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COMPOSITE OXIDE ELECTROLYTES FOR ELECTROCHEMICAL DEVICES

ABSTRACT

This work is focused on the comparative analysis of electrical, electrochemical and mechanical properties of composite ceramic oxide electrolytes, providing a brief overview of the materials having better performance than monophase ones in various high temperature electrochemical devices such as: solid oxide fuel cells, sensors for automotive industry, oxygen probes for controlling metal processing. Introduction of Al_2O_3 inclusions into cubic yttria – zirconia solid solution (8YSZ) matrix, caused the improvement of electrical and mechanical properties compared to pure 8YSZ. The $\text{Nd}_2\text{Ti}_2\text{O}_7$ secondary phase was also able to coexist with 8YSZ matrix and the fracture toughness K_{Ic} of 8YSZ ceramics was also significantly improved by $\text{Nd}_2\text{Ti}_2\text{O}_7$ addition.

Heterophase oxide ionic conductors in the system Calcium zirconate – cubic calcia zirconia solid electrolytes seem to be promising solid electrolytes for application in electrochemical probes for controlling oxygen dissolved in molten steel. The ionic conduction limit for electrolytes based on CaZrO_3 is lower than that for calcia – stabilized zirconia (13CSZ). Hence CaZrO_3 -based materials perform better at low oxygen concentration at molten alloys.

On the other hand composite layered ceramics involving $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2/\text{Bi}_{0.8}\text{Eb}_{0.2}\text{O}_2$ or $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2/\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_3/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ system exhibited better electrolytic stability in gas atmospheres with low oxygen partial pressure at the temperatures 600-800°C. These materials are successfully tested as electrolytes in solid oxide fuel cells. The gradient ceramic oxide electrolytes seems to overcome the limitation of applying them as solid electrolytes in solid oxide fuel cells for long time performance.

Key words : *composite dispersed solid electrolytes, gradient ceramic electrolytes, solid oxide fuel cells (SOFC), electrochemical oxygen probes, ceria, zirconia electrolyte.*

INTRODUCTION

Ceramic oxide ionic conductors have attracted much attention because of their possible application as solid electrolytes in the electrochemical devices such as: solid oxide fuel cell (SOFC), gas sensors, probes for determination of the oxygen dissolved in molten metals, oxygen pumps, thermoelectric generators, coulometric timers or chemical reactors [1-3]. The major scientific applications of ionically conducting solids are electrolytes in galvanic cells, designed to provide fundamental thermodynamic and kinetic data [4-7]. Solid electrolytes satisfy a large number of requirements: fast ionic transport, negligible electronic conduction, and thermodynamic stability over a wide range of temperature and oxygen partial pressure. In addition, they must have a thermal expansion value compatible with that of electrodes and other construction materials,

suitable mechanical properties and negligible interaction with electrode materials under operation conditions [8-9]. Due to a growing interest in environmentally friendly and energy – saving technologies, developments in the field of SOFC and other high temperature electrochemical devices have been considerably intensified in the last 15 years. In particular, some novel oxygen ionic conductors have been reported in the literature, including LaGaO_3 , NdAlO_3 – based perovskites, derivatives of $\text{Bi}_4\text{V}_2\text{O}_{11}$ (BIMEVOX) and $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOXY), several new pyrochlores with relatively high ionic transport such as $(\text{Gd,Ca})_2\text{Ti}_2\text{O}_7$, apatite derived from $\text{Ln}_{10-x}\text{Si}_6\text{O}_{26}$, where Ln is a rare earth cation [10-14].

The well-known MO_2 ($\text{M} = \text{Zr, Ce}$)-based solid electrolytes are still an attractive candidate to be applied in SOFC and other devices. The application of a new method for manufacturing gas-tight thin films, like (spray-pyrolysis deposition, tape-casting, spin-coating, electrophoretic deposition, lithography) is one possibility of obtaining a material with sufficient ionic conductivity to be applied as solid electrolytes in electrochemical devices operating below 800°C [15-18].

To improve electrical and mechanical properties as well, a dispersed heterophase can be introduced into a solid electrolyte matrix [19-21]. Since the first experiments performed by Liang [22] on $\text{LiI-Al}_2\text{O}_3$ composites, numerous studies have been performed on various solid electrolytes composites. The effect of conductivity increase was found in many systems based either on halides (eg. AgCl , BaF_2 , CaF_2) or oxides (ZrO_2 , $\text{Ca-}\beta''\text{-Al}_2\text{O}_3$) with alumina, titania or silica inclusions [23-26].

Generally, in the composite material, the ionic conductivity increases strongly with the concentration of the dispersed phase and then decreases when after reaching maximum. To interpret the results of conductivity measurements in those composites, several theoretical models were proposed. All of them assumed interactions between mobile charged defects and the surface of the dispersed inert phase, leading to space charge region with defect concentrations differing from the intrinsic bulk concentration [27-32]. Uvarov, *et al.* presented a model that considered the surface conductivity and the microstructure of composite solid electrolytes, and he used it to explain their electrical conduction behaviour. He was shown that enhancement in electrical conductivity for such composites strongly depends on the sample preparation conditions, and higher conductivities are expected if a better contact between the solid electrolytes and the dispersoid can be achieved [33].

Solid electrolytes exhibit predominantly ionic conductivity only over a limited range of temperature and chemical potentials. Thus, the electrolytic conduction domain is an important factor limiting the application of these materials in electrochemical devices. Most of ionic conductors operate under a severe chemical potential gradient. Taking into consideration the functional gradient, one can design two or more layers of composite electrolytes with a better performance than for monophase materials in gas sensors, or solid oxide fuel cells [34-38].

K.T. Jacob, *et al.* have given a general analysis of electromotive force (EMF) of a cell incorporating composition gradient solid electrolytes [39-41]. The theoretical analysis of a bilayer ceramic oxide electrolytes in solid oxide fuel cell was also considered [42]. Some experimental studies showed that solid electrolytes with gradient composition were also successfully applied for the thermodynamic data studies in $\text{La}_2\text{O}_3\text{-ZrO}_2$ [43] and $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4$ system [44].

The aim of this paper is to give an overview of the electrical and mechanical properties of composite oxide solid ionic conductors and their possible application as

solid electrolytes with a better performance than monophasic material in solid oxide fuel cells, electrochemical gas sensors or probes for controlling metal processing.

ZIRCONIA –BASED ELECTROLYTES

Zirconia-yttria (8 % mol Y_2O_3 in ZrO_2 - 8YSZ) with fluorite structure is the oxygen ion conductor mostly used as a solid electrolyte in electrochemical gas sensors, probes, solid oxide fuel cells, pumps or solid galvanic cells. Due to its high values of ionic oxide conductivity, low manufacturing costs, chemical stability under oxidizing or reducing gas atmospheres [45-48].

A conventional SOFC using YSZ as a solid electrolyte requires a high – operating temperature (1000°C), resulting in serious problems as: chemical reaction between components, thermal degradation of materials or cracking during cycles. This implies a short service life of cell and requires expensive metallic materials for interconnectors. Lowering the operation temperature of SOFC is the main goal of technology of solid fuel cells, and it constitutes a challenge for the materials under design and development [49-51].

Planar solid oxide fuel cells are currently being developed in two main geometrical variants with different structural support (*Fig. 1*). SOFC concepts based on electrode substrates (mostly anode) allow to reduce the electrolyte thickness to thin layers [52-55].

Fig 1. SOFC single cell configuration. Reprinted from [52] with permission Elsevier.

In the electrolyte supported variant, a much thicker membrane (~100-200 nm) is required for mechanical robustness. The main advantages of electrolyte – supported cells are: a relatively strong support from dense electrolyte, lower susceptibility to failure due to anode reoxidation and cathode reduction. In this case, the cell resistance strongly depends on electrolyte thickness; the anode supported SOFC concept has the attractive advantage for intermediate temperature performance. The difference in the thermo-elastic behaviour between the individual layers in the planar SOFC cell composite generates residual stresses that can cause mechanical integrity problems.

However, there are some specific advantages of electrolyte supported cell in respect to mechanical integrity. The electrolyte supported cell has a more or less symmetric layer structure, and thus, residual stresses generate smaller curvature, i.e the cells are essentially flat [56,57].

This consideration indicates that the application of 8YSZ in solid ionic devices means not only high conductivity, but also better mechanical properties (flexural strength and fracture toughness). The thin solid electrolyte in SOFC configuration needs to be strong and tough enough to withstand room temperature assembly stresses and to be mechanically stable for long periods at high temperatures in reducing and oxidizing atmospheres. Therefore, the enhancement of mechanical properties of the solid electrolyte is an important problem to be solved [58-61].

The electrical and mechanical properties of composites 8YSZ with Al_2O_3 inclusions have been studied for more than 20 years. In spite of such interest in zirconia-alumina – based composites, some results described in the paper quoted are far from being complete, and their interpretation is rather difficult. Generally, samples 8YSZ containing up to 7– 9 wt. % at temperatures 200 - 800°C showed electrical conductivity values higher than those of cubic ZrO_2 stabilized yttria, although in some cases a deterioration in ionic conductivity was observed. The increase in electrical conductivity of cubic zirconia-alumina particulate composites is generally attributed to the interaction between alumina and silica, which modifies interfaces and grain boundaries as a result of purification from the silica –rich glassy phase [62-64].

An addition of Al_2O_3 enhanced also the flexural strength and fracture toughness of 8YSZ / Al_2O_3 composites as compared to the monophase 8YSZ. However, some data also indicates that such an addition improves mechanical properties, but reduces electrical conductivity [65-67]. Controversial increase in flexural strength up to 480 MPa, without changes of ionic conductivity, have also been reported [68].

Guo summarizes and analyzes the positive and negative effects of Al_2O_3 additions on the electrical properties of ZrO_2 . An Al_2O_3 addition may cause an increase in bulk resistivity, mainly because of formation of defect associates and insulating Al_2O_3 second-phase particles. Al_2O_3 inclusions content within the solubility limit increases the grain boundary space-charge potential, but when Al_2O_3 content is over the solubility limit; however, it scavenges the silica-rich phase from grain boundaries, thereby decreasing the grain boundary resistivity [69,70].

Systematic research on the influence of both alumina content and microstructure on the electrical and mechanical properties was also reported in detail [71-73]. To visualise the influence of $\alpha\text{-Al}_2\text{O}_3$ inclusions on electrical conduction properties of the composites, the relative total conductivity (σ/σ_0), where σ_0 is the conductivity of pure 8YSZ matrix, was plotted against the alumina content - *Fig 2* - for two series of (HG) and (HA), samples. Materials originating from gamma-alumina powder were marked as HG –series, while those prepared from alpha-alumina powder - as HA –series.

In both cases, inclusions of 7.5 wt. % of $\alpha\text{-Al}_2\text{O}_3$ caused the maximum enhancement in the conductivity by factors 6.5 and 13, which depended, respectively, on the sample and microstructure. The composites obtained from gamma – aluminium powder show a higher increase in conductivity than those prepared from alpha-alumina powder. The average grain sizes of the zirconia matrix are practically the same in the (HG) and (HA) – series, whereas the average grain sizes of alumina inclusions in both series differ by a factor 2 [72].

Fig.2. Changes of the relative total conductivity (σ/σ_0 , σ_0 -conductivity of pure ZrO_2 matrix) for both series as a function of alumina content at 400°C . Reprinted from [72] with permission PTCer.

In both the series investigated, after the maximum (at higher alumina content), the conductivity value decreases rapidly. The influence of chemical composition and microstructural features on mechanical properties of cubic zirconia-alumina was also investigated. The maximum values of fracture toughness K_{Ic} was reached at 5 and 10 % alumina inclusions for the composites of the HA and HG, respectively. The highest increase in fracture toughness K_{Ic} (up to $3.9 \text{ MPa}\cdot\text{m}^{0.5}$) has been found when inclusions size was comparable to the matrix grain [73]. These results indicate that the microstructure (size of inclusions and matrix) has a strong influence on the electrical and mechanical properties.

Recently, Chan and Yang have developed a new toughening process, called piezoelectric secondary phase toughening, in which a piezoelectric secondary phase is introduced into the ceramics matrix as a toughening agent, and the energy dissipation resulting from domain wall motion and piezoelectric effect is considered to be the toughening mechanism. The piezoelectric secondary phase toughening approach has been applied successfully to several systems: $\text{BaTiO}_3/\text{Al}_2\text{O}_3$, $\text{Nd}_2\text{Ti}_2\text{O}_7/\text{Al}_2\text{O}_3$ [74]. $\text{Nd}_2\text{Ti}_2\text{O}_7$ as a secondary phase was able to coexist with an 8YSZ matrix, and the fracture toughness K_{Ic} was scientifically improved by a $\text{Nd}_2\text{Ti}_2\text{O}_7$ addition. An optimal value of $8 \text{ MPa}\cdot\text{m}^{0.5}$ was obtained for 8YSZ including 15 % mol $\text{Nd}_2\text{Ti}_2\text{O}_7$ composite material, and this value was 2.5 times higher than that of the monophase 8YSZ [75].

CERIA –BASED ELECTROLYTES

Ceria is a promising solid electrolyte for application in solid oxide fuel cells, on-board diagnostic sensors for monitoring hydrocarbons and other exhaust gases at intermediate temperature range $600 - 800^\circ\text{C}$ [76-80]. The primary problem encountered in using ceria-based electrolytes for IT-SOFC is the partial reduction of ceria in fuel atmospheres [81-85]. This results in n-type electronic conductivity, causing partial internal electronic short circuits in the cell. It also results in an expansion of the crystal

lattice, which leads to mechanical degradation either inside the electrolyte or at the electrolyte - electrode interface. It has been reported that the reduction of ceria can be neglected at a lower temperature - around 600 -700°C. However, such low temperatures are not suitable for singly doped ceria - $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Sm}, \text{Gd}, \text{Y}$ where $x = 0.15-0.20$) as SOFC's electrolyte, due to high resistivity of this material [86,87].

A structural modification of ceria solid solutions is one among the possible ways to improve their electrical conductivity [88,89]. Co-doped ceria of $\text{Ce}_{0.85}\text{Gd}_{0.15-x}\text{Sm}_x\text{O}_2$, wherein $0.05 \leq x \leq 0.1$, showed much higher ionic conductivity at 500-700°C. These materials seem to be more fitting electrolyte materials for IT-SOFC [90]. Maricle, *et al.* also reported that due to co-doping small quantities of praseodymium in $\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$ solid solution, the application region is shifted by two orders to magnitude to lower oxygen partial pressure [91]. The co-doping ceria with calcia and samaria also leads to an improvement in their electrolytic properties when compared to only samaria-doped ceria [92,93].

The application of the layered materials or functionally gradient oxide electrolytes is another possible way to improve their performance in a classical solid oxide fuel cell or single-chamber cell [94-96]. Ceria-zirconia sandwich structured composite film electrolytes were designed in order to offer high ionic and electronic conductivity films. Calculations of oxygen potential profile in the composite film electrolyte indicate that 8YSZ thin films kill the electronic current of ceria without affecting ionic conductivity. Composite films were successfully prepared in a co-firing process. De-lamination between yttria-doped zirconia (YSZ) or gadolina doped ceria (GDC) layers was overcome by the formation of a solid solution phase at the interface of the two films. The resultant composite films showed not only poor electrical conductivity as compared to theoretical values, but also poor mechanical strength values and lattice expansion in reducing atmospheres. The problems of improved mechanical properties still need a solution [97].

Fig. 3. Conceptual representation of an erbia-stabilized bismuth oxide/ samaria-doped ceria (ESB/SDC) bilayer electrolyte showing the effect of relative thickness on interfacial p_{O_2} . Reproduced from [98] with permission ACS

The bilayer electrolyte composed of two highly conductive oxide $(\text{Er}_2\text{O}_3)_2(\text{Bi}_2\text{O}_3)_{0.3}$ (ESB) on the high p_{O_2} side and $(\text{Sm}_2\text{O}_3)_{0.1}(\text{CeO}_2)_{0.8}$ (SDC) on the low p_{O_2} (Fig. 3) seems to be a promising solution [98]. The advantage of this design over the SDC/YSZ bilayer is that SDC and ESB are both conductive enough to serve as intermediate IT-SOFC electrolytes. Thus, at worst, and ESB/SDC bilayer SOFC should

have the conductivity of SDC but with an improved efficiency since the electronic flux barrier prevents the ESB layer from decomposition at very low p_{O_2} as in shown in Fig.4 SDC can act both as electrolyte (ionic) and anode (mixed ionic-electronic) depending on local p_{O_2} . Therefore, a higher t_i can be obtained by bilayer ESB/SDC electrolytes than with SDC. These results also indicate higher values of electrical conductivity and better performance in solid oxide fuel cells. Fig.4 shows a comparison of cell performance of SDC and SDC/ESB electrolytes at 800°C. Cells are 0.8 mm thick with a Pt-H₂/H₂O anode and an Au-O₂ cathode.

Fig. 4. Comparison of cell performance of SDC and SDC/ESB electrolytes at 800°C. Cells are 0.8 mm thick with Pt-H₂/H₂O anode and Au-O₂ cathode. Reproduced from [99] with permission ECS

The increase in values of OCV and power density solid oxide fuel cell with SDC/ESB electrolyte as compared to only SDC electrolyte was observed [99].

The incorporation of a protonic BaCeO₃-based ion conductor into the composite electrolyte structure also leads to a better performance of the electrolyte in SOFC. The multilayered Ce_{0.9}Gd_{0.1}O₂/BaCe_{0.8}Y_{0.2}O_{3-α}/Ce_{0.9}Gd_{0.1}O₂ (GDC/BCY/GDC) electrolyte on a Ni-Ce_{0.8}Sm_{0.2}O_{1.9} anode-support was prepared by tape-casting method. The overall electrolyte thickness ranged from 30 to 35 μm, including 3 μm thick BCY layer. The designed composite material was also successfully tested as ceramic electrolyte in solid oxide fuel cells at the temperature 500-700°C, and reached an OCV of 846-1024 mV, which was higher than for a single layer GDC electrolyte under the same conditions. The investigated composite electrolyte also may be applied as a membrane with direct methane operated SOFC or single chamber fuel cell [100].

CaZrO₃ – BASED ELECTROLYTES FOR OXYGEN ELECTROCHEMICAL PROBES

Electrochemical oxygen sensors based on partially or fully (Y₂O₃, CaO, MgO) stabilized zirconia have been developed, and they are used in steel making, nickel and copper refining processes. Although they are single – reading probes, these sensors

achieved high industrial standard worldwide. However, there is necessity to improve their performance [101,102]. Up to now no suitable oxygen probes for on-line measurements (especially in steel production) have been developed. Steels with very low oxygen content can establish an oxygen partial pressure that is low enough for significant electronic conductivity to occur in zirconia. Significant electronic conductivity in the electrolyte can lead to an erroneous sensor output [103]. One area of improving the performance of electrochemical probes with respect to applying them in on-line measurements in metallurgy is the substitution of zirconia – based solid electrolyte by an alternative ceramic material, which remains a pure oxygen ion conductor to lower oxygen pressure. Good mechanical properties, thermal shock resistance and thermodynamic stability are also required for such applications.

The ionic conduction limit for yttria-doped thoria (YDT) is lower; therefore, these electrolytes perform better at a low oxygen activity. Due to radioactivity and costs, thoria or hafnia-based electrolytes are rather rarely applied in steel industry [104,105].

Calcium zirconate – composite materials with cubic calcia-zirconia solid solution as inclusions seem also to be appropriate solid oxide electrolytes for high temperature application [106-108]. Fig.5 illustrates changes of the CaZrO_3 weight fraction, determined by the Rietveld refinement as function of calcia content in samples investigated. Orthorhombic CaZrO_3 as only singly phase was detected by XRD method in the samples containing from 0.50 to 0.515 mol fraction of CaO . Changes of the phase content in the CaZrO_3 -based materials strongly depended on oxides being in excess. Even in the sample with the smallest ZrO_2 excess a second phase of cubic calcia - zirconia solid solution was observed. In this way composite materials in the system CaZrO_3 -cubic calcia-zirconia solid solutions could be obtained [109, 110].

Fig 5. CaZrO_3 weight fraction as a function of initially assumed calcia to zirconia molar ratio [110].

Electrical properties of CaZrO_3 -based materials, calcia stabilized zirconia and thoria-based electrolytes in the temperature range 200-1600°C are listed in table 1. The values of electronic conduction P_e (defined as the oxygen partial pressure at which the ionic and n – type electronic conductivities are equal) are also given.

Table 1. Electrical properties of CaZrO_3 -based materials, calcia stabilized zirconia and thoria-based electrolytes in the temperature range 1000-1600°C. Data from [111,112].

x in (CaO) _x (ZrO ₂) _{1-x}	σ (S/cm)		Ea, eV	P'_e (bar), $t_{\text{jon}} = 0.5$ at 1600°C
	1000°C	1600°C		
0.5	$1.30 \cdot 10^{-6}$	$5.1 \cdot 10^{-3}$	2.25	
0.48	$6.20 \cdot 10^{-6}$	$2.8 \cdot 10^{-2}$	1.37	$1.5 \cdot 10^{-18}$
0.45	$4.60 \cdot 10^{-5}$	$5.8 \cdot 10^{-2}$	1.34	$1.4 \cdot 10^{-18}$
0.30	$4.14 \cdot 10^{-3}$	$3.2 \cdot 10^{-1}$	1.33	
0.13(13CSZ)	$5.1 \cdot 10^{-2}$	$6.0 \cdot 10^{-1}$	0.72	$1.2 \cdot 10^{-15}$
8% mol Y ₂ O ₃ in ThO ₂ (8YDT)	$2.1 \cdot 10^{-2}$	$1.3 \cdot 10^{-1}$	0.78	$1.2 \cdot 10^{-18}$

The presence of calcia – stabilized zirconia as a second phase in CaZrO_3 -based materials led to improvement of electrical conductivity, due to its better conductive properties compared to CaZrO_3 electrolyte. The 13CSZ or 8YDT – based electrolytes exhibit comparatively high values of electrical conductivity σ from 0.13 to 0.60 (S/cm) at 1600°C. The electrical conductivity of solid oxide electrolytes based on CaZrO_3 is about one order of magnitude lower but still sufficient to apply them as components of electrochemical devices. In order to calculate the oxygen activity in steel melt from EMF measured a knowledge of the parameter P'_e is essential [113, 114]. The CaZrO_3 -based materials exhibited lower values of electronic conduction than that of monophase $(\text{CaO})_{0.13}(\text{ZrO}_2)_{0.87}$ electrolyte. This might indicate a better electrochemical properties of CaZrO_3 – composite electrolytes at lower oxygen partial pressure at high temperature applications [115].

The composite $(\text{ZrO}_2)_{0.55}(\text{CaO})_{0.45}$ was tested as solid electrolyte in electrochemical oxygen probes for liquid iron or steel including 0.0025 to 0.20 % dissolved oxygen at 1600°C. The recorded EMF values for galvanic cell involving composite electrolyte-based on CaZrO_3 were close to theoretical EMF values calculated from Nernst equation. The obtained results were compared with EMF values measured in the same conditions with electrochemical probes including monophase 13CSZ. As opposed to electrochemical probes with only calcia – zirconia solid electrolyte, the values of dissolved oxygen determined by means of electrochemical probes with CaZrO_3 electrolyte did not require any corrections to calculations so as to regard partial electronic conductivity. The composite material performs better than only 13CSZ in solid galvanic cell with low oxygen partial pressure at high temperatures. The chemical stability of CaZrO_3 - based electrolytes in liquid metals such as nickel, copper or iron, was also investigated. Microstructural observations carried out with scanning microscopy and EDS analysis did not reveal any products of the reaction between CaZrO_3 -based samples and metallic melts. The highest thermal resistance in the cyclic temperature conditions and good thermal resistance render the prepared material to be a promising electrolyte for metallurgical application and other application in low oxygen partial pressure [116].

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