# *in situ* and *operando* analysis of electronic structure in carbon-based cathode catalysts for polymer electrolyte fuel cells

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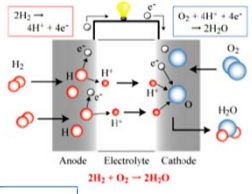
## Background

### Polymer Electrolyte Fuel Cell (PEFC)

- High energy conversion efficiency (83%)
- Clean energy (Products: $H_2O$ only)

- Slow oxygen reduction reaction (ORR).
- Using expensive Pt/C catalysts.

**Non-Pt cathode catalysts**





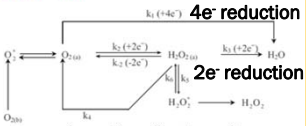
### Carbon-based cathode catalysts

G. Wu *et al.*, Science **332**, 443 (2011).

J. Ozaki *et al.*, Electrocim. Acta, **55**, 1864 (2010).

- Abundant resources
- Low cost
- Low activity

**ORR active sites should be elucidated to improve the activities of carbon-based catalysts.**




Md.R. Miah *et al.*, Electrochim. Acta **56**, 285 (2010).

### Proposed ORR active site

| | |
|---|---|
| Carbon sites | ・Zig-zag edge<br>・Pyrrolic-N, etc. |
| Metal sites | ・Metal-$N_4$ sites<br>・Surface M-N sites, etc. |

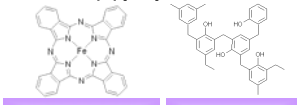
### Objective

To observe the electronic structure of carbon-based cathode catalysts under PEFC working conditions to discuss the ORR active site.

## Catalyst preparation

### FePc-based catalysts

Multi-step pyrolysis method



Iron phthalocyanine (FePc) + Phenolic resin (PhRs)

→ Mix — Fe: 2.3 wt.%

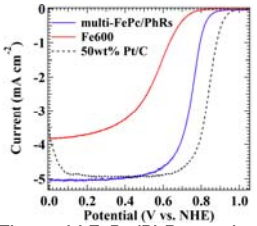
→ Heat Treatment(HT) & Acid Washing (AW) — @ 600°C in $N_2$ flow for 5 h (Fe600)

→ HT & AW — @ 800°C, $NH_3$, 1 h

→ HT — @ 1000°C, $NH_3$, 1 h

→ Multi-FePc/PhRs


TEM image

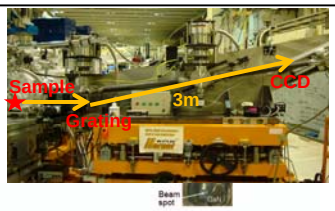


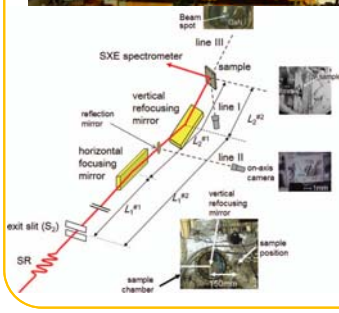

The multi-FePc/PhRs catalyst shows a high ORR activity close to the Pt/C catalyst.

Y. Nabae *et al.*, ACS 246th meeting preprint (2013).

## Experimental

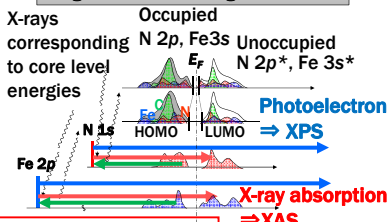
### Valence electronic states analysis by ultra high resolution soft X-ray emission (SXE) spectrometer




- Element specific electronic states near Fermi level.
- High resolution ・Light elements

X-rays corresponding to core level energies

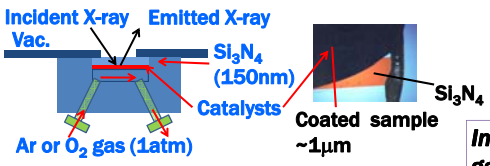



**X-ray emission ⇒SXES**

- Ultra high resolution soft X-ray emission spectrometer @ BL07LSU of SPring-8, Japan.
- Fe 2*p* edge ・Total energy resolving power: ~260 meV @ 710eV ($E/\Delta E$ = ~2700)
- Room temperature

Y. Harada *et al.*, Rev. Sci. Instrum. **83**, 013116 (2012).

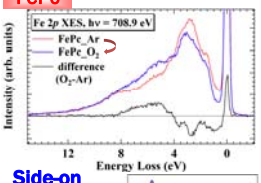
### *in situ* cell for SXE



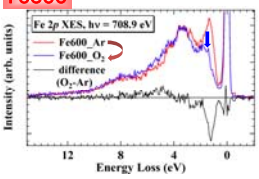

**Condition of ink coating**
Nafion 50μl, Ethanol 50μl, Water 150μl,Catalyst 5.0mg
4μl of Ink was coated by drop casting technique.

***In situ* cell separates ambient gas condition from vacuum.**

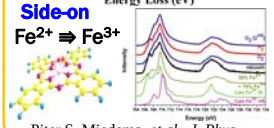
FePc




Fe600




Side-on $Fe^{2+} \Rightarrow Fe^{3+}$

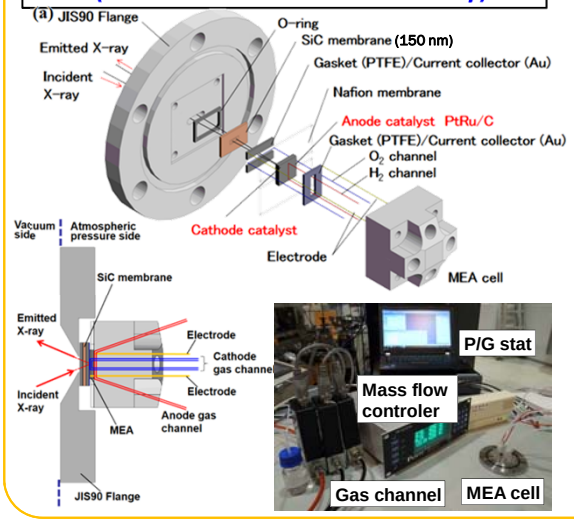


Piter S. Miedema, *et al.*, *J. Phys. Chem. C* **115**, 25422 (2011).

Fe600_Ar → Fe600_$O_2$

**FePc**: Electron donation from Fe (*d*-band) to oxygen ($\pi^*$ orbital) => $O_2$ adsorption in side-on configuration (4e⁻ reduction) by DFT calc.
**Fe600**: Electronic structure of Fe sites is modified by oxygen adsorption. => ORR active site?

### MEA (membrane electrode assembly) cell

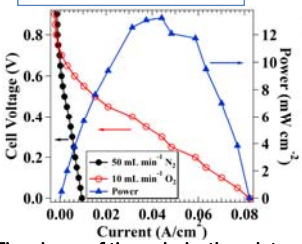






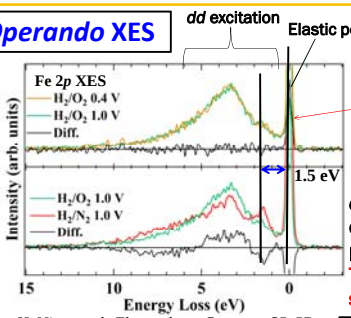
- Room Temperature
- Potential: 1 V, 0.4 V

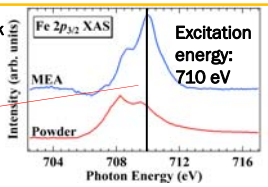
Gas pressure: 1bar
Flow rates:
$H_2/N_2$=10 /50 (ml/min),
$H_2/N_2$-$O_2$=10/45-5 (ml/min)




The shape of the polarization plots of the MEA cell was similar to that of a standard fuel cell, demonstrating that the system can stably produce electricity by $H_2$ and $O_2$ gases.

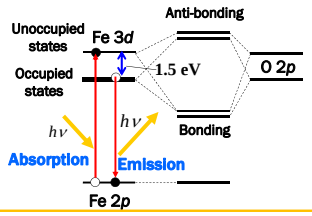
### *Operando* XES



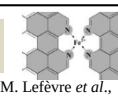

*dd* excitation peak at 1.5 eV is characteristic for Fe species with planar ligand coordination.
The intensity of the 1.5 eV peak is significantly reduced by $O_2$ adsorption.

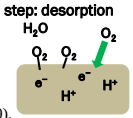
H. Niwa *et al.*, Electrochem. Commun. **35**, 57-60 (2103).




**ORR mechanism**

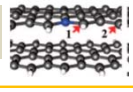
Fe-Nx site






M. Lefèvre *et al.*, Science **324**, 71 (2009).

C-N site



T. Ikeda *et al.*, J. Phys. Chem. C **112**, 14706 (2008).

## Conclusion

- *in situ* cell and MEA cell system which enables *operando* soft X-ray emission measurements under polymer electrolyte fuel cell (PEFC) working conditions have been developed.
- We have successfully observed the electronic structure of iron in an iron phthalocyanine-based catalyst under various working conditions and found the existence of an oxidized iron component active for oxygen adsorption, which is unexpected from the previous *ex situ* results for powder samples.
- The experimental system can also be applied to observe the electronic structure of solid-gas and solid-liquid interfaces under potential control, such as PEFC anode catalysts, metal-air battery electrodes and lithium-ion battery electrodes.

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