白金系燃料電池触媒の電子状態解析
－共鳴非弾性X線散乱で探る酸素吸着特性－

Electronic Structure of Pt-based Fuel Cell Catalysts Studied by Resonant inelastic X-ray scattering

Key words Pt alloy, cathode catalyst, Resonant inelastic X-ray scattering, Fuel cell

共鳴非弾性X線散乱で白金系燃料電池触媒の酸素吸着エネルギーのその場測定が可能に

Resonant X-ray inelastic scattering is an *in-situ* probe of Pt-O bonding for Pt-based catalysts.

固体高分子形燃料電池カソード触媒に適用されるPtナノ粒子触媒表面のPt価電子帯の電子状態密度を共鳴非弾性X線散乱によって観察した。その結果、触媒表面Ptと吸着酸素の結合エネルギーを3.5eVと見積もることができた。
Pt-Co合金、Pt/Auコアシェル触媒においては、Ptと吸着酸素の結合エネルギーがそれぞれ2.5eV、3.0eVであることを見出した。
Pt-Co合金、Pt/Auコアシェル触媒はPt触媒よりも高い比活性を示すことから、酸素との結合が適度に弱いことが、Pt-Co合金触媒、コアシェル触媒における活性向上の原因であることを示唆している。

Using resonant inelastic X-ray scattering, oxygen adsorption energy to Pt-based catalysts was found to be 2.5, 3.0 and 3.5 eV for Pt-Co alloy, Pt/Au core shell and Pt catalysts. Combined with specific activity, these results indicate moderately weak binding energy of oxygen is essential for high performance of Pt-based catalysts.

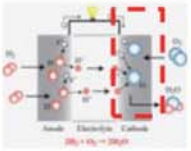
Introduction

Polymer electrolyte fuel cell (PEFC)

Challenge to produce a clean energy, which can reduce CO_2 emission.

FC vehicle

Co-generation home power system "Ene Farm"



Operating at low temperatures (80-100°C)

4-electon reaction
$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$ (1.23 V)

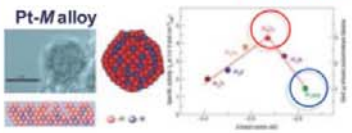
Reaction rate: Anode > Cathode

Cathode catalyst is important to improve the performance of PEFC.

Pt-based cathode catalysts

Improvement of the catalysts is strongly desired! high activity!

Pt-*M* alloy



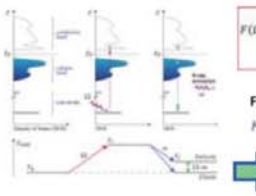
V. R. Satemkovic *et al.*, Nat. Mater. 6, 241 (2007).

Purpose of this study

To understand the changes of the electronic structure of Pt nanoparticles under *in-situ* condition of PEFC

Resonant Inelastic X-ray Scattering (RIXS)

Principle and Experimental



Kramers-Heisenberg formula

$$F(\Omega,\omega) = \sum_f \left| \sum_i \frac{\langle f|T|i\rangle\langle i|T|g\rangle}{E_g + \Omega - E_i - i\Gamma_i} \right|^2 \times \delta\left(E_g + \Omega - E_f - \omega\right)$$

A. Kotani and S. Shin, Rev. Mod. Phys. 73, 203 (2001).

For band model

$$F(\Omega,\omega) \propto \int d\varepsilon \frac{\rho(\varepsilon)\rho'(\varepsilon+\Omega-\omega)}{(\varepsilon-\varepsilon_k-\omega)^2+\Gamma^2}$$

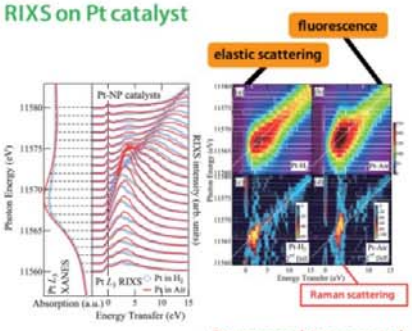
Observation of joint density of states!

Samples Nanoparticles on carbon support
Pt(2.5nm), Pt-Co alloy (6.1nm), *Pt/Au core shell (5.0nm)
*supplied by Prof. Inaba's group at Doshisha University

RIXS
SPring-8 BL11XU, Japan
Edge: Pt $2p$ (11.56 keV)
Resolution: 0.7eV
Atmosphere: 1atm H_2 or air

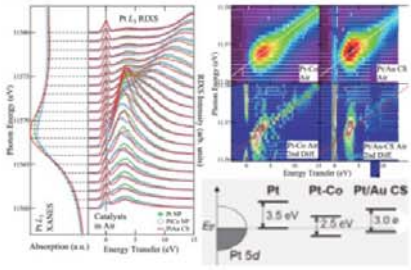
Results and discussion

RIXS on Pt catalyst

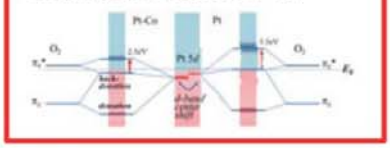


Raman peak is generated by oxygen adsorption.

RIXS on Pt-Co and Pt/Au core shell



Energy diagram (e.g. Pt vs Pt-Co)



→ The Raman shift corresponds to the strength of interaction between Pt 5d-O 2pπ states.

Conclusions

#Using Pt L-edge RIXS, we can measure the surface Pt-O bond strength of Pt-based catalysts, which is more closely related to the catalyst performance than the d-band center.

#Using RIXS technique we will be able to re-plot the volcano plot as a function of Pt-O bond strength in the near future.

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