

# Supported IL Membrane: Stability and Absorption and Permeation Selectivities

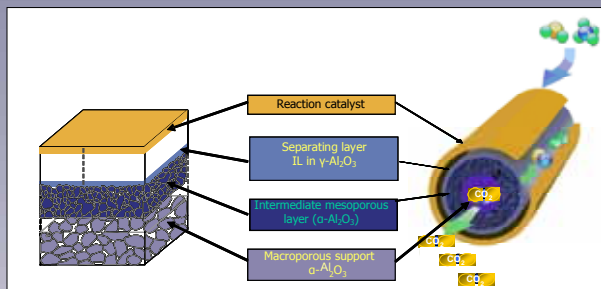
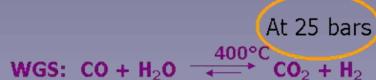
Sona Raeissi<sup>1</sup>, Astrid Schilderman<sup>1</sup>, Cor J. Peters<sup>1</sup>, Wim Haije<sup>2</sup>

<sup>1</sup>Delft University of Technology, Faculty of Mechanical, Maritime and Materials Engineering, Department of Process and Energy, Laboratory of Process Equipment, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

<sup>2</sup>Energy Research Centre of the Netherlands, ECN Department of Hydrogen and Clean Fossil Fuels, PO Box 1, 1755 ZG Petten, The Netherlands

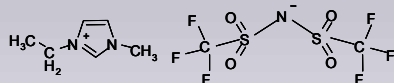
## Goal

Steam reforming and the water gas shift are the key reactions for the production of hydrogen from fossil fuels. By removing carbon dioxide from the reaction mixture as it is produced, the equilibrium can be shifted to the product side. The goal is to develop a membrane reactor based on CO<sub>2</sub>-selective Supported Ionic liquid Membrane (SILM) for the water gas shift reaction. The selected SILM should have both high solubility and high diffusivity.



Schematic diagram of separation-enhanced membrane reactor

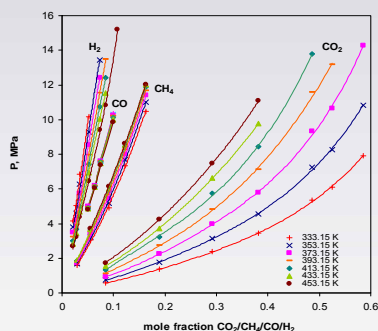
## Selected Ionic liquid for supported ionic liquid membrane



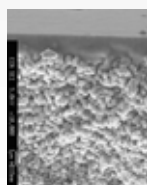
1-ethyl-3-methyl-imidazolium-bis-(trifluoromethylsulfonyl) imide  
abbreviation: [emim][Tf<sub>2</sub>N]

## Results

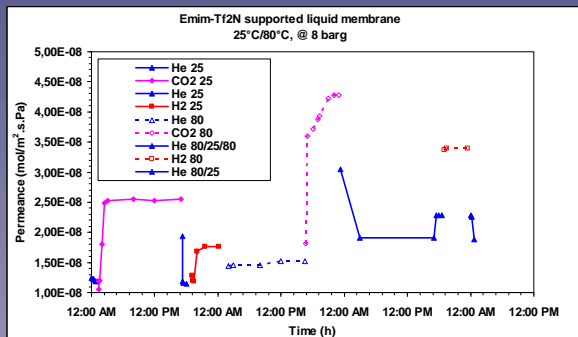
comparison of CO<sub>2</sub>, CO, H<sub>2</sub> and CH<sub>4</sub> solubilities in [bmim][Tf<sub>2</sub>N]



Pressure-concentration → absorption selectivity CO<sub>2</sub>/H<sub>2</sub> between 5 and 15 depending on chosen p, T similar to the emim analogue.



Membrane preparation:  
IL confined to γ-Al<sub>2</sub>O<sub>3</sub> layer



Single gas permeances of He, H<sub>2</sub> and CO<sub>2</sub> at 25 and 80°C

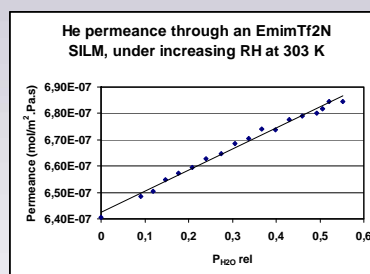
What do we learn from this picture?

- Equilibration is extremely slow
- Permeability of other gases increases after CO<sub>2</sub> has been permeated
- Permeability increases with T
- Permselectivity decreases with T

Table: Average plateau values of the single gas permeances at stable temperature

Condition (°C)	He 25	CO <sub>2</sub> 25	He 25	H <sub>2</sub> 25	He 80	CO <sub>2</sub> 80	He 80/25/80	H <sub>2</sub> 80	He 80/25
Average plateau permeancy (10 <sup>-8</sup> mol/m <sup>2</sup> sPa)	1,2	2,5	1,1	1,7	1,4	4,2	1,9	3,3	1,8

Highest permselectivity measured @ 25°C: 2,3



Stability with water vapour: increasing partial water vapour pressure leads to increasing He flux: SILM degrades

## Conclusions

- Different T absorption fingerprint for CO<sub>2</sub> and CH<sub>4</sub> as compared to CO and H<sub>2</sub>
- Absorption selectivity too low: <15
- Permselectivity even lower: <2,3
- Kinetics too slow
- Decreasing permselectivity with increasing T
- Not stable against water vapour (abundantly present in WGS) degradation likely but not fully proven

So: first investigate and try to understand the changes in liquid structure with different sorbates and then back to drawing table to design a better IL to have higher CO<sub>2</sub> solubility by possible methods such as increasing fluorination of the IL, or using nonfluorinated ILs containing ether linkages and flexible alkyl chains to increase free volume.