Properties of Dense Ceramic Membranes for Energy Conversion Processes

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5 academic partners, 2 industrial partners

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Joint Project MEM-Oxycoal
*Oxygen Permeable Ceramic Membranes for Coal-fired Power Plants*
10 academic partners

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*Gas Separation Membranes for Zero-Emission Power Plants*
13 partners

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Outline

Introduction – why dense ceramic membranes?

Types of membranes and membrane materials

BCFZ - Planar Membranes
  • Oxygen transport: experimental results
  • Modelling of bulk transport and surface exchange

BCFZ - Tubular Membranes
  • Oxygen transport: experimental results
  • Modelling of bulk transport and surface exchange

Conclusion
Dense vs. porous membranes

**Porous Membrane**
- Carbon membranes
- Polymer membranes
- \( T < 100^\circ C \)

**Dense MIEC membrane**
- Oxide membranes
- \( 700 < T < 1000^\circ C \)

Large flux and good selectivity!

\[ \text{BaFe}_{1-x-y}\text{Co}_x\text{Zr}_y\text{O}_{3-\delta} \]

Membrane permeation – pre-requisites for high fluxes

- large driving force
- high electronic partial conductivity
- high oxide ion partial conductivity
  \( \leftrightarrow \) **high oxygen vacancy concentration**

\[
J_b(O_2) = \frac{AT}{nL} \sigma^0_{ion} \left\{ \left( a'_g \right)^n - \left( a''_g \right)^n \right\}
\]

\[
\sigma^0_{ion} = z_{ion} F \cdot u_V \cdot c^0_V
\]

partial pressure \( p \rightarrow \) dimensionless chemical activities \( a \)
Membrane permeation – pre-requisites for high fluxes

- large driving force
- high electronic partial conductivity
- high oxide ion partial conductivity
  
  \[ \text{ <-> high oxygen vacancy concentration} \]

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J_b(O_2) = \frac{AT}{nL} \sigma^0_{ion} \left\{ (a'_g)^n - (a''_g)^n \right\}
\]

\[
\sigma^0_{ion} = z_{ion} F \cdot \gamma_V \cdot c^0_V
\]

partial pressure \( p \) \( \rightarrow \) dimensionless chemical activity \( a \)
Membrane permeation – pre-requisites for high fluxes

- larger driving force
- high electronic partial conductivity
- high oxide ion partial conductivity
  -> high oxygen vacancy concentration
- fast surface kinetics for reduction/incorporation, oxidation/release

high pressure side:

\[ J_s(O_2) = k_{\text{eff}}^0 \cdot \left\{ (a'_g)^m - (a'_s)^m \right\} \]

\[ \frac{1}{2}O_2 + V \rightleftharpoons O^{2-} + 2h^* \]

reduction/incorporation
Membrane permeation – pre-requisites for high fluxes

- large driving force
- high electronic partial conductivity
- high oxide ion partial conductivity
  \( \Leftrightarrow \) high oxygen vacancy concentration
- fast surface kinetics for
  reduction/incorporation, oxidation/release
- fast transport of gaseous oxygen
  to/from membrane surface
  \( \Rightarrow \text{large gas flow rates} \)
  particularly on the feed side

\[
\frac{1}{2} \text{O}_2 + V \rightleftharpoons \text{O}^{2-} + 2 h^*
\]

reduction/incorporation
Membrane materials

\[
\text{J(O}_2\text{)} / \text{m}^3 \text{m}^{-2} \text{h}^{-1} = 8 \times 10^5 \text{ J(O}_2\text{)} / \text{mol cm}^{-2} \text{s}^{-1}
\]

Deviation from stoichiometry

\[ \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \]

\[ \text{BaCo}_{1-x}\text{Fe}_x\text{Zr}_y\text{O}_{3-\delta} \]


oxygen vacancy fraction > 20%

depends on temperature and \( p(O_2) \)

McIntosh et al., Solid State Ionics (2006)
Ba(Co$_x$Fe$_y$Zr$_z$)O$_{3-\delta}$ - Oxygen Permeation

- feed flow rate: 300 ml/min, $p'_g = 0.21$ bar
- sweep flow rate: 40-250 ml/min, $p''_g$ variable

Defect and transport modelling yields
- oxide ion partial conductivity $\sigma^0_{ion}$
- surface exchange coefficient $k^0_{eff}$

assumption: no gas phase transport limitation
Variation of the membrane thickness $L$

- critical thickness $L_c$ may be calculated from ratio of $\sigma_{\text{ion}}$ and $k_{\text{eff}}$ \[ L_c \approx 0.004 \text{ cm (40 } \mu\text{m)} \]
- thick membrane: $L \gg L_c$
  \[ j(O_2) \propto L^{-1} \rightarrow \text{bulk transport limited permeation} \]
- thin membrane: $L \ll L_c$
  \[ j(O_2) \neq f(L) \rightarrow \text{surface exchange limited permeation} \]
Shaping of ceramic hollow fibers

Polymer solution → Oxide powder → Slurry → Spinneret → Green fiber → Sintering → Ceramic hollow fiber

Membranes prepared by: Fraunhofer Institut Grenzflächen und Bioverfahrenstechnik (Stuttgart, Germany)
$J(O_2)/J(O_2)_{ref}$

- 973 K (mea.)
- 1073 K (mea.)
- 1173 K (mea.)

Sweep gas flow rate cm$^3$/min

- without pores
- with pores

Ar

$\text{Air}$

$V_{s,i}$ $a_{s,i}$

$V_{f,i}$ $a_{f,i}$

$J_{b1,i}(O_2)$

$J_{b2,i}(O_2)$

additional gas/solid interfaces

$i$

$\text{bubble}_i$
Local oxygen activities along the tubular membrane
- co-current mode

\[ \dot{V}(\text{Ar}) = 100 \text{ cm}^3/\text{min} \]

![Diagram showing local oxygen activities along the tubular membrane for co-current mode.](image)
Local oxygen activities along the tubular membrane
- counter-current mode

\[ V(Ar) = 100 \text{ cm}^3/\text{min} \]

Oxygen activity

\[ a_s'(O_2), a_g'(O_2), a_g''(O_2), a_s''(O_2) \]
Comparison of co-current and counter-current mode

- 

\[ \frac{J(O_2)}{J(O_2)_{\text{ref}}} \]

Longitudinal position \( x / \text{cm} \)

Sweep gas flow rate \( \text{cm}^3/\text{min} \)

\( \dot{V}(\text{Ar}) / \text{cm}^3 \text{ min}^{-1} \)

- 100
- 200
- 400

\( \dot{V}(\text{Ar}) / \text{cm}^3 \text{ min}^{-1} \)

co-current

- 1073K (co)
- 1073K (counter)
- 1123K (co)
- 1123K (counter)
- 1173K (co)
- 1173K (counter)
Conclusions

- Oxygen transport through thick planar and thin hollow fiber membranes of $\text{Ba(Co}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}}$ was investigated by permeation experiments.

- The oxygen permeation fluxes of planar membranes were sucessfully modelled by a **defect and transport model**.

- The modelling results indicate that:
  - in **thicker planar membranes**, oxygen transport is **predominantly bulk limited**.
  - in **thin tubular membranes**, oxygen transport is **substantially limited by the surface reactions**.

- **Microstructure (e.g. pores) affects the permeation flux**
  Sluggish internal interfaces diminish the flux

- **Tubular membrane in counter-current mode yields slightly higher permeation fluxes** when compared to co-current mode.
End