연료전지용 고체 전해질 막의 개발 및 동향

이 승 재 박사
(삼성종합기술원)

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연료전지용 고체 전해질 막의 개발 및 동향

(Development and Trend of Fuel Cell Membranes)

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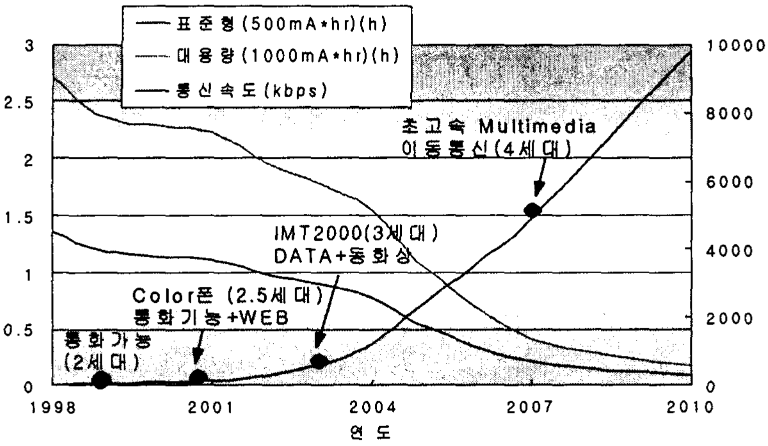
왜 연료전지인가?



다기능화, 고 용량화, 모바일화

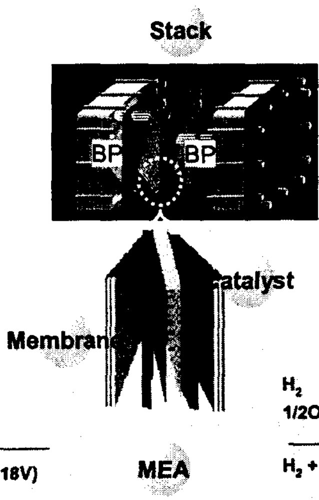
연료전지의 구성

- **Fuel Cell:** 수소와 산소가 반응하여 전기, 물, 열을 생성

Fuel

메탄올 또는 (개질)수소

공기 산소



전기

물

열

DMFC

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

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

$CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2$ (E = 1.18V)

PEMFC

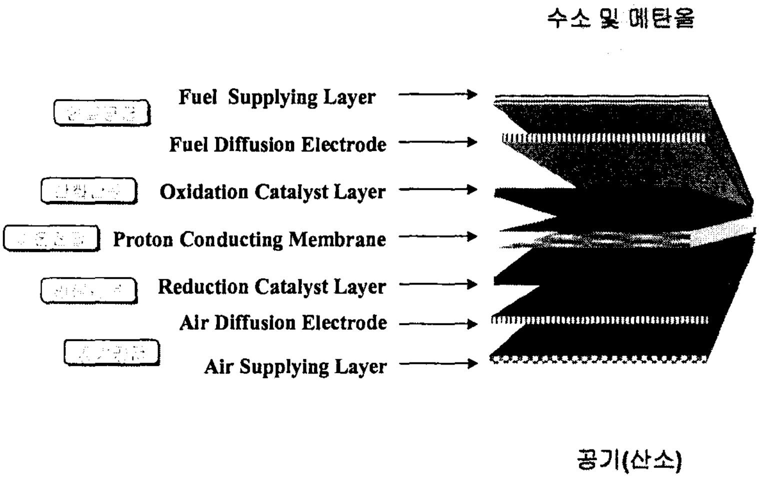
$H_2 \rightarrow 2H^+ + 2e^-$

$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$H_2 + 1/2O_2 \rightarrow H_2O$ (E = 1.23V)

*MEA: Membrane and Electrode Assembly

MEA에서 Membrane



Membrane의 필요조건

- High Proton Conductivity
- Chemical and Mechanical Stability
- Low Gas (PEMFC) and Water (DMFC) Permeability
- Low Methanol Cross-over (DMFC)
- Thermal Stability for High Temperature Membrane (PEMFC)
- Low Cost

High proton conductivity +

- **Chemical stability and water retention above 100oC for high temperature PEMFC**
- **Low methanol and water cross-over for DMFC**

Requirements for High Temperature Mem...

Property	Membrane	Electrode[a]	Methods
Conductivity at 25%RH (see Figure 1)	>0.1 S/cm at 120°C >0.03 S/cm at 25°C	>0.1 S/cm at 120°C >0.03 S/cm at 25°C	2- or 4-point methods (e.g., (7))
H_2-Permeability	below solid black line in Figure 3	above dashed black line in Figure 3	via GC methods (e.g., (12))
O_2-Permeability	below solid black line in Figure 4	above dashed black line in Figure 4	via GC methods (e.g., (12))
Solubility in H_2O	<1% at 150°C for 24h	<1% at 150°C for 24h	Autoclave in H_2O
Swelling in H_2O	<100% H_2O uptake in boiling water	<200% H_2O uptake in boiling water	weight-gain meas. (e.g., (23)
Chemical Stability	stable in presence of peroxyl species	stable in presence of peroxyl species	test with Fenton's reagent (e.g., (20))
Mechanical Stability	critical	less critical	specifications and requirements not yet determined

[a] note that the ionomer in the membrane my be different from the ionomer used in the electrodes.

Membrane의 평가사항

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1. **Water Swelling**
2. **Methanol or Hydrogen Crossover**
3. **Proton conductivity**
4. **Thermal Stability above 100°C**
5. **Chemical Stability in an Aggressive Chemical Environment (free radicals)**
6. **Ease of Fabrication into Thin Membranes**
7. **Adhesion of the Membrane to the Electrodes**
8. **Power Generation in a Laboratory Fuel Cell**
9. **Cost**

Proton conductors as a function of

- Proton conducting material at a temperature < 100°C
- Proton conducting material at a temperature 100~200°C
- Proton conducting material at a temperature 200~350°C
- Proton conducting material at a temperature >350°C

Proton conductors at a temperatures

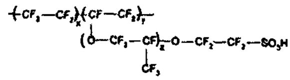
Proton conductivity (σ) and activation energy (E_a) for some representative materials at room temperature

Proton conductor	σ ($S\ cm^{-1}$)	E_a (eV)	Reference
Three-dimensional structure			
$H_2Sb_4O_{11} \cdot 3H_2O$	2×10^{-3}	0.42	[4]
$HSbO_3 \cdot 2H_2O$	3×10^{-3}	0.20	[5]
Tin-mordenite	10^{-2}		[6]
Layered structure			
β''-$NH_4(H_3O)_{0.66}Al_{10.34}Mg_{0.66}O_{17}$	3×10^{-6}–1×10^{-3}	0.27–0.31	[7]
$H_2Ti_4O_9 \cdot 1.2H_2O$	10^{-4}		[8]
$HUO_2AsO_4 \cdot 4H_2O$	5×10^{-3}	0.27	[9,10]
$HUO_2PO_4 \cdot 4H_2O$	5×10^{-3}	0.35	[10,11]
$H_3Sb_3P_2O_{14} \cdot 10H_2O$	4×10^{-3}	0.33	[12]
$HSbP_2O_8 \cdot 10H_2O$	10^{-2}		[12]
α-$Zr(HPO_4)_2 \cdot nH_2O^a$	10^{-4}	0.3	[13]
γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O^a$	3×10^{-4}	0.24	[14]
α-Zr sulfophenylphosphonate	1.6×10^{-2}	0.20	[15]
γ-Zr sulfophenylphosphonate	1×10^{-2}	0.21	[16]
Hydrated oxides			
$SnO_2 \cdot 2H_2O$	4×10^{-4}	0.20	[18]
$Sb_2O_5 \cdot 5.4H_2O$	7.5×10^{-3}	0.16	[19]
Heteropolyacids			
$H_4SiW_{12}O_{40} \cdot 28H_2O$	2×10^{-2}	0.4	[20,21]
$H_3PW_{12}O_{40} \cdot 29H_2O$	8×10^{-2}	0.15–0.25	[20,21]
Sulfonated polymers[b]			
S-PBI[c]	1×10^{-2}	–	[22]
S-PEEK-1.6[d]	3×10^{-2}	–	[23]
NAFION[b]	5×10^{-2}	0.22	[24]
Impregnated membranes			
polyacrylamide · $2.4H_3PO_4$	1.1×10^{-2}	–	[25]

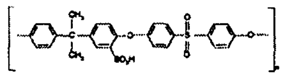
[a] In pellicular form, very suitable as thin separator for gas sensors.
[b] In membrane form.
[c] S-PBI: sulfonated polybenzimidazole.
[d] S-PEEK-1.6: sulfonated polyether ether ketone with ion exchange capacity of 1.6 mEq/g.

Structure of Proton conductors at a

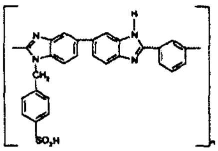
Nafion



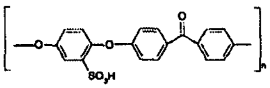
Polysulfone



Polybezimidazole



PolyEtherEtherKetone



- **Nafion or Nafion-like membrane**
- **Non-fluorinated polymers**

- **Nano Composite Membrane : well dispersed hydrophilic nano-particles in the polymer influence on the size of ionic clusters and their hydrophilic interconnections.**
- **Nano particle : silica, titania, etheropolyacids, antimonic acid, layered zirconium phosphate, etc.**

Limitation of Hydrated Proton condu

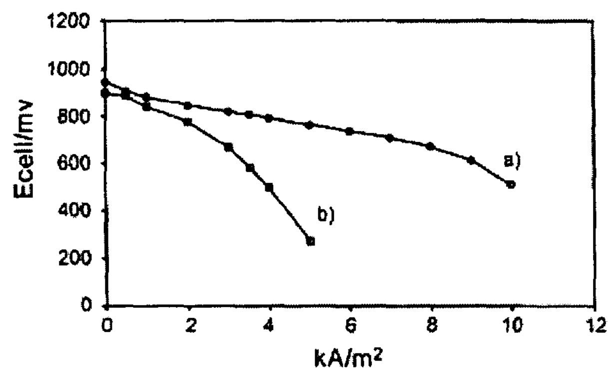


Fig. 7. Typical polarization curves at 70°C and 120°C for a PEM fuel cell using Nafion 117.

Proton conductors at a temperatures

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Table 2
Conductivity (σ) of representative proton conductors in the range 100–190°C

Proton conductor	T (°C)	% r.h.	σ (S cm^{-1})	Reference
α-$Zr(HPO_4)_2 \cdot H_2O$	100	97	1.5×10^{-4}	[28]
$SiO_2 \cdot 0.33\alpha$-ZrP	100	97	3×10^{-3}	[28]
α-$Zr(HPO_4)_2 \cdot$ pyrazole	120	0	1.4×10^{-6}	[29]
γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$	100	95	3×10^{-4}	[30]
α-Zr sulfophenylphosphonate	100	60	1×10^{-2}	[31]
	180	0	1×10^{-5}	[31]
γ-Zr sulfophenylphosphonate	100	95	5×10^{-2}	[32]
	150	80	1.3×10^{-2}	[33]
Nafion[a]	100	100	1.6×10^{-1}	[34]
	150	75	5×10^{-2}	[34]
S-PEEK-2.48[a]	150	75	3×10^{-2}	[34]
S-PEEK-1.6[b]	100	100	5×10^{-2}	[23]
	150	75	3×10^{-3}	[23]
$PAMA^+ H_2PO_4^- 2H_3PO_4$[c]	100	0	1×10^{-2}	[35]
$PBI.xH_3PO_4$[d]	190	11	4×10^{-2}	[36]
$CsHSO_4$	150	0	5×10^{-3}	[27]

[a] S-PEEK-2.48: sulfonated polyether ether ketone with ion exchange capacity of 2.48 mEq/g.
[b] S-PEEK-1.6: sulfonated polyether ether ketone with ion exchange capacity of 1.6 mEq/g.
[c] PAMA: polydiallyldimethylammonium.
[d] PBI: polybenzimidazole.

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Relative Humidity vs. Conductivity

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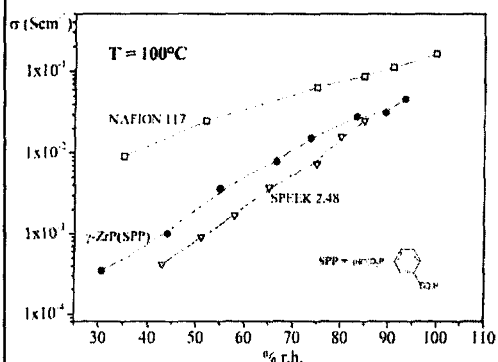

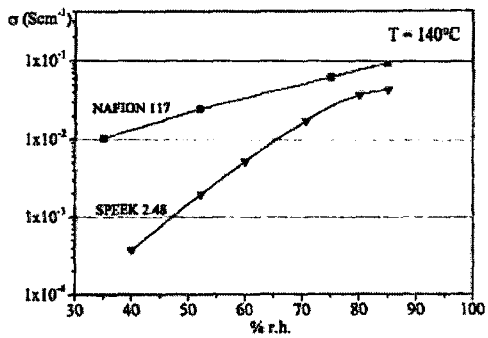

Fig. 3. Conductivity at 140°C as a function of relative humidity for Nafion 117 and S-PEEK 2.48.

- **Acidity influences the ionic conductivity under low relative humidity**
- **Hammett acidity function : Nafion = -12, ZrSPP = -5, SPEEK = -3**

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Comparison of Relative Humidity vs. Cond

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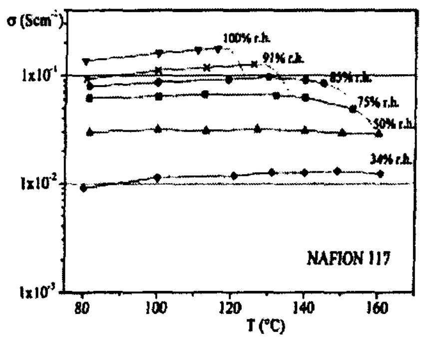

Fig. 11. Conductivity of Nafion 117 in the temperature range 80–160°C at the indicated relative humidity.

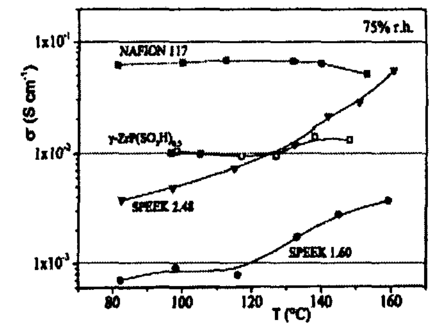

Fig. 12. Conductivity for the indicated materials in the temperature range 80–160°C at 75% r.h.

- **SPEEK may be a solution for high temperature operating *fuel cell due to high* ion conductivity at 160°C**
- **Zirconium sulfophenyl phosphate**
- **Nafion/Hydrophilic compound: SiO2/Nafion**
- **Hybrid membranes are highly promising candidates for the future development of high temperature PEMFC.**

Proton conductors at a temperatures 200

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- **Thermal degradation of the ionomers containing –SOH3 is due to *the decomposition of the sulfonic groups.***
- **Replacement of –SO3H groups with *thermally more stable acid groups* [Phosphonic acid groups], γ-ZrPO4[O2P(OH) –C6H4–PO–(OH)2]nH2O**
- **Condensation reaction of acid group are facilitated at temperatures higher than 190°C. α-zirconium bismonohydrogen phosphate, α -Zr(HPO4)2 : P–OH condensation @ 300°C**

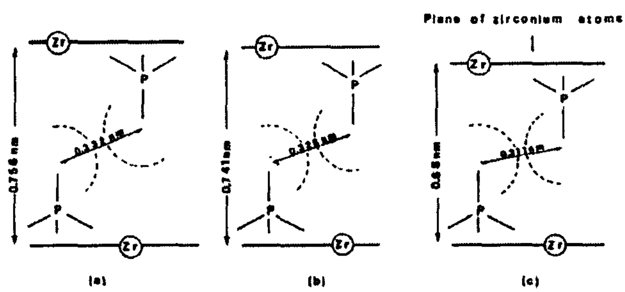

Fig. 4. Distance between the oxygen atoms of the acid P–OH groups belonging to adjacent layers for: (a) monohydrated α-ZrP, (b) anhydrous α-ZrP below 220°C, (c) anhydrous α-ZrP above 220°C.

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Proton conductors at a temperatures

- 350°C 이상의 온도에서는 acid group이 완전히 응축되어 이온전도성을 상실함.
- 응축을 피하려면 acid group간의 거리가 충분히 떨어져 있어야 하지만 그럴 경우 proton jump를 위한 활성화 에너지가 증가하게 되어 전도도가 매우 낮아지게 된다.
- BaPrO3, BaCeO3 : 0.01 S/cm @ 600°C

UTC Program for High Temperature M...

Objectives (high-temp membrane)

- Optimize candidate membranes for operation at 120°C, 50% RH
- Characterize membranes for suitability in high-temperature fuel cell
  - *ex-situ* testing
    - conductivity at various humidity
    - water uptake
    - tensile strength
  - in-cell tests:
    - performance at 120°C and 50% RH, 1.5 kPa
    - 100 hours stability tests
    - fuel crossover
    - elemental analysis of the exhaust water

Technical Barriers and Targets

- DOE Technical Barriers for Fuel Cell Components
  - P. Durability
  - Q. Electrode Performance
  - R. Thermal and Water Management
- DOE Technical Target for Fuel Cell Stack System for 2010

– Durability	5000h
– CO tolerance (2% air bleed)	500ppm ss /1000 ppm transient
– Power density*	650 W/L excluding H2 storage
– Electrode performance	0.2 g Pt/kW

* operate in thermal and water balance

UTC Program for High Temperature Memb...

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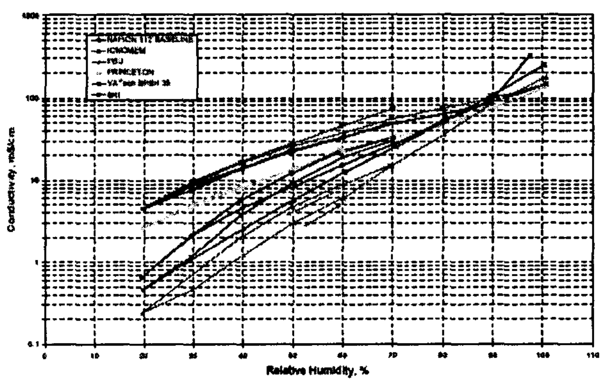
Group	Principal Investigator	Approach
IONOMEM	Mr. Leonard Bonville	Hygroscopic solid ion conductor (e.g., zirconium phosphate,etc) filled Nafion®)
Penn State University	Prof. Digby Macdonald	Sulfones and sulfoxides of aromatic PPBP and aliphatic PVA. Covalent sulfonic acid bonded PEEK, PBI and PPBP
Princeton University	Prof. Andrew Bocarsly	Layered sulfonated Polystyrene/Fluoropolymer system
Stanford Research Institute	Dr. Susanna Ventura	Sulfonated PEEK-PBI-PAN
Virginia Tech	Prof. James McGrath	Sulfonated Poly(arylene ether sulfone)

Conductivity vs. RH % @ 120 C



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연도별 등록 특허 수

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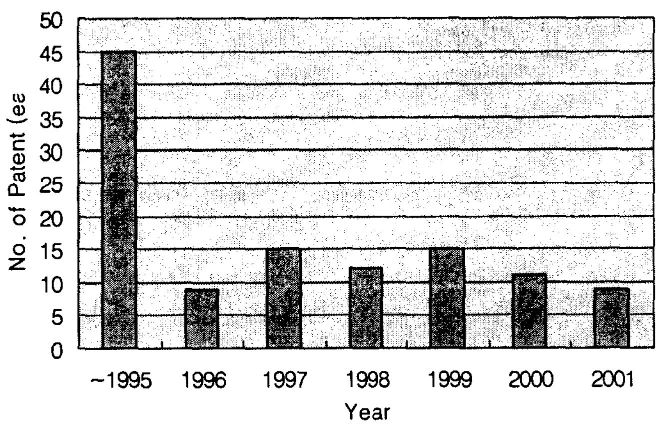

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출원인별 등록 특허 수

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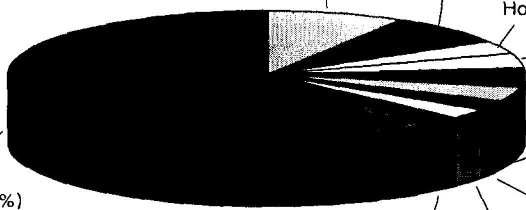

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요약

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- **High Temperature PEMFC용 Membrane**은 고온 , 무가습 시스템 적용을 위한 **heat resistant (**고분자**,** 복합**, cross-linked)**이고**,** 자체 가습형 **(self-humidification, Ionic liquid) Membrane** 개발이 필요하다**.**

- **DMFC**용 **Membrane**은 메탄올과 물의 **crossover**를 극소화하고**,** 가격을 낮추기 위한 재료 **(hydrocarbon polymer) Membrane** 개발이 필수적이다**.**

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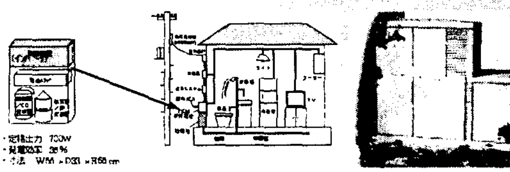
Membrane을 사용한 연료전지의 응용

Portable Devices
(Note PC, Cellular Phone, PDA)



Stationary Power
(On-site Power Supply)

Fuel Cell Vehicle
(ZEV or LEV)