Zeolitic Imidazolate Framework-8 (ZIF-8) Membranes for Kr/Xe Separation

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Xe and Kr Separation in Nuclear Reprocessing

Separating Krypton (Kr) from Xenon (Xe) is a critical step during treatment of spent nuclear fuel
- $^{85}\text{Kr} \rightarrow \text{radioactive}$
- $^{10}\text{Xe}:^{1}\text{Kr}$

Need to store $^{85}\text{Kr}$ for 100 years
- Separating Xe and Kr can save space and money!

Xe used in lighting, medical applications, including neuroprotection, imaging, and anesthesia
- Currently expensive

Benchmark separation technology: cryogenic distillation
- Energy intensive and expensive process.
Distinguishing Xe and Kr

**Membrane Separation (size)**
- Kr: Diameter = 0.37 nm, Boiling point = -153.4 °C
- Xe: Diameter = 0.41 nm, Boiling point = -108.1 °C

**Cryogenic Distillation (temperature)**

**No phase transformation!**

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic diameter (nm)</td>
<td>0.366</td>
<td>0.405</td>
</tr>
<tr>
<td>Polarizability ($10^{-25}$ cm$^3$)</td>
<td>24.844</td>
<td>40.44</td>
</tr>
<tr>
<td>Dipole moment (esu cm)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Quadruple moment (esu cm$^2$)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

ZIF-8

- Family of Metal–organic frameworks (MOFs)
- Zeolitic imidazolate framework, thermally and chemically stable
- Effective aperture size of 0.4–0.42 nm

Crystal structure of ZIF-8: Zn (polyhedral), N (sphere), and C (line)

Gas Separation Process

- Adsorption: electrostatic interaction
- Molecular sieving: membrane and gas size
- Diffusion: molecular radii and weight

- Kr (0.37 nm)
- Xe (0.41 nm)

adsorption

diffusion

membrane

0.4-0.42 nm
ZIF-8 Adsorption and Diffusion Selectivity

Diffusion is the dominant mechanism
Membrane Preparation

1. Place support in mixed solution, then in a Teflon liner.

2. Solvothermal treatment:
   - 120 °C for 4-12 hours.

3. Crystallization.
Membrane Separation Results

**Permeance** = pressure - normalized flux, membrane property

**Separation factor α** for a ratio of Kr permeance/Xe permeance.


<table>
<thead>
<tr>
<th>Membrane ID</th>
<th>Kr permeance (mol/m²·s·Pa)</th>
<th>Separation selectivity (α)</th>
<th>Separation index (π)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>0.33x10⁻⁸ (9.9)</td>
<td>5.9</td>
<td>13.6 x10⁻⁴</td>
</tr>
<tr>
<td>1B</td>
<td>0.17x10⁻⁸ (5.1)</td>
<td>10.8</td>
<td>13.9 x10⁻⁴</td>
</tr>
<tr>
<td>2A</td>
<td>1.7x10⁻⁸ (50.8)</td>
<td>12.3</td>
<td>162 x10⁻⁴</td>
</tr>
<tr>
<td>2B</td>
<td>1.3x10⁻⁸ (38.8)</td>
<td>16.1</td>
<td>164 x10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>0.5x10⁻⁸ (14.9)</td>
<td>7.9</td>
<td>28.9 x10⁻⁴</td>
</tr>
</tbody>
</table>

²¹A, 1B, 2A, 2B are two layer membranes. 3 is three-layer membrane. Numbers in parentheses indicate Gas permeation units (GPU). \( \pi = \text{Kr permeance} \times (\text{selectivity}-1) \times \text{permeate pressure} \)
SEM Images of ZIF-8 2-Layer Membranes
Conclusion and Future work

- Successfully synthesized continuous ZIF-8 membranes and first to demonstrate Kr/Xe gas separation with MOF membrane
  - Average Kr permeances as high as $1.5 \times 10^{-8} \pm 0.2$ mol/m$^2$s Pa and average separation selectivities of $14.2 \pm 1.9$ for molar feed compositions in air ratio
  - Molecular sieving, competitive adsorption, and differences in diffusivities were the prevailing separation mechanisms.
  - Promising alternative to the benchmark technology cryogenic distillation currently employed to separate Kr/Xe

- Next step:
  - Optimize synthesis parameters to improve selectivity and permeance
Thank you!

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Co-authors: Xuhui Feng, Sameh K. Elsaidi, Praveen K. Thallapally
• Kr: 83.798 g/mol
• Xe: 131.293 g/mol
Membrane Performance Parameters

**Permeance** = pressure - normalized flux, membrane property

\[
\Pi_i (mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}) = \frac{N_i}{\Delta P_i}
\]

**Permeability** = permeance * membrane thickness, material property

\[
P_i (mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}) = \Pi_i l
\]

**Separation factor** \( \alpha \) for a binary mixture of component A(CO\(_2\)) and B(CH\(_4\)):

\[
\alpha_{A/B} = \frac{(c_A / c_B)_{permeate}}{(c_A / c_B)_{feed}}
\]