H_2O selectivity of carbon alloy catalysts for PEMFC cathode

Naokatsu Kannari, Takafumi Suzuki and Jun-ichi Ozaki

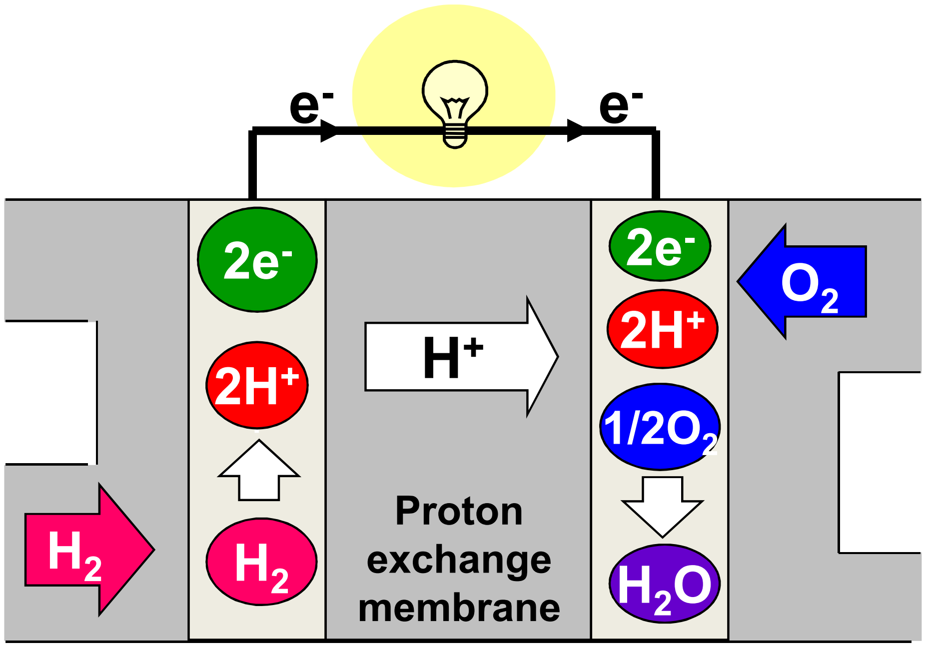
Gunma University

Outline

- **Introduction**
  - — Proton exchange membrane fuel cell
  - — Nanoshell-containing carbon
  - — Reaction pathway of oxygen reaction reaction
- **Experimental**
- **Results and discussion**
  - — Deference of the selectivity between Co-NSCC and Fe-NSCC
- **Conclusion**

Introduction

Proton exchange membrane fuel cell (PEMFC)



anode   **cathode** ←Oxygen Reduction Reaction (ORR)

Advantages

- high energy density
- low working temperature
- cleanliness

Problems The cathode requires more platinum than the anode, because the cathode reaction is quite slow

⇩

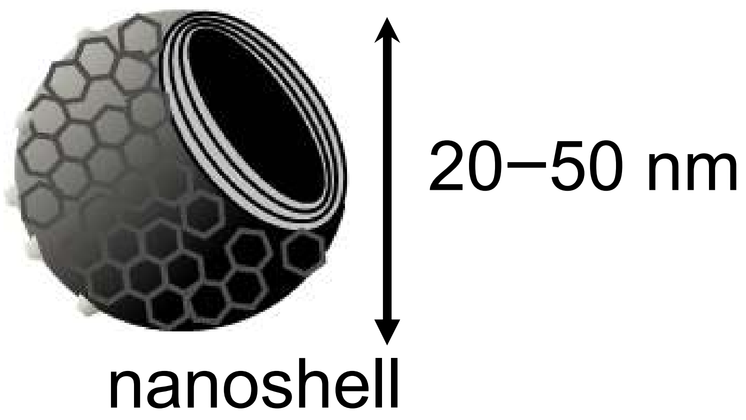
Exploration of the non-platinum cathode catalysts is needed to replace the costly platinum catalyst

Introduction

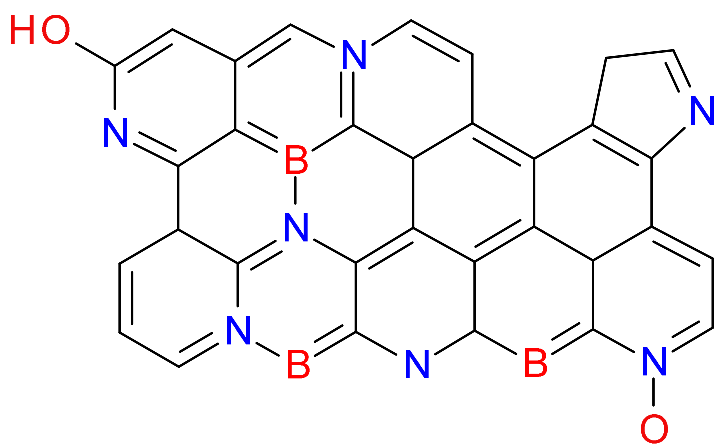
Non-platinum cathode catalyst for PEMFC ⇨ Carbon alloy catalyst

Carbon alloy catalyst

① Nanoshell structure



② Heteroatoms doping



Highly active catalysts for ORR

Introduction –Nanoshell-containing carbon as an ORR catalyst –

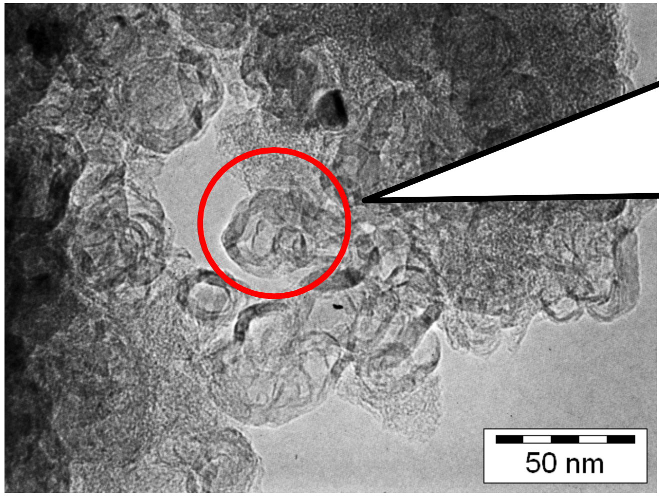
Preparation and structure of nanoshell-containing carbon (NSCC)

Starting polymer

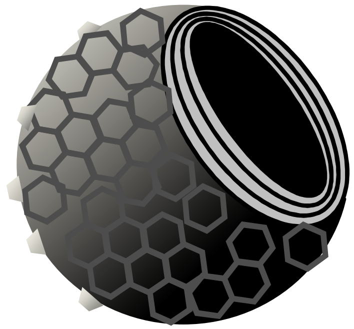
Transition metal complex

ex.) Co or Fe phthalocyanines

Carbonization



TEM image of NSCC



20-50 nm

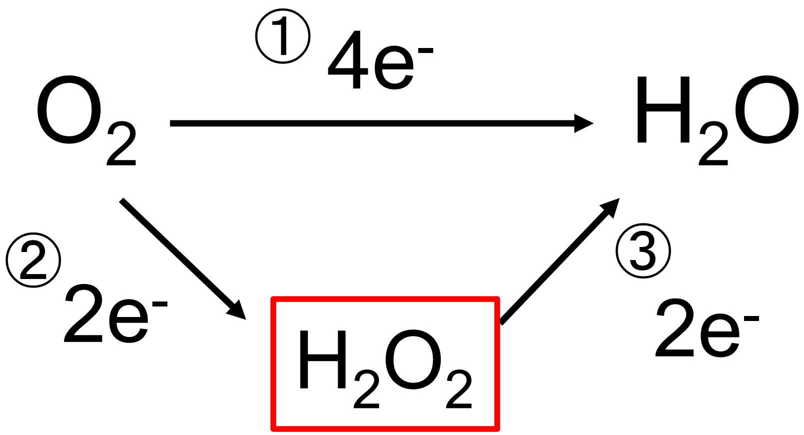
Model structure of nanoshell (NS)

Hollow spherical shape, whose wall is composed of graphitic layers

NSCCs show ORR activity

Promising candidate for the cathode catalyst

Reaction pathways of ORR



①: Direct 4-electron pathway

②+③: 2+2-electron pathway

Strong oxidant to damage the polymer electrolyte and the catalyst

⇨ Need to develop ORR catalysts with no or low H_2O_2 formation

Our previous study

Nanoshell forming catalyst	$\%H_2O$
Fe	High
Co	low

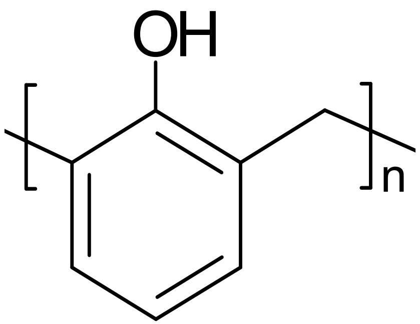
What is the controlling factor for the selectivity?

Objective of this study

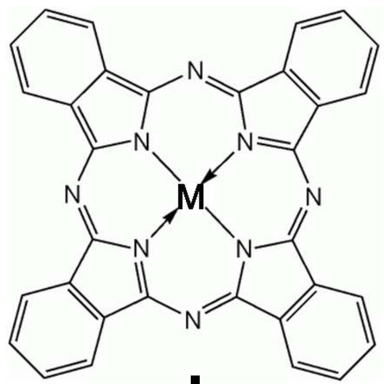
To clarify the factors determining the H_2O selectivity of NSCCs

Experimental –Preparation of NSCCs –

Phenol-formaldehyde resin(PF)



Metallophthalocyanine（Fe or Co：3 wt%）



Precursor

Carbonization

Ball-milling

Acid washing

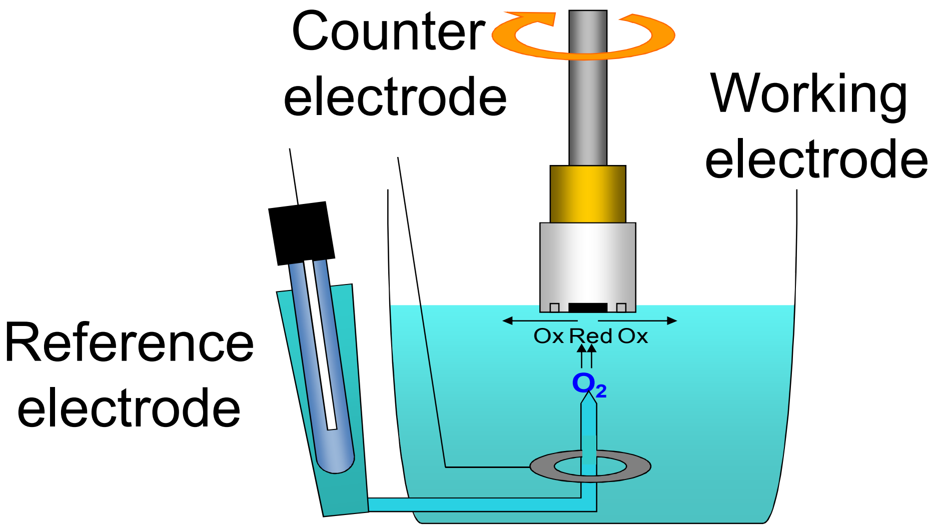
M-NSCC (M = Co or Fe)

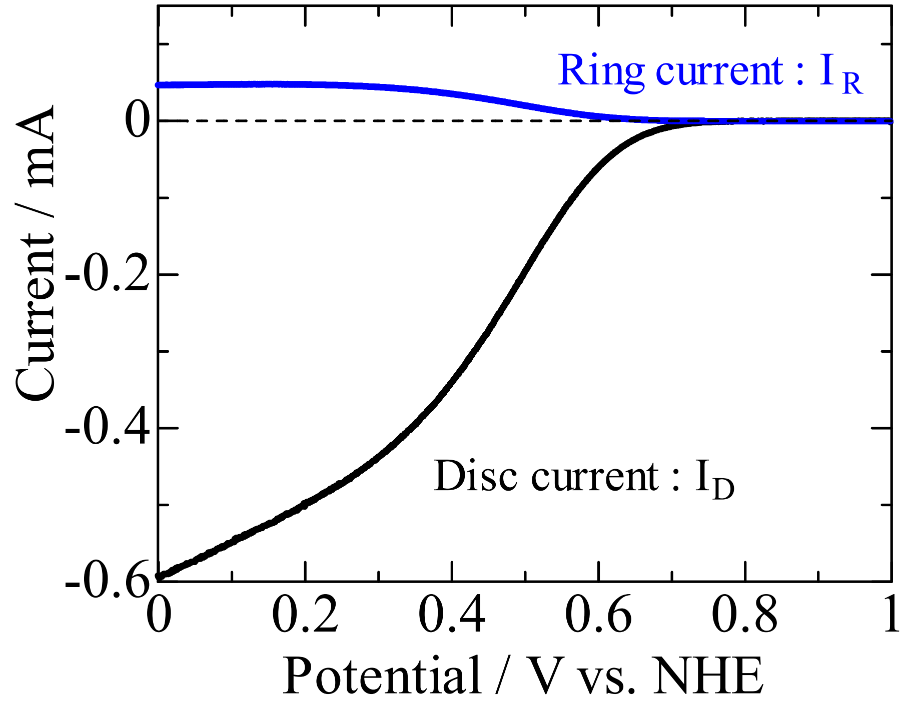
Carbonization conditions

In a nitrogen stream,
Heating rate：10℃/ min
Temperature：800 (Fe)
or 1000℃ (Co)
Time：1 h

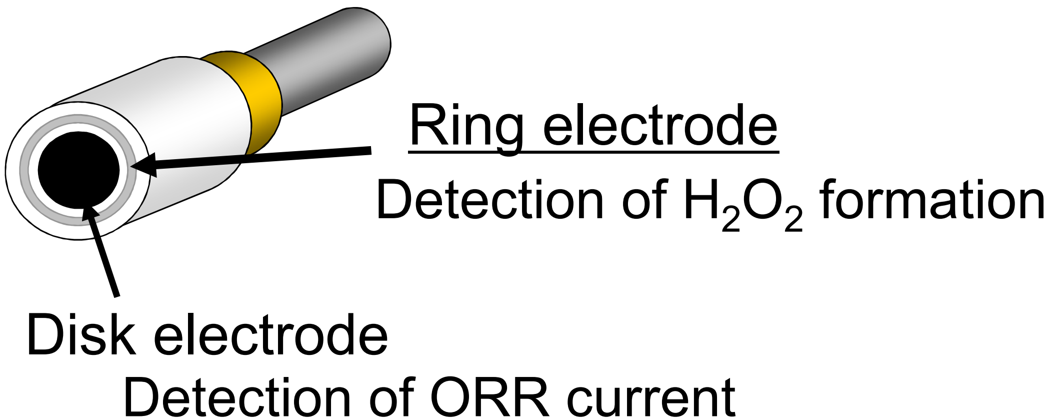
Evaluation of ORR activity and selectivity

Rotating ring-disk electrode (RRDE) method



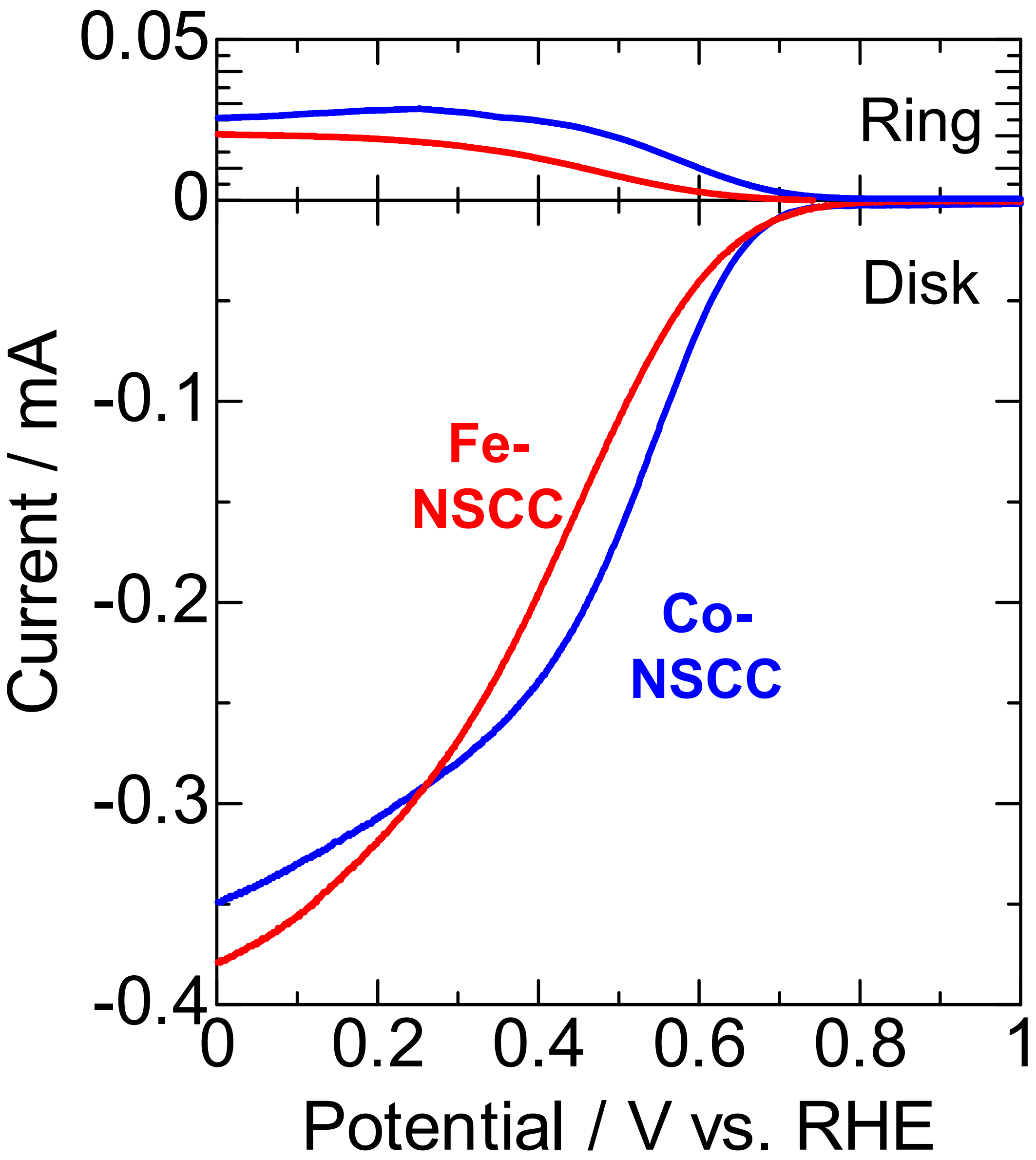


Working electrode



Calculation of the selectivity to H_2O from O_2 (%H_2O) by both disk and ring currents

ORR activities and selectivies of NSCCs



Sample	E_{O2} (V vs. RHE)	$\%H_2O$ (%)
Fe-NSCC	**0.78**	**86**
Co-NSCC	**0.78**	**59**

E_{O2}: Potential at -10 μA cm^{-2}

E_{O2} ··· Fe-NSCC **=** Co-NSCC
$\%H_2O$ ··· Fe-NSCC **>** Co-NSCC

Selectivity depended on the types of nanoshell forming catalysts, Fe or Co.

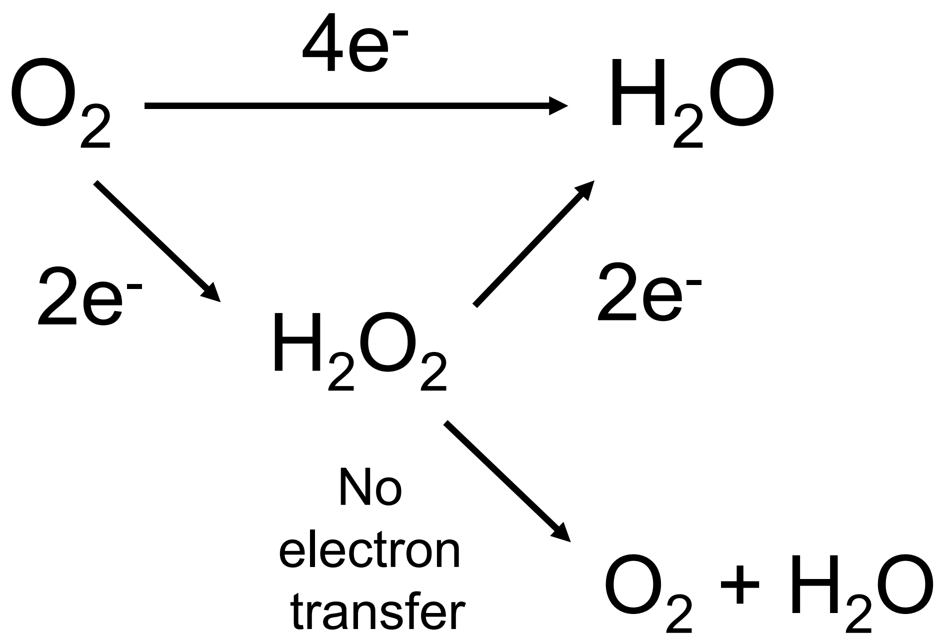
Possible explanations for the Fe-NSCC's high H_2O-selectivity compared to Co-NSCC's

Fe-NSCC promotes ….

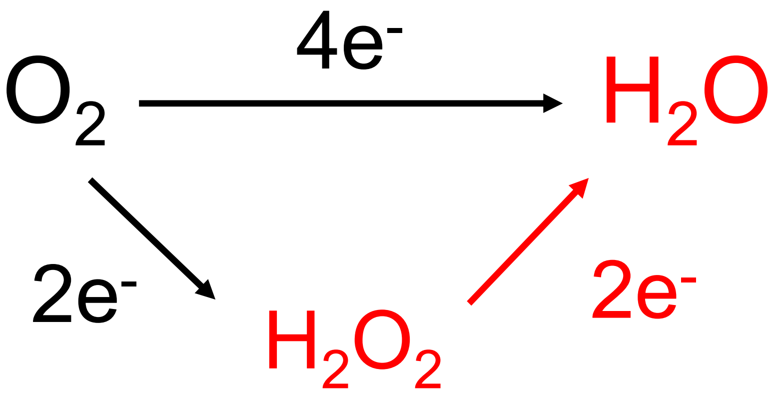
① Direct 4-electron pathway (difficult to occur in carbon catalysts)

② 2+2-electron pathway

③ H_2O_2 decomposition by disproportionation reaction

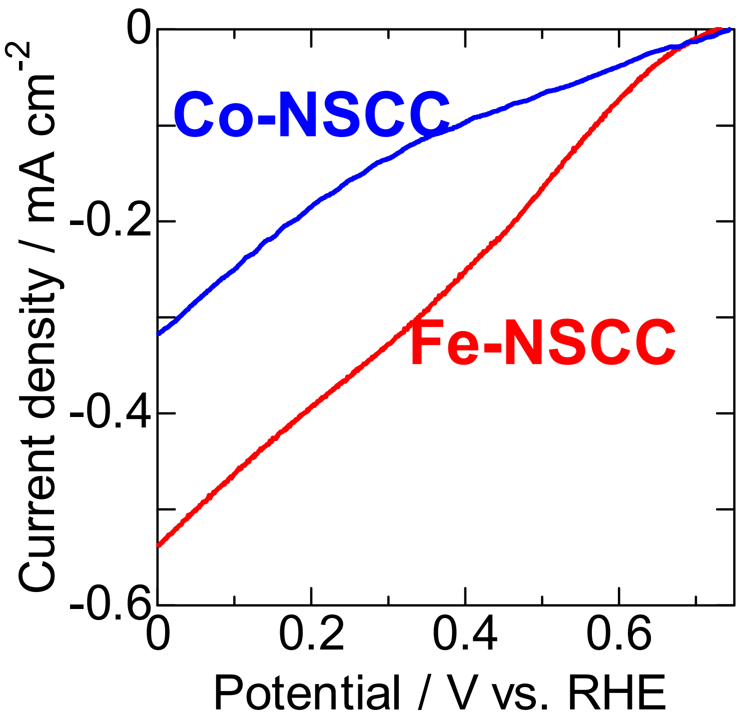


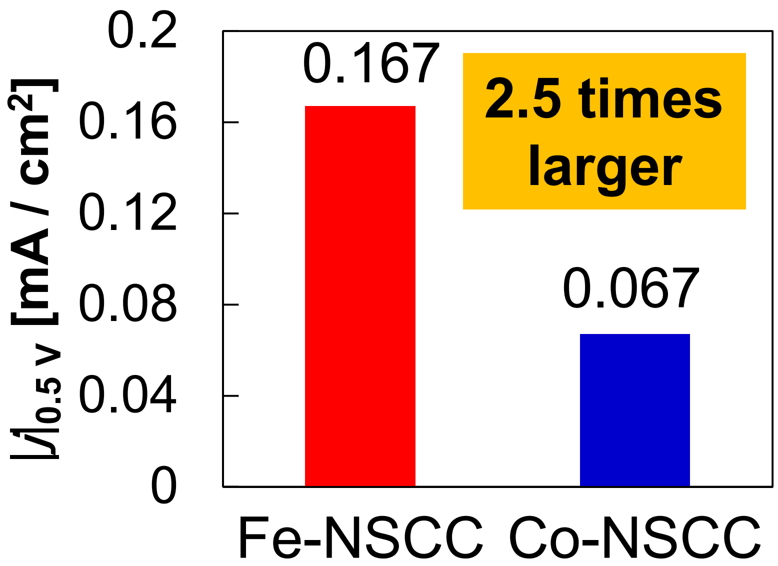
H_2O_2 reduction activity



Conditions of H_2O_2 reduction

Electrolyte	: 1 mM H_2O_2 / 0.5 M H_2SO_4
Counter electrode	: Glass-like carbon
Reference electrode	: Reversible hydrogen electrode
Scanning region	: 1 ～ 0 V vs. RHE
Scanning speed	: 1 mV/s
Rotating speed	: 1500 rpm





Fe-NSCC shows higher catalytic activity for H_2O_2 reduction than Co-NSCC

How dose Fe-NSCC promote the H_2O_2 reduction?

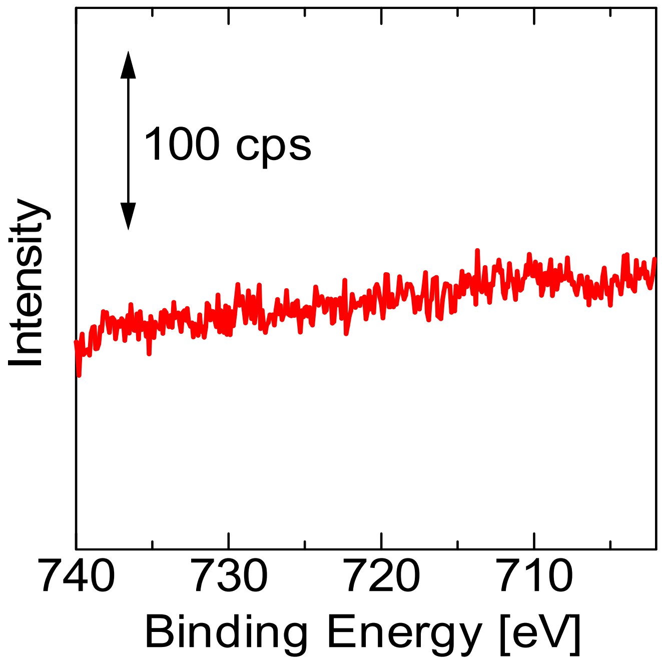
Possible controlling factors

① Surface metal species

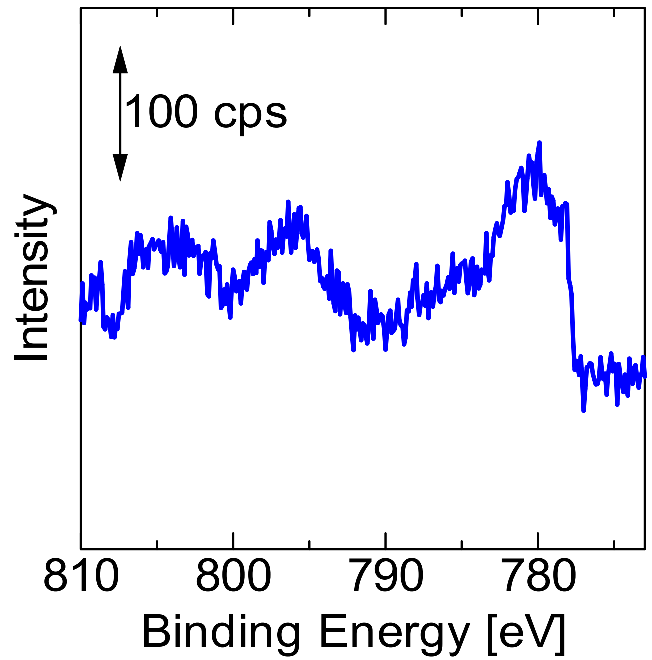
② Surface chemical structure

Surface metal species

Fe 2p XPS spectrum of Fe-NSCC



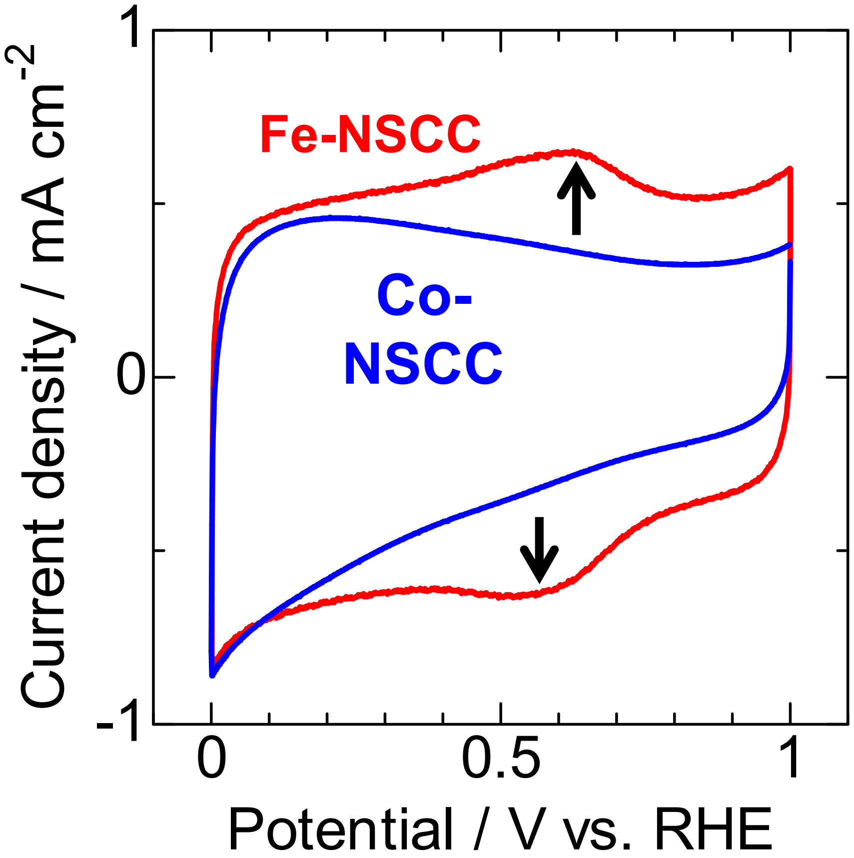
Co 2p XPS spectrum of Co-NSCC



Sample	M/C (M = Fe or Co)	H_2O_2 Reduction activity
Fe-NSCC	0	High
Co-NSCC	0.002	low

Metal species is not the controlling factor

Electrochemically active species on NSCC



Conditions for CV

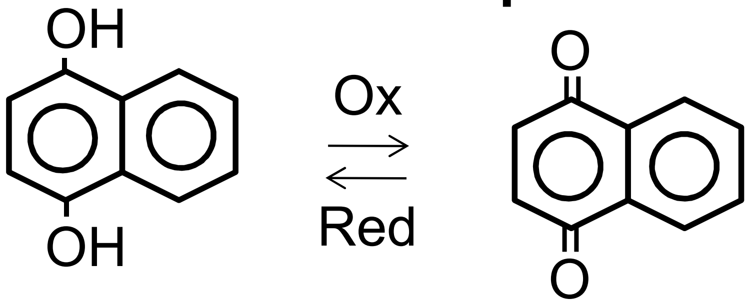
Electrolyte	**: 0.5 M H_2SO_4**
Counter electrode	**: Glass-like carbon**
Reference electrode	**: Reversible hydrogen electrode (RHE)**
Scanning range	**: 1 ～ 0 V vs. RHE**
Scanning speed	**: 50 mV/s**

<u>Fe-NSCC showed a redox peak at ca. 0.6 V</u>

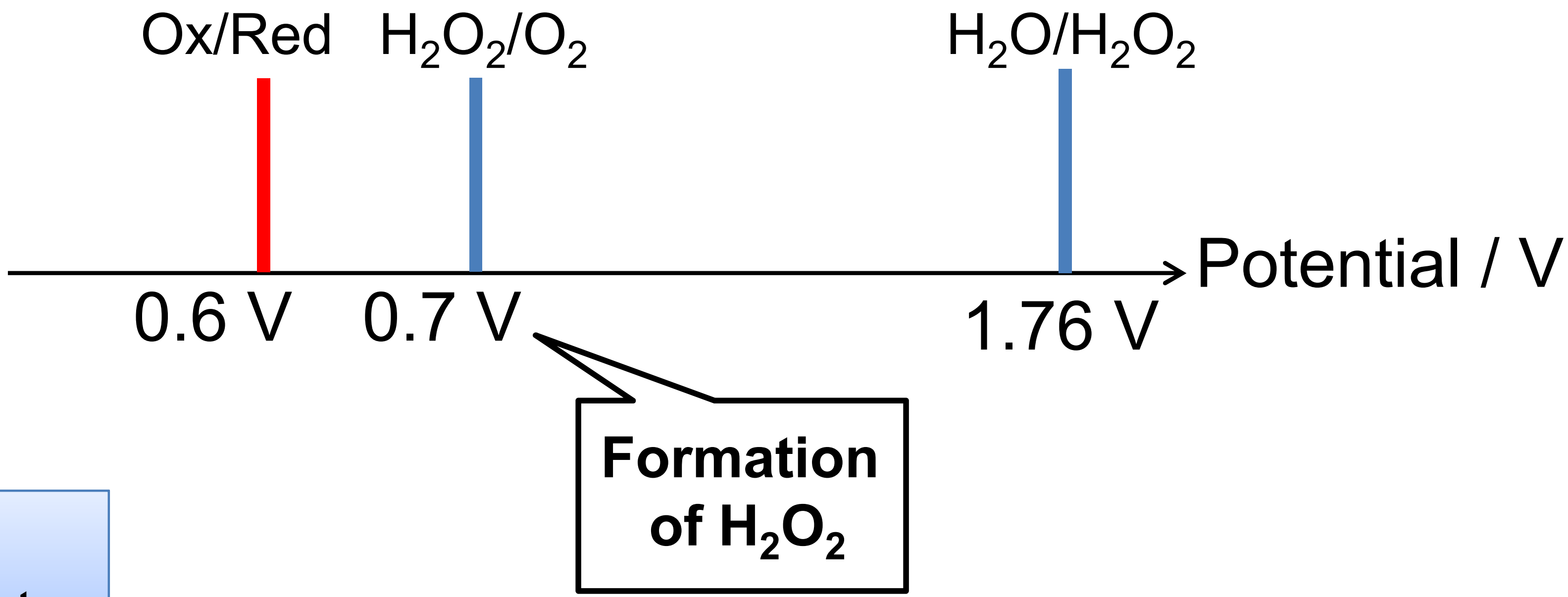
Possible factor for the promotion of H_2O_2 reduction

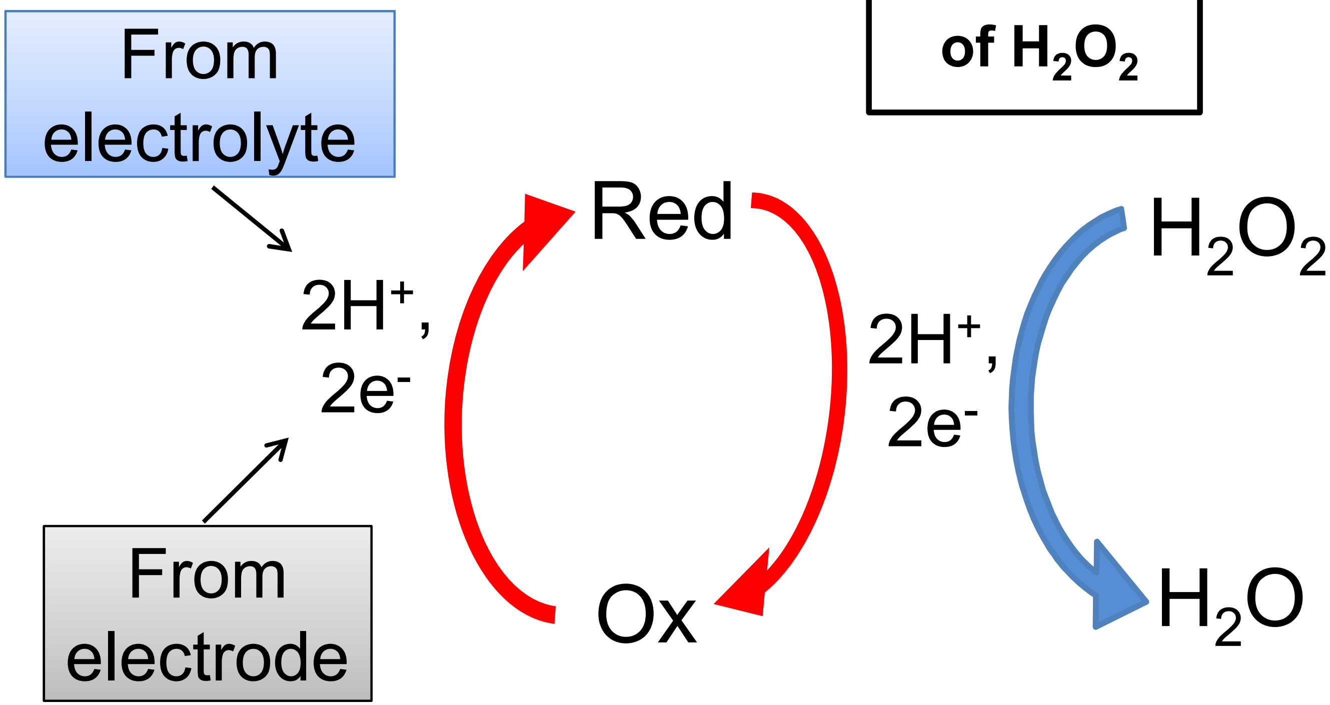
The redox species should be introduced by the addition of Fe, which does not mean the direct action of Fe

Quinone groups are the candidates for the redox species



Mechanism for the promotion of H_2O_2 reduction by the redox species





The redox cycle with the redox potential at 0.6 V promoted H_2O_2 reduction

Conclusion

In this study, we investigated the controlling factor for the ORR selectivity of NSCCs.

Comparison of Fe-NSCC and Co-NSCC

・Fe-NSCC shows the higher selectivity than Co-NSCC
the higher H_2O_2 reduction activity than Co-NSCC
the redox species at 0.6 V

⇩

The redox species promotes the selectivity of the ORR