

CERIA BASED ELECTROLYTE MATERIALS FOR ADVANCED SOLID OXIDE FUEL CELL (SOFC) APPLICATIONS

Abstract

For the last few decades, alternative and sustainable energy sources have been approached which deplete the environmental-issues and provides the clean energy conversion towards world energy demands. Fuel cells which convert chemical (Fuel) energy directly into electrical energy (electricity) via electro-chemical reaction mechanism are more advantageous when compared with the other conventional energy conversion technologies. Among the various available fuel cells, Solid oxide fuel cell (SOFC) has proven as most promising, efficient, eco-friendly energy conversion device due to its longer life time, variety choice of fuels and less environmental impact. The fundamentals of fuel cell technologies, background, working mechanism, different components of SOFC, brief note on traditional materials, and development of novel materials for the advanced SOFC were addressed. Working/operating temperature plays a key role in the development of SOFC because high operating temperature curbs the commercialization. Enormous efforts have been done in reducing the operating temperature by introducing various doped /co-doped /triple-doped ceria based materials with enhanced electrical properties which led to the development of intermediate temperature SOFCs. On the way of reducing the operating temperature, R&D introduced a composite approach using doped ceria and alkali carbonates which pave a way for the development of low operating temperature SOFC. The recent developments regarding ceria-carbonate composites with emphasis on the ionic conductivity have been discussed towards the electrolytes for advanced SOFC applications at relatively lower temperatures.

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I. INTRODUCTION

The energy-requirement in the world has been increased rapidly with the fast-growing population of the world. According to international energy outlook-2009, it is expected to increase fifty percent by 2030. The fossil fuels are the main source for the energy-requirement and maximum of required energy is produced from the combustion of coal, petroleum and natural gases. Regrettably, these combustions lead to the emission of unwanted hazardous gasses causing global-warming due to the pollution of environment [1–5]. In this case of interest, the world demands the alternative and sustainable energy sources which deplete the environmental-issues and provides the clean-energy. The fuel energy, solar energy and wind energy sources etc. have been addressed as alternative(s) to those conventional sources. Among the alternative energy sources, the reliable energy source is fuel energy i.e. Hydrogen energy. An Electro-chemical energy-conversion device is required to avail the alternative energy using a source of hydrogen as fuel energy, known as fuel cell [3–8].

The scientist named H Davy demonstrated the concept of the fuel cell in 1801. He observed the electricity when small amount of water added to the some alkali compounds [9]. The physicist as well as chemist named W R Grove invented the fuel cell in 1839 and demonstrated practically by naming it as gas-voltaic-battery. W R Grove was used two electrodes dipped in acidic medium and he observed the flow of current takes place between the electrodes when they were in contact with the hydrogen and oxygen [10]. In 1889, the scientists named C Langer and L Mond developed this invention and named it as Fuel Cell [11]. In 1905, Haber filed the first patent on the solid electrolyte based fuel cells [12]. Later the term Fuel Cell is defined as an electro-chemical energy conversion device. One of the vital sources for the fuel energy is hydrogen gas. In general, a fuel cell is an identical to that of a battery; both are having three modules namely cathode, anode and the electrolyte. The principle of operation is also same as that of a battery, in which the fuel and the oxygen (air) have been electro-chemically combined and generates electricity. However, a battery needs recharge as it is consumes internally stored fuel where as a Fuel cell need not to be recharged because in fuel cell, the fuel energy (fuel and oxidants) supplied externally. As long as with the supply of fuel energy it can work continuously and generates electricity, thus it can convert chemical (Fuel) energy directly into electrical energy (electricity) via electro-chemical reaction mechanism [13–17]. The block diagram of fuel cell represented as a Fig. 1.

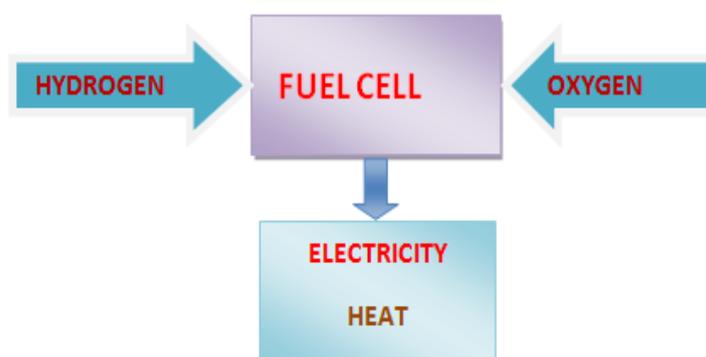


Figure1: Fuel Cell block diagram

II. DESIGN AND WORKING MECHANISM OF A FUEL CELL

Designing a fuel cell is vary from very simple to complex and is depending upon the application and desired efficiency. The schematic-diagram of a characteristic fuel cell consists of three modules namely a porous anode, cathode and electrolyte as shown in the Fig. 2. The hydrogen as a basic fuel and the oxygen as oxidant are used in the fuel cell and supplied to the electrodes known as anode and cathode respectively. The anode and cathodes are separated by the electrolyte. Initially, hydrogen fed to a porous anode, oxygen fed to the cathode and are electro-chemically combined through the electrolyte and generates electricity. Heat and water are produced in addition to that of electricity and this cycle repeats.

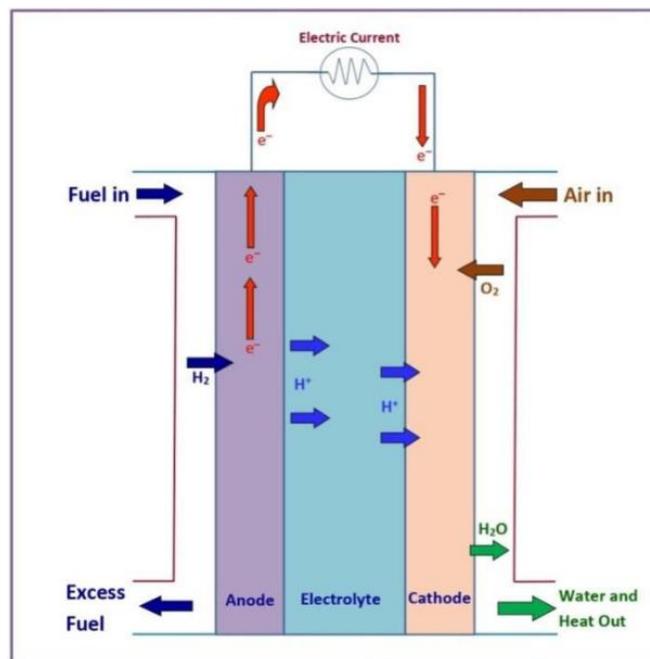


Figure 2: Schematic-diagram of Fuel Cell

The energy-conversion can be done via following chemical-reactions in a fuel cell and are shown below:

Chemical energy of a fuel = Electrical energy + Heat energy+ Water.

At the side of Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

At the side of Cathode: $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

Overall net reaction: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$

1. Advantages and applications of a Fuel Cell: Fuel Cell(s) are more advantageous when compared with the conventional power-sources like combustion engines and batteries etc. In comparison with the conventional combustion engines, the fuel cell(s) are most efficient ones, can show low environmental impact as they have low chemical and thermal emissions. Hydrogen gas is most important fuel for the fuel cell; however fuel cells can have the ability to use wide range of fuels. Fuel cells can operate noiselessly, so they can use as a stationary power sources in residential or hospital areas. In combustion

mechanism, burning the fossil fuel leads to the environmental-pollution where as in case of a fuel cell the environmental damage is reduced and it releases only heat and water as residual products in addition to the electricity. Durability of a fuel cell is high when compared to the batteries. No recharge is required for the fuel cell to produce electricity. Fuel cell uses a hydrogen gas as fuel energy to produce clean electricity since it does not require the oil or gasoline. Fuel cell(s) can have the ability of high energy conversion efficiency with reduced noise, thermal and environmental pollutions. Fuel cell has low maintenance cost and the performance is very high. Design of a fuel cell is simple (modular design) and can work on various fuel(s).

Fuel cells have many vital applications in the industrial, residential and commercial fields. Fuel cells can be used in automotive fields, stationary power units, isolated houses, telecom tower-backup units, portable applications such as mobiles, laptops, notebook computers, etc. The co-generation of heat as well as electricity by the fuel cell is well suited for residential applications. Fuel cells can be used as a power sources for remote locations (such as spacecraft's, space shuttle, large parks, weather stations, and research stations). Fuel cells are also useful in transportation applications (such as electric vehicles) as well as few military applications [6, 17 and 18].

- 2. Categories of Fuel Cell:** Principle of working of all types of fuel cells is similar. However, the fuel cell is later categorized by the type of electrolyte used and the operating temperature range. Among various categories of fuel cells, some may have the low-operating temperature and other may have high-operating temperatures. Certain operating temperature range is suitable for a particular electrolyte material; so the electrolyte material can play a vital role in the classifications of fuel cells. Therefore, depends upon type of the electrolyte used in the fuel cell that can able to classify as certain category [6, 17–19].

The following fuel cells are categorized based on the type of an electrolyte.

- Polymer Electrolyte Membrane Fuel Cell (PEMFC)
- Alkaline Fuel Cell (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)

Among these fuel cell technologies, the high-operating temperature range fuel cells are SOFC and MCFC and the low-operating temperature range fuel cells are PAFC, AFC and PEMFC. The brief explanation of above said fuel cells are as follows:

Polymer Electrolyte Membrane Fuel Cell (PEMFC)

- Type of electrolyte used: Ion exchange membranes
- Example of electrolyte: Nafion (Polymer type)
- Operating Temperature: 50 to <100 °C
- Fuel: Hydrogen, Methanol
- Oxidant: O₂/Air

- Efficiency: 35 to <60 %
- Ion to be conducts via electrolyte: H^+
- Advantage(s): Quick start up, reduced corrosion due to membrane electrolyte and low temperature
- Disadvantage(s): high purity fuel, expensive catalysts
- Application(s): Stationary, transportation and portable electronic devices
- Chemical reaction(s):
- At the side of Anode: $H_2 \rightarrow 2H^+ + 2e^-$
- At the side of Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Alkaline Fuel Cell (AFC)

- Type of electrolyte used: Mobilized or immobilized alkaline hydroxide
- Example of electrolyte: NaOH, KOH
- Operating Temperature: 50 to 150 °C
- Fuel: Hydrogen, Methanol
- Oxidant: O_2 /Air
- Efficiency: 60 %
- Ion to be conducts via electrolyte: OH^-
- Advantage(s): Fast cathode reaction in alkaline media, low temperature, low cost
- Disadvantage(s): Design problem, electrolyte management and sensitive to CO_2 in fuel & air
- Application(s): Stationary, military, transportation and portable electronic devices
- Chemical reaction(s):
- At the side of Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
- At the side of Cathode: $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Phosphoric Acid Fuel Cell (PAFC)

- Type of electrolyte used: Immobilized liquid Phosphoric acid
- Example of electrolyte: H_3PO_4
- Operating Temperature: 150 to 200 °C
- Fuel: Hydrogen
- Oxidant: O_2 /Air
- Efficiency: 40 %
- Ion to be conducts via electrolyte: H^+
- Advantage(s): Increased tolerance to fuels and enables CHP
- Disadvantage(s): Structural design problem, long start up time and Pt catalyst
- Application(s): Transportation, stationary power generators with output up to 400kW.
- Chemical reaction(s):
- At the side of Anode: $H_2 \rightarrow 2H^+ + 2e^-$
- At the side of Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Molten Carbonate Fuel Cell (MCFC)

- Type of electrolyte used: Immobilized liquid molten carbonate
- Example of electrolyte: Molten K_2CO_3 , Li_2CO_3
- Operating Temperature: 600 to 700 °C

- Fuel: Hydrogen, Natural gas, carbon monoxide, Propane
- Oxidant: O₂/ CO₂/Air
- Efficiency: 50 %
- Ion to be conducts via electrolyte: CO₃²⁻
- Advantage(s): Fuel flexibility, variety of catalysts and enables CHP due to high temperature
- Disadvantage(s): High temperature corrosion of the cell parts, long start up time.
- Application(s): Distributed power generation
- Chemical reaction(s):
- At the side of Anode: $\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$
- At the side of Cathode: $\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$

Solid Oxide Fuel Cell (SOFC)

- Type of electrolyte used: Solid/ Ceramics
- Example of electrolyte: (Solid form) Yttria Stabilized Zirconia or Doped ceria
- Operating Temperature: 600 to 1000 °C
- Fuel: Hydrogen, CO, Natural gas, Propane
- Oxidant: O₂/Air
- Efficiency: >60 %
- Ion to be conducts via electrolyte: O²⁻
- Advantage(s): High efficiency, modularity, fuel flexibility, avoids expensive catalysts, suitable CHP/ CHHP, hybrid/GT cycle, cogeneration and potential for internal reformation of hydrocarbons.
- Disadvantage(s): Corrosion of the cell parts at high temperatures, lengthy start up time.
- Application(s): Distributed and stationary power generation to auxiliary power units in vehicles
- Chemical reaction(s):
- At the side of Anode: $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
- At the side of Cathode: $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$

Among the fore mentioned fuel cells, SOFC has proven as most promising and efficient electrochemical energy conversion device. SOFC technology has a great interest due to its clean electrical energy production from chemical energy and in the process of conversion only heat and water produced as derivatives. Solid oxide fuel cell (SOFC) is an environmentally-friendly energy conversion device due to its longer life time, choice of a fuel and less environmental impact. In addition to this, SOFC uses a solid electrolyte which can minimize the corrosion problems when compared to MCFC and eliminates the water management issue when compared to PEMFC. Apart from the advantages, the SOFC has important applications such as distributed power generation, stationary power generation to auxiliary power units in vehicles, remote power generation and uninterruptable power supplies. This makes the SOFC as a most efficient and favorable electro-chemical energy conversion device [4, 6, 17–19].

III. DESIGN AND WORKING MECHANISM OF SOLID OXIDE FUEL CELL (SOFC)

SOFC is one of the important fuel cell types, which is emerged as an efficient electro-chemical energy conversion technology over other categories of fuel cells [17–20]. In 1937, the SOFC was demonstrated and developed first by Bauer and Pries [21]. SOFC is mainly comprises of three parts, out of which two electrodes (cathode and anode) connected by a dense solid electrolyte. SOFC can be constructed in planar form called as planar SOFC and tubular form called as tubular SOFC. The working mechanism of SOFC is straightforward. Fig. 3 depicts the schematic-diagram of simple SOFC design. In a typical SOFC, oxygen is supplied to cathode side and fuel i.e. hydrogen is supplied to anode side. The reduction of oxygen atoms to oxygen ions takes place by the electrons ($1/2O_2 + 2e^- \rightarrow O^{2-}$). The resultant oxygen ions (O^{2-}) diffused via solid electrolyte towards the porous anode. Hydrogen fuel is then supplied at the porous anode. The reaction between the hydrogen and diffused oxygen ions gives off electrons to the external circuit ($H_2 + O^{2-} \rightarrow H_2O + 2e^-$).

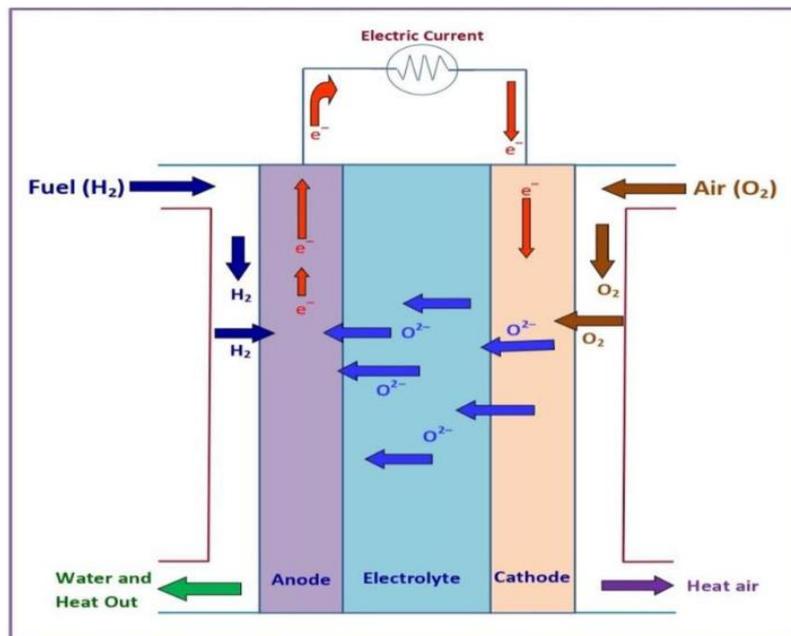


Figure 3: Schematic-diagram of simple SOFC design

The hydrogen and diffused oxygen ions are electro-chemically combined through the electrolyte to generate electricity. Therefore, it can efficiently convert the fuel-chemical energy to clean electrical energy besides it releases water and heat and this cycle repeats [6].

1. Anode: Important role of this component is to access the fuel and electro-oxidize the hydrogen fuel via chemical reaction and subtraction of product. Therefore, the material to be withstanding as a good anode and to achieve this role, the material must possess the following properties.

- High porosity for the fast diffusion of fuel through it
- High electronic-conductivity

- Sufficient ionic-conductivity
- Chemical stability in fuel and oxidizing environment and operating conditions
- Enough catalytic activity to oxidize the hydrogen
- Matched coefficient of thermal expansion (CTE) with adjacent SOFC components
- Physical, chemical and mechanical compatibility with adjacent components
- Lower cost

These above mentioned properties confines the choice of anode materials. The most important materials in the choice of anode materials are nickel and the noble-metals. One of the vital anode materials for the SOFC is consists of nickel due to its low cost with feasible properties over noble-metals. However, this material is not used as anode material due to the high value of CTE when compared to solid electrolyte lead to thermal mismatch between the components. In addition to this, Nickel is not stable at high temperatures over oxidation in air. To minimize the problem associated with this, research & development has suggested the several perovskites and also composite material such as $\text{SrMo}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$, and Nickel-Doped Ceria which can offer above said desired properties [22–25]. Furthermore, the composite anodes such as (LaSr)(TiFe) O_3 -Ceria, $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{O}_{2-\square}$ -GDC, $\text{Ni/SrTi}_{1-x}\text{Cr}_x\text{O}_3$ as well as some layered perovskite anodes like Y- and Al- substituted SrVO_3 , etc. have been developed as a novel materials which offering desired properties [26–29].

2. Cathode: Important role of this component is to access the oxygen and reduction of molecular form of the oxygen to oxygen ions via chemical reaction and transports these reduced oxygen ions to the solid electrolyte. Therefore, the material to be withstanding as a good cathode and to achieve this role, the material must possess the following properties.

- Sufficient mixed (electronic–ionic) conductivity
- Chemical stability in oxygen environment and operating conditions
- Enough catalytic activity in the reduction of oxygen
- Matched coefficient of thermal expansion (CTE) with adjacent SOFC components
- Physical, chemical and mechanical compatibility with adjacent components
- Lower cost

These mentioned properties confines the choice of cathode materials. The most important materials in the choice of cathode materials are the manganese and cobalt based perovskites. The materials such as perovskite structured Lanthanum Cobaltite (LaCoO_3) and Lanthanum Manganite (LaMnO_3) are the most commonly used cathode materials. Numerous research was done on novel materials to enhance the said properties such as (LaSr)(CoFe) O_3 , (BaSr)(CoFe) O_3 , (SmSr)(CoFe) O_3 , $\text{Sr}_{2.7}\text{Nd}_{0.3}\text{Fe}_2\text{O}_{7-\square}$, $\text{Sr}_{2.4}\text{Ca}_{0.3}\text{Nd}_{0.3}\text{Fe}_{1.4}\text{Co}_{0.6}\text{O}_{7-\square}$, $\text{Sr}_{2.4}\text{Ca}_{0.3}\text{Nd}_{0.3}\text{Fe}_{1.4}\text{Co}_{0.6}\text{O}_{7-\square}$ etc. Later, the number of investigations was made to explore new cathode materials such as $\text{Sm}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.25}\text{Co}_{0.75}\text{O}_{2.8}$, $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Cu}_2\text{O}_{5+\square}$, $\text{Bi}_{0.5}\text{Ba}_{0.5}\text{FeO}_{3-\square}$ and other materials based on double perovskite as well as layered structured materials. Furthermore, to minimize the problem associated with the thermal expansion compatibility, the research & development has suggested that the composite materials can be suitable as a novel cathode material for operating conditions in SOFC. The composite cathodes made up of

two different materials such as $(\text{BaSr})(\text{CoNb})\text{O}_3\text{-GDC}$ and $(\text{LaSr})(\text{CoSb})\text{O}_{3-\delta}\text{-SDC}$, LSCF-GDC , etc. have been developed as a novel materials which offering desired properties [30–37].

3. Solid Electrolyte: The vital component of SOFC is solid electrolyte, which plays an important role in providing the ionic conduction i.e. migration of oxygen ions from cathode to anode for SOFC applications. Therefore, the material to be withstanding as a good solid electrolyte and to achieve this role, the material must possess the following properties.

- Highest oxygen ion (O^{2-}) conductivity
- Negligible electronic (e^-) conductivity
- High density
- Chemical stability in different oxygen partial pressures and operating conditions
- Similar thermal expansion coefficient (TEC) with adjacent electrode components
- Physical, chemical and mechanical compatibility with adjacent components
- Lower cost

These fore mentioned properties confines the choice of solid electrolyte materials. The electrolyte material's highest ionic conduction property influences the SOFC performance. Stabilized zirconia (such as Ytria stabilized zirconia / Scandia stabilized zirconia) and ceria (i.e. CeO_2) have been used as typical solid electrolyte materials for SOFC [4, 17–20]. Traditional stabilized zirconia is the principal solid-electrolyte, due to its high ion conductivity at higher operating temperatures ($\sim 1000^\circ\text{C}$) of SOFC. Unfortunately, the usage of stabilized zirconia as electrolyte at these higher temperatures cause some drawbacks such as material (physical and /or chemical) degradation due to unfavorable reactions between the neighboring cell parts. This further leads to the degradation, thermal mismatch, and also short circuit in SOFC which in turn reduces the life time. In view of this, enormous research work is focused on novel electrolytes to get rid of complications in developing the SOFC [4, 17, 20, 38–40]. In order to decrease the operating temperature and to protect the SOFC from the fore mentioned drawbacks, researchers concentrated on ceria as a novel solid electrolyte material over stabilized zirconia.

The performance of electrolyte materials plays a key part in defining the operating temperature and categorization of SOFC like High Temperature-SOFC ($\sim 1000^\circ\text{C}$), Intermediate Temperature-SOFC ($600^\circ\text{C}\text{-}800^\circ\text{C}$), and Lower Temperature/ advanced-SOFC ($<600^\circ\text{C}$). The enhancement in performance at relatively lower operating temperature is prerequisite for optimized electrolyte towards the advanced SOFC applications.

IV. DOPED/CO-DOPED CERIA ELECTROLYTES FOR IT-SOFCs

The intermediate temperature solid oxide fuel cell (IT-SOFC) is a breakthrough towards the development of SOFC. Ceria as a solid electrolyte has been extensively studied due to its high ionic conductivity when compared to zirconia at comparatively lower temperatures. In addition to this, ceria has a relatively same thermal expansion coefficient at

when compared to stabilized zirconia [38–40]. Un-doped ceria i.e. Pure CeO_2 is a poor conductor and requires structural changes that creates considerable oxygen vacancies to improve the ionic conductivity. In view of this, studies suggested that the fractional replacement of Ce ions with trivalent ions such as Sm, Gd, Pr, Y, La, Gd and Nd could generates concentration of oxygen vacancies in the lattice of ceria which in turn lead to the high ionic conductivity of doped ceria when compared to pure ceria.

The local defect structures created by dopants, concentration of oxygen vacancies will affect the electrical properties of doped ceria. The superior total ionic conductivity of doped ceria when compared to un doped ceria pave a way for the development of novel electrolyte towards SOFC. Several rare earth and alkaline earth elements like La, Nd, Sm, Gd, Y, Yb, Dy, Er, Eu, Ho, Ca, Sr, Ba and Mg etc., have been approached towards the optimization of dopants for ceria to enhance the electrical properties. So far, enormous doping efforts have been made on ceria and reported the enhanced electrical properties of doped ceria for the intermediate temperature SOFC applications [38–43].

However, the ionic conductivity in single doped ceria electrolyte materials is dominated by the electronic conductivity which lead to the short circuit of SOFC. So, R&D focused on the co-doping approach in ceria. Researchers have been extensively investigated various co-doped ceria system of materials and suggested the optimized solid electrolytes such as $\text{Ce}_{0.85}\text{La}_{0.075}\text{Sm}_{0.075}\text{O}_{2-\delta}$ [44], $\text{Ce}_{0.8}\text{Sm}_{0.12}\text{Pr}_{0.08}\text{O}_{2-\square}$ [45], $\text{CeO}_2\text{-}8\text{Gd}_2\text{O}_3\text{-}2\text{Nd}_2\text{O}_3$ [46], $\text{Ce}_{0.8}\text{Er}_{0.18}\text{La}_{0.02}\text{O}_{1.9}$ [47], $\text{Ce}_{0.8}\text{Nd}_{0.18}\text{Ca}_{0.02}\text{O}_{1.89}$ [48], $\text{Ce}_{0.83}\text{Dy}_{0.14}\text{Ca}_{0.03}\text{O}_{1.90}$ [49], $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Ca}_{0.1}\text{O}_{2-\square}$ [50], $\text{Ce}_{0.80}\text{Pr}_{0.10}\text{La}_{0.10}\text{O}_{2-\square}$ [51], $\text{Ce}_{0.85}\text{La}_{0.10}\text{Sr}_{0.05}\text{O}_{2-\square}$ [52] and $\text{Nd}_{0.20}\text{Gd}_{0.05}\text{Ce}_{0.75}\text{O}_{1.90-x/2}$ [53] etc. whose electrical properties are superior than single doped ceria.

Further improvement of structural, thermal and electrical properties of ceria, recently, triple/multi-doping concept has been approached to develop a new ceria based electrolyte. Several triple doped ceria systems were investigated and succeeded in reporting the enhanced performance of optimized electrolytes like $\text{Ce}_{0.7}\text{Pr}_{0.15}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{O}_2$ [54], $(\text{La}_{0.77}\text{Sr}_{0.2}\text{Ca}_{0.03})_{0.15}\text{Ce}_{0.85}\text{O}_{1.908}$ [48] and $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Ca}_{0.05}\text{Gd}_{0.05}\text{O}_{2-\square}$ [55] etc.

On the other hand, to enhance the electrical properties of ceria, previous studies proposed the density-functional theory (DFT) based on which the choice of dopants have been made. According to these studies, Promethium is an ideal dopant for ceria because in Pm^{3+} no site is preferred for occupation of vacancies (due to the balanced elastic and electronic interactions between the dopants and vacancies). So, the creation of oxygen vacancies without traps lead to the enhanced ionic conductivity of ceria [56]. However, Pm^{3+} is a radioactive-element and can not used as dopant in ceria. In view of this, studies suggested the choice of dopants whose average atomic number and ionic-radius nearer to Pm^{3+} or lie in between Pm (61) and Sm (62) [43, 56]. To improve the ionic conductivity of ceria, this concept has been approached for the choice of dopants the dopants and succeeded in getting enhanced properties of doped ceria materials such as $\text{CeO}_2\text{-}8\text{Gd}_2\text{O}_3\text{-}2\text{Nd}_2\text{O}_3$ [46], $\text{Ce}_{0.84}\text{Gd}_{0.08}\text{Pr}_{0.08}\text{O}_2$ [57], $\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Nd}_{0.05}\text{O}_{2-\delta}$ [58] and $\text{Ce}_{0.7}\text{Pr}_{0.15}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{O}_2$ [54] etc.

- 1. Ceria based composite Electrolytes for LT-SOFCs:** The operating temperature is a crucial aspect in SOFC community i.e. reducing the operating temperature from intermediate to lower is prerequisite as intermediate temperature i.e. $>600^{\circ}\text{C}$ results in expensive interconnectors, element compositional changes, poor performance, insufficient ionic conductivity, and costly fabrication etc which leads to a barrier for commercialization of SOFC. On the other hand, decrease in operating temperature results in increased internal resistance of cell and decreased ionic conductivity of electrolyte, which reduces the SOFC performance. In view of this, to sustain SOFC commercially, the electrolyte should possess high value of total-ionic-conductivity at relatively low operating temperature. So, the creation of density of oxygen vacancies without traps to maximize the total-ionic-conductivity of electrolyte is prerequisite towards the commercialization of SOFC at relatively low operating temperatures (i.e., below 600°C) [59–62].

In this context, R&D approached the composite materials in developing the novel solid-electrolyte with a working temperature of below 600°C for the low temperature–SOFC (LT–SOFC) applications. Especially ceria - carbonate composite materials have been extensively studied and revealed that these materials can facilitate the enhanced total ionic conductivity towards the advanced SOFC applications within the temperature below 600°C . In ceria - carbonate composite facilitates multiple ion conductivity i.e. in addition to the oxygen ion conductivity, carbonate content (sodium/ potassium/ lithium carbonates) offers protonic as well as carbonate ions conductivity together enhance the total ionic conductivity of composite electrolyte. The ceria - carbonate composite approach pave a way for the development of advanced SOFCs [60–64].

- 2. Reaction mechanism and conductivity in ceria - carbonate composite electrolytes:** The reaction mechanism of molten carbonate fuel cell is combined with the SOFC makes the superficial conduction in the proposed low temperature-SOFC / advanced SOFC. The combined reactions in advanced SOFC with proposed ceria - carbonate composite electrolyte as follows [65 and 66]

Anode side:

- $\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$
- $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
- $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode side:

- $\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$
- $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$
- $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

Overall reaction:

- $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

The above reactions in advanced SOFC indicates that the diffusion of H^+ ions and CO_3^{2-} ions takes place in addition to that of O^{2-} ions diffusion. In this multiple ion diffusion, the CO_3^{2-} ion contribution is negligible due to the small amount of CO_2 in air.

So, the total ionic conductivity is mostly contributed by H^+ ions diffusion through carbonate phase and O^{2-} ions diffusion through doped ceria phase as represented in the Fig.4 [65].

The softening of carbonates below the melting temperature, create an extra interfacial space for the transportation of ions i.e. ion conducting paths by connecting the carbonate as well as ceria phases which leads to the enhanced total ionic conductivity in doped ceria - carbonate composite. The soft carbonate phase can act as a glue among the two phases in composite to get a dense microstructure and to minimize the interfacial polarization losses. In this way the enhanced electrical properties of ceria - carbonate composites makes its suitability for the advanced SOFC applications [62, 65, and 66].

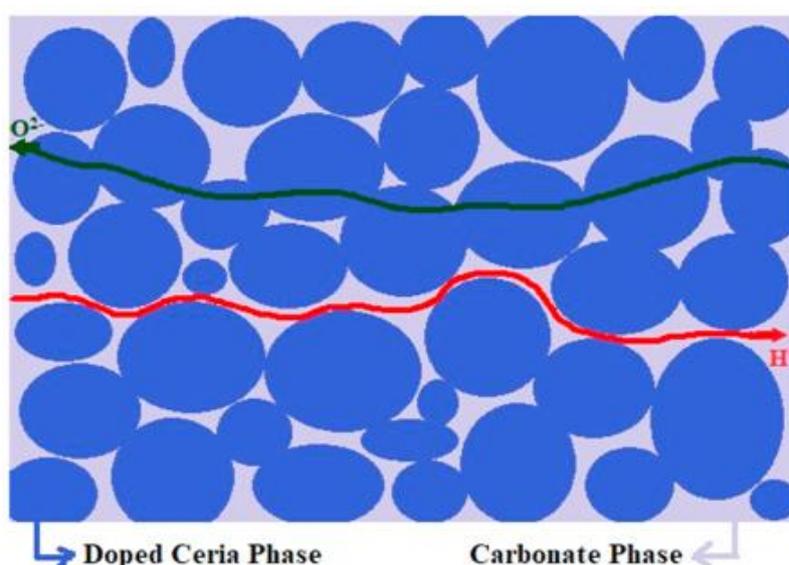


Figure 4: Schematic ionic conduction mechanism in doped ceria-carbonate composite electrolyte [62].

Noteworthy research has been carried with the choice of doped ceria materials and the carbonates to develop a novel doped ceria-carbonate composite electrolyte such as SDC- Na_2CO_3 , SDC- K_2CO_3 , SDC- Li_2CO_3 , SDC- $(Na/K)_2CO_3$, SDC- $(Li/Na)_2CO_3$, SDC- $(Li/K)_2CO_3$, SDC- $(Li/Na/K)_2CO_3$, $Ce_{0.90}Eu_{0.10}O_{2-\delta}-(Li/Na)_2CO_3$, $Ce_{0.85}Er_{0.15}O_{2-\delta}-(Li/Na/K)_2CO_3$, $Ce_{0.85}La_{0.15}O_{2-\delta}-(Li/Na/K)_2CO_3$, $Ce_{0.95}Sr_{0.05}O_{2-\delta}-(Li/Na/K)_2CO_3$, $Ce_{0.85}Sm_{0.15}O_{2-\delta}-(Li/Na/K)_2CO_3$, GDC- Na_2CO_3 , GDC- K_2CO_3 , GDC- Li_2CO_3 , GDC- Sr_2CO_3 , GDC- $(Na/K)_2CO_3$, GDC- $(Na/Sr)_2CO_3$, GDC- $(Li/Na)_2CO_3$, GDC- $(Li/K)_2CO_3$ and GDC- $(Li/Na/K)_2CO_3$ [63, 64, 67–70].

Recently, significant work has been made on co-doped / triple-doped ceria-carbonate composite electrolytes and reported the optimized materials such as $Ce_{0.93}Ca_{0.05}Sr_{0.02}O_{1.93}-(Li_{0.52}Na_{0.48})_2CO_3$, $Ce_{0.90}Mg_{0.06}Sr_{0.04}O_{1.90}-(Li/Na)_2CO_3$, $Ce_{0.83}Dy_{0.14}Ca_{0.030}O_{2-\delta}-(Li_{0.52}Na_{0.48})_2CO_3$, $Ce_{0.80}Sm_{0.2-x}Ca_xO_{2-\delta}-Na_2CO_3$, and $Ce_{0.8}M_{0.1}Gd_{0.1}O_{2-\delta}$ ($M = Sm^{3+}, Sr^{2+}, Ca^{2+}$)- Na_2CO_3 , $65[Ce_{0.82}La_{0.06}Sm_{0.06}Gd_{0.06}O_{2-\delta}] - 35[(Li-Na)_2CO_3]$, $70[Ce_{0.76}La_{0.08}Pr_{0.08}Sm_{0.08}O_{2-\delta}] - 30[(Li-Na)_2CO_3]$, and $70[Pr_{0.08}Sm_{0.08}Gd_{0.08}Ce_{0.76}O_{2-\delta}] - 30[(Na-K)_2CO_3]$ [62, 71–76].

Fig. 5 indicates the Arrhenius plots of total conductivity of the sintered La, Sm, Gd triple-doped ceria LSG ($\text{Ce}_{0.82}\text{La}_{0.06}\text{Sm}_{0.06}\text{Gd}_{0.06}\text{O}_{2-\delta}$) and its carbonate composite LSG-LN ($\text{Ce}_{0.82}\text{La}_{0.06}\text{Sm}_{0.06}\text{Gd}_{0.06}\text{O}_{2-\delta} - (\text{Li-Na})_2\text{CO}_3$) [62] as well as Pr, Sm, Gd triple-doped ceria PSGC ($\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{Ce}_{0.76}\text{O}_{2-\delta}$) and its carbonate composite PSGC-NK ($\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{Ce}_{0.76}\text{O}_{2-\delta} - (\text{Na-K})_2\text{CO}_3$) samples [76].

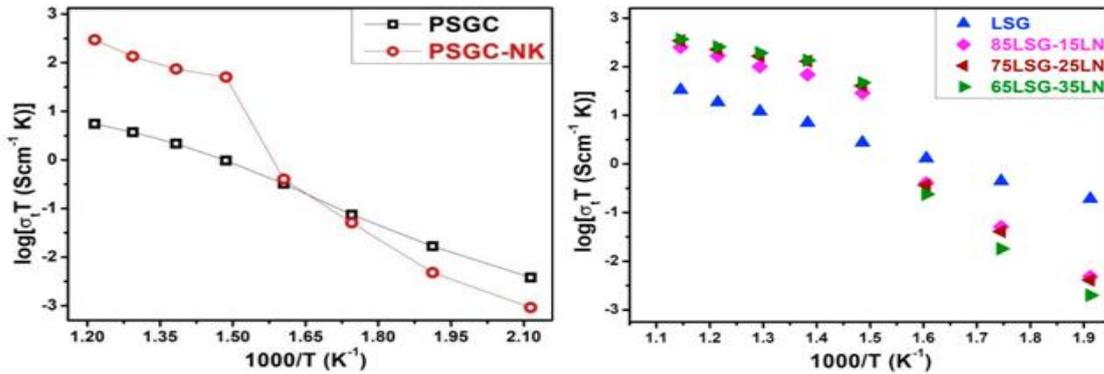


Figure 5: Arrhenius plots of total conductivity of LSG and LSG-LN [62] & PSGC and PSGC-NK [76].

Total-ionic-conductivity comparison was made in Table 1 with recently studied ceria based compositions such as doped / co-doped / triple-doped ceria as well as doped ceria-carbonate composite materials for advanced SOFC applications.

Table 1: Total-ionic-conductivity comparison of recently studied ceria based solid electrolytes for advanced SOFCs.

Composition	Sintering Temperature	Total Ionic Conductivity (S/cm)	Ref
$\text{Ce}_{0.85}\text{La}_{0.075}\text{Dy}_{0.075}\text{O}_{2-\delta}$	1300°C	2.08×10^{-2} at 600°C	[38]
$\text{Ce}_{0.8}\text{Ga}_{0.05}\text{Cu}_{0.15}\text{O}_{1.825}$	1300°C	2.03×10^{-2} at 700°C	[39]
$\text{Ce}_{0.76}\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{O}_{2-\delta}$	1300°C	1.86×10^{-2} at 600°C	[40]
$\text{Ce}_{0.82}\text{La}_{0.06}\text{Sm}_{0.06}\text{Gd}_{0.06}\text{O}_{2-\delta}$	1300°C	3.81×10^{-2} at 600°C	[42]
$\text{Ce}_{0.85}\text{La}_{0.075}\text{Sm}_{0.075}\text{O}_{2-\delta}$	1300°C	1.95×10^{-2} at 600°C	[44]
$\text{Ce}_{0.7}\text{Pr}_{0.15}\text{Sm}_{0.075}\text{Eu}_{0.075}\text{O}_{2-\delta}$	600°C	3.05×10^{-4} at 500°C	[54]
65[$\text{Ce}_{0.82}\text{La}_{0.06}\text{Sm}_{0.06}\text{Gd}_{0.06}\text{O}_{2-\delta}$] – 35[(Li-Na) $_2\text{CO}_3$]	700°C	4.2×10^{-1} at 600°C	[62]
(Li/Na/K) $_2\text{CO}_3$ -GDC	680°C	2.9×10^{-1} at 600°C	[63]
(Li/Na) CO_3 -SDC	800°C	3.1×10^{-1} at 600°C	[64]
CM6S4/20LNCO	700°C	2.95×10^{-1} at 500°C	[72]
CC5S2/30LNCO	700°C	2.00×10^{-1} at 500°C	[73]
CDC/30LNCO	700°C	1.05×10^{-1} at 500°C	[74]
70[$\text{Ce}_{0.76}\text{La}_{0.08}\text{Pr}_{0.08}\text{Sm}_{0.08}\text{O}_{2-\delta}$] – 30[(Li-Na) $_2\text{CO}_3$]	700°C	4.6×10^{-1} at 600°C	[75]
70[$\text{Pr}_{0.08}\text{Sm}_{0.08}\text{Gd}_{0.08}\text{Ce}_{0.76}\text{O}_{2-\delta}$] – 30[(Na-K) $_2\text{CO}_3$]	700°C	3.6×10^{-1} at 550°C	[76]

It is noticed from the earlier investigations that the co-doped ceria-carbonate composites showed highest total-ionic-conductivity over single-doped ceria-carbonate composites and pure co-doped ceria materials as well. The research & development is still going on to report improved nanocomposite ceria-carbonate electrolyte materials with enhanced electrical properties towards advanced SOFC applications at relatively lower temperatures.

V. CONCLUSION

Present study focused the fundamentals of fuel cell technologies, background, working mechanism, different components of SOFC, brief note on traditional materials, and development of novel materials for the advanced low temperature SOFC applications have been discussed. In the way of enhancing the electrical properties i.e. total ionic conductivity of ceria electrolyte significant efforts have been done on doping, as well as co-doping. Studies suggested that the fractional replacement of Ce ions with trivalent ions such as Sm, Gd, Pr, Y, La, Nd, Yb, Dy, Er, Eu, Ho, Ca, Sr, Ba and Mg generates concentration of oxygen vacancies in the lattice of ceria which in turn lead to the high ionic conductivity of doped/co-doped ceria when compared to pure ceria. Further triple-doping in ceria has been introduced to develop suitable electrolyte towards the intermediate temperature SOFCs. The optimal doping of lower valance elements in ceria eases the decrease of grain boundary resistance and as a result increases the total ionic conductivity. The trend of increased total ionic conductivity of ceria electrolytes is achieved using single-doping, and followed by co-doping, triple-doping respectively. R&D suggested the ceria - carbonate composites which facilities the multiple ion conduction i.e. in addition to the oxygen ion conductivity, carbonate content (sodium/ potassium/ lithium carbonates) offers protonic as well as carbonate ions conductivity together enhance the total ionic conductivity of composite electrolyte. The suggested ceria-carbonate composite electrolytes not only enhance the performance of advanced SOFC but also reduce operating temperature as well as cost of the SOFC.

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