Humidity Dependent Structure of Surface Water on Perfluorosulfonated Ionomer Thin Film Studied by Sum Frequency Generation Spectroscopy

Hidenori Noguchi, Kento Taneda, Hiroshi Minowa, Hideo Naohara, and Kohei Uosaki

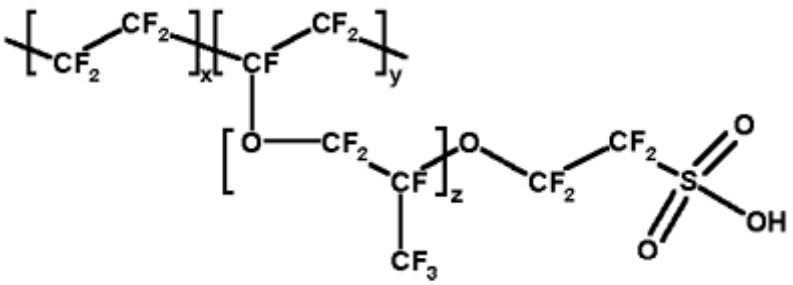
J. Phys. Chem. C, 2010, 114 (9), pp 3958

Introduction

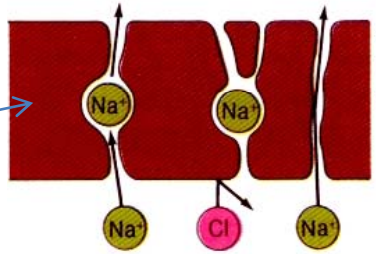
Nafion is Polyperfluorosulfonic acid (PFSA) membrane

proton-exchange membrane

make good use of fuel cell



Structural formula of Nafion



PFSA membrane

Motivation

proton conductivity of the membrane

is depend on temperature and the water content within the membrane

The hydration behavior of a Nafion membrane is importance

Electrochemical reactions take place at gas/Nafion/electrode interfaces

Here, the SFG measurement was used to

understanding the structure of water at Nafion thin film interface

under various relative humidity.

Nafion film preparation

Nafion Solution

substrate cleaning : piranha solution (30 minutes)

substrate rinse : Milli-Q water

Spin coating on quartz prism substrate (2000 rpm)

Drying : vacuum desiccator (room temperature/ overnight)

Nafion thin film (thickness = 500 nm)

The experimental arrangement for SFG measurements

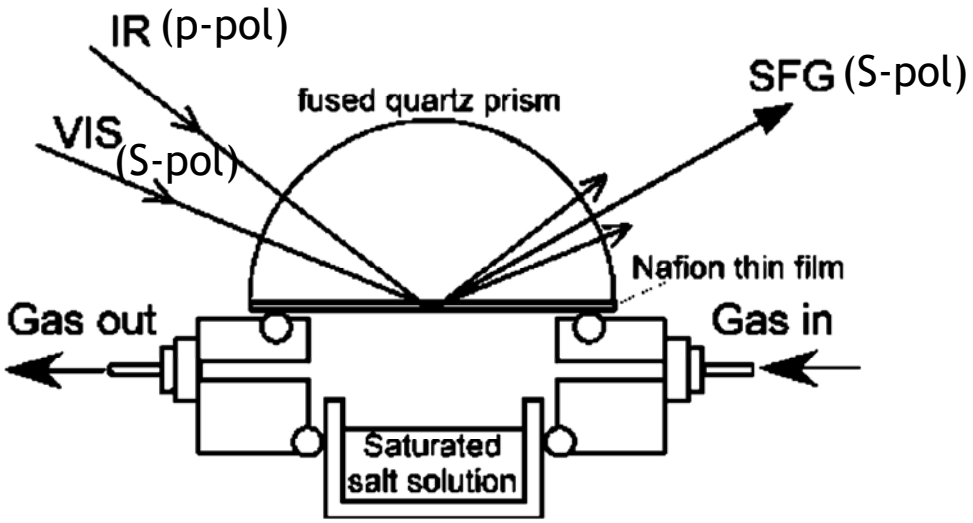


TABLE 1: Saturated Salt Solutions Used in the Present Experiment and the Actual RH Measured by the Present Hygrometer

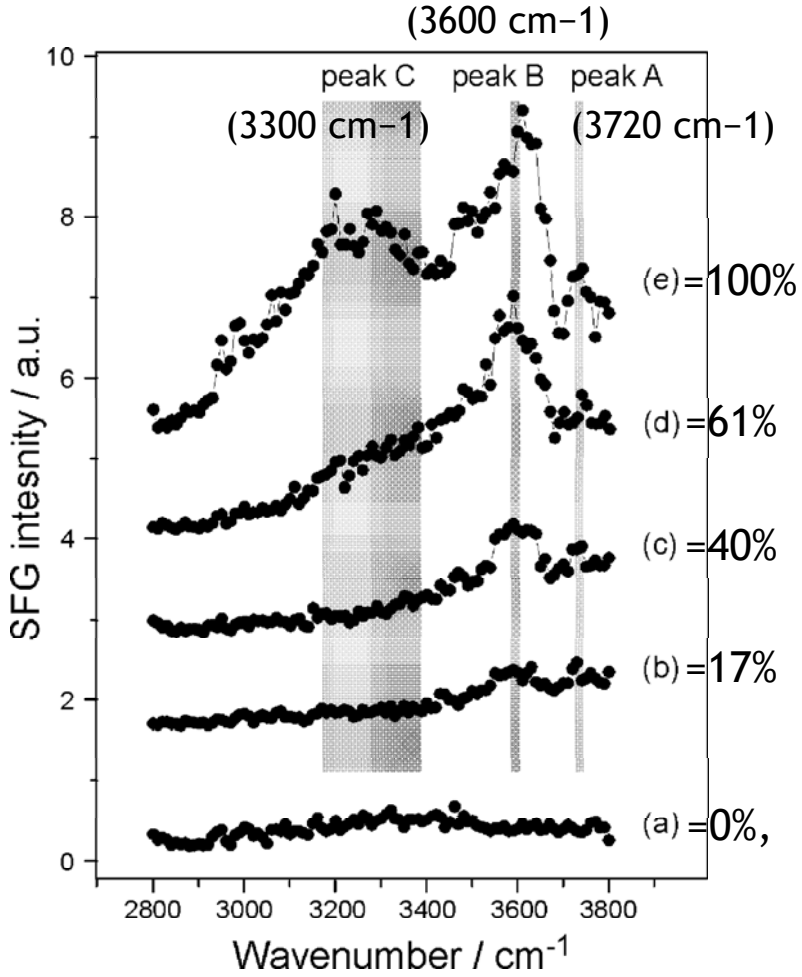
hygrostat at 22 °C	RH (%)
dry Ar gas	0
LiCl	17
$MgCl_2$	40
NaBr	61
H_2O	100

The Nafion thin film was in contact with the Ar gas flow or nonflowing water vapor with various Relative humidity (RH)

RH values was obtained by positioning a saturated salt solution

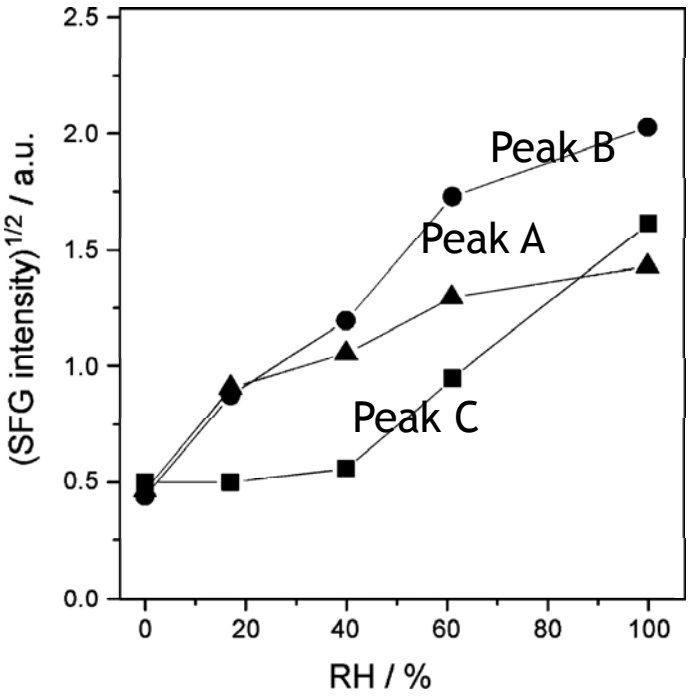
Results & Discussion

1.Humidity-Dependent SFG Spectra



SFG spectra at the Nafion thin film/water vapor interface under various RH conditions

SFG peak intensity summarize



Square root of SFG peak intensities observed as a function of RH.

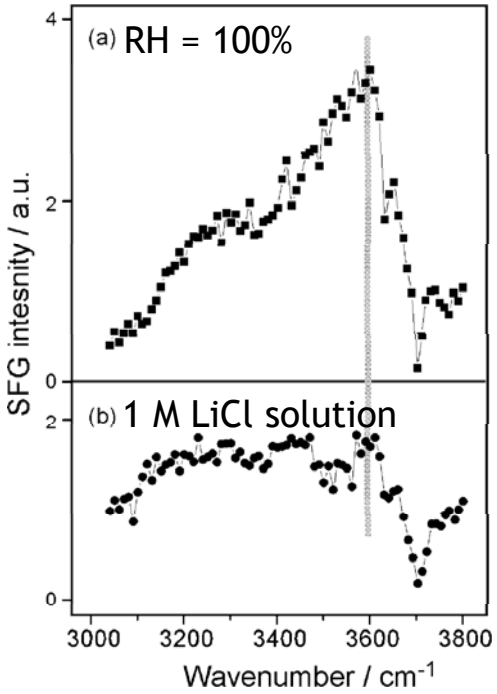
2. Peak Assignment

- peak A (3720 cm-1):

  come from water molecules expose to the vapor phase at the Nafion surface

- peak B (3600 cm-1):

  due to water molecules are hydrogen bond with sulfonate groups within the proton channel



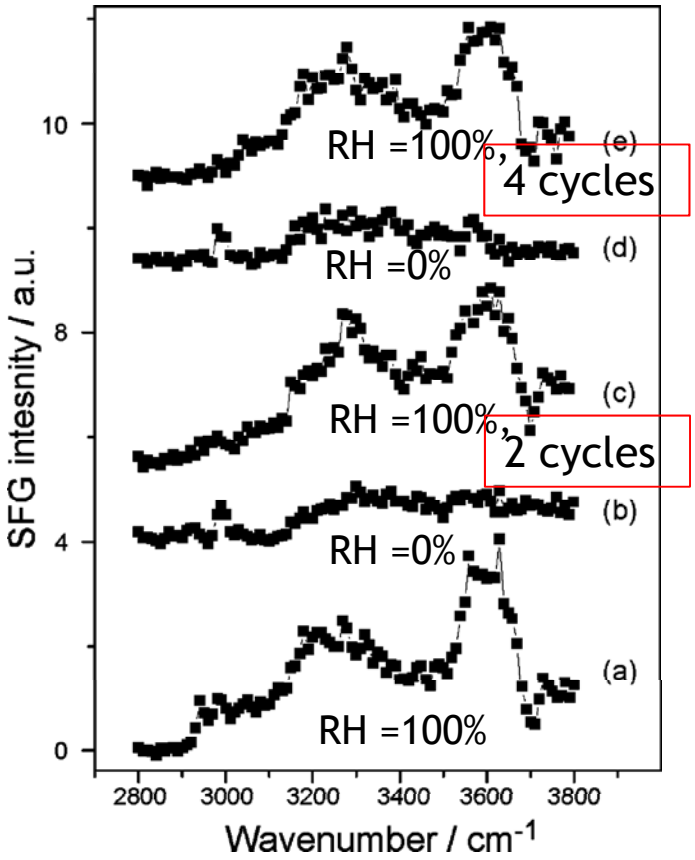
water molecules interact with sulfonate groups of the Nafion surface

SFG spectra of the Nafion thin film/water vapor (RH = 100%) interface (a) before and (b) after Nafion was immersed in 1 M LiCl solution for 1 h

- peak C : Ice-like water peak

  Because water molecules adsorb on fluorocarbon sites of the Nafion surface

3. Effect of Dry/Wet Cycles on the Spectra



The SFG spectra is reversible

The surface properties of the Nafion did not change

SFG spectra after RH change: (a) 100%, (b) 0% after spectrum a, (c) 100% after 2 cycles of RH change between 100% and 0%, (d) 0% after spectrum c, and (e) 100% after 4 cycles of RH change between 100% and 0%

4. Comparison between the RH-Dependent Structures of Water Molecules at the Surface and Inside of Nafion.

4.1 The behaviors of water Molecules at the Surface (SFG Spectra)

-In low RH condition : the intensity of peak C is very low

Why so ?

water molecules adsorb at sulfonate sites on the Nafion surface

-As RH was increased to ca. 40% : the intensities of peak C did not change

Why so ?

water molecules of increase adsorb at the sulfonate site

-In higher RH condition : the intensity of peak C increase rapidly

Why so ?

water molecules adsorb at fluorocarbon sites on the Nafion surface

4.2 The behaviors of water Molecules Inside of Nafion (FTIR Spectra)

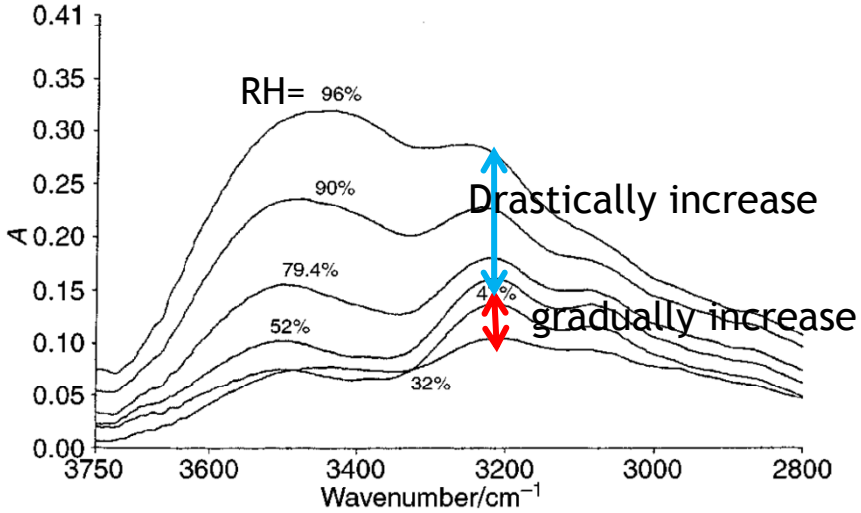


Fig. 15 IR spectra of water OH stretching in Nafion at different humidities.

FTIR measurements showed two main broad peaks centered around 3500 and 3250 cm-1 in the OH stretching region under various RH conditions

Phys. Chem. Chem. Phys., 1999, 1, 4619

-In low RH region : The 3250 cm-1 peak gradually increase

The water uptake slowly increase with the increase of RH

Why so ?

The amount of water molecules increases within the channel inside

-In high RH region : peak intensities drastically increase

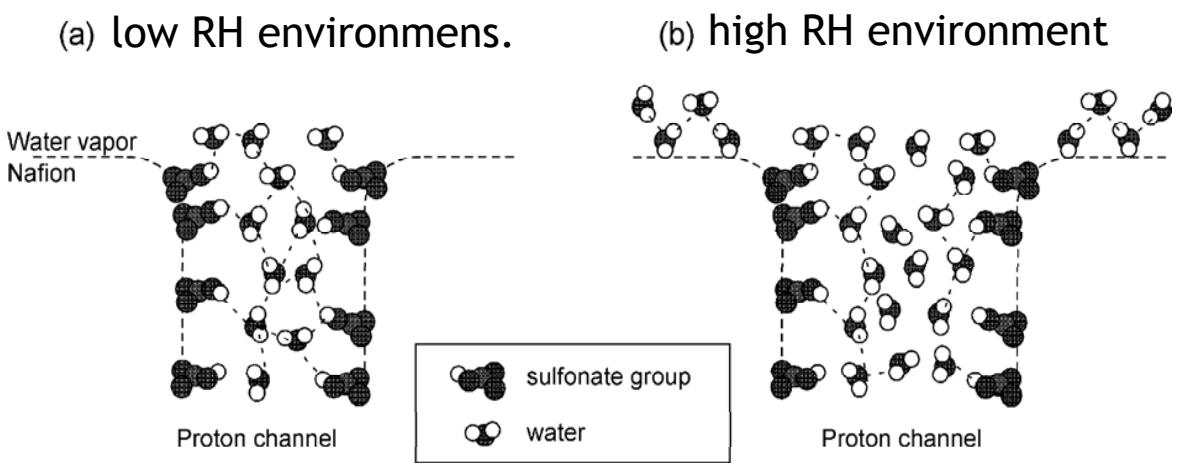
The high wavenumber OH peak position red-shifted (3500 → 3400 cm^{-1})

Why so ?

More loosely bound water form inside Nafion

Schematic model

A model of the Nafion/water vapor interface



- At low RH environment, water molecules are present
  interacting strongly with the sulfonate site
  & forming water clusters in the channel

- At high RH environment (more than 70%), water molecules are present
  bulk water inside the Nafion membrane
  & an adsorption at the very fluorocarbon site

Conclusion

- 3720 cm^{-1} peak is to the “dangling OH” or “free OH” of water molecules

- 3600 cm^{-1} peak was assigned to be due to water molecules interacting with sulfonate groups of the Nafion surface

- In high RH environment (RH > 60%),
water adsorbed on fluorocarbon sites of Nafion