New polymeric proton conductors for water-free and high temperature fuel cells

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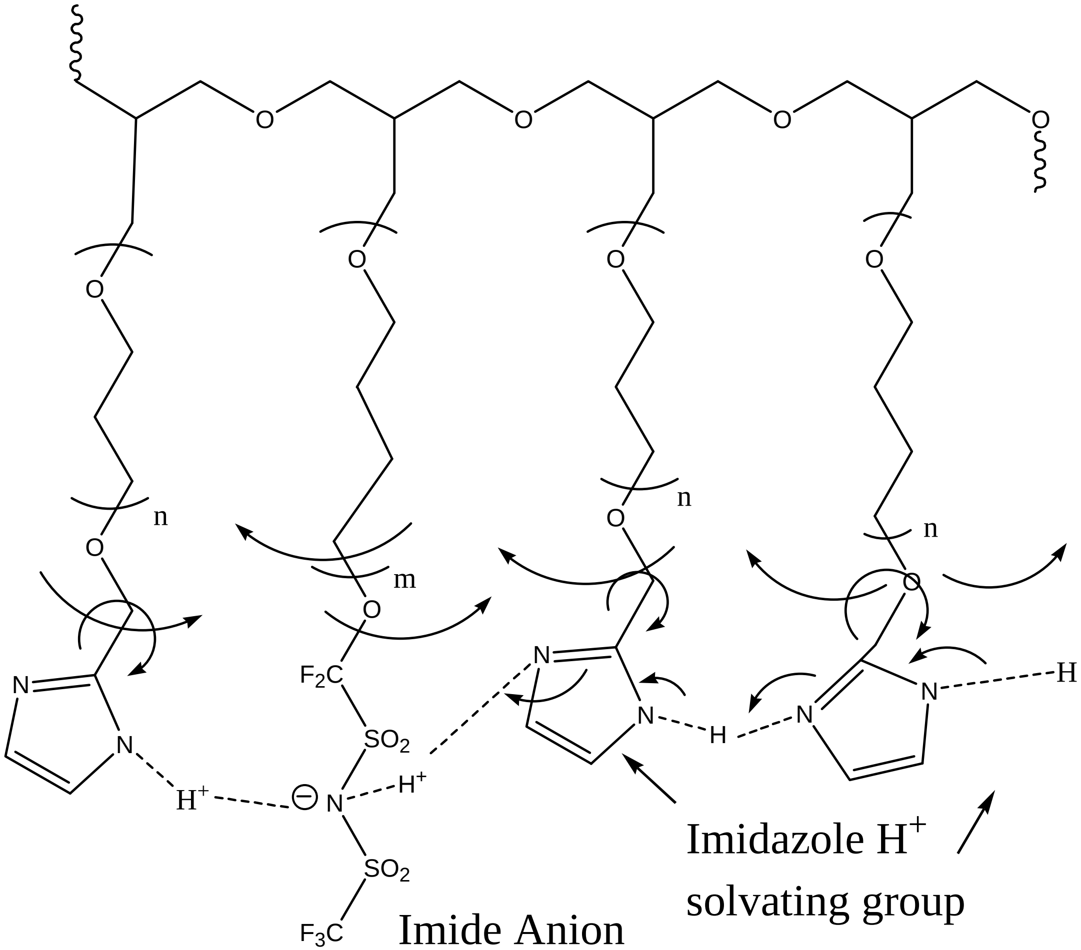
Objectives

- Investigate the feasibility of use of solvent free solid polyelectrolytes for water-free and high temperature operation.
  - Measure conductivity, mechanical/thermal properties of Nafion® and Polyether polyelectrolytes doped with imidazoles.
  - Covalently attach imidazoles to appropriate polymer backbones and test for conductivity, mechanical/thermal behavior and gas permeability

Approach

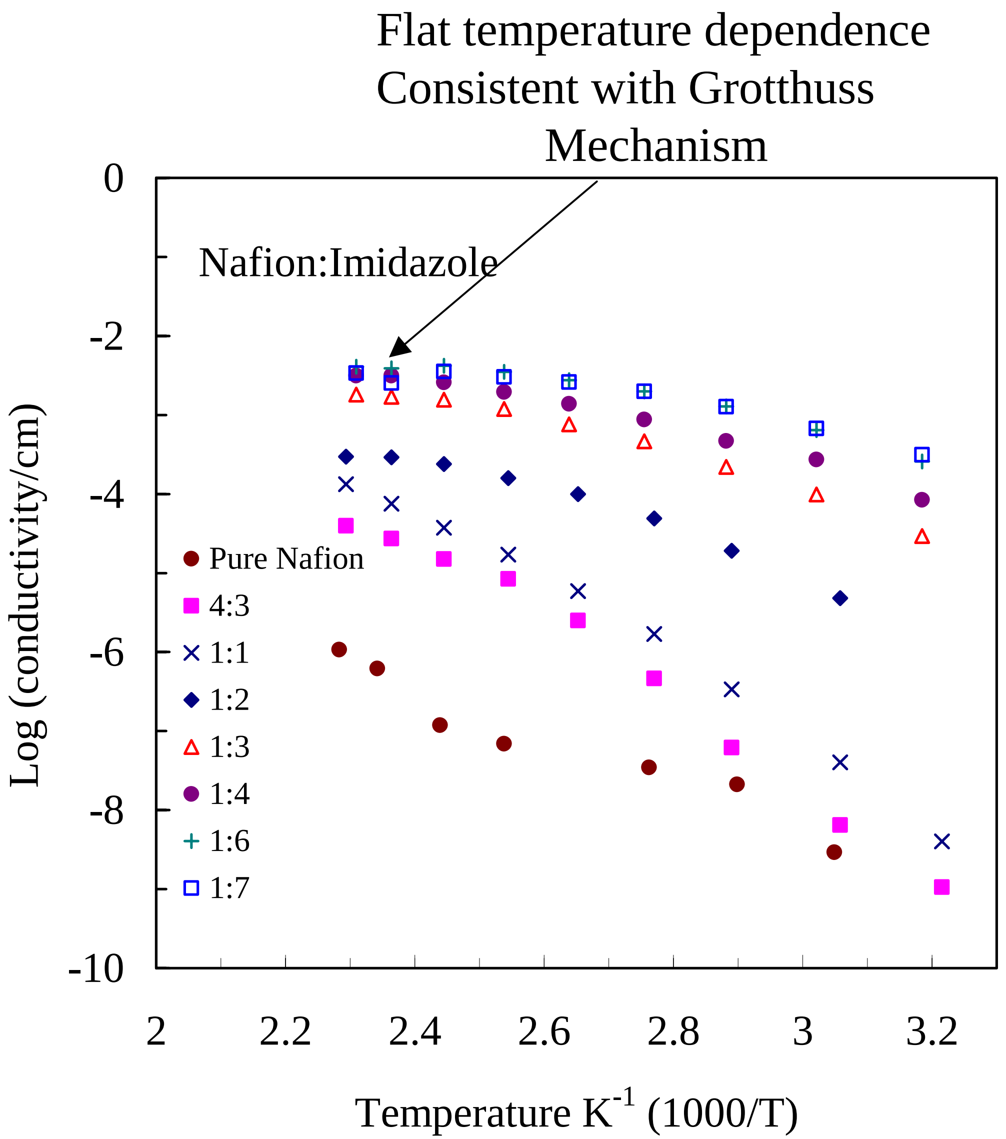
1. Prepare polyelectrolyte gels from Nafion® and Imidazole or N-methylimidazole to replace water. Measure properties (conductivity, thermal/mechanical properties)
2. Prepare polyelectrolyte gels with imidazoles and polyether polyelectrolytes prepared under NASA PERS program for lithium batteries. Measure properties for variety of polyelectrolytes with different structures and pendant anions.
3. Attach imidazoles covalently to modified polyether polyelectrolyte backbones using results from 2. as guidance. Measure properties and optimize for use in separator membrane(high t_g, low gas permeability, high conductivity) or MEA (low t_g, high gas permeability, high conductivity).
4. Optimize structures for durability.

New Polymer Architectures for Imidazole Solvating groups (Kreuer), Anion Mobility and Flexibility



- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature (pdo/bdo) and length of side chain to control chain mobility.
- Backbone (PE, polystyrene, polysiloxane) and cross-link density to control mechanical & morphological properties.
- Degradation results in Release of small fragments - facilitates failure analysis.

Conductivities of Imidazole Doped Nafion Films



Details of film casting

Nafion: acid form

Equivalent MW: 1,100

Solvent used: aliphatic alcohol and water mixed solvent.

Drying condition: 65° C for 2 hours.

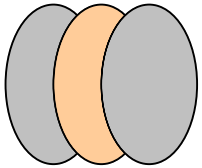
Film thickness: 100 μm ±20 μm

Testing conditions

Film between two parallel stainless steel plate.

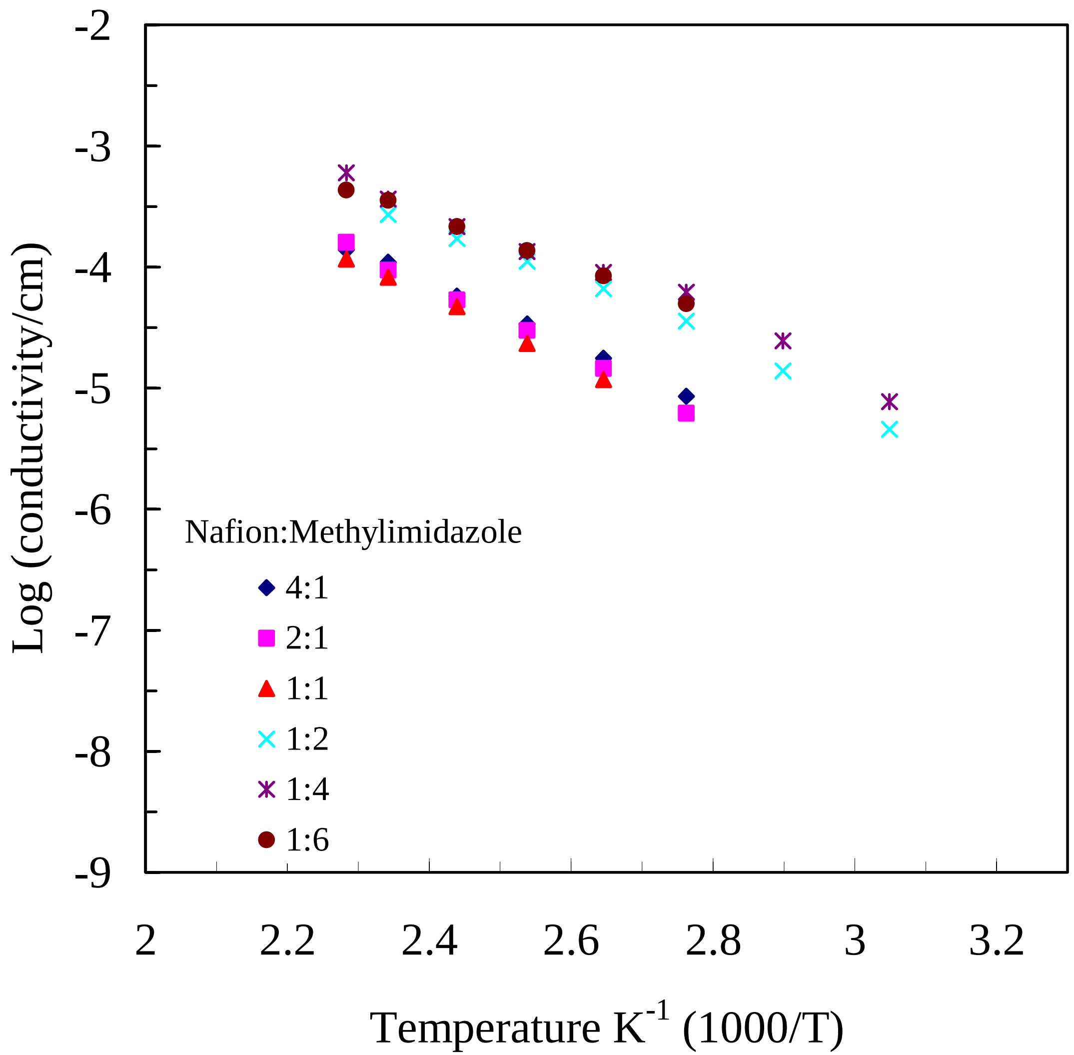
Impedance measurements.

Decreasing temperature from 170° C to 25° C.



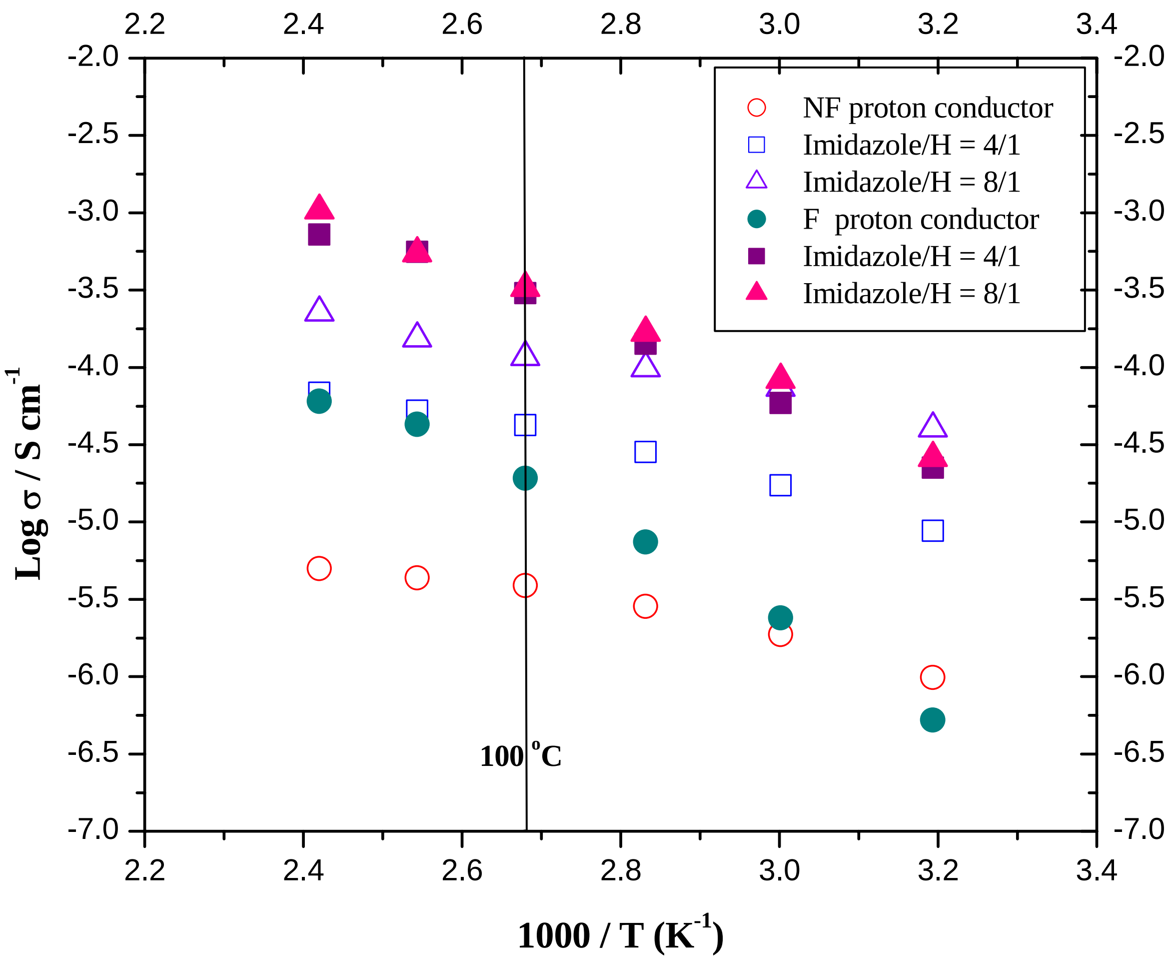
Stainless steel disc-Membrane-Stainless steel disc

Conductivities of Methylimidazole Doped Nafion Films



N-methyl Imidazole unable to particpate in Grotthuss mechanism of proton transport. Only segmental motion responsible for proton mobility, hence larger activation energy and steeper slope. Compare with Imidazole doped Nafion where Grotthuss mechanism is possible.

Polyether Polyelectrolytes doped with Imidazole - Acid Strength increases Conductivity.



Polyether polyelectrolytes prepared from $PE(EO)_5$co-Allyl$(EO)_2$ and $CH_2=CHCH_2OC_2H_4OC_2H_4SO_3Li$ (NF conductor) and $CH_2=CHCH_2C_2F_4OC_2F_4SO_3Li$ (F proton conductor).

Exchange Li^+ for H^+ with Dowex® -HCR-W2 ion exchange resin.

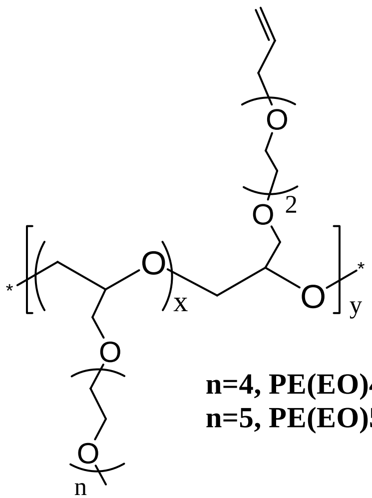
Vacuum dried over P_2O_5

Co-cast polyelectrolyte with Imidazole from EtOH soln.

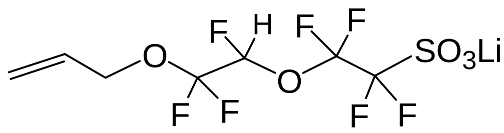
Dry over P_2O_5.

Temperature dependence indicates no Grotthuss mobility.

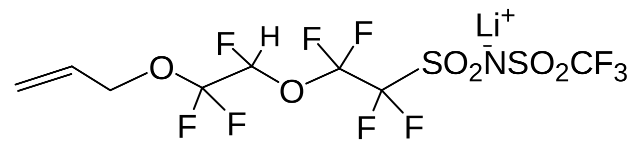
Low T_g Pre-polymers and Salts for Testing as Proton Conductors



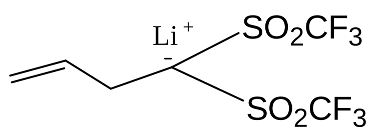
n=4, PE(EO)4
n=5, PE(EO)5



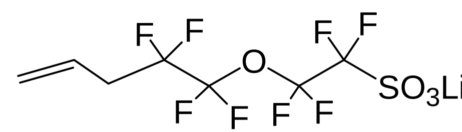
Salt I



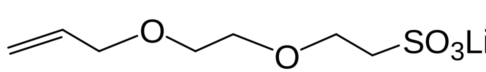
Salt II



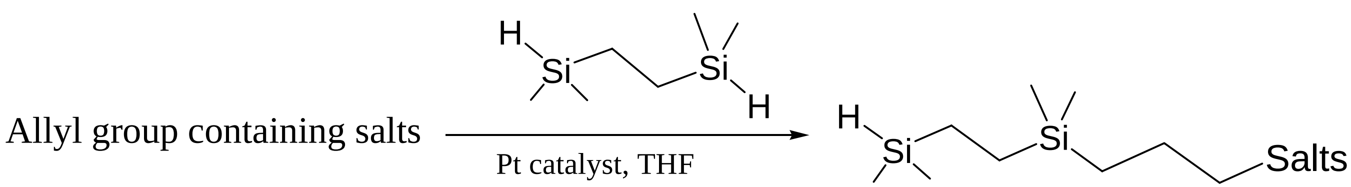
Salt III



Salt IV

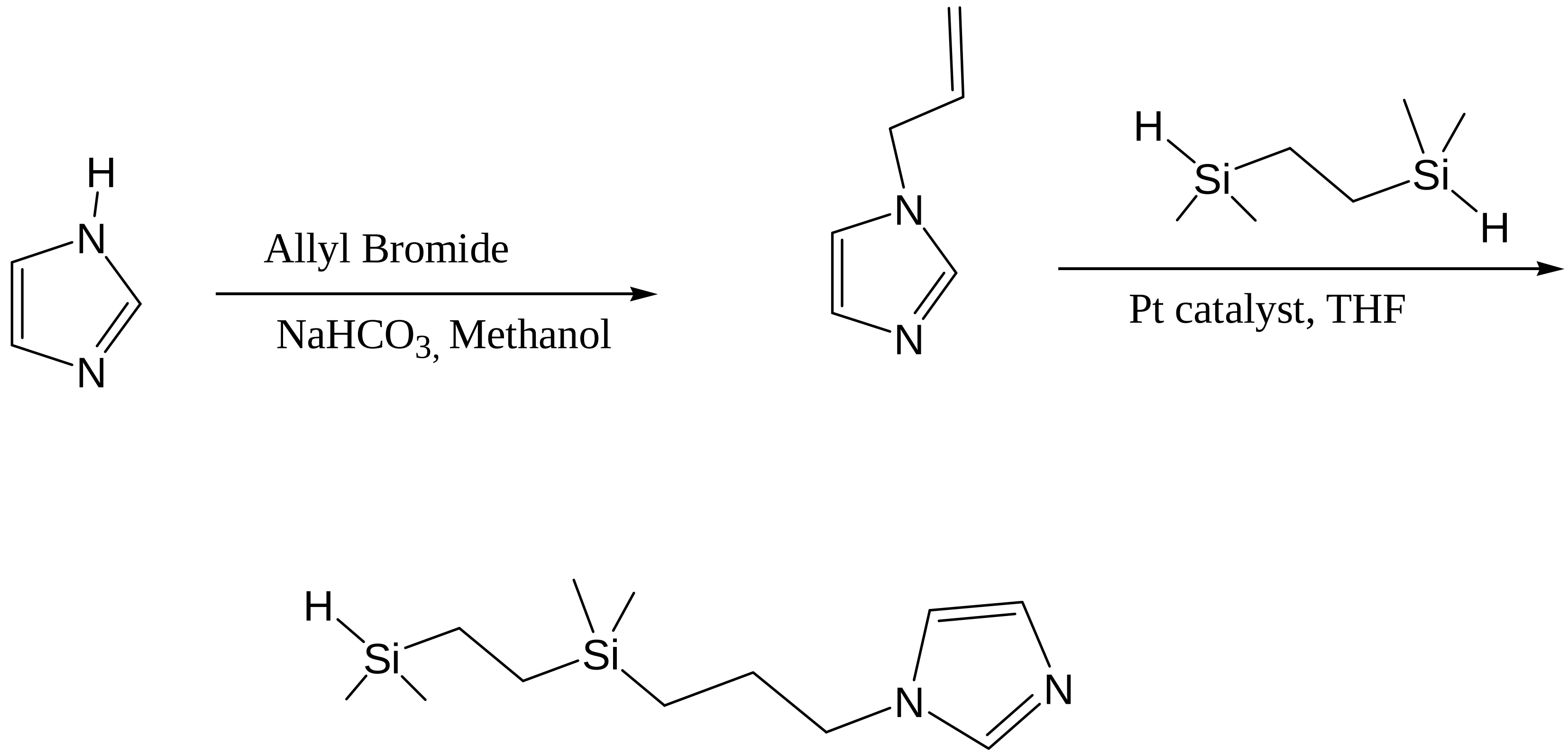


Salt V



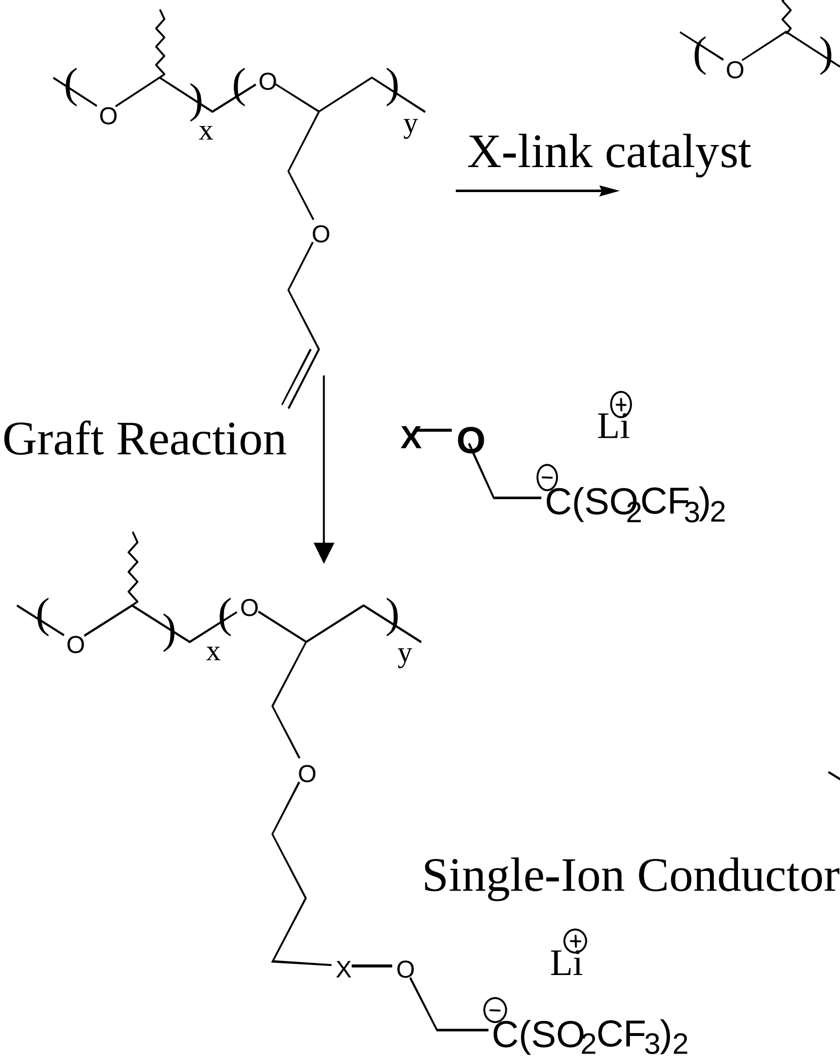
Intermediates

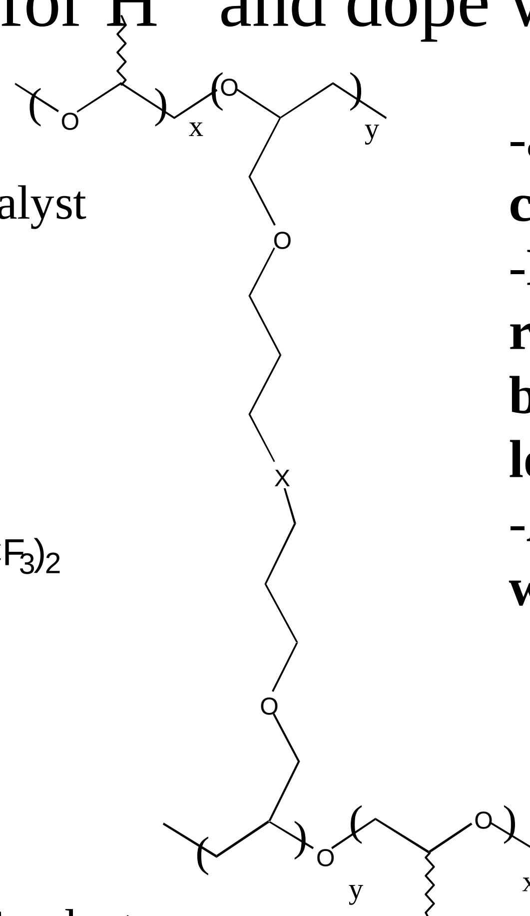
Synthesis of N-allyl Imidazole and intermediate for grafting



Polyether Polyelectrolytes under construction for Lithium Batteries - NASA

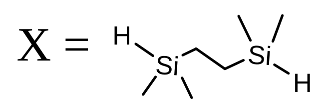
Exchange Li^+ for H^+ and dope with Imidazole



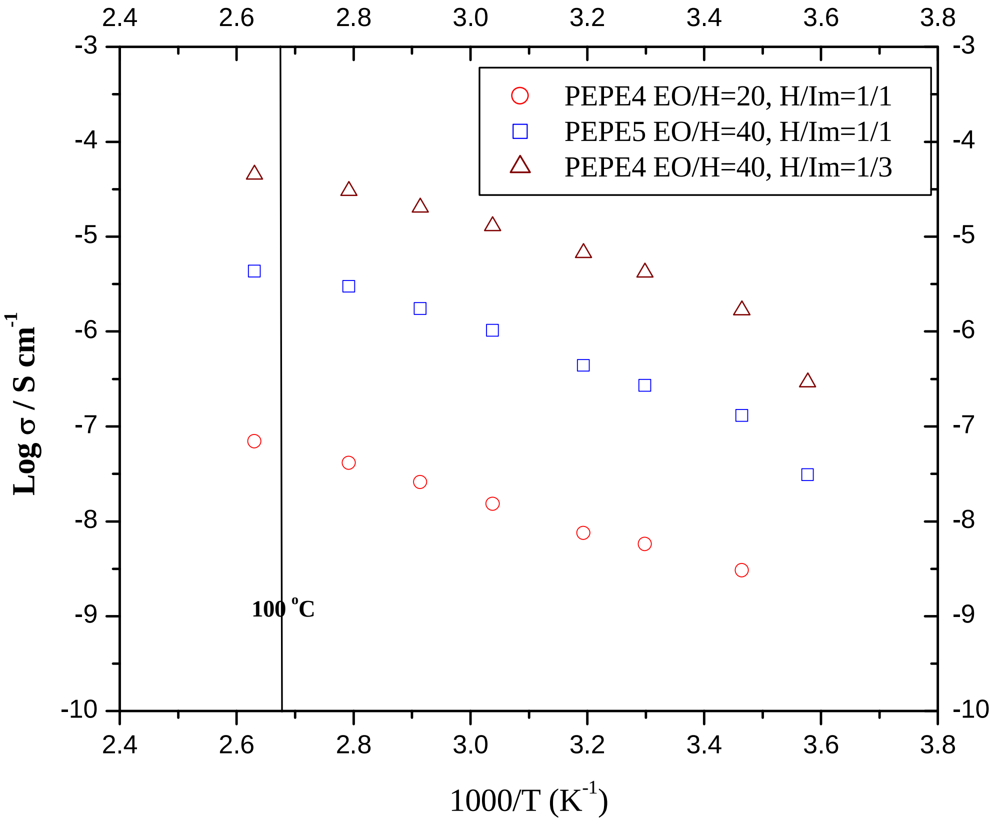


X-Linked Network
- may link different polymers to stabilize blends for cost savings

-allyl groups are reactive centers in this chemistry.
-Hydrosilation is reproducible, provides better uniformity and leaves no residues.
-Allyl groups do not react with radical initiators



Conductivity of grafted imidazole-based proton conductors – alkylsulfonic acid. All solid state – only the proton moves

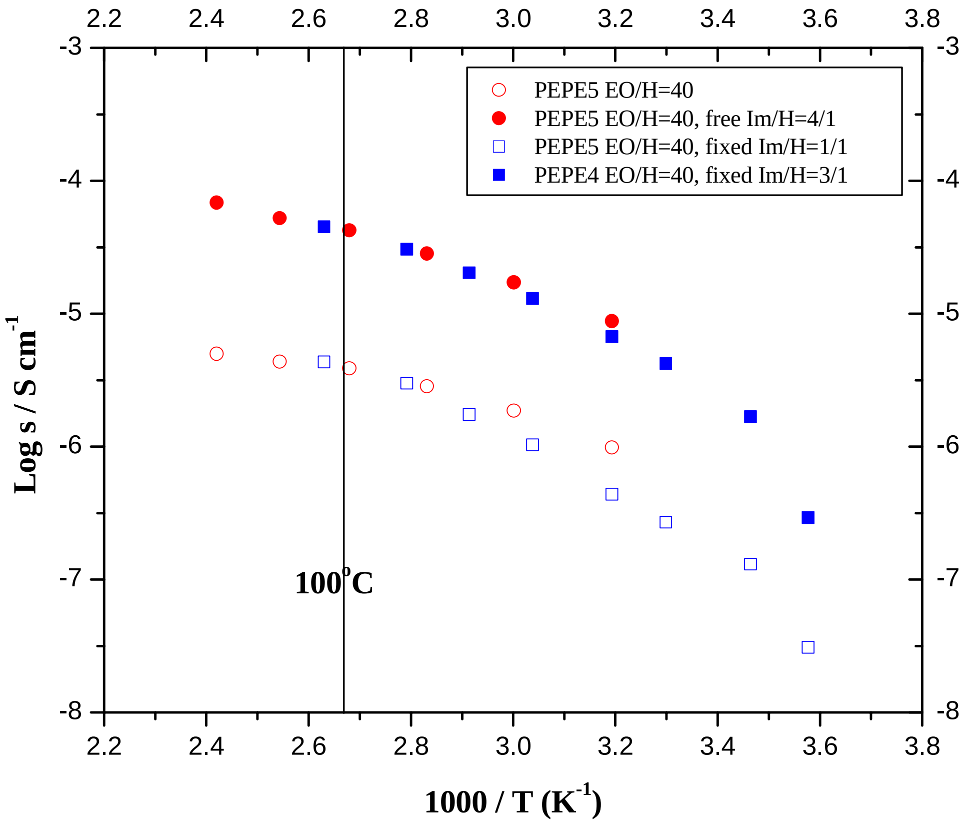


Physical Properties of Polyepoxide Ether Polyelectrolytes.

Polymer	EO/H	Im/H	T_g /ºC
$PEPE_4$	20:1	1/1	-69.7
$PEPE_5$	40:1	1/1	-75.1
$PEPE_4$	40:1	3/1	-75.2

Low T_g polymer is better for MEA
-Polymer is permeable to gases and can adhere to electrode surfaces better

Comparison of conductivities of free imidazole and fixed imidazole based proton conductors. Fixed alkylsulfonic acid groups.

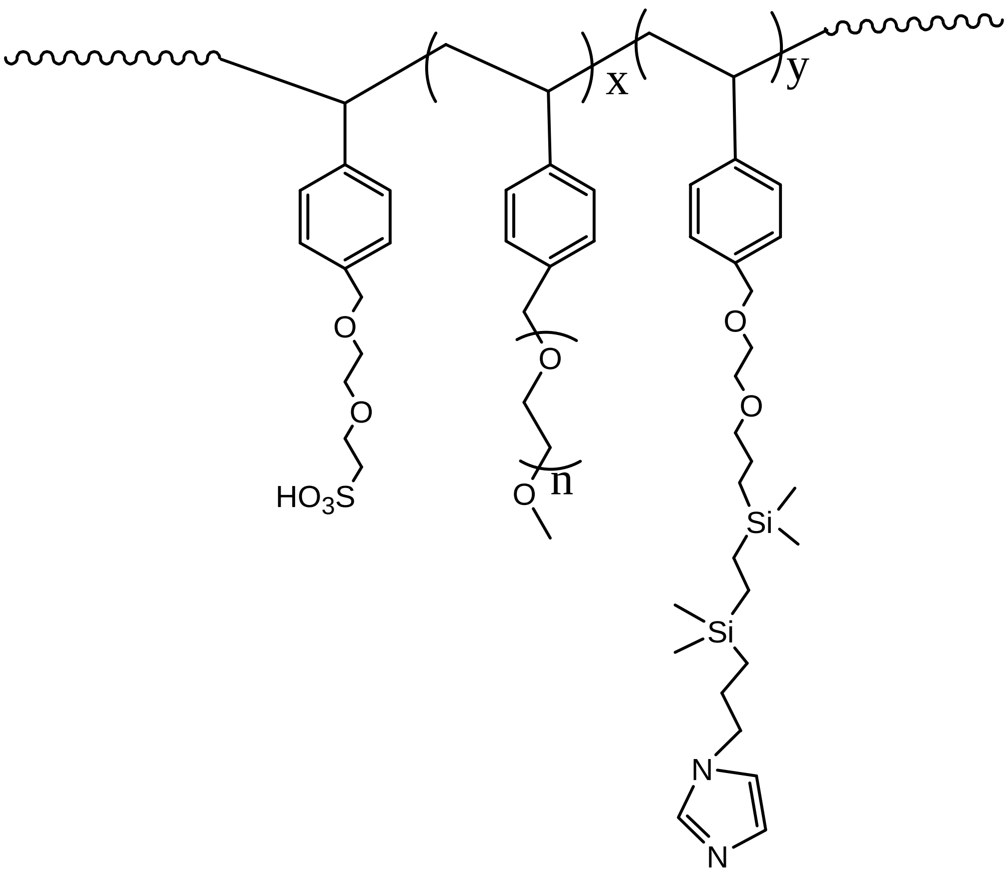


Conductivity of fixed Imidazole polymer equal to the conductivity of the polymer doped with free imidazole solvent.
Relative concentration of Imidazole to acid group is critical.
Increase conductivity by optimization of tether length, acid/base concentration, nature of the acid group (Fluoroalkylsulfonylimides vs. Alkylsulfonate.

➔**Road Map to solvent-free conductivity above 10^{-2}S/cm exists.**

High T_g Pre-polymer

Better for Bulk Membrane – glassy phase impermeable to gases, phase separation favors Grotthuss Transport.



Styrene Backbone provides matrix stiffness, hydrophobicity, phase separation and low gas permeability.

Side chain length provides solvent and ion mobility.

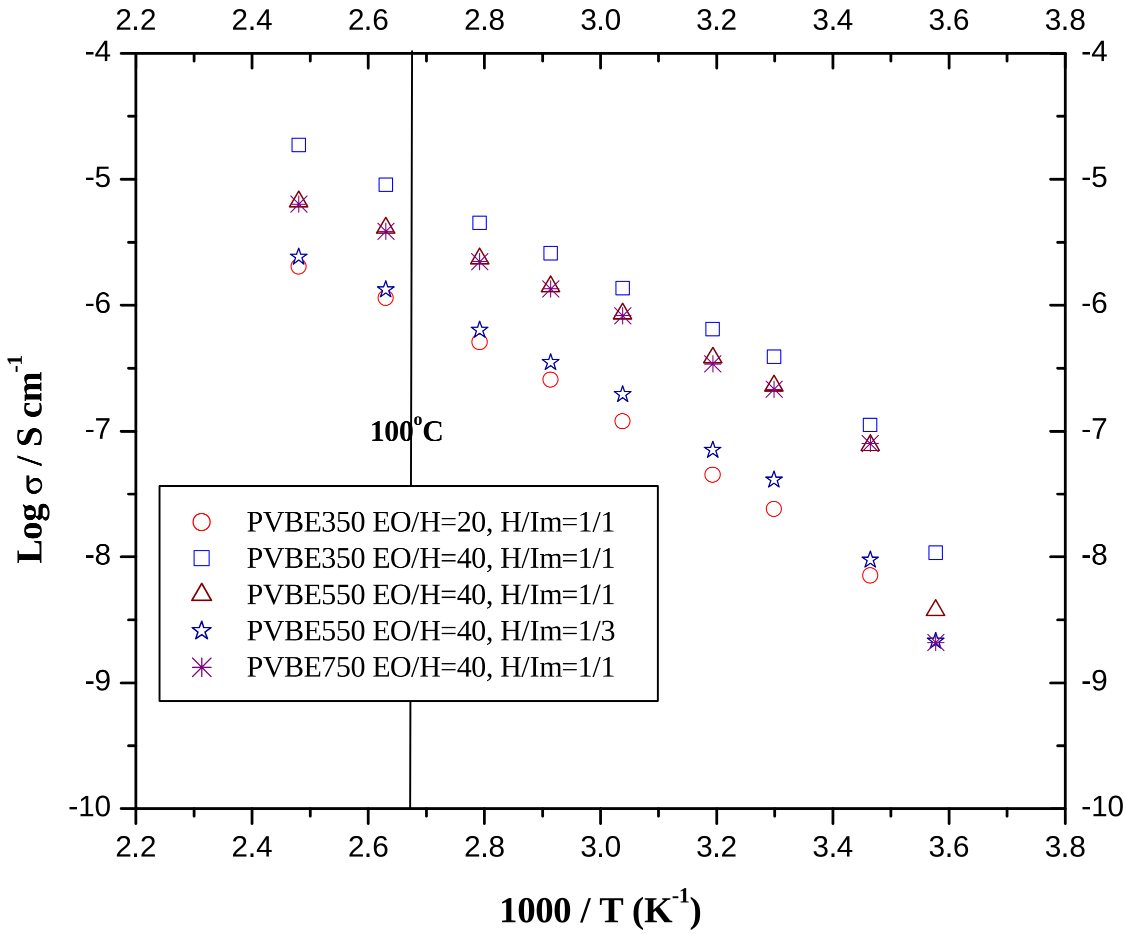
Side chains also used to cross-link structure and lock in morphology.

Multiplet cluster size dependent on relative concentration of solvent imidazole and anions in addition to side chain length. This may control gas permeability.

Physical Properties of Polystyrene-backbone polyelectrolytes.

Polymer	M_w	M_n	PDI	EO/H	Im/H	T_g /ºC
PVE350	6.7×10^3	8.14×10^3	1.21	20:1	1/1	-55.6
PVE350	1.39×10^4	2.56×10^4	1.84	40:1	1/1	-69.5
PVE550	1.21×10^4	1.74×10^4	1.44	40:1	1/1	-64.1
PVE550	1.34×10^4	2.23×10^4	1.66	40:1	3/1	-72.3
PVE750	1.46×10^4	2.01×10^4	1.37	40:1	1/1	-71.5

Polystyrene based proton conductors Tethered N-alkylimidazole and alkylsulfonic acid – only the protons move.



Conclusions

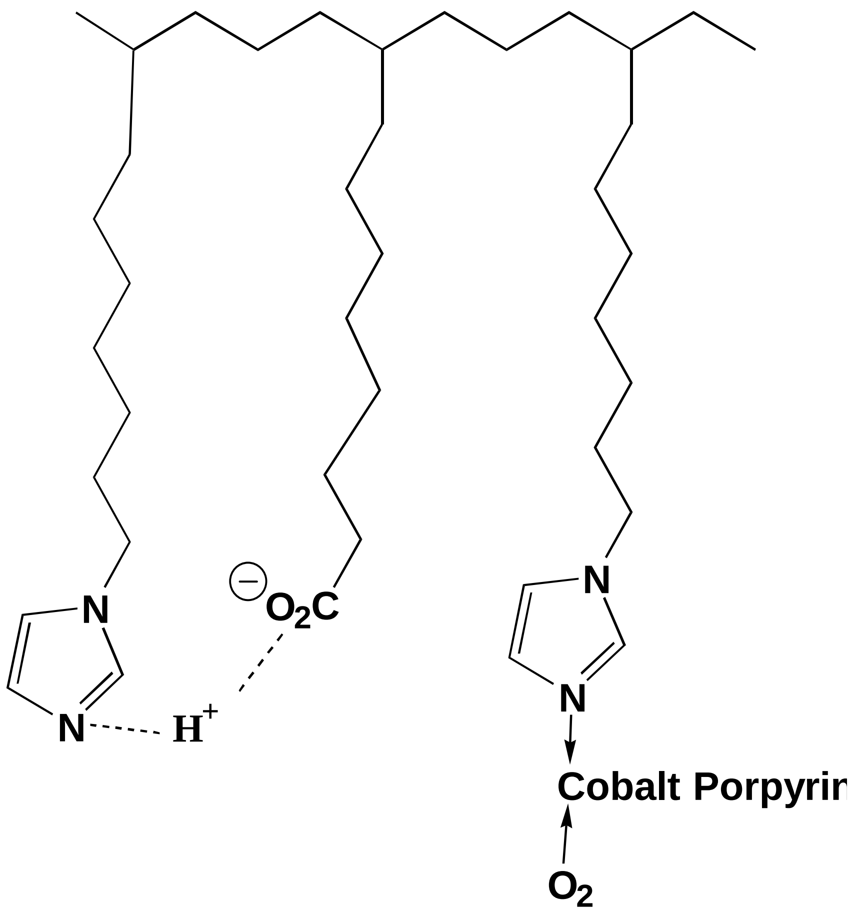
- Imidazole solvation groups are feasible for high temperature and water-free membranes.
- Temperature dependence of conductivity of free imidazole is consistent with the Grotthuss mechanism of proton transfer.
- The morphology of the polymer matrix plays a role on the promotion of the Grotthuss mechanism.
- The imidazoles must be tethered to the polymer matrix due to volatility. This results in a loss of conductivity.
- The conductivity loss due to tethering of imidazoles is small.
- Stronger acid groups such as fluoroalkylsulfonylimides promote higher conductivities.
- Longer tethers for the acid groups promotes conductivity.
- Imidazole groups in the MEA must be protonated to avoid catalyst poisoning. This results in a loss of conductivity.

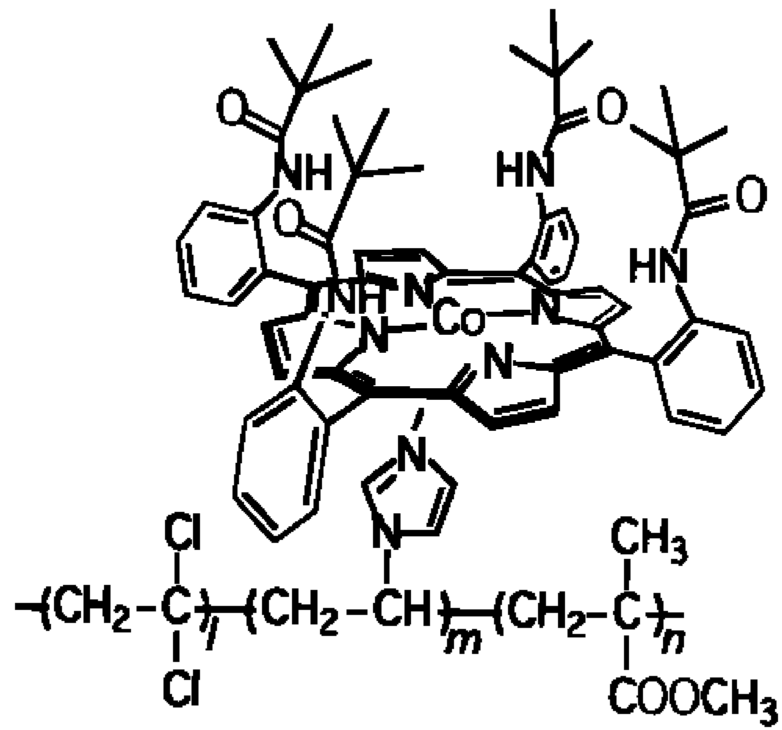
Next Steps

- Attach C-tethered imidazoles – Grotthus transport possible.
- Attach triflate and fluoroalkylsulfonyl imides.
- Increase hydrophobic content in backbone
  - Polymers specifically designed for this program that phase separate – promote Grotthuss transport.
- Prepare MEAs and test full cell performance
- Investigate water uptake and low temperature performance.
- Degradation studies and failure analysis.

Oxygen Separation Membrane

Vinyl Imidazole used rather than vinyl pyridine.

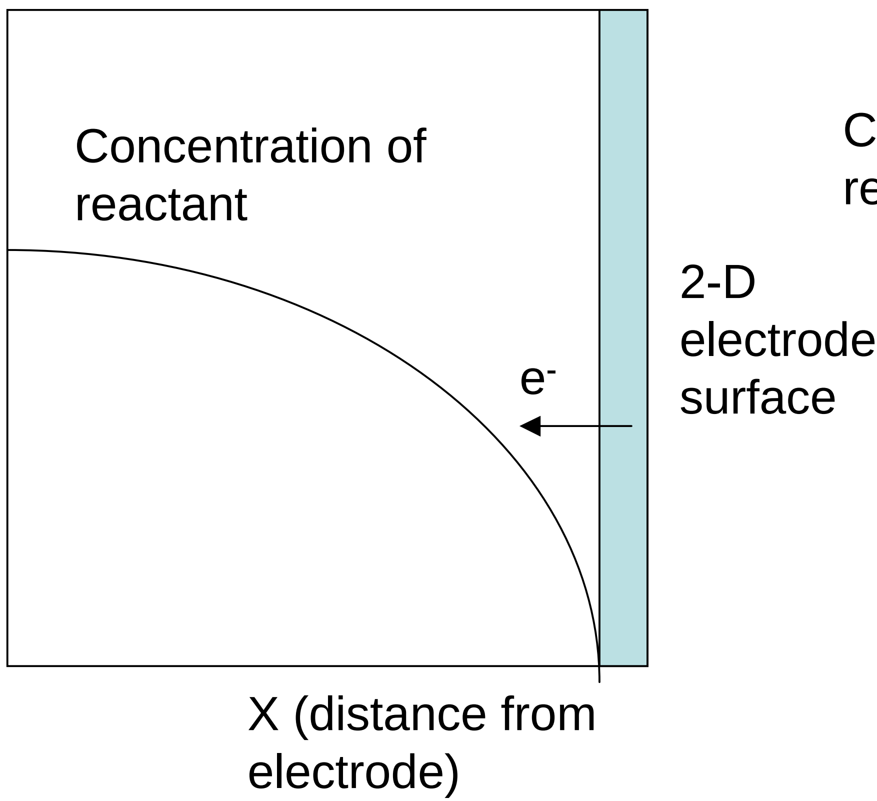


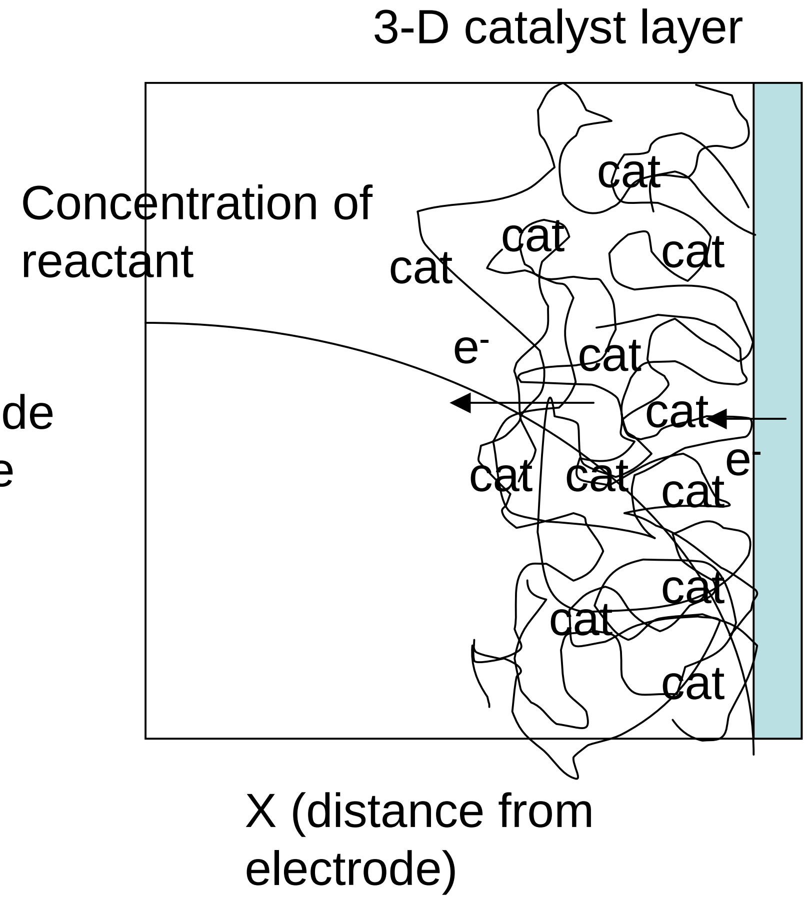


Hiroyuki Nishide,* Yukihiro Tsukahara, and Eishun Tsuchida,
J. Phys. Chem. B, 102 (44), 8766 -8770, 1998.

Two vs. Three Dimensional Catalysts

Polymer-coated electrode provides dynamic 3-D catalyst layer that makes up for slow kinetics of the catalyst by 3-D supply of substrate. Polymer chains must be mobile to allow catalyst to move to the electrode to pick up electrons.





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