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The changes of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite oxide on heating in oxygen and carbon dioxide atmospheres

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Abstract: In the first part of this study, the oxygen deficiency, δ, in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was measured by means of thermogravimetry as a function of the oxygen partial pressure, $p(O_2)$, in the range of 1.1×10^{-6}–41.67 % at elevated temperatures in the range 873–1073 K. It was shown that δ becomes more pronounced with increasing T and with decreasing $p(O_2)$. The isotherms δ *vs*. $p(O_2)$ were determined. The second part of this study relates to the reaction of CO_2 with $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.8}O_{3-\delta}$ perovskite oxide in the absence and presence of O_2 at temperatures ranging from 673 to 973 K, also by thermogravimetry. The reactivity of CO_2 with BSCF increased with increasing temperature and increasing exposure to CO_2. The reaction of CO_2 with BSCF was described by equilibrium reaction isotherms. The results of X-ray diffractometry evidenced that exposure to CO_2 leads to the formation of carbonates.

Keywords: BSCF; perovskite; oxygen; carbon dioxide.

INTRODUCTION

Among mixed conducting perovskite-type oxides, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) has recently received much attention.[1–4] BSCF has been proposed as the cathode material for a new SOFC (solid oxide fuel cell)[5,6] and as an oxygen permeable membrane material.[7] After a first report by Shao *et al.*,[8] the preparation, phase structure, thermal expansion coefficient and performance of BSCF materials were investigated.[9–16]

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McIntosh *et al.*[17] investigated oxygen non-stoichiometry of BSCF up to 1273 K in the $p(O_2)$ range 1.01325×10^5 to $1.01325\cdot10^2\times$Pa using a neutron diffraction technique. It was found that BSCF maintained cubic symmetry at all temperatures and oxygen partial pressures covered by the performed experiments. Zeng *et al.*[18] measured the non-stoichiometry of BSCF at room temperature using iodometry and found a high oxygen non-stoichiometry of $\delta = 0.318$ (2.682) for an air-calcined sample. They also measured the oxygen partial pressure and temperature dependence of the oxygen non-stoichiometry by the thermogravimetric analysis (TGA) method up to 1273 K under an air and nitrogen atmosphere. Bucher *et al.*[19] also investigated the oxygen non-stoichiometry of BSCF by thermogravimetry at temperatures ranging from 873 to 1173 K and $p(O_2)$ pressures from 10 to 4×10^4 Pa. In addition, oxygen exchange kinetics was measured by electrical conductivity relaxation and the chemical diffusion coefficients and surface exchange coefficient were calculated from the relaxation experiments.[20] Vente *et al.*[21] measured the oxygen transport, oxygen non-stoichiometry of BSCF and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ for oxygen transport membranes. Combined TGA, temperature programmed desorption (TPD) and neutron diffraction measurements were performed. The oxygen non-stoichiometry measurements were realized in oxygen partial pressures from 100 to 1×10^5 Pa in the temperature range 873 to 1073 K. Using TGA, Wang *et al.*[22] determined the oxygen content of the starting material to be $3-\delta = 2.79$ at room temperature. They determined the oxygen ion–electron hole diffusion coefficient, the oxygen content and the diffusion coefficient of the oxygen vacancy. Perovskite oxides of type $A_{1-a}A'_aB_{1-b}B'_bO_{3-\delta}$ (with A A′ = La, Ba, Sr and B B′ = Mn, Fe, Co) were investigated by Giradauskaite *et al.*[23] The non-stoichiometry of oxygen was measured using a micro-thermo balance with partial oxygen pressures from 10^{-3} to 10^5 Pa.

The use of BSCF in practical applications, such as fuel cell cathodes, demands a certain degree of chemical stability. It is well known[24–28] that some perovskites containing alkaline elements react with CO_2. As CO_2 is one of the components of air, which is often used as an oxidizer for the fuel cell, there may be a chemical interaction between a BSCF and CO_2, leading to degradation of the cathode.

Yan *et al.*[29] investigated the interaction between CO_2 and BSCF using TPD in the presence and absence of O_2 and H_2O. They found that CO_2 could be adsorbed and reacted with BSCF in the temperature range from 673 to 973 K, thereby forming $Sr_{0.6}Ba_{0.4}CO_3$. In the case of adsorption of CO_2 without O_2, the reactivity of CO_2 on the surface of BSCF increased with increasing temperature. CO_2 and O_2 were competitively adsorbed on the BSCF. At 973 K, the oxygen adsorption was the dominant reaction on the surface of BSCF. The presence of water accelerated the "toxicity" of CO_2, which probably resulted in the formation of bicarbonate. Moreover, Yan *et al*. calculated important kinetic parameters, such as activation energy, to see how strongly the adsorbent was bound to the surface of the adsorbate.

Nomura *et al*.[30] emphasized that oxygen vacancy in perovskite structures could contribute to the formation of carbonates. They suggested that the perovskite oxides with oxygen vacancy in the crystal lattice, which are formed at elevated temperatures, could easily adsorb CO_2. The higher the temperature at which the pretreatment was performed, the more oxygen vacancies were present, which, as explained by the author, may be the reason for the reaction of BSCF with CO_2 being facilitated at high temperatures.

Arnold *et al*.[31] reported the competitive adsorption of CO_2 and O_2. They noticed strong acceleration in the degradation of a BSCF membrane with increasing CO_2 content in the supply air.

Yan *et al*.[32] found that CO_2 desorption starts at 713 K and reaches its peak at 980 K. Small particles of $SrCO_3$, $BaCO_3$ and $Sr_xBa_{1-x}CO_3$ may decompose from 873 to 1023 K. They concluded that complete decomposition of carbonate requires temperatures above 973 K. Finally, they indicated that extremely clean air should be used as an oxidizer when a BSCF cathode is operated at low temperatures. In another study, Yan *et al*.[33] examined the effects of CO_2 concentration and temperature on the performance of BSCF cathodes in SOFC at temperatures from 673 to 1023 K and CO_2 concentrations from 0.28 to 3.07 %. They concluded that BSCF cathode is not suitable for single chamber fuel cells that use hydrocarbons as fuel, especially at lower temperatures.

Yang *et al*.[34] reported on the catalytic activity of $Ba_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$, which was degraded in a carbon dioxide atmosphere from 773 to 1073 K due to the formation of carbonate on the surface.

In this paper, we present the results of an investigation of the reactivity of BSCF with oxygen and carbon dioxide, in various gas mixtures and under various temperatures. Six different gas mixtures were used. Results were fitted to reaction isotherms based on the well-known mathematical models 1 (Freundlich) [35] and 2 (Langmuir).[36] The performed calculations based on the reaction isotherms provided valuable insight into the *in situ* behavior of BSCF.

EXPERIMENTAL

Phase pure BSCF powder (Praxair) was annealed in air at 1273 K for 6 h. XRD analysis (Siemens D5000 diffractometer using a Cu-K_α X-ray tube (λ = 154 nm)) was performed on the resulting material, confirming the presence of single phase BSCF. The employed BSCF had a specific surface area close to 2 m^2 g^{-1} as determined by the Brunauer–Emmett–Teller (BET) method.

Non-stoichiometric ratios of oxygen and CO_2 adsorption were measured by a set of TGA measurement (Netzsch STA 449 C with rhodium–platinum furnace) as a function of oxygen partial pressure and temperature. The gas flows were controlled using flow meters (Bronkhorst, GmbH, Germany) with magnetic valves. The platinum crucible and slip-on plate were conditioned for the measurement by heating to 1073 K. The non-stoichiometric ratio of oxygen was measured under isobaric conditions under an atmosphere of Ar or Ar and O_2. Six different gas mixtures were used (60 cm^3 min^{-1} Ar, 55 cm^3 min^{-1} Ar + 5 cm^3 min^{-1} O_2, 50 cm^3 min^{-1} Ar + 10 cm^3 min^{-1} O_2, 45 cm^3 min^{-1} Ar + 15 cm^3 min^{-1} O_2, 40 cm^3 min^{-1} Ar + 20 cm^3 min^{-1} O_2 and 35 cm^3 min^{-1} Ar + 25 cm^3 min^{-1} O_2). Temperature program included heating to1073 K at a heating rate of 10 K min^{-1} with a 30-min-long isothermal dwell time. Isothermal dwell times were chosen in order to keep the system in a state of dynamic equilibrium. Subsequently, the sample was cooled to 973 K and then to 873 K at a cooling rate of 0.5 K min^{-1} with 30-min-long isothermal dwells. In all experiments, the samples were considered in a thermodynamic equilibrium when the sample mass attained a constant value. The equilibration time was chosen according to this condition. After cooling to873 K, samples were again heated to 1073 K with an isothermal dwell at 973 K.All measurements were corrected by the results of a correction measurement, which was performed under the same conditions as a sample run. For each measurement, the sample mass was 700 mg.

The absolute oxygen non-stoichiometry was determined by complete reduction of a BSCF sample in a 5 vol. % mixture of Ar and H_2 under isothermal conditions at 1073 K for about 24 h. The oxygen partial pressure of the reducing atmosphere was measured by a Rapidox 2100 oxygen sensor (Cambridge Sensotec Ltd., UK). After the reduction experiment, the X-ray diffraction pattern of the sample confirmed the complete decomposition of the perovskite phase into the constituent oxides. Experiments measuring carbon adsorption were performed using different CO_2/O_2 gas mixtures with a constant gas flow (10 cm^3 min^{-1}). $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.8}O_{3-\delta}$ was subjected to the initial treatment in air at 773 K for 60 min in order to remove traces of moisture. The sample weight in all experiments was 200 mg. All measurements were performed in a Pt crucible. The TG analysis of CO_2 adsorption onto BSCF was performed at 673, 773, 873 and 973 K. Each isothermal step lasted 480 min with the intention of system mass equilibration. Gas mixtures of 1, 10 and 100 % CO_2 were used for the adsorption, as presented in Table I. The rate of heating/cooling was 10 K min^{-1} in all experiments. The corrective measurement was performed with the same temperature and atmospheric parameters as used for the measurement in 100 % CO_2.

TABLE I. Gas mixtures used for measurements of CO_2 adsorption by $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Gas mixture	Purity	Other characteristics	Producer
100 % CO_2 gas	CO_2 > 99.998 %, O_2 < 2 ppm, H_2O < 3 ppm, N_2 < 8 ppm, H_2 < 0.5 ppm, CO < 1 ppm, C_nH_m < 5ppm	40 dm^3 Quality 48	Carbagas, Switzerland
10 % CO_2 gas in O_2	CO_2 by analysis 10 % (±2 % rel.)	40 dm^3, CO_2 quality 40, O_2 quality 48	Carbagas, Switzerland
1 % CO_2 gas in O_2	CO_2 by analysis 0.997 % (± 2 % rel.)	40 dm^3 CO_2 quality 40, O_2 quality 48	Carbagas, Switzerland

RESULTS AND DISCUSSION

Non-stoichiometric ratio of oxygen in oxidizing atmosphere ($p(O_2) > 21000$ Pa) was largely influenced by the temperature, as shown in Fig. 1. Change of the oxygen non-stoichiometric ratio by the oxygen partial pressure showed that, regardless of the temperature, a plateau of the partial pressure of oxygen occurred, near to the one that exists in the Earth's atmosphere, indicating temporary stabilization of the oxygen level in the material. Of course, such stabilization could be interpreted as a relative change in the diffusion energy of the oxygen ions in the BSCF material.

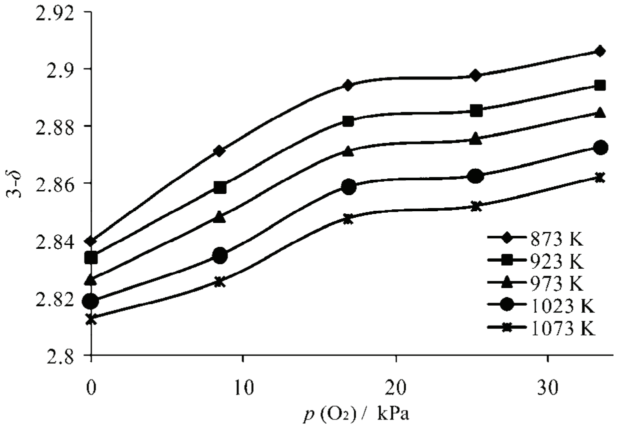

Fig. 1. Oxygen stoichiometry (3–δ) of BSCF as a function of oxygen partial pressure at different temperatures.

Although the process of change in the oxygen non-stoichiometric ratio in BSCF cannot be understood as an adsorption process, it is possible to determine the relation between the partial pressure of oxygen and the change in the mass of the sample. Reaction isotherms based on mathematical model 1, as shown in Fig. 2, followed a linear dependence that opened the possibility of determining the oxygen non-stoichiometric ratio in relation to oxygen partial pressure. The linear correlation coefficients had high values (>0.99) with a tendency to increase with temperature.

The sample mass changes obtained upon cooling were in strong agreement with those obtained upon heating. Between 973 and 873 K, the non-reversibility in mass change between the cooling and the heating process at a rate of 0.5 K min^{-1} was around 0.06 %. (Fig. 3) As shown in Fig. 4, the sample morphology, followed by scanning electron microscopy (SEM), remained the same before and after the experiment, implying that the non-reversibility was not a consequence of grain growth. Oxygen sorption and desorption are chemical processes responsible for the stoichiometric change of BSCF material. Thus, it could be concluded that the adsorption hysteresis is due to the different chemical processes during heating and cooling.

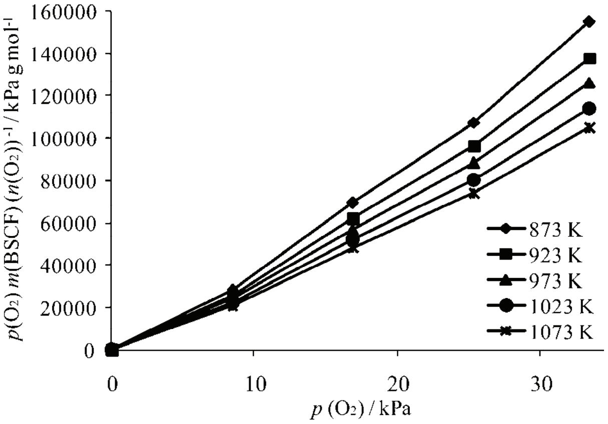

Fig. 2. Reaction isotherms based on mathematical model 1 for the system BSCF–O_2 with the corresponding equations and linear correlation coefficients (y(873 K) = 4636.9x – 5982, $R^2 = 0.9924$; y(923 K) = 4123.1x – 4974, $R^2 = 0.9934$; y(973 K) = 3779.3x – 4430, $R^2 = 0.9937$; y(1023 K) = 3412.2x – 3818, $R^2 = 0.9942$; y(1073 K) = 3144.5x – 3229, $R^2 = 0.995$).

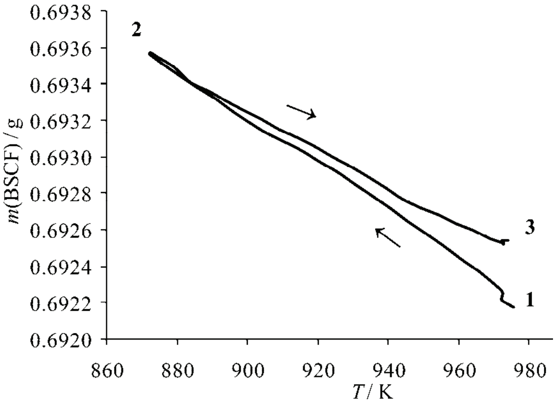

Fig. 3. The mass change of the BSCF sample at 0.5 K min^{-1} cooling (1→2) and heating (2→3) between 973 and 873 K under 10 cm^3 min^{-1} O_2 + 50 cm^3 min^{-1} Ar gas mixture.

The value of the initial oxygen stoichiometry obtained by the complete reduction of BSCF was $3–\delta \approx 2.6$. Initial oxygen stoichiometry, as found by various authors, is presented in Table II. Its value is determined by many factors, including the method of synthesis, and the values can vary from 2.48 to 2.79.

Concerning BSCF, it was assumed that the non-stoichiometry is governed by the reduction of iron from Fe^{3+} to Fe^{2+}, and cobalt from Co^{3+} to Co^{2+}. It is well known that Sr and Ba always keep their valence states and, therefore, do not influence oxygen non-stoichiometry.[37]

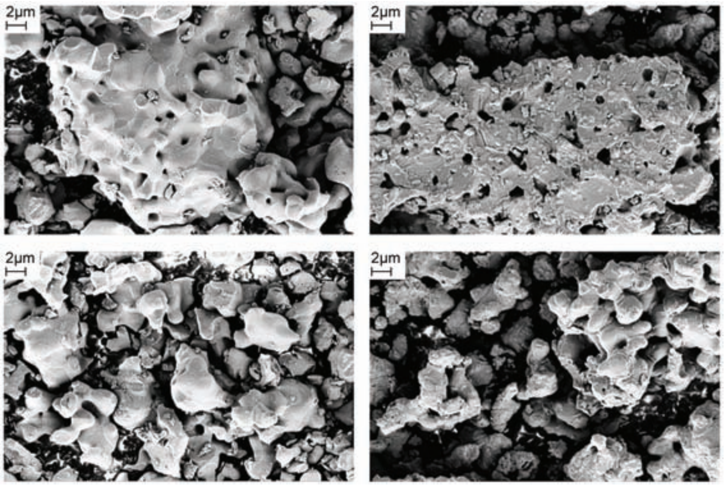

Fig. 4. Morphology of the BSCF samples before (left) and after (right) oxygen non-stoichiometry TG measurement.

TABLE II. Summary of the experimental results for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ initial oxygen stoichiometry found by various authors

Authors	Initial oxygen stoichiometry
McIntosh *et al.*[17]	2.48
Zeng *et al.*[18]	2.68
This study	2.60
Girdauskaite *et al.*[23]	2.75
Wang *et al.*[22]	2.79

Taking into consideration that Co^{3+} is reduced at a lower temperature[38] than Fe^{3+}, and that in BSCF, the molar fraction of Co is greater than the mole fraction of Fe; it could be presumed that oxygen non-stoichiometry is guided mainly by Co^{3+} reduction.

The BSCF sample mass as a function of temperature and CO_2 concentration was followed during reaction with CO_2 by thermogravimetry (Fig. 5). It should be noted that the equilibrium mass ratio established at a given temperature caused by the reaction with CO_2 was not corrected for changes in mass resulting from the temperature-dependent oxygen content in the material. There was no significant reaction with CO_2 at 673 K regardless of the relative CO_2/O_2 ratio in the atmosphere. Considerable variation in the reactivity of the BSCF–CO_2 system was observed at 773, 873 and 973 K. Increasing temperature and partial pressure of CO_2 resulted in an increased reaction rate and the creation of carbonate at the surface of BSCF. The reaction rate in 1 % CO_2 was relatively small and therefore, no weight stabilization could be observed during 480 min isothermal heating. Reaction rates in 10 % and especially in 100 % CO_2 were higher than in the previous case, leading to equilibration of the BSCF sample mass. In the case of two-component gas mixtures (10 and 1 % CO_2 in oxygen), there was a possibility of competitive adsorption and reaction of both molecules. Oxygen is absorbed and desorbed from the perovskite structure depending on the oxygen partial pressure in the surrounding atmosphere and temperature. The concentration of surface oxygen vacancies depends on the stoichiometric ratio of oxygen in the BSCF structure. These surface vacancies represent possible active sites for further reaction of oxygen and other small molecules, in the present case, CO_2. Oxygen vacancies could play the role of active adsorption centers, enabling a chemical molecular mechanism. In the case of reaction with CO_2 and related reactions on the surface, various chemical forms may occur, bonded linearly or through a chemical bridge. Based on the experimental results related to the non-stoichiometric ratio of oxygen, it is clear that the change in the oxygen content in the material (due to changes in temperature and the oxygen partial pressure) occurs rapidly and that the system is continuously in a state of dynamic equilibrium. In this regard, after equilibration of the system (after a short time) at a constant temperature and partial pressure of oxygen in the atmosphere, the competitive adsorption and reaction of oxygen and CO_2 should not be considerable.

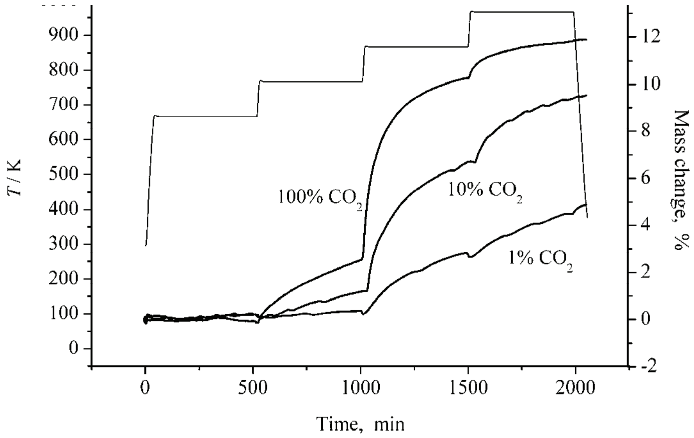

Fig. 5. Mass change of BSCF samples during isothermal steps (673, 773, 873 and 973 K) due to adsorption from 1, 10 and 100 % CO_2 mixtures.

After adsorption, a molecule of CO_2 reacts with BSCF material to form carbonates.[34] It could be assumed that penetration and reaction of oxygen is provided through the entire structure of BSCF, while the penetration of CO_2, followed by the creation of carbonate is limited to the surface only.[34] It is clear from the experimental results that with increasing temperature, such a monolayer does not prevent further reaction with CO_2. Simultaneously with the temperature change, there is also a change in number and availability of oxygen vacancies and a change in the reactivity of CO_2. The increase in the reaction rate with temperature and partial pressure of CO_2 could be explained by the above-mentioned effects. At 673 K in an atmosphere of CO_2, no reaction was recorded. The explanation for this may be the low reactivity of CO_2 with BSCF at this temperature and a slightly lower concentration of defects associated with the non-stoichiometric ratio of oxygen. As the experiments were realized in a dynamic (permanent fluctuating) atmosphere and that elemental carbon (C) is practically absent from the whole system, it could be assumed that the 100 % CO_2 system behaves in Boudouard balance[39] ($2CO \leftrightarrows CO_2 + C$) and only negligible amounts of CO were formed. In the two-component systems, *i.e.*, with 10 and 1 % CO_2 in the O_2 mixture, the possibility of CO formation is even smaller.

Already at this stage and based on the very slow mass equilibration of the system, it could be concluded that studied interaction of CO_2 with BSCF may be described as chemical adsorption and reaction. At lower concentrations of carbon oxides (1 %), the adsorption process did not proceed to completion, which means that the weight at the end of the process is not the maximal and that the decrease in concentration increased the time required for equilibration, and the uncertainty in the formulation of the maximum adsorbed mass.

Adsorption is a very complex phenomenon.[40] For this main reason, there is no single model of adsorption that would give a universal mathematical description of adsorption isotherms that could be used at the borders of all phases and when any physical or chemical adsorption is present. In this study, the reaction of CO_2 on the surface of BSCF perovskite was described by reaction isotherms based on two mathematical models. As the content of oxygen in BSCF varies and the mass is dependent on temperature and partial pressure of oxygen in the surrounding atmosphere, it was difficult to obtain correct molar mass and amount of BSCF in a continually varying atmosphere. Therefore, in this study, the reaction isotherm based on mathematical model 1 was used in such a way that the amount of reacted substance was included as the mass (Fig. 6). An additional benefit of this approach is that the precise chemical form of the carbon oxides deposited on BSCF does not modify the used relation. The parameters k and $1/n$ of the corresponding line equation (Table III) were deter-mined from the linear form of reaction isotherms based on mathematical model 1 (Fig. 7).

The reaction isotherm based on mathematical model 2 was modified in the same way as for the reaction isotherm based on the mathematical model 1 and it was applied to describe the reaction of CO_2 with BSCF (Fig. 8). The reaction isotherms based on mathematical model 2 are expressed by the equation given in Table IV, where k_1 and k_2 are constants. Experimental data are well described by this reaction isotherm, especially at 873 and 973 K, at which temperatures completion of the reaction was observed and it could be concluded that the system was in thermodynamic equilibrium. The coefficients of determination R^2 increase

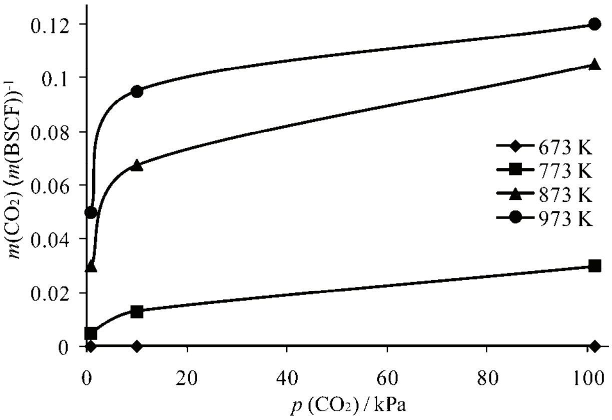

Fig. 6. Reaction isotherm based on mathematical model 1 for the system BSCF–CO_2.

TABLE III. Linear form of the reaction isotherm based on mathematical model 1. Values of the constants *k* and 1/*n*

Parameter	*T* / K		
	773	873	973
k / $kPa^{-1/n}$	7.9712	5.3278	4.2434
$1/n$	0.3891	0.272	0.1901

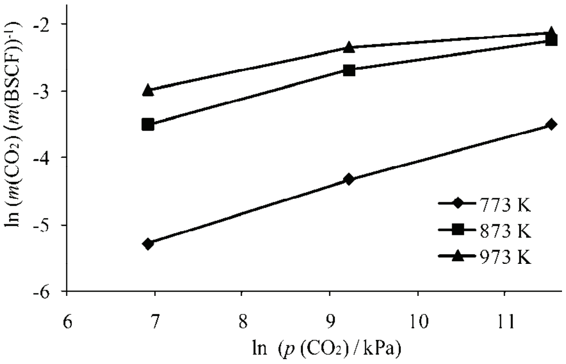

Fig. 7. Linear form of the reaction isotherm based on mathematical model 1 for the system BSCF–CO_2 with the corresponding equations and linear correlation coefficients ($y(973\ K) = 0.190x - 4.243$, $R^2 = 0.932$; $y(873\ K) = 0.272x - 5.327$, $R^2 = 0.971$; $y(773\ K) = 0.389x - 7.971$, $R^2 = 0.998$).

with temperature for both linear isotherms, while their absolute values are in favor of the reaction isotherm based on mathematical model 2. Thus, it could be concluded that the reaction isotherm based on mathematical model 2 better described the reaction of CO_2 at the surface of the BSCF system.

The comparison of the XRD results of the different samples after completion of the experiments presented in Fig. 9 indicates that a chemical reaction of carbon oxides occurred during which the $Sr_{0.6}Ba_{0.4}CO_3$ phase forms. The intensity of the peaks attributed to the perovskite phase decreased with increasing concentration of carbon oxides in the atmosphere.

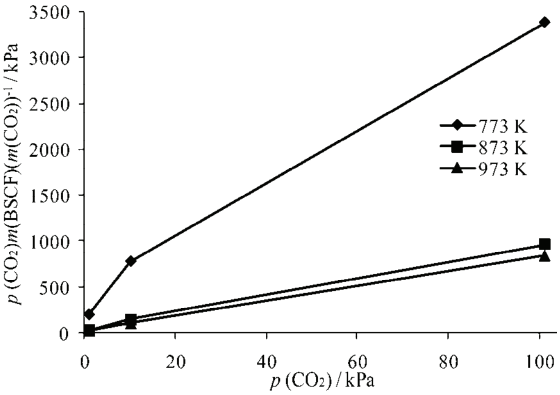

Fig. 8. Linear form of the reaction isotherm based on mathematical model 2 for the system BSCF–CO_2 with the corresponding equations and linear correlation coefficients (y(773 K) = 30.36x + 314.6, R^2 = 0.992; y(873 K) = 9.142x + 40.20, R^2 = 0.998; y(973 K) = 8.164x + 17.67, R^2 = 0.999).

TABLE IV. Linear form of the reaction isotherm based on mathematical model 2. Values of the constants k_1 and k_2

Parameter	T / K		
	773	873	973
k_1 / Pa^{-1}	0.0965	0.227	0.462
k_2	0.0329	0.109	0.122

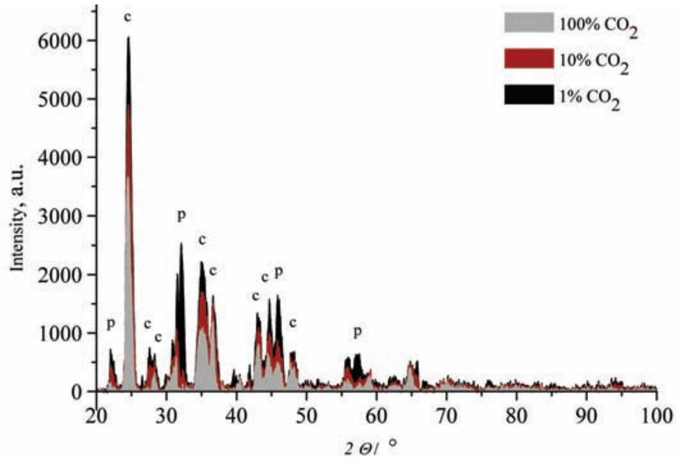

Fig. 9. Comparison of the XRD patterns of the BSCF samples after adsorption from 100, 10 and 1 % CO_2. p: perovskite, c: $Sr_{0.6}Ba_{0.4}CO_3$.

CONCLUSIONS

Oxygen non-stoichiometric property of BSCF has been presented and discussed in conjunction with the findings of other authors. Oxygen non-stoichiometry was investigated by thermogravimetry as a function of oxygen partial pressure in the temperature range 873–1073 K. The absolute oxygen non-stoichiometry was determined by the complete reduction of BSCF. Non-stoichiometry in an oxidizing atmosphere ($p(O_2) > 21000$ Pa) was found to be largely influenced by the temperature. Due to the higher molar fraction of Co *vs*. Fe and the greater affinity for Co^{2+} reduction, it could be argued that the oxygen non-stoichiometry is guided mainly by Co reduction. The defined reaction isotherms for the BSCF––O_2 system follow a linear dependence, opening the possibility for controlling the oxygen non-stoichiometry ratio by changing the partial pressure of oxygen.

The reaction of carbon oxides with BSCF perovskite was observed at 773, 873 and 973 K. The reaction rate increased with increasing temperature and with increasing concentration of CO_2 in the atmosphere. A reaction of CO_2 with BSCF perovskite was not observed at 673 K. The increase of reaction rate with the increasing temperature for the same mixture of gases (in terms of the initial concentrations) could be attributed to the increased concentrations of oxygen vacancies and/or increased reactivity of the CO_2–BSCF system. Since there is no reaction present at 673 K, despite the presence of oxygen vacancies, it can be assumed that CO_2 does not react with BSCF at or below this temperature.

The XRD measurements clearly showed the presence of $Sr_{0.6}Ba_{0.4}CO_3$ phase indicating that chemical reaction occurred in the system. Such an interaction of adsorbate and adsorbent implies the presence of Lewis active sites on the surface of the perovskite, very likely oxygen vacancies sites. This chemical reaction of BSCF perovskite and CO_2 can be completely described by:

$$2ABO_{3-\delta} + 2CO_2 \rightleftarrows 2ACO_3 + B_2O_3 + \left(\frac{1-\delta}{2}\right)O_2 \qquad (1)$$

where ABO_3 is the general chemical formula for perovskite compound with A and B standing for cations of very different sizes The formation of carbonate ions was realized by interactions with the negatively charged atomic oxygen ions $O^{\delta-}$ (Lewis bases) of the complex metal oxides and the positively charged carbon atoms $C^{\delta+}$ (Lewis acid).[41]

The maximum measured weight gain (at 973 K and in 100 % CO_2) was 12 %. During 480-min-long reaction with CO_2 from 1 and 10 % mixtures, no mass equilibration was attained, which suggests that the reaction of CO_2 with BSCF from these gas mixtures was not completed. Due to the very rapid changes in the material regarding the oxygen content related to the temperature and partial pressure of O_2, it does not seem likely that competitive adsorption and reaction of O_2 and CO_2 is present during the period of 480 min.

It is recommended that extremely pure air be used as an oxidant when BSCF is operated as a cathode material at low temperatures. Furthermore, a BSCF cathode is not suitable for single-chamber fuel cells that use hydrocarbons as a fuel, especially at lower temperatures.

By careful observation of the isotherm, it could be noticed that the reaction at 973 K went to completion and that a plateau formed. At 873 and especially at 773 K the plateaus were poorly defined. Both types of reaction isotherms, (linear forms) sufficiently describe the BSCF–CO_2 system. However, based on the results of the linear correlation coefficient, the linear form of reaction isotherm based on mathematical model 2 was more successful in describing the system, especially at higher temperatures. The reaction isotherms registered only one “plateau”.

ИЗВОД

ПРОМЕНЕ ПЕРОВСКИТНОГ ОКСИДА $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ ПРИ ГРЕЈАЊУ У АТМОСФЕРИ КИСЕОНИКА И УГЉЕН-ДИОКСИДА

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Мањак кисеоника, δ, у формули перовскита $Ba_{0,5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) мерен је термогравиметријски у функцији парцијалног притиска кисеоника, $p(O_2)$, у опсегу $1,1\times10^{-6}$–41,67 % на повишеним температурама (873–1073 K). Мањак кисеоника постаје већи са повећањем T и са смањењем $p(O_2)$. Одређене су изотерме δ–$p(O_2)$ за различите температуре. Испитивана је реакција CO_2 са BSCF у одсуству и присуству O_2 на температурама од 673 до 973 K такође методом термогравиметрије. Реактивност CO_2 са BSCF се повећавала са повећањем температуре и изложености CO_2 гасу. За ову реакцију одређене су равнотежне реакционе изотерме. Резултати XRD указују да се реакцијом са CO_2 формирају карбонати.

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