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Ceramic materials for SOFCs: Current status

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It is well known that the main parts of Solid Oxide Fuel Cells (SOFCs) are build from ceramic materials. Namely the ceramic materials and composites, used for SOFCs manufacturing, are objects of the overview in the present work. The analysis carried out covers the last current publications in the field discussed. Special attention and examination in details have been done on patents state-of-the-art. After a background and short classification of the ceramic SOFCs materials the attention is focused on cathode, electrolyte, anode, interconnection and sealing materials. Their requirements, structure, thermal stability, composition control and behavior, processing and performance are the object of overview. A correlation has been made between the phase diagrams oxygen incorporation and transport, and SOFC advantages, generally for materials of lanthanum- base perovskite family. In order to analyze the innovative investigations regarding the patent branch of the SOFCs development and application, an object of review was patents from Japan, USA, Germany and European Union. Some examples of the inventions with accent on the ceramic materials are shown. In addition the tendency regarding R & D activities of SOFCs development materials from the leading companies in the world is analyzed. On the base of the most important technological and economical parameters of cell cathode/electrolyte/anode materials an attempt for evaluation and correlation has been made and innovative conceptions are shown.

Key words: Ceramic materials, SOFCs, current analysis, patent status, cathodes, electrolytes, anodes, lanthanum – base perovskites, phase diagrams

Materiales cerámicos para SOFCs: Situación actual

Es bien sabido que los componentes principales de las celdas de combustible de óxido sólido (SOFCs) estan constituidos por materiales cerámicos. Dichos materiales cerámicos y materiales compuestos que se utilizan en la fabricación de SOFCs son objeto de estudio en el presente trabajo. El análisis llevado a cabo incluye la revisión de las últimas publicaciones en la materia, con una especial atención y examen minucioso sobre las patentes más relevantes. Después de una revisión y breve clasificación de los materiales SOFCs cerámicos, el estudio se centra en la descripción del cátodo, electrolito y ánodo, así como de la unión y materiales de sellado. También se han estudiado sus requisitos, estructura, estabilidad térmica, control composicional y de comportamiento, procesado y rendimiento. Se ha establecido una correlación entre los diagramas de fase de incorporación y transporte de oxígeno y las ventajas de los SOFC, generalmente para materiales de la familia de las perovsquitas basadas en lantano. Con el fin de analizar las investigaciones innovadoras que conciernen al campo del desarrollo y aplicación de SOFCs, se han revisado patentes de Japón, Estados Unidos, Alemania y la Unión Europea. Se dan algunos ejemplos de dichas patentes en las que destaca el papel de los materiales cerámicos. Además, se ha analizado la tendencia en actividades de I + D sobre los SOFCs en compañías líderes mundiales. Se ha intentado realizar una evaluación y correlación en base a los parámetros tecnológicos y económicos más importantes de los materiales de celda cátodo/electrolito/ánodo y se han mostrado conceptos innovadores.

Palabras clave: Materiales cerámicos, SOFCs, análisis actual, estado de patentes, cátodos, electrolitos, ánodos, perovsquitas basadas en lantano, diagramas de fase.

1. INTRODUCTION

It is well known that in the next decades the human civilization will meet the challenges of exhausting the energy sources of our planet. In this context many efforts have been made to decide the worldwide energy problem. The intensive action in the field of fuel cells (1) today gives us one of the best decision of the problem to convert energy from one form to another. There are mainly three zones of powerful R&D, innovations and activities to the fuel cell science and application; namely Europe, North American and Asia Pacific Zone & Japan (2). As a selection the following companies actively operate in relation to innovative investigations, fuel cells development and market application: in Europe (Siemens, Research Center Uluch, BMW, PSA Peugeot, Citroen, British Gas), North America (Argonne National Labs, Siemens Westinghouse Co., Exxon, Texaco) and in Japan (Toyota, Toto, Toho Co., Tokyo Electric Power and etc.).

The electrolyte used defines the key properties of a fuel cell and according to its nature there are four distinguished types of inorganic fuel cells (excluded PEMFC and DMFC, which are on polymer base) namely:

(i) alkaline fuel cells (AFC),
(ii) phosphoric acid fuel cells (PAFC)
(iii) molten carbonate fuel cells (MCFC) and
(iv) solid oxide fuel cells (SOFCs).

The term *FUEL CELL* means Electrochemical Energy Generator (Electricity production by chemical reaction) (1) and *SOFC*- is a solid oxide ceramic base unit for generation of electricity from hydrocarbon fuels.

It should be noted that a worldwide progress exists for SOFCs systems development. For example Siemens Westinghouse Power Co. has published tubular design SOFCs to provide 300 kWe of electricity. There is another project for production of 1 MWe- Class of power, both with a SOFC/GT hybrid stack- gas turbine arrangement. There are many companies, which offer SOFCs systems for residential (stationary heat generation) application. Another applications are in the military transport, and auxiliary power units for trucks, and automobiles as well (3).

The advantages of a SOFCs include the use of i) high temperature heat to reform hydrocarbon fuels to produce a mixture of H2 and CO (syngas) ii) a high cell electrical efficiency, iii) usage of mixed conducting ceramic elements as electrodes and solid electrolyte i.e. lack of noble catalysts used, iv) relatively simple reformer technology and compatibility with of a variety of hydrocarbon fuels v) an ability to use syngas (CO + H_2) as a fuel, and vi) no preliminary humidification procedure of the reactants is necessary. The disadvantages are high temperature enhances breakdown of cell components and need to insulate the technology equipment to protect from injury, i.e. requirements of more costly construction materials.

Nowadays, there are two major SOFCs designs widespread which are available on the market, namely: tubular (t-SOFCs) (2,4,5) and planar (p-SOFCs) (2,4,5). According to ref. (4) the operating principle of a SOFC is shown in Fig. 1. Evidently is that state-of-the-art SOFC cell incorporates four ceramic components. First a cathode (air electrode) as Sr-doped lanthanum manganite, second an YSZ solid state electrolyte, third a cermet anode, usually Ni-YSZ and fourth Sr- doped lanthanum chromite interconnect or bipolar plate. The sealing materials are glass, ceramic or glass-ceramic composite materials. The chemical nature and structure of the materials use predominantly the respective useful properties and effective performance. The SOFCs materials must possess ionic, i.e. oxygen anionic conduction for the electrolyte and mixed ionic and electronic conduction (electrodes). Other requirements are far beyond mechanical strength and toughness, thermo- mechanical and thermo-chemical stability, to maximum low temperature operating range, to high catalytic activity and virtually high perm selectivity behavior at a high temperature treatment.

Regarding materials for SOFCs applications there are some review papers. For example the work of Kawada and Yokokawa (6) where the materials used for SOFCs are reviewed in correlation with thermodynamic calculations. A useful selection of chemical potential diagrams in parallel to calculated phase diagrams are applied to study the structural-chemical stability and compatibility of the materials. Ref. (7) is addressed to development of new SOFCs materials that can operate at lower temperatures. The data are extracted from the recent research performed at Argonne National Laboratory. Functionally graded cathodes for SOFCs are object of experiments and review in ref. (8). In the same direction can be marked the work of Kilner (9). He offers a work with accent on the cathode (air electrode) kinetics phenomena discussion, oxygen self-diffusion and surface exchange transport as well as an overview of the defect chemistry of the mixed conductive perovskites. There is a perfect overview presented by Singhal (10) regarding the materials and fabrication methods used for the different cell components. We must underline the extended review (over 400 ref.) of Minh (11) which paper reviews the science and technology of the ceramic fuel cells, commonly referred as SOFCs. Discussion on materials and processing studies and recently built power generation systems is presented, as well. Useful information is located into the current issue of ECS for SOFC(V), SOFC(VI), and SOFC(VII) conferences. The last one has been held in Tsukuba, Japan, where 126 papers have been presented. In the proceedings there are special sections developed with a focus on processing and performance of electrolyte materials, cathode materials, anode materials, and interconnection materials (12). In this context can be also treated the review paper (2) about state-of-the-art of the patent issue and innovations steps regarding SOFCs materials and application in systems. A bibliography analysis from Chemical Abstracts for a period of 1996 to 2001 shows an increasing of publications of SOFCs as is shown in Fig. 2.

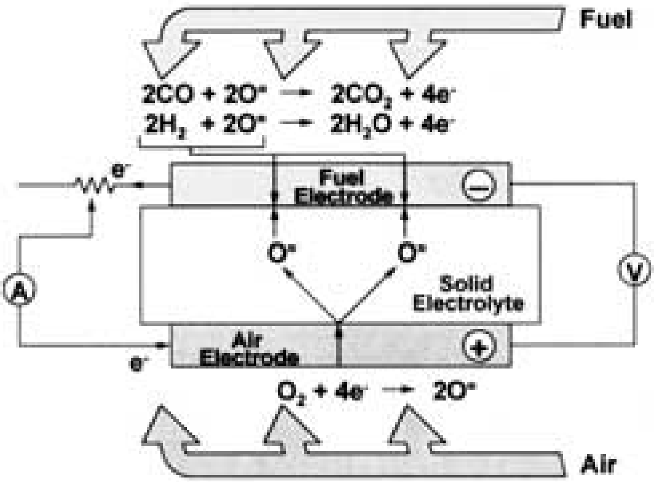

Figure 1 Operating principle of a SOFC according to (4).

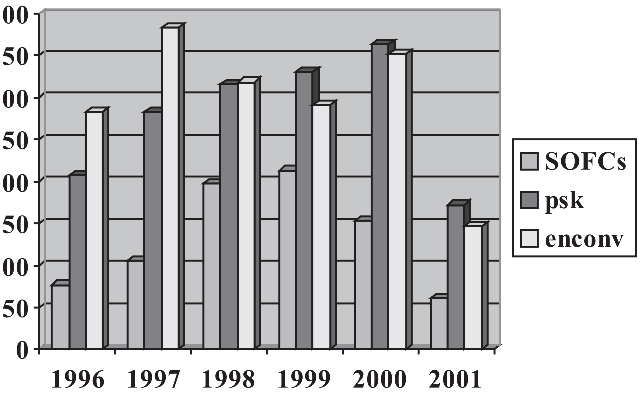

Figure 2 A bibliography analysis for a period of 1996 to 2001 shows an increasing of publications of the field of SOFCs; A correlation is shown in comparison to perovskites (psk) and materials for energy conversion (enconv).

The aim of the present paper is to present an overview regarding the ceramic materials used for SOFCs development. The analysis carried out cover the last current publications about cathode, electrolyte, anode, interconnection and sealing materials used. In order to analyze the innovative investigations regarding the patent branch of the SOFCs development and application object of review will be JP, US, DE and EP class of patents.

2. CERAMIC MATERIALS

2.1. Cathode materials

The cathode materials have to meet the following requirements:

(i) To ensure a stable layer with a sufficient porous microstructure parallel with good adhesion to the another SOFCs ceramic components (13)
(ii) To possess high electronic conductivity (> 100 S.cm^{-1})
(iii) To possess an effective ionic (oxygen) conductivity (~10^{-1} S.cm^{-1})
(v) High catalytic activity to O_2 dissociation and next reduction process ($1/2O_2 + 2e^- = O^{2-}$).
(vi)Compatibility and minimum reactivity with the electrolyte and the interconnection with which air electrode comes into contact (10)

The thermal expansion coefficient must to be equivalent to the other cell components (10,14).

The most effective ceramic materials covered the above requirements are those from perovskite ABO_3 family. Fig.3 shows an ideal perovskite structure. In the case of site structural substitution the value of Goldschmidt factor is important (15). Stable perovskite structure requires t – factor value in the range from 0.75 to 1. According to the crystallographic data in [(16) a typical perovskite structure of BaTiO3 after a calculation by us is presented in Fig. 4.

Usually for SOFCs cathode material A is a rare- earth element and B is a 3d- transition element (Fe,Mn,Ni,Co). Rare- earth is substituted with alkali-earth (Ca^{2+}, Sr^{2+}, Ba^{2+}) element/s for creation p-type perovskite oxide. A good selection and correlation of electrical conductivity of the perovskites vs. the temperature is presented in Fig. 5 (6,17). It is evident that in dependence of the composition (A- and B- type of substitution) there is wide variety in the conductivity that is in close relation to the oxygen partial pressure, as well.

It is necessary to underline that $La_{1-x}Sr_xMnO_3$ perovskite is an attractive material for cathode application. The solid solution of $La_{1-x}Sr_xMnO_3$ possesses a high electron conductivity, but the ionic conductivity is low i.e. not enough oxygen vacancies exists. The performance of such electrodes is a function of the microstructure, which can change during the exploitation period (18). The electronic conductivity of $La_{1-x}Sr_xMnO_3$ is due to electron hopping effect between the Mn^{4+} and Mn^{3+} valence states. The defect chemistry, electrical conductivity, thermodynamic characteristics at high temperature, chemical potential diagrams (6) and the polarization behavior of substituted lanthanum manganites are well known in the literature. It was established that the alkaline earth doped lanthanum manganites have been found to satisfy all the requirements for an effective cathode material. This is a logical consequence following the innovative ideas presented into the patents (19-23).

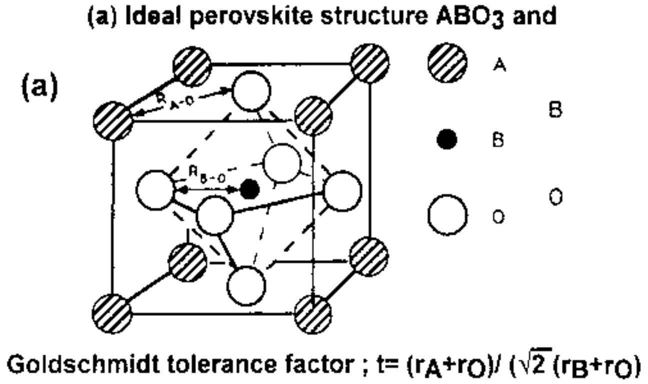

Figure 3 ABO_3 ideal perovskite structure.

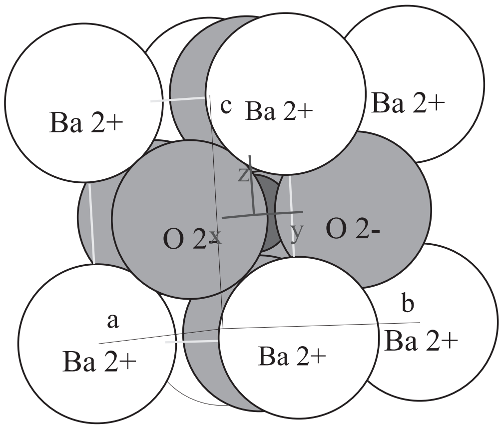

Figure 4 Perovskite crystal unit of BaTiO3 (tetragonal); space group ? 123, (P4/mmm) a = 3.993 Å; c = 4.033Å Ba 2+ (0,0,0); Ti 4+ (1/2,1/2,1/2) ;O 2- (0,1/2,1/2), (1/2,1/2,1),(1/2,1/2,0); data according to (16).

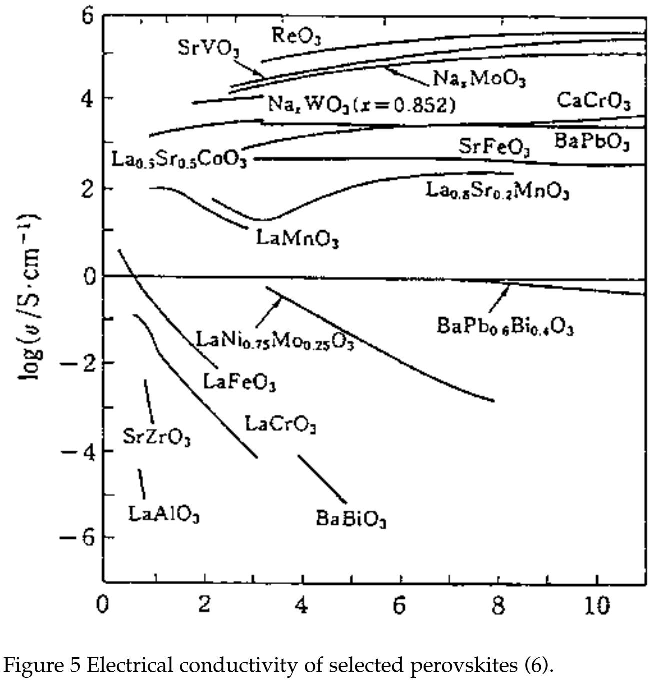

Figure 5 Electrical conductivity of selected perovskites (6).

The solid solutions of $La_{1-x}Sr_xCoO_{3-\delta}$ are mixed conducting ceramic materials. They possess both good electron and ionic conductivity. It is necessary to underline that A and B doping effect influences on the electrical conductivity. The relation of substitution is investigated in details by Petric et al. (14). A good relation is established and the behavior is presented in Fig.6. The maximum conductivity values are checked at 20% Sr content. The Sr-doping effect has a strong influence on one side, for creation of oxygen vacancies and on another side the Sr^{2+}-ions acts as acceptors. Those stimulate the chemical transition from Me^{3+} to Me^{4+}. The authors have established that the electrical conductivity decreases with Fe-side substitution instead of Co- doped samples. That doping effect stimulates the oxygen nonstoichiometry of the substituted perovskites. The phenomenon is very interesting but it is out of the scope of the present work. We would like only to mention that Mizusaki et al. (24), Kawada and Yokokawa (6) and Sakai at el. (25-27) have a significant contribution on the problem discussed. The surface behavior of Sr- doped lanthanide perovskites has been investigated, as well (28).

The binary phase diagrams of $La_2O_3 – Me_nO_m$ class, are well known and can be found in (29). Fig.7 shows the phase equilibrium diagram of the La_2O_3 - FeO_3 system, as an example. The phase analysis shows that an incongruent melting compound of $LaFeO_3$- perovskite is established only. Any liquid phase cannot be checked up to 1490°C. There is a new study on the phase equilibrium diagram of the La_2O_3 – CoO – NiO system (30). It was established that all binary compounds $LaCoO_{3-\delta}$, La_2NiO_4, $La_3Ni_2O_7$, $La_4Ni_3O_{10}$ exist and there are formed corresponding solid solutions as $LaCo_{1-x}Ni_xO_{3-\delta}$ (0≤ x ≤ 0.6), $La_2Ni_{1-y}Co_yO_{3-\delta}$ (y = 0.1), $La_3(Co_{1-y}Ni_y)_2O_7$ (0≤ y ≤ 0,025) and $La_3(Co_{1-x}Ni_x)_3O_{10}$ (0≤ y ≤0,6), which are checked into the fields of crystallization, as is shown in the Fig. 8 . Structural studies on $LaCoO_3$ and $LaNiO_3$ perovskites, after Sr^{2+} and Ni^{2+}– substitutions are carried out by Huang et al.(31). Some selected parameters of the $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-ä}$ crystal cell are shown in the Table 1 in correlation to $LaCoO_3$ and $LaNiO_3$ crystal phases. It can be checked, that the cell parameter is equal to those of $LaNiO_3$ - perovskite structure. A deviation to the higher values of the α- angle can be accepted when the Ni content is increased at equal strontium amount.

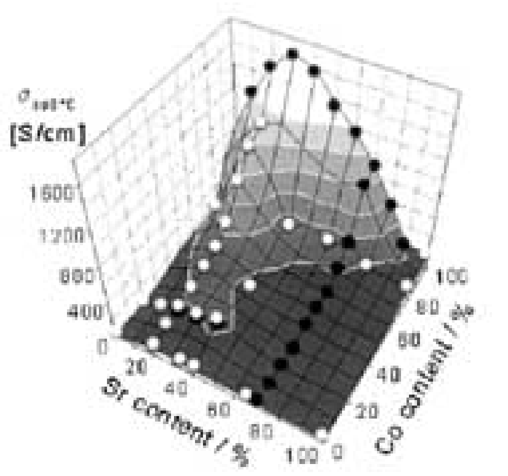

Figure 6 Electrical conductivities at 800 ºC for $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ system, a correlation of the experimental data with literature data from (14).

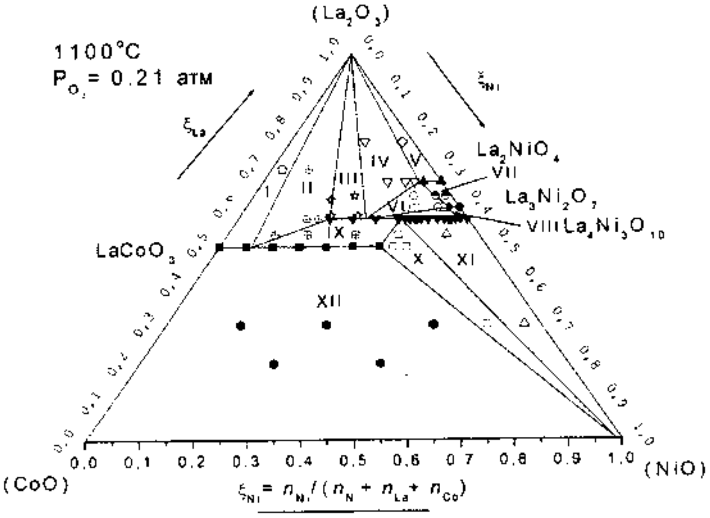

Figure 8 Phase equilibrium of La_2O_3 – CoO – NiO at 1100 ºC in air (30).

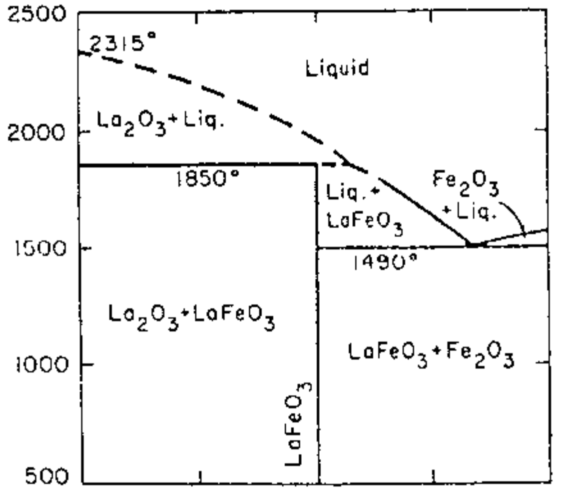

Figure 7 Phase equilibrium diagram of La_2O_3 – Fe_2O_3 system (29).

TABLE 1. PARAMETERS OF $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-ä}$ CRYSTAL CELL, ACCORDING TO (31)

Phase	a(r), Å	á(r),^{0}
$LaCoO_3$	a(h)=5,441	á=â=90^0
(S.G.=R3m,z=6)	c(h)=13,088	ã=120^0
$LaCo_{0,6}Ni_{0,4}O_{3-ä}$	3,839	90,75
$LaCo_{0,4}Ni_{0,6}O_{3-ä}$	3,839	90,72
$La_{0,9}Sr_{0,1}Co_{0,9}Ni_{0,1}O_{3-ä}$	3,84	90,58
$La_{0,9}Sr_{0,1}Co_{0,8}Ni_{0,2}O_{3-ä}$	3,842	90,62
$La_{0,8}Sr_{0,2}Co_{0,9}Ni_{0,1}O_{3-ä}$	3,841	90,49
$La_{0,8}Sr_{0,2}Co_{0,8}Ni_{0,2}O_{3-ä}$	3,843	90,52
$La_{0,7}Sr_{0,3}Co_{0,9}Ni_{0,1}O_{3-ä}$	3,84	90,38
$LaNiO_3$	a(r)=3,838	90,38
(S.G.=R3m,z=1)		

To consider oxygen incorporation reaction on the cathode surface is an interesting topic. According to (32) only, in the case of electronic conducting cathodes, this incorporation occurs via adsorption of oxygen on the electrode surface, surface diffusion of oxygen species to the tree phase boundary (TPB), ionization and incorporation into the electrolyte close to the TPB. Mixed ionic and electronic conducting electrodes are assumed to broaden the incorporation zone since a reaction via a bulk path is also possible. In other words, we can accept oxygen adsorption, next incorporation into the electrode volume, transport to the two phase- boundary and finally ion transfer across this two phase boundary. These two possibilities of oxygen adsorption, surface path and bulk path, are well illustrated in the next Fig. 9. The authors proposed model geometry of a porous mixed conducting cathode, as a perovskite one after the structural substitution. The calculated lines with equivalent potential of the oxygen vacancies in part of the model cathode are also presented. It is concluded that if the ionic transport in the cathode is rate limiting, the current density distribution is constructed to the region close to the TPB. A major fraction of the total current flows in narrow stripes close to the TPB. It has been accepted that a slow oxygen incorporation reaction activates generally the entire two-phase boundary mechanism i.e. bulk path. From this point of view, the active sites indicating the oxygen interface reduction, have been studied by $^{16}O^{-}$ and $^{18}O^{-}$ isotope SIMS analysis (33).

The effect of the water vapor on electrochemical reaction of SOFCs is investigated and a model is presented in (34). It was found that the surface reaction rate constant for oxygen isotope exchange on YSZ, was approximately 500 higher in wet atmosphere (28hPa O_2 + 22hPaH_2O) than that value in dry atmosphere (28hPaO_2 at 873°C). The authors present a model of water vapor cathode reaction (Fig.10) and accepted that the effect of water will be very important at low temperatures exploitation regime where the electrode reactions are rate limited by charge transport processes. It is clear (Fig.10) that after the surface adsorption of the oxygen (O_{ad}) and next diffusion process to the TPB, the O_{ad} reacts with the interstitial proton (H_i), generated from the water vapor, after transportation through YSZ. The authors accepted that the reaction rate of step 4 shown in the figure is much faster than the reaction in dray O_2.

A functionally graded cathode has been reported in ref. (8). The cathodes have been prepared from $La_{0.85}Sr_{0.15}MnO_3$ and YSZ mixtures using screen-printing techniques. The authors used a bi- layer cathode made from $La_{0.8}Sr_{0.2}CoO_3$ (LSCO) and $La_{0.85}Sr_{0.15}MnO_3$ (LSM) deposited on YSZ electrolyte. After microstructure, compositional analysis and AC impedance spectroscopy characterization, the authors established that as the level of LSM-YSZ graded within the cathode increased, the polarization resistance decreased.

There is relatively limited number of studies on cathode materials for intermediate temperatures operating SOFCs. As an alternative cathode materials can be treated $Ba(La)CoO_3$ (35). On the base of the cathode over-potential, measured at 1073K, the authors established that the $Ba_{0.6}La_{0.4}CoO_3$ is the optimal composition for a cathode operation. The experiments are carried out on a $LaGaO_3$ – based electrolyte. The results from ref. (36) can be adopted as alternative cathode materials. The authors have investigated compositions as $La_{0.8}Sr_{0.2}CoO_3$, $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$, $Ga_{0.8}Sr_{0.2}CoO_3$, $Ga_{1-x}Sr_xCoO_3$ (0.5<x<0.8,), $LaNiO_3$ and etc. vs. reactivity between electrolytes (gadolinium – doped ceria; CGO) and the cathodes. It was established that the novel cathode $SrFeCo_{0.5}O_{0.35}$, performed the best at higher temperatures, achieving the lowest area resistances measured. New data for SmCoO3 – perovskites containing fine Pt particles are reported in ref. (37).

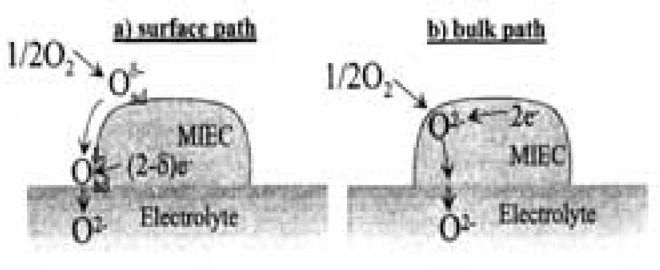

Figure 9 Sketch of two possible oxygen incorporation paths in mixed conducting cathodes (32).

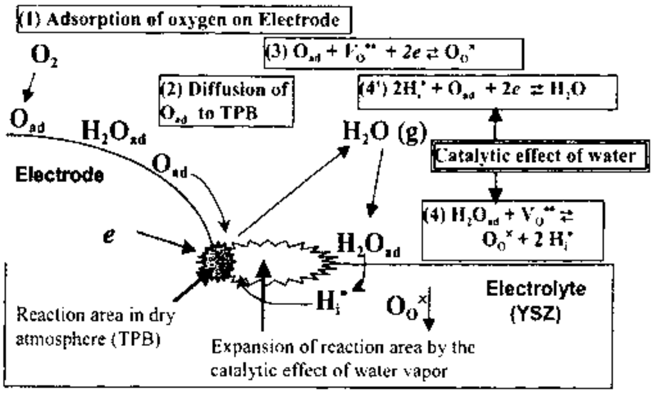

Figure 10 Effect of water vapor on cathode reaction in SOFC (34).

2.2. Electrolytes

The nature of a SOFC is based on the transport of oxide ions (O^{2-}) from the air electrode side to fuel electrode (anode) side. The electrode materials have to possess the following properties:

(i) Electrochemical: high ionic conductivity with σ- value at about > 0.1 Scm^{-1} at 1000°C (38)

(ii) Chemical: structural stabilization at high temperature, no reactivity to the other component materials and lack of instability to oxygen and fuel gas at high temperature treatment (39); lack of phase immiscibility is also necessary.

(iii) Thermal: thermal phase stability and low thermal expansion coefficient ($<10.10^{-6}.1/°C$) close to those values of the other cell components (14).

(iv) Mechanical: durability and high strength of fracture, dense and not gas permeation phenomena

As solid-state electrolytes usually are used fluorite-structured oxide materials as YSZ, rare earth doped bismuth oxide and rare earth doped ceria. Following the literature about electrolyte materials processing and performance it can be concluded that YSZ is the most widely and successfully applied. According to the Y_2O_3 – ZrO_2 phase diagram (29) the doping effect of over 8 % Y_2O_3 leads to high temperature cubic phase stabilization, parallel to the oxygen vacancies (Vö) creation; the last one contribution is equivalent to every mole of Y_2O_3 amount. As is shown in the Fig. 11 the electrolyte must be dense to protect from any free migration of the gases from one side of the electrolyte to the other. Important requirement is to possess high level of oxygen vacancies, i.e. high oxygen ion conductivity, at an optimal thickness value to minimize the resistance losses. The recommended electrolyte thickness is from 40 to 50 µm thick layer, deposited by different technology as plasma spraying, sol – gel route, polymer precursor spin coating process, MCVD, EVD and etc. According to (4) the mechanism of the oxygen transport from one occupied anion lattice site to a vacant anion site in a fluorite oxide and defect concentration in YSZ vs. P_{O2} is presented in Fig. 12. The diagram shows three regions: low, intermediate and high P_{O2}. The same material can exhibit n-type, ionic-, and p- type conductivity in dependence of P_{O2}. Each of the mobile species is then transported through the material in response to the applied chemical potential due to the ΔP_{O2} or the electrical one (4).

It is well known that the δ- Bi_2O_3 exhibits the highest oxygen- ion conductivity, due to its extremely open crystal structure. The problem is that all bismuth- based electrolytes possess high reduction ability of Bi^{3+} to Bi^0- metallic. As a result they cannot be use as alternative electrolyte materials. Ceria doped with alkaline earths (e.g. Ca- and Mg-) or rare earths (e.g. Ga- (CGO) and Sm- oxides) samples are more stable by comparison with bismuth- base electrolytes. If a reduction is carried out, the Ce^{4+} ions are reduces to Ce^{3+}, and electron conductivity will appear. The electron conductivity acts as a short- circuit pathway through the electrolyte and effectively reduces the SOFC efficiency. Below 700°C the degree of electronic conductivity is low enough to allow acceptable SOFC operation. But for low temperature operation (500-700°C) doped ceria electrolytes can be classified as good candidate materials (7) and next experiments are needed.

New compositions from the lanthanum gallate system are under development and they can be treated as original materials for electrolyte application. The perovskite lattice is less open than the fluorite related lattice (AO_2) (40) but it was established that the conductivity of these perovskites is higher than those of doped- zirconia electrolytes. Phase relations in quasi-ternary systems, e.g. $LaGaO_3$- $SrGaO_{2.5}$-$LaMgO_{2.5}$, have been published in ref. (41) and the phase equilibrium of the Ga_2O_3-La_2O_3 system is presented, as well (42). The authors established a large field of stable $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ (LSGM) perovskite phase at 1673K. In the literature the phase $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ is an object of high interest of synthesis and study. A comparison of mechanical and thermal properties of the tubular LSGM, CGO and YSZ electrolytes is reported in (43). It was established that the thermal expansion coefficients increase in the order YSZ< LSGM< CGO and all samples possess an excellent thermal shock resistance.

It is interesting only to note the study of K. Nomura regarding the transport properties of $(La_{0.9}Sr_{0.1})M^{III}O_{3-\delta}$ (where M^{III} is Al, Ga, Sc and In) perovskites and new rare- earth silicate electrolytes ($RE_{9.33}(SiO_4)_6O_2$) for medium operating temperature SOFCs by Ch. Barthet, works published in SOFC VII proceedings (12), as well.

Regarding the innovation level for electrolytes there are lot of patents in the field discussed. We would like only mention that some actual information about materials used as electrolytes the reader can find in the review paper about patents state-of-the-art (2).

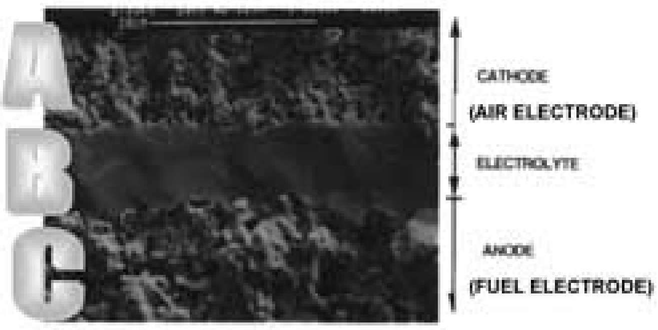

Figure 11 Cross section of a SOFC illustrating the morphology of A- cathode, B- electrolyte and C- anode elements.

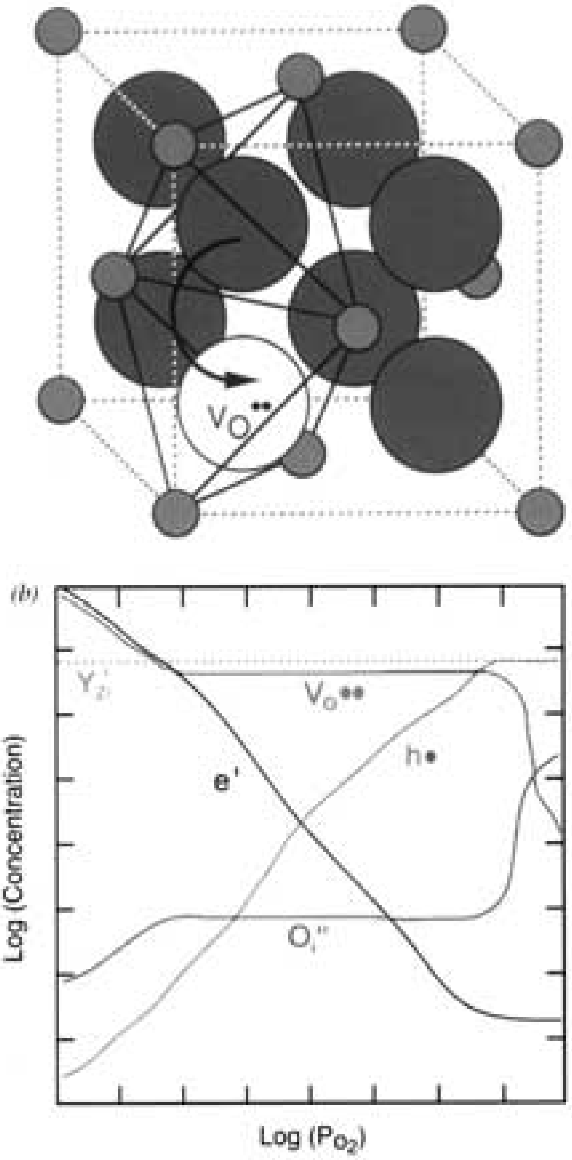

Figure 12 Mechanism of transport from an occupied anion lattice site to a vacant anion site in a fluorite oxide – (a) and (b) –concentration of defects, potential profile and mass transport illustration after (4).

2.3. Anode materials

The anode (fuel electrode) must possesses:

(i) High stability at reduction atmosphere;
(ii) To have high temperature stability;
(ii) To be porous;
(iii) To possess high catalytic activity and
(iv) Should be electronically conducting parallel with
(v) High corrosion stability.

The function of the anode is to absorb H_2, CO and to oxidize them. CH_4 or other hydrocarbon fuels are usually separately treating in a stream reforming reactor (reaction $CH_4 + H_2O \rightarrow CO + 3H_2$) and after that the reaction products are introduced into the SOFC. In high temperature SOFCs this reaction is expected to proceed on the anode itself ("internal reforming") (6). On the electrolyte/fuel electrode interface the fuel oxidation reaction ($O^{2-} + H_2 = H_2O(g) + 2e^-$) takes place.

The transition metals are potential candidates because they possess high catalytic activity. A high incompatibility of the thermal expansion coefficient exists between them and YSZ electrolyte. As a result an interface mechanical- thermal effect occurs and the electrolyte is separated during the thermal exploitation cycles. After applying of high-dispersed metal-YSZ cermet (usually Ni:YSZ is used, where Ni is 50 ± 10vol.%) a high interface thermal, mechanical and corrosion stability is established. The Ni:YSZ- cermet anode (alternatively Co or Ru), however, exhibits a problem of carbon deposition during the exploitation. According to Singhal (10) a skeleton of YSZ- units is formed around the nickel particles. As a result the YSZ skeleton prevents sintering of the Ni- particles, decreases the anode thermal expansion coefficient bringing it closer to that of the electrolyte and stimulates a better adhesion of the fuel electrode with the electrolyte also. According to (6) the most important point in the processing of Ni:YSZ electrode is to keep nickel-to-nickel contact. After reducing in the operating atmosphere, Ni- particles tend to sinter and become separated from each other. The size ratio of Ni- particles to YSZ is another important factor to make better Ni contacts. It is also important to keep the ionic path through YSZ to YSZ contact to make a high O^{2-} transport and good performance electrode. This is well illustrated by the model presented in Fig. 13. According to Mizusaki's Labs investigations a conception and idea of the electrolyte/fuel electrode interface fuel oxidation reaction $O^{2-} + H_2 = H_2O$ (g) + $2e^-$ is shown in Fig. 14 (44).

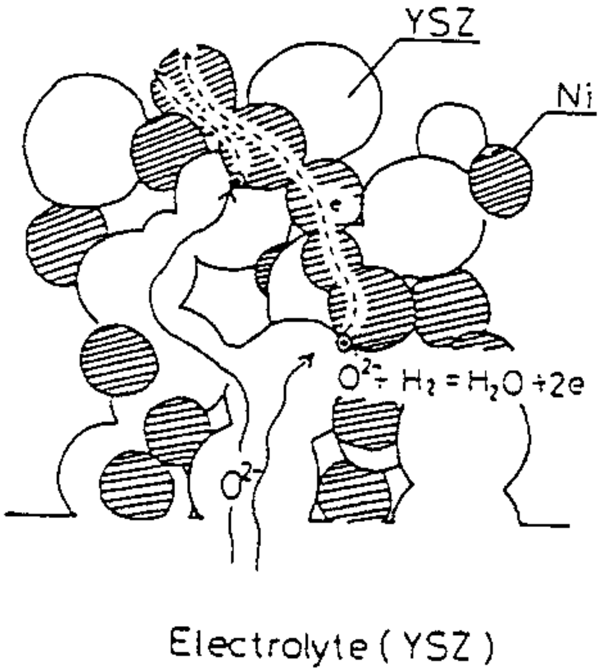

Figure 13 Schematic view of Ni : YSZ cermet after Kawada et al. (6).

Regarding the fuel electrode innovations few patents can be cited. Patent (45) discussed a honeycomb structural SOFC build with Ni:YSZ fuel electrode. The same material for anode is used in (46) where the fuel electrode material is Ni:YSZ in a ratio 60: 40 at 50 μm thick. Patents (47,48) are related to development of fuel electrodes from NiO:YSZ and Ni: ZrO_2, respectively. Patent (49) relates to SOFC anode enhanced performance stability and method for manufacturing the same. The method is based on reaction of NiO-MgO (ss) with CeO_2 to stabilize Ni against coarsening. There is an European patent (50), aiming to develop SOFC with anode built from cermet Ni:, Co:CeO_2 and -:ZrO_2 deposited on Y(Ca,Mg):ZrO_2 solid electrolyte.

Following the current literature there are experiments and new tests about alternative materials for fuel electrodes. According to (7) a number of groups are now evaluating the benefits and long- term stability of a Ni:[ceria-samaria (CSO)] cermet. In a reducing environment the Ce^{4+} tends to reduce to

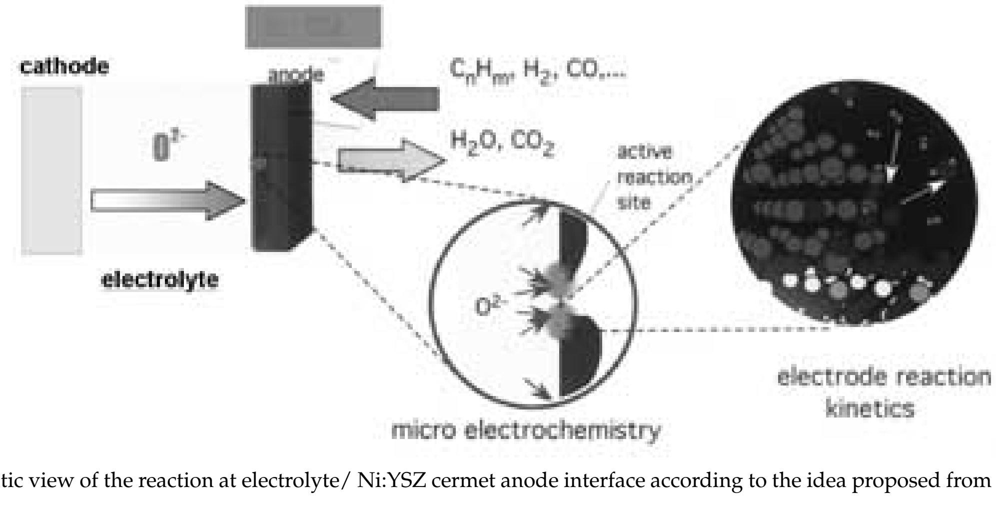

Figure 14 Schematic view of the reaction at electrolyte/ Ni:YSZ cermet anode interface according to the idea proposed from Mizusaki Labs. (44).

Ce^{3+} and this reduction introduces electrons into the ceria lattice. It is necessary to mark that on one side, the CSO does not fit its thermal expansion coefficient to those of YSZ, and on the other some undesirable reactivity may occur between CSO and YSZ electrolyte. In the same context, cerium-gadolinium anodes and correlation with Ni: YSZ ones, are object of study in (51). The tests are carried out in the temperature range from 600ºC to 800ºC with both, humidified hydrogen and methane as a fuel. It was established that Ni:CGO anodes are superior to Ni:YSZ anodes especially at low temperature operation and when CH_4 is used. A high performance electrode for medium- temperature SOFCs activation on Ytria- Doped Ceria (YDC) anode with highly dispersed Ru electro catalyst is an object of study in (52). YDC $(CeO_2)_{1-x}(Y_2O_3)_x$ (x=0.2 and 0.3) exhibit about 3 times higher σ_e than that of SDC, while its value of σ_{ion} is moderate. New mixed conducting oxides for SOFC anodes, have been investigated in (53). The idea of the authors is to introduce early transition metal oxide e.g. TiO_2 into zirconia ss. Ionic and electronic conductivity of selected samples from the Y_2O_3-Sc_2O_3- ZrO_2 -TiO_2 system are studied.

It is interesting to mark that some experiments have been carried out on perovskite oxides suitable for anode applications. There is an innovation idea in publication (54) proposed Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC). The purpose is to achieve zero emission power generation using the all perovskite fuel cell using methane as a fuel. Developments of the ceramic materials for a perovskite/ perovskite/ Ni: perovskite oxide cermet anodes as $La_{0.4}Ba_{0.6}CoO_3$ (cathode)/ $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ / Ni: cermet anode as (Ni; Ni/ $SrTi_{0.93}Mg_{0.07}O_3$; Ni/ $Sc_{0.18}Zr_{0.82}O_2$; Ni/$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ and etc.) are described together with the introduction of a novel methane processing. There is a study on donor doped $SrTiO_3$ (STO) which is stable in both, reduction and oxidation atmosphere (55). The attention is focused on compositions as $SrTi_{1-y}Nb_yO_3$ and $La_xSr_{1-x}NbO_3$. TPB length is estimated after measurements by analyzing of SEM images of the cross sections around porous electrodes/YSZ interfaces. It was accepted that LSTO composition should be used to compare STNO for hydrogen-generating electrode of steam electrolysis.

There are few patents regarding intermediate layer deposited between electrolyte /electrode configuration. Among them the German patents (56-58) proposed Ti or Nb:ZrO_2, Nb and/or Gd:CeO_2, CeO_2 doped with Ga and Sc ions.

2.4. Interconnect

Interconnect (Separator or Bipolar plate) is applied in a SOFC for electric contact to the air electrode and also for its protection from the reducing environment of the fuel used. The requirements to these ceramic elements include the following:

(i) To possess high (100%) electronic conductivity.

ii) To possess low permeability to oxygen and hydrogen to minimize direct combustion during the cell operation process.

(iii) Chemical durability of the composition at high temperature exploitation and stability to both oxidation and reduction atmospheres, since it is exposed to air on the one side and to the fuel on the other side.

(iv) To have high chemical stability i.e. non- reactivity with the other cell components

(v) To possess thermal expansion coefficient close to that α-value of the air electrode and the electrolyte used.

(vi) To satisfy these requirements both kinds of materials are used, namely on ceramic base and on metallic base.

Usually ceramic-based materials from the perovskite La_2O_3- Cr_2O_3 systems are used. The materials from this system are p- type conductors, in whose structure a small polaron hopping effect exists up to 1400ºC. After low valence ions substitution of La- and /or Cr- ions by Ca, Sr, Mg, better conductivity and low temperature (< 1700ºC) sintering process can be achieved. For the Siemens Westinghouse t-SOFC, the bipolar plate layer in ~ 85 µm thick is deposited by plasma spraying along the air electrode tube length. After small reduction in operating temperature the bipolar plate material modifies itself to the desired conductivity. European patents (50,59) are related to interconnect materials on doped lanthanum chromite.

There are limiting data checked for other alternative bipolar plates on ceramic base. Air- sintering characteristics of Ti- doped lanthanum strontium chromites with B-site substitution are an object of the study in ref. (60). The effect of B-site dopants in the $La_{0.8}Sr_{0.2}Cr_{0.9}Ti_{0.1-y}Co_yO_3$ perovskites ($0.15 \le x \le 0.20$ and $0 \le y \le 0.02$) and $La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1}M_xO_3$ perovskites (M = V and Ni; $0 \le x \le 0.05$) is studied. The samples are prepared from fine powders made through the Pechini method. The authors proposed the composition $La_{0.8}Sr_{0.2}Cr_{0.88}Ti_{0.1}V_{0.02}O_3$ as a promising candidate material for SOFC separators, regarding thermal expansion and sintering characteristics.

It is well know that the separators can be made from metal alloys. The metallic materials are out of scope of the present study, so that we intend only to draw the attention of the reader. The metals and alloys possess a big problem regarding corrosion stability and protection at high temperature treatment. In this context, oxide scale forms on the metallic surface especially in the air atmosphere on the cathode side. As a result, the conductivity decreases and seriously reduces the time of SOFCs performance.

2.5. Sealing materials

The requirements to the sealing materials in SOFCs include the following:

(i) To possess high chemical and thermal stability at high temperature treatment.

(ii) To possess good isolating effect and not to exhibit any gas (to oxygen and hydrogen especially) permeability during the cell operation process.

(iii) To possess thermal conductivity and to be stable towards thermal shock regimes or cycling processes of the cell stack.

(iv) The thermal expansion coefficient could be matched to that α- value of the other SOFCs components

In the literature there are not so much data published on the problem discussed. On a laboratory scale, both compression seals and gold gaskets have been used to seal single cells. To use gold gaskets it is not so practical for industrial application. The most widely used sealing materials are selection of glasses (generally of "3.3" type of glass), ceramics and glass-ceramics compositions. Borosilicate glasses with commercial names as "Pyrex, Simax, Duran 8330 and etc." are suitable to be used as a base. It is necessary to modify the composition by rare- earth and Sr, Ba, Mg – oxides incorporation into the vitreous structure. The best materials are glass ceramics compositions close to the industrial mica and those, which are doped with suitable nucleates or surfactants for next devitrification process, after additional thermal treatment. SOFCs operating at lower temperatures will be more adaptable for a sealants selection and testing procedure.

Limited number of patent data exists regarding the sealing materials. There is a patent (61) with a proposal for binding material with good mechanical and electrical properties. Another patent (62) relates to rare- earth silicate glasses with appropriate coefficient of thermal expansion and good adhesion effect.

5. CONCLUSIONS

The following conclusions may be drown, based on the present work:

1. There are intensive works (papers and patents) registered regarding the ceramic materials fabrication processes, and performance of different SOFCs components. There are few review papers, but those with focus on materials used, are limited.

2, All aspects of SOFCs production, assembling and market distribution are with an accent on the wide number of powerful companies in USA, Europe, Asia and especially Japan.

3. The best cathode materials are these from the perovskite $La_{1-x}Sr_xMnO_3$ family covering the requirements. There is a research for functionally grated cathodes i.e. bi-layer structure made from $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.85}Sr_{0.15}MnO_3$ deposited on YSZ electrolyte. As alternative cathode materials perovskite compositions as $La_{0.8}Sr_{0.2}CoO_3$, $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$, $Ga_{0.8}Sr_{0.2}CoO_3$, $Ga_{1-x}Sr_xCoO_3$ ($0.5<x<0.8$,), $LaNiO_3$, $SrFeCo_{0.5}O_{0.35}$ and etc. after A- and B- substitution are investigated, as well.

4. Regarding electrolyte materials processing and performance it can be concluded that the YSZ is the most widely and successfully employed. Alternative electrolytes are these from Ga_2O_3 -La_2O_3 system e.g. $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ perovskite and ceria doped with alkaline earths and/or rare earths samples.

5. It was established that the Ni:YSZ- cermet anode (alternatively Co or Ru, instead of Ni), is most widely used. There is a study on Ni:CGO anodes which are acceptable at low temperature operation and when CH_4 is used. High performance electrode for medium- temperature SOFCs activation on Ytria- Doped Ceria (YDC) and incorporation of early transition metal oxide e.g. TiO2 into zirconia ss from Y_2O_3-Sc_2O_3- ZrO_2 -TiO_2 system are potential candidates following their ionic and electronic conductivity.

6. The leading materials for interconnect are these from the perovskite La_2O_3- Cr_2O_3 system. The effect of B-site dopants in the $La_{0.8}Sr_{0.2}Cr_{0.9}Ti_{0.1-y}Co_yO_3$ perovskites ($0.15 \le x \le 0.20$ and $0 \le y \le 0.02$) and $La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1}M_xO_3$ perovskites (M = V and Ni; $0 \le x \le 0.05$) is studied and the composition $La_{0.8}Sr_{0.2}Cr_{0.88}Ti_{0.1}V_{0.02}O_3$ is a promising candidate material for SOFC separator.

7. There are limiting data regarding the sealing materials. Borosilicate glass compositions by rare- earth and Sr, Ba, Mg – oxides incorporation into the vitreous structure are applicable. The best sealing materials are glass ceramics compositions close to the industrial mica and these doped nucleates or surfactants for next devitrification process.

8. It appears that the materials processing for SOFCs application is now maturing and the leading companies are focus their attention on stack and systems application to the market (12,63).

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