Mixed Matrix Membrane
For Gas Separation:
PDMS Filled with Ionic liquid
Coated Zeolite (ZSM-5)

By
Muhammad Hussain
Axel König

Lehrstuhl für Thermische Verfahrenstechnik
Friedrich-Alexander-Universität Erlangen-Nürnberg
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  • Diffusivity vs Solubility-Based Gas Separation

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Membrane-Based Gas Separation

- Advantages of Membrane-Based Gas Separations
  - Low capital and operational cost
  - Low energy cost
  - Ease of Operation

- Disadvantages of Membrane-Based Gas Separations
  - Fouling
  - Difficult to get both high selectivity (separation) and high throughput
Membrane-Based Gas Separation

Gas Separation Membranes

Polymeric Dense Membranes e.g. PDMS;

Poros Inorganic Membranes e.g. Zeolite, Pyrolyzed carbon

Hybrid Membranes Materials

1-Solubility selective
2-Separation mechanism (Solution Diffusion)

1-Size Exclusion
2-Solubility – selectivity through surface effects e.g. Cappillary condensation
Hybrid Membran Materials

- Combine the best characteristics of Porous and polymeric materials

- Different types of orgaine-inorganic hybrids
  - Incorporation of inorganic materials into the polymer matrix
    Chandak et al. (1997), Merkel et al. (2002)
  - Organic-Inorganic sol-gel materials Smaihi et al. (1996)
  - Chemical attachment of organic groups to the inorganic surface
  - Present work is focused on incorporation of Zeolite materials into the polymer matrix Kiran (2005), Oksoyuglu (2008), Hussain (2009)
Theory

Permeability = Flux * Thickness/Driving Force

Permeability = Solubility (S) * Diffusivity (D)

\[ P_A = \frac{\delta_M}{(p_{A,F} - p_{A,p})} \times \frac{nA}{A_M} \]

\[ P_B = \frac{\delta_M}{(p_{B,F} - p_{B,p})} \times \frac{nB}{A_M} \]

\[ \alpha_{A/B} = \frac{P_A}{P_B} = \left( \frac{D_A}{D_B} \right) \times \left( \frac{S_A}{S_B} \right) \]

Diffusivity-Based

Solubility-Based

\[ P_A = \frac{\delta_M}{A_M(p_{A,F} - p_{A,p})} \times \frac{V_{Autoclave}}{RT} \times \frac{dp_{A,F}}{dt} \]
Experimental Setup

Autoclave
1,4 Litre

CO2
N2
CH4

Room Temperature

Feed

Permeate

Retantate

Screw Valve
Needle Valve

0.00515 m2

PIR
1
2
PR
1
2
PSV
1
2
DPIR
1

PRESSURE

Room Temperature

Vent

TR
1
2

CIR
1

PI
1
2

FR
1
2
Mixed-Matrix Membrane

Continuous polymer phase $P_c$

Zeolite particles as dispersed phase $P_d; \phi$

$\phi$ Volume fraction of the dispersed phase

$P_{c/d}$ Permeability of continuous/ dispersed phase
Maxwell Model: Permeability of CO₂ as function of ZSM-5 Content

\[ P_{d,c} = P_c \cdot \frac{P_d + 2P_c + 2\phi(P_d - P_c)}{P_d + 2P_c - \phi(P_d - P_c)} \]

\[ P_{overall} = \frac{P_d \cdot P_c}{(1-\phi) \cdot P_d + \phi \cdot P_c} \]

- Maximum (parallel model)
- Maxwell model [2]
- Minimum (series model)


* Measured Result
Maxwell Model: Permeability of CO\textsubscript{2} as function of Zeolite Content

\[ P_{d,c} = P_c \cdot \frac{P_d + 2P_c + 2\phi(P_d - P_c)}{P_d + 2P_c - \phi(P_d - P_c)} \]


Fig. a) : SEM image showing the interfacial gap ‘sieve in cage morphology’ [4]
b) : SEM image showing the interfacial Void [3]


Continuous polymer phase

\( P_c \)

Zeolite particles as dispersed phase

\( P_d; \phi \)

\( \phi \) Volume fraction of the dispersed phase

\( P_{c/d} \) Permeability of continuous/ dispersed phase
Filling of Interfacial Organic Inorganic Void: Concept

Continuous polymer phase

IL coated zeolite particles as dispersed phase

$P_d$
Membrane Preparation: Concept

Zeolite

Zeolite ZSM-5

Zeolite particle
Membrane Preparation: Concept

Zeolite ZSM-5

Zeolite

Ionic Liquid

EMIM [TFO]

10%  20%  30%

EMIM [TF2N]

10%  20%  30%

Zeolite particle

IL-layer after coating

mass-% IL in ZSM-5
Membrane Preparation

1.) Dispersing in Acetonitril
2.) Adding IL
3.) ~3h mixing at 60°C & 100 mbar until solvent has evaporated

Filled in PDMS

1.) Dispersing in PDMS
2.) Adding Crosslinker
3.) Membrane Casting
4.) ~5 h Curing

Zeolite particle

IL-layer after coating

Filled in PDMS
Porosity Comparison (Pycnomatic)

- Due to small atomic size of Helium, it could penetrate into the pores like $10^{-10}$ m in diameter.
- Solid density of the sample could be measured.
- Porosity $\varepsilon = 1 - (\rho_b / \rho_s)$

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Filling level

- Without IL-coating
- 20 wt-% TF2N in Filler
Varying Coating Level With Constant Filling Level

56 wt% IL coated Zeolite in PDMS

Permeability / [Barrer]

CO₂

CH₄

N₂

Coating level

10 wt%  20 wt%  30 wt%

[EMIM TF2N-allwt%-56wt%-CO₂]
[EMIM TF2N-allwt%-56wt%-CH₄]
[EMIM TF2N-allwt%-56wt%-N₂]
Varying Filling Level With Constant Coating Level

Permeability / [Barrer]

Filling level

CO₂

CH₄

N₂

16wt% 38wt% 56wt%

Filling level

[EMIM TF2N-20wt%-allwt%-CO2]

[EMIM TF2N-20wt%-allwt%-CH4]

[EMIM TF2N-20wt%-allwt%-N2]
Modeling Part: Modified Maxwell Model

\[ P_{d,c} = P_c \cdot \frac{P_d + 2P_c + 2\Phi(P_d - P_c)}{P_d + 2P_c - \Phi(P_d - P_c)} = f(P_c; P_d; \Phi) \]

\[ P_d = P_{IL} \]

\[ P_c = P_{PDMS} \]

IL-Polymer-model

\[ P_{overall} = f(P_c = P_{PDMS}; P_d = P_{IL}; \Phi_{Fil}) \]
### Modeling Part: Modified Maxwell Model

Table 1: Permeability values for CO₂, N₂ and CH₄ in pure components

<table>
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<tbody>
<tr>
<td>Units</td>
<td>[Barrer]</td>
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<tr>
<td>CO₂</td>
<td>1171</td>
<td>1702</td>
<td>17622</td>
<td>3800</td>
<td>3500</td>
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<tr>
<td>N₂</td>
<td>29</td>
<td>74</td>
<td>4182</td>
<td>400</td>
<td>325</td>
</tr>
<tr>
<td>CH₄</td>
<td>63</td>
<td>139</td>
<td>9558</td>
<td>1200</td>
<td>1000</td>
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</tbody>
</table>

*Measured Results


IL-Polymer Model: CO$_2$

- $P_d = P_{IL}$
- $P_c = P_{PDMS}$

Coated Zeolite In PDMS

- Pexp/Pmaxwell: 20% EMIM[TF2N]
- Pexp/Pmaxwell: 10% EMIM[TF2N]

Graph showing the relationship between $P_{maxwell}$ and $P_{exp}/[Barrer]$ with different coating percentages.
IL-Polymer Model : $N_2$

\[ P_{d} = P_{IL} \]

\[ P_{c} = P_{PDMS} \]

$P_{d} = P_{IL}$

$P_{c} = P_{PDMS}$

\[ P_{exp}/P_{maxwell} \]

Coated Zeolite

20% EMIM[TF2N]

10% EMIM[TF2N]

Coated Zeolite

Coated Zeolite In PDMS

56%  38%  16%

IL-Polymer-model
IL-Polymer Model : CH$_4$

$P_d = P_{IL}$

$P_c = P_{PDMS}$

Coated Zeolite in PDMS

$P_{exp}/P_{maxwell}$

- 25%
- 0%
+ 25%

$P_{maxwell} / [Barrer]$

$P_{exp} / [Barrer]$

- P$_{exp}$/P$_{maxwell}$ 20% EMIM[TF2N] Coated Zeolite
- P$_{exp}$/P$_{maxwell}$ 10% EMIM[TF2N] Coated Zeolite
Conclusion

• Successful coating of IL on zeolite surface has been achieved.
• Permeabilty of CO$_2$, N$_2$ and CH$_4$ has been reduced by either increasing the coated level of IL on zeolite particals or by increasing the filling level of IL coated zeolite in PDMS.
• Modified Maxwell Model Results are in good conformance with the experimental results.
Our Group

Axel König
Thank you For Your Attention
TGA Analysis of IL-Coated Zeolite

![Graph showing weight loss versus temperature for different samples.]

<table>
<thead>
<tr>
<th></th>
<th>Decomposition Or Boiling Temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
</tr>
<tr>
<td>Zeolite (ZSM-5)</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>EMIM[TF2N]</td>
<td>~ 440</td>
</tr>
</tbody>
</table>
Varying Filling Level With Constant Coating Level

Permeability / [Barrer] vs. Filling level

- CO2
- CH4
- N2

[EMIM TFO-20wt%-allwt%-CO2]
[EMIM TFO-20wt%-allwt%-CH4]
[EMIM TFO-20wt%-allwt%-N2]

20 wt % IL Coated Zeolite

Fig. 4.2: Permeability decrease with increasing filling level in [TF2N-allwt%-allgases].
EMIM TF2N
1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

EMIM TFO
1-Ethyl-3-methylimidazolium trifluoromethanesulfone