Communications

Evidence of a Strong Correlation Between Oxygen Nonstoichiometry (d) and Oxygen Uptake Capacities of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4)

Edoardo Magnone, Jung Ryoel Kim, Jung Hoon Park,[*] and Seong-Kyu Park[†]

Dongguk University, Wonheung-gwan F619, Seoul 100-715, Korea. [*]E-mail: pjhoon@dongguk.edu
[†]KOFIRST R&D Center, KF E&E Co. Ltd., Gyeonggi-do 435-833, Korea

Recently, there has been a growing interest in utilizing nonstoichiometric $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-d}$ perovskite-type oxide as sorbents for high-temperature production of oxygen-enriched carbon dioxide stream.[1-4] During the past decades, many studies have been conducted on these solid solutions, and in order to achieve higher oxygen uptake capacities, the La^{3+} lanthanide was substituted by bivalent Sr^{2+} alkaline-earth ions to decrease the ionicity of the Ln–O bond which could result in an increased number of hole.[5-7]

As far as we know, the correlation between the oxygen content (3-d) or the oxygen nonstoichiometry (d) and the oxygen uptake capacities of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4) has not been studied systematically. In the present study, $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ with different bivalent Sr^{2+} dopant contents were selected because the solubility of the selected ion in the sintered perovskite-type oxide was limited to Sr_x < 0.4.[7] For this reason, the main goal was to verify the possible influence of oxygen nonstoichiometry (d) on the oxygen adsorption properties of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4), and also to verify the relationship (if any) between these data to enable a material modeling to improve the chemical structural design for use in advanced applications.

$La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4) have been synthesized by combustion synthesis method[8] and have been further heated at ~1300 °C under atmospheric air pressure.[9] The details of the experimental procedure are described elsewhere.[8] The quality of the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < x < 0.4) was studied by X-ray Diffraction (XRD) analysis. The XRD analyses indicated that there were no additional phases in the prepared perovskite-type oxide solid solution $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ (0.1 < x < 0.4).

Thermogravimetric (TG) measurements were performed to investigate (1) the oxygen nonstoichiometry (d) in reduction condition (*i.e.*, He), and (2) the oxygen uptake capacities (*i.e.*, Air) of the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4). Every reduction process to determine the oxygen nonstoichiometry (d) was studied in He flow (100

mL/min) from room temperature to 950 °C, while in each adsorption process a synthetic air flow (100 mL/min) was used in isothermal mode (900 °C). Based on these data, all parameters related to the oxygen content and oxygen storage process could be established for studying these relationships. In particular, as it can be seen in Figure 1, TG analyses reveal that the observed TG weight loss (%) in the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4) in He is due to the reduction steps (called α and β by Teraoka *et al.*[10]) in oxygen content (3-d). Oxygen contents (3-d) in the first (α) and second (β) large desorption onsets for various $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ compositions (0.1 < Sr_x < 0.4) are plotted in function to the Sr contents (Sr_x) in Figure 1 (right side). According to Tai *et al.*,[7] on the replacement of La^{3+} by Sr^{2+}, the oxygen nonstoichiometry (d) increases with increasing Sr^{2+} dopant content between Sr_x = 0.1 and Sr_x = 0.4. This effect can be understood when taking into account the changes of oxygen content (3-d) of the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxide, when trivalent La^{3+} lanthanide is substituted by bivalent Sr^{2+} alkaline-earth ion.[7,10]
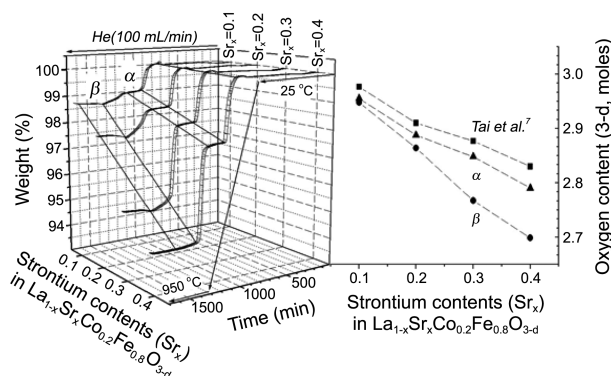

Figure 1. Relative TG weight loss (%) of various $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ compositions (0.1 < Sr_x < 0.4) with time with He as reduction gas from room temperature to 950 °C, and relative oxygen content (3-d) in function to Sr content (Sr_x) in He (α and β)[10] and in air after Tai *et al.*[7]
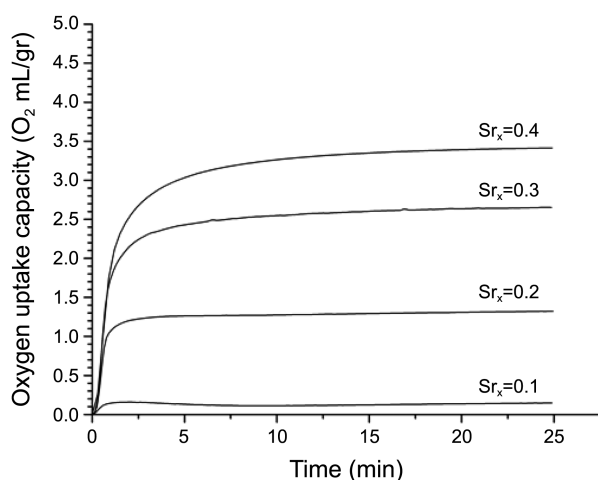
Figure 2. Comparison of the isothermal oxygen uptake capacities (O_2 mL/gr) of various $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ compositions (0.1 < Sr_x < 0.4) in Air after long equilibration in He at 900 °C.

Figure 2 shows the oxygen adsorption curves in volumes of O_2 for mass of sample (O_2 mL/gr) in various $La_{1-x}Sr_x$-$Co_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4) when the surrounding gas is switched from He to air under atmospheric pressure at 900 °C. Clearly, in the selected experimental conditions, the oxygen adsorption capacities of the $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4) increase when increasing the Sr^{2+} dopant content from Sr_x = 0.1 to Sr_x = 0.4.

In order to rationalize these experimental data, a graph of the coordinates "oxygen nonstoichiometry (d) - oxygen uptake capacity" of perovskite-type oxide solid solution La_{1-x}-$Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ (0.1 < Sr_x < 0.4) is presented in Figure 3, where the data shows the total oxygen nonstoichiometry (d) derived from the second large desorption onset (β) of synthesized $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4) and the maxima in oxygen uptake for the same oxides in Air at 900 °C.

It is clear from Figure 3 that an increase in oxygen nonstoichiometry (or decrease in oxygen content) results in a progressive linear shift of the maximun oxygen uptake capacity at 900 °C to higher values. Moreover, as shown in Figure 3, the experimental results show a high correlation that confirms the authenticy of the mathematical analysis with a regressing coefficient, indicating the strength of the association between oxygen nonstoichiometry (d) and oxygen uptake capacities at high temperature (900 °C), of 0.9990. According to this regression (linear) model, the standard deviation is low (SD = 0.07845) because the experimental points are for the most part within the line of best fit (95% confidence limits).

In summary, the communication provided clear evidence of a strong correlation between the nonstoichiometry oxygen
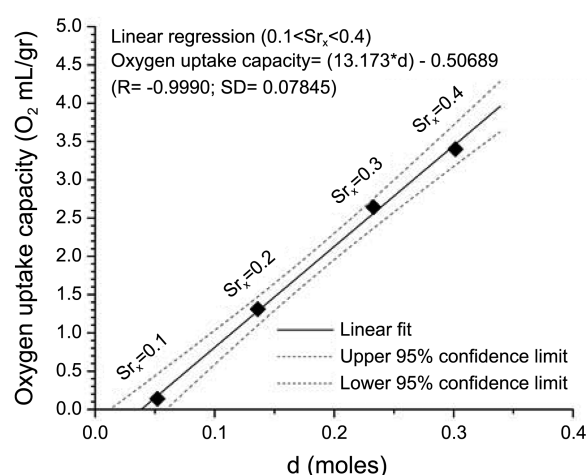

Figure 3. A measure of the mathematical (linear) relationship between oxygen nonstoichiometry content (d) and oxygen uptake capacities at high temperature (900 °C) and of the dependency of oxygen uptake capacities on oxygen content (3-d) of $La_{1-x}Sr_x$-$Co_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < Sr_x < 0.4).

content (d) or oxygen content (3-d) and the maximum oxygen uptake capacity of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-d}$ oxides (0.1 < x < 0.4). The results may be considered as a provisional basis for further research, allowing the prediction of the oxygen uptake capacities at low temperature by easy determination of oxygen contents.

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