

# Recent Advances In Ceria Based Electrolytes For Solid Oxide Fuel Cells

P Sharma

K. L. Singh

D.A.V Institute of Engineering and Technology,  
Jalandhar, Punjab.

C Sharma

A. P. Singh

Punjab Technical University,  
Kapurthala, Punjab

**Abstract:** Ceria based oxides have attracted a great deal of attention in low and intermediate temperature solid oxide fuel cells applications, distinctly due to easy and inexpensive availability of base material, high chemical stability, high redox activity and high oxygen ion conduction. Rare earth oxide doped ceria (RDC) shows outstanding properties compared with yttria stabilized zirconia (YSZ), which is conventional oxide ion conductor used as electrolyte material for SOFC. RDC shows ionic conductivity one order of magnitude higher as compared to YSZ. Also the aliovalent cations (valency < +4) doping in  $CeO_2$  causes an increase in the defect concentration producing anions vacancies in the structure and enhancing  $O^{2-}$  ion conduction. Co-doping of two or more aliovalent cations has also been reported as more efficient strategy to increase the conductivity. The processing method also has an effect on the material properties and hence on the performance of electrolyte.

**Keywords:** Ceria, SOFC, electrolyte, ionic-conductivity.

## I. INTRODUCTION

A fuel cell is an electrochemical device, which can continuously convert the chemical energy of a fuel and an oxidant to electrical energy, by a process involving an essentially invariant electrode-electrolyte system. Apart from the high efficiency of fuel cells, they also exhibit very low emissions. SOFCs are a class of fuel cells which are characterized by the use of a solid oxide material as the electrolyte. SOFCs consist of three main parts, including, macro porous anode, dense solid electrolyte and macro porous cathode. These are all made up of ceramic materials. In a working SOFC, the solid electrolyte conducts oxygen ions from the cathode (the air side) to the anode, where oxidation of the oxygen ions with the fuel (usually hydrogen) occurs. SOFCs operate at high temperatures, typically between  $700^{\circ}C$  and  $1000^{\circ}C$ , because the typical materials used in an SOFC are not sufficiently electrically and ionically conducting at lower temperatures [1]. Even at such high operating temperature of solid oxide fuel cells, highly polluting nitrogen oxides, ashes, solid combustion products etc. are not produced

and  $CO_2$  is produced in very less quantities. SOFCs use a ceramic membrane for the conduction of ions at temperatures above  $600^{\circ}C$ . On the basis of temperature of operation SOFCs are classified into intermediate and high temperature SOFCs. Intermediate temperature SOFCs (IT-SOFC) operate in the range of  $(600-800)^{\circ}C$ , generally using ceria-doped rare earth electrolyte, whereas high temperature SOFCs (HT-SOFC) generally use doped zirconia electrolytes [2].

An ideal SOFC electrolyte possess minimum electronic conductivity, maximum ionic conductivity ( $>0.1 \text{ Sm}^{-1}$ ) and a thermal expansion coefficient that is closely matched between the contracting components and the electrodes. Also the thermal and chemical relationship between the contracting electrodes should be effectively stable and entire structure should be dense enough to block the electronic movement & to maximize the ionic conductivity [3]. Standard electrolyte materials based on stabilized zirconia, require SOFCs to be operated at  $(900-1000)^{\circ}C$  to ensure sufficient ionic conductivity and hence high output current density. But apart from the high efficiency of stacks using YSZ, which theoretically can reach upto 100%, the high operating

temperature leads to degradation of the materials and overall system cost also increases. Further in real SOFC devices, some of the potential energy is lost in the electrolyte in the form of ohmic loss. Reduction in the electrolyte losses is accomplished by making the electrolyte membrane very thin (5-15 $\mu\text{m}$ ), by using anode supported configuration and by choosing a material with a high ionic conductivity even at lower temperature [4].

Also for an optimum performance and life time of the stack as well as for reduction of the overall cost of the system, there is a need to the develop low temperature electrolytes, like, different cationic doped ceria electrolytes  $\text{Ce}(\text{Re})\text{O}_{2-\delta}$  where (Re: rare-earth or alkaline-earth cations), Scandia stabilized zirconia electrolytes, doped bismuth electrolytes etc. All of these materials have fluorite structure [5-10]. These also include GDC (gadolinium doped ceria), YDC (Yttrium doped ceria) and SDC (samarium doped ceria) etc. These electrolytes have permitted the SOFCs to operate at temperature below 600 $^{\circ}\text{C}$ . These electrolytes have advantages over high temperature electrolytes because if the operating temperature could be replaced to intermediate temperature of say (500-700) $^{\circ}\text{C}$ , less expensive materials such as steel could be used in these auxiliary components [11]. The operating temperature can be further decreased to 600 $^{\circ}\text{C}$  by employing highly conductive solid electrolytes such as gadolinium doped ceria or strontium and magnesium doped lanthanum gallate etc. [12].

#### A. ELECTROLYTE MATERIALS

In the literature, a number of electrolyte materials with greater oxygen conductivity than 8mol% Yttria stabilized zirconia (8YSZ), which is most commonly used electrolyte, have been studied. The electrolyte material 10 mol%  $\text{Gd}_2\text{O}_3$  doped CeO (10CGO), is frequently considered to replace 8YSZ for low temperature (LT-SOFCs). At temperatures more than 500 $^{\circ}\text{C}$ , CGO is not considered as SOFC electrolyte because there is reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  at high temperature. Scandia-doped Zirconia is an other material which may be considered as SOFC electrolyte. SDZ has high ionic conductivity relative to other doped zirconia compounds. Scandium is however a rare element and is very expensive [13].  $\text{Bi}_2\text{O}_3$  systems have the highest ionic conductivity, but their limited stability in reducing atmosphere limits their applicability.  $\text{LaGaO}_3$  systems (e.g. LSGM) are also considered as candidates for the temperature range below 500 $^{\circ}\text{C}$ , but the conductivity of CGO in this range is slightly higher. But it should also be considered that Gallium is also a rare and very expensive element. The electrical conductivity of various types of fluorite oxides discussed so far can be arranged in an order like  $\text{Bi}_2\text{O}_3 > \text{CeO}_2 > \text{ZrO}_2 > \text{ThO}_2 > \text{HfO}_2$ . Among these  $\text{Bi}_2\text{O}_3$  has an oxygen deficient fluorite structure where 1/4 of the normal fluorite anion sites are vacant and shows the highest oxygen-ion conductivity so far reported for the solid oxide electrolytes. It is monoclinic structure at low temperatures and becomes cubic and hence shows higher ionic conduction at high temperatures but it is easily reduced at low oxygen partial pressures [14].

Current developments in the electrolytes for intermediate temperature solid oxide fuel cell (IT-SOFCs) focuses on the

rare earth (RE)-doped (RE = Gd, Sm, Pr etc.) ceria, which have been regarded as promising oxide electrolytes for IT-SOFCs due to their higher oxygen-ion conductivity below 800 $^{\circ}\text{C}$  than YSZ at the same temperature [15-16]. Recently most research have been investigated in understanding the effect of different acceptor dopants and dopant concentration on the ionic conductivity of ceria, suggesting that GDC ( $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ) for the compositions with  $x = 0.1$  and  $0.2$  is one of the most frequently used electrolytes for IT-SOFCs [17-20]. It is known that the total electrical response of a polycrystalline solid oxide electrolyte is determined by the bulk and grain boundary conductivities especially in the low and intermediate temperature range. Carlos et al. reported that the specific grain boundary conductivity for Dy doped ceria enhances as the grain size decreased. Hence, it can be believed that the change of grain boundary conductivity with decreasing grain size possibly gives rise to the increase of the total conductivity for the prepared Gd-doped ceria [21].

#### II. DOPED CERIA AS SOFC ELECTROLYTE

Doped ceria has been studied over the last many years as catalysts, structural and electronic promoters of heterogeneous catalytic reactions [22] and also as an oxide ion electrolyte possibly due to its higher conductivity than the conventionally used yttria stabilized zirconia at lower temperatures in solid oxide fuel cells [23,24]. It also have better oxygen surface exchange coefficient at cathode side interface of SOFC and therefore excellent functionality as an interlayer between doped zirconia electrolyte and cathode. Doped ceria is also preferred due to its lower cost in comparison to electrolytes like lanthanum gallate [25]. It lowers the operating temperature from 1000 $^{\circ}\text{C}$  to 600 $^{\circ}\text{C}$ , which in turn facilitates the choice of electrode and interconnects and also increases the life span of cell. This would allow the use of cost effective, environmentally gentle materials, such as chromia forming ferritic stainless steels as interconnectors or other construction materials. On the other hand thermal degradation processes are also slowed down at lower temperatures and it is possible to shorten the starting time and off-time of the generator. The chemical stability of the electrode material also increases due to lower operating temperature [26].

#### A. DOPING OF CERIA

Doping of ceria is usually performed by substituting lower valence cations into the lattice, with the additional effect of introducing oxygen vacancies, however overall charge neutrality in lattice is maintained. These oxygen vacancies supply the equivalent sites allowing the oxygen ions to migrate (by hopping mechanism) and are the requirement for high ionic conductivity. A further remarkable feature of the fluorite structured ceria is that it is able to sustain a high degree of substitution and consequent non-stoichiometry, making these structures very highly disordered materials. Doping of the fluorite structured oxide for improvement in oxide ion conductivity is usually achieved by substitution of the host cation with a rare earths. Examples of such materials are doped zirconia, doped ceria etc. with the general formula

$Re_{1-x}A_xO_{2-\Delta}$ , where 'A' is cations and 'Re' is the rare earth dopants. The ionic motion in fluorite-based systems is the well-established vacancy based hopping mechanism, where one vacancy shifts position with a neighbouring oxygen ion in a normal lattice position.

### III. SYNTHESIS OF DOPED CERIA ELECTROLYTE

Various synthesis methods like solid state reaction (SSR), co-precipitation, Hydrothermal, sol-gel, combustion synthesis etc. may be used to synthesis the electrolyte material for SOFC. Various factors such as kinetic control, activation energy, surface morphology, particle size distribution, density and porosity etc. are needed to be taken care of, while fabricating a SOFC electrolyte.

Solid state powder preparation method is simplest and most common method used both in industry and laboratory. In this method heating of non-volatile solids take place in order to form desired products. But there are some disadvantages like high temperature required, ion diffusion problems, even by grinding the material carefully the particle size would only be reduced to  $0.1\mu\text{m}$  which is not enough.

Co-precipitation is used in order to obtain the starting materials, where a stoichiometric mixture of soluble salts of the metal ions is dissolved and then precipitated as hydroxides, citrates, oxalates. Then this mixture is filtered, dried and then heated to give the desired product. In sol-gel method, colloidal particles, dispersed in a suspension (a sol) undergo further reactions, which cause the colloidal particles to join together in a continuous network called a gel. The gel is dried, calcined and in the case of powder milled. The major drawback of the co-precipitation method is the fact that the stoichiometry of the precipitates may not be exact, in case one or more ions are left in the solution, whereas in sol-gel process the reactants never precipitate. Initially the "sol" is prepared, which is basically a concentrated solution or colloidal suspension of the reactants, and finally is concentrated to form the "gel", which is then heated to form the product [27].

### IV. PROPERTIES OF DOPED CERIA

Pure ceria is fundamentally a poor oxide ion conductor. Ceria possesses cubic fluorite structure from room temperature to its melting point while in case of zirconia it is only possible at high temperatures. This distinct property of ceria is advantageous to design SOFCs which can operate at comparatively less temperature.

#### A. XRD ANALYSIS

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. X-rays are a form of electromagnetic radiation that have high energies and short wavelengths (in the order of the atomic spacing of solids). Diffraction pattern help to find crystal structure as well as to determine the phase of the material. Figure 1 Shows the XRD spectrum of doped

ceria, which indicates a phase-pure face-centred-cubic fluorite-type structure of  $\text{CeO}_2$  [28].

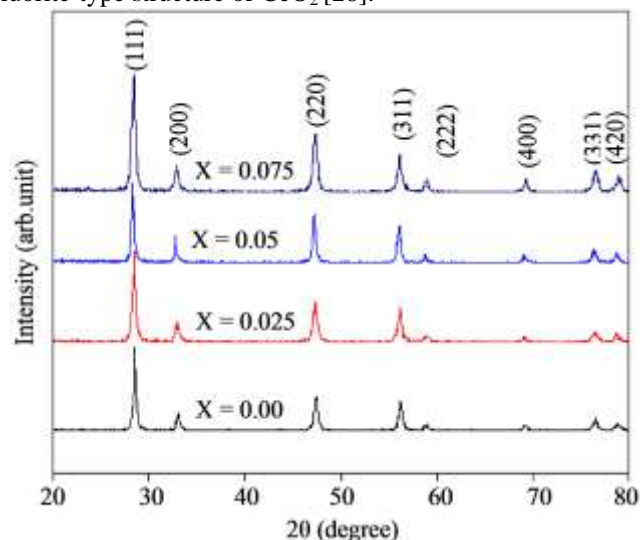


Figure 1: Shows the XRD spectrum of doped ceria, which indicates a phase-pure face-centred-cubic fluorite-type structure of  $\text{CeO}_2$  [28]

#### B. SEM CHARACTERIZATION

Electron microscopy is used to study the structure, morphology, defects and to determine the distribution of elements. A conventional microscope uses visible radiation (400-700 nm) and so cannot resolve images of objects, which are smaller than half the wavelength of light. On the contrary, electron microscopes allow resolution down to 0.1 nm. The electron beam is produced by heating a tungsten filament, and focused by magnetic fields in a high vacuum. In SEM, the electrons are rastered across the surface of the sample. Electrons reflected by the surface of the sample and emitted secondary electrons are detected to give a map of the surface topography of the sample. The typical SEM image shown in Figure 2 and corresponding size distribution suggest that the mean diameter of nanoceria powders is about 6 nm [29].

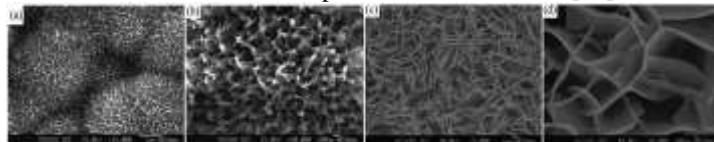


Figure 2: SEM images of the porous  $\text{CeO}_2$  (a, b) and Gd-doped  $\text{CeO}_2$  (c, d) prepared by an electrochemical deposition route [29]

#### C. ELECTRICAL PROPERTIES

##### a. IONIC CONDUCTIVITY IN DOPED CERIA

The oxide ion conductivity in ceria can be increased by substitution of a lower-valent metal ion for cerium. While the zirconia lattice structure is too small to accommodate a wide range of rare earth dopants, the host lattice of ceria is compatible with a wide range of rare-earth ion substitutions. Various alkaline-earth and rare earth oxides form solid solutions with ceria. The lower valencies of the dopant cations are charge compensated by the introduction of mobile oxygen

vacancies, which makes these doped ceria, promising solid electrolytes over an extended range of temperature and partial oxygen pressure. Gadolinium doped ceria is considered to be one of the best ceria based solid electrolytes [30]. Comparison of variation of electrolyte conductivity with temperature of doped ceria and YSZ is shown graphically in Figure 3 [31].

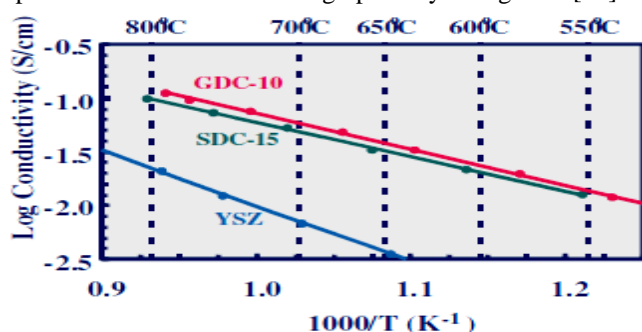


Figure 3: Ionic-conductivity of ceria based electrolytes<sup>[31]</sup>

Further in case of ceria based electrolytes existence of large ionic radius of  $\text{Ce}^{4+}$  ( $0.97\text{\AA}$ ) compared to  $\text{Zr}^{4+}$  ( $0.72\text{\AA}$ ) leads to much more open structure through which oxygen ion can easily migrate [32]. So, key factor in design of modified ceria is the choice of element as dopant as well as amount of dopant to be introduced. The ceria can be doped with  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Gd}^{3+}$  etc. to enhance conductivity [32,34]. But Doped ceria have weak structural stability under reducing conditions yet the feasibility of doped ceria as single electrolyte for LT- SOFC is reported at temperature below  $500^{\circ}\text{C}$  because ceria reduction is limited to electrolyte surface and there abouts only [35,36]. It is known that structural stability of ceria under reducing conditions is poor due to structural change of ceria from  $\text{CeO}_2$  to  $\text{CeO}_3$ , which has often prevented the doped ceria from being widely utilized for SOFCs [37]. The ionic conductivity is significantly increased by the impurity atoms such as  $\text{Na}_2\text{O}$ ,  $\text{CaO}$  and  $\text{SrO}$  when the sample of 3N purity of  $\text{CeO}_{2-x}$  is used [38]. The additive effect of alkaline earth oxides as dopants in ceria such as  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{MgO}$  and  $\text{BaO}$  was studied by Arai et al [39-40]. The addition of  $\text{CaO}$  and  $\text{SrO}$  enhances electrical conductivity of ceria and makes the activation energy lower. The addition of  $\text{BaO}$  and  $\text{MgO}$ , however, do not increase the electrical conductivity very much as compared with  $\text{CaO}$  and  $\text{SrO}$ . The additive effect of various rare earth oxides as dopants in ceria on the electrical conductivity has been studied by many investigators [41-48]. Electrical conductivity of ceria doped with 10 mol%  $\text{Sm}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$  reported by Yahiro et al. and concluded that  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ , is seen to have the highest electrical conductivity among ceria-based oxides. Balags and Glass observed the similar results using ten rare earth elements as dopants. The electrical conductivities of ceria doped with 10 mol% rare earth and alkaline earth oxides (MO) at 1073K obtained by the doping of  $\text{Sm}^{3+}$  ion among rare earth oxides and  $\text{Ca}^{2+}$  ion among alkaline earth oxides with an ionic radius of about 0.11 nm gives the maximum electrical conductivity. The maximum electrical conductivity at this radius of dopant ion is due to the similar ionic radius as the host ion resulting in the minimum association enthalpy between dopant ion and oxygen vacancy, which will be discussed in the next section. The electrical conductivities doped with  $\text{MgO}$  and  $\text{BaO}$  are exceptionally low, which may be ascribed to the insufficient

solubility of these oxides in ceria [50]. Depending on the type and amount of dopant, ceria oxide electrolytes reveal different electrochemical properties. Sintering agents can also influence the electrochemical behaviour of ceria oxide electrolytes, since they have an effect on the electrical conductivity and impurities [51]. Dopants with ionic radii similar to  $\text{Ce}^{4+}$  have a high solubility in structure and hence have high ionic conductivities. Co-doping of two or more aliovalent cations has also been reported as more efficient strategy [52-57]. Pure stoichiometric  $\text{CeO}_2$  has the calcium fluorite type of structure over temperature range from room temperature to melting point. The Ceria structure is known to tolerate a considerable reduction without phase change especially at elevated temperatures [58] and when  $\text{CeO}_2$  is reduced to  $\text{CeO}_{2-x}$  defects are formed in the form of  $\text{Ce}^{3+}$ . As the  $\text{Ce}^{3+}$  has one negative charge compared to normal lattice, these substitutional defects are balanced by oxide ion vacancies [59]. Oxide vacancies may also be introduced by doping with oxides of metals with lower vacancies like by dissolution of  $\text{CaO}$  or  $\text{Gd}_2\text{O}_3$  [60]. These Oxygen ion vacancies are responsible for ionic conductivity observed in doped ceria [61]. CGO-10 seems to be the most promising electrolyte for IT-SOFC. The ionic radii of  $\text{Gd}^{3+}$  is closer to the ionic radii of  $\text{Ce}^{4+}$  keeping in that manner the enthalpy of association  $\Delta H_a$  as small as possible hence the activation energy is also low. CGO-10 according to Steele performs better electrochemically with respect to CGO-20, revealing higher lattice ionic conductivity and better stability in reducing atmospheres below  $730^{\circ}\text{C}$  according to Kharton. But in this direction one of the main difficulties encountered is to obtain densified electrolyte at low temperature which usually needs to be exposed to high temperature over  $1600^{\circ}\text{C}$ , when solid state reactions are applied, leading to electrochemical performance degradation. Moreover single phase ceria based electrolytes have met a number of challenges that limit its the applications as SOFC electrolyte such as its low conductivity ( $5 \times 10^{-3}$  -  $10^{-2}$ )  $\text{Scm}^{-1}$  at  $600^{\circ}\text{C}$  for which is not sufficient for high performance SOFC that require  $0.1 \text{Scm}^{-1}$ . Also there is partial reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  in the operating fuel cell causing electronic conduction and a significant decrease in power output. Moreover ceria electrolytes have poor mechanical properties. These problems can be overcome by using two phase nanocomposite ceria based materials which exhibit improved ionic properties as compared to single phase materials below  $600^{\circ}\text{C}$  [62-64].

## V. CONCLUSIONS

This review highlights the recent advances of ceria based electrolytes in synthesis, electrical and mechanical studies. It is concluded that ceria-based electrolytes are strong candidates for SOFC electrolytes. After doping with certain amount of dopant conductivity can be increased. Gadolinium doped ceria is most commonly used electrolyte material at low temperature due to its high conductivity and high stability. Different dopants with different doping percentage can be synthesized with different synthesis methods in order to optimize the conductivity, cost as well as the overall performance of the electrolyte.

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