Study the Effect of Electric Field on Polymer Electrolyte Membrane for Fuel Cell

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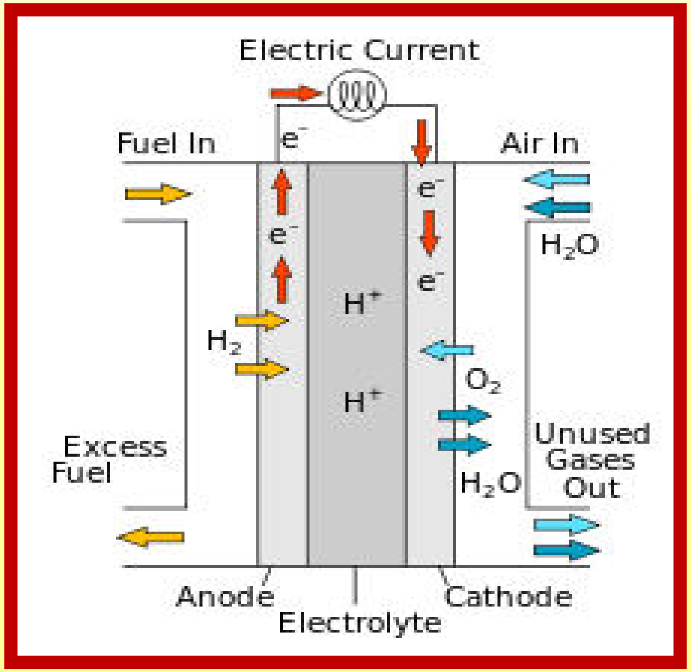
Outline

1. Introduction

Polymer electrolyte fuel cell (PEFC)



Polymer electrolyte fuel cell (PEFC)

BALLARD Cars
http://www.youtube.com/watch?v=oy8dzOB-Ykg

- **The PEFC's offer the promise of a low-polluting, highly efficient energy source → They are under intensive investigation.**
- **The polymer electrolyte membrane (PEM) → the most important parts on PEFC's.**
- **The PEM is a key element ↑ the performance of the PEFC's.**

Requirements for the polymer electrolyte membrane for fuel cells

- **Low permeation of H_2 and O_2 gases.**
- **High proton conductivity.**
- **No electron conductivity.**
- **High chemical stability.**
- **High mechanical stability.**

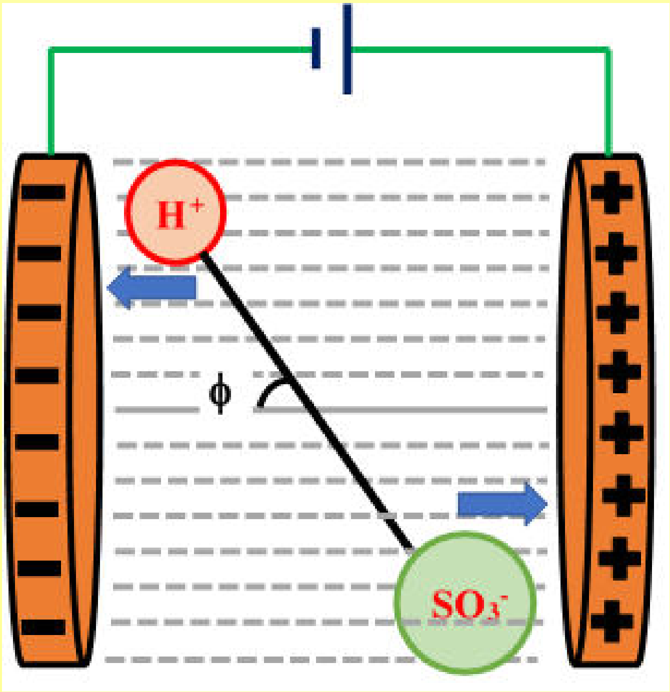
Many polymers are under investigation as PEM for example; *Perfluorinated PEMs (Nafion® and Aquivion®).*

Motivation

- The electric field impact on the Nafion membrane is the center of the current investigation.
- Appling an electric field to the Nafion membrane at a temperature between T_g and T_m provides energy to the molecular motion.
- Also, the electric field causes the polar sulfonic acid groups of Nafion to move along the direction of the electric field.
- Furthermore, applied electric field to the Nafion membrane has its effect on the structure of the ion channels.
- The ionic cluster channels of Nafion membranes after applying an electric field have smaller diameters and thus lower gas/methanol crossover than those for as received membrane.

Motivation (Cont.)

- In the electric field effect, the electric force is applied according to the dipoles of the Nafion 112, particularly $-SO_3^-$ and H^+ .
- When every section regarding dipole has a positive charge (*Q*+) or negative charge (-*Q*), the dipoles have a torque as *EQD* sin (*ϕ*), [*E* → electric field strength, *D* → split in the poles, *ϕ* is the angle].
- In real systems, a more complicated situation is demanded in explaining the structural changes, especially, at high temperatures (~ 90 °C).



A dipole in an ion channel for Nafion 112 membrane subject to an electric field

Objectives

- *Investigation of the electric field impact a 90 ^{o}C on the properties of Nafion 112 as a polymer electrolyte membrane (PEM) for the fuel cell applications.*
- *Studying the influence of the electric field strength on the nanostructure of PEMs such as free volume holes.*
- *Studying the effect of the electric field strength on mechanical properties, water uptake, and proton conductivity.*
- *Studying the correlation between the free volume and mechanical properties and proton conductivity.*

Outline

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2. Experimental and data analysis

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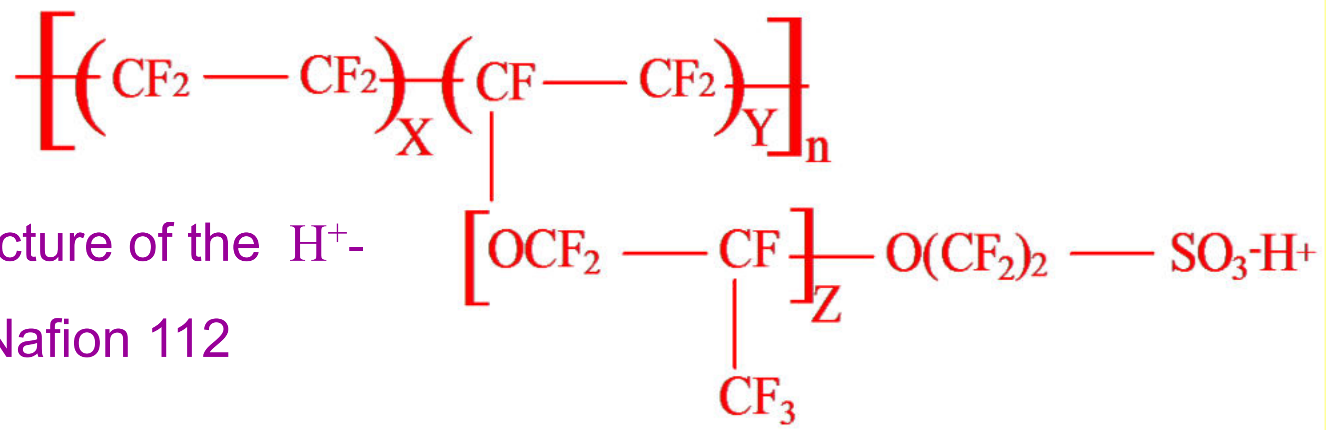
Samples under study

- Nafion 112 with ion exchange capacity (IEC) = 0.91 meq/g and thickness 50 μm which was purchased from DuPont, USA.



Chemical structure of the H^+-form of Nafion 112

- Electric field process to the membranes was done using DC high voltage power supply.
- The electric field strength changed from 0 to 140 KV/m at 90 °C.

Techniques

Many different techniques were used;

- Fourier Transform Infrared (FTIR).
- Water uptake.
- Wide angle x-ray diffraction (WAXD).
- Thermogravimetric analysis (TGA).
- Mechanical properties.
- Proton conductivity.
- Positron annihilation lifetime (PAL).

Outline

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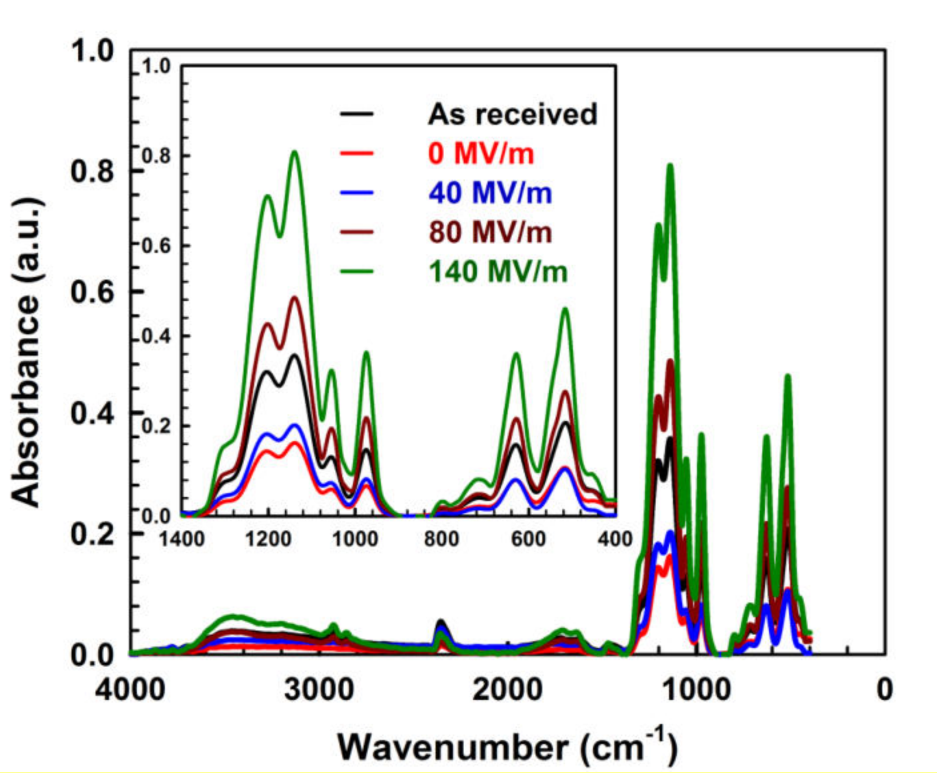
Fourier Transform Infrared (FTIR)

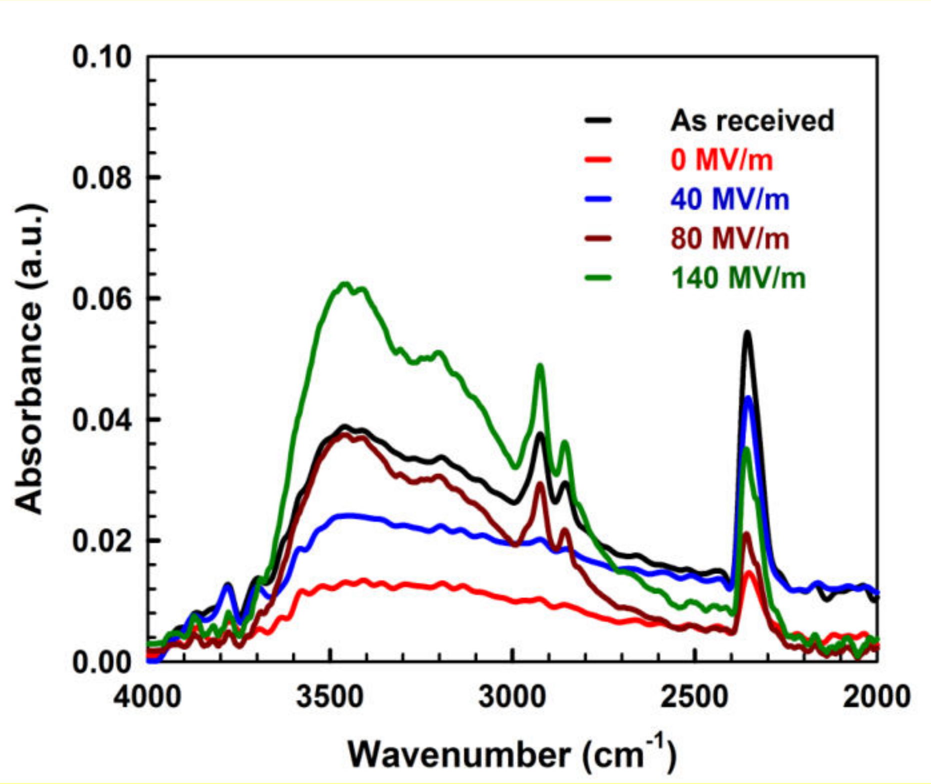
- No significant change in the peak positions.
- The absorbance of the bands showed variations with temperature and electric field effects.
- The absorbance for as received membrane > that for the heated one at 90 °C (0 MV/m).
- The absorbance ↑ with ↑ in the electric field strength at 90 °C.



- The change of the membrane structure can influence the extinction coefficient of different functional groups → the substituent within the absorption remains affected by the interchange between the coefficient.
- However, there is a specific point at which the surface and mass have undergone clear changes during the electric field effect.

Fourier Transform Infrared (FTIR) (Cont.)

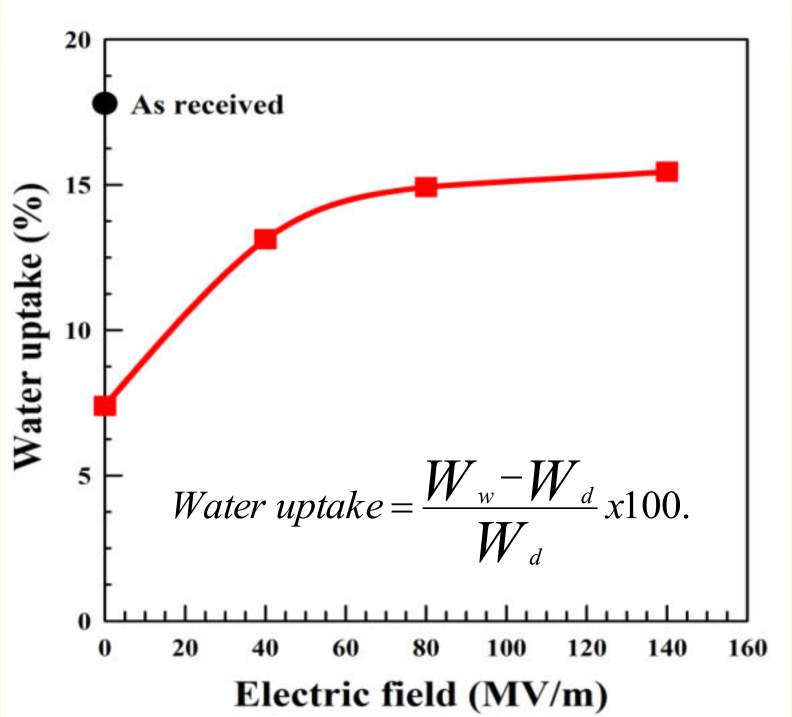
- The absorbances at the range from 2500-3700 cm^{-1} show a decrease in the O-H signal by heating the as received membrane at 90 ^{o}C → loss of water sorption by temperature.
- The water uptake measurement confirms this as a result of the reduction in the size of the free volume measured by PAL.



- The absorbances show an increase in the O-H signal by increasing the electric field's strength on the membrane at 90 ^{o}C → an increase in water sorption by the electric field.
- Also, increasing the water uptake is consistent with the expansion in the free volume size by increasing the electric field strength.

Water uptake

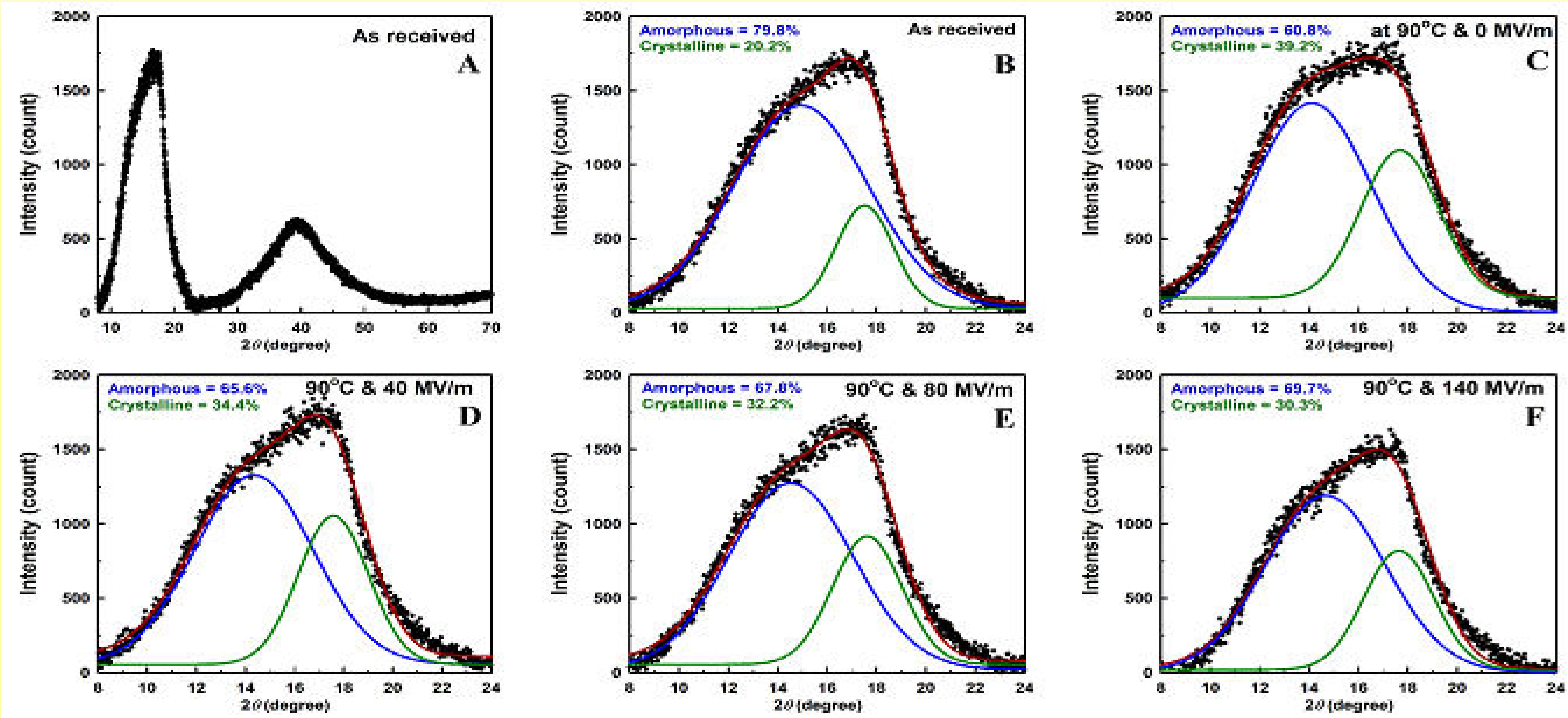
- The water uptake at 90 °C & 0MV/m is < as received membrane → due to an irreversible reorganization of the membrane structure and changes in the size of the ionic clusters, which happen under the heat treatment of the membrane and impacts the properties of water uptake.
- It increases with an increase in the electric field's strength up to 80 MV/m and then leveled off.



$$Water\ uptake = \frac{W_w - W_d}{W_d} x100.$$

- The high strength of the electric field prompts more separations of the functional groups [(-SO_3^-) and (H^+)], and afterward, more water molecules were absorbed until saturated.
- The present data of water uptake are consistent with decreasing the degree of crystallinity with an increase in the electric field strength.

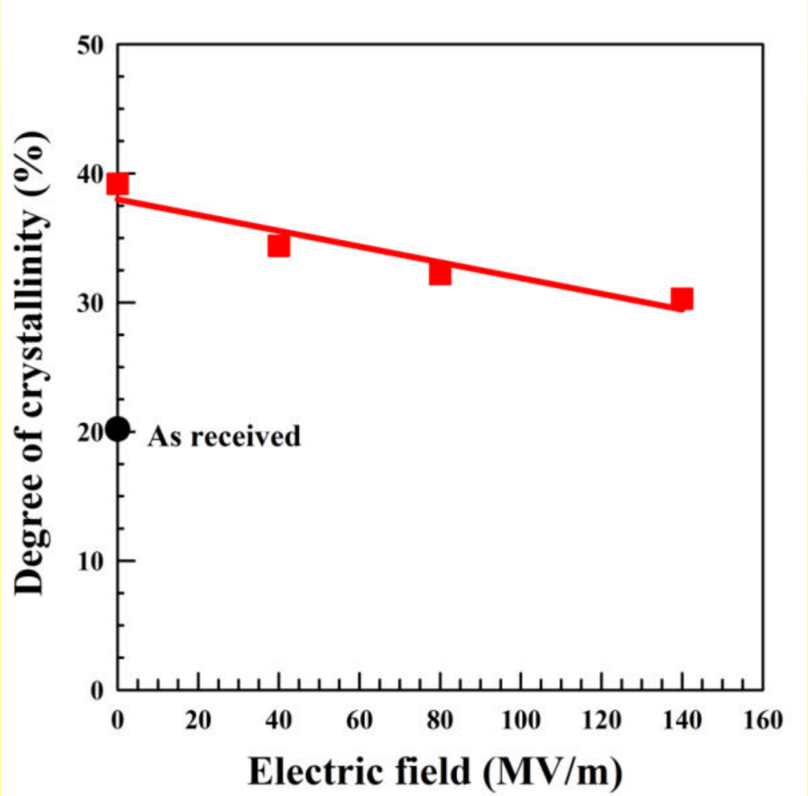
Wide angle x-ray diffraction (WAXD)



- There is an amorphous hump over a range of 2θ = 12-22°, which could be analyzed into two peaks;
  1) at low θ peak is attributed to the amorphous domain.
  2) at high θ peak presents the crystalline domain.

Degree of crystallinity

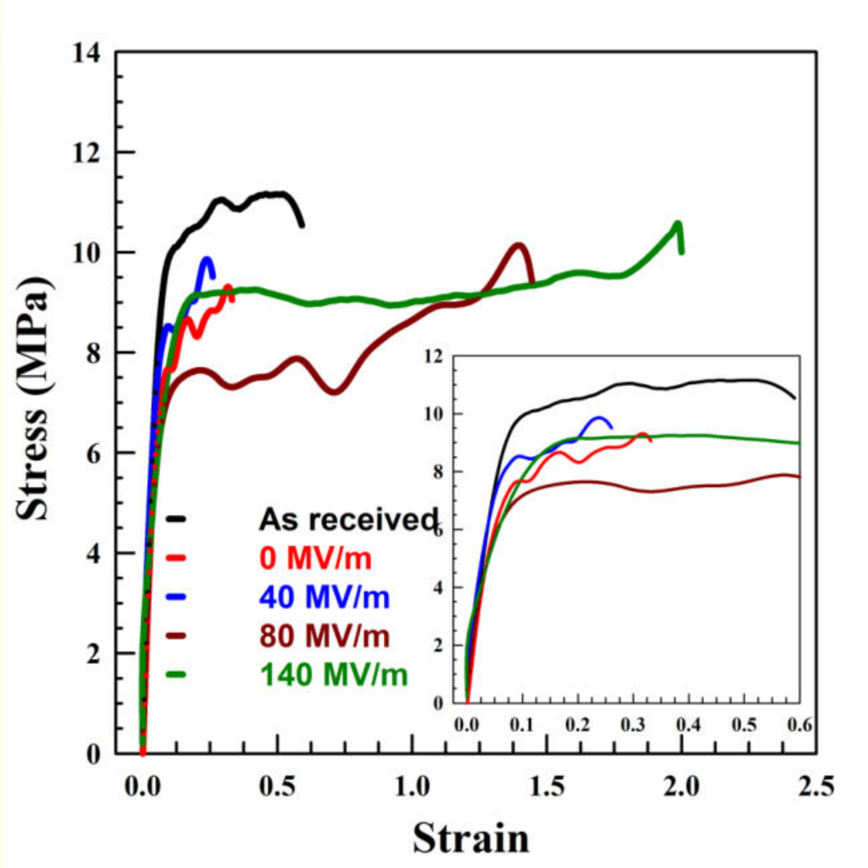
- The degree of crystallinity of the as received sample is < the one heated at 90 ºC & 0 MV/m → the effect of heating the membrane closer to their Tg and the loss of the water molecules.
- The degree of crystallinity ⬇ with ⬆ in the electric field strength at 90 ºC → the electric field destroyed the crystalline structure of Nafion 112 and the amorphous region increases.



- Increasing the electric field strength leads to an increase in the aggregation of the ionic groups and reduces the polymer backbone chain's mobility.
- The data about diminishing the degree of crystallinity are reliable with the FTIR result above and free volume size point of view.

Mechanical properties (stress-strain curve)

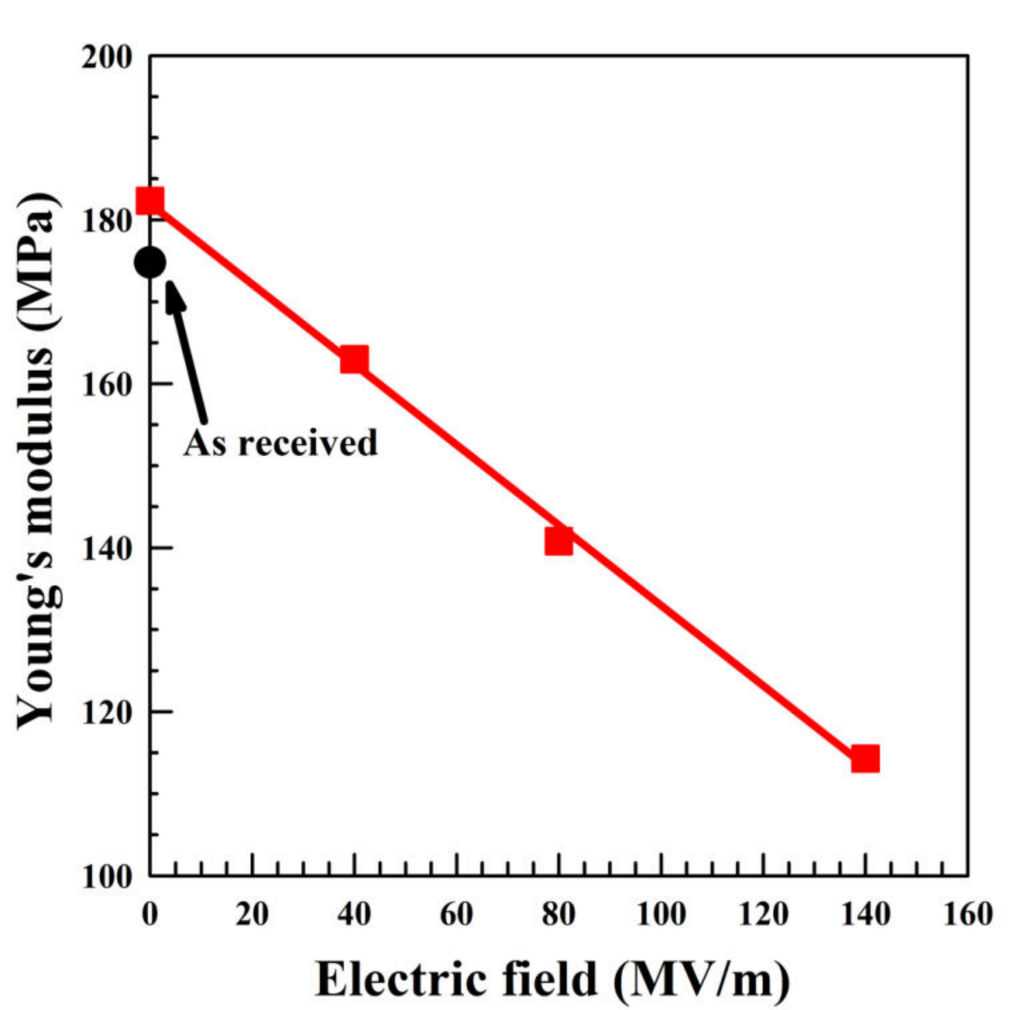
- The strain ⬆ with ⬆ in the electric field strength, while the stress for all membranes beyond the yield point is almost constant.
- So, the membrane with 140 MV/m has the highest strain → indicating that this sample is the most flexible sample compared with the others.
- These results could also be connected to the highest water uptake for the membrane with 140 MV/m at 90 °C as discussed before.



- Increasing water uptake prompts a decrease in the initial slope of the stress-strain curve (minimizing Young's modulus) and improvement of the strain (degree of elongation).

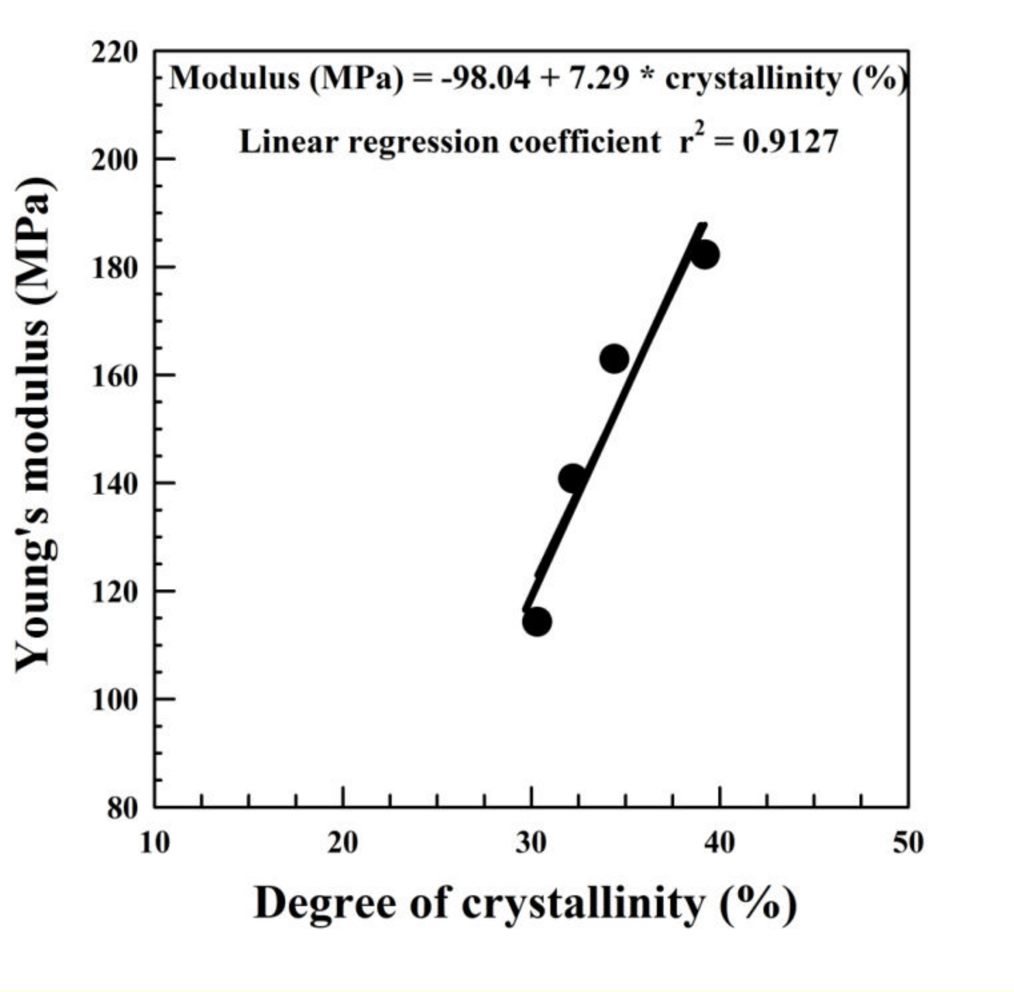
Mechanical properties (Young's modulus)

- Young's modulus ⬇ with ⬆ in the electric field strength → the membrane became more flexible due to the electric field effect.
- Electric field ⬆ the intermolecular forces and ionic interaction.
- The increase in temperature will destroy the Nafion cluster structure and the membrane chain will gain more mobility ⬇ both of Young's modulus and degree of crystallinity.



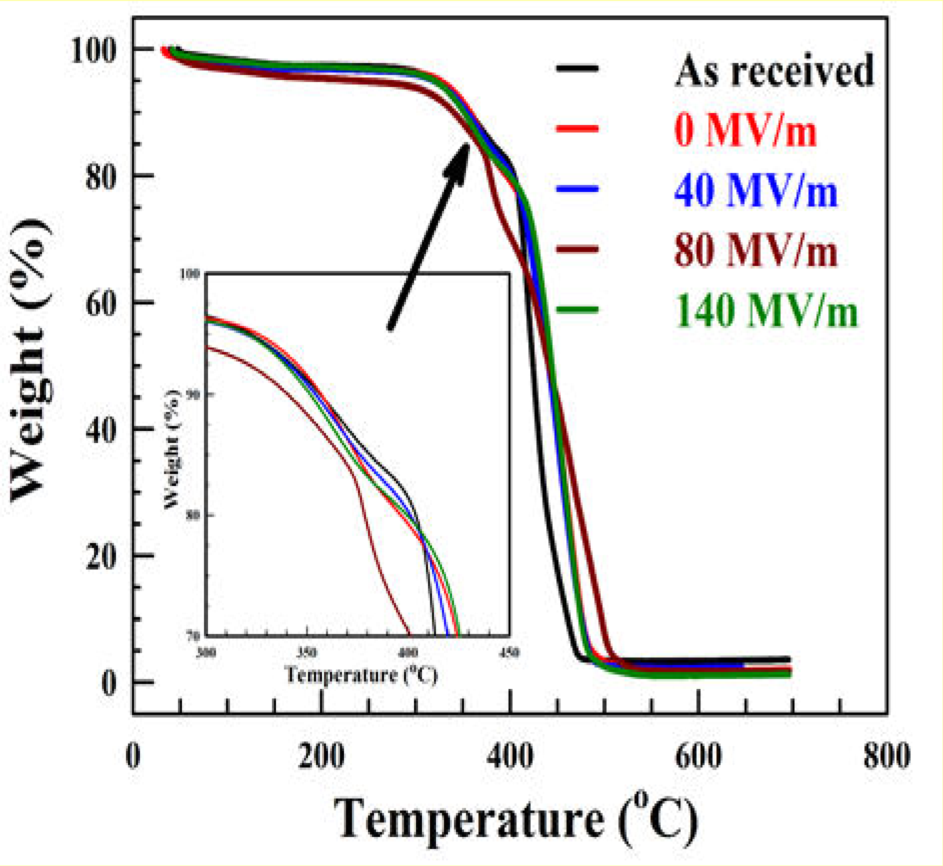
Correlation between the Young's modulus and the degree of crystallinity

- This interpretation is consistent with the present data, where Young's modulus is correlated with the degree of crystallinity.
- The Young's modulus increases linearly with an increase in the degree of crystallinity.



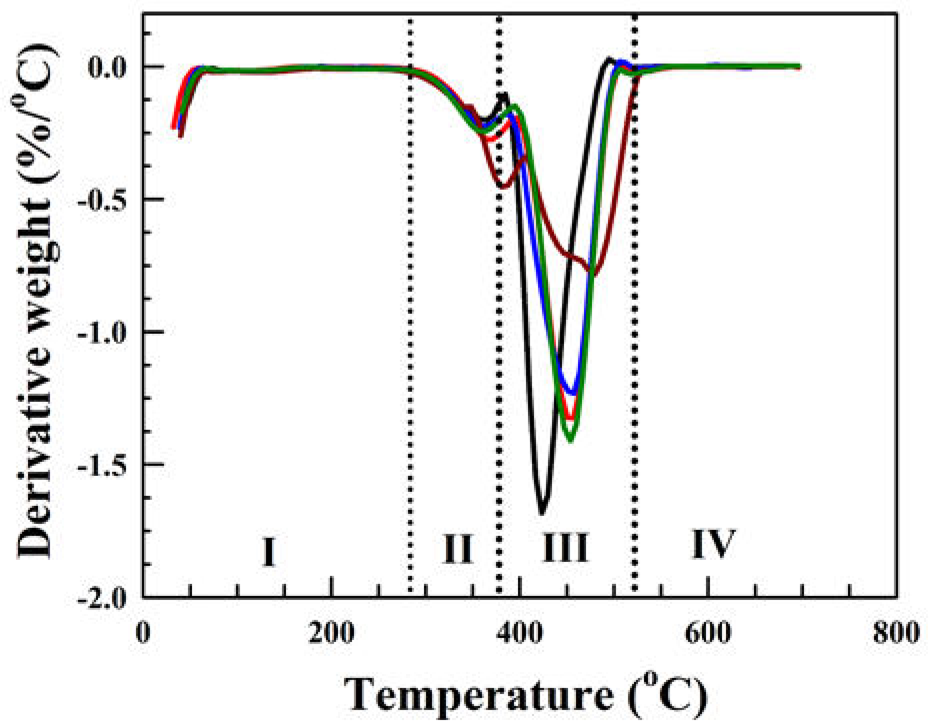
Thermogravimetric analysis (TGA)

- At 0 ~ 280 °C, the weight loss is due to the removal of trapped and free water from the Nafion 112 membranes.
- At 280-380 °C, the changes of the weight are from the desulfonation process.
- At 380-520 °C, the change of the weight is a result of the degradation of the side chain in the membrane.
- At > 520 °C, the membrane backbone is decomposed or degraded.



Derivative Thermogravimetric analysis (TGA)

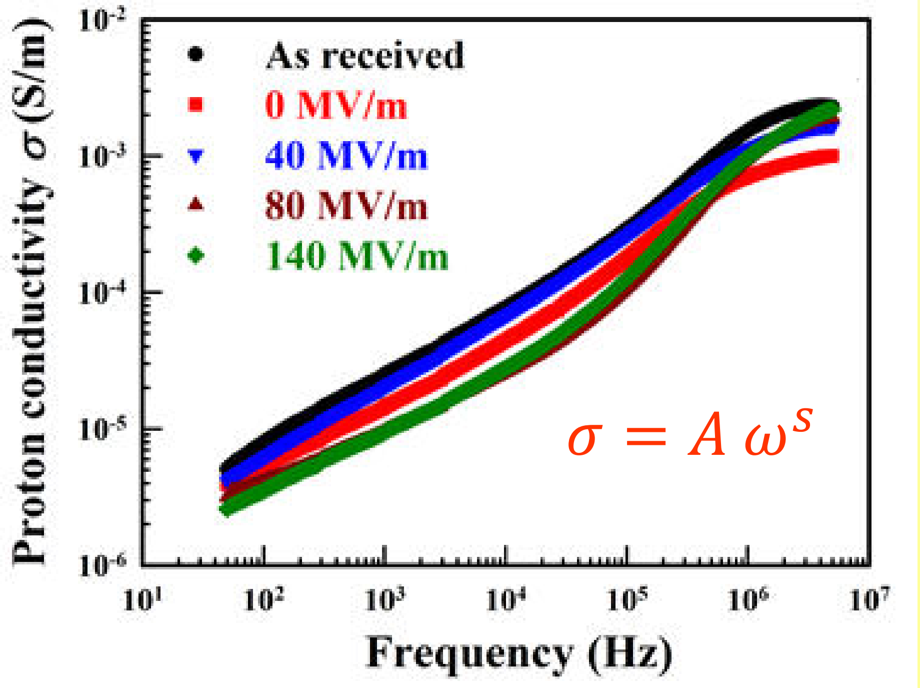
- The decomposition of the membrane mainly occurs in the third region (380-520 ^{o}C).
- The peak temperature for the as received membrane is at 423 ^{o}C, while these peaks are shifted to higher temperature at about 455 ^{o}C for the samples heated at 90 ^{o}C and influenced by the electric field.



- There is no significant difference between the heated at 90 ^{o}C and influenced by the electric field samples → all the samples have the same thermal stability, which is higher than the as received one.

Proton conductivity

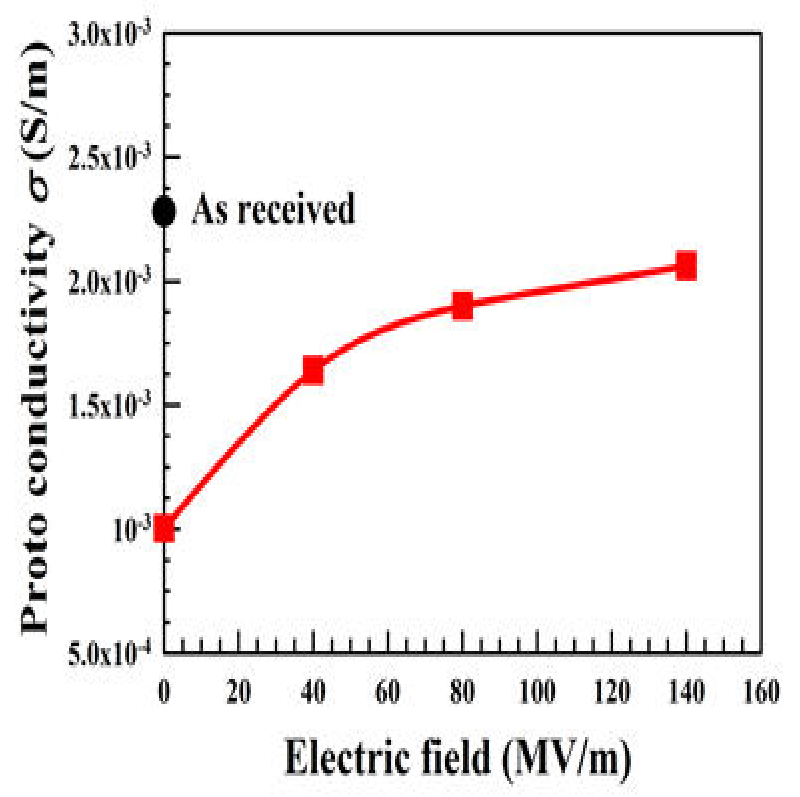
- The behavior between σ and frequency can be divided into two regions;
  1) At low frequency, σ indicates almost no frequency dependence.
  2) at a high frequency, the behavior is stated the diffraction region is the same in imitation of σ .



- The obtained value of index *s* for the as received is 0.56, where they are 0. 53, 0.55, 0.59, and 0.61 for membranes with an electric field strength of 0, 40, 80, and 140 MV/m, respectively.
- These values forecast hopping conduction in the present Nafion 112 membranes.

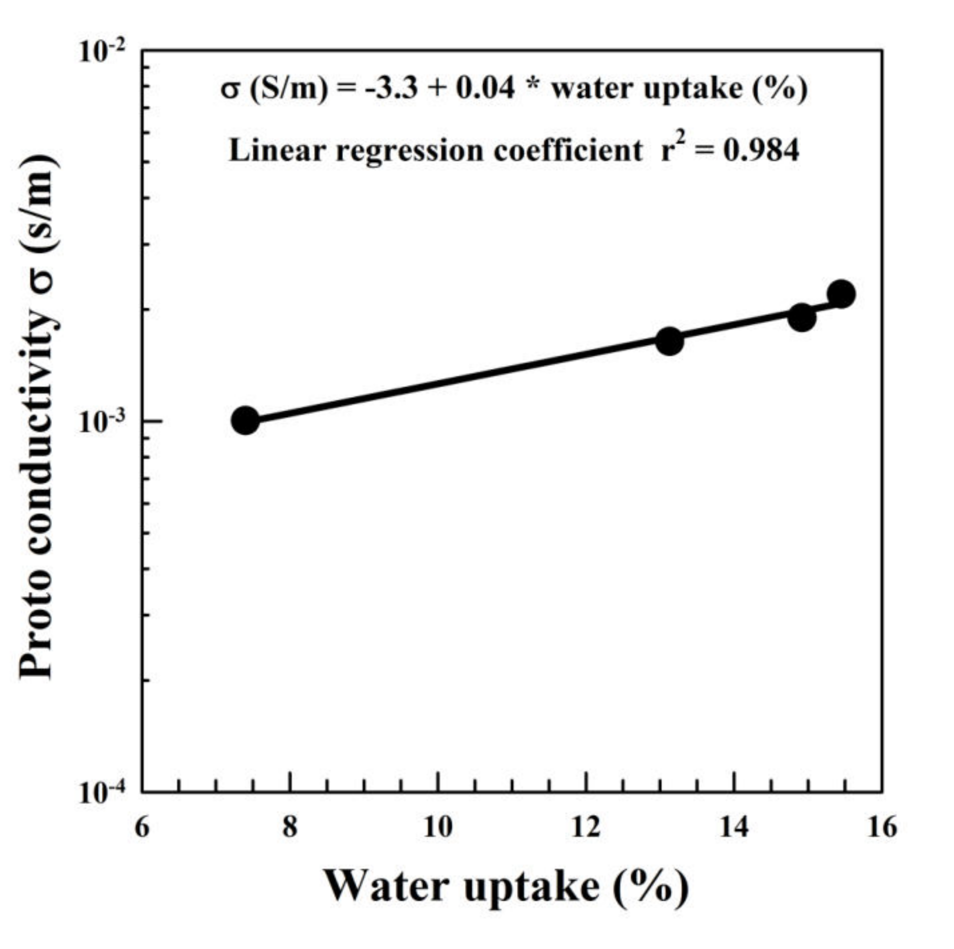
Proton conductivity (Cont.)

- **σ of the as received membrane is higher than that for the membrane heated at 90 ºC & 0MV/m → heating the membrane leads to the removal of the water molecules and then decreases σ.**
- **Increasing the electric field's strength leads to an increase in σ → due to the alignment of the ionic groups or the nonstop contact among conductive ions when aligned via the electric field.**
- **Without the electric field, the particle shape has fewer nonstop channels for proton transport across the membrane.**



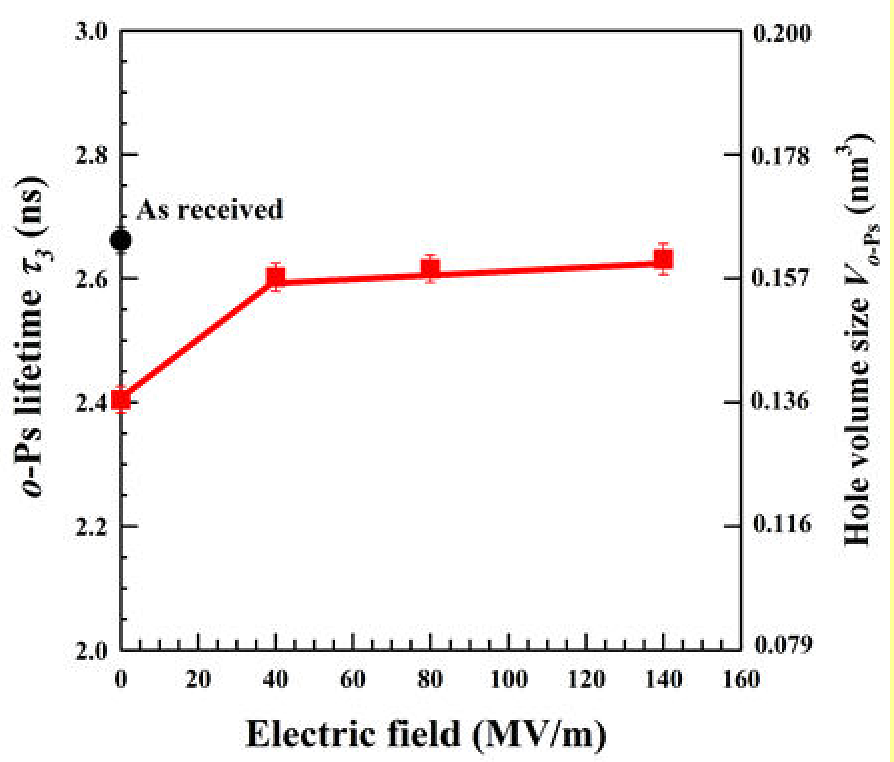
Correlation between proton conductivity and water uptake

- σ increases exponentially with expanding the water uptake of the membrane.
- More water molecules form more channels for the proton to transport through membranes.
- In Nafion membranes, σ depends on many factors such as water uptake, crystallinity, free volume, nanostructure, the balance between the local interactions with charges, nanoscale connectivity, and spatial confinement inside ionic domains.



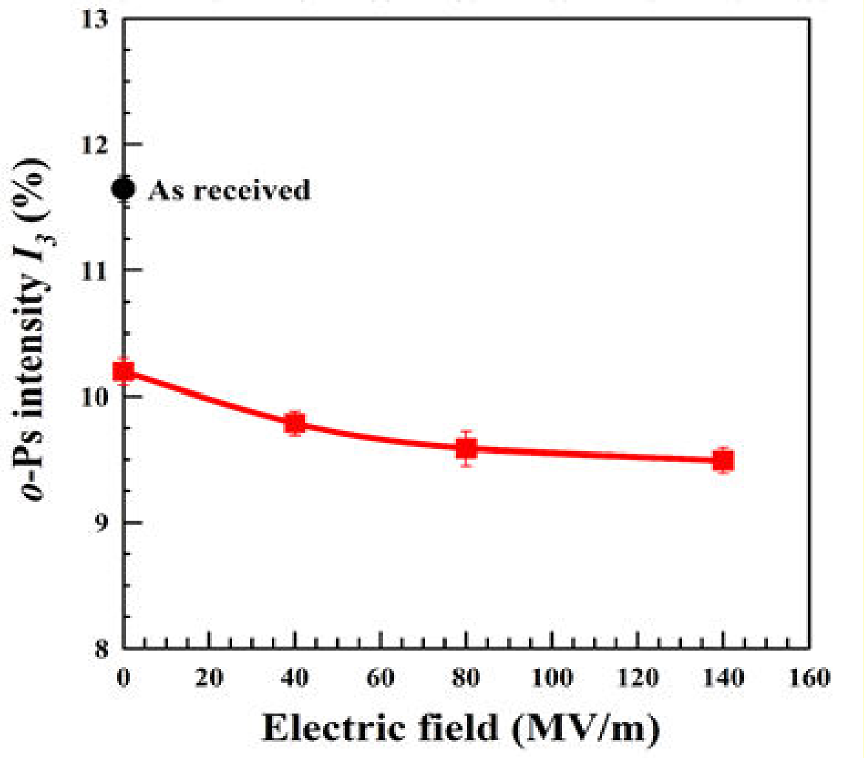
The o-Ps lifetime (hole volume size, $V_{o\text{-}Ps}$)

- $V_{o\text{-}Ps}$, for the heated membrane at 90 °C & 0MV/m is < for the as received membrane → the amorphous part on the membrane ⬆ because heating the membrane leads to the removal of water and ⬆ n the degree of crystallinity.
- With ⬆ electric field strength, $V_{o\text{-}Ps}$, ⬆ → ⬆ the amorphous region as a result of ⬆ the migration of the dipoles due to the electric field.



The o-Ps intensity I_3 (Ps formation)

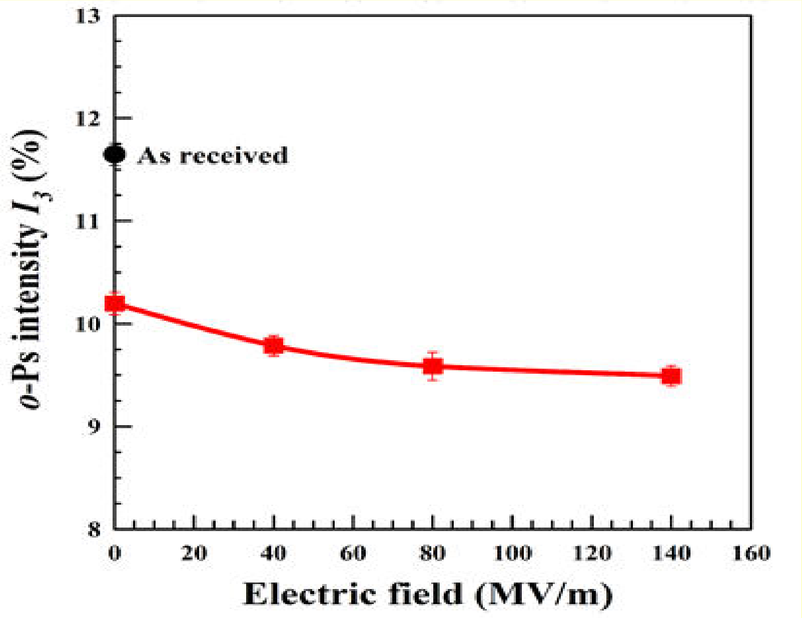
- I_3 decreases with heating the Nafion 112 membrane after heating at 90 °C as a result of increasing the degree of crystallinity.
- With ⬆ electric field strength at 90 °C, I_3 decreases smoothly.
- It is well known that I_3 can be correlated with the crystalline region on the sample, i.e., lower I_3 is as a result of a higher degree of crystallinity.



- Here, this is not the case where I_3 decreases, and the degree of crystallinity decreases too.
- Along these lines, this change in I_3 is not because of the difference in the number of holes or hole volume content on the membrane.

The o-Ps intensity I_3 (Ps formation) (Cont.)

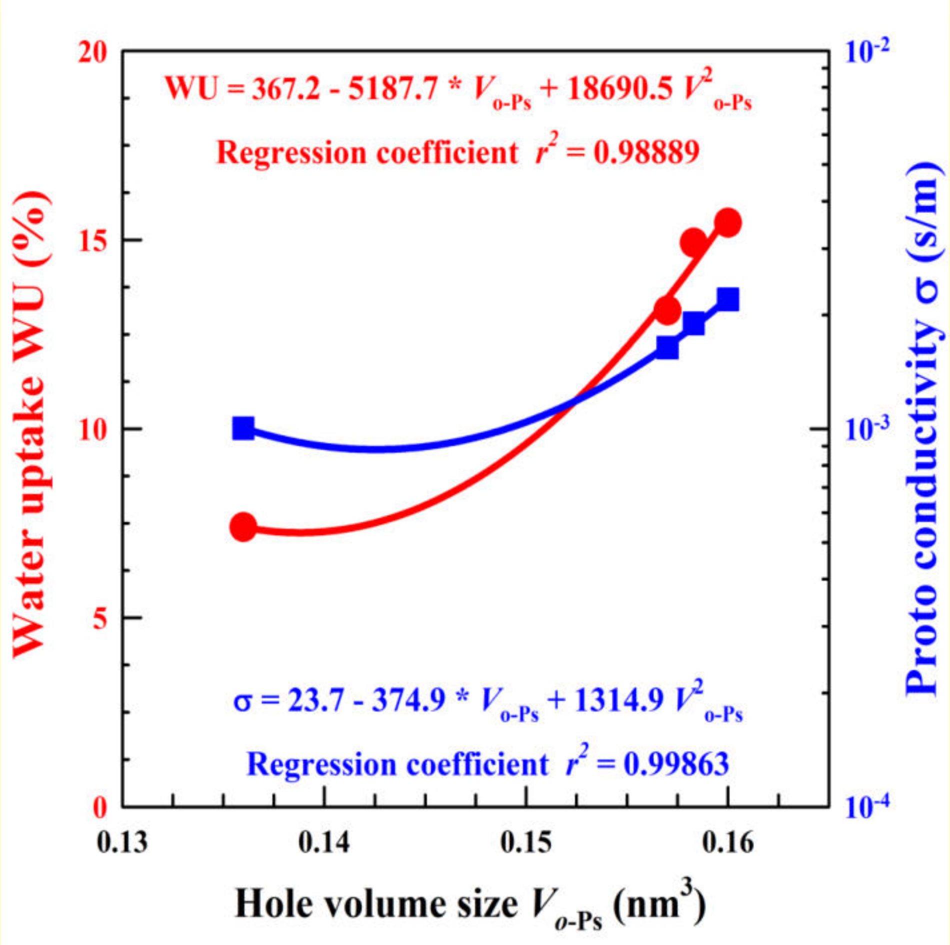
- In addition, because Nafion is a polar polymer, so the result could be interpreted by a spur model (Ps is formed by combination of an electron removed from the substance and a thermalized positron, so, after the positron and electron are completely thermalized, Ps will form.



- Many reactions will compete with the spur reaction for Ps formations, such as escaping of positron and electron from the spur and recombination between ion and electron.
- It is well known that the interaction between the electrons and positrons is not strong because it is a Coulomb reaction. So, using the electric field can easily separate the electron from the positron and decrease the Ps formation, *i.e.*, decrease I_3).

Correlations

- **Increasing the water uptake and proton conductivity at different electric field strengths on Nafion 112 membranes at 90 ºC could be correlated with increasing hole volume size.**
- **This correlation indicated that the water uptake and proton conductivity mechanisms are controlled with the hole volume size.**



Outline

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4. Conclusion

Conclusion

1] The chemical structure of the membranes is not affected by the electric field.

2] The electric field enhances water uptake, proton conductivity, thermal stability, mechanical strength, and hole volume size while it reduces the degree of crystallinity.

3] The present data of both water uptake and proton conductivity are linearly good correlated with the hole volume size $V_{o\text{-}Ps}$ of Nafion 112 membranes, suggesting a considerable role played by free volume.

4] The electric field affected the o-Ps intensity I_3 because of increasing the separation between the electron and positron, thus decreasing Ps formation.

5] So, the electric field at 90 ^oC improved all properties of the Nafion 112 membranes, which consequently improve the performance of the PEMFCs and DMFCs.

THANKS FOR YOUR ATTENTION

Acknowledgment

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