Ceramic Membranes for Oxyfuel Power Plants

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IEF-1: Materials Synthesis and Processing
Outline

1. Introduction

2. Sample preparation of asymmetric structures

3. Permeation experiments

4. Conclusion and outlook
1 Introduction

- Development of a $O_2/N_2$-separation membrane for application in Oxyfuel power plants.

- Different conditions for the membrane are possible that require different materials (vacuum, CO$_2$-sweep, etc.).

- $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is a highly oxygen permeable mixed ionic and electronic conductor (MIEC).

- BSCF can be a suitable material for conditions without flue gas contact of the membrane - e.g. vacuum (CO$_2$ $\rightarrow$ Carbonates, SO$_2$ $\rightarrow$ Sulfates).

- Satisfying the demanded permeation rate of at least $j=3$ ml/(min·cm$^2$) a decrease of the layer thickness is favorable.
1 Introduction

- Diffusion controlled transport according to Wagner-Equation

\[ j = -K \frac{T}{L} \int_{\ln \rho_i}^{\ln \rho_n} \frac{\sigma_i \sigma_e}{\sigma_i + \sigma_e} \ d \ln P_{O_2} \]

- Below a characteristic thickness \( L_c \) the Wagner-Equation does not apply any more.

→ **Surface kinetics** take control of the permeation rate.

- Thin membrane layers (<100 µm) need to be mechanically supported.

- Differences in TEC and shrinkage behavior can lead to cracked structures
1 Introduction

- Not matching expansion behavior due to chemical expansion of BSCF
- Chemical compatibility has to be provided

\[ \text{first approach: same support material BSCF} \]
2 Sample preparation

Porous support via Tape Casting

Slurry preparation
- BSCF ($d_{50}=1.7 \, \mu m$)
- 20 wt-% rice starch (2-8 µm) as pore forming material
- solvent, dispersing agent, binder and plasticizers
  are homogeneously mixed and degassed

Tape casting
- $h$ (doctor blade) = 1.9 mm
- $h$ (tape green state) $\approx$ 1 mm
- Casting speed = 200 mm/min
2 Sample preparation

Porous support
Tape casting facilities

- small tapes (width around 14 cm)
- large tapes (width up to 50 cm)

Slow debinding of organic matter (24 h)
Presintering step at 900°C/3h with a shrinkage of 13%
2 Sample preparation

Porous support
Permeability \( (D_s = 1 \cdot 10^{-10} \text{ cm}^2 \) according to DIN 51058)
Average pore size = 1,1 µm (Hg-porosimetry)
Porosity of 23 Vol-% (optical analysis)

Average pore size = 1,1 µm (Hg-porosimetry)

Permeability measurement

SEM picture

Graph: Porosity [%] vs. Pore size [µm]

Porosity [%] vs. Relative volume [%]

Average pore size (APS) 1,1 µm
2 Sample preparation

Dense layer via Screen Printing

BSCF-powder is mixed with ethyl cellulose binder, dispersing agent and terpineol as transport media.

Homogenization with 3 roller mill and characterization of pastes.

Multiple printing with wet layer thickness of 95 µm per step.
2 Sample preparation

Asymmetric membrane
Sintering at 1100°C/5h with subsequent characterization

Layer thickness: 120 µm

Substrate thickness: 860 µm

Machined to Ø15mm by cylindrical grinding

He-Leak rate: 7·10⁻⁹ mbar·l /cm²·s
3 Permeation measurement

Setup and parameters

- Feed: Air-O$_2$-mixture
  \[ F = 250 \text{ ml/min} \]
- Sweep: Argon
  \[ F = 50-300 \text{ ml/min} \]
- Quartz glass recipient
- Membrane: Ø 15 mm
- Dense layer on feed side
- Sealing with gold rings
- Temperature controlled by thermocouple
- Permeate concentration measured by mass spectrometry
3 Permeation measurement

Temperature

Decrease in thickness leads to higher permeation

Bulk: \( j = 1,53 \text{ ml/min} \cdot \text{cm}^2 \)

Asymm.: \( j = 1,94 \text{ ml/min} \cdot \text{cm}^2 \) \((T=900°C)\)

According to Wagner:

\[
\frac{L(\text{bulk})}{L(\text{asymm.})} = \frac{1000 \mu\text{m}}{120 \mu\text{m}} = 8,3
\]

Feed (Air): \( F=250 \text{ Nml/min} \)
Sweep (Ar): \( F=50 \text{ Nml/min} \)

Dense layer on feed side
3 Permeation measurement

Sweep flow rate

Feed (Air): 250Nml/min
Variation of $F(\text{Ar})$

**Low driving force:**
$F(\text{Ar})=50$ Nml/min
$P_i^*=0.041$ atm
$j(O_2)=1.74$ ml/min·cm$^2$

**High driving force:**
$F(\text{Ar})=2000$ Nml/min
$P_i^*=0.002$ atm
$j(O_2)=3.21$ ml/min·cm$^2$

+ 85%
3 Permeation measurement

Partial pressure gradient

$F(\text{Air/O}_2) = 250 \text{ Nml/min}$

$F(\text{Ar}) = 50-300 \text{ Nml/min}$

$$j \propto \frac{1}{L} \cdot \ln \left( \frac{p_h}{p_l} \right)$$

different permeation rates for same ratio of partial pressures

$\rightarrow$ absolute values of partial pressures have influence
3 Permeation measurement

Partial pressure gradient

Permeation rate $[\text{ml/min} \cdot \text{cm}^2]$

- Asymm
- Bulk

Feed 84% O$_2$
Feed 20% O$_2$

$F(\text{Air/O}_2)=250 \text{ Nml/min}$
$F(\text{Ar})=50-300 \text{ Nml/min}$

Difference more evident for asymmetric structures

Oxygen partial pressure ($p$) at the surface not detectable

$\rightarrow$ measurement of the oxygen partial pressure in the permeate gas stream ($p^*$)
3 Permeation measurement

Partial pressure gradient

Substrate changes oxygen partial pressure

$F(Air/O_2) = 250 \text{ Nml/min}$

$F(Ar) = 50-300 \text{ Nml/min}$

Difference more evident for asymmetric structures

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3 Permeation measurement

Partial pressure gradient

\[ F(\text{Air/O}_2) = 250 \text{ Nml/min} \]
\[ F(\text{Ar}) = 50-300 \text{ Nml/min} \]

Difference more evident for asymmetric structures

Oxygen partial pressure \((p)\) at the surface not detectable

\(\rightarrow\) measurement of the oxygen partial pressure in the permeate gas stream \((p^*)\)
Gas tight asymmetric membrane structures of BSCF can be prepared via tape casting and screen printing. Increase in permeation rates but no Wagner relation.

4 Conclusion and outlook
4 Conclusion and outlook

For high flux membrane structures the dependencies need to be clarified and quantified.
Thank you for your attention....

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