High Temperature Direct Methanol-Fueled Proton Exchange Membrane Fuel Cells

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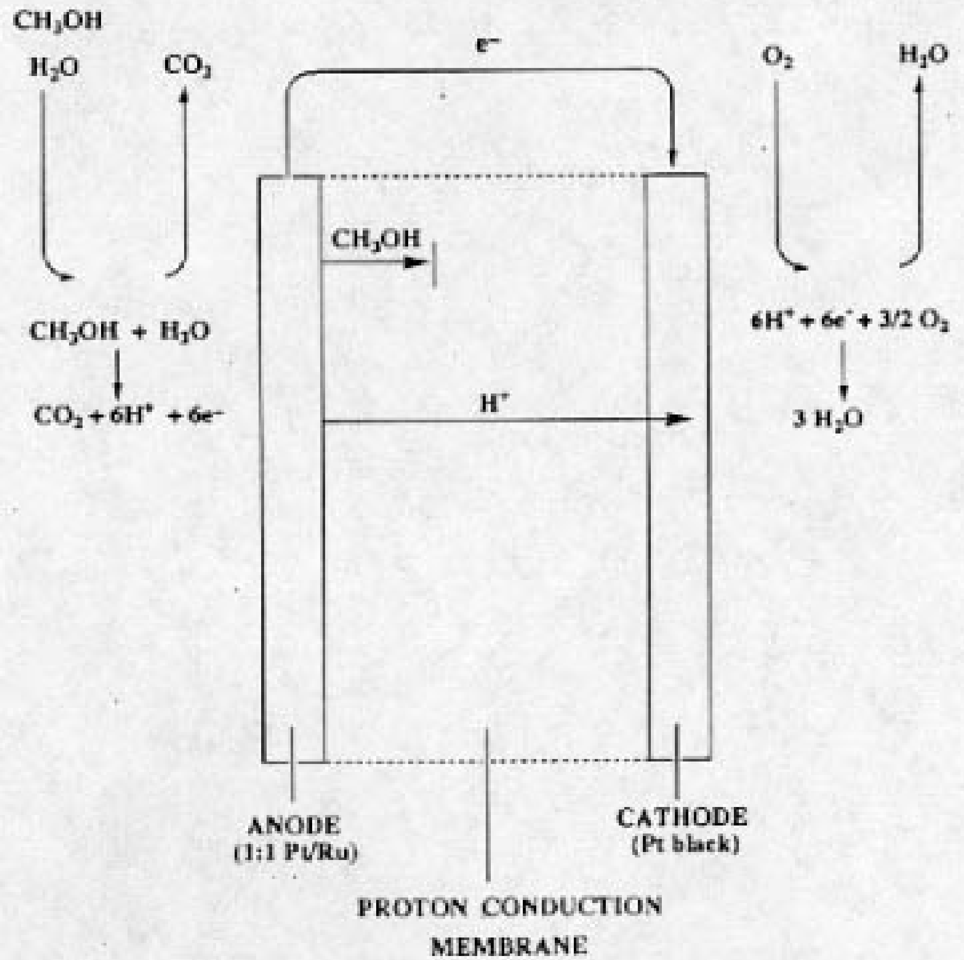
METHANOL - FUELED FUEL CELL



Our objective is to develop a better proton-conduction membrane for methanol-fueled fuel cells

(a) It must conduct protons at temperatures above 100°C

(b) It must prevent methanol crossover

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A Membrane for a Direct Methanol Fuel Cell must be -

1. **Chemically and physically stable at elevated temperatures (100-200^{0}C) in contact with acidic, oxidizing, reducing, and free radical environments.**

2. **Conduct protons**

3. **Resist methanol crossover**

Very few polymers have these three combined characteristics

WEAKNESSES OF MOST POLYMERS FOR FUEL CELL APPLICATIONS

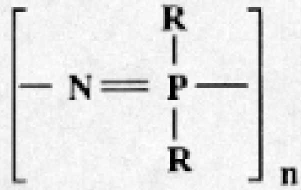
1. They contain carbon atoms in the backbone and are, therefore, decomposed by oxidizing agents such as $HO^{\cdot}$ free radicals

2. They are limited by the types of side groups and density of functional groups (such as SO_3H, PO_3H_2, etc.)

3. Tend to be soluble in organic solvents at high temperatures and to allow the transmission of organic vapors and liquids such as methanol

4. The backbone elements can only rarely be used to immobilize acid functional groups

WHY POLYPHOSPHAZENES FOR FUEL CELL APPLICATIONS ?



n = 15,000

1. **Backbone of inorganic elements (no carbon). Highly resistant to oxidation, reduction, and free-radical decomposition**

2. **Method of synthesis allows very high loadings of side groups (R) with acidic functional groups**

3. **Presence of inorganic backbone, coupled with a wide choice of side groups, allows polymers to be tailored <u>at the molecular level</u> for resistance to organic solvents and fuels**

4. **The backbone nitrogen atoms, as well as the side groups, can be the sites for binding acidic functional groups**

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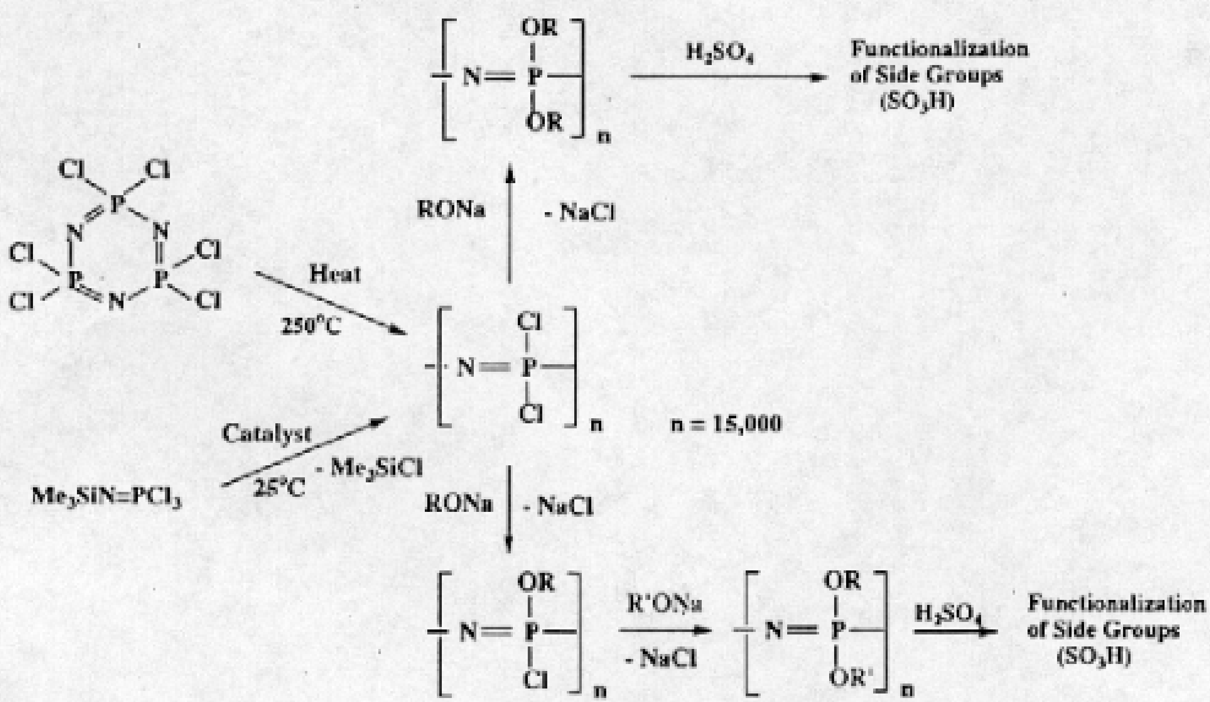
SYNTHESIS OF THE POLYMERS

Single-Substituent Polymers



Mixed-Substituent Polymers

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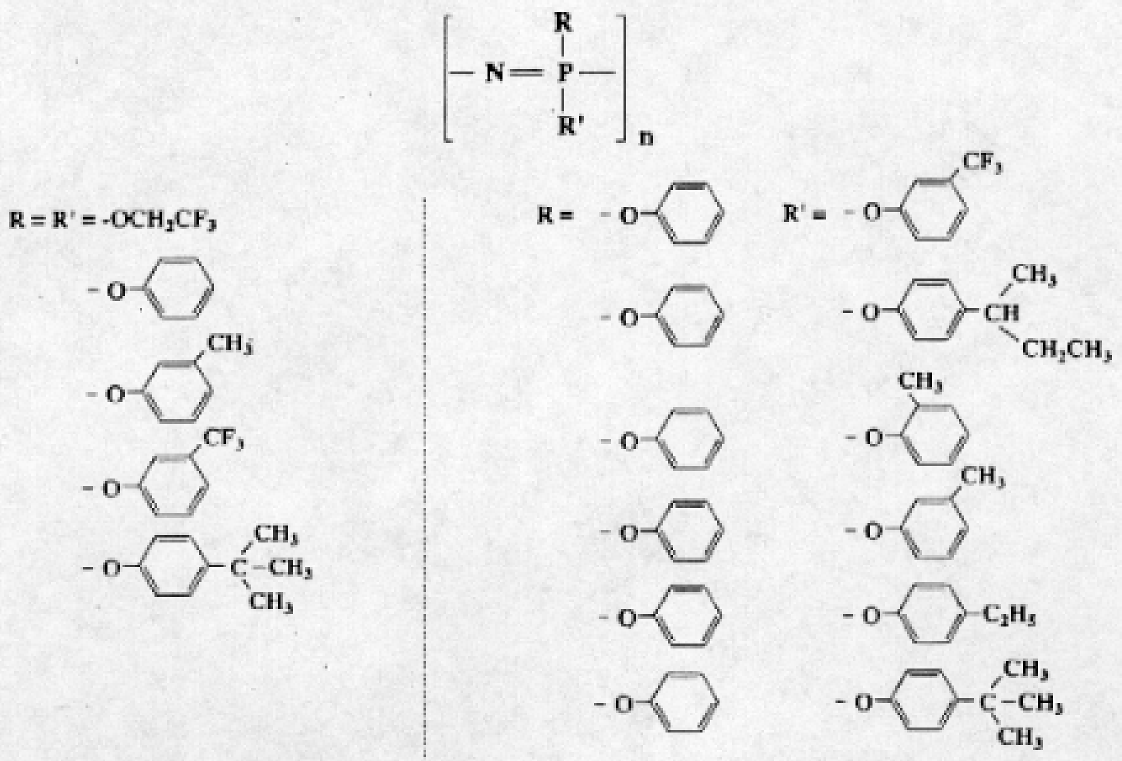
RANGE OF SIDE GROUPS UTILIZED



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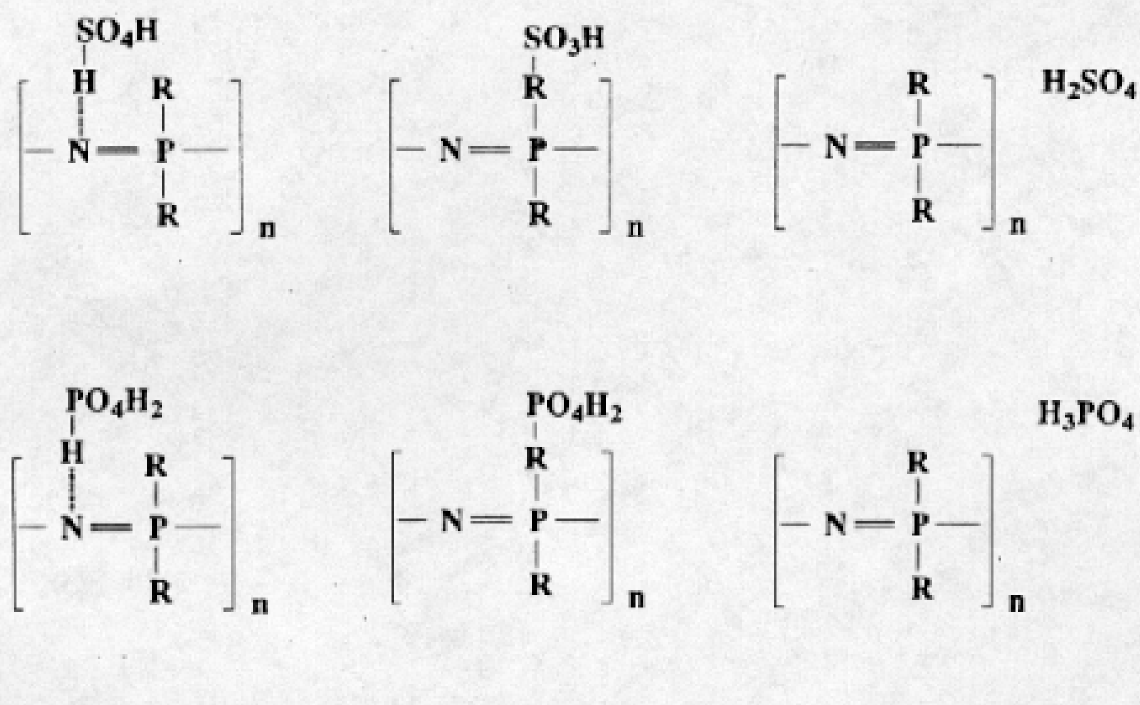
ALTERNATIVE WAYS TO INCORPORATE ACID FUNCTIONAL GROUPS



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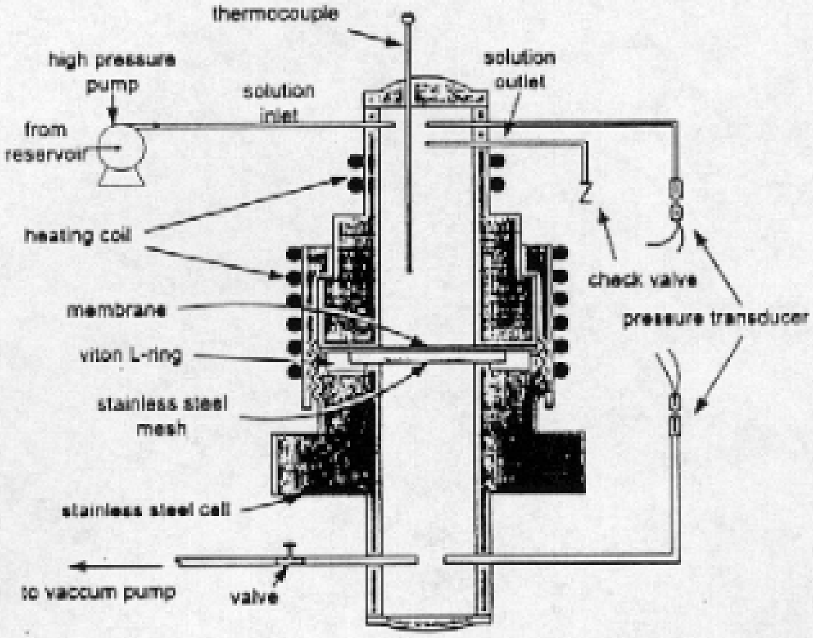
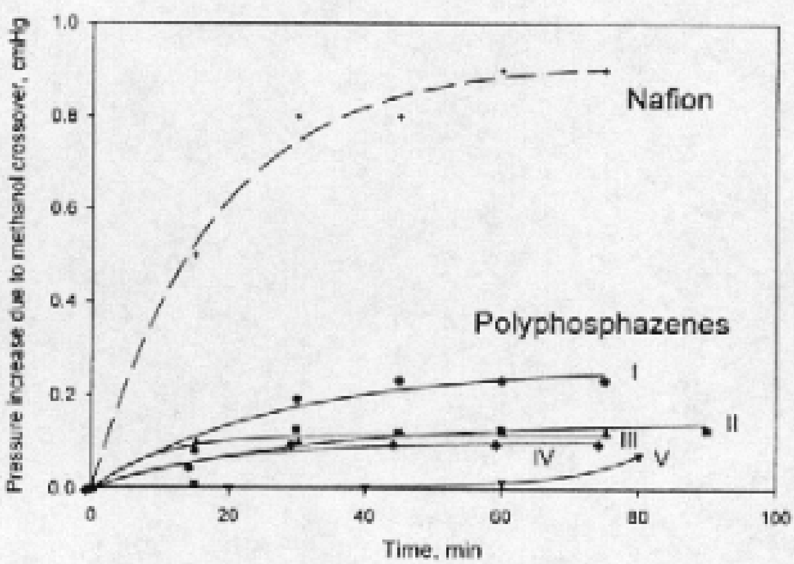
Schematic of the Apparatus for Crossover Measurements at Elevated Temperatures

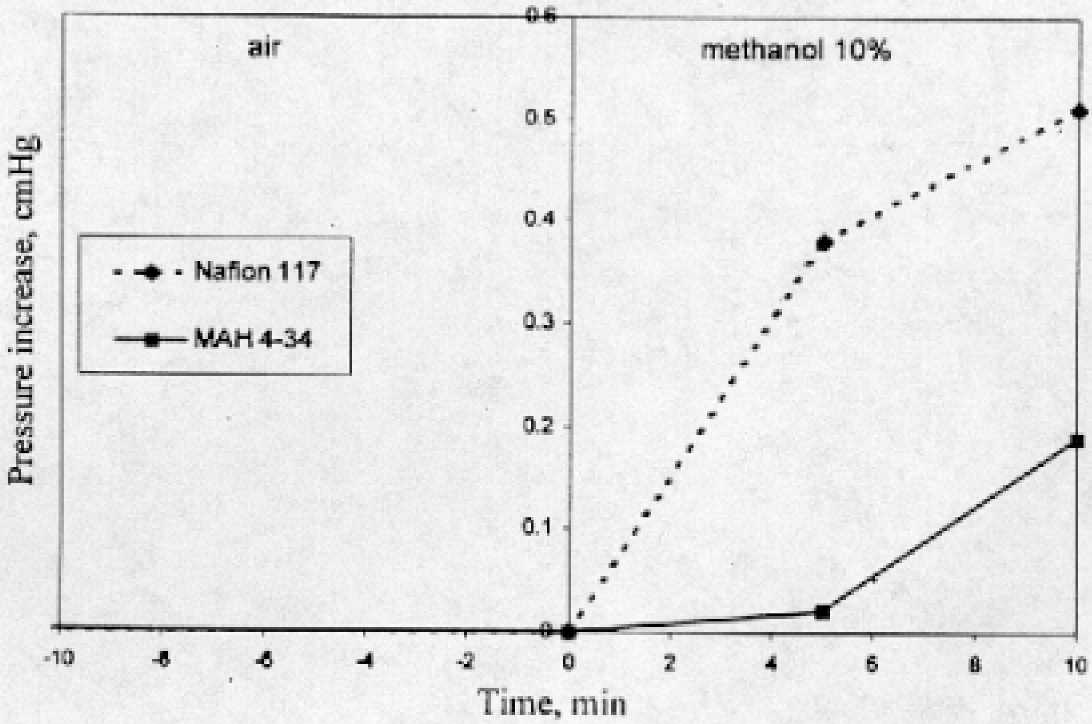


Methanol Crossover of Polyphosphazenes



Methanol crossover was measured using the pressure increase method. The volume of the vacuum chamber is 4.1 cm^3

Methanol Crossover at 40 °C



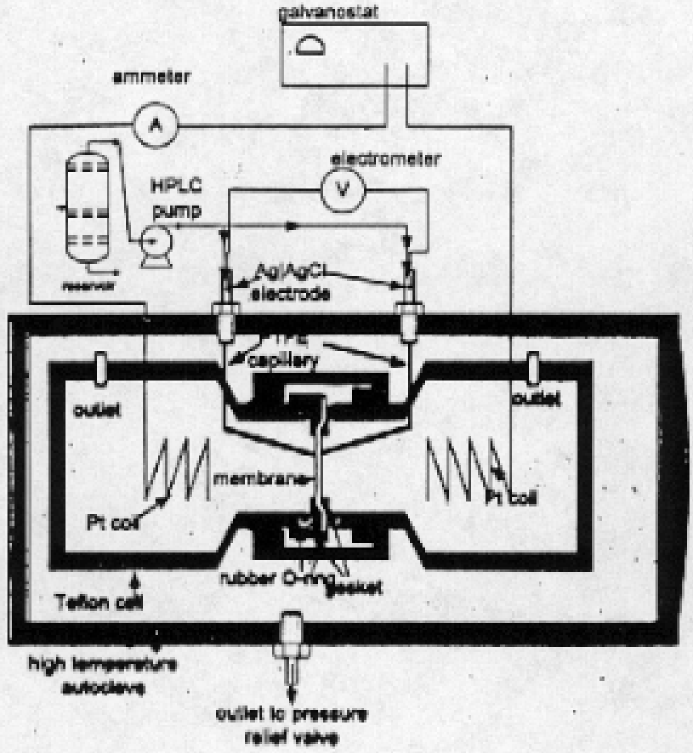
Experimental conditions:

temperature, 40°C; pressure of water or solution, 1 atm; volume of the vacuum chamber, 4.1 cm^3;

thickness of the Nafion 117 film, 0.023 cm; exposed area, 7.57 cm^2; conductivity, 8.1 x 10^{-3} S/cm.

thickness of MAH 4-34 film, 0.029 cm; exposed area, 7.57 cm^2; conductivity, 7.9 x 10^{-3} S/cm.

Electrochemical Cell for Membrane Conductance Measurements in Liquid Phase at Elevated Temperatures

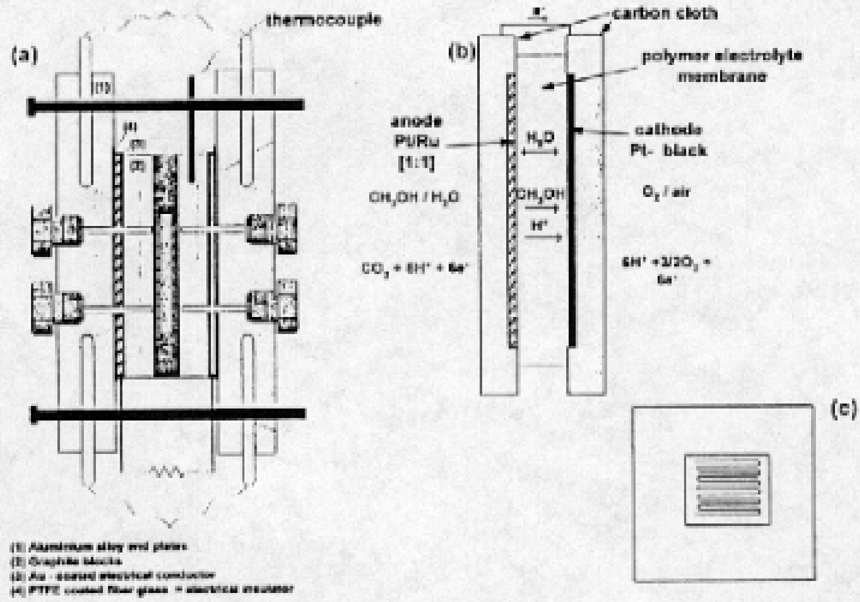


Results of Membrane Conductance Measurements

Membrane Code	Ionic conductivity, (S/cm)	Ionic Conductivity of Nafion 117, (S/cm)
MAH-Phosphate 3	3.27×10^{-3}	1.10×10^{-2}
MAH-Phosphate A	4.34×10^{-3}	
MAH-Phenoxy Phosphate 1-1	2.29×10^{-3}	
MAH-Phenoxy Phosphate 2-2	3.76×10^{-3}	
MAH-Phenoxy Phosphate 3-3	1.36×10^{-3}	
MAH-Phenoxy Phosphate 2	1.63×10^{-2}	
MAH-Phenoxy Phosphate 3	6.79×10^{-3}	

Los Alamos Design of Fuel Cell

(a) Side view of the cell assembly
(b) Details of the PEM assembly
(c) Top view of the graphite block



ECONOMICS

Scale-up of polymer synthesis to 1-10 Kg per batch level being carried out by Phosphazene Custom Synthesis (PCS Inc.) State College, PA (a Penn State spin-off company)

Development work to be carried out by PCS in preparation for scale-up to an initial manufacturing level of 1000-10,000 Kg (2000-20,000 lb) per year

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Initial cost of polymer at the research level estimated to be \$5-10 per 20 x 20 cm membrane

At the full scale manufacturing level, assuming a 9-membrane (20 x 20 cm) stack, and \$1 per membrane, the polymer costs would be \$9 per Kilowatt

IN WHAT WAYS ARE THESE MEMBRANES BETTER THAN NAFION ?

1. Greater resistance to methanol crossover.
2. Less expensive than Nafion
3. Membrane performance and properties can be tuned over a much wider range by changes to the polymer side groups
4. Allow acid phosphates to be used as the proton conduction phase which improves conduction and membrane physical properties

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