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A Highly Efficient Electrocatalyst for Oxygen Reduction Reaction: N-doped Ketjenblack Incorporated into Fe/Fe_3C Functionalized Melamine Foam

Jang-Soo Lee, *Gi Su Park, Sun Tai Kim, Jaephil Cho**

Interdisciplinary School of Green Energy and
Converging Research Center for Innovative Battery Technologies
Ulsan National Institute of Science and Technology (UNIST), Korea

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Outline

- **Introduction:**

— Recent developments in non-precious metal catalysts for oxygen reduction reaction (ORR)

— Requirements for desired properties of non-precious metal catalysts

- **Our strategy inspired by a tetrapod structure of a breakwater**

— Proper combination of micro-sized melamine foam and nano-sized Ketjenblack

— Better catalytic activity and mass transport

- **Catalysts obtained by heat treatment of melamine foam, ketjenblack, and Iron metal precursors:**

— Melamine foam and ketjenblack derived catalysts

— ORR activity based on electrochemical, physical, and chemical analysis

- **Practical application of melamine/KB-derived catalysts**

- **Summary**

- **Acknowledgements**

Recent developments in non-precious metal catalysts for oxygen reduction reaction (ORR)

- The sluggish oxygen reduction reaction (ORR) contributes a majority of the loss in metal-air and fuel cell technology

- Platinum based catalysts have been widely used as cathode catalysts, but Its High cost and scarcity must be considered

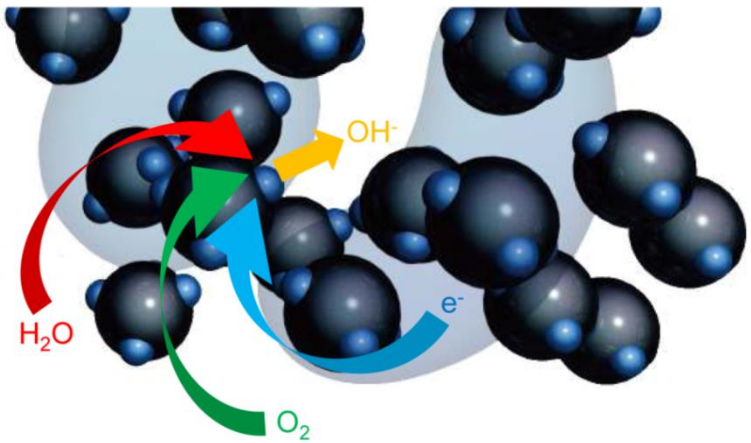
- Pyrolysis of transition metal precursor, nitrogen-carbon moiety, and other supporting materials (M/N/C-) have gained some significant attraction recently although the debate about TMN4/C and TMN2/C is ongoing[1-5]

1. Jasinski, R., *Nature,* 1964, 201, 1212.
2. Lefevre, M., J. P. Dodelet, Science, 2009, 324, 71.
3. Wu, G., P. Zelenay., Science, 2011, 332, 443.
4. Proietti, E, J. P. Dodelet., Nat. Commun., 2011, 2, 416.
5. Wen, Z. et al., Advanced Materials, 2012, 24, 1399.

Introduction

Requirements for desired properties of non-precious metal catalysts

Oxygen Reduction Reaction (ORR) in alkaline solution



Oxygen diffusion — Electronical conductivity

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline solution)

Hydrophobicity/ Hydrophilicity

Unfavorable to active sites

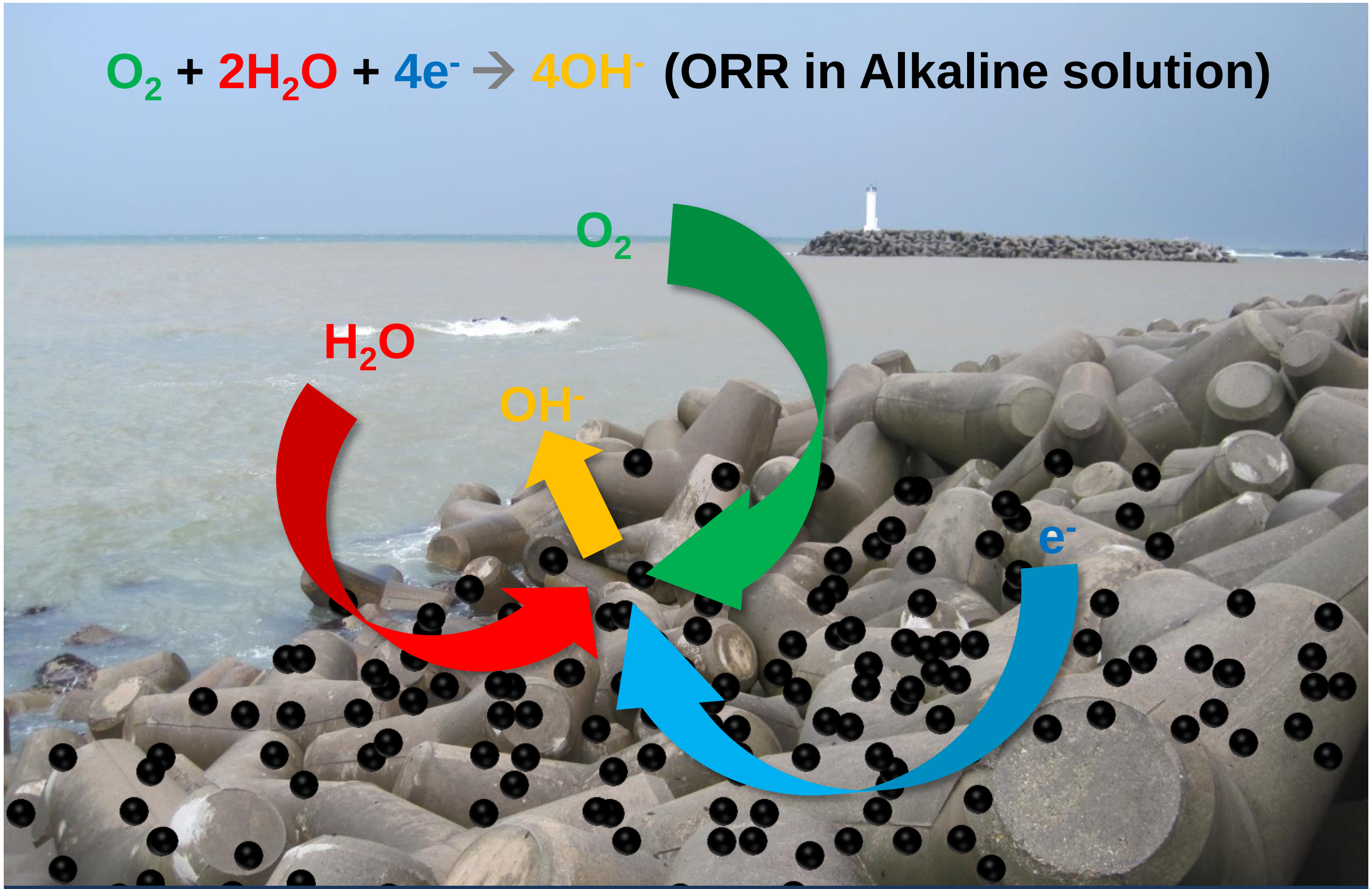
Kinetic rate: catalytic activity for Oxygen Reduction Reaction

<Requirements>[1-5]

- "High ORR onset potential"
- "High active site density & uniform distribution"
  – high mass and volumetric activities (> 1/10 of Pt/C)
- "High surface area and pore size control"
- "High mass transport and electronical conductivity"
- "High stability"

1. H. A. Gasteiger, et. al. , Appl. Catal. B, 2005, 56, 9.
2. F. Jaouen, et. al., Appl. Mater. Interfaces, 2009, 1, 1623.
3. Lee, J. S. et al., Nano Letters, 2011, 11, 5362. ; 4. Lee, J. S. et al., Energy Environ. Sci., 2011, 4, 4148.
5. D.-J. Liu, Fuel Cell Seminar & Exposition San Antonio, TX, 2010

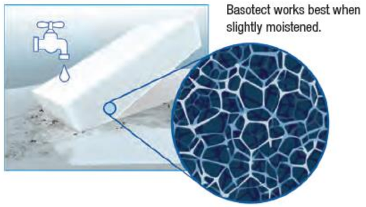
Our strategy inspired by a tetrapod structures of a breakwater



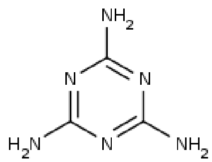
1. Connecting pores into which air and electrolyte can easily invade
2. Superior mechanical strength

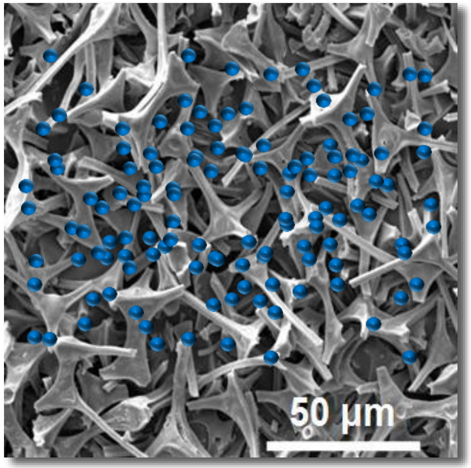
This photo taken in *Jung-Ja* harbor in Ulsan, Korea.

How to realize this idea?

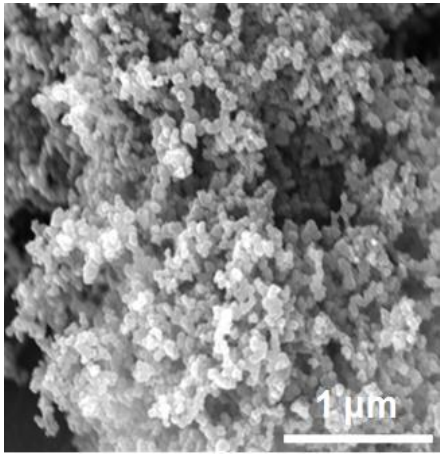


pyrolysis





Micro sized structure of carbonized Melamine foam[2] affording skeleton and active site by Fe functionalization

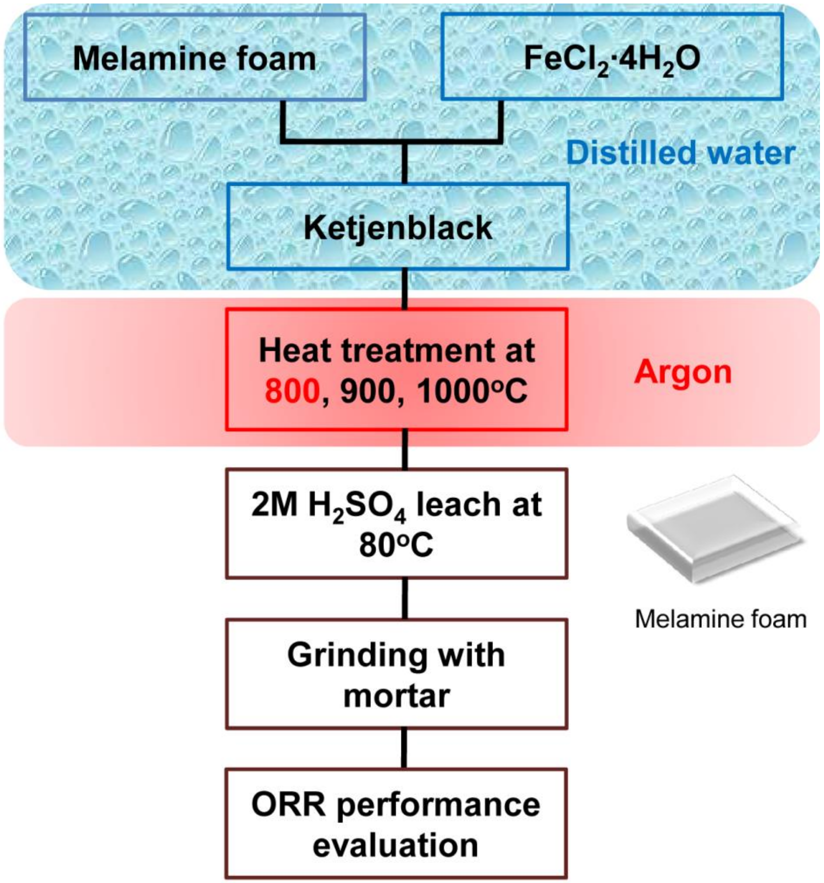


- Proper combination of micro sized melamine foam and nano-sized Ketjenblack can afford both many active sites and better mass transport

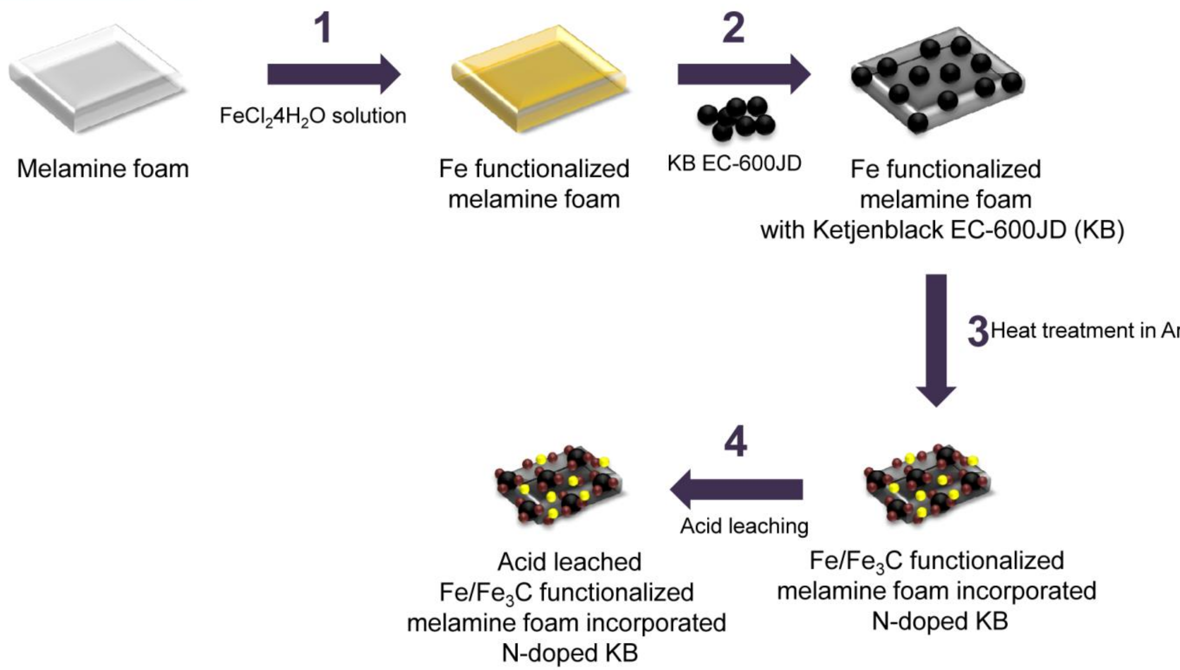
Nano sized structure of Ketjenblack EC-600JD (High surface area (~ 940m^2/g)) affording many active sites and electronical conductivity

1. http://www.basf.com/group/corporate/en/brand/BASOTECT
2. Kodama, M, et. al., Carbon, 2007, 45, 1105

High-Temperature Synthesis of melamine/KB-derived catalysts



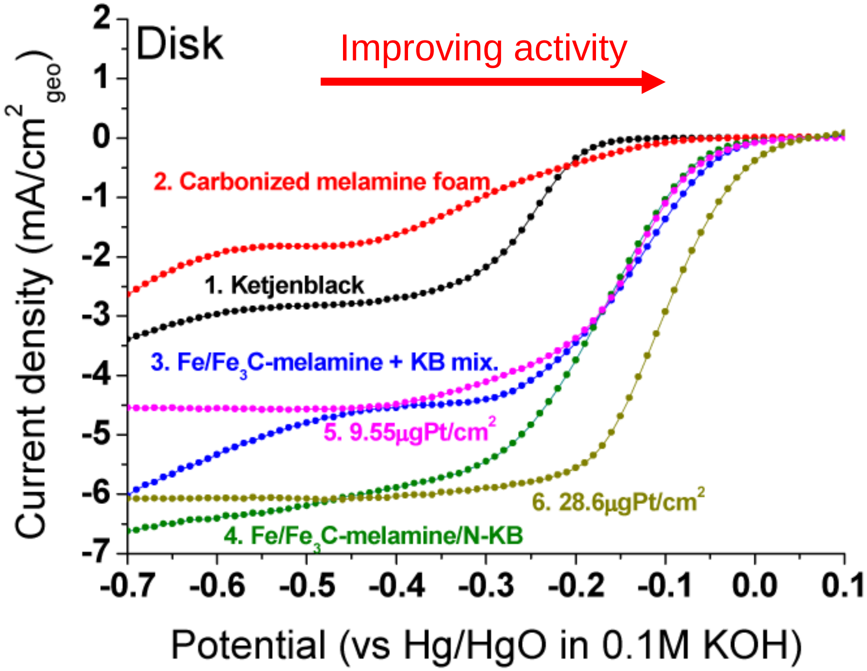
- Facile one-pot pyrolysis synthesis
- Starting materials is very cheap
- Melamine foam acting as nitrogen source to Ketjenblack during pyrolysis

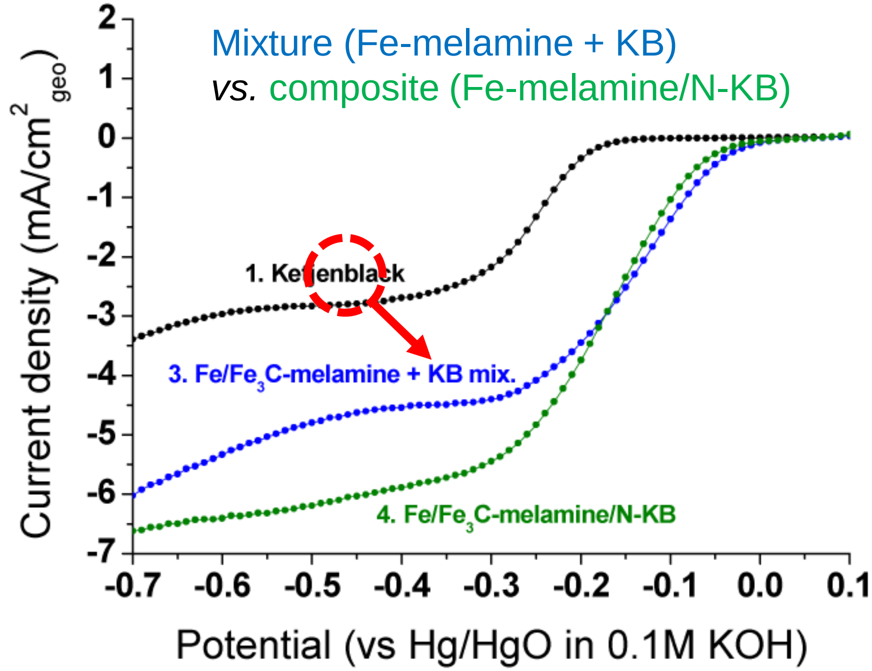


Melamine/KB-derived Catalysts: ORR Activity and 4e- Selectivity

Rotating Ring Disk Electrode (RRDE) Data

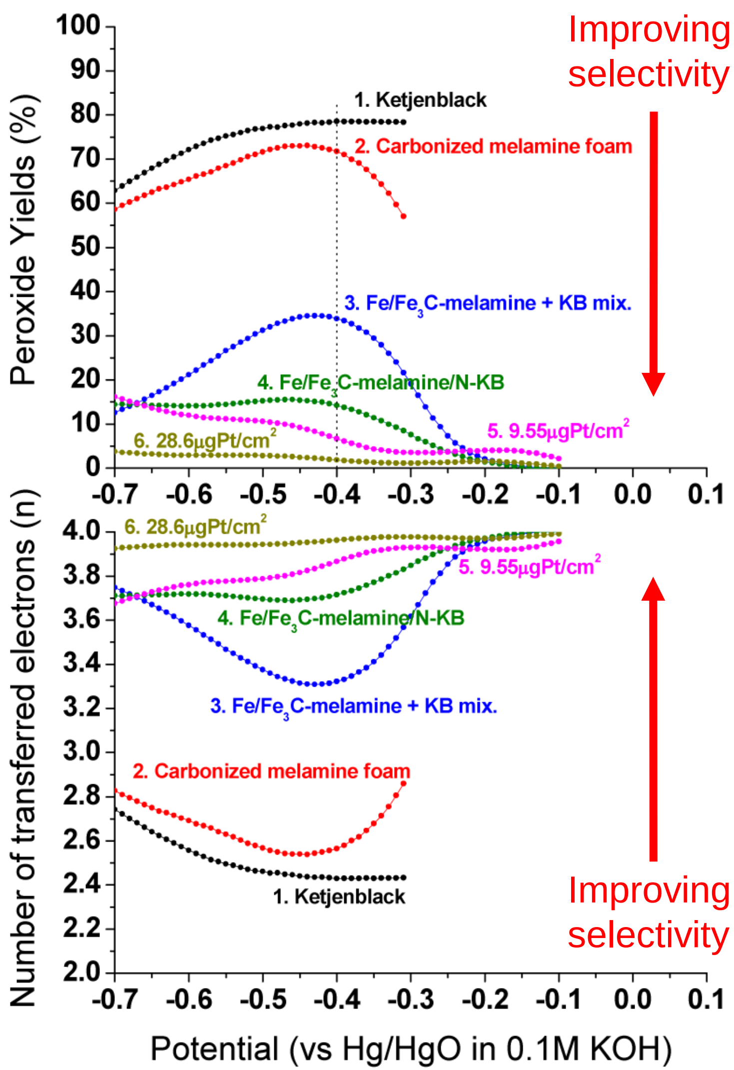
- Non-precious metal catalysts loading are $0.286 mg_{cat}/cm^2$ (10 times higher than 28.6 $\mu gPt/cm^2$)
- 0.1M KOH and 2000rpm





- Comparative kinetic activity in low overpotential with Pt/C
- Further gradually increasing current at high overpotential region
- Mixture and composite showed different shape in LSV (synergic effect)

Melamine/KB-derived Catalysts: ORR Activity and 4e$^-$ Selectivity



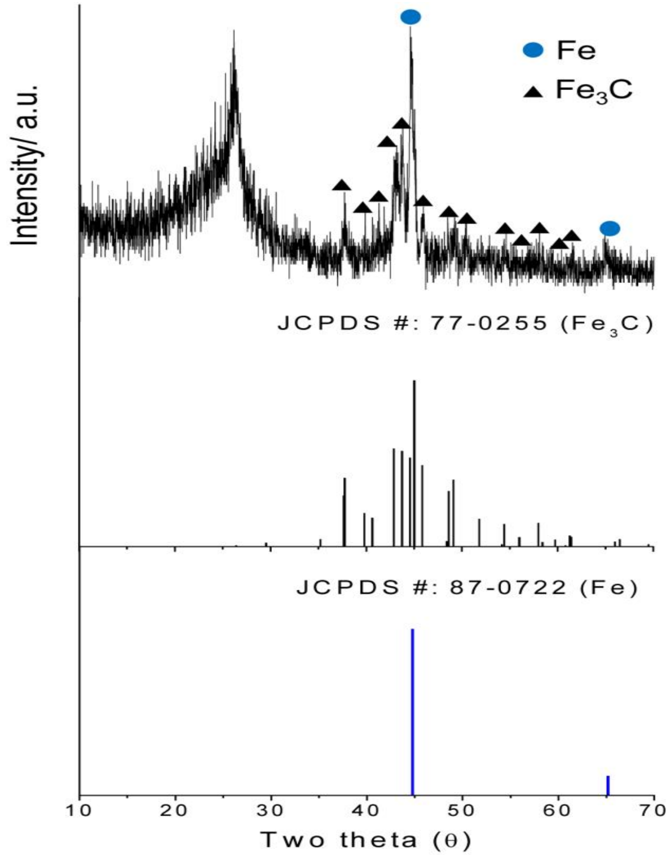
Number of electrons: $n=(4I_{disk})/(I_{disk}+I_{ring}/N)$
Peroxide yield: $\%HO_2 = (200I_{ring}/N)/(I_{disk}+I_{ring}/N)$

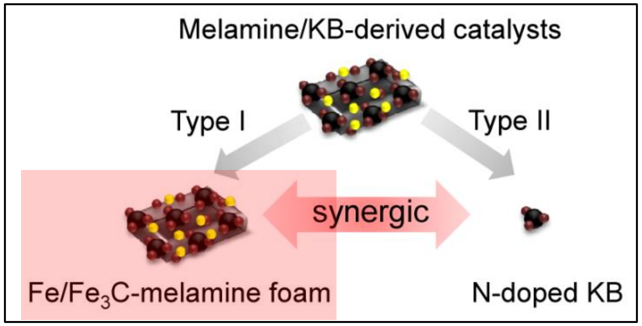
Catalyst	Potential at 0.1mA/cm² (V vs. Hg/HgO)	Current density at -0.45V (mA/cm²)
Ketjenblack	**-0.17**	**-1.793**
Carbonized melamine foam	**-0.11**	**-2.79**
Fe/Fe_3C-melamine + KB mix.	**-0.01**	**-4.62**
Fe/Fe_3C-melamine /N-KB	**-0.02**	**-6.03**
9.55$\mu g_{Pt}/cm^2$	**-0.01**	**-4.55**
19.1$\mu g_{Pt}/cm^2$	**0.025**	**-5.65**
28.6$\mu g_{Pt}/cm^2$	**0.035**	**-6.06**

For the melamine/KB-derived catalysts
- Peroxide generation around 15% at -0.4V
- # n is 3.7~3.85, which is direct pathway

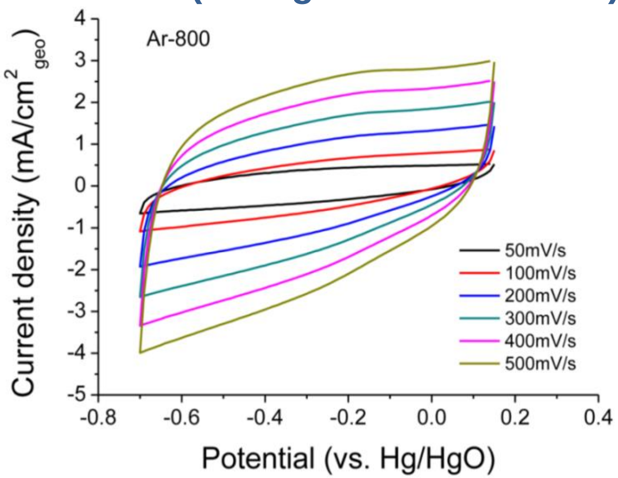
Origin of activity for ORR in melamine/KB-derived catalysts

Chemical composition: Structure 1. Fe/Fe_3C-melamine foam





No $Fe^{2+/3+}$(Background scan in Ar)



- Our catalysts is composed of metallic Fe and Fe_3C in XRD
- Iron coordinated N-C species (Fe/N/C) could not participate in ORR

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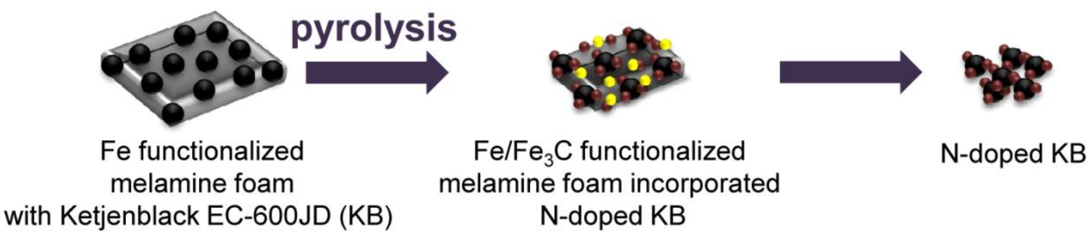
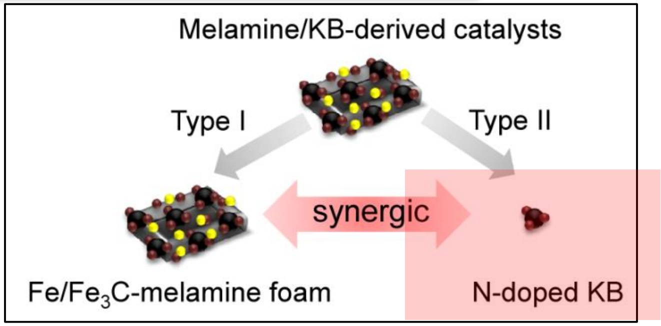
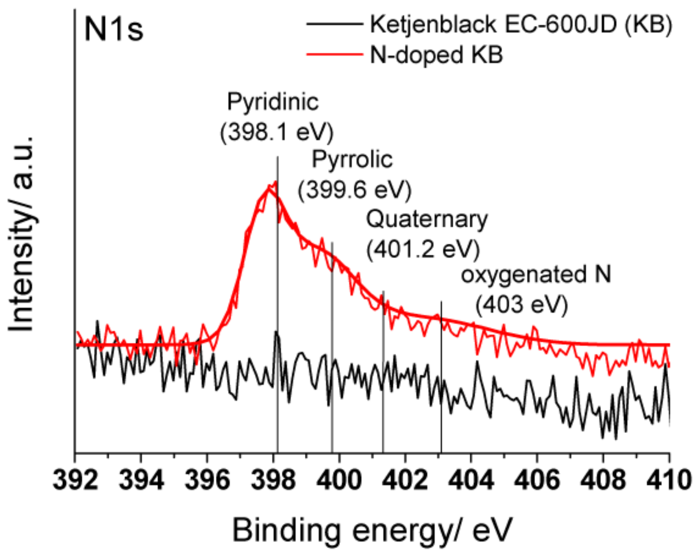
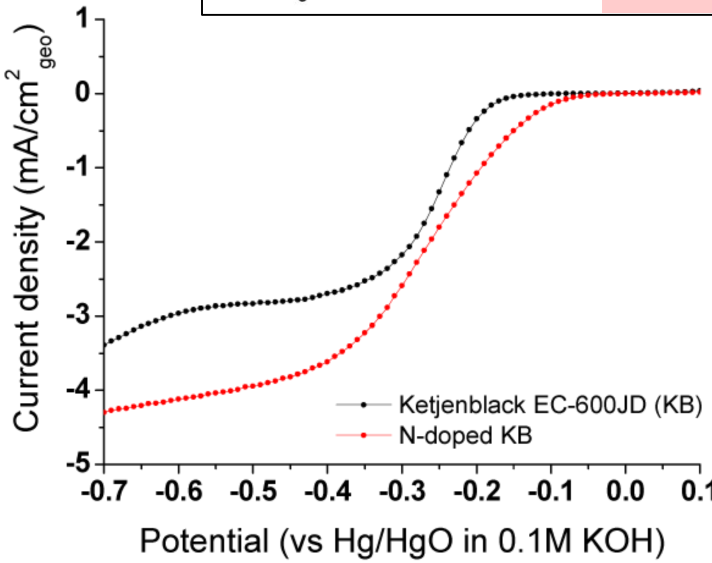
Origin of activity for ORR in melamine/KB-derived catalysts

Chemical composition: Structure 2. N-doped Ketjenblack









- N-doped ketjenblack foamed during pyrolysis and positive effect on ORR
- Melamine foam can act as N-source during pyrolysis

Origin of activity for ORR in melamine/KB-derived catalysts

Chemical composition:
Structure 1. Fe/Fe_3C-melamine foam + 2. N-doped Ketjenblack (KB)

N-doped KB

Oxygen diffusion

Electronical conductivity

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline solution)

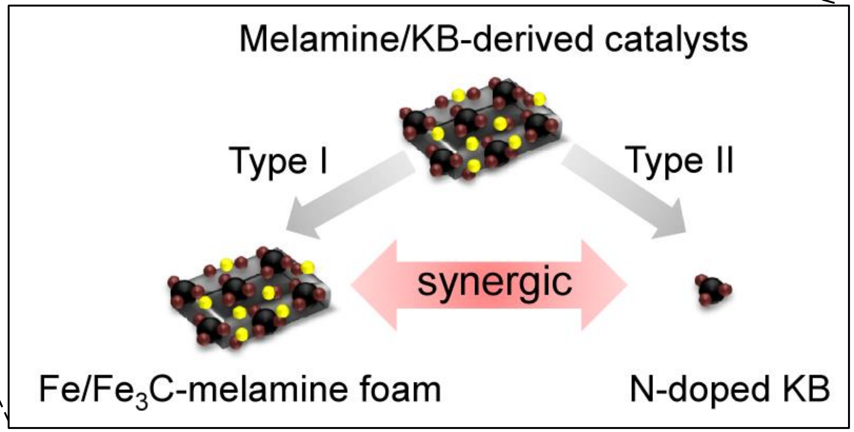
Hydrophobicity/ Hydrophilicity

Unfavorable to active sites

Kinetic rate: catalytic activity for Oxygen Reduction Reaction

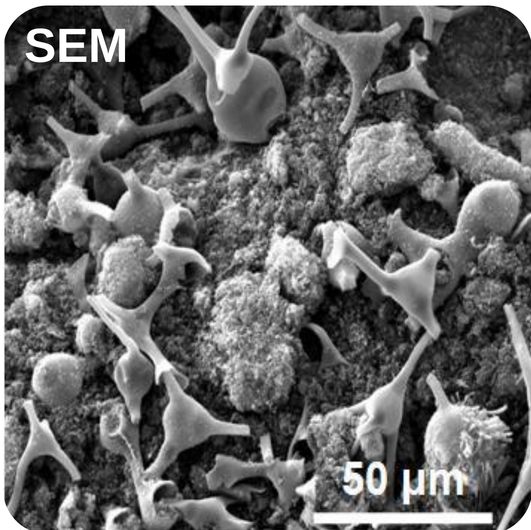
- Oxygen diffusion
- Hydrophilicity

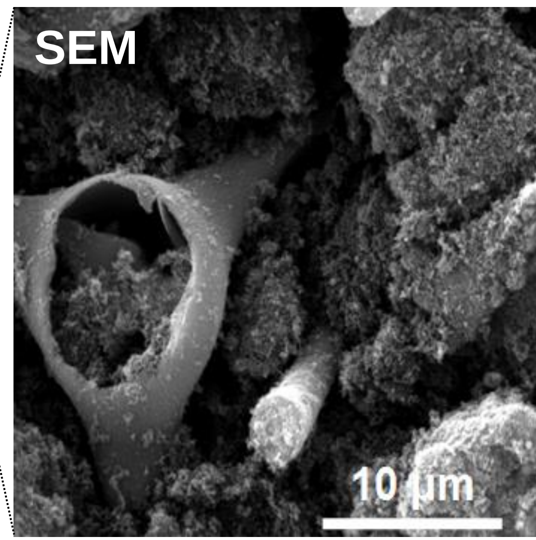
- Better mass transport (?)

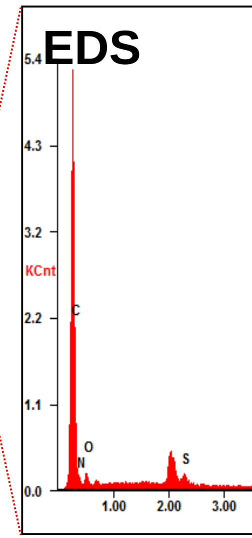


Origin of activity for ORR in melamine/KB-derived catalysts

Physical shape: Microstructure of melamine/KB-derived Catalysts: FE-SEM Images

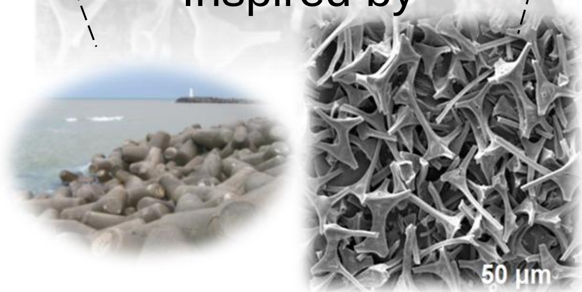






	Elemental composition by EDS (Wt. %) of Ar-800
C	75.1
N	14.2
O	4.99
Fe	3.30
S	2.30

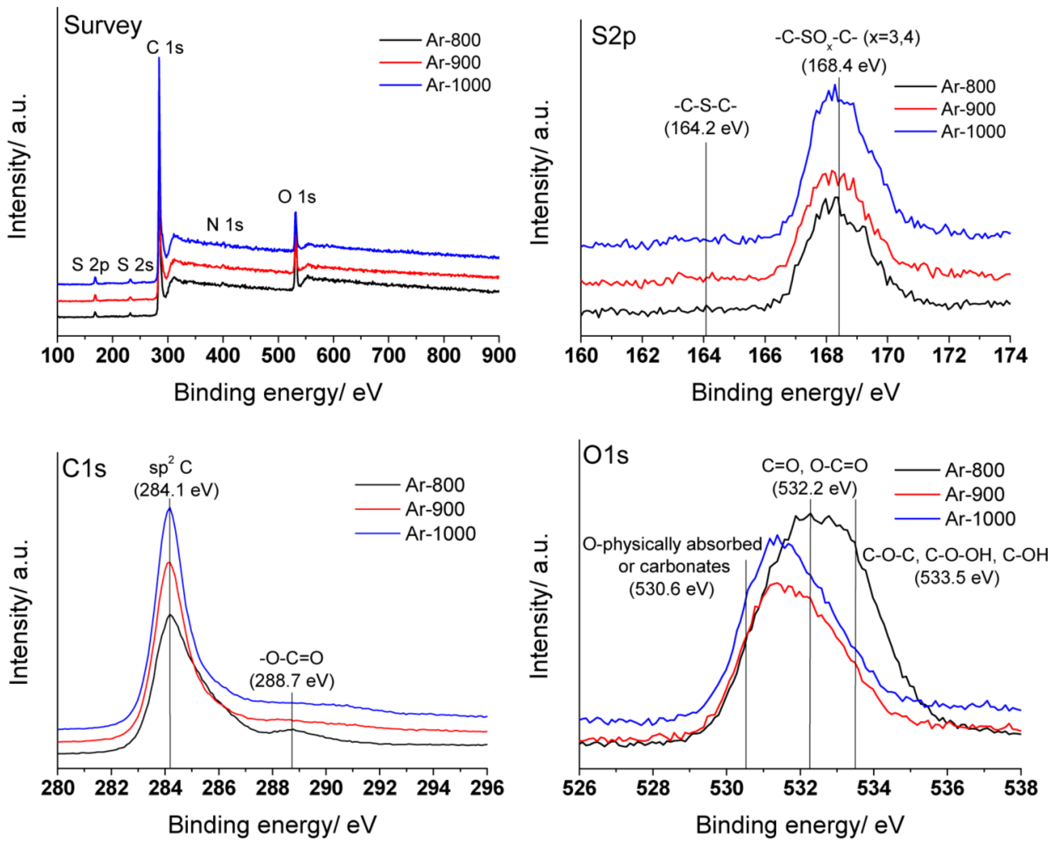
Inspired by



- Micro & nano structure combination
- Better porosity → better mass transport
- Good attachment of KB on melamine moiety
- Fe and Fe_3C based on XRD and EDS

Origin of activity for ORR in melamine/KB-derived catalysts

Chemical composition: melamine/KB-derived Catalysts: XPS



- Increased Hydrophilicity based on -O-C=O, C=O, and -C-SO$_x$-C- (x=3,4)[1,2]
- S-doped effect on ORR is negligible (-C-S-C-)[2,3]
- Proper combination of hydrophobic and hyrophilicity could be better than only one property → enhanced mass transport

1. Datsyuk, V. et. al., Carbon, 2008, 46, 833.
2. Yang, Z. et. al., ACS Nano, 2011, 6, 205.
3. Choi, C. H. et. al., Green chemistry, 2011, 13, 406.

Origin of activity for ORR in melamine/KB-derived catalysts

Physical & Chemical composition: better Mass transport with Structure 1. Fe/Fe_3C-melamine foam + 2. N-doped Ketjenblack (KB)

N-doped KB

Oxygen diffusion

Electronical conductivity

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline solution)

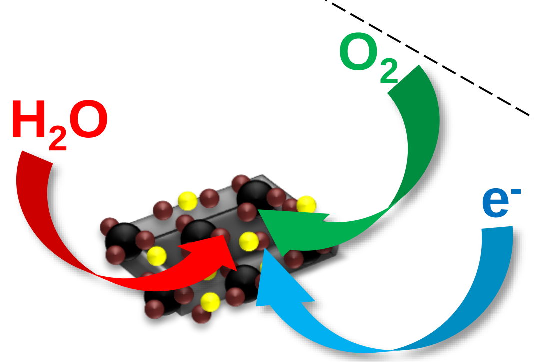
Hydrophobicity/ Hydrophilicity

Unfavorable to active sites

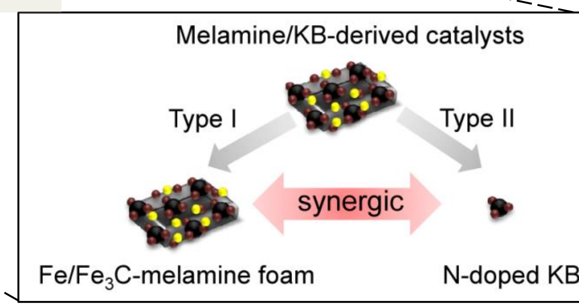
Kinetic rate: catalytic activity for Oxygen Reduction Reaction

- Oxygen diffusion
- Hydrophilicity

- Better mass transport

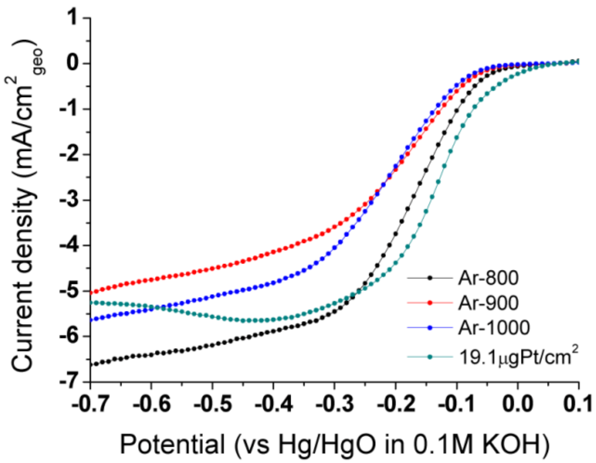


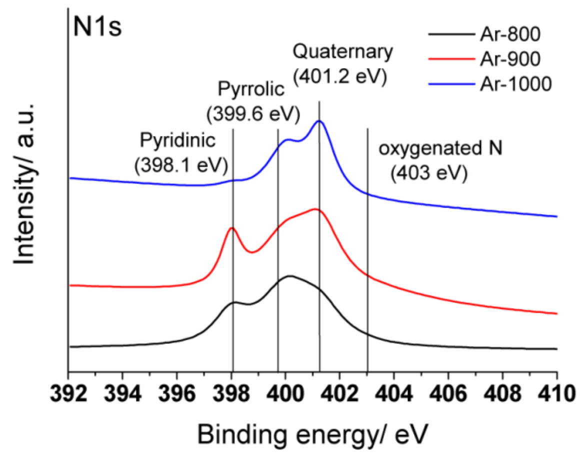
melamine/KB-derived catalysts



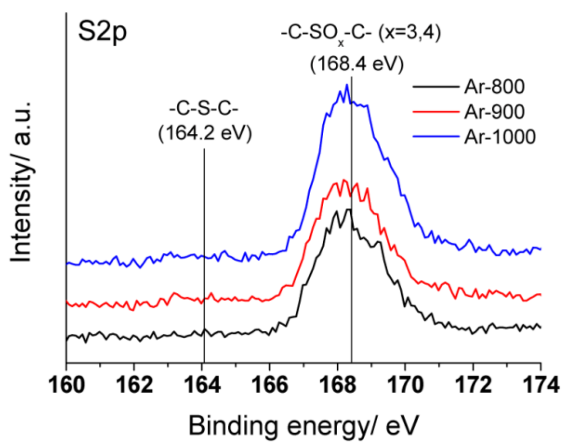
Origin of activity for ORR in melamine/KB-derived catalysts

Temperature effect on melamine/KB-derived Catalysts: RRDE and XPS





C-N···Fe/Fe_3C



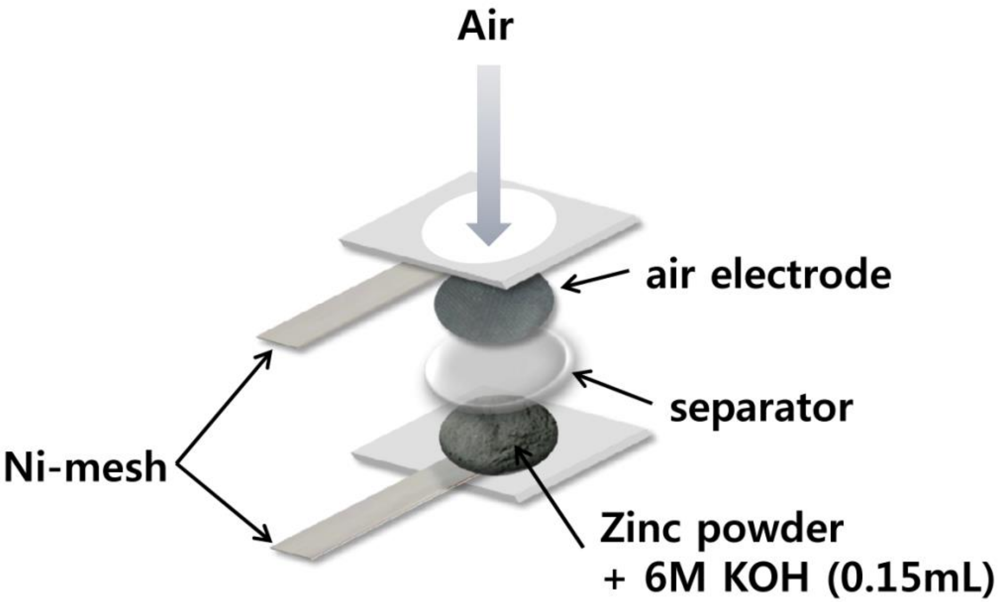
- Ar-800 is our best non-precious metal catalysts
- Pyridinic + pyrolic N: major binding site for Fe + Fe_3C
- Sulfur does not be affected under Heating T
- Sulfur could exist as (-C-SO_x-C- (x=3,4)),

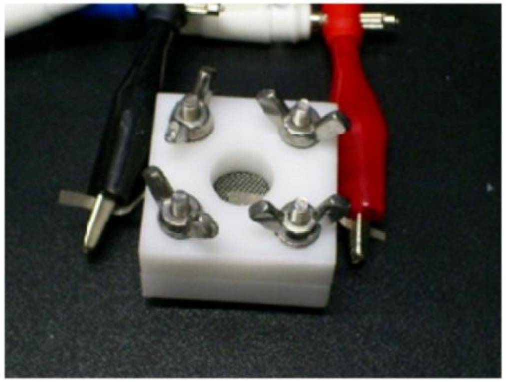
not (-C-S-C-) (coming from bisulfite of melamine foam)

→ Could not affect electronic structure of carbon

Practical application of melamine/KB-derived catalysts

Application 1: Zinc-air battery[1-3]





- Catalysts loading density

1) Non-precious metal catalyst loading: $0.3mg_{cat}/cm^2$

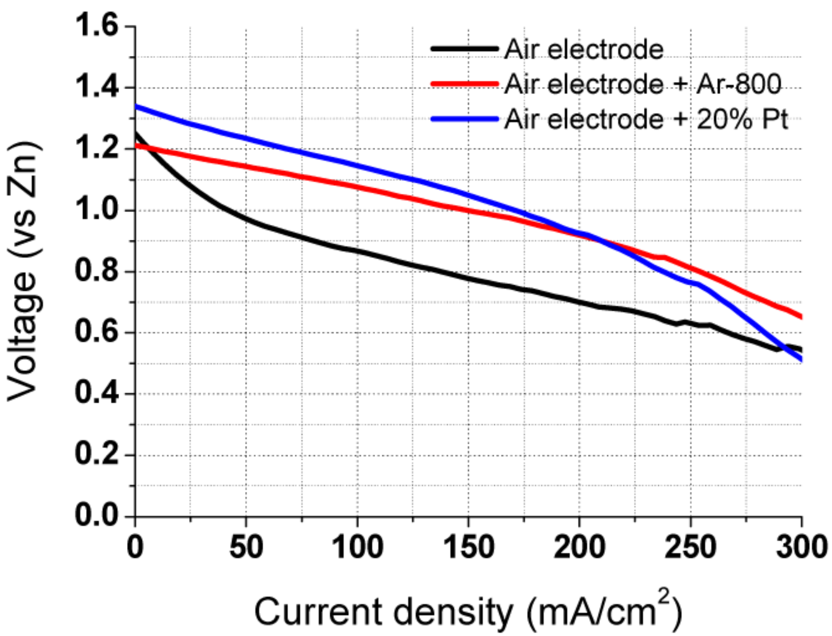
2) 20%Pt/C catalysts (E-TEK) (For reference material):

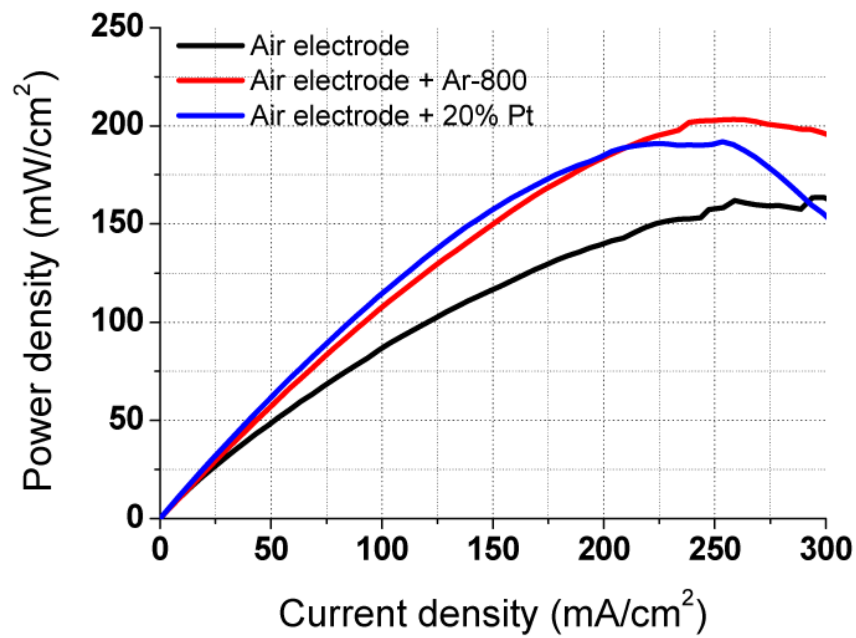
$0.2mg_{cat(Pt+carbon)}/cm^2 = 40\mu g_{Pt}/cm^2$

1. Lee, J. S. et al., Nano Letters, 2011, 11, 5362.
2. Lee, J. S. et al., Energy Environ. Sci., 2011, 4, 4148.
3. Lee, J.-S. et al., Advanced Energy Materials, 2011, 1, 34.

Practical application of melamine/KB-derived catalysts

Application 1: Zinc-air battery

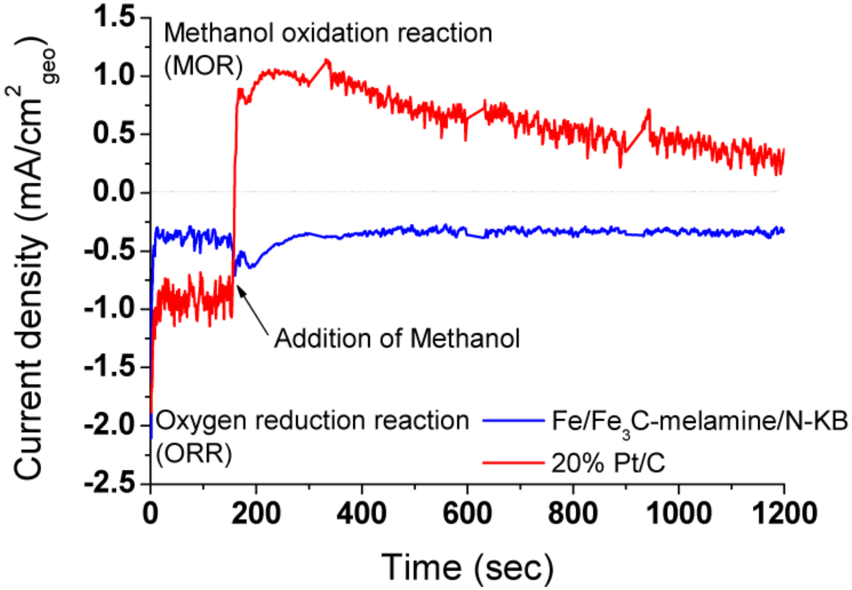


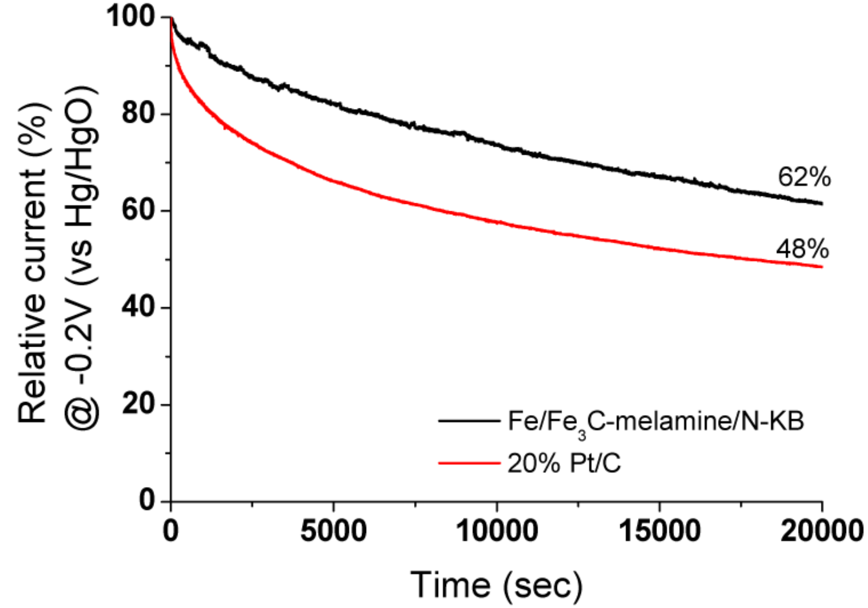


- Similar activity trend observed in both RDE and Zn-air Fuel cell testing
- Enhanced mass transport at high current density based on physical & chemical analysis
- Better power density of ~200mW/cm^2 using melamine-KB derived catalysts

Practical application of melamine/KB-derived catalysts

Application 2: Methanol cross over (for DMFC) and durability





- Our melamine/KB derived catalysts (Ar-800) showing better tolerance for methanol crossover and durability than Pt/C catalysts
- Our melamine/KB catalysts can be used as cathode catalysts for DMFC
- Further detail analysis and optimization is required for better catalysts

Summary

Without any detail optimization of Fe contents in the sample

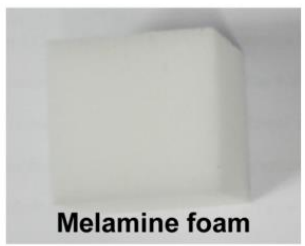
- Melamine/KB derived catalysts has

(1) High activity (reasonable selectivity for 4 e^- process and low peroxide yield)

(2) Better mass transport (Of course, Further more systematic analysis is needed such as volumetric or gravimetric activity)

(3) Reasonable tolerance for methanol cross over and good durability

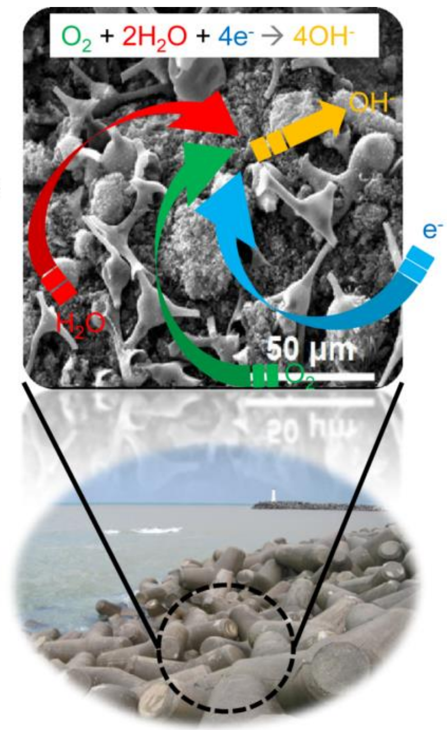
(4) Facile and cost effective mass production is possible

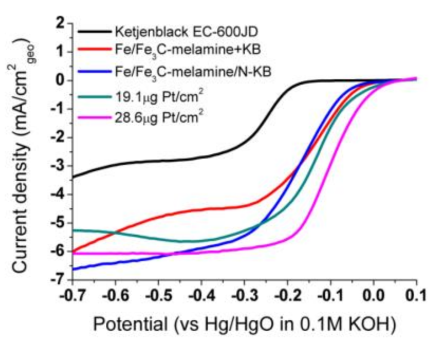


pyrolysis

$FeCl_2 \cdot 4H_2O$

Ketjenblack





Acknowledgments

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Thank you for your attention

Jung-Ja harbor in Ulsan, Korea