Carbon Capture using a Nitrogen-Selective Membrane Process

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Clean Energy Conversions

**Mission Statement:** Tune and test materials for advanced energy conversion processes that minimize environmental impact

**Ongoing Projects**

1. **Carbon Capture**
   - N$_2$-selective membrane technology (EPA/NSF/ARL)
   - CO$_2$-selective adsorption (GCEP)

2. **Carbon Sequestration**
   - CO$_2$ transport and adsorption in micro/mesoporous systems, gas shale with kerogen and clay (DOE-NETL/BP/Aramco)

3. **Trace Metal Capture**
   - Hg, Se, As sorbent/catalyst testing (NSF/Johnson Matthey/EPRI/Novinda)

4. **Hydrogen Fuel Cells and Storage**
   - Oxygen reduction across Pt nanoparticles (Air Force/DOE)
   - Hydrogen production and storage (Shell/ARL/DOE)
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Agenda

Appreciating the Scale of CO$_2$ Emissions

N$_2$-Selective Membranes
Appreciating the Scale

- US population ≈ 311,591,000
- CH population ≈ 1,344,130,000
- Annual emissions per capita:
  - US ≈ 17.5 tons CO₂
  - CH ≈ 5 tons CO₂
- Flight from SF to Chicago RT ≈ 0.8 ton CO₂
- Drive – Toyota Prius ≈ 0.7 tons CO₂
- Drive – BMW M3 convertible ≈ 1.5 tons CO₂
- Depending on sorbent loading and performance (cycling)
  - 17.5 tons → total 150 tons material

Just the CO₂ per person in US!

Just the sorbent + CO₂ per person in US!
Capture and Regeneration are Both Key

- Capturing CO$_2$ is only ½ the story
- MUST regenerate
- Options for usage:
  - Chemical feedstock?
    - Challenge – market is small
  - Enhanced oil recovery (aka EOR)
    - Seems to be best near-term option
  - Conversion to fuel
  - Storage
    - Challenges include public perception and overcoming risks of potential seismic events

Amine Scrubbing - Current State-of-the-Art Technology for Point-Source Capture of CO$_2$
To Prevent 2 °C Warming ...

• Between 2000-2050 if cumulative emissions are less than:
  – 1,000 Gt → 25% probability global warming beyond 2 °C
  – 1,440 Gt → 50% probability global warming beyond 2 °C

Ref: Allen et al., Nature, 2009

Where we’re projected to go (BAU):
  – Assuming annual increases:
    • Coal – 0.3%
    • Oil – 0.9%
    • Natural Gas – 2.3%
  – ≈ 31 Gt CO₂ emitted in 2011
  – ≈ 44 Gt CO₂ projected in 2050
  – 1790 cum. Gt CO₂ in 2050!

Ref: BP Statistical Rev. of World Energy, 2012
Expanding the Impact of CCS

**Scenario Cumulative Gt CO₂**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Cumulative Gt CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replace Coal w/ NG</td>
<td>1512</td>
</tr>
<tr>
<td>90% Capture (Point Source Electric Sector)</td>
<td>1288</td>
</tr>
<tr>
<td>90% Capture (Point Source Electric Sector) + 50% Transport (on-board capture; EV; DAC)</td>
<td>1083</td>
</tr>
</tbody>
</table>
The Majority of the CO\textsubscript{2} Sources are Moderate to Extremely Dilute

<table>
<thead>
<tr>
<th>Category</th>
<th>% CO\textsubscript{2} (vol)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Pressure</td>
<td>varies</td>
<td>Gas Wells (e.g., Sleipner) Synthesis Gas (e.g., IGCC)</td>
</tr>
<tr>
<td>High Purity</td>
<td>90-100%</td>
<td>Ethanol Plants Oxy-Combustion Exhaust</td>
</tr>
<tr>
<td>Dilute to Moderate</td>
<td>10-20%</td>
<td>Coal-Fired Power Plants Cement Plants Cracker Exhaust</td>
</tr>
<tr>
<td>Very Dilute</td>
<td>3-7%</td>
<td>Natural Gas Boilers Gas Turbines</td>
</tr>
<tr>
<td>Extremely Dilute</td>
<td>0.04 – 1%</td>
<td>Ambient Air transport sector</td>
</tr>
</tbody>
</table>
CCS Progress to Date

- 4 large-scale CCS projects have carried out monitoring sufficient to ensure injected CO₂ is permanently sequestered
- Combined, ~50 MtCO₂ has been stored
- 9 additional projects under construction + ~13 MtCO₂/yr and expected to be operational by 2016
- 2 possible demonstration projects at iron and steel plants and one at coal-to-chemicals/liquids – advanced stages of planning
- CO₂ pipeline transport is a mature technology w/ more than 3700 miles of pipelines in the U.S.
- CCS may be the primary large-scale option for emissions reductions from the industrial sector, e.g., cement, iron and steel, chemicals and refining, which represent ~20% of total global emissions
- CO₂ emissions from current systems under construction as of 2011 (e.g., power plants, industrial facilities, etc.) will total ~550 GtCO₂ through 2035

IEA CCS Roadmap, 2013; Global CCS Institute, 2013
Where CCS should be by 2050 - IEA

- IEA analysis shows that CCS is an integral part of any climate model where average global temperate increases are $< 2\text{-}4^\circ C$ (Edmonds et al., 2010; IPCC, 2007)
- Growth needs to increase from tens of Mt$\text{CO}_2$/yr $\rightarrow$ Gt$\text{CO}_2$/yr from 2013 to 2050

**Steps Required**

- By **2020**, CO$_2$ capture must be successfully demonstrated in at least 30 projects across sectors - leading to over 50 Mt$\text{CO}_2$/yr and safely and effectively stored
- By **2030**, CCS is routinely used to reduce emissions and is successfully demonstrated for industrial applications leading to over 2 Gt$\text{CO}_2$/yr of storage
- By **2050**, CCS is routinely used to reduce emissions across power and industry sectors w/ over 7 Gt$\text{CO}_2$ stored annually
Considering *other* Separation Process
Membranes and Adsorption

- **Benefits of Adsorption:**
  - Absence of water
  - Absence of corrosive solvents
  - Greater options for choosing heat properties

- **Benefits of Membranes:**
  - No regeneration
  - Space efficiency
  - No phase change

Wilcox et al., Annu. Rev. Chem. Biomol. Eng., to be published
... and finding ways not to bend CO$_2$

From Springer site:
Agenda

Appreciating the Scale of CO$_2$ Emissions

N$_2$-Selective Membranes
The Team - Theory, Experiments, and Optimization

Theory and Experiments

PhD students:
Ni Rochana, Ekin Ozdogan, Kyoungjin Lee

Optimization

PhD students:
Mengyao Yuan, Tao Narakornpijit

Post-doc:
Dr. Reza Haghpanah
**N\textsubscript{2}-Selective Membrane for Carbon Capture**

**Flux:**

\[
J = \frac{Q}{L} \left( P_{\text{feed}}^n - P_{\text{permeate}}^n \right)
\]

- Capture CO\textsubscript{2} on the high-pressure side of the membrane may lead to cost savings in terms of compression energy.
- Separate solubility and diffusivity studies indicate N\textsubscript{2} can move through metals.
- Potentially produce ammonia at lower energy costs.


U.S. Patent 8,440,000
N and O Diffusivity in Vanadium

Permeability = Diffusivity × Solubility

Flux Measurements

- Feed or Sweep gases (N₂, Ar, He, H₂, CO₂, etc.)
- Bubble flow meter or Mass spectrometer
- Membrane Module (in the furnace)
- Retentate
- Feed
- Sweep gas
- Permeate
- High temperature furnace (500 -1000°C)
- Back-pressure regulator
Nitrogen permeability measurement

- Nitrogen permeability through vanadium is higher by two orders of magnitude than its permeability through niobium.
- Compare to the hydrogen permeability through Pd membrane \((1.6 \times 10^{-8} \text{ mole/m\cdot s\cdot Pa}^{0.5})\) – how can we increase this?
CO₂ permeability is lower than nitrogen by 5 orders of magnitude in vanadium.

CO₂ is expected to diffuse through the defects in the metals.
Membrane *Bulk* After Permeation

**X-ray Diffraction (XRD) on V membranes**

*Bulk* vanadium nitride phases formed after exposure to $N_2$ at high temperature
Material Screening and DFT

1. Surface activity
   • N₂ adsorption mechanism
   • N₂ dissociation pathway
   • Comparison to other typical ammonia synthesis catalysts

2. Solubility and Diffusivity
   • Atomic N binding mechanism
   • Comparison to atomic H binding

3. Effect of alloying
   • Ru
   • Effect on binding
   • Implications for permeability

Computational Methodology

VASP (Vienna ab initio Simulation Package)

Density functional theory (DFT)
   • Projector-augmented wave (PAW) potential
   • GGA – PBE

<table>
<thead>
<tr>
<th>Bulk vanadium</th>
<th>Lattice constant [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>2.98</td>
</tr>
<tr>
<td>Previous calculation</td>
<td>2.93-2.94</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.021</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.024</td>
</tr>
</tbody>
</table>

### Increase Permeability by Alloying

<table>
<thead>
<tr>
<th>Pure Vanadium</th>
<th>Distance (N-Ru)= 0.5 Å</th>
<th>Distance (N-Ru)= 0.71 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Lattice Constant= 3.01 Å</td>
<td>Lattice Constant= 3.02 Å</td>
<td>Lattice Constant= 3.01 Å</td>
</tr>
<tr>
<td>$E_b$= -2.132 eV</td>
<td>$E_b$= -0.889 eV</td>
<td>$E_b$= -1.48 eV</td>
</tr>
<tr>
<td>Lattice Expansion= 1.01%</td>
<td>Lattice Expansion= 1.34%</td>
<td>Lattice Expansion= 1.01%</td>
</tr>
</tbody>
</table>

H binding in V:  O-site = -0.076eV; T-site = -0.280eV

![Abou and Wilcox, J. Phys. Chem. C, 2010; Pauling-Scale Electronegativities: N = 3.04; V = 1.63; Ru = 2.2](image4.png)
Making Alloy-Based Membranes is Difficult!
Alloy metal deposition strategy

**Sputtering**
- Conformal and good adhesion
- Slow (roughly 10-20 nm/min)
- Limited thickness

**Evaporation**
- Directional, moderate adhesion
- Slow & limited thickness

**Chemical Vapor Deposition (CVD)**
- Metal oxide deposition (diffusion barrier)
- Conformal & fast

**Availability**
- Shared equipment at Stanford Nanofabrication Facility (SNF)
  - Prof. William Chueh (Stanford)
  - Dr. Steve Paglieri (TDA)

- Shared equipment at SNF and Stanford Nano Center (SNC)

- Shared equipment at SNF
### Shared facilities at Stanford for metal deposition

<table>
<thead>
<tr>
<th>Name</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>KJ Lesker e-beam evaporator</td>
<td>Installed targets: Ti, Ta, Al, Au, Pd, Pt, Nb, and Ag. Additional materials possible based on user demand. Thickness limited to couple of hundred nm. Contact: Cliff Knollenberg (Spilker basement)</td>
</tr>
<tr>
<td>E-Beam Evaporator, Innotec</td>
<td>Installed targets: Ag, Al, Au, Co, Cr, Cu, Fe, Ge, In, Mo, Ni, Pd, Pt, Si, Ti, Ta, and W. Allowed but not installed: Er, Hf, Ir, Ru, Tb, and Y. Precious metal is limited to 200 nm; Others &lt; 1µm</td>
</tr>
<tr>
<td>Magnetron sputtering, Metallica</td>
<td>Installed targets: Ag, Al, Au, Cr, Cu, Mo, NiCr, Pd, Pt, Ti, W and TiW 90/10wt%. Rate: Au 60 nm/min, Ti, Cr 4 nm/min, Cu at 20 nm/min (one wafer at a time). Ferromagnetic materials (Co, Ni, Fe) cannot easily be sputtered. Max: 1µm (sputter should cool down after 10 min). Reasonably conformal film. Maybe able to bring our own target (1” dia, 1/8” thick).</td>
</tr>
</tbody>
</table>
Improvements in membrane sealing in module

Previous
- One graphite gasket
- Temperature limited
- Ceramic breakage

Improvement
- Two SOFC gasket (made of clay)
- Higher operating temperature (>700°C)
- Buffering ceramic disk
Consideration of Realistic Flue Gas

$H_2O, NO, NO_2, SO_2$
Experimental setup

- Expose clean vanadium to each gas species (in N₂) at 600 °C for 1 hr, 3 hrs, and 5 hrs
- Follow up by XPS characterization (SSI and PHI)

<table>
<thead>
<tr>
<th>component</th>
<th>reference flue gas* conc.</th>
<th>experimental conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(g) [vol%]</td>
<td>7.22%</td>
<td>10%</td>
</tr>
<tr>
<td>SO₂ [ppm]</td>
<td>425</td>
<td>495</td>
</tr>
<tr>
<td>NO [ppm]</td>
<td>231</td>
<td>245</td>
</tr>
<tr>
<td>NO₂ [ppm]</td>
<td>12</td>
<td>14</td>
</tr>
</tbody>
</table>

* coal: Appalachian Low Sulfur in IECM
Blank V samples - unsputtered

Surface C and Na removed by N$_2$
SO$_2$-exposed (495 ppm) V samples, unsputtered

Difference from SSI vs. PHI?
NO-exposed (245 ppm) V samples, unsputtered

- O(1s)
- V(2p3)
- C(1s)
- Na(1s)
- N(1s)

Bar chart showing the percentage of each element for different time periods:
- 1hr-SSI: 2.9%
- 1hr-PHI: 0.5%
- 3hr-PHI: 2.4%
- 5hr-PHI: 4.9%
NO$_2$-exposed (14 ppm) V samples, unsputtered

Same sample

Difference – SSI vs. PHI

- O(1s)
- V(2p3)
- C(1s)
- Na(1s)
- N(1s)
H$_2$O-exposed (10 vol%) V samples, unsputtered

![Graph showing the percentage of elements O(1s), V(2p3), C(1s), and Na(1s) after exposure times of 1hr-SSI, 3hr-SSI, and 5hr-PHI.]
Where Does this Technology Fit Best?

...in a power plant, ammonia synthesis optimization helps to answer this
Membrane Configurations: \( \text{N}_2 \)-Selective Membranes

**Config. 1:** Single-stage \( \text{N}_2 \)-selective membrane

**Config. 2:** 2-stage \( \text{N}_2 \)-selective membranes, with pressurization on 1\(^{st}\)-stage feed

**Config. 3:** 2-stage \( \text{N}_2 \)-selective membranes, \textbf{no} pressurization on 1\(^{st}\)-stage feed

Hybrid Configurations: $\text{N}_2^-$ + $\text{CO}_2^-$-Selective Membranes

**Config. 4**: 1$^{\text{st}}$-stage $\text{N}_2^-$-selective membrane with feed pressurization, 2$^{\text{nd}}$-stage $\text{CO}_2^-$-selective membrane

**Config. 5**: 1$^{\text{st}}$-stage $\text{N}_2^-$-selective membrane with no feed pressurization, 2$^{\text{nd}}$-stage $\text{CO}_2^-$-selective membrane

**Config. 6**: 1$^{\text{st}}$-stage $\text{CO}_2^-$-selective membrane with feed pressurization, 2$^{\text{nd}}$-stage $\text{N}_2^-$-selective membrane

Optimization Results

Promising Application
“CO₂ Enrichment”

In Summary

• Proof of Concept: nitrogen permeates through Group V metals and is selective over CO$_2$ via a solution-diffusion mechanism
• From DFT, atomic N draws significant charge from V leading to stabilization and “bonding” in the lattice
• Alloying with Ru significantly reduces atomic N stability in V
• Vanadium seems to be able to withstand acid gases, but further work is required
• N$_2$-selective membranes have shown great potential as feed CO$_2$ enrichers for CO$_2$-selective membranes
• Future work will involve investigation (ASPEN) of impact removal of N2 has on remainder of power plant operations
• Future work will include investigation of alloy synthesis and testing
Acknowledgements

Helpful Discussions (Membrane Research)
Dr Steve Paglieri, TDA Research

Funding
• Membranes: NSF, Catalysis Division; EPA; Army Research Lab
• Supercomputing: CEES (Stanford), NSF Teragrid, UT Austin

Additional Information
Clean Energy Conversions Website: http://cec-lab.stanford.edu/
Questions?

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