Development of multilayered ferrite-based ceramic membranes for partial oxidation of hydrocarbons.

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Technologies for natural gas conversion

Steam reforming

$CH_4+H_2O=CO+3H_2$

$$\Delta H^0_{298} = 206\ \mathrm{kJ/mol}$$

Partial oxidation

$CH_4+0.5O_2=CO+2H_2$

$$\Delta H^0_{298} = -36\ \mathrm{kJ/mol}$$

highly endothermic reaction

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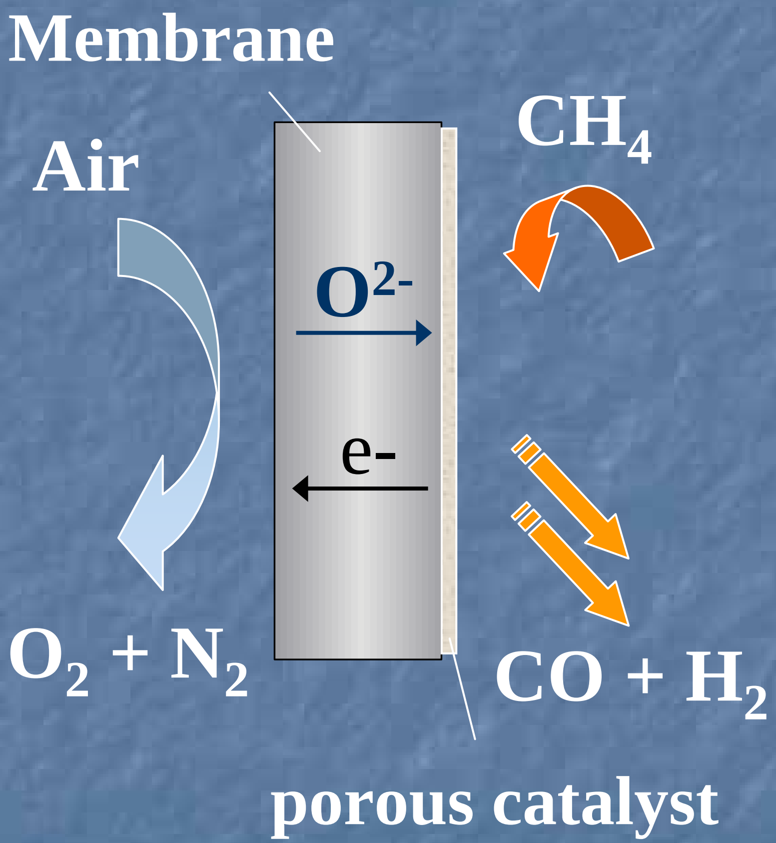
Energy expensive

The main cost – cryogenic oxygen plant

The advantage of mixed-conductive membranes

possibility to integrate oxygen separation and partial oxidation in a single reactor

Operation principles



Membrane

Air

CH_4

O^{2-}

e-

$O_2 + N_2$

$CO + H_2$

porous catalyst

Feed (air) side:

$$O_2 + 4e^- = 2O^{2-}$$

Permeate side:

$$2O^{2-} + 2CH_4 = 2CO + 4H_2 + 4e^-$$

Oxygen permeation flux:

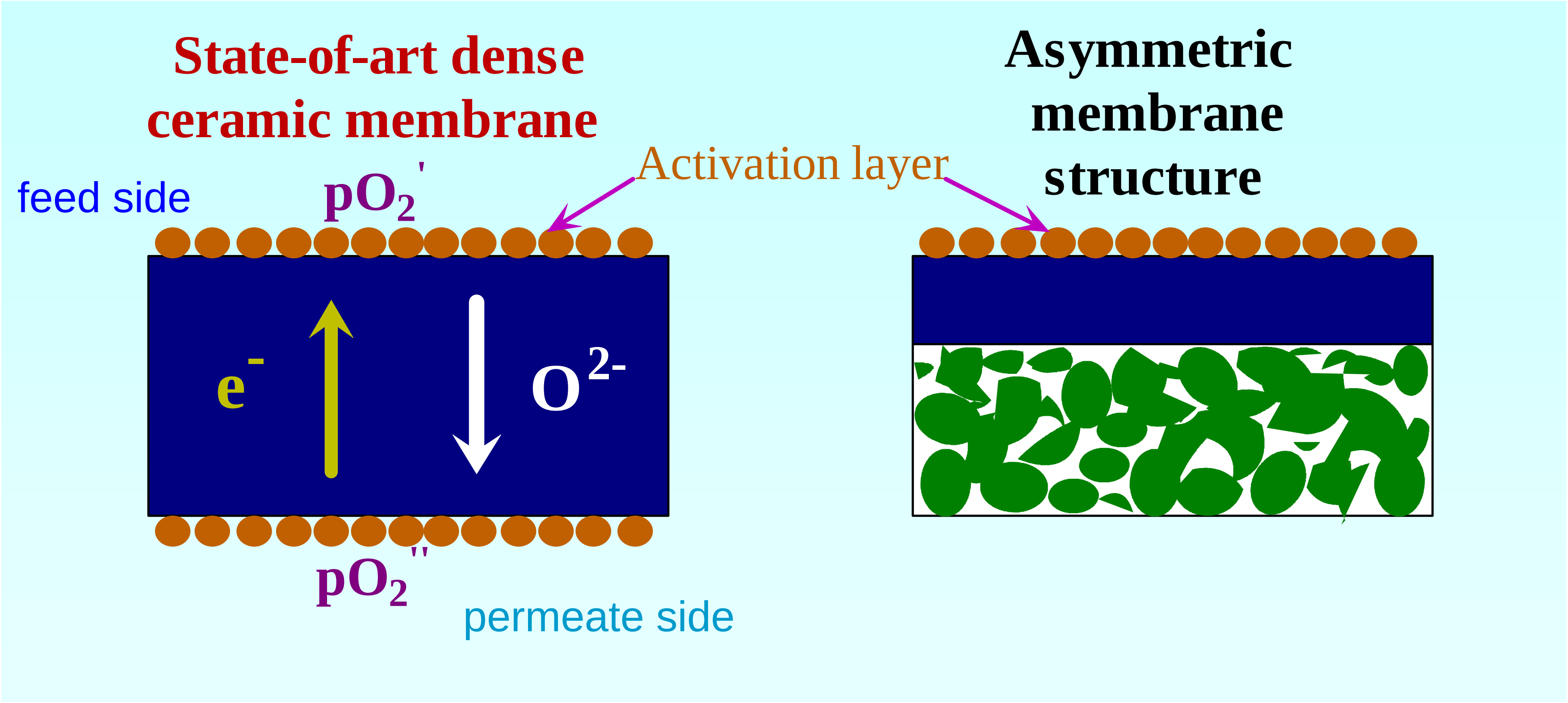
$$j = \frac{RT}{16F^2 d} \int_{p_1}^{p_2} \frac{\sigma_O \sigma_e}{\sigma_O + \sigma_e} d \ln p(O_2)$$

d – membrane thickness

σ_O and σ_e – partial oxygen-ionic and electronic conductivities

p_2 and p_1 – oxygen partial pressures at the membrane feed- and permeated-side

Dense membrane concepts



- *Relatively low oxygen permeation fluxes*
- *Chemical instability under reducing conditions*

- *High oxygen permeation rates*
- *Possibility to increase membrane stability by forming diffusion barrier*
- *Possibility to provide higher CO and H_2 selectivity*

Requirements to support material

- similar thermal and chemical expansion with dense layer;
- sufficient mechanical strength;
- stable microstructure with narrow pore size distribution;
- ability to withstand the membrane operation conditions;
- low resistance to gas flow;

- catalytic activity towards POM → fast attainment of equilibrium condition providing higher CO and H_2 selectivity of partial oxidation

Oxygen permeability and stability of perovskite-type materials

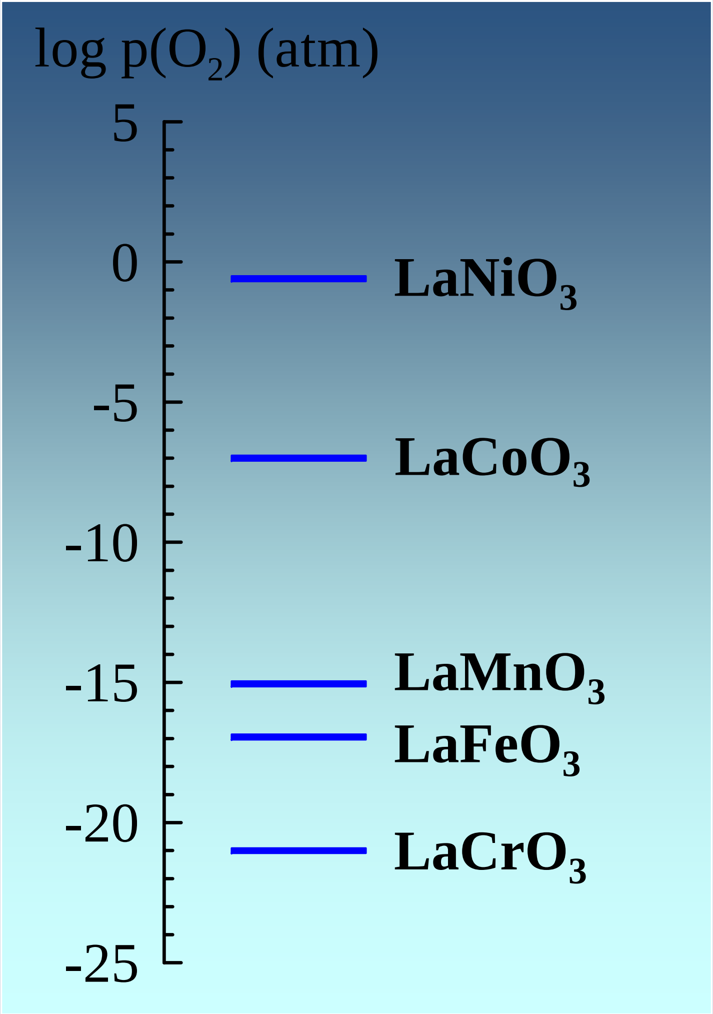
La-A-Co-O and ***La-A-Fe-O*** solid solutions (A = alkaline earth element)

↓

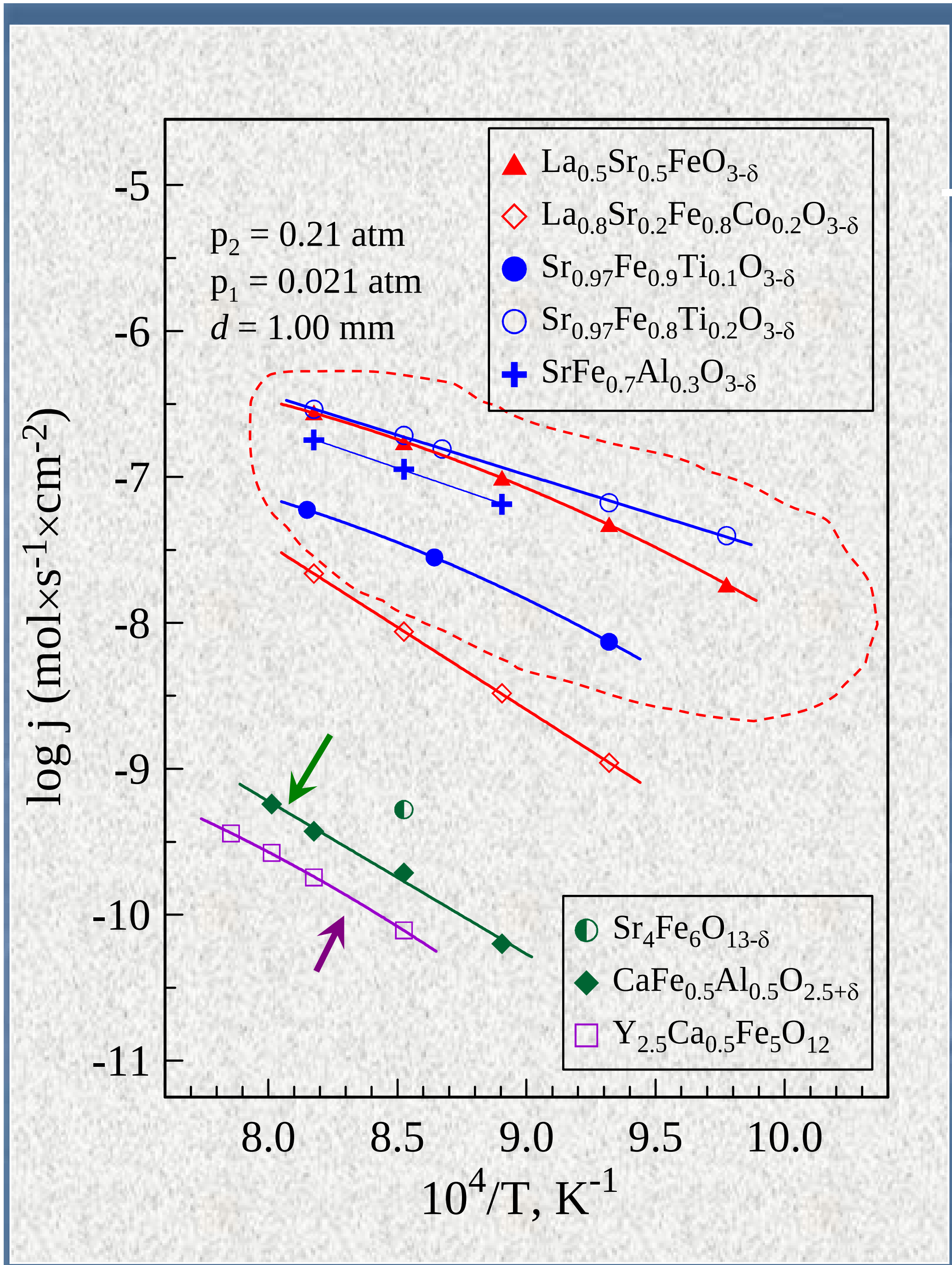
highest oxygen permeability level

Ferrite – based mixed conducting oxides seem to be the most promising candidate materials for membranes for oxygen separation and methane conversion, if one relates to the optimal ratio between oxygen permeability and thermodynamic stability in reducing environment.

Low-p(O_2) stability limits at 1273 K



Selection of the components: oxygen permeation



Garnet-type: low oxygen deficiency and low vacancy mobility

Brownmillerite-type: ordering in the oxygen sublattice

Perovskite-type: substantial ionic transport

↓

$SrFe(Al)O_{3-\delta}$ $La_{0.5}Sr_{0.5}FeO_{3-\delta}$

$Sr_{0.97}Fe_{0.8}Ti_{0.2}O_{3-\delta}$

V.V. Kharton, A.L. Shaula, E.N. Naumovich et. al., *J. Electrochem. Soc.*, 150 (2003) J33.

V.V. Kharton, A.L. Shaula, F.M.M. Snijkers et.al., *J. Membrane Sci.*, 252 (2005) 215.

V.V. Kharton, A.V. Kovalevsky, E.V. Tsipis et.al., *J. Solid State Electrochem.*, 7 (2002) 30.

E.V. Tsipis, M.V. Patrakeev, V.V. Kharton et.al, *Solid State Sci.*, 7 (2005) 355.

Refs.

Selection of the components: thermal expansion

Membrane material	Phase composition	Average TEC in air	
		T, K	
$Gd_{2.5}Ca_{0.5}Fe_5O_{12}$	G	370-1150	
$Y_{2.5}Ca_{0.5}Fe_5O_{12}$	G	370-1150	
$CaFe_{0.5}Al_{0.5}O_{2.5+\delta}$	B	370-850 / 930-1300	
$Sr_4Fe_6O_{13\pm\delta}$	L	770-1100	10.8
$SrFe_{0.2}Co_{0.8}O_{3-\delta}$	C	300-700 / 800-1100	18.8 / 29.4
$SrFe_{0.7}Al_{0.3}O_{3-\delta}$	C	370-920 / 920-1220	15.4 / 23.0
$SrFe_{0.5}Al_{0.5}O_{3-\delta}$	C + I	370-920 / 923-1220	13.5 / 19.1
$Sr_{0.97}Fe_{0.9}Ti_{0.1}O_{3-\delta}$	C	350-700 / 700-1040	14.7 / 28.0
$Sr_{0.97}Fe_{0.8}Ti_{0.2}O_{3-\delta}$	C	300-780 / 780-1040	13.8 / 27.0
$La_{0.3}Sr_{0.7}FeO_{3-\delta}$	C	300-770 / 770-1150	13.0 / 24.9
$La_{0.3}Sr_{0.7}Fe_{0.8}Ga_{0.2}O_{3-\delta}$	C	300-920 / 920-1110	12.9 / 25
$La_{0.5}Sr_{0.5}Fe_{0.6}Ga_{0.4}O_{3-\delta}$	C	330-850 / 850-1070	11.9 / 19.3
$La_{0.3}Sr_{0.7}Fe_{0.8}Ti_{0.2}O_{3-\delta}$	C	400-790 / 790-1260	13.6 / 21.7
$La_{0.3}Sr_{0.7}Fe_{0.8}Al_{0.2}O_{3-\delta}$	C	350-680 / 680-1300	12.9 / 27.4
$La_{0.3}Sr_{0.7}Fe_{0.6}Al_{0.4}O_{3-\delta}$	C + I	350-760 / 760-1300	12.1 / 23.2
$La_{0.3}Sr_{0.7}Fe_{0.6}Al_{0.3}Cr_{0.1}O_{3-\delta}$	C + I	380-980 / 980-1350	13.1 / 22.7

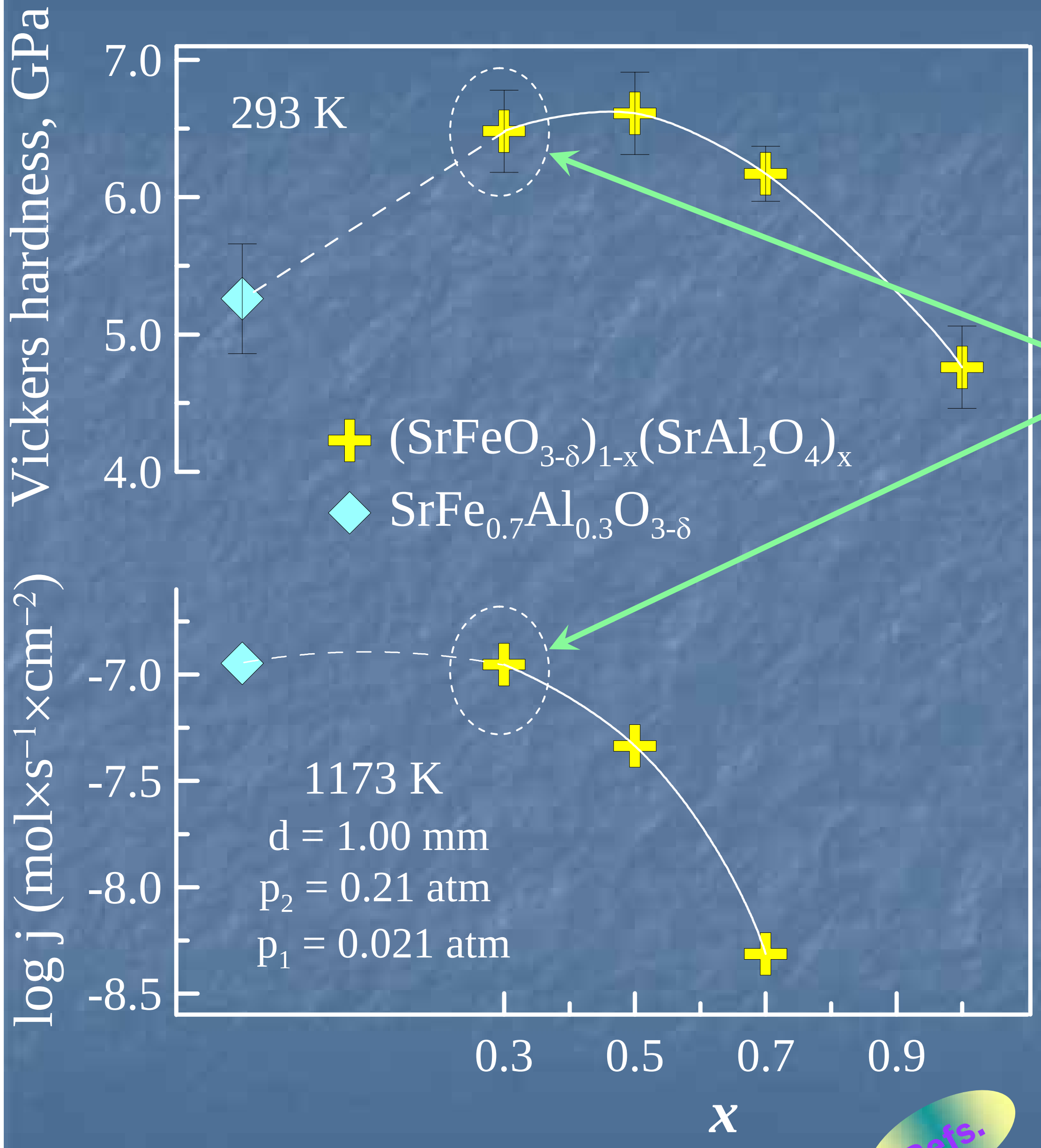
High expansion of $Sr_{0.97}Fe(Ti)O_{3-\delta}$ makes it rather impossible to use these materials to form a thermally-stable dense layer in asymmetric membranes

Refs.

V.V. Kharton, A.A. Yaremchenko, M.V. Patrakeev et.al, *J. Europ. Ceram. Soc.,* 23 (2003) 1417.

V.V.Kharton, A.A.Yaremchenko, E.N.Naumovich, *J. Solid State Electrochem.*, 3 (1999) 303.

Selection of the components: Sr-Fe-Al-O system



Moderate additions of monoclinic $SrAl_2O_4$ to perovskite-type $SrFe(Al)O_{3-\delta}$ mixed conductors improve the sinterability and thermomechanical properties.

$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ dual phase composite demonstrates an attractive combination of thermomechanical and oxygen transport properties.

Selected asymmetric architectures:

SFSA-LSF: $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ - dense
$La_{0.5}Sr_{0.5}FeO_{3-\delta}$ - porous

SFSA-2: $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ - both dense and porous layers

A.A. Yaremchenko, V.V. Kharton, A.L. Shaula et.al, *J. Electrochem. Soc.* 153 (2006) J50

Refs.

V.V. Kharton, A.V. Kovalevsky, A.A. Yaremchenko et.al, *J. Solid State Electrochem.*, 10 (2006) 663.

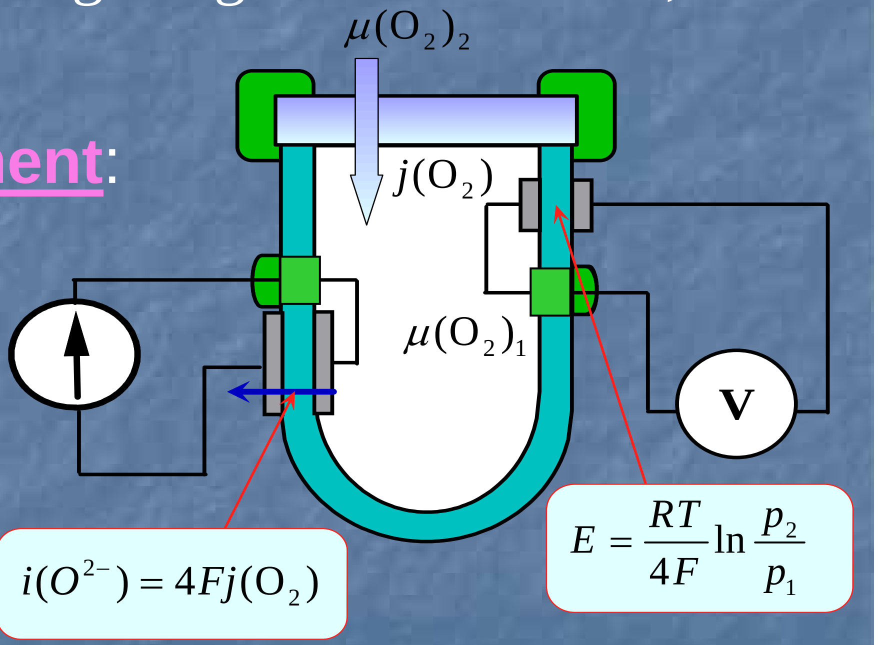
Experimental

Synthesis: **$La_{0.5}Sr_{0.5}FeO_{3-\delta}$** - standard ceramic route,
$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ - combustion spray pyrolysis

Characterization: X-ray diffraction and SEM/EDS analysis, mercury intrusion porosimetry, gas-tightness control, dilatometry

Oxygen permeation measurement:

temperature range: 1023 – 1223 K,
$p(O_2)$ range – feed side: 0.21 atm
permeate side: 0.1 – 0.02 atm



$$i(O^{2-}) = 4Fj(O_2)$$

$$E = \frac{RT}{4F}\ln\frac{p_2}{p_1}$$

Refs.

V.V.Kharton, A.A.Yaremchenko, A.V.Kovalevsky et.al., *J. Membr. Sci.* 163 (1999) 307.

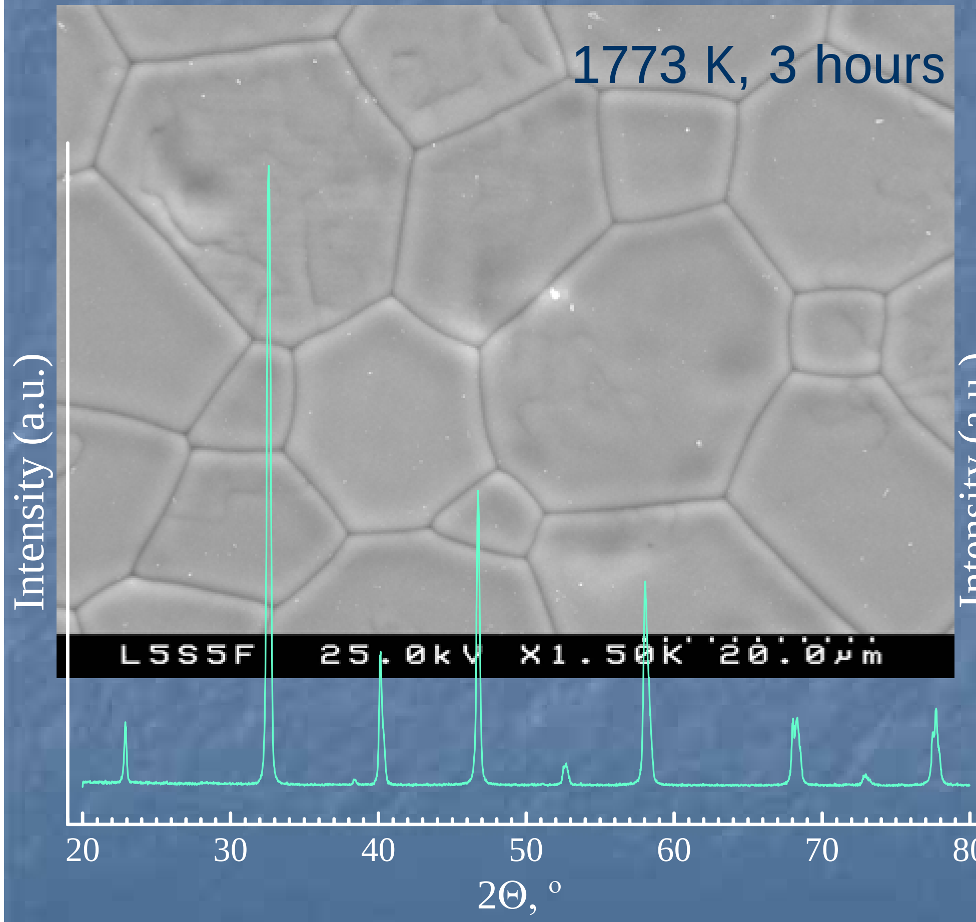
V.V. Kharton, A.V. Kovalevsky, A.P. Viskup et.al., *J. Solid State Chem.* 156 (2001) 437.

A. V. Kovalevsky, V. V. Kharton, V. N. Tikhonovich et.al, *Materials Sci. Eng. B*, 1998 (52) 105.

Characterization of single components

$La_{0.5}Sr_{0.5}FeO_{3-\delta}$

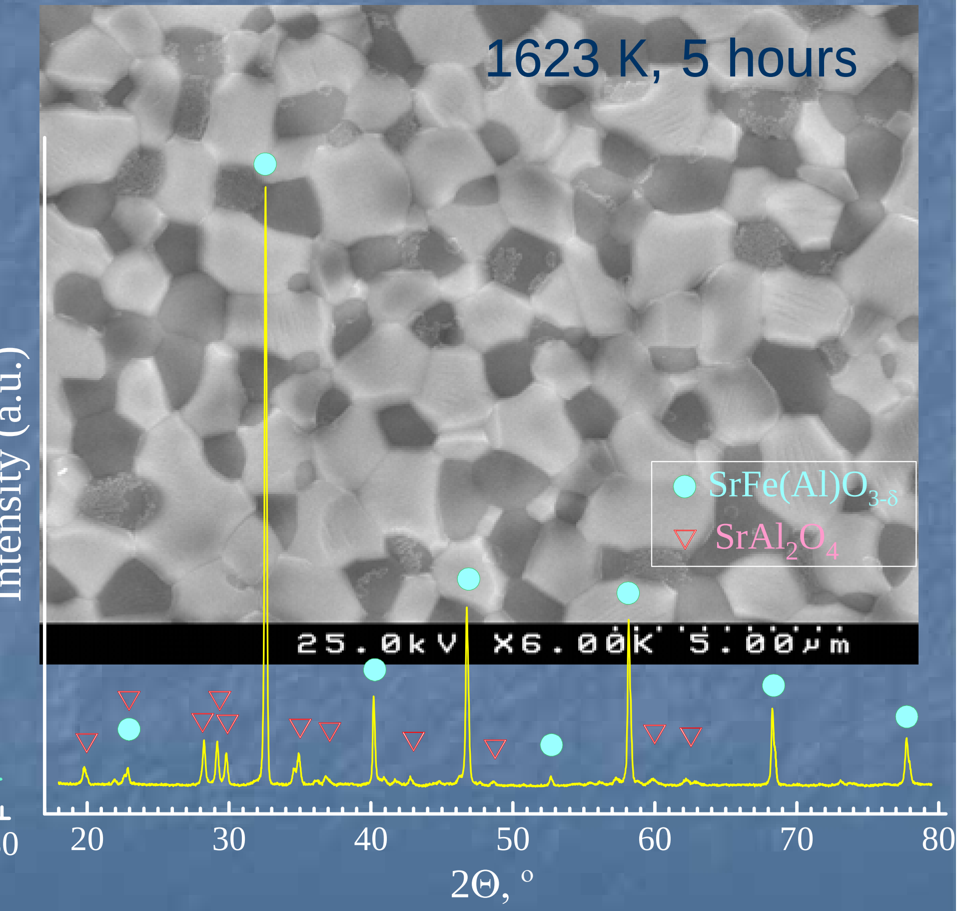
Rhombohedrally-distorted perovskite (S.G. $R\bar{3}c$)



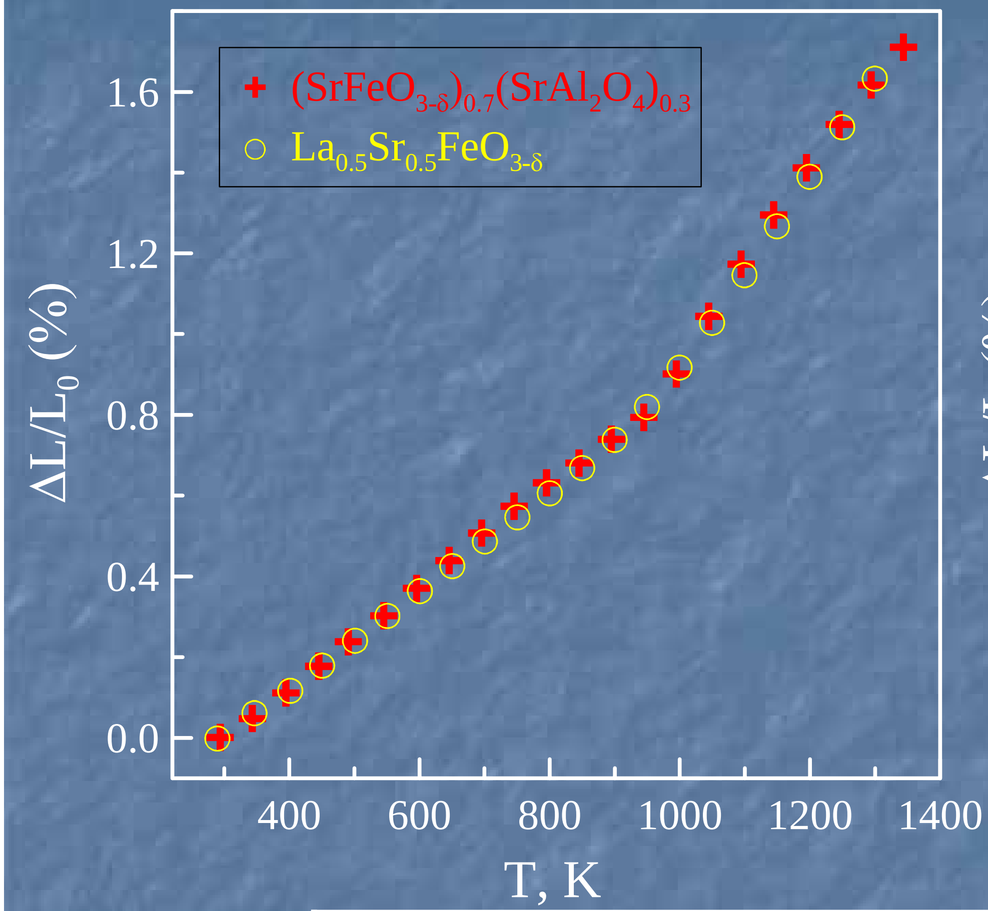
$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$

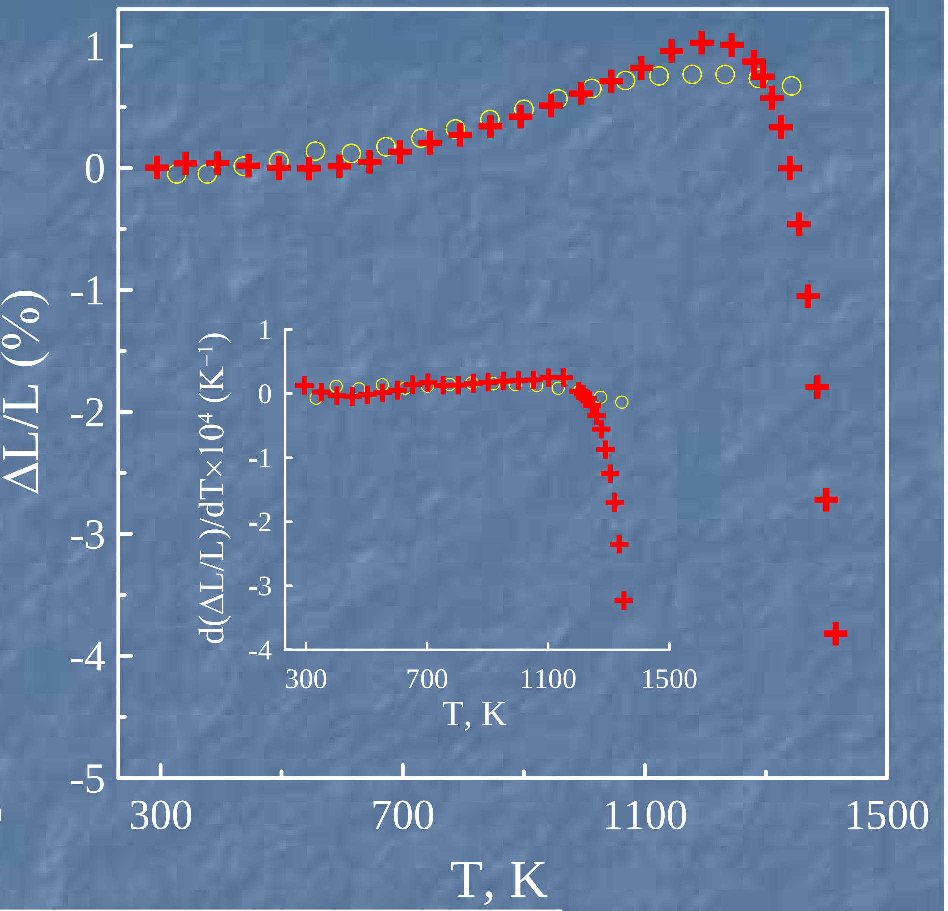
Phase 1: $SrFeO_{3-\delta}$ - based cubic perovskite (S.G. $Pm\bar{3}m$)

Phase 2: monoclinic $SrAl_2O_4$ (S.G. $P2_1$)



Characterization: shrinkage and thermal expansion



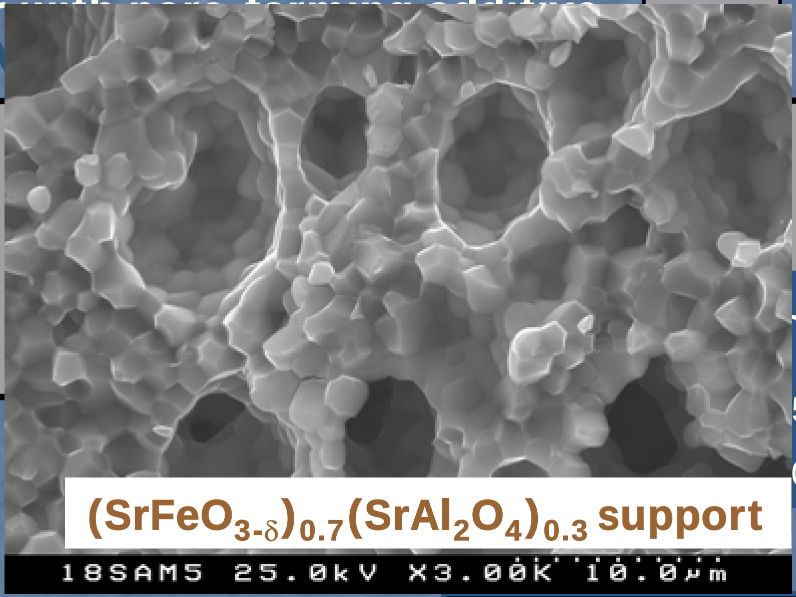


Composition	T, K	$\alpha\times10^6$, K-1
$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$	350 – 950 950 -1310	12.6 ± 0.1 24.1 ± 0.1
$La_{0.5}Sr_{0.5}FeO_{3-\delta}$	350 – 950 950 -1310	12.4 ± 0.1 23.7 ± 0.2

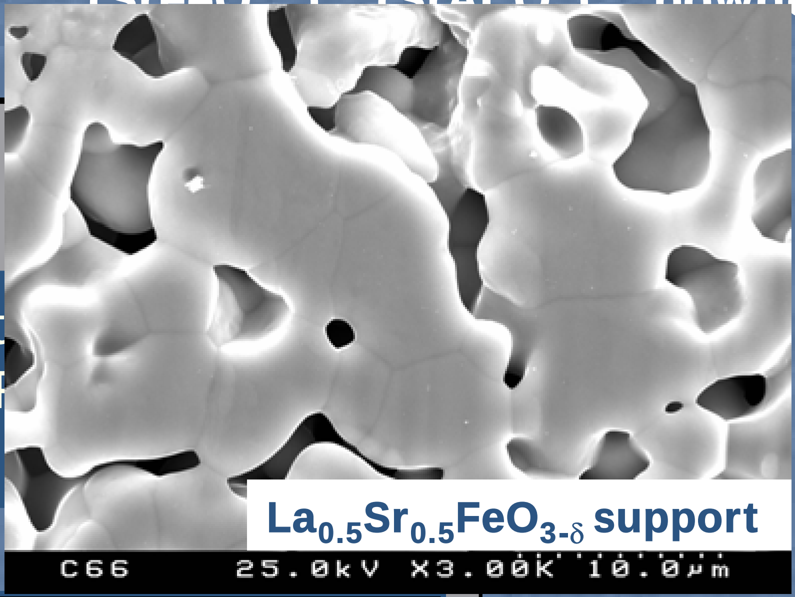
Experimental: fabrication route for asymmetric membranes

Powder

powder



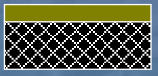
$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ support



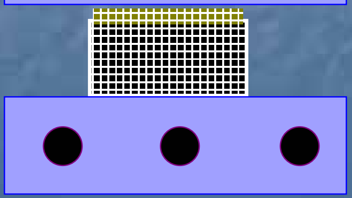
$La_{0.5}Sr_{0.5}FeO_{3-\delta}$ support

Open porosity: 20-30 %

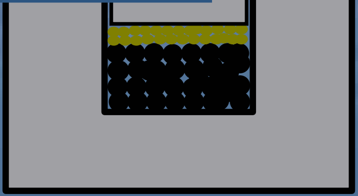
(mercury intrusion porosimetry)



Asymmetric membrane



Sintering

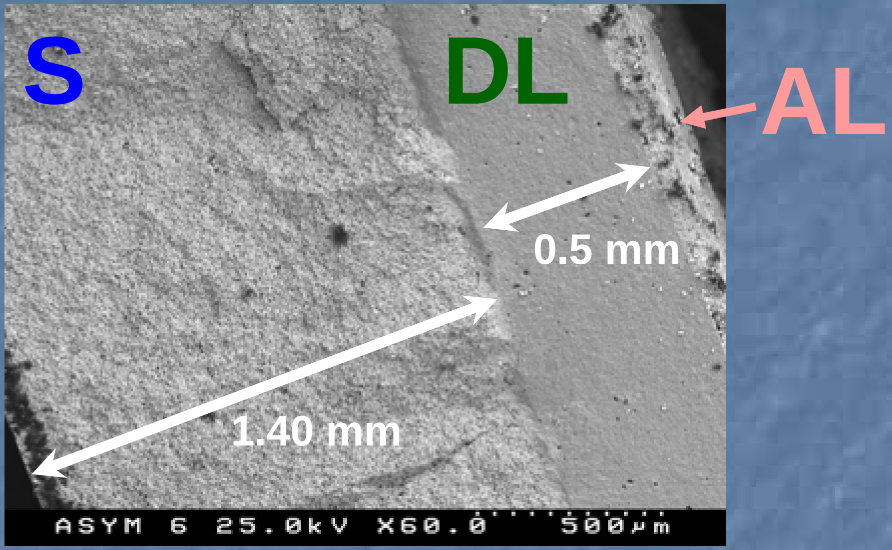


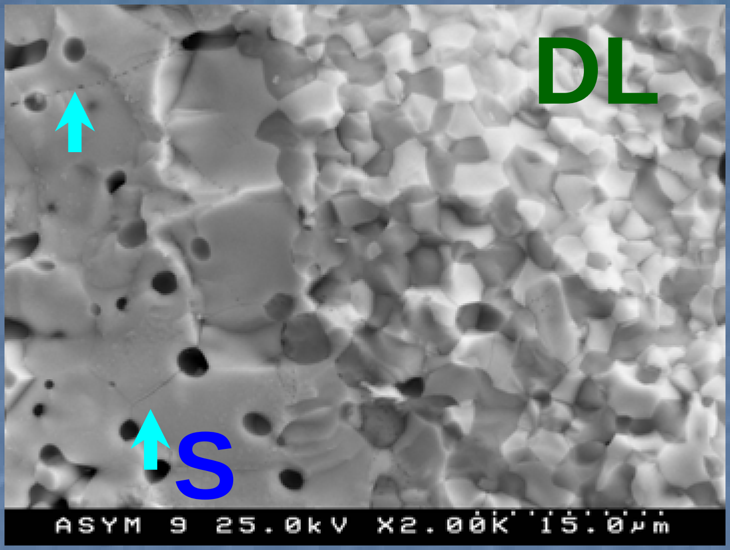
Pressing at 65-150 MPa

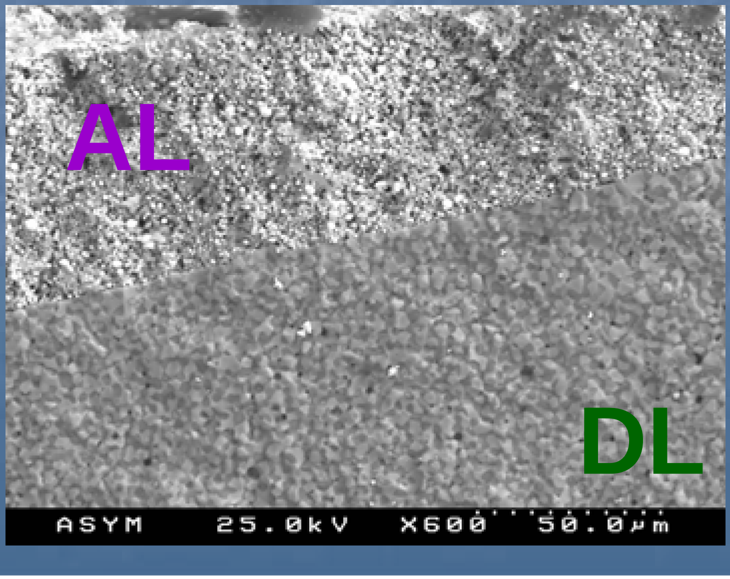
A.V. Kovalevsky, V.V. Kharton, F. Maxim et.al, *J. Membrane Sci.*, 278 (2006) 162.

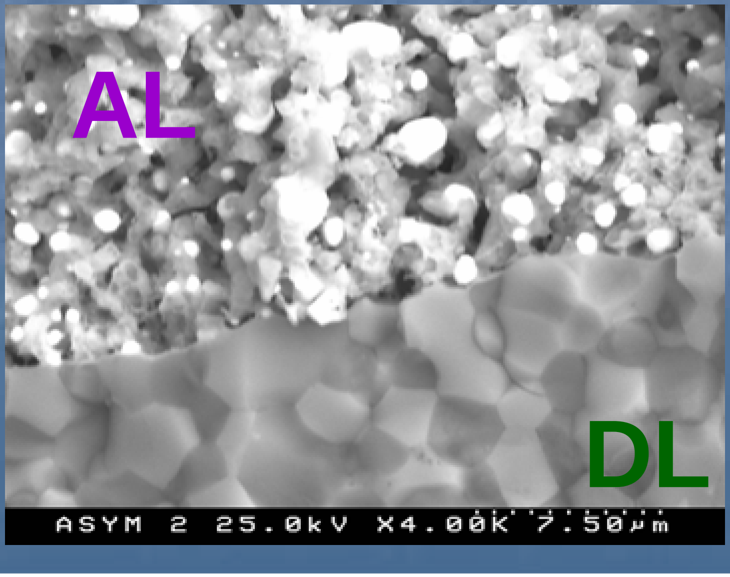
$La_{0.5}Sr_{0.5}FeO_{3-\delta}$ -supported composite membrane (SFSA-LSF)

Activation layer (**AL**): $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ + Pt (50:50 wt. %)



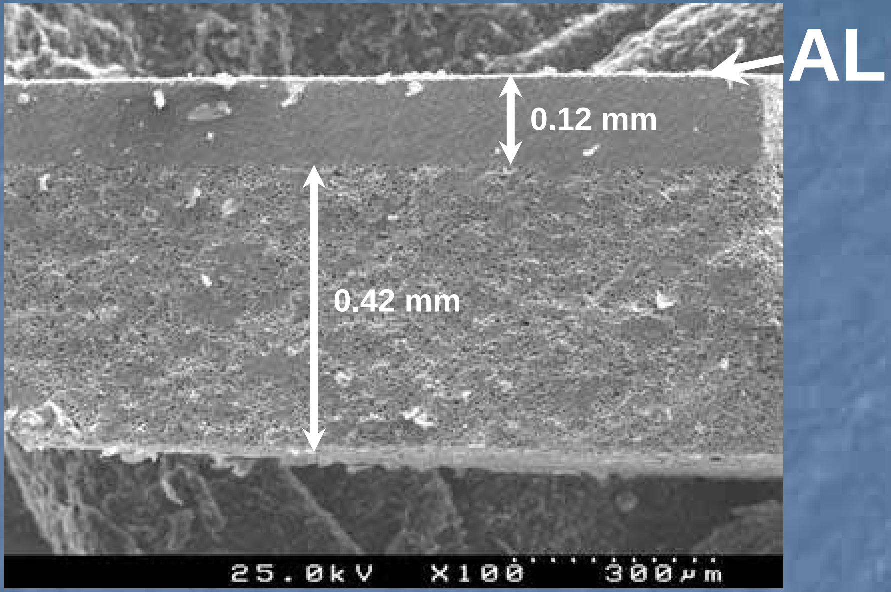


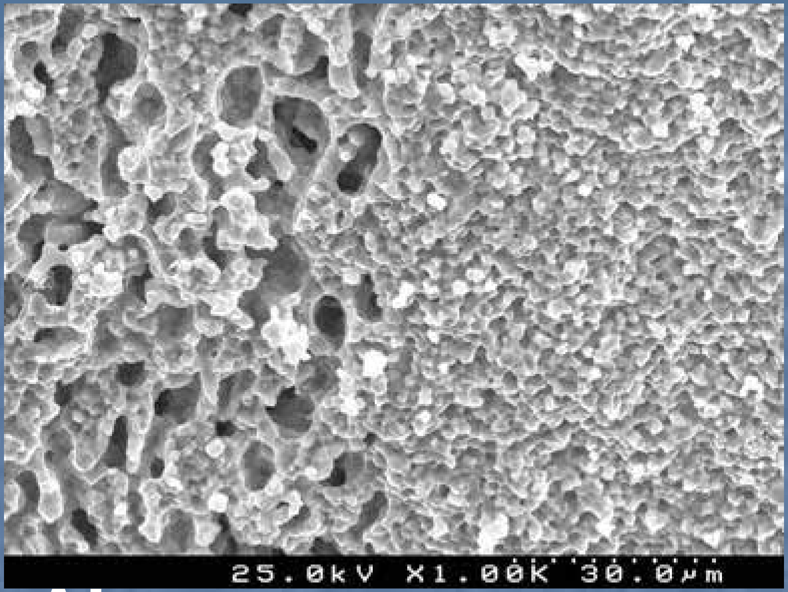


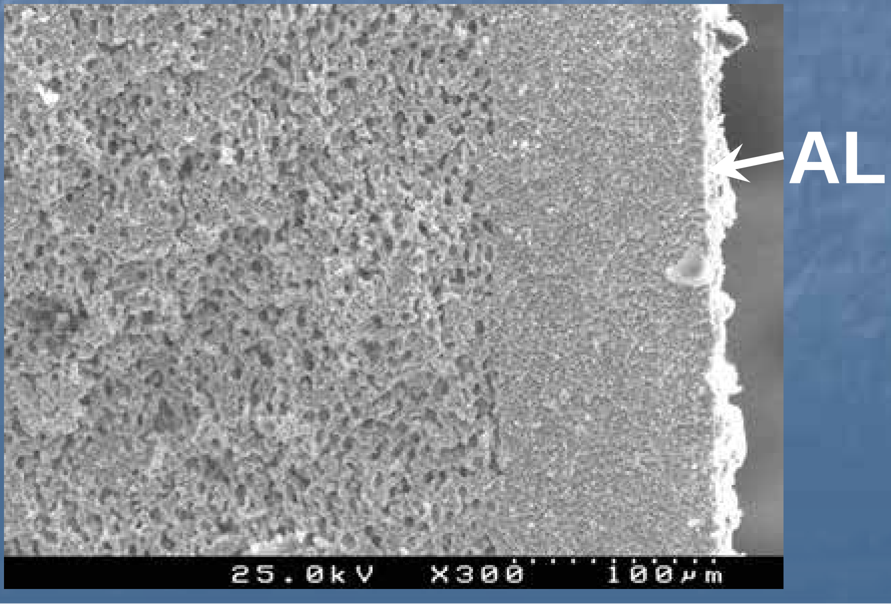


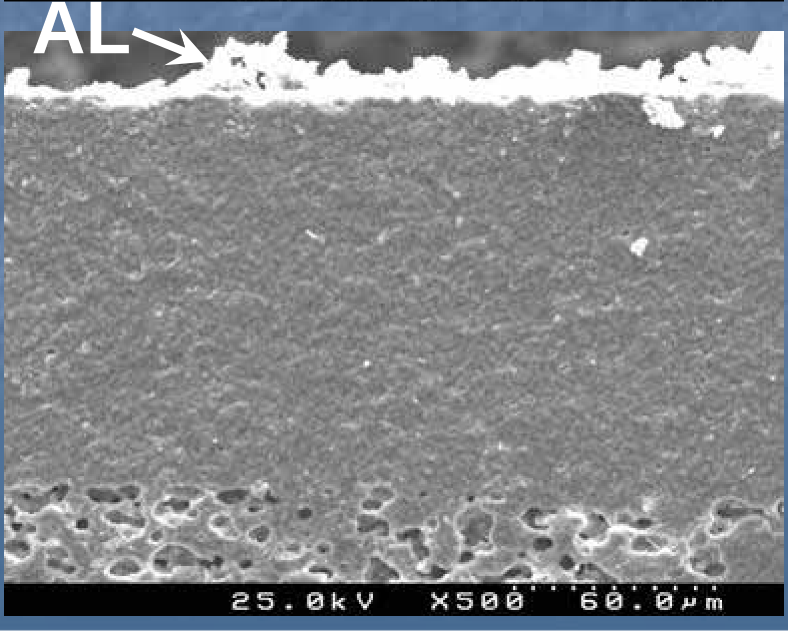
Self -supported $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ composite membrane (SFSA-2)

Activation layer (**AL**): $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ + Pt (50:50 wt. %)

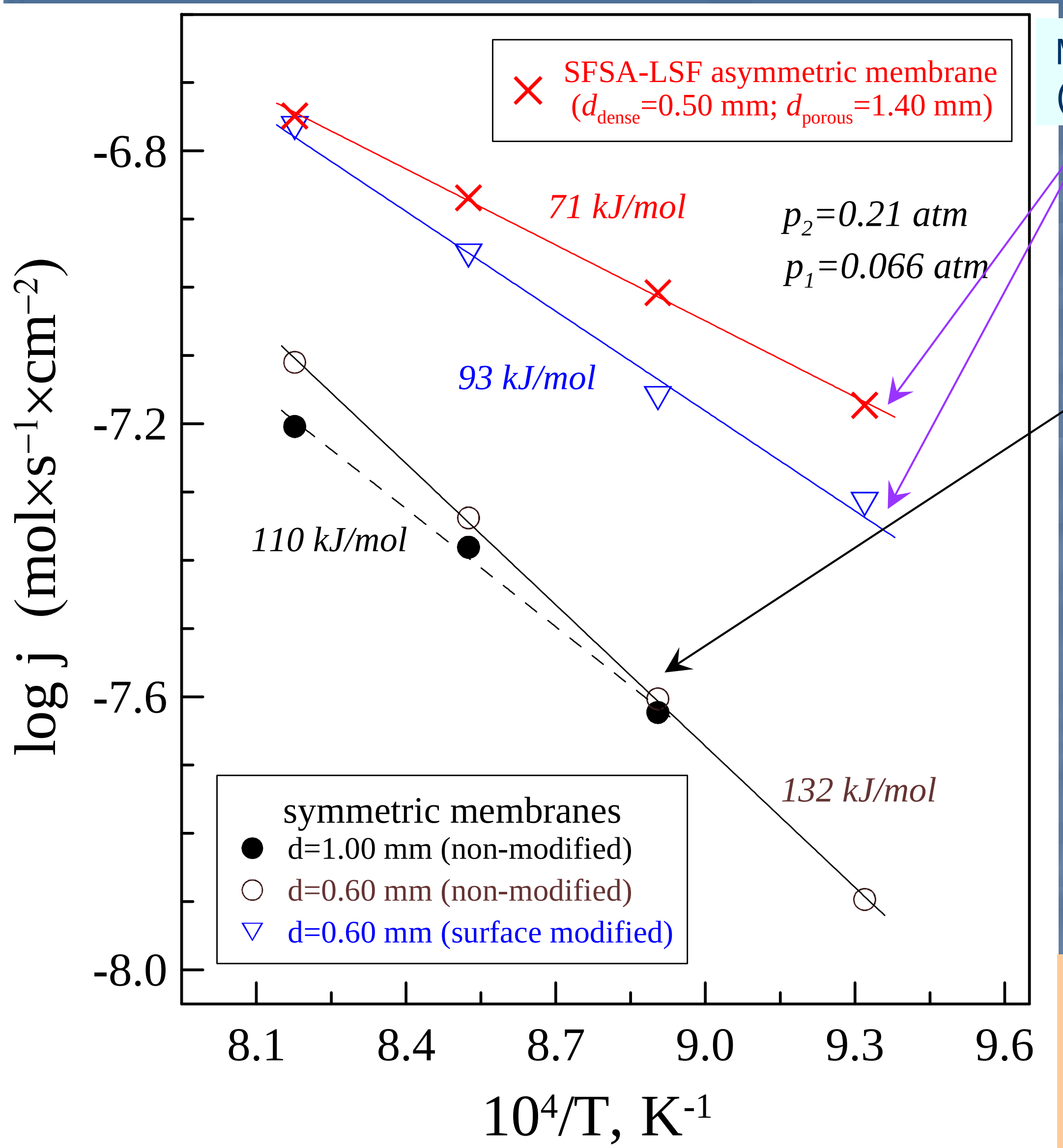








Oxygen permeation: limiting effect of surface oxygen exchange



Modified with
$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ + Pt (50:50 wt. %)

The overall transport is strongly affected by exchange processes at the membrane/gas boundary.

The activation energy (E_a) for surface oxygen exchange is higher than that for the bulk ambipolar conductivity.

The exchange limitations to oxygen transport may completely inhibit positive effects expected on decreasing thickness of the membrane dense layers.

For symmetric membranes, surface activation leads to a substantial decrease in the apparent E_a values, from 132 down to 93 kJ/mol at 1073-1223 K.

SFSA-LSF asymmetric membrane concept

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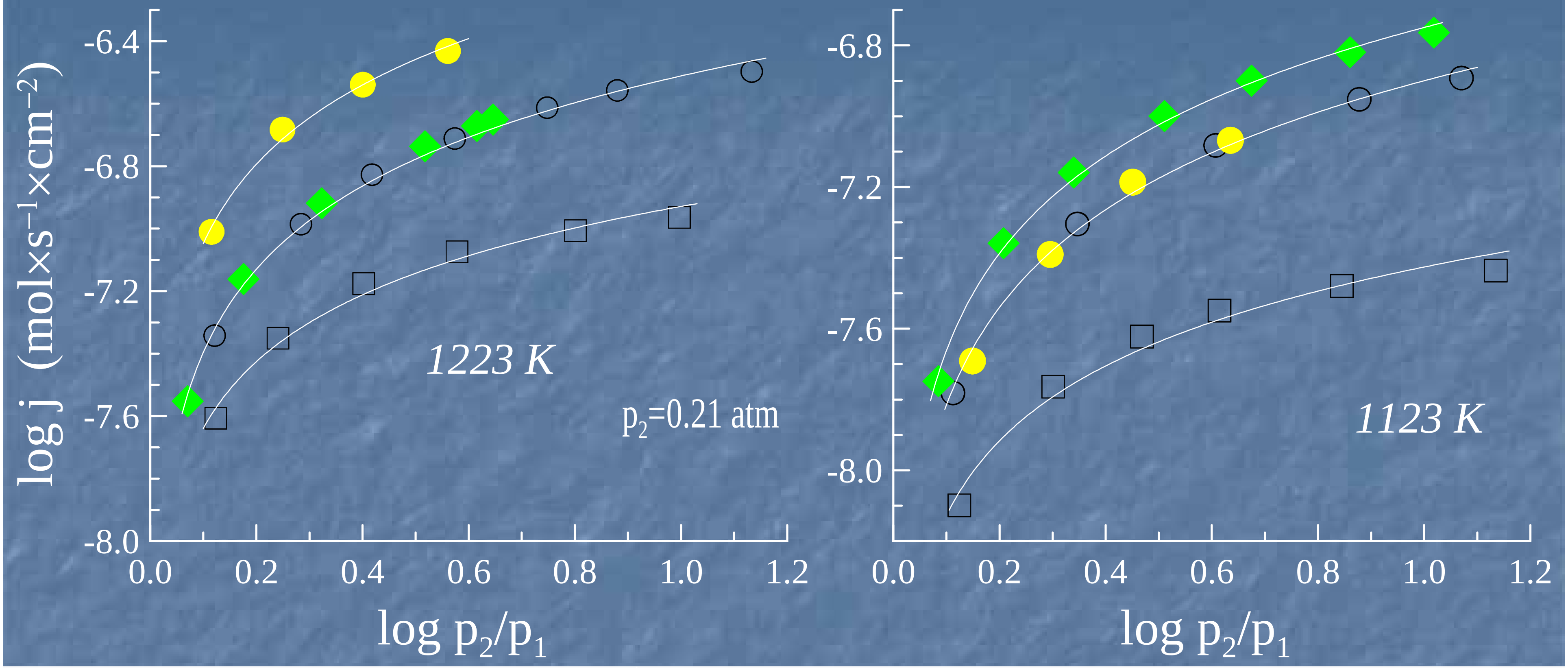
noticeable improvement in oxygen permeation fluxes at 1073-1173 K

The activation agent is not effective enough.

Oxygen permeation: impact of membrane architecture



□ d=0.60 mm (non-modified)

○ d=0.60 mm (surface-modified)

◆ SFSA-LSF asymmetric membrane

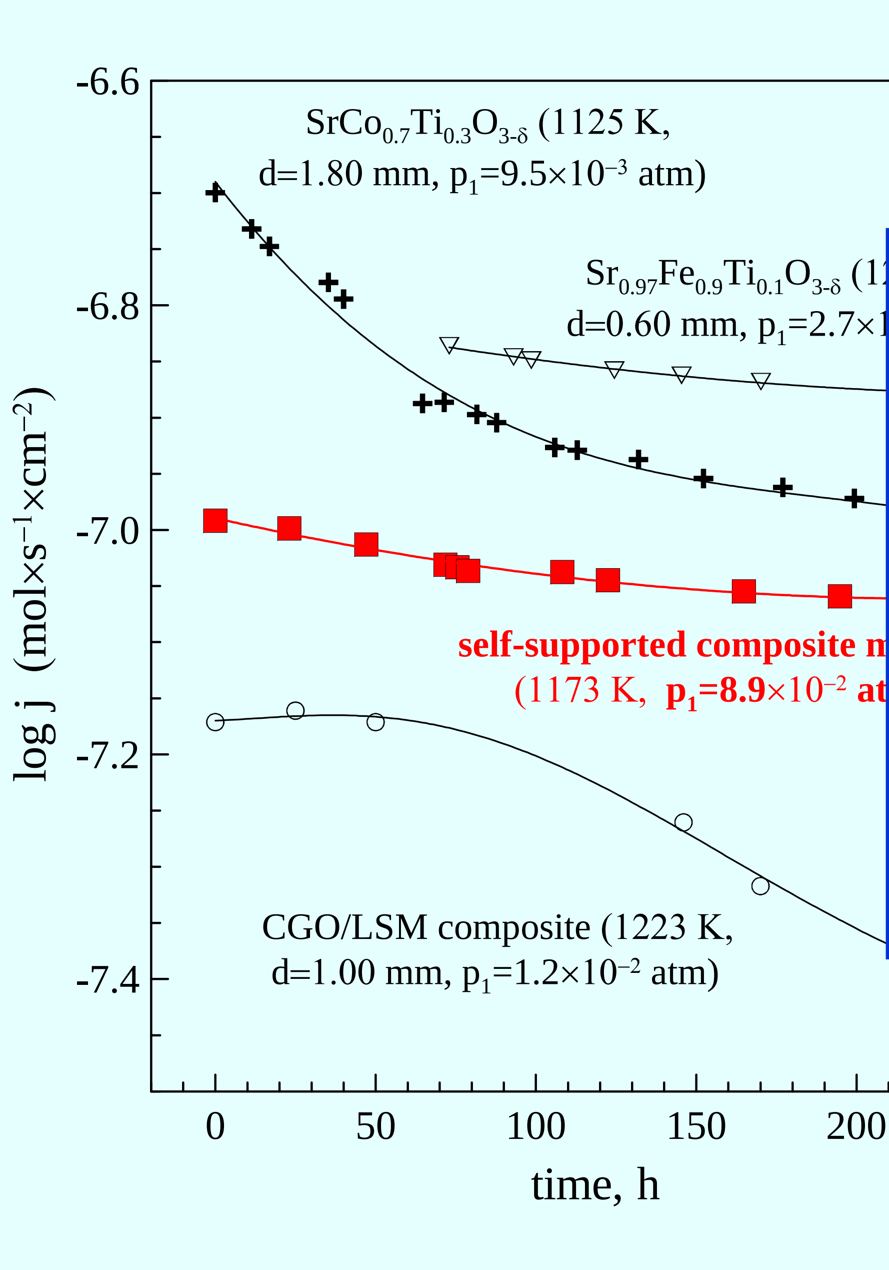
● SFSA-2 asymmetric membrane

At T<1223 K the catalytic activity of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ is apparently higher than that of $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ + Pt mixture

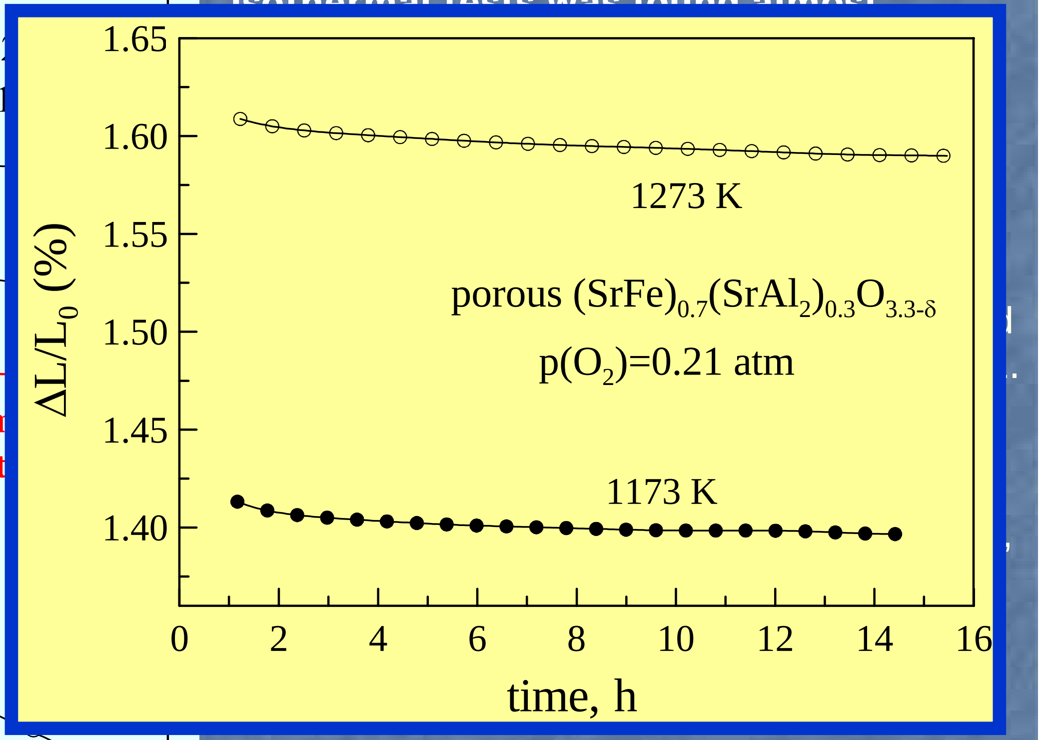
The improvement for self-supported concept of the composite membrane was observed only at temperatures higher than 1173 K.

At 1223 K the oxygen permeation through self-supported composite membrane is still limited by oxygen exchange on the surface.

Oxygen permeation: stability



Self-supported $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ membranes exhibit a sufficiently stable performance; the degradation on either temperature cycling or during prolonged isothermal tests was found almost



The decrease in oxygen permeability with time is minor and may be associated with microstructural factors, namely a slow but continuous sintering of the porous support.

Conclusions

- Similar thermal expansion of $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ and $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ enables to assemble them in one asymmetric membrane structure by uniaxial compacting in two steps, followed by thermal treatment.

- The results show an applicability of the asymmetric membrane concept for improvement of the oxygen permeation fluxes through ferrite-based ceramic membranes.

- $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ supported $(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$ membrane performs at considerably good level at 1073-1173 K, reaching values close to the ideal intrinsic materials performance.

- An architectural approach using perovskite-type $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ as a composition for porous support was found to provide a moderate improvement of oxygen exchange rate on the boundary between dense and porous layers.

- For self supported composite –based asymmetric membrane, a reasonable improvement of transport properties was observed only at high temperatures above 1173 K.

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