Part V. Functional Polymers for Energy Applications

Outline of Part

Fuel Cell

- Introductions for Fuel Cell
- Basic Principle & Structure of Fuel Cell
- Types of Fuel Cell
- DMFC
- Application Field & Market Prospect

DMFC

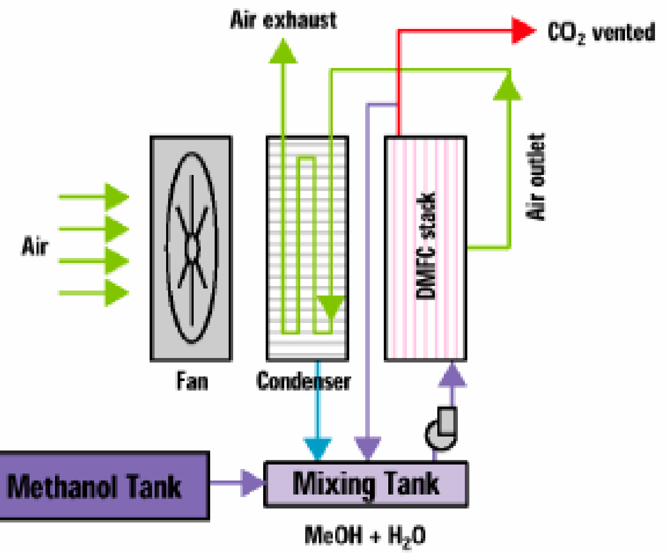
- **Electrochemistry of DMFC**

Anode : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode : $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3\ H_2O$

Overall : $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

- A DMFC system does **not** require a bulky and heavy **hydrogen storage system** or **a reforming subsystem**.
- Liquid methanol is the fuel being oxidized directly at the anode.



Schematic of DMFC system

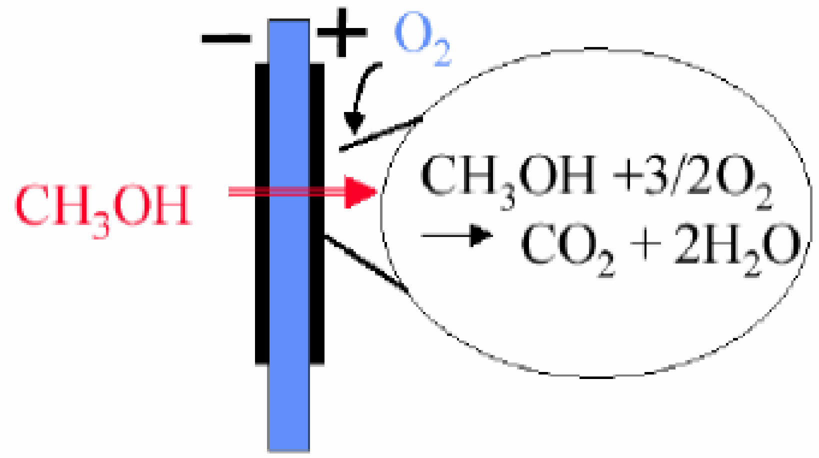
Advantage of DMFC

- Simpler than a reformer system
- Simpler stack design
- Lower temperature of operation compared to a reformer system
- Capable of an ambient temperature start-up
- Good thermal control of stack
- Infrastructure built for gasoline can be used with a little change

Issues

Core Technologies	Technical Issues
MEA	·High Efficient Catalyst & Support Material ·Catalyst Electrode Process ·High Power Density MEA ·Low Catalyst Loading ·CO Tolerant Catalyst
Membrane	·High Proton Conductivity / Conductance ·Chemical / Mechanical Stability ·Low Cost ·Low Methanol Cross-over & Water Permeation
Stack & System	·Thin & Light Material ·Stack Design / Fuel Distribution / Flow Channel Design ·Fuel Mixing / Sensor ·Miniaturization

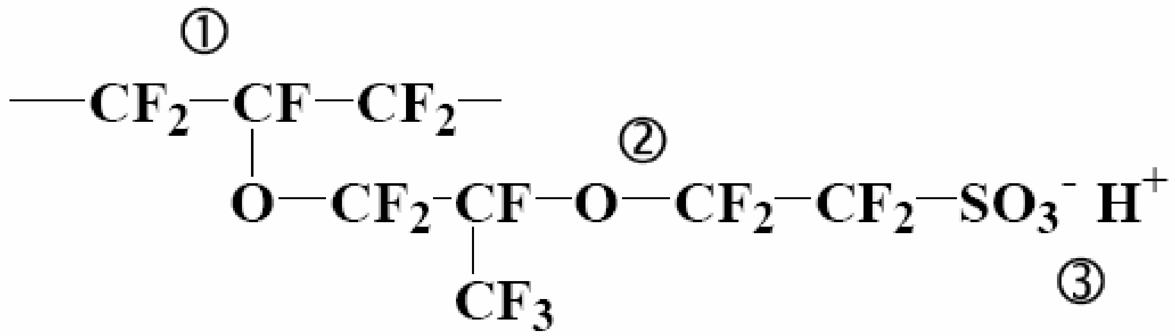
MeOH Crossover



Implications :

Parasitic fuel loss ; 20%
Lower cell voltage ; by 0.1V
Reduction in efficiency

Chemical Structure of Nafion



Nafion[TM] *by Dupont*

Poly(perflurosulfonic) acid, *Nafion*[TM], consists of three regions.

① Teflon-like, fluorocarbon backbone

② Side chains, -O-CF_2-CF-O(-CF_3)-CF_2-CF_2-, which connect the molecular backbone to ③

③ Ion cluster of sulfonic acid ions, $SO_3^-H^+$

Structure of Cluster

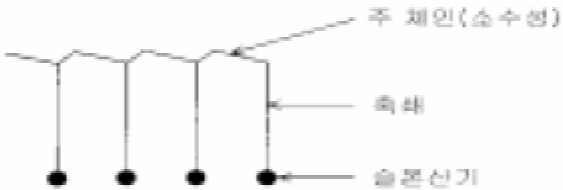
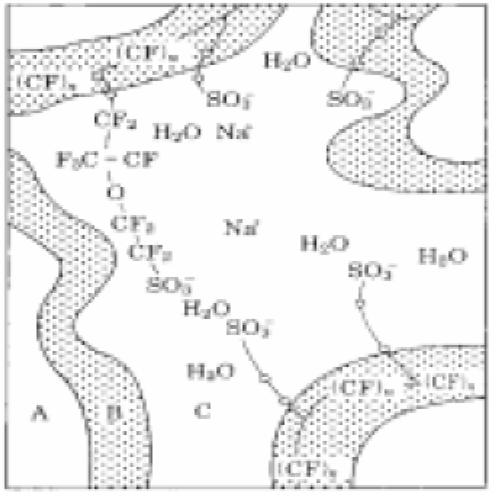


그림. 전해질막 구조의 모델
(미쯔다 2000)



A : 주 체인 골격 소수성영역
B : 가스 투과성 공간영역
C : 친수성 이온 클러스터영역

그림. 전해질막의 미세구조
(Ogumi, et al., 1985)

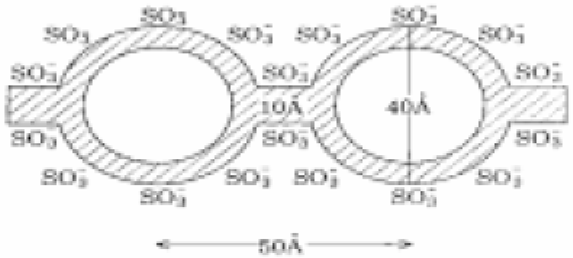
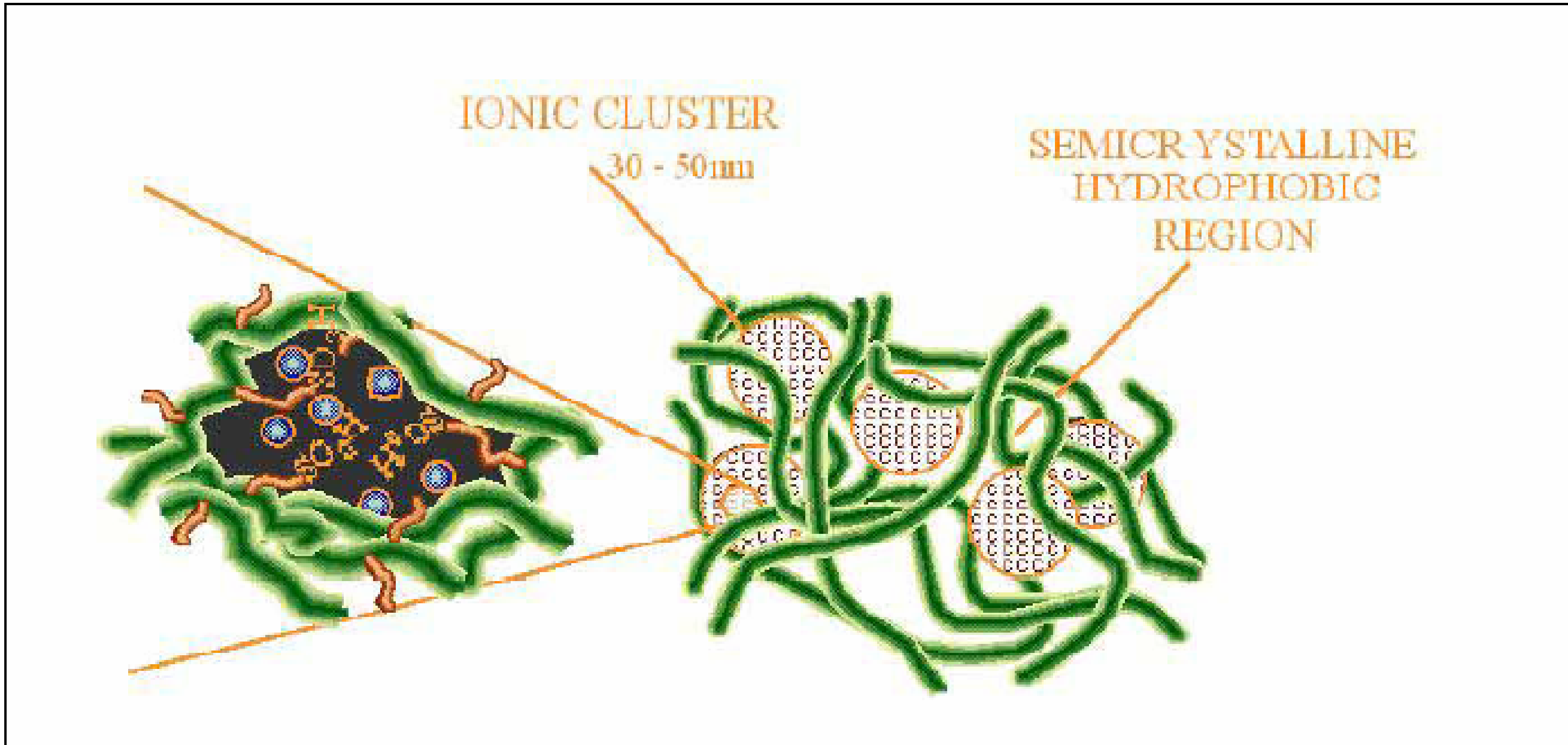


그림. 클러스터 구조
(Gierke, et al., 1981)

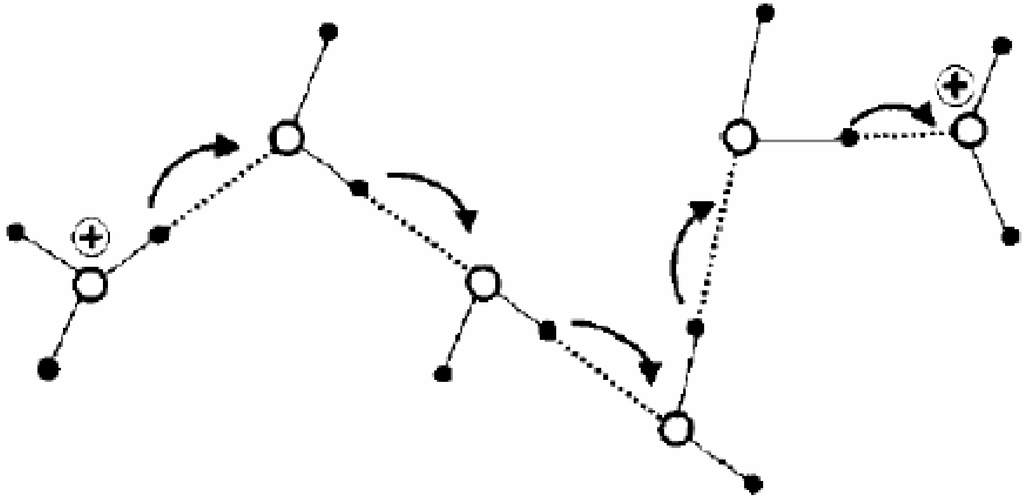
Structure of Hydrated Nafion



H^+ conductivity of Nafion 117 = 0.10 S/cm

Methanol diffusivity of Nafion 117 = 2.3×10^{-6} cm^2/s

Grutthus Mechanism



Proton conductivity according to the Grotthuss mechanism presented in most textbooks

Proton hopping from a H_3O^+ moiety to a freely rotating nearest-neighbor water molecules

Mobility

Ion	λ_o / Sm^2mol^{-1}	$u/m^2s^{-1}V^{-1}$
H^+	349.8×10^{-4}	36.25×10^{-8}
Li^+	38.7×10^{-4}	4.01×10^{-8}
Na^+	50.1×10^{-4}	5.19×10^{-8}
K^+	73.5×10^{-4}	7.62×10^{-8}
NH_4^+	73.4×10^{-4}	7.61×10^{-8}
Ca^{2+}	119.0×10^{-4}	6.17×10^{-8}
Cd^{2+}	108.0×10^{-4}	5.60×10^{-8}
Zn^{2+}	105.6×10^{-4}	5.47×10^{-8}
OH^-	198.3×10^{-4}	20.55×10^{-8}
Cl^-	76.34×10^{-4}	7.91×10^{-8}
Br^-	78.4×10^{-4}	8.13×10^{-8}
I^-	76.9×10^{-4}	7.96×10^{-8}
NO_3^-	71.4×10^{-4}	7.40×10^{-8}
CH_3COO^-	40.9×10^{-4}	4.24×10^{-8}
ClO_4^-	68.0×10^{-4}	7.05×10^{-8}
SO_4^{2-}	159.6×10^{-4}	8.27×10^{-8}

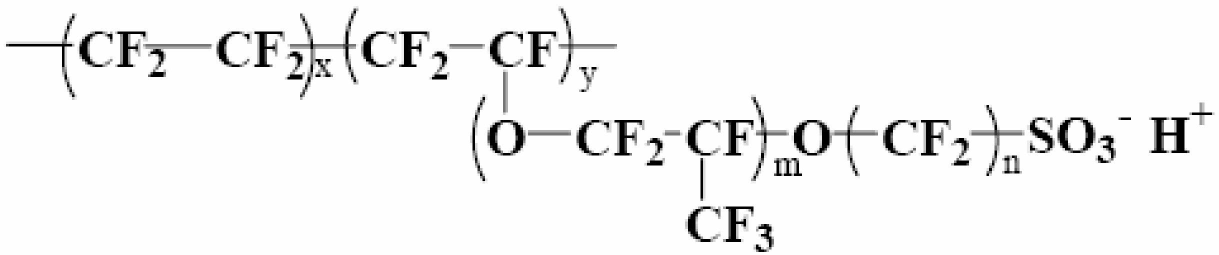
Types of Membrane

1. Fluorinated membrane

2. Non- Fluorinated membrane

- Polybenzimidazole membrane doped with Phosphoric acid
- Hydrocarbon membrane
- Poly(vinyl alcohol)/H_3PO_2 gels
- Crosslinked polyphosphazene-based membrane
- Inorganic-organic proton conducting membrane

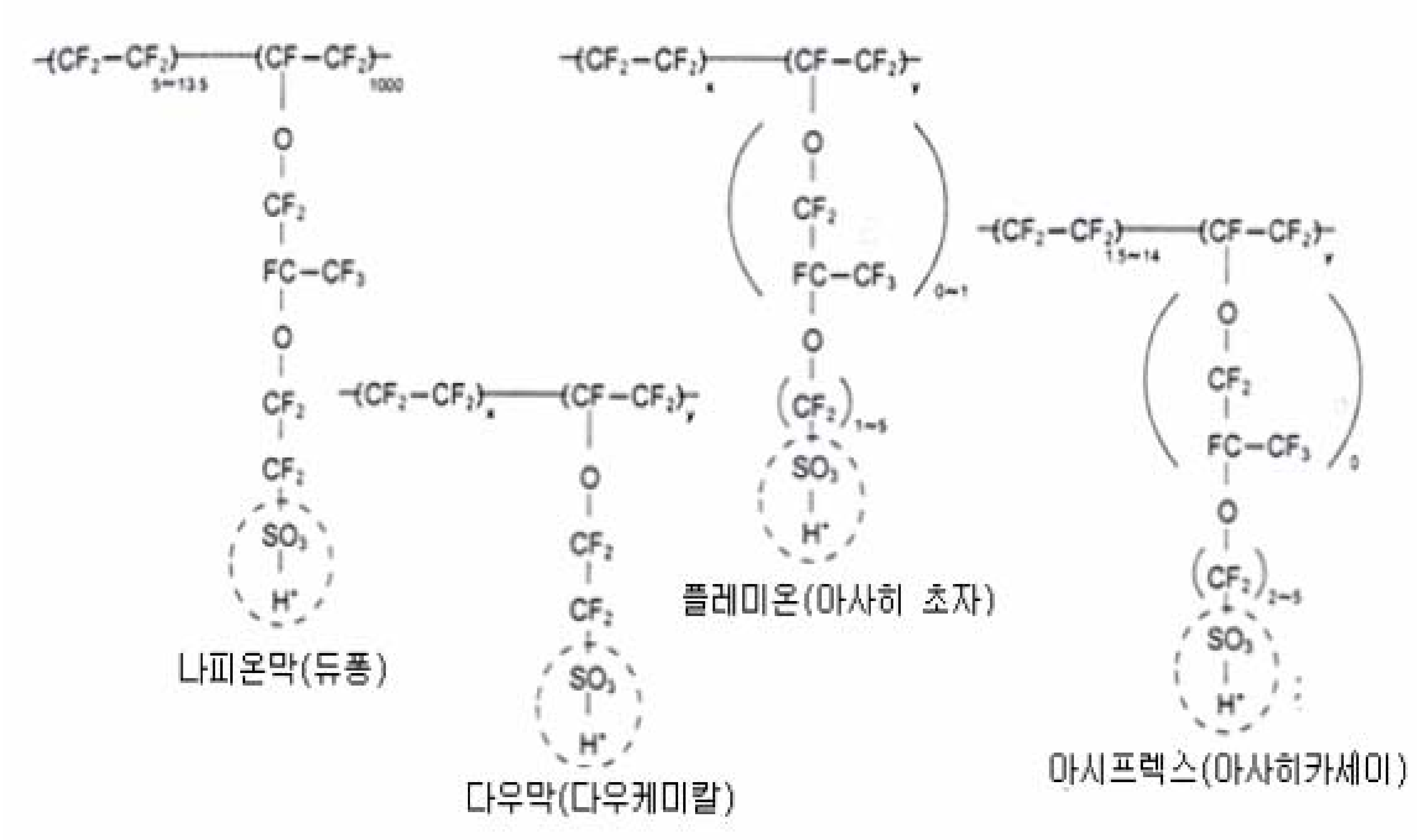
Poly(perfluorinated) Acid Membrane



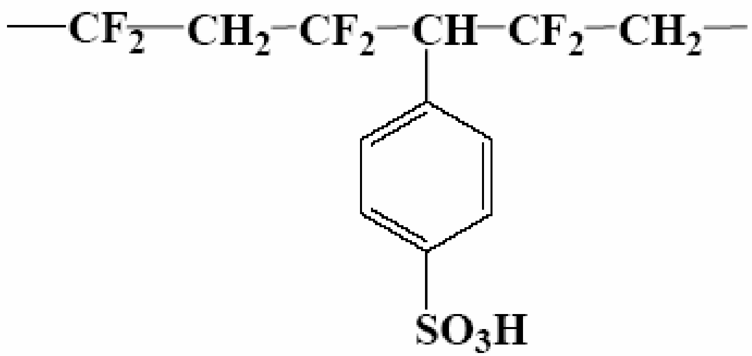
Nafion®117	m≥1, n=2, x=5-13.5, y=1000
Flemion ®	m=0,1; n=1-5
Aciplex ®	m=0,3; n=2-5, x=1.5-14
Dow membrane	m=0, n=2, x=3.6-10

- Good chemical stability and proton conductivity

Poly(perfluorinated) Acid Membrane



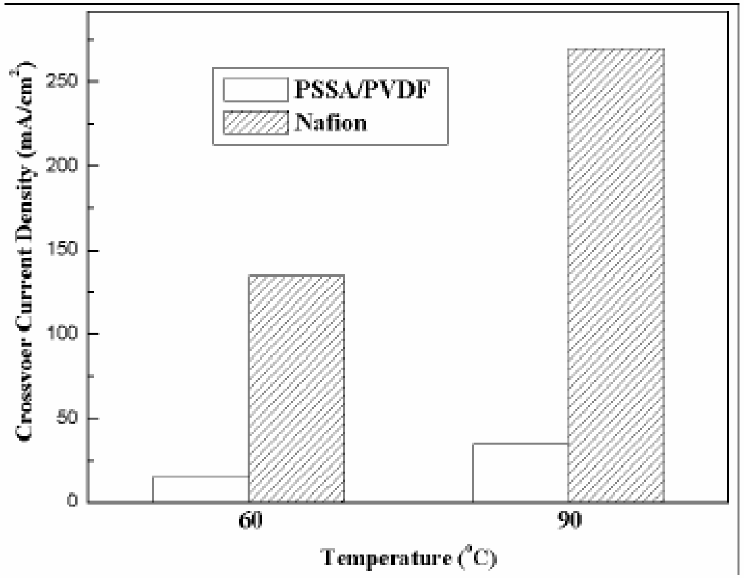
Radiation Induced PVDF-g-PSSA



(Ref.) T. Lehtinen et al, Electrochimica Acta., 43, 1881 (1998)

- Kynar films are grafted with styrene followed by sulfonation with chlorosulfonic acid
- High protonic conductivity (0.1 S/cm at 40% grafting) and water uptake
- Acceptable cell performance: 0.85 V for 150 hrs
- The film thickness of the membrane should be reduced

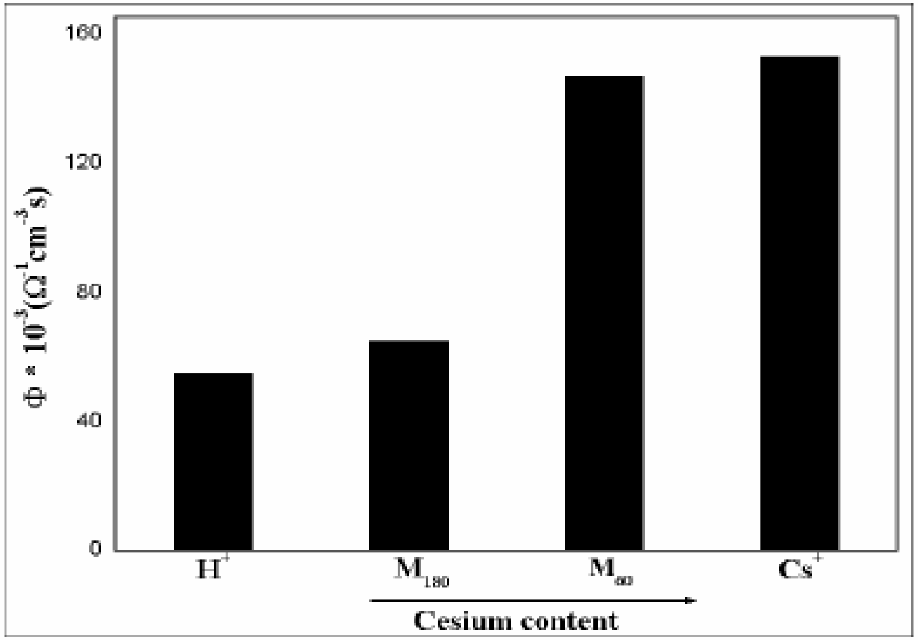
X-linked PSSA/PVDF Membrane



NASA's Jet Propulsion Laboratory, Pasadena, California

1. A PVDF membrane matrix is prepared
2. The membrane matrix is impregnated with a solution of styrene, divinylbenzene, and initiator(AIBN)
3. The styrene and divinylbenzene are copolymerized within the membrane matrix
4. The membrane is sulfonated
5. The membrane is sandwiched between electrode films

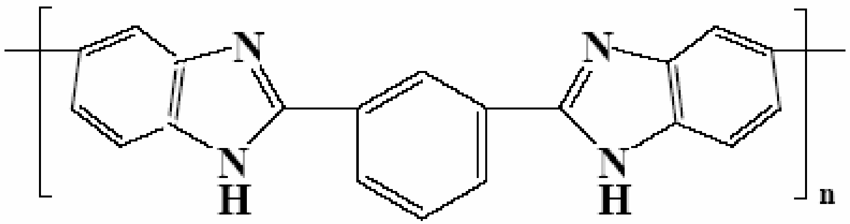
Poly(perfluorosulfonte) Membrane Containg Cs



(Ref.) V. Tricoli, J. Electrochem. Soc., 145, 11 (1998)

- Cesium ions have a considerably smaller hydration energy compared to protons

PBI / H_3PO_4 Membrane

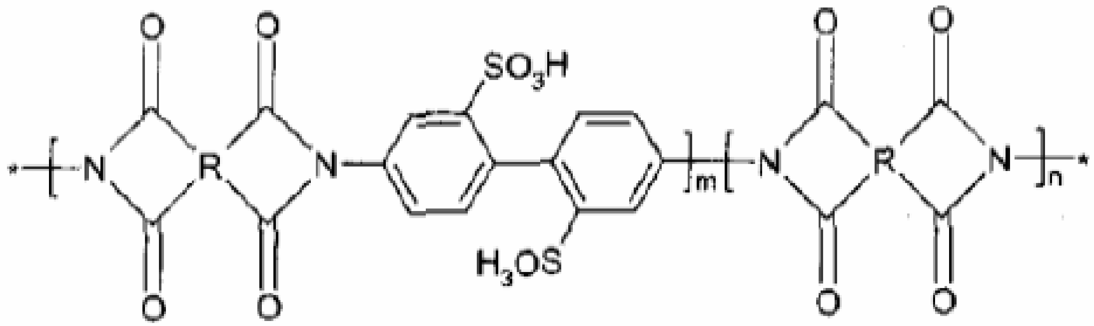


PBI (poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole))

(Ref.) S. R. Samms, J. Electrochem. Soc., 143, 1225 (1996)

- Good mechanical flexibility, excellent oxidative and thermal stability at elevated temperature (200°C)
- Almost zero electro-osmotic drag number (0.6-2.0 for Nafion®)
- Good proton conductivity (0.035 S/cm at 190°C)
- Low methanol gas permeability
  (the methanol crossover rate of acid doped PBI(80μm) is one-tenth of that of Nafion®(210 μm))

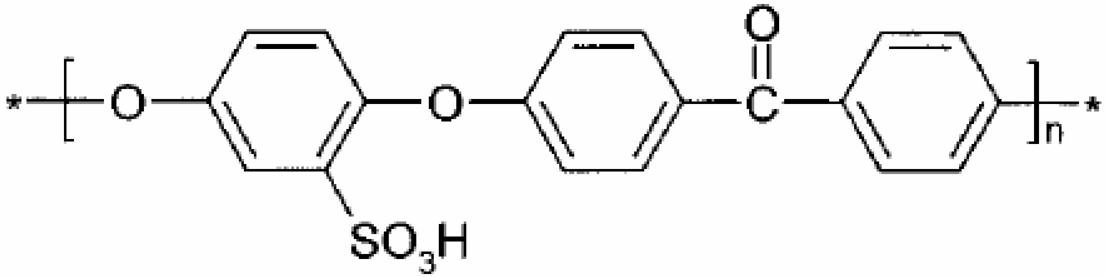
Sulfonated Polyimide



Hydrophobic sequence	Hydrophilic sequence	Hydrophobic sequence

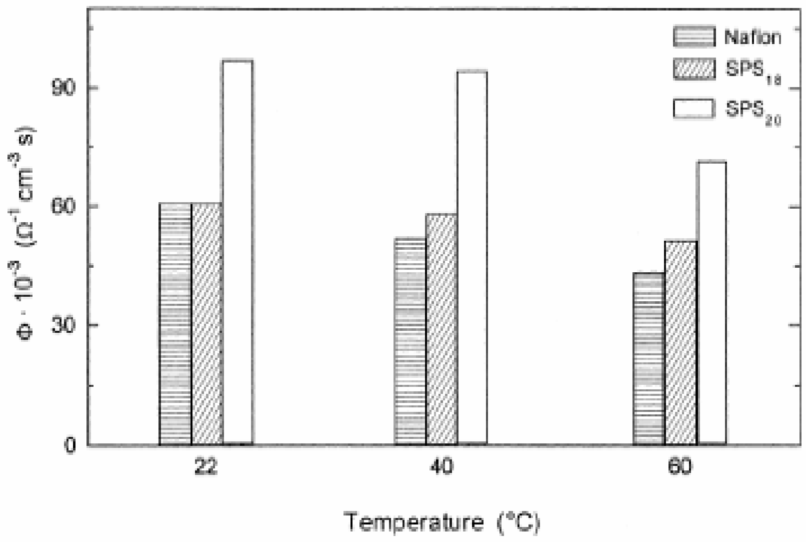
- Low gas permeability
- Good chemical stability and mechanical flexibility
- High protonic conductivity
- Proton permeates through the domains made by continuous ionic groups

SPEEK



- Commonly blended with PBI to earn good ionic conductivity and prevent water and MeOH crossover
- Hydrophilic channel formed between hydrophobic and hydrophilic areas
- Low cost

Sulfonated Poly(styrene) Membrane



(Ref.) N. Carretta, et al., J. Membrane Sci., 166, 189 (2000)

- **Cheaper than perfluorinated ionomers**
- **Easily recycling by conventional methods**
- **High water uptakes over wider temperature range**

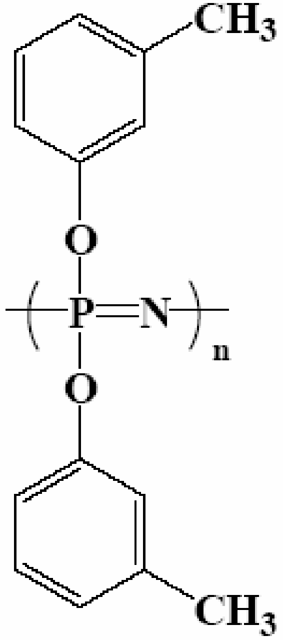
PVA + H_3PO_4 + H_2O Gels

- Gel type proton conductors made of poly(vinyl alcohol) (PVA), hypophosphorous (H_3PO_2) and water

(Ref.) M. A. Vargas, Electrochimica Acta., 45, 1399 (2000)

- 0.1 S/cm at room temperature

Crosslinked Polyphosphazene



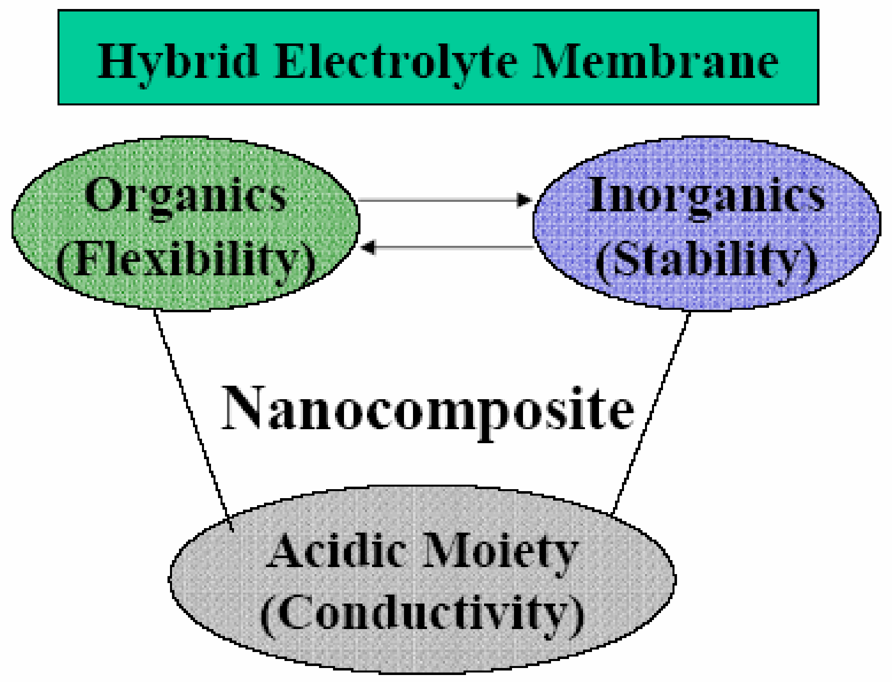
Poly[bis(3-methylphenoxy) phosphazene]

(Ref.) Q. Guo, J. Membrane Sci., 154, 175 (1998)

1. Sulfonation of polyphosphazene
2. Dissolving benzophenone in the casting solution of membrane
3. Crosslinking the polymer solution by UV light

- High proton conductivity (0.04S/cm at 25°C)
- Low methanol diffusion coefficient (8.5×10^{-8} cm^2/s at 45°C)

SiO_2/PEO Membrane



(Ref.) Q. Guo, Solid State Ionics, 120, 255 (1999)

- SiO_2/PEO nanocomposite membrane synthesized by sol-gel process
- Good protonic conductivity(10^{-4} S/cm) at high temp(above 100°C)

Potential Applications