Taking Fundamentally New Materials for CO₂ Capture Toward Applications: A Synergistic Effort

Presented by Jeff Kortright, LBNL (for Berend Smit)
Acknowledgements

Researchers

E. Albenze 1
T.H. Bae 4
S. Bowser 3
K. Damodaran 3
W. Drisdell 5
M. Haranczyk 1
J. Kim 5
J. Duldeep 6
J.B. Kortright 5
M. Lartey 1
J.R. Long 4,5
D. Luebke 1
J. Meyer-Ilse 5
J.B. Neaton 5,4
H. Nulwala 1,2
D. Prendergast 5
R. Poloni 4
B. Smit 4,5
R.L. Thompson 1,7
F. Yang 4,2

1NETL
2CMU
3U. Pittsburgh
4U.C. Berkeley
5LBNL
6eMolecules
7URS Corp

DOE facilities

NERSCC, LBNL
Advanced Light Source, LBNL
Molecular Foundry, LBNL

Funding (to LBNL)

DOE, Fossil Energy, Carbon Capture Program
FWP MSKCBS
~250K$/year for 3 years
Combine strengths of Berkeley & NETL

• Synthesis of MOFs tailored for gas separations & other applications
• Computational methods, *ab initio* theory
• Advanced characterization development (NMR, soft x-ray synchrotron techniques)
• National facilities (NERSCC, ALS, MF)

• Mitigating strategies for fossil fuel use
• Novel membranes for CO₂ capture
• Ionic liquids for CO₂ capture
Open metal site & functionalized MOFs

**Mg$^{2+}$-MOF-74**

Amine-functionalized variant exhibits phase-change isotherm relevant to CO$_2$ capture.

**Tom McDonald, et al., JACS 2012, 134, 7056**  
(see poster)

**Sumida, et al., Chem. Rev. 2012, 112, 724**
CO₂ adsorption isotherm via Mg K-edge absorption in Mg-MOF-74

- Reversible spectral changes as CO₂ adsorbs & desorbs at open Mg²⁺ sites.
- Ab initio theoretical & experimental spectra agree.
- Direct confirmation of 1ˢᵗ principles description of MOFs that includes VdW interactions.

Mixed matrix membranes incorporating Mg-MOF-74

- Mg-MOF-74 nanocrystals in polyimide membranes perform nearly as well as bulk material.
- CO₂/N₂ selectivity maintained.
- Rubbery polymers reduce CO₂ adsorption by blocking access to pores.
- Possible approach to implement MOFs in CO₂ capture.

T.H. Bae, T. McDonald, J.R. Long, *Energy Environ. Sci.* 2013, 6, 3565
Intermolecular interactions in ionic liquids for CO$_2$ capture

- Major interaction between CO$_2$ and anion
- Cation interacts strongly with anion
- Tuning cation may indirectly but significantly affect CO$_2$ solubility
Towards a Materials Genome Approach for Ionic Liquids: Synthesis Guided by *Ab Initio* Property Maps

**F. Yang**, M. Lartey, K. Jariwala, S. Bowser, K. Damodaran, E. Albenze, **D. Luebke**, H. Nulwala, B. Smit, M. Harancyzk,

*J. Phys. Chem. (submitted for publication)*
Consider unexplored triazolium based ILs

- Limit $R_1$, $R_2$, $R_3$ to hydrocarbons C1 – C8
- 33 common anions in including Tf$_2$N$^-$
- Limit IL combinations to ~200,000 (from ~2M)
- Develop \textit{ab initio} force fields for 20 ILs spanning large set, calculate:
  - Density
  - Ion diffusivity, viscosity
  - Henry coefficients for CO$_2$, etc.
- Find most strongly correlated chemical descriptors (maximum projection area, maximum projection volume, VdW volume)
- Use neural network and other methods to extrapolate properties over entire IL set.

Property maps for $\rho$, $k_H$, $D_+$, etc.

Projected onto 2 strongest principal components, PC1, PC2

Blue = full force field simulation for training algorithms
Red = experimental calibration (synthesize & test)
Comparison with experiment

Simulated property maps

Experimental verification (E1-E15)

CO₂ Henry coefficient

![CO₂ Henry coefficient graph]

Predicted Henry coefficient [1/bar]

Experimental Henry coefficient [1/bar]

y = 2.4195x - 16.853
R² = 0.8964

Cation diffusivity

![Cation diffusivity graph]

Predicted D⁺ at 400K [m²/s]

Experimental D⁺ at 303K [m²/s]

y = 1.3294x + 7 × 10⁻¹²
R² = 0.9614
Further extrapolation of calculated properties w.r.t. trend lines
Final results: strong anion dependence

\[ B(CN)_4^- > FEP^- > PF_4(C_2F_5)_2^- > Tf_2N^- \]
Comparative study of 4 ILs w/ Tf$_2$N$^-$ anion: effect of isomeric cation branching

- ILs with various degree of branching were synthesized.
- Simulated density and CO$_2$ solubility do not match with experimental trends.
- Unusual thermodynamic trends not systematic w/ branching

<table>
<thead>
<tr>
<th>IL</th>
<th>Number of branches</th>
<th>Density / g.cm$^{-3}$</th>
<th>Molar volume / cm$^3$.mol$^{-1}$</th>
<th>Henry’s Law Constant CO$_2$ / bar</th>
<th>$H$ / cP</th>
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</thead>
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<tr>
<td>(I)</td>
<td>0</td>
<td>1.366</td>
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<tr>
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<tr>
<td>(IV)</td>
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<td>1.346</td>
<td>354.1</td>
<td>32.2</td>
<td>103.2</td>
</tr>
</tbody>
</table>
XAS at C, N, O, and F K-edges reveals unexpected dependence on branching

- Spectra of ILs I & IV (II & III) are nearly identical.
- Specific C-A interactions depend on symmetry of distribution of R groups.
- O & N differences may relate to Tf2N\(^-\) conformational differences.
- C differences sense R-group C-H & C-C bonds; H bonding(?).
Summary

• Materials Genome approach combines many types of algorithms to screen ~ 200,000 ILs for their CO$_2$ capture potential. Impressive demonstration.

• Should be extendable to other well-defined problems.

• MGA relies on experimental calibration points.

• MGA effectively coarse-grains over fine details of intermolecular interactions.

• Experiments can observe trends that do not follow coarse-grained MGA predictions, evidently due to fine details of C-A interactions. Can *ab initio* theory capture these subtle trends?