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SOME STRUCTURAL ASPECTS OF IONIC CONDUCTIVITY IN CO-DOPED CERIA-BASED ELECTROLYTES

WYBRANE STRUKTURALNE ASPEKTY PRZEWODNICTWA JONOWEGO W ROZTWORACH STAŁYCH NA BAZIE TLENKU CERU DOMIESZKOWANEGO DWOMA KATIONAMI

The sinters of co-doped ceria solid solutions with the formula of $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, where $\text{R} = \text{Y, Gd, Pr, Tb}$, $0 < x < 0.15$, were obtained from powders synthesised by Pechini method. The linear variation of cell parameter a vs. chemical composition was observed for $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, where $\text{R} = \text{Y, Gd, Tb}$, $0 < x < 0.15$ samples. However, the introduction of Pr^{3+} into $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{Pr}_x\text{O}_{1.9}$ caused a small deviation from linearity due to possible changes in the valence from Pr^{3+} to Pr^{4+} .

The determined values of oxide transference number t_{ion} for $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, $\text{R} = \text{Y, Gd}$ in the temperature range 400-750°C and partial oxygen pressure from 10^{-6} to 1 atm were close to 1, which indicated that materials investigated exhibited practically pure ionic oxide conductivity.

On the other hand, the introduction of Tb^{3+} or Pr^{3+} higher than $x > 0.05$ into solid solution $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, $\text{R} = \text{Tb, Pr}$ caused a decrease in the ionic transference number t_{ion} below 1 due to an increase in partial electronic conduction. This fact limiting investigated co-doped ceria and samaria or samaria and praseodymia ceria-based solid solutions for the further application as oxide electrolytes in solid oxide fuel cells. The analysis of bulk and grain boundary values indicated that partial substitution of Sm^{3+} by Y^{3+} or Gd^{3+} caused slight improvements in the ionic conductivity of $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$. The highest ionic conductivity was found for solid solution with chemical composition $\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Y}_{0.05}\text{O}_{1.9}$.

The selected co-doped ceria samples were tested as solid electrolytes in solid oxide fuel cells operating in the intermediate temperature range 500-750°C.

Keywords: solid oxide fuel cells, ionic conductivity, co-doped ceria solid solutions, fluorite structure

Spieki roztworów stałych tlenku ceru (IV) domieszkowanego dwoma kationami $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, gdzie $\text{R} = \text{Y, Gd, Tb, Pr}$, zaś $0 < x < 0.15$ otrzymano z proszków syntezowanych metodą Pechiniego. Dla roztworów stałych $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, gdzie $\text{R} = \text{Y, Gd, Tb}$, zaś $0 < x < 0.15$ zaobserwowano liniowe zmiany stałej sieci a wraz ze zmianą składów chemicznych badanych próbek. Z kolei zastąpienie w roztworze stałym $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{Pr}_x\text{O}_{1.9}$ kationów Sm^{3+} kationami Pr^{3+} powoduje już odstępstwa od liniowych zmian wielkości stałej sieci a badanych materiałów. Przyczyną tego zjawiska jest prawdopodobna zmiana stopnia utlenienia kationów Pr^{4+} na Pr^{3+} w badanym roztworze stałym.

Wyznaczone wielkości liczb przenoszenia jonów tlenkowych t_{ion} dla grupy spieków roztworów stałych $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, gdzie $\text{R} = \text{Y, Gd}$, gdzie $0 < x < 0.15$ są bliskie 1, co wskazuje na praktycznie czysto jonowy mechanizm przewodnictwa elektrycznego. Z kolei dla spieków tlenku ceru (IV) domieszkowanego kationami samaru i terbu lub samaru i prazeodymu $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, $\text{R} = \text{Tb, Pr}$, gdzie $x > 0.05$ stwierdzono spadek liczby przenoszenia jonów tlenkowych t_{ion} poniżej 1. Wzrost składowej przewodnictwa elektronowego w tych materiałach ogranicza ich potencjalne zastosowanie jako elektrolitów tlenkowych w stałotlenkowych ogniwach paliwowych. Spiek $\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Y}_{0.05}\text{O}_{1.9}$, charakteryzuje się najwyższą przewodnością jonową z pośród badanych materiałów. Wybrane materiały na bazie tlenku ceru (IV) domieszkowanego dwoma kationami przetestowano jako elektrolity tlenkowe w stałotlenkowych ogniwach paliwowych pracujących w temperaturach 500-750°C.

1. Introduction

Solid oxide fuel cells (SOFCs) represent the cleanest, most efficient, and most versatile system of conversion of chemical energy to electrical energy. The flexibility of fuel sources for SOFCs is an important advantage over polymer membrane fuel cells. It is possible to feed hydrocarbons directly into the cell anode. Especially interesting is the use not only of natural gas, diesel, gasified coal, and biomass but also

of solid fuels based on waste carbon particles [1÷3]. Lowering the temperature of operation is of significant technical importance to both conventional large-capacity and portable miniaturised SOFCs, ensuring reliability and cost-effectiveness, as well as providing a pathway for commercialisation of the former as well as facilitating thermal management, resulting in a reduction in size of the latter [4, 5].

In terms of the electrolyte, there are two key approaches to decreasing the operating temperature: the first is to utilise

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an alternative electrolyte material, such as yttria-stabilised zirconia (YSZ), possessing higher ionic conductivity than conventional electrolyte materials; the second is to reduce the physical thickness of the conventional electrolyte to reduce ohmic resistance [6, 7]. Ceria-based electrolytes still seem to be the most attractive oxide electrolytes for solid oxide fuel cells operating at intermediate temperature ranges (IT-SOFC) of 600-800°C.

Gadolina and samaria-doped ceria $Ce_{1-x}M_xO_{1.9}$, $M = Sm, Gd$, $0.1 < x < 0.2$ are the most-studied materials due to their higher oxide ionic conductivity compared to 8YSZ, chemical stability with cobalt – containing cathodes and thermal expansion coefficient (TEC) match with adjacent nickel involving cermet anodes.

However, ceria-based materials at 800°C become mixed conductors in reducing conditions because of the partial reduction of Ce^{4+} to Ce^{3+} , including cell voltage and efficiency losses due to internal short-circuiting. It has been reported that the electrolytic boundary domains of ceria-based solid solutions shifted to lower oxygen partial pressure at intermediate temperature ranges (500-700°C), but under these conditions the ionic conductivity of these membranes is too low to avoid unacceptably high ohmic losses during IT-SOFC operation [8, 9].

Structural modification of ceria-based solutions by co-doping is one possible way to increase the ionic oxide conductivity of ceria-based electrolytes at an intermediate temperature range (500-700°C) [10, 11]. The incorporation of co-doped ceria electrolytes into IT-SOFC produced higher power and current densities from this cell compared with the same SOFC utilised with an oxide membrane single-doped ceria $Ce_{1-x}M_xO_{1.9}$, $M = Gd, Sm, Y$ and $0.1 < x < 0.3$ [12-14].

The aim of this paper was to summarise research on the structural modification of $Ce_{0.85}Sm_{0.15-x}R_xO_{1.9}$ solid solution, where $R = Y, Gd, Pr, Tb$, and its impact on the variation of ionic conductivity. Comparative analyses of performance of IT-SOFC involving singly- or co-doped ceria-based materials are also presented and discussed.

2. Experimental

2.1. Sample preparation

Samples of $Ce_{0.85}Sm_{0.15-x}R_xO_{1.9}$, $R = Y, Gd, Pr, Tb$ were sintered at 1500°C for 2 h from fine powders obtained using the Pechini method. The details of fine powder synthesis of CeO_2 -based powders have been described in previous papers [15, 16]. $NiO-Ce_{0.85}Sm_{0.15}O_{1.9}$ was also synthesised using a modified Pechini method. In this method the thermal decomposition of the organic precursor at 600°C for 1 h, followed by a calcination at 1100°C for 2 h, enabled the acquisition of the desired composite anode materials. All CeO_2 -based prepared powders were grounded in a planetary mill (Retsch PM 100).

2.2. Analytical methods of evaluating co-doped ceria-based materials

The phase compositions of all powders and sintered bodies were identified by X-ray diffraction analysis based on the ICDD data base. XRD measurements were done using the

PANalytical X'Pert Pro system with monochromatic CuK_{α} radiation. The lattice parameters a of co-doped ceria solid solutions $Ce_{0.85}Sm_{0.15-x}R_xO_{1.9}$, $R = Gd, Y, Pr$ and Tb were determined using the Rietveld method. Scanning electron microscopy (SEM) augmented with an Energy-Dispersive X-ray analysing system (EDX) was used for the observation of fractures in etched sintered samples and small prepared solid oxide fuel cells (button-sized, with an active surface area of ca. 2 cm^2).

The electromotive force of the cell (1) was measured as a function of temperature (500-800°C) and oxygen pressure ranging from $1 \cdot 10^{-6}$ to 0.21 atm.



The ionic transference number (t_{ion}) of co-doped ceria based samples was estimated as the ratio of the observed $E_{(obs)}$ to the theoretical electromotive force (E_t). The electromotive force measurement of cell (1) in the same condition was also performed for samples of 8% mole Y_2O_3 in ZrO_2 (8YSZ), which is known and commonly used as a solid oxide electrolyte in electrochemical oxygen sensors and other electrochemical devices [16].

The electrical properties of ceria-based electrolytes were determined using the a.c impedance spectroscopy method at the temperature range 100-700°C and at frequencies from 0.01 Hz to 1 MHz.

2.3. Electrochemical tests of solid button oxide fuel cells

The electrochemical tests of electrolytes in solid oxide fuel cells were conducted for:

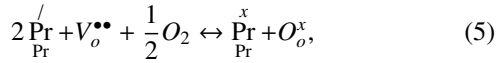


where 15SDC, 10S5YDC, and 10S5GDC were electrolytes consisting of $Ce_{0.85}Sm_{0.15}O_{1.9}$, $Ce_{0.85}Sm_{0.1}Y_{0.05}O_{1.9}$, and $Ce_{0.85}Gd_{0.1}Y_{0.05}O_{1.9}$; LSCF was a $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3$ porous cathode material deposited by screen printing; LSCF-GDC was a composite cathode material consisting of LSCF+10 mol. % Gd_2O_3 in CeO_2 (GDC); and Ni-15SDC was a cermet anode material. The family of current (I -voltage (U) and current (I)-power (P) curves of tested solid oxide fuel cells was also measured using the cyclic voltammetry (CV) method and an Autolab electrochemical station.

3. Results

Only CeO_2 -based solid solutions were identified by the XRD analysis in all prepared powders and sintered electrolytic shapes. No phases, other than cubic CeO_2 -based solid solutions, were found in the XRD diffraction patterns of co-doped samples exposed in a (H_2 -Ar) gas mixture. The variation lattice parameter a of $Ce_{0.85}Sm_{0.15-x}R_xO_{1.9}$, $R = Y, Gd, Pr, Tb$ vs. chemical composition is presented in Fig. 1. The linear decrease of cell parameter a vs. chemical composition was obtained for analysed co-doped solid solution $Ce_{0.85}Sm_{0.15-x}R_xO_{1.9}$, $R = Y, Gd, Tb$. Only in case of

$\text{Ce}_{0.85-x}\text{Sm}_{0.15-x}\text{Pr}_x\text{O}_{1.9}$ solid solution, a slight deviation from linearity was noticed. According to Shunk et al. [17], one of the main reasons for such a relationship could be a change of valence of $\text{Pr}^{3+}/\text{Pr}^{4+}$ at atmospheric pressure [18]. The equilibrium between Pr^{3+} and Pr^{4+} , determined by temperature and oxygen partial pressure, can be expressed by equation (5):



where: $[\text{Pr}_{\text{Pr}}^{\bullet\bullet}] = \text{Pr}^{3+}$, $[\text{Pr}_{\text{Pr}}^x] = \text{Pr}^{4+}$.

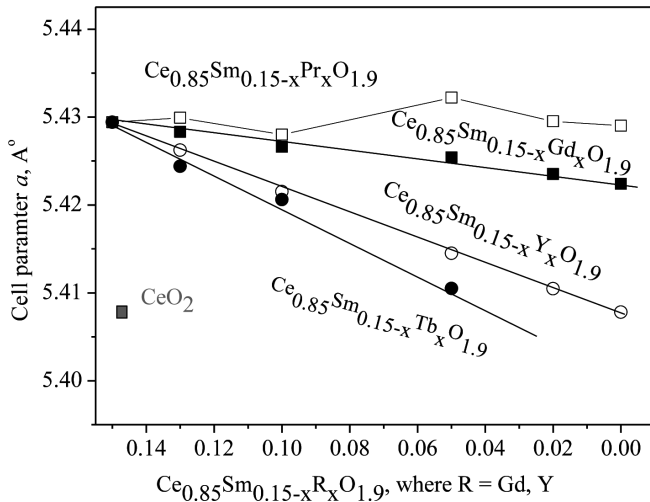


Fig. 1. The cell parameter a of co-doped ceria electrolytes

Ionic conductors considered as oxide electrolytes for SOFC application should have an oxide ionic transfer number (t_{ion}) close to 1. In this study, ionic oxide transference numbers t_{ion} were determined based on electromotive force (E_{ob}) measurements. The (E_{ob}) values for cell (1), measured at a temperature range of 500-700°C, were compared with the (E_T) values obtained for a cell containing 8YSZ. The data are collected in Table 1.

TABLE 1
Temperature dependence of oxide ion transference t_{ion} of co-doped ceria electrolytes

Composition	Temperature, °C				
	550	600	650	700	750
$\text{Ce}_{0.85}\text{Sm}_{0.13}\text{Pr}_{0.02}\text{O}_{1.9}$	1	0.99	0.98	0.98	0.97
$\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Pr}_{0.05}\text{O}_{1.9}$	0.92	0.90	0.90	0.9	0.88
$\text{Ce}_{0.85}\text{Sm}_{0.05}\text{Pr}_{0.1}\text{O}_{1.9}$	0.70	0.72	0.74	0.75	0.74
$\text{Ce}_{0.85}\text{Sm}_{0.05}\text{Tb}_{0.1}\text{O}_{1.9}$	0.82	0.84	0.84	0.85	0.86
$\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Tb}_{0.05}\text{O}_{1.9}$	0.88	0.87	0.88	0.90	0.91
$\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.9}$	1	1	1	1	1

As can be seen, the transference number was close to 1 for samples from the $\text{CeO}_2\text{-Gd}_2\text{O}_3\text{-Sm}_2\text{O}_3$ or $\text{CeO}_2\text{-Gd}_2\text{O}_3\text{-Y}_2\text{O}_3$ systems. On the other hand, in the case of co-doped samaria and praseodymia or samaria and terbium $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, $\text{R} = \text{Pr}, \text{Tb}$, where x increase of higher values than 0.05 a considerable decrease of values of t_{ion} was noticed.

One of the main reasons for such behaviour is an increase in partial electronic conduction in samples at the investigated temperature and partial pressure range. This agrees well with possible changes in valence $\text{Pr}^{3+}/\text{Pr}^{4+}$. In the cases of samaria- and terbium-doped ceria solid solutions, changes in valence Tb^{3+} to Tb^{4+} and their impact on increase electronic conductivity is also possible.

The a.c impedance spectroscopy method was applied to determine the electrical properties of single- or co-doped ceria-based samples obtained using the Pechini method. Fig. 2. presents the typical impedance spectra recorded for $\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Y}_{0.05}\text{O}_{1.9}$ at 400°C. The equivalent circuit $(\text{R-CPE})_b\text{-(R-CPE)}_{gb}\text{-(R-CE)}_{el}$ was used to fit the impedance data to calculate bulk (R_b) and grain boundary resistance (R_{gb}).

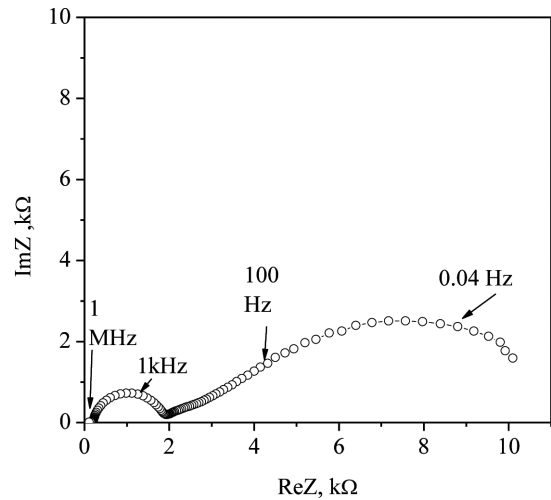


Fig. 2. The impedance spectra recorded for $\text{Ce}_{0.85}\text{Sm}_{0.1}\text{Y}_{0.05}\text{O}_{1.9}$ sample at 400°C

The Arrhenius plot of bulk conductivity (σ_b) for $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.9}$ (a), $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.9}$ (b) and $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Y}_{0.05}\text{O}_{1.9}$ (c) samples is shown in Fig. 3. in $\log(\sigma T)$ vs. $1/T$ coordination. These results indicated that co-doped ceria with Sm_2O_3 and Y_2O_3 or Sm_2O_3 and Gd_2O_3 exhibits slightly higher values of bulk conductivity compared to a $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.9}$ sample with the same dopant concentrations. The ionic conductivity of doped ceria electrolytes is affected not only by distribution of oxygen vacancies but also lattice strain. The introduction of Sm_2O_3 and Y_2O_3 in to solid solution $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{Y}_x\text{O}_{1.9}$ may suppress the ordering of oxygen vacancies, thereby lowering activation energy conduction and improving ionic conductivity. The typical dependence of bulk and grain boundary conductivity vs. temperature recorded for $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.9}$ sample is presented in Fig. 4. The detailed analysis of bulk and grain boundary conductivities for all investigated samples in $\text{CeO}_2\text{-Sm}_2\text{O}_3\text{-R}_2\text{O}_3$, $\text{R} = \text{Gd}, \text{Y}$ at 600°C reveals that bulk and grain boundary conductivities reached a maximum value for $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{Y}_{0.05}\text{O}_2$ and $\text{Ce}_{0.85}\text{Sm}_{0.05}\text{Gd}_{0.1}\text{O}_{1.9}$ samples. The maximum values of bulk and grain boundary conductivities – correspond to minimum energy activation in agreement with the compensation rule of Mayer-Neldel. Although the values of electrical conductivity are higher in the case of $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{R}_x\text{O}_{1.9}$, $\text{R} = \text{Pr}^{3+}$ and Tb^{3+} , the previously-detected presence of electronic conduction limits their application as solid oxide electrolytes.

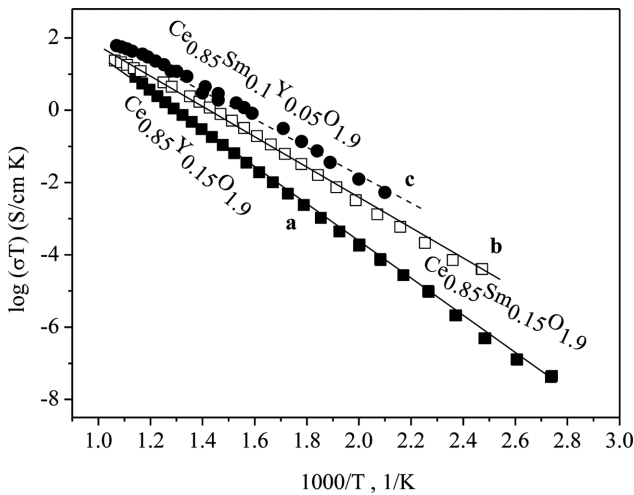


Fig. 3. Temperature dependence of bulk conductivity (σT) v.s $1000/T$ for $Ce_{0.85}Y_{0.15}O_{1.9}$ (a) $Ce_{0.85}Sm_{0.15}O_{1.9}$ (b), $Ce_{0.85}Sm_{0.1}Y_{0.05}O_{1.9}$ (c)

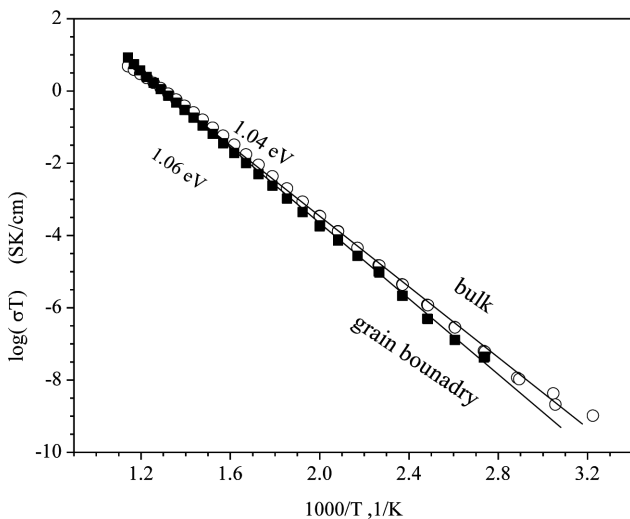


Fig. 4. Temperature dependence of bulk conductivity and grain boundary (σT) v.s $1000/T$ for $Ce_{0.85}Sm_{0.1}Y_{0.05}O_{1.9}$ sample

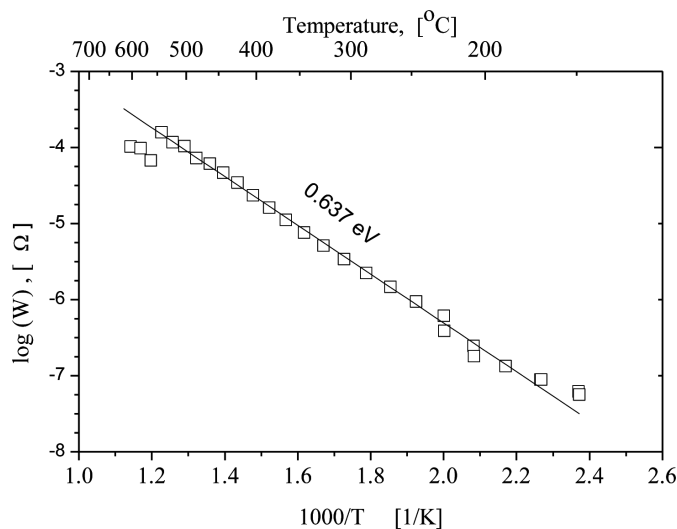


Fig. 5. The dependence of Warburg element (W) vs. temperature

The linear dependence of Warburg impedance (W) vs. temperature (Fig. 5) was also noticed in investigated tem-

perature range. The calculated values of energy activation for oxygen diffusion in thin layer electrode are close to data obtained for the same process but for other oxide ionic conductors. These results clearly indicate that co-doped ceria solid solutions in the $CeO_2-M_2O_3-Y_2O_3$, $M = Gd, Sm$ system seem to be adequate ceramic electrolytes for IT-SOFC application. The $Ce_{0.85}Sm_{0.15}O_{1.9}$ (15SDC) and $Ce_{0.85}Sm_{0.1}Y_{0.05}O_{1.9}$ (10S5YDC) samples were chosen for further investigations as components of solid oxide fuel cells filled with gaseous hydrogen.

TABLE 2
Electrical conductivities σ at $600^\circ C$ of the CeO_2 -based samples

Composition	σ [S/cm]		Ea , [eV]	
	bulk	grain boundary	bulk	grain boundary
$Ce_{0.85}Sm_{0.15}O_2$	$6.21 \cdot 10^{-3}$	$4.71 \cdot 10^{-3}$	0.93	1.01
$Ce_{0.85}Sm_{0.1}Y_{0.05}O_2$	$9.84 \cdot 10^{-3}$	$6.83 \cdot 10^{-3}$	0.88	0.98
$Ce_{0.85}Sm_{0.12}Y_{0.08}O_2$	$8.14 \cdot 10^{-3}$	$5.65 \cdot 10^{-3}$	0.92	1.03
$Ce_{0.85}Y_{0.15}O_2$	$4.41 \cdot 10^{-3}$	$3.28 \cdot 10^{-3}$	1.04	1.06
$Ce_{0.85}Sm_{0.1}Gd_{0.05}O_2$	$6.89 \cdot 10^{-3}$	$5.14 \cdot 10^{-3}$	0.91	1.01
$Ce_{0.85}Sm_{0.05}Gd_{0.1}O_2$	$8.40 \cdot 10^{-3}$	$6.13 \cdot 10^{-3}$	0.96	0.99
$Ce_{0.85}Sm_{0.1}Tb_{0.05}O_{0.2}$	$7.81 \cdot 10^{-3}$	$5.23 \cdot 10^{-3}$	0.78	0.84
$Ce_{0.85}Sm_{0.05}Tb_{0.1}O_{0.2}$	$1.3 \cdot 10^{-2}$	$6.40 \cdot 10^{-3}$	0.73	0.82
$Ce_{0.85}Sm_{0.05}Pr_{0.1}O_{0.2}$	$1.8 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$	0.70	0.79

Fig. 6. shows the family of voltage (U) – current density (I) recorded for an SOFC with 15SDC and 10S5YDC samples as electrolytes at a temperature range of $500-750^\circ C$. The power (P) density, as well as current (I) density, of an SOFC with the $Ce_{0.85}Sm_{0.1}Y_{0.05}O_{1.9}$ (10S5YDC) electrolyte reached higher values than the same SOFC with the $Ce_{0.85}Sm_{0.15}O_{1.9}$ (15SDC) electrolyte. This could be attributed to a decrease in the resistance of the cell. As can be seen, the utilisation of a solid oxide electrolyte with higher ionic conductivity led to a reduction in ohmic losses during IT-SOFC performance.

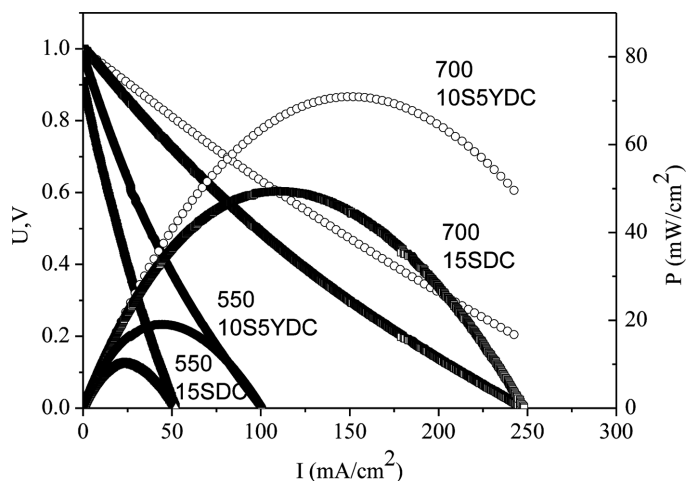


Fig. 6. The family curves $U - I$ and $P - I$ recorded for 15SDC and 10S5YDC at 550 and $700^\circ C$

4. Conclusions

The co-doping approach seems to be an adequate way to improve the ionic conductivity of ceria-based electrolytes at an intermediate temperature range. It was found that partial substitution of Sm^{3+} by Y^{3+} in $\text{Ce}_{0.85}\text{Sm}_{0.15-x}\text{Y}_x\text{O}_{1.9}$, where x is not higher than 0.05, caused a small improvement in ionic conductivity. Comparative electrochemical SOFC investigations indicated that elaborating electrolytic materials seems to be prospective components for intermediate temperature solid oxide fuel cells application.

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