containing LnBaCo₂O_{5+δ} layered double perovskite oxides are proposed as potential cathode materials for (LT, IT, HT-SOFCs) because of their high electrical and ionic conductivity, high rates of O²⁻ ion diffusivity and surface oxygen exchange [Kim et al., 2008; Zhang et al., 2008; Burriel et al., 2012]. Current research work focuses on Ln-containing double perovskite oxide materials doped with alkaline earth cations (Ba, Ca, Sr etc.) at A site in addition to substitution of transition metals (Cr, Co, Mn, Cu, Fe, etc.) at B site as shown in Figure 1.5. PrBaCoMn₂O_{5+δ} having A-site layered perovskite structure have been discussed using structure-property correlation. In recent investigations, the layered perovskite anode materials, PrBaMn₂O_{5+δ} NdBaMn₂O_{5+δ} PrBaCo₂O_{5+δ} have been studied with concern to their structure and electrical property [Afroze et al., 2019].

1.7.4 Ruddlesden-Popper Perovskites

Ruddlesden-Popper (RP) phases composed of Rare-earth transition metal cations $A_{n+1}M_nO_{3n+1}$ ($A=La, Pr, Nd, Sr, Ca$ etc.), ($B = Cu, Co, Ni$ etc.), where ($n = 1, 2$ and 3) are related perovskite structured materials having wide range of elements and provide interstitially oxygen ions transport along layers of rock salt. The electronic conductivity shown by these materials are not as good as other perovskite-associated cathode materials, under low operating temperature condition. Some chemical reactions also occur between Ruddlesden-Popper (RP) phases, and commonly used electrolyte materials, but their coefficients of thermal expansion are closely comparable to those of electrolyte materials [Woolley et al., 2014; Takahashi et al., 2010]. A comparative representation of Ruddlesden-Popper (RP) structure along with perovskite and double perovskite structures are shown in Figure 1.5

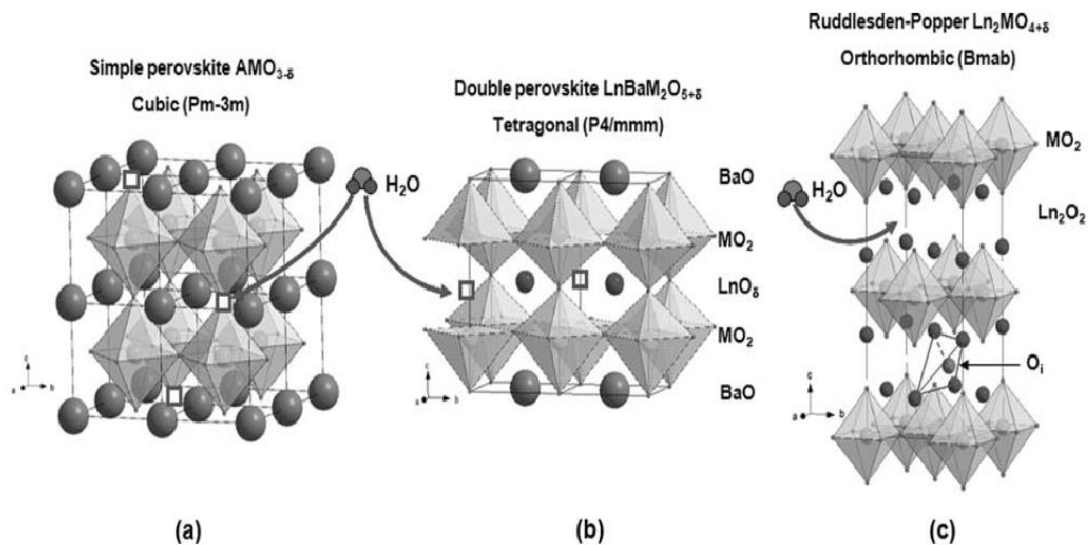


Figure 1.5 Schematic interpretations of the crystal structures of: a) Simple Cubic perovskite, b) Layered double perovskite oxide and c) Ruddlesden-Popper perovskite oxide. Water insertion sites are displayed: oxygen ion vacancies for the cubic perovskites and interstitials for Ruddlesden-Popper $Ln_2MO_{4+\delta}$ structure [Grimaud et al., 2012]

1.8 Anode Materials

In fuel cell, the second main component is the anode part which catalyzes the oxidation-reaction of fuel gas with oxygen. It must have chemical stability in highly reducing atmosphere, active catalytic reaction site in the microstructure and ionic conductivity in certain limit to permit ion diffusion between the anode materials and electrolyte, in addition to electronic conductivity to allow the transport of electrons. Furthermore, it should be sufficiently porous (20-40%) for fuel supply as well as chemically inactive with respect to the commonly used electrolyte materials. The Nickel/Yttrium oxide stabilized zirconia (Ni/YSZ) cermet is the extensively used anode material in the high temperature SOFC using H₂ as a fuel [Rafique et al., 2019]. Several reasons are associated for the selection of this material, such as low price, good catalytic activity for oxidation reaction of fuel, chemically inactive and TEC matching with the YSZ electrolyte. However, the major drawback of Ni/YSZ anode materials is degradation through the supply of fuels having sulphur contents which result in dramatic performance loss with time via poisoning of nickel. Apart from the Ni based anode materials, several conducting anode materials were explored with the aim to improving their conductivity measured under oxidizing and reducing conditions e.g. La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O₃, Sc_{0.1}Y_{0.1}Zr_{0.6}Ti_{0.2}O_{1.9}, Ti_{0.34}Nb_{0.66}O₂, (La_{0.7}Sr_{0.3})_{1-x}Ce_xCr_{1-x}Ni_xO₃, La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O₃, CrTi₂O₅, LaSrTiO₂, Ni-SDC, Cu-CeO₂, Ni-GDC, CrTi₂O₅, Cu-GDC as mentioned in Table 1.3 [Rafique et al., 2019; Shaikh et al., 2015]. Moreover, various possible synthesis methods of SOFC anode materials is also crucial in selecting the most beneficial method with desired properties for anode applications [Rafique et al., 2019; Shaikh et al., 2015].

Table 1.3 List of materials developed as anode and their dc conductivities at 800°C [Shaikh et al., 2015].

| Materials | dc conductivity (S cm ⁻¹) | Advantage/Disadvantage |
|--|---------------------------------------|---------------------------------------|
| La _{0.8} Sr _{0.2} Fe _{0.8} Cr _{0.2} O ₃ | 0.5 | Low conductivity |
| Sc _{0.1} Y _{0.1} Zr _{0.6} Ti _{0.2} O _{1.9} | 0.14 | work at high temperature |
| La _{0.8} Sr _{0.2} Cr _{0.95} Ru _{0.05} O ₃ | 0.6 | Costly |
| Sr _{0.88} Y _{0.08} TiO ₃ | 64 | High working temperature |
| (La _{0.7} Sr _{0.3}) _{1-x} Ce _x Cr _{1-x} Ni _x O ₃ | 5.03 | Carbon deposition |
| CrTi ₂ O ₅ | 177 | Costly |
| Ti _{0.34} Nb _{0.66} O ₂ | 340 | Very Expensive |
| Ni-YSZ | 250 | High working temperature |
| Ni-SDC | 573 | Compatibility issue |
| LaSrTiO ₂ | 360 | Coke formation |
| Ni-GDC | 1070 | Coke formation |
| Cu-GDC | 8500 | degradation of electronic performance |
| Cu-CeO ₂ | 5200 | electronic conductivity |

1.9 Electrolyte Materials

In an SOFC, the primary role of solid electrolyte is to conduct ions either O²⁻ or H⁺ (a nature of the specific material) between the electrodes, in order to avoid blocking of electrons internal conduction, driving the electrons to move through the outside external circuit to complete the overall electrochemical reaction. Materials used as electrolytes in SOFCs must have high oxygen ion conductivity, chemically, thermally and mechanically companionable with the adjoining cell components, highly dense microstructure, low electronic conductivity to avoid internal short-circuits during electrochemical reaction [Singhal et al., 2014; Jiang et al., 2011; Holtappels et al., 2010]. In last few decades, SOFC electrolyte materials have received great attention among materials researchers and scientists in order to achieve good performance of SOFCs [Fergus et al., 2006; Kharton et al., 2004]. So, a wide variety of compounds have been investigated as suitable candidate of electrolyte materials for SOFC. The major research work has been focused mainly around four categories of electrolyte materials, viz. Ytria-stabilised zirconia (YSZ), Gadolinium/Samarium doped ceria

(GDC/SDC), doped bismuth and doped lanthanum gallate [Arabacı et al., 2012; Sammes et al., 1999; Fergus et al., 2006]. In order to improve the ionic conductivity of these systems, single or multiple dopants in each of these four systems of materials have been further sub categorized.

The ionic conductivity of electrolytes, such as, doped ceria originate through ion movement in lattice under the effect of an electric field. The electrical conductivity σ can be expressed as:

$$\sigma = ne\mu \quad \text{Eq. 1.1}$$

Where, σ , n , e , μ represent the ionic conductivity, concentration of charge carrier in a given volume of lattice, electronic charge and mobility of charge carrier respectively. In case of pure oxygen ion conductor, ion conduction takes place via oxygen ion vacancies.

Therefore, the ionic conductivity of such conductors can be also expressed as:

$$\sigma = (1 - [V_O^{\bullet\bullet}]) N_o q_i \mu_i \quad \text{Eq. 1.2}$$

The N_o is number of oxygen vacancies, $V_O^{\bullet\bullet}$ represents the fraction of oxygen vacancies and μ_i is the oxygen-ions mobility having charge denoted as q_i . [Jaiswal et al., 2019]

1.9.1 Yttria Stabilized Zirconia (YSZ)

Stabilized zirconia is most extensively investigated and most commonly used SOFCs electrolyte materials working at high temperature. In order to stabilize cubic fluorite structure of zirconia, several divalent and trivalent oxide dopants are incorporated in to cation sublattice such as CaO, Y₂O₃, MgO, Sm₂O₃, Yb₂O₃. Among these compositions, 8 mol% yttria stabilized zirconia (8YSZ) provides the best properties for electrolyte material, having required characteristics for SOFCs application, such as improved ionic conductivity, durability, chemical and thermal stability in reducing and oxidizing

environments [Strickler et al., 1964; Dixon et al., 1963; Yeh et al., 2005; Yamamoto et al., 1995]. Figure 1.6 demonstrates the maximum ionic conductivity in systems of $\text{ZrO}_2\text{-Ln}_2\text{O}_3$, and the oxygen ion migration and association enthalpy with variation of ionic radius of Ln^{3+} dopant. Despite several advantages, due to high fabrication cost associated through high working temperature, and material degradation, great efforts are being done to reduce the operating temperature of these electrolytes. However, a major concern in this task is the point that with the lowering of operating temperature, the ionic conduction of the solid electrolyte also decreases significantly. Moreover, another disadvantage of YSZ electrolyte is the chance of chemical reactivity with the cathode material that can be detrimental to the performance of fuel cell. As stated in earlier section, cathode materials containing La and Sr react with YSZ at high working temperature forming insulating phases like SrZrO_3 and $\text{La}_2\text{Zr}_2\text{O}_7$ along the cathode-electrolyte interface and blocking the ions transportation. [Jacobson et al., 2010].

In further investigation of alternative electrolyte materials, Scandium doped ceria (ScSZ) exhibits extensively higher ionic conductivity as compared to YSZ. Further, 1 mol% substitution of Bi_2O_3 in Scandia-stabilized zirconia (ScSZ) exhibits an improved ionic conductivity 0.33 S/cm at temperature 1000 °C. At room temperature, the undoped system has a rhombohedral crystal structure, which occur lower ion conductivity as compare to cubic phase structure. A cubic phase transformation occurs at higher temperatures. The 2 mol% addition of Bi_2O_3 in 10ScSZ leads to lower temperature range stability of cubic phase and exhibits highest conductivity value (0.18 S/cm) at temperature 600 °C [Sarat et al., 2006]. However, the high cost of the scandium limits it for practical use in SOFC application as an electrolyte on a huge scale [Hirano et al., 1999].

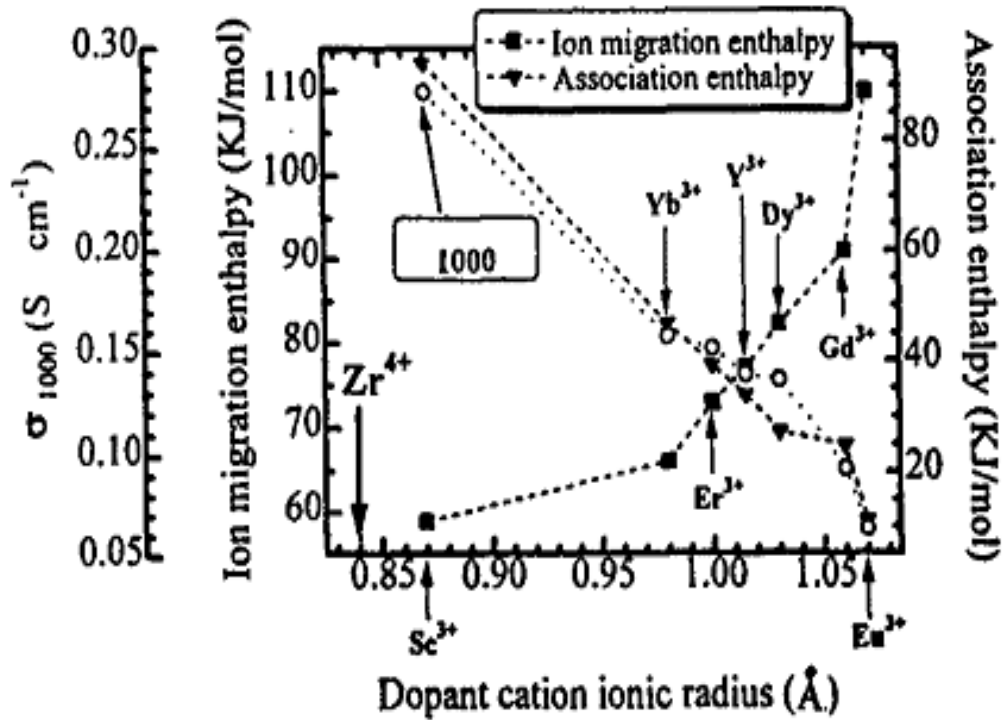


Figure 1.6 Maximum ion conductivity in the mixture of binary systems $ZrO_2-Ln_2O_3$ at 1273 K and the association enthalpies and ion migration enthalpy with ionic radius of Ln^{3+} dopant cations [Yamamoto et al., 1998].

1.9.2 Doped Lanthanum Gallate

Lanthanum gallate $LaGaO_3$ based oxides with cubic perovskite structure have been widely investigated as oxygen conductor electrolyte for IT-SOFCs applications. In crystal lattice, La^{3+} cations are situated in twelve coordination site of O^{2-} anions and Ga^{3+} cations occupy six-coordinated octahedral sites with corner-sharing arrangement of GaO_6 octahedra. The GaO_6 octahedral tilting causes a deviation from ideal cubic unit cell [Malavasi et al., 2010]. In order to obtain higher ionic conductivity, La can be partly substituted by Ca, Sr, Ba, Nd and Sm, whereas Ga may also be partly substituted by Mg, Al, In or Zn, thereby increasing the concentration of oxygen vacancies, as in $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM). In this regard, Sr and Mg substituted lanthanum gallate

with general formula $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM) showed higher value of ionic conductivities than that of YSZ in the temperature range, 770-1100K. The TEC are also similar to the other common components of cell. The composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ was found to exhibit higher value of ionic conductivity ($\sigma_{\text{ion}} = 0.17 \text{ S}\cdot\text{cm}^{-1}$ at 800 °C) [Ishihara et al., 1994; Feng et al., 1994]. However, these electrolytes still have some demerits such as being unstable under reducing atmospheres, new phases are formed due to volatility of Ga at high temperatures, and high chemical reactivity with Ni is observed which leads to formation of LaNiO_3 phase which is ionic insulator. The temperature dependence of ionic conductivity of various LaGaO_3 -based solid electrolytes, in air, is illustrated in Figure 1.7.

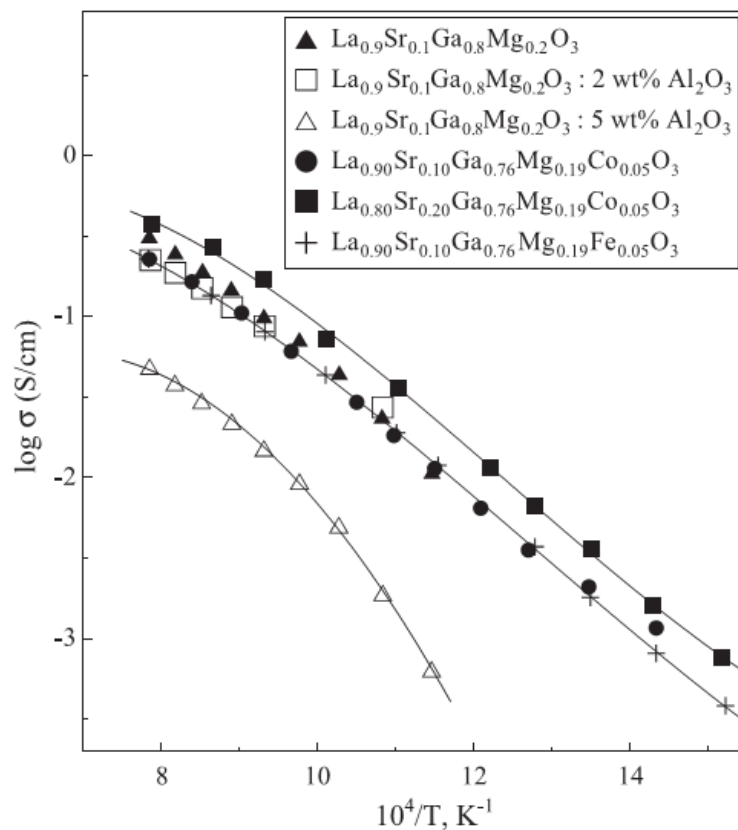


Figure 1.7 Variation of conductivity of LaGaO_3 -based solid electrolytes with temperature in air [Kharton et al., 2004].

1.9.3 Bi₂O₃-based Electrolytes

Among various oxide ion conducting electrolyte materials, the series of oxides derived from Bi₂O₃ are particularly attention-grabbing because of their high oxide ion conductivity as compared many solid oxide electrolytes. Bi₂O₃ exhibits a noteworthy polymorphism having α and δ as two stable phases [Takahashi et al., 1972]. The δ -phase having fluorite crystal structure shows high ionic conductivity in high temperature region. The phase stability of δ -phase appears above 730°C [Malavasi et al., 2010]. The ion migration path and local structure within δ -Bi₂O₃ were revealed using total scattering technique of neutron diffraction [Hull et al., 2009; Mohn et al., 2009]. It was debated that the Bi³⁺ ion having nearby asymmetric electron density is essential for promoting wide spread disorder of anions inside δ -Bi₂O₃, with diffusion of ion assisted both by the substantial relaxation and flexible cation sublattice of the neighboring anions. At temperatures below 973-1073 K, the phase stability of the δ -Bi₂O₃ phase can be attained by doping of rare-earth cations like Y, Er or Dy in bismuth and their groupings with upper oxidation state cations, for example V, Nb or W [Kharton et al., 2009]. The total oxide ion conductivity of various Bi₂O₃-based solid oxide electrolytes is illustrated in Figure 1.8. The maximum ionic conductivity has been obtained in Y(Bi_{1-x}Y_xO_{1.5}, x=0.23-0.25) and Er (Bi_{1-x}Er_xO_{1.5}, x=0.20) doped compounds. The Phase stability of these systems appear only in the temperature region 1043-1143°C. These systems suffer a phase transition afar this limit which causes a reduction in the ion conductivity. The 20 mol% addition of Er₂O₃ in Bismuth oxide (ESB) also exhibits the maximum conductivity among all reported electrolytes of stabilized Bi₂O₃. However, ESB, cannot be employed as oxide ion conductor solid electrolyte for IT-SOFCs because of its low phase stability in reducing environment (<10-13atm) [Wang et al., 2012; Fruth et al.,2006; Shuk et al.,1996]. Current research efforts have tried to simplify

this condition, looking for optimal dopant concentrations and proper selection of dopants that give both maximum ion conductivity and longtime stability.

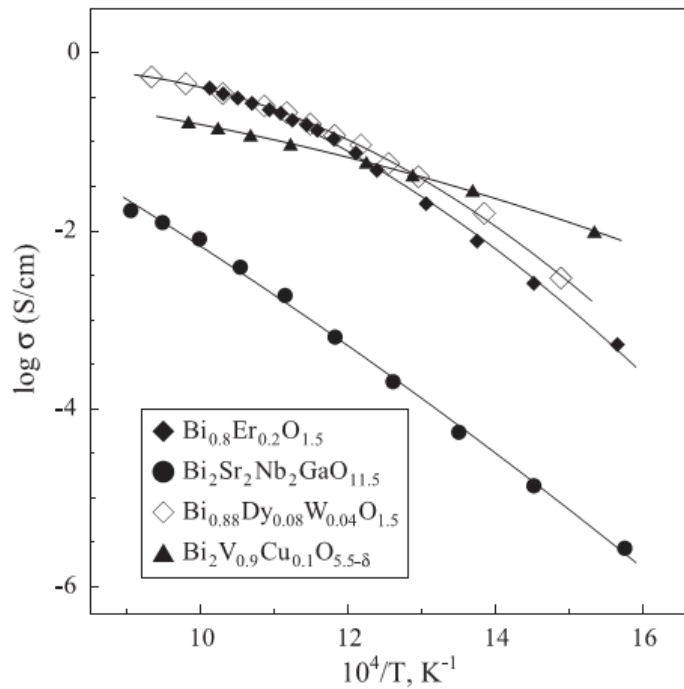


Figure 1.8 Total oxide ion conductivity of various Bi_2O_3 -based solid oxide electrolytes [Kharton et al., 2009].

1.9.4 Doped/Co-doped Ceria based Electrolytes

Analogous to ZrO_2 , CeO_2 exhibits cubic fluorite crystal structure which possesses easy oxygen-ion transport inside lattice due to relatively large interionic open space inside lattice as shown in Figure 1.9. It is a widely spread material employed as common electrolyte in SOFCs applications [Inaba et al., 1996]. Although pure ceria itself is not a good ionic conductor as it does not possess any defects like oxygen vacancy and dopants. The partial substitution of acceptor cations into ceria lattice introduces oxygen vacancy defects which influences the ionic conductivity at relatively low operating temperatures. These defects mainly oxygen vacancies are responsible to influence electrical and many other properties of solid oxides [Steele et al., 2000; Mogensen et al., 2000]. In order to generate oxygen vacancies, generally, trivalent rare

earth and divalent alkaline earth metals are incorporated as dopants in to ceria lattice. The formation of oxygen vacancy can be written via the resultant defect mechanism using Kröger-Vink notation.

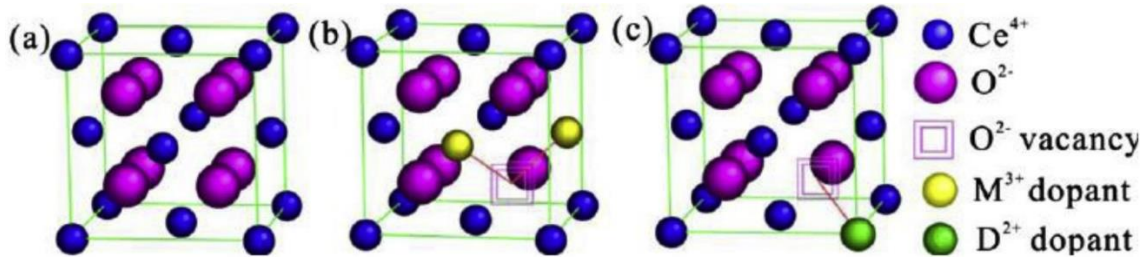
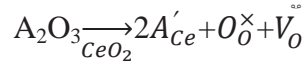


Figure 1.9 (a) illustration of fluorite crystal structure of Ceria (b) position of M^{3+} dopant ions and resulting oxygen ion vacancy (c) location of D^{2+} doped positive ions and resulting oxygen vacancy [Li et al., 2013].

Among several rare earth dopants, Gadolinium (Gd) and Samarium (Sm) doped ceria were observed as best ionic conductors for IT-SOFCs. The value of ionic conductivity of $Ce_{0.90}Gd_{0.10}O_{1.95}$ (CGO10) was found to be 0.01 S/cm at 500 °C [Suda et al., 2006; Sha et al., 2007; Shimonosono et al., 2005]. The oxygen-ion conduction of doped ceria is significantly influenced by the type of dopant. Generally, it is considered that the oxide-ion conductivity of doped ceria can be associated with ionic radii mismatch between the dopants and host cations and concentration of dopants. Based on this fact, various regression analyses were performed to develop an empirical model to interpret these correlations. One interpretation proposed by Kim is based on critical ionic radius (r_c) of dopants which leads to negligible lattice distortion in host ceria lattice on doping [Kim et al., 1989]. However, this model could not describe the oxide-ion conductivity of Sm_2O_3 and Gd_2O_3 doped CeO_2 that give higher ionic conduction as compared to Y_2O_3 doped ceria while the ionic radius of Y^{3+} (1.019 Å) is nearer to r_c (1.038 Å) than that of Sm^{3+} (1.079 Å) and Gd^{3+} (1.053 Å). Arai et.al have investigated

the influence of addition of divalent alkaline earth cations in CeO₂ for example SrO, MgO, CaO, and BaO. The substitution of SrO and CaO increase the ionic conductivity of ceria very much than that of BaO and MgO because of large size mismatch of Ba²⁺ (1.42 Å), Mg²⁺ (0.89 Å) and the Ce⁴⁺ (0.97 Å) [Arai et al., 1988]. Further, Kilner and Brook predicted that in doped ceria, ionic conductivity is determined by the value of $(|r_d - r_c|)$, where r_d defines the ionic radius of dopant cations. The lesser value of the $|r_d - r_c|$ for a system containing specific dopant cation predicts the higher value of the oxygen ion conductivity [Kilner et al., 1982]. Omar et al. have investigated a co-doping approach in ceria in order to observe the validity of minimum strain's assumption. Using this methodology, Lu³⁺ and Nd³⁺ were substituted in ceria lattice such as the weighted average of ionic radius of Lu³⁺ and Nd³⁺ equals the value of r_c [Omar et al., 2009]. On estimating the lattice parameter, the elastic lattice strain was found to be almost negligible in these systems (see Figure 1.10). However, the ionic conductivity of Gd³⁺ doped ceria was observed to be higher than that of La³⁺ and Nd³⁺ co-doped ceria. Thus, although the co-doping in ceria lattice shows minimal elastic strain but its value of oxide-ion conductivity remains lower as compared to Gd³⁺-doped ceria.

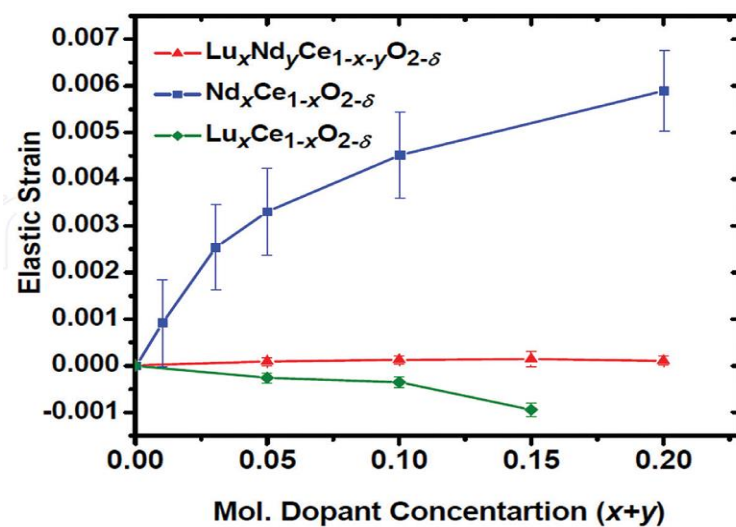


Figure 1.10 Plot of Elastic strain for Nd_xCe_{1-x}O_{2-δ} against the Mol. dopant concentration [Omar et al., 2009; Stephens et al., 2009].

Further, the activation energy plot in trivalent rare earth cation doped ceria suggests that the Sm^{3+} doped system possesses least activation energy value for charge conduction, which has a much higher ionic radius value than the r_c value. Therefore, after doing such experimental analysis via co-doping approach, it was concluded that co-doping results as well as acquired activation energy data for charge conduction do not favor the assumptions proposed by Kilner and Brook that the system having negligible elastic lattice strain possess highest oxygen-ion conductivity. Although, it is important to discuss that all the reported r_c values are derived from the empirical formula in the literature which are expressed as a function of lattice expansion data estimated at RT [Kilner et al.,1982]. Generally the oxide-ion conductivity of doped ceria system is measured in the temperature range 400°C to 700°C , there is a probability that the as temperature increases, r_c value also increases. This hypothesis is tested by Omar et al. through evaluating the lattice distortion at higher temperatures for different cations with 10 mol. % dopant concentration in ceria systems [Omar et al., 2009]. The value of r_c was then calculated, where the mismatch of lattice parameter between pure ceria and doped ceria occurs to zero (see Figure 1. 11).

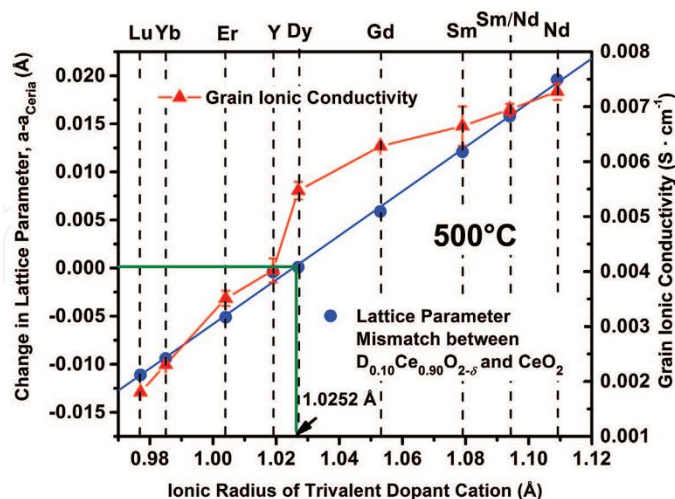


Figure 1.11 Plot of lattice parameter mismatch between CeO_2 and $\text{A}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$ versus the ionic radius of positive ions (A^{3+}) dopant at temperature 500°C . The oxide ion conductivity along bulk (grain) of $\text{A}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$ at temperature 500°C is also presented [Omar et al., 2009].

It was observed that with the rise in temperature, the value of r_c reduces and the expected trend of conductivity is not followed. The acquired outcome evidently points out that the ionic conductivity is not completely reliant on strain, and consequently, a critical ionic radius based concept of structure-conductivity relationship is not sufficient to explain the oxygen-ion conduction behavior in doped CeO_2 .

From the earlier investigations, it has been reported that the oxygen vacancies created via adding aliovalent cation dopants are not movable. Moreover, they are related with the charged ions to form dopants vacancy associates or clusters [Huang et al., 1998]. In ceria lattice, there are numerous relative sites between dopants charged ions and oxygen vacancies. It has been observed by Li et al. that variety of dopant vacancy associates and clusters of dopant cations containing oxygen vacancies are situated at either the first or second neighbor site of associated dopants [Li et al., 2013]. In trivalent rare-earth dopants, the small size cations prefer to occupy the first nearest neighboring (NN) site to related vacancy associated to oxygen having a lattice vector of $(1/2 \ 1/2 \ 1/2)$ and larger size cations occupy second next nearest neighboring (NNN) site having the lattice vector of $(1/2 \ 1/2 \ 1)$. In situation of the divalent charged ion dopants, the NN is suitable site which do not significantly depend on the dopant ionic radius and dopant vacancy. The divalent charge clusters possess relatively higher binding energy as compared to the trivalent, as a result, they generate strong defect associations between oxygen vacancies and dopant cations. The doping of trivalent positive ions in ceria shows higher oxide ion conductivity than divalent positive ions ceria [Jaiswal et al., 2019]. However, oxygen ion conductivity of doped/co-doped ceria materials depend not only type of dopant but also concentration. The oxide ion conductivity increases with increasing doping level and attains a maximum conductivity at a certain doping level but after that it decreases even if it is far below the dopant solubility limit. One

most likely reason is the defects clustering. When point defects of charge (A_{Ce}') are merged within the crystal lattice, to conserve neutrality of charges, point defects having reverse charges must be formed. The presence of electrostatic attraction among oppositely charged defects, cause strong interaction with each other. Further, the elastically originated interactions also reduce the local stresses neighboring these charge defects. Such as, an open space of vacancy may be attracted by an oversized substitutional impurity cation. This phenomena cause to the creation of local defect clusters for example $(A_{Ce}'-V_o^{**})^{\bullet}$ and $(A_{Ce}'-V_o^{**}-A_{Ce}')$. The oxygen vacancies are trapped by these clusters and efficiently decrease the quantity of mobile charged oxide-ions. In most of the reported research work, it is believed that the formation of defect cluster is the main cause for the significant reduction in oxygen ion conductivity of doped/co-doped ceria at higher concentration of doping. In addition, one more reason reported to be the presence of space charge layer and silicon impurities along the grain boundaries which originate resistance [Omar et al., 2019].

In the past few decades, both theoretically and experimentally, various co-doped ceria based materials have been extensively observed as solid electrolytes for SOFCs applications such as $Ce_{1-x}Ho_{0.1}Sr_xO_{2-\delta}$ [Anirban et al., 2018], $Gd_{0.2-x}Dy_xCe_{0.8}O_{1.9}$ [Khakpour et al., 2014], $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5}$ [Wang et al., 2004], $Sm_xNd_{0.15-x}Ce_{0.85}O_{2-\delta}$ [Rai et al., 2014], $Ce_{1-x}(Y_{0.5}Dy_{0.5})_xO_{2-\delta}$ [Tadokoro et al., 2007], $Ce_{0.8}Sm_{0.2-x}Pr_xO_{2-\delta}$ [Lin et al., 2015], $Ce_{1-x}(Gd_{0.5}Pr_{0.5})_xO_{2-\delta}$ [Ramesh et al., 2012], etc. Nonetheless, expensive elements in precursor such as Sm and Gd are still the reason which inhibits to develop these materials as foremost electrolytes in market for SOFC applications. It has been reported that incorporation of numerous transition metal ions (Cu, Fe, Mn, Ni, Cr, Co) as sintering aid in minor amount ($< 1-2$ mol%) in ceria, reduces the temperature of sintering and blocking effect along grain boundary [Arun kumar et al., 2014; Zajac et

al., 2009; Zhang et al., 2006; Kang et al., 2009; Myung et al., 2015]. In view of above requirements, a number of research works have concentrated on the progress of new co-doped ceria as promising solid electrolyte for ITSOFCs as well as LTSOFCs applications. Nicollet et al. have observed a significant reduction in sintering temperature of GDC electrolyte via addition of sintering aids such as Zn, Li and Cu (3 wt. %) [Nicollet et al., 2017]. Ji et al. has achieved value of oxide ion conductivity 0.029 S cm^{-1} at temperature 800°C via co-doping of Cu-Y in ceria [Ji et al., 2015]. Gil et al. have revealed that the addition of Bi_2O_3 in GDC electrolyte can improve the sinterability of solid electrolyte material [Gil et al., 2007].

1.9.5 Carbonate/Oxide Electrolytes

An emerging research & development growth in the LT-SOFC field has been resulted by recent activities on the composite electrolytes, especially the doped ceria–alkali carbonate composites. One of the most important benefits of the doped ceria–carbonate composites is to resolve the reduction problem of ceria as reported in many earlier research [Zhu et al., 2003; Jain et al., 2010; Raza et al., 2010]. In addition, the core-shell structure of composite electrolytes addresses the localized electrons within ceria lattice, which are unable to travel from one particle of ceria to the other, since the amorphous carbonate shell does not permit electrons to move or conduct [Fan et al., 2014]. To certain point, the system of doped ceria-alkali carbonate composite can be assumed as a new combined cell technology of fusion between the MCFC (molten carbon fuel cell) and SOFC which uses equally the essential features of carbonates having a vital relation to MCFC. Still, the alkali carbonate anions do not support the major functions in doped ceria-carbonate that leads to composite's composition adjustment, for example, when two phases of the similar particle sizes are used, the

60:40 weight ratio works as a critical point of the system. If the content of ceria is on or above this point, the composite system follows the SOFC model; for lower content of Ceria, it follows the MCFC model. Even though the device does not work in MCFC gases due to lack of external carbonate ion supply the device has to work in the SOFC mode. Furthermore, if the temperature during operation does not achieve the melting point of carbonate, then MCFC mode does not occur. Depending on the applications requirement, it favors the SOFC mode as an easier operation, that can sustain the solid phase having very less side-effect of melting carbonates. The nanocomposite method is used to synthesize 20 wt% or less alkali carbonates forming a nano meter shell layer of carbonates bounded by solid structure of ceria core which is not easily molten, to create a new kind of core-shell structure composite particles. Thus, the joint SOFC and MCFC mode for electrolyte can be a better approach to give a noteworthy improvement of device working performance [Xia et al., 2009].

Earlier studies on ceria-alkali carbonate composites focused on different rare earth doped or co-doped ceria, containing $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC), $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{1.9}$ (SNDC), $\text{Ce}_{0.8}\text{Gd}_{0.05}\text{Y}_{0.15}\text{O}_{1.9}$ (GYDC), $\text{Ce}_{0.8}\text{Sm}_{0.2-x}\text{Ca}_x\text{O}_{2-\delta}$ (CSDC) etc., while the carbonates as second phase are single Na_2CO_3 salt, eutectic binary $\text{Li}/\text{Na}_2\text{CO}_3$, $\text{Li}/\text{K}_2\text{CO}_3$, $\text{Na}/\text{K}_2\text{CO}_3$, or ternary $\text{Li}/\text{Na}/\text{K}_2\text{CO}_3$ mixtures. The rare earth co-doped ceria have been prepared by numerous chemical routes, e.g. carbonate co-precipitation, oxalate co-precipitation, glycine nitrate combustion method, sol-gel method, etc. Furthermore, the composite of doped/co-doped ceria and alkali carbonates was sintered for measuring ionic conductivity and working performance measurement of the cell. Table 1.4 reviews the ionic conductivity as well as related performances of fuel cells of different composite electrolyte materials reported by various research groups. From the values in Table 1.4, it can be seen that ceria carbonate composite

electrolytes show fairly good ionic conductivity as compared to single phase ceramic oxide solid electrolyte in intermediate to low temperature region SOFCs [Wang et al., 2012].

Table 1.4 Conductivity with different composition of ceria-carbonate composite electrolyte from literature [Wang et al., 2012].

| Doped Ceria | T (°C) | Salt | Conductivity (S cm ⁻¹) |
|---|---------|--|------------------------------------|
| Ce _{0.8} Sm _{0.2} O _{1.9} | 240-650 | No salt | 10 ⁻⁶ -0.03 |
| Ce _{0.8} Sm _{0.2} O _{1.9} | 500-650 | 30 wt.% of Li/Na/K ₂ CO ₃ (43.5/31.5/25, mol%) | 0.05-0.07 |
| Ce _{0.8} Sm _{0.2} O _{1.9} | 500-650 | 30 wt.% of Li/Na ₂ CO ₃ (50/50, mol%) | 0.1-0.16 |
| Ce _{0.8} Sm _{0.2} O _{1.9} | 500-600 | 20 wt.% of Li/Na ₂ CO ₃ 50/50, mol%), | 0.071-0.093 |
| Ce _{0.8} Sm _{0.2-x} Ca _x O _{2-δ} | 350-560 | Na ₂ CO ₃ | 0.1-0.3 |
| Ce _{0.8} Sm _{0.2} O _{1.9} | 450-600 | 20 wt.% of Li/Na ₂ CO ₃ (52/48, mol%) | 7×10 ⁻³ -0.5 |
| Ce _{0.8} Sm _{0.2} O _{1.9} | 450-600 | 20 wt.% of Li/Na ₂ CO ₃ (53/47, mol%) | 3.7×10 ⁻³ -0.029 |
| Ce _{0.8} Gd _{0.2} O _{1.9} | 450-550 | 25 wt.% of Li/Na ₂ CO ₃ (53/47, mol%) | 5×10 ⁻⁴ -0.175 |
| Ce _{0.8} Gd _{0.05} Y _{0.15} O _{1.9} | 400-650 | 40 wt.% of Li/Na ₂ CO ₃ (52/48, mol%) | 3×10 ⁻⁴ -0.4 |

In doped Ceria-alkali carbonate composite electrolytes, the effect of the adding amorphous phase of alkali carbonates on the crystalline phase of ceria, its particle morphology, phase structure and electrical properties are constantly an area of great research concern. For example, Huang et al. examined the effect of different composition of carbonate mixtures on the ion conduction behavior of the composite electrolyte materials. The cell having composite electrolyte of the composition SDC/(Li-Na)₂CO₃ exhibited the best cell performances (600 mWcm² at 600°C) [Huang et al., 2010]. Xia et al. designed SDC via three different preparation techniques with

different morphologies. They observed that the thickness of SDC electrolyte and surface properties possess a great impact on the performance of fuel cell [Xia et al., 2010]. The rod-like morphology of SDC based composite electrolyte displayed the best performance of cell; meanwhile it favors the development of successive layer along the interface of double phase designed for the fast ionic transport mechanism. Ferreira et al. observed the effect of synthesis and processing methods on the morphology and cell working performance with composite electrolytes, proposing that creation and precise location of minor secondary phases of carbonate in ceria particle might perform a vital part on working performance of cell [Ferreira et al., 2011]. The particle size of doped ceria is one more significant factor that influences the outcomes of ceria-carbonate composite electrolytes. Thus, a number of researchers have investigated the size effect of composite particles. For instance, Tang et al. perceived that carbonate composites having nano-scale range particles size showed higher conductivities at relatively low working temperatures on the other hand extra effects of complex boundaries were observed to particles having size in micrometer range [Tang et al., 2010]. In a latest research work, a noteworthy conductivity improvement of the SDC/Na₂CO₃ nanocomposite was also observed than that of the SDC/Na₂CO₃ composite with size of micro-level, that can be attributed to the larger surface area and added homogeneously distributed interfaces between the host phase SDC and NaCO₃ phases [Gao et al., 2011]. As a result, nanostructured ceria-alkali carbonate composite electrolytes are currently becoming a main focus in the fuel cell research field. The interfacial conduction is leading in whole charge transport mechanism for nanocomposites electrolytes, which may determine a vast conductivity enhancement. For instance, the fabrication of core-shell nanostructured SDC/Na₂CO₃ composite was firstly reported by Wang et al., which exhibited high oxygen ion conduction value 0.1 S cm⁻¹ above 300°C temperature and

attained better performance of fuel cell 0.8 W cm^2 at 550°C [Wang et al., 2008]. The novel fabrication of 1D SDC nanowires based nanocomposites and its application were demonstrated for the first time as electrolyte for SOFC by Ma et al [Ma et al., 2010]. The optimum values of power densities of 417 mW cm^2 at temperature 550°C , and 522 mW cm^2 at temperature 600°C , have been obtained, indicating a promising candidate for low-temperature SOFCs applications. Therefore doped ceria-alkali carbonate nanocomposite fabrication method has grown into an effective technique to develop LT-SOFCs solid electrolytes. In particular latest work, material scientists tried several other techniques to make uniform 3D structured ceria-alkali carbonate nanocomposites electrolytes [Cai et al., 2011; Zhang et al., 2011]. For example, Zhang et al. designed SDC-alkali carbonate nanocomposite via the pre fabrication of porous matrix of SDC through a “template” method followed by impregnation of alkali carbonate in molten phase. The microstructure of porous SDC matrix shows homogeneous micro-pores with uniform distribution as evidenced by both 3D X-ray tomography and 2D SEM imaging [Zhang et al., 2011]. Similar molten carbonate infiltration route has been adopted to synthesize SDC-alkali carbonates nanocomposite by Cai et al. They observed that the performance of cell containing composite electrolytes is much enhanced by employing this sample fabrication technique [Cai et al., 2011]. To further investigate the charge conduction mechanism along interfaces, few unconventional methods, such as electron microscopy, are frequently used to illustrate the interface of ceria-carbonate composite electrolytes. For example, Marques et al. have used SEM to characterize the ceria-carbonate composite materials and reported uniform distribution of each phases, having the ceria ceramic phase as skeleton based percolating network on grain size of nano scale level enclosed by the secondary phase of molten carbonate salts, having large interfacial area among constituent particles [Marques et al., 2010]. Xia et al. also

characterized interface using SEM imaging and reported that the ceria- carbonate composites sintered at temperature 675 °C always exhibit the optimum microstructure of interfaces and the Li/Na₂CO₃ distribution in SDC electrolyte is at the best, as presented in Figure 1.12a. They established that the moderately good connection among doped ceria and alkali carbonates would offer extra likely “superionic highway” for charge conduction of ions [Xia et al., 2011]. Tang et al. used wet-mixture method to achieve semi-micrometer level size homogeneous composite. The large image contrast difference between the outer and the inner surface specifies a core-shell structure of nanocomposite, as examined by Wang et al. using TEM technique. The core-shell microstructure via TEM image is further displayed in Figure 1.12b. The dominant fringes of ceria lattice are seen evidently in the core and the lattice fringe due to Na₂CO₃ shell layer cannot be observed which confirms the amorphous nature of carbonate. Simultaneously the interfacial region between core-ceria and shell-carbonate is also observed evidently [Wang et al., 2008].

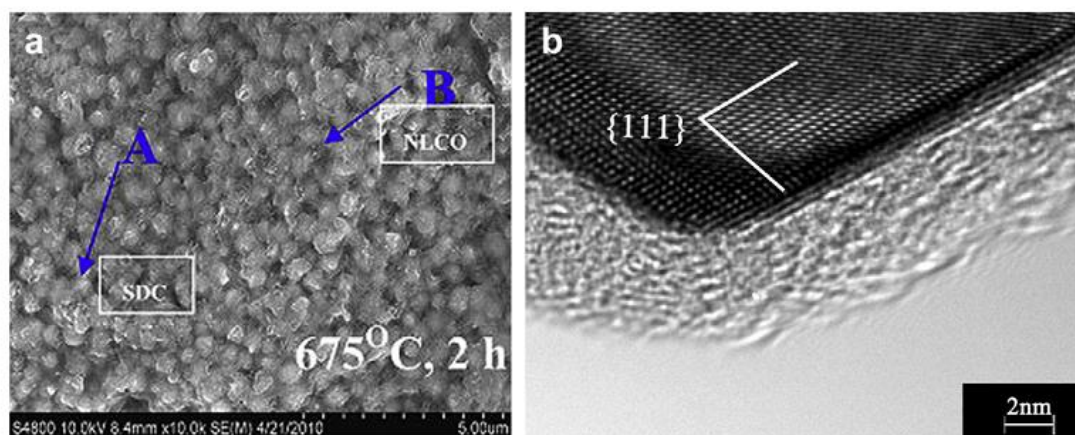


Figure 1.12 The FE-SEM image of SDC and Li/Na₂CO₃ composite sintered sample at temperature 650°C for 2 h [Xia et al., 2011] (b) The image of HRTEM of SDC/Na₂CO₃ nanocomposite informed by Wang [Wang et al., 2008].

1.10 Charge conduction Mechanisms in Ceria-Carbonate Solid Electrolytes

There is still not well understood description of the mechanism of charge conduction in ceria-carbonate composite materials. Numerous hypotheses have been proposed in recent years and this section will concisely review the same. Bin Zhu proposed the oxide ions conduction in the oxide phase in addition to proton conduction in the carbonate salt phase in his first work on carbonate-ceria materials as illustrated in Figure 1.13 [Zhu et al., 2006].

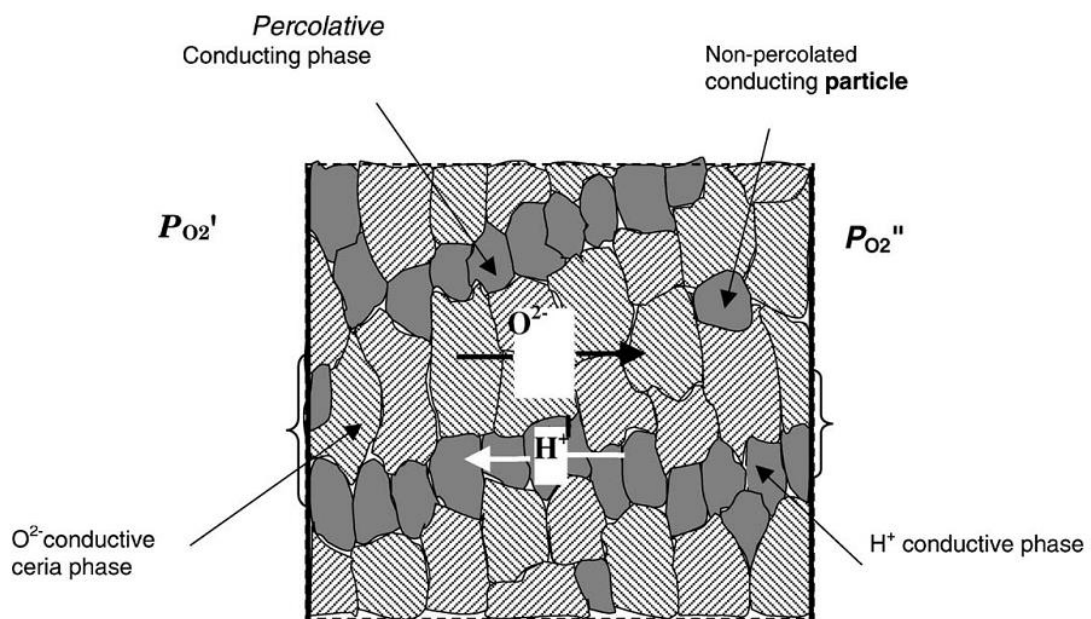


Figure 1.13 Two percolative interpenetrated phases with an oxide as oxide ion conductor and a carbonate salt as proton conductor according to Zhu [Zhu et al., 2006]

Zhu et al, highlighted that in depth study of oxygen ion and proton conduction mechanism along with the strong enhancement in conductivity were not clear even. The utmost common description for the appealed interfacial superionic conductivity persists to the Maier's "space charge" layer theory [Maier et al., 1995]. The space charge region formed along the phase boundaries as a result of the interfacial interaction between carbonate-oxide phases is usually believed to be responsible for the superior

electrochemical properties, for instance, cations of the carbonate in addition to oxygen ions could accumulate along the interface. The enrichment the defects/ions along the interfaces than that of the bulk phase of ceramic essentially provide ‘superionic conduction highways’ at the interfaces between the two constituents. Zhu et al. proposed that various types of negatively charged oxygen species (O_2^- , O^- , and O^{2-}) covering the oxide surface can also occur and distinct consideration should be paid to the interfacial interactions among the oxygen ions and the alkali cations M^+ (Li^+ , Na^+ , or K^+) of the molten carbonate phase that create an induced electrical field along the interfaces between the two phases (see Figure 1.14). They considered that the formation of this electric field distribution plays vital role to recognize interfacial ionic conduction, particularly oxide ions charge conduction, permitting ions to transport along the interfaces as high conductivity highways [Zhu et al. 2006; Zhu et al., 2008]. Also Schober, using the space charge layer theory, considered that the space charge layer nearby to the interfacial region containing higher concentration of defects than that of the bulk phases of ceramic is the main source of the superior ionic conductivity [Schober et al., 2005]. Huang et al. suggested more systematic explanation of enhanced conduction mechanism using defect chemistry. For the alkali carbonate phase (M_2CO_3 , $M=Li, Na, \text{ or } K$), there could be a surface reaction, owing to the interfacial surface interaction, resulting enrichment in vacancies of cation in the bulk phase of carbonate. Thus a space charge layer is created increasing cation disorder which offers rise to improved conductivity in ceria-carbonate composites below the melting point temperatures of the carbonate phase in air atmosphere [Huang et al., 2010].

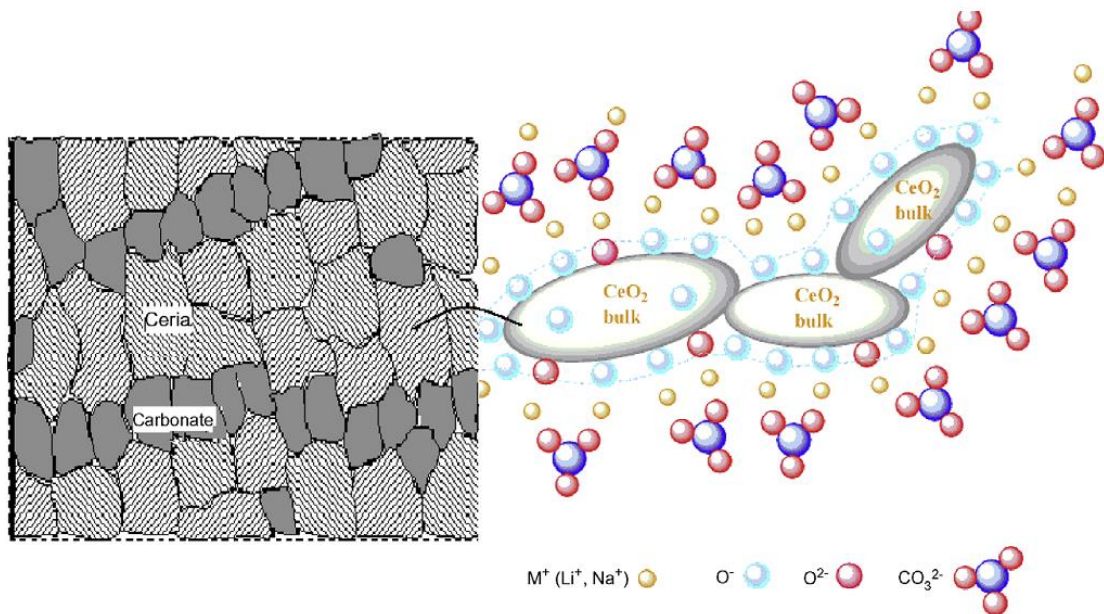


Figure 1.14 Interfacial charge conduction pathway based on space charge layer theory giving by Zhu et al. [Zhu et al., 2008]

1.11 Motivation and Objective of the Thesis

The major objective of the present thesis is the development of electrolyte and electrode materials of SOFCs having lower TECs and favorable compatibility with SOFC components with reduced operating temperature, using cost effective and easy fabrication processing. With this aim, to synthesize and characterize novel materials, I mainly focused on materials with the fluorite and perovskite structure for Solid oxide fuel cells applications. The novel ceria based electrolytes by co-doping of cheaper elements were developed and the effects of co-doping on structural, morphological and conductivity properties of materials were investigated. The development of doped ceria-carbonate composite ionic conductors as solid electrolyte for LT-SOFCs and effect of formation of space charge layer on ionic conductivity and charge transport behavior of materials were also evaluated. A small part of the thesis is also dedicated to studying the

chemical and electrical performance of A-and B-site co-doped perovskite structured cobalt free cathode for IT-SOFCs. The key objectives of this thesis are following:

- Investigation of Ga³⁺ and Cu²⁺ co-doped ceria in the series Ce_{0.8}Ga_{0.2-x}Cu_xO_{2-δ} (for x=0.00, 0.05, 0.10, 0.15, and 0.20) on the structural, morphological and electrical properties for IT-SOFCs applications.
- Study of effect of binary alkali carbonate (mixture of Na₂CO₃ and Li₂CO₃) addition on the structural, electrical and charge transport properties of tri-doped ceria based composites to explore potential electrolyte materials for low temperature applications.
- Investigation of Mo⁶⁺ and W⁶⁺ co-doping effects in SrFeO_{3-δ} as cathode material in order to study synergistic effects of higher valence transition metals in relation to thermal and electrochemical properties for SOFCs.