INFULENCES OF HUMIDITY ON PROPERTIES OF NAFION® MEMBRANE

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1 Introduction

Fuel cell is a device that directly converts chemical energy into electrical energy. At each of fuel electrodes has the functionality of oxidative reaction and the oxygen reduction reaction. Fuel cells, the basic structure, are a composition that contains catalytic pole in between the membrane and the electrode. At catalytic pole/membrane composition, the membrane act as a pathway to deliver hydrogen ion from one electrode to another electrode and also as isolation wall to prevent oxygen mixing with the fuel. [1]

Fuel cells classify by type of electrolyte. As PEMFC (Poly Electrolyte Membrane Fuel Cell), PAFC (Phosphoric Acid Fuel Cell), AFC (Alkaline Fuel Cell), MCFC (Molten Carbonate Fuel Cell), SOFC (Solid Oxide Fuel Cell).

Fuel cells normally have the efficiency of 40-70% of the electricity generation. Present mobile power supply research is mainly on the substance of PEMFC as polymer matrix and stationary power generation supply research is based on ceramic membranes using SOFC. Currently the Nafion is used as a bench mark membrane in a fuel cell.

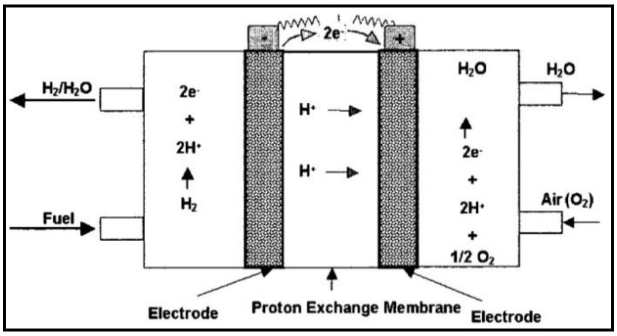

Fig. 1. The Fuel cell concept[1]

Nafion ionomers were developed by the Dupont Company. It is generated by copolymerization of a perfluorinated vinyl ether comonomer with TFE (tetrafluoroethylene). [2] The performance of Nafion membrane is depended on the ratio of TFE and surfonly comonomer. Sulfornic acid group at the end of side chains congregates then they have high proton conductivity around 0.1 S/cm at room temperature.Most of the polymer membranes of PEMFC have ion channel like Nafion membrane. Controlling the size and the stabilization of ion channel is the way to optimize the moisture absorption by capillary force. And also the way to optimize the penetration of MeOH by water channel.

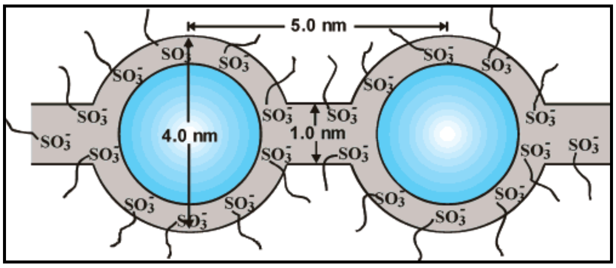

Fig. 2. Cluster-network model for the morphology of hydrated Nafion.[2]

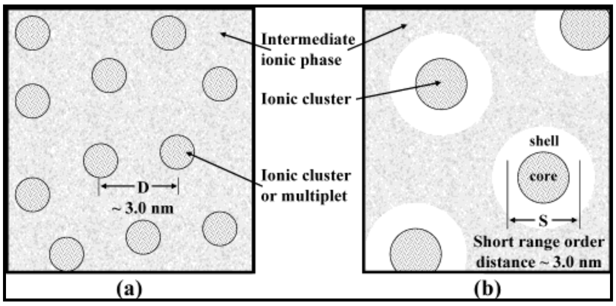

Fig. 3. Two morphological models used to describe the origin of the ionic SAXS maximum observed for Nafion: (a) the modified hard-sphere model depicting interparticle scattering and (b) the depleted-zone core-shell model depicting intraparticle scattering.[2]

Anode : $CH_3OH(l) + H_2O(l) \xrightarrow{Pt/Ru} CO_2(g) + 6H^+ + 6e^-$

Cathode : $3/2\,O_2(g) + 6e^- \xrightarrow{Pt} 3\,H_2O(l)$

Overall: $CH_3OH(l) + 3/2\,O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

Fig. 4. Half reaction and overall reaction

DuPont™ Nafion® PFSA NRE-212 membranes are non-reinforced dispersion-cast films based in Nafion® PFSA polymer, a perluorsulfonic and/TFE copolymer in the acid form. Nafion® PFSA membranes are widely used for PEMFCs and water electrolyzers. The membrane performs as separator and solid electrolyte in a variety of electrochemical cells that require the membrane to selectively transport cations across the cell junction. The polymer is chemically restant and durable.

The membrane is positioned between a backing film and a coversheet. This composite wound on a 6 inch ID plastic core, with the backing film facing out, as shown in Fig. 5.

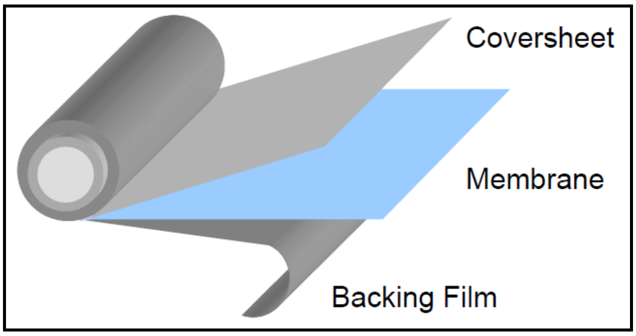

Fig. 5. Roll unwind orientation

The backing film facilitates transporting the membrane in to automated MEA fabrication processes, while the coversheet protects the membrane from exposure to the environment during intermediate handling and processing. In addition, the coversheet (in combination with the backing film) eliminates rapid changes in the membrane’s moisture content, and stabilizes the dimensions of the membrane as it is removed from the roll.[3]

Nafion membrane shows superior physical and chemical properties due to its TFE backbone. Therefore Nafion membrane is frequently used as the membrane of PEMFCs. However proton conductivity of Nafion membrane is easily affected by temperature and humidity and is drastically decreased in high temperature (>80℃) and/or low humidity state, because of ion channel is sensitive for temperature and the percentage of water content.

Previously the decrease of proton conductivity, ion exchange capacity (IEC), water uptake, and thermal stability changes of Nafion membrane had been researched. The primary object of this investigation was to research the changes of Nafion membrane with humidity relationship, also the connection between ion exchange capacity (IEC) and water uptake.

A. Thickness and Basis Weight Properties[1]

Membrane Type	Typical Thickness (micrometer)	Basis Weight (g/m^2)
NRE-211	25.4	50
NRE-212	50.8	100

B. Physical Properties

	Typical Values				
	NRE-211		NRE-212		
Property[2]	MD	TD	MD	TD	Test Method
Physical Properties					
- measured at 50% RH, 23 °C					
Tensile Strength, max., MPa	23	28	32	32	ASTM D 882
Non-Std Modulus, MPa	288	281	266	251	ASTM D 882
Elongation to Break, %	252	311	343	352	ASTM D 882

C. Other Properties

Property	NRE-211	NRE-212	Test Method
Specific Gravity[1]	1.97	1.97	DuPont
Available Acid Capacity[3] meq/g	0.92 min.	0.92 min.	DuPont NAE305
Total Acid Capacity[4] meq/g	0.95 min.	0.95 min.	DuPont NAE305
Hydrogen Crossover[5], ($ml/min \cdot cm^2$)	< 0.020	< 0.010	DuPont

D. Hydrolytic Properties

Property	Typical Value	Test Method
Hydrolytic Properties		
Water content, % water[6]	5.0 ± 3.0%	ASTM D 570
Water uptake, % water[7]	50.0 ± 5.0%	ASTM D 570
Linear expansion, % increase[8]		
from 50% RH, 23 °C to water soaked, 23 °C	10	ASTM D 756
from 50% RH, 23 °C to water soaked, 100 °C	15	ASTM D 756

[1]Measurements taken with membrane conditioned to 23℃, 50% RH

[2]Where specified, MD - machine direction, TD - transverse direction. Condition state of membrane given

[3]A base titration procedure measures the equivalents of sulfonic acid in the polymer, and used the measurements to calculate the available acid capacity of the membrane (acid form).

[4] A base titration procedure measures the equivalents of sulfonic acid in the polymer, and used the measurements to calculate the total acid capacity or the equivalent weight of membrane (acid form)

[5] Hydrogen crossover measured at 22℃, 100% RH and 50-psi delta pressure. This is not a routine test.

[6] Water content of membrane conditioned to 23℃ and 50% RH (dry weight basis).

[7] Water uptake from dry membrane to conditioned in water at 100℃ for 1 hour (dry weight basis).

[8] Average of MD and TD, MD expansion is similar to TD expansion for NR membranes.

Table 1. Properties of DuPont™ Nafion® PFSA membrane [3]

2 Experimentation

2.1 Materials

The Nafion-212 membrane (50.8 ㎛ thick, EW value 1100) purchase from the Dupont company. Nafion-212 membrane is treated with Sulfuric acid (Daejung 95%).

Sodium chloride (Samchun Pure Chemical Co., Ltd, 99%) and sodium hydroxide (Samchun Pure

Chemical Co., Ltd, 98%) which was used to test IEC of Nafion membrane needed no purification to use Sulfuric acid is constant, 95% sulfuric acid dilution in deionize water as used.

2.3 Acid treatment

Nafion membrane is immerged in boiling 0.5M H2SO4 aqueous solution during 2hr.
After then wash by deionize water. And Nafion 212 membrane immerged in boiling deionize water during 2hr.
Store the Nafion 212 membrane in deionize water.

2.4 Proton Conductivity

Conductivity assembling tool, SH-241 Bench-Top Temperature and Humidity chamber (Espec) in measured.
Impedance value measure 5Hz to 10MHz by 4192A LF Impedance Analyzer (Yokogawa, Hewlett Packard).
Impedance measurement is 90℃ in humidity 80% and 50% of the measured

$$\sigma = \frac{L}{RS} \quad (1)$$

σ is proton conductivity (S/cm). R is measured impedance value. S is cross section area of cation exchange membrane (cm2). L is distance between each electrode.
During 48hr, acid treated Nafion 212 membrane's proton conductivity at each humidity were measured.

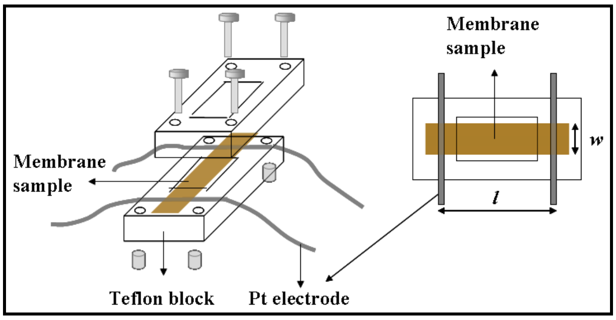

Fig. 6. Schematic illustration of conductivity assembling tool

2.5 Ion Exchange Capacity.

IEC measured by end point titration.
Acid treated Nafion 212 membrane keep in the SH-241 Bench- top Temperature and Humidity chamber (Espec). After 48hr, steep Nafion 212 membrane in 2M NaCl aqueous solution during 24hr.
And end point titration use 0.024M NaOH aqueous solution.

$$IEC = \frac{0.025 \times V_{NaOH}}{W_{dry}} \quad (2)$$

V_{NaOH} is the volume of consumed0.024M NaOH aqueous solution. And W_{dry} is the weight of dry sample weight.

2.6 Water uptake

Water uptake of Nafion membrane is measured by the following method.
At first Nafion membrane is immerged into the deionize water during 3days. After then wipe the Nafion membrane's surface and immediately measure its weight.
And the Nafion membrane dry in vacuum oven at 80℃ until the weight stabilizes.

$$Water\ uptake = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (3)$$

Wwet is the weight of saturated Nafion membrane. And Wdry is the weight of dry Nafion membrane.

3. Result

3.1 Conductivity

At 98% humidity, the Nafion 212 membrane's proton conductivity shows 1.42 × 10-1 S/cm. Also at 80% 50% humidity, each proton conductivity are 3.58 × 10-2 S/cm and 2.74 × 10-2 S/cm. As lower humidity, proton conductivity of Nafion 212 membrane is low in the balance.

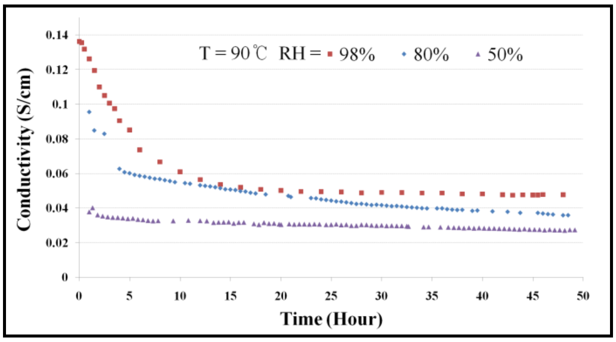

Fig. 7. Time dependent proton conductivity.

5 Conclusion

Proton conductivity of Nafion membrane decreased as humidity decreased. After aging at elevated temperature, the proton conductivity of Nafion membranes decreased due to chemical structure change into sulfonic anhydrides formation. Sulfonic acid anhydride formation was reversible.

6 References

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[2] Kenneth A. Mauritz, Robert B. Moore. "State of Understanding of Nafion". *Chemical Reviews*, Vol. 104, No. 10, pp 4535-4585, 2004

[3] Product information DuPont™ Nafion® PFSA Membranes.