Perovskite powders synthesis for oxygen separating membranes and oxy-combustion processes

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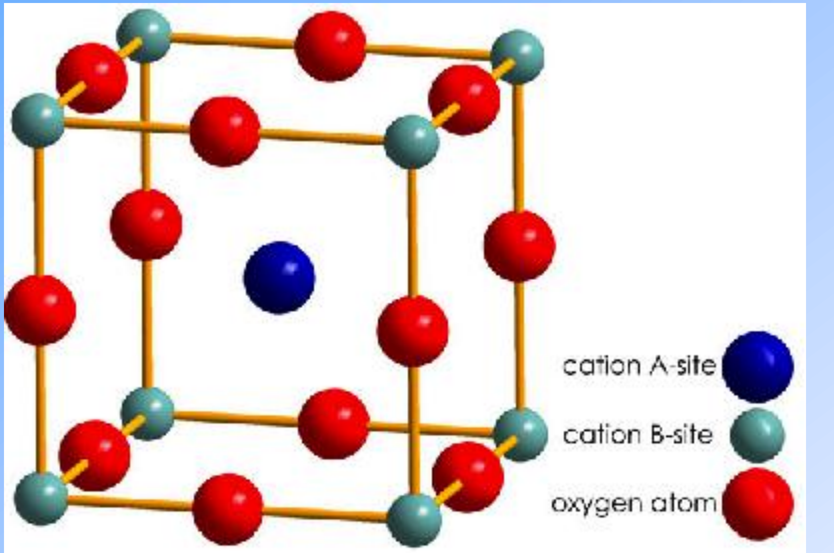
On the perovskite type oxides



Perovskite structure [1]

The characteristic feature of perovskite:

- high thermal stability,
- oxygen mobility,
- variety of elements enable to create ABO_3 structure.

1. Maciej Stodólny, Perovskite-based materials as an anode for Solid Oxide Fuel Cells (SOFCs).

Application of perovskite materials

- ✓ **membranes for the pure oxygen production from air and oxy-combustion processes,**
- ✓ **cathodes and anodes in Solid Oxide Fuel Cells,**
- ✓ catalysis - active and selective catalysts in processes of the exhaust gas purification; catalysts of the oxidation reaction (methane, carbon black),
- ✓ electronics – electric condensers, component of different sensors,
- ✓ electrolysers,
- ✓ hydrogen gaining in the process of photo decomposition of water,
- ✓ others.

Requirements of perovskite membranes for oxygen separation

- mixed electronic and ionic conductivities,

- **such electric conductivity so that the oxygen permeation flux through the membrane is greater than 10 ml O_2 /cm^2 x min,**

- chemical and structural stabilities at high temperature and changeable partial oxygen pressure (*T* of membranes ~1000°C),

- mechanical strength (resistance of the membrane on assembly and operation stresses),

- high catalytic activity towards oxygen reduction and reoxidation.

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The oxygen permeation flux through the membrane

In the range controlled by diffusion processes:

$$J_{O_2} = \frac{RTG_e G_i}{16F^2(G_e + G_i)L} \ln \frac{p_h}{p_l}$$

R – gas constant

T – temperature of the process

G_e – electronic conductivity

G_i – ionic conductivity

F – Faraday constant

L – thickness of the membrane

p_h – partial oxygen pressure on feed side (high pressure)

p_l - partial oxygen pressure on loan side (low pressure)

The oxygen permeation flux through the membrane

In the range controlled by surface processes:

$$J_{O_2} = \frac{c_i k}{2}\left(\sqrt{\frac{p_h}{p_o}} - \sqrt{\frac{p_l}{p_o}}\right)$$

c_i – membrane density

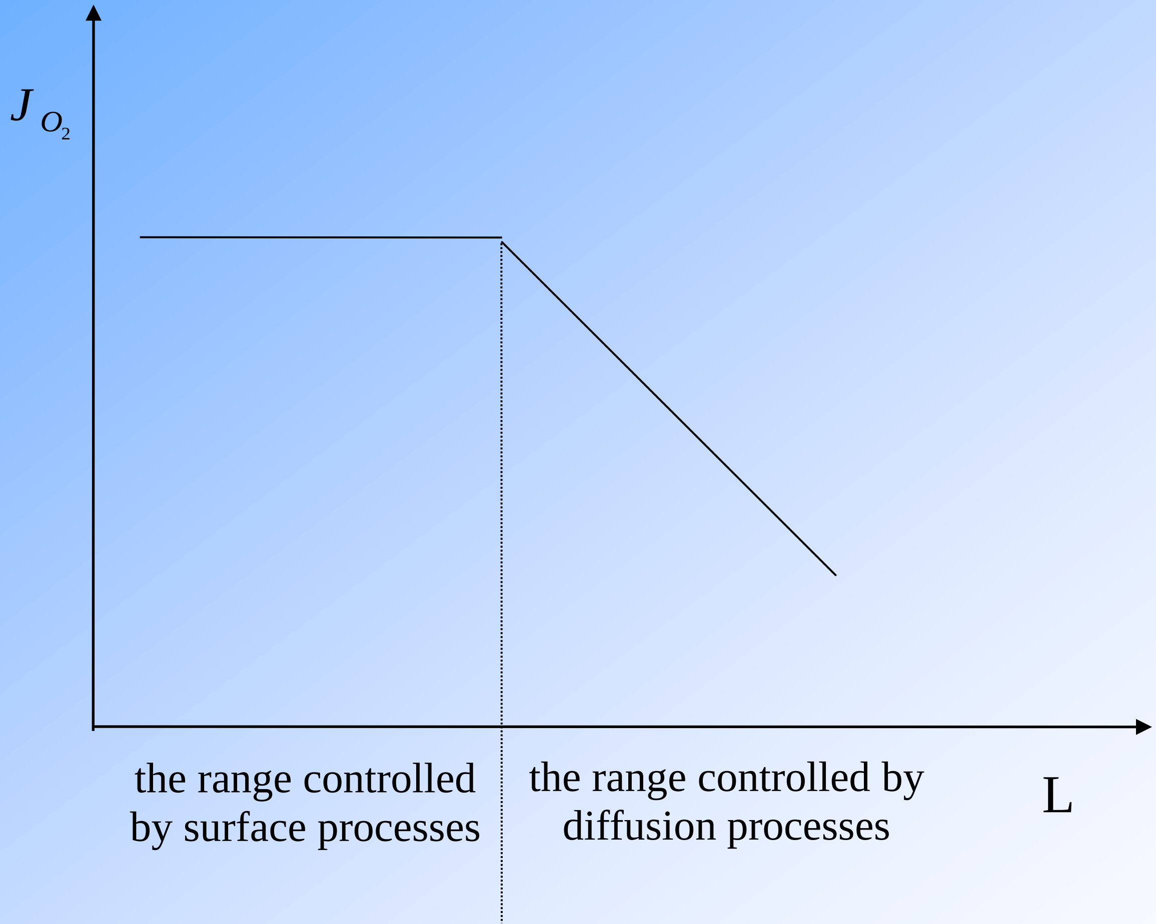
k – surface exchange coefficient

p_o – atmospheric pressure

p_h – partial oxygen pressure on feed side (high pressure)

p_l - partial oxygen pressure on loan side (low pressure)

The oxygen permeation flux through the membrane via the thickness of the membrane



Plan of this research

- Selection of a standard sample: $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (S0; Praxair)
- Fabrication of the material by different methods
- Determination of an optimal synthesis method with respect to physicochemical properties of final product
- Manufacture of the membranes by the optimal method

Experimental part

Methods of the synthesis:

- solid-state - S1

- sol-gel: S2 – with citric acid
    - S3 – with maleic acid
    - S4 – with ethylene glycol
    - S5 – with propionic acid
    - S6 – with EDTA

- chemical combustion - S7

- hydrothermal - S8

- co-precipitation - S9

All materials were calcined for 6 h at 850°C.

Properties

Sample	Specific surface, m^2/g	Chemical composition
S0	7.71	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$
S1	3.36	$La_{0.6}Sr_{0.37}Fe_{0.8}Co_{0.2}O_3$
S2	5.43	$La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$
S3	6.65	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$
S4	5.04	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$
S5	4.06	$La_{0.59}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$
S6	5.28	-
S7	4.35	-
S9	4.38	$La_{0.6}Sr_{0.38}Fe_{0.8}Co_{0.2}O_3$

The perovskite phase did not appear by hydrothermal method (S8).

XRD analysis

Monophase samples

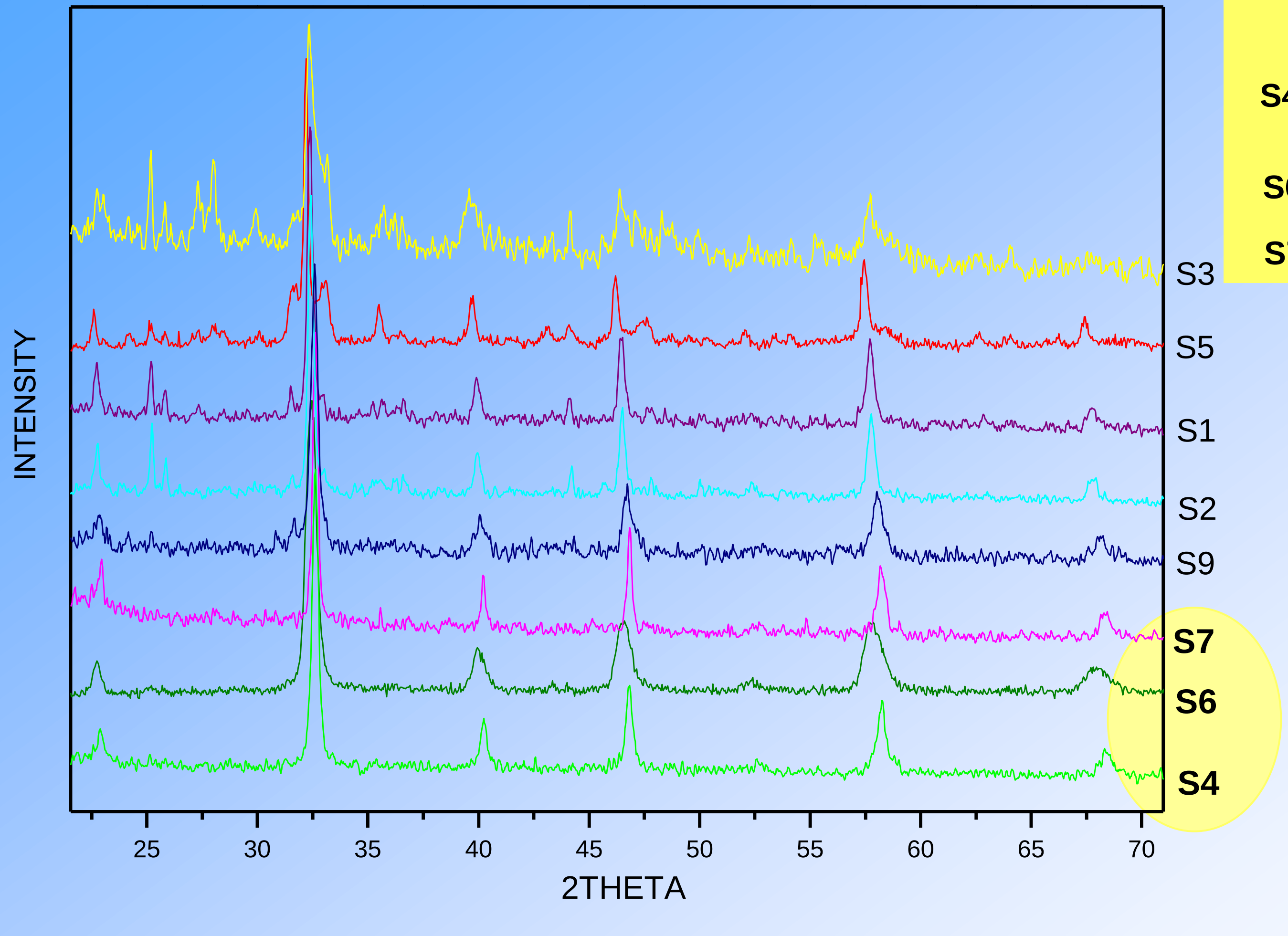
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$

R-3 c R

S4: $a = 5.467(1)$ Å $\alpha = 60.26^o$

S6: $a = 5.497(9)$ Å $\alpha = 60.24^o$

S7: $a = 5.469(1)$ Å $\alpha = 60.25^o$



XRD patterns of samples obtained by different methods and calcined for 6h at 850°C.

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Preparation of sintered disks in Cerel

- formation: the die of inside diameter of 11,5 mm
- uniaxial pressing under pressure of 1 MPa
- isostatic pressing under pressure of 250 MPa
- determination of the density of green disks
- disks sintering in supercanthal furnace: heating and cooling rate of 100°C/h

max temp. 1350°C

dwell time 2 h

Preparation of sintered disks in Cerel

- absorbability, apparent density and porosity of the sintered disks

	Green disks	Sintered disks		
Samples	Density g/cm^3	Absorbability %	Density g/cm^3	Porosity %
S0	**3,62**	**0,00**	**5,76**	**0,00**
S1	**3,29**	**0,00**	**6,09**	**0,00**
S2	3,09	3,57	4,69	16,73
S3	3,02	8,68	4,06	35,2
S4	**2,98**	**0,06**	**5,86**	**0,33**
S5	3,43	5,30	4,66	24,7
S9	3,64	0,96	5,42	5,21

XRD analysis

$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$
R-3 c R

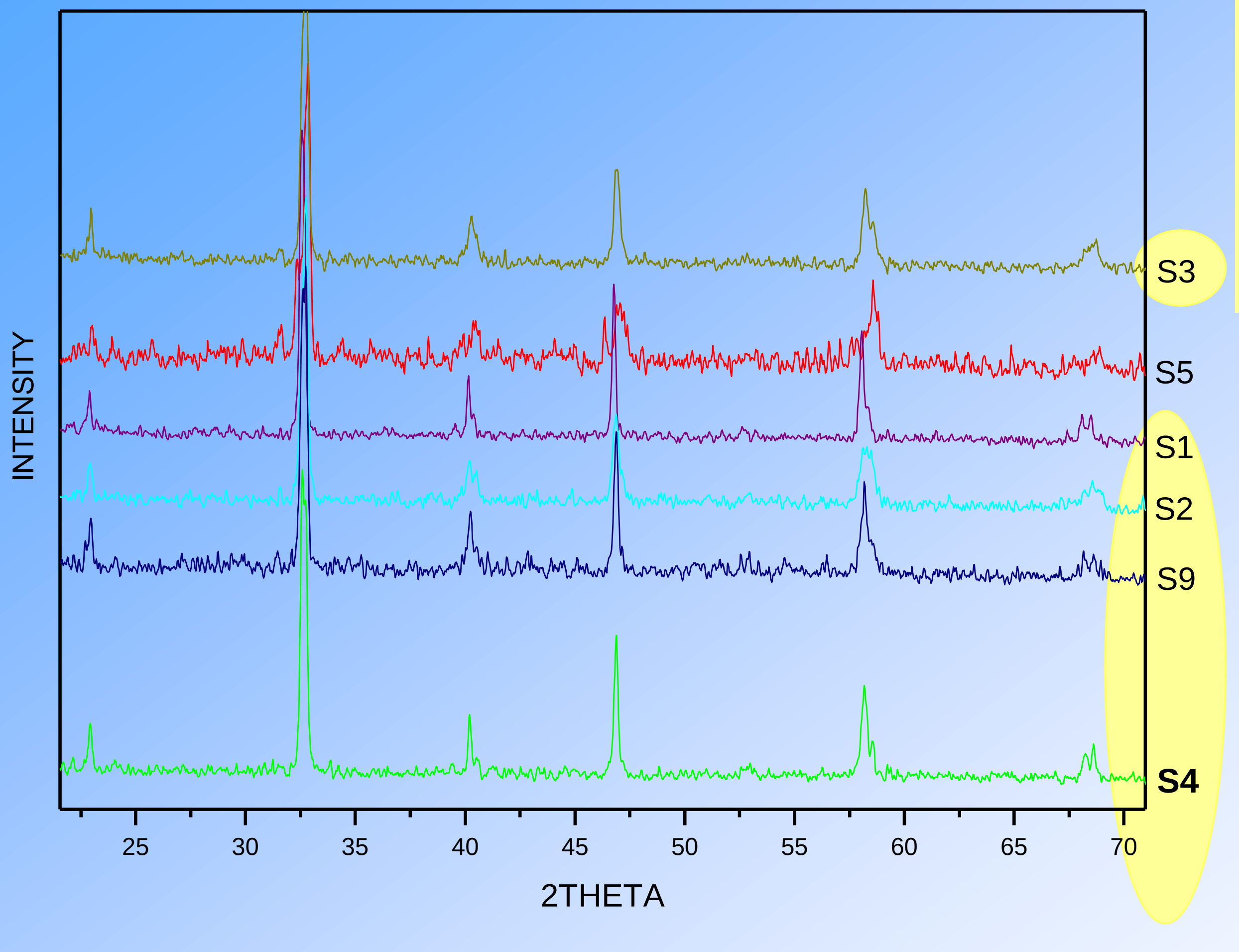
S4: a = 5.465(1) Å α = 60.33°

S9: a = 5.468(9) Å α = 60.35°

S2: a = 5.469(1) Å α = 60.34°

S1: a = 5.478(1) Å α = 60.27°

S3: a = 5.470(1) Å α = 60.34°



XRD patterns of powders obtained from disks sintered at 1350^{0}C

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Preliminary conclusions

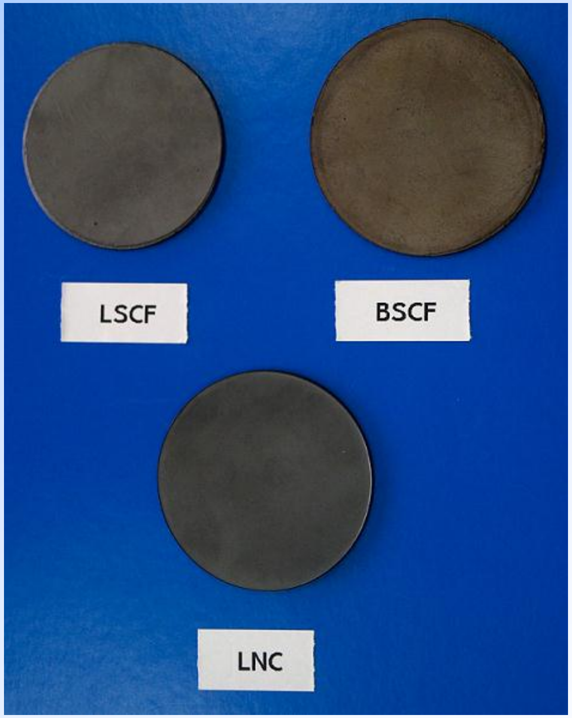
- LSCF powder fabrication method strongly influences on the phase composition and physicochemical properties.

- The monophase sinter of LSCF can be obtained from the single-phase powder as well as powders containing other phases than those of the basic perovskite.

- **The solid-state method seems to be the most promising to fabricate the dense sintered perovskite-structured membranes.**

Fabrication of perovskite membranes in CEREL

- selection $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (**LSCF**), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (**BSCF**) and $LaNi_{0.5}Co_{0.5}O_{3-\delta}$ (**LNC**)
- synthesis of perovskite powders
- preparation of granulated powders
- membranes pressing (inside diameter of the die - 55 mm)
- sintering in supercanthal furnace



thicknesses: 1.7 - 2 mm

diameters: 42 - 46 mm

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Fabrication of perovskite membranes in CEREL

- absorbability, apparent density and porosity of the membranes

Materials	Absorbability %	Density g/cm^3	Porosity %
LSCF	0.00	6.14	0.02
BSCF	0.01	5.47	0.08
LNC	0.00	7.01	0.03

Dense perovskite-structured membranes were obtained

Further work

- measurements of electrical conductivity and oxygen permeation flux.
- manufacture of square membranes of the side dimension of 100 mm and the thickness of 1 mm.
- work out the optimal technology of membranes production for oxygen separation and oxy-combustion processes.

Thank you
for your attention