Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture

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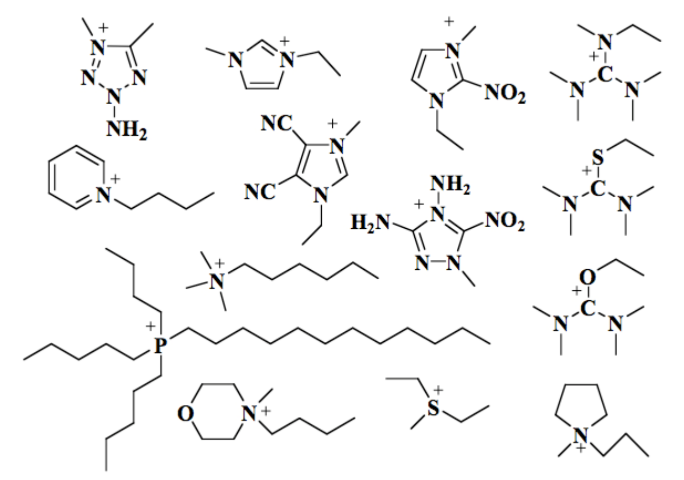
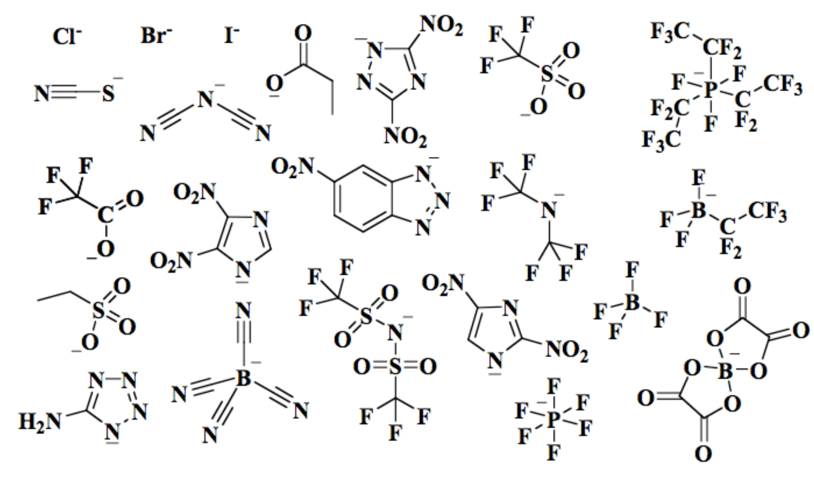
Ionic Liquids

- Pure salts that are liquid around ambient temperature
  - Not simple salts like alkali salts
- Many favorable properties
  - **Nonvolatile**
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity

Examples of cations



Examples of anions

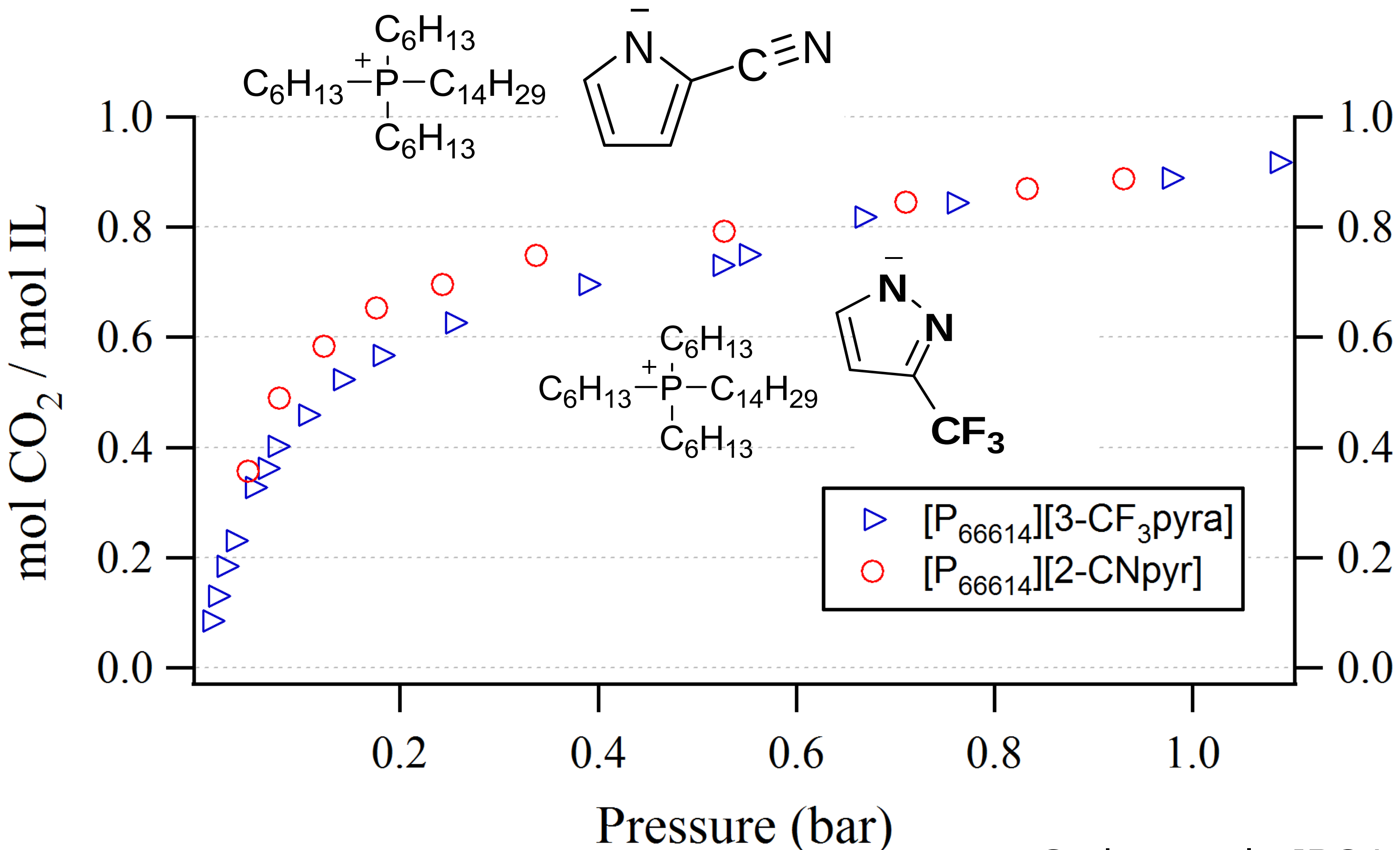


Ionic Liquids for CO_2 Capture – Previous Work

- Equimolar capacity – 1 mol CO_2/mol IL

AHA – aprotic heterocyclic anions

- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding

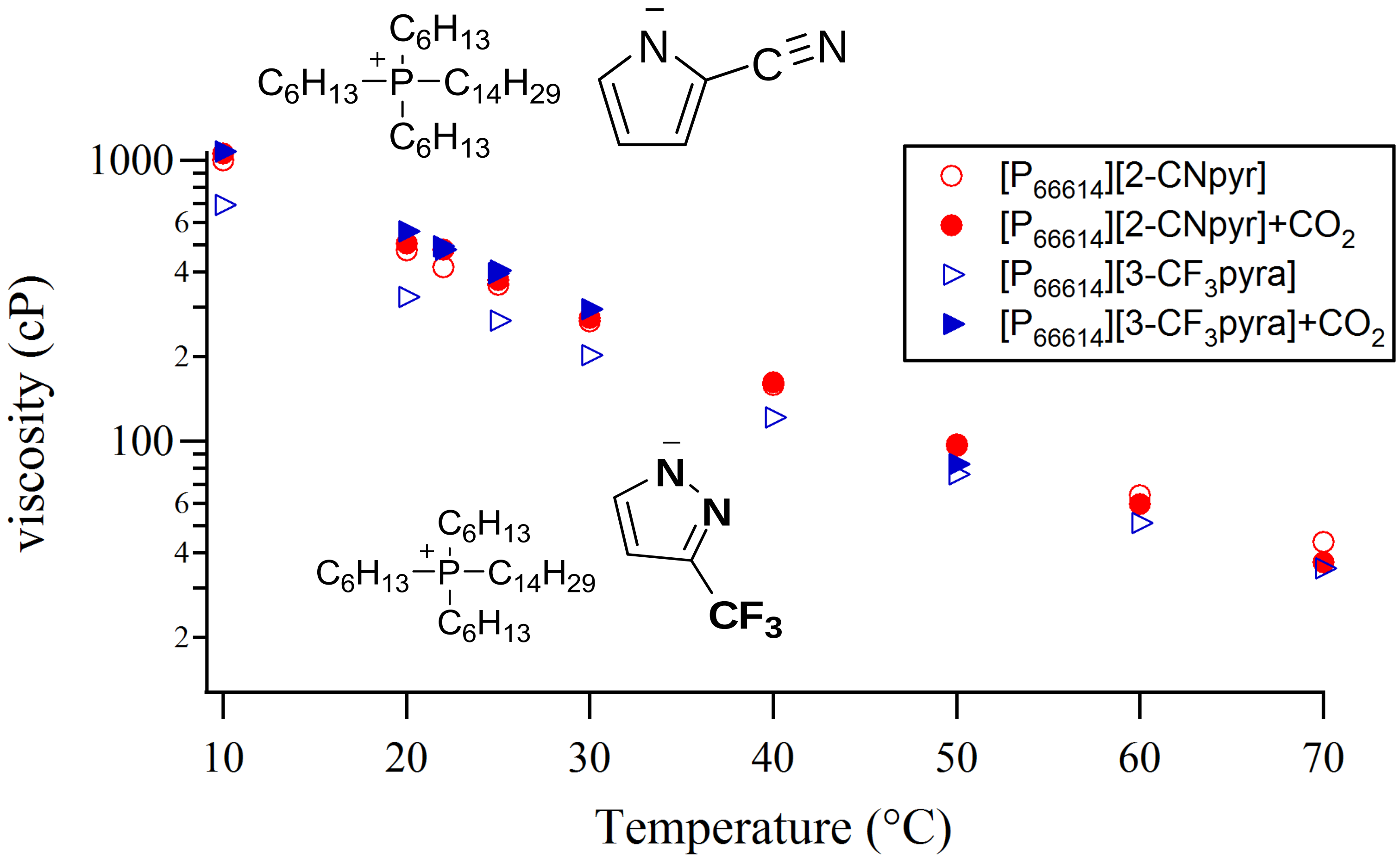


Gurkan et al., JPC Lett, 2010

Ionic Liquids for CO_2 Capture – Previous Work

- Equimolar capacity – 1 mol CO_2/mol IL
- No viscosity increase upon reaction with CO_2

Eliminate Viscosity Increase by Using AHA – aprotic heterocyclic anions

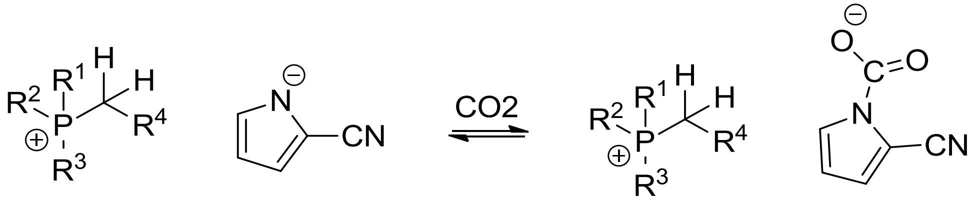


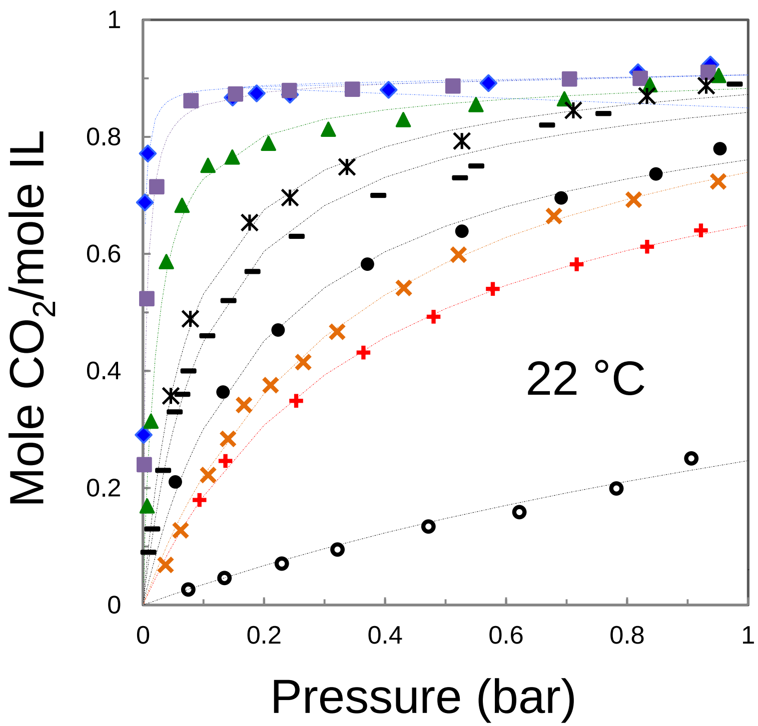
Gurkan et al., JPC Lett, 2010

Ionic Liquids for CO_2 Capture – Previous Work

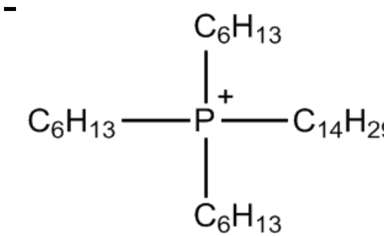
- Equimolar capacity – 1 mol CO_2/mol IL
- No viscosity increase upon reaction with CO_2
- Tunable enthalpy of reaction

Tuning Reaction Enthalpy of AHA ILs





	ΔH_{rxn} (kJ/mol)
[Inda]	-54
[BnIm]	-52
[6-BrBnIm]	-48
[2-SCH_3BnIm]	-41
[2-CNPyr][a]	-45
[3-CF_3Pyra][a]	-44
[3-CH_3-5-CF_3Pyra]	-41
[3-Triaz]	-37
[4-Triaz]	-42



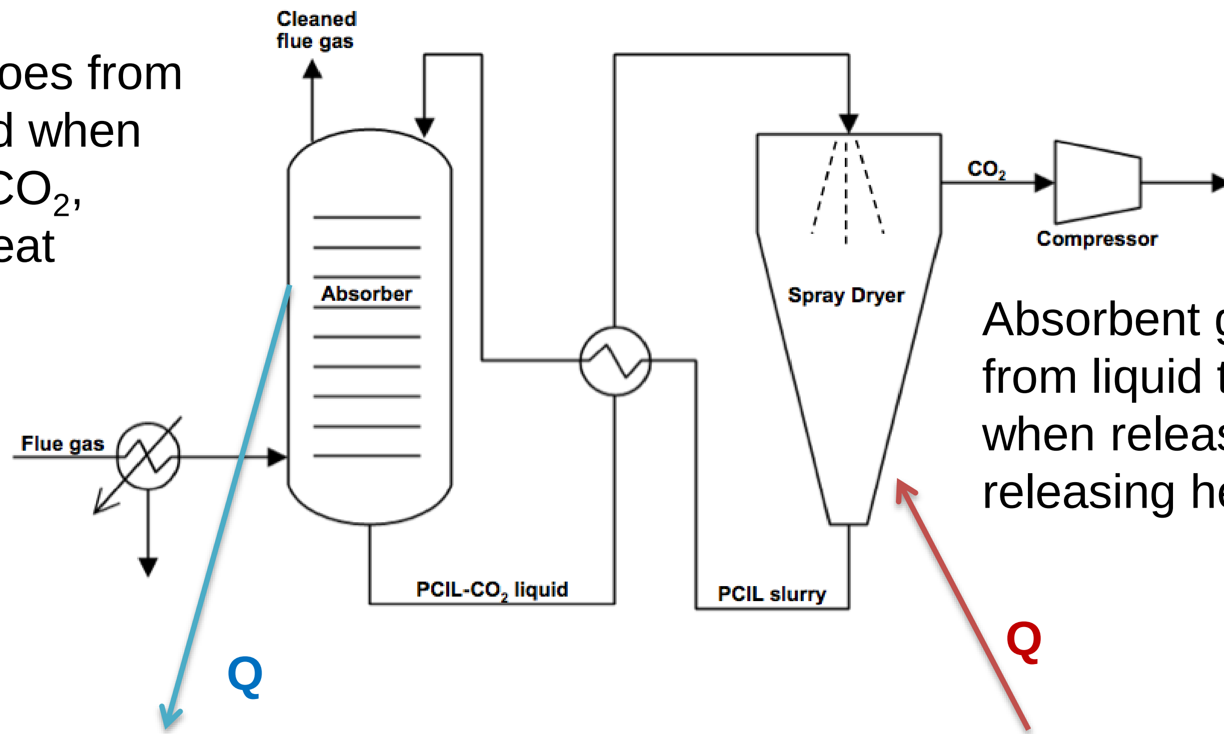
Seo et al., JPC B, 2014, 118, 5740

Ionic Liquids for CO_2 Capture – Previous Work

- Equimolar capacity – 1 mol CO_2/mol IL
- No viscosity increase upon reaction with CO_2
- Tunable enthalpy of reaction
- Phase change ionic liquids

CO_2 Capture with Phase Change Material

Absorbent goes from solid to liquid when reacts with CO_2, absorbing heat



Absorbent goes from liquid to solid when releases CO_2, releasing heat

'Melting' of absorbent reduces cooling duty

Heat duty in stripper reduced by the heat of fusion of the phase change material

CO_2 Capture with Phase Change Material

Absorber

Remove
50 kJ/mol

$[C^+][A^-]\ (s) + CO_2 \longrightarrow [C^+][ACO_2^-]\ (s)$

exothermic

$[C^+][ACO_2^-]\ (s) \longrightarrow [C^+][ACO_2^-]\ (l)$

endothermic

Add
20 kJ/mol

Q_{net} = Remove 30 kJ/mol

Regenerator

Add
50 kJ/mol

$[C^+][ACO_2^-]\ (l) \longrightarrow [C^+][A^-]\ (l) + CO_2$

endothermic

$[C^+][A^-]\ (l) \longrightarrow [C^+][A^-]\ (s)$

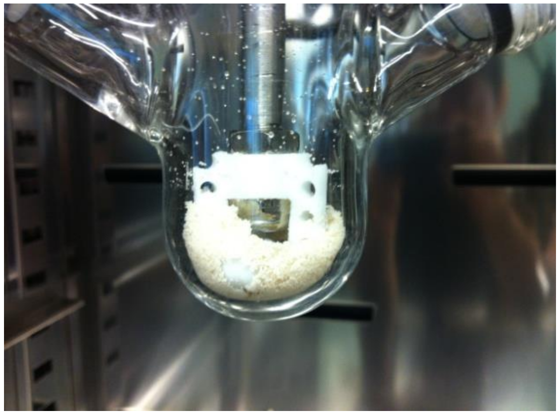
exothermic

Remove
20 kJ/mol

Q_{net} = Add 30 kJ/mol

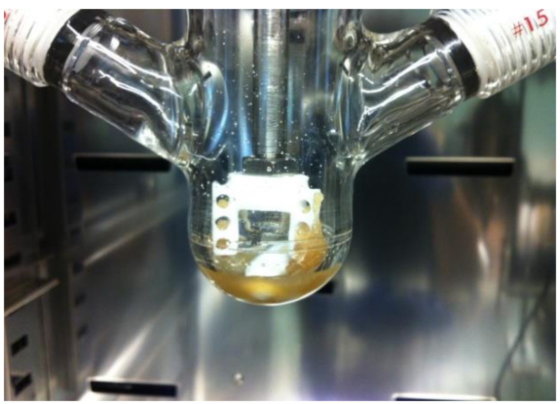
Phase Change Ionic Material

70 °C

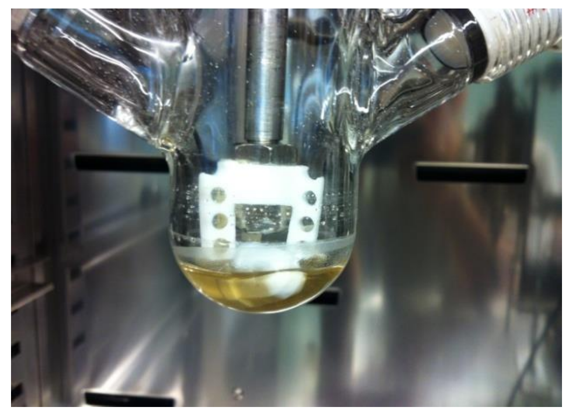


Pure material; T_m=166 °C; no CO_2

60 mbar CO_2

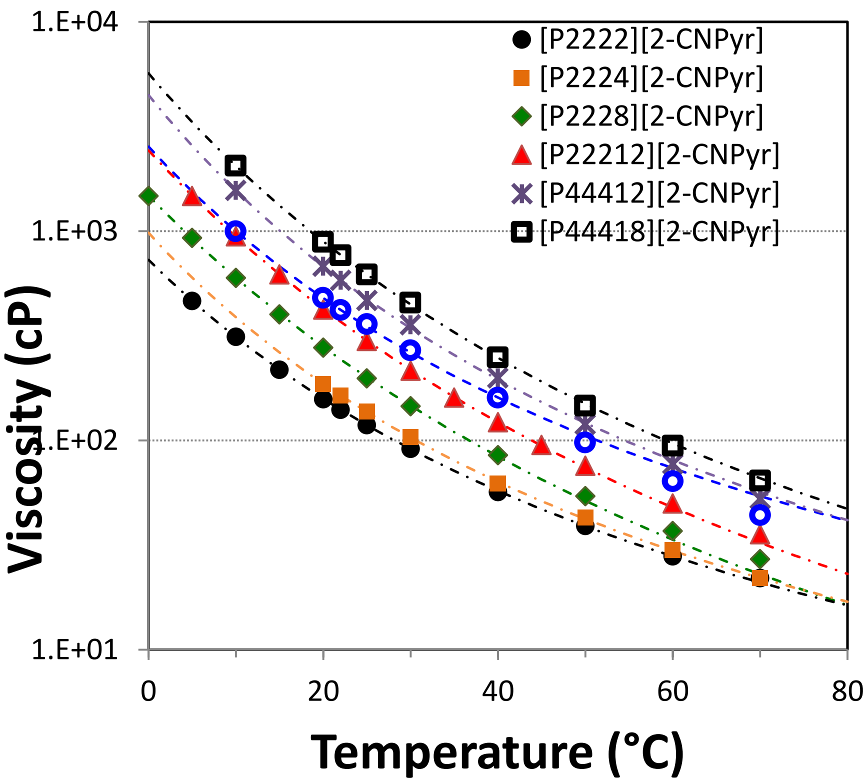


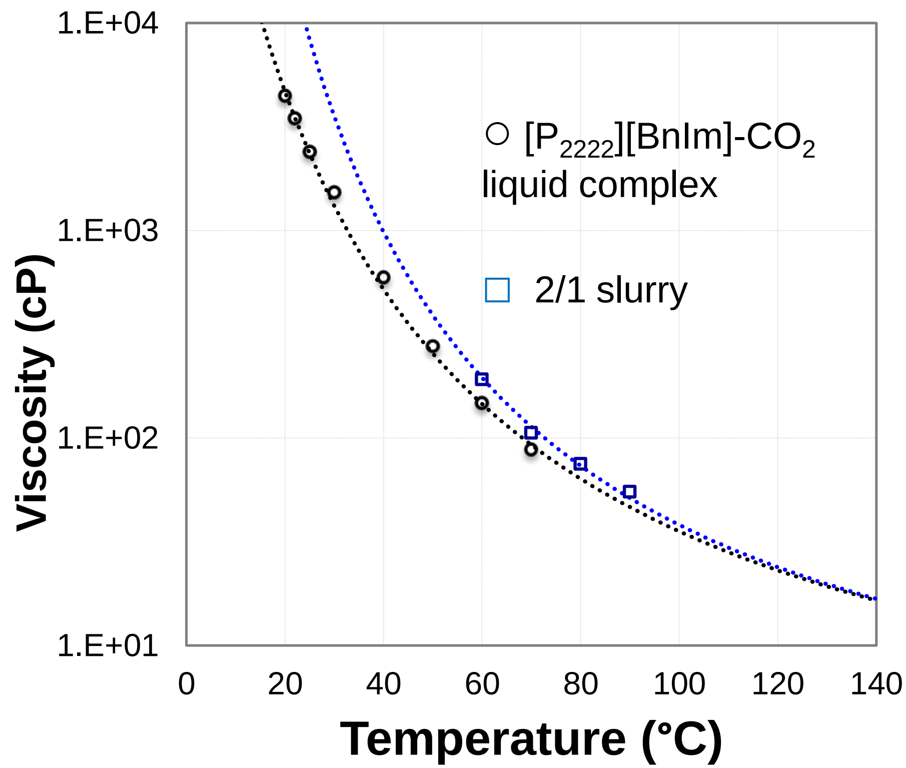
100 mbar CO_2



150 mbar CO_2

Challenge: High Viscosity/Poor Mass Transfer



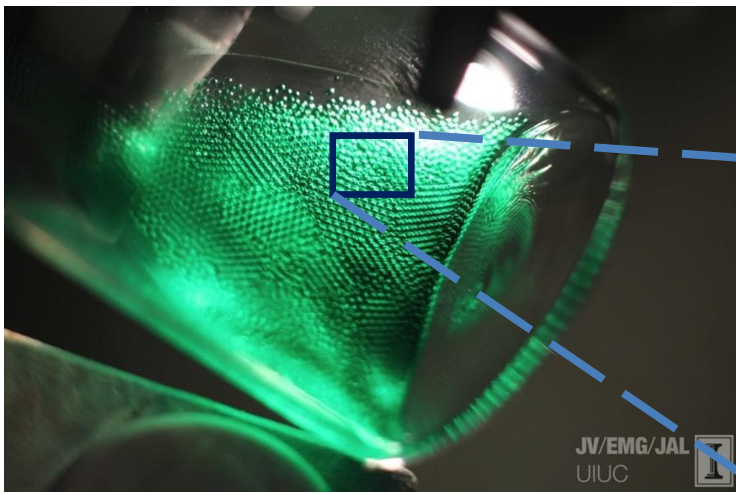


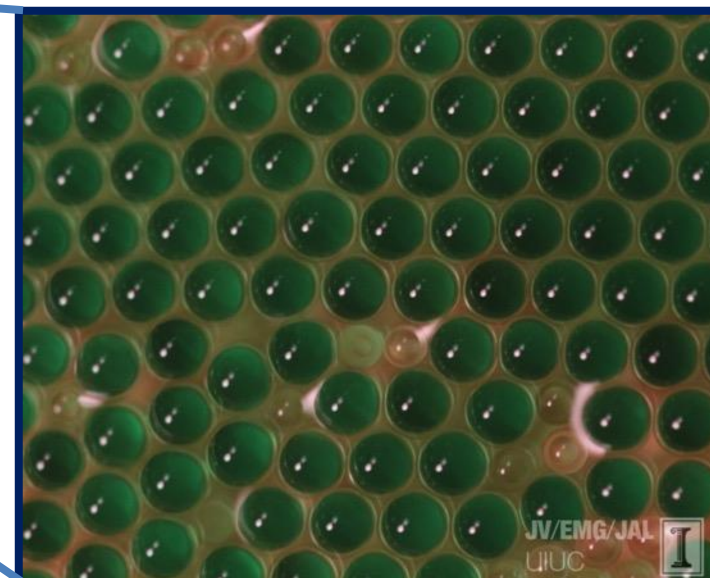
Seo et al., Energy & Fuels, 2014, 28, 5968-5977

Microencapsulation

• Idea: improve mass transfer by increasing mass transfer AREA

• Successfully demonstrated by LLNL for other CO_2 sorbents





- Multiple solvents, shell materials, and sizes produced

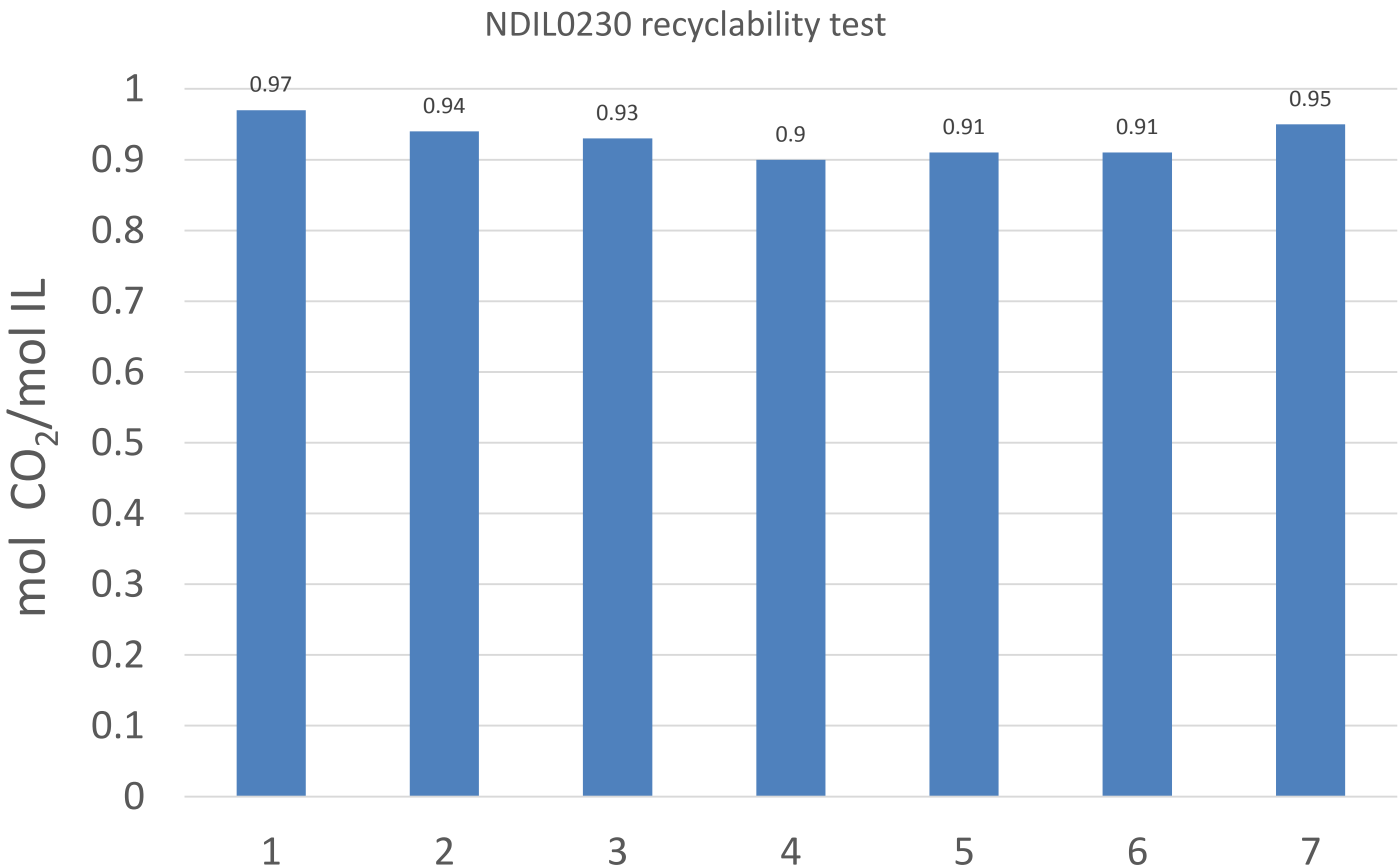
Selection of ILs and PCILs

- Evaluated 9 IL and 10 PCIL candidates
- Criteria
  - Melting point
  - Thermal stability
  - Enthalpy of reaction with CO_2 between -45 and -60 kJ/mol
  - Viscosity
  - $T_m^{complex} < T_m^{pure}$ for PCIL
- ILs: NDIL0230 and NDIL0336
- PCILs: NDIL0309 and NDIL0335

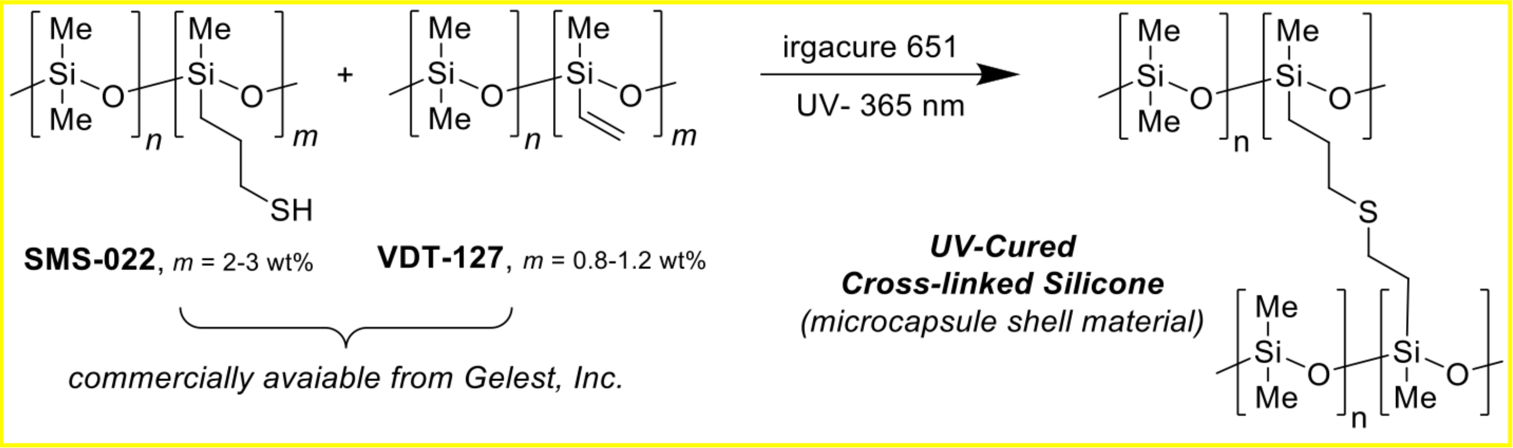
Bulk IL Recyclability Testing

- Leading IL candidate – PCIL0230
- Room temperature in volumetric apparatus
- Exposed to CO_2 at 1 bar; determine equilibrium uptake
- Heat at 60 °C and vacuum (~5 torr) for 5 hours to desorb
- Reabsorb at RT and 1 bar CO_2
- Repeat

IL Recyclability Testing



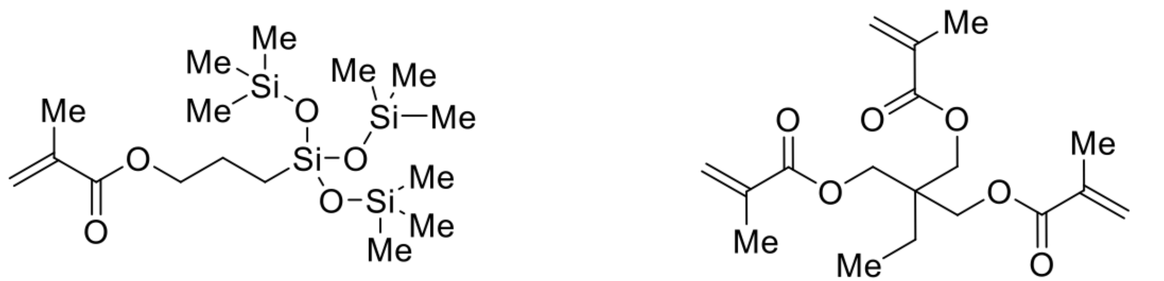
Identification of IL and PCIL-compatible shell material and/or curing process



Scheme 1: Formulation of thio-lene shell material

Two new shell materials were created for CO_2 capture solvents

Active Monomer | *Crosslinker*

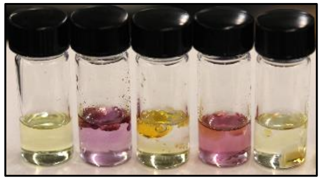


SiTRIS 3-[Tris(trimethylsiloxy)silyl]propyl methacrylate

TMPTMA Trimethylolpropane trimethacrylate

Scheme 1: Formulation of SiTRIS shell material

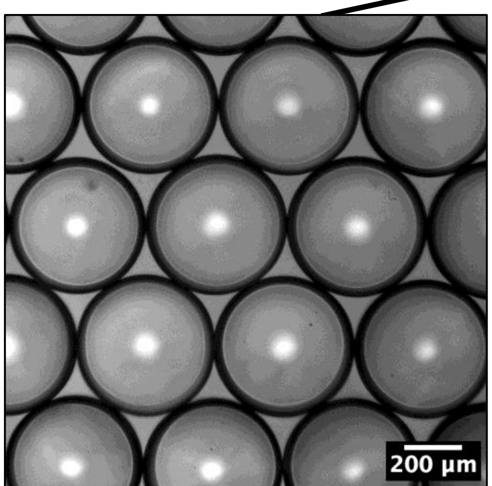
Identification of IL and PCIL-compatible shell material and/or curing process

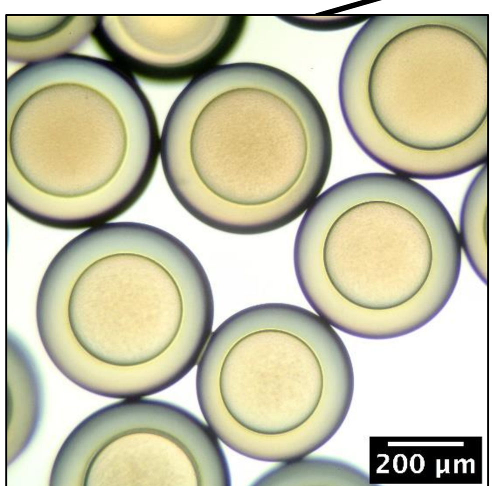


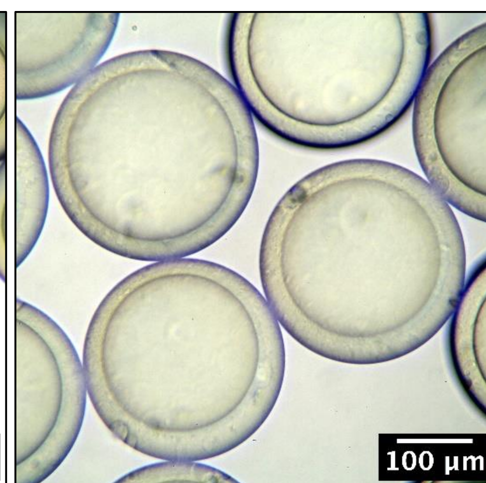
Systematic core-shell screening identified promising pairs

Good properties for encapsulation	Marginal properties for encapsulation	Not compatible

	NDIL0274	NDIL0252	NDIL0231	NDIL0231 1:1 wt. water	NDIL0230	NDIL0230 1:1 wt. water	NDIL0309 (solid powder)	NDIL0309 w/ 1:1 wt. water
Semi-cosil				×		×		
Thiol-ene				×				✓
SiTRIS (80:20)				✓		✓ (w/ 1:3)		







× encapsulation attempted and failed

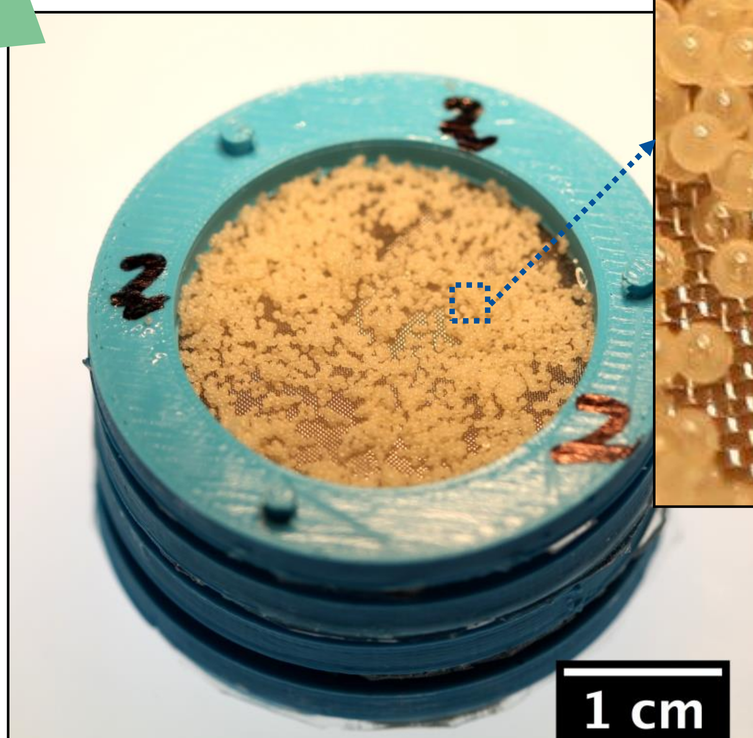
✓ encapsulation succeeded

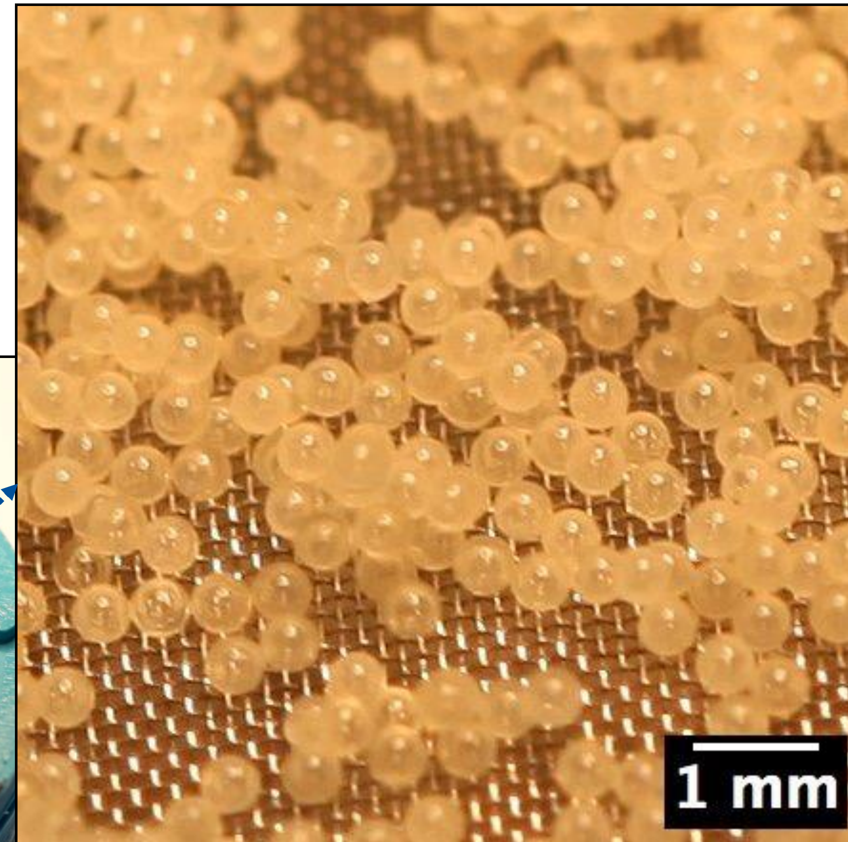
Encapsulated IL Production

NDIL0231-SiTRIS microcapsules washed and dried at 60 °C x 6 hours:

Washed with DI water repeatedly and then dried on mesh holder

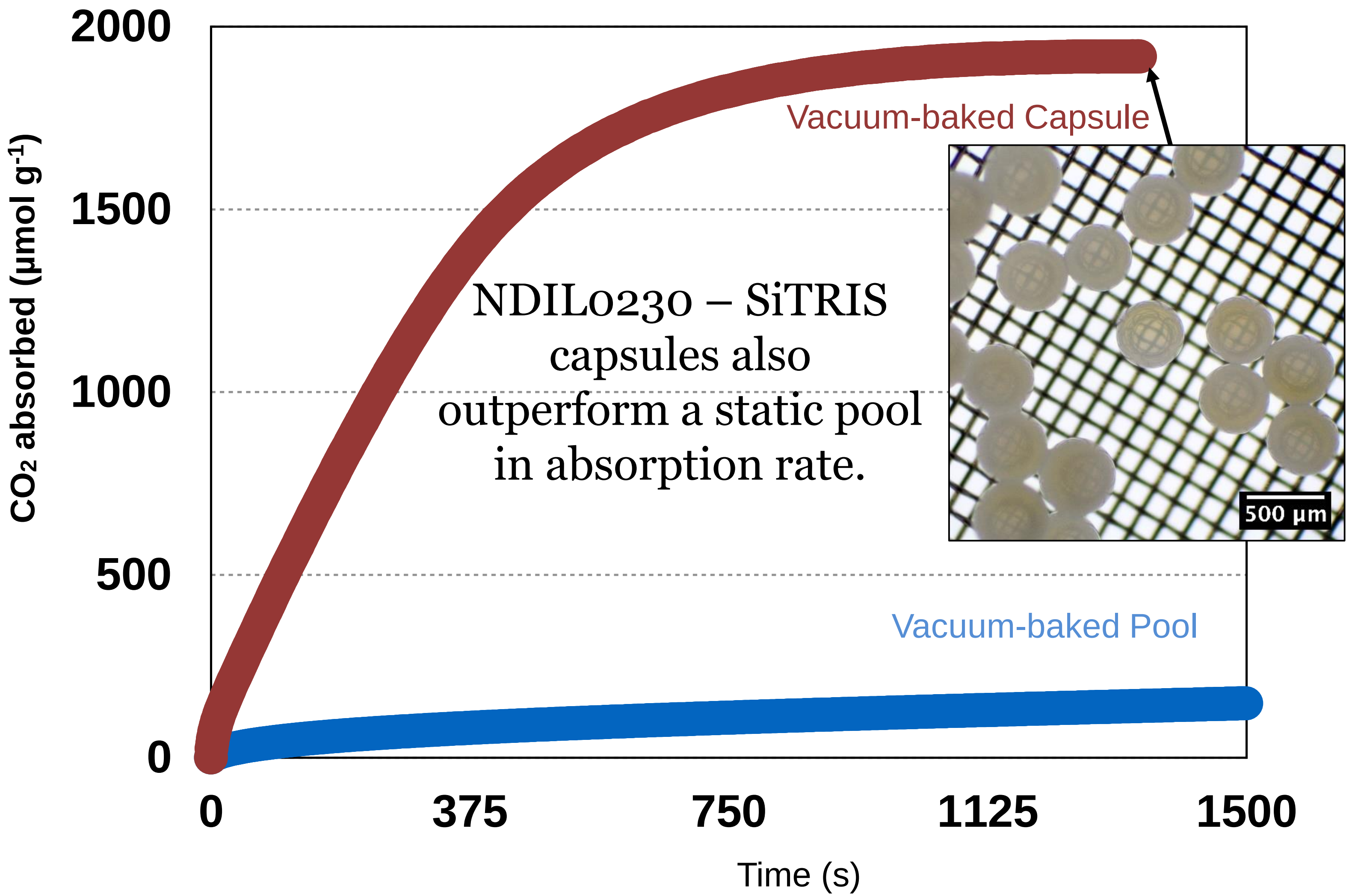
Encapsulating neat ILs remains challenging. Current strategy: dilute ILs in water and dry them after production



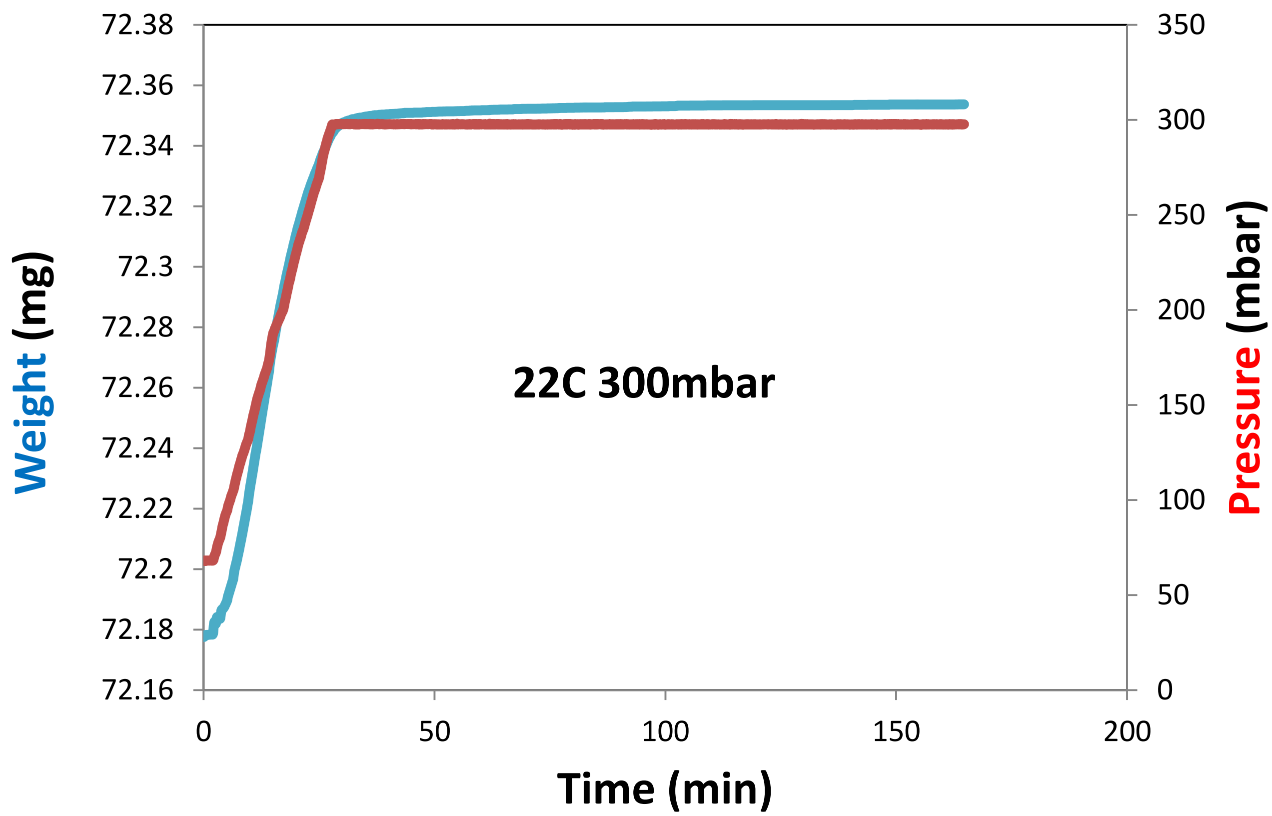


Great core-shell integrity and uniformity

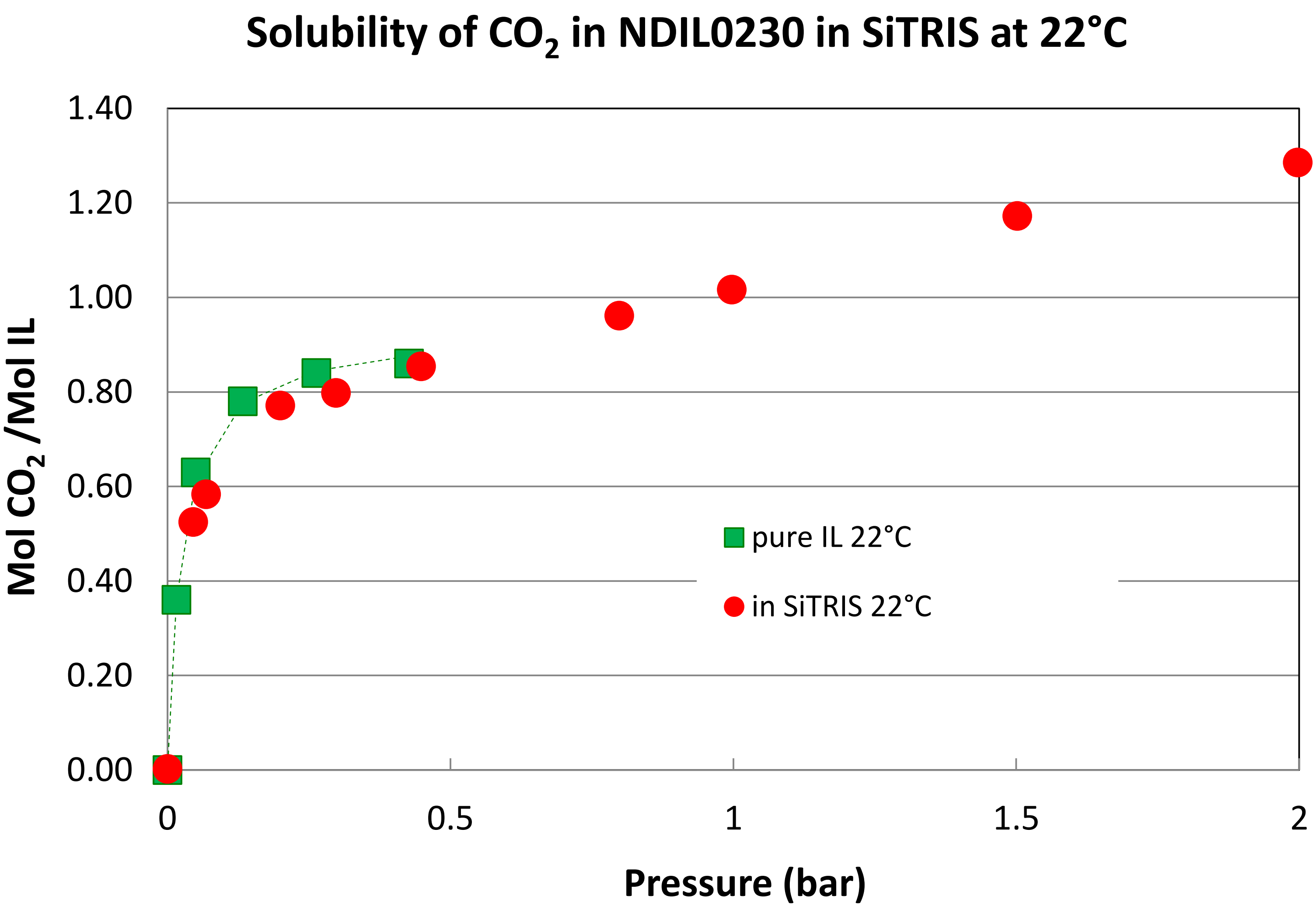
Fast CO_2 Uptake by Encapsulated ILs



Fast CO_2 Uptake by Encapsulated ILs



Encapsulate IL Maintains Capacity



Summary

- Successful synthesis, purification and testing of ILs and PCILs
- Successful encapsulation of ILs and PCILs
- Demonstration of fast CO_2 uptake by encapsulated IL
- Encapsulated IL maintains capacity
- Future work
  - Further shell material improvements
  - Dealing with water and impurities
  - Demonstration in laboratory scale unit

Reprotonation Equilibrium and Kinetics

Desired

$$C^+ A^- + CO_2 \rightleftharpoons C^+ ACO_2^-$$

Not Desired

$$C^+ A^- + H_2O \rightleftharpoons C^+ OH^- + AH$$

Not Desired

$$C^+ A^- + H_2O + CO_2 \rightleftharpoons C^+ HCO_3^- + AH$$