SOFC CATHODE MATERIAL BASED ON RARE EARTH COBALTITES
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ABSTRACT
The electrical conductivity and oxygen permeability of \( \text{Ln}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) (\( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}; x = 0-0.5 \)) and \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) (\( x = 0-1.0 \)) ceramics were measured. The thermal expansion and crystal structure of cobaltites was investigated. It was found that ionic conductivity of cobaltites decreases in the \( \text{La} > \text{Pr} > \text{Nd} \) sequence.

INTRODUCTION
Perovskite-like cobaltites of rare-earth elements (REE) and strontium are promising materials for solid oxide fuel cells due to their high ionic conductivity, compared to such oxide ion conductors as zirconia based solid solutions (1-4). The presence of oxide ionic conductivity on the background of high electronic conductivity for electrode materials leads to a substantial improvement in the electrochemical properties of electrodes, owing to the expansion of the electrochemical reaction zone. The purpose of the present work is to investigate the physico-chemical properties of \( \text{Ln}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) and oxide ion transference parameters of these solid solutions.

EXPERIMENTAL
Synthesis of \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) (\( x = 0.0-1.0 \)) and \( \text{Ln}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta} \) (\( \text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}; x = 0.0-0.5 \)) polycrystalline samples was carried out by standard ceramics technology from oxides, nitrates and carbonates at temperatures 1370 - 1570 K for 15 - 35 hours in the air. During the process of synthesis the multiple powder milling was used. The X-Ray diffraction patterns were taken with DRON-3M diffractometer using Cu\( K_\alpha \) and Co\( K_\alpha \) radiation (Ni and Fe filters). Error in the crystalline lattice constants was \( \pm 0.0001 \) nm.

Ceramic samples were pressed from of powders synthesised cobaltites under pressure of 300 - 600 MPa, in the shape of bars (4×4×30 mm) and tablets (diameter 15 or 28 mm, thickness 3 - 4 mm). Ceramics were calcimined at the temperatures 1470 - 1670 K during 20 - 35 h. Ceramic samples' density (\( d_{\text{exp}} \)) was 80-95 % with respect to the theoretical density. Obtained ceramics were tested for
gas tightness (absence of open porosity) using spirit solution of "Sudan" dye-stuff and by means of helium-vacuum method with leak-detector GTI-3.

The methods of synthesizing cobaltites, making ceramics, investigating crystal structure, electrical conductivity and linear thermal expansion are described in detail in our previous papers (4-6).

Oxygen permeability measurements were carried out with the help of the electrochemical cell outfitted with an oxygen pump and sensor. The investigation procedure is described in detail in previous papers (5,6). Oxygen permeability was determined subject to the condition that the flow of the oxygen coming to the cell through a tightly glued sample owing to the ionic conductivity of cobaltite should be equal to the flow of the oxygen removed from the cell by the oxygen pump. Oxygen permeability was measured over the temperature range from 950 to 1370 K with difference of the partial pressures of oxygen in the internal and external space of measuring cell between 1×10⁴ and 1×10³ Pa. The time for the cell to reach a steady state was 0.5 to 6 hours. Measurements were made on ceramics whose gas tightness was determined preliminary by the vacuum-helium method using a GTI-3 detector. The variance of reproducibility for the oxygen permeability of cobaltites did not exceed 5 % with respect to the measured value.

The effective activation energy of oxide ionic conductivity was calculated using the regression model

\[ \sigma_o = A_o \frac{1}{T} \exp\left( \frac{-E_a}{RT} \right) \]  

(1),

where \( E_a \) is the effective activation energy; \( A_o \) is the preexponential factor. The ionic conductivity \( (\sigma_o) \), and oxide ionic transference numbers \( (t_o) \) were calculated using the equations

\[ t_o \times (1-t_o) \times \overline{\sigma} = \frac{d}{S} \times \frac{dI}{dE} \]  

(2),

\[ \sigma_o = t_o \times \overline{\sigma} \]  

(3),

where \( \overline{\sigma} \) is the mean specific electrical conductivity over the given interval of partial pressures of oxygen; \( d \) and \( S \) are the thickness and effective area of investigated sample respectively; \( I \) is the intensity of the current through the
measuring-cell oxygen pump, which evacuates oxygen from the internal to the external space of the cell; $E$ is the e.m.f of the oxygen sensor of the cell.

For the calculation of oxide ionic conductivity we used experimental data corresponding to values of the correlation coefficient of the linear dependence $I = f(E)$ that were not less than 0.995.

RESULTS AND DISCUSSION

X-Ray diffraction testing results of synthesised samples $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\delta$ ($x = 0..0.7$) $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3\delta$ ($x = 0..0.1$) and $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3\delta$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}; x = 0.0..0.5$) showed that formation of series of perovskite-type solid solutions with cubic, orthorhombic or rhombohedric structures took place in the investigated region. Thermodynamic stability of cobaltites was confirmed by DTA methods, high-temperature X-Ray diffraction analysis and also by maintenance of phase composition and structure in long annealing session (up to 100 hours) in the temperature region from 870 to 1270 K. The type of perovskite structure (Table I) is mostly dependent from synthesis conditions (temperature, atmosphere, heating and cooling rate) and oxygen non-stoichiometry (7). The ceramics of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3\delta$ for $x > 0.1$ are not single phase. Calculated values of elementary cell volume rise with $x$ increase because the ion radius of Sr$^{2+}$ cation is greater than those of Ln$^{3+}$.

The results of cobaltites specific conductivity investigations were published earlier (6). Temperature dependencies of electrical conductivity of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3\delta$ are in agreement with the literature data (8, 9). The addition of strontium leads to sharp conductivity increase and transition to a metallic type of conductance at $x > 0.2$. Temperature resistance coefficients (TRC) of investigated materials are given in Table II. TRC values were calculated using the equation:

$$\rho = \rho_o \times (1 + \beta \times T) \quad (4),$$

where $\beta$ is TRC, $\rho$ is the specific resistance, $\rho_o$ - is the specific resistance at 298 K.

The conductivity of cobaltites does not depend on oxygen partial pressure at temperatures lower than 700 K (Fig.1-3). The reversible conductance decrease with oxygen partial pressure drop was observed at $T > 900$ K. The variation of conductivity increases with increasing the strontium concentration and increasing temperature.

The geometrical calculation of distance between cations in the most probable anion jump direction for REE and strontium cobaltites confirms that anion transfer
channel size decreases in a La → Nd sequence. Nevertheless the ionic conductivity value is to a large degree defined by O\(^{2-}\) ion interaction with the nearest cation neighbouring (4 A-ions and 2 B-ions of the ABO\(_3\) perovskite structure). From that point of view lanthanide ion radius decrease causing further weakening of B - O bond and A - O bond energy increase, can lead to oxide ionic conductivity decrease. B\(^{4+}\) ion existence means B - O bond covalence rising. In this case ionic conductivity decreases.

The ionic conductivity variations in Ln\(_{1-x}\)Sr\(_x\)CoO\(_{3-δ}\) systems (Fig.4) are in agreement with the previous conclusion. The ionic conductivity decreases as \(x\) increases at \(x\) values between 0 and 0.4. Then oxide ionic conductivity increases with \(x\) increase from 0.5 to 0.7. The most probably, the discussed change of the ionic conductivity is due to corresponding variation of concentration of oxygen vacancy and Co\(^{4+}\) ions (10). Then ionic conductivity decreases with \(x\) increase from 0.8 to 1.0 because these complex oxides are not single phase. The value of ionic conductivity diminishes in the La > Pr > Nd sequence. The values of effective activation energy for oxide ion conductivity derived from Arrhenius law and oxide ion transference numbers are given in Table II.

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Fig. 1. Oxygen partial pressure dependence of conductivity for $\text{La}_0.5\text{Sr}_0.5\text{CoO}_3$ at 670 K (1), 970 K (2), 1070 K (3).

Fig. 2. Oxygen partial pressure dependence of conductivity for $\text{Ln}_0.5\text{Sr}_0.5\text{CoO}_3$ at 1070 K for $\text{Ln} = \text{La}$ (1), Pr (2), Nd (3), Sm (4).
Fig. 3. Oxygen partial pressure dependence of conductivity for Nd$_{1-x}$Sr$_x$CoO$_{3-\delta}$ at 1070 K for $x = 0$ (1); 0.1 (2); 0.3 (3).

Fig. 4. Oxide ionic conductivity dependence on the strontium content for La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (1) at 1105 ± 5 K; Pr$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (2) and Nd$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (3) at 1115 ± 4 K.
### Table I. Properties of Ln$_{1-x}$Sr$_x$CoO$_3$$_\delta$ ceramics

| Ln  | x   | Structure$^a$ | a, nm  | b, nm  | c, nm  | $\alpha$,° | $d_{exp}$, kg/m$^3$ | TEC $\times 10^6$, K$^{-1}$ |
|-----|-----|---------------|--------|--------|--------|-----------|----------------|------------------|
|     |     |               |        |        |        |           |                   |                  |
| La  | 0.0 | R             | 0.5388 |        |        | 60.80     | 6100             | 200-1100         | 22.9±0.3        |
|     | 0.1 | R             | 0.5390 |        |        | 60.62     | 6020             | 200-1100         | 19.9±0.2        |
|     | 0.2 | R             | 0.5407 |        |        | 60.56     | 5840             | 300-1100         | 18.3±0.1        |
|     | 0.3 | R             | 0.5411 |        |        | 60.44     | 5590             | 300-1100         | 17.8±0.2        |
|     | 0.4 | R             | 0.5414 |        |        | 60.32     | 5410             | 300-1100         | 18.9±0.2        |
|     | 0.5 | R             | 0.5418 |        |        | 60.24     | 5360             | 300-1100         | 22.2±0.4        |
|     | 0.6 | C             | 0.3830 |        |        |          | 5250             | 300-750          | 14.5±0.9        |
|     | 0.7 | C             | 0.3834 |        |        |          | 5170             | 300-750          | 19.6±0.5        |
| Pr  | 0   | C             | 0.7561 |        |        |          | 6370             | 650-1100         | 28.3±0.2        |
|     | 0.1 | C             | 0.7587 |        |        |          | 6360             | 300-800          | 22.0±0.3        |
|     | 0.2 | C             | 0.7595 |        |        |          | 5950             | 400-1100         | 18.3±0.1        |
|     | 0.3 | C             | 0.7600 |        |        |          | 5790             | 400-1100         | 18.6±0.2        |
|     | 0.4 | C             | 0.7606 |        |        |          | 5560             | 400-800          | 19.5±0.4        |
|     | 0.5 | C             | 0.7614 |        |        |          | 5500             | 400-800          | 18.2±0.3        |
| Nd  | 0   | C             | 0.7548 |        |        |          | 6600             | 300-1100         | 27.9±0.2        |
|     | 0.1 | C             | 0.7562 |        |        |          | 6680             | 300-1100         | 23.8±0.1        |
|     | 0.2 | R             | 0.5340 |        |        | 59.40     | 6170             | 300-800          | 20.7±0.1        |
|     | 0.3 | R             | 0.5363 |        |        | 60.22     | 6000             | 300-700          | 15.8±0.1        |
|     | 0.4 | O             | 0.5354 | 0.5333 | 0.7644 |          | 5880             | 700-1100         | 21.9±0.9        |
|     | 0.5 | O             | 0.5352 | 0.5408 | 0.7614 |          | 5730             | 300-850          | 15.7±0.1        |
| Sm  | 0   | O             | 0.5285 | 0.5353 | 0.7497 |          | 7230             | 800-1150         | 22.5±0.6        |
|     | 0.1 | O             | 0.5336 | 0.5409 | 0.7480 |          | 6900             | 800-1100         | 20.9±0.9        |
|     | 0.2 | C             | 0.7552 |        |        |          | 6410             | 650-1100         | 20.1±0.8        |
|     | 0.3 | C             | 0.7578 |        |        |          | 5480             | 300-1100         | 18.2±0.1        |
|     | 0.4 | C             | 0.7587 |        |        |          | 5570             | 300-900          | 17.1±0.1        |
|     | 0.5 | C             | 0.7594 |        |        |          | 5560             | 300-850          | 18.1±0.3        |
| Gd  | 0   | O             | 0.5208 | 0.5397 | 0.7449 |          | 6940             | 800-1100         | 23.6±0.3        |
|     | 0.1 | O             | 0.5214 | 0.5389 | 0.7441 |          | 6720             | 850-1100         | 24.4±0.2        |
|     | 0.2 | O             | 0.5217 | 0.5384 | 0.7437 |          | 6680             |                  |                  |
|     |     | C             | 0.3784 |        |        |          |                  |                  |                  |
|     | 0.3 | O             | 0.5218 | 0.5384 | 0.7436 |          | 6610             |                  |                  |
|     |     | C             | 0.3788 |        |        |          |                  |                  |                  |
|     | 0.4 | O             | 0.5217 | 0.5384 | 0.7436 |          | 6390             |                  |                  |
|     |     | C             | 0.3792 |        |        |          |                  |                  |                  |
|     | 0.5 | O             | 0.5217 | 0.5383 | 0.7437 |          | 6100             |                  |                  |
|     |     | C             | 0.3794 |        |        |          |                  |                  |                  |

$^a$ C - cubic structure of perovskite, R and O - perovskite structure having rhombohedral and orthorhombic distortions respectively, $^b$ $d_{exp}$ - density of ceramic, $^c$ TEC - thermal expansion coefficient

518
Table II. Transference parameters of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$-

| Ln  | $x$ | $TRC \times 10^4$, $K^{-1}$, 300-700K | $E_a$, kJ/mol | $t_0$ a | $T$, K | Value |
|-----|-----|-----------------------------------|--------------|---------|-------|--------|
| La  | 0.0 | -                                 | 1100-1250    | 16 ± 2  | 0.0007|
|     | 0.2 | 1.9 ± 0.2                          | 1100-1250    | 25 ± 7  | 0.0003|
|     | 0.3 | 7.5 ± 1.0                          | -            | -       | -     |
|     | 0.4 | 6.4 ± 0.3                          | 1100-1250    | 33 ± 6  | 0.0001|
|     | 0.5 | 10.3 ± 0.3                         | 1100-1200    | 29 ± 5  | 0.0005|
|     | 0.6 | 10.6 ± 0.2                         | -            | -       | -     |
|     | 0.7 | 11.4 ± 0.5                         | 1100-1250    | 23 ± 7  | 0.0012|
|     | 0.8 | -                                 | 1150-1300    | 17 ± 3  | 0.0008|
| Pr  | 0   | -                                 | 970-1200     | 49 ± 5  | 0.0002|
|     | 0.1 | -                                 | 970-1120     | 46 ± 4  | 0.0002|
|     | 0.2 | -                                 | 970-1200     | 47 ± 4  | 0.0002|
|     | 0.3 | 0.9 ± 0.2                          | 970-1200     | 54 ± 3  | 0.0001|
|     | 0.4 | 8.3 ± 0.5                          | 970-1200     | 51 ± 5  | 0.0001|
|     | 0.5 | 10.7 ± 2.2                         | -            | -       | -     |
| Nd  | 0.2 | -                                 | 970-1200     | 48 ± 7  | 0.0001|
|     | 0.3 | 1.3 ± 0.3                          | 970-1200     | 51 ± 3  | 0.0001|
|     | 0.4 | 6.0 ± 0.4                          | 970-1200     | 43 ± 5  | 0.0001|
|     | 0.5 | 8.6 ± 0.6                          | -            | -       | -     |
| Sm  | 0.3 | 1.5 ± 0.8                          | -            | -       | -     |
|     | 0.4 | 5.8 ± 0.5                          | -            | -       | -     |
|     | 0.5 | 7.9 ± 0.7                          | -            | -       | -     |

a $t_0$ - oxide ion transference number $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ at 1105±5 K and $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ (Ln=Pr,Nd) at 1115±5 K