Local Atomic and Electronic Structures of Pt Catalysts Using EXAFS

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Recently, direct methanol fuel cells (DMFCs) have been much attracted as portable power sources for mobile applications. In this cells methanol uses as fuel for the anode electrode and oxygen in air as oxidant for the cathode electrode. The methanol oxidation and the oxygen reduction reactions are generally caused by the Pt–based electrocatalyst supported on carbon. In order to improve the cell performance, it is important to realize exactly the characteristics of the Pt- catalysts because the catalytic activity is affected from various factors. In this study we have investigated the electronic structure of Pt 5*d*-band and the local atomic structures for Pt catalysts by using XAFS.

XAFS measurements were performed at BL16B2 in Spring-8. The XAFS data were collected around the Pt L_3-edge by the transmission mode. The used samples were 50 wt %Pt / carbon catalysts with a various particle size of Pt. The average particle size is determined from XRD data. Fig.1 shows the Pt L_3-edge XANES spectra for the Pt/carbon catalysts. It is found that the white-line intensity increase gradually and its peak position shift to high-energy side as the particle size of Pt become small. These results indicate that the 5*d* band of Pt atoms on the surface is different from that on bulk because the ratio of atoms on surface to total atoms increases in Pt catalysts with a small particle size.

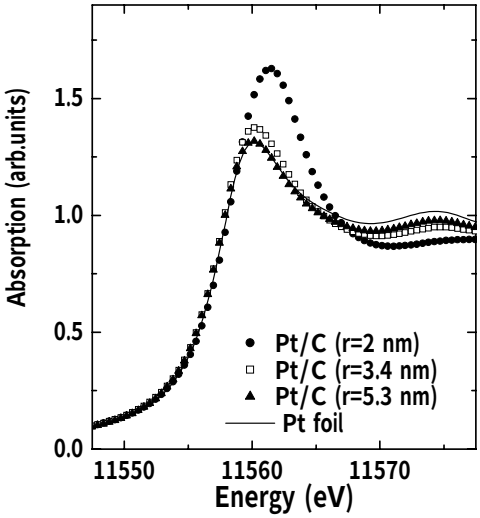

Fig.1 The XANES spectra at Pt L_3-edge for Pt /Carbon catalysts and Pt foil.

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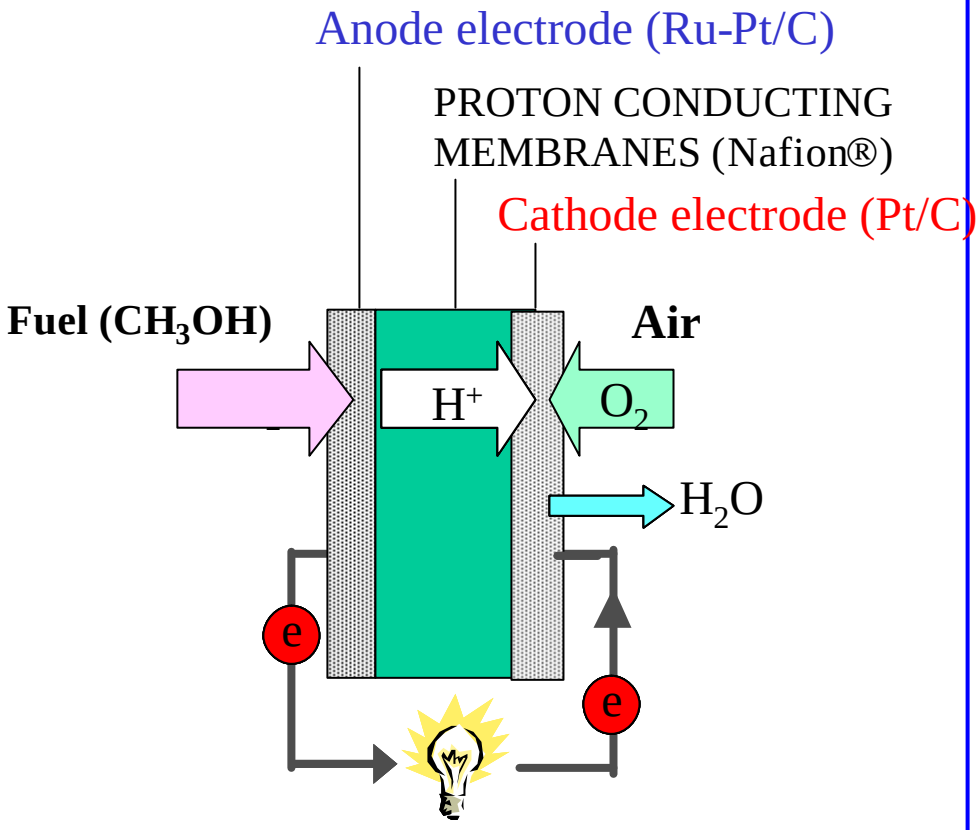
Introduction

☆Direct methanol fuel cells (DMFCs)

— a future power source for portable devices.

☆Technological improvements

- Catalyst supporting electrodes
- Polymer electrolytes
- Fuels for portable devices
- Design for portable cell



Schematic drawing of DMFCs

☆Electrocatalysts for DMFCs

Carbon-supported Pt or Pt-based alloys **are effective electrocatalysts for methanol oxidation and oxygen reduction.**

We need overcome many problem. (*ex*. CO poisoning, overpotential, *etc*.)

Case1 : *Particle size effect*

- Increasing of surface area in small particle size

  → Improvements of catalytic activity

- Existence of optimum particle size Pt /C : 2 ～ 3 nm

  below 2nm → Decreasing of catalytic activity

- Catalytic activity is sensitive to surface structure.

(arrangement, coordination, shape, electronic structure)

☆Characterization of Electrocatalysts by SR-XAFS

Various characterization tools for surface structure

(ex. TEM, XRD, XPS, FTIR etc.)

- **SR-XAFS** is a powerful tool to characterize the structure of the catalysts.

  EXAFS — coordination number, interatomic distance, disorder

  XANES — unoccupied state, chemical bond, oxidation state

☆Purpose of this study

As first step, ***particle size dependence*** of electronic and local structures for carbon-supported Pt electrocatalyts using EXAFS

Sample ☆Carbon-supported Pt electrocatalysts

【preparation】

Colloidal method

H_2PtCl_6 solution

⇓ ← $NaHSO_3 + H_2O_2$

Pt oxide colloids

⇓ ← Carbon black

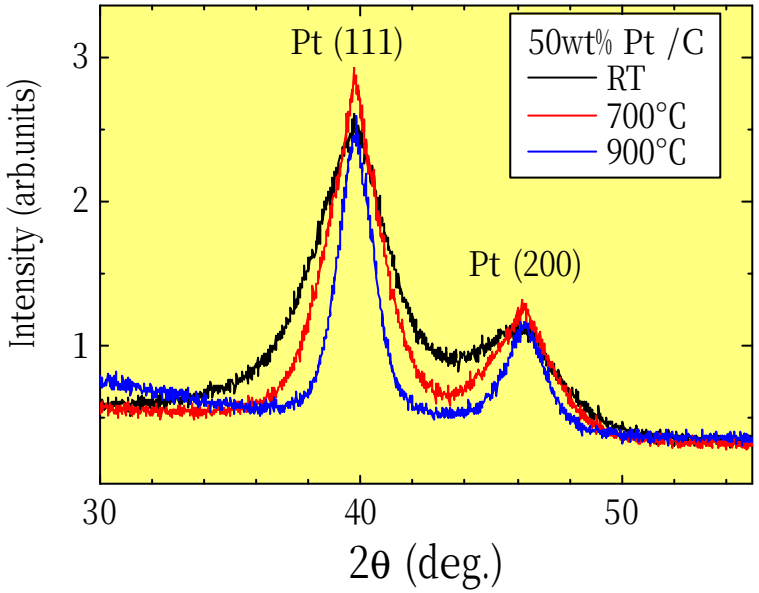
Adsorption of Pt oxide colloids on carbon surface

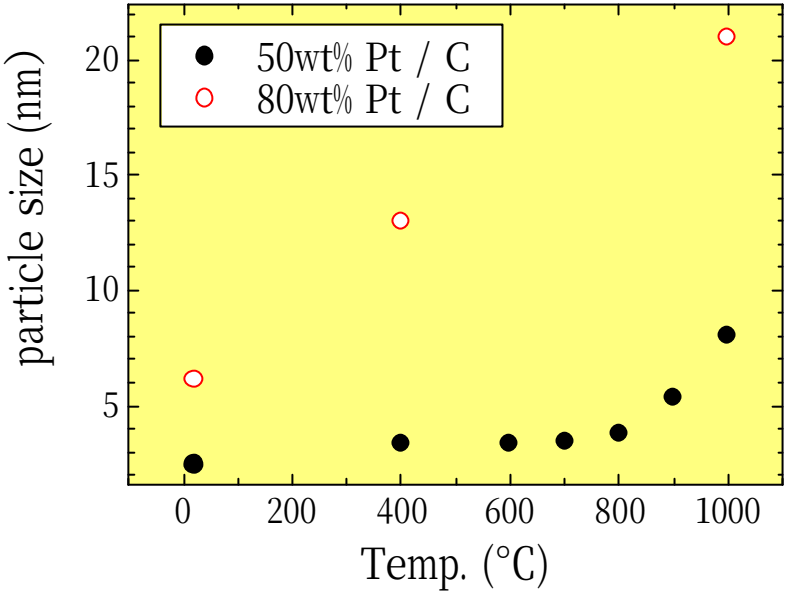
⇓ ← Reduction and annealing in H_2 atmosphere

Metallic Pt particles on carbon

- Pt loading 50, 80 wt%

XRD of carbon-supported Pt electrocatalysts





☆Pt particle size

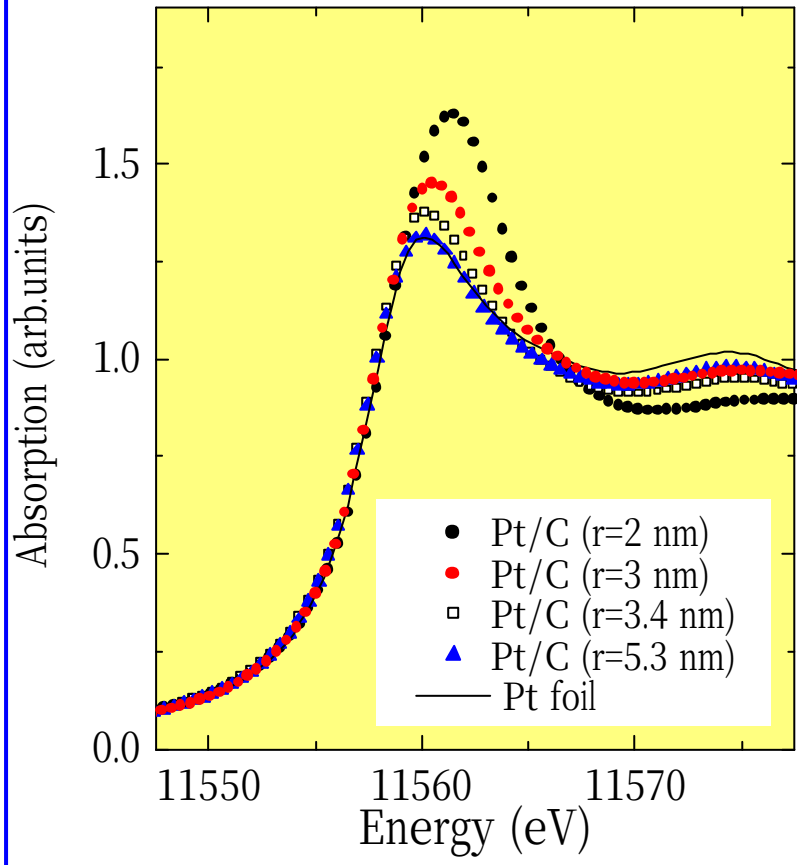
- was obtained from Scherrer formula.
- increased above 700℃ in 50wt% Pt /C.
- increased gradually with temperature in 80wt% Pt /C.

XAFS measurements

☆Sunbeam BL16B2 at SPring-8

- Si (311) double-crystal monochromator + Rh coating mirror
- beam size : 0.5 (V) × 2 (H) mm^2
- Pt L_3-edge
- transmission method
- ionization chamber gas: I_0: N(75)+Ar(25) , I: Ar(100)

XANES of carbon-supported Pt electrocatalysts (1)

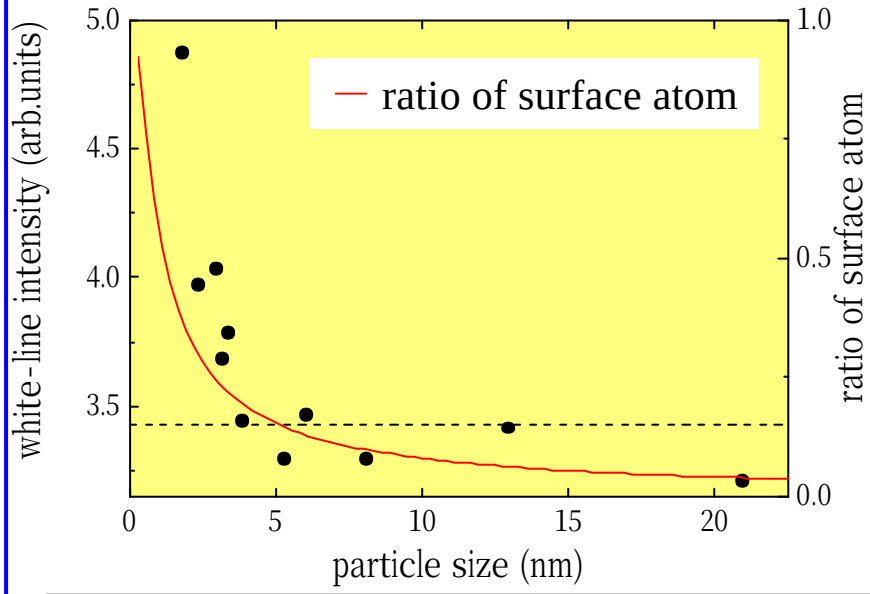


White-line → Pt 5d-band

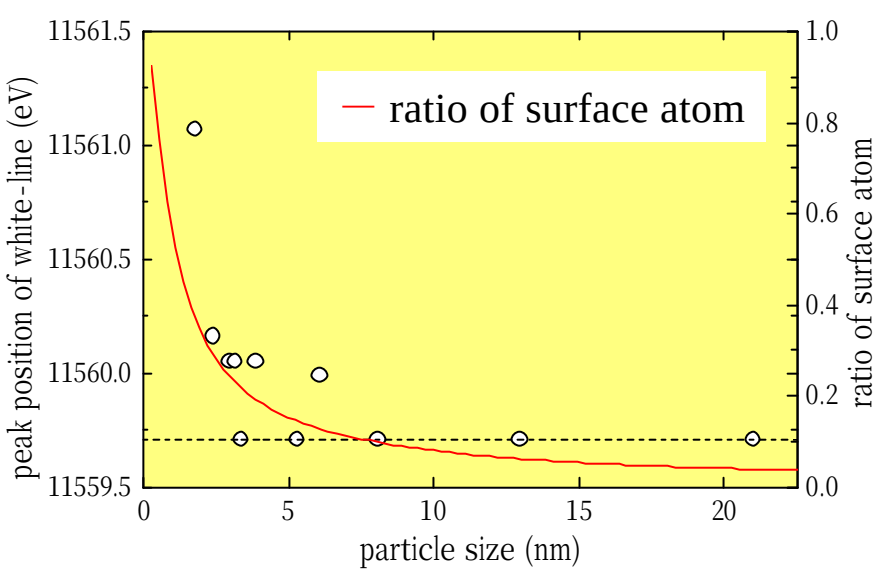
- Remarkable size effect
- In the small particle
  - white-line intensity increase
  - peak shift to higher energy side

XANES of carbon-supported Pt electrocatalysts (2)

White-line intensity



White-line peak position



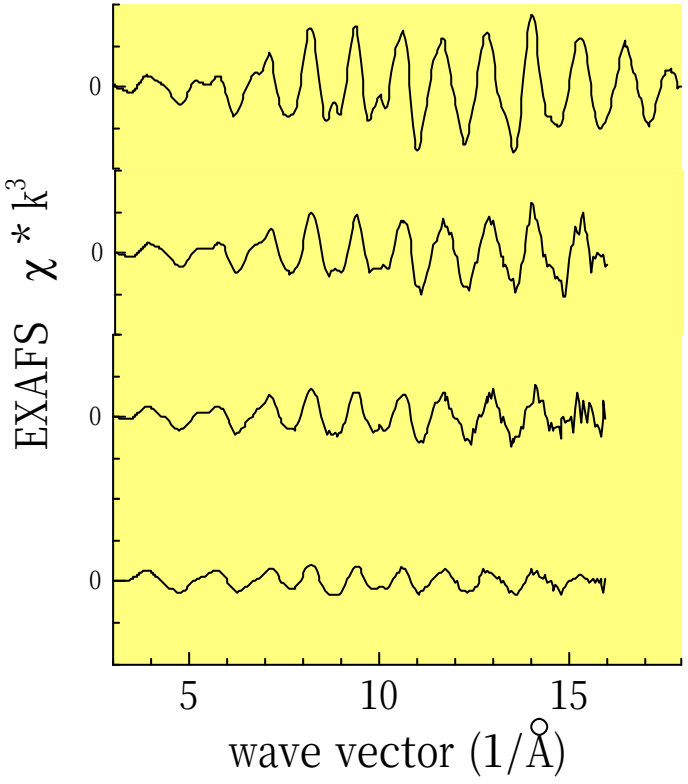
- Particle size dependence of white-line is corresponding to ratio of surface atoms.
- Pt 5d-band of surface atoms is different from that of bulk Pt.

→ Increasing of Pt 5d-band vacancies in surface Pt atoms.

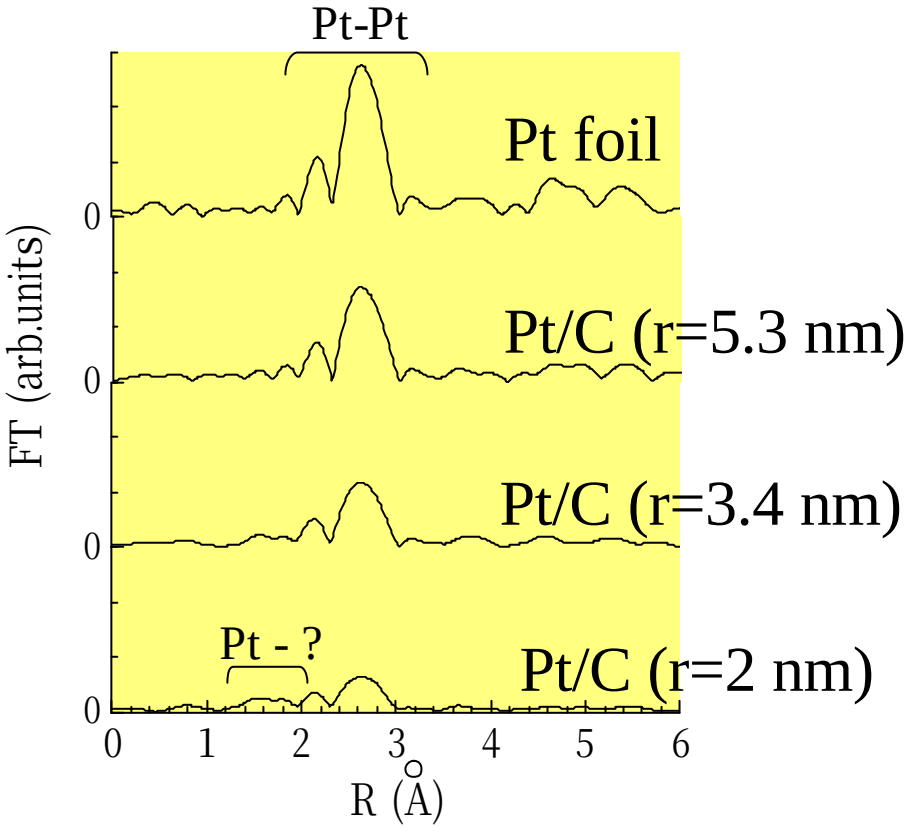
→ Charge transfer between Pt 5d-band and carbon support, adsorption atoms.

EXAFS of carbon-supported Pt electrocatalysts (1)

EXAFS signal



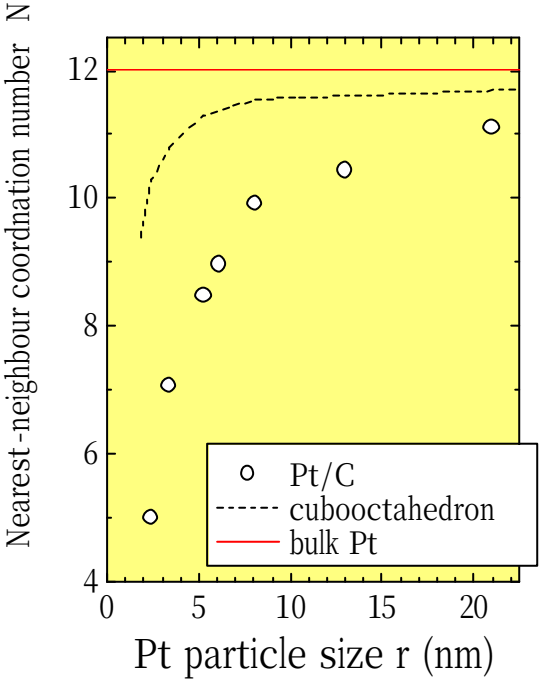
FT of EXAFS signal



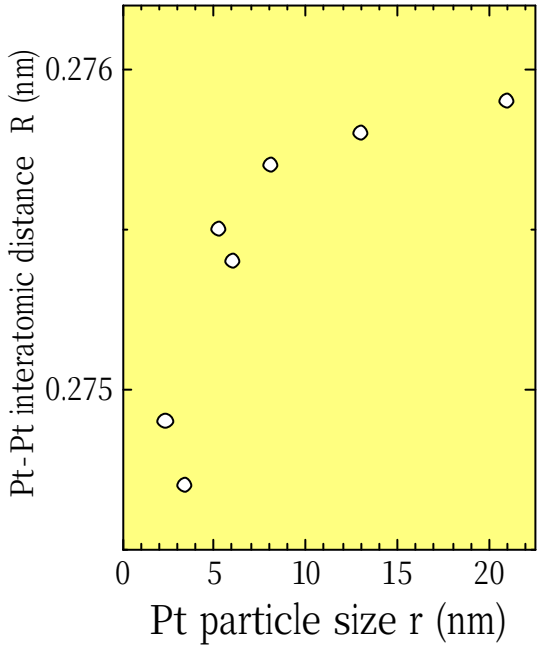
- Decreasing of EXAFS and FT amplitude in small Pt particle size.
- Bonding with other atoms in surface Pt-site. (carbon supports or adsorping oxygen)

EXAFS of carbon-supported Pt electrocatalysts(2)

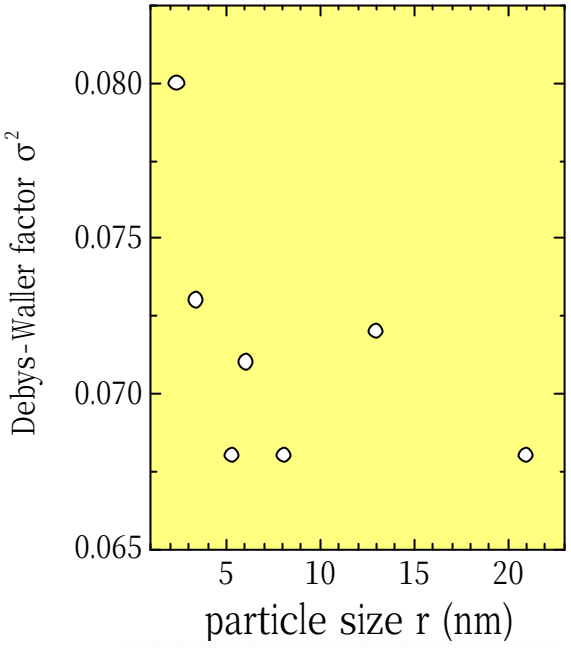
Coordination number



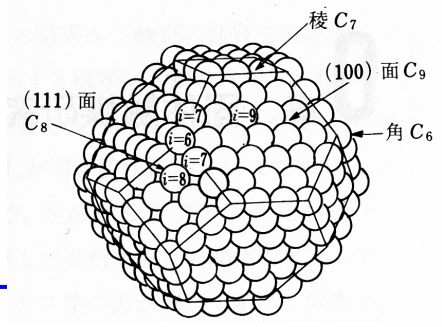
interatomic distance



Debye-Waller factor



- E_0 , λ was fixed to value obtained in Pt foil.
- Reasonable CN calculated from Pt cluster model with cuboctahedron*.



* R.E. Benfield: J. Chem.Soc. Faraday Trans. **88**(8) , 1107-1110 (1992).

EXAFS of carbon-supported Pt electrocatalysts(3)

【Coordination number (CN) for Pt-Pt bond 】

- CN for the Pt-Pt bond decreased gradually below the particle size of 8nm.
  →This trend is consistent with that calculated from the simple cuboctahedron.
- The observed CN were reduced in small particles with respect to the calculated value.
  → We need to consider the cluster model with other geometry or third cumulants term in Debye-waller factor.

【Interatomic distance】

- Interatomic distance for the Pt-Pt bond also decreased gradually below the particle size of 8 nm
- Existence of bonding with other atoms in surface Pt site.

Summary

Remarkable particle size dependence of local and electronic structures have been observed in carbon-supported Pt catalysts .

XANES

- Variation of white-line intensity and its peak position with particle-size

→ reflect to the electronic structure of surface Pt atom.

Increasing of Pt 5d-band vacancies (charge transfer to neighbouring other atoms)

EXAFS

- Decreasing of CN and interatomic distance in Pt particle size below 8 nm.
- Existence of bonding with other atoms in surface Pt site.

Future plan

- Investigation for Pt/C below 2 nm
- In-situ XAFS measurements combined with voltammetric technique.
- Application to other catalysts
  - Ru-Pt (anode), 3dTM-Pt (cathode)