

Thermochemical compatibility between selected (La,Sr) (Co,Fe,Ni)O₃ cathodes and rare earth doped ceria electrolytes

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Available online 21 May 2007

Abstract

In this paper the results of thermal expansion coefficient measurements of different singly and doubly doped ceria electrolytes, together with results for selected cathode materials from (La,Sr)(Co,Fe,Ni)O₃ system are given. A high temperature chemical stability of the cathode–electrolyte interface was measured on 1:1 wt. mixtures of previously characterized ceria and perovskite powders. The samples were heated at 800, 1000 or at 1200 °C in air for 6 or 100 h. Chemical reactivity investigations were conducted using XRD with Rietveld analysis.

For all heated samples the crystal structure of both components were preserved. However, their lattice parameters evolved to a different extent, suggesting the existence of cation exchange. A formation of the solid state solution between Ce_{1-x}RE_xO_{2-x/2} and La(Co,Fe,Ni)O_{3-δ} was found, with mobile La cation. On the basis of the obtained results a qualitative mechanism of the observed reaction was proposed.

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Keywords: Solid oxide fuel cell; Ceria; Perovskite oxides; Thermal extension coefficient; Thermochemical compatibility

1. Introduction

Among several important properties the compatibility between component materials used in the solid oxide fuel cells (SOFC) plays an important role [1]. Compatible materials must fulfill strict requirements concerning fitting of their thermal expansion coefficients (TEC) and lack of chemical reaction between them in working conditions of the cell, as well as during a stack construction.

Up-to-date, most promising cathode materials for an intermediate temperature SOFC (IT-SOFC) belong to the perovskite type oxides with a wide range of compositions Ln_{1-x}A_xMO₃ (Ln: La, Sm, Nd, Gd, Dy, Pr; A: Ca, Sr, Ba; M: 3d metals; usually Co, Fe, Ni used in various proportions) [2–4]. In case of the electrolytes one of the most promising materials are rare earth doped ceria, e.g. Ce_{1-x}Gd_xO_{2-x/2} [5]. Recently also doubly doped oxides, e.g. Ce_{1-x}(RE1,RE2)_xO_{2-x/2} (RE: rare earth element) were studied [6,7].

2. Experimental

Singly (Ce_{0.85}Gd_{0.15}O_{1.925}, Ce_{0.8}Gd_{0.2}O_{1.9}) and doubly (Ce_{0.85}(Gd_{0.5}Y_{0.5})_{0.15}O_{1.925}, Ce_{0.85}(Gd_{0.5}Nd_{0.5})_{0.15}O_{1.925}, Ce_{0.85}(Gd_{0.5}Sm_{0.5})_{0.15}O_{1.925}, Ce_{0.85}(Gd_{0.5}Dy_{0.5})_{0.15}O_{1.925}) doped ceria powders were obtained by means of a coprecipitation method from corresponding nitrate solutions (p.p.a.). The solution with concentration of ions equivalent to desired electrolyte stoichiometry was dropwise added to the intensively mixed, concentrated ammonia solution. The obtained gel was washed with water and next with isopropyl alcohol. Then, the gel was filtered, dried at 90 °C to yield a xerogel and finally was calcinated in air at 700 °C for 1 h. To obtain dense pellets for TEC measurements synthesized powders were compacted uniaxially (100 MPa) and sintered for 4 h at 1500 °C.

LaFe_{1-x}Ni_xO₃, La_{1-x}Sr_xCo_{1-y}Fe_yO₃, La_{1-x}Sr_xCo_{1-y-z}Fe_yNi_zO₃ and GdFe_{0.6}Ni_{0.4}O₃ perovskites with different compositions were synthesized using a modified citric acid method. Stoichiometric amounts of La(NO₃)₃·6H₂O, Sr(NO₃)₂, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O and Ni(NO₃)₂·6H₂O (p.p.a.) were dissolved in deionised water. A 1.5 M excess of citric acid was used. The solutions were heated in air up to 400 °C. A

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formation of sol followed by gel, which decomposed producing NO_x and CO_x gases, was observed. The precursors were mixed in mortar and pressed into pellets. The samples were initially heated in air for 12 h at 600 °C, re-grounded, uniaxially compacted (100 MPa) and finally heated in the 1000–1200 °C range, depending on the sample chemical composition. In case of the $\text{GdFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ and LaNiO_3 samples the final heating was performed at 800 °C due to their lower chemical stability. Crystallographic structure of obtained materials was determined by XRD measurements, using Philips X'Pert Pro diffractometer with $\text{Cu K}\alpha$ radiation. Structural parameters of the samples were refined by Rietveld method. The linear TEC was measured on dense samples by means of a standard dilatometric method using custom-made dilatometer.

Chemical stability studies were conducted on pellets consisting of 1:1 weight ratio mixture of the electrolyte and the perovskite material, and heated in 800, 1000 and 1200 °C for 6 and 100 h. Heated mixtures were characterized by XRD measurements with Rietveld refinement. Different cathode materials were tested in relation to standard ceria electrolyte $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, whereas electrolyte materials were tested in relation to typical cathode material $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$.

3. Results and discussion

3.1. Thermal expansion coefficient

Two phases forming an interface designed to work in elevated temperatures should be characterized with similar TEC values. It is recognized, that the highest accepted mismatch of TECs between electrolyte and cathode materials cannot exceed about 30%. In Table 1 a set of thermal expansion coefficients obtained for $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and different doubly doped ceria: $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Y}_{0.5})_{0.15}\text{O}_{1.925}$, $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Nd}_{0.5})_{0.15}\text{O}_{1.925}$, $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Sm}_{0.5})_{0.15}\text{O}_{1.925}$, $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$ is shown together with literature data for yttria stabilized zirconia, $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$, and doped lanthanum gallate: $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.9}\text{Mg}_{0.1}\text{O}_{2.85}$ [8]. In Table 2 a similar set of data is presented for LaFeO_3 , $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$, $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_3$, $\text{LaFe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$, $\text{LaCo}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3$, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.6}\text{Ni}_{0.2}\text{O}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite cathode materials. Also data for LaNiO_3 [9], $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ [10], $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ [11], $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_3$ [10], $\text{LaCo}_{0.7}\text{Ni}_{0.3}\text{O}_3$ [12],

Table 1
Thermal expansion coefficients for electrolyte materials

Material	TEC ($\times 10^{-6} \text{ K}^{-1}$)	Reference
$\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$	10.5	[8]
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$	10.9	[8]
$\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Sm}_{0.5})_{0.15}\text{O}_{1.925}$	11.4	This work
$\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$	11.6	This work
$\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$	11.9	This work
$\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Y}_{0.5})_{0.15}\text{O}_{1.925}$	12	This work
$\text{Ce}_{0.85}\text{Gd}_{0.20}\text{O}_{1.9}$	12.5	This work
$\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Nd}_{0.5})_{0.15}\text{O}_{1.925}$	12.7	This work

Table 2
Thermal expansion coefficients for cathode materials

Material	TEC ($\times 10^{-6} \text{ K}^{-1}$)	Reference
LaNiO_3	10	[9]
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$	11.7	[10]
LaFeO_3	11.8	This work
$\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$	12	[11]
$\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$	12.2	This work
$\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_3$	12.9	This work
$\text{LaFe}_{0.9}\text{Ni}_{0.1}\text{O}_3$	12.9	This work
$\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$	13.4	This work
$\text{LaCo}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3$	14.9	This work
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3$	15.8	This work
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_3$	16.1	[10]
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.6}\text{Ni}_{0.2}\text{O}_3$	16.9	This work
$\text{LaCo}_{0.7}\text{Ni}_{0.3}\text{O}_3$	17.3	[12]
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	17.5	This work
$\text{LaCo}_{0.9}\text{Ni}_{0.1}\text{O}_3$	19.6	[12]
LaCoO_3	22	[10]
$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	24	[13]
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	27.1	[13]

$\text{LaCo}_{0.9}\text{Ni}_{0.1}\text{O}_3$ [12], LaCoO_3 [10], $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ [13] and $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ [13] taken from other articles is shown.

It can be noted that for all electrolytes TEC values change within a relatively narrow range, from $11 \times 10^{-6} \text{ K}^{-1}$ for $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$ to $12.7 \times 10^{-6} \text{ K}^{-1}$ for $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Nd}_{0.5})_{0.15}\text{O}_{1.925}$. On the contrary, TECs of the perovskite materials is spread over a much wider range, from $10 \times 10^{-6} \text{ K}^{-1}$ for LaNiO_3 to $27.1 \times 10^{-6} \text{ K}^{-1}$ for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$. Generally, perovskite oxides exhibiting the highest activity towards oxygen reduction (for instance $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$) are characterized by high TEC values. On the other hand, cathodes with substantial nickel content fit well to ceramic electrolytes in terms of TEC, values but their stability at high temperatures is insufficient (see Section 3.2). If the fuel cell is to endure large number of heating–cooling cycles, one has to find a compromise between thermomechanical and other important properties.

3.2. High temperature stability

SEM analysis (Fig. 1a) performed on the heated mixtures of doped ceria and perovskite oxide revealed that the obtained samples compose of close packed grains and exhibit relatively low porosity. Fig. 1b presents one of the XRD patterns of the starting materials, in this case $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, before mixing and after heating at 1200 °C for 6 h. XRD pattern obtained after heating revealed no new phases present in the examined system.

Also in almost all examined cases (except three presented below) no new phases were observed and crystallographic structure of both: cathode and electrolyte materials was preserved. This indicates a reasonable chemical compatibility of tested materials. There are three exceptions: perovskite oxides with composition $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Fe}_{0.4}\text{Ni}_{0.4}\text{O}_3$ and $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ decomposed after heating at 1200 °C. For these samples on the XRD pattern new reflexes appeared, indexed to NiO phase. The

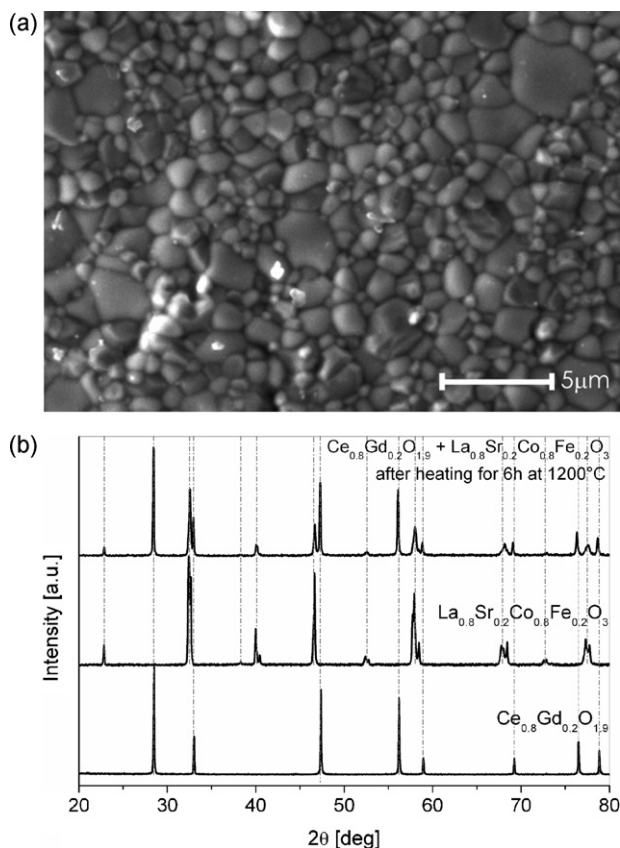


Fig. 1. (a) Scanning electron micrograph of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ mixture heating at $1200\text{ }^\circ\text{C}$ for 100 h and (b) set of XRD patterns for the starting materials and for the mixture after heating.

NiO amount increased with the increasing heating time and after 100 h of heating NiO content raised to over 10 wt.%. Both materials have 0.4 mol of nickel per 1 mol of compound and probably this causes their instability. For LaNiO_3 , the decomposition temperature is below $1000\text{ }^\circ\text{C}$.

For all heated mixtures small shifts of XRD peaks position were observed. For instance, in Fig. 2 an evolution of the (111) peak of the ceria electrolyte $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ is presented. The results were obtained after heating the electrolyte with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathode material. The first peak on the right-hand side relates to $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ oxide heated sep-

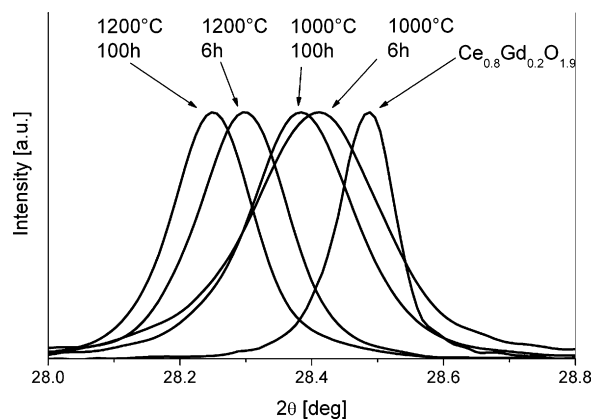


Fig. 2. Evolution of ceria (111) peak position for the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}-\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ mixture after heating at different temperatures and for different times.

arately at $1200\text{ }^\circ\text{C}$ for 6 h and it occurs at the same position as for unheated sample (the result not shown). For the mixture of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ the position of this reflex shifts towards smaller 2θ values. This process intensifies for longer heating times and for higher heating temperatures. Such dependence may indicate an existence of cation exchange between materials being in contact. The shift of the peaks during separate annealing of cathode or electrolyte material is negligible.

Table 3 shows an example of lattice constants evolution for the $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ in the 50/50 wt.% mixture as a function of heating time. Number in bracket denotes a standard deviation of the corresponding value. For all the temperatures the most intensive changes were observed during a first 6 h of process. Similar results were obtained for all examined mixtures.

In Table 4 a comparison of relative changes of lattice constants is presented for different ceria electrolytes heated for 100 h at 800, 1000 and $1200\text{ }^\circ\text{C}$ with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite oxide. In the case of $800\text{ }^\circ\text{C}$, which is close to supposed working temperature of the solid oxide fuel cell with ceria electrolyte, changes of lattice parameters are small and do not exceed 0.2% for both cathode and electrolyte materials. At higher temperatures the observed changes are more substantial and reach 0.85% for c parameter of

Table 3

Lattice constants evolution for the $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ in the 50/50 wt.% mixture as a function of heating time

Composition	Annealing time (h)	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$		$\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$
		a (Å)	c (Å)	a (Å)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, $1200\text{ }^\circ\text{C}$	0	5.5226(3)	13.3894(8)	5.4204(1)
	6	5.5092(2)	13.4527(7)	5.43295(7)
	100	5.5041(3)	13.4612(6)	5.4350(4)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, $1000\text{ }^\circ\text{C}$	0	5.5226(3)	13.3894(8)	5.4204(1)
	6	5.5150(2)	13.4380(9)	5.42713(7)
	100	5.5121(2)	13.4441(8)	5.42750(6)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, $800\text{ }^\circ\text{C}$	0	5.5226(3)	13.3894(8)	5.4204(1)
	6	5.5215(2)	13.4162(7)	5.4234(2)
	100	5.5189(1)	13.4143(5)	5.4231(1)

Table 4
Relative changes of lattice constants for different ceria electrolytes heated together with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite for 100 h at 800, 1000 and 1200 °C

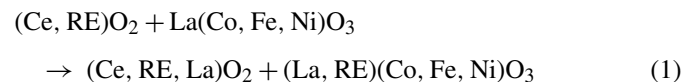
Composition	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$		Ceria
	a (Å)	c (Å)	a (Å)
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Y}_{0.5})_{0.15}\text{O}_{1.925}$, 800 °C	−0.06%	0.17%	0.03%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Y}_{0.5})_{0.15}\text{O}_{1.925}$, 1000 °C	−0.20%	0.43%	0.09%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Y}_{0.5})_{0.15}\text{O}_{1.925}$, 1200 °C	−0.25%	0.09%	0.16%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Nd}_{0.5})_{0.15}\text{O}_{1.925}$, 800 °C	−0.05%	0.18%	−0.01%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Nd}_{0.5})_{0.15}\text{O}_{1.925}$, 1000 °C	−0.20%	0.39%	0.07%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Nd}_{0.5})_{0.15}\text{O}_{1.925}$, 1200 °C	−0.24%	0.50%	0.18%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Sm}_{0.5})_{0.15}\text{O}_{1.925}$, 800 °C	−0.06%	0.19%	0.01%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Sm}_{0.5})_{0.15}\text{O}_{1.925}$, 1000 °C	−0.22%	0.40%	0.09%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Sm}_{0.5})_{0.15}\text{O}_{1.925}$, 1200 °C	−0.25%	0.50%	0.23%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$, 800 °C	−0.06%	0.16%	0.01%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$, 1000 °C	−0.41%	0.77%	0.35%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$, 1200 °C	−0.61%	0.93%	0.24%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, 800 °C	−0.07%	0.19%	0.05%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, 1000 °C	−0.19%	0.41%	0.13%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$, 1200 °C	−0.34%	0.53%	0.27%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{CeO}_2$, 800 °C	−0.05%	0.20%	0.05%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{CeO}_2$, 1000 °C	−0.16%	0.52%	0.08%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{CeO}_2$, 1200 °C	−0.26%	0.60%	0.21%

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ being in contact for 100 h at 1200 °C with $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$. In all cases the lattice parameter a of perovskite decreases, while parameter c and ceria lattice constant increase. As can be seen in Table 4, all ceria based oxides show similar behavior independently on the composition. The largest modifications were observed for compositions containing ceria doped with dysprosium. Quite surprisingly, for $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Y}_{0.5})_{0.15}\text{O}_{1.925}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system change of perovskite lattice constant c is higher during annealing at 1000 °C than at 1200 °C. Similarly, for $\text{Ce}_{0.85}(\text{Gd}_{0.5}\text{Dy}_{0.5})_{0.15}\text{O}_{1.925}$ – $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system change of doped ceria lattice constant a is more substantial at 1000 °C than at 1200 °C. Also, for $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ in contact with ceria, nonlinear changes are observed. We cannot explain these facts on the basis of our results and further studies are needed.

Available literature data for the changes of the lattice constant during heating of $\text{Ce}_{0.8}\text{Y}_{0.18}\text{Ca}_{0.02}\text{O}_{1.89}$ together with $\text{YNi}_{0.33}\text{Mn}_{0.67}\text{O}_3$ shows different behavior [14]. After heating for 4 h at 1250 °C the decrease (−0.07%) of ceria lattice parameter was observed. However, such characteristic is expected and will be discussed below.

Table 5 presents the variation of relative lattice constant changes for different perovskite oxides heated for 100 h together with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ electrolyte. In this table perovskites with two crystallographic structures are collected: hexagonal $R\text{--}3c$ (LaNiO_3 , $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Fe}_{0.4}\text{Ni}_{0.4}\text{O}_3$) and orthorhombic $Pnma$ (LaFeO_3 , $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$). At 800 °C the observed changes are minor and do not exceed 0.2%. A strong dependence on the nickel content may be observed. The increase of the nickel amount in the perovskite causes intensification of the observed changes.

Experimental data presented in Tables 4 and 5 suggest an appearance, to some extent, of a chemical reaction between the cathode material and the electrolyte. Changes of the lattice parameters in case of different perovskites are diversified and cannot be easily explained, however, the increase of lattice constant is observed in every case for ceria oxides. On the basis of the results, a qualitative model of reaction occurring in the $\text{Ce}_{1-x}(\text{Gd}_{0.5}\text{RE}_{0.5})_x\text{O}_{2-x/2}$ – $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y-z}\text{Fe}_y\text{Ni}_z\text{O}_3$ system can be proposed. By analyzing ionic radii of all the cations present in the system (Table 6) [15], we conclude that the 3d metal cations cannot induce such an increase (they are much smaller than Ce^{4+} in cubic coordination), particularly that 3d metals practically do not form solid solutions with ceria, because of large difference in ionic radii. Among cations only La^{3+} and Sr^{2+} introduced into ceria (due to their larger ionic radius) might cause such a behavior. The majority of the tested samples contained the perovskite without strontium content, and for them the lanthanum cation must be a mobile element. We suggest that a following reaction (1) occurs, that is the formation of a solid solution (in a few percent range) between two oxides:



In order to verify the above assumption the $\text{GdFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ perovskite was synthesized and compared (in terms of chemical stability) with $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$. If the lanthanum is the mobile element, its substitution with gadolinium (which induces far smaller changes of the ceria lattice constant—compare [16]) should attenuate observed modification. The results obtained during heating at 800 °C for 100 h a mixture of $\text{GdFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ are presented in Fig. 3. The observed changes of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ lattice constant are much smaller,

Table 5

Relative changes of lattice constants for different perovskite cathodes heated together with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ for 100 h at (a) 800 °C, (b) 1000 °C and (c) 1200 °C

Composition	Perovskite			$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ <i>a</i> (Å)
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
$\text{LaNiO}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	-0.01%	–	0.03%	0.18%
$\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	0.01%	-0.02%	-0.05%	0.11%
$\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1000 °C	0.10%	0.04%	-0.05%	0.34%
$\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1200 °C	0.36%	0.45%	-0.04%	0.80%
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Fe}_{0.4}\text{Ni}_{0.4} + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	0.03%	–	-0.09%	0.12%
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Fe}_{0.4}\text{Ni}_{0.4} + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1000 °C	-0.02%	–	-0.06%	0.25%
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Fe}_{0.4}\text{Ni}_{0.4}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1200 °C	0.05% (NiO appears)	–	0.05%	0.83%
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	-0.08%	–	-0.07%	0.12%
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1000 °C	-0.08%	–	-0.07%	0.09%
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1/3}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1200 °C	-0.06%	–	-0.03%	0.49%
$\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	0.04%	-0.04%	0.00%	0.07%
$\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1000 °C	-0.01%	0.02%	-0.03%	0.17%
$\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1200 °C	0.14%	-0.02%	-0.02%	0.41%
$\text{LaFeO}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	0.01%	-0.01%	-0.03%	0.07%
$\text{LaFeO}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1000 °C	0.03%	-0.04%	-0.08%	0.21%
$\text{LaFeO}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1200 °C	0.02%	-0.10%	-0.18%	0.27%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 800 °C	-0.07%	–	-0.07%	0.05%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1000 °C	-0.21%	–	0.40%	0.13%
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 + \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, 1200 °C	-0.21%	–	0.34%	0.19%

Table 6

Ionic radius of cations present in the studied system [15]

Cation	Ionic radius (Å)		
	Octahedral	Cubic	Dodecahedral
Ce^{4+}	0.87	0.97	1.14
Gd^{3+}	0.938	1.053	–
La^{3+}	1.032	1.16	1.36
Sr^{2+}	1.18	1.26	1.44
Co^{3+}	0.545 (LS), 0.61 (HS)	–	–
Fe^{3+}	0.55 (LS), 0.645 (HS)	0.78	–
Ni^{2+}	0.69	–	–
Ni^{3+}	0.56 (LS), 0.6 (HS)	–	–

LS: low spin; HS: high spin.

when heated together with $\text{GdFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$. The reaction (1), proposed above, can also explain results from [14], in which a decrease of lattice constant of $\text{Ce}_{0.8}\text{Y}_{0.18}\text{Ca}_{0.02}\text{O}_{1.89}$ heated with $\text{YNi}_{0.33}\text{Mn}_{0.67}\text{O}_3$ was observed, as Y^{3+} (ionic radius in

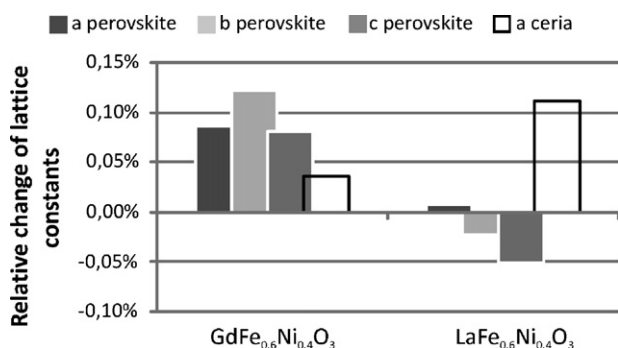


Fig. 3. Comparison of lattice constants relative change for $\text{GdFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ and $\text{LaFe}_{0.6}\text{Ni}_{0.4}\text{O}_3$ both heated with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ for 100 h at 800 °C.

cubic coordination equals 1.019 Å) is smaller than Ce^{4+} cation. Summarizing, in all of these cases it is the A cation (in ABO_3 perovskite) which is mobile. For instance in $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$ perovskites observed changes may be attributed to lanthanum mobility. At the same time, a vast lattice parameters change was observed for cathode material, but the interpretation of this fact is rather complicated due to many possible explanations. Variable factors in perovskite oxides are: possibility of nonstoichiometry in both cation sublattices and oxygen sublattice, and possibility of mixed valency of nickel and iron. Each of these may cause observed variations of lattice constants.

4. Conclusions

When analyzing TEC data of ceria based electrolytes and different perovskites one may note that in order to obtain suitable match of thermal expansion it is the chemical composition of the cathode material that should be optimized, because it varies in much wider range.

Taking into consideration the obtained results, the thermochemical compatibility between measured perovskites and ceria based electrolytes is sufficient under working conditions of IT-SOFC. The observed changes of cell parameters were relatively low, comparing to chemical stability data for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3\text{-YSZ}$ system available in literature [17].

We proposed the chemical reaction suggesting cation mixing between ceria and perovskite oxides due to the mobility of cation from perovskite sublattice A. The proposed reaction seems to explain the observed changes of ceria lattice constant during annealing with perovskite oxides. In order to clarify cause

of changes of perovskite lattice constants further studies are needed.

It must be pointed out, that operating temperature of IT-SOFCs with $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ or similar cathodes and $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ electrolytes is supposed to be in the 600–800 °C range. However, in order to obtain mechanically stable cell with appropriately formed microstructure and porosity, and satisfactory adhesion between the cell components much higher temperatures are required. Stack construction must be carried out in the lowest possible temperatures and for shortest time, in order to minimize disadvantageous processes (cation mixing) taking place at the electrolyte–cathode material interface.

Acknowledgement

This work is supported by Polish Committee for Scientific Research under grant KBN PBZ–100/1/3/2004.

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