# Carbon Dioxide Separation with Supported Ionic Liquid Membranes

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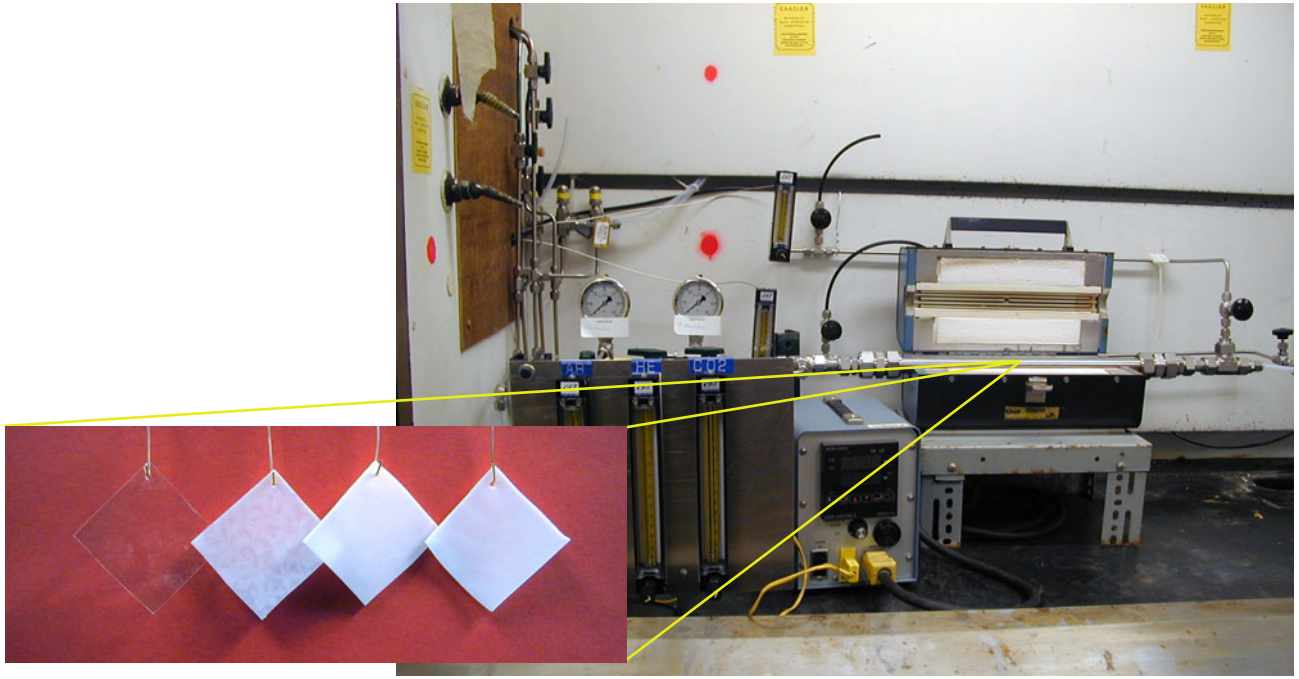
A practical form of $CO_2$ capture at water-gas shift conditions in the IGCC process could serve the dual function of producing a pure $CO_2$ stream for sequestration and forcing the equilibrium-limited shift reaction to completion enriching the stream in $H_2$. The shift temperatures, ranging from the low temperature shift condition of 260°C to the gasification condition of 900°C, limit capture options by diminishing associative interactions which favor removal of $CO_2$ from the gas stream. Certain sorption interactions, such as carbonate formation, remain available but generally involve exceptionally high sorbent regeneration energies that contribute heavily to parasitic power losses. Carbon dioxide selective membranes need only establish an equilibrium between the gas phase and sorption states in order to transport $CO_2$, giving them a potential energetic advantage over other technologies.

Supported liquid membranes take advantage of high, liquid phase diffusivities and a solution diffusion mechanism similar to that observed in polymeric membranes to achieve superior permeabilities and selectivites. The primary shortcoming of the supported liquid membranes demonstrated in past research has been the lack of stability caused by volatilization of the transport liquid. Ionic liquids, which possess high $CO_2$ solubility relative to light gases such as $H_2$, are excellent candidates for this type of membrane since they have negligible vapor pressure and are not susceptible to evaporation.

A study has been conducted evaluating the use of ionic liquids including 1-hexyl-3-methyl-imidazolium bis(trifuoromethylsulfonyl)imide in supported ionic liquid membranes for the capture of $CO_2$ from streams containing $H_2$. In a joint project, researchers at the University of Notre Dame synthesized and characterized ionic liquids, and researchers at the National Energy Technology Laboratory incorporated candidate ionic liquids into supports and evaluated the resulting materials for membrane performance. Improvements to the ionic liquid and support have allowed testing of these supported ionic liquid membranes at temperatures up to 300°C without loss of support mechanical stability or degradation of the ionic liquid. Substantial improvements in selectivity have also been observed at elevated temperature with the best membrane currently achieving optimum performance at 75°C.

# Carbon Dioxide Separation with Supported Ionic Liquid Membranes

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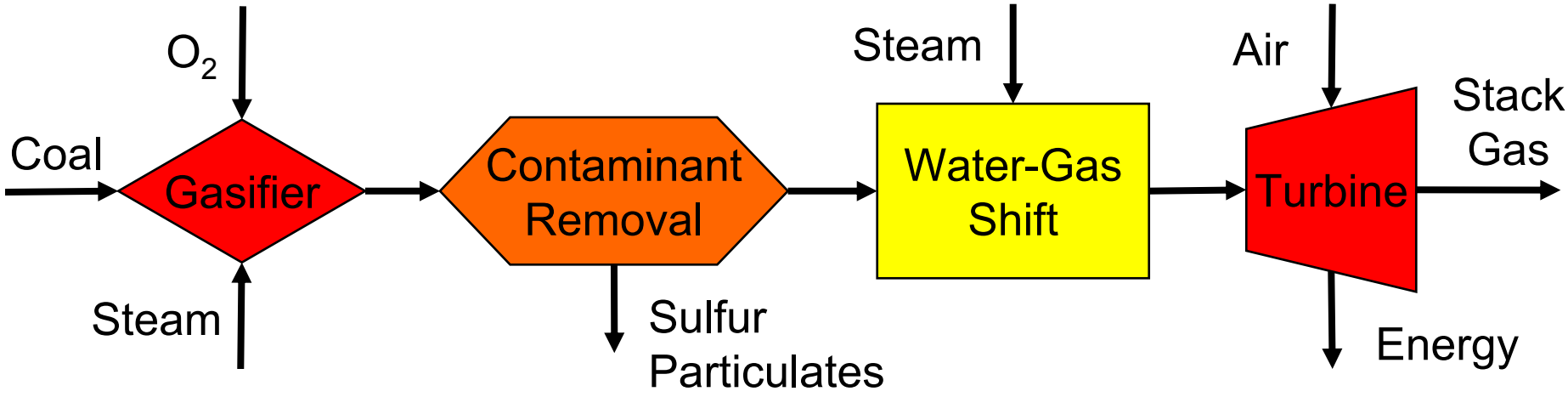
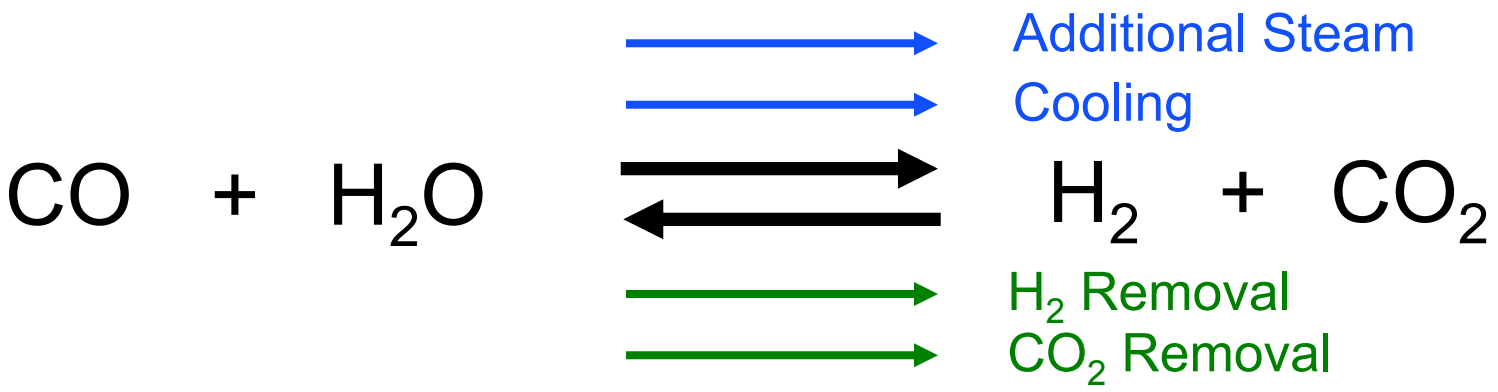
*Sixth Annual Conference on Carbon Capture & Sequestration*

# Integrated Gasification Combined Cycle (IGCC)



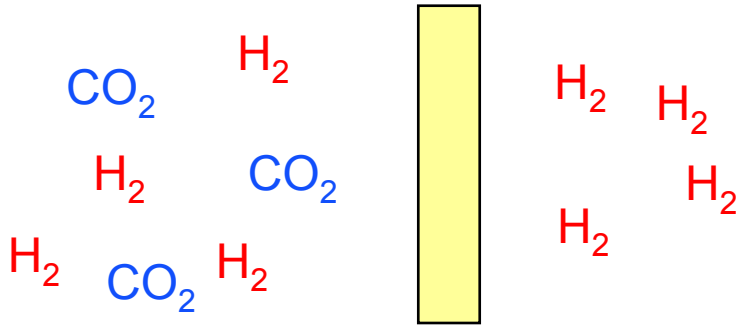

- **Significant component of future power generation**
- **Possible efficiency enhancement**
- **Potential to produce $H_2$ or electricity**

# Water-Gas Shift



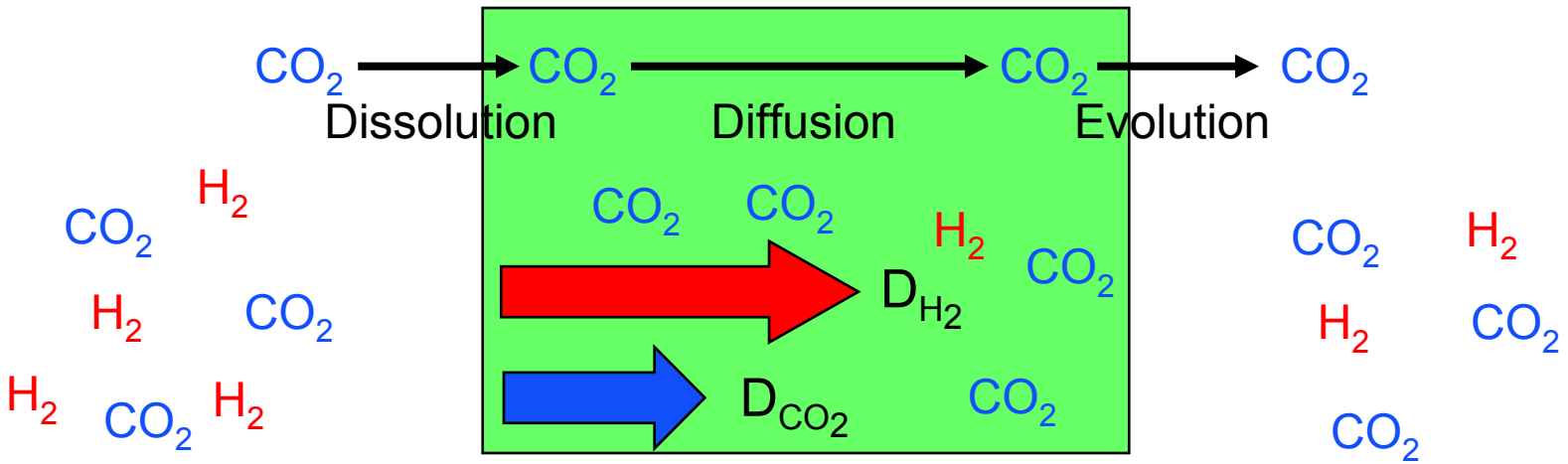

- **Conventional**
  - Catalyst Needed
  - Cooling to 260°C
  - Additional Steam
- **Improvement through Separation**
  - Separation above 500°C: No Catalyst
  - Cooling Only to Separation Temperature
  - Only Stoichiometric Steam Required

# $CO_2$ Selective Membranes: Solution Diffusion



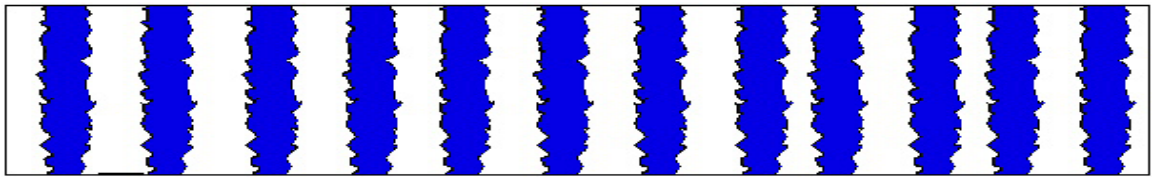

Knudsen Diffusion/
Molecular Sieving

Solution Diffusion



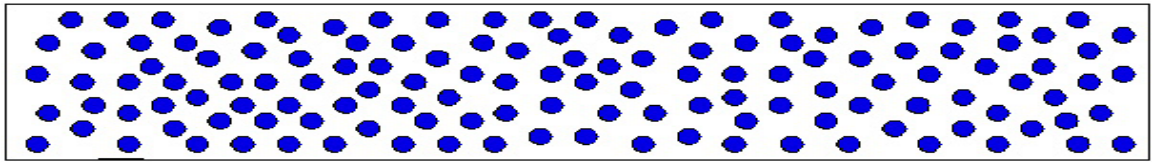

Permeability = Solubility X Diffusivity

# Supported Liquid Membranes



Porous Substrate

Scovazzo, J. Membr. Sci. 238 (2004) 57.



Dense Substrate

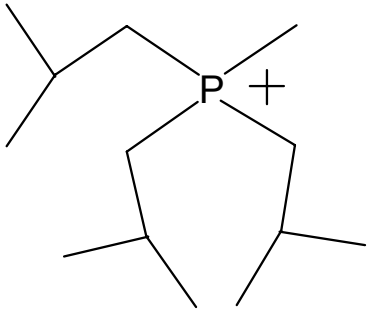
Zou and Ho, J. Membr. Sci. 286 (2006) 310.

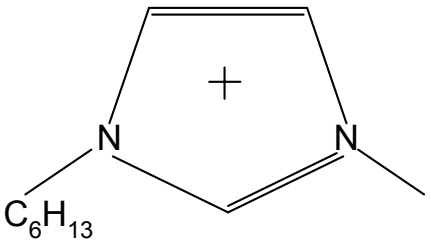
Polymerized Liquid

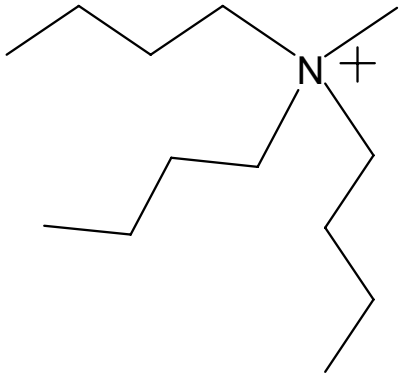
Tang, Macromolecules 38 (2005) 2037.

# Potential of Ionic Liquids

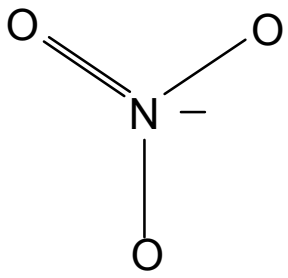
Cations

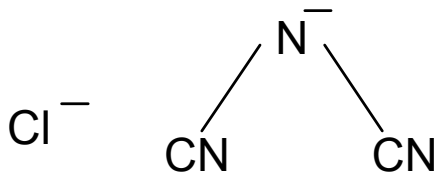


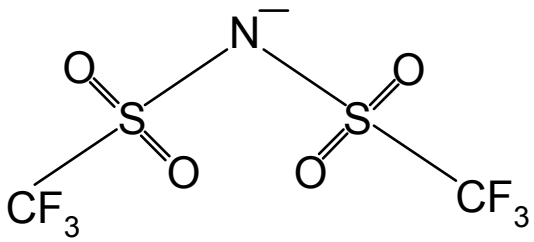




Anions



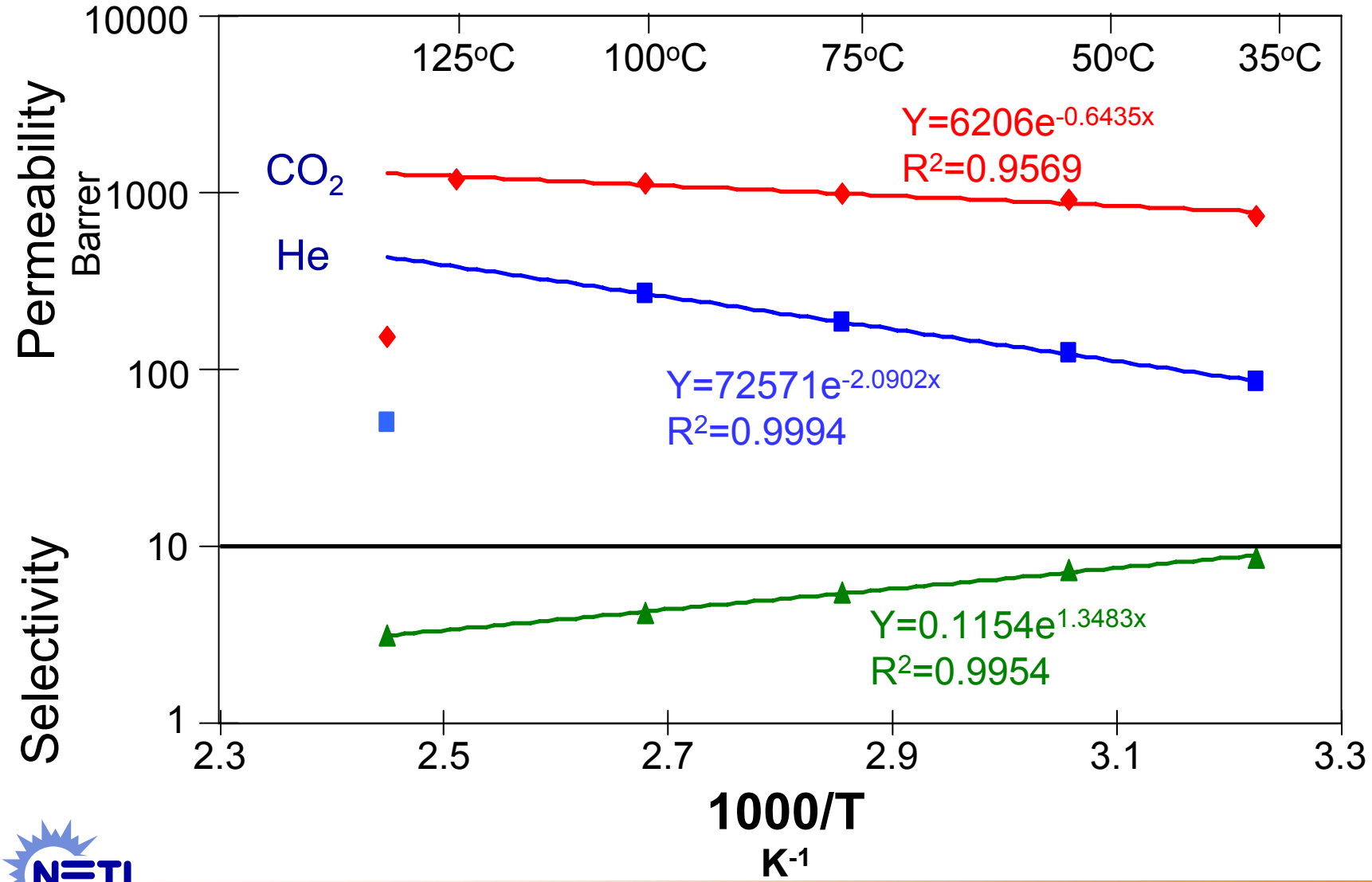

- **Negligible Vapor Pressure**
- **Thermally Stable above 200°C**
- **High $CO_2$ Solubility Relative to $H_2$, $N_2$, and $CH_4$**

# Step 1: Proof of Concept
## Membrane Testing

- Ionic liquids in porous polymer supports
- Ionic liquid saturated with water before testing
- Constant pressure flow system
- Pressure slightly greater than 1 atm
- Argon sweep
- Mixed gas permeabilities and selectivities

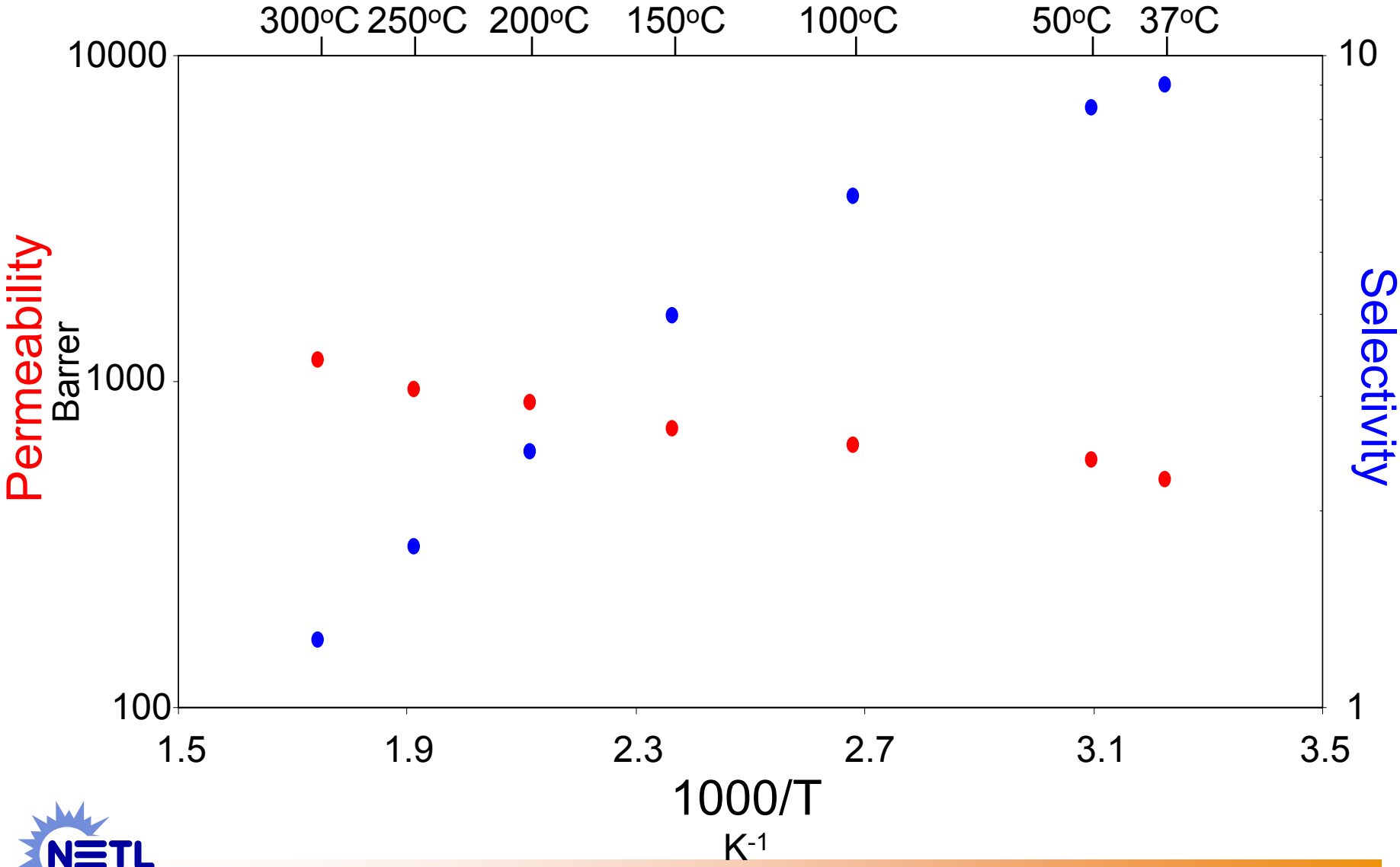
# Step 1: Proof of Concept

## Support Failure Limits Performance



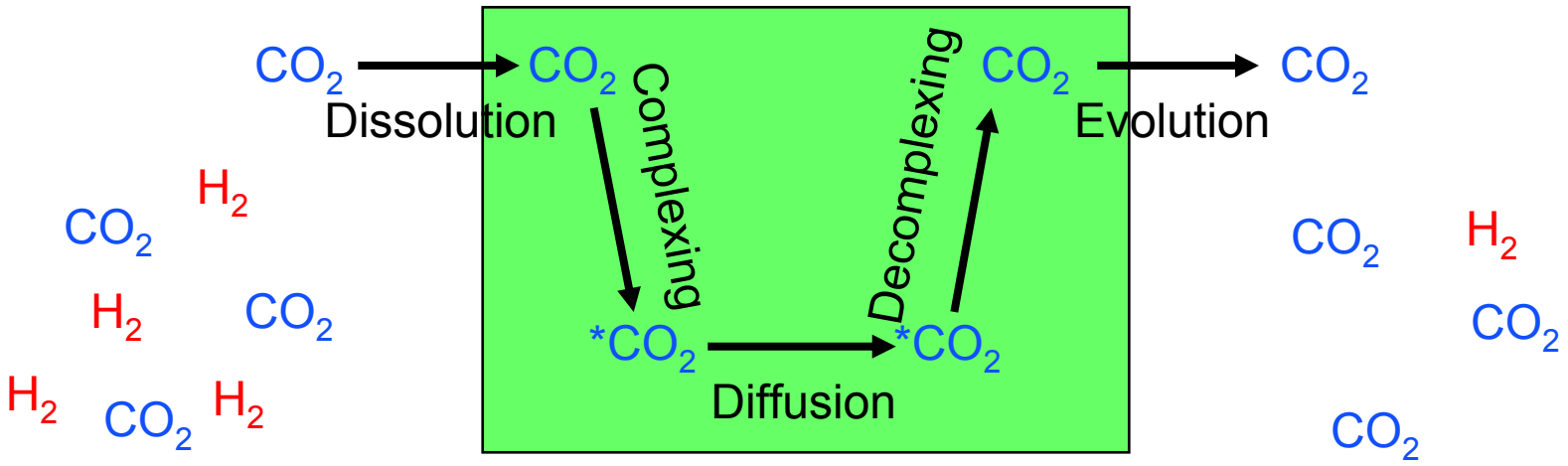
# Step 2: Support Improvement

## Cross-linking Stabilizes Support



# Step 3: Ionic Liquid Improvement

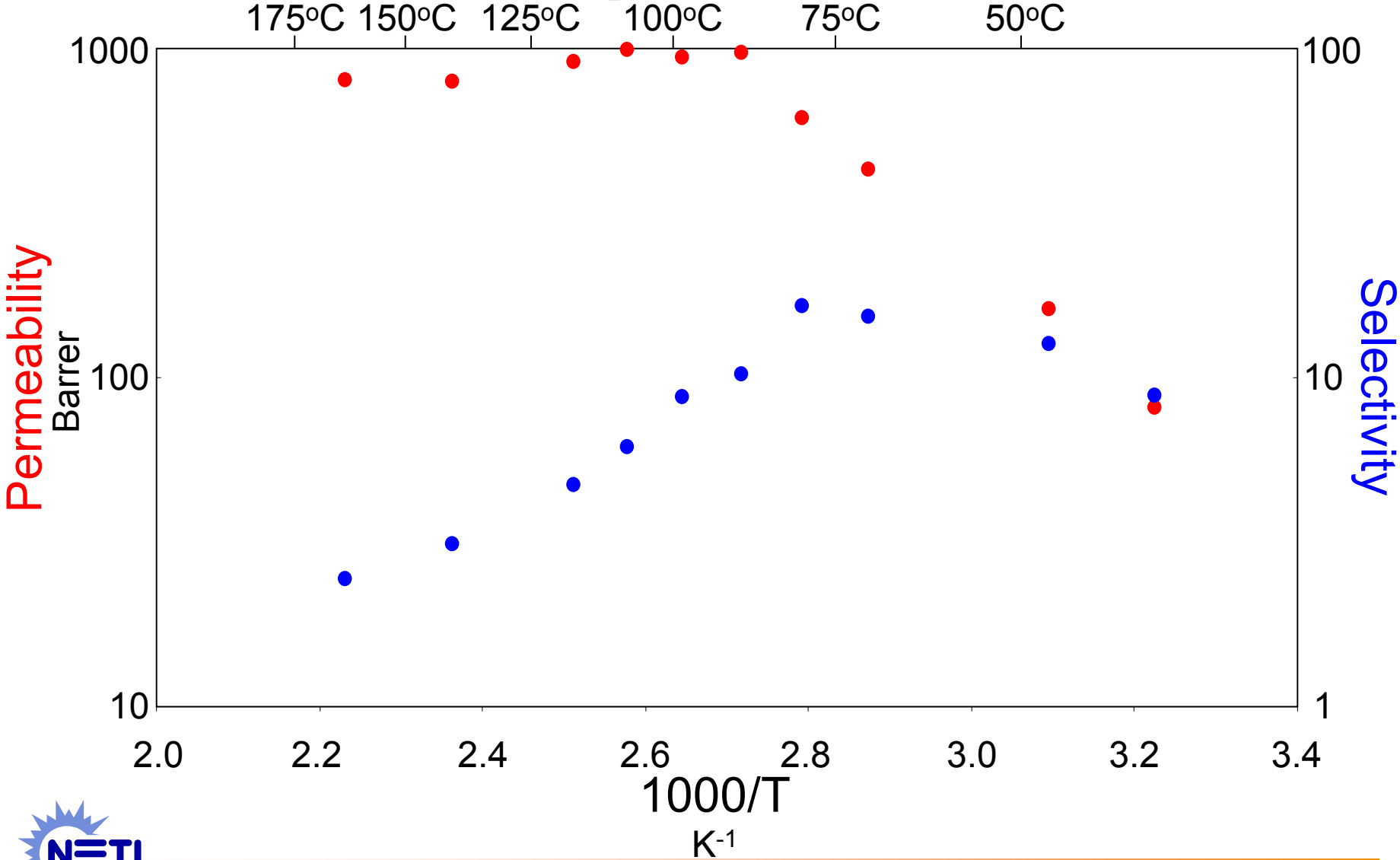
## Facilitated Transport?




- **Probable Increase in Solubility**
- **Potential to Optimize for Higher Temperature**
- **New Rate Limiting Step at Low Temperature**

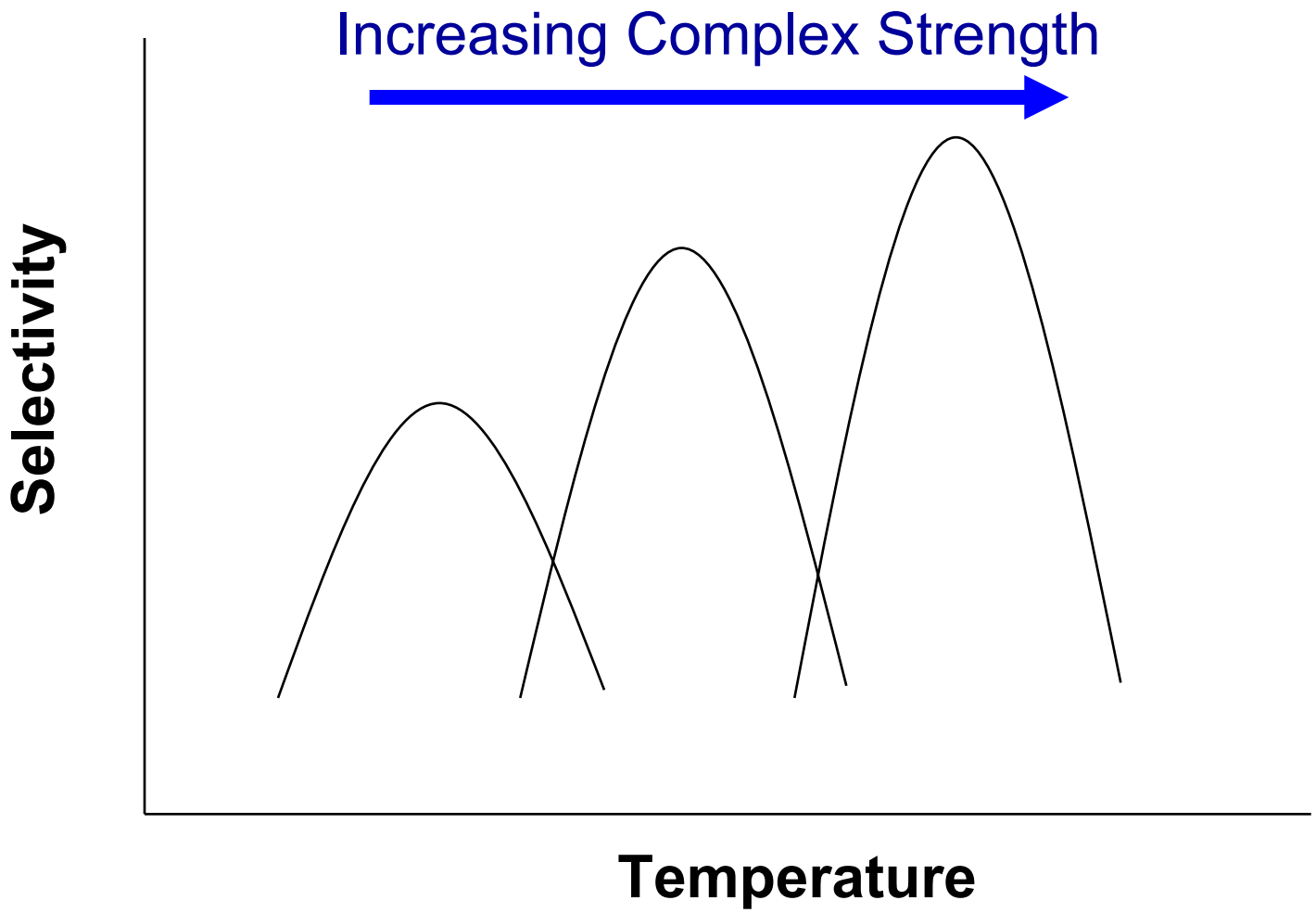
# Step 3: Ionic Liquid Improvement

## Facilitated Transport Increases Performance

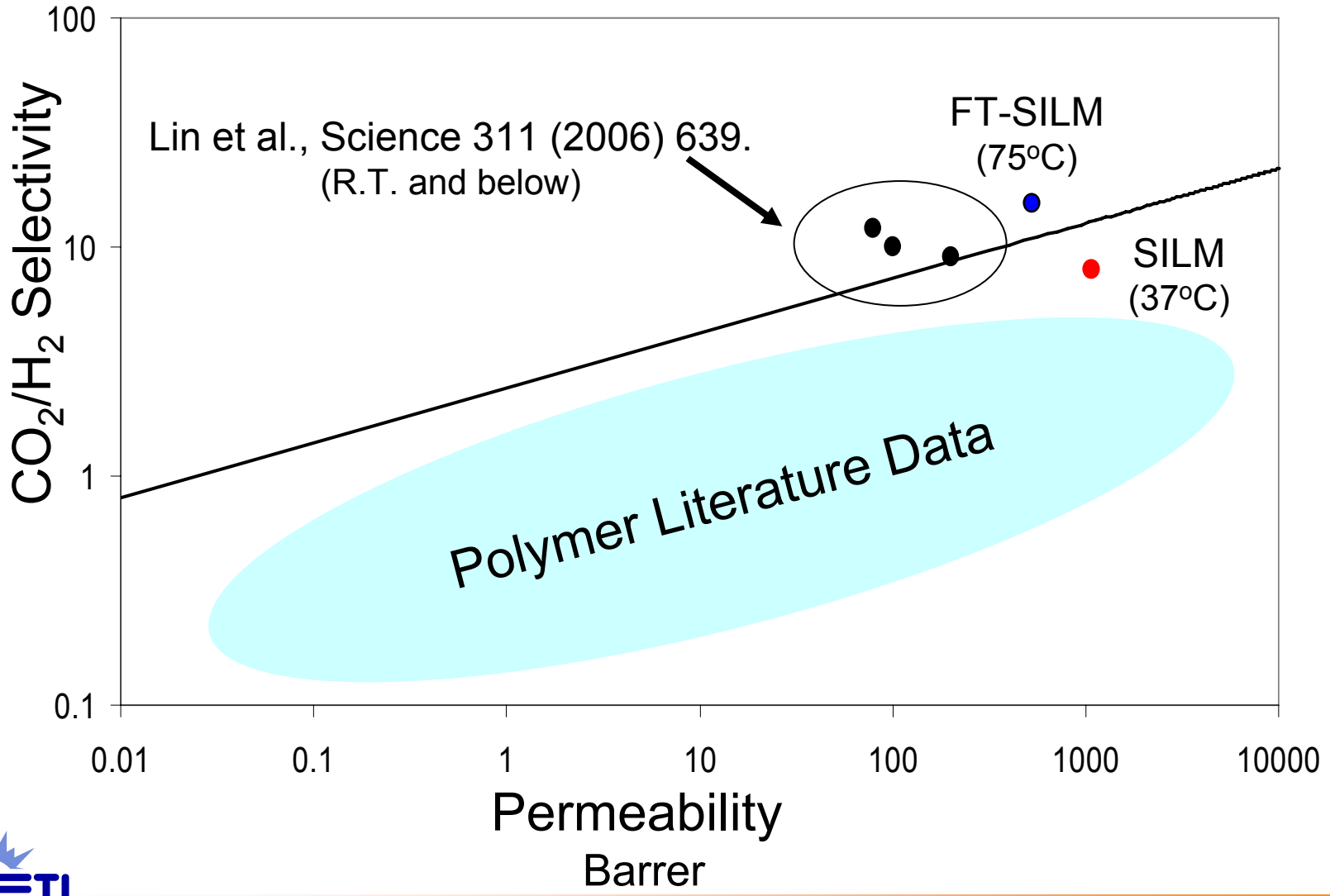


# Step 3: Ionic Liquid Improvement

## Stronger Complexes for Better Performance



# SILMs versus Polymers



# Summary

- High temperature $CO_2$ selective membranes may facilitate water-gas shift and enhance IGCC efficiency
- Ionic liquid membranes with cross-linked supports may be employed at water-gas shift conditions
- Ionic liquid based facilitated transport membranes have the potential for superior performance at elevated temperatures.

# Acknowledgements

The authors gratefully acknowledge the Brennecke and Maginn research groups at the University of Notre Dame. Their efforts in the synthesis and characterization of the ionic liquids along with their invaluable expertise in these areas have been very beneficial in the development of this exciting new technology. We look forward to continued fruitful collaboration.