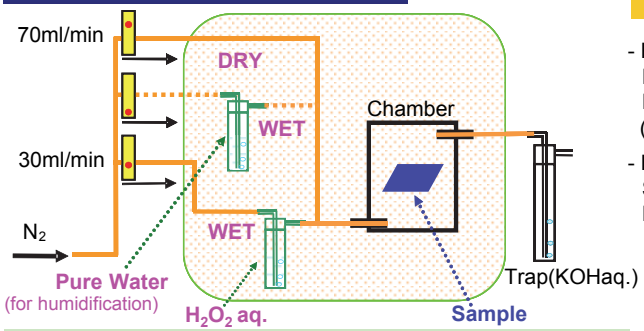
Degradation analysis in perfluorinated and hydrocarbon polymer electrolyte membranes

H_2O_2 exposure tests* simulating the membrane degradation caused by H_2O_2 generated on the electrodes in polymer electrolyte fuel cells were conducted on perfluorinated and hydrocarbon electrolyte membranes to study the difference between the degradation behaviors of the two types of membranes.

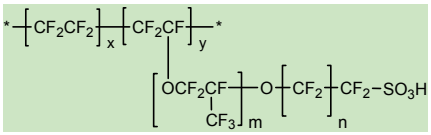
1. H_2O_2 exposure test method and tested electrolyte membranes

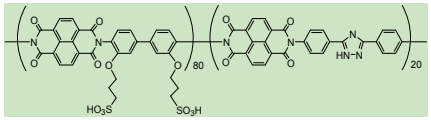


System specifications
Temperature: Room temperature - 100 °C, Humidity: 20 - 90%RH, Sample size: 7 cm x 7 cm

Polymer electrolyte membranes

- Perfluorinated membranes
  Nafion® 112 (thickness: 50 μm)
  Nafion® 1035 (thickness: 90 μm)
  (Sulfon content: 112<1035)
- Hydrocarbon electrolyte membranes
  SPI-8 (80)** (Thickness: 50 μm)
  Polyimide electrolyte membrane





* Honmura, et al., *Polymer Preprints Japan*, 54 (2), 2005

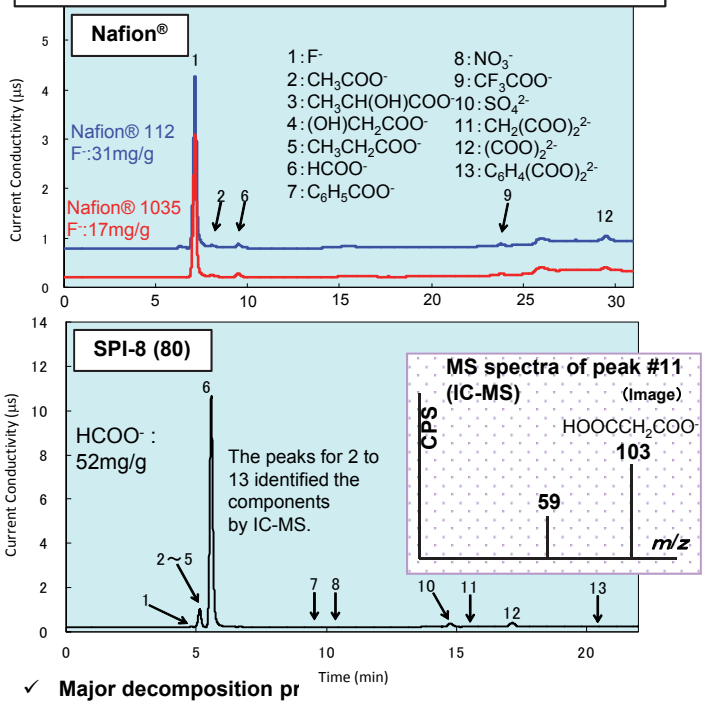
** Saito, et al., *Macromolecules*, 2008

Exposure test conditions

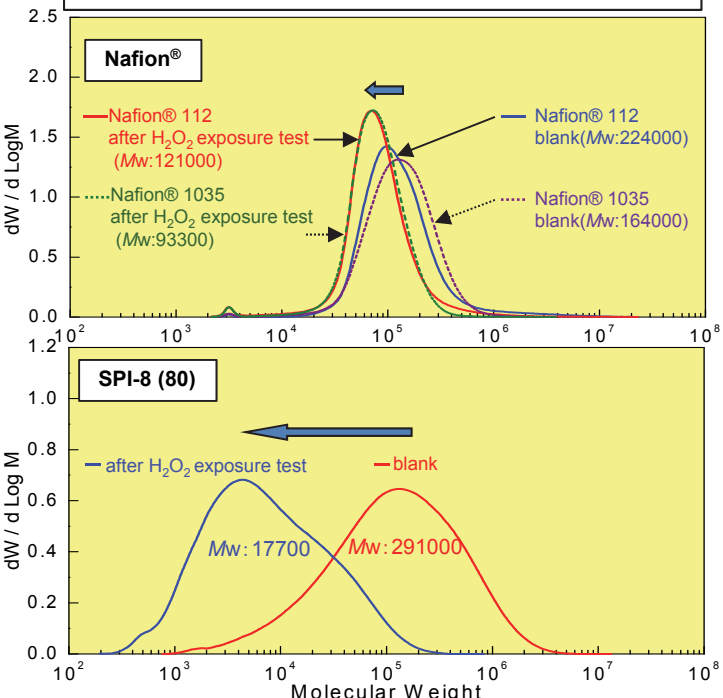
Chamber temperature: 90 °C, relative humidity 30%RH, test time 100 hr
- Perfluorinated electrolyte membrane: H_2O_2 solution concentration 30%
- Hydrocarbon electrolyte membrane: H_2O_2 solution concentration 3%

2. Analysis results for the decomposition products and electrolyte membranes obtained in the H_2O_2 exposure test

Ion chromatograph (IC-MS) for the decomposition products (collected fluid)



Changes in the membrane molecular weight (GPC)



- ✓ **Major decomposition pr**
  Nafion® : Fluoride ion , SPI-8(80): Formic acid.
- ✓ **The amount of F^- produced per unit weight was larger with Nafion® 112.**

- ✓ **The weight average molecular weight (M_w) of Nafion® was decreased to about 1/2 in Nafion, that of SPI-8 (80) was decreased to 1/10 after H_2O_2 exposure test, respectively.**
- ✓ **There was no significant difference between the molecular weight reduction rates in Nafion® 112 and Nafion® 1035.**

- Perfluorinated electrolyte membranes have relatively high resistance to H_2O_2. Although production of H_2O_2 on hydrocarbon electrolyte membranes with low gas permeability is presumed to be low in an actual cell, the presence of H_2O_2 will readily degrade the membranes easily.
- Production of fluoride ion/formic acid, and reduction in the membrane molecular weight are also observed in the degradation analysis using an actual cell, and the present study is considered to be an effective accelerated degradation test.

Part of the present study was commissioned by the New Energy and Industrial Technology Development Organization (NEDO).