

# A Study on the Present Status of Zirconia based Electrolytes for Solid Oxide Fuel Cell

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## Short Communication

Received date: 22/08/2016

Accepted date: 28/10/2016

Published date: 02/11/2016

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**Keywords:** Electrolytes, SOFC, YSZ, ScSZ

### ABSTRACT

Aim of the present study is to provide an insight of development of electrolyte material for Solid oxide fuel cells (SOFCs). In the recent years the major interest is to reduce the working temperature of SOFC, so that, the problems like thermal instability, high chemical reactivity, etc. can be minimized as well as life of a fuel cell can be increased with reduction in the cost. Also the reduction of the working temperature of SOFCs is urgently required for its broad commercialization. But as the operating temperature of SOFCs depends upon the choice of electrolyte material, this requires the development of electrolyte materials with sufficient ionic conductivity even in low temperature range. The most commonly used electrolyte material in SOFC is ZrO<sub>2</sub> doped with trivalent oxides to introduce vacancies into the oxygen lattice through which the O<sub>2</sub><sup>-</sup> ions can be transported. In this paper prospects and problems of doped Zirconia as SOFC electrolyte are discussed and comparative study of performance of various materials as electrolyte is done. but none of them fully assure the growing need of waste management in major cities. In this work we have compared various methods of waste management and suggested a better method of plasma gasification, in which pyrolysis of solid waste takes place at very high temperature thus ensuring syngases as the output of gasifier. The method not only treats all types of waste, but also produces many useful by-products and electricity.

### INTRODUCTION

Because of our limited resources and increasing environmental concerns there is a need of environment friendly and efficient energy conversion technology. In this direction, fuel cells are promising candidates. These have very low environmental impact and also offer high efficiency, so they can be used in clean energy generating technologies. Among the various kinds of fuel cells, solid oxide fuel cells (SOFCs) are very important as they offer high efficiency, fuel flexibility, very less emission and use solid ceramics as electrolytes. Also solid electrolytes overcome the problems related with liquid electrolyte management <sup>[1]</sup>.

SOFC devices allow the direct conversion of chemical energy into the electrical energy through an electrochemical reaction. They consist of three parts anode, cathode and electrolyte. The major roles of the electrolyte in SOFCs are to give ions transportation from cathode to anode and to prevent gas diffusion or leakage from both cathode and anode sides. Apart from being an ionic conductor, a typical SOFC electrolyte should meet several important requirements, such as good thermal stability and chemical compatibility with other components of the cell. The electrolyte acts as a barrier between the electrodes and helps in transferring the oxide ions in between the electrodes. In order to avoid gas leaks between the cathode and the anode compartment, its relative density must approach the theoretical one and ionic conductivity should be sufficiently high, for the overall SOFC operation to be efficient <sup>[2]</sup>. To meet these requirements, a fully dense YSZ electrolyte is necessary. So, there is a need to densify the YSZ electrolyte at reduced temperature. Further, much of the research carried out nowadays on SOFCs is focused on optimizing the ionic conductivity of the solid electrolyte. Moreover, if the conductivity for oxygen ions in SOFC can remain high even at lower temperature, material choice for SOFC will broaden and many existing problems can be dealt with. We can optimize the fabrication and processing techniques, in order to improve performance of an electrolyte material. The main effect of the introduction of aliovalent cations in the zirconium oxide lattice is the creation of oxide ion vacancies, which are the charge carriers for enhanced ionic conductivity. Moreover, in these defective oxides, the high temperature cubic phase becomes stable at room temperature.

Oxide ion conducting electrolytes cover a wide range of materials including fluorite, perovskite, brown millite structured materials etc. Four main types of solid electrolyte systems which have been the subject of much attention are those based on fully or partially stabilized zirconia, doped ceria, doped LaGaO<sub>3</sub> and doped Bi<sub>2</sub>O<sub>3</sub> [3-7]. Amongst each system, there are a number of sub categories of materials with one or more dopant content, which enhance ionic conduction or increase phase stability. The type of dopant and its concentration has a significant effect on phase stability, chemical reactivity, and ionic conductivity, thermal and mechanical properties. Also there is a possibility that microstructures of these materials can be designed and optimized which leads to increased interest in pure and doped zirconias. For high ionic conductivity electrolyte materials that have been considered are doped zirconia, doped Ceria, doped Bismuth oxides etc. Addition of little amount of sintering additive has the possibility to change the sintering activity of YSZ as well as its ionic conductivity. Scandia doped zirconia is particularly interesting because they are stable even in such a reducing conditions as well as, their thermal and mechanical properties are similar to those of yttria stabilized zirconia, which is most widely used material as SOFC electrolyte [8,9].

### **Doped Zirconia as SOFC Electrolyte**

#### **Yttria stabilized zirconia as electrolyte**

As reported by Subhash C. Singhal (2007), Yttria-doped zirconia (YSZ) is the most widely used material for the electrolyte in SOFCs because of its sufficient ionic conductivity, chemical stability and mechanical strength. Pure zirconia (ZrO<sub>2</sub>) has a monoclinic structure up to a temperature of about 1446 K, above 1446 K it changes to the tetragonal modification. For temperatures higher than 2643 K zirconia adopts a cubic fluorite structure. The high temperature phases can be partially or completely stabilized at room temperature by doping with aliovalent oxides such as yttria (Y<sub>2</sub>O<sub>3</sub>), calcia (CaO), Scandia (ScO) or magnesia (MgO). Cubic stabilized zirconia has improved mechanical and thermal properties such as high strength, toughness, and thermal-shock resistance [10]. The ionic conductivity of stabilized zirconia depends on the size and concentration of the dopant. Yttria is the most commonly used dopant for stabilizing the cubic phase of zirconia. The addition of Y<sub>2</sub>O<sub>3</sub> stabilizes the zirconia cubic fluorite structure to room temperature and changes the non-conducting zirconia into an ion conducting material. In doping of ZrO<sub>2</sub> with Y<sub>2</sub>O<sub>3</sub>, the Zr<sup>4+</sup> cations in the ZrO<sub>2</sub> lattice are substituted by the Y<sup>3+</sup> cations, thereby forming oxygen vacancies to maintain charge neutrality in the lattice. The cubic fluorite structure has a face-centered cubic (FCC) zirconia lattice and a cubic oxygen lattice placed in the FCC lattice. The Zr<sup>4+</sup> cations occupy the tetrahedral sites and the O<sub>2</sub><sup>-</sup> anions the octahedral sites. The remaining octahedral sites are occupied by the Zr<sup>4+</sup> cations. Among various electrolytes, yttria stabilized zirconia (YSZ) is widely used as an electrolyte for SOFCs due to its high oxygen ion conductivity at high temperature. However, high temperature causes a thermal degradation, thermal expansion mismatch and even the interfacial reaction between electrodes and electrolyte [11]. Yttria doped zirconia poly crystals exhibit excellent strength and fracture toughness. Hence, upon the addition of a few percent of Y<sub>2</sub>O<sub>3</sub>, the cubic phase can be obtained at lower temperatures. The crystal structure of ZrO<sub>2</sub> transforms from monoclinic to tetragonal when the content of Y<sub>2</sub>O<sub>3</sub> increases, while a Y<sub>2</sub>O<sub>3</sub> addition of up to 8 mol% promotes further phase transformation from tetragonal to cubic. To avoid the phase transformation during the heating and cooling cycles, YSZ ceramics with the sole cubic phase is desirable for high temperature applications, such phase is called fully stabilized phase and this stabilized ZrO<sub>2</sub> has been used widely in several fields. Among these stabilized systems, yttria stabilized zirconia (YSZ) is the most common [12]. A fully (cubic) stabilized zirconia is obtained with an Y<sub>2</sub>O<sub>3</sub>-content of >7 mol%, while an Y<sub>2</sub>O<sub>3</sub>-content of about 2-6 mol% gives a partially stabilized zirconia [13]. Furthermore the addition of substitutional cation like Ca<sup>2+</sup>, Mg<sup>2+</sup> or Y<sup>3+</sup>, which have lower valency than zirconium ion (Zr<sup>4+</sup>), induces the generation of oxygen vacancies for charge compensation. For example, the substitution of Zr<sup>4+</sup> with Y<sup>3+</sup> causes the negative net charge in the lattice. The oxygen vacancies make it possible for oxygen ions to move through the electrolyte by hopping from vacancy to vacancy in the lattice. The concentration of oxygen vacancy is determined by the concentration of the dopant [14].

The only drawback of stabilized ZrO<sub>2</sub> is the low ionic conductivity below 750°C. This problem can be solved by decreasing the thickness of the YSZ electrolyte and to find other acceptors like Scandia to replace Y. The use of scandia stabilized zirconia (ScSZ) has recently shown more than double the power density achieved with conventional electrolyte materials for solid oxide fuel cells at intermediate temperature of (600-800°C) [15]. Although 8YSZ possesses high ionic conductivity, its low mechanical properties limit its applications. In order to increase the mechanical properties of 8YSZ, some factors like particle size and grain size should be considered and different sintering methods may be used [16].

#### **Scandia stabilized zirconia as SOFC electrolyte**

Scandia stabilized zirconia (ScSZ) is another candidate electrolyte for an application in SOFC that can operate below 800–850°C and development of ScSZ based electrolytes with high and long stable conductivity is of great importance. Though much higher ionic conductivity is found for cubic fluorite-type phase of ScSZ with Sc<sub>2</sub>O<sub>3</sub> content around 10 mol% compared to yttria-stabilized zirconia (YSZ), the system is poly phase and the conductivity is not very stable during extended annealing at operating temperatures. One way to avoid detrimental phase transformations and to stabilize the cubic modification of ScSZ is partial substitution of Sc by Y. It has been reported that substitution of Scandia by yttria in more than 10% successfully eliminates the cubic–rhombohedral phase transition. Along with composition the conductivity of Y doped ScSZ and its stability at that time are influenced by the presence of tetragonal phase in a minute amount which depends on the sintering temperature and yttria content as well [17]. ScSZ has been proved to have a high electrical conductivity and the highest ionic conductivity and specific conductivity

among zirconia doped with rare-earth ions materials. At the operating temperature of 700-1000°C the ionic conductivity of ScSZ materials is highest at around 10 mole percent  $\text{Sc}_2\text{O}_3$  [18]. ScSZ has been proved to have a high electrical conductivity and the highest ionic conductivity and specific conductivity among zirconia doped with rare-earth ions materials [19,20]. This has been attributed to the low association enthalpy of the defect reactions and the similarity between the  $\text{Sc}^{3+}$  and  $\text{Zr}^{4+}$  ionic radii. At the operating temperature of 700-1000°C the ionic conductivity of ScSZ materials is highest at around 10 mol%  $\text{Sc}_2\text{O}_3$  [21]. The ionic conductivity of 9 mol%  $\text{Sc}_2\text{O}_3$ - $\text{ZrO}_2$  is almost twice that of 8YSZ at 1000°C. Scandia doped Zirconia has high ionic conductivity compared with YSZ electrolyte because scandium has smaller ionic radius than yttrium which is very close to that of zirconium leading to highest conductivity [22]. The cubic phase in the ScSZ system has the highest ionic conductivity, so it is suitable for use as a solid electrolyte for SOFC [23]. However the cubic phase is not stable at lower temperatures (below 650°C), which has been causing an abrupt decrease in ionic conductivity. To suppress an undesirable phase transition doping with  $\text{Al}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{HfO}_2$ ,  $\text{Ga}_2\text{O}_3$  etc. can be done [24]. The ionic conductivity of 9 mol%  $\text{Sc}_2\text{O}_3$ - $\text{ZrO}_2$  is almost twice that of 8YSZ at 1000°C. However,  $\text{Sc}_2\text{O}_3$  is scarce and expensive for practical use as an electrolyte for large scale SOFC deployment [25].

As reported by Raj Singh et al. (2007) a composition with 9.2 mole%  $\text{Sc}_2\text{O}_3$  in  $\text{ZrO}_2$  was studied as an electrolyte for the SOFC operation at intermediate temperature range of 600°C-800°C. The new ScSZ ceramic is made by adding scandia ( $\text{Sc}_2\text{O}_3$ ) to zirconium oxide ( $\text{ZrO}_2$ ) to optimize the crystal structure. The new ScSZ exhibits improved ionic conductivity and mechanical strength as compared to YSZ, while its coefficient of thermal expansion is about the same as yttria stabilized zirconia (YSZ). According to Osamu Yamamoto et al. (2004) ScSZ with 8 mol%  $\text{Sc}_2\text{O}_3$  exhibited the cubic phase and those with 11 mol% and 12 mol%  $\text{Sc}_2\text{O}_3$  exhibit the rhombohedral phases at room temperature. As reported by S. Sarat (2000) addition of  $\text{Bi}_2\text{O}_3$  to ScSZ electrolyte is found to stabilize the cubic crystalline phase. Also 2 mol%  $\text{Bi}_2\text{O}_3$  doped ScSZ gives electrical conductivity of 0.18  $\text{S cm}^{-1}$  at 600°C.  $\text{Sc}_2\text{O}_3$ -doped zirconia poly crystals also have high fracture strength. According to Hirano, et al. (2000) significant improvement in the fracture strength, accompanied by an enhancement in the electrical conductivity, of zirconia poly crystals that were doped with 3-7 mol%  $\text{Sc}_2\text{O}_3$  has been obtained. As reported by J.T.S. Irvine et al (2005), it has been shown that 2 mol% yttria in Scandia stabilized zirconia results in formation of cubic phase and so avoids major phase changes which we believe to be detrimental to long term electrolyte stability. This addition of yttria can be achieved without significant impairment of the electrical conductivity of the scandia-stabilised zirconia. Further, SSZ has a higher conductivity than YSZ, at 780°C even higher than that of YSZ at 1000°C.  $\text{ZrO}_2$  with 11 mol%  $\text{Y}_2\text{O}_3$  shows no aging on annealing at 1000°C for more than 6000 hrs. Shows a phase transition from rhombohedral structure to cubic structure at 600°C with a volume change. This cubic phase can be stabilized at room temperature by the addition of small amount of  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$ . Scandia-doped zirconia has higher conductivity than YSZ but high cost of scandium and detrimental ageing effects in Scandia doped  $\text{ZrO}_2$  make it less attractive in commercializing SOFCs. However, the limited availability and high cost of Scandia have generally limited interest in its application in fuel cells. Many progresses on single-phase electrolyte materials with the enhanced ionic conductivity have been made, but they are still far from the criteria of commercialization. Further Scsz can be coped with dopant like Bismuth to improve properties. It has been reported that by varying the amount of  $\text{Bi}_2\text{O}_3$  in the ScSZ in the range of 0.25–2.0 mol% many structural as well conductivity behavioral changes are possible. The original ScSZ samples indicated a rhombohedral crystalline structure that in general has lower conductivity than the cubic phase. However, the addition of  $\text{Bi}_2\text{O}_3$  to ScSZ electrolyte was found to stabilize the cubic crystalline phase as detected by XRD. Impedance spectroscopy measurements in the temperature range between 350 and 900°C indicated a sharp increase in conductivity for the system containing 2 mol% of  $\text{Bi}_2\text{O}_3$  that is attributed to the presence of the cubic phase. In addition, impedance spectroscopy measurements revealed significant decrease of both the grain bulk and grain boundary resistances with respect to the temperature change from 600 to 900°C and concentration of  $\text{Bi}_2\text{O}_3$  from 0.5 to 2 mol%. The electrical conductivity at 600°C obtained for 2 mol%  $\text{Bi}_2\text{O}_3$  doped ScSZ was 0.18  $\text{S cm}^{-1}$  [26]. Also a small addition of 2 mol% yttria to Scandia stabilized zirconia results in stabilization of the cubic phase and so avoids the major phase changes that occur on thermal cycling of Scandia substituted zirconias, which might be expected to be detrimental to long term electrolyte stability.

## CONCLUSION

Yttria stabilized zirconia is a state of art material used for electrolyte in SOFC. Among various possible compounds as SOFC electrolyte, Scandia-stabilized zirconia shows the highest value of electrical conductivity in the electrolytic region. For the same ionic conductivity value of yttria-stabilized zirconia electrolytes, the working temperature of SOFCs with ScSZ electrolytes can be lowered. Scandia stabilized zirconias offer much better electrical performance than conventional yttria stabilized materials. However, the limited availability and high cost of Scandia have generally limited interest in its application in fuel cells. Political and economic changes over the last decade have significantly enhanced Scandia's availability, rendering it worth considering for commercial application, even though there is still some uncertainty about its ultimate market price.

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