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Efficient oxygen reduction reaction electrocatalysts for Zn-Air battery

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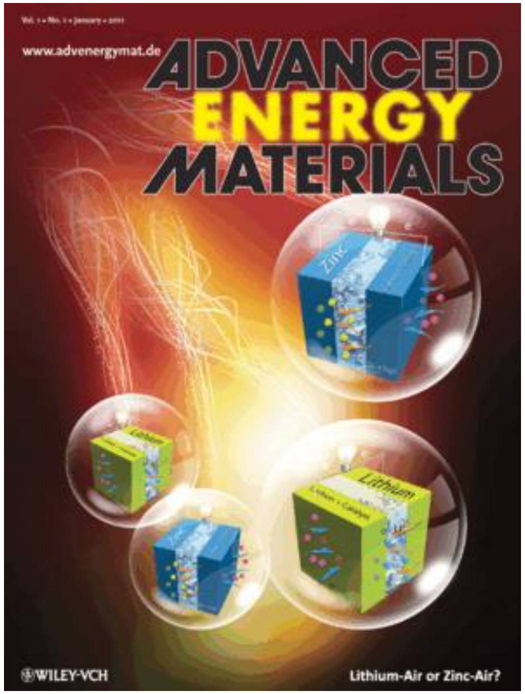
This presentation does not contain any proprietary or confidential information

Our studies in Zinc-air battery

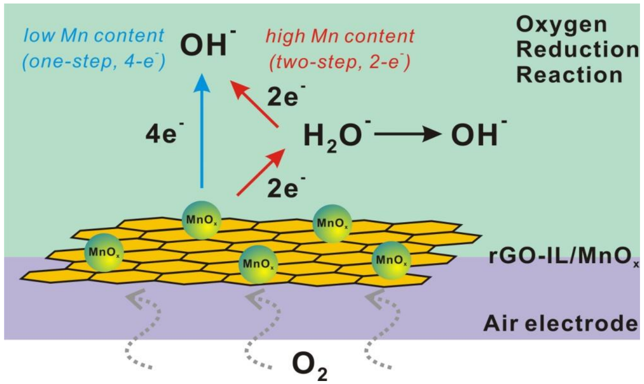
1. Jang-Soo Lee, Sun Tai Kim, Ruiguo Cao, Nam-Soon Choi, Meilin Liu, Kyu Tae Lee*, Jaephil Cho*, "Metal–Air Batteries with High Energy Density: Li–Air versus Zn–Air", 1, 1, 34-50, 2011, ***Adv. Energy Mater.***



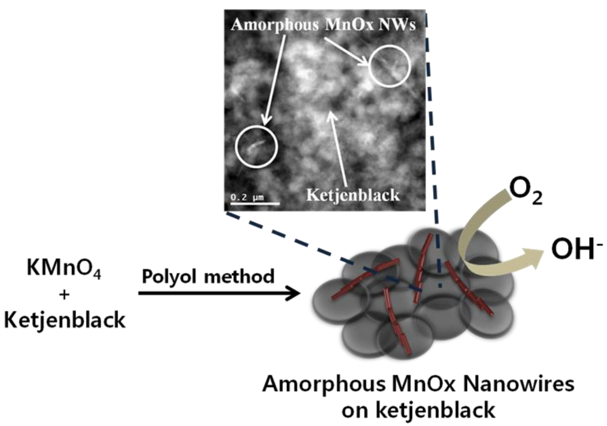
2. Min-Kyu Song, Soojin Park, Faisal M. Alamgir, Jaephil Cho*, Meilin Liu*
"Nanostructured electrodes for lithium-ion and lithium-air batteries: the latest developments, challenges, and perspectives", 2011, ***Mater. Sci. Eng. R*** (doi:10.1016/j.mser.2011.06.001)

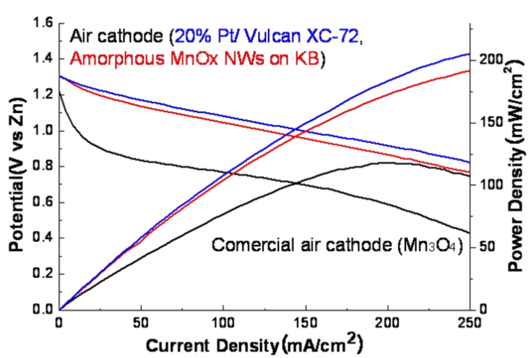
Our studies in Zinc-air battery

3. Jang-Soo Lee, Taemin Lee, Hyun-Kon Song, Jaephil Cho* and Byeong-Su Kim*
"Ionic liquid modified graphene nanosheets anchoring manganese oxide nanoparticles as efficient electrocatalysts for Zn–air batteries", 4, 4148-4154, 2011, ***Energy Environ. Sci.***



4. Jang-Soo Lee, Gi Su Park, Sun Tai Kim, Ruiguo Cao, Meilin Liu*, and Jaephil Cho*
"Ketjenblack carbon supported amorphous manganese oxides nanowires as high efficient electrocatalyst for oxygen reduction reaction", 11, 5362-5366, 2011, ***Nano Lett.***



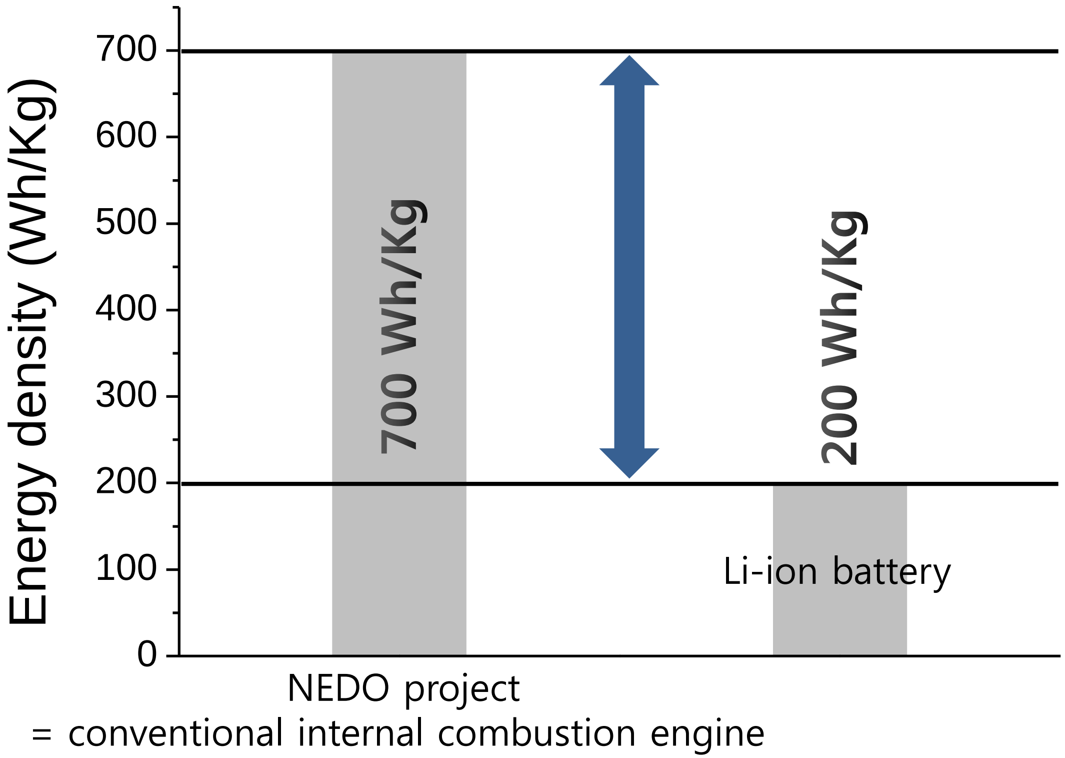


Contents

1. Lighter energy storage devices[1,2]

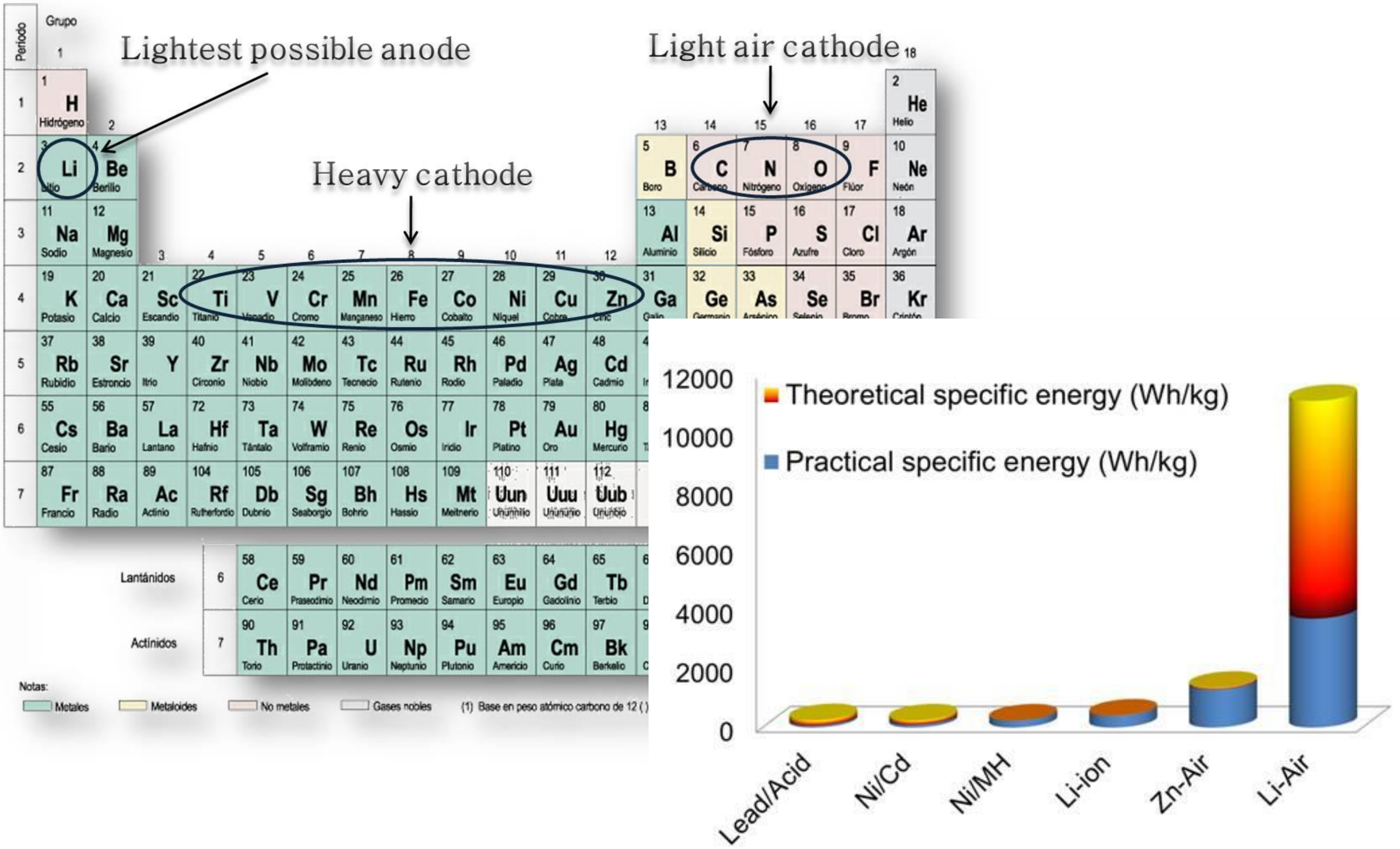
NEDO New Energy and Industrial Technology Development Organization

In Japan, **the final target** of the New Energy and Industrial Technology Development Organization (NEDO) project for batteries in **next-generation EV**



The theoretical specific energy density of **Zn-air batteries**: 1084 Wh/kg (?)

1. Lighter energy storage devices[1,2]



1. Promise and Challenges: Li-Air Batteries, IBM Almaden Research Center, May 6, 2010
2. Lee et al, **Metal–Air Batteries with High Energy Density: Li–Air versus Zn–Air**, *Adv. Energy Mater.*, 1, 34-50, 2011

1. 1 Metal-air battery (Zinc-air battery)

V vs NHE

Eo= +0.4 — $\mathbf{O_2(g)} + 2H_2O + 4e^- \leftrightarrow 4OH^-(aq)$ (ORR)

Eo = -0.9 — Fe (metal) → Fe/Air

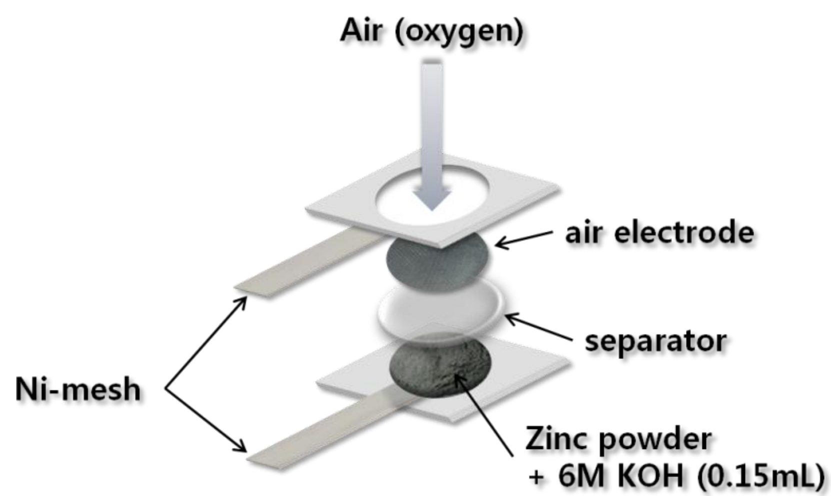
Eo = -1.25 — $Zn(OH)_4^{2-} + 2e^- \leftrightarrow \mathbf{Zn} + 4OH^-(aq)$

Zn-air battery

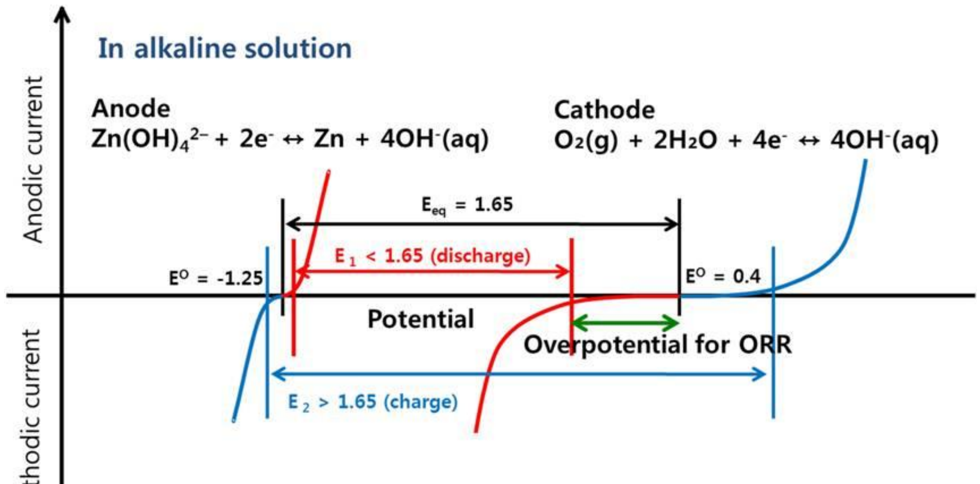
Eo = -2.3 — Al (metal) → Al/air

Eo = -2.7 — Mg (metal) → Mg/air

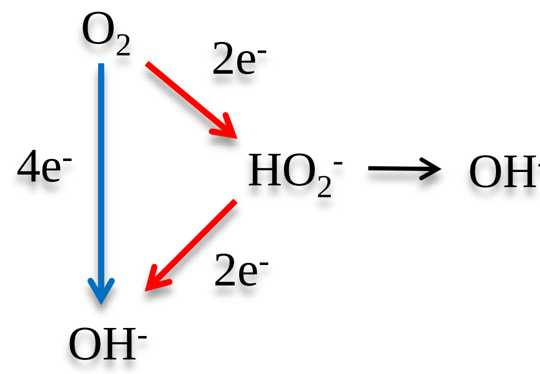
Eo = -3 — Li (metal) → Li/air



1. 2 Oxygen reduction reaction (ORR)

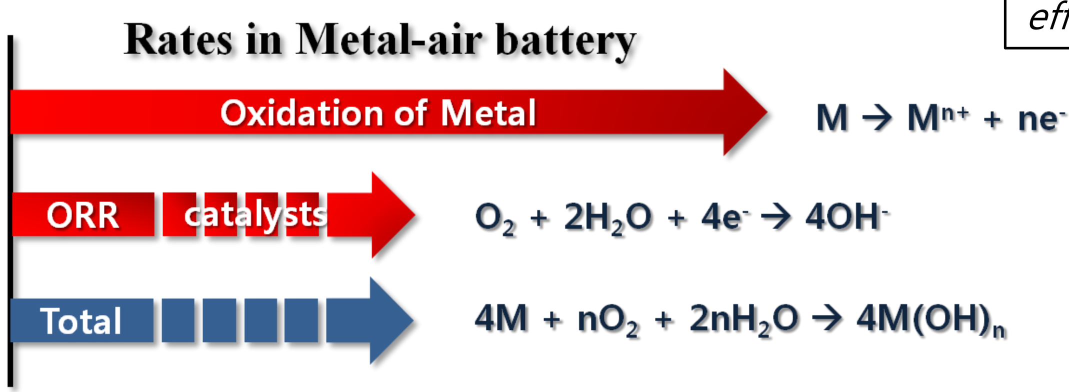


Schematic polarization curves of zinc-air cell[1]



ORR pathway ($4e^-$ *vs* $2e^-$)
(according to Anastasijevic's model)[2,3]

Four-electron process is desirable due to its higher efficiency and non-corrosive product

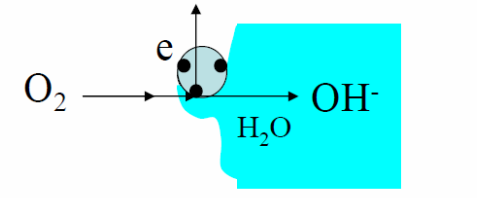


1. Lee et al, **Metal–Air Batteries with High Energy Density: Li–Air versus Zn–Air**, *Adv. Energy Mater.*, 1, 34-50, 2011
2. Anastasijevic et al, **Determination of the kinetic parameters of the oxygen reduction reaction using the rotating ring-disk electrode: Part I. Theory**, *J. Electroanal. Chem.*, 229, 305-316, 1987
3. B. Viswanathan et al, **On the search for non-noble metal based electrodes for oxygen reduction reaction**, *Photo/Electrochemistry & Photobiology in the Environment, Energy and Fuel*, 43-101, 2006

1. 3 ORR catalysts approach

Oxygen diffusion → O_2
Electronic conductivity → $4e^-$
Hydrophobicity/ Hydrophilicity → $2H_2O$
Affinity to active sites → $4OH^-$

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



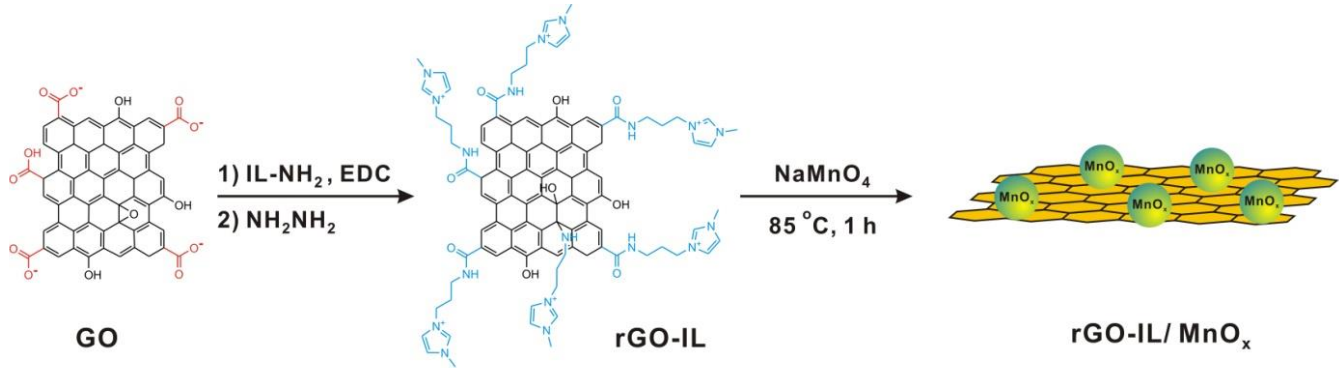
Gas, liquid, solid three phase zone

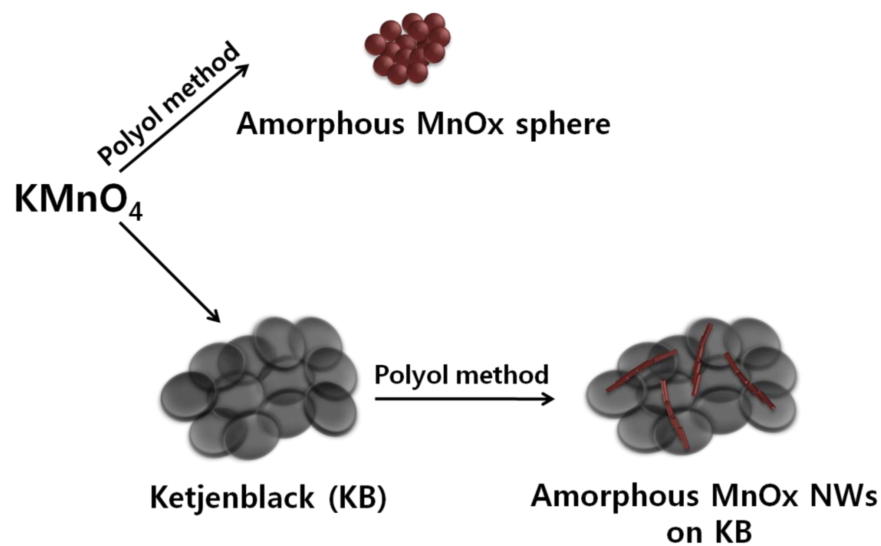
Non-Precious Transition Metal Oxide composite

- Fact: Mn oxides are claimed to decompose hydrogen peroxide in ORR
- Objective: Increase Electronic conductivity and active sites
  Adjust Hydrophobicity/ Hydrophilicity
- Approach: 1) reduced Graphene Oxide (rGO)
  Ionic liquid moiety increasing affinity to oxygen molecule
  2) Ketjenblack carbon
  Amorphous Mn Oxide structure
- Choice: 1) rGO-IL/Mn_3O_4 composite
  2) Amorphous MnOx Nanowires on Ketjenblack composite

2. Efficient ORR catalysts in alkaline solution

Approach





2. 1 Approach 1: rGO-IL/Mn_3O_4 composite

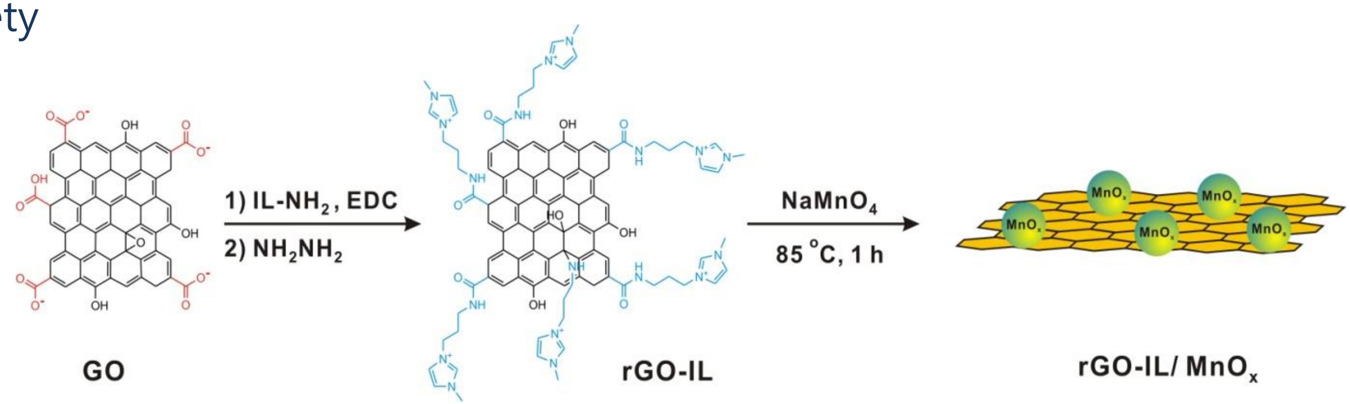
Graphene Oxide

↓ *(i)* Ionic liquid moiety
(ii) Reduction

rGO-IL

↓ *(i)* Mn precursor
(ii) Reduction

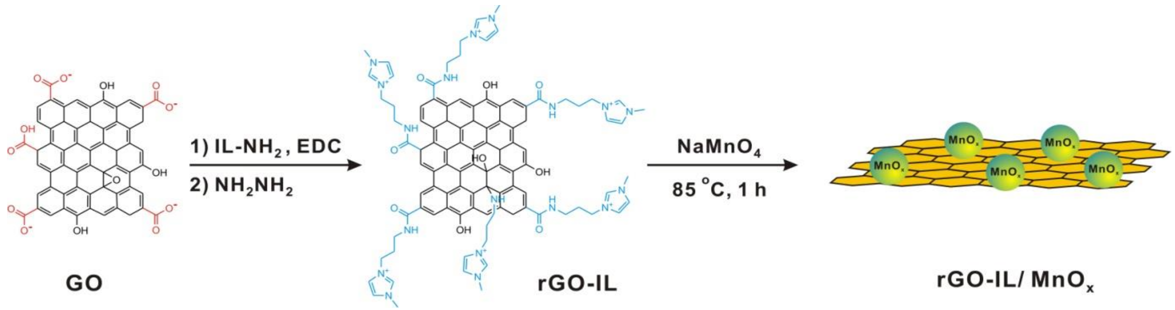
rGO-IL/Mn_3O_4



Lee et al, **Ionic Liquid Modified Graphene Nanosheet Anchoring Manganese Oxide Nanoparticles as Efficient Electrocatalysts for Zn-Air Battery**, 4, 4148-4154, *Energy Environ. Sci.* 2011 (DOI: 10.1039/c1ee01942b)

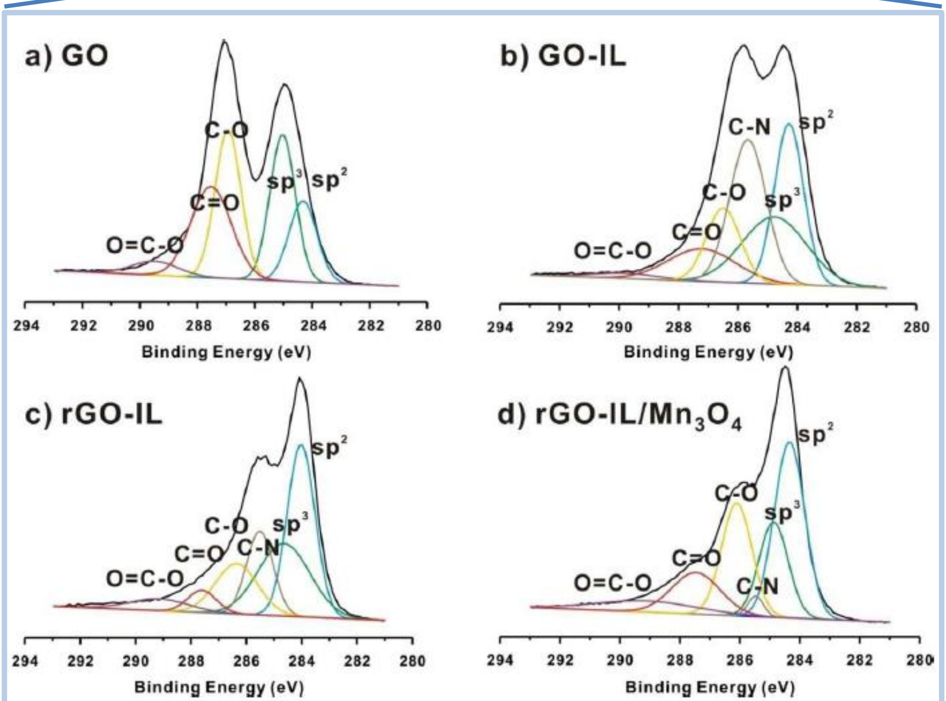
Physical characterization for rGO-IL/Mn_3O_4

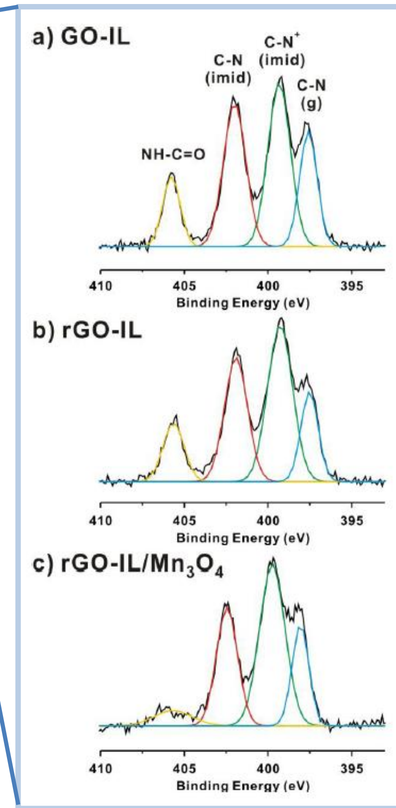
Proof synthesis procedure using XPS



SP³ carbon↓, N atom formation

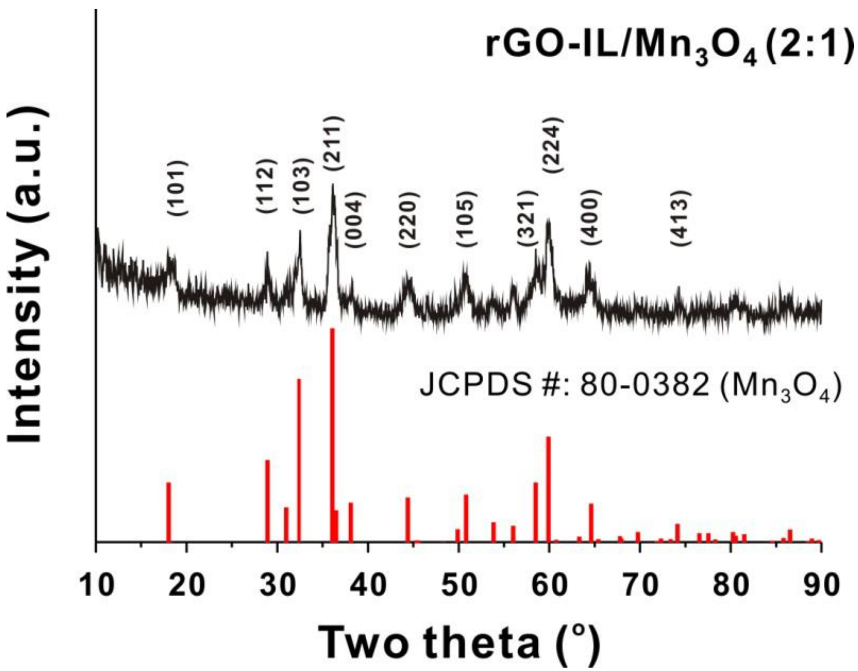
NH-C=O↓

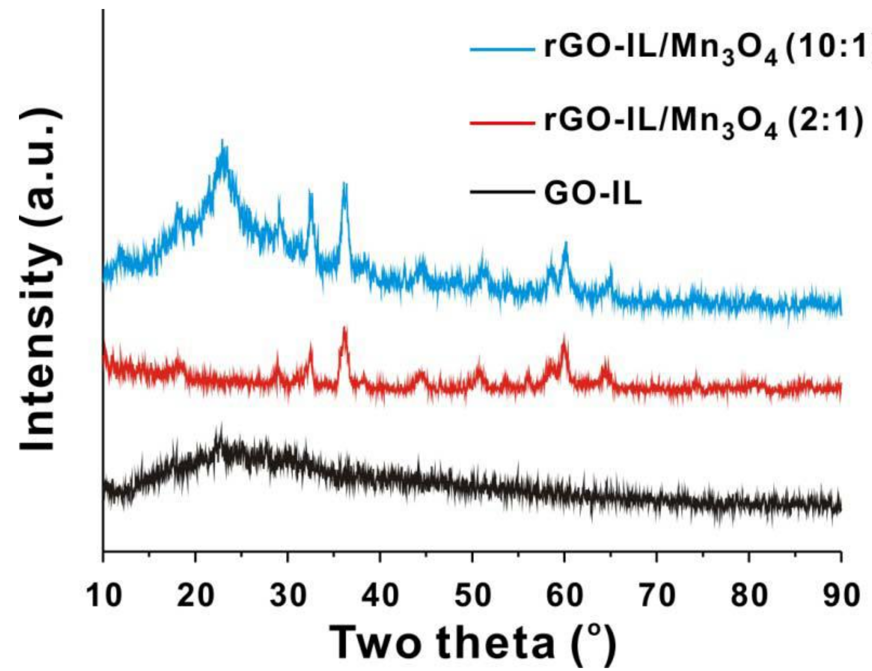




Physical characterization for rGO-IL/Mn_3O_4

XRD data (Mn Oxide phase)



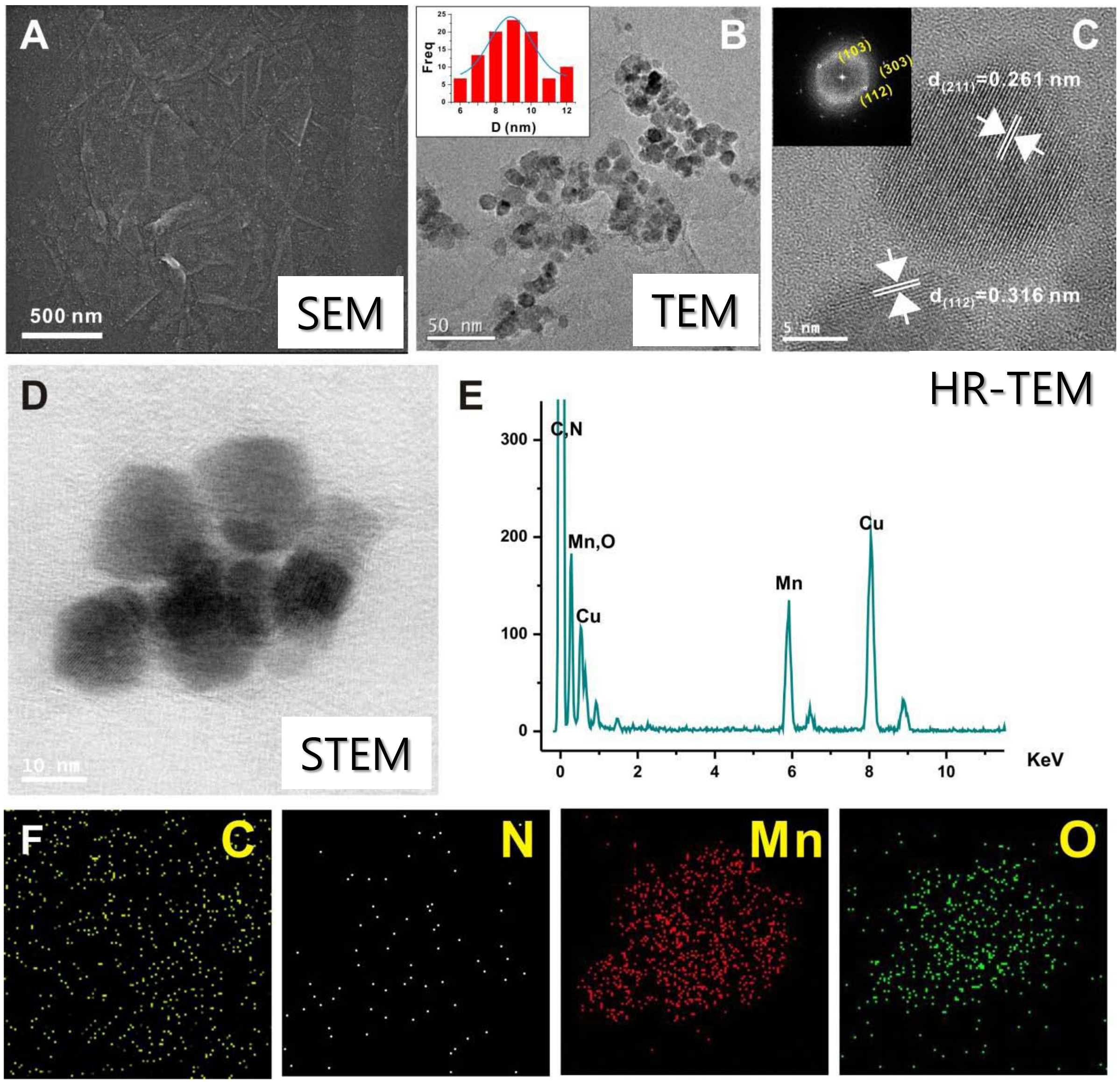


<ORR catalytic activity>
β-MnO_2 < λ-MnO_2 < γ-MnO_2 < α-MnO_2 ~ δ-MnO_2 [1]
Mn_5O_8 < **Mn_3O_4** < Mn_2O_3 < MnOOH [2]

1. Lanqun Mao et al, **Electrochemical Characterization of Catalytic Activities of Manganese Oxides to Oxygen Reduction in Alkaline aqueous Solution**, Journal of The Electrochemical Society, 149 (4) A504-A507, 2002
2. Y.L. Cao et al, **The mechanism of oxygen reduction on MnO_2-catalyzed air cathode in alkaline solution**, Journal of Electroanalytical Chemistry 557, 127-134, 2003

Physical characterization for rGO-IL/Mn_3O_4

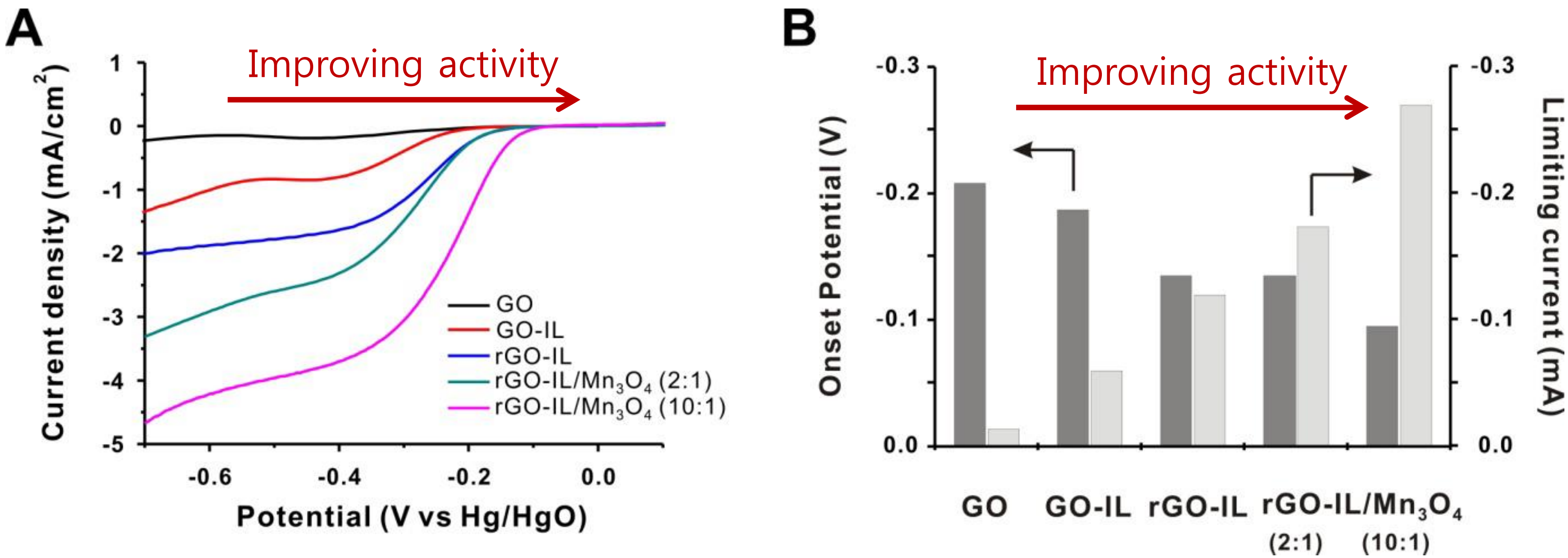
SEM and TEM images of rGO-IL/Mn_3O_4



- Non-uniform coating of Mn_3O_4 nanoparticles (*avg. d*= ca 10nm), but the graphene–nanoparticle Interaction allows good dispersion
  → Avoid potential aggregation of nanoparticles
- SAED → crystalline nature of the Mn_3O_4 nanoparticles
- In the elemental mapping → C, O and N (from rGO-IL) Mn and O (from Mn_3O_4)

rGO-IL/Mn_3O_4 catalysts: Evolution of ORR Activity

Rotating Disk Electrode (RDE) Data



<Surface resistance of air electrode>

rGO-IL/Mn_3O_4 (2:1): 61.1 ohm/sq (52.5% Mn contents by TGA)

rGO-IL/Mn_3O_4 (10:1): 120.3 ohm/sq (19.2% Mn contents by TGA)

Both **electrical conductivity** and **catalytic activity** should be considered in designing proper ORR catalysts.
ionic liquid also affects ORR activity.[1,2]

1. Snyder et al, **Oxygen reduction in nanoporous metal-ionic liquid composite electrocatalysts**, Nature Materials , 9, 904–907, 2010
2. James F. Wishart, **Energy applications of ionic liquids**, Energy Environ. Sci., 2, 956-961, 2009

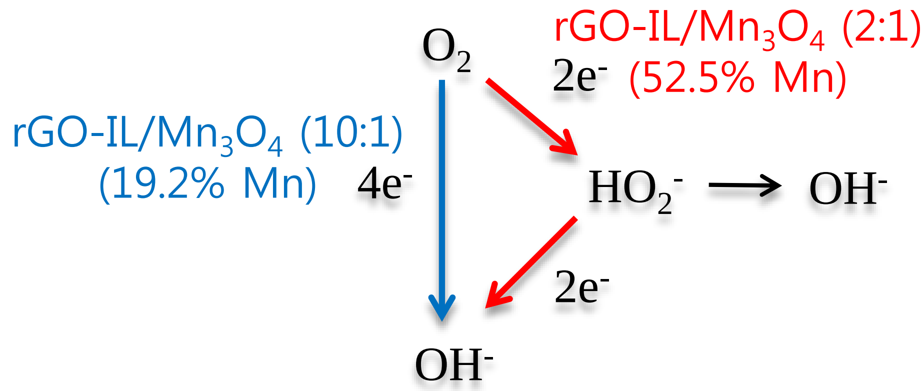
rGO-IL/Mn_3O_4 catalysts: Evolution of ORR Activity

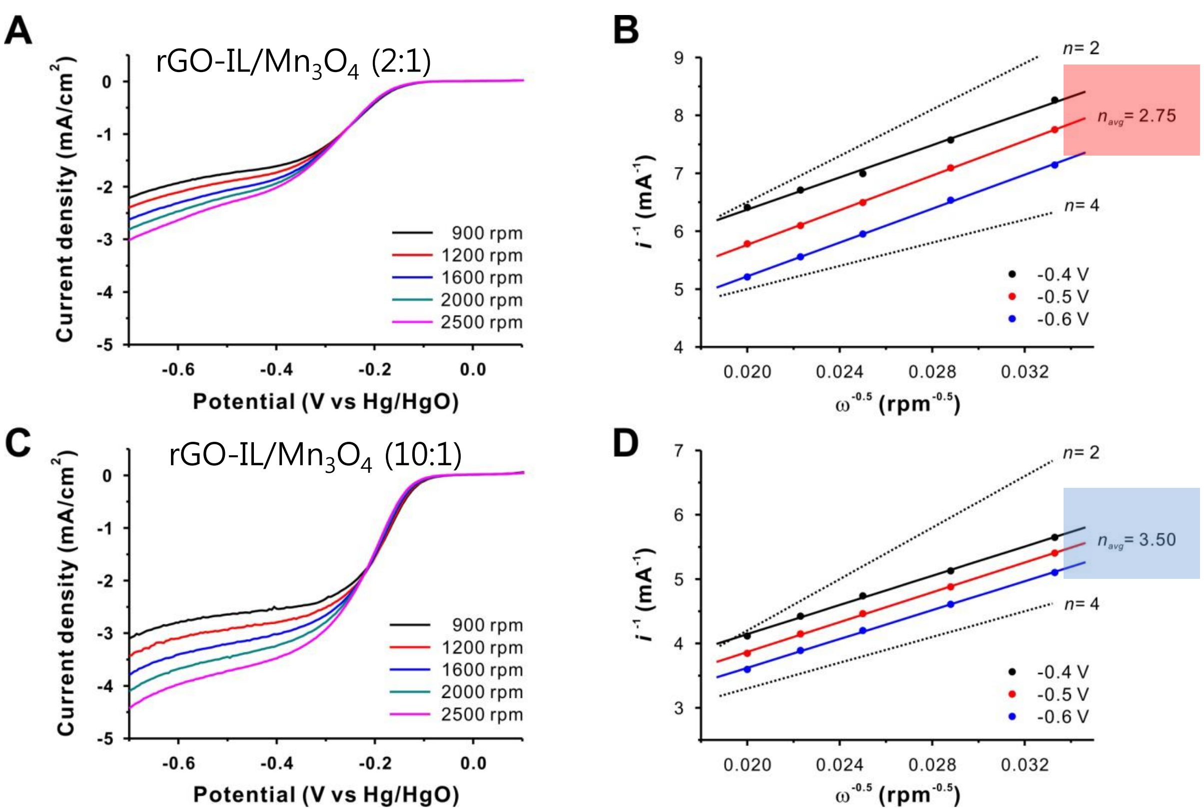
Koutecky-Levich (K-L) plot

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{dl}} = \frac{1}{i_k} + \frac{1}{B\omega^{1}} \quad (1)$$

$$i_k = nFAkC_t \ \textit{(kinetic current)} \quad (2)$$

$$i_{dl} = 0.20nFAC_{O_2}D_{O_2}{}^{2/3}\nu^{-1/6}\omega^{1} \ \textit{(diffusion limiting current)} \quad (3)$$

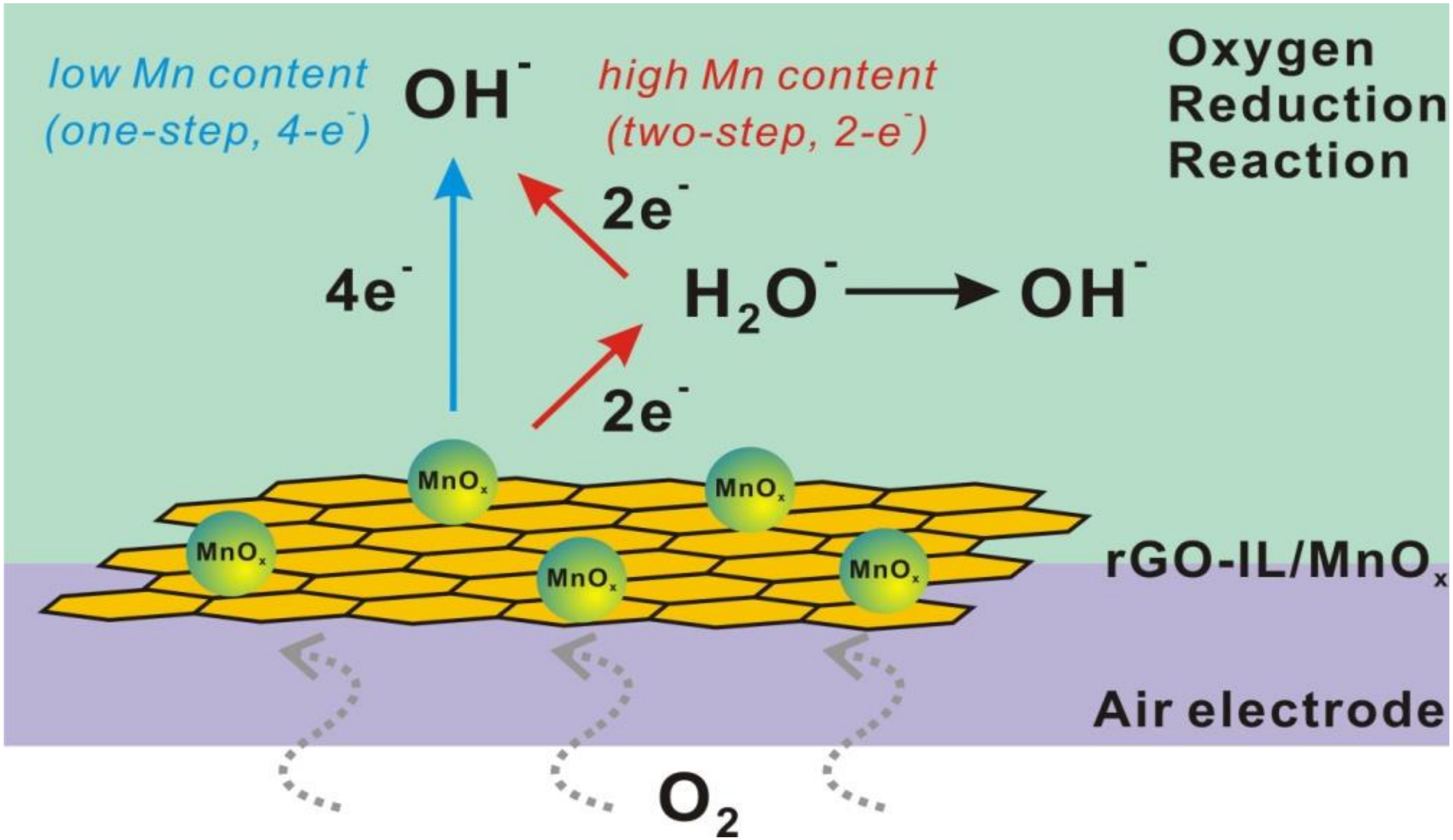




- Average number of transferred electrons (n) of
rGO–IL/Mn_3O_4 (2 : 1): 2.75
rGO–IL/Mn_3O_4 (10 : 1): 3.50

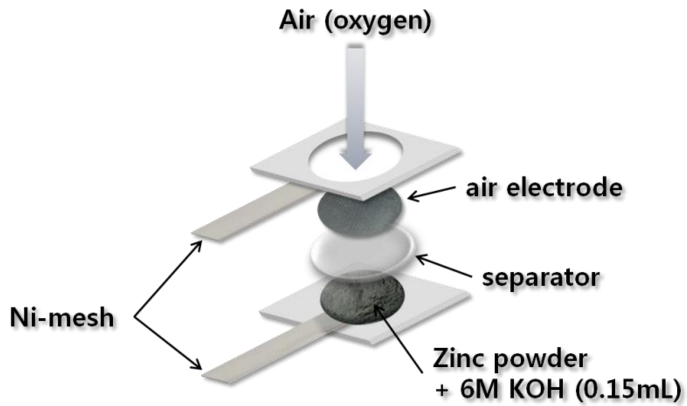
→The reaction mechanism is tunable with amount of Mn_3O_4

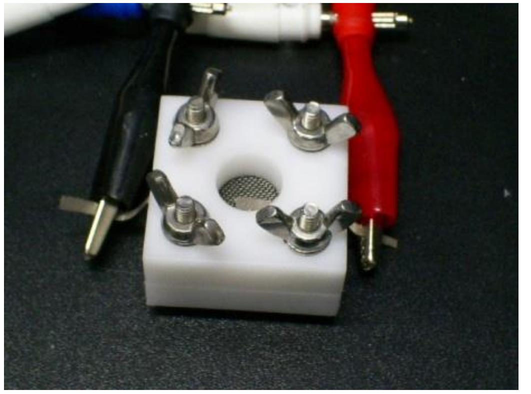
ORR pathway in our system

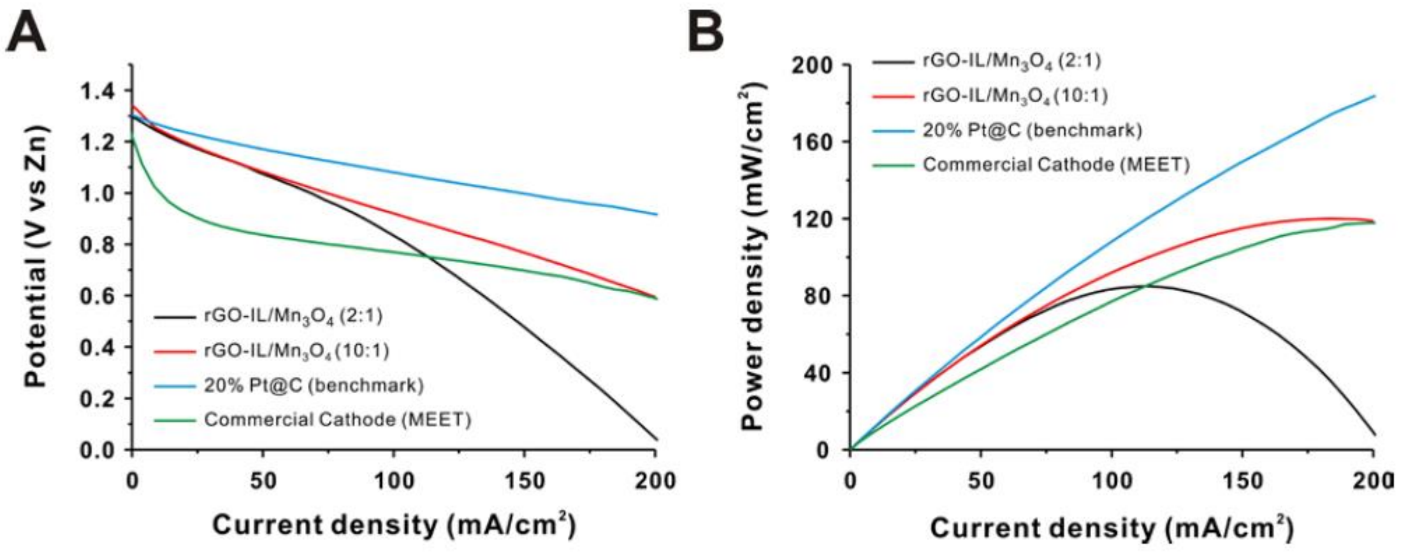


- Electrical conductivity could affect ORR pathway
- Reaction mechanism is tunable simply with the relative amount of nanoparticles supported onto the graphene sheets

Practical application on Zn-air battery







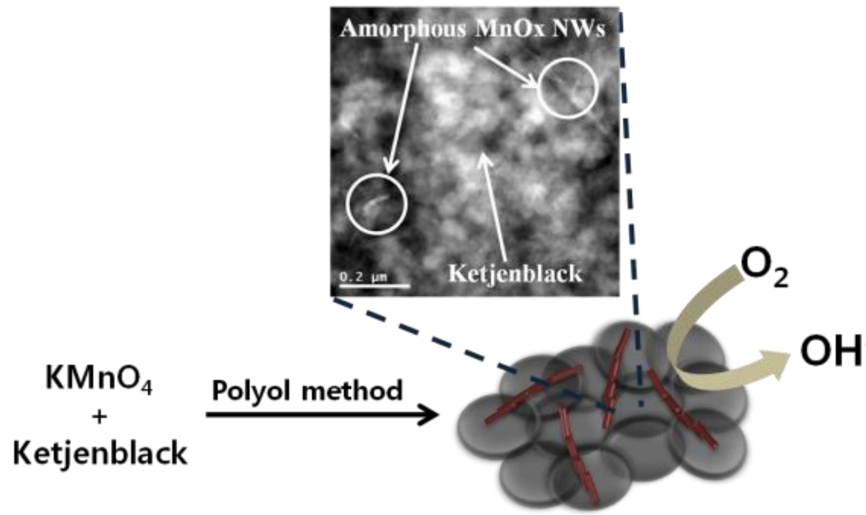
- Maximum peak power density of 120 mW/cm^2 can be obtained.
- This hybrid catalyst could be used as a potential candidate in low-cost electrocatalysts.

2. 2 Approach 2: Amorphous MnOx Nanowires on Ketjenblack

Ketjenblack carbon

↓ *(i)* Mn precursor
(ii) Polyol Reduction

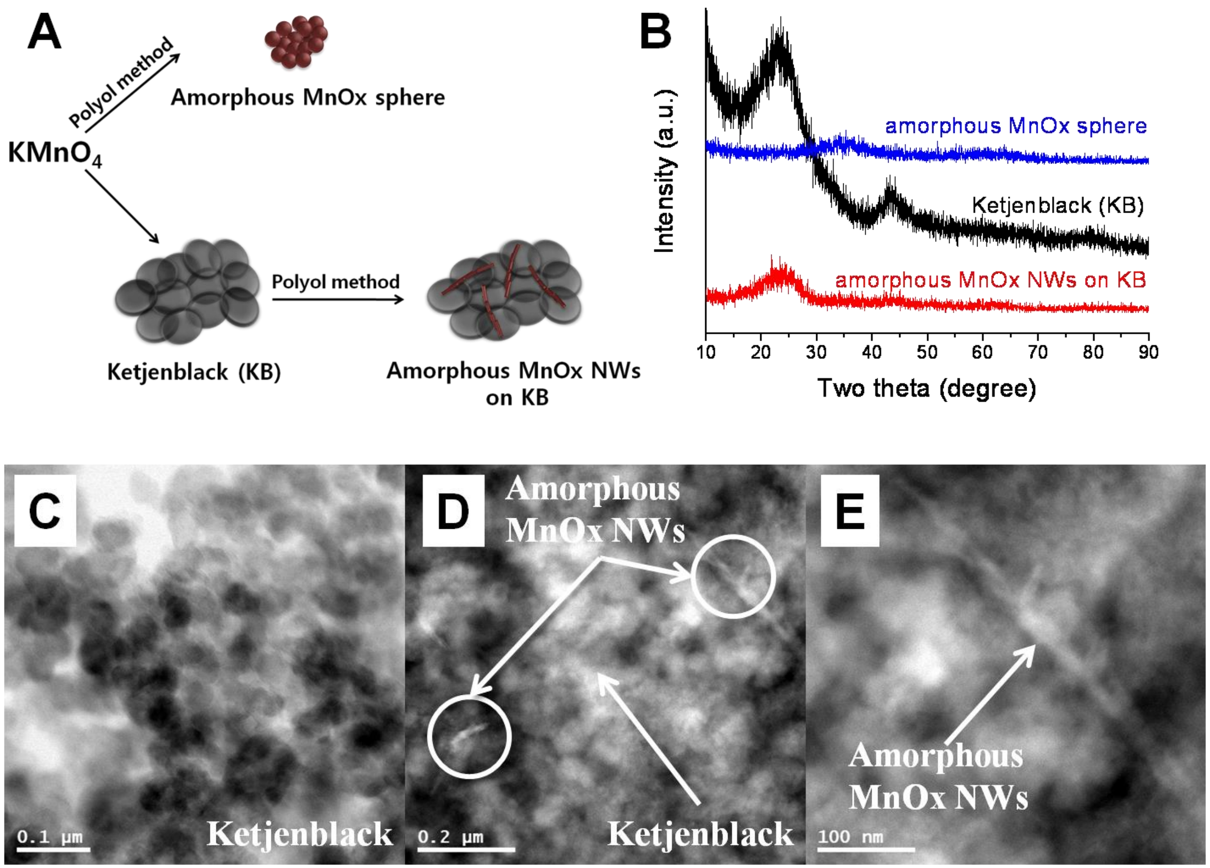
Amorphous MnOx NWs on KB



Lee et al, **Ketjenblack carbon supported amorphous manganese oxides nanowires as high efficient electrocatalyst for oxygen reduction reaction**, 11, 5362-5366, 2011, ***Nano Lett.***

Physical characterization for catalysts

XRD data (Mn Oxide phase) and TEM image of catalysts

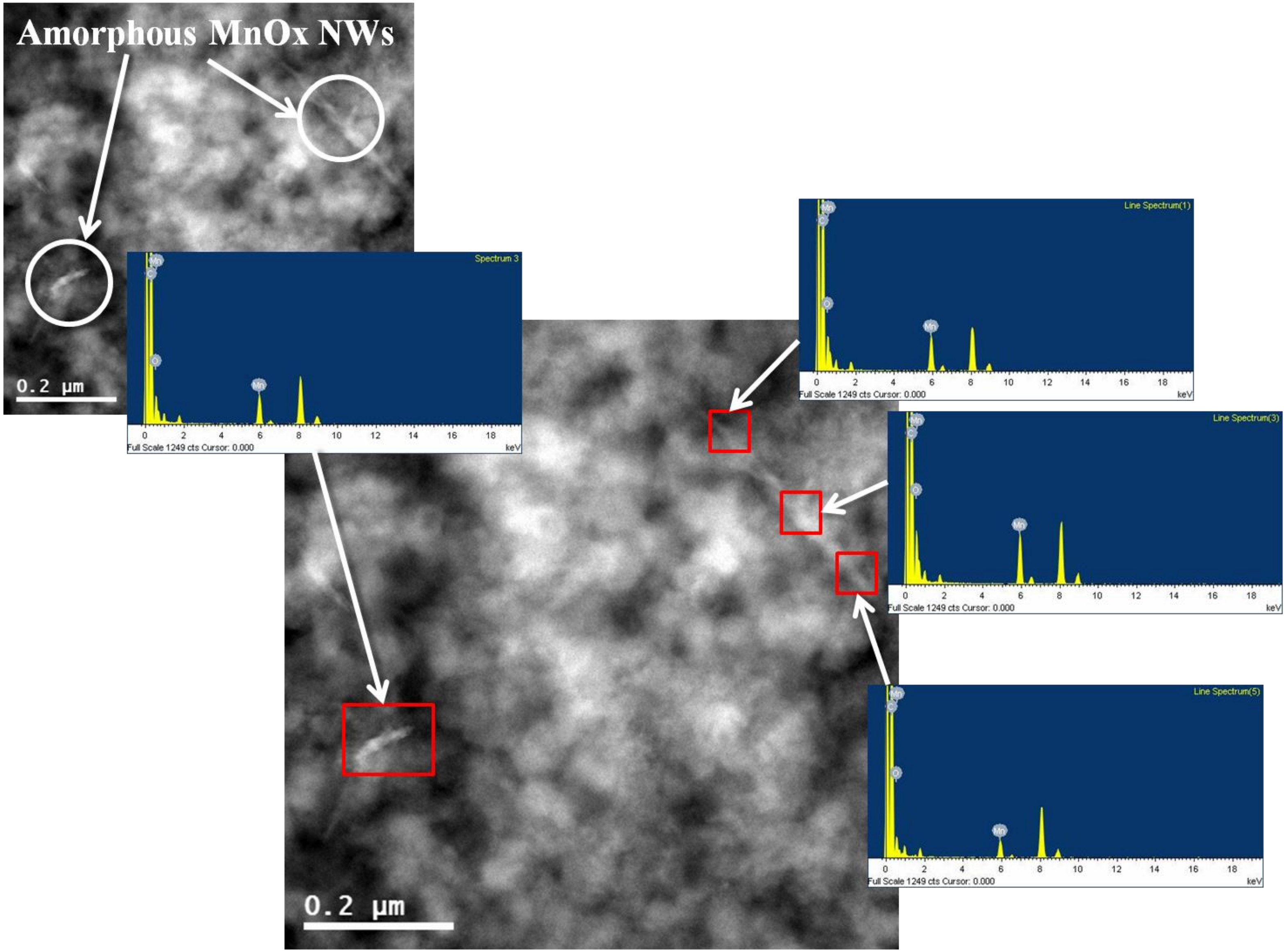


- Mn Oxide structure is amorphous (in XRD)

- Amorphous Nanowire structure (in TEM)
→ Large and rough surface area of amorphous MnOx NWs
→ High concentration in lattice defects[1]

1. Yang, J.; Xu, J. J., **Nanoporous amorphous manganese oxide as electrocatalyst for oxygen reduction in alkaline solutions**, Electrochemistry Communications, 5 (4), 306-311, 2003

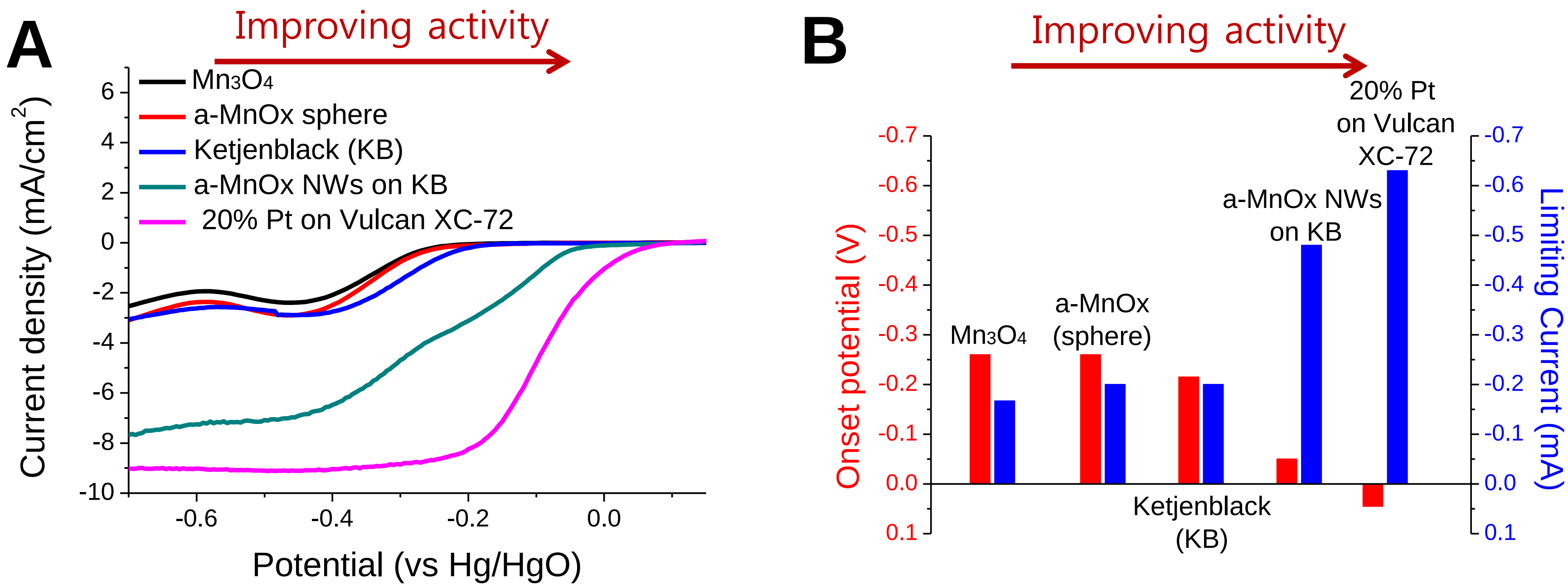
Physical characterization for catalysts



· Amorphous MnOx NWs (line mapping: Mn, O in TEM)

Catalysts: Evolution of ORR Activity

Rotating Disk Electrode (RDE) Data

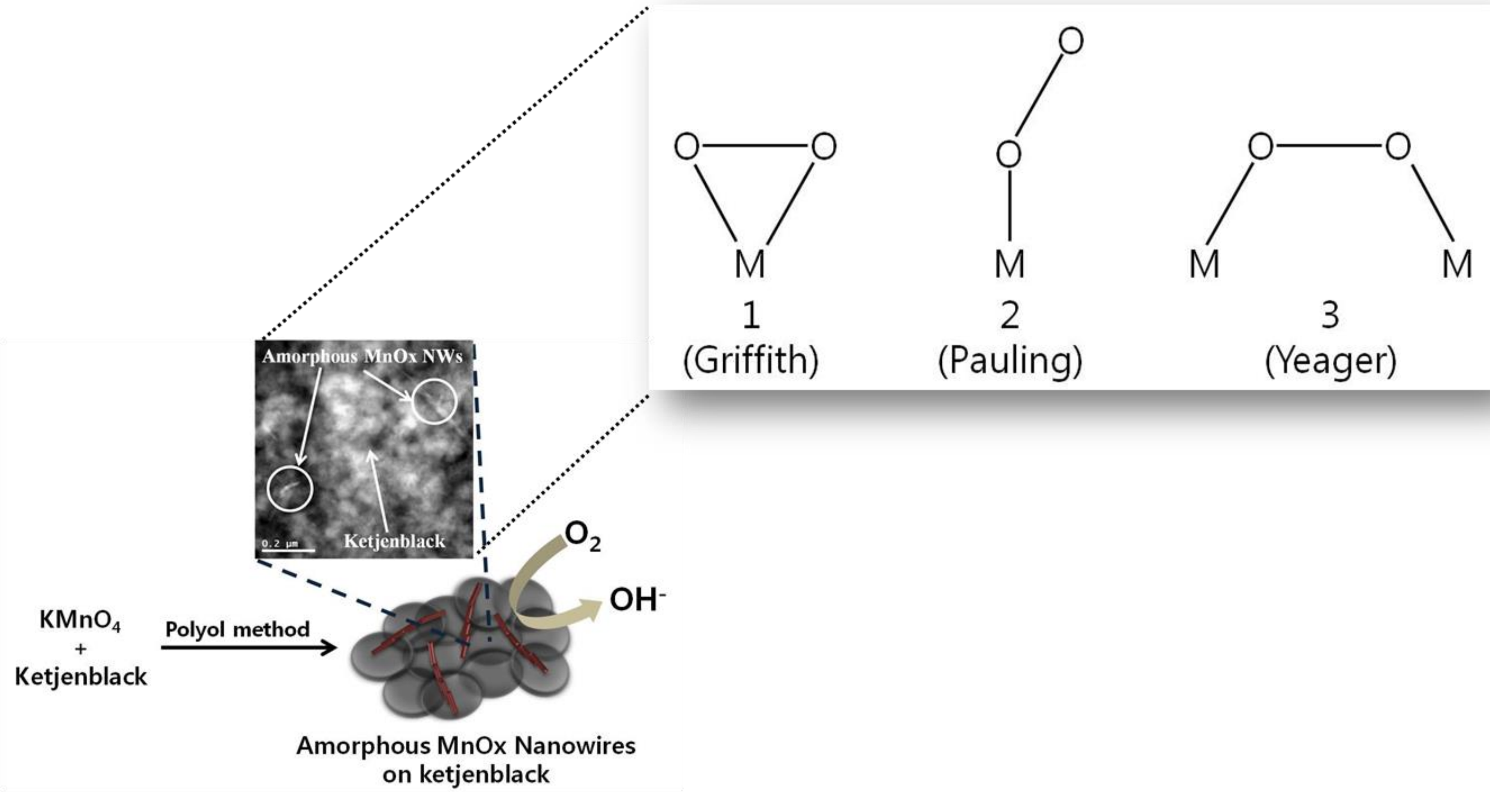


· Ketjenblack carbon (large surface area and good electrical conductivity)
\+ amorphous MnOx (large surface area and high concentration in defect sites)

Enhanced ORR activity

Catalysts: Evolution of ORR Activity

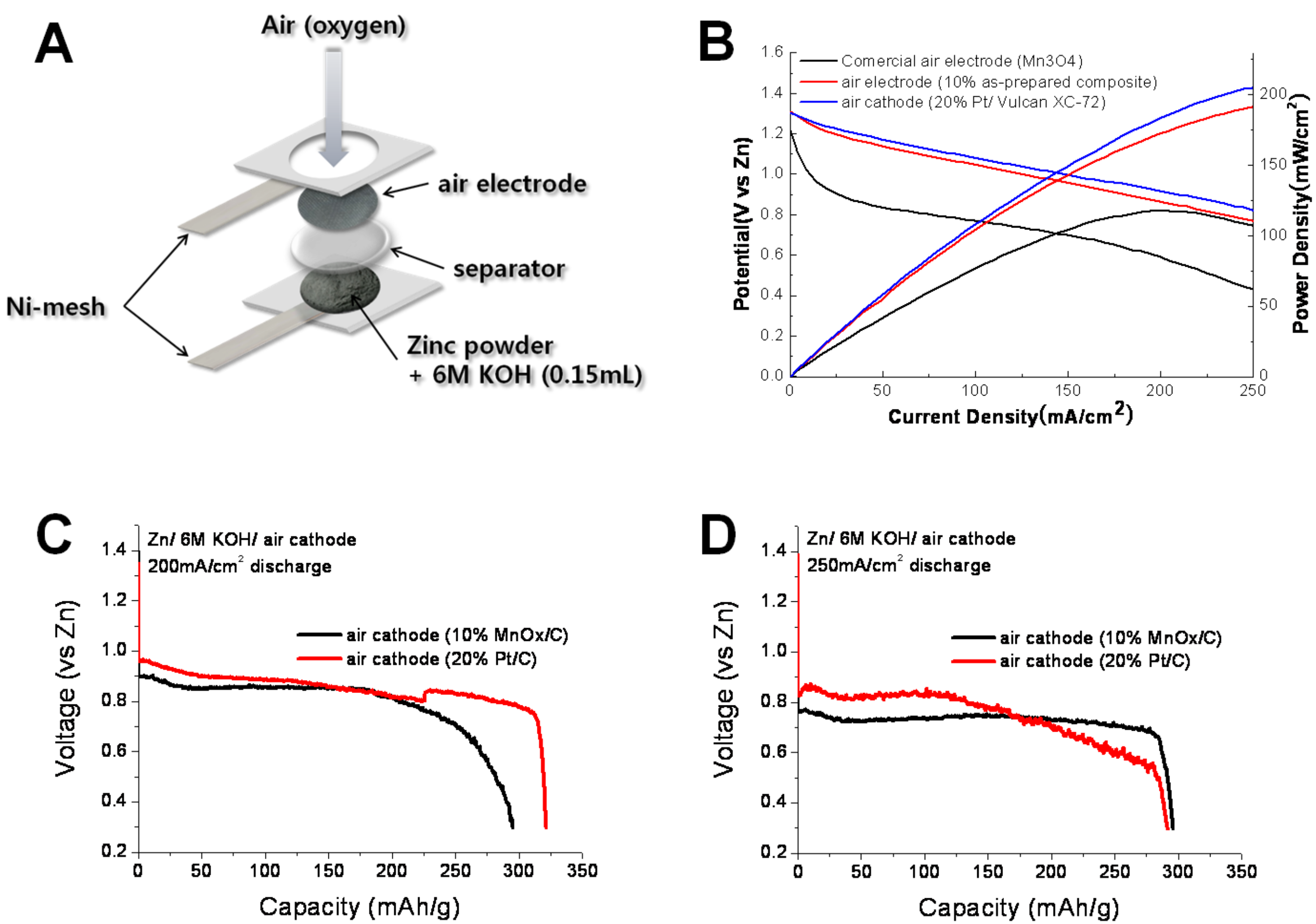
Geometrical effect on enhenced ORR activity



- Amorphous MnOx NWs structure has less selectivity to certain one model unlike other crystalline MnOx

1. J. S. Griffith, **On the Magnetic Properties of Some Haemoglobin Complexes**. Proc. R. Sot. London Ser. 23, A 235, 1956
2. L. Pauling, **Nature of the Iron-Oxygen Bond in Oxyhaemoglobin**, Nature 203, 182, 1964
3. E. Yeager, **Recent Advances in the Science of Electrocatalysis**, J. Electrochem. Soc. 128, 160C, 1981

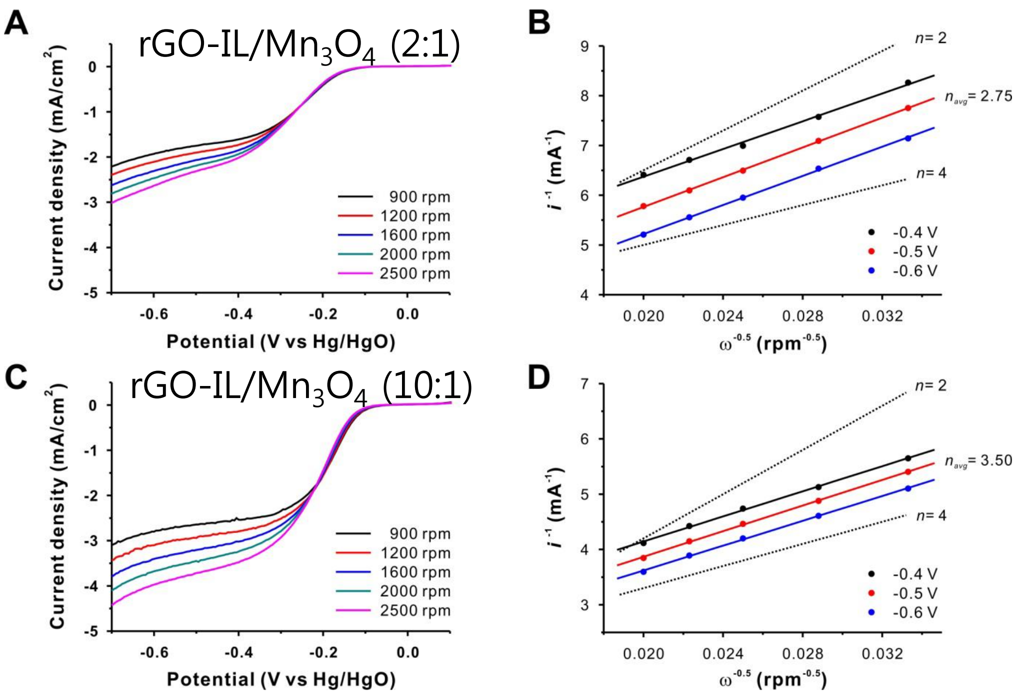
Practical application on Zn-air battery

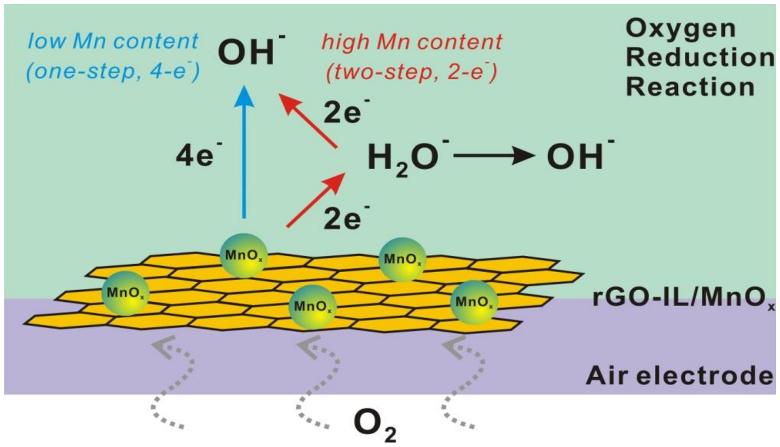


- Maximum peak power density of ca. 190 mW/cm^2 can be obtained. (similar to 20% Pt@Vulcan carbon catalyst)
- This hybrid catalyst could be used as a potential candidate in low-cost electrocatalysts.

3. Conclusions

Approach 1: rGO-IL/Mn_3O_4 composite





- Electrical conductivity, ionic liquid moiety affect ORR catalytic activity and pathway.
- Reaction mechanism is tunable simply with the relative amount of nanoparticles supported onto the graphene sheets

3. Conclusions

Approach 2: Amorphous MnOx Nanowires on Ketjenblack

1) Good electrical conductivity (Ketjenblack)+
2) large surface area and high concentration in defect sites (amorphous MnOx NWs) +
3) Amorphous MnOx NWs structure has less selectivity to certain one model unlike other crystalline MnOx

Improved ORR activity