

Radiation Grafting of Ionic Liquids to Synthesize Polymer Electrolyte Membrane Fuel Cells

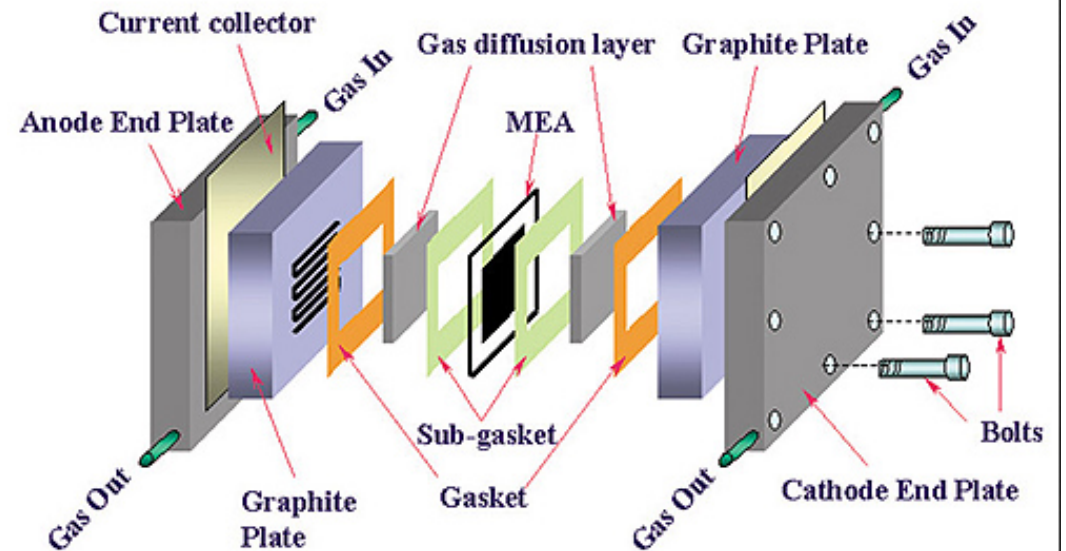
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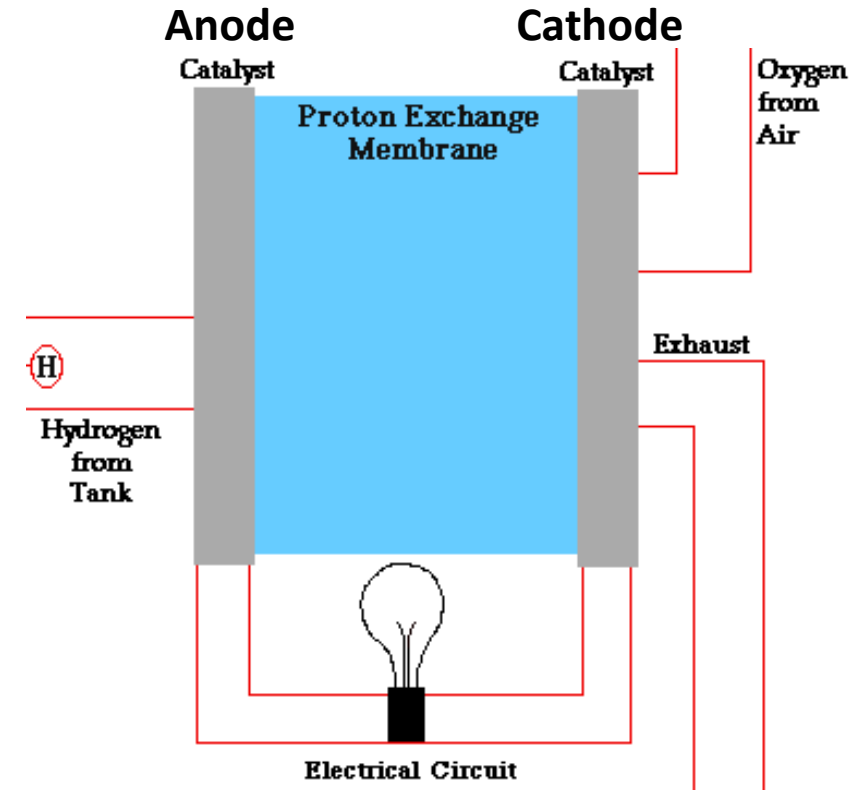
Membrane Electrode Assembly (MEA)



<https://www.scientific-computing.com/images/scwjnfeb03fuelcell1.jpg>

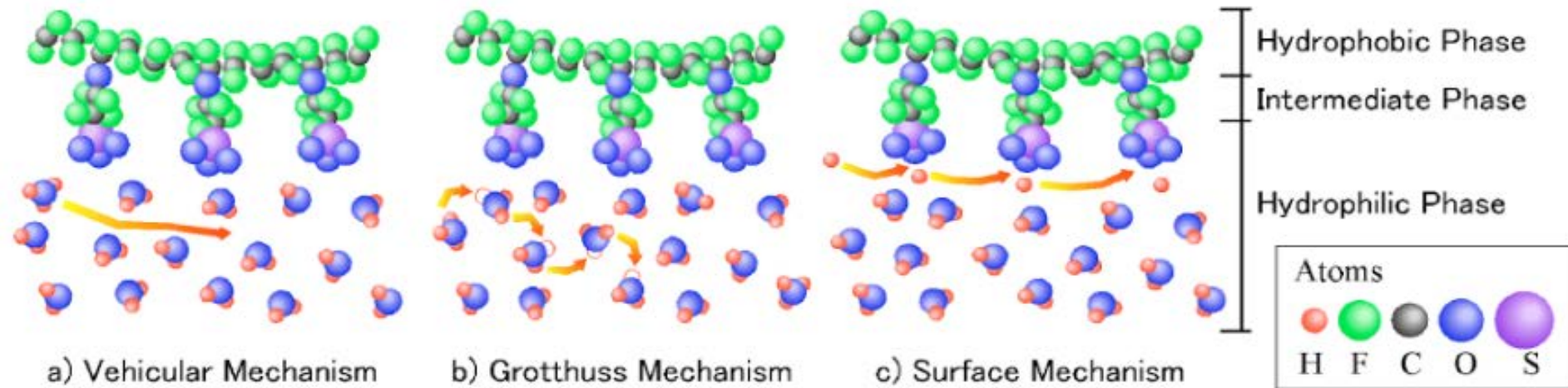
Polymer Electrolyte Membrane Fuel Cell

- PEMFC rely on proton conducting membranes to convert the chemical potential of hydrogen combustion into electrical power
- Traditional PEM operate using water as the medium to transport protons from anode to cathode
- Operating temperature and humidity have significant impact on proton conductivity and performance



Marc Marshall, Schatz Energy Research Center: <http://www.schatzlab.org/index.html>

Proton Transport Mechanism in PEMFC



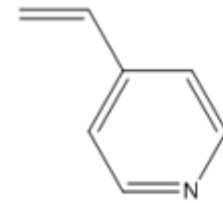
Tsushima, S. et al. "Elucidation of Proton Conducting Mechanism in a Polymer Electrolyte Membrane of Fuel Cell by Nuclei Labeling". *MRI. ECS Trans.* **3**, 91–96 (2006).

- PEM micro structure, temperature, water content and localized electric field are the main factors that influence the proton conductivity mechanism
- Water needs to be substituted with another medium for high temperature PEM operation

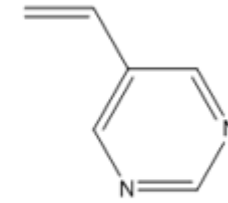
Sun, H., Yu, M., Li, Z. & Almheiri, S. A molecular dynamic simulation of hydrated proton transfer in perfluorosulfonate ionomer membranes (Nafion 117). *J. Chem.* **2015**, (2015).

Design: High Temperature PEMFC

Cyclic amine ionic liquids were used to achieve proton conductivity at high temperature



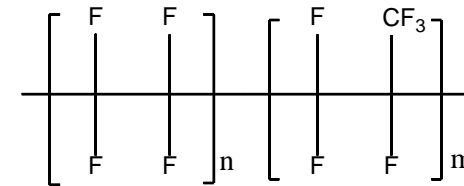
4-Vinylpyridine
pKa 5.62



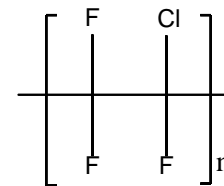
5-vinylpyrimidine
pKa 1.82

Indirect radiation grafting was used to attach monomers onto fluorocarbon thin films:

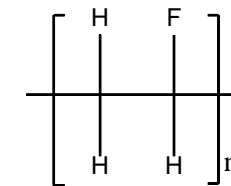
- Fluorinated ethylene propylene (FEP)
- Polychlorotrifluoroethylene (PCTFE)
- Polyvinylfluoride (PVF)



FEP



PCTFE

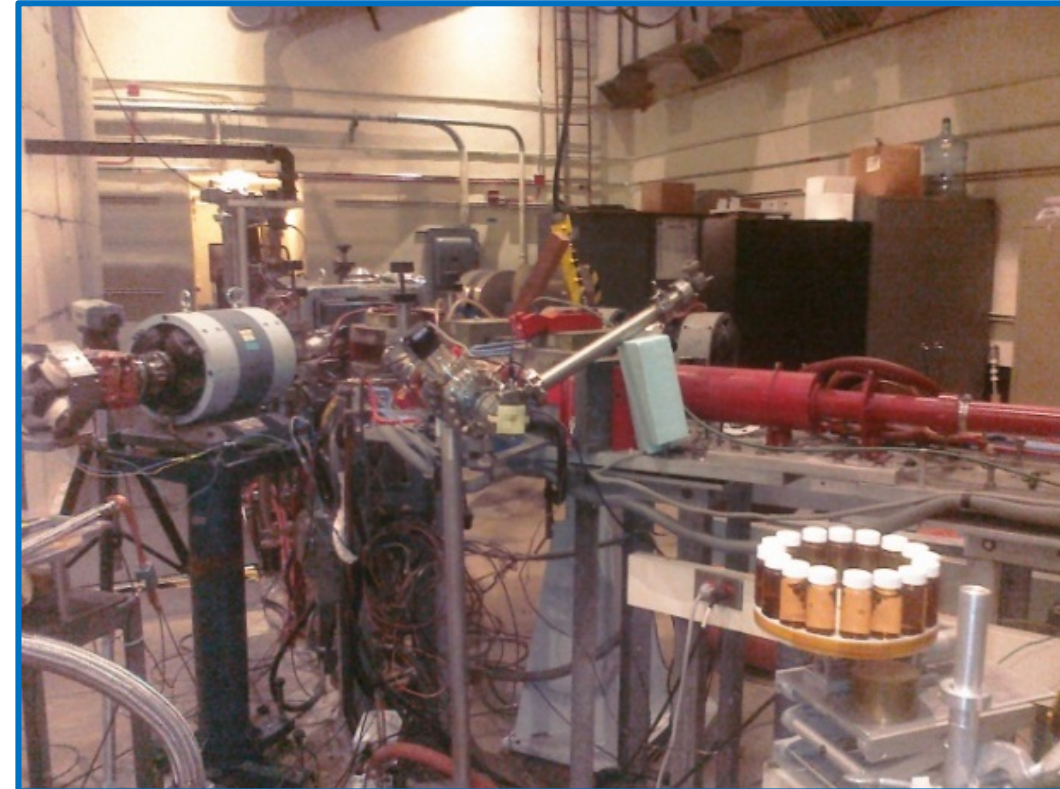
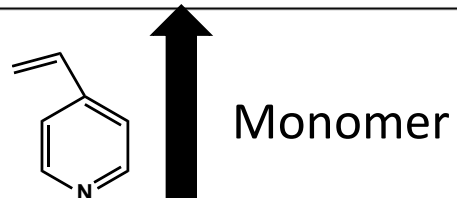
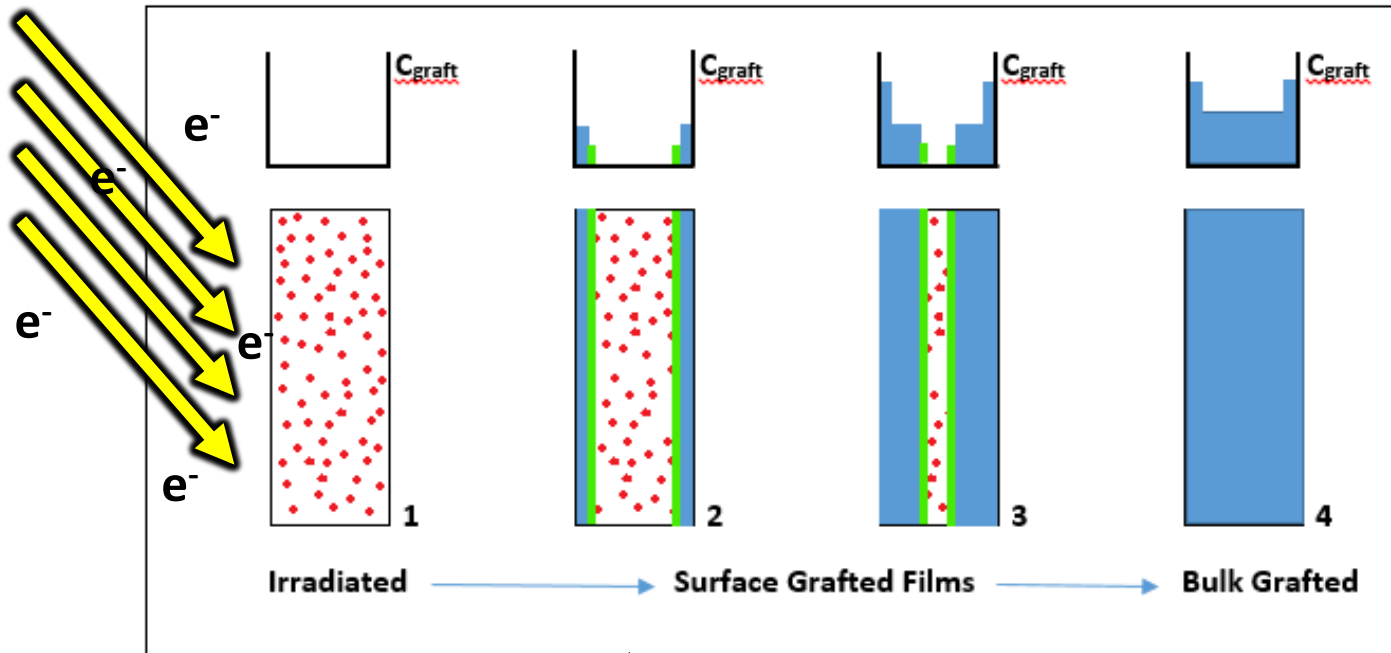


PVF

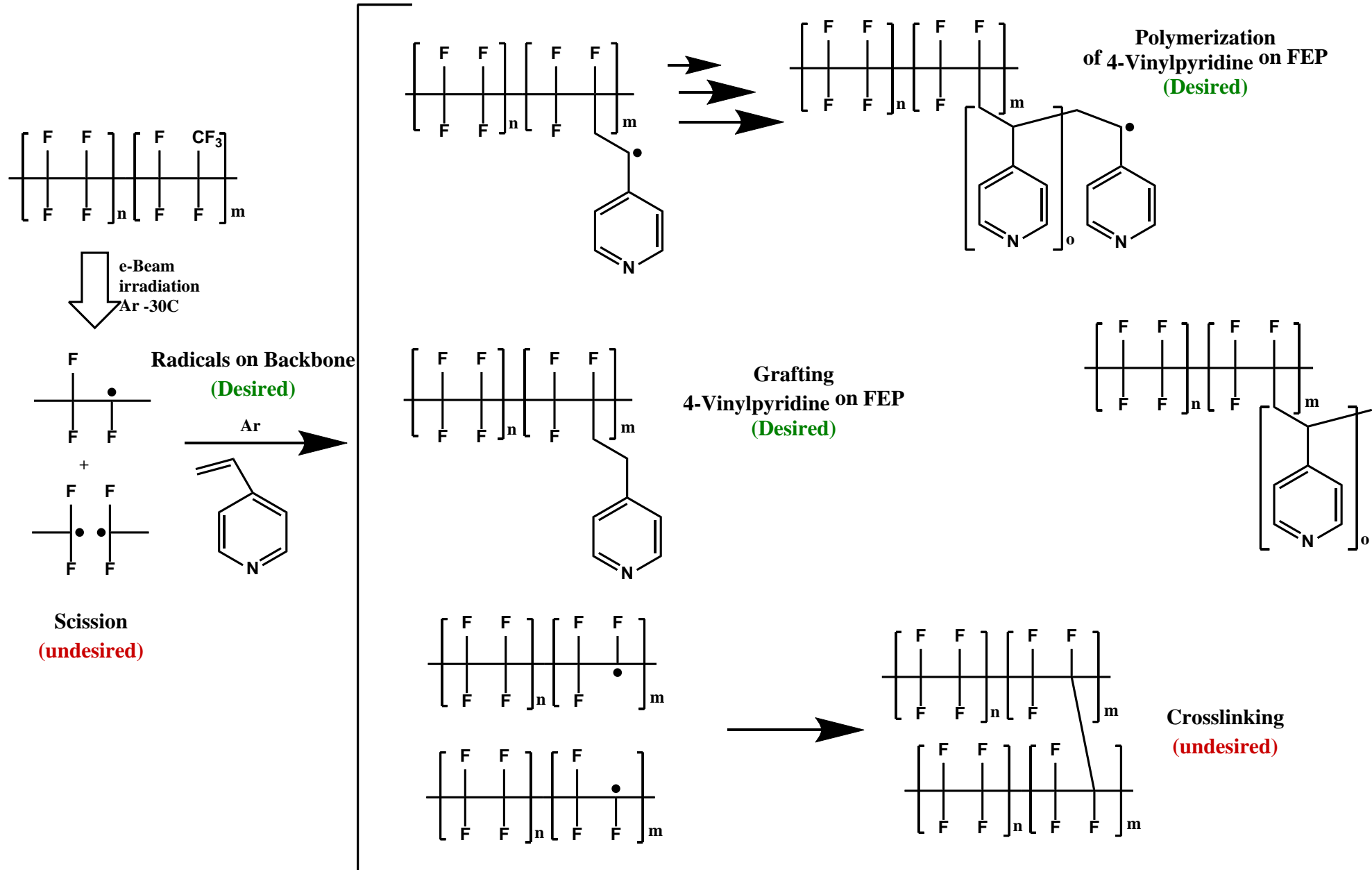
Synthesis: Electron Beam Radiation Grafting

Medical Industrial Radiation Facility (MIRF) NIST

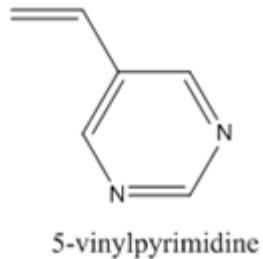
Grafting Front Model



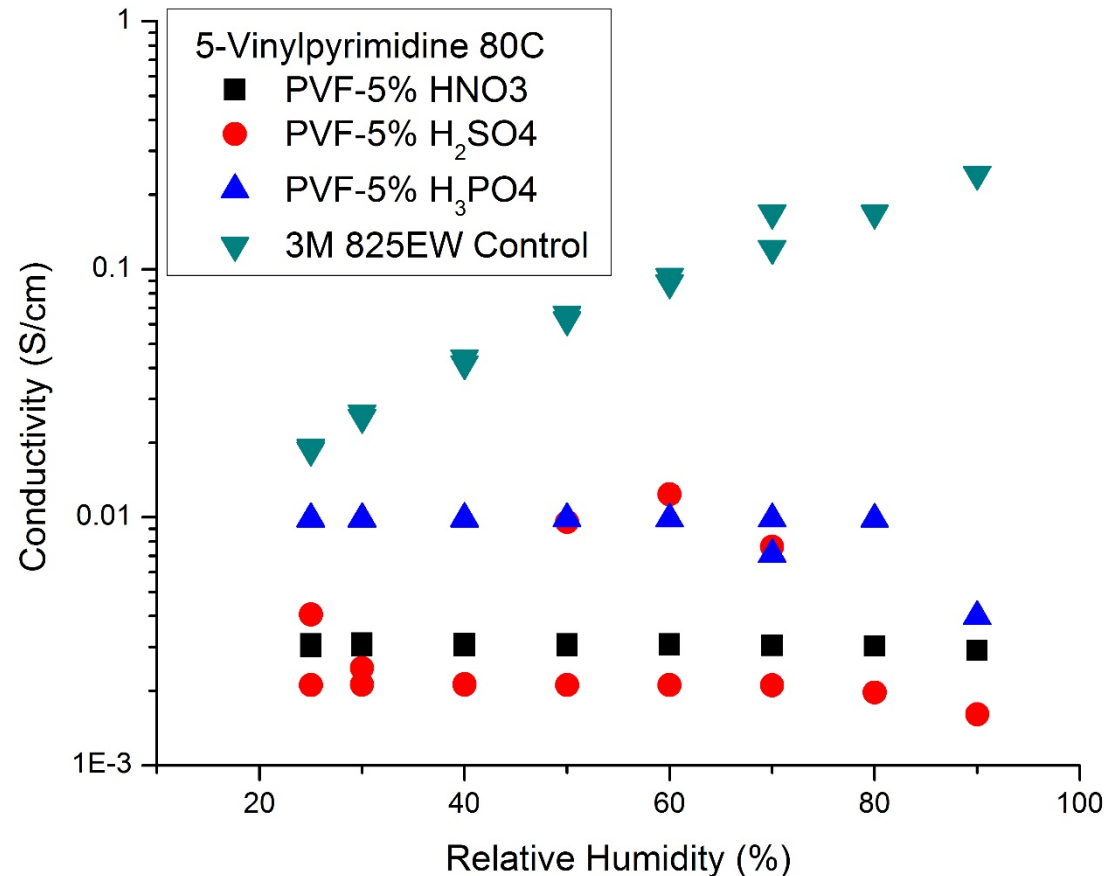
Indirect Grafting Competing Reactions



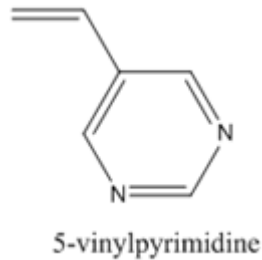
Conductivity: 5-vinylpyrimidine 80°C



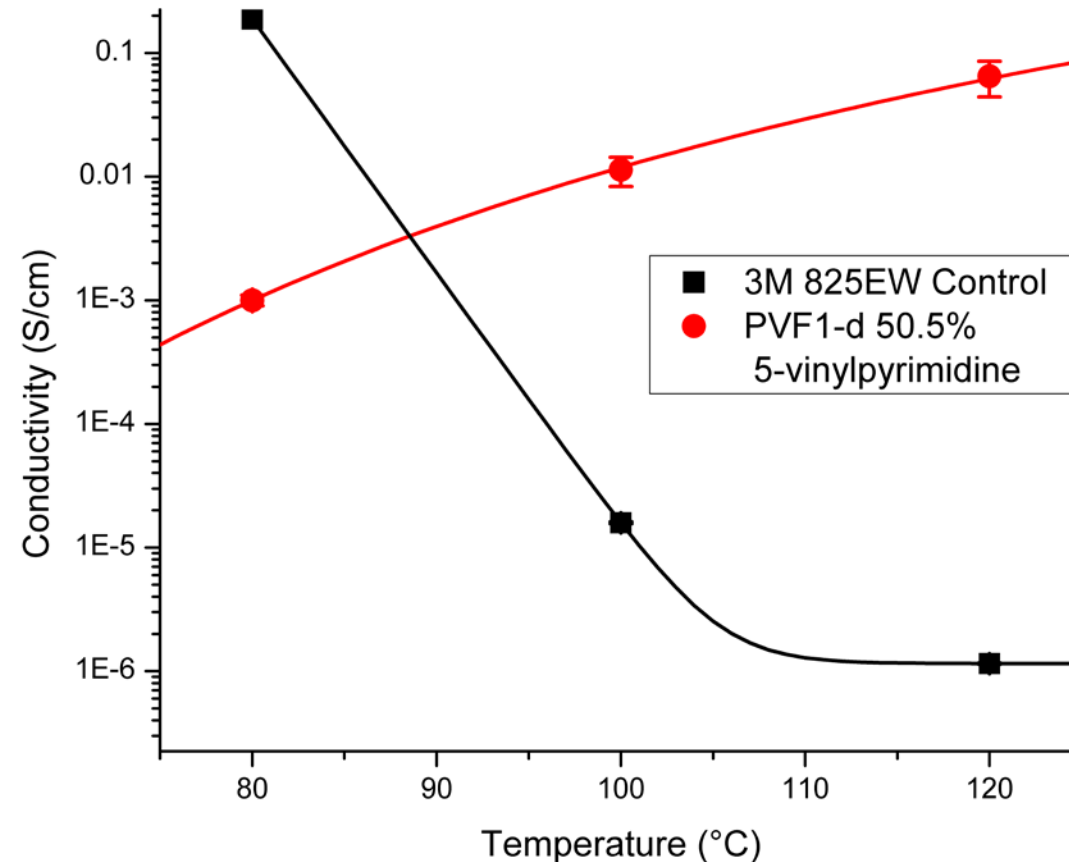
- Proton conductivity in these PEM show humidity independent
- Humidity independent was most likely due to the symmetry of 5-vinylpyrimidine group low activation energy proton conductivity
- After acid treatment one nitrogen is protonated allowing pyrimidine groups to form a solid-state network for proton conductivity



High Temperature Conductivity



- Ionic liquid proton conductivity increases with temperature
- Does not require humidity control
- Higher operating temperature PEMFC operate more efficiently and reliably



Significance

- The goal of this research is to design, synthesize and analyze **novel solid-state PEM** that incorporate protic ionic liquids and to assess them for high temperature fuel cell application
- The performance of PEMFC can be significantly improved by increasing their **operating temperature above 120°C** but their current design is limited by their reliance on water for proton conductivity
- Confirmed proton conductivity of protic ionic liquids, **heterocyclic amines** to be used to substitute water as a proton conductive medium at high temperatures
- Trends found in this research will help the development of future anhydrous PEM with higher conductivity, durability and higher operating temperatures

Acknowledgments

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- Dr. Joseph Robertson, Engineering Physics NIST
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