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^{o}C to the gasification condition of 900^{o}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(trifluoromethylsulfonyl)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^{o}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^{o}C.

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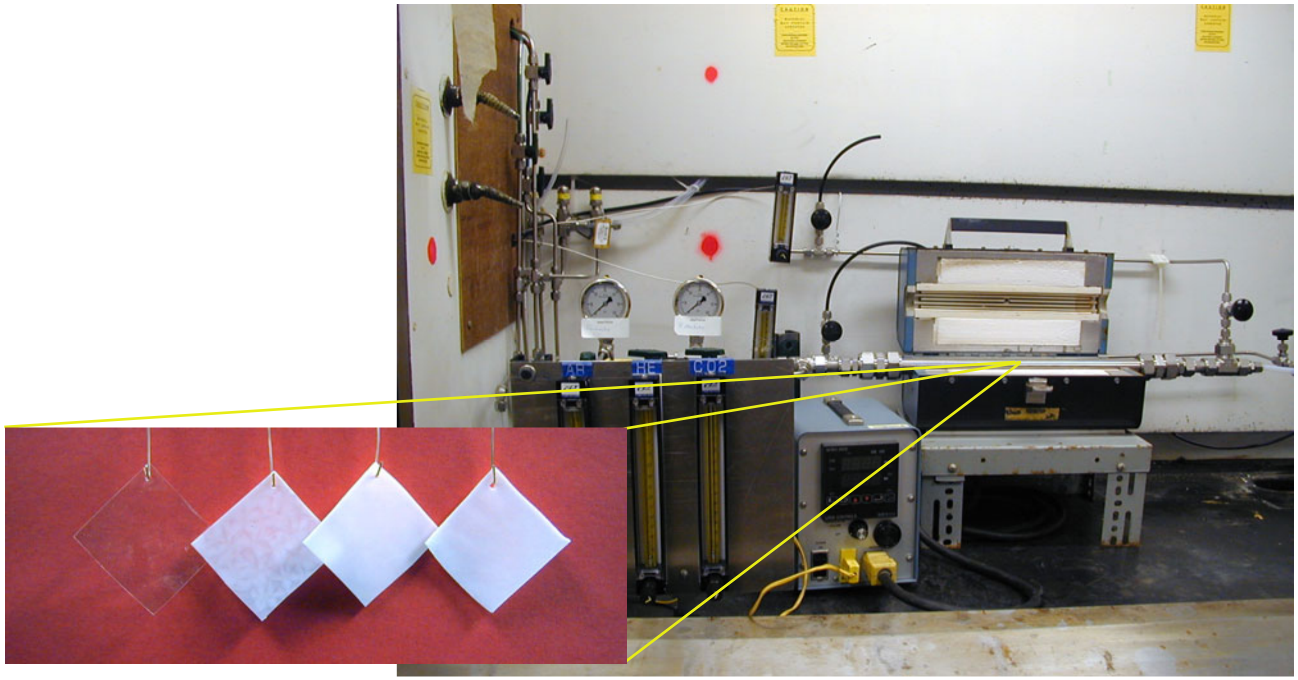

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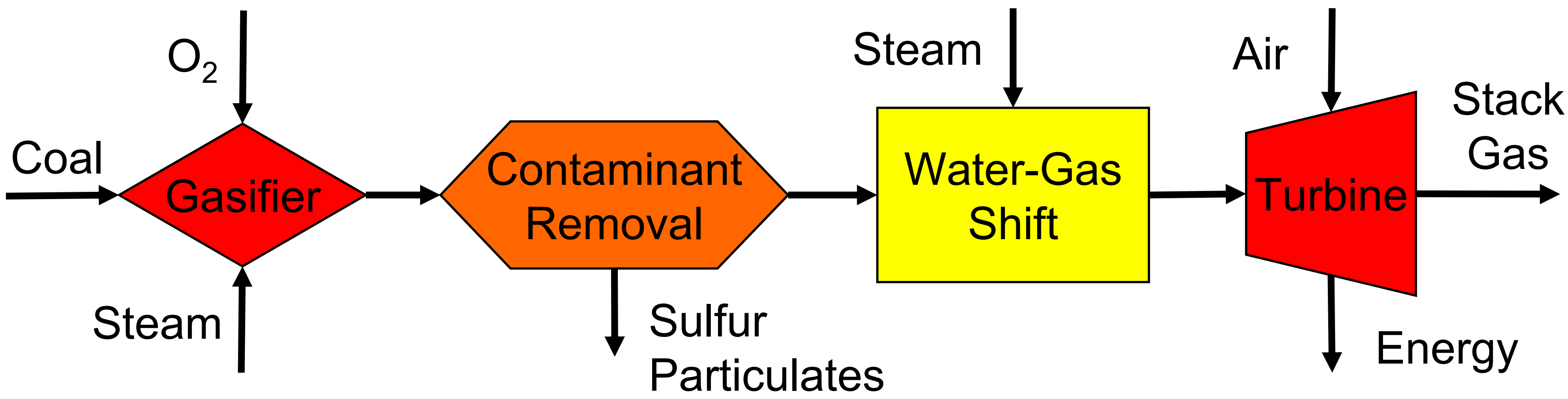
Integrated Gasification Combined Cycle (IGCC)



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

Water-Gas Shift

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Shift to the right ($\rightarrow$):

- Additional Steam
- Cooling
- H_2 Removal
- CO_2 Removal

- **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

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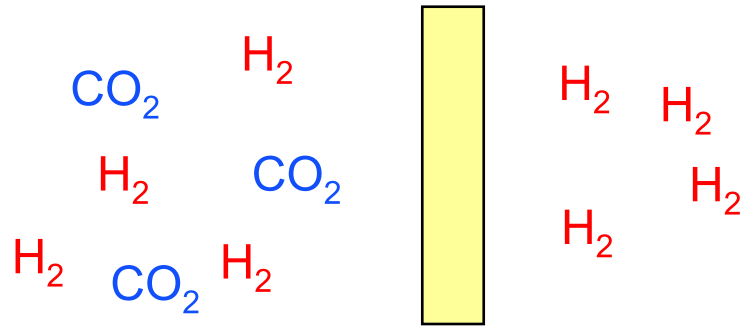
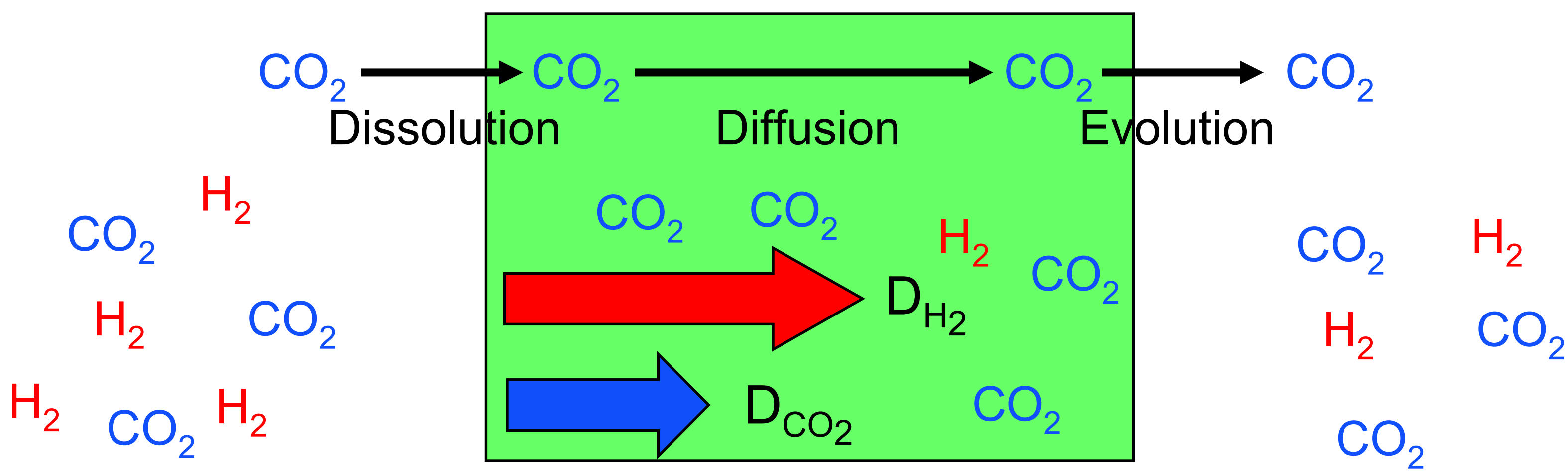
CO_2 Selective Membranes: Solution Diffusion



Knudsen Diffusion/ Molecular Sieving



Solution Diffusion

Permeability = Solubility X Diffusivity

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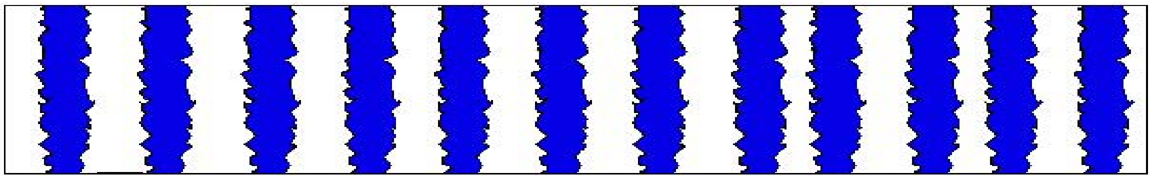
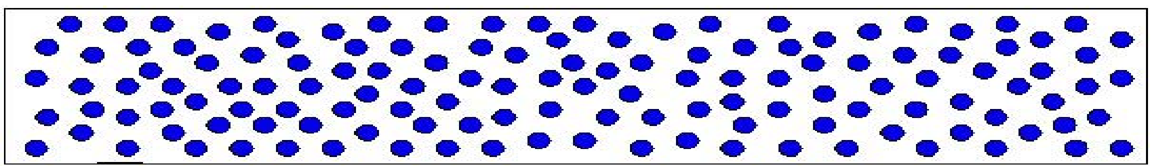
Supported Liquid Membranes



Porous Substrate

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



Dense Substrate

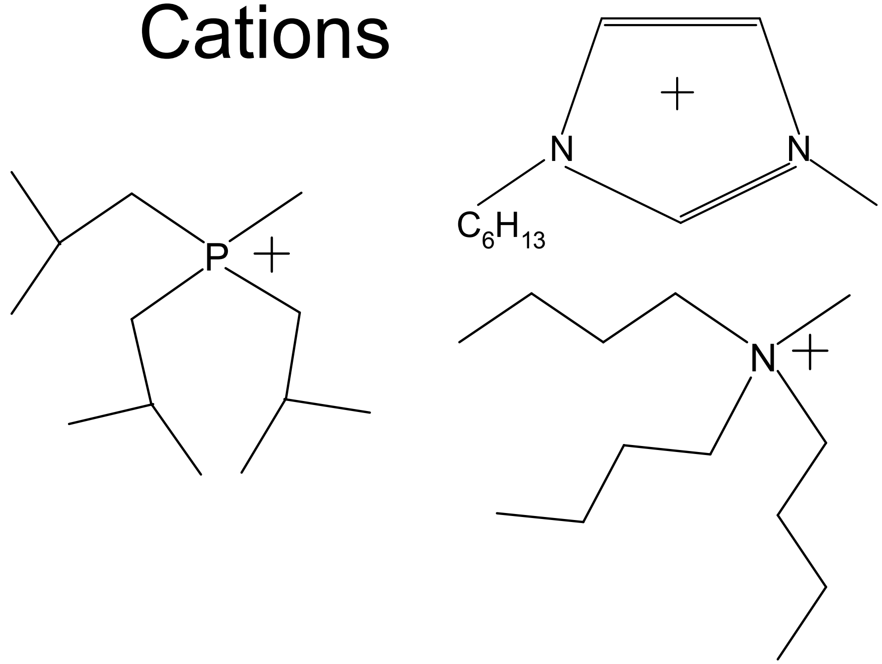
Zou and Ho, J. Membr. Sci. 286 (2006) 310.

Polymerized Liquid

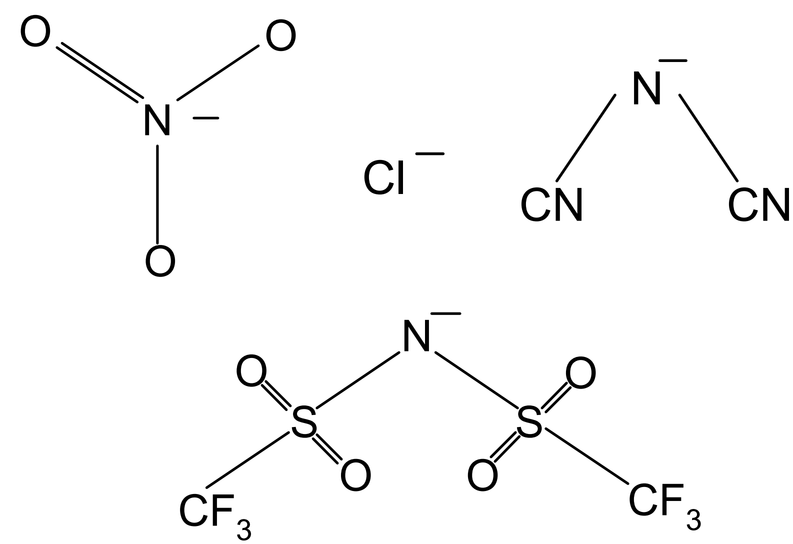
Tang, Macromolecules 38 (2005) 2037.

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**

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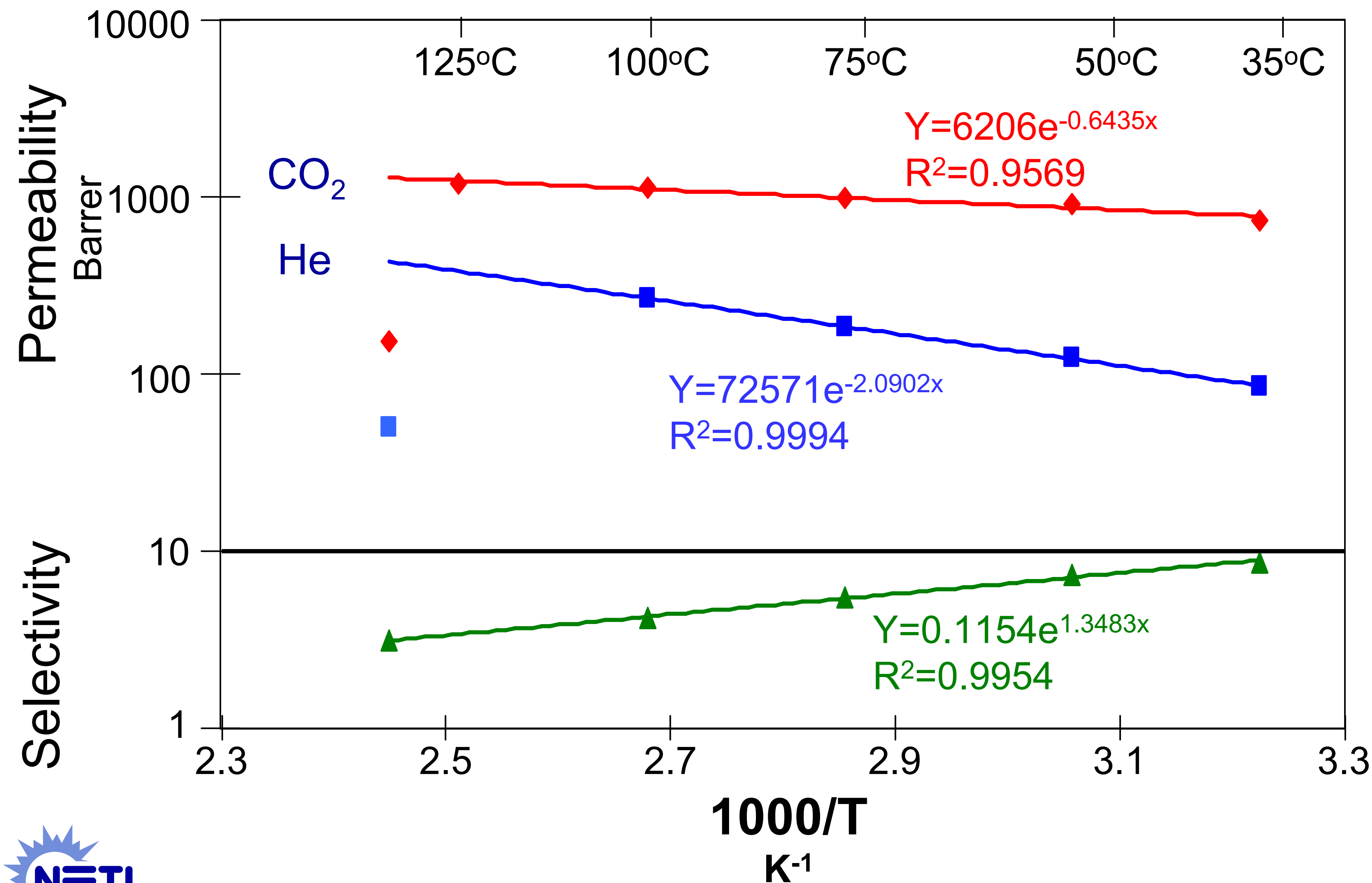
Step 1: Proof of Concept

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



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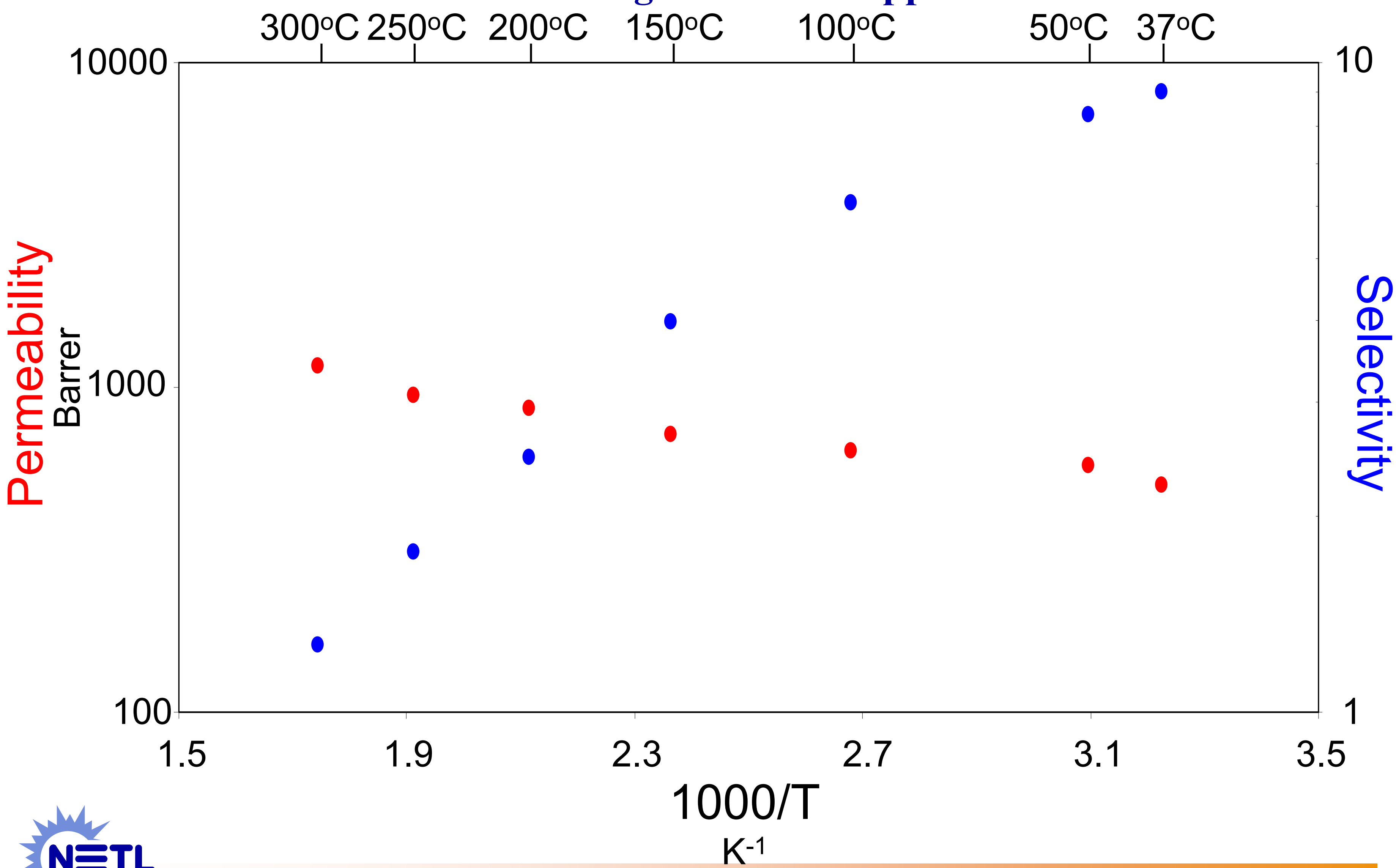
Step 2: Support Improvement

Cross-linking Stabilizes Support



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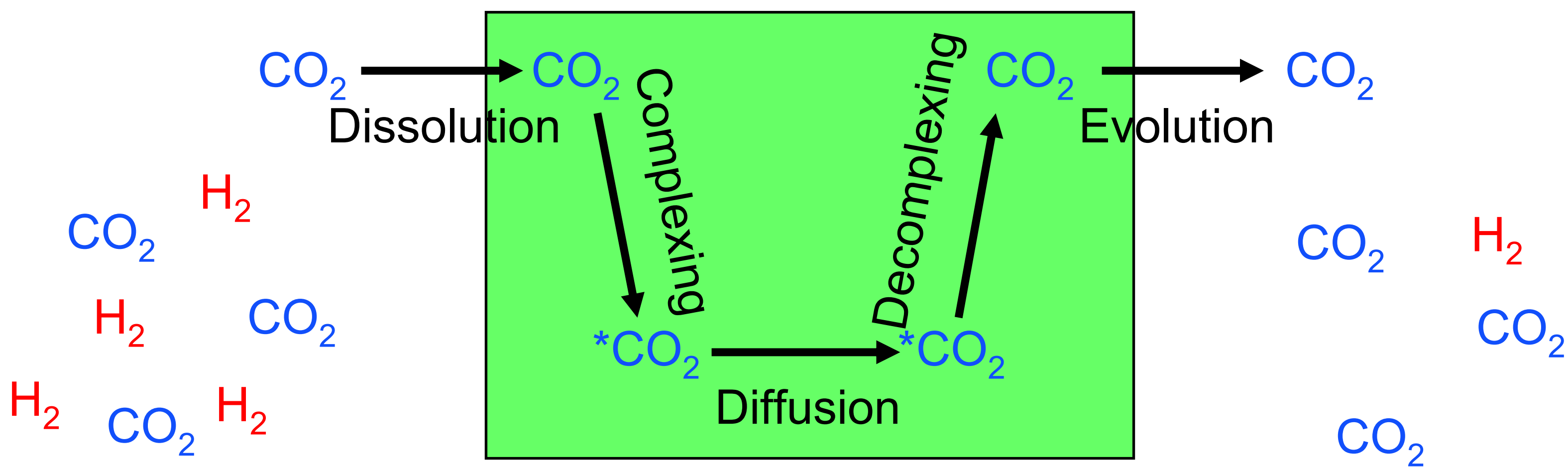
Step 3: Ionic Liquid Improvement

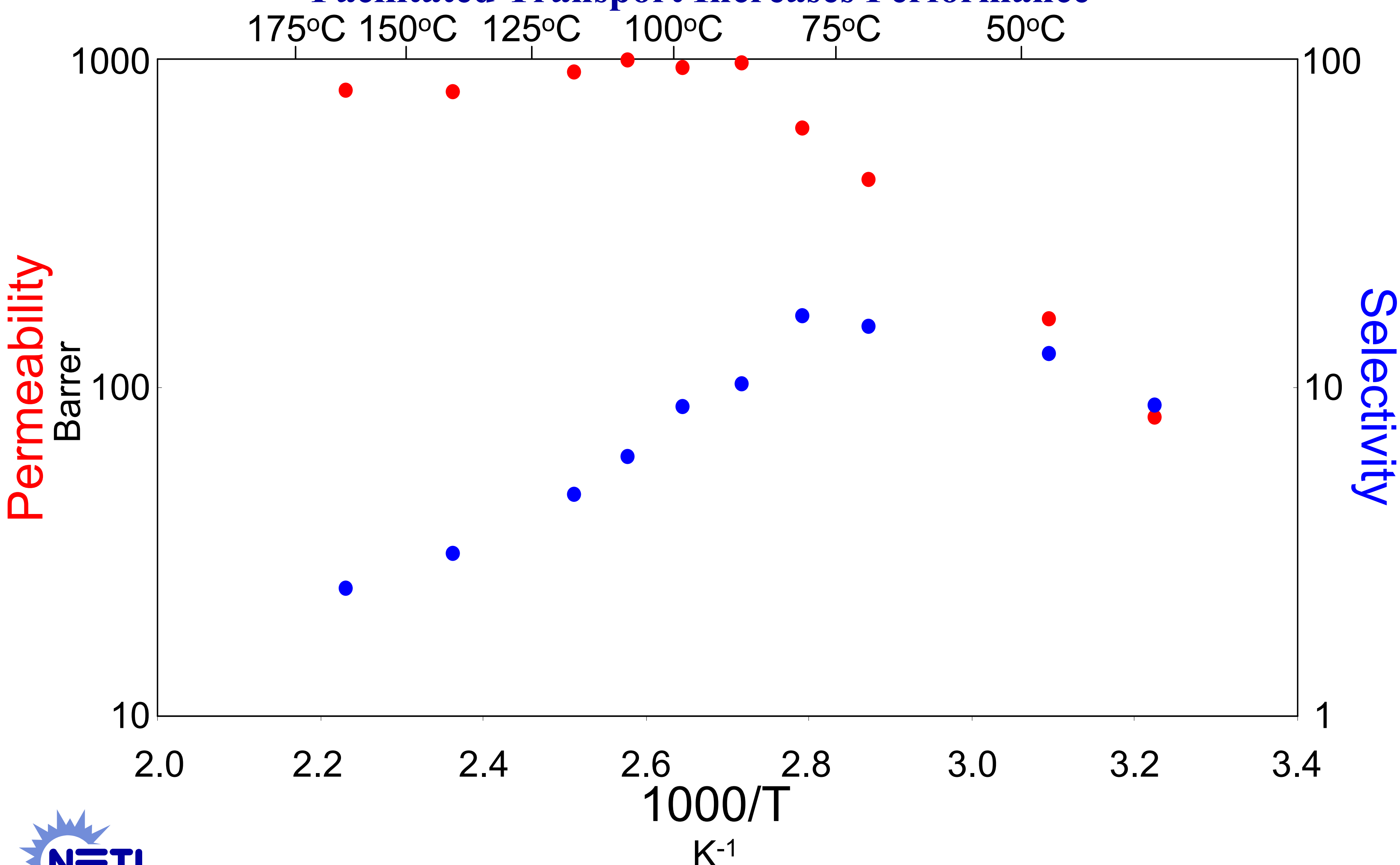
Facilitated Transport?



- **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



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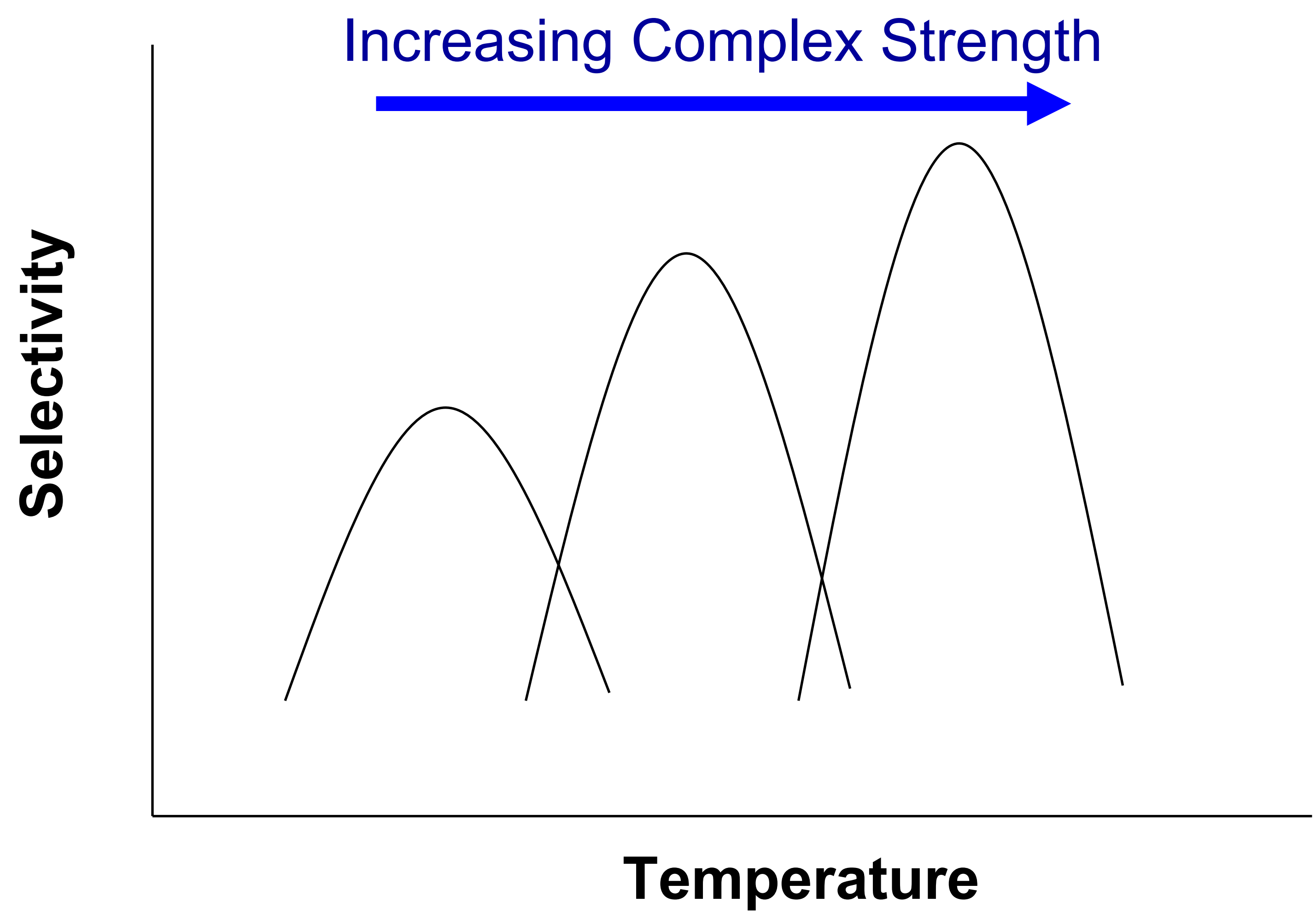
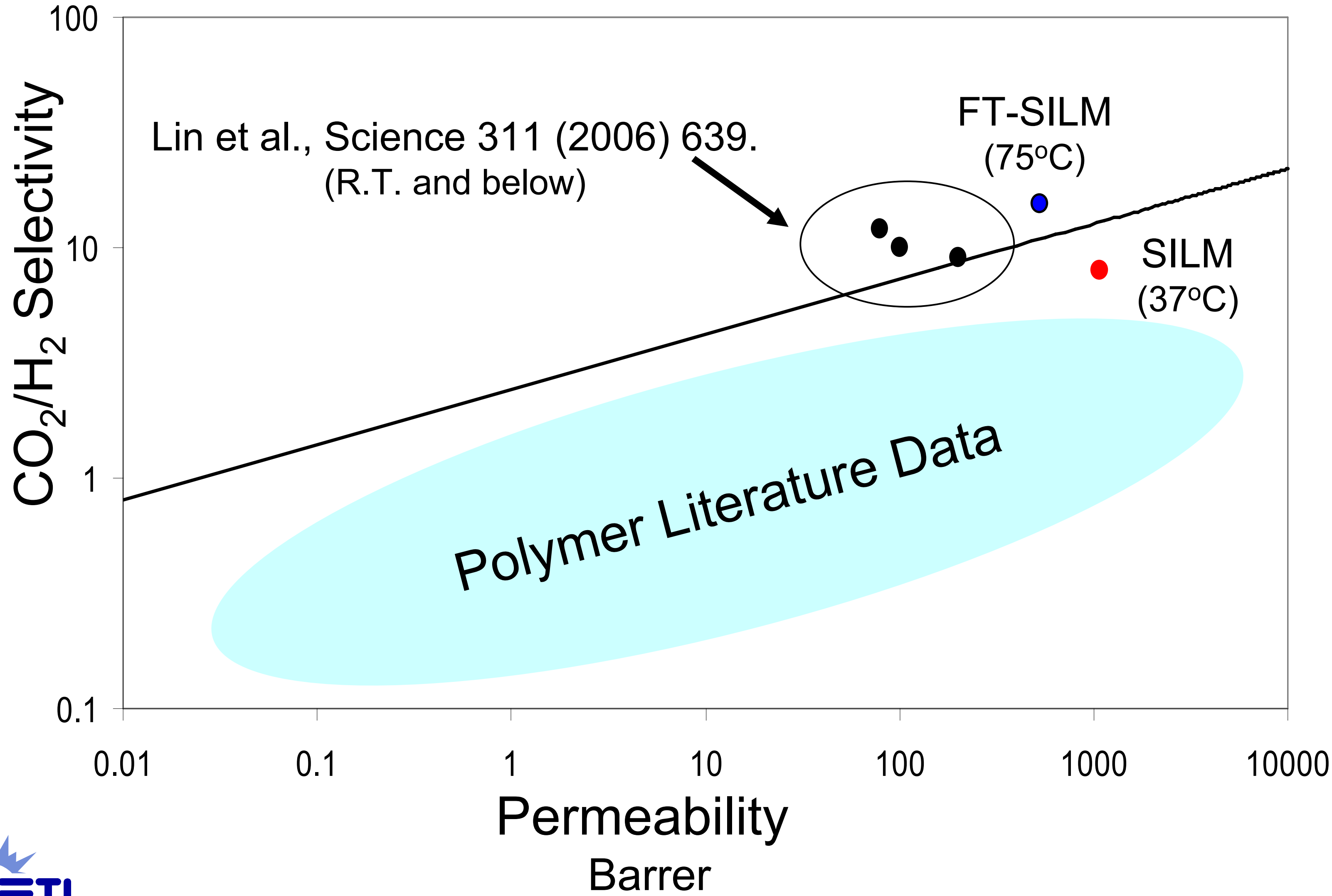
Step 3: Ionic Liquid Improvement

Stronger Complexes for Better Performance



SILMs versus Polymers



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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.**

NETL

Acknowledgements

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