Perovskite capillaries for high temperature oxygen separation

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What can you expect?

» Introduction
  » CO₂ capture in fossil fuel power plants
  » Mixed ionic-electronic conducting (MIEC) perovskite membranes
  » Capillaries using phase-inversion spinning technique

» Development and performance of Ba₀.₃Sr₀.₃Co₀.₈Fe₀.₂O₃₋₅ (BSCF) capillaries
  » Challenges
    » Avoid macrovoids
    » Overcome sulfur contamination effect

» Conclusions
**CO₂ capture in fossil fuel power plants**

(A) Post combustion

- Fossil fuel
- (90%N₂/10%CO₂)
- CO₂ + ev. N₂

- Energy production
- N₂/CO₂ separation

(B) Oxyfuel

- Fossil fuel
- N₂/CO₂ separation
- Energy production
- CO₂ + H₂O
- Condensing

(C) Pre combustion (methane, gasified coal)

- Fossil fuel
- N₂/CO₂ separation
- Partial oxidation
- CO₂ shift (N₂)
- H₂O
- Energy production
- (N₂), H₂O
- Condensing
- CO₂ + H₂O

**Mixed ionic-electronic conducting (MIEC) perovskite membranes**

- 100% oxygen selectivity provided no cracks or connected-through porosity
- Simultaneous transport of oxygen ions and electrons
- ΔpO₂ + high temperature (>700°C)
- No electrodes or external electrical loadings
- Allow integration in high temperature combustion processes
- N₂/O₂ separation: Ba₀.₅Sr₀.₅Co₀.₄FeₓO₃₋ₓ (BSCF)

**Permeate side**

- High pO₂ (air)
- 2 O₂⁻ = O₂ + 4 e⁻

**Feed side**

- Low pO₂ (vacuum, sweep gas)
- 2 O₂⁻ = O₂ + 4 e⁻
Transport mechanism: cubic doped $\text{ABO}_3$ structure

![Diagram of cubic doped $\text{ABO}_3$ structure]

Why capillaries/hollow fibers?

<table>
<thead>
<tr>
<th>Membrane geometry</th>
<th>Surface/volume ratio</th>
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<tbody>
<tr>
<td>Flat (plate &amp; frame)</td>
<td>100-400 m$^2$/m$^3$</td>
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<tr>
<td>Tubular (d &gt; 10 mm)</td>
<td>360 m$^2$/m$^3$ (r = 5 mm)</td>
</tr>
<tr>
<td>Capillaries (0.5 &lt; d &lt; 10 mm)</td>
<td>3600 m$^2$/m$^3$ (r = 0.5 mm)</td>
</tr>
<tr>
<td>Hollow fibers (d &lt; 0.5 mm)</td>
<td>36000 m$^2$/m$^3$ (r = 0.05 mm)</td>
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→ Especially interesting for large-scale gas separation applications
Phase-inversion

- Preparation of polymer membranes (flat, capillary, hollow fiber)
- Exchange of solvent and nonsolvent for polymer
- ‘liquid-liquid’ demixing into polymer-rich and polymer-poor phase
- Polymer-rich phase → solid membrane structure
- Polymer-poor phase → membrane pores

- Phase-inversion spinning technique:
  - Tunable diameter, wall thickness, length
  - Flexible green products → complex structures (U-forms)

Fabrication Process

- Suspension
  - Polymer
  - Solvent
  - Ceramic powder
- Spinning
  - Suspension
  - Pump
- Calcination and sintering

Synthesis parameters:
- Suspension rheology
- Choice of coagulation bath
- Choice of bore liquid
- Flow rate suspension
- Flow rate bore liquid
- Height of air gap
Challenge 1: avoid macrovoids

We like to avoid macrovoids:
» Large pores up to 100 μm
» No densification during sintering
» No control over size and location of appearance
» Weak spots
» Affecting stability of dense top layer
» Affecting overall mechanical strength

Proper choice of:
» Polymer/solvent/nonsolvent system
» Rheology spinning suspension

Role of rheology in formation of macrovoids

Polysulphone based membranes

\[ d_{50} = 0.7 \text{ μm} \]
85 % < 1μm

\[ d_{50} = 3 \text{ μm} \]
20 % < 1 μm

\[ d_{50} = 2 \text{ μm} \]
30 % < 1 μm
Sintered BSCF capillaries

Cross sections

Outer surface

Inner surface

XRD of sintered BSCF capillaries

Phase impurities

- ▼ BaSO₄ (7%)
- ○ Fe₃O₄ or Co₃O₄ (7%)

• Due to the use of polysulfone
• Influence on oxygen flux?
**EDS mapping of outer surface S-containing BSCF capillary: visualizing impurities**

**Setup for oxygen permeation measurement of capillaries: principal scheme**

Oxygen sensor EMF (Nernst eq.):

\[ E = \frac{RT}{4F} \ln \left( \frac{0.21 \times P}{p(O_2)_{atm}} \right) \]

\[ j(O_2) = \frac{V}{RT \cdot S} \left( p(O_2)_{atm} - p(O_2)_i \right) \left( 1 - \frac{p(O_2)_i}{P} \right) \]

- \( j(O_2) \) – oxygen permeation flux;
- \( V \) – total gas flow rate;
- \( T_s \) – flow meter temperature;
- \( S \) – membrane surface area;
- \( p(O_2)_i \) – inlet oxygen partial pressure;
- \( p(O_2)_{atm} \) – outlet oxygen partial pressure;
- \( P \) – total pressure.
Decomposed (S-containing) BSCF capillaries: dependence of oxygen flux on sweep gas flow rate

- Literature data for gastight, pure BSCF disk membranes (~ 400 μm thickness) at sweep flow rate of 100 Nml/min:
  - 3.4 Nml/cm²/min (800°C) → factor 8 lower
  - 5.1 Nml/cm²/min (900°C) → factor 4 lower

- Activation energy: ±110 → 142 kJ/mol
- Limitation flux by surface exchange kinetics?

-Z. Chen et al., Ceramics International-35 (2009) 2455
Challenge 2: how to counteract influence of sulfur contamination?

- Catalytic activation of membrane surfaces
  - Suitable catalyst: PrO$_x$
  - S-contamination remains

- Preparation of phase-pure BSCF capillaries
  - No S-contamination
  - New phase inversion system
  - Further performance improvement using catalysts?

Catalytic activation of membrane surfaces using PrO$_x$

- Immersion in Pr(NO$_3$)$_3$ solution
- Porous, mechanically stable layer of ~ 4µm thickness
- Surface density ~ 1.1 mg/cm$^2$
- Pr-containing perovskite layer, no Pr-intrusion
Production of S-free BSCF capillaries (1)

- New phase-inversion system
  - Rheological study → no macrovoids!
    - Polymer solution
    - Ceramic suspension
- Key parameters polymer solution
  - Water content
  - Polymer concentration
  - Molecular weight polymer
- Key parameters ceramic suspension
  - Powder morphology
  - Ratio powder/binder

Production of S-free BSCF capillaries (2)

- Pure BSCF structure (minor Co$_3$O$_4$ impurity)
- Macvoid-free
- High density
- Gastight

- Phase diagram showing the regions of 1-phase and 2-phase
- X-ray diffraction pattern showing pure BCSF perovskite phase after calcination of S-free binder and sintering

- Density (%) vs. dwell time at 1100°C
SEM images S-free BSCF capillaries

Oxygen permeation results for capillaries with $D_o = 3.6$ mm and $D_i = 2.8$ mm (1)

- Activated S-containing BSCF capillaries:
  - Noticeable surface activation effect $\rightarrow$ confirmation strong oxygen flux limitation by surface exchange kinetics

- Superior performance S-free BSCF capillaries
**Oxygen permeation results for capillaries with** $D_0 = 3.6 \text{ mm}$ and $D_i = 2.8 \text{ mm}$ (2)

- Activated S-containing and S-free BSCF capillaries show lower activation energy due to improved surface exchange rates $\rightarrow$ increase in bulk diffusion contribution
- $T \geq 850^\circ \text{C}$:
  - Decrease in activation energy, indicating increase in bulk diffusion contribution
  - Reduced effect of the improved performance of activated S-containing and S-free BSCF capillaries

**Conclusions**

- S-containing BSCF capillaries show lower oxygen permeation fluxes compared to literature
  - Significant amount of BaSO$_4$

- Catalytic activation of membrane surfaces
  - Significant increase in oxygen permeation
  - Confirmation severe limitation by surface exchange reactions

- Sulfur-free BSCF capillaries
  - Superior performance
  - Oxygen flux mainly governed by bulk diffusion limitation
    - Confirmation first tests with PrOx activation
  - Increase oxygen flux $\rightarrow$ lower membrane thickness
Acknowledgements

» Raymond Kemps
» Myriam Mertens
» Bart Molenberghs
» Wim Doyen
» Herman Beckers