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

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Technologies for natural gas conversion

- **Steam reforming**
  \[ \text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \]
  \[ \Delta H_{298}^0 = 206 \text{ kJ/mol} \]
  highly endothermic reaction
  Energy expensive

- **Partial oxidation**
  \[ \text{CH}_4 + 0.5\text{O}_2 = \text{CO} + 2\text{H}_2 \]
  \[ \Delta H_{298}^0 = -36 \text{ kJ/mol} \]
  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**

**Feed (air) side:**
\[ O_2 + 4e^- = 2O^{2-} \]

**Permeate side:**
\[ 2O^{2-} + 2CH_4 = 2CO + 4H_2 + 4e^- \]

**Oxygen permeation flux:**
\[
j = \frac{RT}{16F^2d} \int \frac{p_1}{p_2} \left( \frac{\sigma_O \sigma_e}{\sigma_O + \sigma_e} \right) d \ln p(O_2)
\]

- \( d \) – membrane thickness
- \( \sigma_O \) and \( \sigma_e \) – partial oxygen-ionic and electronic conductivities
- \( p_2 \) and \( p_1 \) – oxygen partial pressures at the membrane feed- and permeated-side
Dense membrane concepts

State-of-art dense ceramic membrane

Asymmetric membrane structure

- 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 H₂ 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 \( \rightarrow \) 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

Low-p(O_2) stability limits at 1273 K

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.
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

\[ \text{SrFe(Al)O}_{3-\delta} \quad \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \]

\[ \text{Sr}_{0.97}\text{Fe}_{0.8}\text{Ti}_{0.2}\text{O}_{3-\delta} \]

References:


## Selection of the components: thermal expansion

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Phase composition</th>
<th>Average TEC in air, $\alpha \times 10^6$, K$^{-1}$</th>
<th>T, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Gd}<em>{2.5}\text{Ca}</em>{0.5}\text{Fe}<em>5\text{O}</em>{12}$</td>
<td>G</td>
<td>370-1150</td>
<td></td>
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<td>$\text{Y}<em>{2.5}\text{Ca}</em>{0.5}\text{Fe}<em>5\text{O}</em>{12}$</td>
<td>G</td>
<td>370-1150</td>
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<tr>
<td>$\text{CaFe}<em>{0.5}\text{Al}</em>{0.5}\text{O}_{2.5+\delta}$</td>
<td>B</td>
<td>370-850 / 930-1300</td>
<td></td>
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<tr>
<td>$\text{Sr}_4\text{Fe}<em>6\text{O}</em>{13+\delta}$</td>
<td>L</td>
<td>770-1100</td>
<td>10.8</td>
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<tr>
<td>$\text{SrFe}<em>{0.2}\text{Co}</em>{0.8}\text{O}_{3-\delta}$</td>
<td>C</td>
<td>300-700 / 800-1100</td>
<td>18.8 / 29.4</td>
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<tr>
<td>$\text{SrFe}<em>{0.7}\text{Al}</em>{0.3}\text{O}_{3-\delta}$</td>
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<td>370-920 / 920-1220</td>
<td>15.4 / 23.0</td>
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<tr>
<td>$\text{SrFe}<em>{0.5}\text{Al}</em>{0.5}\text{O}_{3-\delta}$</td>
<td>C + I</td>
<td>370-920 / 923-1220</td>
<td>13.5 / 19.1</td>
</tr>
<tr>
<td>$\text{Sr}<em>{0.97}\text{Fe}</em>{0.5}\text{Ti}<em>{0.1}\text{O}</em>{3-\delta}$</td>
<td>C</td>
<td>350-700 / 700-1040</td>
<td>14.7 / 28.0</td>
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<tr>
<td>$\text{Sr}<em>{0.97}\text{Fe}</em>{0.5}\text{Ti}<em>{0.2}\text{O}</em>{3-\delta}$</td>
<td>C</td>
<td>300-780 / 780-1040</td>
<td>13.8 / 27.0</td>
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<tr>
<td>$\text{La}<em>{0.3}\text{Sr}</em>{0.7}\text{FeO}_{3-\delta}$</td>
<td>C</td>
<td>300-770 / 770-1150</td>
<td>13.0 / 24.9</td>
</tr>
<tr>
<td>$\text{La}<em>{0.3}\text{Sr}</em>{0.7}\text{Fe}<em>{0.8}\text{Ga}</em>{0.2}\text{O}_{3-\delta}$</td>
<td>C</td>
<td>300-920 / 920-1110</td>
<td>12.9 / 25</td>
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<tr>
<td>$\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{Fe}<em>{0.6}\text{Ga}</em>{0.4}\text{O}_{3-\delta}$</td>
<td>C</td>
<td>330-850 / 850-1070</td>
<td>11.9 / 19.3</td>
</tr>
<tr>
<td>$\text{La}<em>{0.3}\text{Sr}</em>{0.7}\text{Fe}<em>{0.8}\text{Ti}</em>{0.2}\text{O}_{3-\delta}$</td>
<td>C</td>
<td>400-790 / 790-1260</td>
<td>13.6 / 21.7</td>
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<tr>
<td>$\text{La}<em>{0.3}\text{Sr}</em>{0.7}\text{Fe}<em>{0.8}\text{Al}</em>{0.2}\text{O}_{3-\delta}$</td>
<td>C</td>
<td>350-680 / 680-1300</td>
<td>12.9 / 27.4</td>
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<tr>
<td>$\text{La}<em>{0.3}\text{Sr}</em>{0.7}\text{Fe}<em>{0.6}\text{Al}</em>{0.4}\text{O}_{3-\delta}$</td>
<td>C + I</td>
<td>350-760 / 760-1300</td>
<td>12.1 / 23.2</td>
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<tr>
<td>$\text{La}<em>{0.3}\text{Sr}</em>{0.7}\text{Fe}<em>{0.6}\text{Al}</em>{0.3}\text{Cr}<em>{0.1}\text{O}</em>{3-\delta}$</td>
<td>C + I</td>
<td>380-980 / 980-1350</td>
<td>13.1 / 22.7</td>
</tr>
</tbody>
</table>

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

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

(SrFeO$_{3-\delta}$)$_{0.7}$(SrAl$_2$O$_4$)$_{0.3}$ dual phase composite demonstrates an attractive combination of thermomechanical and oxygen transport properties.

Moderate additions of monoclinic SrAl$_2$O$_4$ to perovskite-type SrFe(Al)O$_{3-\delta}$ mixed conductors improve the sinterability and thermomechanical properties.

(SrFeO$_{3-\delta}$)$_{0.7}$(SrAl$_2$O$_4$)$_{0.3}$ dual phase composite demonstrates an attractive combination of thermomechanical and oxygen transport properties.

Selected asymmetric architectures:

**SFSA-LSF:** $(\text{SrFeO}_{3-\delta})_{0.7}$(SrAl$_2$O$_4$)$_{0.3}$ - dense La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ - porous

**SFSA-2:** $(\text{SrFeO}_{3-\delta})_{0.7}$(SrAl$_2$O$_4$)$_{0.3}$ - both dense and porous layers


**Experimental**

**Synthesis:** \( \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \) - standard ceramic route, 
\( (\text{SrFeO}_{3-\delta})_{0.7}(\text{SrAl}_2\text{O}_4)_{0.3} \) - 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

\[
\mu(O_2)_2 \quad \mu(O_2)_1
\]

\[
i(O^{2-}) = 4Fj(O_2)
\]

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


Characterization of single components

**La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$**

Rhombohedrally-distorted perovskite (S.G. $\overline{R3c}$)

1773 K, 3 hours

**Phase 1: SrFeO$_{3-\delta}$ - based cubic perovskite (S.G. $Pm\overline{3}m$)**

**Phase 2: monoclinic SrAl$_2$O$_4$ (S.G. $P2_1$)**

**SrFeO$_{3-\delta}$**$_{0.7}$**SrAl$_2$O$_4$**$_{0.3}$

1623 K, 5 hours

**Intensity (a.u.)**

20 30 40 50 60 70 80

20°, °
Characterization: shrinkage and thermal expansion

<table>
<thead>
<tr>
<th>Composition</th>
<th>T, K</th>
<th>$\alpha \times 10^6$, K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{SrFeO}<em>3_\delta)</em>{0.7}(\text{SrAl}_2\text{O}<em>4)</em>{0.3}$</td>
<td>350 – 950</td>
<td>12.6 ± 0.1</td>
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<tr>
<td></td>
<td>950 - 1310</td>
<td>24.1 ± 0.1</td>
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<tr>
<td>$\text{La}<em>{0.5}\text{Sr}</em>{0.5}\text{FeO}_3_\delta$</td>
<td>350 – 950</td>
<td>12.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>950 - 1310</td>
<td>23.7 ± 0.2</td>
</tr>
</tbody>
</table>
Experimental: fabrication route for asymmetric membranes

Powder with pore-forming additive:

- (SrFeO$_{3-\delta}$)$_{0.7}$(SrAl$_2$O$_4$)$_{0.3}$ powder
- La$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ powder

Pressing at 65-150 MPa

Sintering

Open porosity: 20-30 %

(mercury intrusion porosimetry)

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 \((\text{SrFeO}_{3-\delta})_{0.7}(\text{SrAl}_2\text{O}_4)_{0.3}\) composite membrane \((\text{SFSA-2})\)

Activation layer \((\text{AL})\): \((\text{SrFeO}_{3-\delta})_{0.7}(\text{SrAl}_2\text{O}_4)_{0.3}\) + Pt (50:50 wt. %)
**Oxygen permeation: limiting effect of surface oxygen exchange**

Modified with \((\text{SrFeO}_{3-\delta})_{0.7}(\text{SrAl}_2\text{O}_4)_{0.3} + \text{Pt (50:50 wt. %)})\)

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**

noticeable improvement in oxygen permeation fluxes at 1073-1173 K

*The activation agent is not effective enough.*
Oxygen permeation: impact of membrane architecture

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$_2$O$_4$)$_{0.3}$ + 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.
Self-supported (SrFeO$_{3-\delta}$)$_{0.7}$(SrAl$_2$O$_4$)$_{0.3}$ membranes exhibit a sufficiently stable performance; the degradation on either temperature cycling or during prolonged isothermal tests was found almost negligible.

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 \( (\text{SrFeO}_{3-\delta})_{0.7}(\text{SrAl}_2\text{O}_4)_{0.3} \) and \( \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \) 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.

- \( \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \) supported \( (\text{SrFeO}_{3-\delta})_{0.7}(\text{SrAl}_2\text{O}_4)_{0.3} \) 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 \( \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta} \) 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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