Outline – Ionic Conducting Cells – From Laboratory Scale to Market

- Potential applications of mixed ionic electronic conductors
- Development strategies and microstructures
- From membrane button cell to industrial relevant size – manufacturing challenges
- Planar module designs
- Cost evaluation – examples OTM for carbon capture in a oxyfuel cement plant and SOFC

- This lecture shows concepts and is not focused on a single material
Applications of Mixed Ionic Electronic Conductors

Gas Supply
Power Plants, Cement Industry (GREEN-CC), Glass Industry, Steel Industry, Medical, etc.

Membrane Reactors
Syngas-Production, Methanation, Dehydration, Water Gas Shift Reaction, etc.

Separation of single gases e.g. O₂, H₂, CO₂

CO₂ + 4 H₂ → 2 H₂O + CH₄

CO₂ Utilisation
Commodity Chemicals / Chemical Energy Carriers
Environmental Applications

Methane Synthesis
Potential Applications of Membranes in Catalytic Membrane Reactors (CMR)

CO$_2$-Utilisation, Chemical Energy Carriers, Environmental Applications

![Diagram of potential applications of membranes in CMR](image)

W. Deibert, M. E. Ivanova, S. Baumann, O. Guillon, W. A. Meulenberg
Journal of Membrane Science (2017)
Potential Applications of Membranes in Catalytic Membrane Reactors (CMR)

CO₂-Utilisation, Chemical Energy Carriers, Environmental Applications

W. Deibert, M. E. Ivanova, S. Baumann, O. Guillon, W. A. Meulenberg
Journal of Membrane Science (2017)
Exemplary Catalytic Membrane Reactors

Catalytic Partial Oxidation of Methane
Production of Syngas
Reaction: \( \text{CH}_4 + 0.5 \text{ O}_2 \rightarrow \text{CO} + 2 \text{ H}_2 \)

\( T = 900 \, ^\circ \text{C} \), catalyst: Ni

Water-Gas Shift Reactor
Separation of Pure Hydrogen
Reaction: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)

\( T = 550-900 \, ^\circ \text{C} \)
Ceramic Gas Separation Membranes

Microporous Membranes

Dense Mixed Ion-Electron Conducting Membranes

SiO₂ Top layer

T ≈ 200°C

T = 400-900°C
Development Strategy and Challenges

Materials Development

- high ionic / electronic conductivity
- stability in aggressive environment
- thermal stability
- compatibility
- low cost material
- availability of materials

Microstructuring

- thin films for high performance
- porous catalytic layers
- low polarisation in support
- no deformation of membrane
- no delamination of single layers
- thermomechanical stability

Component Manufacturing

- adjustment of sintering steps
- module design and sealing
- no deformation of membrane
- thermomechanical stability
- fast, scalable and low cost processing technologies
Manufacturing Steps

e.g. Sequential tape casting and screen printing

- Tape cast support (slurry containing pore former)
  - Pre-sintering of support
  - Screen printing on support
  - Co-sintering

- Tape cast membrane layer (slurry without pore former)
  - Tape cast support (slurry containing pore former)
  - Co-sintering

Tape casting + screen printing

Sequential tape casting
Similar Membrane Microstructure

....with different materials

• Tape cast membranes with thicknesses between 15 and 30 µm

• Comparable porosity

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness Membrane (µm)</th>
<th>Porosity Membrane (%)</th>
<th>Porosity Support (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STF30</td>
<td>14</td>
<td>&lt; 5</td>
<td>38</td>
</tr>
<tr>
<td>STF50</td>
<td>20</td>
<td>&lt; 1</td>
<td>25</td>
</tr>
<tr>
<td>STF70</td>
<td>22</td>
<td>&lt; 1</td>
<td>27</td>
</tr>
<tr>
<td>BSCF</td>
<td>25</td>
<td>&lt; 5</td>
<td>26</td>
</tr>
<tr>
<td>LSCF</td>
<td>30</td>
<td>&lt; 1</td>
<td>30</td>
</tr>
</tbody>
</table>

[Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$]

[Ba$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$]
Similar Membrane Microstructure

….with different materials

- At high temperature flux nearly independent from material
- Polarisation effect in support

Polarisation depends on:

- Thickness
- Open porosity
- Pore diameter and shape
- Tortuosity
- Gas species
Modelling: Understanding the Limitations

**Effect of tortuosity**
- Large effect of substrate thickness
- Straighter pores significantly better

**Effect of pore shape**
- CFD / Fluent μCT data phase inversion tape casting
- U-shaped pores enhance flow velocity

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**Flux relative to thin bulk membrane**

- Large effect of substrate thickness
- Small pores limit transport

**Support on feed side permeate side**

**Source:** Unoako Unije and Robert Mücke

**DTU support**

Co-Sintering of Membrane and Support

Temperature above 1450°C is required for full densification of thin membrane

Curvature rate proportional to the difference in free sintering rates

Modelling of sintering behaviour possible

Video made by Kwati Leonhard in Jülich

O. Guillon et al. Woodhead Pub. 2010
Manufacturing of Asymmetric Membranes
Successful Materials Combinations

La$_{6-x}$WO$_{12-\delta}$ (LWO)

BaZr$_{0.8}$Y$_{0.15}$Mn$_{0.05}$O$_{3-\delta}$

Scale-Up of Membrane Components

Evaporation of residual solvents and melting of plasticisers and binder

Pyrolysis of organic components
- Plasticisers
- Binder
- Starch (pore former)

Scale-Up of Membrane Components

Evaporation of residual solvents and melting of plasticizers and binder

Pyrolysis of organic components
  - Plasticisers
  - Binder
  - Starch (pore former)

Next step:

Simulation-Supported Module Design
GREEN-CC Project (Coordination: W. A. Meulenberg)

Key issues/activities
- Mechanical stress analysis
- Homogeneous gas flow
- Joining techniques for ceramic-metal materials

CFD modelling shows homogeneous velocity distribution of air flow

Membrane element
Development of Membrane Components

Lamination of single tapes

La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$

- Tape casting
- Tape casting/cutting or milling
- Tape casting

Assembling of OTM Module:
Dec. 2017, Area: 420 cm$^2$

Size: 4 x 7 cm$^2$

Size: 7 x 10 cm$^2$
Cost estimation of the prototype membrane

<table>
<thead>
<tr>
<th>Batch / Amount [kg]</th>
<th>Price [€/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 - 50</td>
<td>430</td>
</tr>
<tr>
<td>51 - 100</td>
<td>390</td>
</tr>
<tr>
<td>101 - 500</td>
<td>290</td>
</tr>
<tr>
<td>501 – 1.000</td>
<td>260</td>
</tr>
<tr>
<td>1.001 – 10.000</td>
<td>210</td>
</tr>
<tr>
<td>10.001 – 50.000</td>
<td>150 - 180</td>
</tr>
<tr>
<td>50.001 – 100.000</td>
<td>100 - 130</td>
</tr>
</tbody>
</table>

Powder Price of LSCF in dependence of amount of delivery

Source Solvay Flour
Cost estimation of the prototype membrane

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)
- membrane material costs: ceramic material cost is 700 €/m²
- membrane-manufacturing costs: 4200 €/m²
- costs for the housing and sealing: 11500 €/m²

- total membrane module costs: 16400 €/m²
- drastically decrease is expected for a commercial module design

large potential for cost reduction

Calculated by Sonja Paul, AVT RWTH Aachen
Cost estimation of the prototype module

- Ceramic material Costs: 4%
- Work time for housing: 24%
- Membrane manufacturing: 26%
- Braze: 9%
- Metal costs for housing: 37%

Costs:
- 328 €/component
- 16400 €/m²

Calculated by Sonja Paul, AVT RWTH Aachen
## Cost estimation of the prototype membrane

### Oxyfuel Power Plant

<table>
<thead>
<tr>
<th>Product costs:</th>
<th></th>
<th>Cement Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTM (without membrane)</td>
<td>9.87 c€/kWh\text{el}</td>
<td>7.41 €/t</td>
</tr>
<tr>
<td>Cryogenic ASU</td>
<td>11.85 c€/kWh\text{el}</td>
<td>11.29 €/t</td>
</tr>
<tr>
<td>Plant Capacity</td>
<td>623.4 MW\text{gross (OTM)}</td>
<td>3,000 t/d</td>
</tr>
</tbody>
</table>

| Oxygen demand | 99 kg/s | 8,8 kg/s |
| Average oxygen flux | 0.9 Nml/min cm² | 0.9 Nml/min cm² |
| Membrane area (for LSCF) | ~500,000 m² | ~44,000 m² |

<table>
<thead>
<tr>
<th>Membrane lifetime:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>35 years</td>
<td>1050 € per m²</td>
<td>3367 €/m²</td>
</tr>
<tr>
<td>4 years</td>
<td>120 € per m²</td>
<td>385 €/m²</td>
</tr>
</tbody>
</table>

### Power plants should be a long-term application

Since the cement industry is price sensitive these supplementary costs have to be forced by governmental regulation.

*Calculated by Sonja Paul, AVT RWTH Aachen*
Cost reduction potential

Material:
- Using cheap support materials (ZrO$_2$, MgO, etc.....)

Membrane unit:
- Reduction of manufacturing steps or using of other routes (e.g. extrusion, 3D-Printing)
- Using of advanced sintering methods, e.g. FAST

Housing:
- Using of cheaper steels or ceramics - MIEC membrane does not require conductive housing material
- Using of cheap sealants

Overall:
- Long life means low cost / Lifetime more important than performance /
- Continuous operation must be guaranteed
Stack components Jülich design

Drawings: Martin Bram

supplied by Norbert Menzler and Siri Harboe
Two different Jülich stack designs

1: Stationary design ($T_{\text{op.}} \approx 700^\circ \text{C}$) : $P_e/A = 0.37 \text{ W/cm}^2$
   - Alloy Crofer22APU, thicker plates
   - Machined by milling & creep feed grinding

2: Light-weight design ($T_{\text{op.}} \approx 770^\circ \text{C}$) : $P_e/A = 0.25 \text{ W/cm}^2$
   - Alloy Crofer22H thinner sheets
   - Hydroforming

supplied by Norbert Menzler and Siri Harboe

SOFC manufacturing cost model

SOFC stacks scale-dependent processing-lines evaluated

\[ \Sigma = \text{Direct costs} \]

- **Material costs**
  - net demands, scraps, price

- **Machine costs**
  - machine cycle time, CAPEX depreciation, maintenance

- **Labor costs**
  - duration of manufacturing, labor rate

- **Energy cost**
  - duration of machines in use, energy demand and price

- Costs of SOFCs manufacturing
- Costs: Pros & cons of stack designs
- Costs reduction R&D aspects

supplied by Norbert Menzler and Siri Harboe

Scale-up possibilities - example Solid Oxide Cells

JuCast 3-500: Sequential tape caster with three casting heads

N.H. Menzler et al. Fuel Cells 14/1 (2014), 96-106
Differences MIEC Membrane - SOFC

Membrane unit and materials:
- Only membrane layer and support required, sometimes also active surface layer
- No requirements regarding electrical conductivity for support, cheap ceramics can be used
- Reaction catalyst required

Housing and interconnect/gas separators:
- Using of cheaper steels or ceramics possible compared to SOFC
  MIEC membrane does not require conductive interconnect material
- Using of different sealants including metals are possible

Operation:
- Pressure controlled instead of power controlled (higher pressure and reaction harder to control)
- Often more aggressive environment
- No electricity required
Thank you for your attention