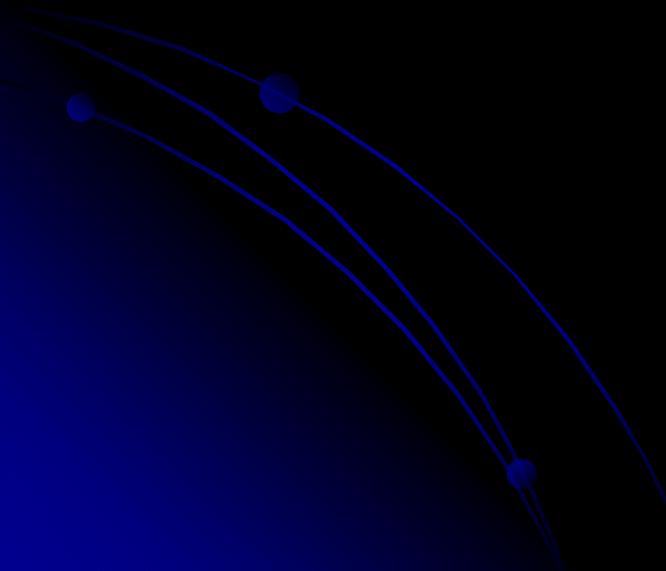

**Structural and Electronic properties of
platinum nanoparticles studied by
in situ x-ray diffraction and
in situ x-ray absorption spectroscopy**

Hideto Imai

Fundamental and Environmental

Research Laboratories

NEC Corporation



Micro Fuel Cells

Empowered by Innovation

NEC

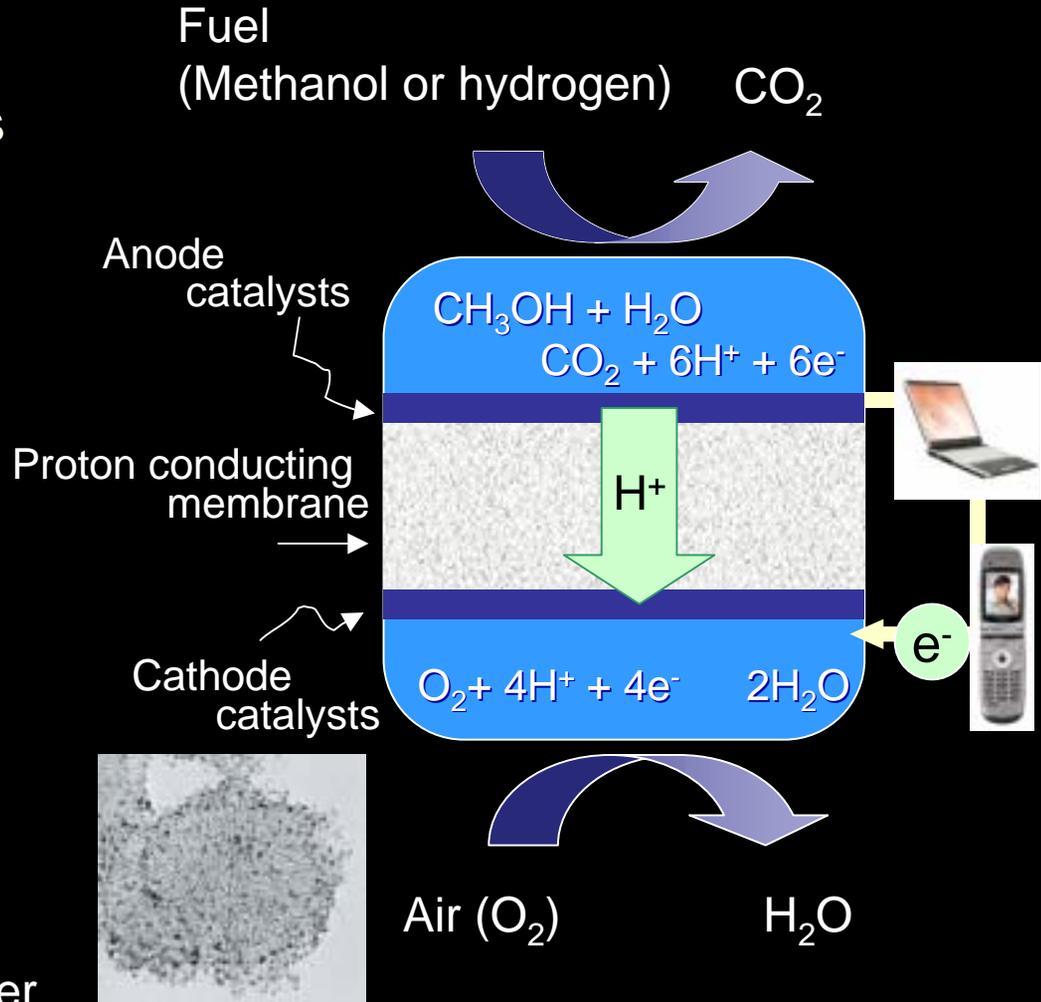
Portable batteries in the Ubiquitous Networking Society

Potential successor to Li - ion batteries

- ✓ Higher energy capacity
 - Longer usage period
 - Smaller size
- ✓ Instantly rechargeable



Fuel cell-powered laptop computer
(A prototype)



Technological hurdles

Energy Loss at the cathode electrode

Cathode Reaction

Oxygen Reduction Reaction



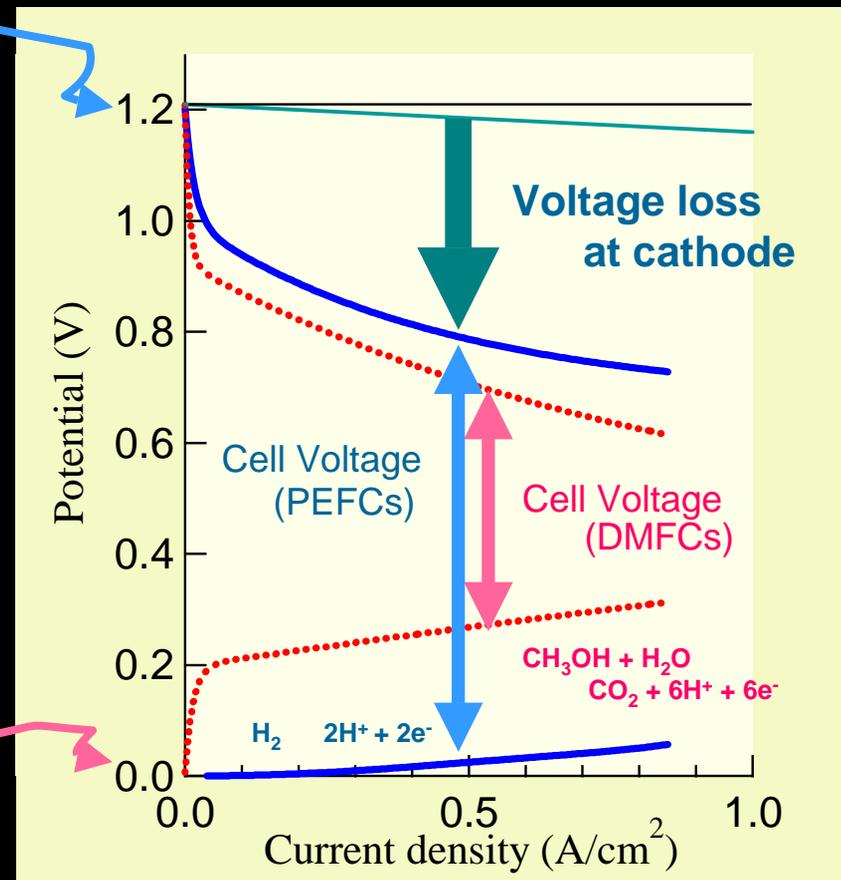
$$E^0 = 1.23 \text{ V}$$

- ✓ Catalytic activity of the current catalyst (Pt) is not enough

Elucidation of ORR mechanism

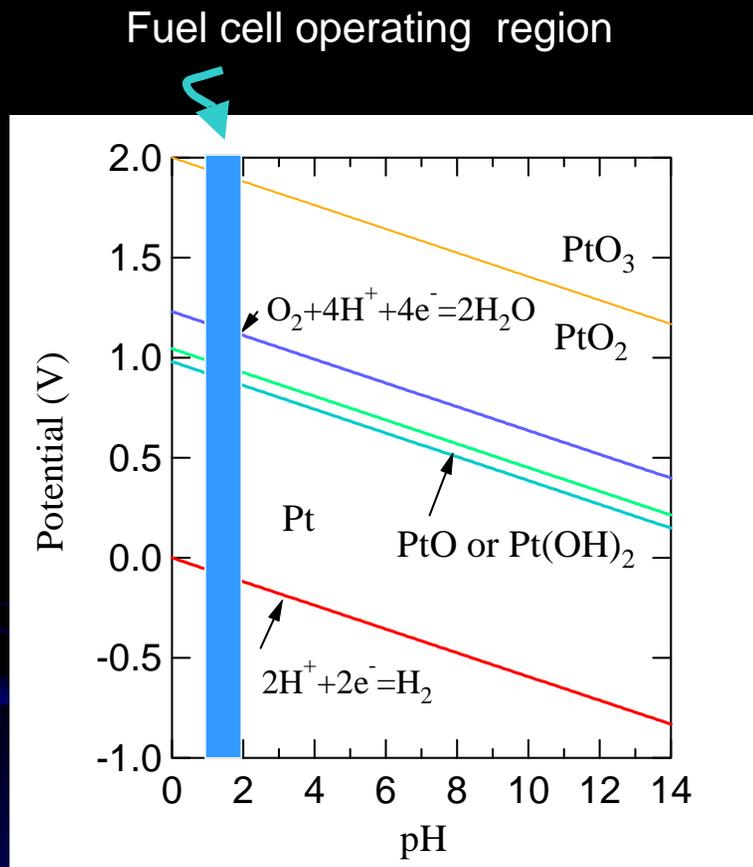
- Surface morphology
- Intermediate species
- Electronic state of platinum

Cathode

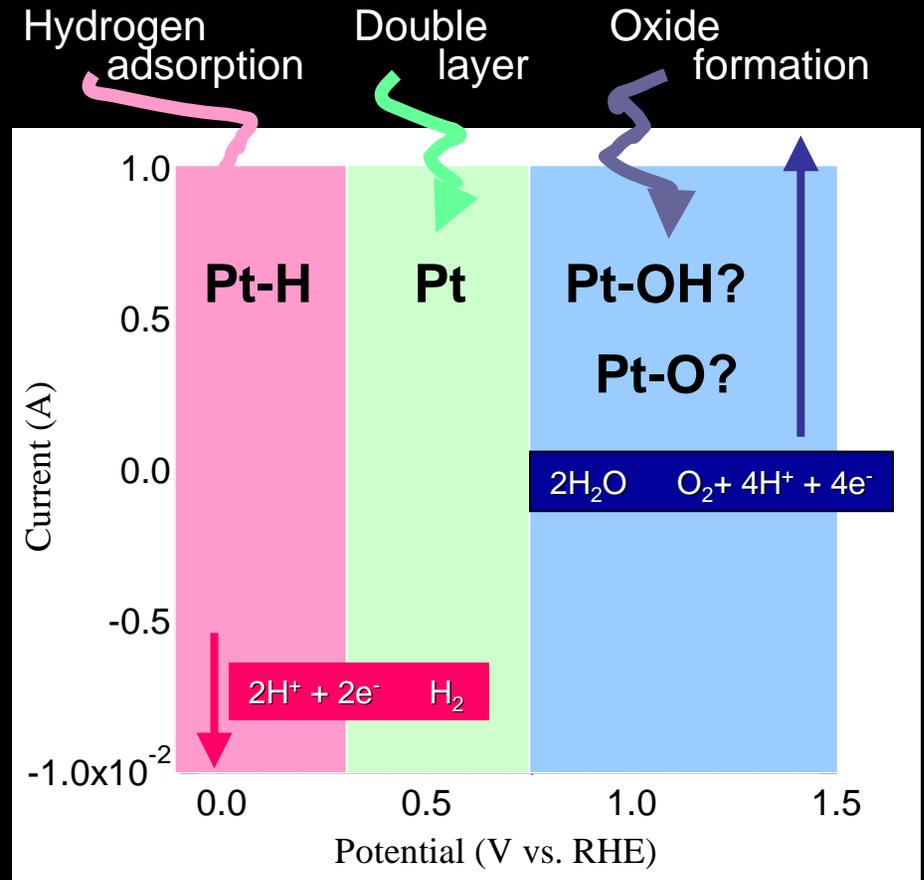


Current vs. Voltage (Polarization) curve for PEFCs and DMFCs

Stability of platinum in aqueous systems



The potential - pH equilibrium diagram for the system platinum - water

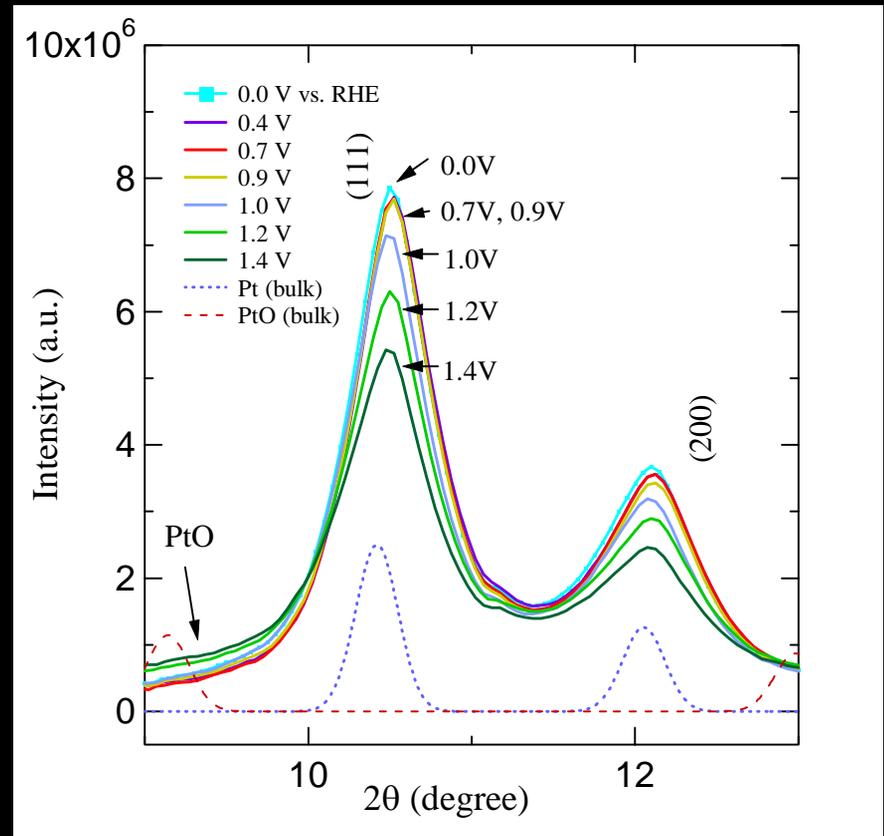
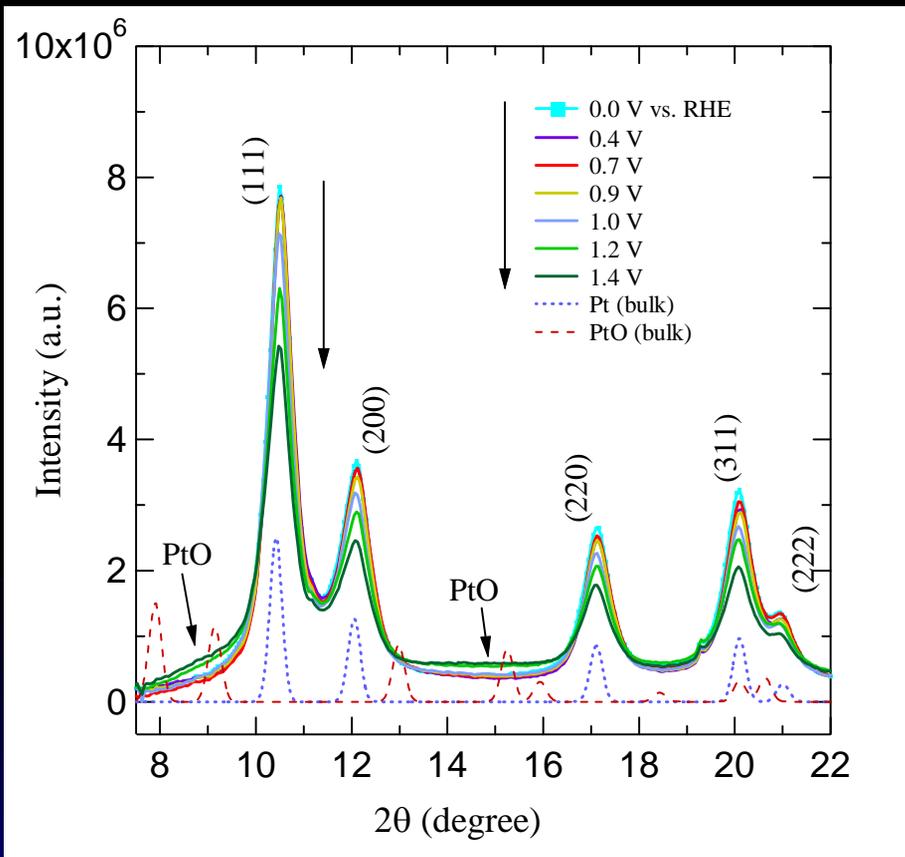


Cyclic voltammogram for carbon supported platinum nanoparticles in 0.5 M H_2SO_4

In situ XRD and XAFS measurements

- Platinum nanoparticles (supported on a carbon)
 - ca. 3 nm, 50 wt% - Pt loading
- Potential control
 - Home made three electrode electrochemical cell
 - 0.5M H₂SO₄ electrolyte
 - Potentiostatic mode
- In situ XRD BL16XU
 - Photon energy 30 keV ($\lambda = 0.041\text{nm}$)
 - Transmission mode, Imaging plate
- In situ XAFS BL16B2
 - L_3 and L_2 absorption edges
 - Transmission mode

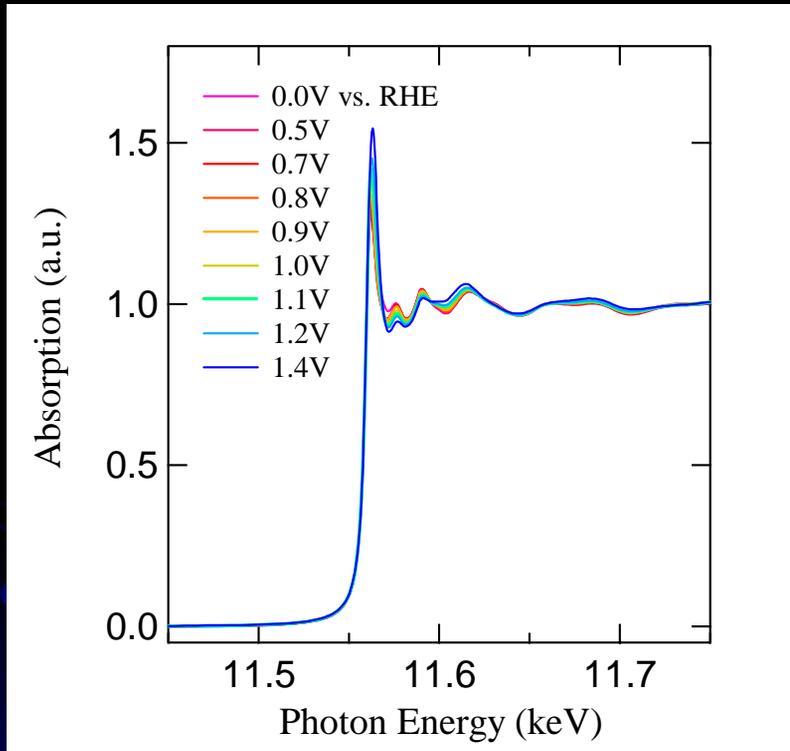
In situ x-ray diffraction



The potential dependence of x-ray diffraction patterns for carbon supported platinum nanoparticles

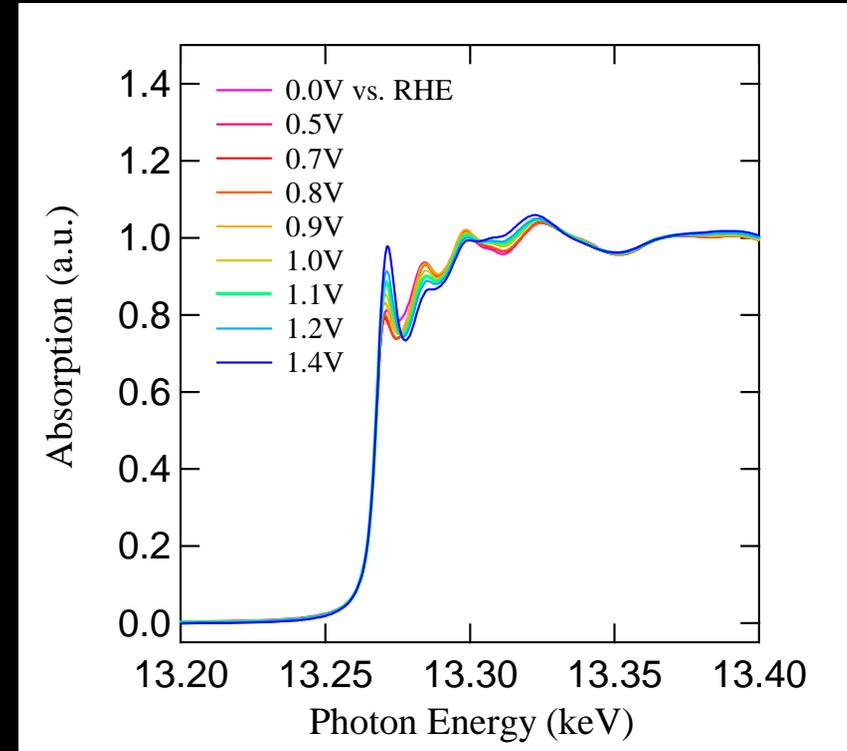
In situ x -ray absorption spectroscopy

L_3 absorption edge



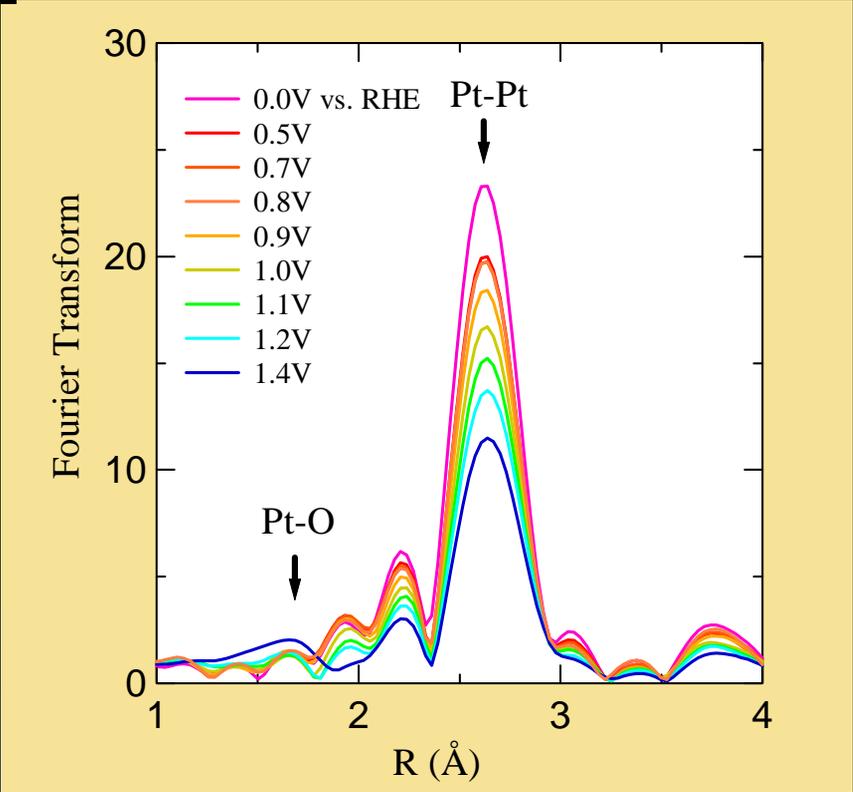
The potential dependence of XAS spectra at the L_3 absorption edge

L_2 absorption edge

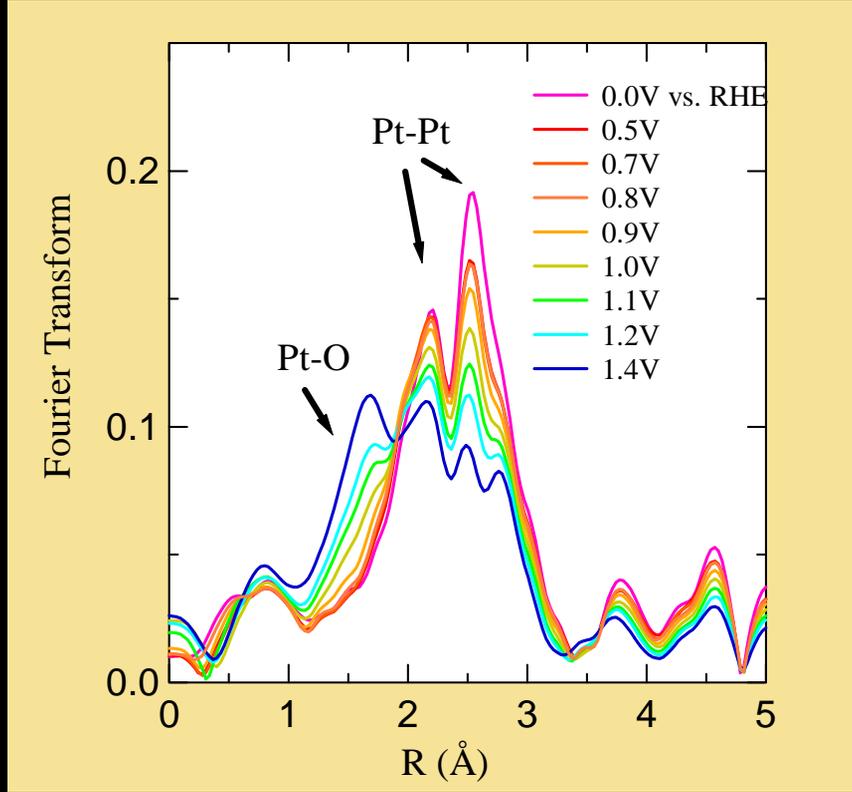


The potential dependence of XAS spectra at the L_2 absorption edge

Fourier transform of Pt L₃ EXAFS



The k^3 -weighted Fourier transform of Pt L₃ EXAFS

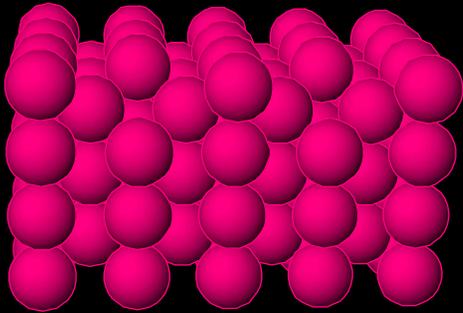


The k -weighted Fourier transform of Pt L₃ EXAFS

Structural models for the platinum nanoparticle surface

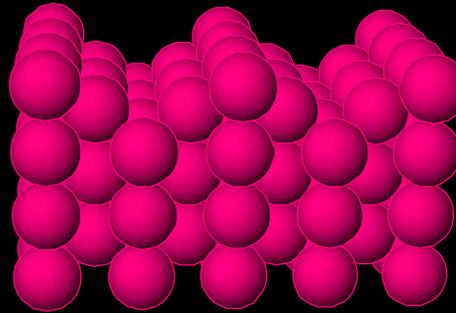
0.5 ~ 0.7 V

Clean Pt surface
(Double layer region)



cf. Pt-O distance 2.58Å (bulk PtO₂)

Surface reconstruction

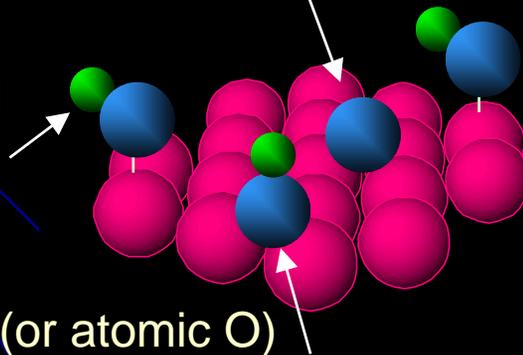


on-top site Pt-OH
~ 2.02Å

hollow site Pt-O
~ 2.06Å

0.8 ~ 1.0 V

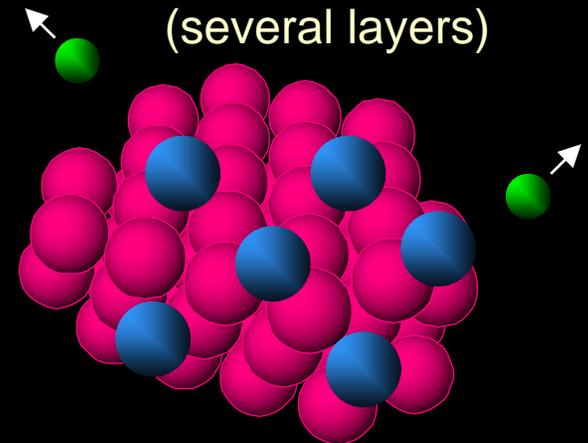
Irreversible OH (or atomic O)
adsorption



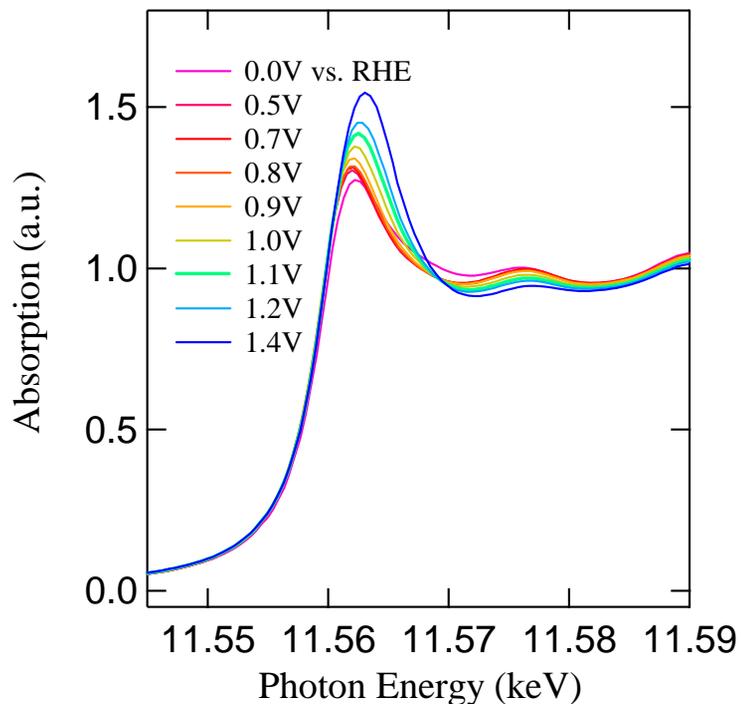
bridge site Pt-OH
~ 2.26Å

1.1 ~ 1.4 V

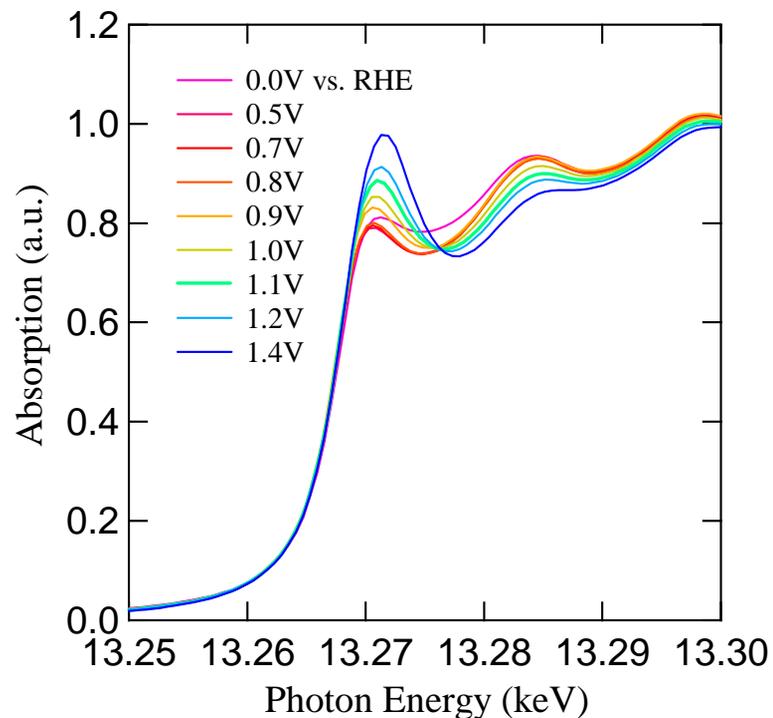
Amorphous like PtO_x
(several layers)



XANES spectra

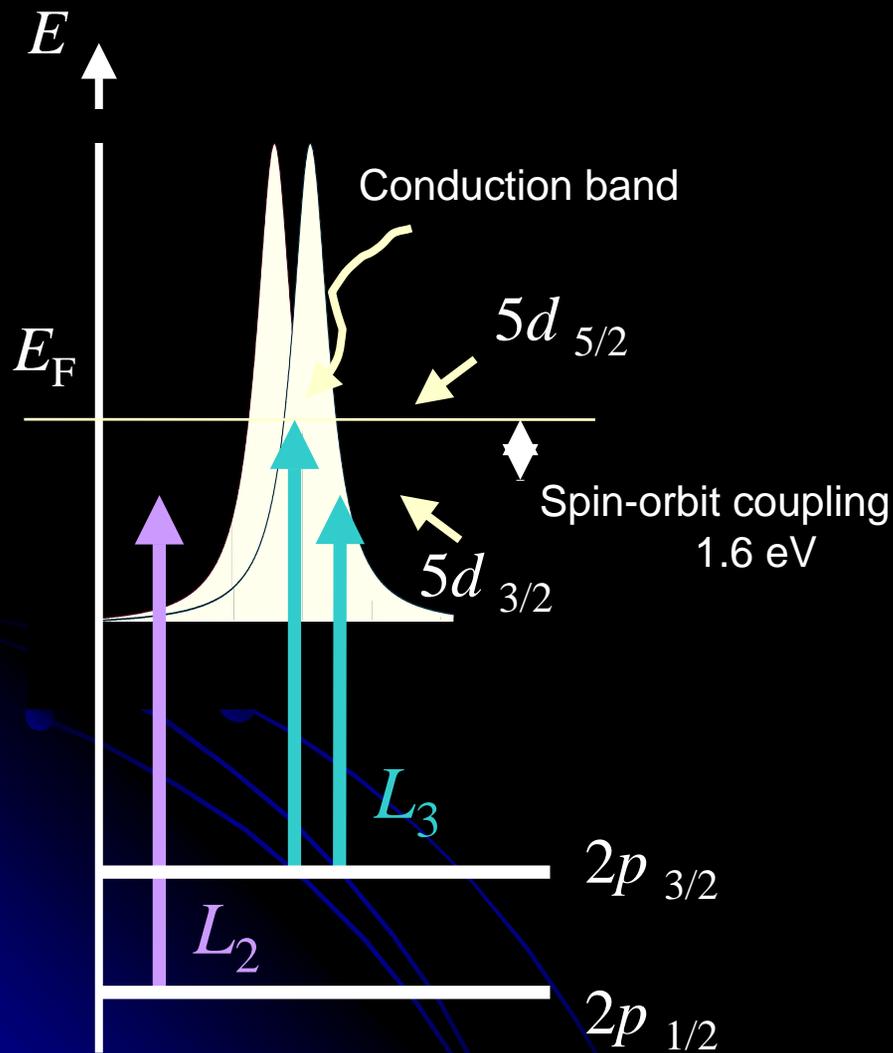


The potential dependence of XANES spectra at the L₃ absorption edge



The potential dependence of XANES spectra at the L₂ absorption edge

L_3 and L_2 absorptions in platinum



The fractional change in the number of unoccupied d states from that of bulk Pt

$$f_d = \frac{\Delta h_T}{h_{\text{TPt}}} = \frac{(\Delta A_3 + 1.11\Delta A_2)}{(A_3 + 1.11A_2)_{\text{Pt}}}$$

$$h_T = (1 + f_d) h_{\text{TPt}}$$

A_i : edge area for the i th edge

$$\Delta A_i = A_{\text{isample}} - A_{\text{iPt}}$$

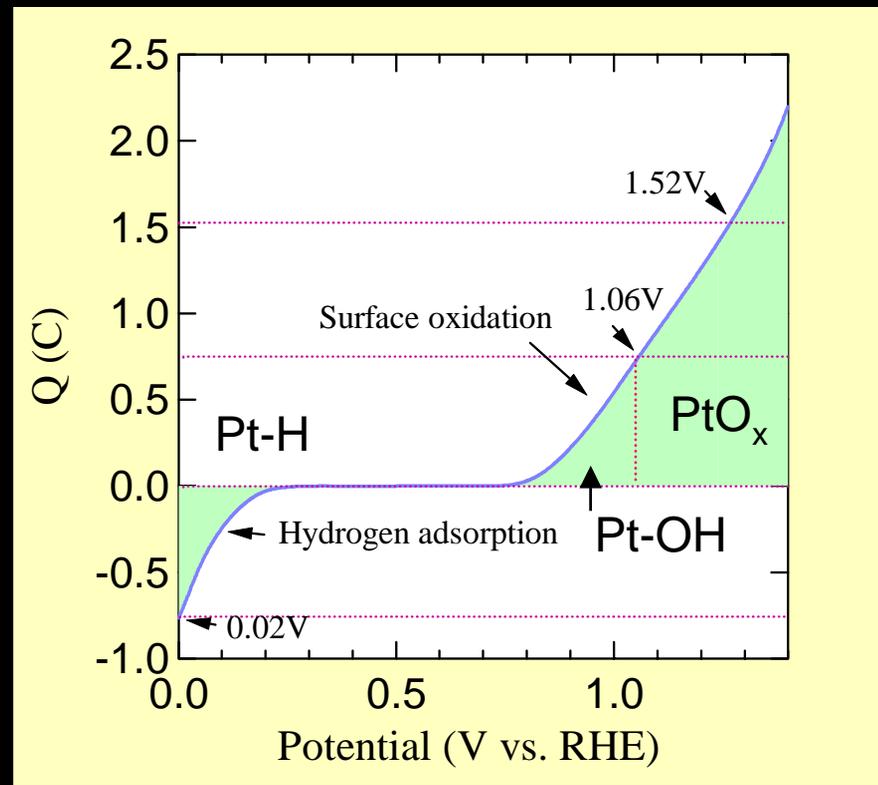
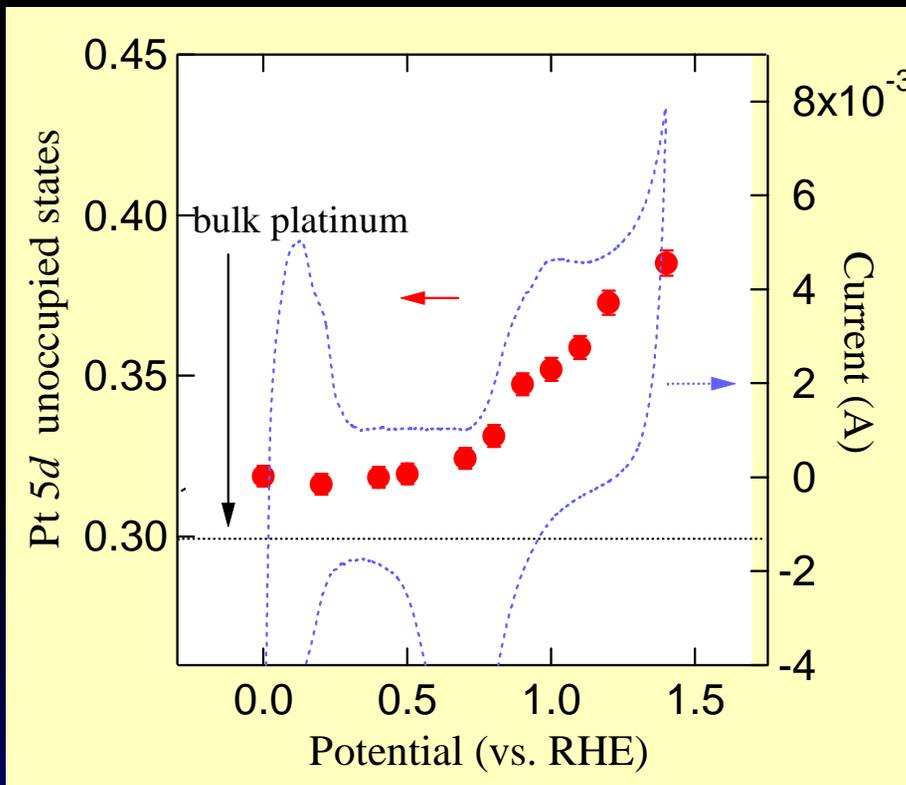
h_T : total number of unoccupied d states

$$\Delta h_T = h_{\text{Tsample}} - h_{\text{TPt}}$$

$$h_{\text{TPt}} = 0.30 \text{ (tight-binding + spin-orbit coupling)}$$

Electronic states

Unoccupied states in platinum 5d orbitals



The potential dependence of unoccupied states in platinum 5d orbitals

The total charge due to the hydrogen adsorption and the surface oxide formation estimated from the cyclic voltammogram

Summary

In situ XRD and XAFS studies clearly showed the followings :

In the oxygen reduction reaction potential region....

- Surface reconstruction, adsorption of oxygen species, and formation of platinum oxides
 - Irreversible OH adsorption (0.8 ~ 1.0V)
 - Pt-OH at on-top site
 - Pt-O at 3 fold or 4 fold hollow sites
 - Surface oxide formation (1.1 ~ 1.4 V)
 - amorphous like PtO_x (several layers)
- Charge transfer from platinum
 - The number of unoccupied states in Pt 5*d* orbitals linearly depends on the potential and the coverage of oxygen species

The formation of surface oxygen species may significantly reduce the catalytic activity of platinum on oxygen reduction reaction