KYUSHU UNIVERSITY 九州大学 エネルギーウィーク 2021 Energy Week 2021 Q-PIT Kyushu University Platform of Inter-/Transdisciplinary Energy Research

DEVELOPMENT OF HIGH OXYGEN BARRIER PEM FOR DURABLE PEFC SYSTEMS

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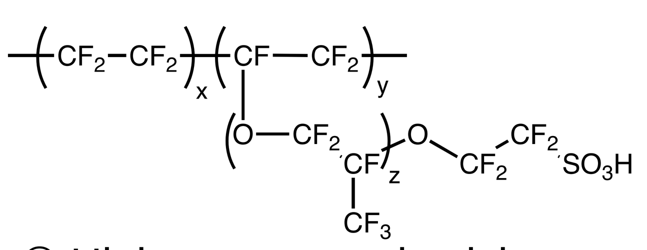
【Scientific Background of Research Proposal】

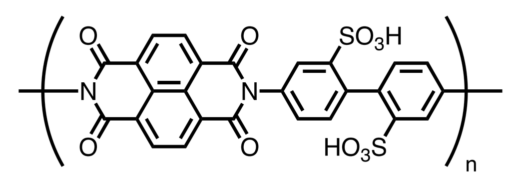
Polymer Electrolyte Membrane (PEM) Material Used for Fuel Cells

Nafion（Fluorine-based）



☺ High proton conductivity
☺ High chemical durability
Standard PEM for fuel cells

Alternative PEM（Hydrocarbon）



☺ Simple structure and easy to modify
☺ High proton conductivity and heat stability

【Current problem for PEM】
Chemical decomposition of PEM due to the attack from radicals generated during operation

Traditional research approach

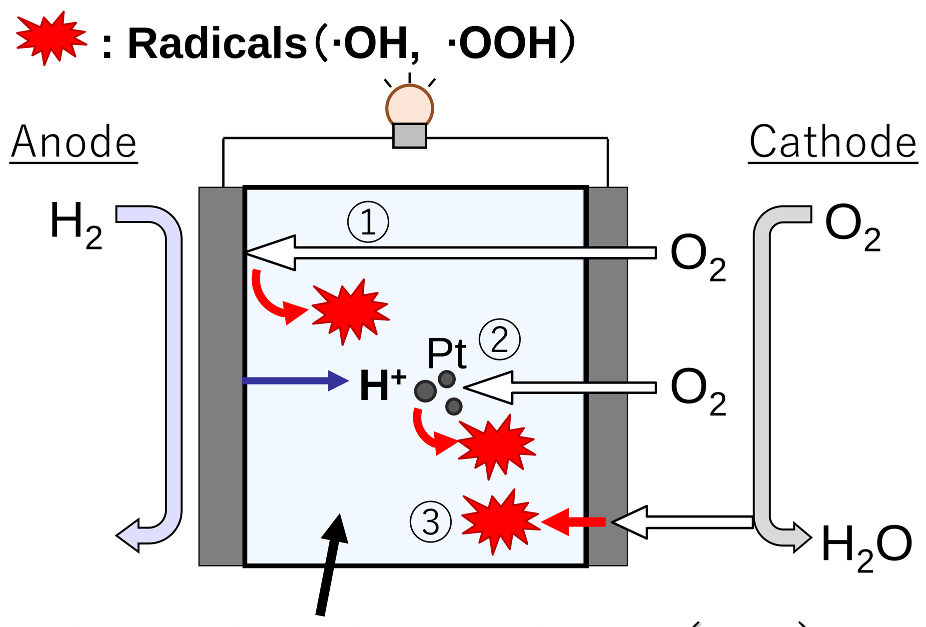
- Introduction of molecular structure (polyphenylene, fluorine-based) with high chemical durability
- Blending with radical scavengers (CeO_2 ,etc.）

Problems such as limited structure and uneven distribution of radical scavengers inhibit these approaches to be a fundamental solution

Decomposition of PEM

Attack from radical species (•OH, •OOH) on PEM leads to PEM decomposition

Radical formation on PEM



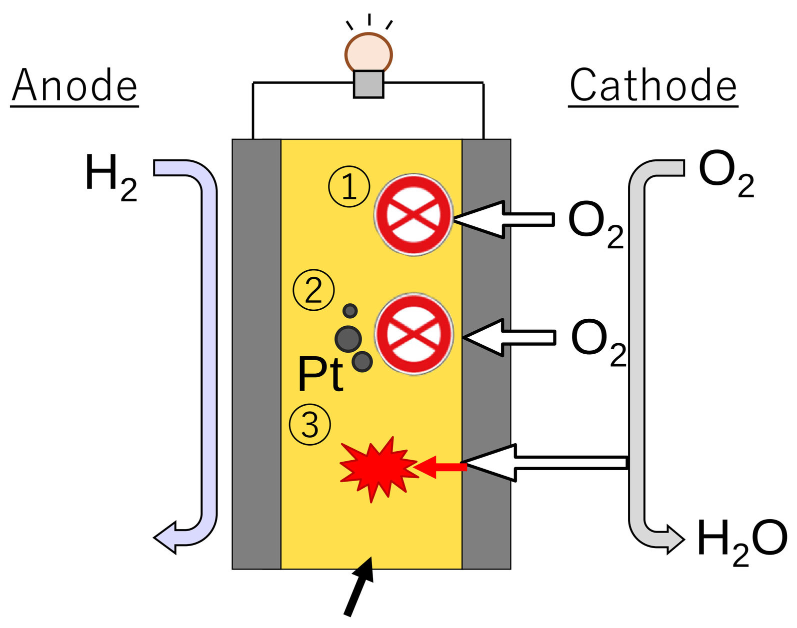
1. Penetrated oxygen gas to the anode side
2. Penetrated oxygen gas to the eluted Pt
3. Radical formation by two-electron reaction at the cathode

"Oxygen penetration through PEM is the main cause of radical formation"

[Question]
Can we suppress PEM decomposition by less radical formation if oxygen gas never penetrate PEM ?

【Research Objective】

By developing high oxygen gas barrier Polymer Electrolyte Membrane (PEM) to suppress the radical's generation due to oxygen permeation through PEM, the decomposition of PEM is fundamentally solved.



- PEM with 100 times more O_2 barrier than Nafion
- Thinner PEM can be applied

【Research Direction】
Develop high oxygen gas barrier PEM
・To reduce radicals derived from oxygen permeation and suppress PEM decomposition
・Higher performance by thinner PEM
PEM redesign
・PEM redesign based on durability analysis result

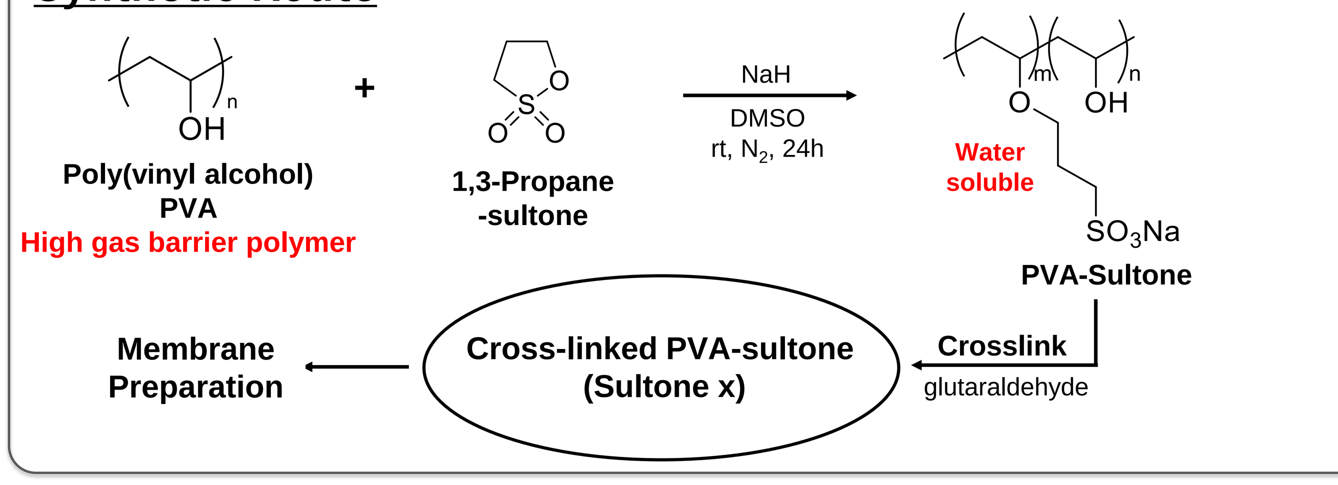
【Research Impact】
Possibility of using various materials
→ Material Chemistry
Application to water electrolysis
→ Hydrogen energy field

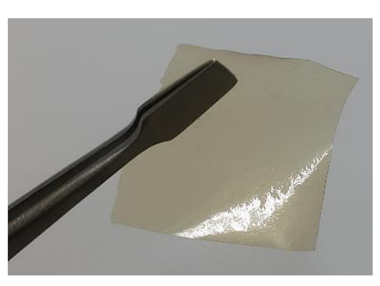
【Research Plan】

Full Ph.D. Project Time Schedule

2020 - 2021	2021 - 2022	2022 - 2023
➢ **Development of High Oxygen Barrier PEM** * Preparation * Characterization * PEM durability evaluation * Article publication	➢ **Optimized High Oxygen Barrier PEM** * Improved durability * Article publication ➢ **Development of High Oxygen Permeable Ionomer** * Improved catalytic performance * Article publication	➢ **Combination of High Oxygen Barrier PEM and High Oxygen Permeable Ionomer for PEFCs Application** * Improved performance and durability * Article publication * Ph.D. thesis writing

Synthetic Route

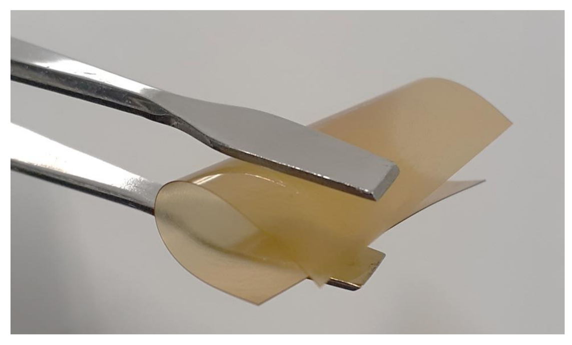




High Oxygen Barrier PEM

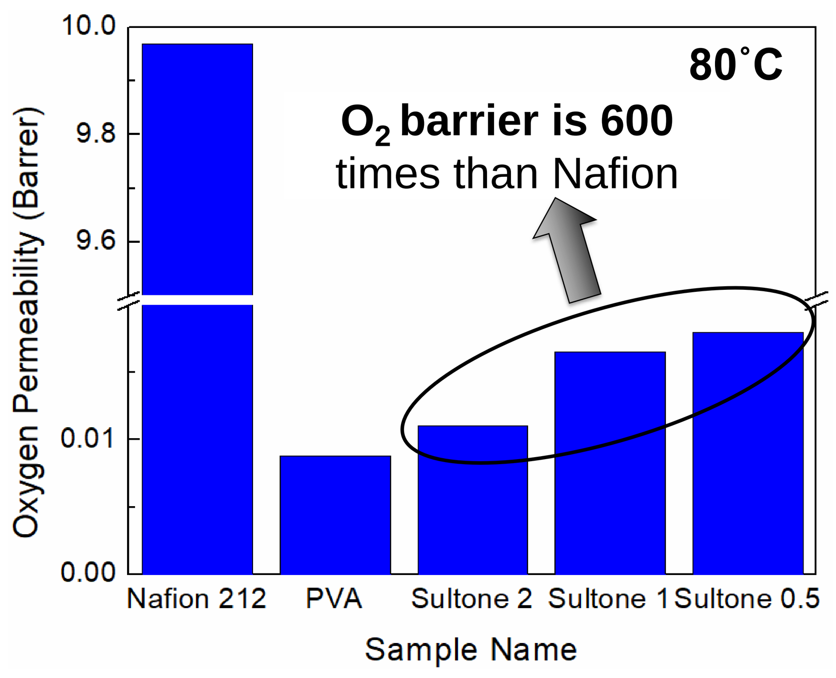
【Current Research Results】

Sample Name	PVA (meq.)	1,3-propane sultone (meq.)	Sulfonation Degree (%)	IEC (mmol/g)
Sultone 2	1	2	53	1.80
Sultone 1	1	1	**59**	**2.41**
Sultone 0.5	1	0.5	51	1.09

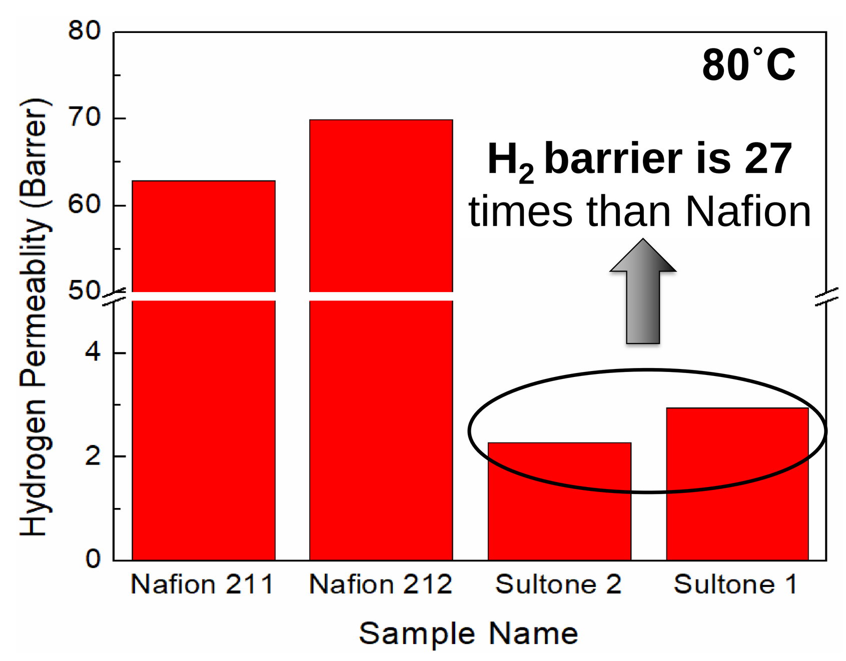


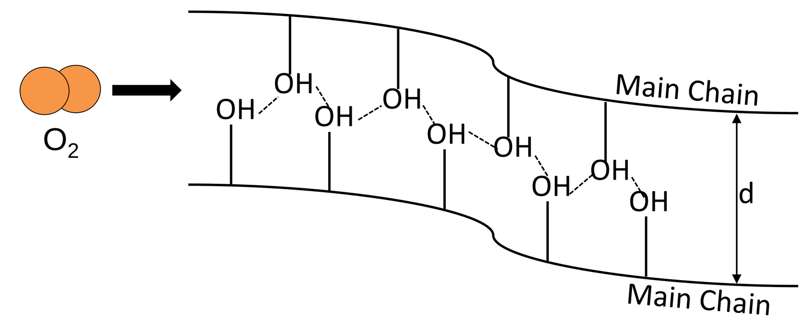
Gas Barrier Properties

Oxygen Barrier



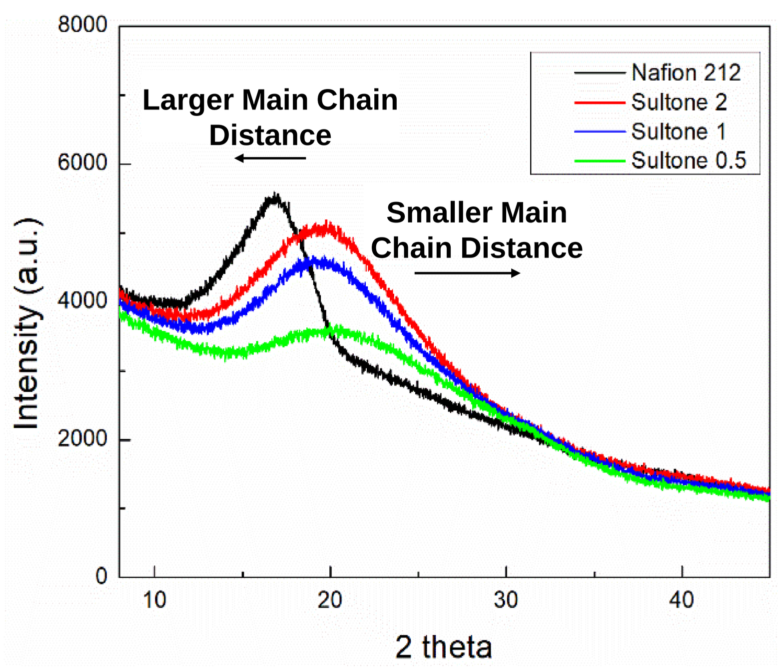
Hydrogen Barrier





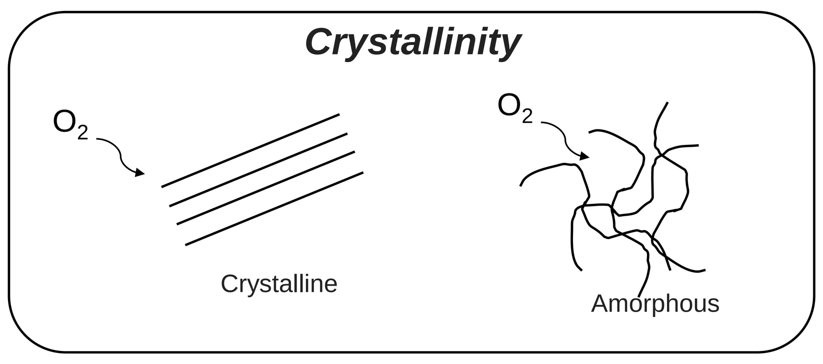
- High oxygen barrier property of PVA is obtained from strong intermolecular force between OH groups. → small main chain distance
- After sulfonation, strong intermolecular force remains existed between sulfonic acid groups.

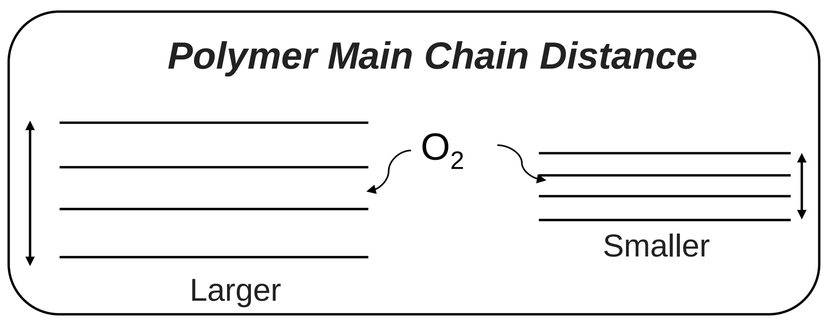
X-ray Diffraction



- Nafion 212 is slightly more crystalline than Sultones.
- However, Sultones show smaller distance between its polymer main chain.

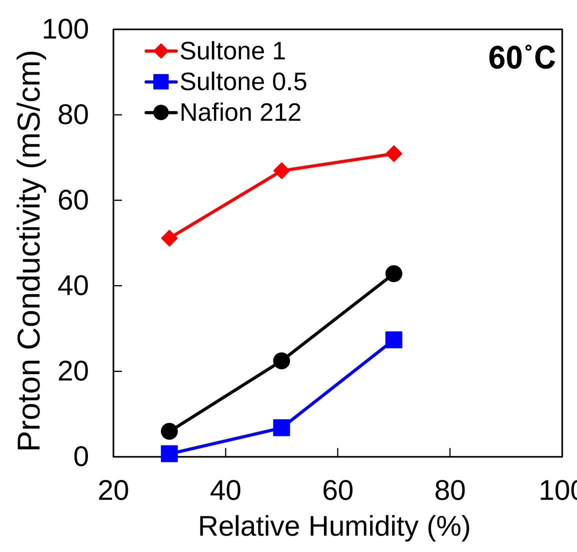
Structure vs Oxygen Permeability





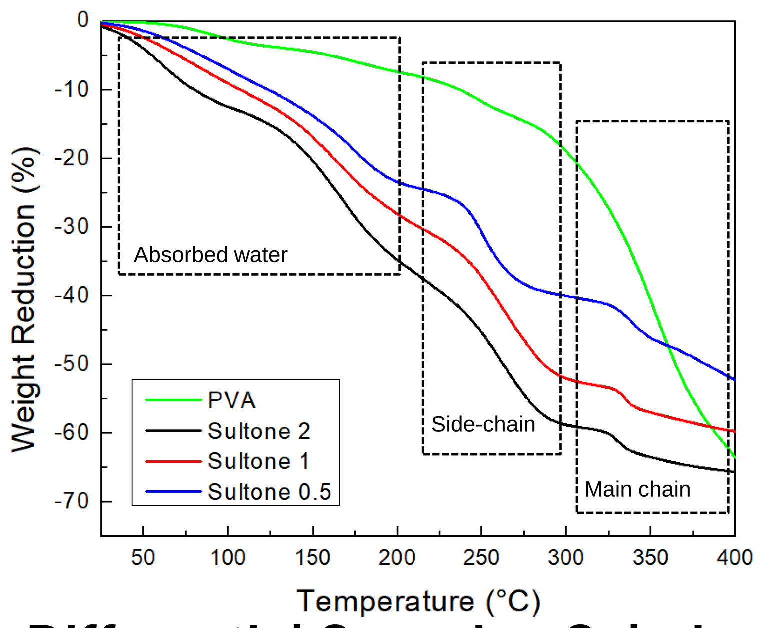
Although crystallinity relates to gas barrier property, the dominant factor for Sultones was given by "polymer main chain distance".

Proton Conductivity



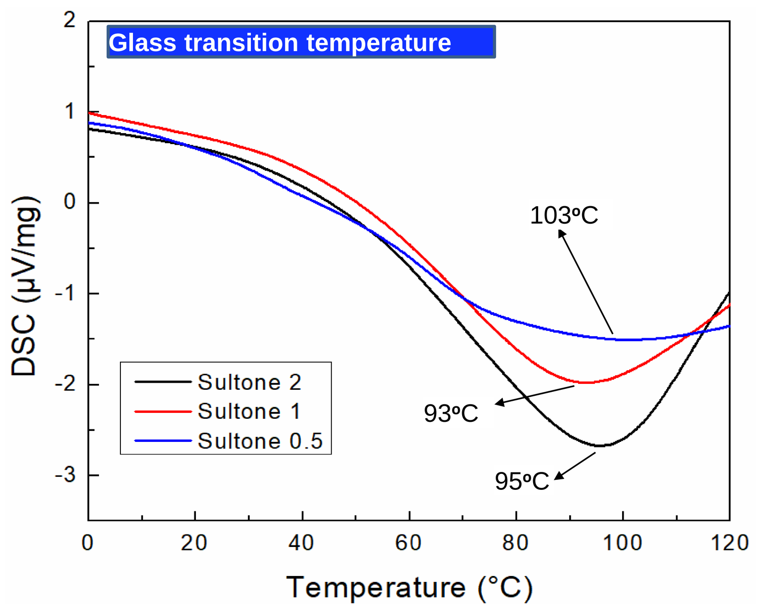
- The optimum proton conductivity is achieved by Sultone 1 (70 mS/cm), higher than Nafion 212 at the same condition.
- Proton conductivity in higher temperature and humidity is not available yet due to thermal stability issue and swelling, respectively.

Thermogravimetric Analysis



- Evaporated and bound water molecule were decomposed at the first step.
- Second step relates to de-sulfonation.
- Main chain degradation was recorded at the third step.

Differential Scanning Calorimetry



- Glass transition temperature of Sultones are lower than Nafion (130˚ C) → optimizing test condition
- Sultones with lower sulfonation degree need to be measured for negative control

【Summary and Future Plan】

1. The developed PEM shows significant high O_2 and H_2 barrier compared to Nafion 212.
2. The high gas barrier properties of Sultones comes from its small main chain distance.
3. The optimum proton conductivity was shown by Sultone 1 (70 mS/cm) (60ºC, 70%RH).

1. Thermal stability improvement by modifying crosslinking method.
2. SAXS analysis to investigate the distance between sulfonic acid group of PEM.
3. **OCV holding test** for PEM chemical durability measurement.