Structural Analysis of Metal Ion Distribution in Polymer Film by Anomalous Small-Angle X-ray Scattering

Research Reactor Institute, Kyoto University

Masaaki Sugiyama, Takashi Sato,

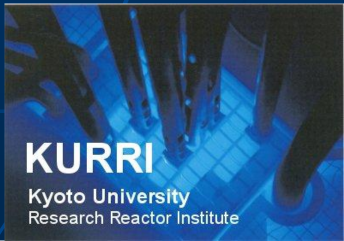
Keiji Itoh, Kazuhiro Mori, Toshiharu Fukunaga

Research and Development Center for Higher Education, Kyushu University

Yuji Soejima

Department of Applied Science and Engineering, Hokkaido University

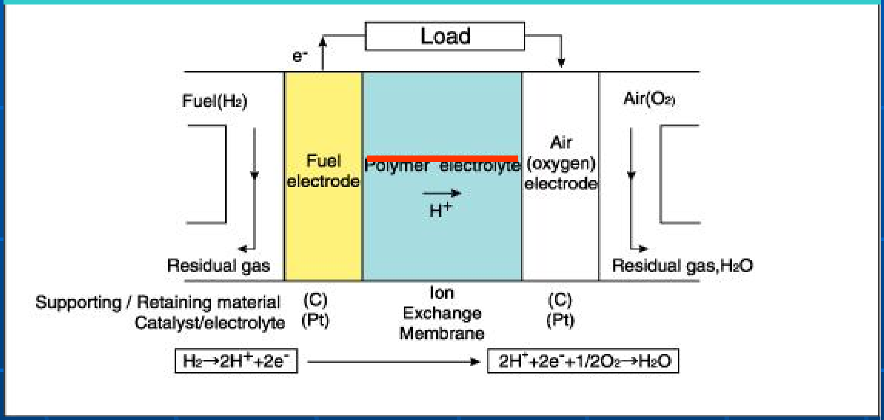
Hiroshi Orihara, Yang Ho Na



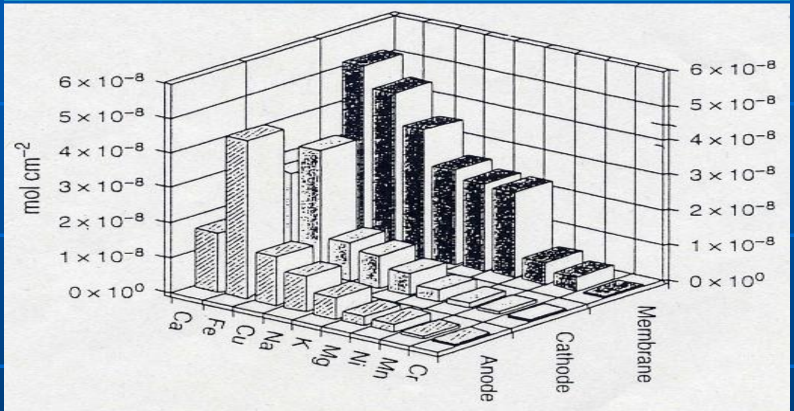
Introduction

- In long time operation of a fuel cell (FC), a membrane, which is used for a separator between electrodes, gradually absorbs metal ions from the environment.

Proton-Exchange membrane Fuel cell（PEFC）



Accumulation of metal ions (in 9000hrs)



from *Handbook of Fuel Cells*

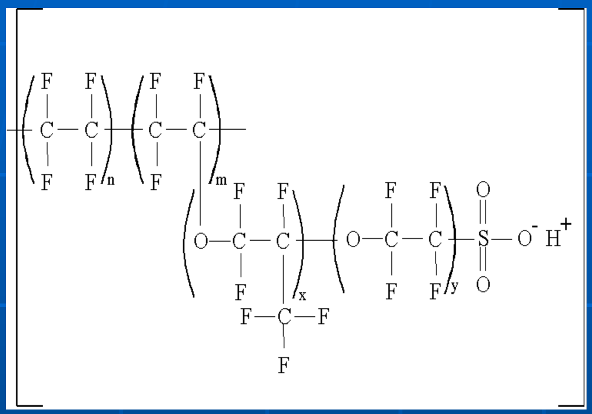
- It makes degradation of electric conductivity of Nafion.

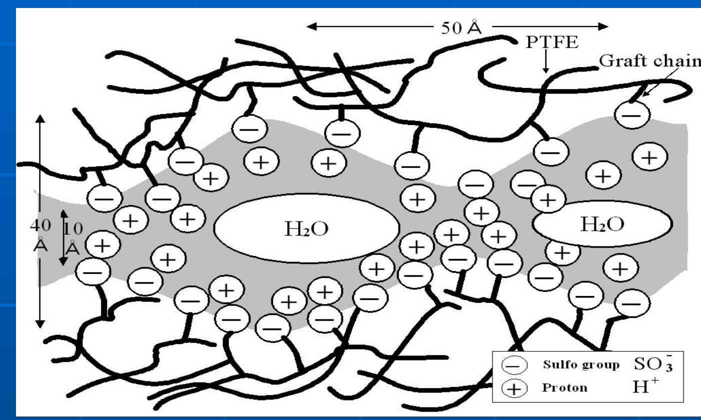
absorbed substance	electric conductivity
Water	0.04583 S/cm
Water + Cu (0.1mol/l)	0.00509 S/cm

KURRI
Kyoto University
Research Reactor Institute

Questions

- What structure does the polyelectrolyte film (Nafion) have? *Is the present accepted model correct?*

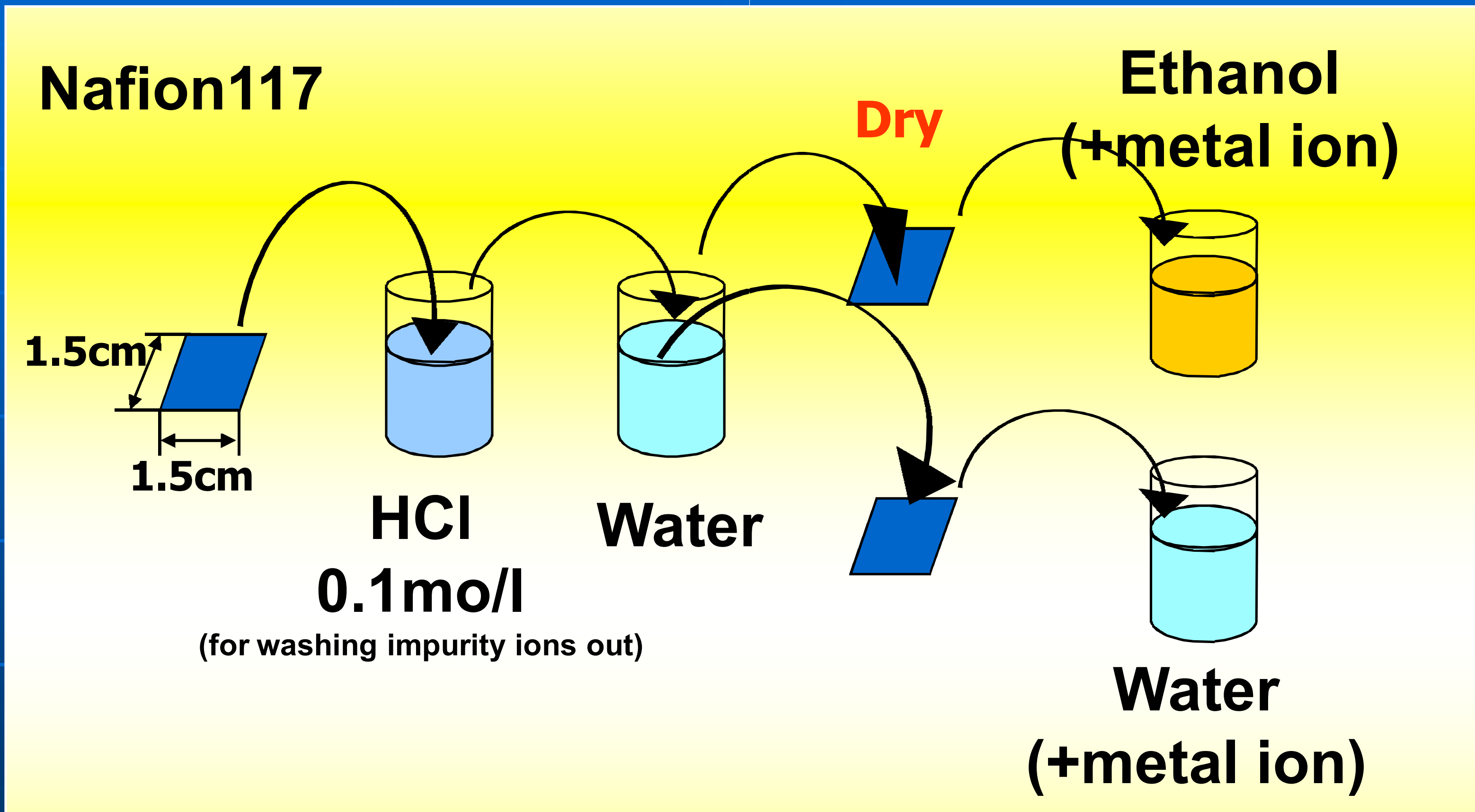




- How does the structure concern about its electric property?
- Where are the absorbed metal ions located in the structure of Nafion film?
- How is the electric conductivity of Nafion dropped by the absorption of metal ion?

KURRI
Kyoto University
Research Reactor Institute

Samples preparation



$$R = \frac{M_b - M_a}{M_b} \times 100$$

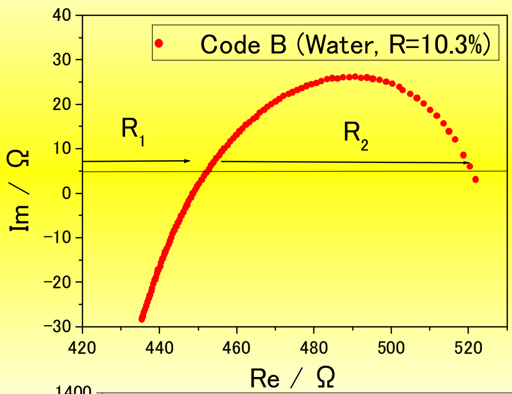
R: Content ratio [%]

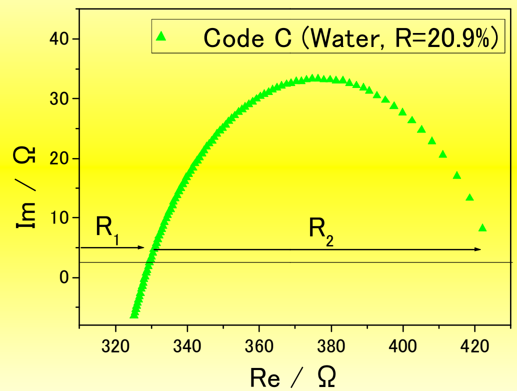
M_a: Complete dry weight [g]

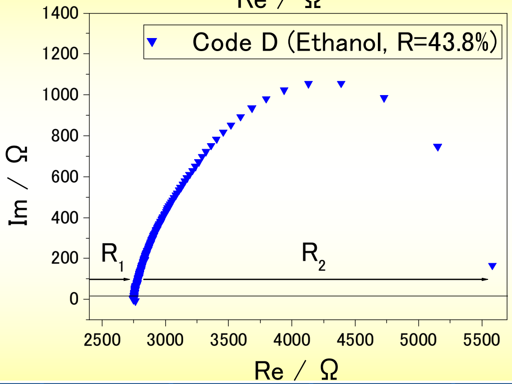
M_b: Wet weight [g]

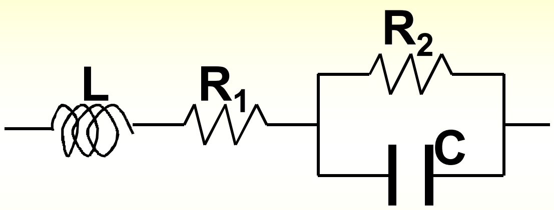
KURRI
Kyoto University
Research Reactor Institute

Electric conductivity



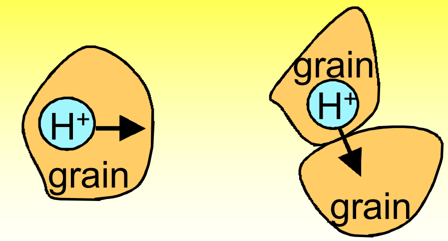






Cole-Cole plots and their equivalent circuit

Two kinds of resistances in a ion conducting ceramic

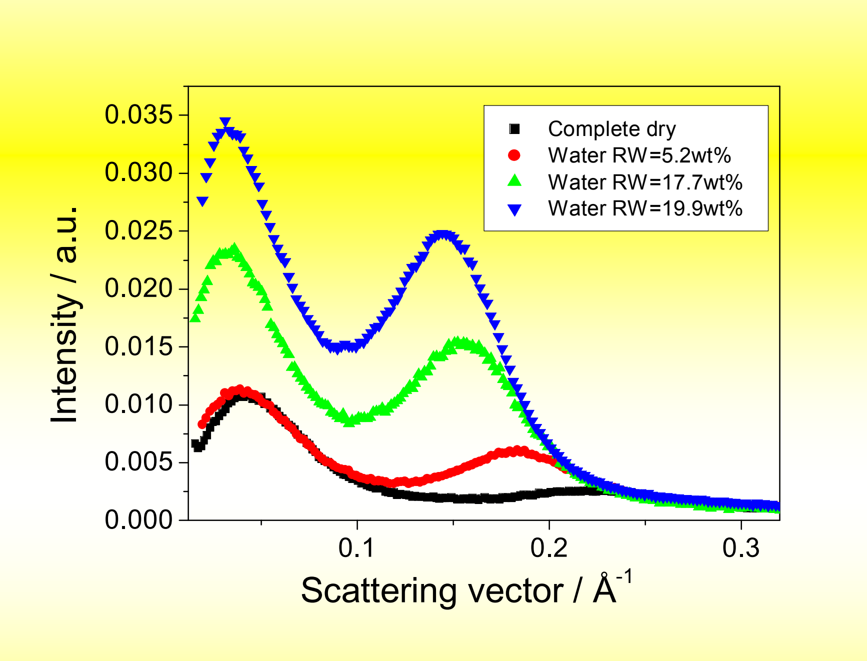


Bulk Resistance R_1

Grain-boundary resistance R_2

Code	σ_1 [S/cm] (bulk)	σ_2 [S/cm] (g.b.)	C [F]	L [H]
A	$< 8.40 \times 10^{-8}$	$< 8.40 \times 10^{-8}$	-	-
B	4.61×10^{-2}	1.28×10^{-1}	4.50×10^{-10}	1.58×10^{-6}
C	4.90×10^{-2}	1.58×10^{-1}	2.94×10^{-10}	1.31×10^{-6}
D	6.84×10^{-3}	4.07×10^{-3}	1.93×10^{-13}	4.68×10^{-7}

Nano structure



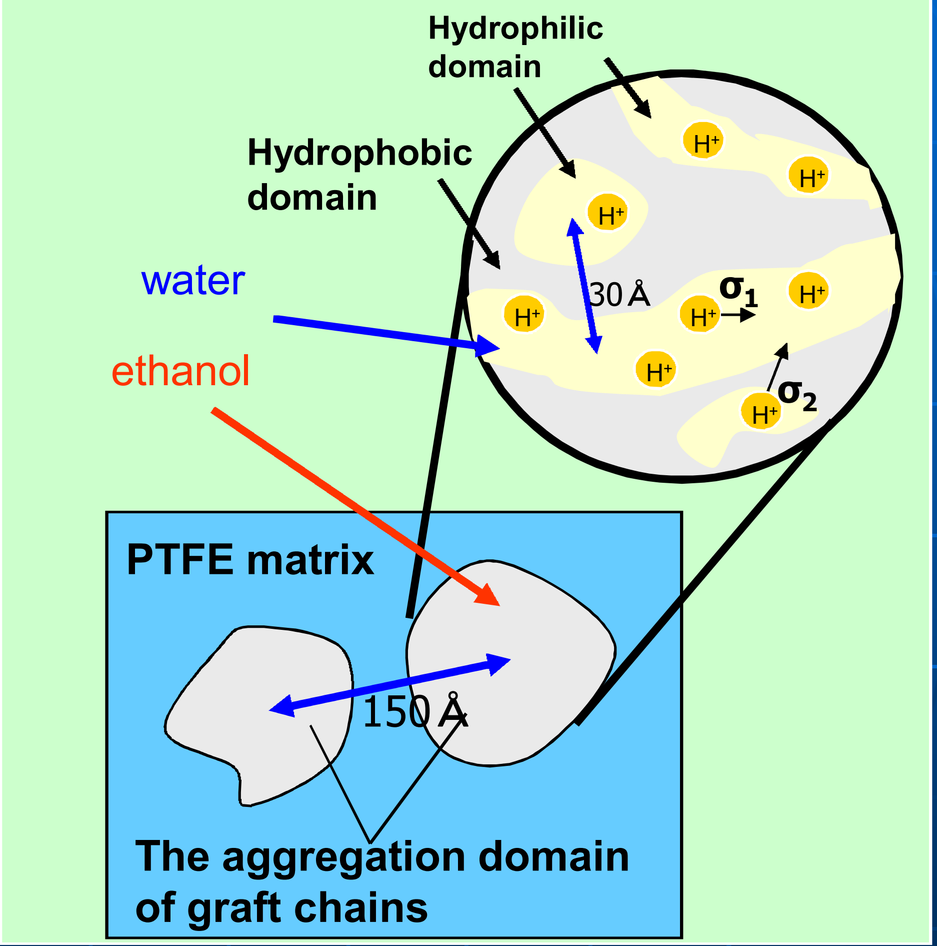
Nafion shows two peaks in the SAXS profiles.

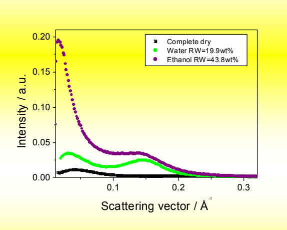
⇒Hierarchic structure

The second peak shifts to the lower *q* with increase of the water content but the first one does not move.

⇒Water penetrates into the domain corrsponding to the second peak .

Nano-structure model of Nafion film

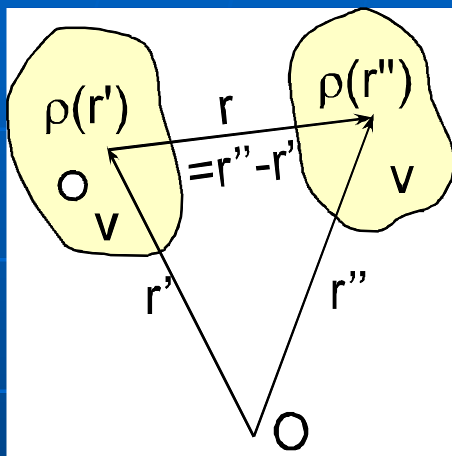




KURRI
Kyoto University
Research Reactor Institute

Problems

- As shown in the previous figure, small-Angle X-ray Scattering (SAXS) is a very powerful tool to investigate a nanostructure.



$$\rho(\mathbf{r}) = \frac{1}{v}\sum_j b_j$$

Average of scattering length

$$I(\mathbf{q}) = \iint_V \rho(\mathbf{r}')\rho(\mathbf{r}'')\exp(i\mathbf{q}(\mathbf{r}''-\mathbf{r}'))d^3\mathbf{r}'d^3\mathbf{r}''$$

$$= \int_V C(\mathbf{r})\exp(i\mathbf{q}\mathbf{r})d^3\mathbf{r}$$

$$C(\mathbf{r}) = \int_V \rho(\mathbf{r}')\rho(\mathbf{r}'')d^3\mathbf{r}' = \int_V \rho(\mathbf{r}')\rho(\mathbf{r}+\mathbf{r}')d^3\mathbf{r}'$$

- BUT it is difficult to distinguish between density fluctuation and distribution fluctuation.
- *Where are metal ions absorbed?*

What does make difference
between ρ(r) and ρ (r′),
density fluctuation or atom distribution ?

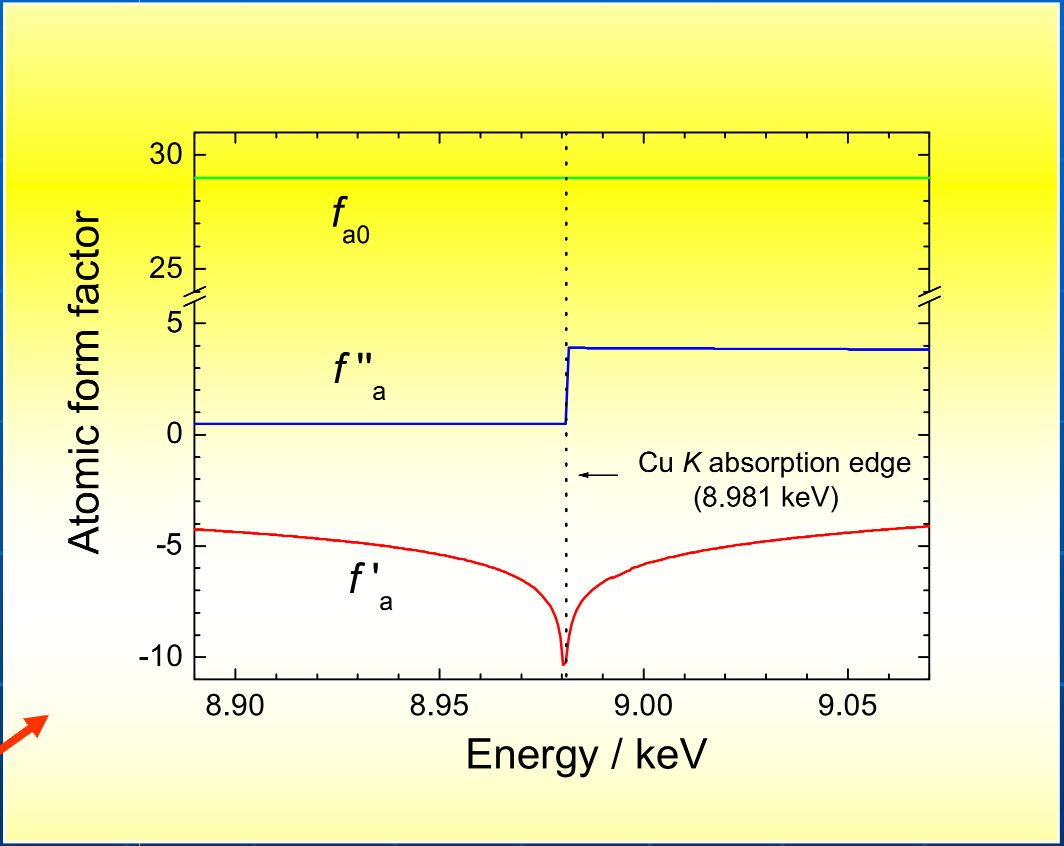
KURRI
Kyoto University
Research Reactor Institute

X-ray anomalous dispersion effect

Atomic form factor

$$f = f_0 + \underline{f' + if''}$$

Around an absorption edge, energy dependent terms add to an atomic form factor

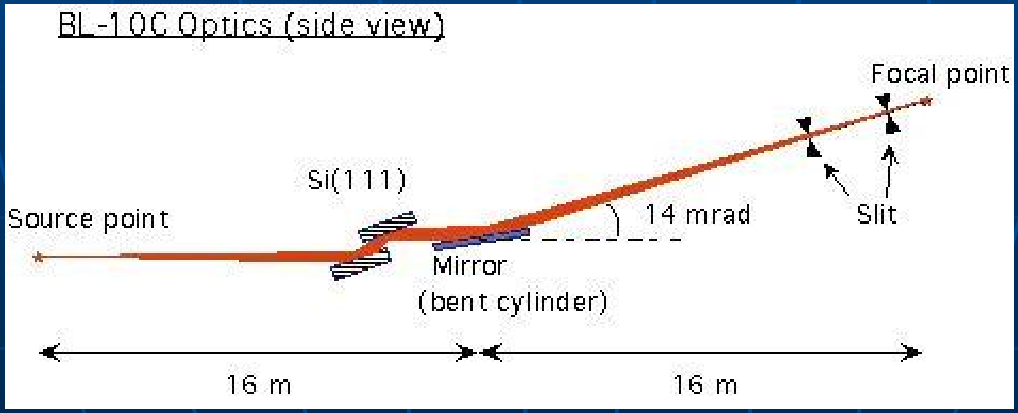


Energy dependence of Cu atomic form factor

→Around the absorption edge, scattering length density of an only domain where Cu ion aggregates becomes lower.

SAXS utilizing anomalous dispersion effect experiment

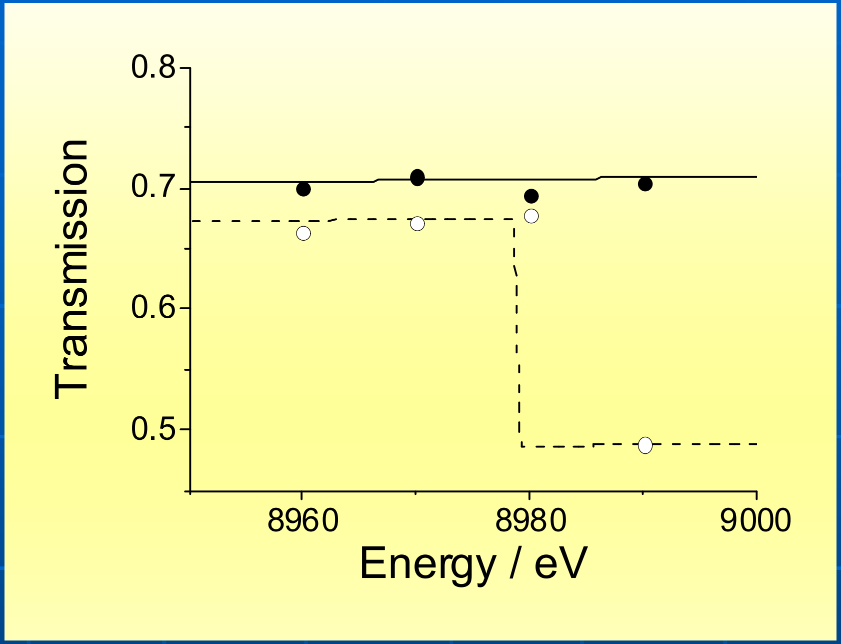
- **SAXES** installed at BL10C of Photon Factory (PF) in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan
- X-ray wavelength : 1.373 Å to 1.389 Å (Step : 0.004 Å)
  8.930 keV to 9.030 keV (Step : 10 eV)
  Cu absorption edge = 1.381 Å (=8.980 keV)
- Detector : one-dimensional position sensitive detector
- Q-range : 0.02 - 0.45 $Å^{-1}$
- Measurement time : 600 sec

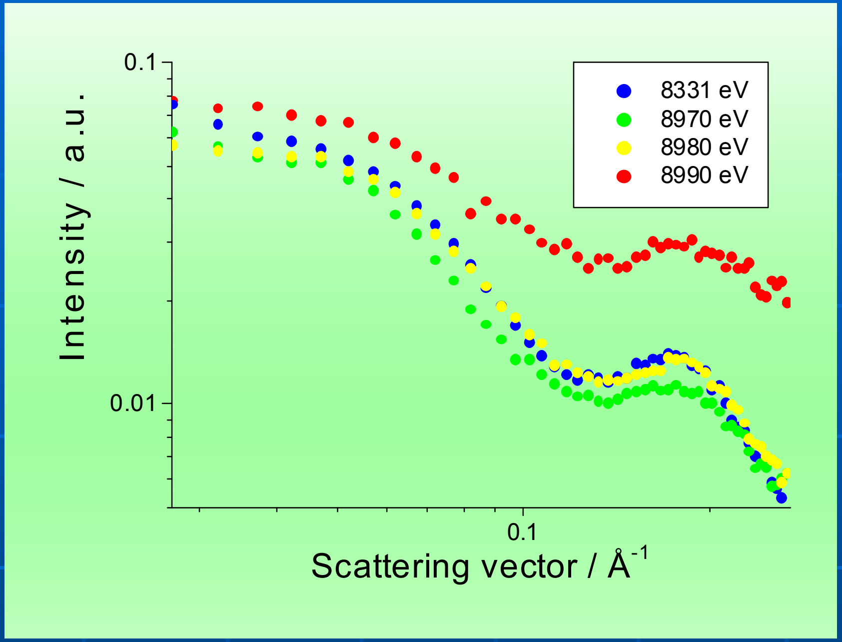


From KEK-PF HP (http://pfwww.kek.jp/users_info/station_spec/bl10/bl10c.html)

KURRI
Kyoto University
Research Reactor Institute

Anomalous SAXS (Water & $CuCl_2$)





Transmission drastically dropped at an absorption edge of Cu.

⇒Nafion absorbed Cu ion.

The first and second peaks becomes intensive at the absorption edge.

⇒Cu ion absorbed in the domain where sulfate group aggregates.

KURRI
Kyoto University
Research Reactor Institute

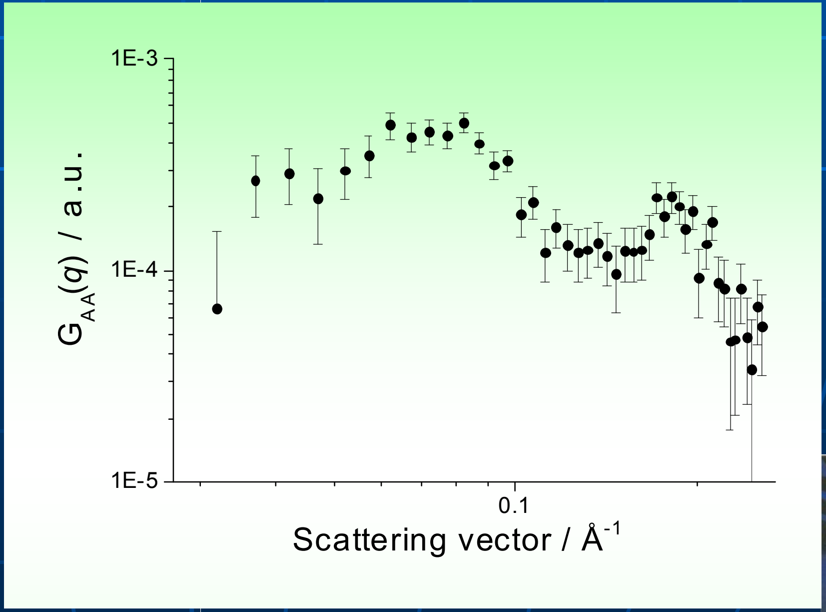
Anomalous SAXS (Water & $CuCl_2$)

$$I_{metal}(q) = \left[\frac{\Delta I(q, E_2, E_1)}{\Delta f'_{metal}(E_2, E_1)} - \frac{\Delta I(q, E_3, E_1)}{\Delta f'_{metal}(E_3, E_1)} \right] \frac{1}{F(E_1, E_2, E_3)}$$

$$F(E_3, E_2, E_1) = \frac{\Delta f^2_{metal}(E_2, E_1)}{\Delta f'_{metal}(E_2, E_1)} - \frac{\Delta f^2_{metal}(E_3, E_1)}{\Delta f'_{metal}(E_3, E_1)}$$

$$\Delta f^2_{metal}(E_m, E_n) = \left| f_{metal}(E_m) \right|^2 - \left| f_{metal}(E_n) \right|^2, \Delta f'_{metal}(E_m, E_n) = f'_{metal}(E_m) - f'_{metal}(E_n)$$

Energy	f	f’	f”
8831	29	−2.35	0.550
8970	29	−6.64	0.484
8980	29	−10.34	0.483



KURRI
Kyoto University
Research Reactor Institute

Summary & Future

- We propose a hierarchic structure for Nafion, phase separation between graft chain domains and PTFE chain domains is upper class structure and domains where sulfates groups gather exist in the graft chain domain, film from electric conductivity measurement. and conventional SAXS measurements.
- Water aggregates in the domain where sulfates groups gather and then expands that domain: it does not effect the upper class structure.
- We conducted to SAXS utilizing anomalous dispersion effect for revealing distribution of metal ions in Nafion film.
- With tri-points method, partial scattering intensity from only Cu ion distribution has been analyzed.
- Cu ion gathers the domain where the water aggregates.