Oxygen Transport Membranes BIGCO2 Achievements

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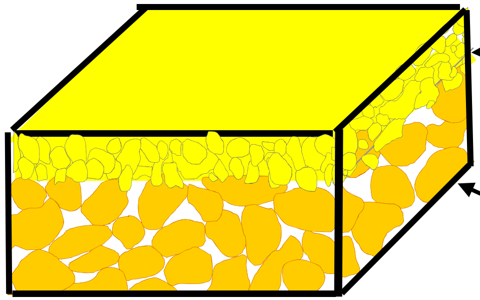
Outline

- Introduction
  - Air separation with OTM
  - Applications and integration concepts
- BIGCO2 Task A achievements
  - Membrane fabrication
  - Sealing technology
  - Membrane testing
  - Material development
- Summary

Air separation
Oxygen transport membranes (OTM)

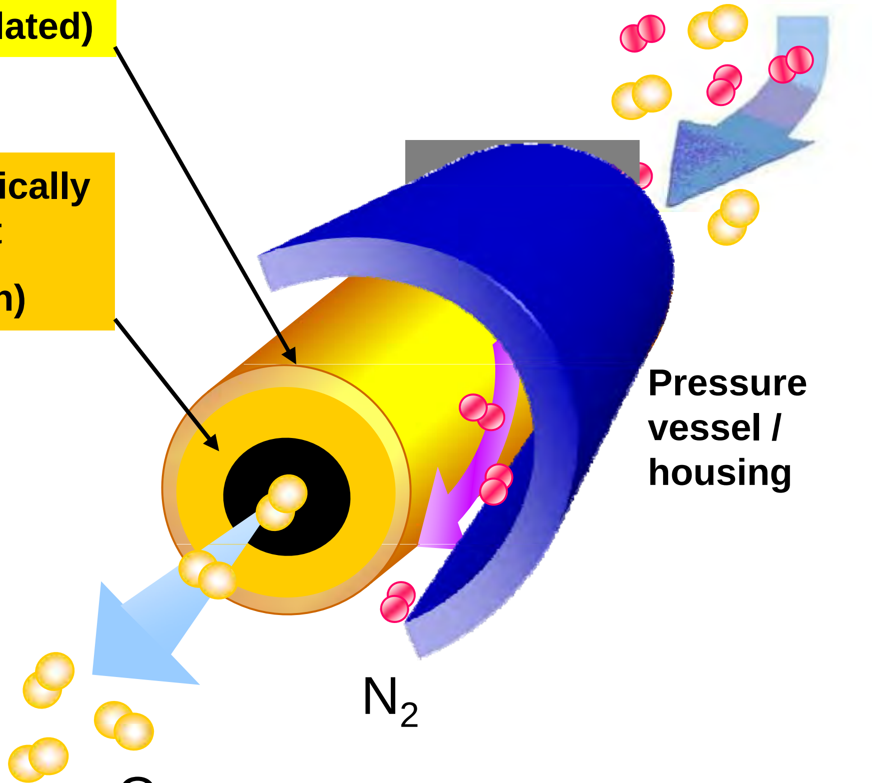


Dense layer

(perovskite related)

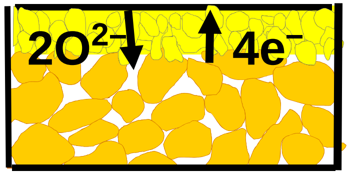
Macroporous mechanically strong support

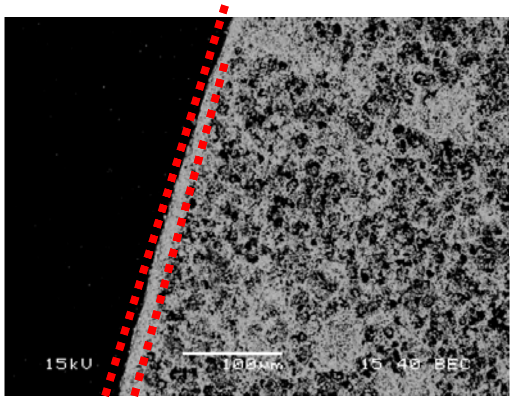
(same composition)



Driving force

Feed side:
High p(O_2)

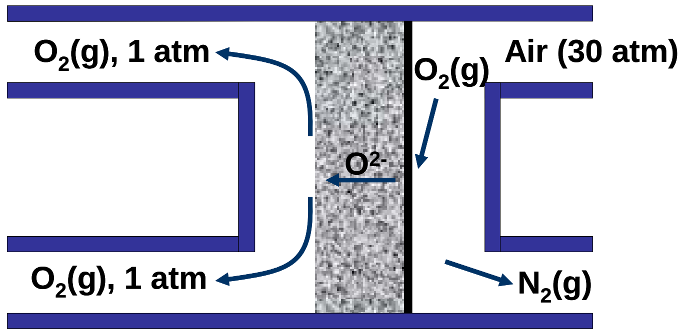




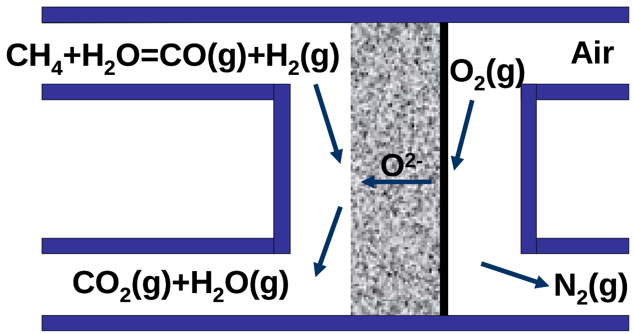
Permeate side:
Low p(O_2)

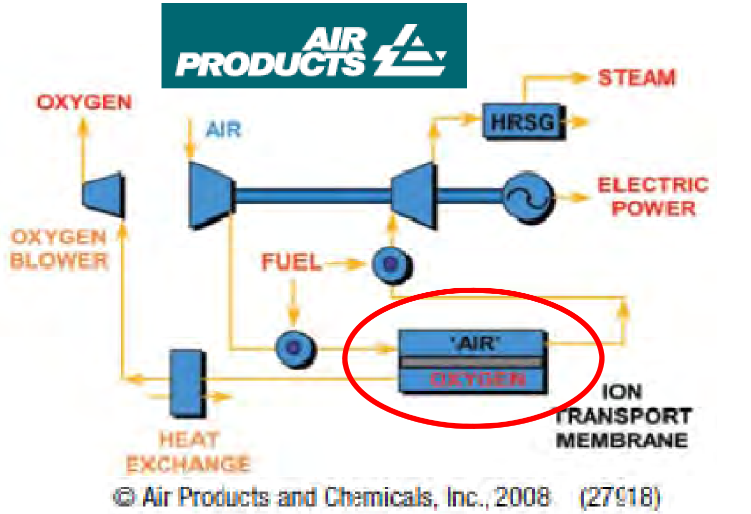
Applications and integration concepts

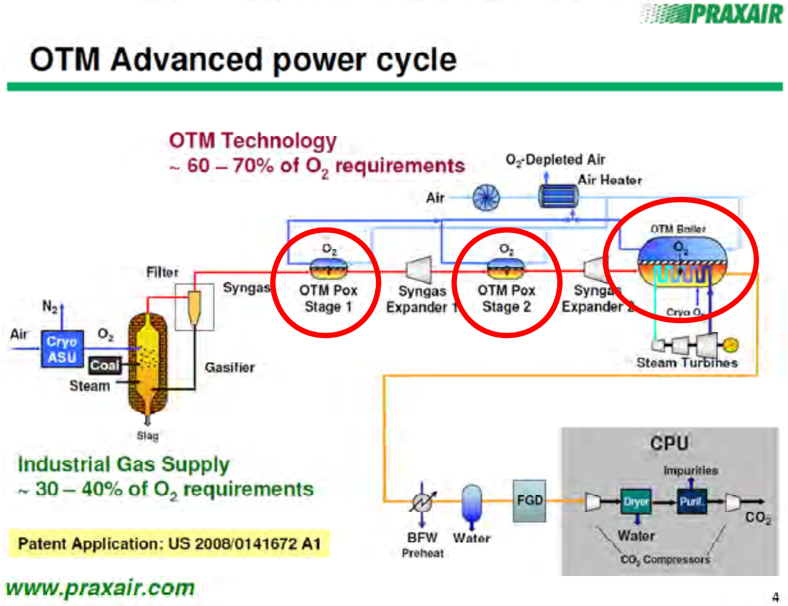
- Oxygen production, i.e. for oxy-fuel processes



- Syn-gas production
- Catalytic membrane reactor







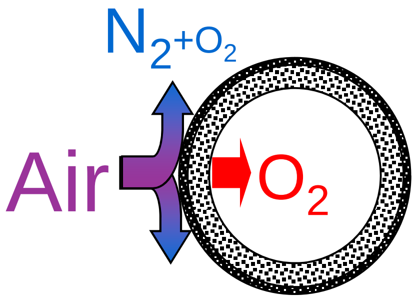
BIGCO2 Task A
High temperature membranes

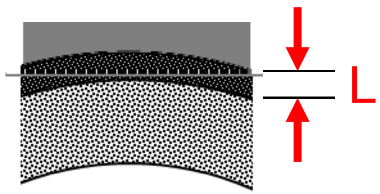
- Overall objectives (2007-2011)
  - Establish and develop fabrication and sealing technology for ceramic high temperature membranes
  - Use the technology for fabrication of membrane modules for oxygen and/or hydrogen separation

- Main activities
  - Membrane fabrication
  - Sealing technology
  - Testing and characterization
    - Including material development

BIGCO2 Task A – Achievements

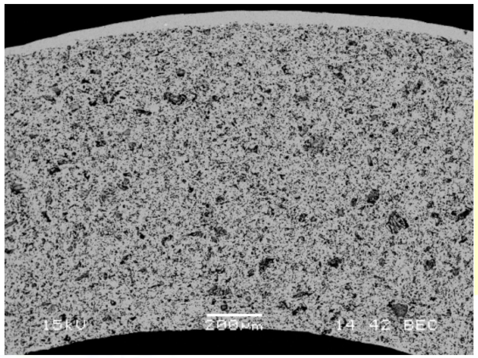
- Fabrication of asymmetric tubular membranes





$$J_{O_2} = -\frac{RT}{16F^2 L}\int_{\ln p^{I}_{O_2}}^{\ln p^{II}_{O_2}} \frac{\sigma_{el}\sigma_{ion}}{\sigma_{el}+\sigma_{ion}}\,\partial \ln p_{O_2}$$

- Tubular membranes
  - o Extrusion of porous support
  - o Coating of thin dense membrane layer



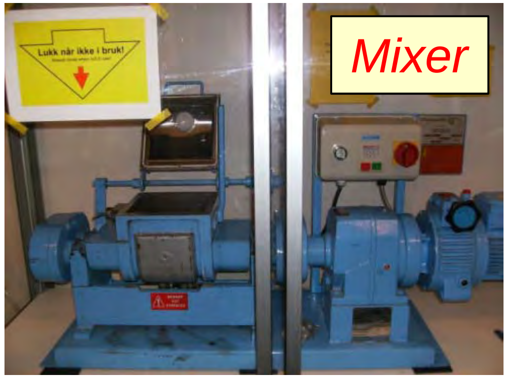
Dense membrane layer coated onto porous support

Extruded tubular support

BIGCO2 Task A – Achievements

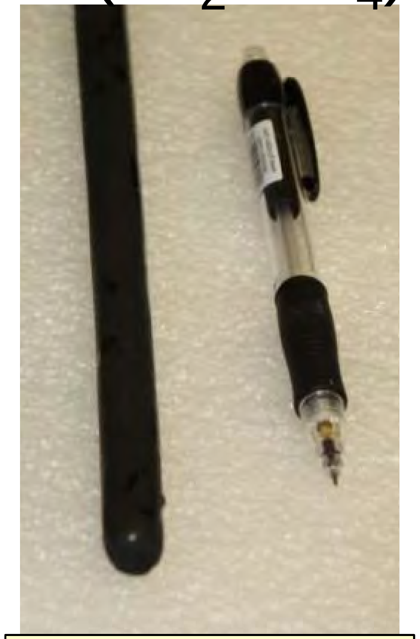
- Paste formulation and ceramic extrusion (La_2NiO_4)

Mixer



Piston extruder

As extruded tubular supports



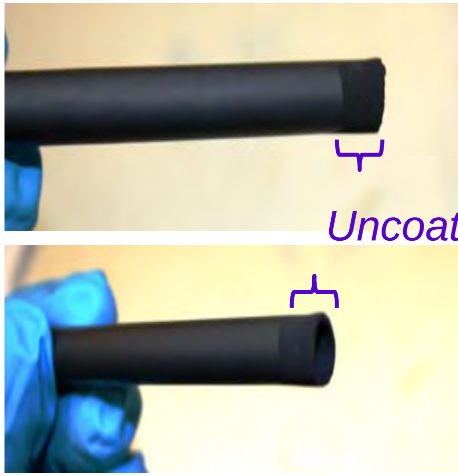
Tubular supports with close ends

BIGCO2 Task A – Achievements

- Slurry preparation and coating of dense membrane layers (La_2NiO_4)

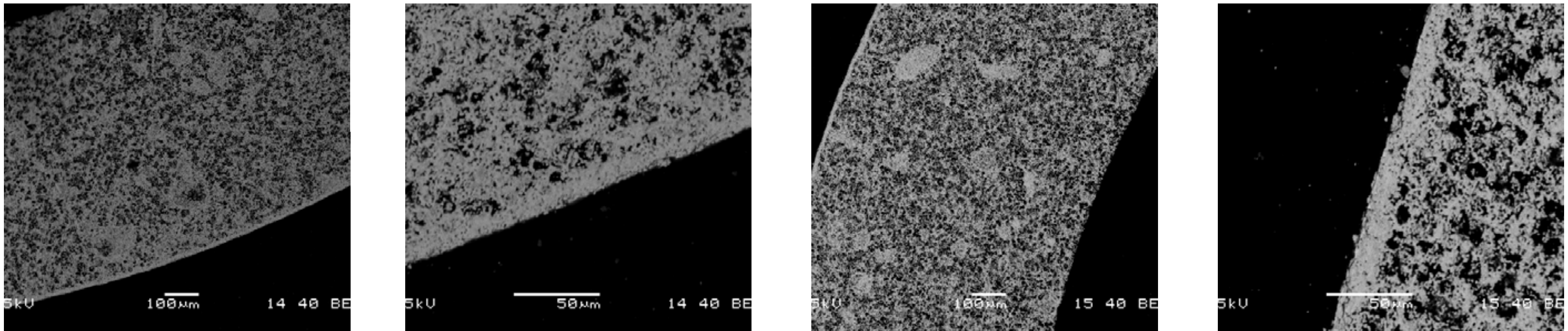
Stability of various dispersions investigated

Coated supports



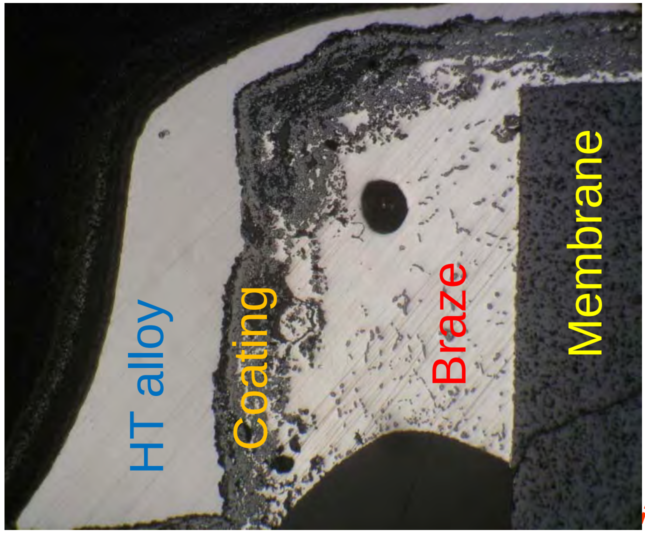
Uncoated areas

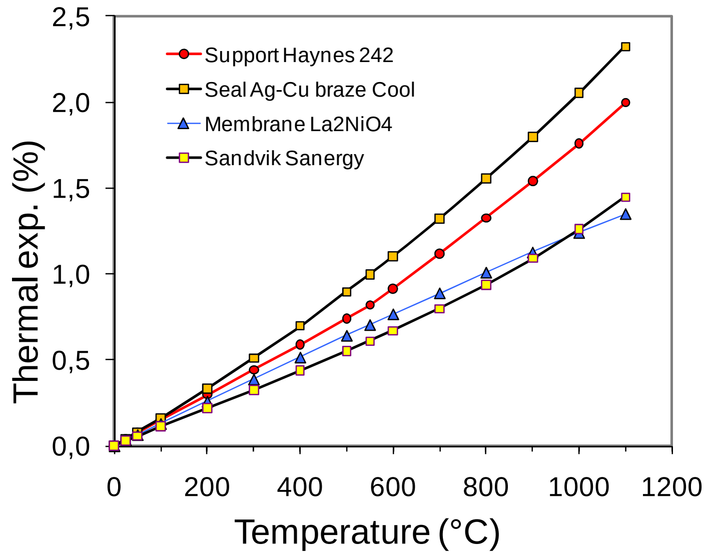
SEM micrographs (cross-section) of selected asymmetric membranes



BIGCO2 Task A – Achievements

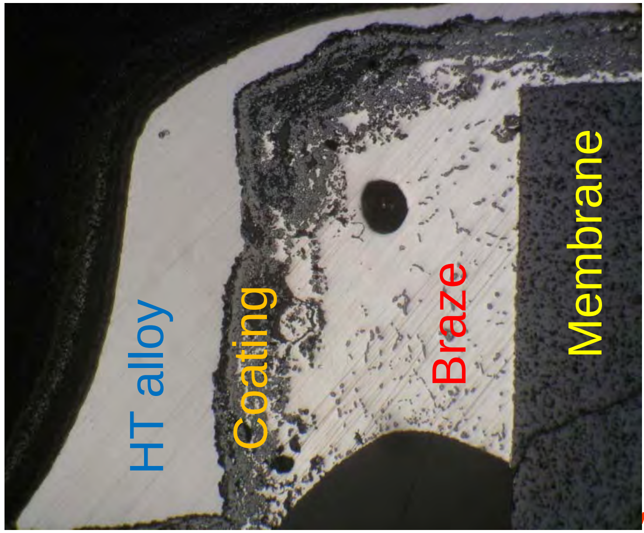
- Sealing development – air braze
  - Thermo-chemicall˛ com˛ atible with membrane material
  - Matching thermal expansion behaviour of braze, membrane/ housing material (HT alloy)

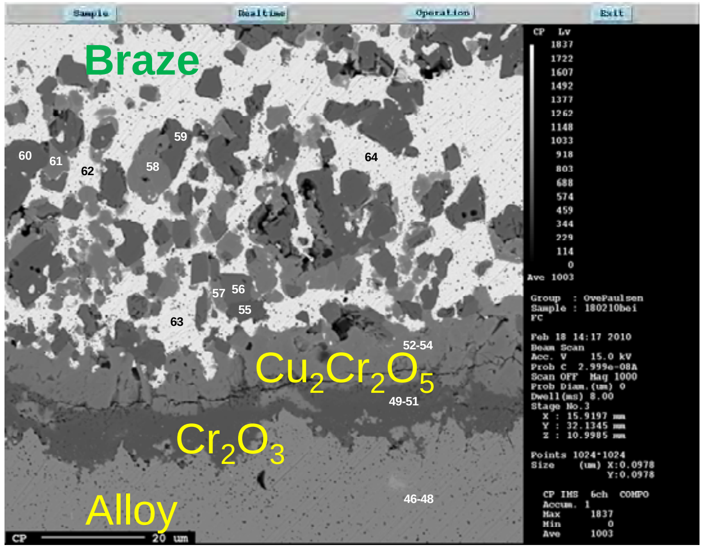




BIGCO2 Task A – Achievements

- Sealing development – air braze
  - o Thermo-chemically compatible with membrane material
  - o Matching thermal expansion behaviour of braze, membrane/ housing material (HT alloy)



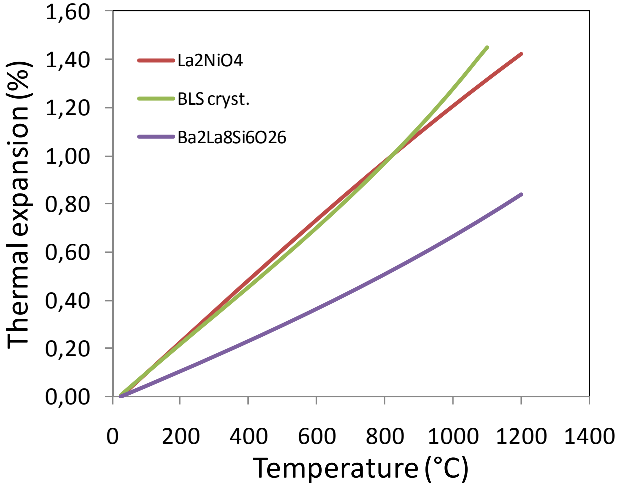


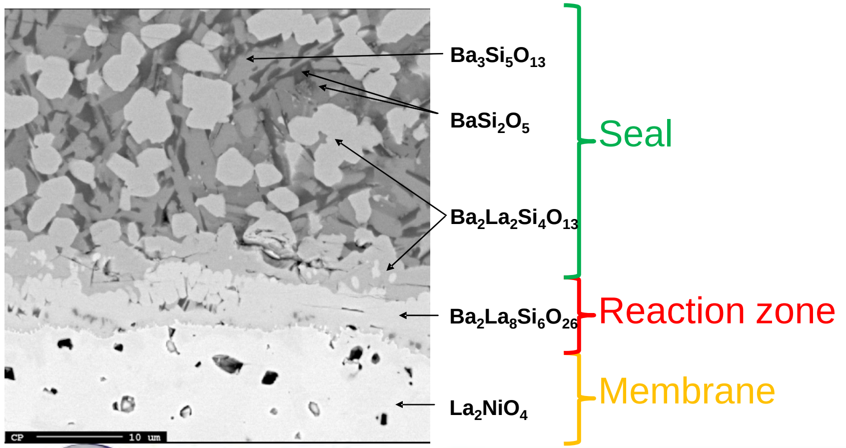
  - o Detected challenges after 4 weeks at high temperature (900-960°C):
    - Undesired interaction between braze and protective coating
    - Thermal expansion mismatch between formed chromium oxide and cupper-chromium oxide (formed from reacton with Cu in braze)

BIGCO2 Task A – Achievements

- Sealing development – glass ceramics

$BaO-La_2O_3-SiO_2$ glass (BLS)

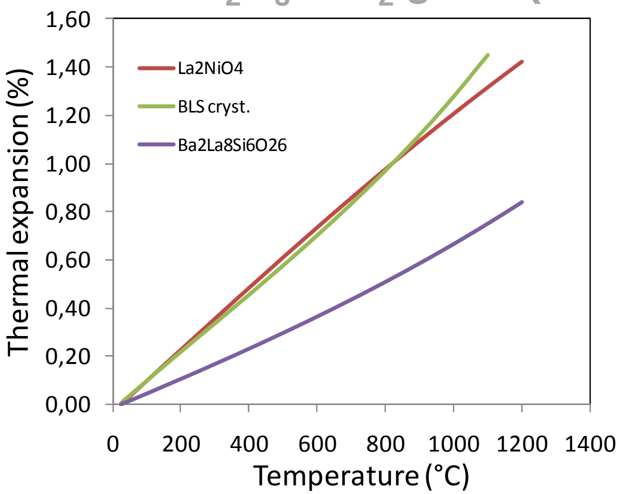




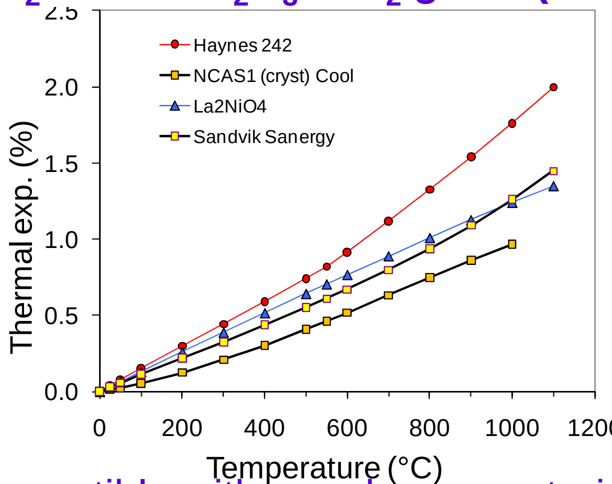
BIGCO2 Task A – Achievements

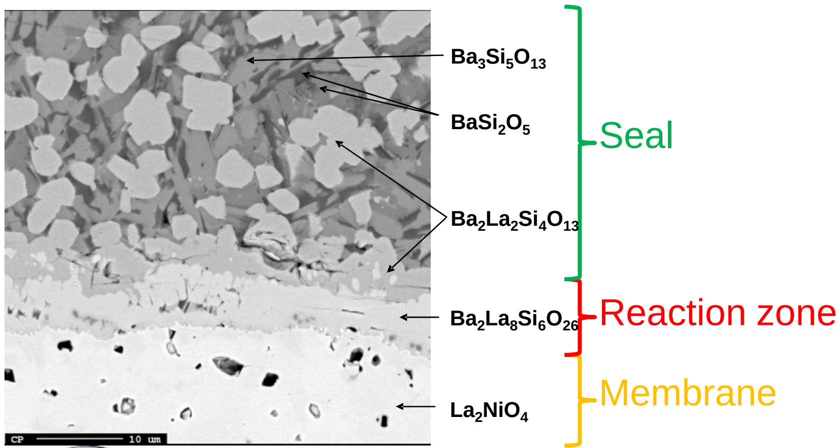
- Sealing development – glass ceramics

BaO-La$_2$O$_3$-SiO$_2$ glass (BLS)

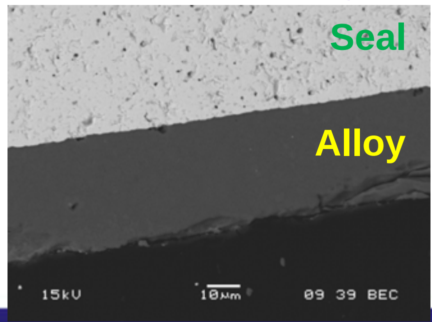


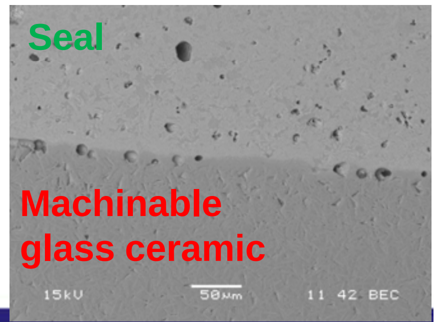
Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ glass (NCAS1)





- ❑Compatible with membrane material
- ❑Cracks on interface seal – alloy housing
- ❑Compatible with alternative housing
  - oMachinable glass ceramic

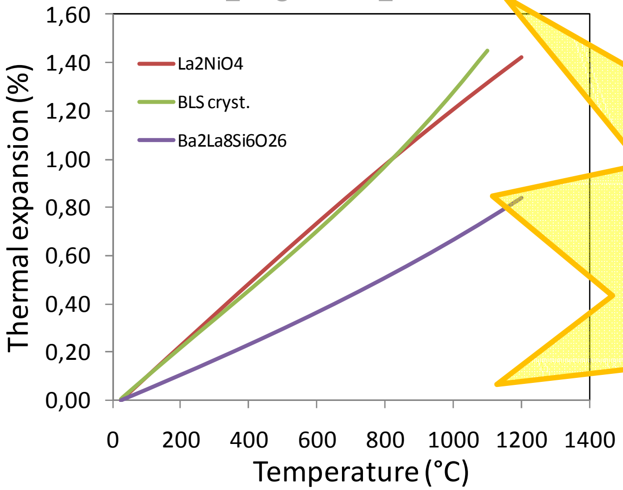




BIGCO2 Task A – Achievements

- Sealing development – glass ceramics

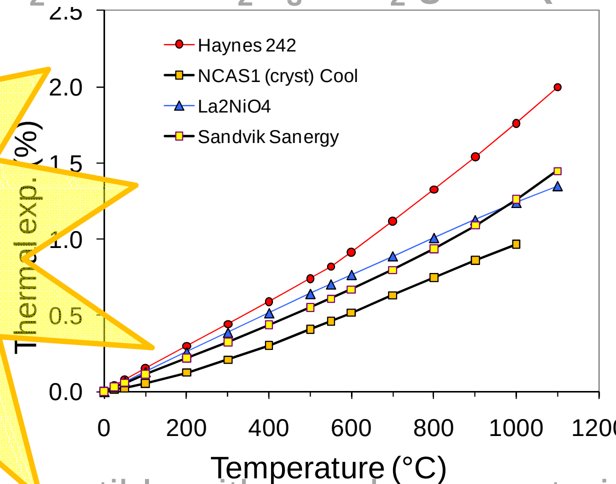
BaO-La_2O_3-SiO_2 glass (BLS)

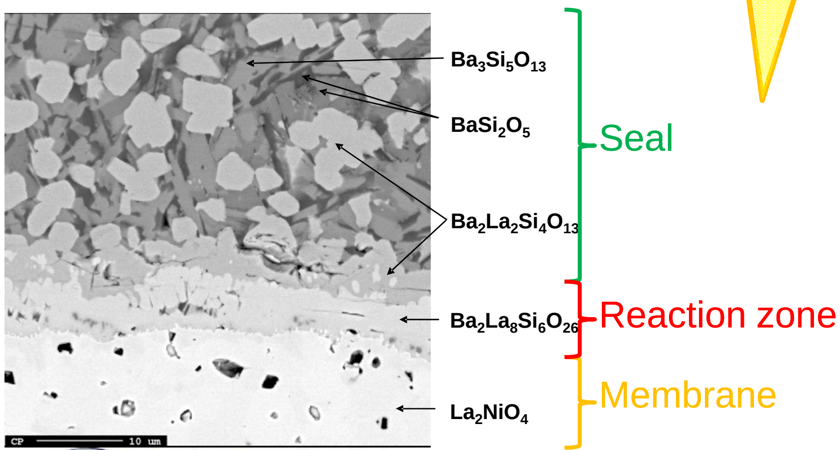


Complex material systems

Many possible reaction products to consider

Na_2O-CaO-Al_2O_3-SiO_2 glass (NCAS1)





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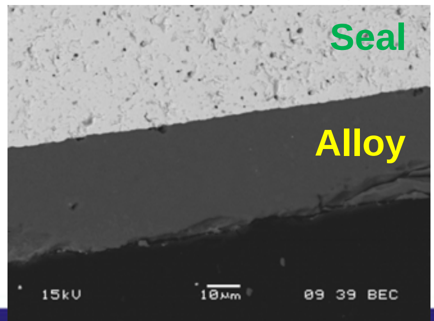
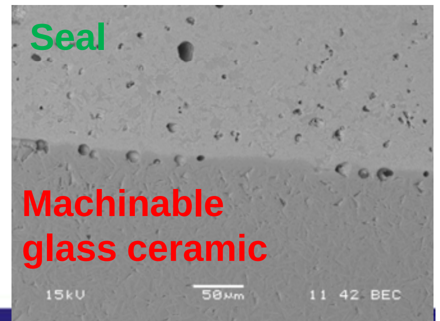




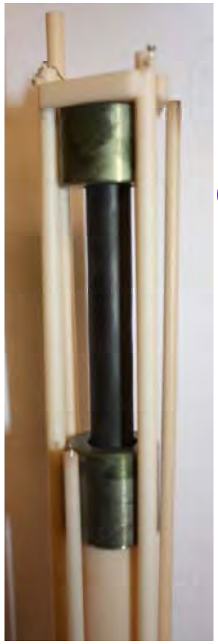
BIGCO2 Task A – Achievements

- Membrane testing
  - Various single tube modules investigated

Tubular membranes tested in Probostat™ cells up to 8 bars and 80% O_2 (32 bar air equivalent)

Gold seals

Dense alumina base



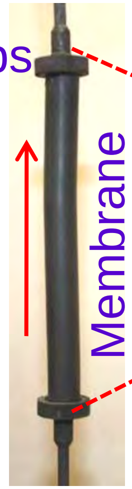
Glass ceramic seal

Machined alloy caps

Sweep gas

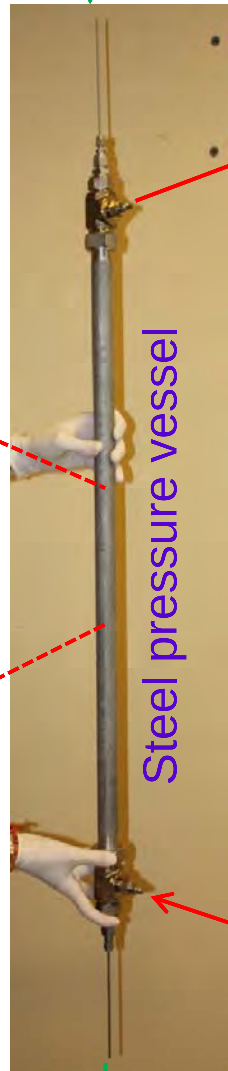
Brazed alloy caps

Air flow



Membrane

Oxygen + Sweep gas



Steel pressure vessel

Air out

Air in

BIGCO2 Task A – Achievements

- Membrane testing
  - Dense tubular membrane (reference material La_2NiO_4) tested over <u>2500 hours</u> at various conditions
    - Pressurized up to 8 bars and 80% O_2 in feed (32 bars air equivalent)
    - Varying gas flows and temperature ranging from 800 to 1000°C

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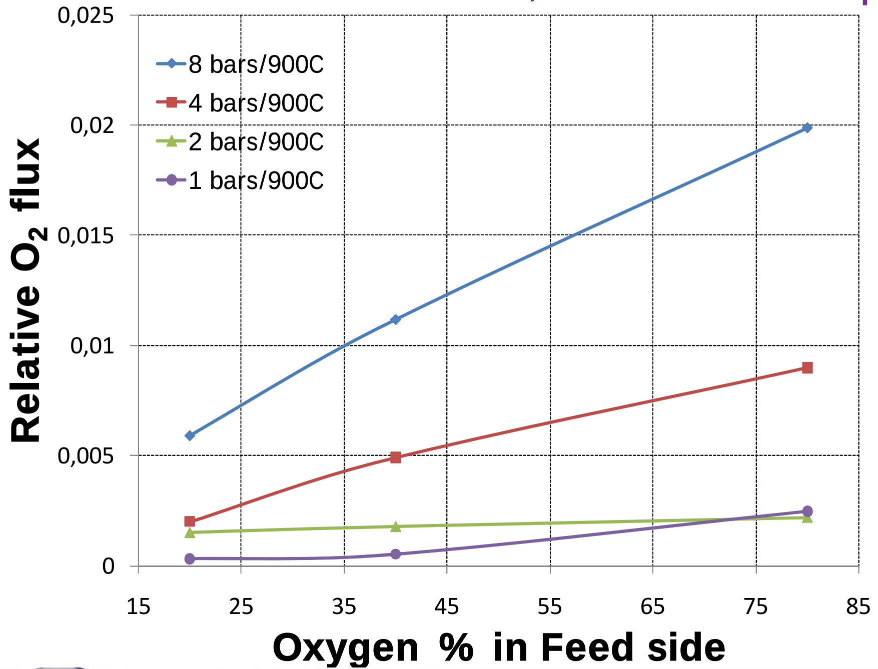
Measurements at 2-8 bars, constant sweep flow



- o Data currently being processed for modelling purposes
  - Ambipolar conductivity
  - Flux model as function of T, pO_2 and membrane thickness
  - Preliminary model indicates flux goal of 10 mL/(cm^2·min) is achievable

BIGCO2 Task A – Achievements

- Material development
  - Improved stability in reducing atmosphere by B-site substitution with iron ($La_2Ni_{1-x}Fe_xO_4$, $x < 0.3$) and no CO_2 absorption (from HPTGA)
  - Improved transport properties by A-site deficiency ($La_{2-x}NiO_4$, $x<0.5$)

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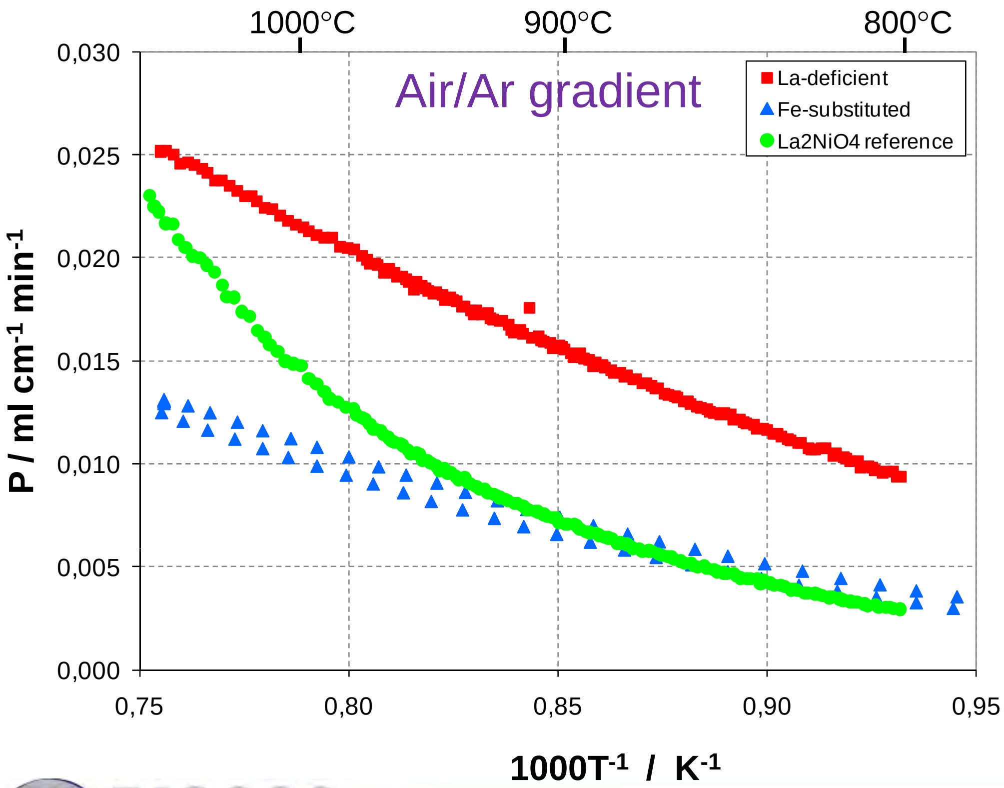

- o Improved O_2 flux of $La_{2-x}NiO_4$ compared to reference material (La_2NiO_4)
  - Doubled at 900°C
- o Decreased activation energy:
  - From measurements in Air/Ar gradient
  - La_2NiO_4: 86 kJ/mol
  - $La_{2-x}Ni_2O_4$: 45 kJ/mol

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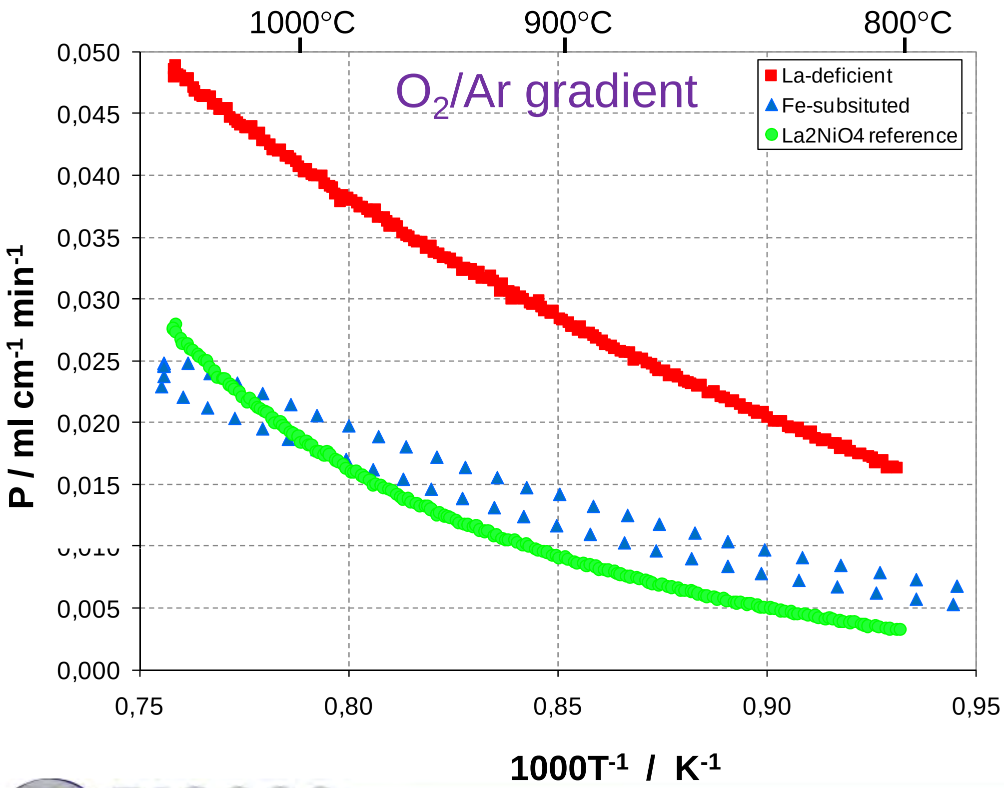

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  - La_2NiO_4: 86 kJ/mol
  - $La_{2-x}Ni_2O_4$: 45 kJ/mol
- o $La_2Ni_{1-x}Fe_xO_4$: Flux comparable to reference material at high pO_2

Summary

- **BIG!!!** BIGCO2 achievements on OTM
  - Membrane fabrication
    - Long porous tubular supports (up to 1 m)
    - Asymmetric membranes with thin dense layers (10-20 µm)
  - Material development
    - Increased stability with Fe-substitution
    - Increased transport properties by La-deficiency
  - Membrane testing
    - Long term tests (2500+ hours) of tubular membranes
    - Pressurized tests up to 8 bars (32 bars air pressure equivalent)
    - Modeling using experimental results in progress
  - Sealing with brazing or glass ceramics in progress

- OTM: high potential for various applications when integrated in high temperature systems (oxy-fuel, Pox,…)

Acknowledgement

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And supporting industrial partners:

Thank you for your kind attention!