2023 Nov. 20
TechTalks

High-performance and high durable polymer electrolyte materials for PEFC application

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KYUSHU UNIVERSITY

1. Decarbonization of transportation sector and contribution of fuel cell (PEFC) system

2. Polymer electrolyte Membrane (PEM)

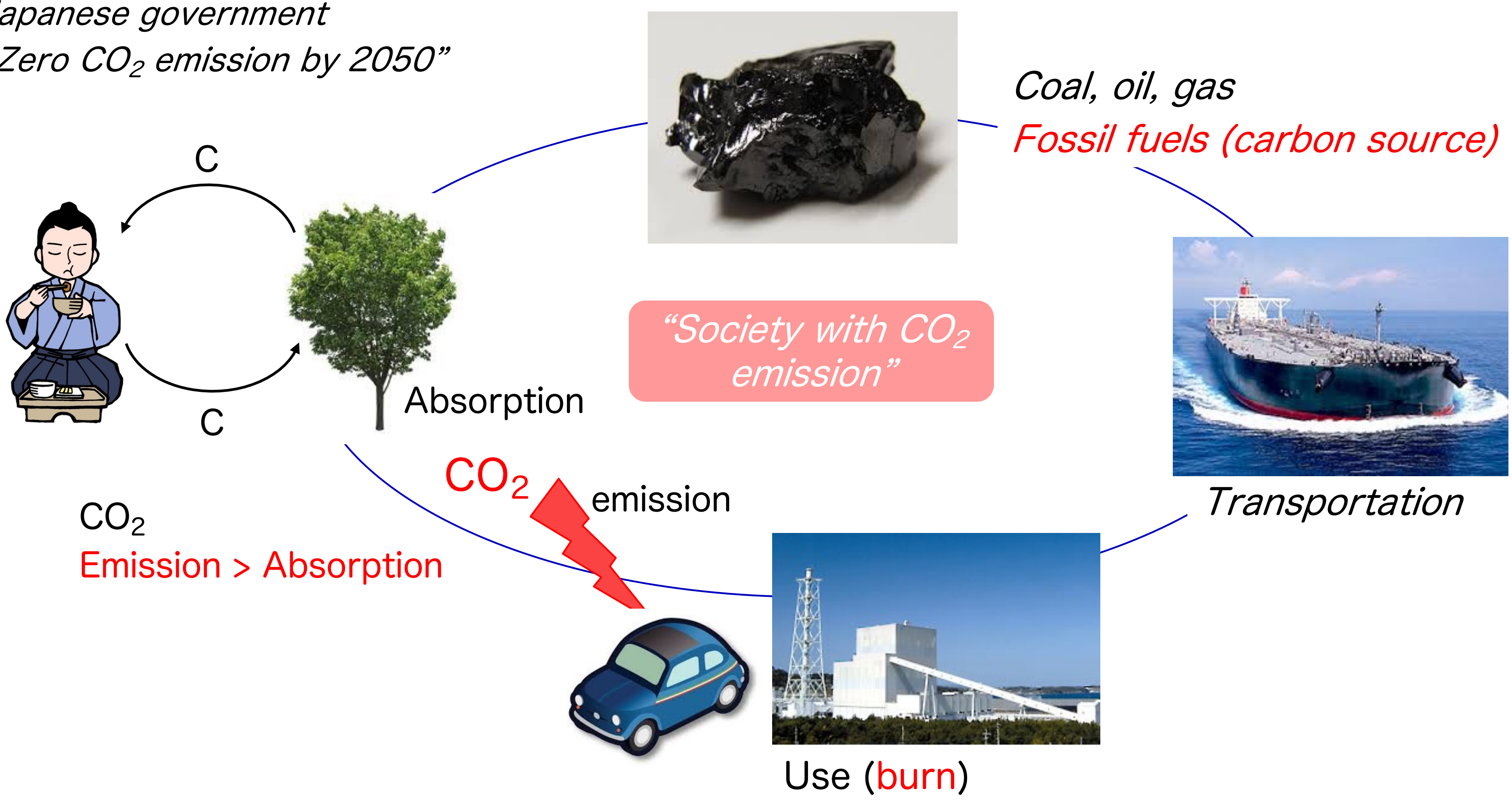
- High gas barrier PEM for high durability

3. Ionomer

- High gas permeable ionomer for high performance

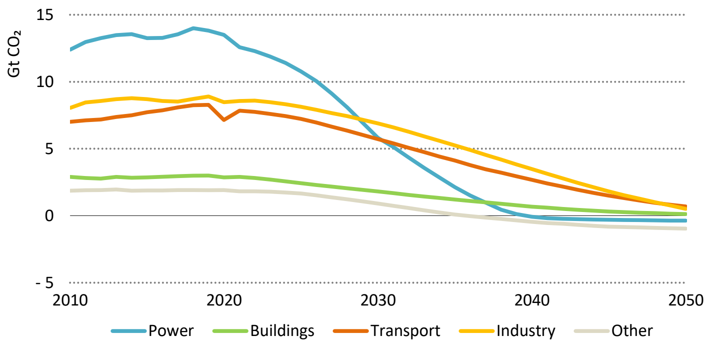
Current Energy Situation (Japanese case)

Japanese government
"Zero CO_2 emission by 2050"



Decarbonization of transportation sector

Figure 3.1 ▷ CO_2 emissions by sector in the NZE

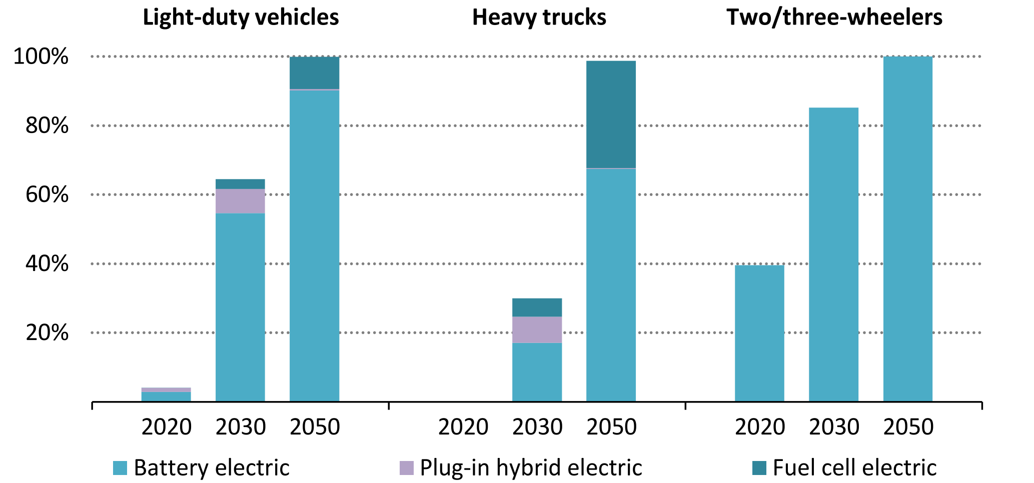


Emissions fall fastest in the power sector, with transport, buildings and industry seeing steady declines to 2050. Reductions are aided by the increased availability of low-emissions fuels

Note: Other = agriculture, fuel production, transformation and related process emissions, and direct air capture.

IEA, Net Zero by 2050 , p100

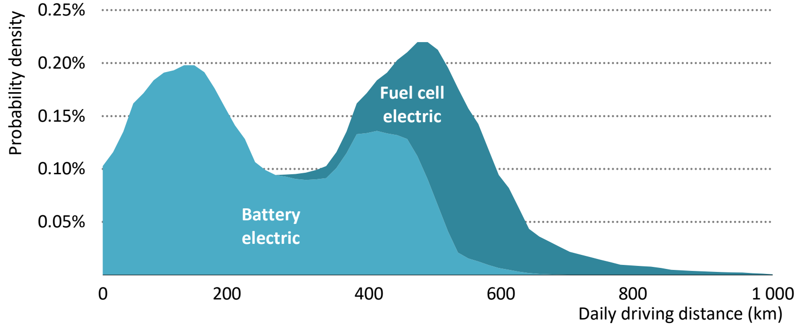
Figure 3.23 ▷ Global share of battery electric, plug-in hybrid and fuel cell electric vehicles in total sales by vehicle type in the NZE



Sales of battery electric, plug-in hybrid and fuel cell electric vehicles soar globally

IEA, Net Zero by 2050 , p134

Figure 3.24 ▷ Heavy trucks distribution by daily driving distance, 2050



Driving distance is the key factor affecting powertrain choice for trucks

IEA, Net Zero by 2050 , p135

Electrification of transportation sector is important for decarbonization.

Current research target of FCVs

Passenger car

©Toyota

Lifetime: 5,000hs

Heavy duty vehicles (HDVs)

©Hyundai

Lifetime: 50,000 hs
+ high power generation
(target in 2030 for 25t truck)

It is hard to realize the targets by using current technology and its modification.

Potential demand of FC application for HDVs

Target of H2 usage in Japan (2050):
20Mt/year (Current: 2Mt/year)
For HDV application: ca 6Mt/year

Global market of HDVs (2050):
Max 1.5M cars (ca 300 T¥ (2T$))

Fuel cell application for HDVs
- Contribution to decarbonization of transportation sector
- Driving force to glow automotive industry

Current research target of FCVs
Development of new materials, system and concept for HDV application

NEDO, Roadmap of fuel cell development –FCV•HDV application- (2023 Feb.)

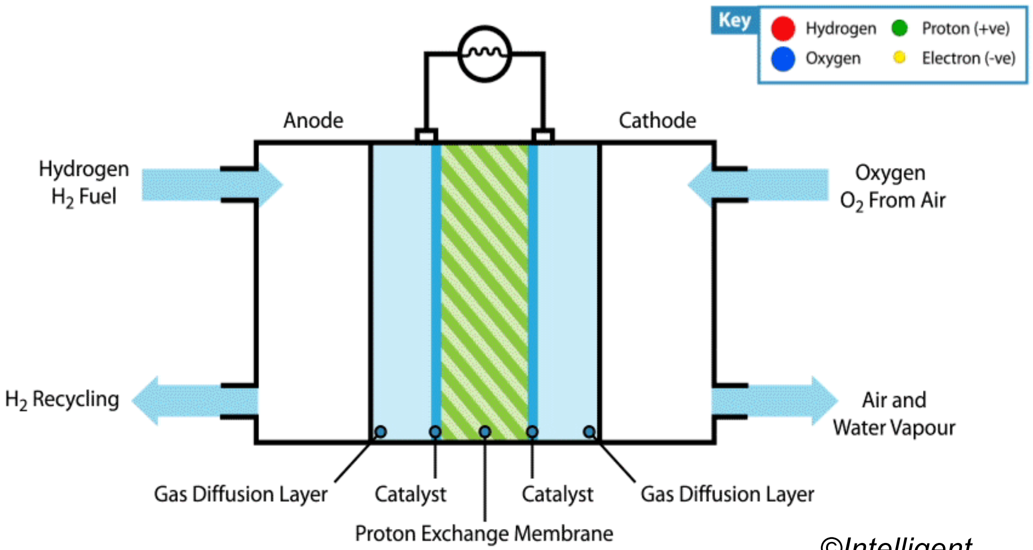
Polymer electrolyte fuel cell (PEFC)

Hydrogen + Oxygen → Water + Electricity

Hydrogen Oxidation Reaction (HOR): $2H_2 \rightarrow 4H^+ + 4e^-$

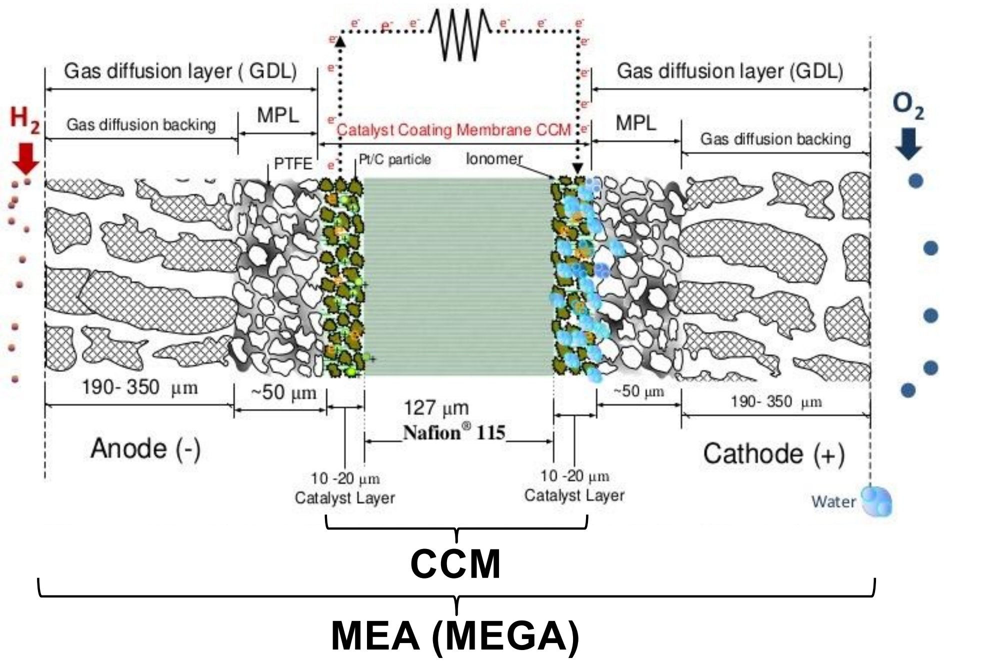
Oxygen Reduction Reaction (ORR): $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Catalyst Coating Membrane (CCM)
Membrane Electrode Assembly (MEA)
Membrane Electrode GDL Assembly (MEGA)



©Intelligent Energy

https://newagemetals.com/pgm-based-fuel-cells-applications-for-industry/



https://www.openpr.com/news/2192967/global-membrane-electrode-assembly-market-analysis

1. Decarbonization of transportation sector and contribution of fuel cell (PEFC) system

2. Polymer electrolyte Membrane (PEM)

- High gas barrier PEM for high durability

3. Ionomer

- High gas permeable ionomer for high performance

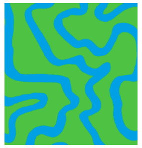
PEM

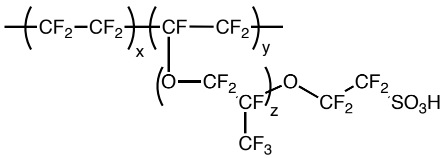
Ionomer

Technical problems of polymer electrolyte materials

Fluoro polymer electrolytes (Standard)

- **Nafion**





K.D. Kreuer, et. al., *Macromolecules 48, 8534-8545 (2015)*

☺ High chemical durability
☺ High proton conductivity

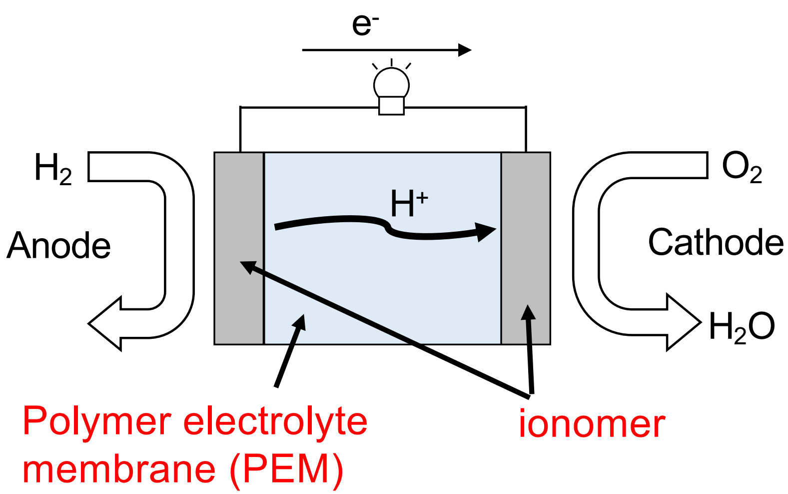
☹ Expensive
☹ Less structural variations
☹ Hard to synthesize

Hydrocarbon polymer electrolytes

☺ Relatively cheap
☺ Much structural variations

Current design of polymer electrolytes

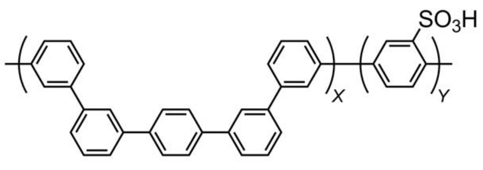
1. ***High durable polymer Polyphenylene etc.***
2. ***Radical scavengers***



Alternative polymer electrolyte materials

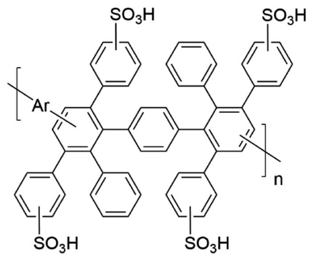
1. High durable polymer

Polyphenylene, crosslink etc.



SPP-QP

K. Miyatake, et. al., *Sci. Adv.*, 2017;3:eaao0476.



M. Breitwieser, et. al., *Sustainable Energy Fuels*, 2021, 5, 3687–3699.

☺ **Higher durability than Nafion**
☹ Limited chemical structures

2. Radical scavengers

- CeO_2
- Heteropoly acid (HPA) (11-silicotungstic acid (HSiW11) etc.)

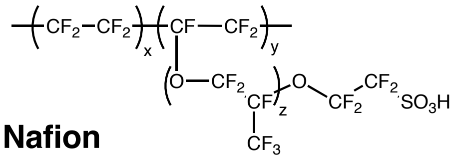
☺ **Higher ability of radical neutralization**
☹ Limited numbers of the materials

Needs new concept to develop better materials than now

PEM

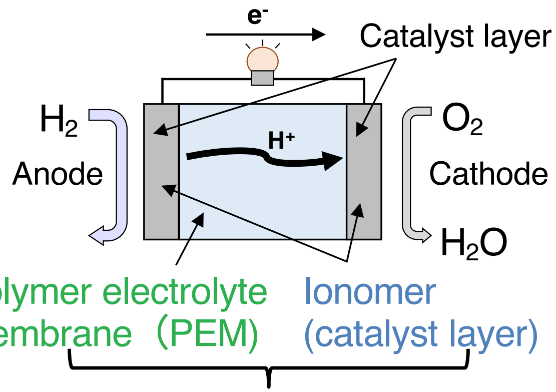
Ionomer

New Material designs for Polymer Electrolytes

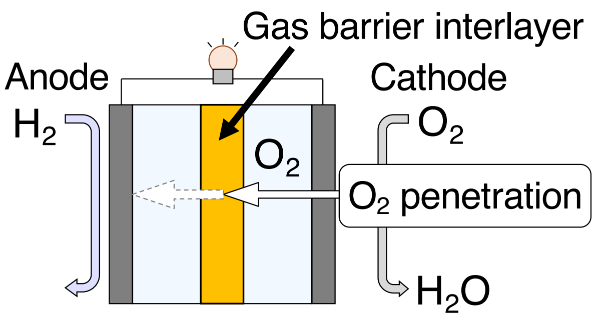


Nafion
(Standard polymer electrolyte for PEFC)

Polymer electrolyte fuel cell (PEFC)



PEM **High durability**

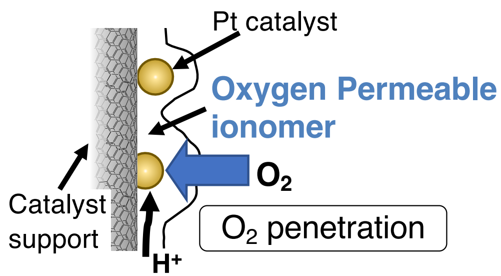


Suppression of PEM by O_2 barrier

Z. Gautama, et. al., ***J. Memb. Sci.***, *658, 120734 (2022).*

Gas transport of polymer electrolytes

Ionomer **High Performance**

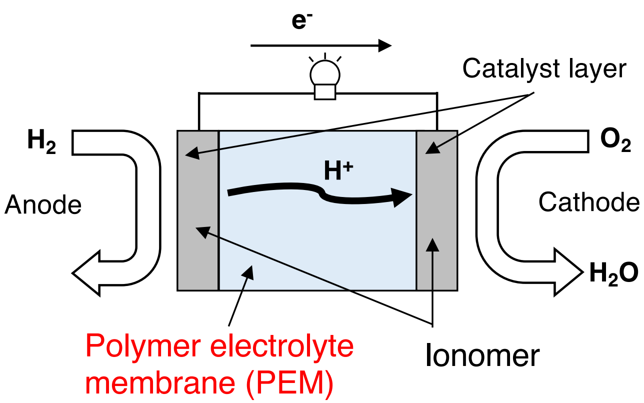


Enhancement of catalytic activity by O_2 transport

Y. Hutapea, et. al., ***J. Power sources***, 556, 232500 (2023).

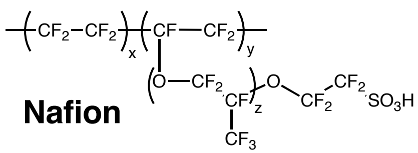
Polymer electrolyte materials (PEM, ionomer) with high chemical durability and high performance.

For High Durability – Durable Membranes with High Gas Barrier-



Polymer electrolytes

Perfluoro polymer electrolytes



- ☺ Good chemical & mechanical durability
- ☺ High proton conductivity
- ☹ Cost

Alternative polymer electrolytes

- Chemical durable polymers
- Radical scavengers etc.

⇨ Material design
"**Defense from radical attack**"

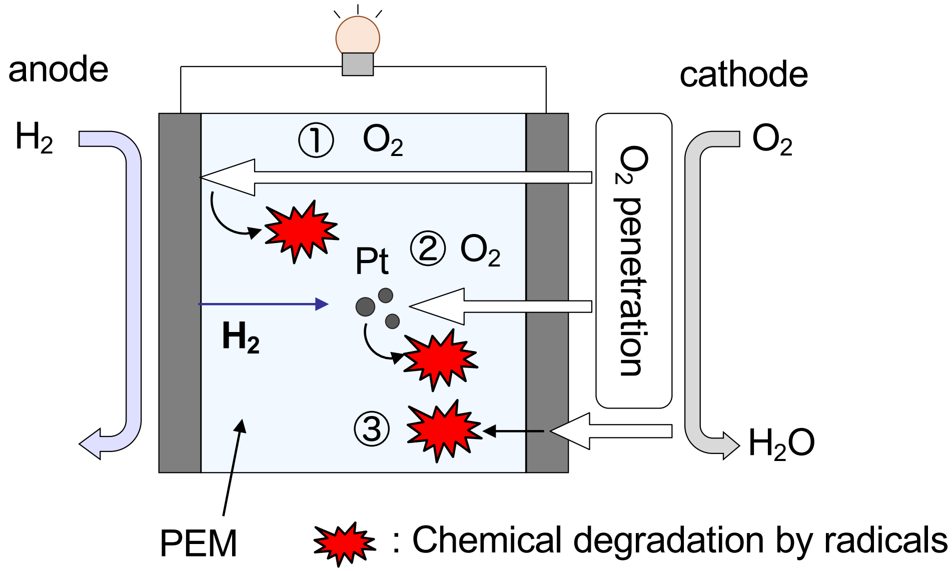
O_2 → H_2O_2 → **•OH** Origin of degradation → durable design

Achieved theoretical limitation of molecular design

Chemical degradation mechanism of PEMs

Radical species

•OH (hydroxy radical), •OOH (perhydroxy radical), •H (hydrogen radical or atom)



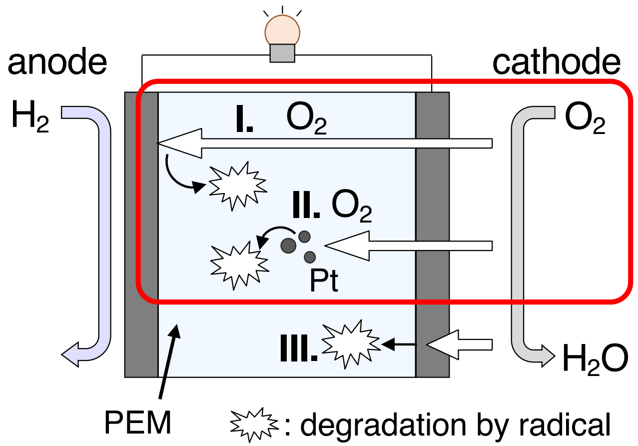
I. Radical formation at anode by **the penetrated oxygen** through PEMs
II. Radical formation on the deposited Pt in PEMs by **the penetrated oxygen** through PEMs
III. Two electron reaction at cathode

"Oxygen penetration through PEMs" is a main cause of radical formation.

Inaba et al, Electrochimica Acta 51 (2006) 5746–5753
Ohma et al, ECS (2007) 154 (8) B757-B760

Degradation of PEMs and Concept of This Work

Generation mechanism of radicals



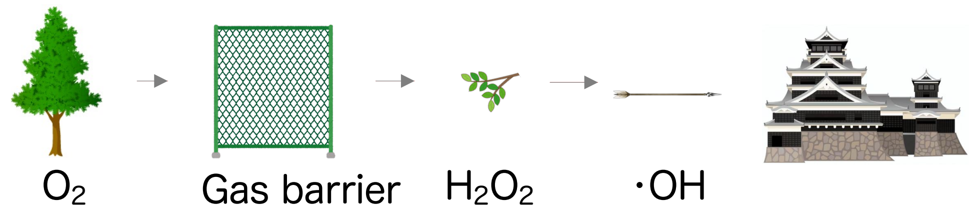
I. Radical formation at anode by **the penetrated oxygen** through PEMs
II. Radical formation on the deposited Pt in PEMs by **the penetrated oxygen** through PEMs
III. Two electron reaction at cathode

"Oxygen penetration through PEMs" is a main cause of radical formation.

Hypothesis
Can we suppress PEM degradation by high oxygen barrier PEMs?

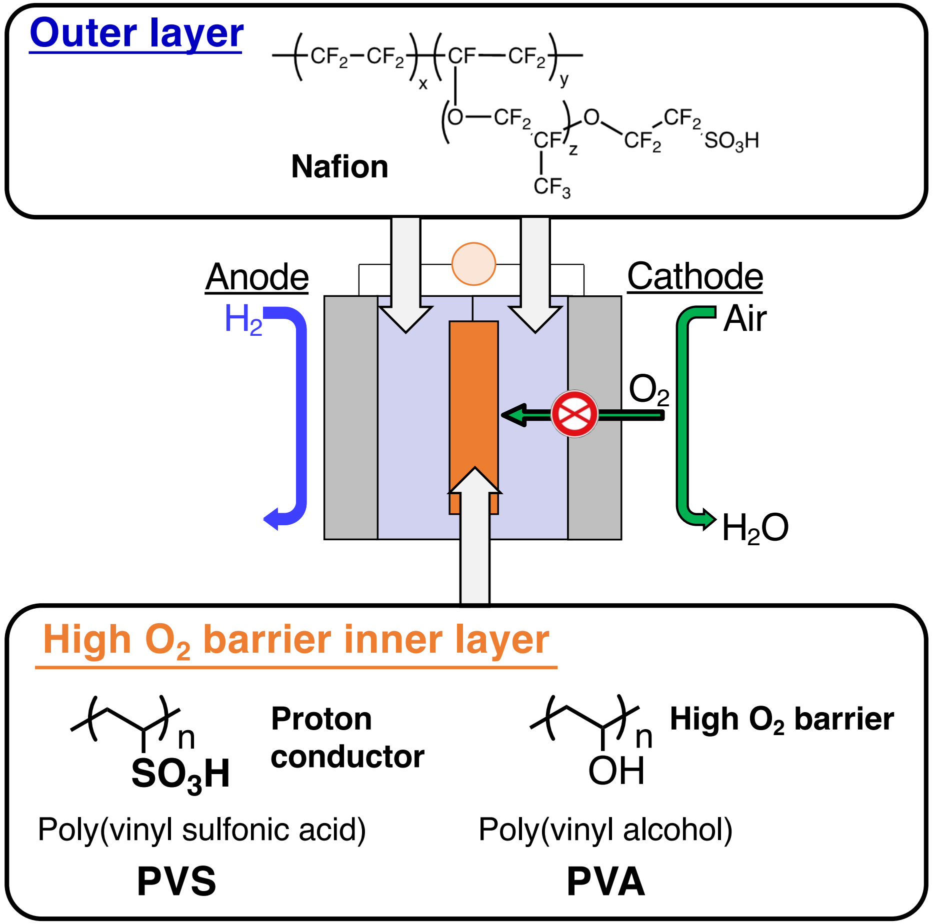
Purpose
Development of high gas barrier PEMs to confirm this hypothesis.

Material design (our research)
"**Reduce radicals**"

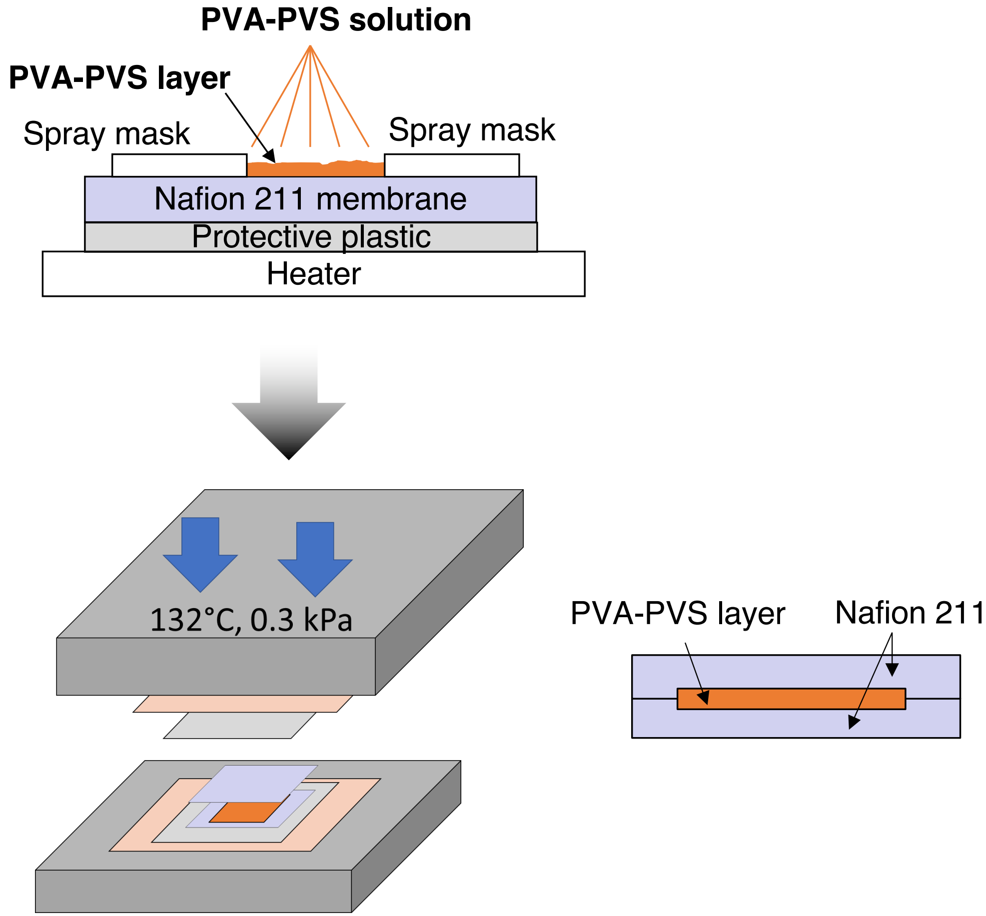


Schematic Image and Preparation of Gas Barrier PEM

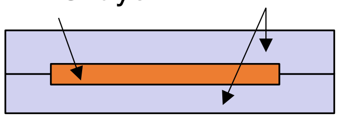
Gas barrier PEM

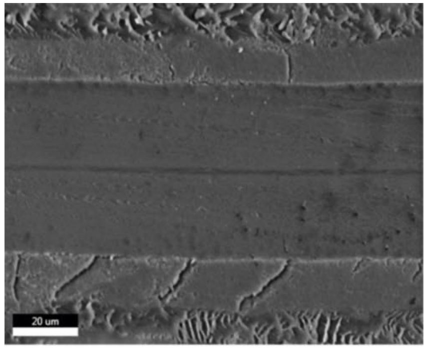


Preparation of Gas barrier PEM



Structure and Gas Permeability of Gas Barrier PEMs

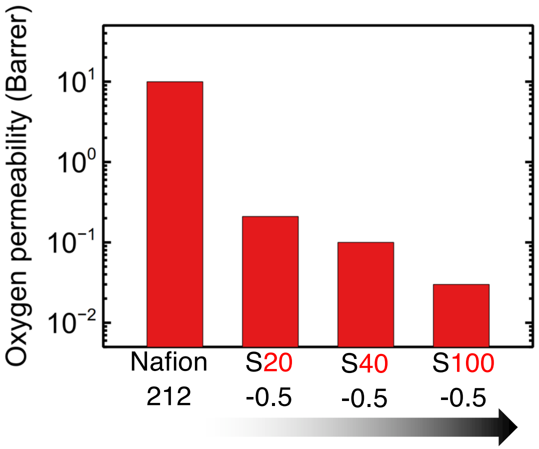




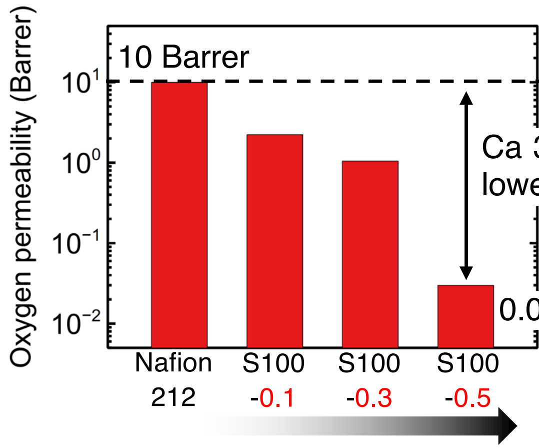
0.5 mg/cm² → **2.2 μm**

Sample	Molar ratio (PVA:PVS)	Areal density (mg/cm²)	Thickness (μm)
S1-0.5	1:1		
S10-0.5	10:1		
S20-0.5	20:1	0.5	2.2
S60-0.5	60:1		
S100-0.5	100:1		
S100-0.1	100:1	0.1	0.5
S100-0.3	100:1	0.3	1.1

Oxygen permeability (80 °C, dry)



High concentration of PVA shows higher O_2 barrier property.



Thicker membranes show higher O_2 barrier property.

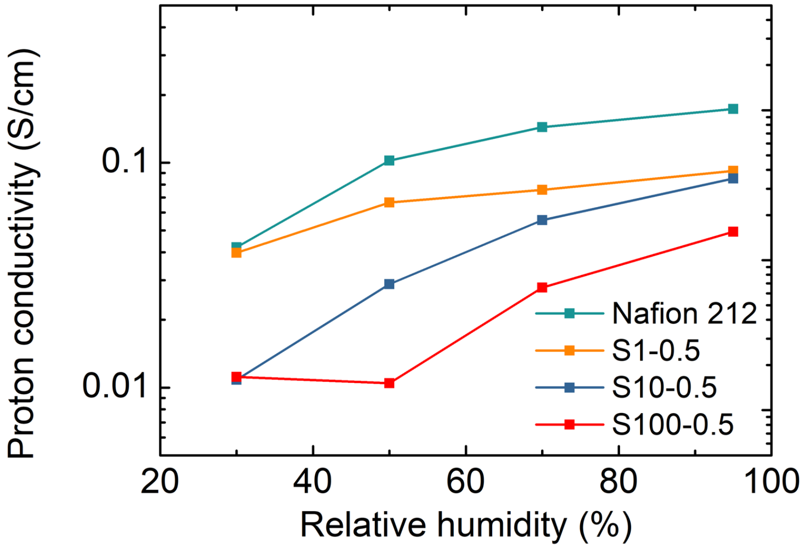
Proton Conductivity and Fuel Cell Performance

Interlayer components

PVA PVS

Sample	Molar ratio (PVA:PVS)
S1-0.5	1:1
S10-0.5	10:1
S100-0.5	100:1

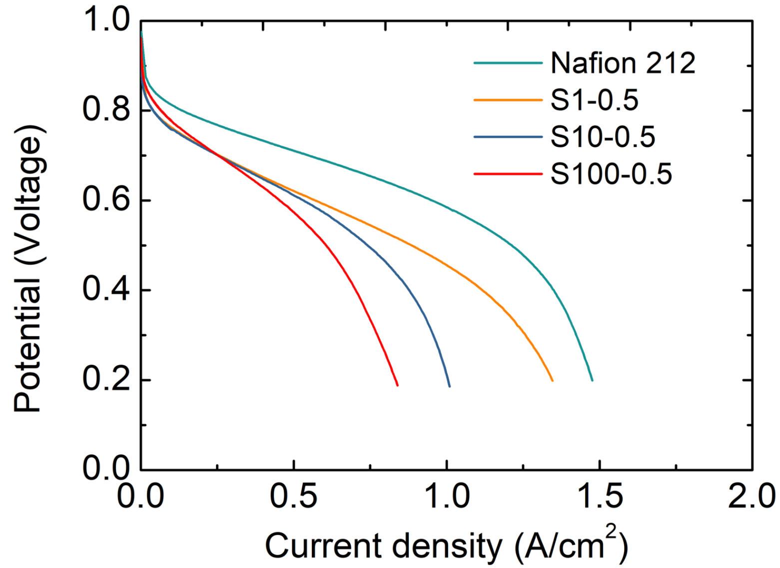
Proton conductivity (80°C)



Low concentration of PVS shows lower proton conductivity.

IV curve

(80°C, 95% RH, H_2:139 mL/ min, air: 332 mL/min)



Low concentration of PVS shows lower fuel cell performance.

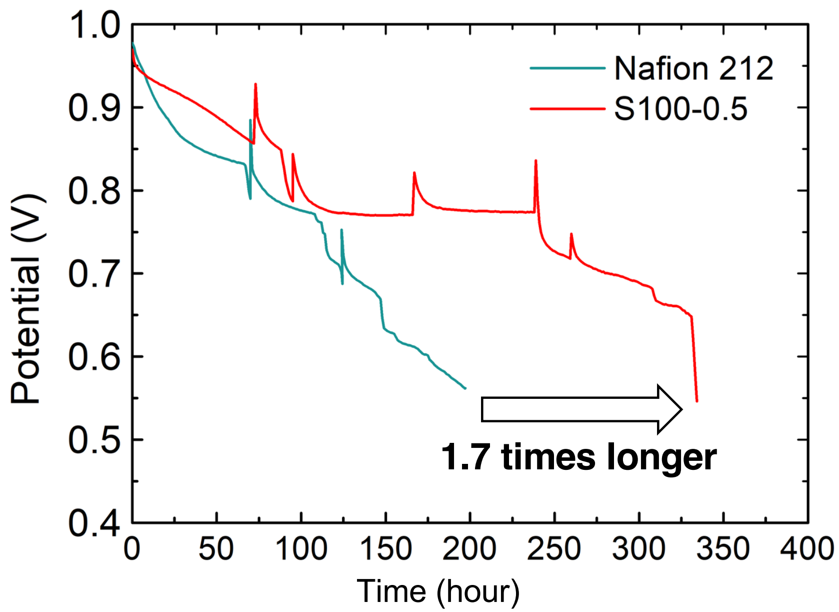
To clarify the hypothesis, high gas barrier PEMs, S100-0.5, was selected for OCV holding test even though IV performance was low.

Chemical Durability (OCV Holding Test)

OCV holding test

S100-0.5 (PVA:PVS=100:1 (mol), 2.2μm)

(1cm^2, 0A/cm^2, 90˚C, 30% RH, H_2: 139 mL/min Air: 332 mL/min)

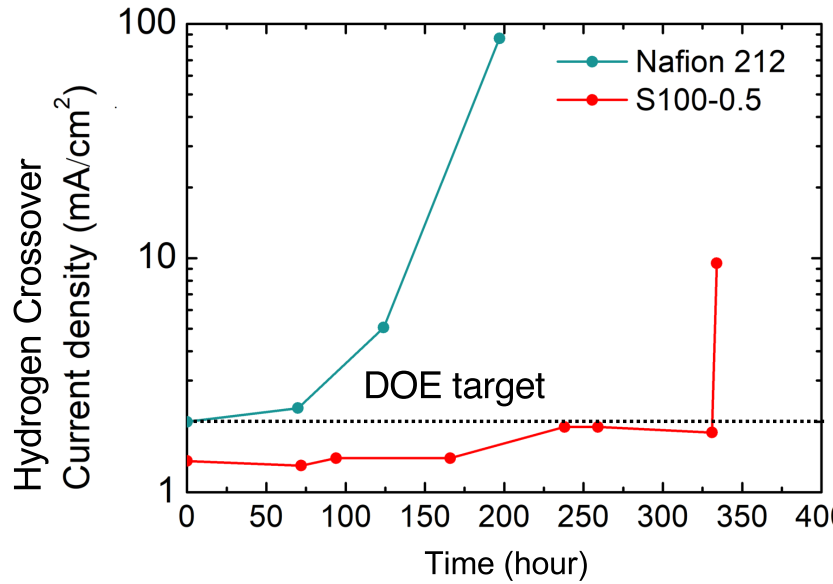


O2 barrier clearly affects chemical durability of PEM.

→ The first example of vinyl hydrocarbon polymer to overcome chemical durability than Nafion.

Hydrogen crossover current density

(80˚C, 95% RH, H_2: 70 mL/min, N_2: 166 mL/min)



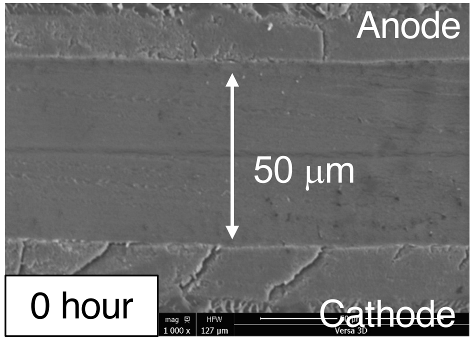
Nafion: Gradually H_2 crossover increased by membrane thinning.

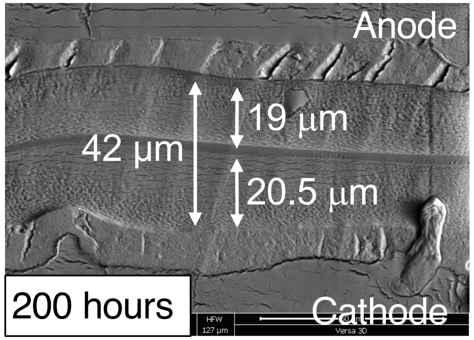
Gas barrier PEM: High gas barrier maintained before a gas barrier interlayer did not have any damages.

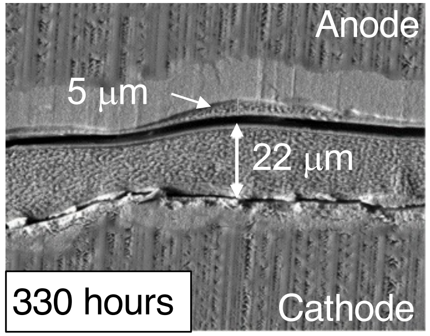
SEM Images after OCV Holding Test

S100-0.5

Ave. membrane thinning rate: **38 nm/h**

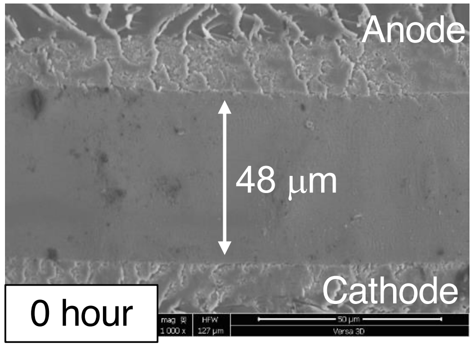


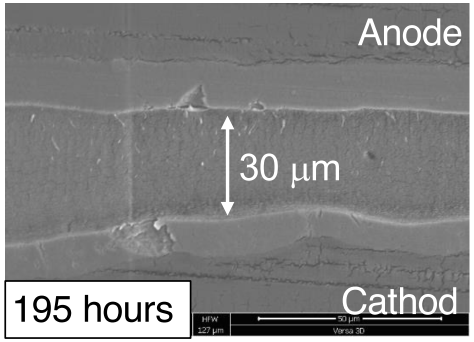




Nafion 212

Ave. membrane thinning rate: **90 nm/h**





- Gas barrier layer could be suppressed O_2 permeation.
- Membrane thinning was also suppressed.
- In OCV holding test, radical formation at anode by penetrated H_2 through PEM is dominant.

Summary of Gas Barrier PEM (50μm Thickness)

Hypothesis

Can we suppress PEM degradation by high oxygen barrier PEMs?

Answer

Gas barrier PEM showed high chemical durability.

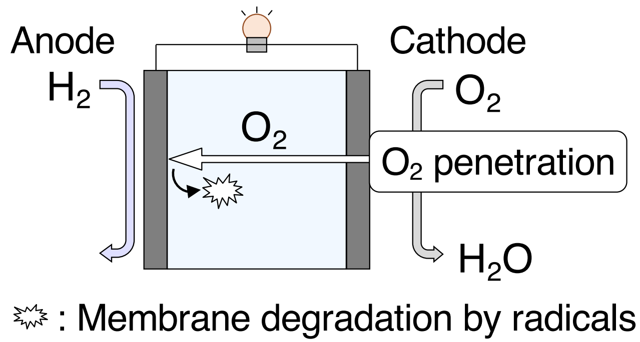
→ Radical formation for O2 permeation is suppressed, and the membrane thinning is also suppressed.

→ The first example of vinyl hydrocarbon polymer to overcome chemical durability than Nafion.

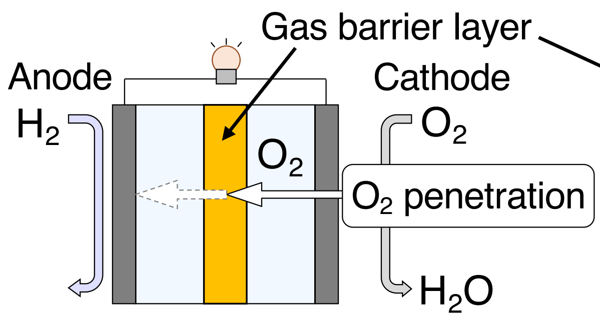
Current problems

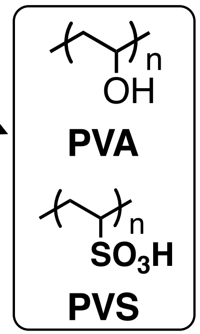
- Low IV performance
- Confirmation of mechanical and thermal durability

Conventional PEM



Gas barrier PEM



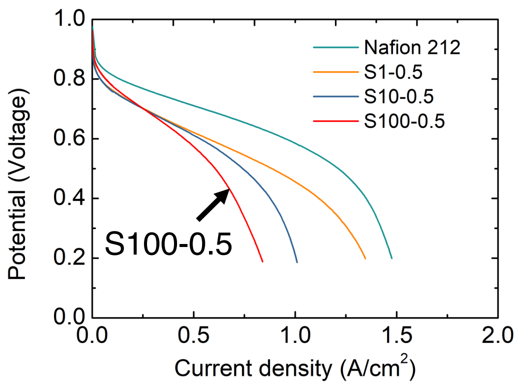


Z. Gautama, et. al., ***J. Memb. Sci.***, *658, 120734 (2022).*
Patent 2021-132396

Preparation of Thin Gas Barrier PEM

Problem: low IV performance

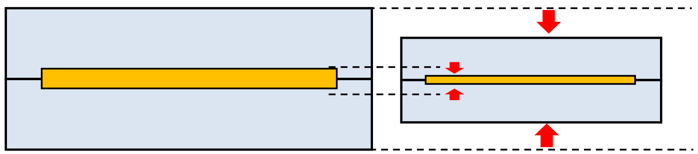
(80˚C, 95% RH, H_2:139 mL/ min, air: 332 mL/min)



PVA **PVS**

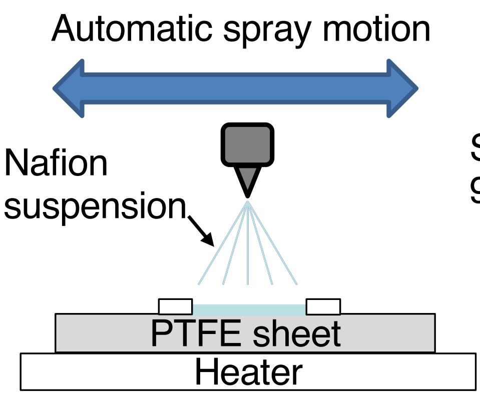
Sample	Molar ratio (PVA:PVS)
S100-0.5	100:1

To improve IV performance, thinning PEM causing reduction of membrane resistance was carried out.

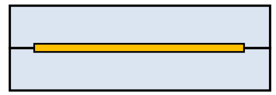


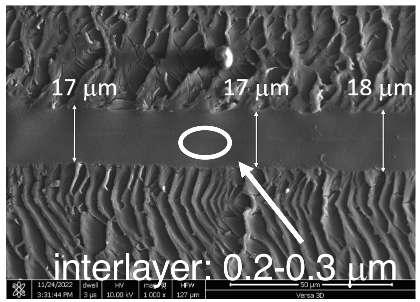
S100-0.5: 50 μm thin PEM: <20 μm

Preparation of thin Gas Barrier PEM



Sprayed Nafion membranes: 9μm





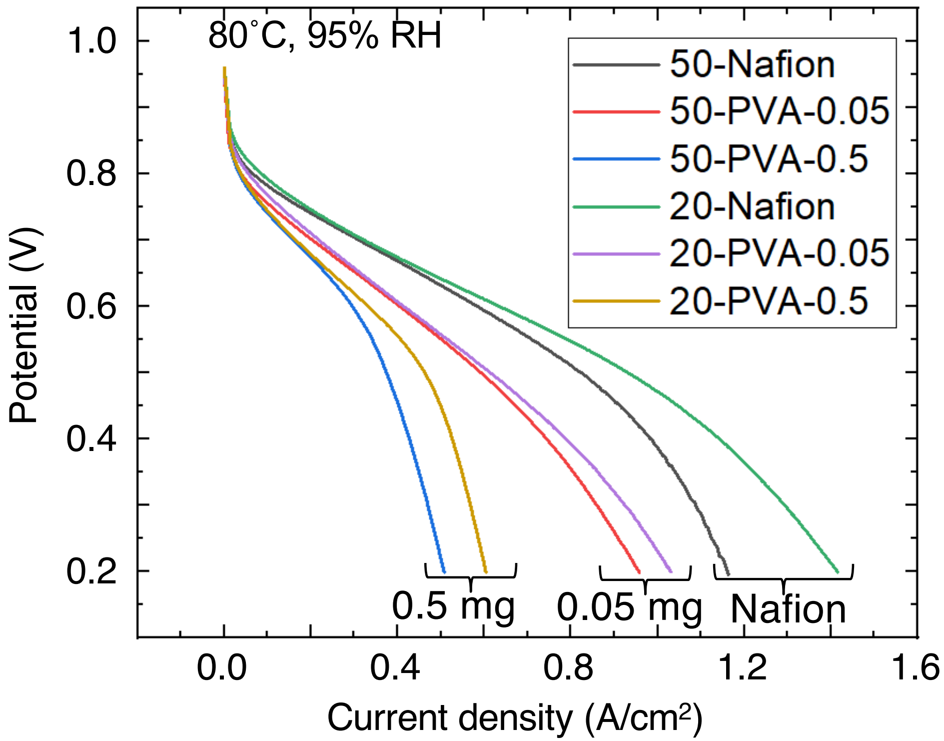
Thin gas barrier PEM： 18 μm (Nafion (9μm) x 2 + interlayer 0.2-0.3 μm)

Z. Gautama, in preparation.

PEM

Fuel Cell Performance of Thin Gas Barrier PEMs

IV Curve



xx-PVA-yy

xx: Nafion thickness (μm)
yy: Gas barrier loading (mg/cm²)

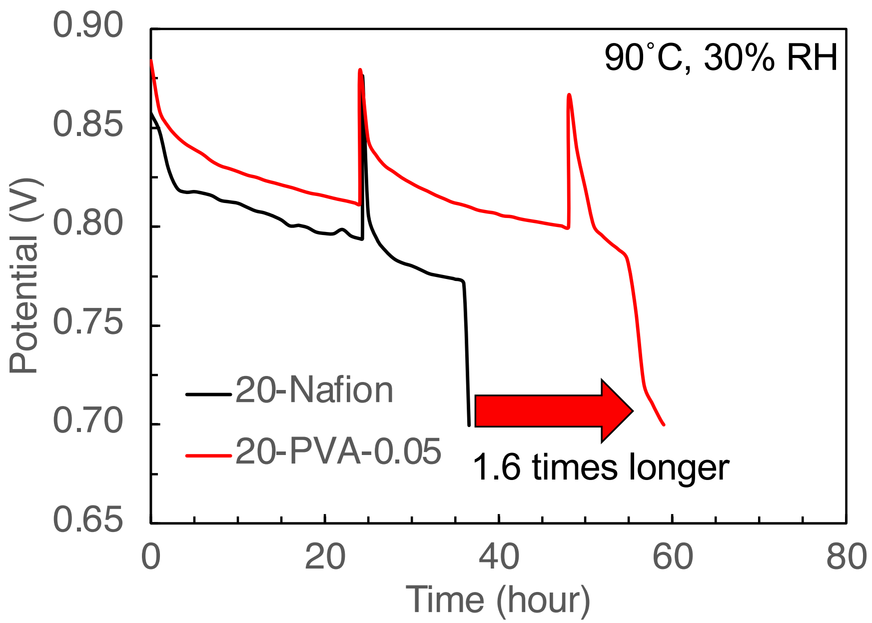
	Max power density	PEM resistance
	W/cm²	mΩ cm²
50-Nafion	0.41	91
50-PVA-0.05	0.3	180
50-PVA-0.5	0.19	288
20-Nafion	0.47	78
20-PVA-0.05	0.32	148
20-PVA-0.5	0.23	274

2 times higher

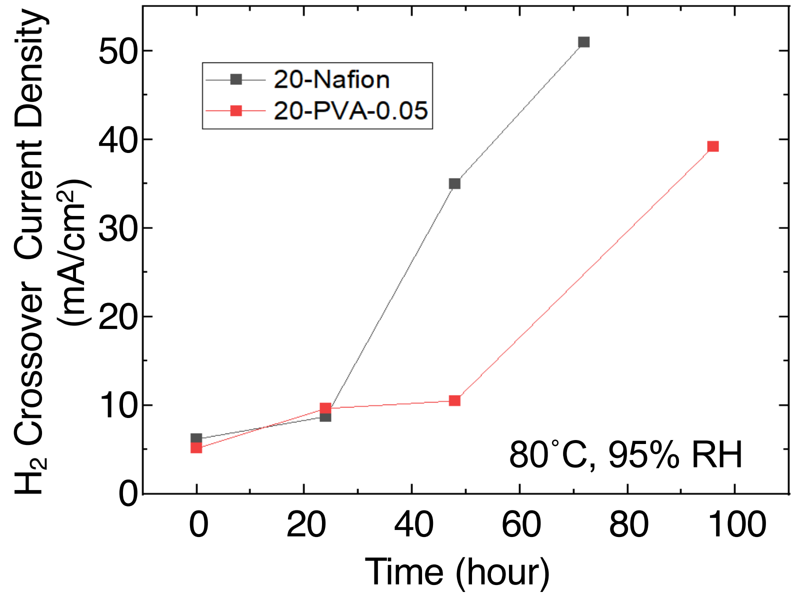
- Reduction of gas barrier loading significantly improves fuel cell performance.
- Utilizing ~0.2 μm gas barrier layer still shows about 2 times higher PEM resistance than Nafion.

Chemical Durability of Thin Gas Barrier PEM

OCV holding test



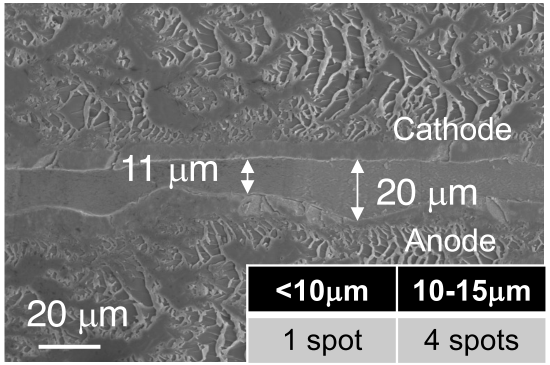
H_2 crossover



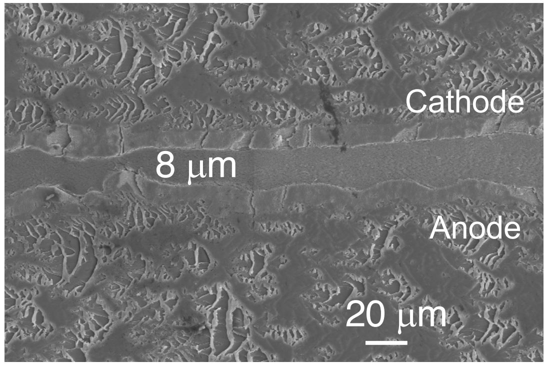
- Even with 0.2 μm gas barrier layer, the chemical durability of Gas barrier PEM was improved significantly.
- The hydrogen crossover trend shows that the gas barrier layer could maintain lower hydrogen crossover.

SEM Images of End-of-life (EOL) Membranes

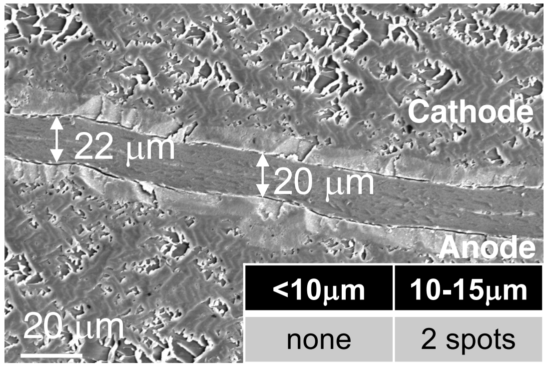
20-Nafion



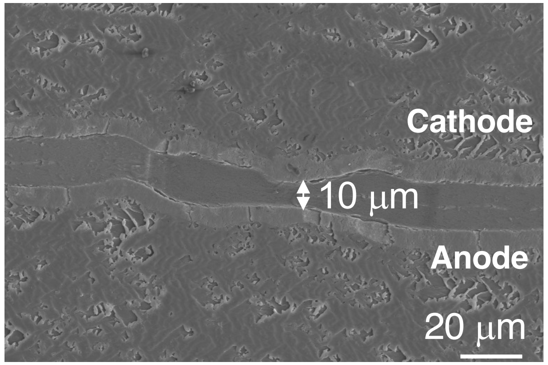
<10μm	10-15μm
1 spot	4 spots



20-PVA-0.05

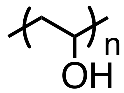


<10μm	10-15μm
none	2 spots

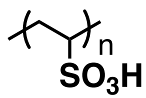


Thin gas barrier PEM：18 μm (Nafion (9μm) x 2 + interlayer 0.2-0.3 μm)

Interlayer components



PVA



PVS

PVA:PVS=100:1 (mol)

- Gas barrier PEM had more homogenous thickness at EOL.
- At EOL, Nafion had more severe membrane thinning.
- Membrane thinning occurred mainly at anode.

Summary –Gas barrier PEM-

Gas barrier PEM

- Gas barrier gives high chemical durability due to effective suppression of radical formation by O_2 barrier.
- Thin gas barrier PEM shows better IV performance with chemical durability.

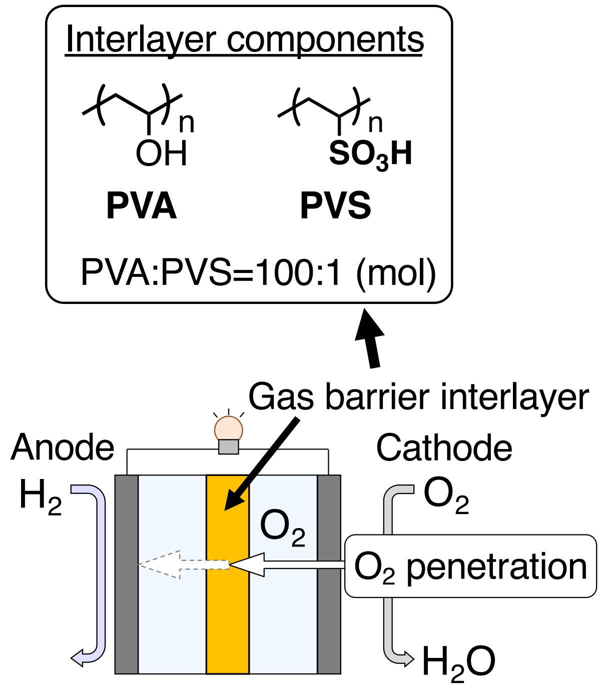
Useful characteristics

- High gas barrier materials would be candidates for gas barrier layer.
- Easy and simple PEM preparation process.

Future works

- Improvement of IV performance more.
- Evaluation of the real durability in fuel cell devises.

Gas barrier PEM



1. Decarbonization of transportation sector and contribution of fuel cell (PEFC) system

2. Polymer electrolyte Membrane (PEM)
• High gas barrier PEM for high durability

3. Ionomer
• High gas permeable ionomer for high performance

Gas permeable ionomers –reported works-

Heavy duty vehicles (HDVs)

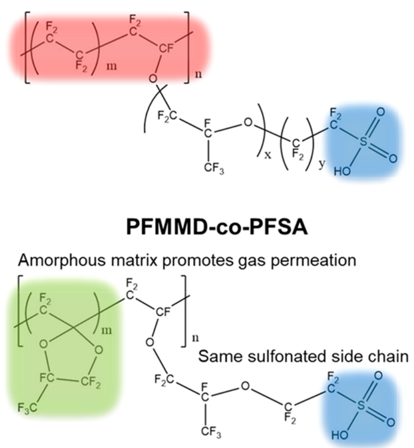
©Hyundai

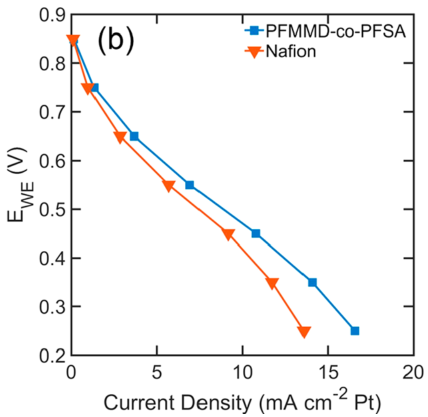
Lifetime: 50,000 hs
+ high power generation
(target in 2030 for 25t truck)

Hypothesis
Can we improve fuel cell performance using high oxygen permeable ionomer?

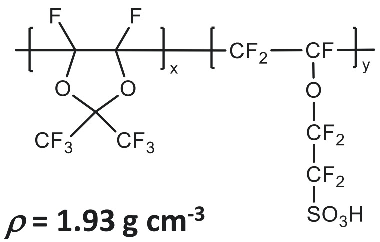
Answer Yes. Possible!!

Gas permeable ionomers (fluoropolymers)

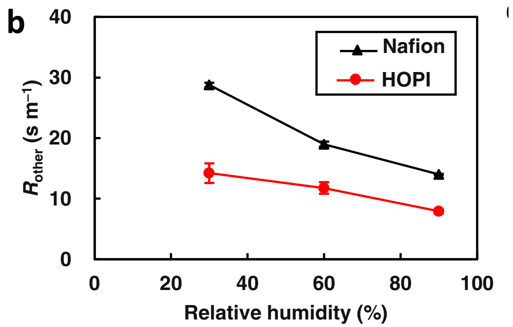




M. A. Modestino et.al, *JACS*. 2020, **142**, 3742–3752.



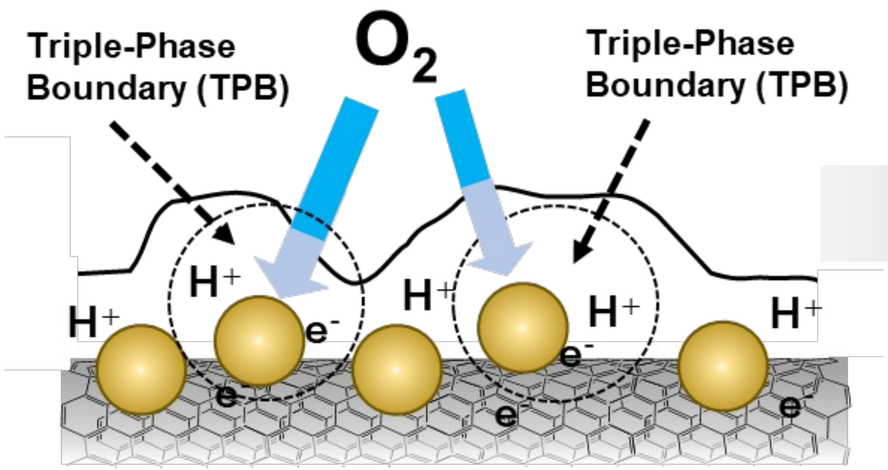
ρ = 1.93 g cm^{-3}
M_n = 3.9×10^4
EW = 735 g mol^{-1}
σ_H = 0.10 S cm^{-1}



R. Jinnouchi, et. al., *Nature Comm.*, 2021,**12,** 4956.

How about hydrocarbon polymers?

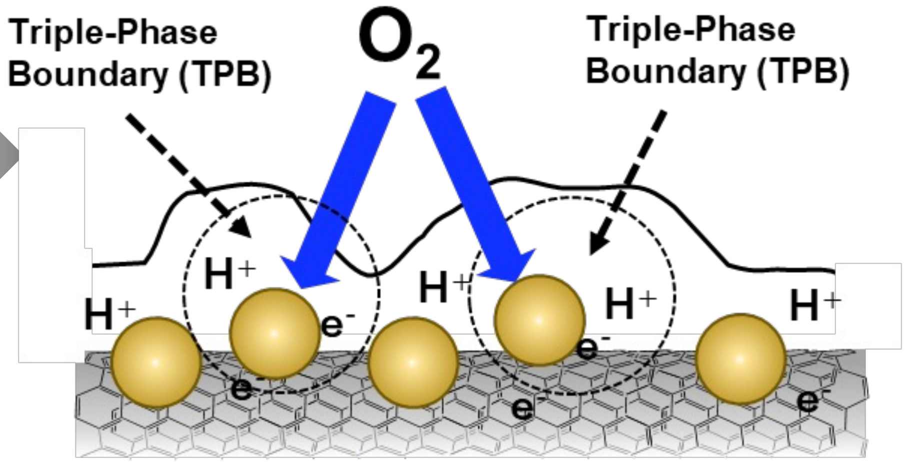
Ionomer at Cathode Catalyst Layer



TPB << active site area

Sci. Adv., **6**: eaaw0870 (2020)

High oxygen permeable ionomer



TPB is enhanced → increased performance

Research objective: reducing oxygen transport resistance in cathode layer by a simple but effective way.

Nafion standard ionomer

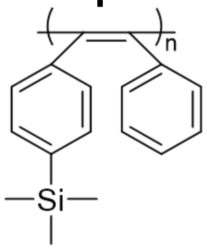
High O_2 permeable polymer

Blended

Gas permeable ionomer blend

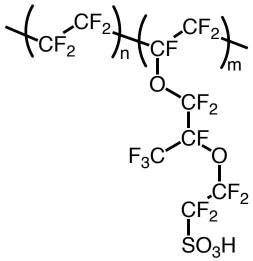
Ionomer Blend

Gas permeable



PTMSDPA
260 Barrer (80°C)

Proton conductive



Nafion
10 Barrer (80°C)

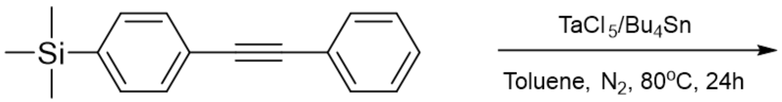
Tsuchihara, et al., *Macromolecules.,* **25**: 5916 (1992)

Ionomer content in MEA → 28wt. %

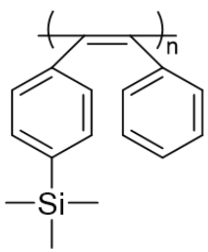
Sample Name	Nafion (wt. %)	PTMSDPA (wt. %)
Nafion	100	0
ACE 1.25%	98.75	1.25
ACE 2.50%	97.5	2.5
ACE 3.75%	96.25	3.75
ACE 5.0%	95.0	5.0

Okumura et al., *J. Electrochem. Soc.*, **164**(9): F928-F934 (2017)

Synthetic Route



PTMSDPA

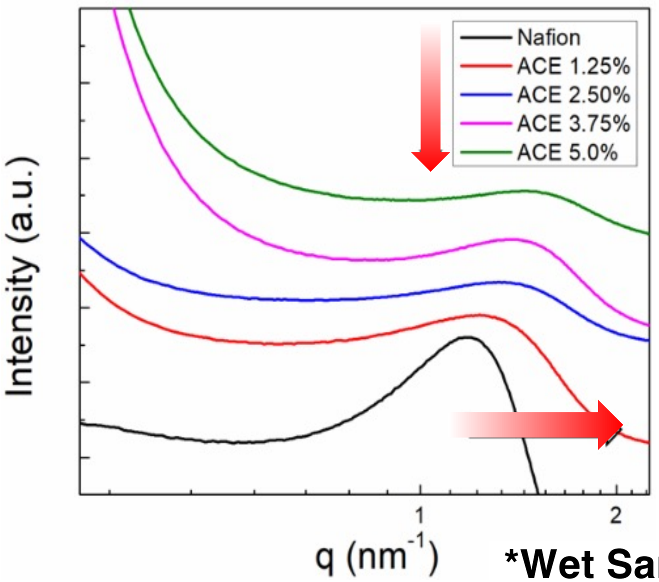


Tsuchihara, et al., *Macromolecules*, 25, 5916-5820, (1992)

Mw : 970,000
PDI : 4.89
Yield: 48%

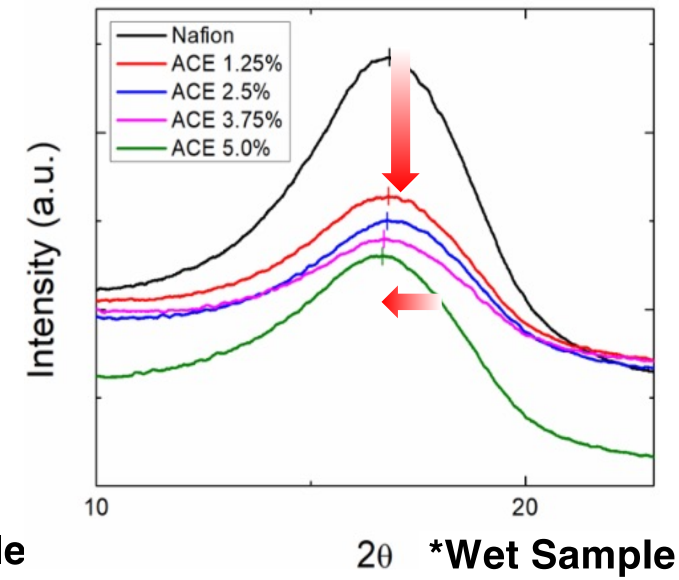
Structural analysis of blend ionomer

Small Angle X-ray Scattering (SAXS)



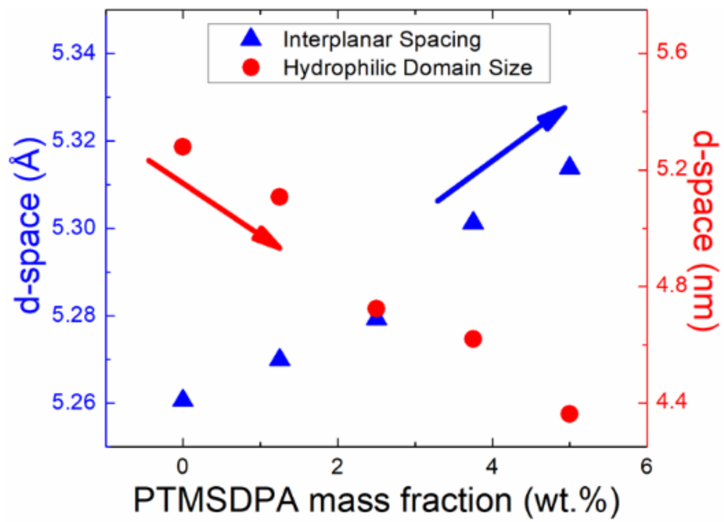
***Wet Sample**

X-ray Diffraction (XRD)



***Wet Sample**

Interplanar Spacing and Hydrophilic Domain Size



Saga light source
λ = 1.38 Å, SiN windows, Pilatus
Camera path: 1087 mm

- Hydrophilic domain size from SAXS

$$d = \frac{2\pi}{q}$$

- Interplanar spacing from XRD

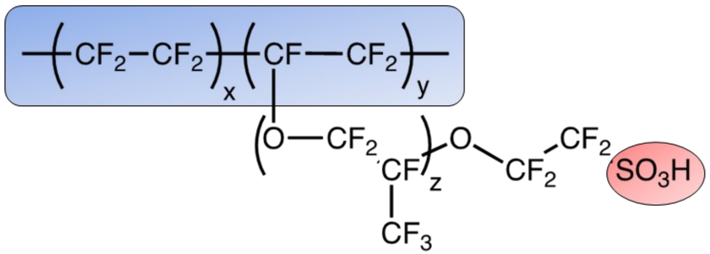
$$d = \frac{n\lambda}{2sin\theta}$$

Effect of PTMSDPA

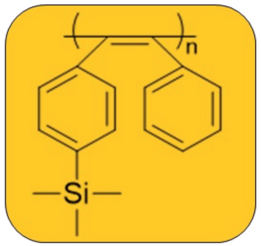
- Expansion of hydrophobic inter-distance (a)
- Compression of hydrophilic domain (d)

Katzenberg et al., *J. Am. Chem. Soc.*, **142**(8): 3742-3752 (2020)

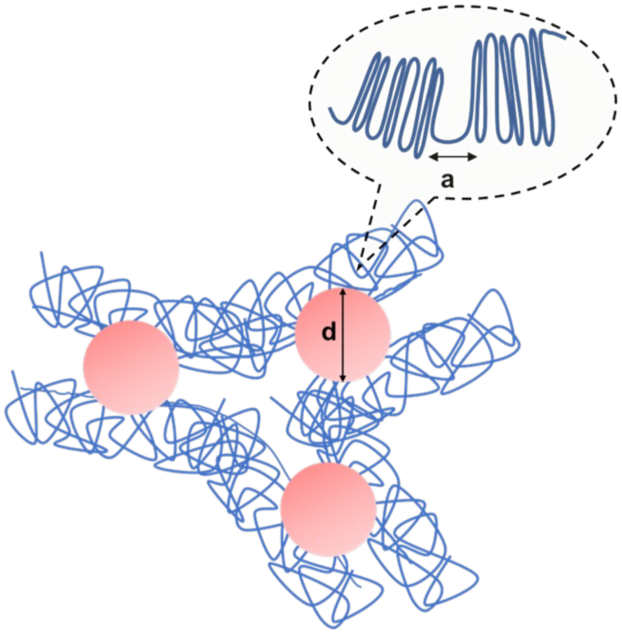
Structural analysis of blend ionomer



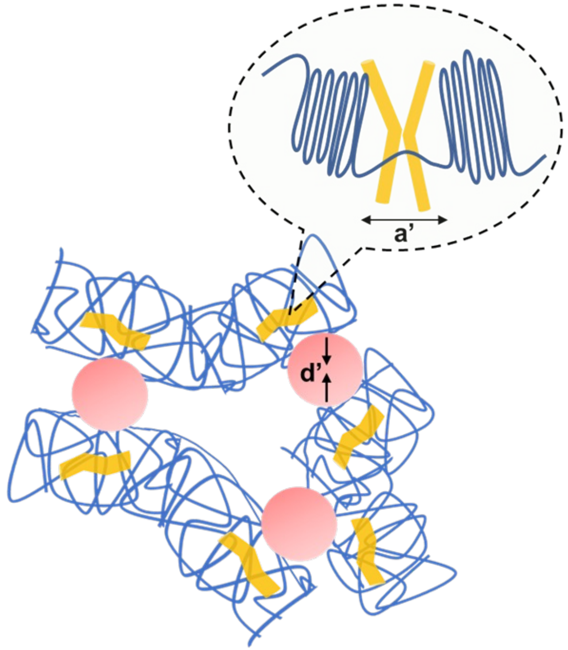
Nafion



PTMSDPA



Nafion



Nafion & PTMSDPA Blend

Fuel cell performance

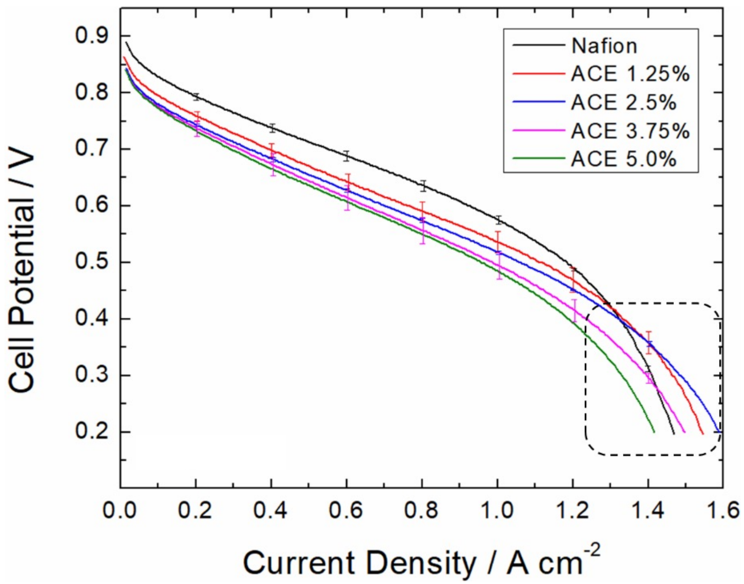
Components	Notes
PEM	Nafion 212
Cell Area (JARI)	1 cm^2
Pt content	0.3 mg/cm^2
GDL	EC-TP1-060T

Components	Conditions
Temperature	80°C
Relative Humidity	95% RH
Hydrogen Flow	0.139 L/min
Air Flow	0.332 L/min

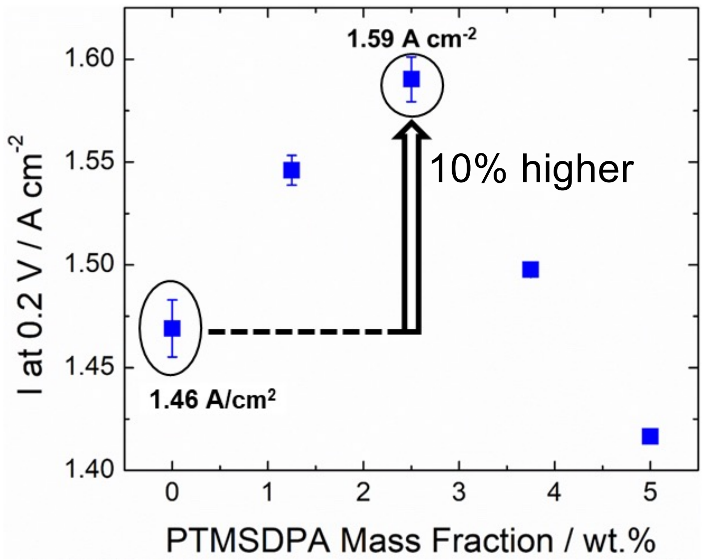
Ionomer content in MEA → 28wt.%

Okumura et al., *J. Electrochem. Soc.*, **164**(9): F928-F934 (2017)

Polarization Curve



Limit Current Density



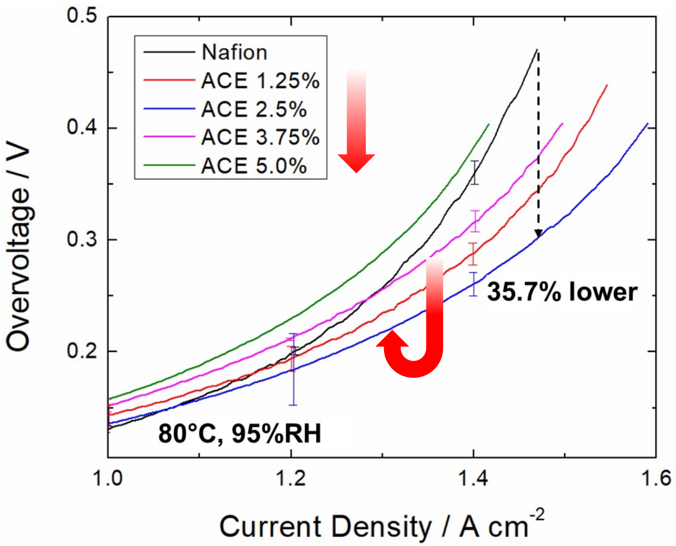
At the higher current density region, the blend ionomers outrun Nafion ionomer performance.

Low performance at low current density

Ionomer

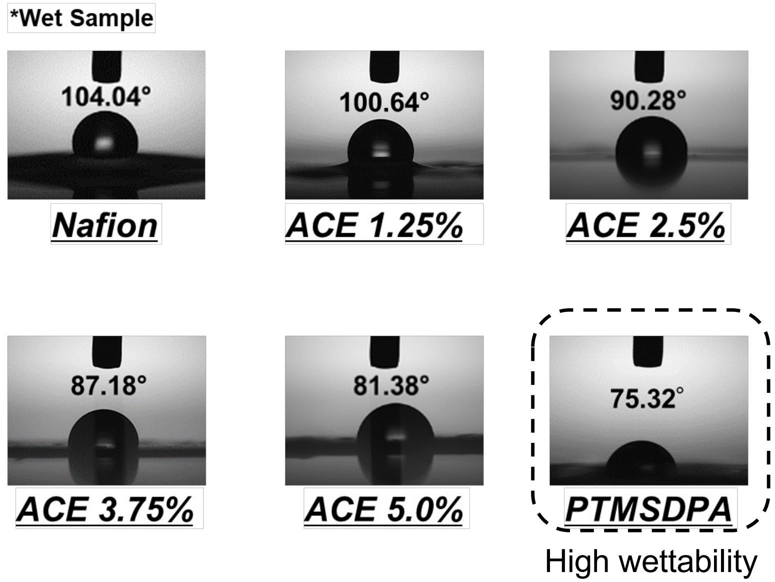
Fuel cell performance

Concentration Overvoltage



Concentration overvoltage: Similar behavior with limit current density

Surface Wettability



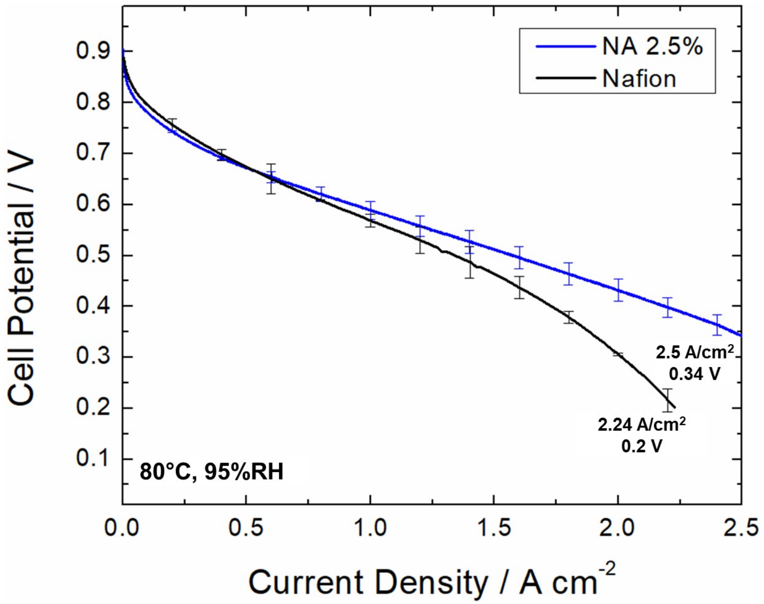
Wettability of PTMSDPA is higher than that of Nafion
→ Hinderance of water emission

Ionomer

Fuel cell performance

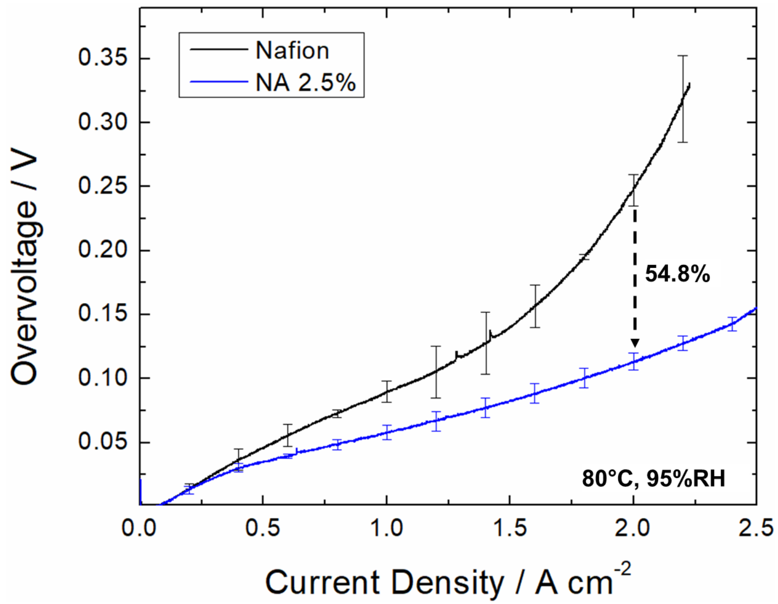
Polarization Curve

NA 2.5%: Nafion 28wt% + PTMSDPA 0.7wt%
(Nafion : PTMSDPA = 97.5 % : 2.5%)
Nafion: Nafion 28 wt%



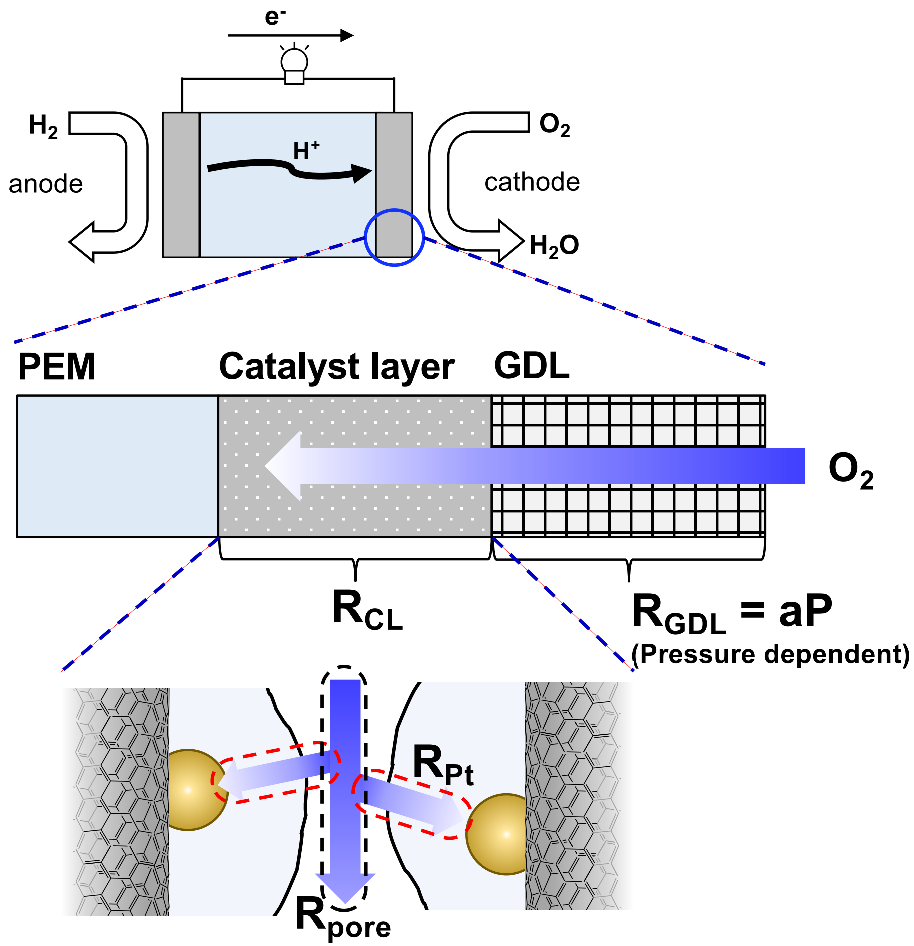
Concentration Overvoltage

Fuel Utilization of 2% at current density of 0.4 A/cm^2



If Nafion amount is the same, performance at low current density is similar with Nafion.

Oxygen transport resistance in catalyst layer



$$R_{Total} = R_{GDL} + R_{CL}$$

R_{total} : Total O_2 transport resistance (s/m)
R_{GDL} : O_2 transport resistance through GDL (s/m)
R_{CL} : O_2 transport resistance through catalyst layer (s/m)

$$R_{CL} = R_{pore} + R_{Pt}$$

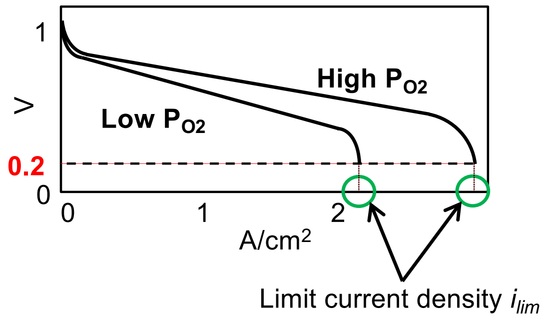
R_{pore} : OTR through catalyst pore
R_{Pt} : OTR around Pt catalyst (ionomer related)

$$R_{Total} = R_{GDL} + (R_{pore} + R_{Pt})$$

Ionomer

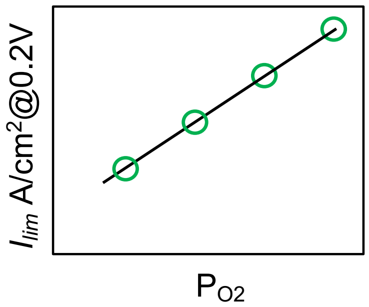
Oxygen transport resistance in catalyst layer

1. Limit current density by different P_{O2}



Measure limit current density by changing O_2 partial pressure.

2. Calculate R_{total} from slope of I_{lim} vs P_{O2}



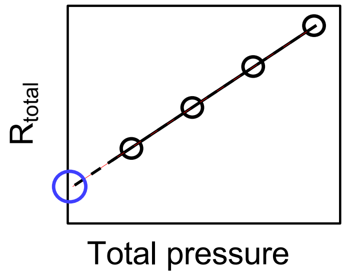
$$i_{lim} = \underbrace{\frac{1}{R_{total}}}_{\text{inverse of slope}} P_{O2} \frac{nF}{RT}$$

inverse of slope

Yasuda et al., *ECS Trans.*, **61**(23): 39 (2014)

R_{total}: Inverse of slope of the graph (P_{O2} vs I_{lim})

3. Calculate R_{CL} from R_{total} with different total pressure



$R_{Total} = R_{GDL} + R_{CL} = aP + R_{CL}$

$$i_{\lim} = nFN = -nFD\frac{dc}{dl} = \frac{nF}{R_{total}}\frac{P_{O_2}}{RT} = nF\frac{P_{O_2}}{RT}\frac{1}{(R_{GDL}+R_{CL})} = nF\frac{P_{O_2}}{RT}\frac{1}{(aP+R_{CL})}$$

$$R_{total} = \frac{P_{O_2}}{i_{\lim}}\frac{nF}{RT} = aP + R_{CL}$$

Yasuda et al., *ECS Trans.*, **61**(23): 39 (2014)

Total pressure: 0 → Resistance of GDL: 0

The rest (intercept of 0 atm): R_{CL} ： O_2 transport resistance through catalyst layer

Oxygen transport resistance in catalyst layer

Total O_2 transport resistance : R_{total} [s/m]

Measurement condition

Components	Measurement Condition
Temp. / Relative Humidity	80°C / 95% RH
Anode Gas	H_2
Cathode Gas / Dilute Gas	O_2 (dry) / N_2
O_2 Gas Concentration	**1, 2, 3, 4 and 5 %**
Gas Flow	0.8 L/min
Cell Voltage	**0.2 V**
Total Pressure	**100, 150, 250, 250 kPa**

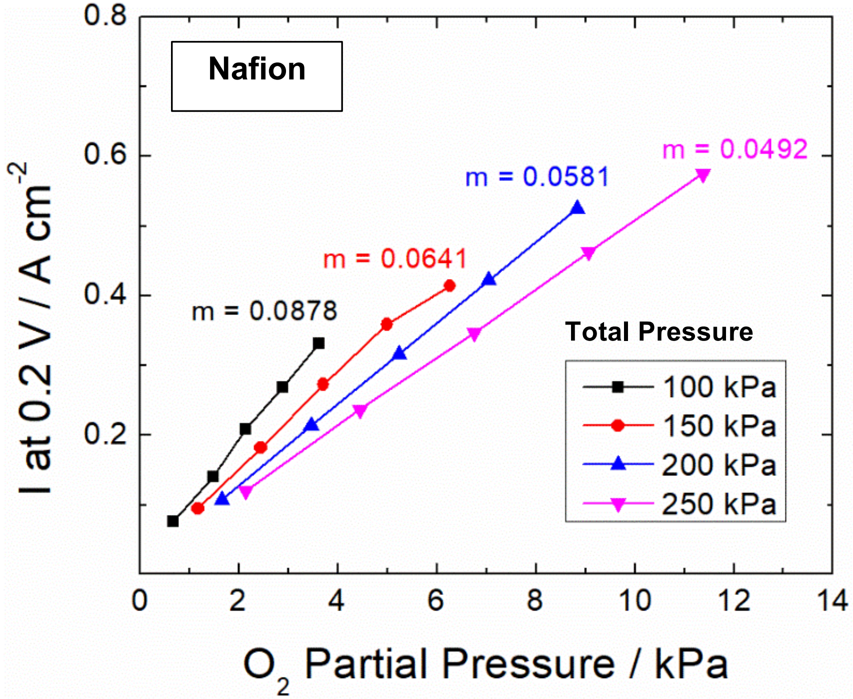
Mashio et al., *ECS Trans.*,**11**(1): 529 (2007)
Yasuda et al., *ECS Trans.*,**61**(23): 39 (2014)
Sakai et al., *ECS Trans.*,**25**: 1193 (2009)

$$i_{lim} = \frac{1}{R_{total}} P_{O2} \frac{nF}{RT}$$

R_{Total} = inverse of slope (s/m)

Resistance to oxygen flux — **Second** — **Meter**

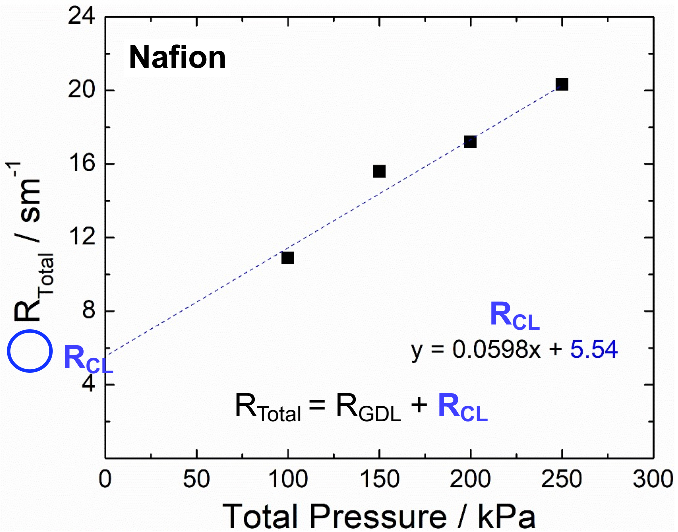
Limit current density vs O2 partial pressure



Oxygen transport resistance in catalyst layer

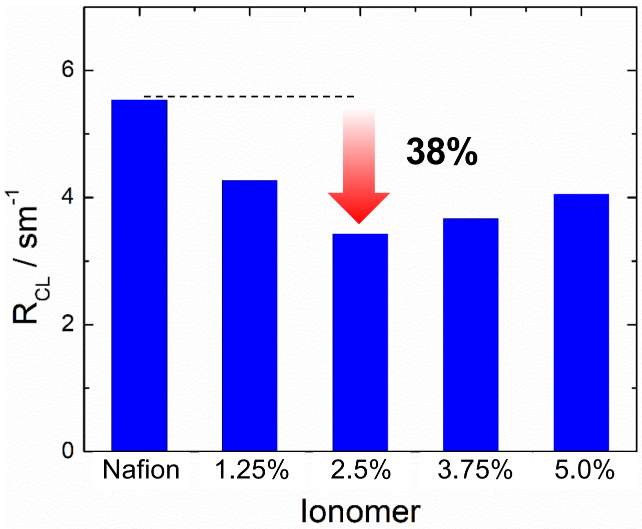
O_2 transport resistance through catalyst layer (s/m): R_{CL} **$R_{Total} = aP + R_{CL}$**

R_{total} as a Function of Total Pressure



Ionomer	R_{CL}(s/m)
Nafion	5.54
ACE 1.25%	4.27
ACE 2.50%	3.43
ACE 3.75%	3.67
ACE 5.0%	4.06

Oxygen Transport Resistance in Catalyst Layer (R_{CL})



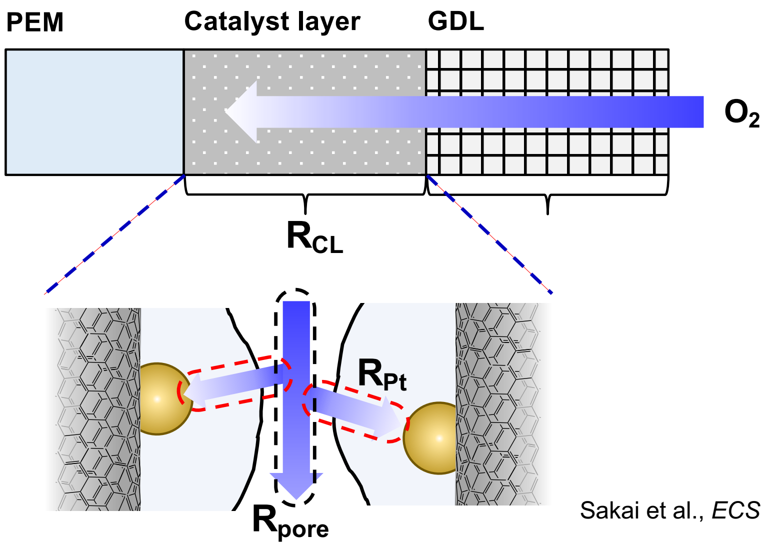
Blend ionomer shows lower R_{CL} than Nafion
→ Effect of gas permeable polymer

Oxygen transport resistance of ionomer

R_{Pt} : OTR around Pt catalyst (ionomer related)

$$R_{CL} = R_{pore} + R_{Pt}$$

R_{pore} : OTR through catalyst pore
R_{Pt} : OTR around Pt catalyst (ionomer related)



Sakai et al., *ECS Trans.*,**25**: 1193 (2009)

$$R_{CL} \times Lo = \frac{R^*_{Pore}\, Lo^2}{3} + R^*_{Pt}$$

Lo: Pt loading

Yasuda et al., *ECS Trans.*,**61**(23): 39 (2014)

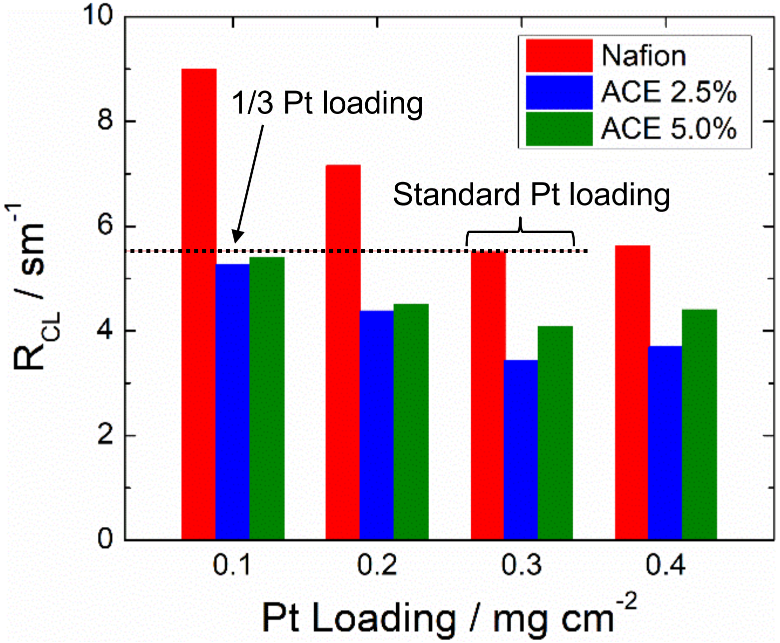
$$R_{CL} = R_{Pt} + R_{pore}$$
$$= R^*_{Pt}/L_O + R^*_{Pore} \times L_O/3$$

R^*_{Pore}, R^*_{Pt}: diffusion resistance parameters in 1mg-Pt loading

R_{CL} is measured by changing Pt loading.
P_{Pt} is calculated from the equation above.

Oxygen transport resistance of ionomer

R_{CL} with different Pt loading



- R_{CL}s of gas permeable ionomer with all different Pt loading are lower than that of Nafion.
- R_{CL}s of gas permeable ionomer with 0.1 mgPt/cm^2 is lower than that of Nafion with 0.3 mgPt/cm^2.

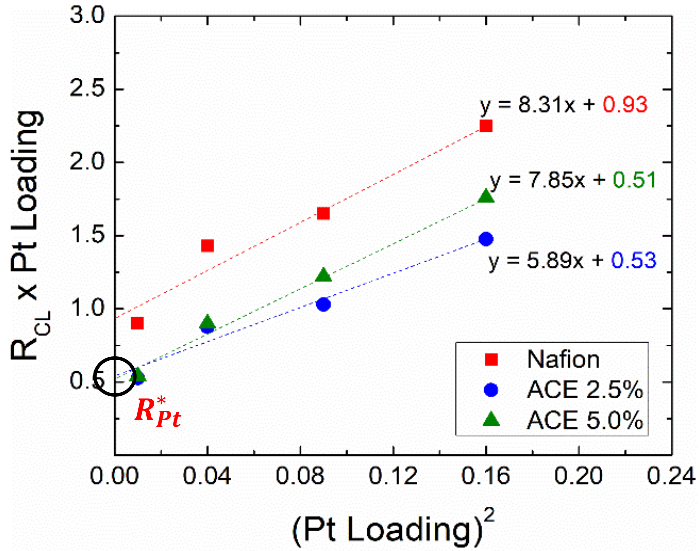
Effective power generation by high gas permeable ionomer with lower Pt loading.
→ **Contribution of reduction of Pt loading**

Ionomer

Oxygen transport resistance of ionomer

$$R_{CL} = R_{Pt} + R_{pore}$$
$$= R^*_{Pt}/L_O + R^*_{Pore} \times L_O/3$$

Oxygen Transport Resistance around the Pt (R_{Pt})



R^*_{Pore} can be obtained from slope and R^*_{Pt} from the intercept of linear fitting.

$$R_{CL} \times Lo = \frac{R^*_{Pore}\, Lo^2}{3} + R^*_{Pt}$$

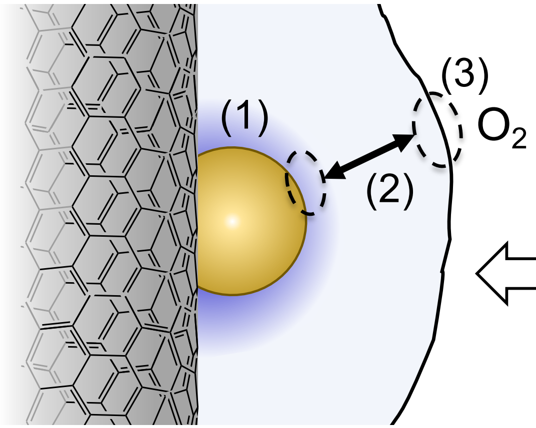
Lo: Pt loading

Yasuda et al., *ECS Trans.*,**61**(23): 39 (2014)

Ionomer	R^*_{Pt} (s/(m•(mgPt/cm2)))	R^*_{Pore} (s•(mgPt/cm2)/m)
Nafion	0.93	24.9
ACE 2.5%	0.53	17.7
ACE 5.0%	0.51	23.5

- R^*_{Pt} of 2.5% gas permeable ionomer is 43% lower than that of Nafion ionomer.
- R^*_{Pore} of 5.0% gas permeable ionomer is higher than that of 2.5% gas permeable ionomer.
  → Hinderance of O2 transport by generated water
- R^*_{Pore} of Nafion is higher than that of 2.5% gas permeable ionomer.
  → Structural change by gas permeable polymer

Ionomer structure in catalyst layer



[Expected ionomer structure in catalyst layer]
Estimated by MD calculation and OTR

• Highly condensed layer at Pt catalyst/ionomer interface (< 0.5nm)
Ave. thickness of ionomer: < 10 nm

(1) Oxygen transport resistance at Pt catalyst/ionomer interface
- Major resistance of R_{Pt}
- Three-seven times higher OTR than bulk OTR
- Dense Nafion layer is formed by Adsorption of sulfonic acid to Pt.
- Affect crystalline structure of Pt catalyst/ionomer

(2) Oxygen transport resistance of bulk ionomer
- No difference from PEM

(3) Interfacial resistance of ionomer/gas phase
- Less contribution than (1)

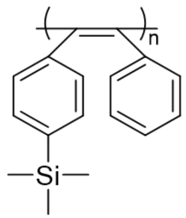
[Further improvement of performance]
- Introduction of hydrophobicity
- Introduction of higher gas permeability
- Less structural relaxation by time

Summary –Gas permeable ionomer-

Gas Permeable ionomer blend PEM

- Gas permeability gives high fuel cell performance due to low oxygen transport resistance.
- 2.5% PTMSDPA shows highest limit current density.

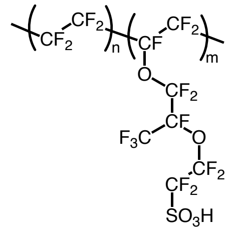
Gas permeable



PTMSDPA

260 Barrer (80°C)

Proton conductive



Nafion

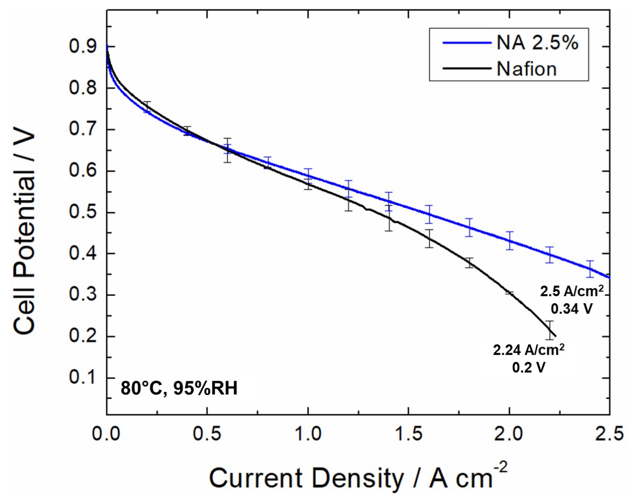
10 Barrer (80°C)

Useful characteristics

- Works well by mixing gas permeable polymer only a few %
- Easy and simple preparation process.

Future works

- Introduction of hydrophobicity
- Introduction of higher gas permeability
- Less structural relaxation by time



Y. Hutapea, et. al., *J. Power Sources,* 556, 232500 (2023).
JP2021-132396

Acknowledgement

KYUSHU UNIVERSITY

Prof. K. Sasaki
Prof. A. Hayashi
Prof. S. Lyth
Prof. J. Matsuda

Ass. Prof. Tachikawa
Ass. Prof. Sugiyama

Prof. Fujikawa

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