The development of electrolytes for intermediate temperature solid oxide fuel cells

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Abstract

This report describes a number of experimental studies on the solid state electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFCs): $Ce_{1-x}Ln_xO_{2-\delta}$ (Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb), some multicomponent systems $Ce_{1-x}Ln_{x/2}Ln'_{x/2}O_{2-\delta}$ (x = 0 – 0.20; Ln = Sm, La, Gd and Ln′ = Dy, Nd, Y), some systems with simultaneous doping by rare earth and alkali earth elements $Ce_{0.8}(Sm_{1-x}M_x)_{0.2}O_{2-\delta}$ (M = Ca, Sr; x = 0.0 – 1.0) and $Ce_{0.8}(Sm_{1-x-y}Ba_yM_x)_{0.2}O_{2-\delta}$ (M = Ca, Sr; x = 0, 0.15, 0.20; y = 0.05, 0.1). Two important aspects are emphasized: the effect of different dopants' ionic radius and concentration on the electrical properties of CeO_2 based solid solutions and the influence of the method of preparation on the structural properties of ceria ceramics and the electrochemical performance of single SOFCs on their base. To describe the electrolytic properties of solid electrolytes the notation of the electrolytic domain boundary (EDB) – the critical oxygen partial pressure ($P_{O_2}^*$) at which the values of the electronic and ionic components of conductivity are equal, were calculated and presented. The interpretation of these data will lead to a better understanding of, subsequent improvements to and ultimately, the commercialization of IT-SOFCs in Russia.
Keywords: alternative energy, SOFC, solid state electrolytes, oxygen conductivity, CeO_2, electrolytic domain boundary.

1 Introduction

Nowadays economic and environmental factors define global changes in energy production and distribution market. Approximately 94% of CO_2 emissions in Europe are attributable to the energy sector as a whole; oil consumption accounts for 50% of CO_2 emissions in EU, natural gas for 22% and coal for 28%, respectively. In the Russian Federation the energy sector is also a major source of pollution. It accounts for over 50 percent of emissions of pollutants into the atmosphere and over 20 percent of waste water discharged into surface watercourses, as well as more than 70 percent of total greenhouse gas emissions. The unpredictability of supply and strong dependence on politically unstable countries, environmental and global warming issues and adherence to the new European legislation related to the deregulation of the energy market all contribute to the introduction of new technologies in the energy field [1–4].

New energy technologies can contribute to the security of supply objectives in several ways, by reducing fuel demand through end-use energy efficiency measures, by utilizing diversified fuel sources, e.g. enabling fuel switching, fuel flexibility and by utilizing renewable energy sources. In the ongoing search for alternative and environmentally friendly power generation facilities, the Solid Oxide Fuel Cells (SOFCs) have generated much interest as a potential economical, clean and efficient candidate for the decentralised generation of heat and power (Table 1).

Table 1: Comparison of the environmental impact of different energy production systems.

Type of power plant and used fuel	Concentration of hazardous components in emissions, mg/m^3				
	SO_x	NO_x	CO	Hydro-carbons	Solid particles
New heat electropower station (coal)	200	200	50	10	10
New heat electropower station (brown coal)	200	200	50	7	10
Mini power plant with internal-combustion engine (gasoline)	2	250	300	115	5
Steam-gas plant (natural gas)	5	100	100	10	2
Electrochemical generator based on SOFCs (natural gas)	0	> 3	> 7	> 3	0

At present however, the techno-economic potential of this technology faces two main critical issues, i.e. the development of a low cost production process for the cell components and their inadequate durability. The current approach of reducing the SOFC's operation temperature allows for a wider choice of low cost materials, particularly for the interconnection (including metallic) and the sealant, a longer cell life-time due to lessened interdiffusion among stack components, improved reliability and a reduced overall cost. In this regard, the electrolyte materials of choice, those that exhibit high conductivity and sufficient stability, are based on ceria and lanthanum gallate [5–8].

Recently, multicomponent electrolytes based on CeO_2 have attracted great interest. It is known that the main disadvantage of ceria-based electrolytes, and this complicates their commercial application, is the appearance of electronic conductivity at low oxygen partial pressures because of Ce^{4+} being partially reduced to Ce^{3+}. Some effort has been made to suppress the electronic conductivity and to extend the electrolyte domain of the ceria-based electrolytes. Structural modification of ceria-based solid solutions by co-doping is one of the possible ways to enhance their electrical conductivity. The ionic radii of Ce^{4+} and Ce^{3+} in CeO_2 are 0.97 and 1.14 Å, accordingly. It was assumed that the fluorite lattice of CeO_2 accepts dopants which have an average ionic radius up to 1.14 Å. It was found that if the trivalent rare earth element sites in CeO_2-Re_2O_3 solid solutions are further partly substituted by univalent or divalent element, so that the trivalent rare earth element sites are made to have a lower valence, the quantity of oxygen vacancies is increased.

Univalent or divalent elements having an ionic radius larger than Ce^{4+} expand the lattice and increase the space in the crystal lattice allowing the oxygen ions to pass through. A large quantity of oxygen vacancies not only increases conductivity in air, but also minimizes change to the defective ceria type compound from $Ce^{4+} \rightarrow Ce^{3+}$ in reducing atmospheres. Mori et al. showed that an electrochemical cell with $(La_{0.75} Sr_{0.2} Ba_{0.05})_{0.175}Ce_{0.825}O_{1.89}$ instead of $Sm_{0.2}Ce_{0.8}O_{1.9}$ as its electrolyte had a power density three times higher at the same temperatures [9].

This report describes a number of experimental studies on solid state electrolytes for intermediate temperature SOFCs. Emphasis is given to two important aspects, the effect of different dopants′ ionic radius and concentration on the electrical properties of CeO_2 based solid solutions and the influence of the method of preparation on the structural properties of ceria ceramics and the electrochemical performance of single SOFCs on their base.

2 Experimental

2.1 The preparation procedure and powder characterization

The solid-state composition $Ce_{1-x}Ln_xO_{2-\delta}$ (Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb), some multicomponent systems $Ce_{1-x}Ln_{x/2}Ln'_{x/2}O_{2-\delta}$ (x = 0 – 0.20; Ln = Sm, La, Gd and Ln′ = Dy, Nd, Y), some systems with simultaneous doping by rare earth and alkali earth elements $Ce_{0.8}(Sm_{1-x}M_x)_{0.2}O_{2-\delta}$(M = Ca, Sr; x = 0.0 – 1.0)

and $Ce_{0.8}(Sm_{1-x-y}Ba_yM_x)_{0.2}O_{2-\delta}$ (M = Ca, Sr; x = 0, 0.15, 0.20; y = 0.05, 0.1) were synthesized by applying three different techniques: solid-state reaction (solid-powders), laser induced evaporation of solid state target (laser-powders) and glycine-nitrate method (chem-powders) (Fig. 1). The temperature of calcinations varied from 600 to 1150°C depending on the procedure.

The specific surface area obtained powders were tested by surface area and porosity analyzer TriStar 3000 V6.03 A. The content of metal oxides in the starting materials and solid-state composition, obtained by different methods, was defined by a Plasma Emission Spectrometer Optima 4300DV (USA). The X-ray diffraction (XRD) technique was employed to identify the phases and to obtain the values of the lattice constants.

The XRD analysis was performed on the milled powders of specimens by using a DMAX-2500 (Rigaku Co. Ltd., Japan) diffractometer with Ni-filtered Cu K_α radiation in the range of $10° \leq 2\theta \leq 120°$. The crystallite size d_x was determined from the broadening of the X-ray diffraction lines according to the Scherer procedure.
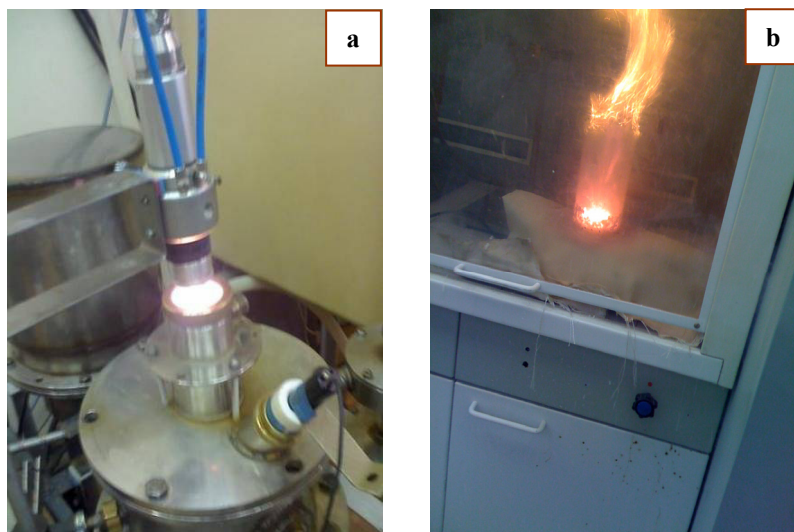

Figure 1:   a. Laser induced evaporation of ceramic target, b. combustion route.

2.2 The preparation and characterization of ceramic samples

Powders prepared by different procedures were compacted by the magnetic pulse technique in the Institute of Electrophysics UB RAS [10] in 2 mm thick pellets with a diameter of 30 mm (pulsed pressure 300 MPa in amplitude and 100 mks in duration) and sintered in air in an electric furnace with controlled heating (heating/cooling rate 5°C/min, maximal temperature was 1600°C with holding time 3 h) (fig. 2b). The dilatometer Dil 402 C was used to investigate the

sintering dynamics. The densities of the samples were determined by hydrostatic weighing in water. The grain size and its distribution on the surface of sintered ceramic samples were investigated by raster electronic microscope JSM-5500 LV JEOL, Japan.

2.3 Investigation of electrical properties

The electrical conductivity measurements of the samples were carried out by employing the four-point dc technique making use of the home-made electrochemical experimental set [11]. The specimens were installed in a tube made from ZrO_2-based electrolyte. Platinum paste stripes, which were deposited on the inner and outer surface of the YSZ tube and connected with platinum wires, were used as the electrochemical oxygen pump and the oxygen sensor. Four Pt electrodes were deposited on the samples' surface and connected with Pt wires. Atmospheres with varying oxygen partial pressures inside the tube were created by pumping in oxygen and they were then registered by the sensor.

Figure 2:   The technology scheme of the ceramic samples preparation. Temperature and oxygen partial pressure were varied automatically by means of a microprocessor system Zirkonia-318 in the range of 350–900°C and 0.21–10−24 atm, respectively.

3   Results and discussion

3.1 Structural properties

The XRD analysis revealed that all the synthesized $Ce_{1-x}Ln_xO_{2-\delta}$ and $Ce_{1-x}Ln_{x/2}Ln'_{x/2}O_{2-\delta}$ compositions were single phase with a cubic fluorite structure like pure CeO_2. The compositions $Ce_{0.8}(Sm_{1-x}M_x)_{0.2}O_{2-\delta}$ (M = Ca, Sr; x = 0.0 – 1.0) with Ca^{2+} were single phase throughout the full range of compositions, while the solubility limit of Sr^{2+} was approximately 8 mol.% , so at x > 0.4 the second phase $SrCeO_3$ was identified. All XRD-patterns of

the compositions $Ce_{0.8}(Sm_{1-x-y}Ba_yM_x)_{0.2}O_{2-\delta}$ (M = Ca, Sr; x = 0, 0.15, 0.20; y = 0.05, 0.1) showed a pure cubic structure without any second phases. However the microstructure of these samples as seen by scanning electron microscopy demonstrated the appearance of second phase in the triple points.

The parameters of elementary cells a and crystallite sizes d_x of powders were determined from the broadening of the X-ray diffraction lines, an average bulk–surface effective diameter of particles d_{BET} was calculated from specific surface area of powders S_{BET}, which was about 1.5–2, 20–25 and 40–45 m^2/g for solid, chem and laser-powders, respectively. In the case of Laser-powders there was close concurrence in crystallite size, calculated from XRD-data and d_{BET}, because they were not agglomerated, having mainly spherical shaped particles (SEM image in Fig. 3a and TEM image in Fig 3b). Chem-powders were agglomerated, but the microsized agglomerates were spongy, so the specific surface area increased, more than in the case of Solid-powders, which were strongly
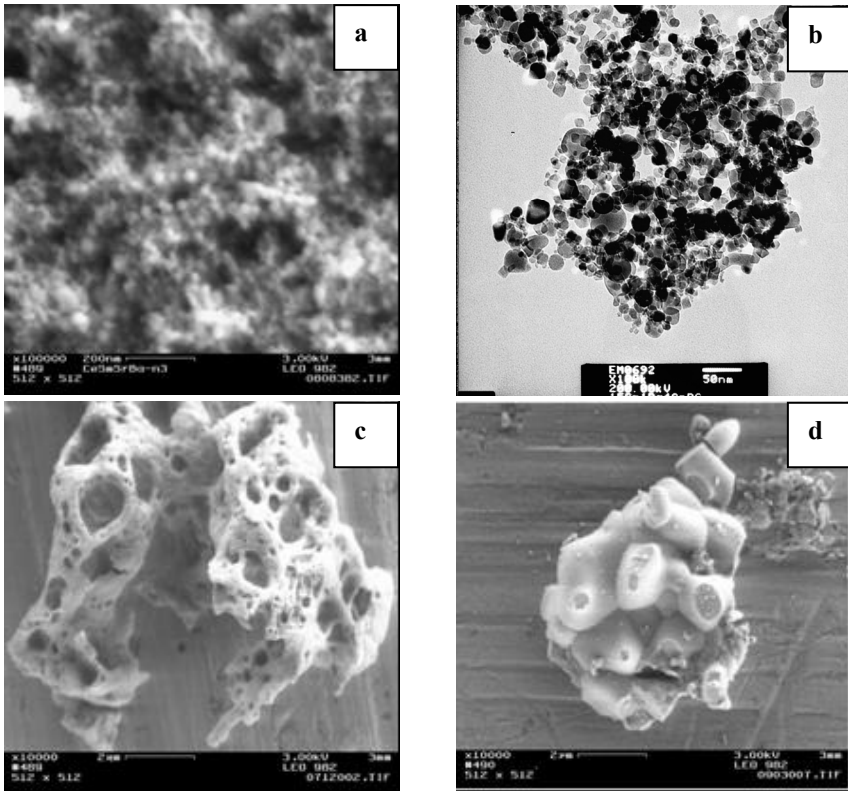

Figure 3:   a, b – Microstructure of powders prepared by laser induced evaporation, c – glycine-nitrate combustion and d – solid state reaction methods.

agglomerated and the procedure of their milling did not significantly alter the picture for some hours (Fig. 3c and d). The dilatometric investigation of sintering kinetics showed that the optimal sintering temperatures for sample preparation with a relative density of no less than 95% were 1400 and 1500, 1600°C for laser, chem and colid-powders, respectively.

3.2 Electrical properties in air

The introduction of the dopant cation (regardless of its radius) significantly increases the total electrical conductivity of CeO_2. The highest value for electrical conductivity in air was found for $Ce_{0.8}Nd_{0.2}O_{2-\delta}$ (14.8×10^{-2} and 13.3×10^{-3} S/cm, at 900 and 750°C, respectively). The dependence of electrical conductivity on the effective radius of the dopant passes through a maximum at $r_d = 0.1109$ nm. According to the classical theory [12], the minimal distortion in the lattice and consequently the maximum electrical conductivity, corresponds to the cation dopant with a radius of 0.1024 nm and any further increase in the dopant's radius will compromise the oxygen anion movement of the diffusion paths overlapping by neighboring cations.

Indeed, we obtained the minimal changes in the lattice's parameters in CeO_2 doped with Dy^{3+} with the effective radius of 0.1027 nm, but the electrical conductivity of samples with this dopant was rather low. Therefore, in order to select a suitable dopant it is necessary to take into account not only the size of the cation, but also the formation of local structures such as cation-oxygen vacancy complexes depending on cation-vacancy binding energy values. It was shown on the base of DFT-calculations [13] that Nd^{+3} and Sm^{+3} have the minimal values of binding energy in CeO_2 lattice and the bulk conductivity of solid solutions based on them are almost equal. For all dopants the conductivity increases with the dopant's concentration excluding Dy^{3+} and Eu^{3+}, whose maximal value of conductivity was found to be at x = 0.15 (8.5×10^{-2} and 12.1×10^{-2} S/cm at 900°C, respectively).

Among $Ce_{1-x}Ln_{x/2}Ln'_{x/2}O_{2-\delta}$ the highest values of conductivity for $Ce_{0.8}La_{0.1}Dy_{0.1}O_{2-\delta}$ and $Ce_{0.8}Nd_{0.1}Sm_{0.1}O_{2-\delta}$ were observed (11.1×10^{-2} and 10.0×10^{-2} S/cm at 900°C). The effect of increased conductivity when co-doping CeO_2 with two rare earth elements was found only under a low concentration of dopants. As a rule the values of conductivity of the three-component systems were equal to the average value of conductivities of the relevant two-component systems. Throughout the entire concentration range for two-component systems the maximum level of conductivity was found when using Nd^{3+} as a dopant. These results are similar to those obtained in [14].

Adding the correct amount of alkaline earth elements Ca^{2+} and Sr^{2+} (2–4 mol.%) significantly increases the conductivity of the samples. The same results were found for $Ce_{0.8}(Sm_{1-x-y}Ba_yM_x)_{0.2}O_{2-\delta}$ (M = Ca, Sr; x = 0, 0.15, 0.20; y = 0.05, 0.1). It was confirmed by the technique of impedance spectroscopy that CaO, SrO and BaO addition increases the grain boundary conductivity by a magnitude of more than 10. It should be noted that the conductivity of the samples with Sr^{2+} is higher due to the lower binding energy of Sr-O (33.4 eV) compared to Ca-O (35.44 eV). The binding energy of Ba-O is minimal among

the alkaline earth elements (31.44 eV), but due to the fact that the effective radius of Ba^{2+} is 0.142 nm, and its solubility in the fluorite lattice is less than 2 mol. %, the number of single-phase solid solutions on the base of BaO is limited. Nevertheless, it was found that the samples with Ba^{2+} have the lowest activation energy for total conductivity. The highest value for total conductivity 16.2×10^{-2} S/cm at 900 °C was attributed to $Ce_{0.8}(Sm_{0.8}Sr_{0.2})_{0.2}O_{2-\delta}$.and $Ce_{0.8}(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}O_{2-\delta}$.

3.3 Electrolytic properties

It is well known that the rate of electrochemical reactions in solid oxide fuel cells is determined by the driving forces of the processes, which, in turn, are determined by the difference between the partial pressure of oxygen in the anode and cathode channels. The greater this difference, the higher is the power output of the electrochemical cell. Usually, with the cathode channel oxygen partial pressure is chosen in the range 0.21^{-1} atm. Problems arise in reducing conditions (anode channel), since at the partial pressure of oxygen below 10^{-15} atm cerium systems are characterized by the appearance of electronic conductivity due to the partial reduction of $Ce^{4+} \rightarrow Ce^{3+}$. The electronic conductivity of solid solutions based on CeO_2 is determined by the dopant's radius, its concentration and temperature. Dependence of total conductivity on $P_{O_2}^*$ was investigated at 750 and 900°C. To describe the electrolytic properties of solid electrolytes the notation of the EDB (electrolytic domain boundary) – critical oxygen partial pressure ($P_{O_2}^*$) at which the values of the electronic and ionic components of conductivity are equal, was used. The minimal value of $P_{O_2}^*$ among $Ce_{1-x}Ln_xO_{2-\delta}$ solid solutions was found for $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ composition (2.76×10^{-21} atm at 750°C). A decrease in the dopant radius results in an increase in $P_{O_2}^*$ and a relevant narrowing of the electrolytic region. The minimal electrolytic domain boundary value was found for the composition $Ce_{0.9}Yb_{0.1}O_{2-\delta}$ (4.57×10^{-13} atm). An increase in the dopant concentration and a lowering of temperature leads to a decrease in the critical partial pressure irrespective of the dopant.

Among the three-component systems the lowest values of $P_{O_2}^*$ equal to 1.16×10^{-18} atm was found for $Ce_{0.8}Nd_{0.1}Sm_{0.1}O_{2-\delta}$. For compositions $Ce_{0.8}(Sm_{1-x}M_x)_{0.2}O_{2-\delta}$ the value of $P_{O_2}^*$ increases with CaO content (with x = 0; 0.2 and 0.5 are 2.76×10^{-21}; 5.05×10^{-18}; 1.31×10^{-18} atm, respectively), while SrO addition decreases it (with x = 0.2 and 0.3 are 3.33×10^{-19} and 9.88×10^{-23} atm). The addition of BaO also leads to expansion of the electrolytic area of co-doped systems. The lowest value 3.30×10^{-23} atm at 750°C was found for $Ce_{0.8}(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}O_{2-\delta}$. In some of the investigations by the Mori group [9, 15] it was also shown that co-doping with alkali earth elements not only leads to an increase in electrical conductivity of solid electrolytes based on CeO_2, but also expands their electrolytic areas.

3.4 Electrochemical performance

Fig. 4 presents the electrochemical characteristics of single SOFCs on the base of $Ce_{0.8}(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}O_{2-\delta}$ and traditionally used in IT-SOFCs $Ce_{0.8}Sm_{0.2}O_{1.9}$ ceramic electrolytes made by different methods. The investigation was carried out using an electrolyte supported electrochemical cell (0.8 mm of electrolyte thickness) with separated cannels: $H_2 + 5\% H_2O$, Pt/electrolyte/Pt, air.

The electrochemical properties of $Ce_{0.8}Sm_{0.2}O_{1.9}$ are strongly affected by the method of their preparation which can give the samples superior density and their electrical properties. The specific power of a single electrochemical cell based on Solid, Chem, and Laser electrolyte was 80, 120 and 130 mW/cm^2 at 750°C (with OCV values, respectively, 0.75, 0.79 and 0.80 V).

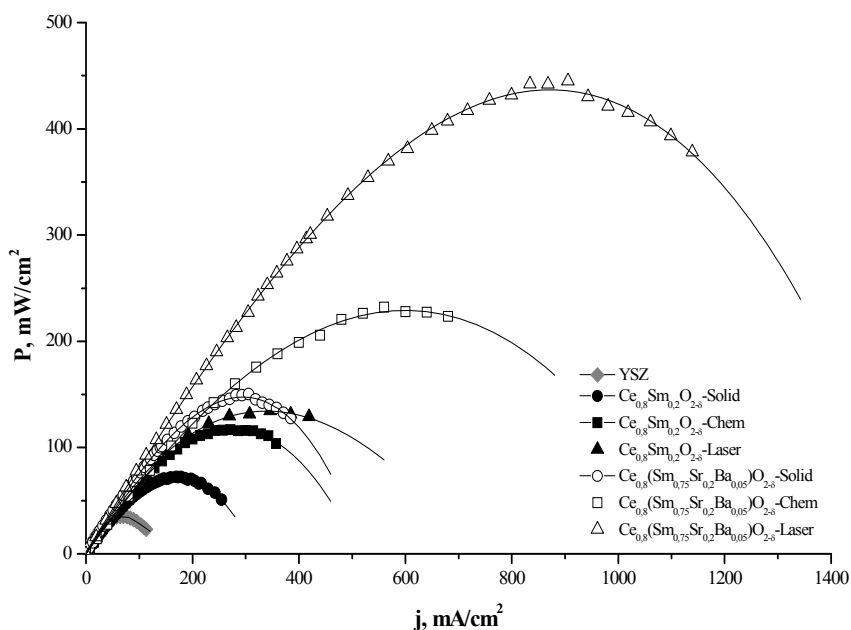Figure 4:   Electrochemical performance (specific power) of single SOFCs with supported electrolyte (0.8 mm) made by different methods, measured at 750°C with fuel $H_2+5\%H_2O$.

It was found that an introduction of Sr^{2+} and Ba^{2+} significantly improved not only the structural and electrical, but also the electrochemical properties of the $CeO_2-Sm_2O_3$ electrolyte. The best characteristics were found in the $(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}Ce_{0.8}O_{2-\delta}$ electrolyte, prepared by the method of laser evaporation of ceramic target. The specific power of a single SOFC on this base reached 450 mW/cm^2 at 750°C (with OCV values of 0.95 V). Compared to the traditional high temperature SOFC electrolyte 8% Y_2O_3-ZrO_2 (the samples were

made from electrolyte elements fabricated by Chepetsk engineering works) it is approximately 9 times higher.

More information about CeO_2 based electrolytes, their structural and electrical properties and their high temperature application was presented in [16].

4 Conclusions

The effect of the cation radius of the dopant and its concentration on the physicochemical properties of solid solutions $Ce_{1-x}Ln_xO_{2-\delta}$ (x = 0 – 0.20; Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb) were investigated. It was found that across the whole concentration range compositions with Nd^{3+} possess the highest values of conductivity at high temperatures, while at low temperatures (below 600°C) – those with Sm^{3+} do. The investigation of multi-component systems $Ce_{1-x}Ln_{x/2}Ln'_{x/2}O_{2-\delta}$ (x = 0 – 0.20; Ln = Sm, La, Gd and Ln´ = Dy, Nd, Y), $Ce_{0.8}(Sm_{1-x}M_x)_{0.2}O_{2-\delta}$ and $Ce_{0.8}(Sm_{1-x-y}Ba_yM_x)_{0.2}O_{2-\delta}$ (M = Cs, Sr) showed that increased conductivity is observed only with the addition of alkaline earth elements.

The highest value for total conductivity 16.62×10^{-2} S/cm at 900°C was obtained for $Ce_{0.8}(Sm_{0.8}Sr_{0.2})_{0.2}O_{2-\delta}$. It was shown that co-doping with SrO and BaO not only leads to increased electrical conductivity for solid electrolytes based on CeO_2, but also expands their electrolytic area. The lowest value 3.30×10^{-23} atm of the critical oxygen partial pressure $P_{O_2}^*$ at which the values of the electronic and ionic components of conductivity are equal was found for $Ce_{0.8}(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}O_{2-\delta}$. The electrochemical properties of electrolytes are strongly affected by the method of preparation which can give superior density of samples and their electrical properties. The specific power of a single electrochemical cell based on $Ce_{0.8}Sm_{0.2}O_{1.9}$ made by solid state reaction, nitrate combustion and laser evaporation methods was 80, 120 and 130 mW/cm^2 at 750°C (with OCV values, respectively, 0.75, 0.79 and 0.80 V). It was found that an introduction of Sr^{2+} and Ba^{2+} significantly improves not only the structural and electrical, but also the electrochemical properties of CeO_2-Sm_2O_3 electrolyte. The best characteristics were found for $(Sm_{0.75}Sr_{0.2}Ba_{0.05})_{0.2}Ce_{0.8}O_{2-\delta}$ electrolyte, prepared by the method of laser evaporation of ceramic target. The specific power of a single SOFC on this base reached 450 mW/cm^2 at 750°C (with OCV values of 0.95 V). These materials can be recommended for use in intermediate temperature electrochemical devises including SOFCs. Our future investigations will be concentrated on the development of electrode supported cells with thin film CeO_2 based electrolyte.

Acknowledgements

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