Oxygen reduction in PEM fuel cell conditions: Heat-treated macrocycles and beyond

J. P. Dodelet

INRS-Énergie et Matériaux
C. P. 1020, Varennes, Québec, Canada, J3X 1S2
dodelet@inrs-ener.uquebec.ca

Collaborators

Michel Lefèvre (INRS)
Sébastien Marcotte (INRS)
Frédéric Jaouen (Royal Inst. of Technology, Sweden)

Prof. Patrick Bertrand (Université Catholique de Louvain, Belgium)

Prof. Göran Lindbergh (Royal Inst. Of Technology, Sweden)

New Orleans workshop
March 21 03.

PEM Fuel Cells

Anode : $2\ H_2 \rightarrow 4\ H^+ + 4\ e^-$

Electrolyte : Perfluorinated polymer – $SO_3\ H$

Cathode : $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

Acidic Medium (pH ~ 1) Low Temperature Fuel Cell (80°C)

↓

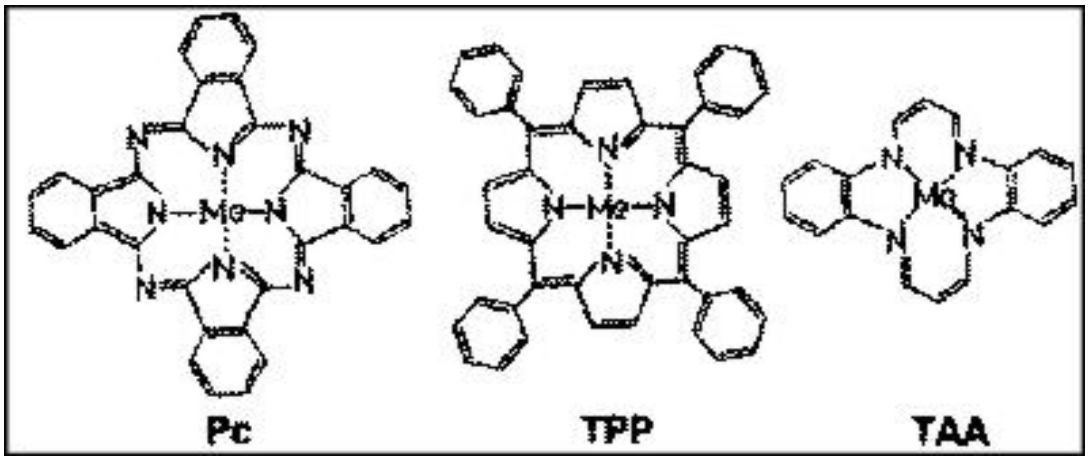
Pt- based Anode and Cathode Catalysts

Pt is not abundant and expensive

Alternatives to Pt

- At the anode : probably not
- **At the cathode: Pyrolyzed N_4 chelates adsorbed on C**

Pyrolyzed N_4 Chelates adsorbed on C



Pyrolysis temperature : 500 – 700 °C

- Low temperature (LT) catalytic site
- **Proposed structure of the catalytic site : FeN_4 /C**

Pyrolysis temperature ≥ 800°C

- High temperature (HT) catalytic site
- **Structure of the catalytic site still unknown but information**
- Not necessary to start from N_4 chelates to obtain HT catalytic site

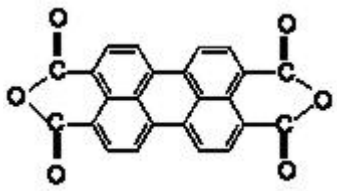
Fe acetate + Polyacrylonitrile + C $\xrightarrow{(900°C)}$ HT catalytic site

Information about the HT catalytic site

1. The simultaneous presence of C, N, and Fe is necessary to obtain the catalytic site

C

Carbon black
Activated carbon
Carbon precursor (PTCDA)

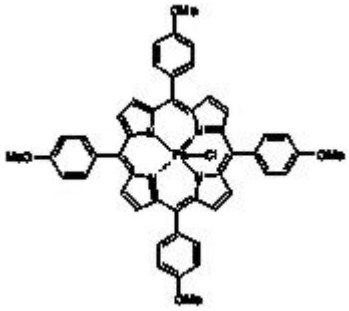


N

NH_3
CH_3CN
N-containing molecules (PAN, N_4Chelates, etc…)

Fe

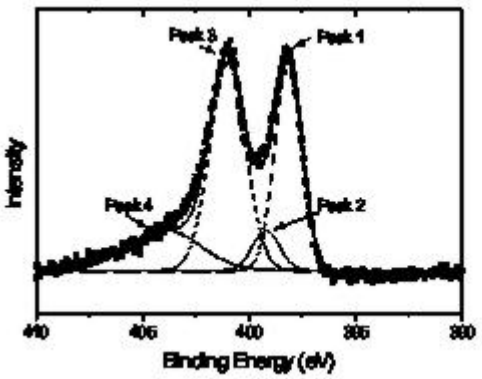
Fe salt (Fe acetate)
Ferrocene
FeN_4 chelate, like ClFeTMPP

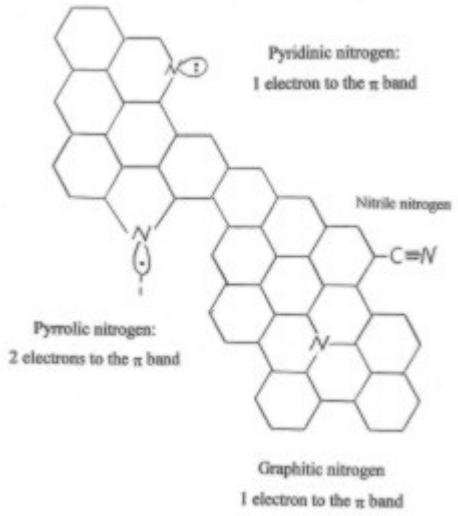


Information about the HT catalytic site (continue)

2. From X-ray Photoelectron spectroscopy (XPS)

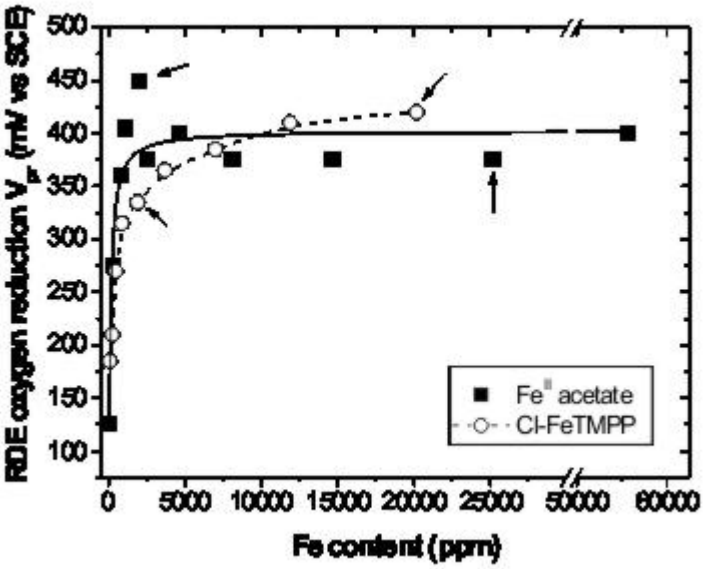
- Fe is oxidized
- Only N of pyridinic type is important





Information about the HT catalytic site (continue)

3. **The catalytic activity rises very quickly with the Fe content.**



4. **Saturation effect at :**
   - ~ 0.5 wt% Fe with Fe acetate
   - ~ 2.0 wt% Fe with ClFeTMPP

   Higher Fe contents produce Fe metal -Fe carbide aggregates surrounded with C. These aggregates are catalytically inactive.

Obtain more information on HT catalytic site using ToF SIMS

Principle of ToF SIMS experiments

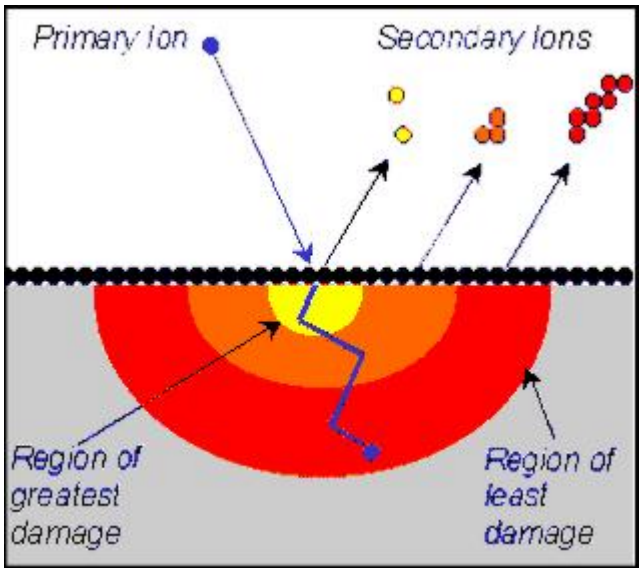
Primary beam of Ga^+ at 15 keV

Analysis between 0-1000 amu

Dose below 10^{12} ions/cm^2 at the first analyzed layer

Mass resolution :

- (m/Δm) of about 4000 at the Si mass (m)
- 0.007 amu



Preparation of Catalysts for ToF SIMS Experiments

Catalysts were prepared with PTCDA as carbon precursor:

- <u>without inactive Fe metal-Fe carbides aggregates</u>
  0.2 wt% Fe with Fe acetate
  0.2 wt% Fe with ClFeTMPP

- <u>with a large range in the catalytic activity</u>

$$\text{PTCDA} \xrightarrow{(900^{\circ}C + NH_3)} \text{pyrolyzed-PTCDA} \downarrow$$

similar to a carbon
but with N in its structure

$$\text{pyro-PTCDA} + \text{Fe precursor} \xrightarrow{(T \text{ variable} + Ar)} \textbf{Type II Catalysts}$$

(Type II Fe (0.2) FeAc)
(Type II Fe (0.2) FeTMPP)
↓
with large range
in catalytic activity

The goal is to <u>look for similarities</u> between:

- changes in the catalytic activity for oxygen reduction
- changes in abundance of typical ions in ToF SIMS spectra
  Only ions of the type Fe N_x C_y^+ are interesting.

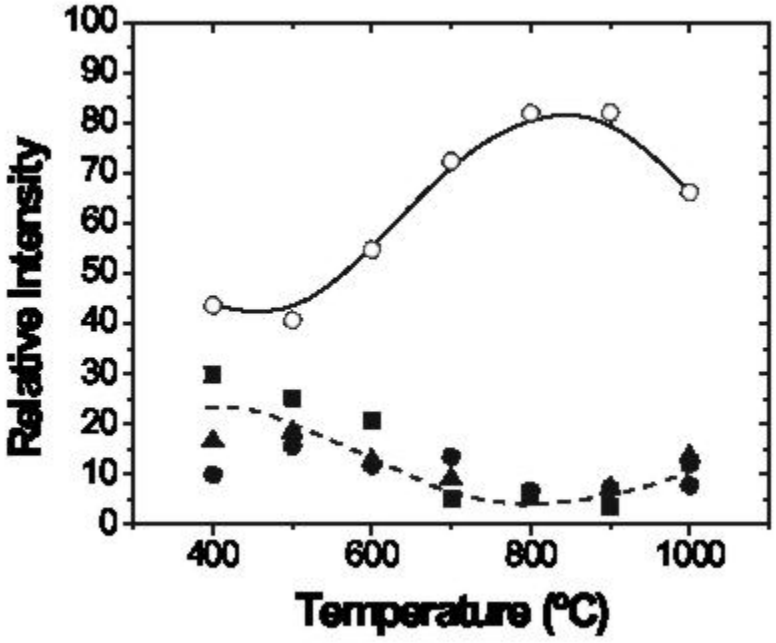
Type II (0.2) FeAc catalysts

Relative abundance in % of $FeN_xC_y^+$ ions as a function of the pyrolysis temperature

Ions	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	1000 °C
$FeNC^+$	28.27	23.82	17.08	0.76	5.76	1.77	2.50
$FeNC_2^+$	0.78	0.00	1.61	2.63	0.00	0.40	2.50
$FeNC_3^+$	0.78	1.41	2.06	1.82	0.63	1.33	7.50
FeN_2C^+	14.94	7.78	4.80	2.38	1.56	2.56	3.75
$FeN_2C_2^+$	1.78	4.70	1.44	0.53	0.63	0.83	0.00
$FeN_2C_3^+$	0.40	1.26	0.53	1.85	0.00	0.93	12.50
$FeN_2C_4^+$	23.92	26.93	46.95	64.89	78.38	76.38	49.86
$FeN_2C_5^+$	1.10	0.00	0.35	2.08	0.00	0.93	0.00
$FeN_2C_6^+$	1.47	0.00	0.64	0.53	1.32	0.40	0.00
FeN_3C^+	1.75	4.97	5.68	1.32	0.00	0.00	2.78
$FeN_3C_2^+$	0.00	1.36	0.00	0.00	1.32	0.42	0.00
$FeN_3C_3^+$	1.78	2.98	1.91	1.82	0.00	0.81	2.78
$FeN_3C_4^+$	0.00	1.10	0.00	1.06	0.00	0.00	0.00
$FeN_3C_5^+$	2.33	0.37	0.29	0.53	1.56	0.85	0.00
$FeN_3C_6^+$	2.64	0.47	0.35	0.76	1.56	0.00	2.78
$FeN_3C_7^+$	0.00	0.00	0.00	0.00	0.00	0.42	0.00
$FeN_3C_8^+$	0.81	3.98	3.36	2.89	0.00	1.67	1.25
$FeN_3C_9^+$	7.33	3.29	1.16	0.76	0.63	3.06	4.03
FeN_4C^+	3.01	0.68	1.12	1.32	0.00	0.42	0.00
$FeN_4C_2^+$	0.34	1.31	1.67	2.38	0.00	0.93	0.00
$FeN_4C_3^+$	0.34	1.89	0.00	0.76	1.56	0.42	0.00
$FeN_4C_4^+$	0.72	0.52	1.08	0.00	0.00	0.42	2.50
$FeN_4C_5^+$	0.40	0.37	2.18	1.32	1.56	0.00	0.00
$FeN_4C_6^+$	0.00	0.00	0.00	0.53	0.00	0.40	1.25
$FeN_4C_7^+$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$FeN_4C_8^+$	5.08	8.05	5.45	4.17	1.88	4.64	4.03
$FeN_4C_9^+$	0.00	1.72	0.29	1.60	0.00	0.00	0.00
$FeN_4C_{10}^+$	0.00	0.68	0.00	0.00	0.00	0.00	0.00
$FeN_4C_{11}^+$	0.00	0.00	0.00	1.32	0.00	0.00	0.00
$FeN_4C_{12}^+$	0.00	0.37	0.00	0.00	1.67	0.00	0.00

Type II (0.2) FeAc catalysts

Relative intensity of
$\Sigma FeN_2C_y^+$ (○),
$\Sigma FeN_1C_y^+$ (■), $\Sigma FeN_3C_y^+$ (7), $\Sigma FeN_4C_y^+$ ( )
as a function of the pyrolysis temperature
Ions belonging to the N_2 family have the same origin:
a catalytic site of the FeN_2 type (HT catalytic site)



Ions belonging to the N_1, N_3, N_4 families have the same origin:
a catalytic site of the FeN_4 type (LT catalytic site)
These ions may be grouped together as:
$\Sigma FeN_1C_y^+ + \Sigma FeN_3C_y^+ + \Sigma FeN_4C_y^+$

Type II (0.2) FeAc catalysts

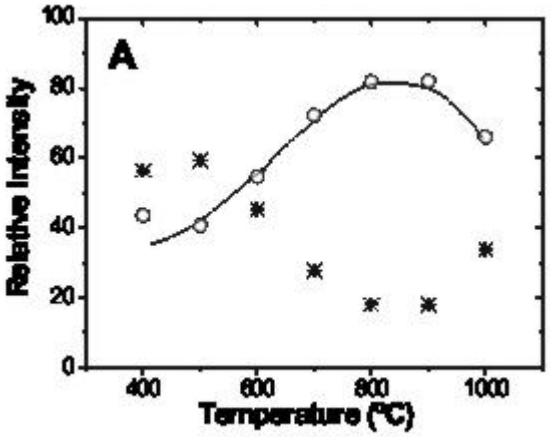
Relative intensity, as a function of the pyrolysis temperature, of :

(○) $\Sigma FeN_2C_y^+$ from **FeN_2/C**

(previously HT catalytic site)

(*) : $\Sigma FeN_1C_y^+ + \Sigma FeN_3C_y^+ + \Sigma FeN_4C_y^+$ from **FeN_4/C**

(previously LT catalytic site)



The two types of catalytic sites coexist at all temperatures

FeN_2/C reaches up to 80% of abundance at 800-900°C
FeN_2/C appears at the expense of FeN_4/C as the pyrolysis temperature rises.

Representative ions of both sites:
FeN_2/C: $FeN_2C_4^+$ up to 78%
FeN_4/C: $FeN_4C_8^+$ 5% (mean)

Type II (0.2) FeTMPP catalysts

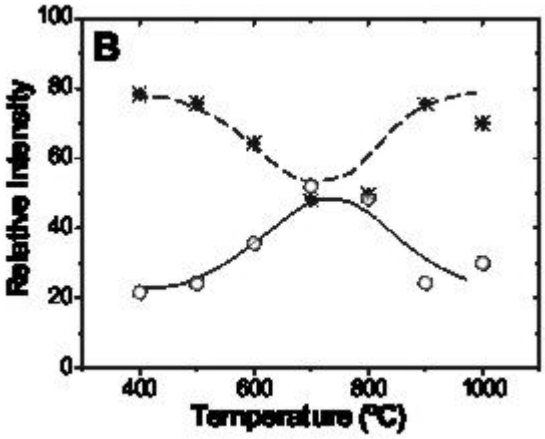
Relative intensity, as a function of the pyrolysis temperature, of :

(○) $\Sigma FeN_2C_y^+$ from FeN_2/C

(previously HT catalytic site)

(*) : $\Sigma FeN_1C_y^+ + \Sigma FeN_3C_y^+ + \Sigma FeN_4C_y^+$ from FeN_4/C

(previously LT catalytic site)



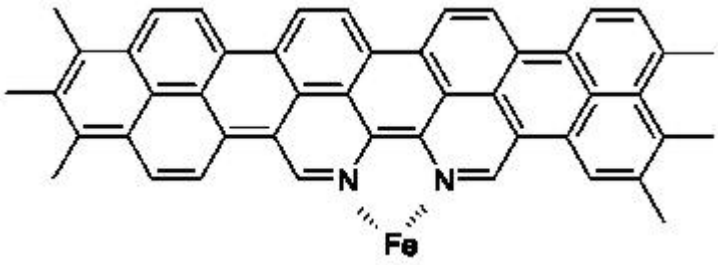
The two types of catalytic sites coexist at all temperatures

FeN_2/C reaches up 50% of abundance at 700-800°C.
FeN_2/C appears at the expense of FeN_4/C as the pyrolysis temperature rises.

Representative ions:
FeN_2/C: $FeN_2C_4^+$ up to 43%
FeN_4/C: $FeN_4C_8^+$ 9% (mean)

Origin of the ions of the $FeN_2C_y^+$ family

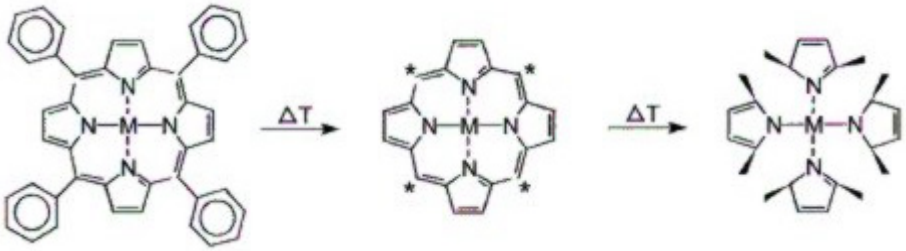
N has to be in a phenanthroline type structure



The remaining of
Fe coordination
is still unknown

FeN_2/C catalytic site

Origin of the ions of the $FeN_1C_y^+$, $FeN_3C_y^+$, $FeN_4C_y^+$ families



FeN_4/C catalytic site

Electrochemical measurements

and comparison between

electrochemical and ToF SIMS measurements

Type II (0.2) FeAc catalysts (variable: pyr. T)

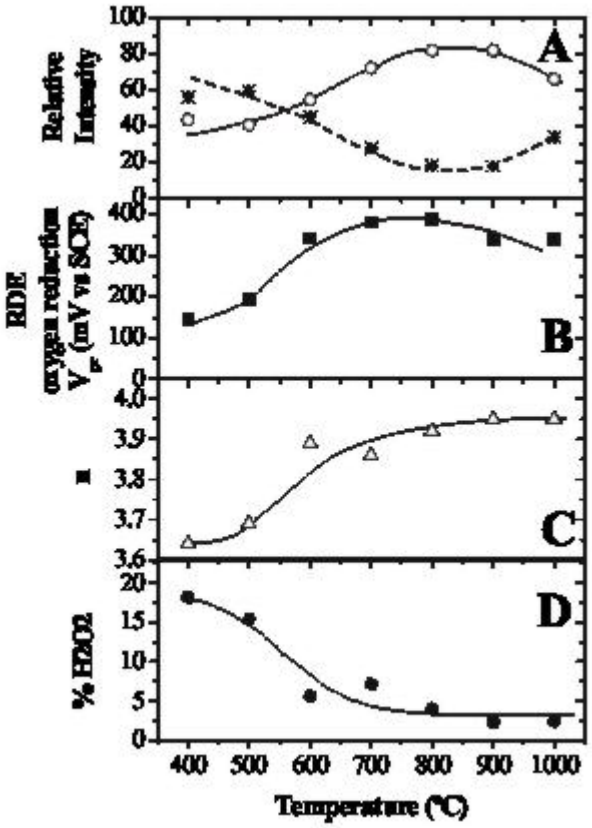
Comparison between :

[A] ToF SIMS abundance : o FeN_2/C and ∗ FeN_4/C

[B] RDE catalytic activity

[C] Number of transferred electrons

[D] $\%H_2O_2$ produced at -0.2V vs SCE



FeN_2/C is the most active site for O_2 reduction

Correlation between changes in FeN_2/C and n or % H_2O_2

Type II (0.2) FeAc catalysts (variable: Fe loading)

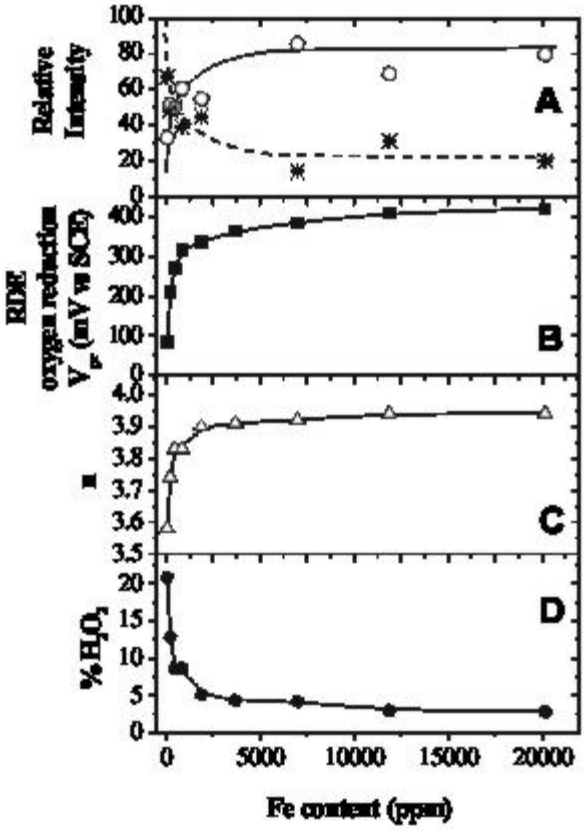
Comparison between :

[A] ToF SIMS abundance : o FeN_2/C and ∗ FeN_4/C

[B] RDE catalytic activity

[C] Number of transferred electrons

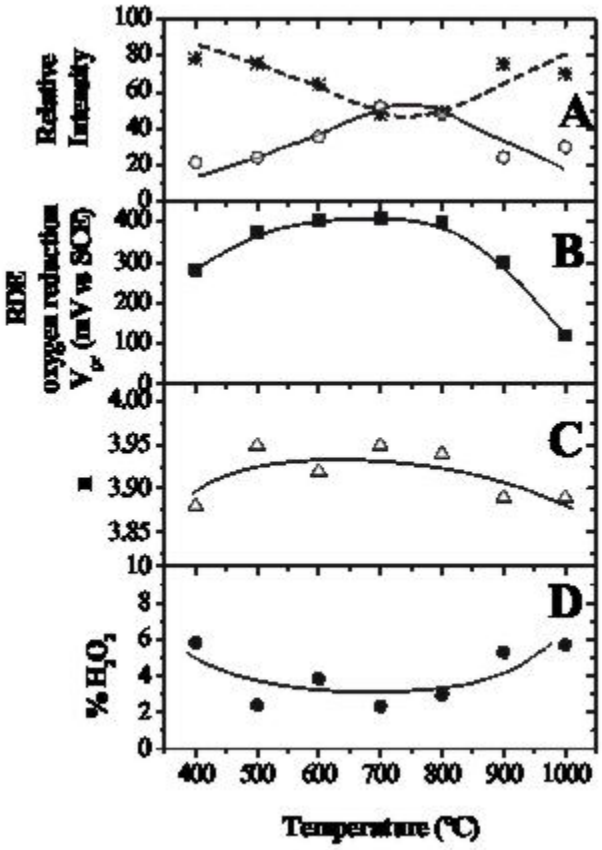
[D] $\%H_2O_2$ produced at -0.2V vs SCE



FeN_2/C is the most active site for O_2 reduction
Correlation between changes in FeN_2/C and n or % H_2O_2

Type II (0.2) FeTMPP catalysts (variable: pyr. T)

Comparison between :
[A] ToF SIMS abundance : o FeN_2/C and ∗ FeN_4/C
[B] RDE catalytic activity
[C] Number of transferred electrons
[D] %H_2O_2 produced at -0.2V vs SCE



FeN_2/C is the most active site for O_2 reduction
Correlation between changes in FeN_2/C and n or % H_2O_2

Conclusions for the **two N-containing catalytic sites**

- Two different catalytic sites - FeN_4/C and FeN_2/C- exist simultaneously at all pyrolysis temperatures in catalysts made with an iron salt (Fe acetate) or a Fe porphyrin (ClFeTMPP) as Fe precursors. Therefore, there is no LT or HT catalytic sites.

- The abundance of the FeN_2/C catalytic site goes through a maximum in the 600-900°C temperature range, at the expense of the other catalytic site: FeN_4/C.

- FeN_2/C is more active than FeN_4/C

- Changes of n and $\%H_2O_2$ follow changes in the relative abundance of FeN_2/C

- Active catalytic sites are characterized by
  $n > 3.9$ and $\%H_2O_2 < 5$, similar to 2 wt% Pt/C.
  It is suspected that some H_2O_2 produced by active Fe-based catalysts may arises from their C support at potentials more cathodic than 300 mV vs. SCE.

Besides FeN_2/C and FeN_4/C,
there is **a third catalytic site for O_2 reduction**

It was discovered when we analyzed the importance of the carbon support on the catalytic activity

Six commercial carbon supports
Printex XE-2
Norit SX Ultra
Ketjenblack EC-600 JD
Acetylene Black
Vulcan XC-72R
Blackpearls 2000

Two developmental carbon supports
HS300 (developmental graphite from Lonza)
RC1 (developmental carbon from Sid Richardson; N enriched)
RC2 (developmental carbon from Sid Richardson; reference)

One synthetic carbon support
Pyrolyzed PTCDA (900°C in [2:1:1] NH_3: H_2: Ar)

Fabrication of the catalysts

Procedure A

Carbon NT + 2000 ppm Fe as Fe acetate

↓ 900°C [2:1:1] NH_3: H_2: Ar

Carbon NT + FeAc 2K

Procedure B

1)

Carbon NT

↓ 900°C [2:1:1] NH_3: H_2: Ar

Carbon T

2)

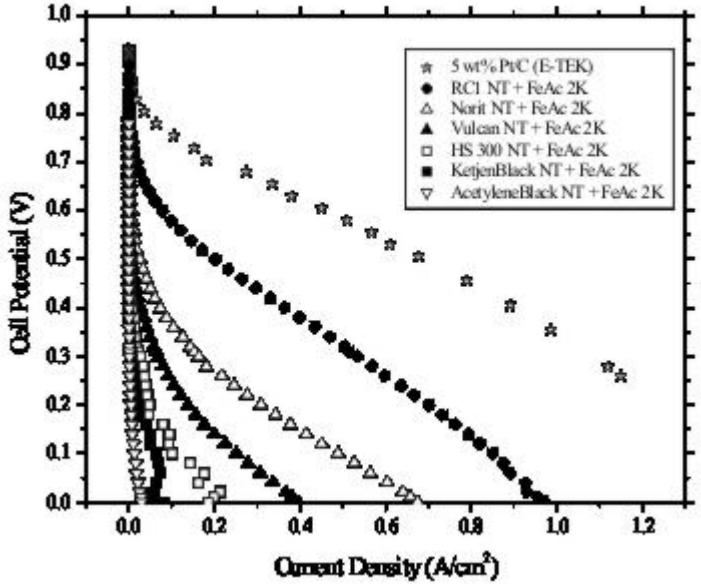
Carbon T + 2000 ppm Fe as Fe acetate

↓900°C [2:1:1] NH_3: H_2: Ar

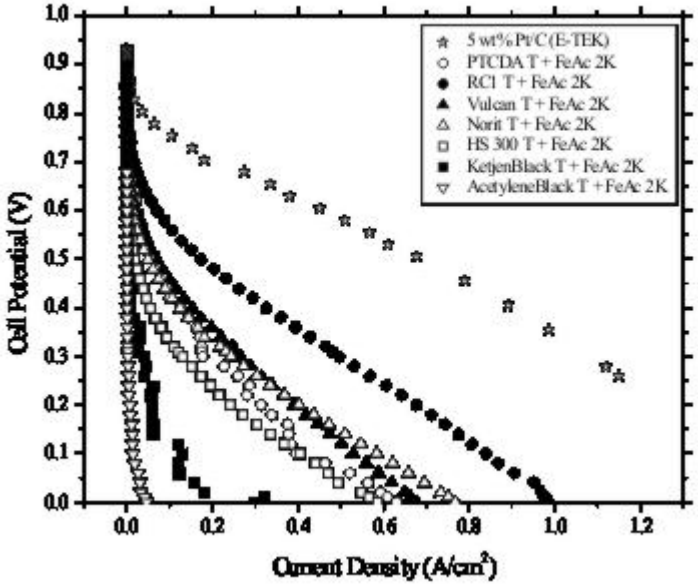
Carbon T + FeAc 2K

Catalytic activity in PEM fuel cells

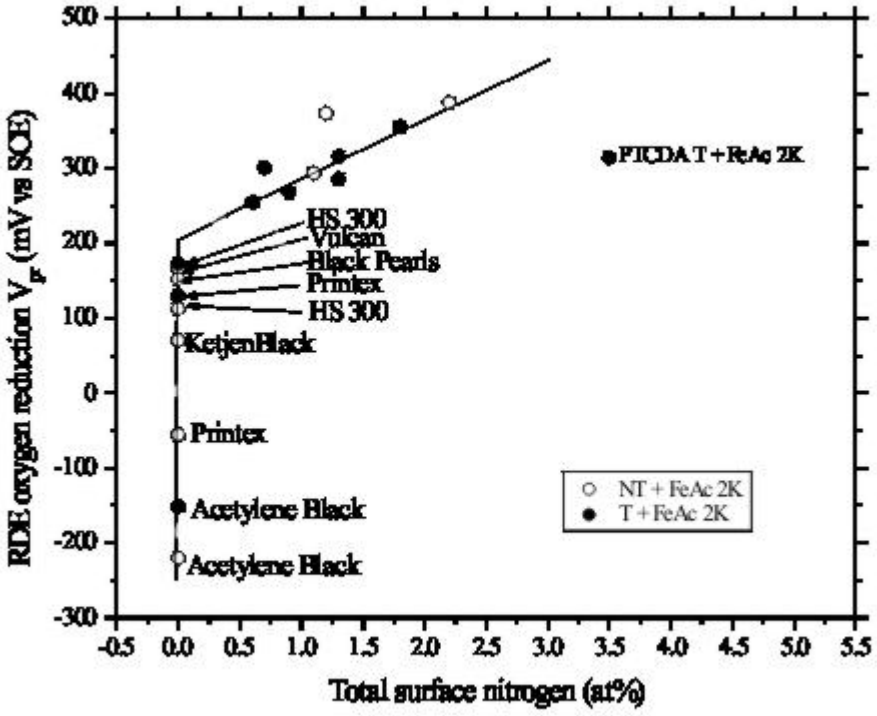
NT + FeAc 2K Catalysts



T + FeAc 2K Catalysts

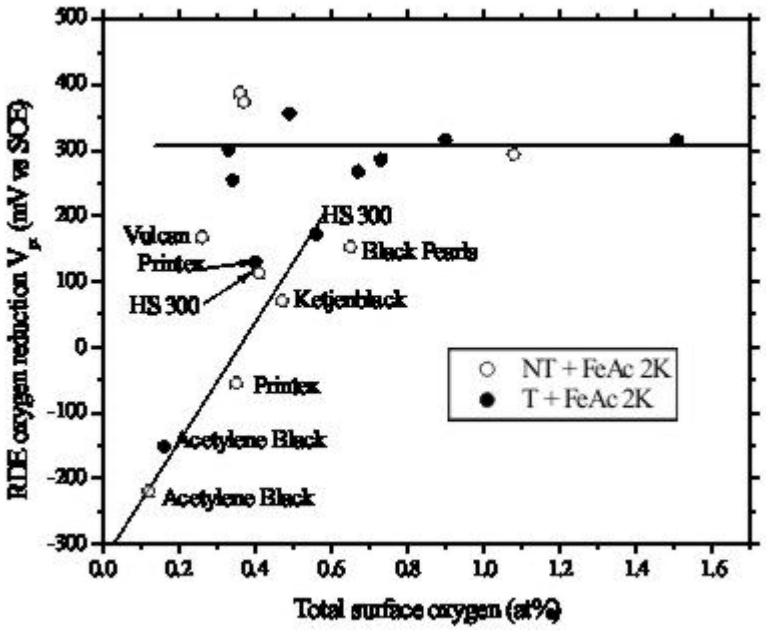


There is a correlation
between the catalytic activity (RDE) and the surface nitrogen concentration (at%) measured by XPS

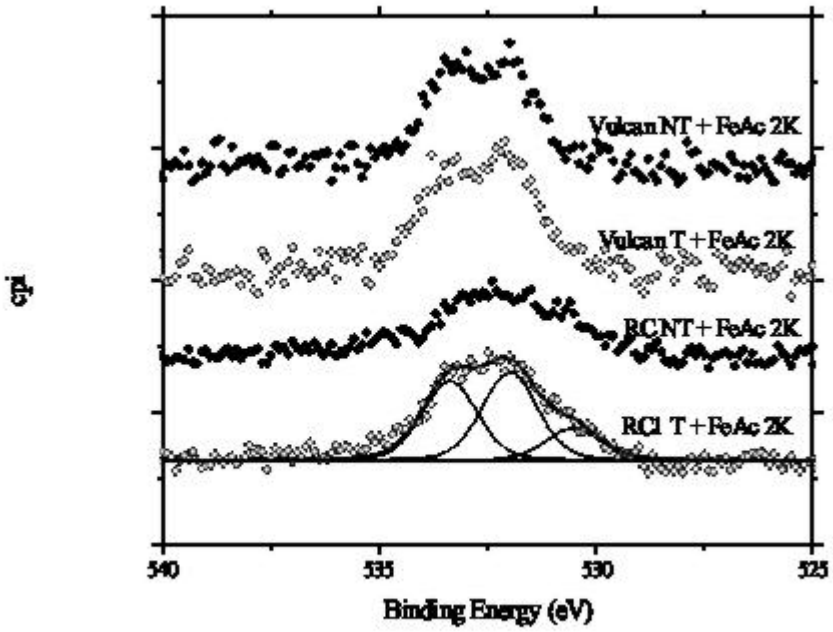


For the catalysts that **do not contain surface N**, there is a correlation between the catalytic activity (RDE) and the surface oxygen concentration (at%) measured by XPS

Detection of a third catalytic site, a Fe oxide/hydroxide



Narrow scans O_{1s} XPS spectra for Vulcan and RC1 carbon supports



Deconvolution of RC1 T

O_A: 533.3 ± 0.02 eV C-OH and / or C-O-C

O_B: 531.8 ± 0.03 eV C=O (aldehydes, ketones, lactones)

O_C: 530.4 ± 0.03 eV Metal-O

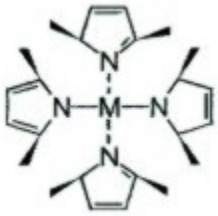
Total O surface concentration (at%) : Vulcan NT (0.3); Vulcan T (0.3)
RC1 NT (0.4) ; RC1 T (0.5)

Take home message about non-noble metal catalysts

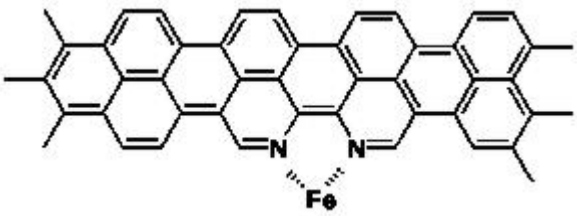
- Fe-based catalysts on C supports are a possible alternative to Pt-based catalysts for PEM fuel cells if it is possible to improve their performance

- Fe-based catalysts on C supports may contain up to three catalytic sites. The abundance of each site depends upon the Fe and the C precursors.

- **The three catalytic sites are:**



1. FeN_4/C



2. FeN_2/C

3. A Fe oxide/hydroxide

- **FeN_2/C is the most active site**

- Future work will be focused on ways to enrich the N content on the surface of the C supports.