HiPerCap – WP3
Membrane based technologies

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WP Leader:	*NTNU*					
Partners:	SINTEF MC	TIPS	CNRS	TNO	EDF	(CSIRO)

Joint EU – Australien workshop Workshop – September 13 – 14, 2017
Oslo - Norway

HiPerCap – WP3

Membrane based technologies

WP Leader:	*NTNU*					
Partners:	SINTEF MC	TIPS	CNRS	TNO	EDF	(CSIRO)

Main Objectives:

To develop high performance membranes based on

1) hybrid membranes with functionalized nanoparticles and with TiO_2 nanoparticles,
2) Ionic Liquid membranes and Supported Ionic Liquid membranes,
3) To develop a simulation tool for the gas transport through the mentioned membranes.

WP 3.1: Hybrid membrane development	NTNU – Sintef MC – TNO
WP 3.2a: Supported Ionic Liquid Membranes	NTNU
WP 3.2b: Nanoporous polymer Ionic Liquid M	TIPS
WP 3.3: Process modelling and simulations	CNRS – NTNU - EDP

WP3: Membrane based technologies

WP 3.1 Hybrid membrane development (NTNU, SINTEF, TNO) - OBJECTIVES

- Develop high flux mixed matrix membrane based on incorporation of nanoparticles in polymer.
  - Target: CO_2 permeance of 2.5 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100.
  - Membrane fabrication and study on transport phenomena.

WP 3.2 Supported ionic liquid membranes (SILM) (NTNU, TIPS) - OBJECTIVES

- Develop contained supported ionic liquid membranes (SILM)
  - Target NTNU: CO_2 permeance above 4 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100
- Develop nanoporous polymer/ILs membranes
  - Target TIPS: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

WP 3.3 Process modelling and simulation (CNRS, EDF, NTNU) - OBJECTIVES

- Develop membrane module simulation model for nanocomposite and SILM membranes.
  - Evaluate the energy requirement & membrane area for different set of operating conditions
- Develop concepts for utilizing the membranes in a post-combustion process.

WP3.1: Hybrid membrane development (NTNU, SINTEF, TNO)

Objectives

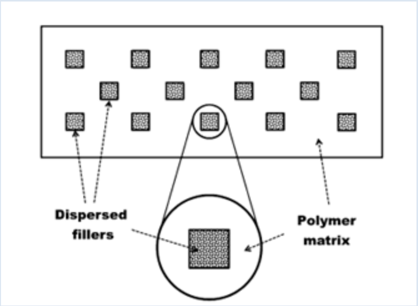
- Develop a high flux mixed matrix membrane based on incorporation of nanoparticles in a polymer.
  - ➢ Target: CO_2 permeance of 2.5 m^3(STP)/ m^2 h bar
    selectivity CO_2/N_2 above 100
  - ➢ Membrane fabrication and study on transport phenomena

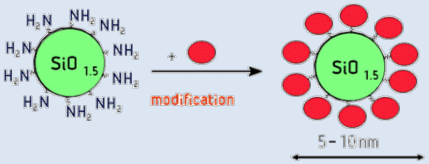
Research Activities

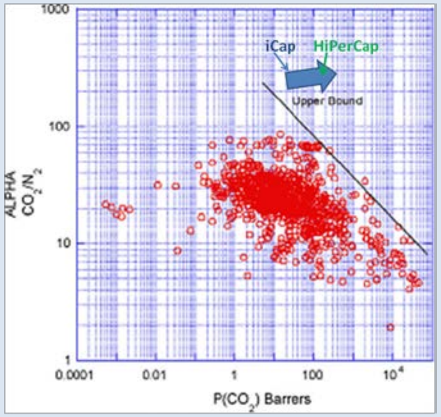
- Study of the transport mechanism and role of the nano-sized particles.
- Tailoring nanoparticles to tune the desired membrane properties such as selectivity and flux.
  - ➢ Nanosized particles prepared and characterized (SINTEF & TNO)
  - ➢ Hybrid membranes prepared and performance tested at NTNU

Expected outcome

- Understanding of hybrid membrane performance
- Dedicated permeability model based on experimental flux data over a wide range of operating conditions







WP3.1: Hybrid membrane development (NTNU, SINTEF, TNO)

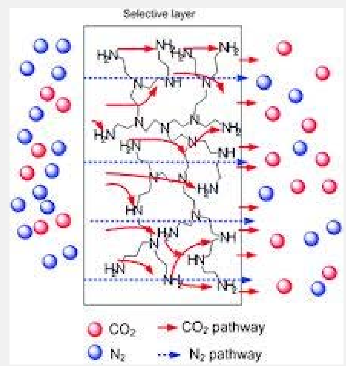
Membrane preparation – PSf-supported amine-POSS® and TiO2 in PVA membranes

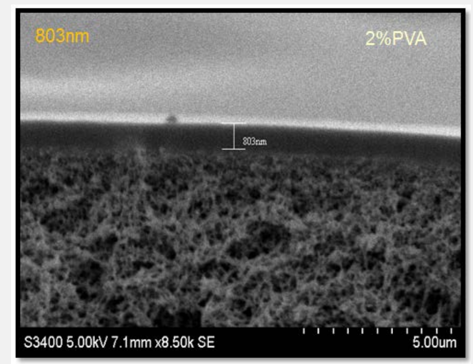
- *Illustration here shows PSf supported flat sheet thin film amine-POSS® in PVA*

1-2 wt.% PVA solution in water → Dipcoating of flat PSF sheet in PVA solution → PSF-supported PVA membrane

Two types of transport for CO_2 through the membrane expected for the amine-POSS® : Fickian diffusion + facilitated transport

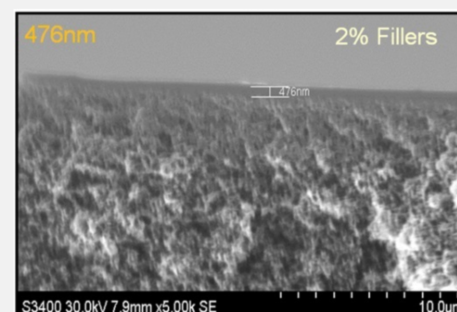
For the hybrid membrane with TiO2 in PVA, only solutions-diffusion was expected





2% PVA

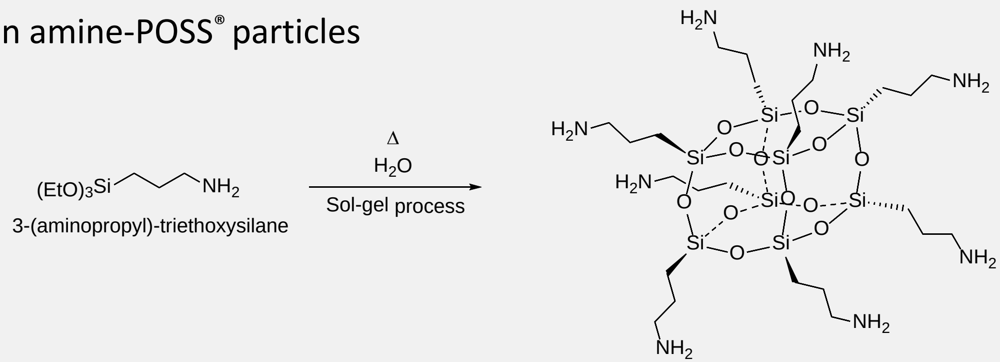
1-2 wt.% PVA solution in water + 10 wt.% HAPS stock solution → Dipcoating of flat PSF sheet in PVA solution with nanofillers → PSF-supported PVA membrane



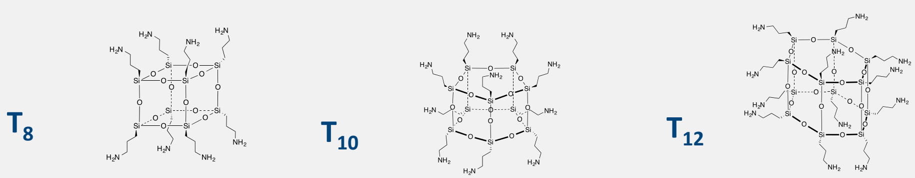
WP3.1: Hybrid membrane development (NTNU, SINTEF, TNO)

Synthesis and optimisation of FunzioNano™ nanoparticles

- Hydrolysis of APS resulting in amine-POSS® particles



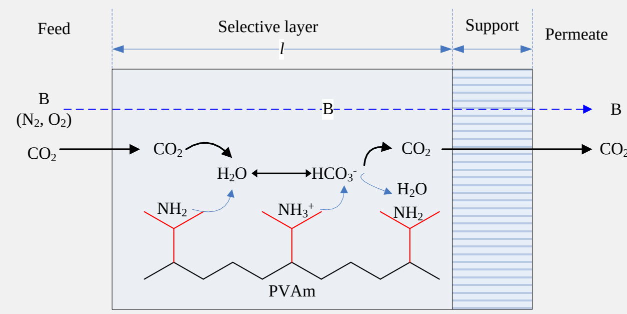
- Controlled synthesis



[29]Si NMR comparison between previous and most optimized FunzioNano® synthesis

- Expected transport mechanism, similar to that in PVAm →

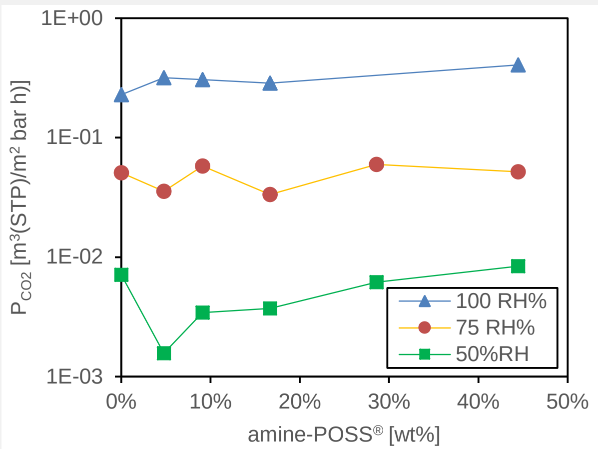
$$J_A = \frac{D_A}{l}\left(c_{A,0} - c_{A,l}\right) + \frac{D_{A,c}}{l}\left(c_{AC,0} - c_{AC,l}\right)$$

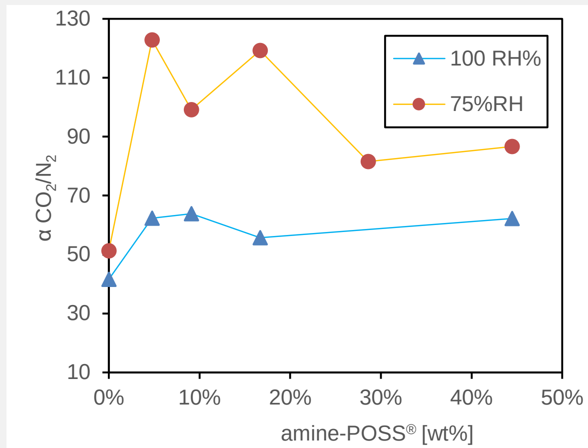


WP3.1: Hybrid membrane development (NTNU, SINTEF, TNO)

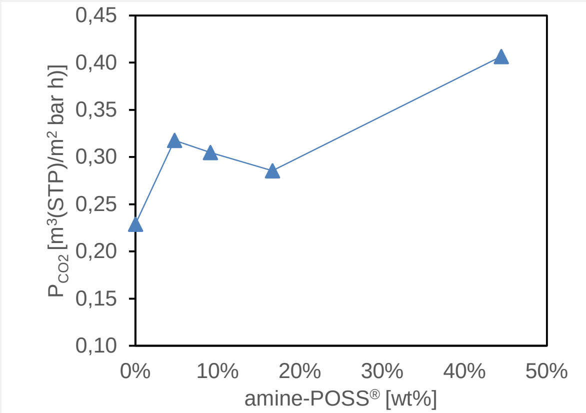
Membrane performance

- Effect of feed humidity and nanoparticle addition





- CO_2/N_2 (10 vol.% CO_2), ~100%RH
  - 25 °C and 1.2 bar
- Transport expected to occur through a combination of solution-diffusion and a "carrier-mediated" mechanism
- Carrier effect could surprisingly not be documented – this has later been thoroughly investigated by PhD-student*
- No increased performance was documented using the TiO2 nanoparticles (range of size 6-8 nm)

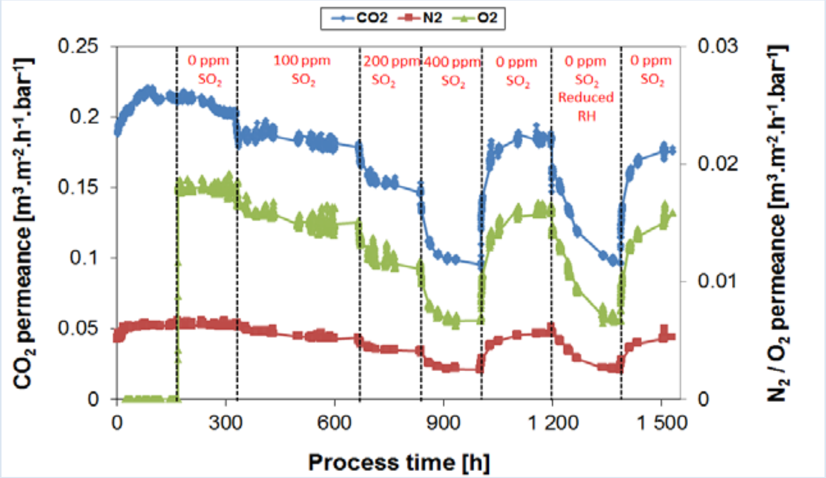


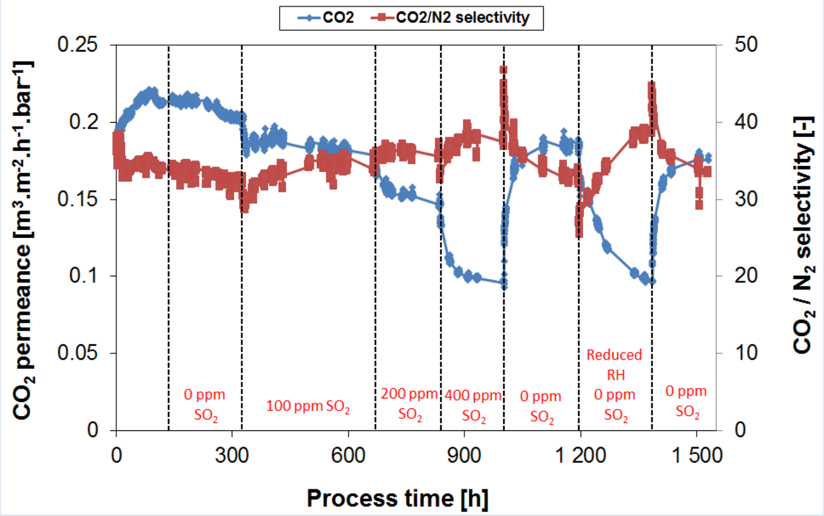
*Guerrero, et al., Energy Proc., 2017

WP3.1: Hybrid membrane development (NTNU, SINTEF, TNO)

SO_2 durability of the HAPS-PVA/PSf membrane

- Membrane PVA:HAPS ratio equal to 1:0.4.
- Experiment performed over a period of 1500 hours under varying SO_2 levels up to 400 ppm at atmospheric pressure at 25 °C.
- Introduction of SO_2 results in a decreasing permeance behavior for all gases at a constant CO_2/N_2 selectivity.
- The decrease in permeance during the SO_2 exposure is explained by the decrease in humidity of the feed gas mixture occurring during the SO_2 exposure.
- SO_2 does not have a permanent negative effect on the membrane performance under the conditions investigated





WP3.1: Hybrid membrane development (NTNU, SINTEF, TNO)

Conclusions for WP 3.1

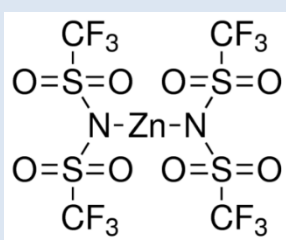
- TiO_2 nanoparticles were prepared (average size 6-8 nm) and prepared as hybrid membranes with PVA as selelctive layer on PSF. No increase in performance was documented
- Amine-POSS® nanoparticles were obtained via sol-gel process through the hydrolysis of 3-aminopropyltriethoxysilane with a mean particles size of 3 nm.
- Functionalized nanoparticles – PVA based films were deposited by dip-coating on PSf supports.
  - SEM cross-section revealed a homogeneous coating on the PSf support and an overall thickness of 3 µm
- The CO_2 permeance of the obtained membranes is strongly influenced by the degree of feed gas humidity
- A CO_2 permeance up to 0.4 m^3(STP)/(m^2 h bar) at a CO_2/N_2 selectivity of up to 60 was obtained
  - These values lie below the original performance target of HiPerCap
- The durability towards SO_2 of the PVA-amine-POSS®/PSf membrane over a period of 1500 hours under varying SO_2 levels was additionally investigated.
  - SO_2 does not seem to have a permanent negative effect on the membrane performance under the conditions investigated

WP3.2a Supported ionic liquid membranes (SILM)

- To develop contained supported Ionic Liquid Membranes (SILM)
  - Target: CO_2 permeance above 4 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100

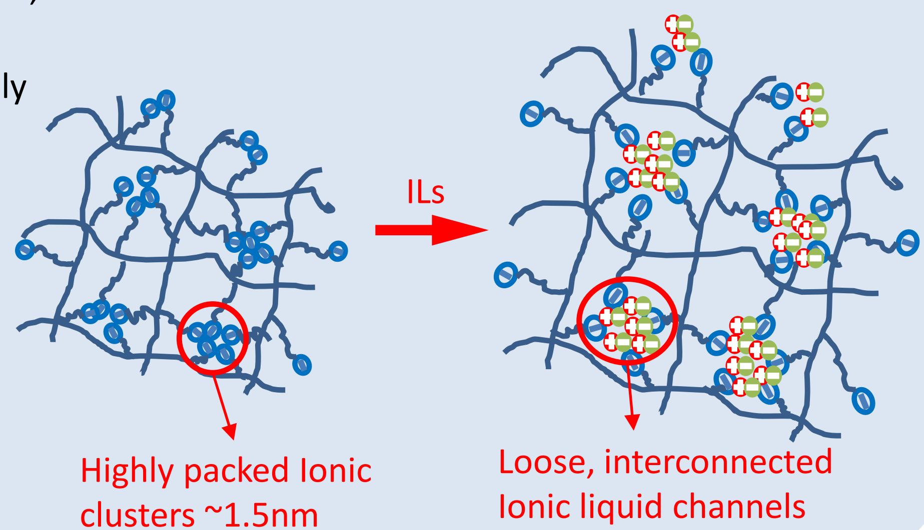
Ionic liquids selection:

- **[TETA][Tfa]** and **amino acid based ionic liquids (AAIL)** are selected due to the high CO_2 solubility and CO_2/N_2 selectivity
- **Metal-containing ILs** (i.e., Zn(II), Fe(II)) are also selected due to the tendency of forming chemical bondings between metal centre and CO_2 molecules, which can greatly enhance CO_2 solubility
- **[Bmim][BF_4]** is selected as a physical Ils. It is finally found the most suitable IL for the membrane.



Polymer selection:

- Nafion™ (Polyperfluorinated sulfonic acid)
- Naxer™ (sulfonated block co-polymer)



Jansen, J. C., et al. (2011). Macromolecules **44**(1): 39-45

WP3.2a Supported ionic liquid membranes

Membrane preparation

- [Bmim][BF4] based membranes are homogeneous and defect free.

Pure Nafion

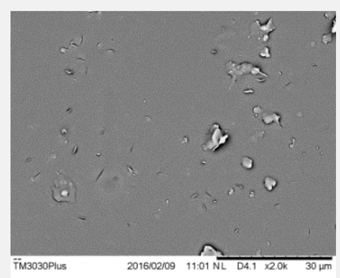
Nafion 30% **[Bmim][BF4]**

Pure Nexar

Nexar 30% **[Bmim][BF4]**

- It was difficult to fabricate membranes from **AAIL, TETA and Zn^{2+}** ILs with the selected polymers (**Nafion, Pebax, PDMS and Naxer)**

Nafion 30% **Zn^{2+} ILs**
(form gel)



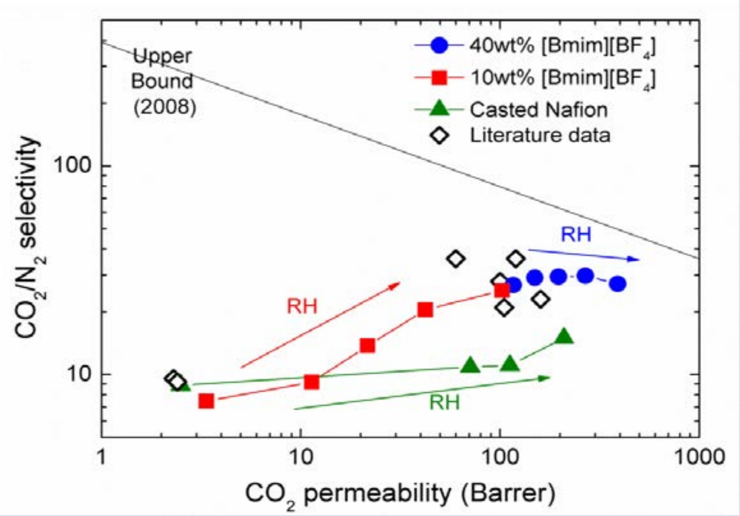
Nafion with [TETA][Tfa] and AAILs
(phase separated)

PI 30% **Zn^{2+} ILs**
(cannot form membrane)

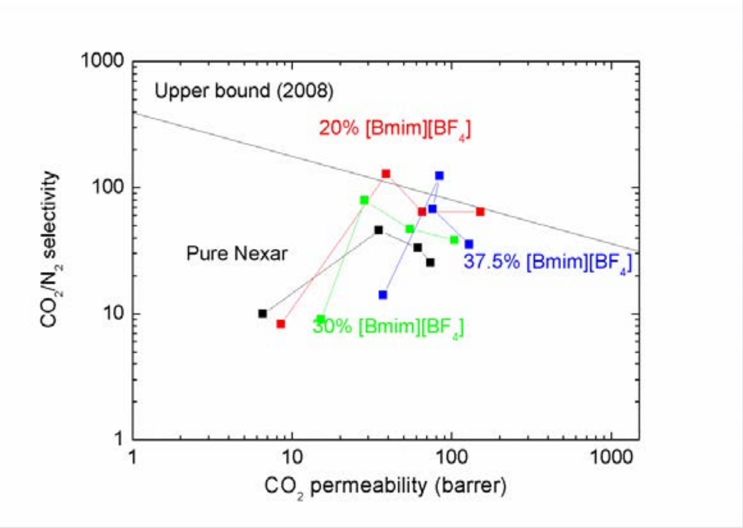
WP3.2a Supported ionic liquid membranes

Results summary

- Nafion/[Bmim][BF_4]



- Nexar/[Bmim][BF_4]



- **Nafion/[Bmim][BF_4]**

  P_{CO2}=365.2 Barrer

  CO_2/N_2 selectivity: 30

- **Nexar/[Bmim][BF_4]**

  P_{CO2}= 151Barrer

  CO_2/N_2 selectivity: 64

  P_{CO2}= 84.3 Barrer

  CO_2/N_2 selectivity: 121

If making composite membrane thickness of 0.2µm

~5 m^3(STP)/ m^2 h bar

~2.07 /~1.65 m^3(STP)/ m^2 h bar

*1Barrer = 365×10^{-6} m^3(STP) m m^{-2} h^{-1} bar^{-1}

WP3.2a Supported ionic liquid membranes

Potential of the membrane and future work

This membrane has the potential to fabricate as thin film composite membrane for large scale production, and it is suitable for CO_2 capture at elevated temperature (>80^oC) and humid conditions with good separation performance.

Future work:

The performance may be further improved through the following:

- To reduce the membrane coating thickness (e.g., 0.1 µm) to enhance CO_2 permeance
- To use chemisorption ILs or blend of chemisorption/physisorption ILs to improve the intrinsic CO_2 permeability and CO_2/N_2 selectivity;
  - membrane preparation conditions must be further optimized
- To adjust the IL nano-channels in membranes (e.g. using polymers containing charged side chains with different length) and to balance the gas transport property and stability;
- To optimize the content of ILs in the polymer matrix

WP 3.2b: Supported Ionic Liquid Membranes

HiPerCap CO_2

TIPS RAS

TIPS objectives:

- Develop contained supported ionic liquid (IL) membranes
    - Targets: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar; selectivity CO_2/ N_2 = 20-30
    - Temperature stability >100°C.

Research activities at TIPS

- ✓ Optimal conditions of cross-linking are developed for high CO_2 permeance TFC support with cross-linked PTMSP gutter layer stable in organic solvents;
- ✓ Developed TFC membranes with selective layer from Polymer of Intrinsic Microporosity (PIM-1) on the top of cross-linked PTMSP gutter layer meet the targeted permeance (13–22 m^3(STP)/m^2 h bar);
- ✓ CO_2/N_2 selectivity of developed TFC membranes meet the targeted value (26-39).

WP 3.2b: Supported Ionic Liquid Membranes

High permeance TFC support: microfiltration MFFK support with cross-linked PTMSP (Ta) thin gutter layer

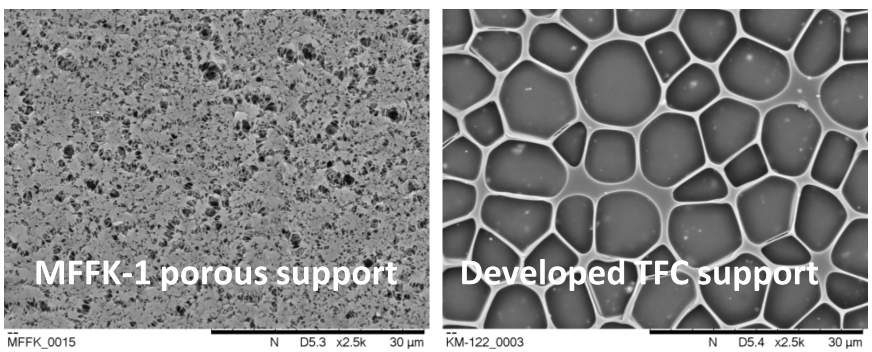
TIPS RAS

Optimal procedure of TFC high permeance support preparation:

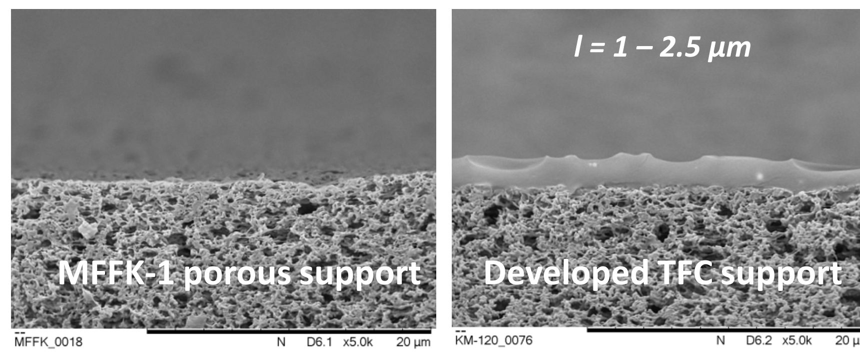
✓4 wt% PEI/PTMSP mixture coated on the MFFK-1 support;
✓crosslinking by 0.5-1.5 wt% solutions of PEGDGE in methanol during 24 h;
✓post-treatment with aqueous ethanol solutions (50 wt% solution and then 25 wt% solution)

CO_2 permeance, $m^3(STP)/m^2h$ bar	N_2 permeance, $m^3(STP)/m^2h$ bar	CO_2/N_2 selectivity
50.2 - 53.4	13.6 - 14.8	3.6 – 3.7

Surface view



Cross-section view



➢**TFC supports with cross-linked PTMSP gutter layer resistant to organic solvent having reproducible high CO_2 permeance of 50 $m^3(STP)/m^2h$ bar are developed;**

➢ **Developed TFC support is excellent for further coating of CO_2 selective layer.**

WP 3.2b: Supported Ionic Liquid Membranes

HiPerCap CO_2

TIPS RAS

TFC membranes with different selective layers on high permeance TFC support

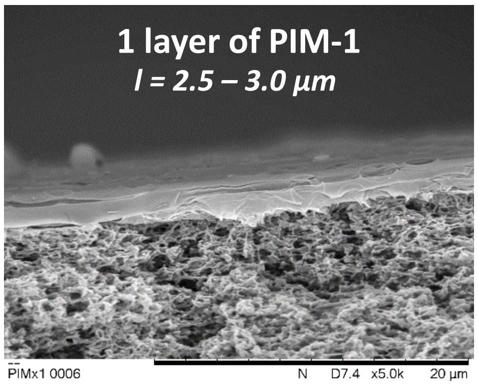
Different selective layers coated on the developed TFC support	CO_2 permeance, m^3(STP)/m^2h bar	N_2 permeance, m^3(STP)/m^2h bar	CO_2/N_2 selectivity
Initial TFC support with cross-linked PTMSP gutter layer	50.2	13.6	3.7
Ionic liquid [Emim][DCA]	3.9	0.5	7.8
PIM-1 - Polymer of intrinsic microporosity (1 layer)	13.0 – 17.9	0.4 – 0.9	10 – 12
PIM-1 - (2 layers)	9.2 – 13.3	0.6 – 1.1	13 – 16
90% PIM-1 + 10% PTMSP	26.5	4.4	6.0
90% Polyvinyltrimethylsilane (PVTMS) + 10% PTMSP	5.9	0.6	9.8

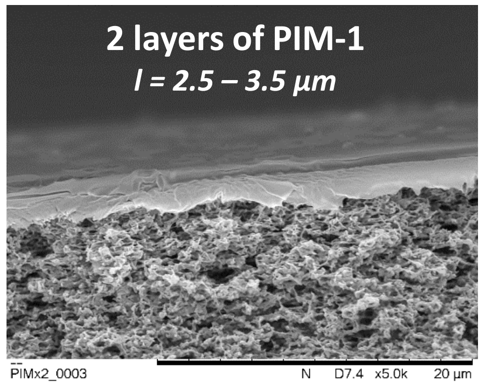
- **TFC membranes with PIM-1 selective layer seem to have most promising properties;**
- **CO_2 permeance of 13.3 m^3/m^2 h bar meets the targeted value;**
- **CO_2/N_2 selectivity of 16 is close to the targeted value of at least 20.**

WP 3.2b: Supported Ionic Liquid Membranes

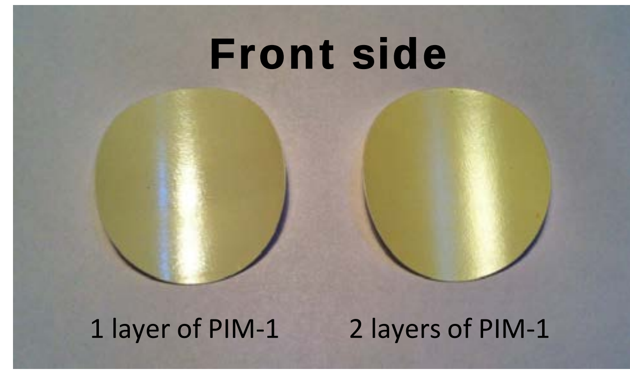
Images of TFC membranes with PIM-1 selective layer on high permeance TFC support

Cross-section view

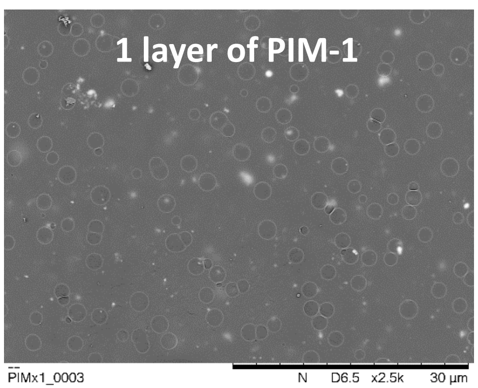


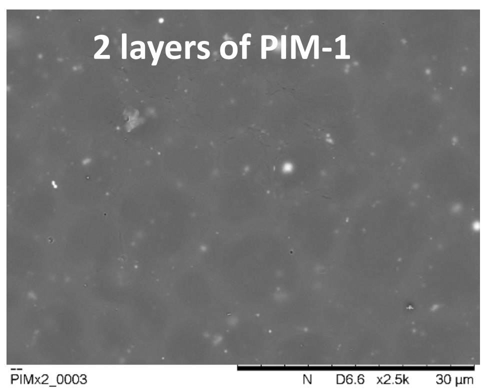


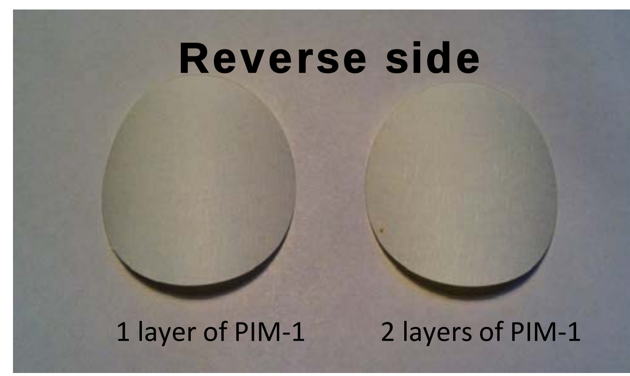
General view



Surface view







- Further extra work on optimization of selectivity was done to meet the target values

WP 3.2b: Supported Ionic Liquid Membranes

HiPerCap CO_2

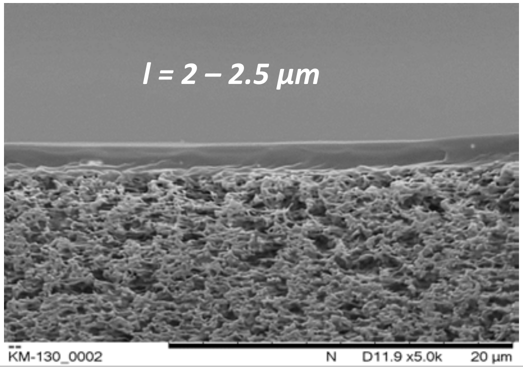
TIPS RAS

High-permeance TFC membranes with targeted properties

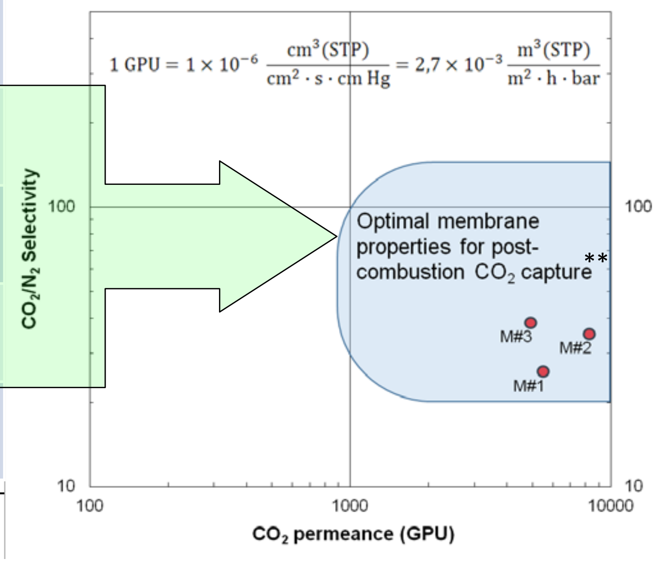
Optimal procedure of PIM-1 TFC membranes preparation:

✓Casting solution: 0.5 wt% of PIM-1 polymer in chloroform/trichloroethylene (1:1) mixed solvent
✓Support: TFC supports with cross-linked PTMSP gutter layer*
✓Method: kiss-coating (meniscus-coating) technique

Cross-section view



Developed TFC membranes		CO_2 permeance, $m^3(STP)/m^2h$ bar	N_2 permeance, $m^3(STP)/m^2h$ bar	CO_2/N_2 selectivity
Initial TFC support with crosslinked PTMSP gutter layer *		50.2	13.6	3.7
TFC membranes with optimized PIM-1 layers	M#1	14.8	0.57	26.0
	M#2	22.3	0.63	35.4
	M#3	13.3	0.34	39.1
Targeted values within HiPerCap		*12-15*	*-*	*20-30*



*- Bazhenov S. et al. *Green Energy and Environment.* 2016, 1 (3), 235-245
** - Merkel T. et al. *Journal of membrane science*. 2010, 359 (1), 126-139

➢ **Developed TFC membranes meet the targeted values of CO_2 permeance and CO_2/N_2 selectivity**

WP3.3: Process modelling and simulation

Objectives:

- ✓ Develop membrane module simulation model
- ✓ Develop concepts for utilizing the membranes in a post-combustion process
- ✓ Evaluate the energy requirement & membrane area for different set of operating conditions

Permeability (barrer)	Case MMM*
CO_2	926
N_2	9.26
H_2O	1500
O_2	30.87
$\alpha_{CO2/N2}$	100
$\alpha_{CO2/O2}$	30
z (µm)	1

*Membrane module parameters in the three different cases (*iCap performance)*

	p_1' (bar)	p_1'' (bar)	p_2' (bar)	p_2'' (bar)	ψ_1	ψ_2	Energy requirement (GJ/t_{CO2})	Specific membrane surface area ($m^2.kg\ de\ CO_2^{-1}.s^{-1}$)
Case 1	2,5	0,2	2,5	0,25	0,08	0,1	2,371	2,10E+04
Case 2	3,125	0,25	2,5	0,25	0,08	0,1	2,537	1,73E+04
Case 3	2,5	0,25	2,5	0,15	0,1	0,06	2,546	2,71E+04
Case 4	2,5	0,25	4,16	0,25	0,1	0,06	2,550	2,65E+04

WP3.3: Process modelling and simulation (CNRS, EDF, NTNU)

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Two stages membrane process

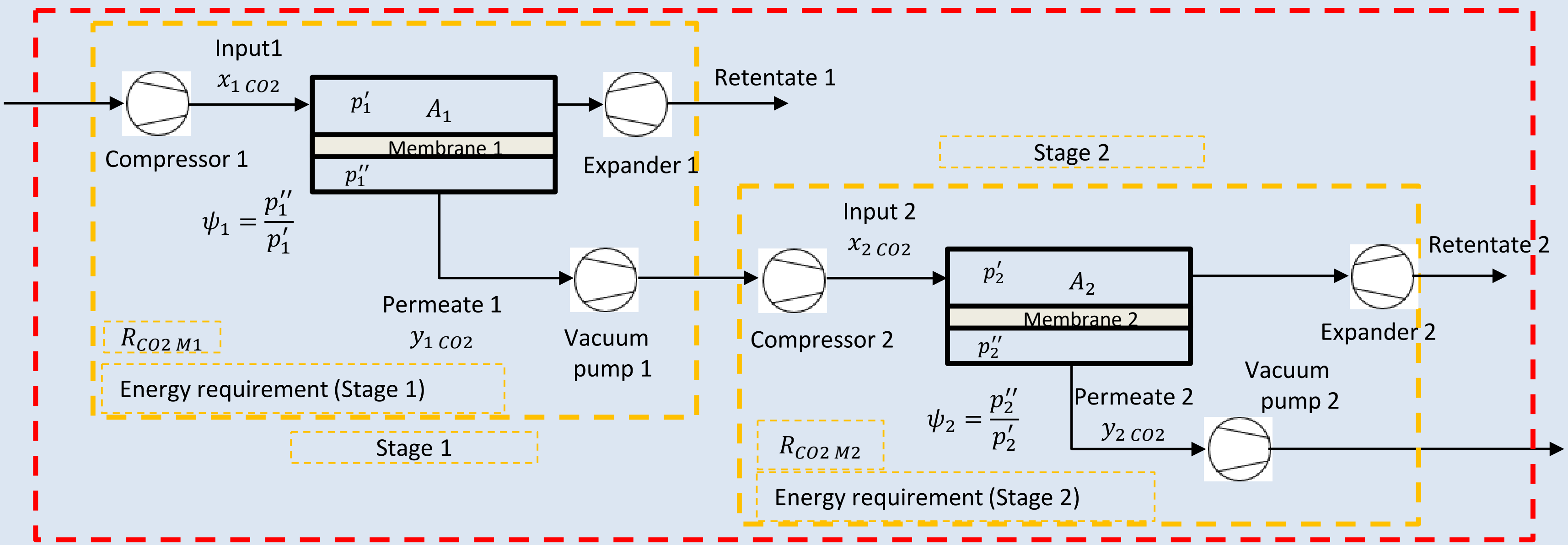
CO_2 (13,597%)
N_2 (71,694%)
O_2 (4,549%)
H_2O (10,16%)

Feed flow
(801,09 kg/s)
(1,05 bar)
(47°C)

Output targets:

$$R_{CO2} = R_{CO2\ M1} * R_{CO2\ M2} = 85\%$$

$$y_{CO2} = y_{2\ CO2} = 95\%$$

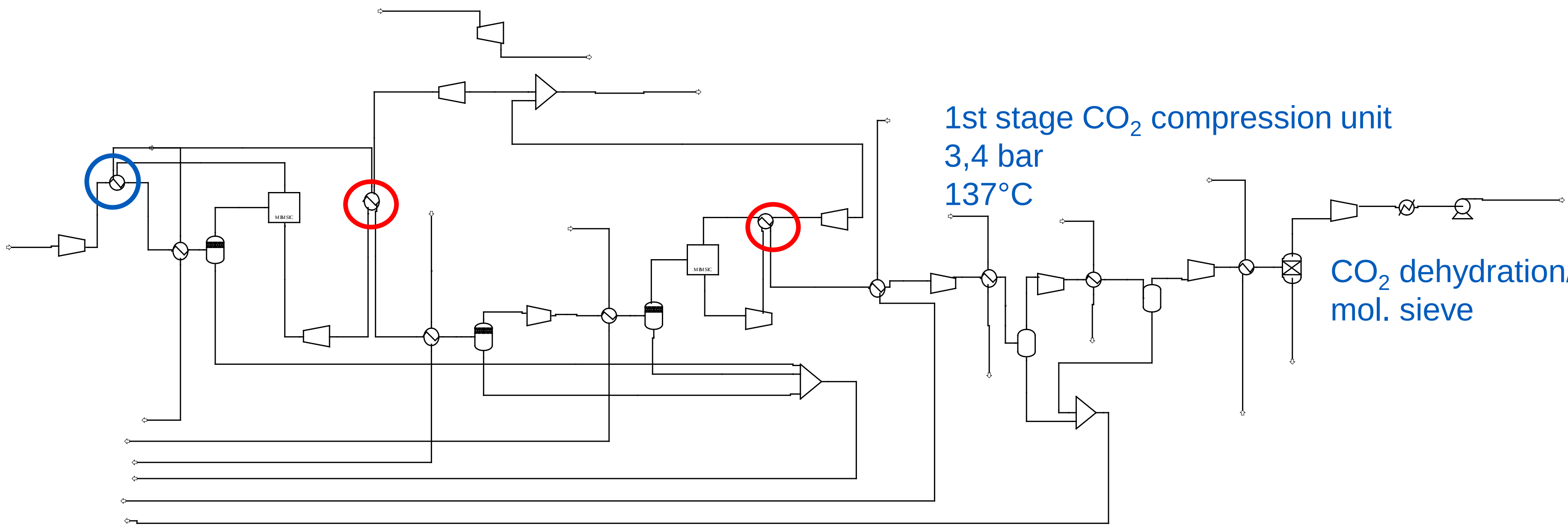


Two-stage membrane process is needed to attain the specification in term of CO_2 purity and recovery

WP3.3: Process modelling and simulation

- Transport mechanism through different membranes (Mixed matrix, Fixed site carrier, Ionic liquid membranes) has been modeled.
- Transport mechanism model parameters for FSCM has been adjusted using data from literature.
- Membrane process simulation code has been developed taking into account of variable permeabilities along the membrane module.
- Required energy and membrane area have been evaluated for different operating conditions and membranes (ION 1, ION2,FSCM, PEIE…) .
- The required energy and membrane area dependant on the compression strategy (vacuum on permeate and/or feed compression), upstream and downstream pressures and on material permeation properties

Two-stage membrane process modelling



	Hipercap				Liao et al (2014)*
	ION1	FSCM2	ION2	FSCM1	PEIE-HT
P (m3 (STP) / m2 h bar)	4,14	2,5	2,31	1,5	15,37
Select. CO2/N2 (-)	64	100	123	100	268
thickness (micro-m)	0,1	1	0,1	1	0,257
Work (kWh/tCO2)	340	280	265	280	242
Area (m2)	500 000	2 059 000	3 420 000	3 490 000	1 355 000

*J. Liao *et al.*, "Fabrication of high-performance facilitated transport membranes for CO2 separation," *Chem. Sci.*, vol. 5, no. 7, p. 2843, 2014.

WP3.3: Process modelling and simulation

Conclusion and perspectives

Limit:

- Trade-off between energy requirement and surface area
  - A technical-economical analysis is required to find an operating optimum (Energy consumption and surface area)

Improvements:

- Determination of new effective membranes (permeability and selectivity) leads to a decrease of the CAPEX and OPEX
  - Higher permeability decreases the surface area
  - Higher selectivity decreases the energy consumption

- Reduction of CO_2 capture ration (R_{CO2}<85%) can show interesting simulation results in terms of energy consumption

WP3 Membrane Based Technologies – Thank you for your attwntion

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__Partners:__

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