Novel Application of Organic Ionic Plastic Crystals to Light Gas Separation

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Introduction

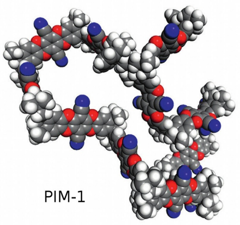
Legacy coal-fired power stations are significant greenhouse gas emitters. Developing a retrofittable separation solution is thus an important goal. Among the technologies being developed for this application are polymeric membranes and ionic liquid physical absorbents. Ionic liquid physical absorbents have also been suspended in polymeric membranes to enhance selectivity through chemical interactions.

Organic ionic plastic crystals (OIPCs) could be thought of as the solid-state cousins of ionic liquids. They are structurally similar to ionic liquids, but can undergo a number of solid-solid phase transitions prior to melting. A hallmark of these intermediate solid phases is mechanical plasticity and an increase in free volume which can aid diffusion. Because of these properties, OIPCs are under investigation as solid-state electrolytes.

This research project is about investigating the permeability and selectivity of light gases through these materials to see if they show potential for application to real-world separations.

Permeability = Diffusivity x Solubility

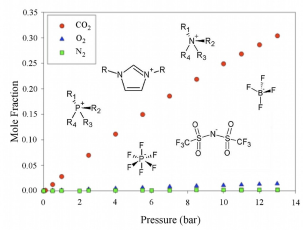
Promoting Diffusion



Current Opinion in Chemical Engineering 2013, 2:238–244

+ Free volume
+ Rigid chains
+ Tuned cavity sizes
- Susceptibility to aging

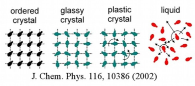
Promoting Solubility



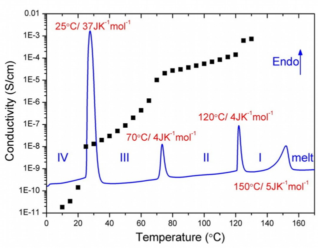
Maginn, Brennecke, McCready, Schneider - NETL CO2 Capture Meeting, September, 2010

+ Free volume
+ Affinity for functional groups
- Low pressure tolerance (SILMs)

Organic Ionic Plastic Crystals



J. Chem. Phys. 116, 10386 (2002)



J. Am. Chem. Soc. 2012, 134, 9688−9697

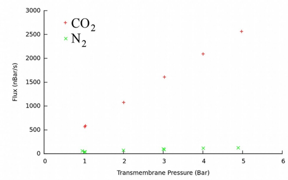
- OIPC constituent ions are often the same as in ionic liquids. In fact, low melting OIPCs <u>are</u> ionic liquids.
- Multiple, increasingly disordered solid phases are observed prior to the melt of an OIPC
- Because of this accumulated disorder, melt entropy is low (typically < 20J/molK)
- Material properties (e.g. conductivity) exhibit a phase-dependence

Research Question

Can the selectivity of ionic liquid chemistry and the diffusion-related properties of organic ionic plastic crystals be developed into a solid-state membrane to separate CO_2 from nitrogen?

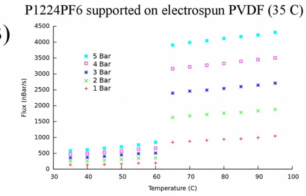
Gas Separation Performance

(A)



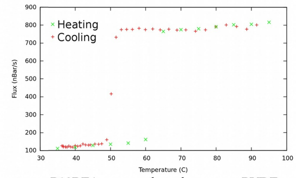
P1224PF6 supported on electrospun PVDF (35 C)

(B)



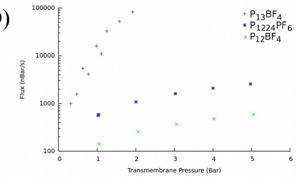
P12BF4 supported on electrospun PVDF

(C)



P12BF4 supported on electrospun PVDF

(D)

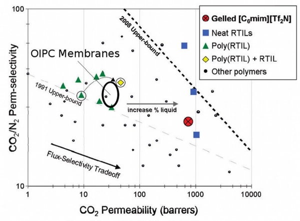


3-way CO2 flux comparison of supported OIPC membranes at 35C

- Selective permeation (CO2/N2) was demonstrated in a supported OIPC membrane (A)
- Robustness against transmembrane pressures of up to 5 Bar was demonstrated (A,B)
- A strong relationship between phase behavior and flux rates was observed (B)
- Transition-related changes in flux were found to be reversible (C)
- Flux was enhanced near the melt transition in the P13BF4/PVDF system (D)
- Ideal selectivity in our membranes is on par with polyRTIL membranes (E) and many high-performance polymers (F)

Significance : This work has direct applicability to the reduction of greenhouse gas emissions as well as the potential to contribute to the understanding of diffusion in OIPCs which could aid in the design of solid-state electrolytes.

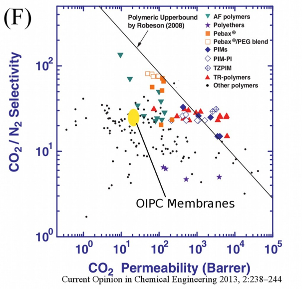
(E)



Chem. Mater., Vol. 21, No. 14, 2009

Our materials versus similar materials

(F)



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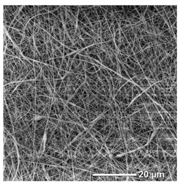
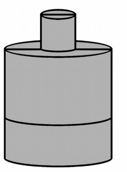
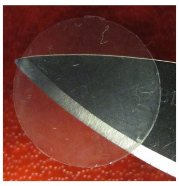
Our materials versus polymers

Sample Preparation

More details in Phys. Chem. Chem. Phys., 2013, 15, 13784--13789







Electrospinning

- PVDF is dissolved in DMF and diluted with acetone
- The solution is then spun onto a drum 15cm away at 15kV

Casting

- Selected OIPCs are then dissolved in methanol
- The solution is then solvent cast onto 13mm discs of the electrospun PVDF fibers and dried

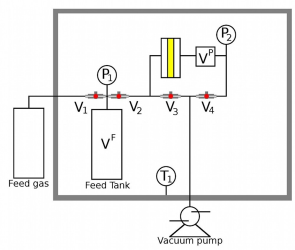
Pressing

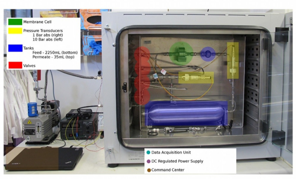
- Composites are then pressed under 1/2 ton for 30 minutes
- The temperature of the die is adjusted to target a suitable phase

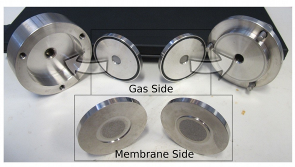
Mounting

- The composite, once pressed, is inspected for defects and then mounted in the cell shown above to begin testing

Time-Lag Permeation Measurements







- On time-lag equipment, gases are tested separately, parameters are calculated on an individual basis, and then relationships are calculated using ideal assumptions.
- On the right is my custom-built equipment including mounting brackets