5th German-Japanese Joint Symposium, Freiberg. July 20, 2015

Carbon alloy catalyst for material-energy conversion

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炭素材料学会
THE CARBON SOCIETY OF JAPAN

日本学術振興会
炭素材料
第117委員会
5th German-Japanese
Joint Symposium
on Carbon Materials

Contents

1. General introduction
2. Introduction to carbon alloy catalysts
3. Exploration of active sites of carbon alloy catalysts
4. Improvements for high performance catalysts
5. Application of carbon alloy catalyst to other reactions than ORR
6. Conclusion

Contents

① Location

Gunma prefecture lies at the end of the Kanto plain and the foot of the Japanese Alps.

Kiryu city is located on a fan-shaped expanse of land, formed by the Kiryu and Watarase Rivers.

② Kiryu textile

◆ Nara Period (710~794)

Kiryu textiles were presented to the Imperial Court.

◆ Civil war (Onin War, 1467-1477)

Decline of the industry.

◆ The triumph of Shogun (1600)

The first Shogun, Ieyasu Tokugawa,
ordered 2,400 silk flags. They made the flags only one night.
Kiryu was selected as a Crown land.
The silk textile industry became a prosperous industry.

◆ Leading weaving centers : Nishijin (Kyoto)
Kiryu (Gunma)

③ Gunma University

Gunma University has three major campuses located in Gunma prefecture. Two campuses are in Maebashi, the capital city of the prefecture, and one campus is in Kiryu city. The school of Science and Technology is located in the Kiryu Campus. The distance between the two cities are 30 km.

Faculty of Engineering
Commemoration Hall

Engineering
Research Center

Population of the organization

	GU	FST
Students	**6,556**	**3,172**
Staffs	**2,204**	

③ Gunma University, Faculty of Science and Technology

100th faculty's anniversary

Founded in 1915

Planning many events to celebrate the anniversary through this year

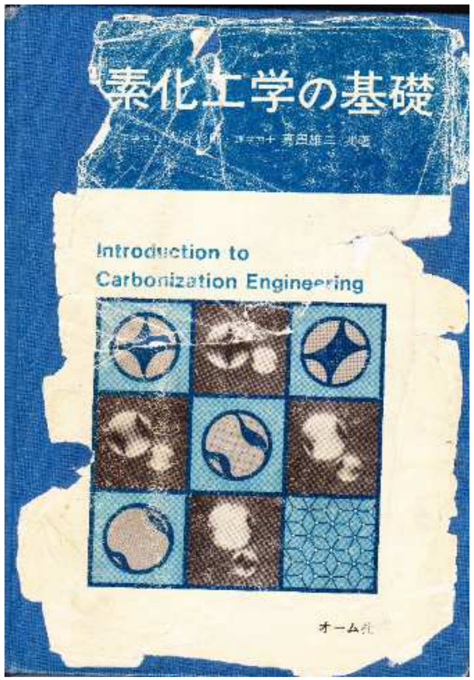
The organization committee may welcome your donation

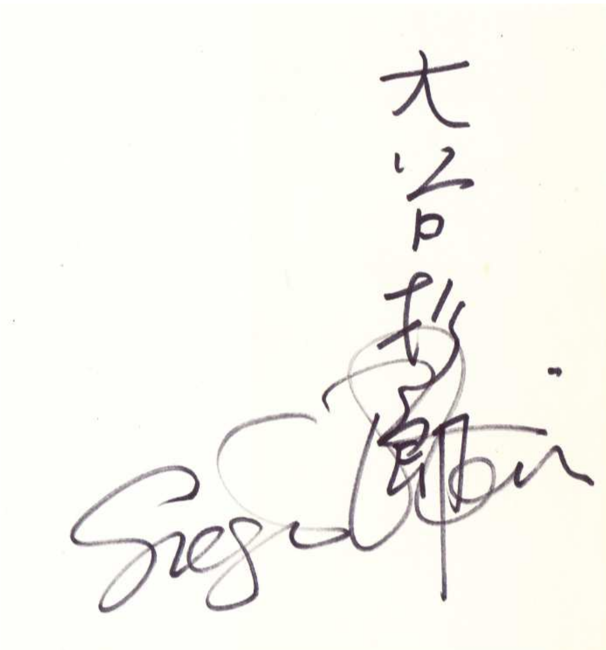
Sugio Otani, Emeritus Professor
～From Black chemistry to Chemistry～

1953 Founded the Carbon Lab.

Invented Pitch-based Carbon Fibers

Studied the chemical process from organic compounds to carbon materials

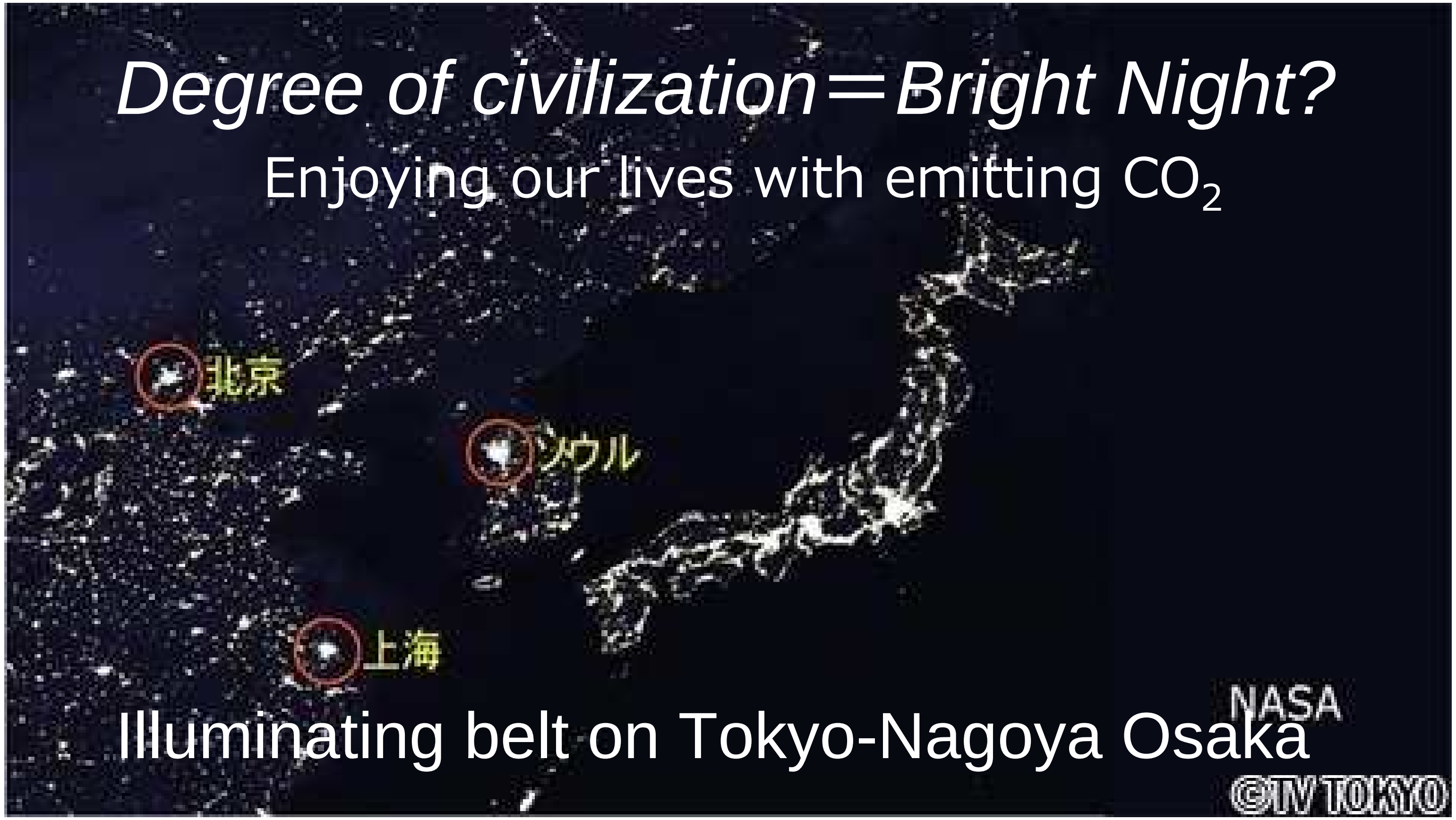




Late Prof. Dr. Sugio Otani

Contents

Low-Carbon Society？

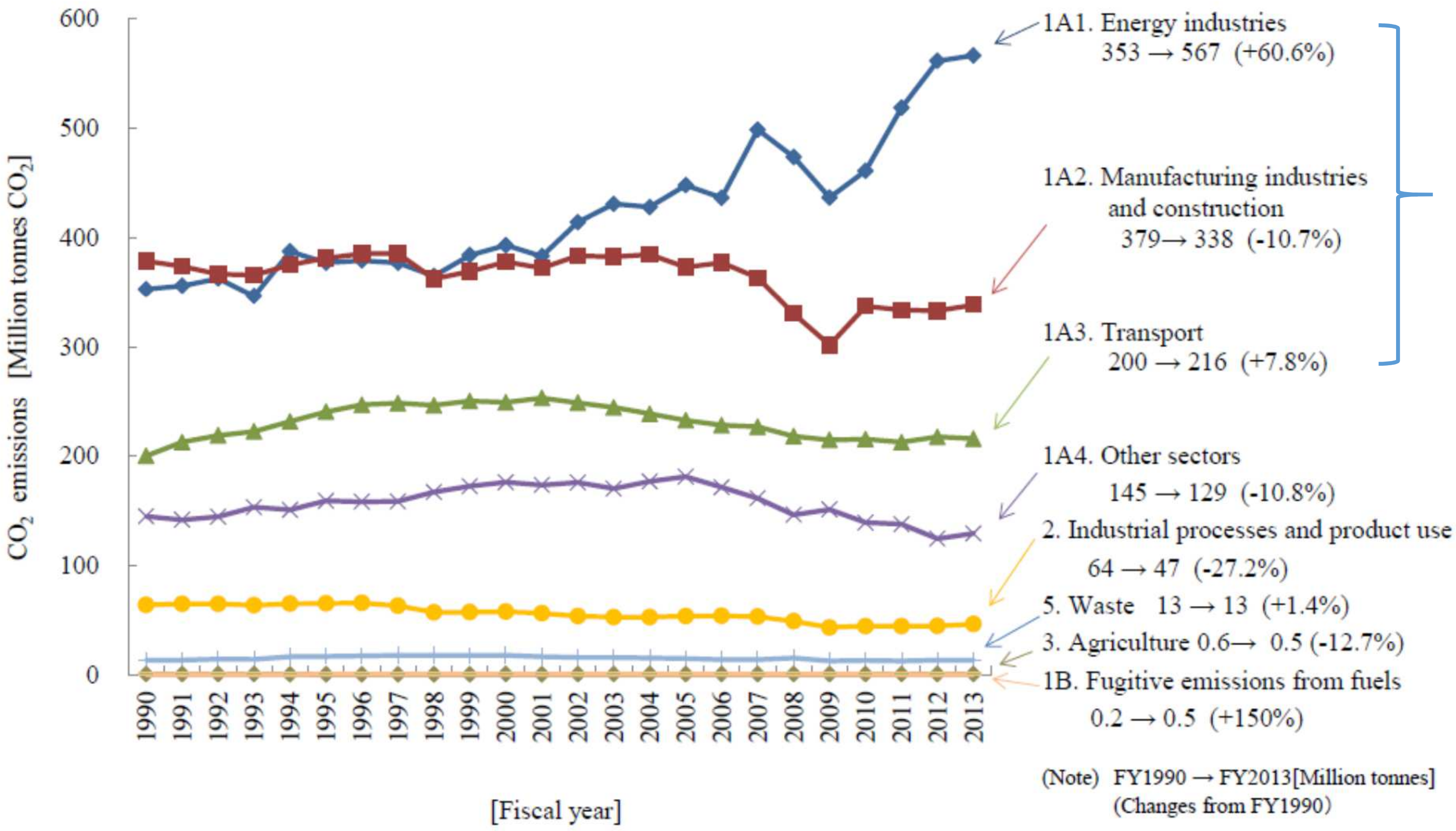


http://www.tv-tokyo.co.jp/newsanswer/blog/kubota/2011/11/post121012.html

Can we go back to the life in Edo era?

Probably, many people say “No!”.

CO_2 emission in Japan



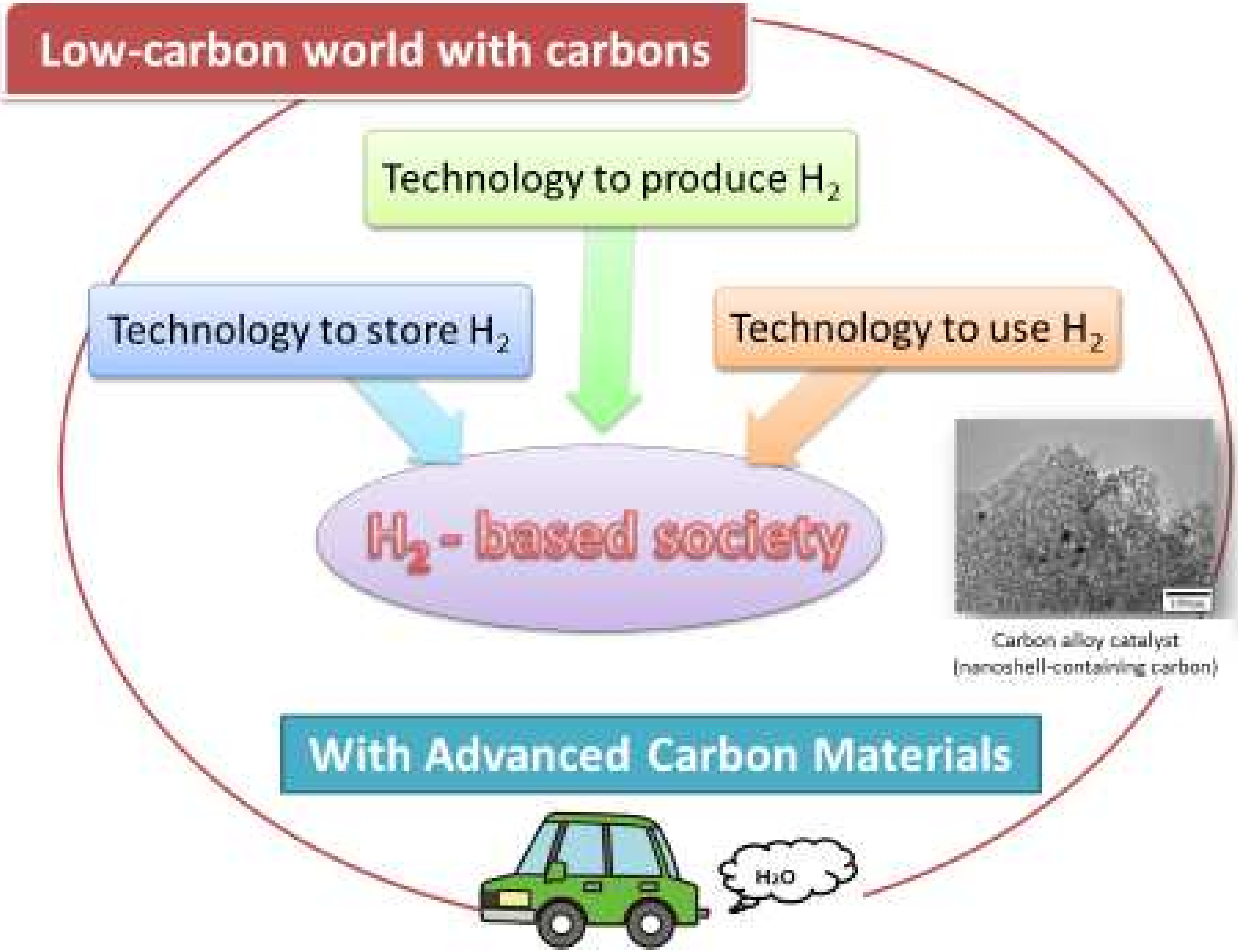
Reduction of CO_2 in these categories are important.

Figure 2-3 Trends in CO_2 emissions in each sector

(Figures in brackets indicate relative increase or decrease to the FY1990 values)

“National Greenhouse Gas Inventory Report of JAPAN”, April, 2015, Min. Environ. Jpn. Greenhouse Gas Inventory Office of Japan (GIO), GGER, NIES

Dream with carbon materials



Introduction of Fuel Cell Vehicle

Toyota introduced an electric vehicle equipped with PEFC to the market on December 15th, 2014

http://toyota.jp/mirai/

Human society, especially Japan, is steadily moving toward the age of hydrogen-based energy

Reduction of Pt in ORR catalyst

35 € /g

46 g/car

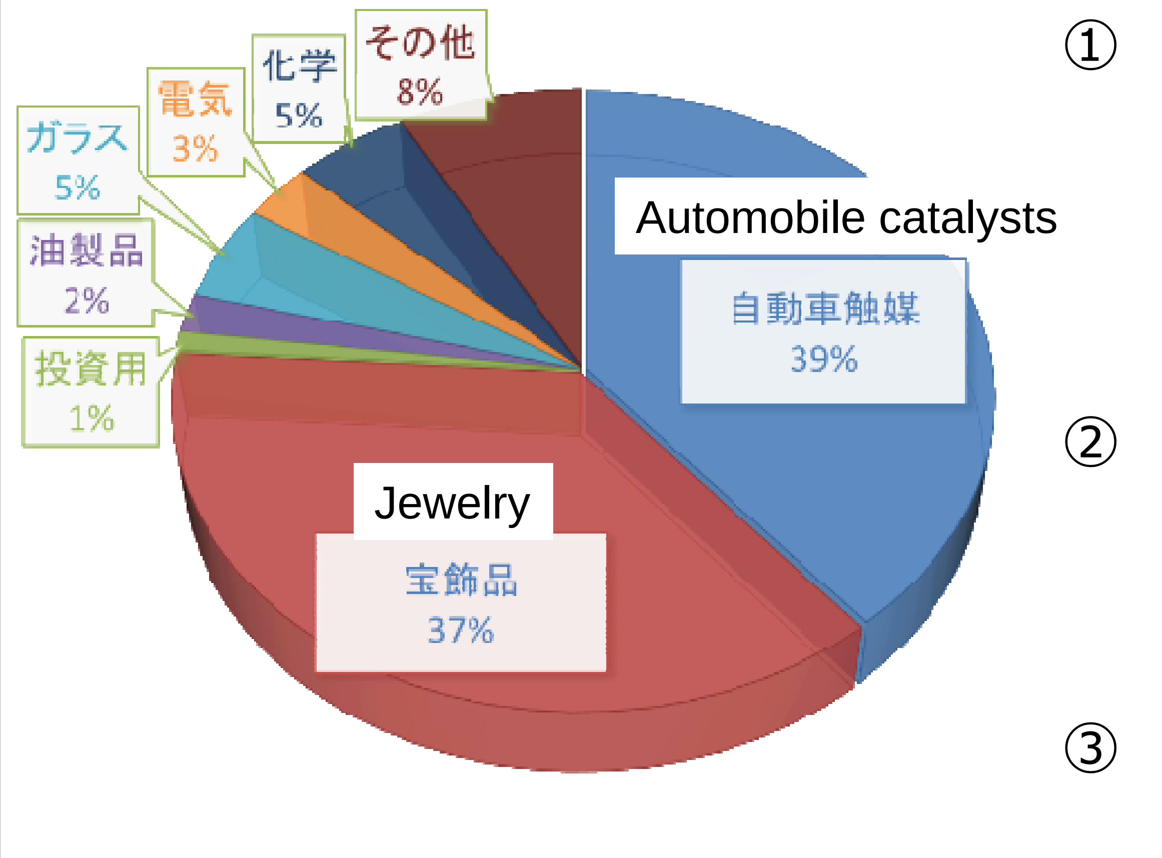
1610 € /car

Reduction of the amount of platinum is critical for further distribution of fuel cell vehicles.

Rare and expensive resource- Pt

Tanaka Kikinzoku Co. Ltd.

1． Used in industry and jewelry 2． Rare resource



① Small amount of mining

Annual global mining :
194 ton (Gold : 4,000 ton)
Accumulated amount since civilization :
4,720 ton (6 m^3 cube)

② Non-uniform distribution of resource

Mines :
South Africa（75%）
Russia（17%）

③ Yield of Pt from oar

3 g of Pt from 1 ton of ore

62% of mined Pt is used in industry

Methods to reduce the amount of Pt

ORR catalysts with reduced amounts of Pt metal

- Alloying platinum with other base metals
- Core-shell structures consisting of a base metal core coated with a platinum shell

Non-platinum ORR catalysts

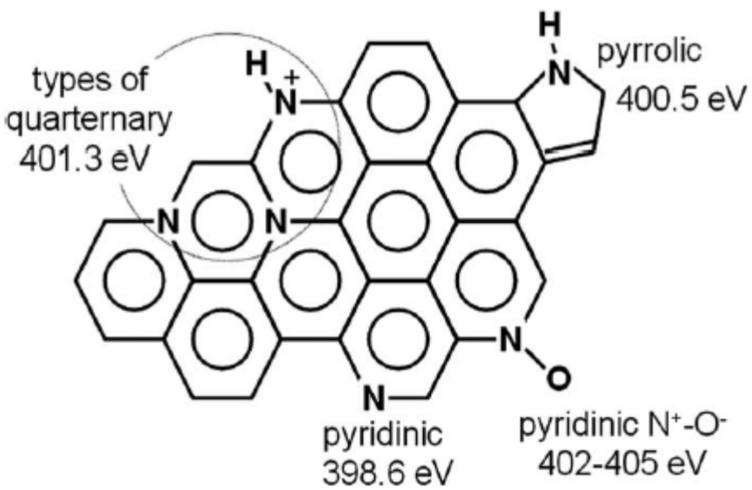
- Chalcogenide compounds: rhodium selenide and ruthenium selenide
- Carbides: tungsten carbides
- Macro-cyclic metal complexes and their thermal derivatives formed on carbon substrates

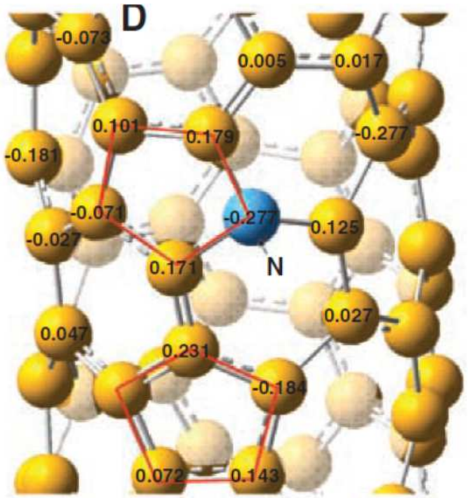
Nitrogen-doped carbon

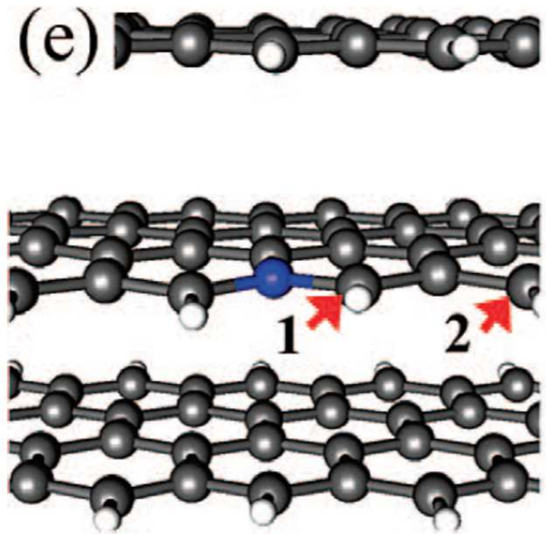
Nitrogen doped carbon is a category of the catalysts without employing Pt at all.

Pyridine-type N

Graphitic N







P.H.Matter et al. J.Catal. 239 (2006) 83

K.Gong et al. Science 323 (2009) 760

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

Identifying the active nitrogen species are very difficult, hence the active sites of the N-doped carbons are still under discussion.

What is CARBON ALLOYS?

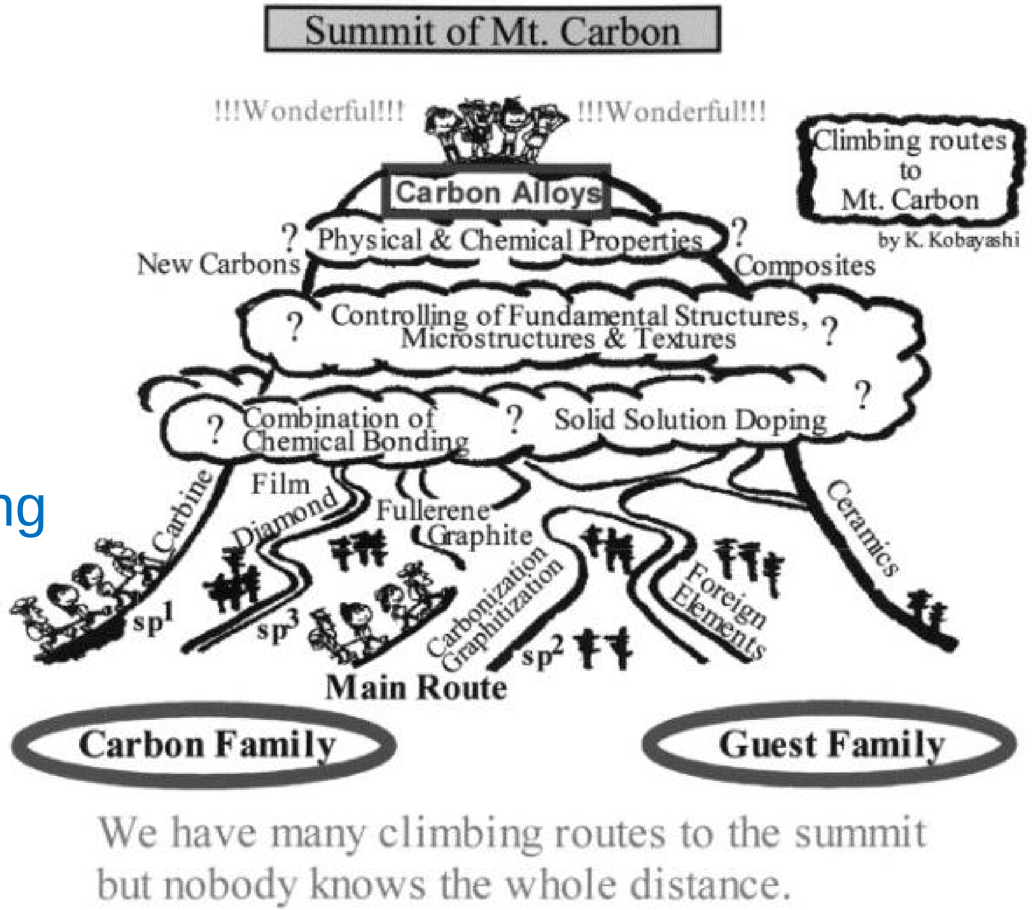
Carbon Alloys

Materials mainly composed of carbon atoms in multi-component systems

Components

Physically and/or chemically interacting

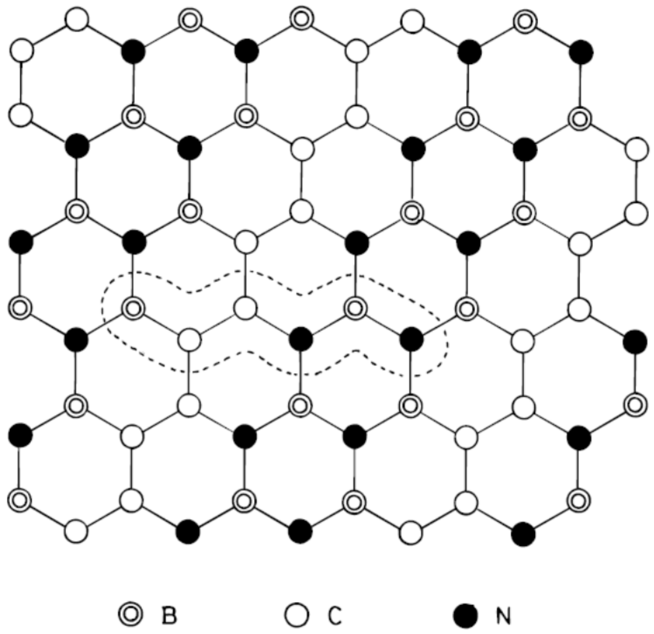
Carbons with different hybrid orbitals



Y. Tanabe, E. Yasuda, Carbon 38 (2000) 329-334

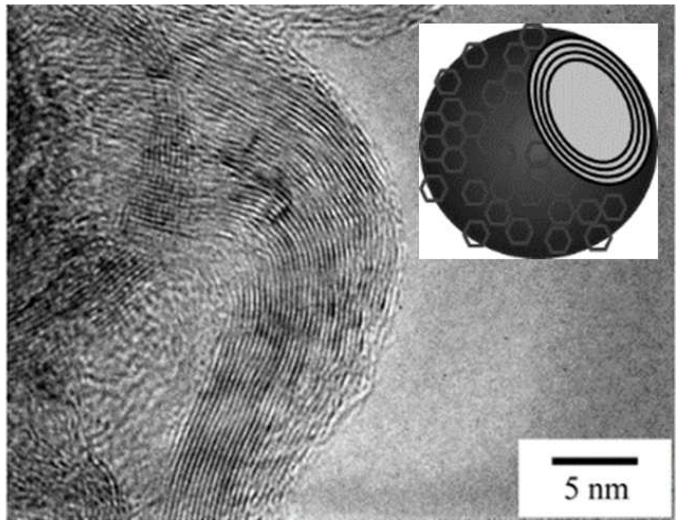
Carbon Alloy Catalysts

BN-doped carbons



M.Kawaguchi et al. Chem.Mater, 9 (1996) 1199

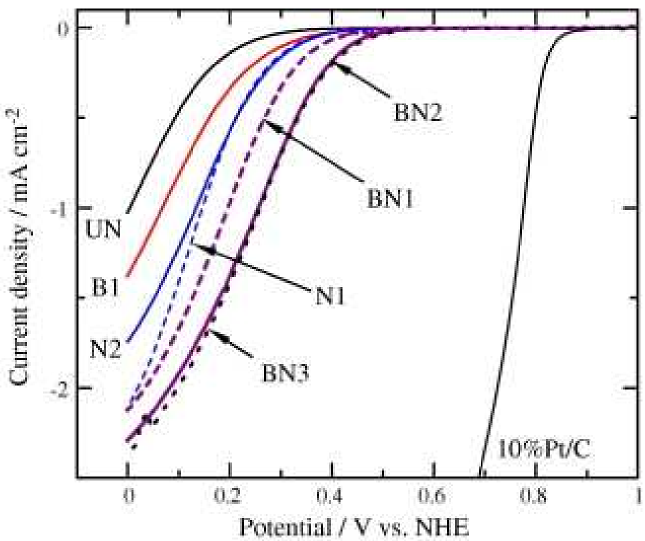
Nanoshell-containing carbon (NSCC)

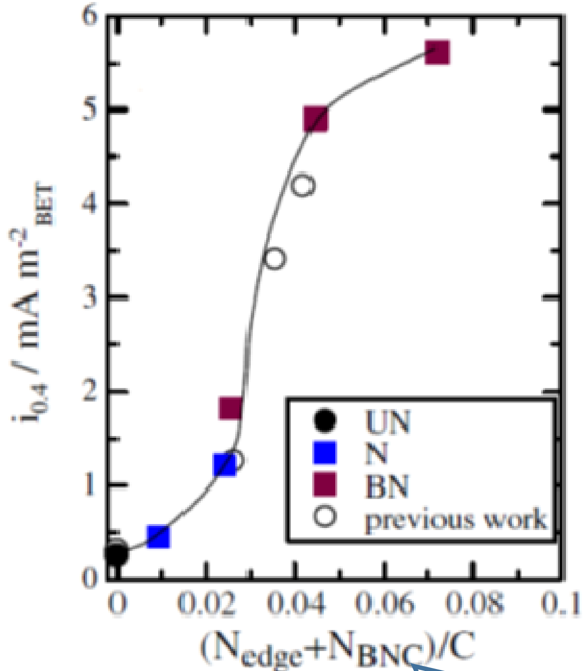


<u>Two types of carbon materials with ORR</u>

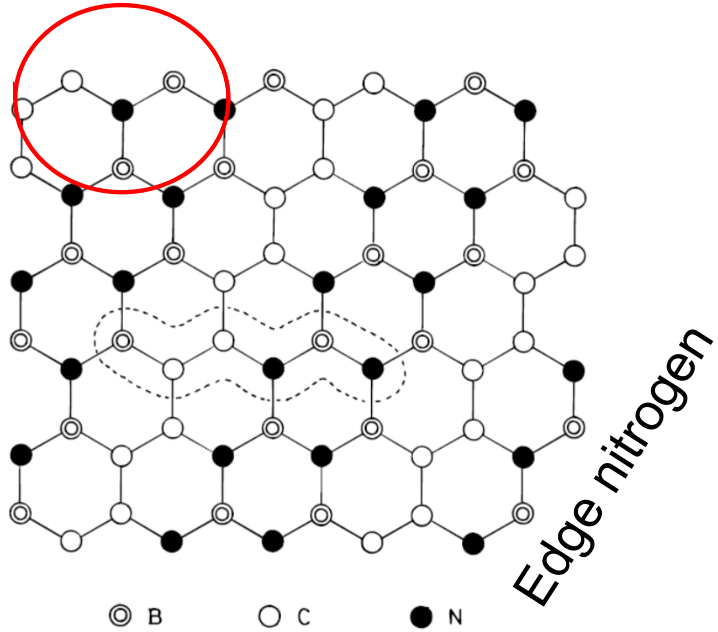
BN-doped carbons

Prepared by carbonizing a polymer with B and N compounds.





B-N-C moieties



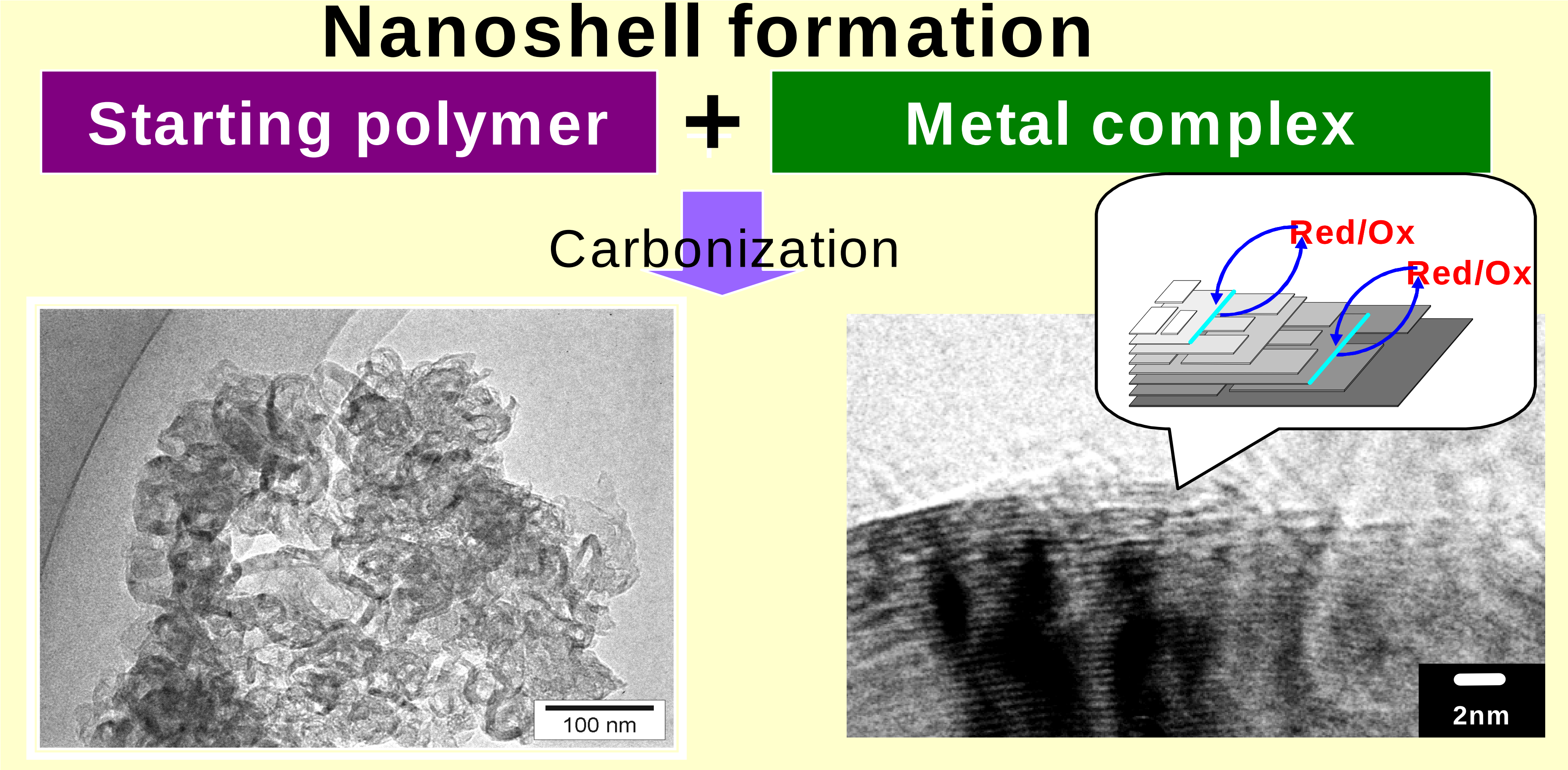
M.Kawaguchi et al. Chem.Mater, 9 (1996) 1199

BN-doping increased the ORR activity.

Edge-N and B-N-C

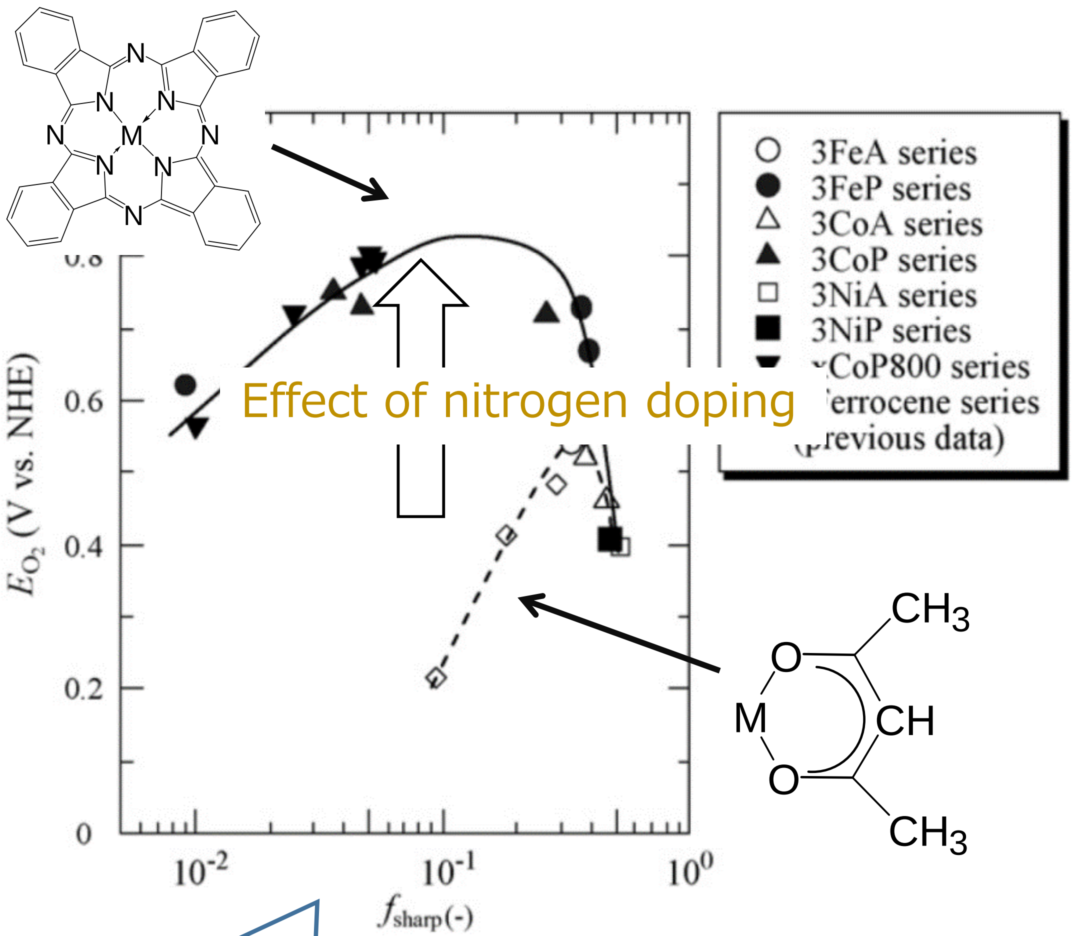
J. Ozaki et al. Carbon 45 (2007) 1847

Nanoshell-containing carbons (NSCC)



1. Carbonization of polymers in the presences of transition metal complexes such as cobalt and iron.
2. Nanoshell has a shell-like form of 20～30 nm of diameter
3. Obtained as a mixture of NS and amorphous carbon

ORR activity of NSCC



Development degree of NS

Optimum development degree

f_{sharp} = 0.3~0.4

Influence of types of metal complexes

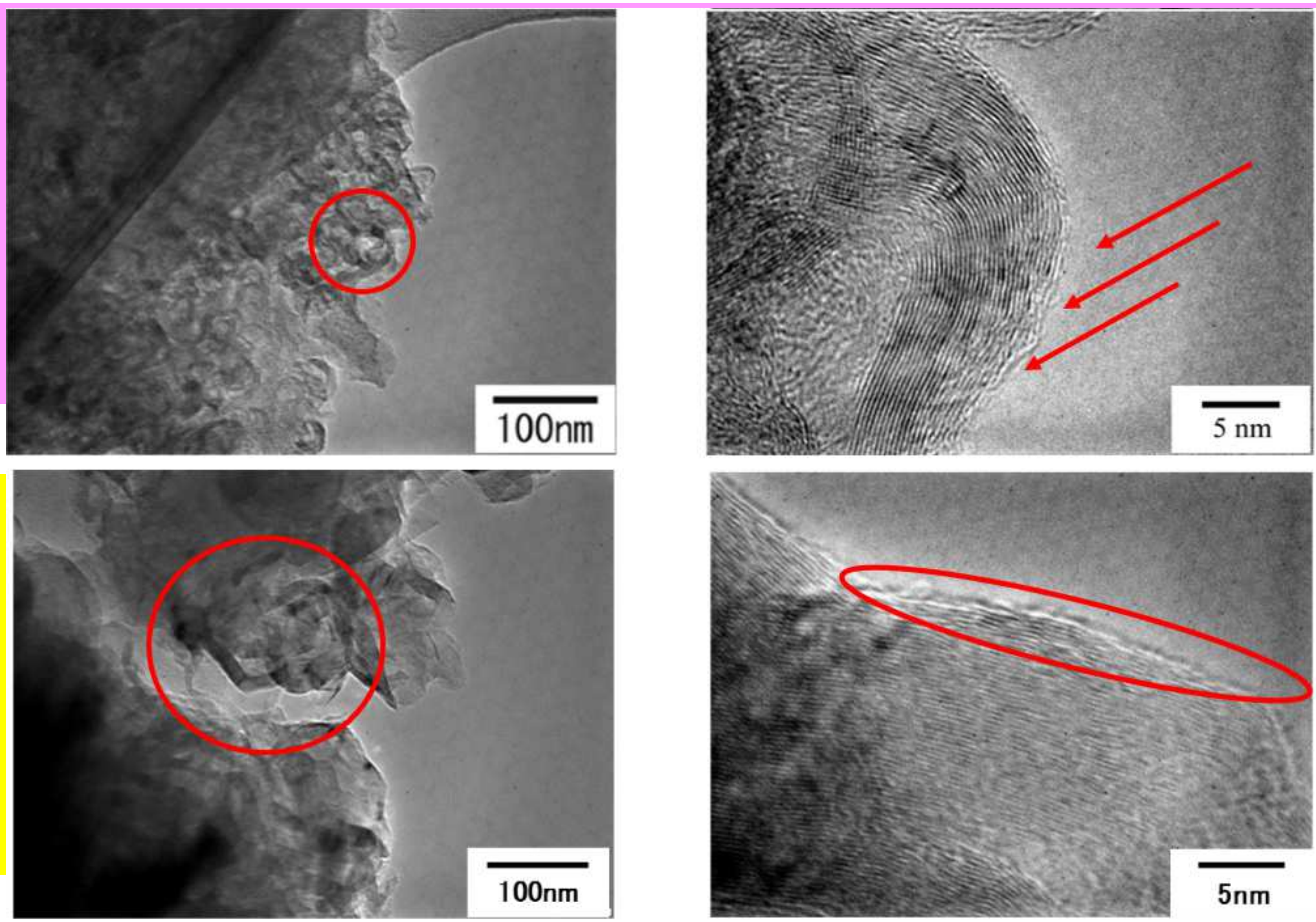
Phthalocyanine > Acetylacetonate

Importance of the carbon structure and the presence of nitrogen

J. Ozaki, et al., Electrochim. Acta, 55, 1864-1871 (2010).

Comparison of surface structure

Surface structure of Nanoshells



Active NSCC

CoPc derived NSCC

- Diameter Approx. 30nm
- Edges and curved layers

Inactive NSCC

NiAA derived NSCC

- Diameter. > 50nm
- Very smooth surface

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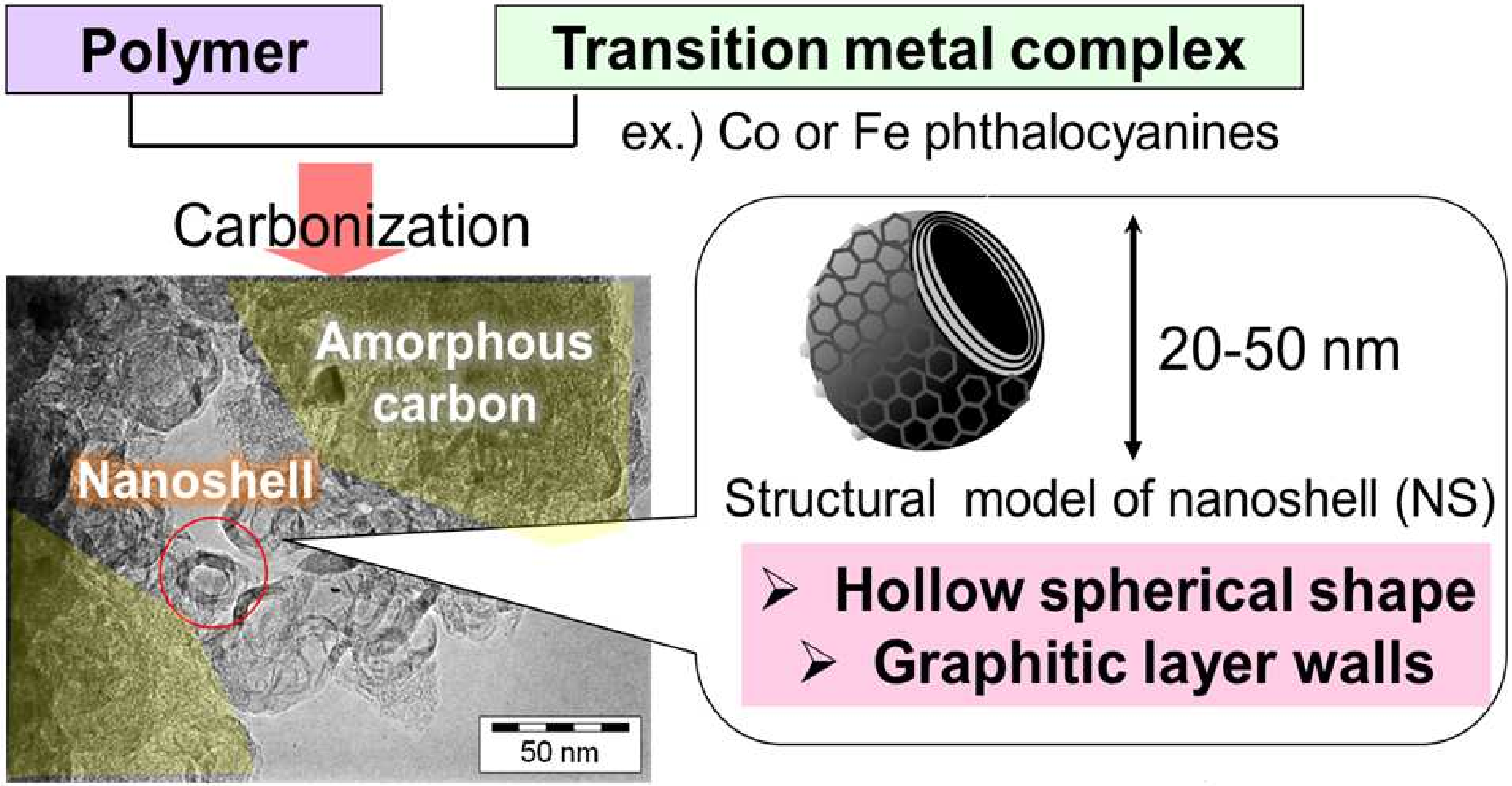
ORR-influencing factors for NSCC



NSCCs: very complex materials

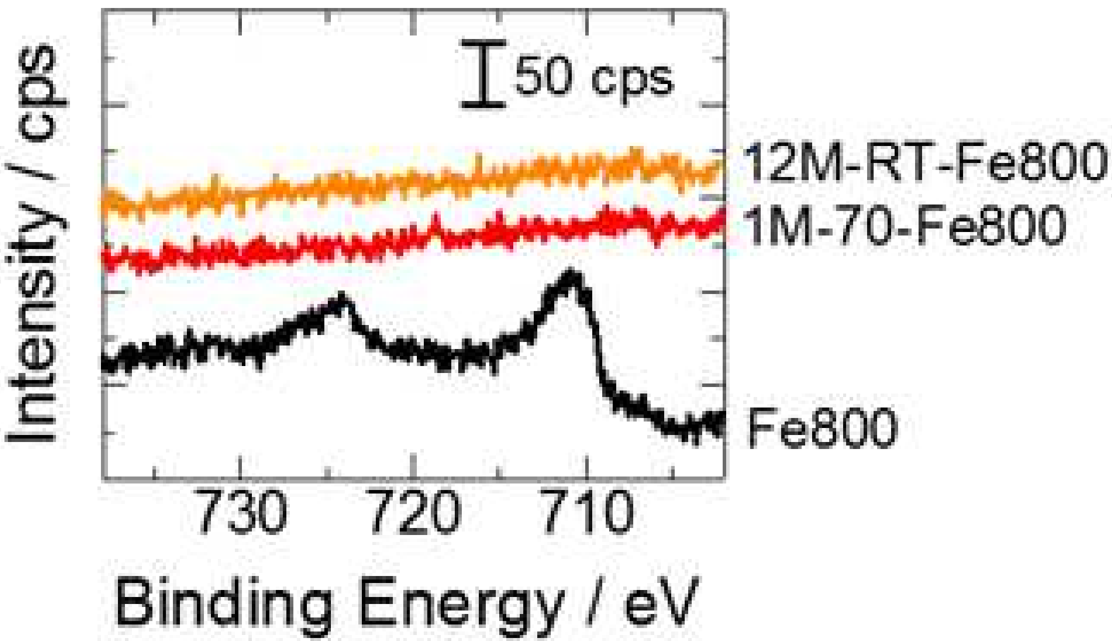
<u>Factors concerning to ORR activity.</u>

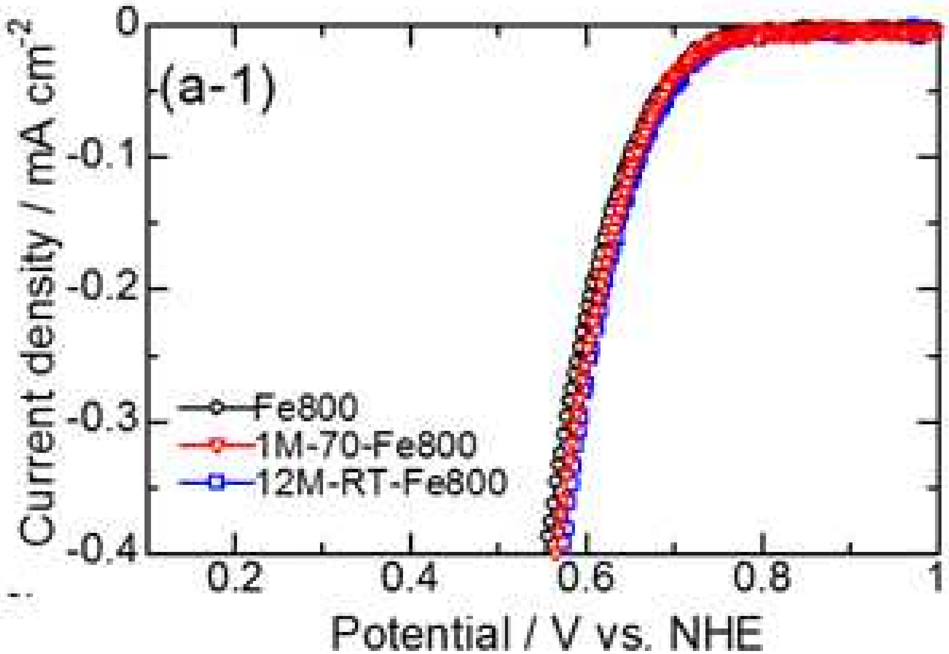
1) Metal species

2) Carbon structure

Influence of metal species on ORR

N. Kannari et al, Tanso (accepted)



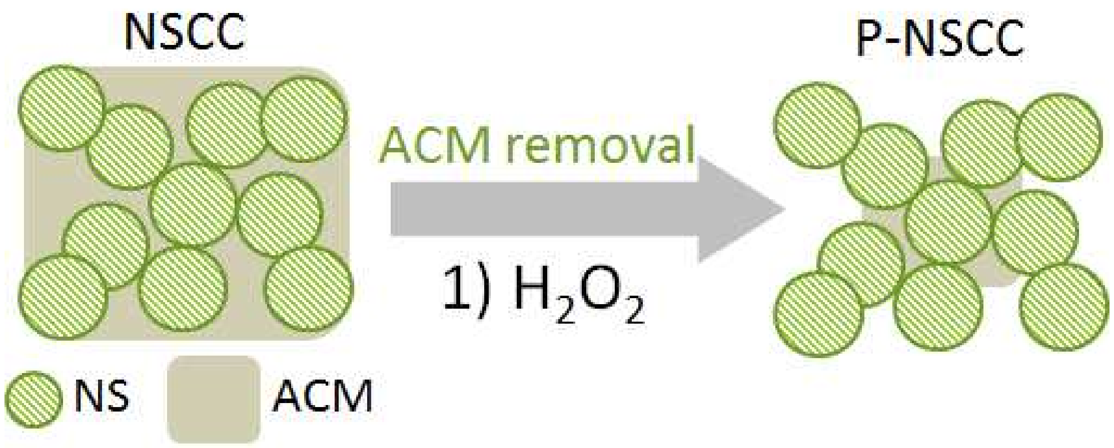


Acid washing
↓
Removed metals from surface

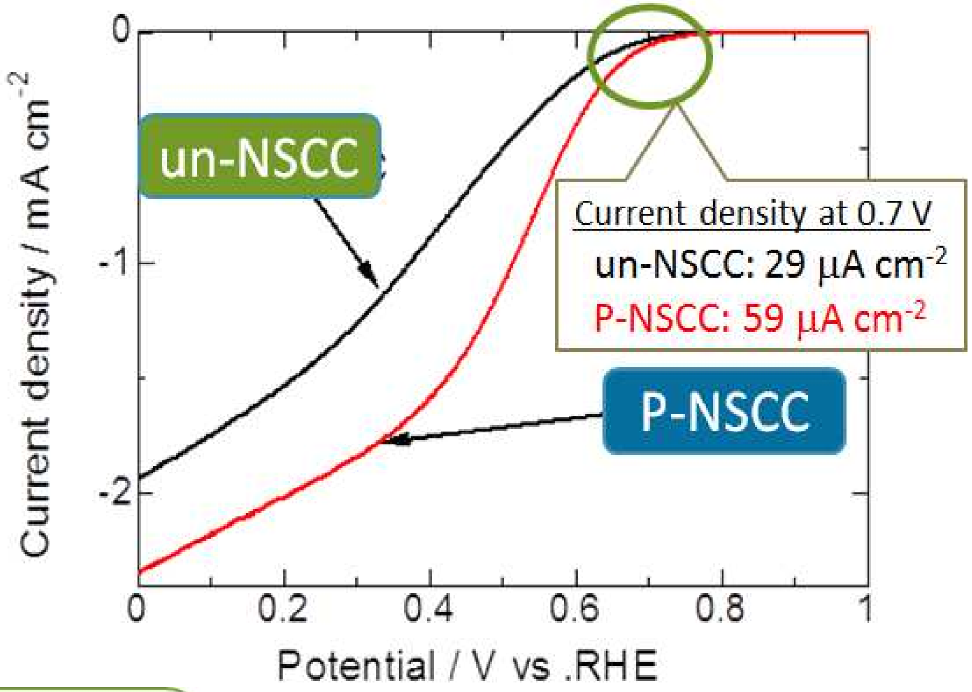
No changes in ORR activity

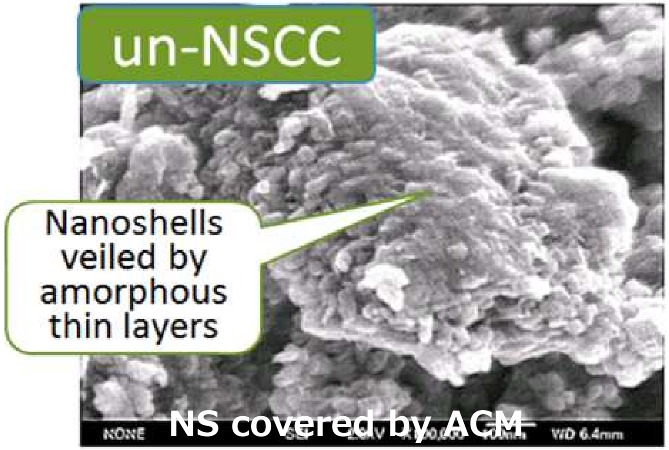
The leachable metal species do not participate ORR.

Carbon structure



Removing ACM by oxidation with H_2O_2



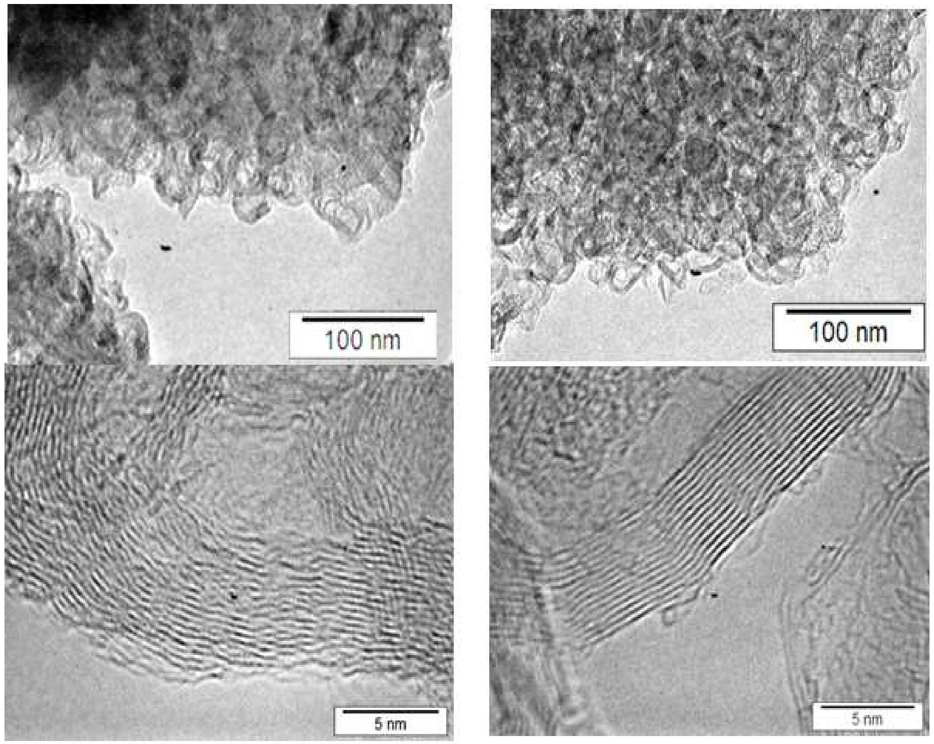


Exposition of NS surface increased ORR activity.

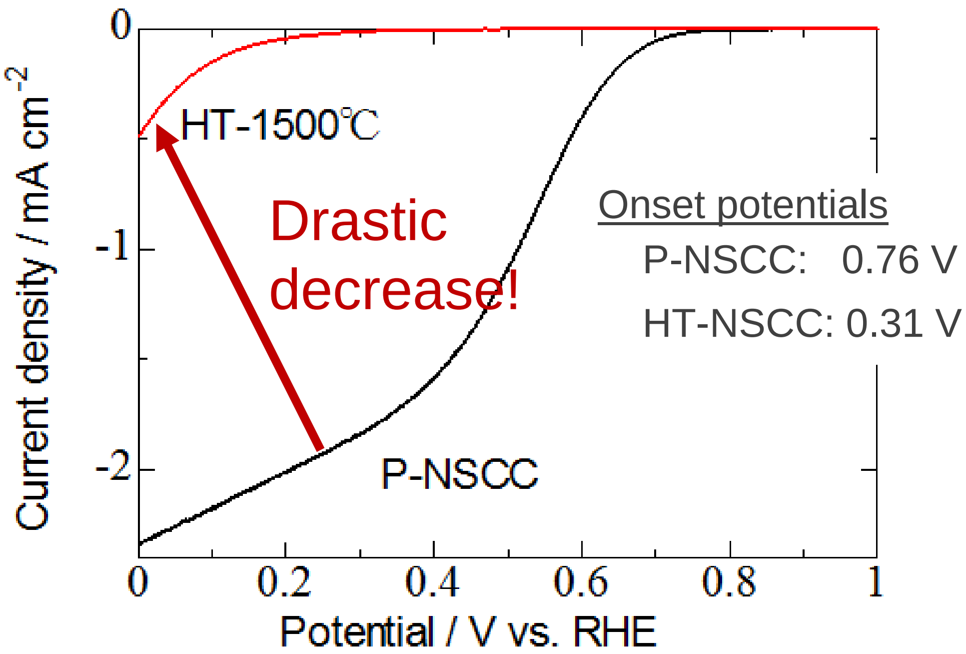
Active sites locate on NS surface.

J. Ozaki et al., Carbon 2013

Removing the defects



P-NSCC HT-NSCC



Formation of finely aligned graphitic layers.

→ Surface defects on NS = Active sites

Influence of defects in carbon to ORR

Artificially introduced defects

Fullerene added carbon ⇨ Edges

Carbonization of pitch with fullerene

Nano onions ⇨ Curved structure and edges

Heat-treatment of nano-diamond

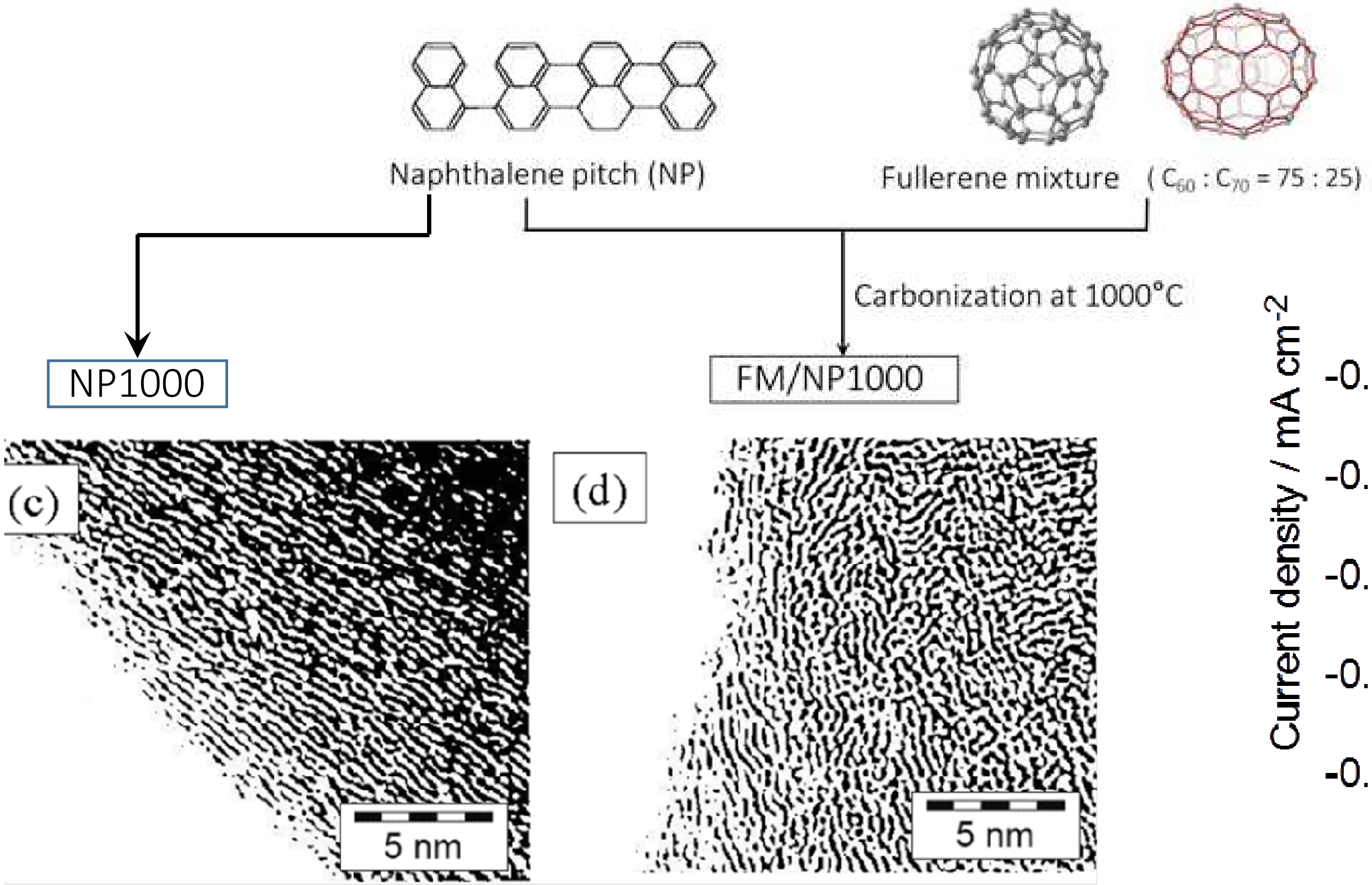
Partial oxidation of fullerene residue

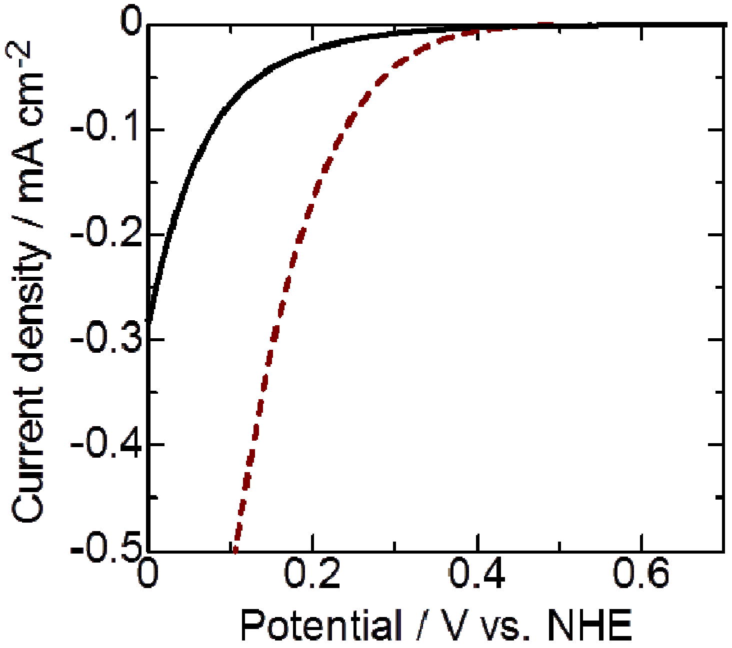
Activated NSCCs ⇨ Edges

H_2 and CO_2 activation of NSCC

Carbon derived from fullerene added pitch

N. Kannari et al, Tanso



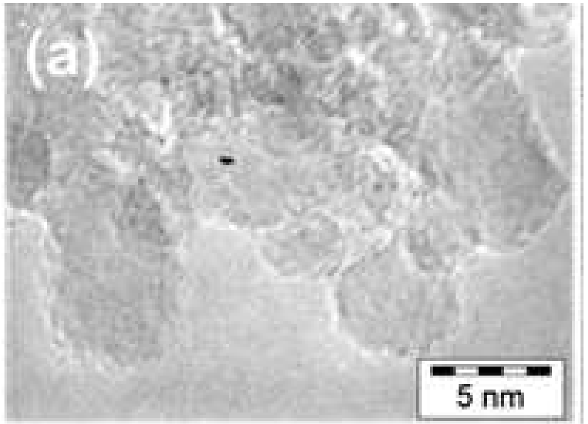


Introduction of disorder. Enhancement in ORR activity

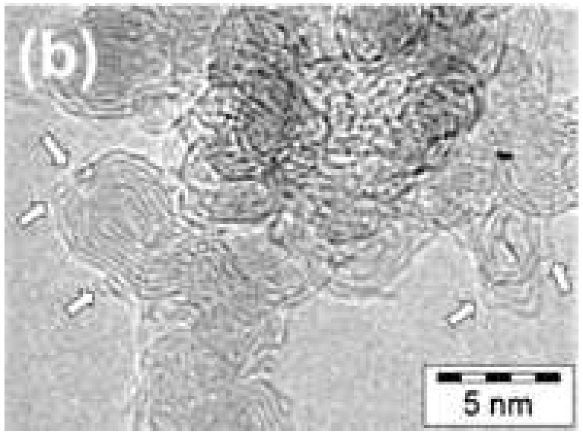
Disordered structure forms ORR active sites.

Carbon nano-onion from nano-diamond

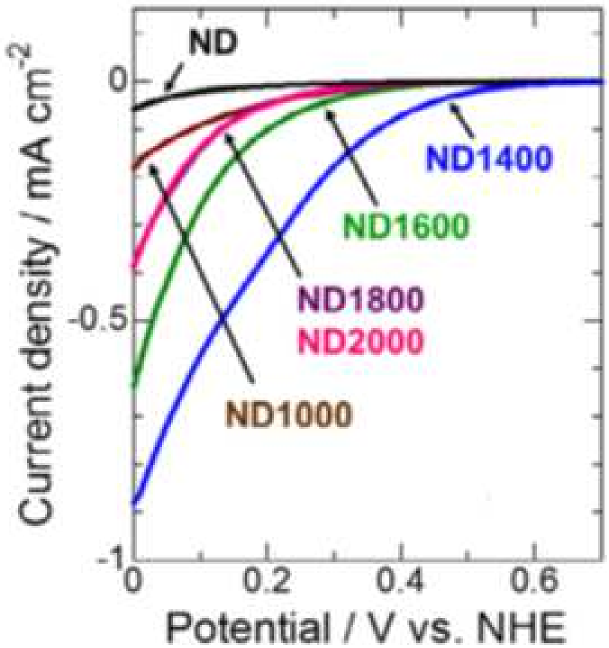
N. Kannari et al, Carbon

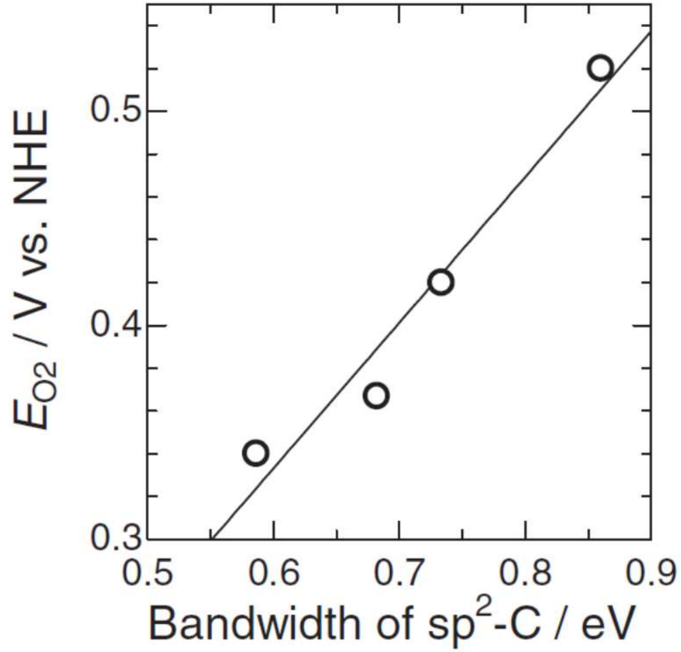


Nano-diamond



1400℃ heat-treated





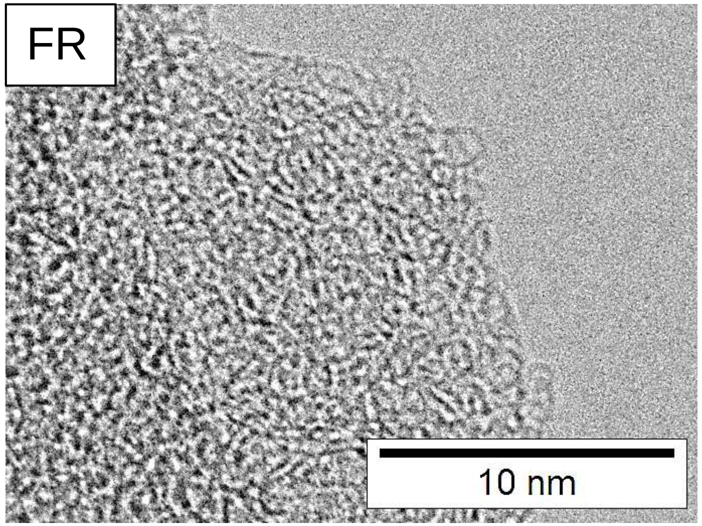
Heat - treatment at 1400ºC

- Formation of nano-onion with many surface defects
- Increase in ORR activity

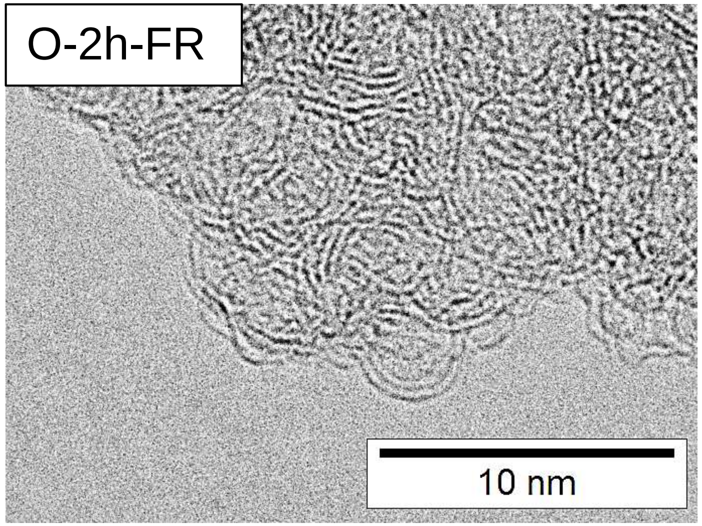
→ Surface defects are the ORR active sites.

Carbon nano-onion from fullerene residue

T. Maie et al, Carbon 2015



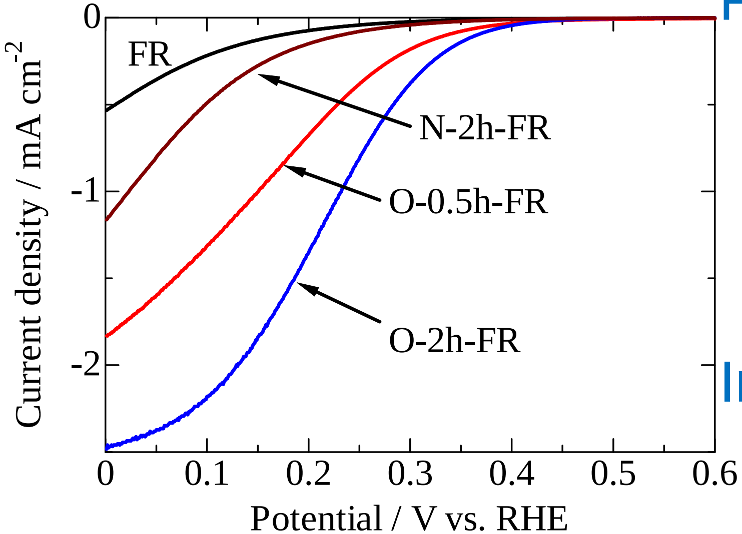
Partial oxidation at 600℃ →



Fullerene Residue (**FR**)

Frontier Carbon Corp.

Product name : NanomBlack



Formation of nano-onions

↓

Increase of ORR activity

→ Curved structure forms ORR active sites.

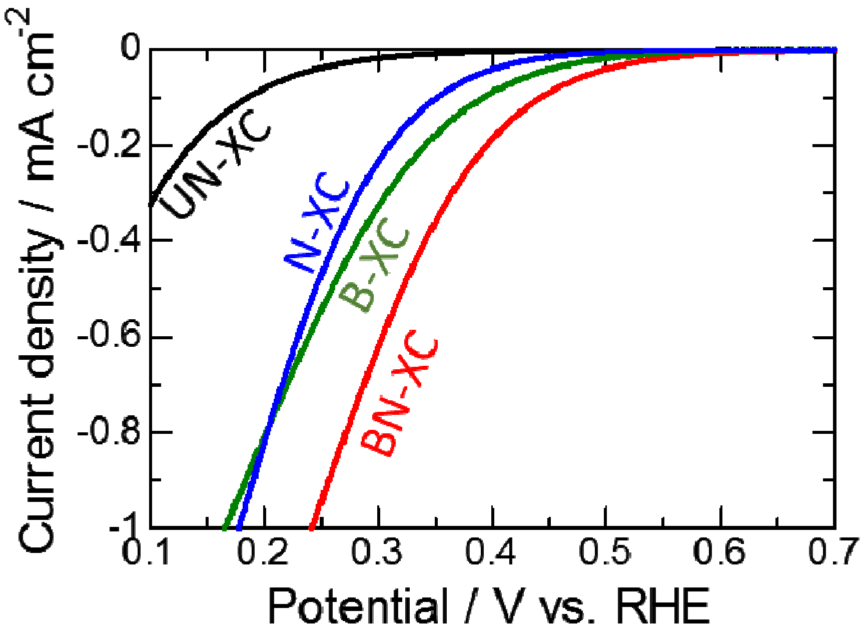
ORR activity of doped carbon blacks

J. Ozaki Carbon 2015, Dresden

Prepared N-, B- and BN-doped carbon blacks to understand the role of B and N atoms in ORR catalysis..

$$\eta = a + b\log|i|$$

η : overpotential i : current density
a : intercept b : Tafel slope



Tafel parameters

	b (mV/dec)	i_0 (mA/cm^2)
UN-XC	183	2.3×10^{-7}
B-XC	171	1.4×10^{-6}
N-XC	152	1.9×10^{-7}
BN-XC	178	4.2×10^{-6}

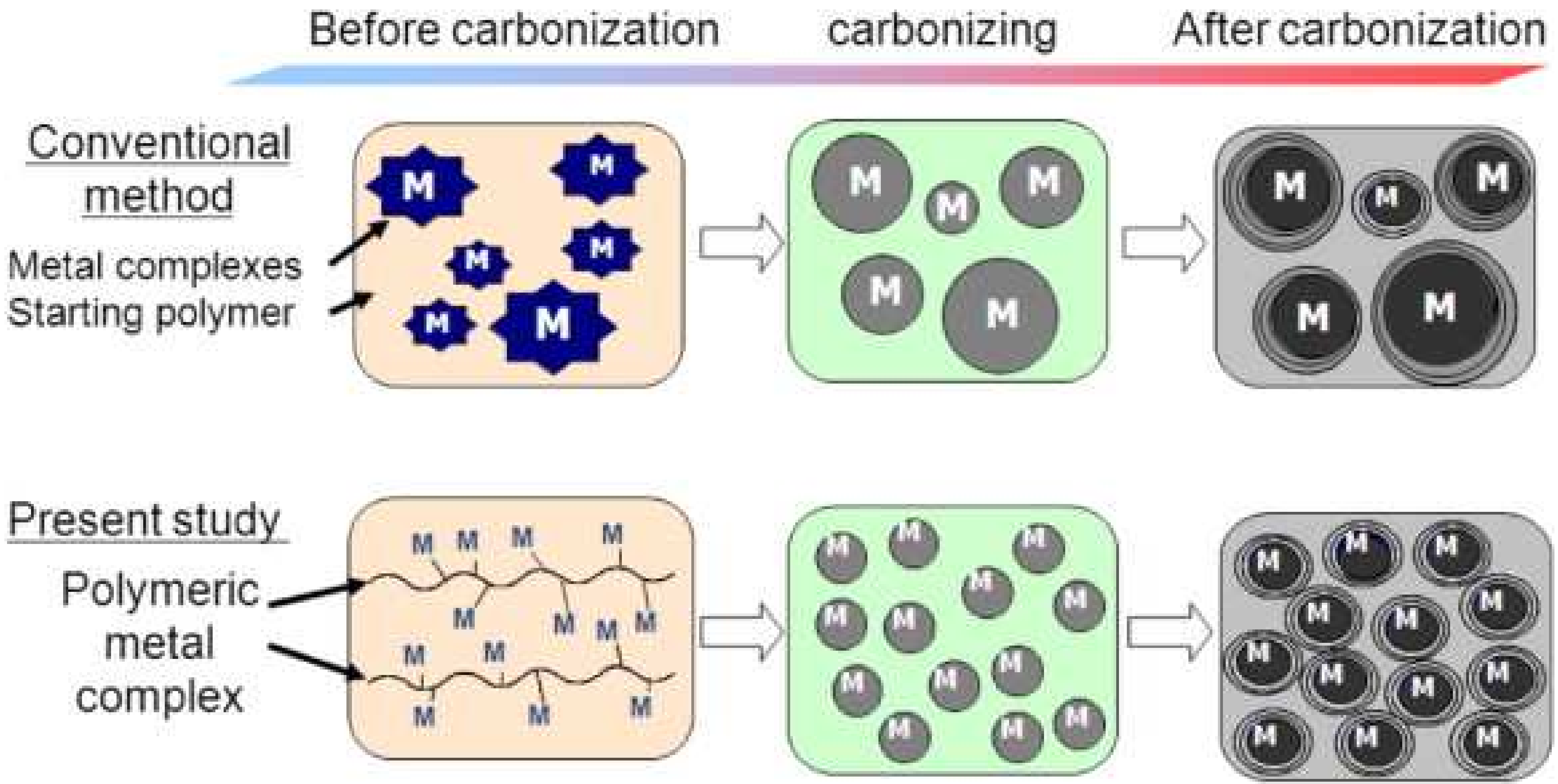
BN-doping increased the surface concentration of active sites or reactant with the same reaction mechanism.

Contents

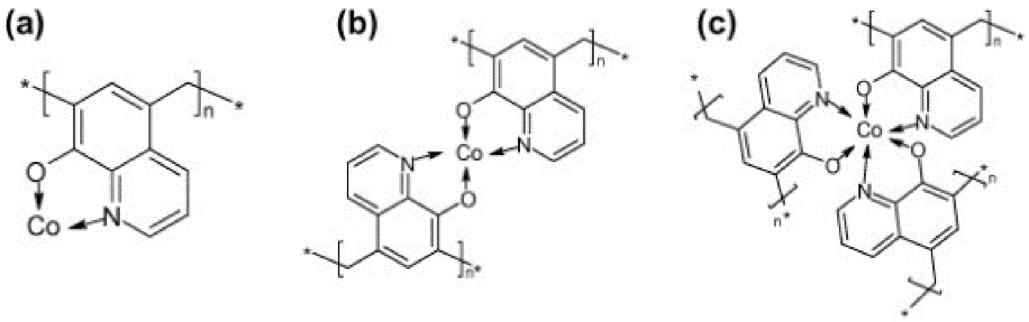
ORR performance improvement

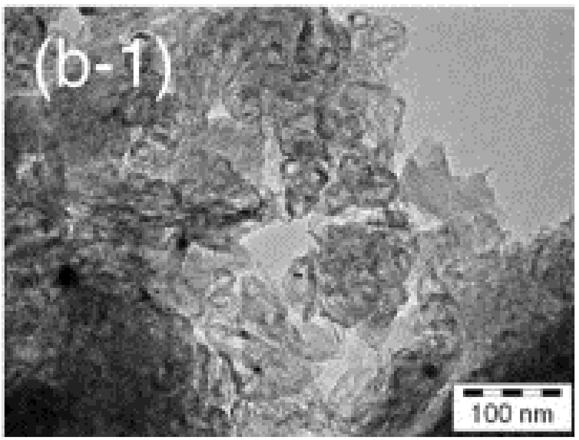
1. Utilization of polymer metal complexes
2. Addition of foreign carbon materials to carbonizing systems

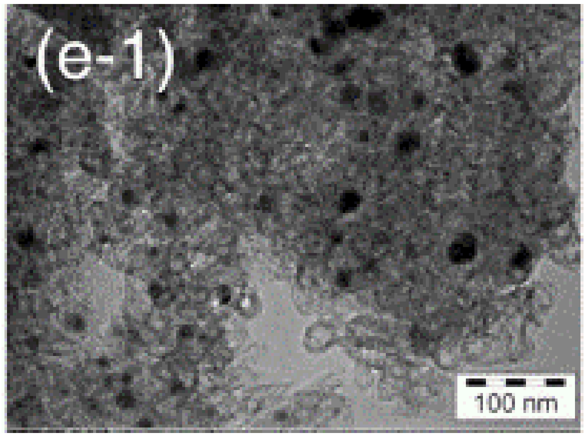
NSCC from polymer metal complex



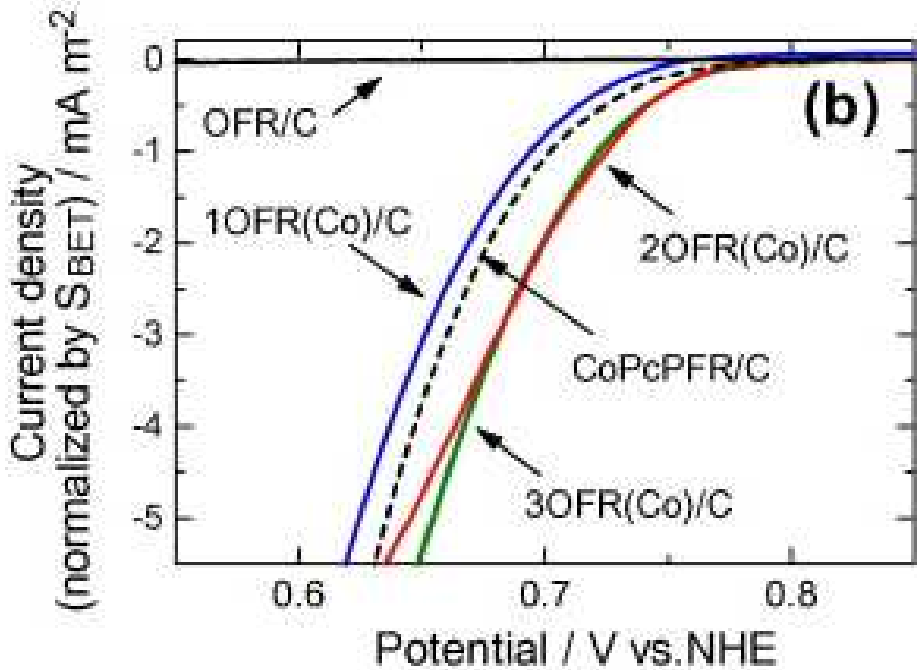
NSCC from polymer metal complex







Formation of small and uniform NS particles



Increased ORR activity

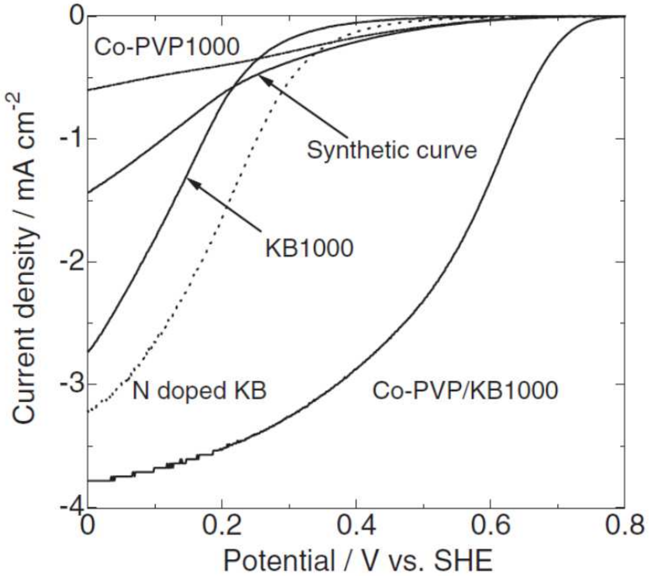
N. Kannari et al. Carbon 50 (2012) 2941-2952

Formation of smaller NS particles are essential to prepare more active catalysts.

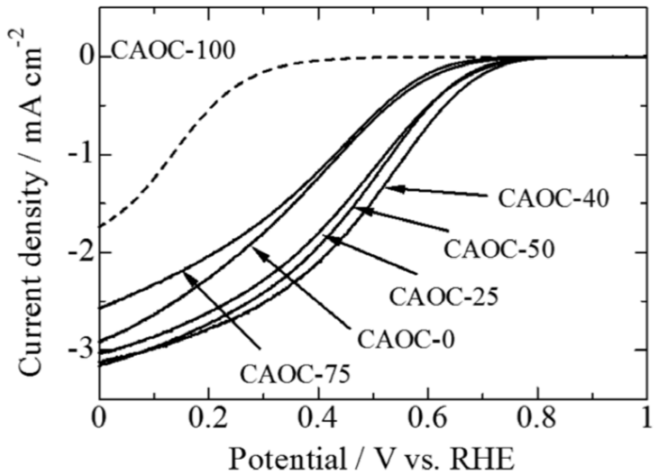
Addition of carbons to NS carbon alloy catalyst precursor

Co-PVP complex with Ketjen Black

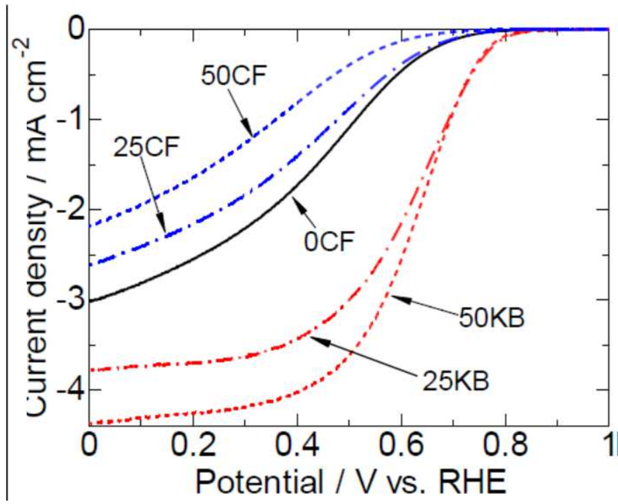
NSCC precursors and various carbon additives



Chemistry Letters Vol.38, No.5 (2009)



Tanso, 2014 (No.265) 159–164



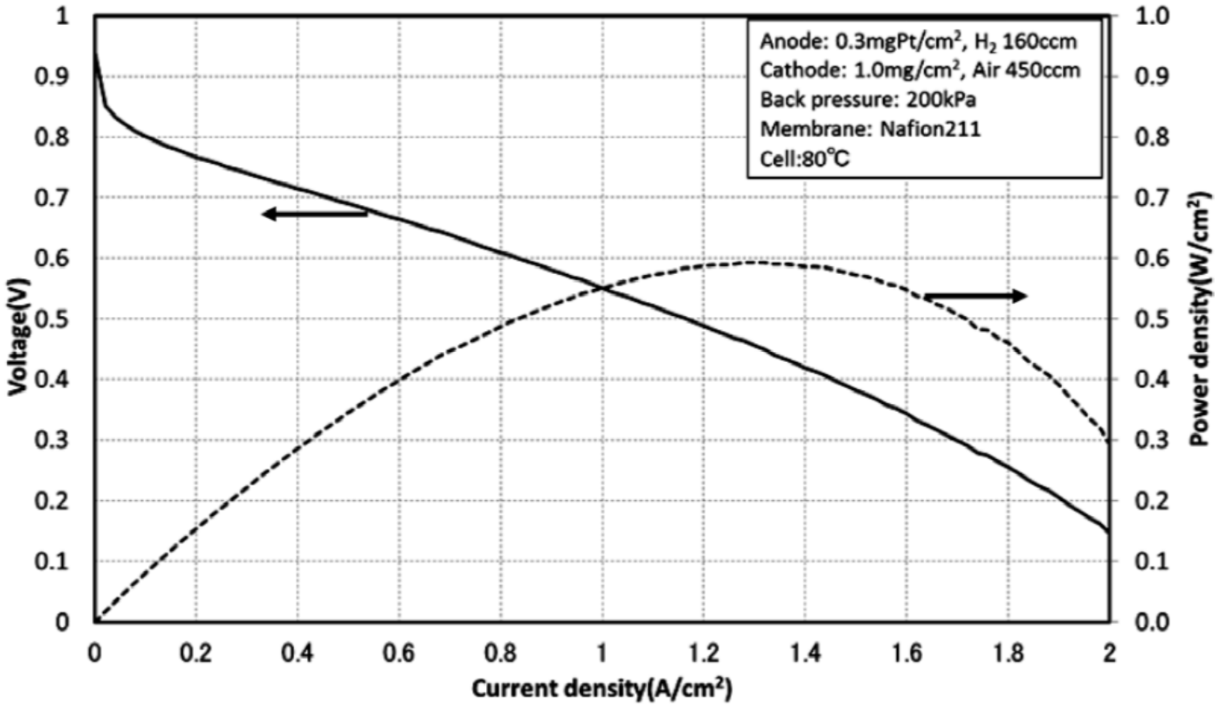
5th GJ–Symposium, 2015

Addition of catalytically inactive carbon additives improved the ORR activity of carbons.

Interaction between the precursor and the additives produces active sites.

Performance of the latest carbon alloy catalyst

Gunma University and Nisshinbo Holdings, Inc.
have developed very active carbon alloy catalyst.



High performance with H_2/air feedings

J. Ozaki et al. Tanso 2014 (No.265) 204-212

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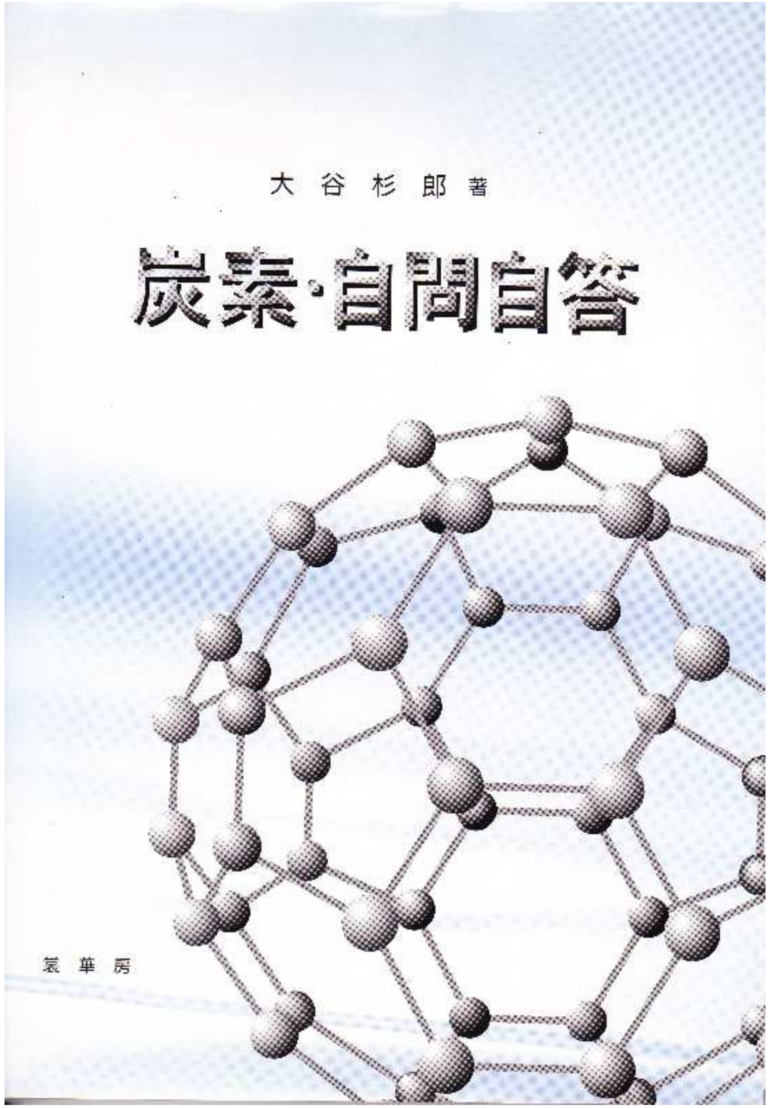
It is not a easy task to prepare desired carbon materials!



"Making carbon from organic compounds" is to eliminate other elements than carbon and to organize the alignment of carbon atoms as the producer designed. Someone would say "You can prepare carbon material just by heating or burn organic substance; no need of any difficult science there." Surely he is right. Heating or burning organic substance will give him carbon material; it is questionable that the obtained carbon material would satisfy his plan. In this case, the material is not produced but accidentally formed.

From: "Tanso Jimon Jitou" by Sugio Otani

Acknowledgment

Thanks to my “very active” students.

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ALCA Advanced Low Carbon Technology Research and Development Program

LCnet 低炭素研究ネットワーク LOW-CARBON RESEARCH NETWORK JAPAN

NISSHINBO

Element Innovation Gunma University, JAPAN

国立大学法人 群馬大学 NATIONAL UNIVERSITY CORPORATION GUNMA UNIVERSITY

Thanks to my colleagues:

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and the laboratory staffs.