

Introduction of Solid-state NMR

Solid-state NMR is useful to ...

- 1) Determine chemical structures for insoluble materials or samples which want avoiding to dissolve in a solvent.
- 2) Evaluate molecular mobility in the solid state.
- 3) Obtain the detail chemical information for observed element selectively.

Measurable elements

^{13}C , ^{29}Si , ^{19}F , ^7Li are nuclei measured frequently, and detailed structural analysis is possible from our abundant databases. From ^{31}P , ^{27}Al , ^{11}B , ^6Li , ^{15}N , ^2H nuclei, it is also possible to obtain useful information. For rubber or gel samples, useful information can also be acquired from ^1H nucleus.

Available information

- 1) About Chemical Structure

Chemical species, coordination number, primary structure, secondary structure (conformation), high-order structure (crystalline and amorphous).

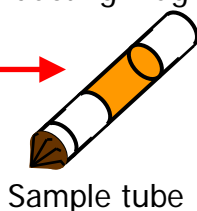
- 2) About Molecular Mobility

Crystallinity, orientation, crosslinking, domain size of polymer alloy (the order of several tens nm or several nm), interaction of active pharmaceutical ingredients or polymers with water or solvents.

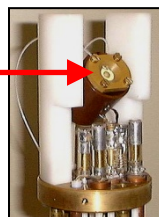
How do measurements?

The sample tube filled up with a sample is installed into a probe, and carried out high speed spinning in the superconducting magnet for measurements.

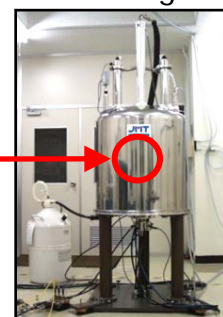
Sample (powder, fiber, cutting film, gel, etc.)



Sample tube

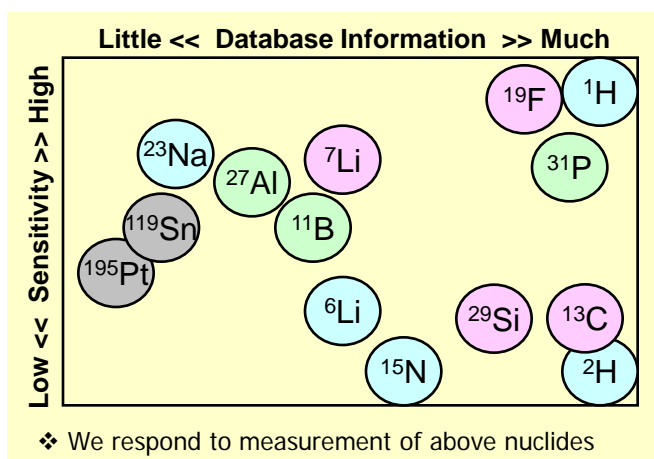


Probe inside



Superconducting magnet

- ❖ Required sample volume is several mg - several hundred mg.
(When the sample amount is sufficient, quantify measurement is possible.)

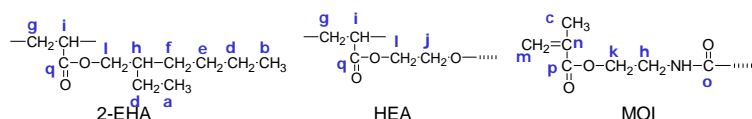


Determining component ratio of polymers.

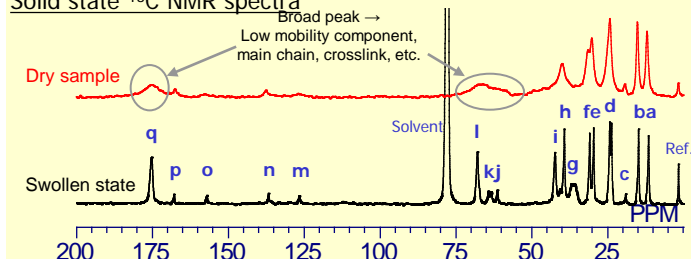
Chemical structure information can be acquired from the peak position (chemical shift value), and the quantity the ratio of each component in the observed elements from the peak area.

Component ratio of adhesive

To determine the composition ratio of three main components of the UV curable adhesive, solid-state ^{13}C NMR measurements were performed.



Solid state ^{13}C NMR spectra



component	2-EHA	HEA	MOI
ratio	71 mol%	19 mol%	10 mol%

In the case of the resin of which monomer composition is unknown, it is effective to carry out IR, pyrolysis GC/MS, and organic analysis of the soluble component in conjunction.

With measuring at high temperature near the melting point or in the swollen state, it is possible to obtain higher resolution spectrum and the accuracy of analysis is improved. we have been carrying out a lot of such high temperature or swelling measurement.

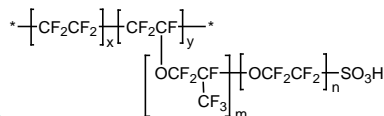
Chemical structure of electrolyte membranes

In order to determine the chain structure for the fluorinated electrolyte membrane in the polymer electrolyte fuel cell, solid-state ^{19}F NMR measurements was effectual.

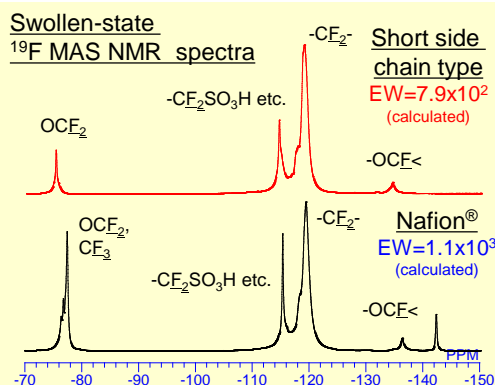
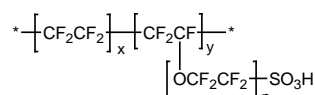
A difference of the chemical structure of the side chain was captured by ^{19}F NMR spectrum for two samples. It is possible to calculate the EW (Equivalent Weight) from the estimated unit ratio summarized in the following table.

	x	y	m	n
NRE212	6.6	1.0	1.1	1.3
Short side chain type	5.1	1.0	—	0.9

【Nafion® NRE212】



【Short side chain type】

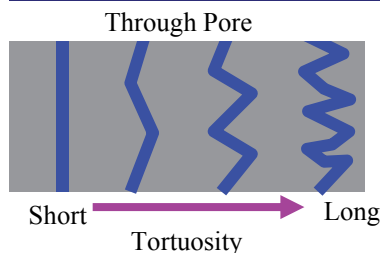


Measurement of tortuosity of porous materials

VII-2

Tortuosity have implications for the performance of porous materials (e.g. the battery separator film used in the lithium-ion secondary battery, the carbon paper used in the fuel cell), as well as pore size distribution, specific surface area, porosity and permeability. Under the assumption of the laminar flow in cylindrical pore, tortuosity can be estimated by Kozeny-Carman equation.

Definition and calculations



Mercury intrusion porosimetry
N₂ or Kr gas adsorption measurements
Air permeability measurements

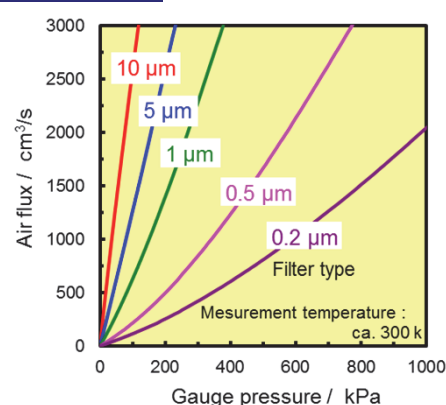
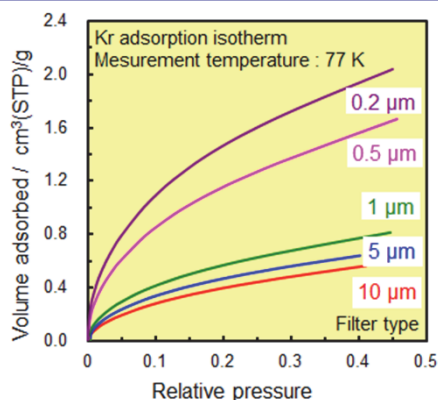
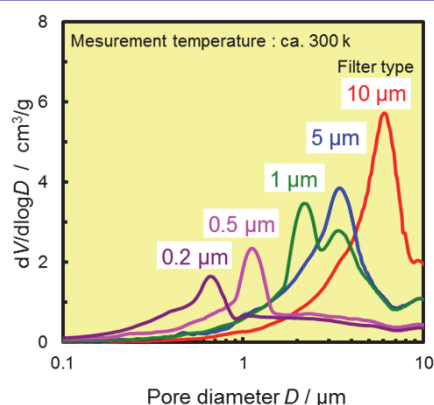
Specific pore volume, Porosity
Specific surface area by BET method
Darcy friction factor

Kozeny-Carman equation

$$\frac{l_e}{l_d} = \sqrt{\frac{\varepsilon}{2k}} \left(\frac{V_p}{S_{BET}} \right)$$

l_e : Pore pathway, l_d : Sample thickness
 V_p : Specific volume of pore, ε : Porosity,
 S_{BET} : Specific surface area by BET method
 k : Darcy friction factor

Separation membranes (Simulation of separators used in the lithium ion battery)

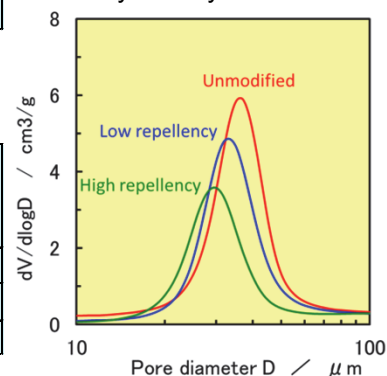


Filter type	Specific pore volume V_p (cm³/g)	Specific surface area S_{BET} (m²/g)	Porosity ε	Air permeability k (Darcy)	Tortuosity
10 μm	2.1	2.2	0.46	0.071	1.7
5 μm	2.0	2.5	0.60	0.028	2.6
1 μm	1.9	2.9	0.53	0.012	3.1
0.5 μm	1.2	5.9	0.60	0.003	2.0
0.2 μm	1.2	7.5	0.64	0.001	2.9

For separation membranes, parameters except tortuosity are related to the pore size. On the other hand, tortuosity is not related to the other parameters. Therefore, it is necessary to obtain the pore volume, porosity and permeability independently, in order to estimate tortuosity exactly.

Carbon papers used in the fuel cell

Sample	Specific pore volume V_p (cm³/g)	Specific surface area S_{BET} (m²/g)	Porosity ε	Air permeability k (Darcy)	Tortuosity
Unmodified	1.7	0.30	0.64	3.3	1.8
Low repellency	1.4	0.16	0.56	3.1	2.6
High repellency	1.1	0.21	0.42	1.5	2.0



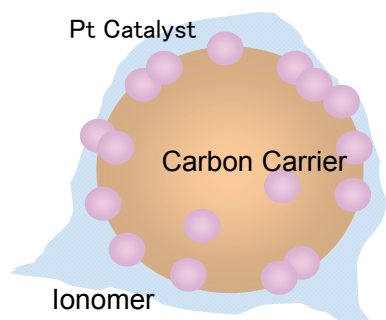
For water-repellent carbon papers, porosity and air permeability become small, as the pore is filled by the water-repellent resin (polytetrafluoroethylene, PTFE). For low water-repellent carbon paper, tortuosity becomes the maximum value, which shows the construction of the most complicated pore structure.

PEFC

3-D Quantitative analysis of Shapes of Catalyst

Estimation for ratio of catalyst which reacts effectively made possible by TEM tomography. In addition, quantitative analysis (ex, coverage of ionomer against carrier) are enabled by detailed analysis for 3-d data.

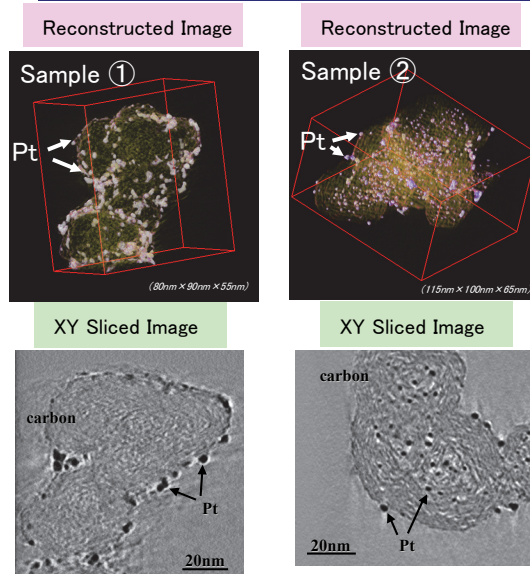
Fuel Cell Catalyst



Information to identify the each sample

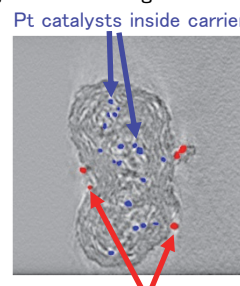
- Where are Pt catalysts?
- How about shapes of catalysts/
- How about diameter of catalysts, or distribution of diameter?
- What is ratio of embeded particles?
- How about carbon particles?
- How about coverage of ionomers?

Numbering and Identification the Catalysts at the Surface and Inside of Carrier



Pt catalyst are observed inside carrier for Sample ②

<Digital Sliced Image of Sample ②>



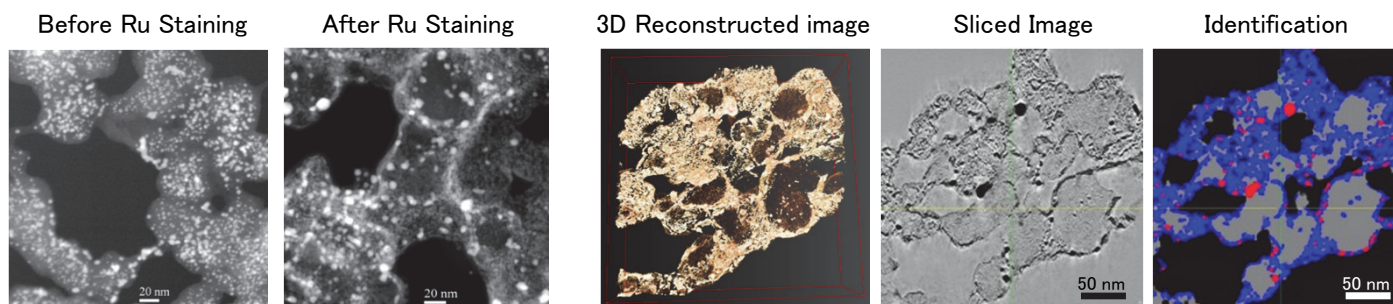
Pt catalysts outside carrier

Total number of Pt catalysts: 1202

Number of Pt catalysts outside carrier: 246

Ratio of catalysts outside Carrier
20 (%)

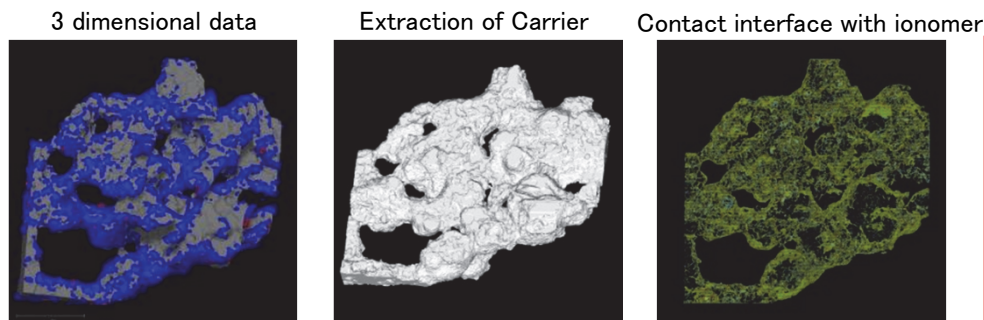
3-D observation of Ionomer Morphology by TEM Tomography and Examples of Quantitative Analysis



Selective contrast acquisition for ionomer

Box size: 305 × 305 × 90 (nm)

• Carbon (Gray)
• Ionomer (Blue)
• Pt catalyst (Red)



- Compositional volume ratio
Carbon = 77 (%)
Ionomer = 14 (%)
Pt Catalysts = 9 (%)
- Surface Area of C = 3.4×10^5 (nm²)
- Contact interface with Ionomer
= 1.9×10^5 (nm²)
- Coverage of Ionomer = 56 (%)

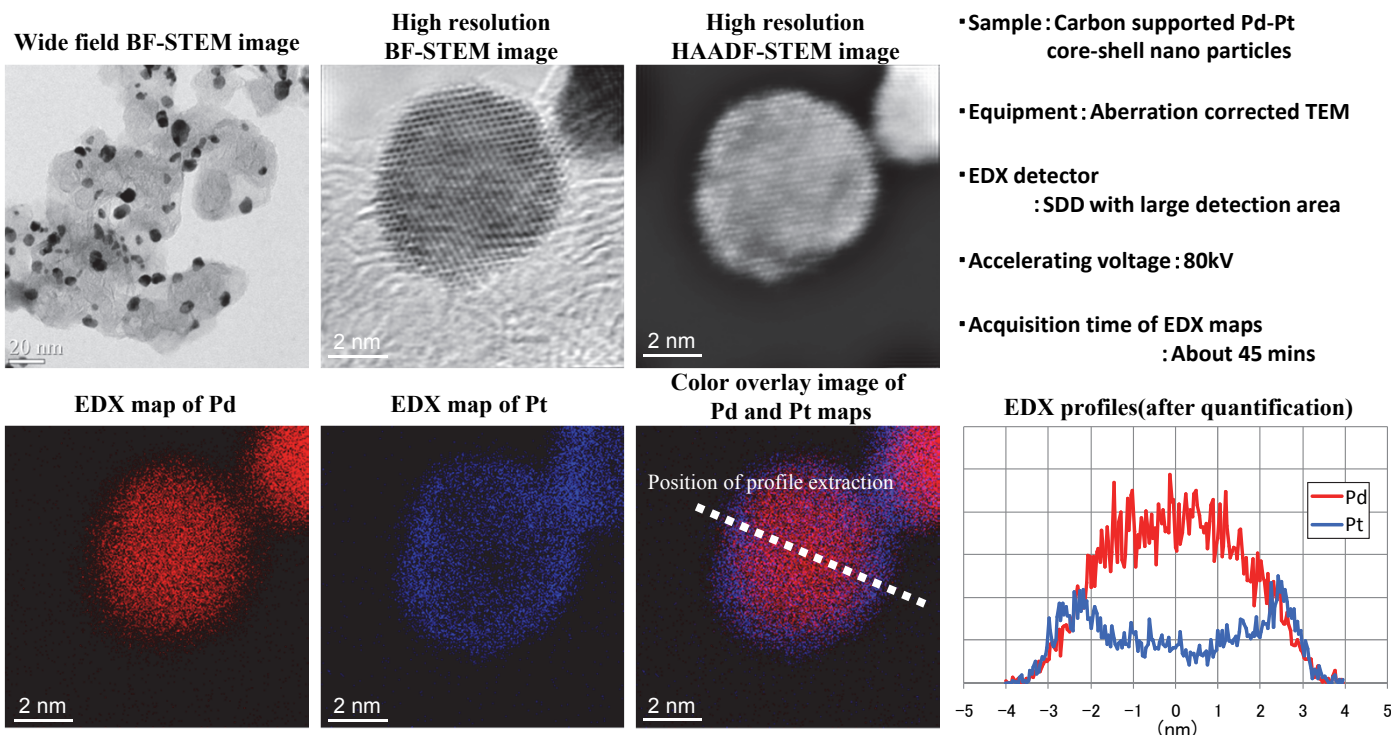
Quantitative analysis of reconstructed 3-D data acquired by TEM Tomography make possible to determine the physical parameters about catalysts for Fuel Cell

※A part of these results are supported by NEDO
"Reducing Platinum for PEFC"

PEFC : Aberration corrected STEM-EDX analysis of core-shell nanoparticles. ^{IV-2}

Clear elemental maps of small nanoparticles can be acquired by combination of aberration correction, high sensitive EDX analysis, and low accelerating voltage measurement (80kV).
Distribution of Pt shell thickness in Pd-Pt core-shell structure can be analyzed precisely.

Aberration corrected STEM-EDX analysis

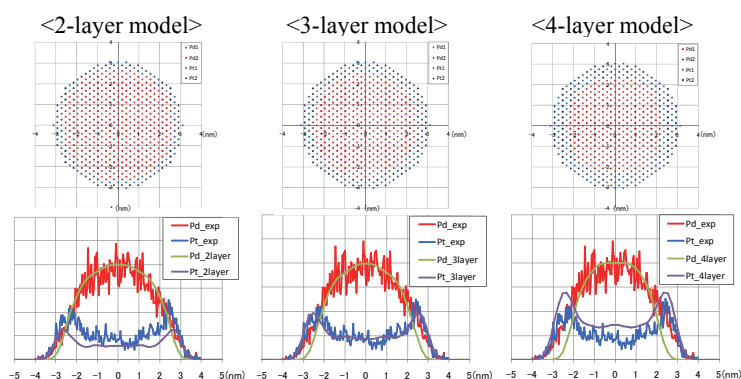


Clear elemental maps of small nanoparticles about 5nm in size can be acquired by combination of aberration correction, high sensitive EDX analysis, and low accelerating voltage measurement (80kV).

Precise analysis of core-shell structure

— Analysis procedure —

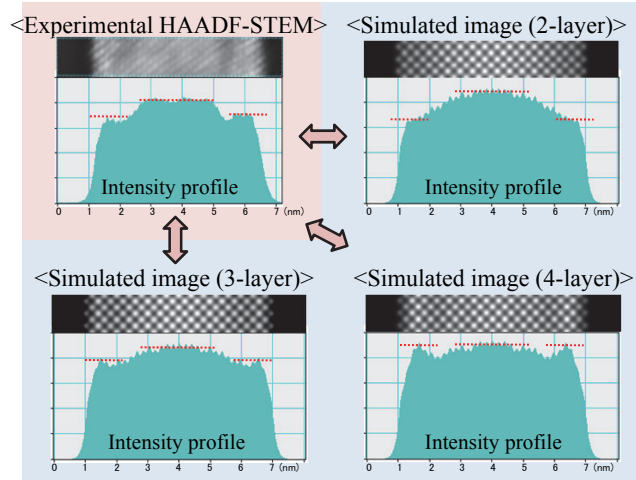
- ①Preparing profiles of the number of Pd and Pt atoms with different shell thickness.
- ②Estimation of effective STEM probe size and convolution it to the profiles.
- ③Comparing with experimental results.



The number of shell layers is determined in an atomic level by fitting core-shell models and experimental EDX profiles. *

* S. Inamoto, Y. Otsuka, K. Kobayashi (Daido univ.), M. Hori (Daido univ.),
The 69th Annual Meeting of the Japanese Society of Microscopy.

Evaluation by STEM image simulations



Results of the HAADF-STEM image simulations show the 3-layer model is similar to the experimental data.

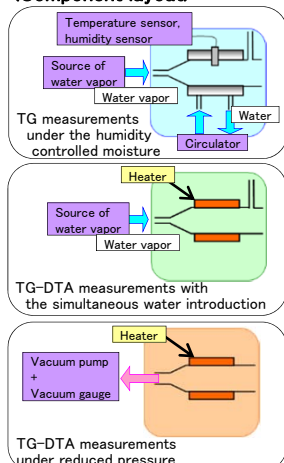
Sample provided by Brookhaven National Laboratory

Thermogravimetry–Differential thermal analysis (TG–DTA) measurements under various atmosphere

Specialized TG–DTA measurement system, which perform under the humidity controlled moisture or reduced pressure, is the powerful tool to clarify the weight change and thermal behavior of a material under the various practical use environment, which can not be investigated using usual TG–DTA measurement system.

Overview of the TG–DTA device

<Component layout>



<Condition>

TG measurements under the humidity controlled moisture

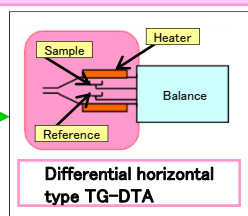
- Temperature: 25~80°C
- Humidity: 20~80%RH (with constraint depending on temperature)

TG-DTA measurements with the simultaneous water introduction

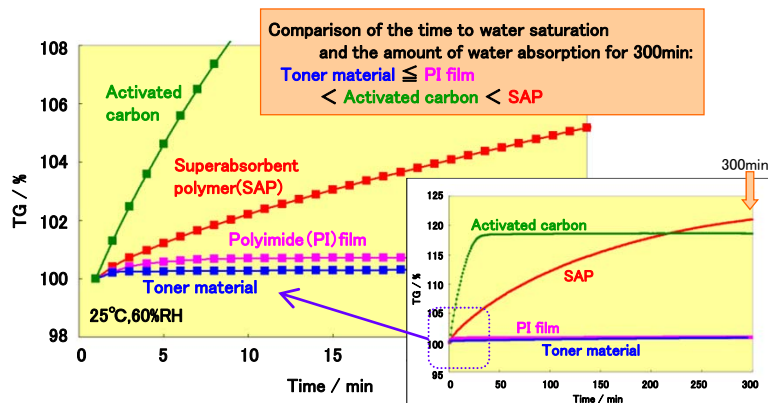
- Temperature: RT(Room temperature)~1000°C
- Atmosphere: Damp gas introduced into water at RT

TG-DTA measurements under reduced pressure

- Temperature: RT~1000°C
- Minimum pressure: 5~10Pa

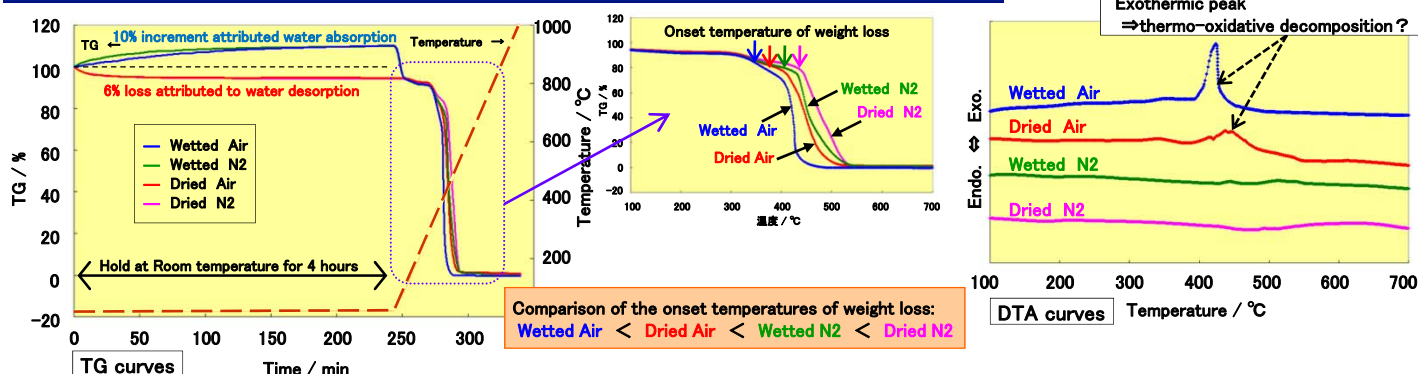


Weight change under the humidity controlled moisture



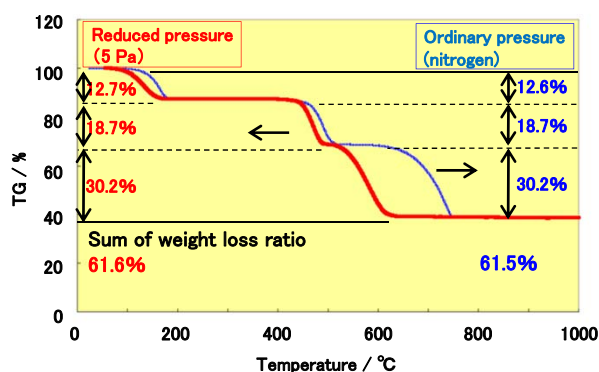
The weight change attributed to water absorption was observed under a given temperature and humidity. The difference of water absorption behavior between materials can be clarified.

TG–DTA measurements for Nafion membrane with the simultaneous water introduction



With introduction of a prescribed gas, the weight change and thermal behavior of Nafion membrane was investigated simultaneously. From TG curves, the difference of the water absorption/desorption behavior in isothermal process at room temperature, the onset temperature of weight loss and weight loss behavior at high temperature can be clarified depending on atmosphere. DTA curves can be used to judge whether weight loss is attributed to thermal or thermo-oxidative decomposition.

TG measurements under reduced pressure for calcium oxalate hydrate



Weight loss ratio in $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ decomposition estimated from chemical equations (theoretical value)

- <1st weight loss> $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ (12.3%)
- <2nd weight loss> $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$ (19.2%)
- <3rd weight loss> $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (30.1%)

<Sum of weight loss ratio> (61.6%)

Despite pressure difference, experimental values of sum of weight loss agree with theoretical one. However, the onset temperature of weight loss in reduced pressure is lower than that of ordinary pressure.