

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

Kazimierz Krząstek, Magdalena Gromada

*Institute of Power Engineering, Ceramic Department „CEREL”, ul. Techniczna 1,
36-040 Boguchwała*

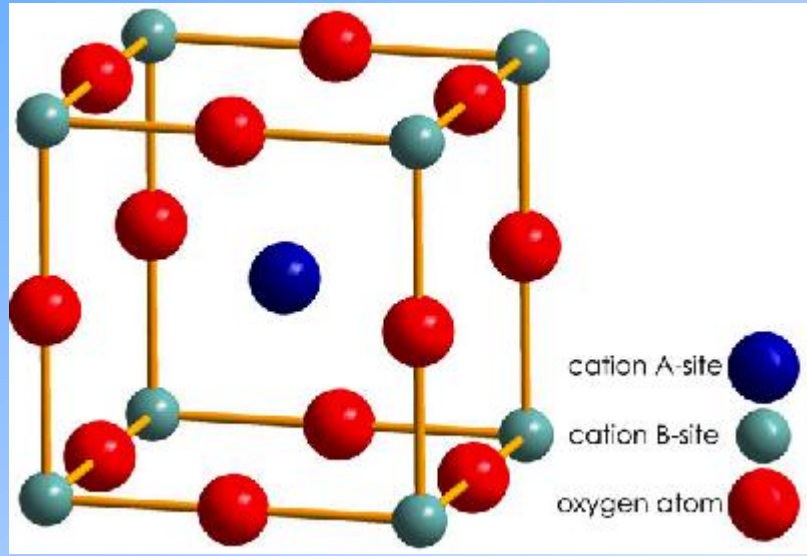
Janusz Trawczyński

Wrocław University of Technology, ul. Wybrzeże Wyspiańskiego 27, 50-370 Wrocław



Politechnika Wroclawska

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 $10 \text{ ml O}_2 / \text{cm}^2 \times \text{min}$,
- ❖ chemical and structural stabilities at high temperature and changeable partial oxygen pressure (T of membranes $\sim 1000^\circ\text{C}$),
- ❖ mechanical strength (resistance of the membrane on assembly and operation stresses),
- ❖ high catalytic activity towards oxygen reduction and reoxidation.



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

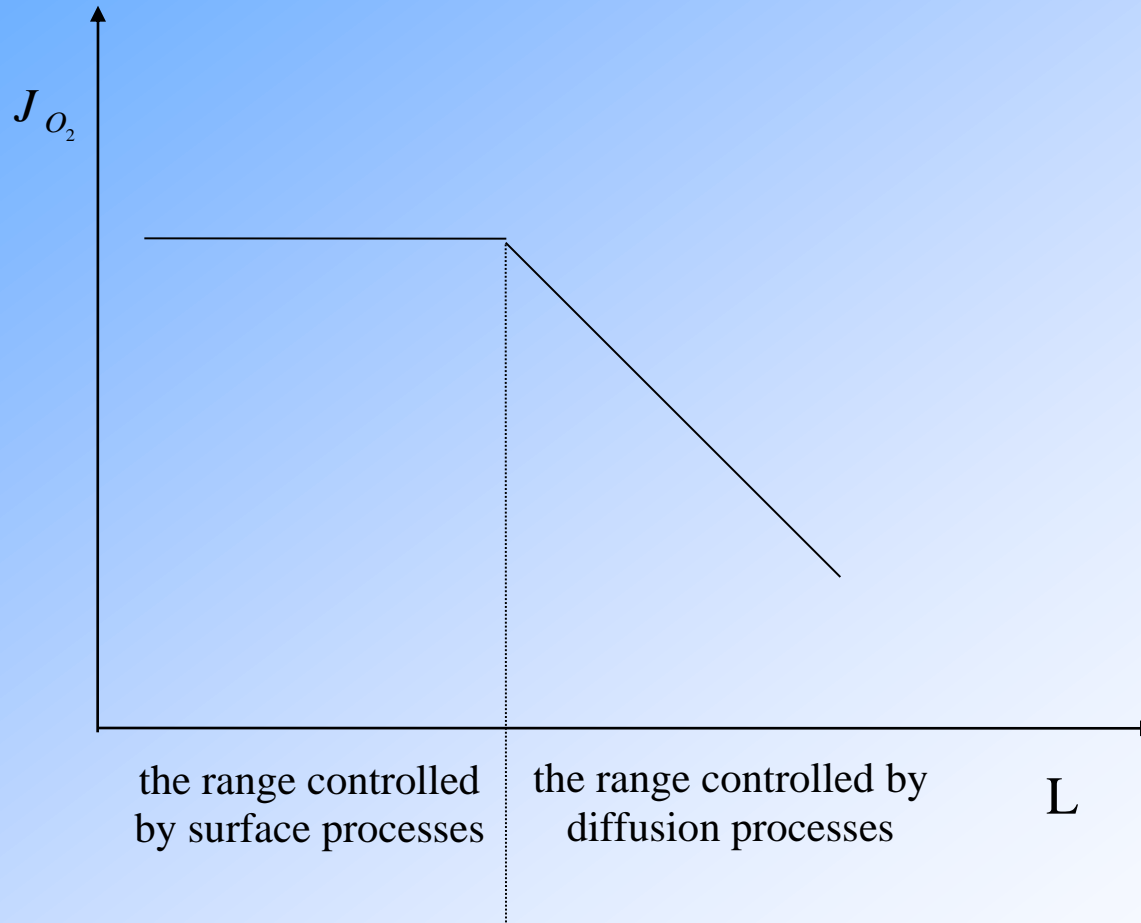
p_o – atmospheric pressure

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: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (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

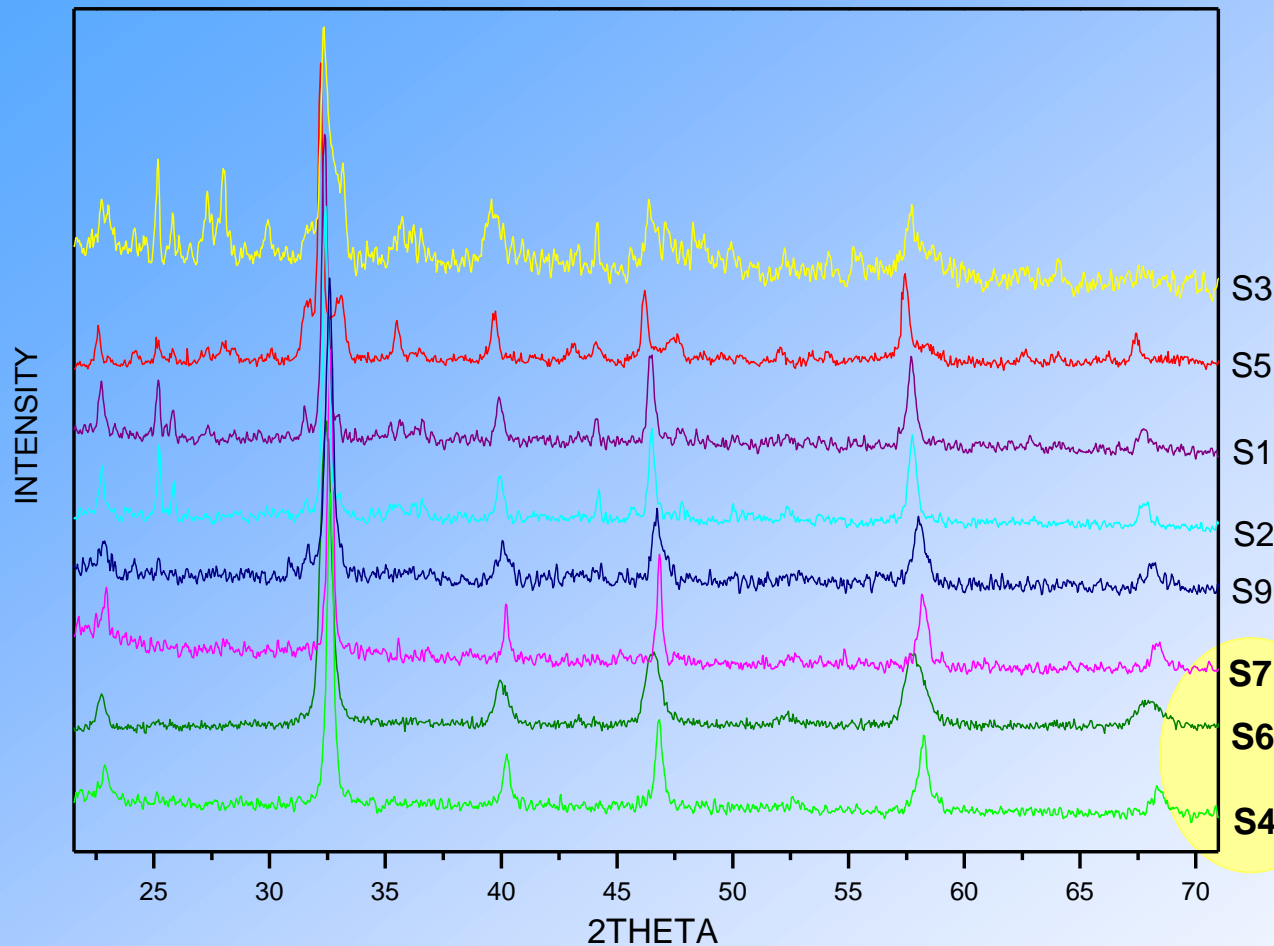


R-3 c R

S4: $a = 5.467(1) \text{ \AA}$ $\alpha = 60.26^\circ$

S6: $a = 5.497(9) \text{ \AA}$ $\alpha = 60.24^\circ$

S7: $a = 5.469(1) \text{ \AA}$ $\alpha = 60.25^\circ$



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



Politechnika Wroclawska

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

dwel time 2 h



Politechnika Wroclawska

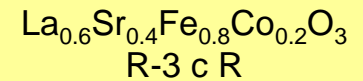
Preparation of sintered disks in Cerel

- absorbability, apparent density and porosity of the sintered disks

Samples	Green disks	Sintered disks		
	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



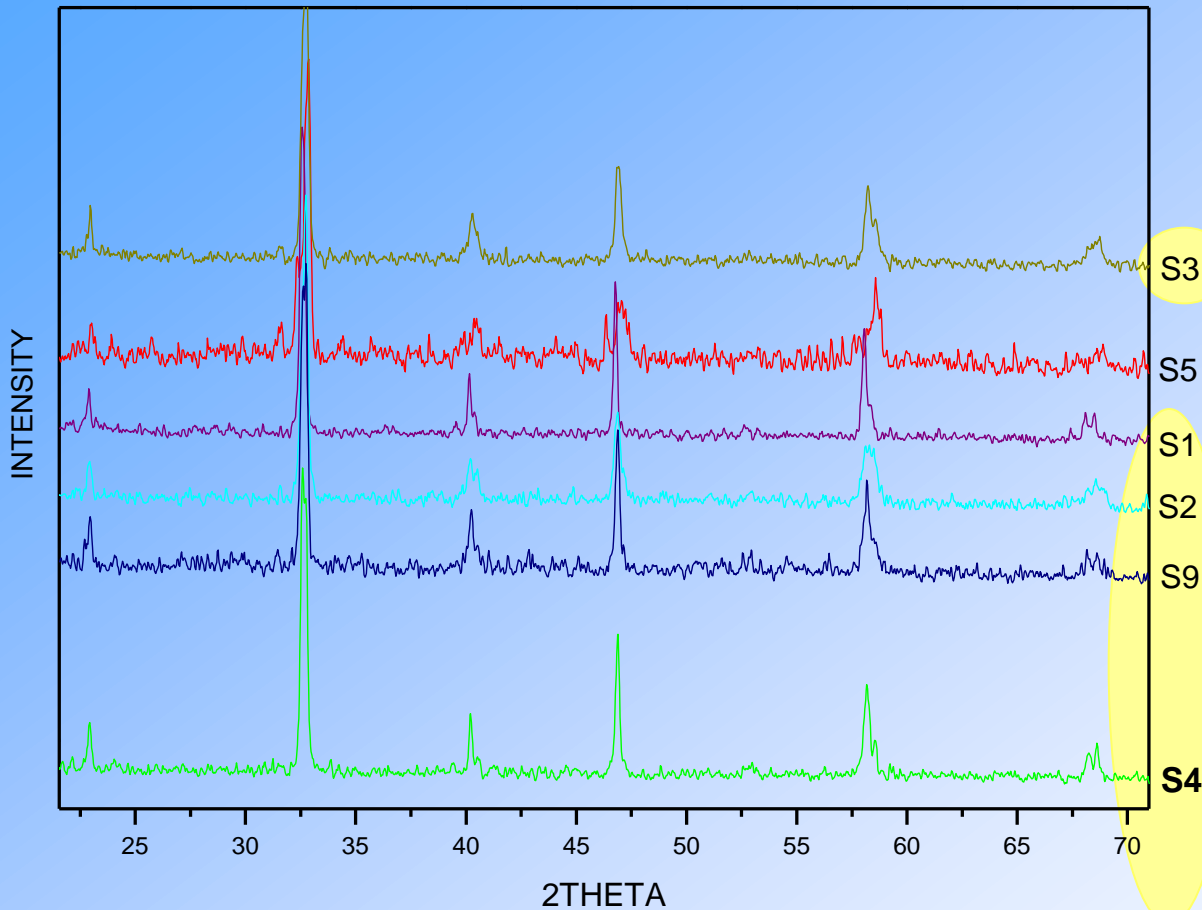
S4: $a = 5.465(1) \text{ \AA}$ $\alpha = 60.33^\circ$

S9: $a = 5.468(9) \text{ \AA}$ $\alpha = 60.35^\circ$

S2: $a = 5.469(1) \text{ \AA}$ $\alpha = 60.34^\circ$

S1: $a = 5.478(1) \text{ \AA}$ $\alpha = 60.27^\circ$

S3: $a = 5.470(1) \text{ \AA}$ $\alpha = 60.34^\circ$



XRD patterns of powders obtained from disks sintered at 1350°C



Politechnika Wroclawska

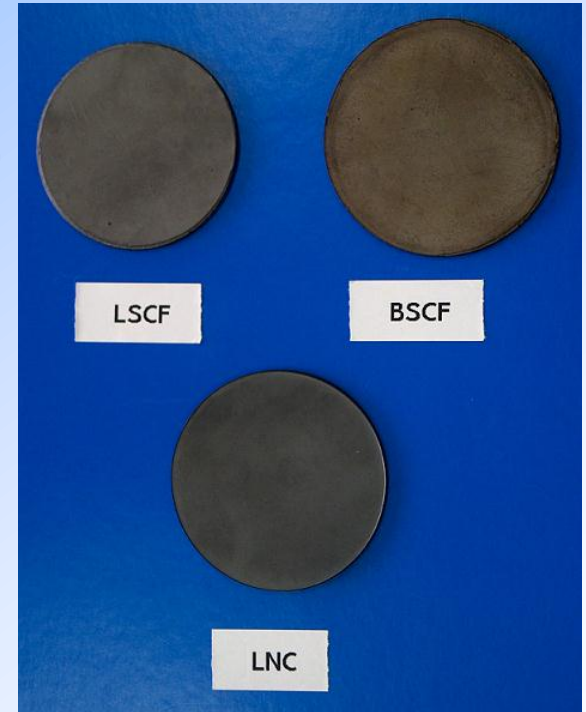
Preliminary conclusions

- LSCF powder fabrication method strongly influences on the phase composition and physicochemical properties.
- The monophasic 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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (**LSCF**),
 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (**BSCF**) and $\text{LaNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ (**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

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**



Politechnika Wroclawska