Perspective of Zn-Air Batteries

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2. Zn-air battery (ZAB) Overview

3. Problems of ZAB

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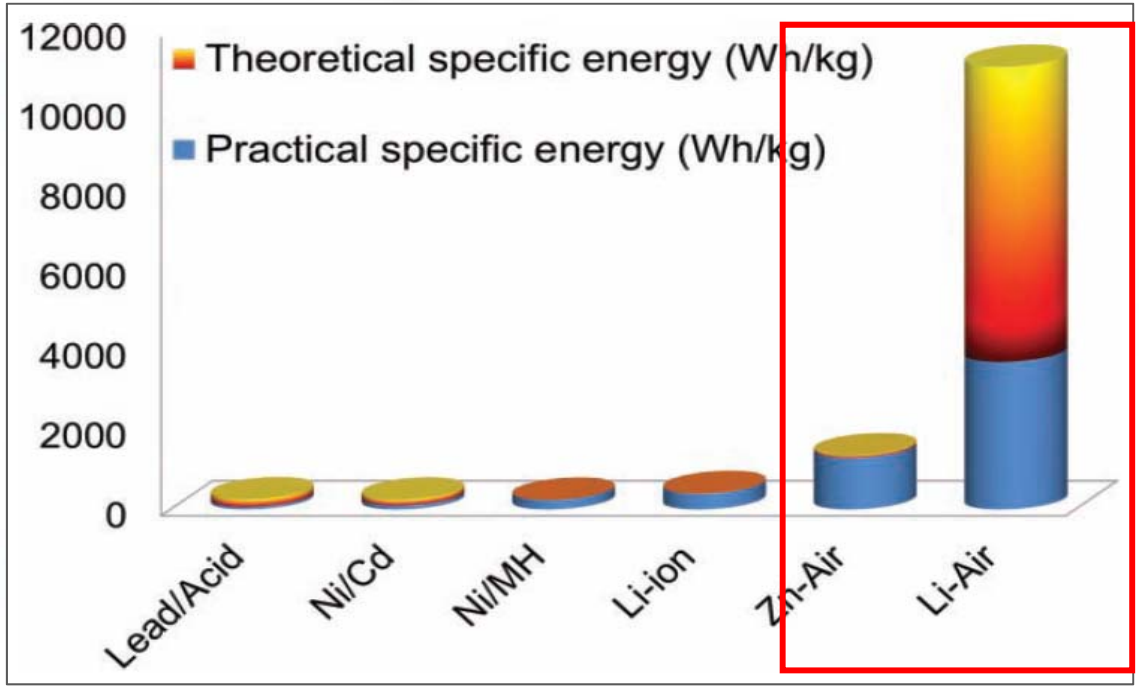
1. Introduction

◆ High energy density of Metal-air battery



Theoretical and practical energy densities of various types of rechargeable battery

<Previous>

Wh/kg

<Current>

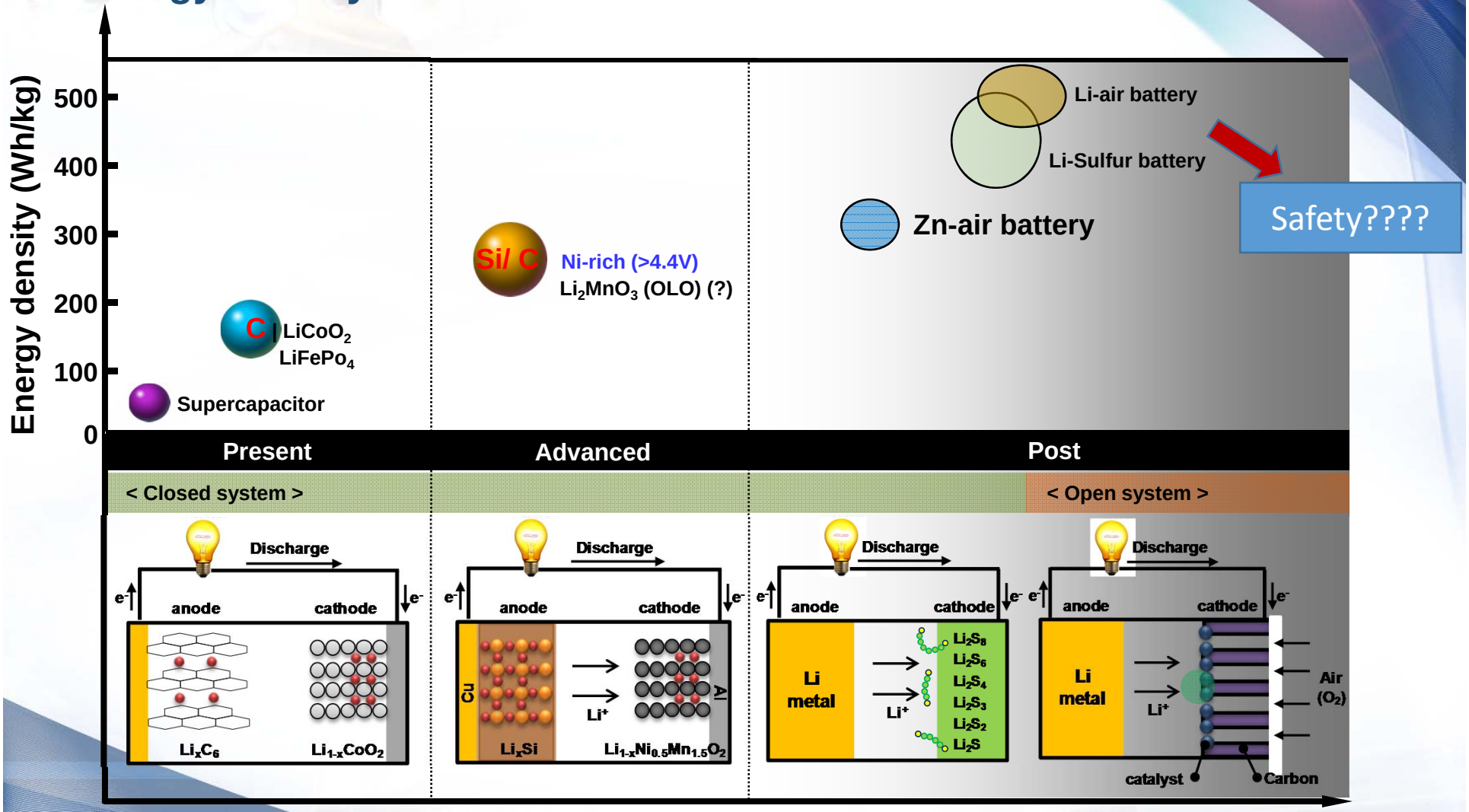
Wh/cc

Battery performance factors

- Power [W], Energy [Wh], Capacity [Ah]

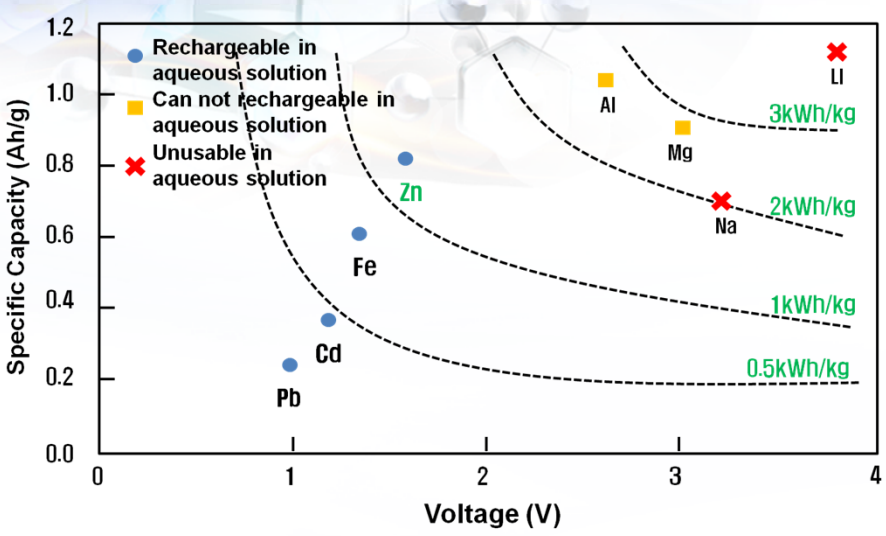
1. Introduction

◆ Energy density evolution



J. Cho et al. Angew. Chem. Int. Ed., 2012, 51, 9994

◆ Metal-air battery in aqueous solution



- **Zn, Fe, Cd, Pb**; Rechargeable
- **Al, Mg**; Not rechargeable

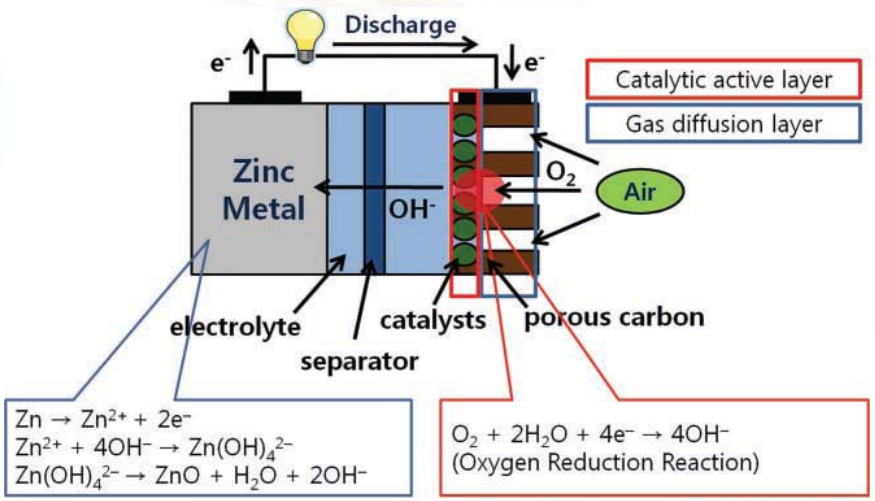
Zhang, Zinc-air technology, Zinc-air technology workshop, International Zinc Association /ZESTEC, Shanghai, 2005

Aluminum	AQUEOUS	▪ High energy density with 6 KWh/Kg ▪ Impossible rechargeability due to instability of aluminum metal under alkaline electrolyte
Zinc		▪ Zinc; low cost, abundance, low equilibrium potential, environmental benignity, flat discharge voltage, long shelf-life

How to maximize the performance?

2. Zn-air battery Overview

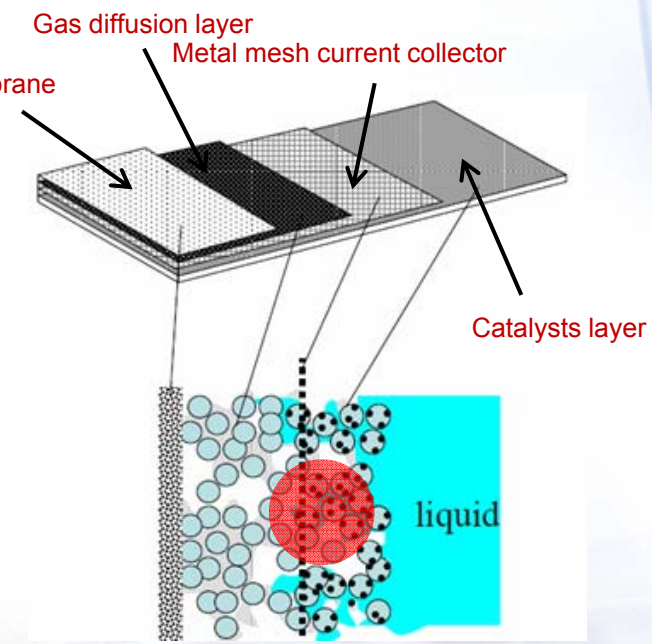
◆ Principle of Zn-air battery



Working principle and each electrode reaction of zinc-air battery

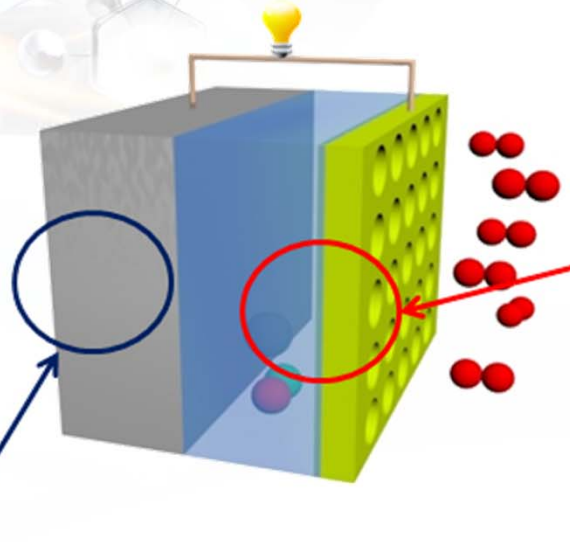
J. Cho et al., Adv. Energy Mater., 2011. 1, 34.

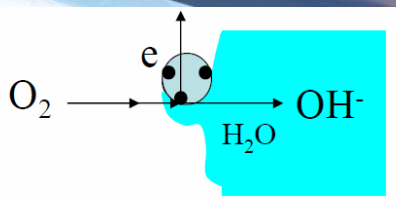
Cathode: $O_2 + H_2O + 4e^- \rightarrow 4OH^-$ (E^o= 0.4 V vs. NHE)
Anode: $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$ (E^o= -1.25 V vs. NHE)
Overall: $2Zn + O_2 \rightarrow 2ZnO$ (E^o= 1.65 V)



- Primary Zn-air battery; fully immersed zinc anode into alkaline electrolyte, separator, partially immersed air cathode.

◆ Principle of Zn-air battery





Gas, liquid, solid three phase zone

<ORR at 3-phase reaction>

Oxygen diffusion

Electrical 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

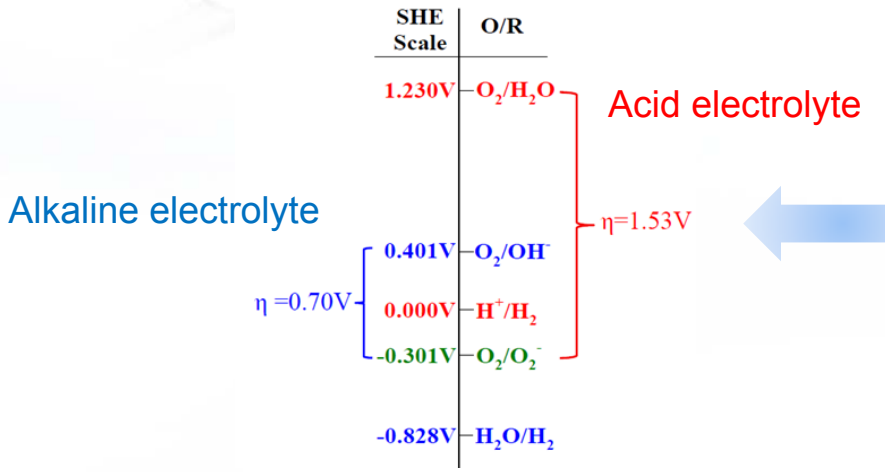
<Zinc oxidation> charge & mass transfer reaction

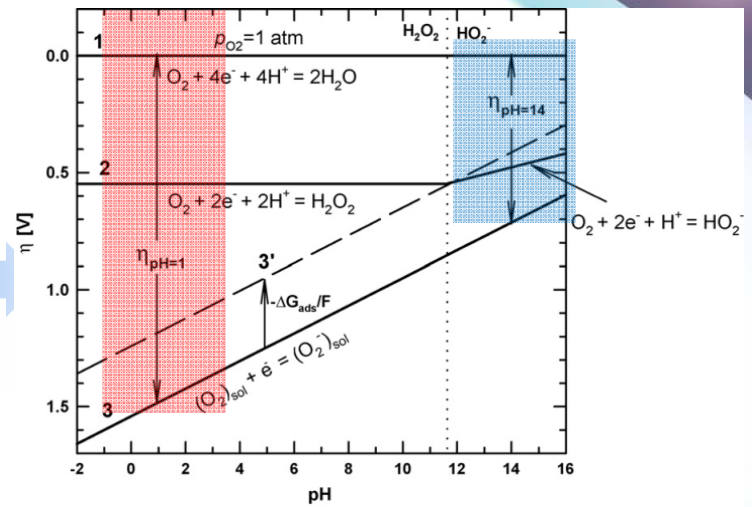
Overall reaction : $2Zn + O_2 \rightarrow \boxed{2ZnO}$ → **Irreversible product**

Hydrogen evolution reaction : $Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2$

Carbonization: $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$ and/or $KOH + CO_2 \rightarrow KHCO_3$

ORR - Acid vs. Alkaline Medium: Thermodynamic Advantages[1,2]



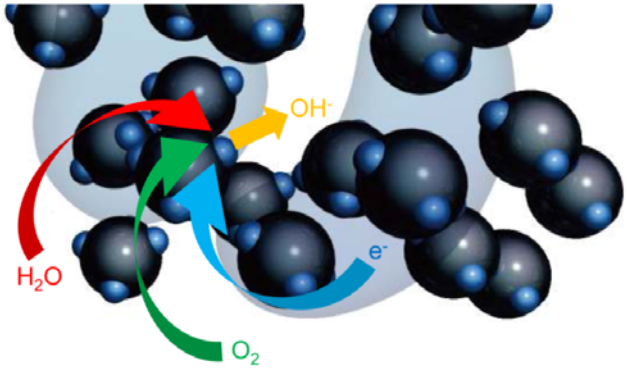


1) Nernstian Potential Shift
   - -0.83 V (-59 mV multiplied by 14 if the pH value changes from 0 to 14)
2) Affects Adsorption Strengths of spectators, and intermediate species

· Overpotential for 1st electron transfer (O_2 + 1e$^-$ → O_2^-) is 0.70V (in alkaline), but 1.53V (in acid electrolyte) → ORR in alkaline is more facile than in acid.
· Generally, rate limiting step (r.d.s) in ORR is 1st electron transfer has been widely accepted.

Requirements for desired properties of non-precious metal catalysts

Oxygen Reduction Reaction (ORR) in alkaline solution



· **Requirements[1-4]**

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

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. et al., Nano Letters, 2011, 11, 5362. ; 4. Lee et al., Angew. Chem. Int. Ed., 2013, 52, 1026
4. D.-J. Liu, Fuel Cell Seminar & Exposition San Antonio, TX, 2010

Thermodynamic electrode potentials of ORR

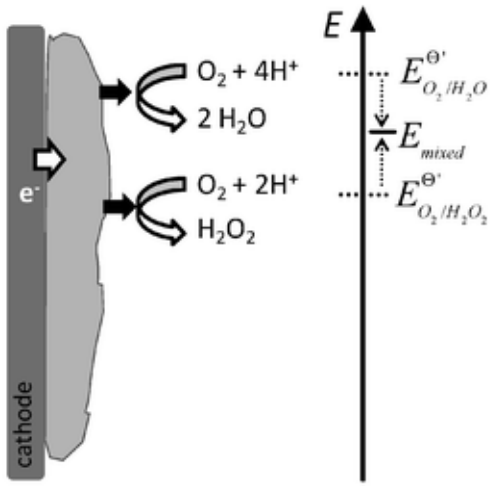


Fig. Schematic illustration of a competing incomplete (or unwanted) reduction reaction and the resulting mixed potential formation for the example of the oxygen reduction reaction at platinum[1]

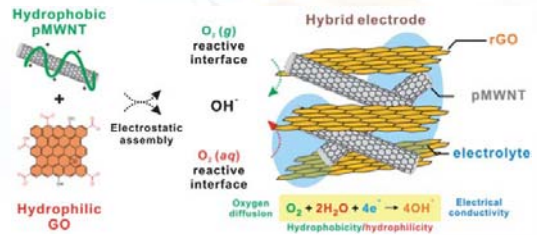
Electrolyte	ORR reactions	Thermodynamic electrode potential at standard conditions, V
Acidic aqueous solution	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.70
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76
Alkaline aqueous solution	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401
	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.065
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.867
	$2HO_2^- \rightarrow 2OH^- + O_2$	chemical disproportionation

Table. Thermodynamic electrode potentials of oxygen reduction reaction.[2]

• • 4-electron direct reduction pathway is much favorable than 2-e indirect pathway.

1. Falk Harnisch and Uwe Schröder, Chem. Soc. Rev. , 2010, 39, 4433
2. Song, C. et al., Electrocatalytic Oxygen Reduction Reaction. In PEM Fuel Cell Electrocatalysts and Catalyst Layers, Zhang, J., Ed. Springer London: 2008; pp 89-134.

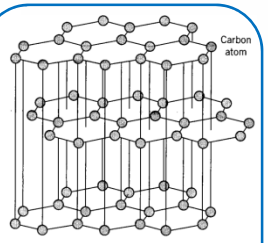
Our Approaches



J. Mater. Chem. A, 2013, 1, 9603

Metal-free

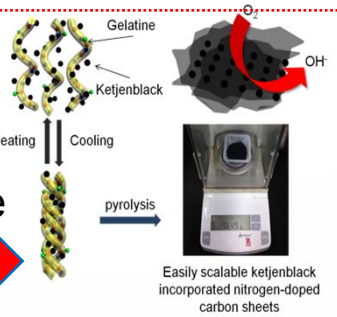
GO



Graphite

Mn_3O_4

Energy Environ. Sci., 2011, 4, 4148

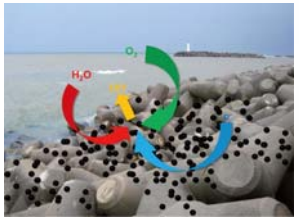


Metal-free

Nano Lett., 2014, 14, 1870

Ketjenblack carbon

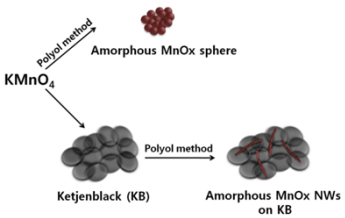
Fe_3C



N-Doped Ketjenblack Incorporated into Fe/Fe_3C-Functionalized Melamine Foam

Angew. Chem. Int. Ed., 2013, 52, 1026

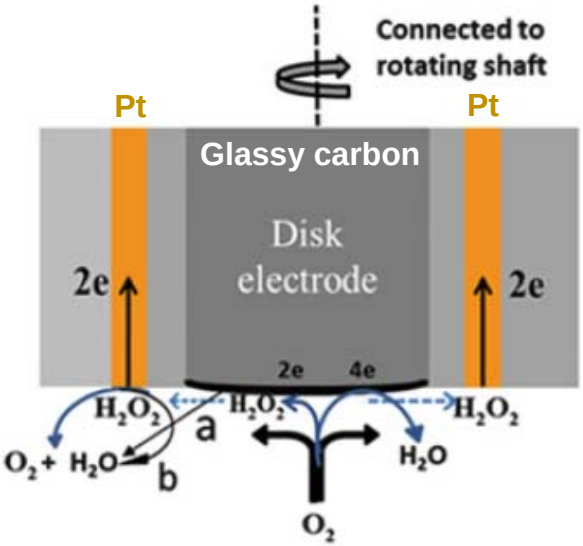
MnOx



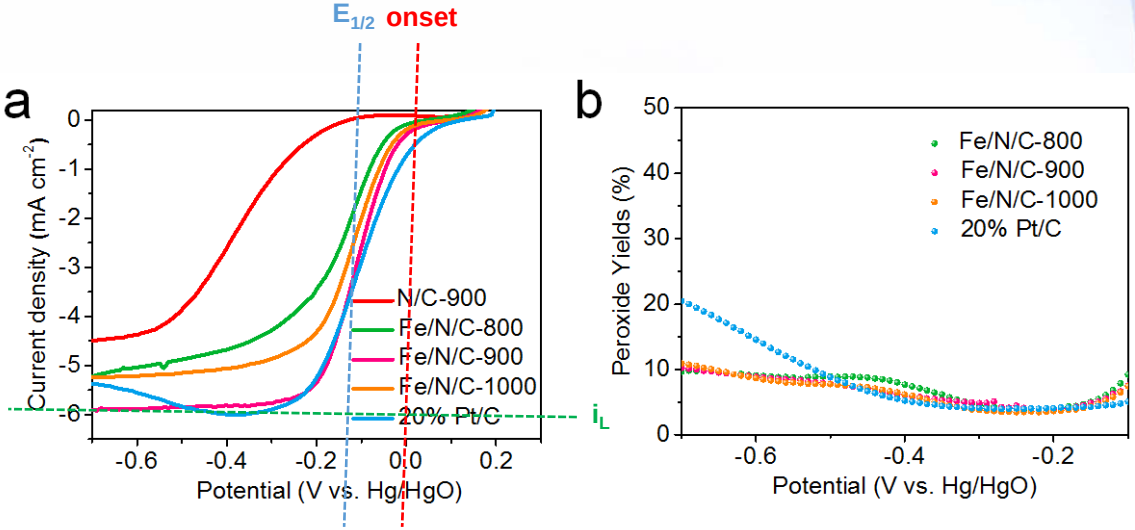
Nano Lett., 2011, 11, 5362

◆ ORR based on RRDE method

- **ORR** : Air electrode is partially immersed in electrolyte to maximize a utilization of gas phase oxygen.
- **Efficient electrocatalyst** : Accelerate sluggish reaction and minimize overall voltage loss.



Schematic of a rotating ring-disk electrode



Electrochemical characterization for Fe/N/Cs catalysts. (a) Steady-state RRDE experiments, (b) Calculated peroxide yields of catalysts. 0.1M KOH (O2 saturated)

Bard AJ, et al., Electrochemical methods. Fundamentals and applications, 2001, 2nd Ed. Wiley, NY

Limiting current, Onset potential, Half-wave potential ($E_{1/2}$)

J. Cho et al., Adv. Mater., 2015, 27, 1396

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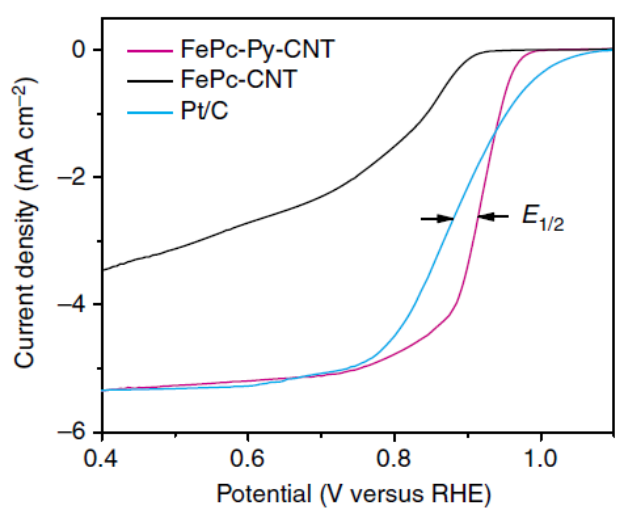
◆ Relationship between half-cell and full cell of ZAB



High limiting current

High negative onset potential

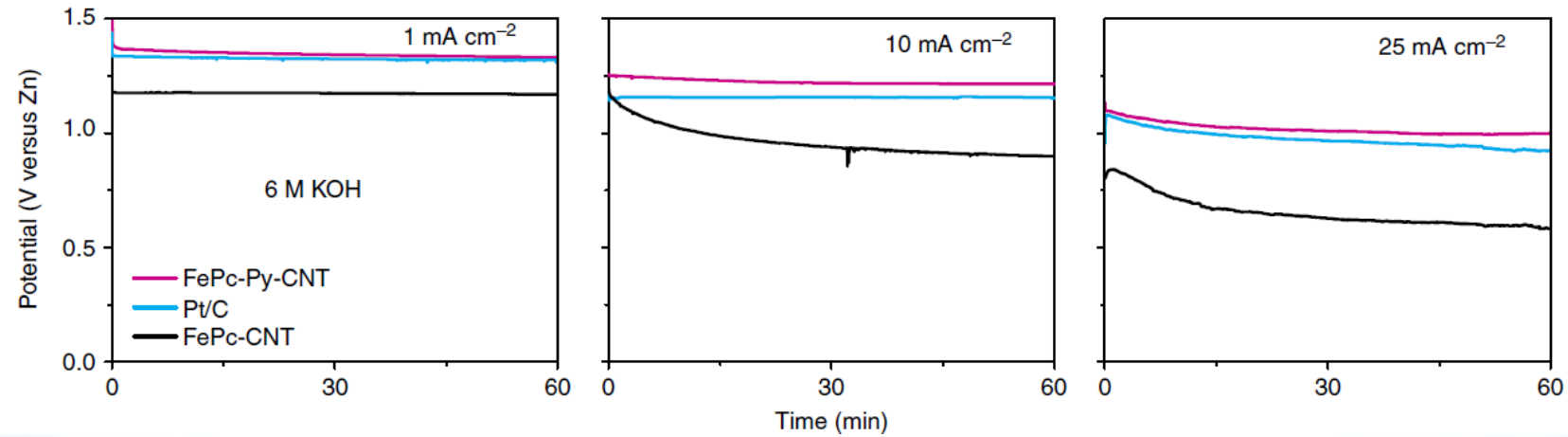
High negative half-wave potential ($E_{1/2}$)

Half-cell

Low overpotential

High capacity

Full-cell (6M KOH)



Discharge profiles for several electrocatalysts at various current densities in ZAB with 6 M KOH electrolytes

J. Cho et al., *Nat. Comm.*, 2013, 4, 2076

◆ Anode; zinc oxidation

$$Zn\ (0.140\ cm^3/g) + 4OH^- \rightarrow Zn(OH)_4^{2-}\ (soluble) + 2e^-$$

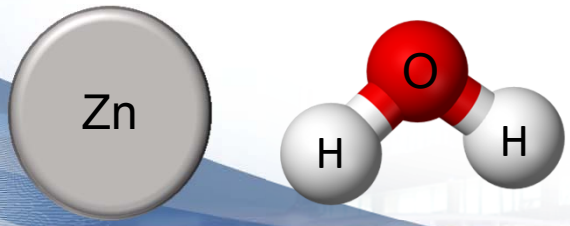
(via charge transfer reaction)

$$Zn(OH)_4^{2-} \rightarrow ZnO\ (0.147\ cm^3/g) + 2OH^- + H_2O$$

(via mass transfer reaction)

◆ Anode; hydrogen evolution reaction (HER)

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \uparrow \text{ (Hydrogen evolution reaction)}$$



Low utilization of zinc
Low ionic conductivity
Low capacity

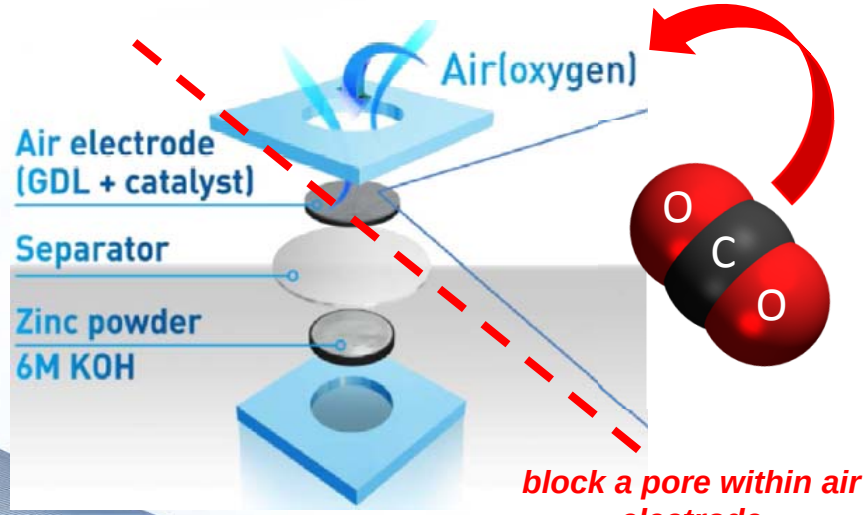
◆ Cathode & Anode

1.65 V → 1.4 V

∵ *Internal loss of the cell due to activation, and ohmic and concentration loss*

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O \text{ and/or } KOH + CO_2 \rightarrow KHCO_3$$

(carbonization)

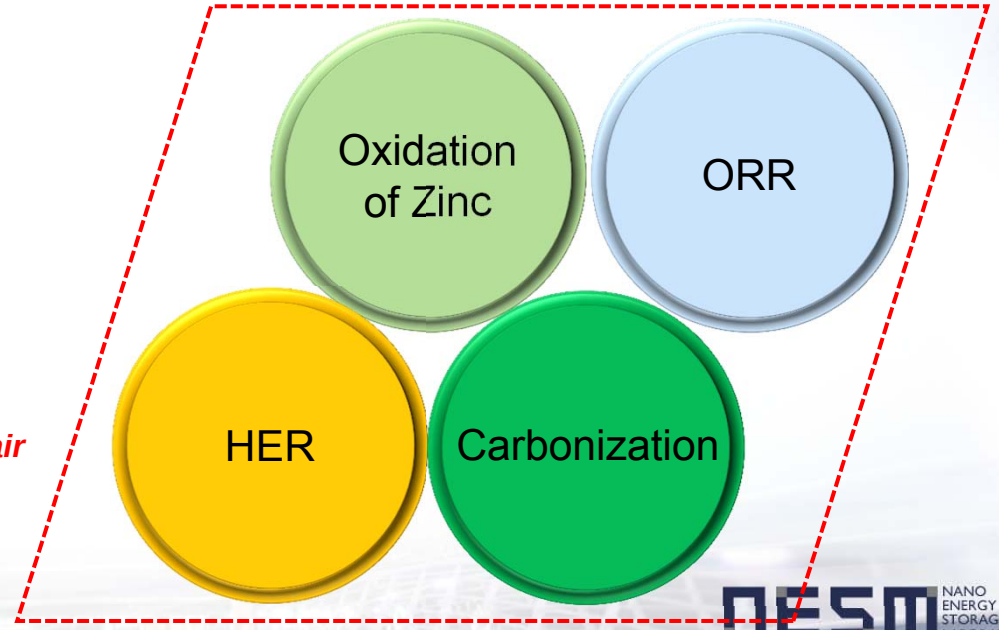


block a pore within air electrode

Open type Zn-air battery system

J. Cho et al., J. Power Source, 2013, 243, 267

<For better ZAB>



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3. Problems of Zn-air battery

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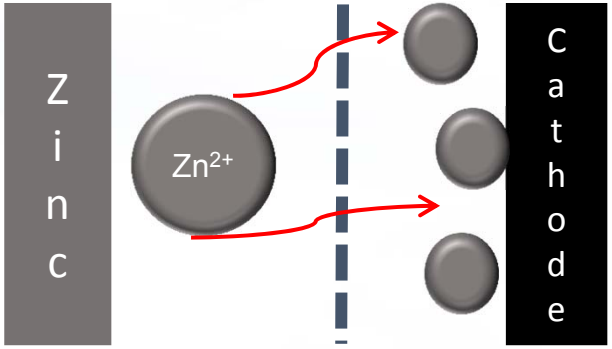
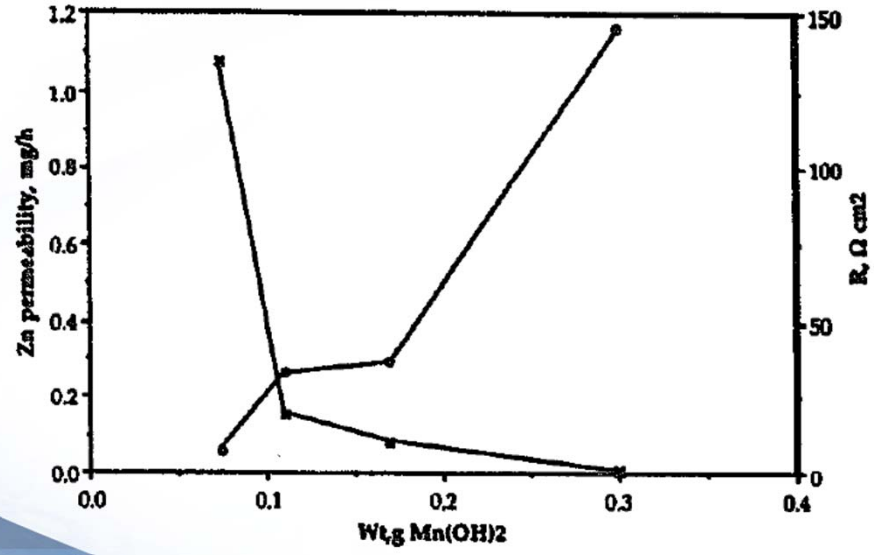
◆ Permeation of Zinc in alkaline electrolyte



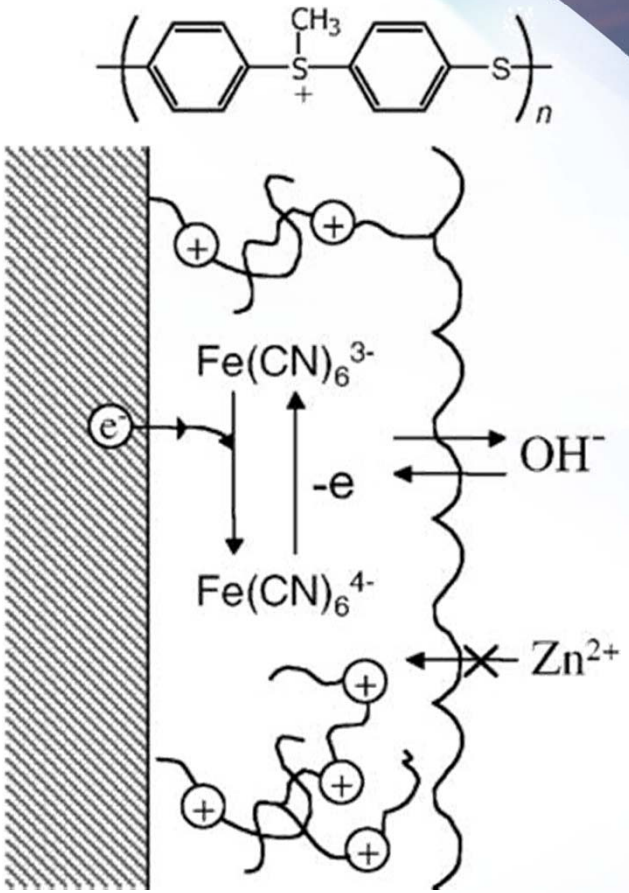
Polarization ↑

Capacity ↓



Amount of $Mn(OH)_2$ coated on the separator as function of zinc permeability and resistance

Kiros, Y. et al., J. Power Sources, 1996, 62, 117.



Scheme of modified electrode using polysufonum

Tsuchida, E., et al., J. Power Sources, 2003, 115, 149.

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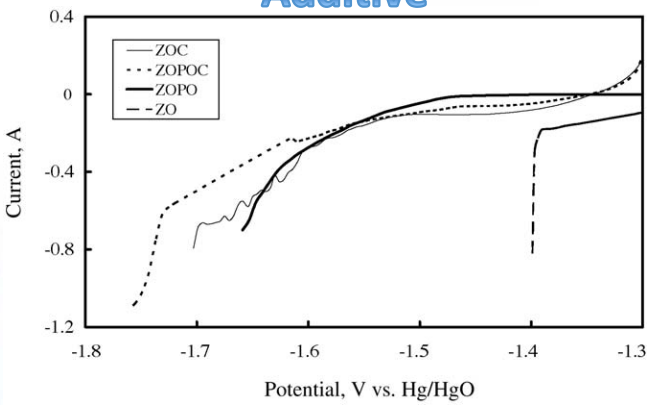
◆ HER of Zinc in alkaline electrolyte

V_{eq} of Zn < V_{eq} of H_2 → Capacity ↓, Ionic conductivity of electrolyte ↓

H_2 ↑ with slow kinetic rate

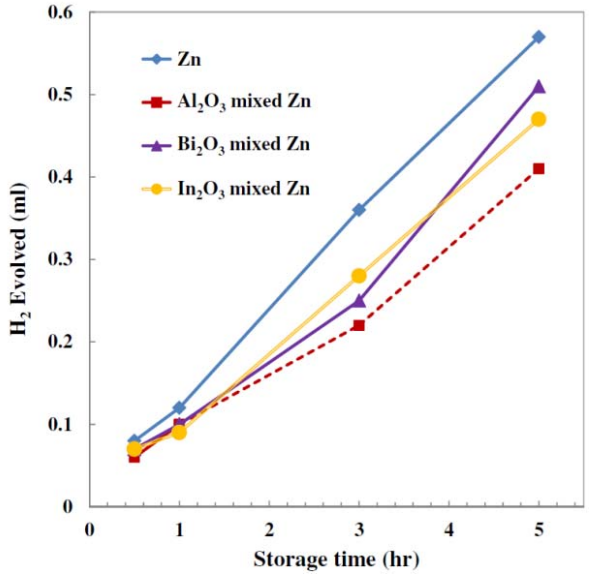
Additive



Effect of additives to a zinc oxide electrode on HER

S. Cho., et al., J. Power Sources, 2013, 227, 177

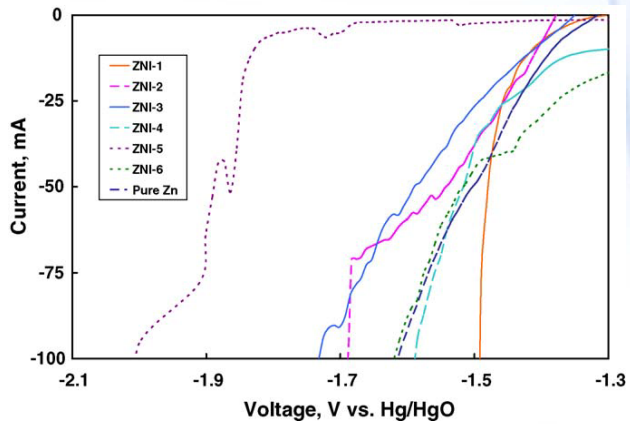
Surface coating



Volumetric measurement of hydrogen spontaneously evolved on the surface of Zn gel anode at 60℃

M. Yun., et al., J. Power Sources, 2006, 160, 161

Alloy



Effect of zinc and its alloy electrode on HER

M. Yun., et al., J. Power Sources, 2006, 160, 1436

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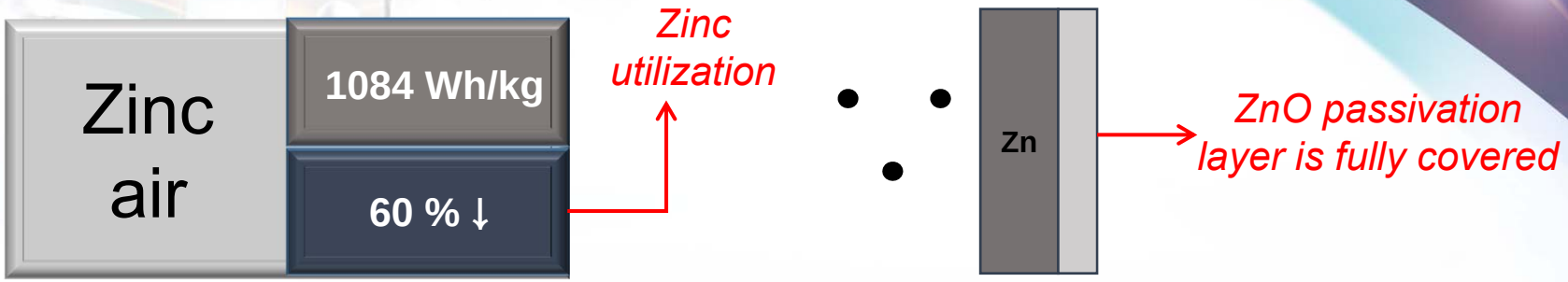
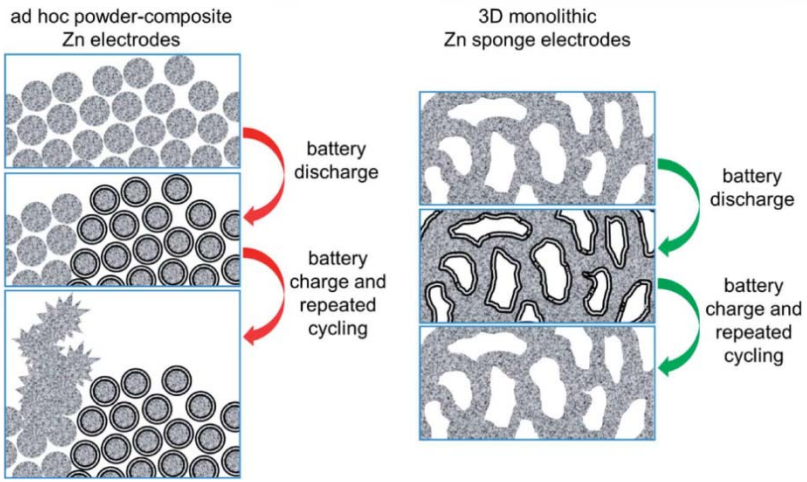
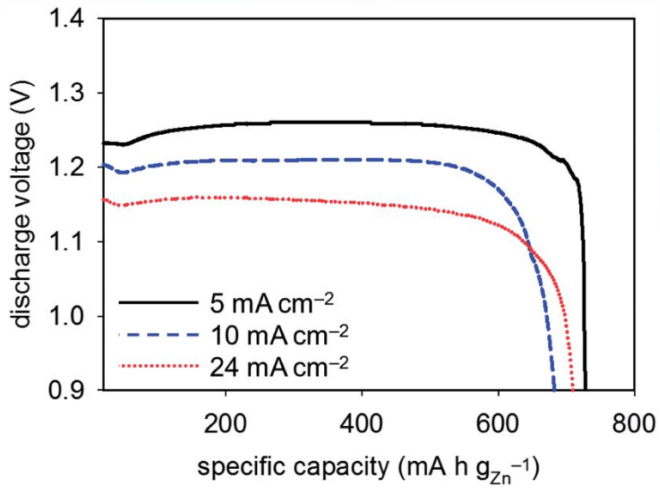
◆ Low Zinc utilization





Effect of zinc and its alloy electrode on HER.



Effect of zinc and its alloy electrode on HER.

Zinc sponge with a porous monolithic, 3D aperiodic architecture and they demonstrated that zinc utilization approaches 90% (728 mAh/g_{Zn}) as a primary zinc-air cell.

Jeffrey W. Long., et al., Energy Environ. Sci, 2014, 7, 1117.

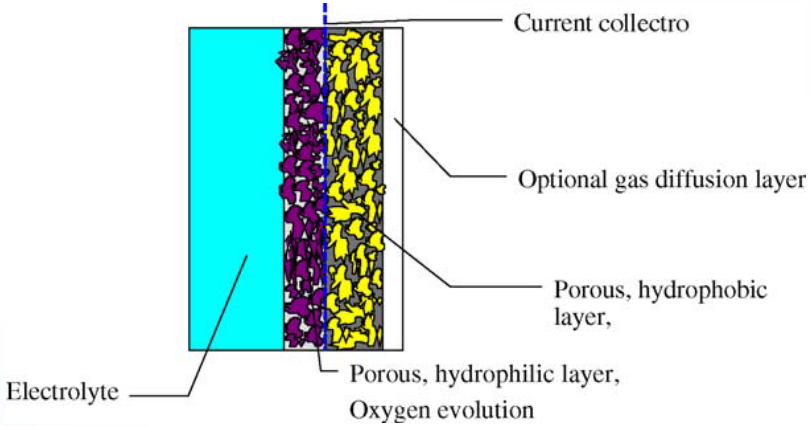
◆ Degradation of hydrophobicity in air electrode

Air electrode

Hydrophobic carbon in gas diffusion layer

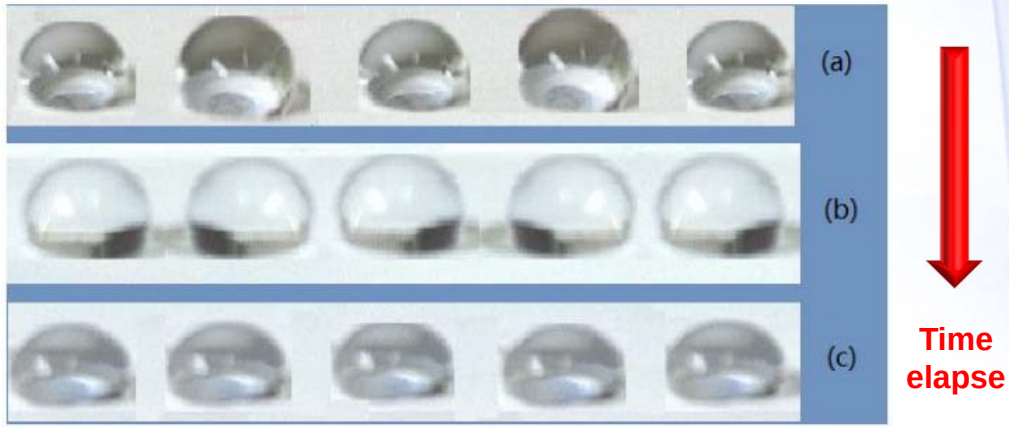
Hydrophilic carbon in catalyst layer

O_2



Possible microstructure of a multi-layered electrode

- **Natural Degradation**



Results of surface property experiment of PTFE film, (a) unhandled PTFE film, (b) Soak for 72 hours, (c) Soak for 148 hours PTFE film.

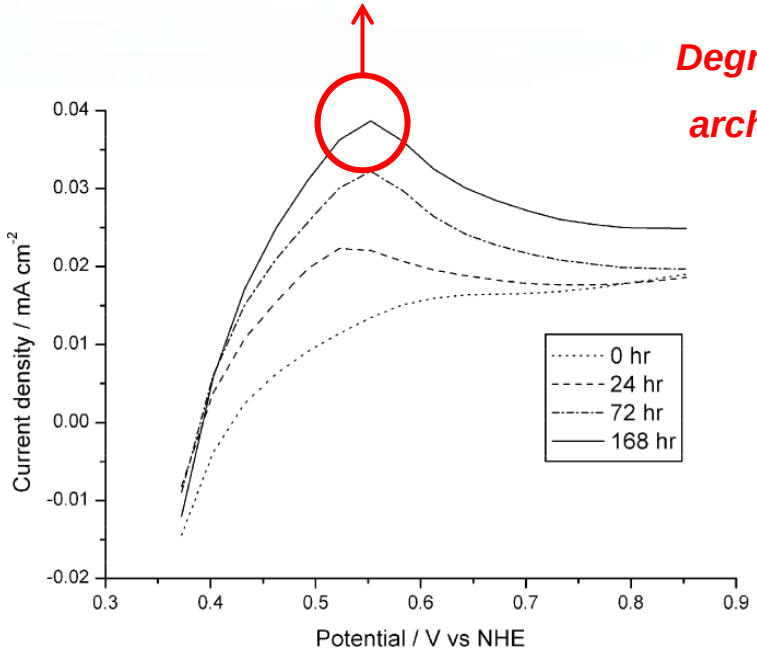
- **Electrochemically Degradation**

During discharge, generated heat affects electroosmosis of electrolyte and PTFE hydrophobic binder, causing air electrode polarization due to electrolyte infiltration.

Zhang, J., et al., Int. J. Electrochem. Sci., 2013, 8, 11805.

◆ Degradation of air electrode in charging process

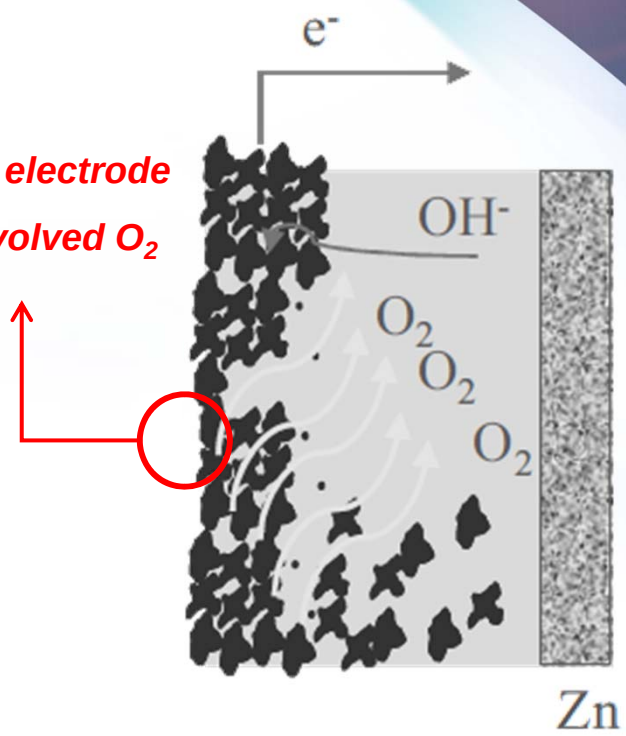
Carbon oxidation peak at the range of Zn-air battery charging process



Forward scan of the cyclic voltammogram of Vulcan XC-72

Yushan Yan., et al., J. Power Sources, 2006, 158, 154.

Degradation of air electrode architecture by evolved O_2

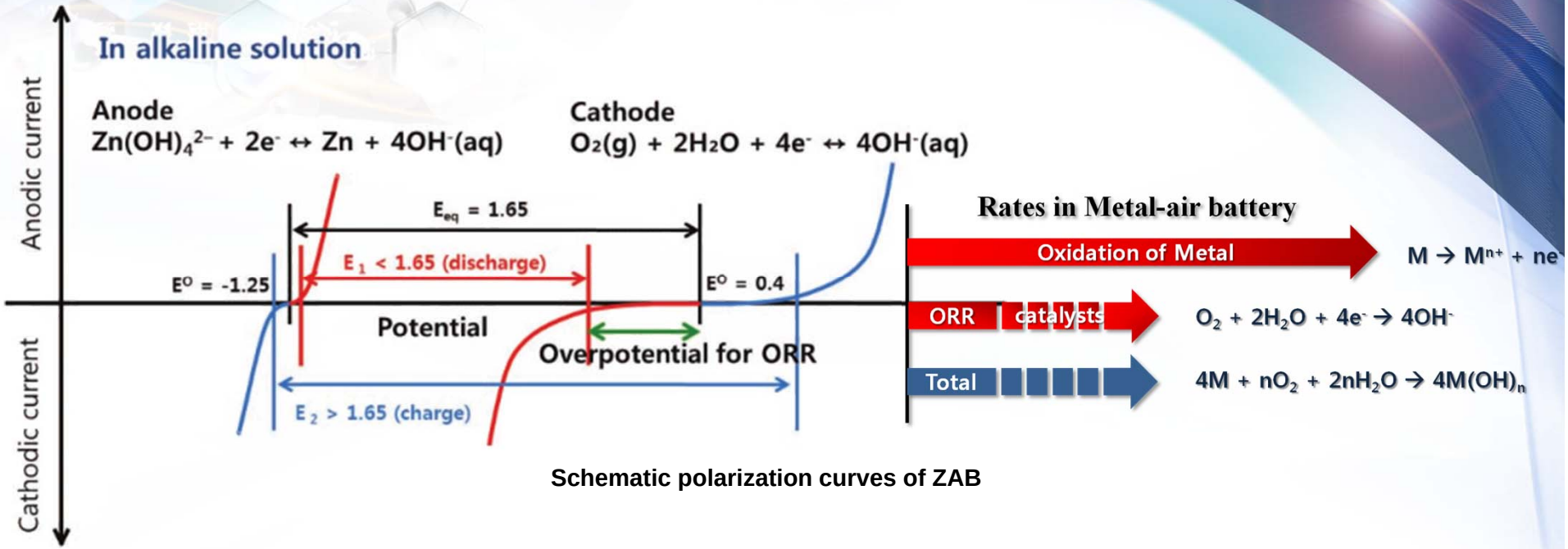


Air electrode during charge

Fabrice Fourgeot., et al., ECS Trans, 2010, 28, 25.

Reversible air electrode ⟸ **ORR OER** **Minimize Carbon content in Catalyst**

◆ Necessity of bi-functional electrocatalysts



Schematic polarization curves of ZAB

<u>Overpotential : Zinc anode < Air cathode</u>

Discharge process : Working voltage is smaller than 1.65 V (red line)

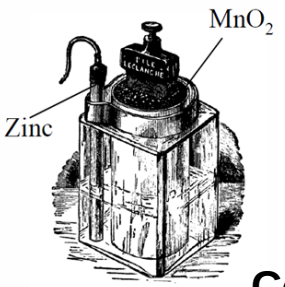
Charge process : Working voltage is larger than 1.65 V (blue line)

Bi-functional electrocatalyst

J. Cho., et al., Adv. Energy Mat., 2011. 1, 34

Progress of Zn-air Technology[1]

· 1868 – Leclanche invented Zn-C battery
He noted : the MnO_2 cathode improved the battery Performance – discovered the principle of Zn-air battery
· 1879 – first Zn-air battery invented

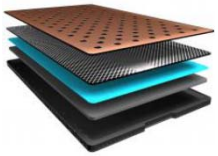


First mechanically
Rechargeable battery

Commercialization
Low current

Button cell
Hearing aids

New Era:
Large batteries
Motive power applications
- Better air cathodes
- Moisture control systems
- New ways of recharging



Revolt

EOS

1879 | 1932 | 1950 | 1950 | 1990 | 2000

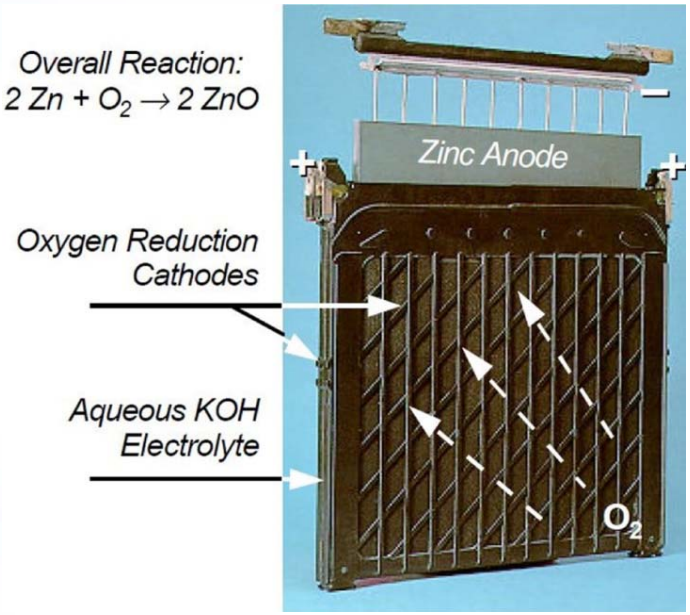
<Progress of Zn-air Technology>

1. Zhang, Zinc-air technology, Zinc-air technology workshop, International Zinc Association /ZESTEC, Shanghai, 2005

4. Rechargeable ZAB

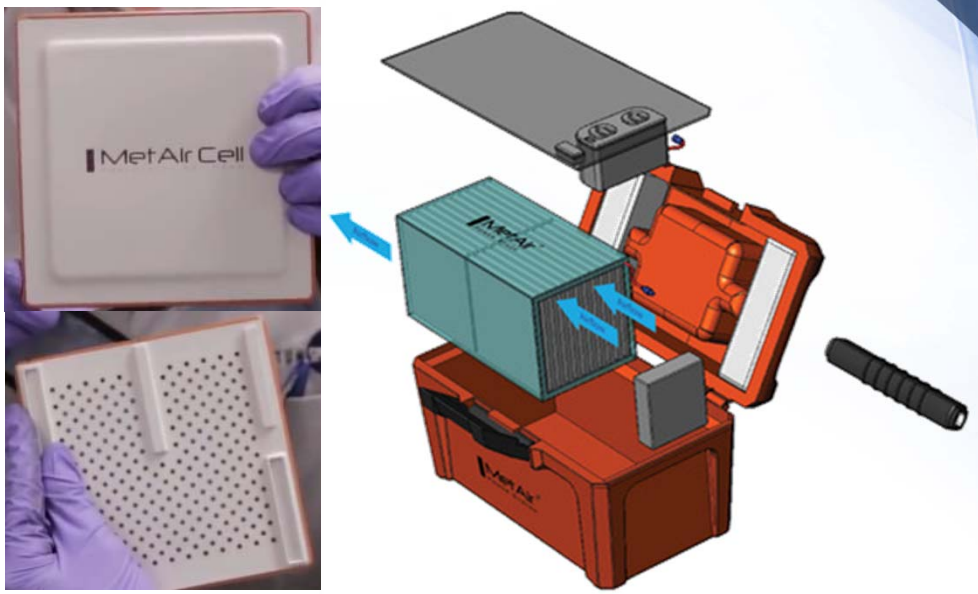
◆ Mechanically rechargeable ZAB

Zinc replacement



Mechanically rechargeable Zn-air battery

K. Kim., et al., J. Korean Electrochem. Soc., 2013, 16



Commercialized Zn-air battery of Met-air

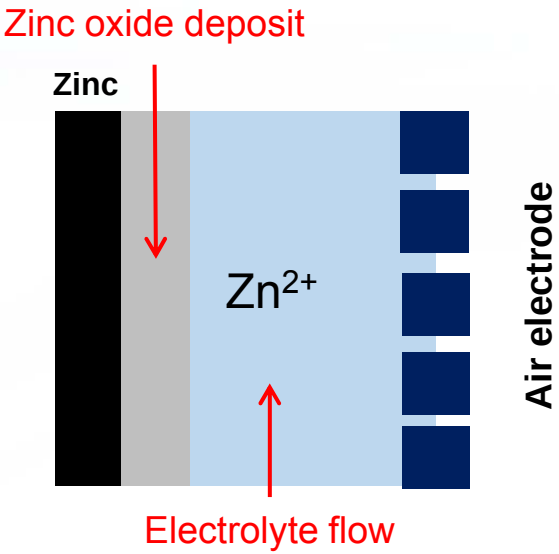
http://www.metair.co.za

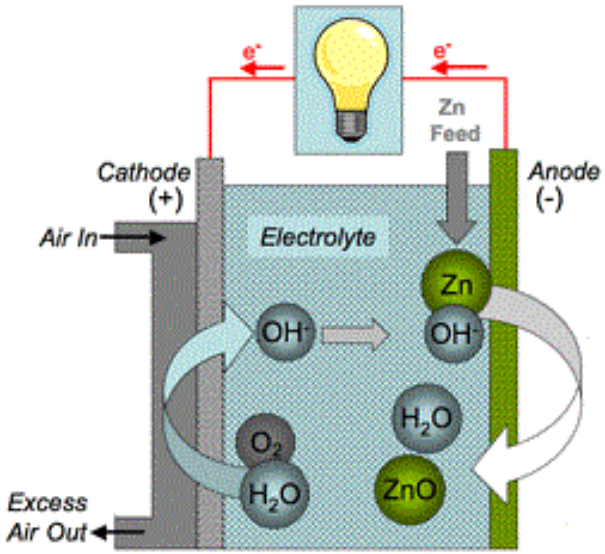
Irreversible phase of ZnO at zinc anode → necessity of change whole zinc side

Zinc is cheap metal which can be used as disposable material (~ 0.9 USD/lb)

◆ Mechanically rechargeable ZAB

Zinc air flow battery





http://cleantechnica.com/2008/11/26/company-introduces-zinc-fuel-cell-power-pack/

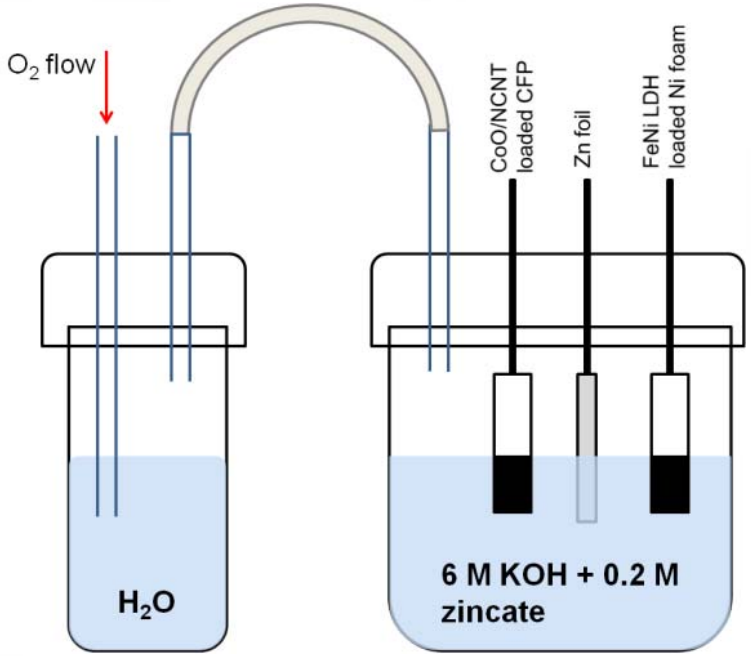
Schematic of the new zinc air flow system

Passivation layer of ZnO at Zinc anode is problem for ZAB rechargeability

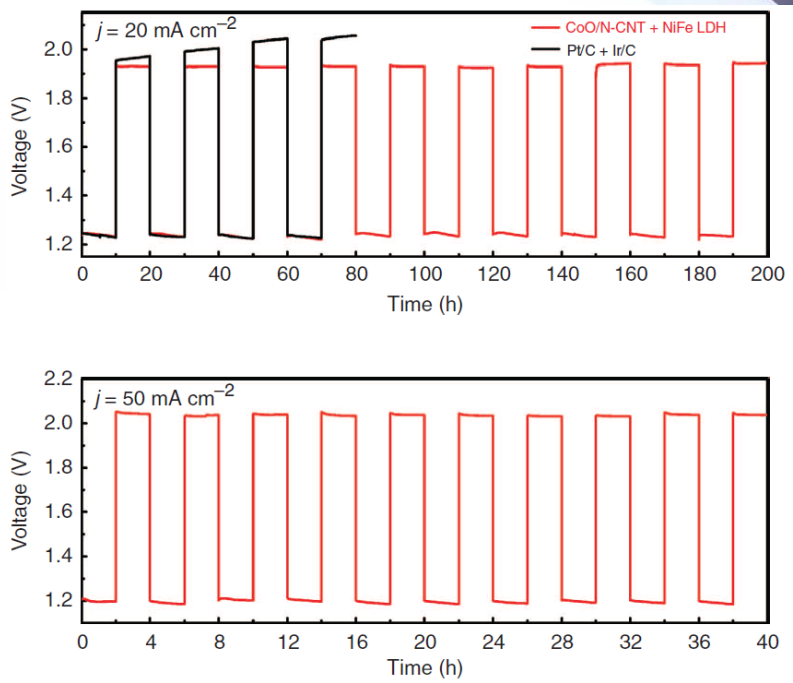
ZnO can be removed by the flowing electrolyte

◆ Electrically rechargeable ZAB

3-electrode system (with O_2 blowing)



Schematics of electrochemical cells for the measurements of rechargeable ZAB with three electrodes and oxygen blowing.



Cycling performance of the tri-electrode ZAB at 20 mA cm^{-2}, 20 hours cycle period and 50 mA cm^{-2}, 4 hours cycle period.

Electrode separation for ORR and OER with O_2 blowing; artificial system

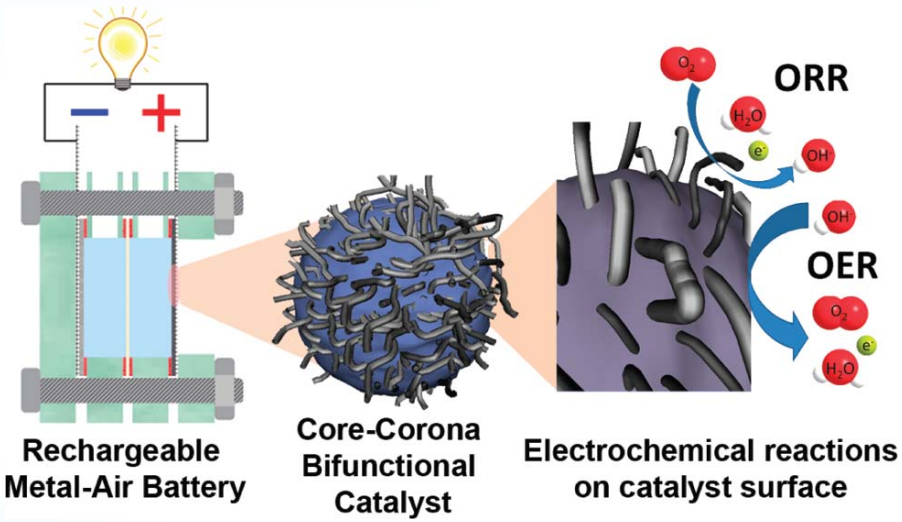
Relatively high DOD (~ 12 %, 14 %) with stable property

H. Dai., et al., Nat. Comm., 2013, 4, 1805

◆ Electrically rechargeable ZAB

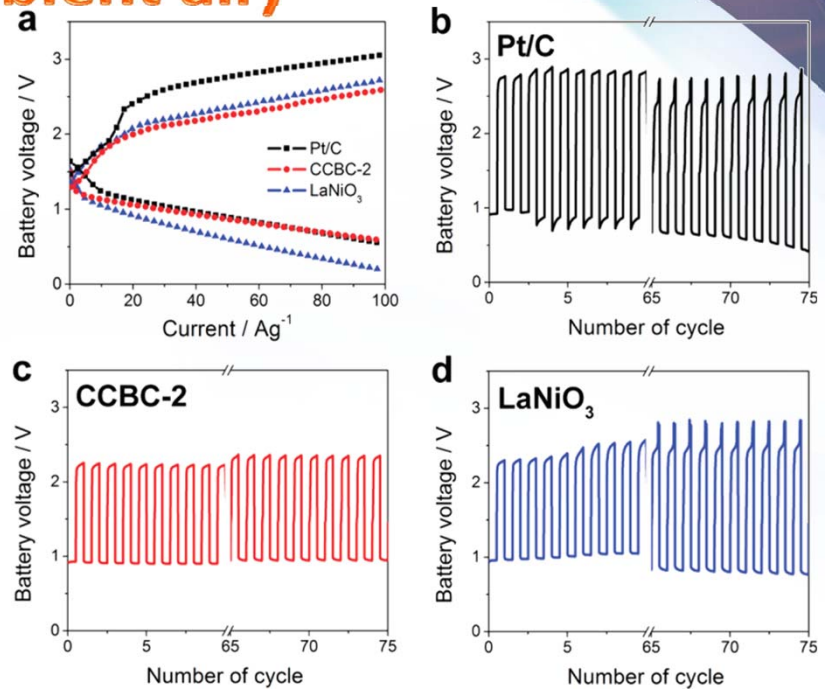
2-electrode system (with ambient air)

$LaNiO_3$/NCNT electrocatalyst



Schematics of electrochemical cells for the measurements of rechargeable ZAB with three electrodes and oxygen blowing

Z. Chen., et al., Nano Lett., 2012, 12, 1946.



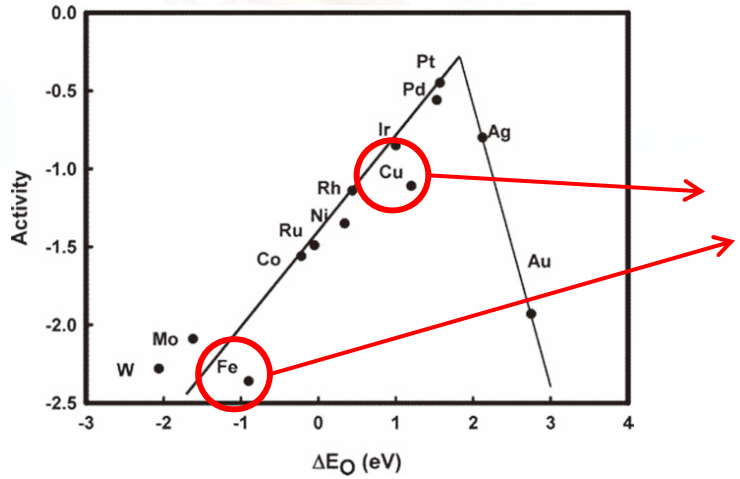
(a) Discharge and charge polarization curves of electrocatalysts, (b-d) ZAB cycling performance of each electrocatalysts. Current density : 17.5 mA cm^{-2}, cycled 75 times.

No electrode separation for ORR and OER in ambient air condition; natural condition

Relatively high overpotential in low DOD about 1 %

5. ZAB research in our group

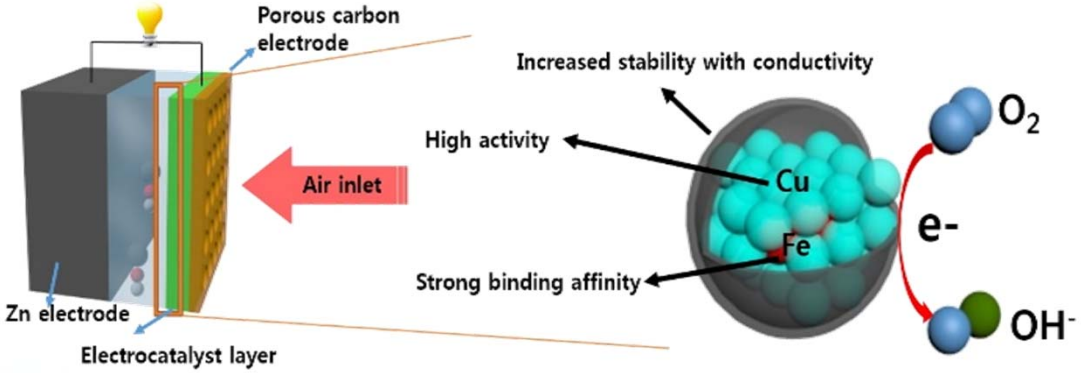
◆ Cu-Fe Bi-functional Electrocatalyst



With high activity of Cu and high absorptivity of Fe → Alloy could be solution!

J.K. Norskov et al., J. Phys. Chem. B., 2004, 108, 17886

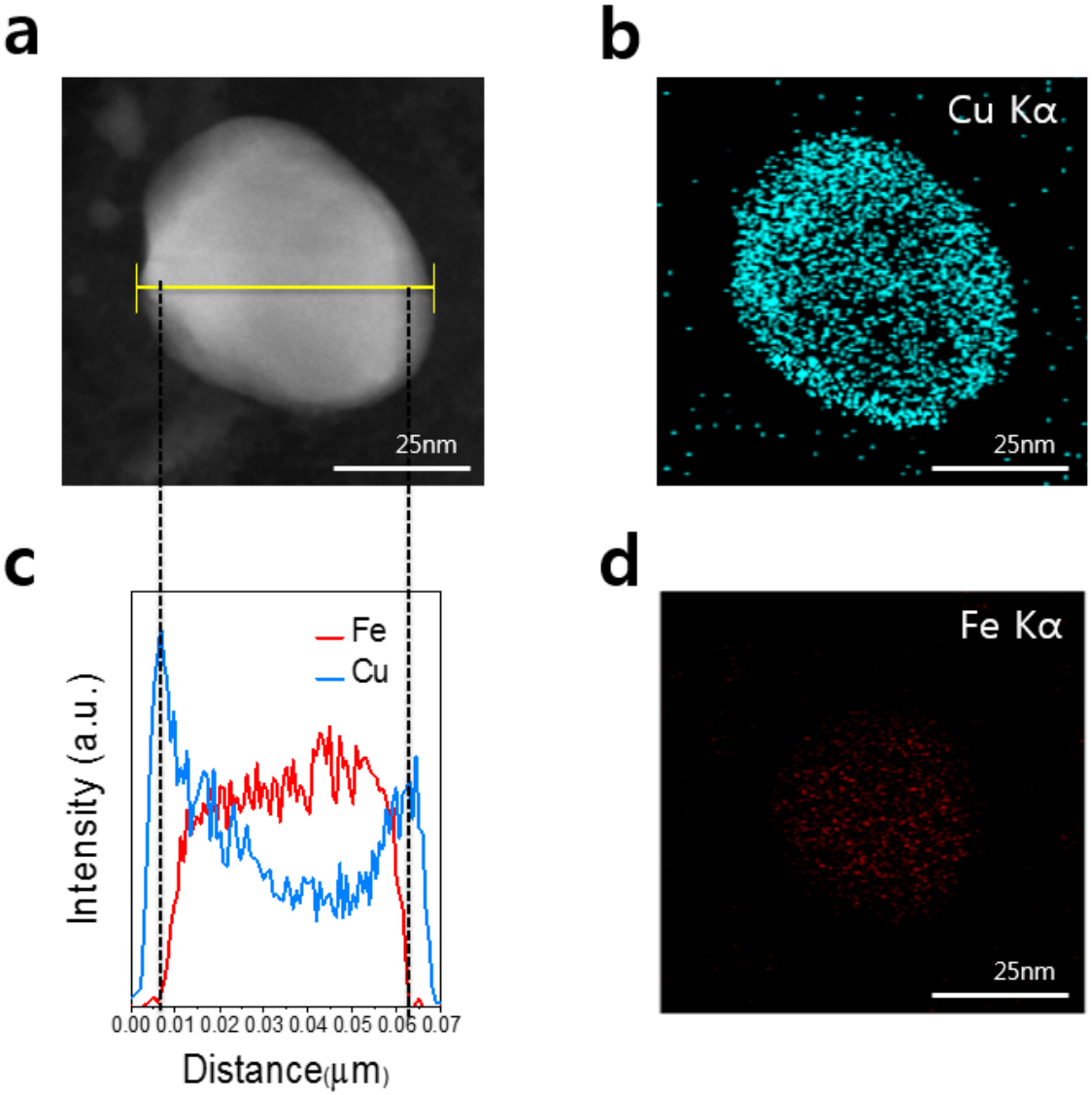
Trends in oxygen reduction activity plotted as a function of the oxygen binding energy

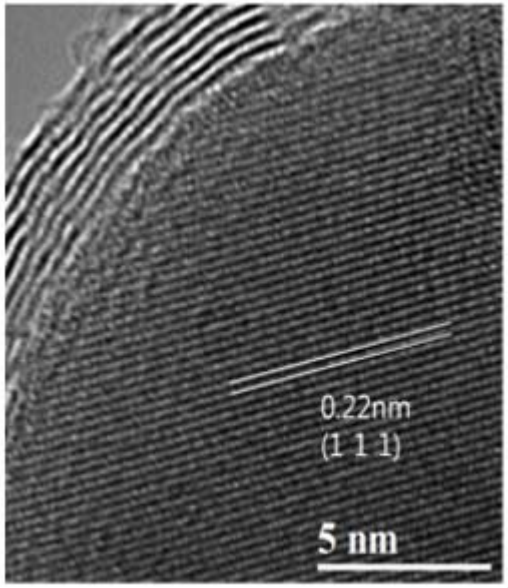


Oxygen reduction reaction of carbon coated Cu-Fe alloy electrocatalyst

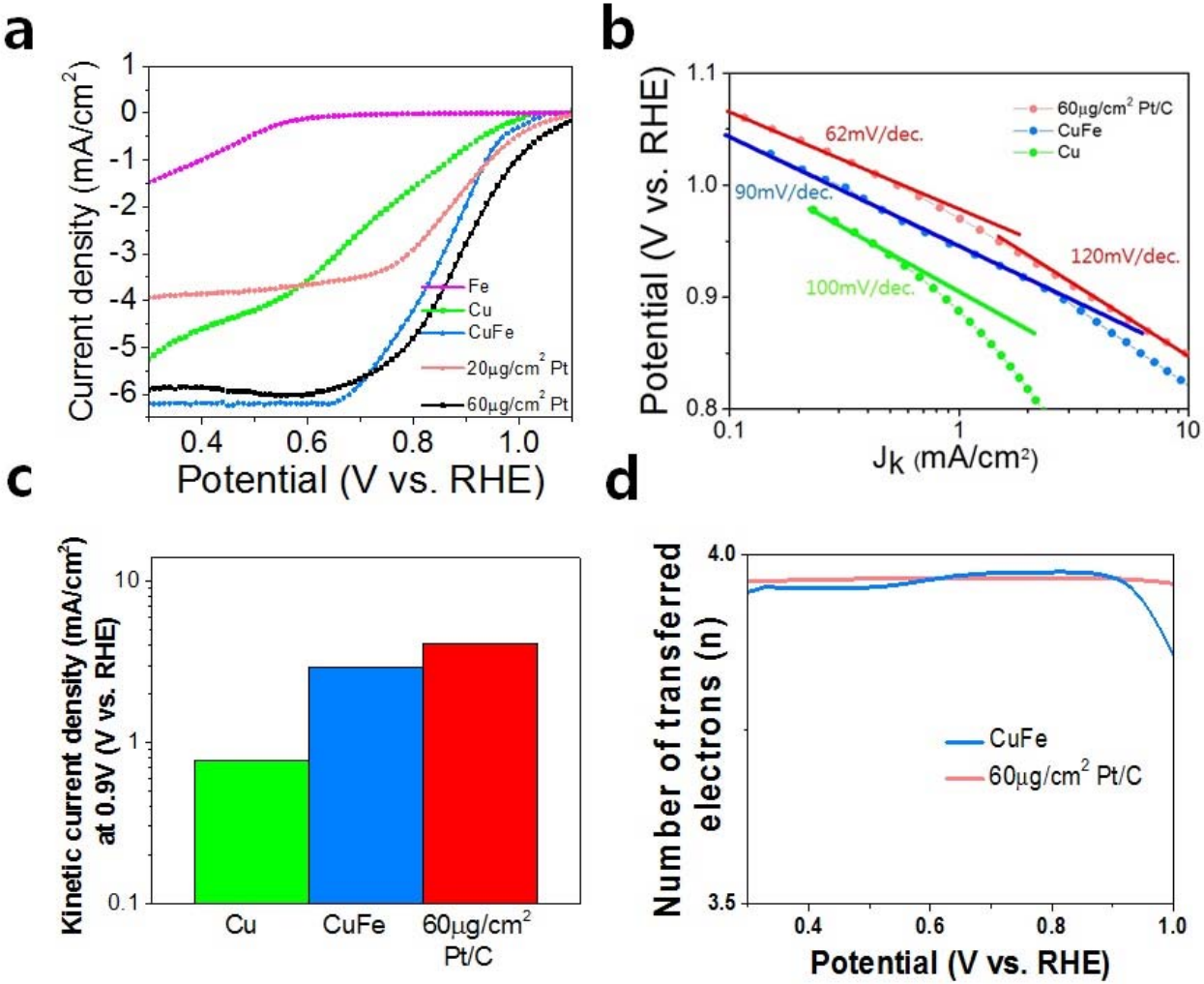
ACS NANO 2015

Microstructure of CuFe Alloy





Electrocatalytic activity of CuFe alloy

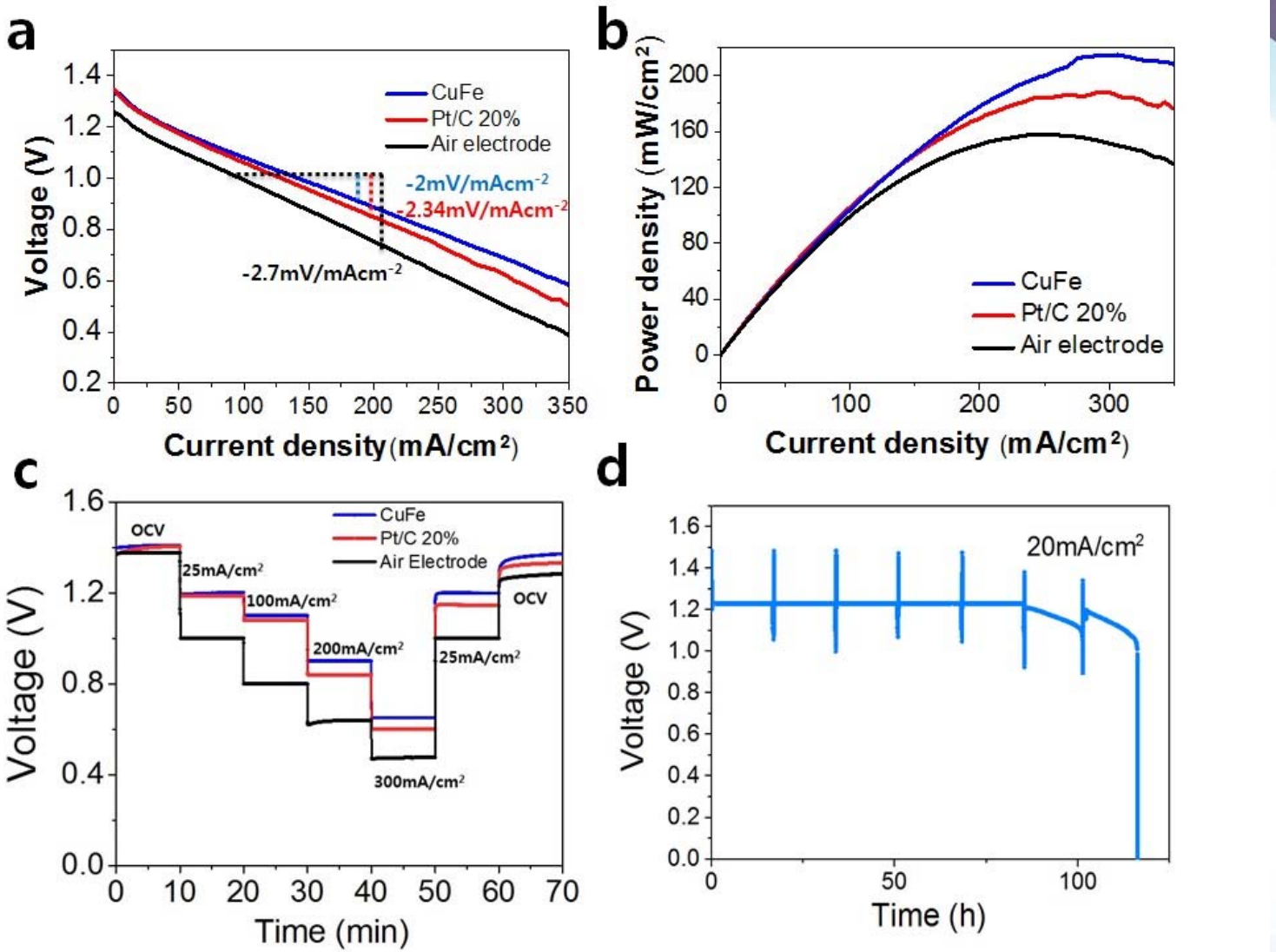


Tafel plot: the rate-determining steps during CuFe alloy catalysis of the ORR may be both the migration of intermediates and electron transfer.

CuFe: 0.389mg/cm^2

Pt/C : 0.318mg$_{(20\%\ Pt/C)}$/cm^2 (60μg$_{pt}$/cm^2)

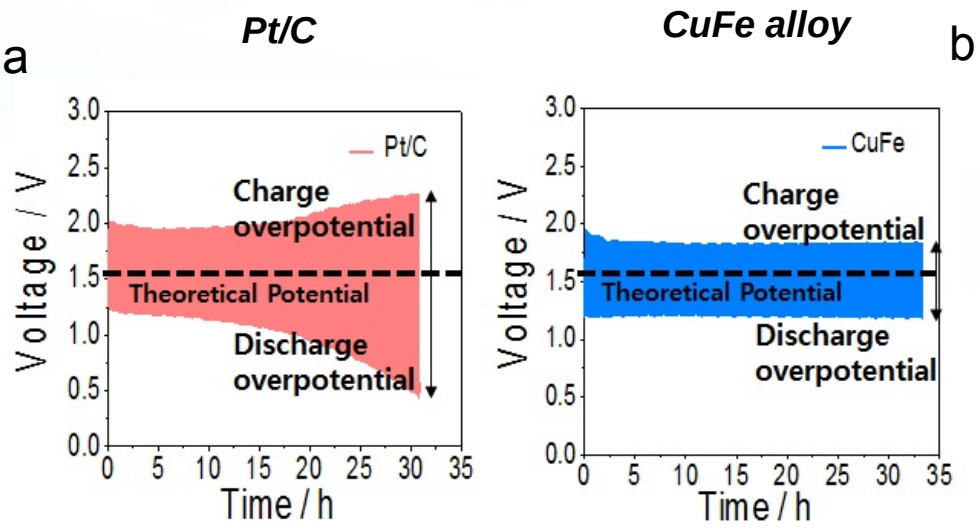
Zn-Air cell performance



◆ Cu-Fe Bi-functional Electrocatalyst

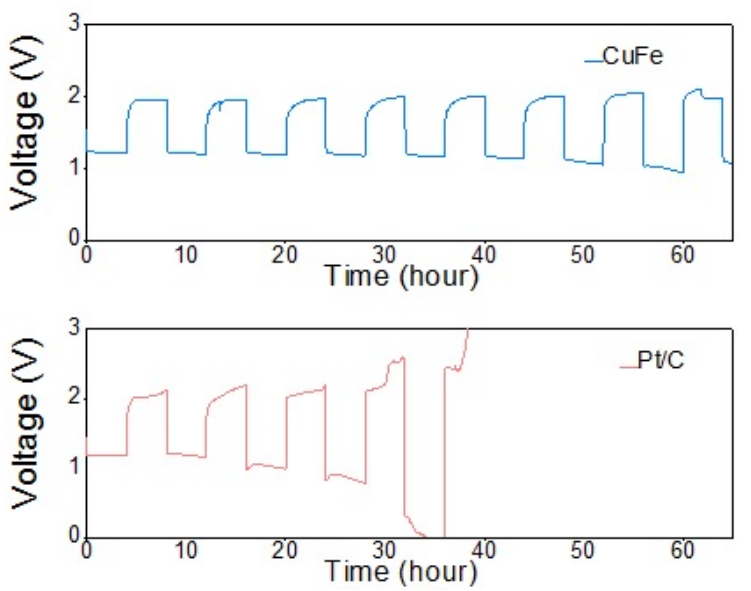
2-electrode system (with ambient air)

a



(DOD 1%)

b



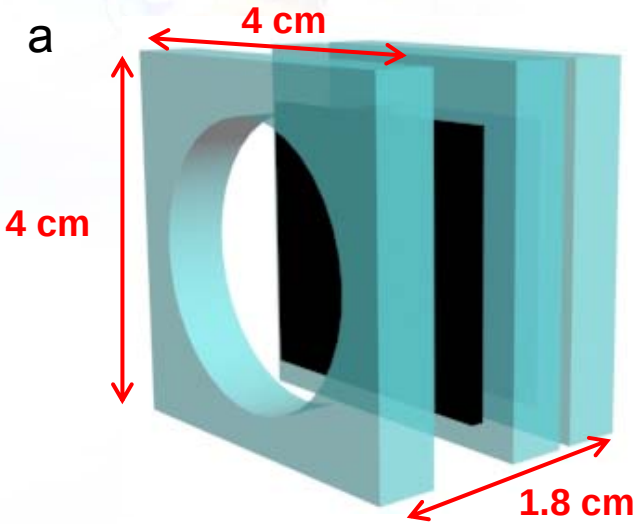
(DOD 10%)

Rechargeable ZAB of Pt/C, CuFe, (a) 5 mins and (b) 4 hours discharge and charge time for each process.

Stable Zn-air battery performance with Cu-Fe electrocatalyst (DOD 1% and 10%)

Unpublished

◆ Wh/cc of Zn-Air cell



(a) Schematic diagram and (b) photograph of the stack-type Zn-air battery

Specification of Stack-Type ZAB

Cell total weight : 33.5 g

Zinc anode weight : 0.8 g

Air electrode weight : 0.3 g

[Dimension]

Width x length : 4 cm x 4 cm

Thickness : 6 mm x 3

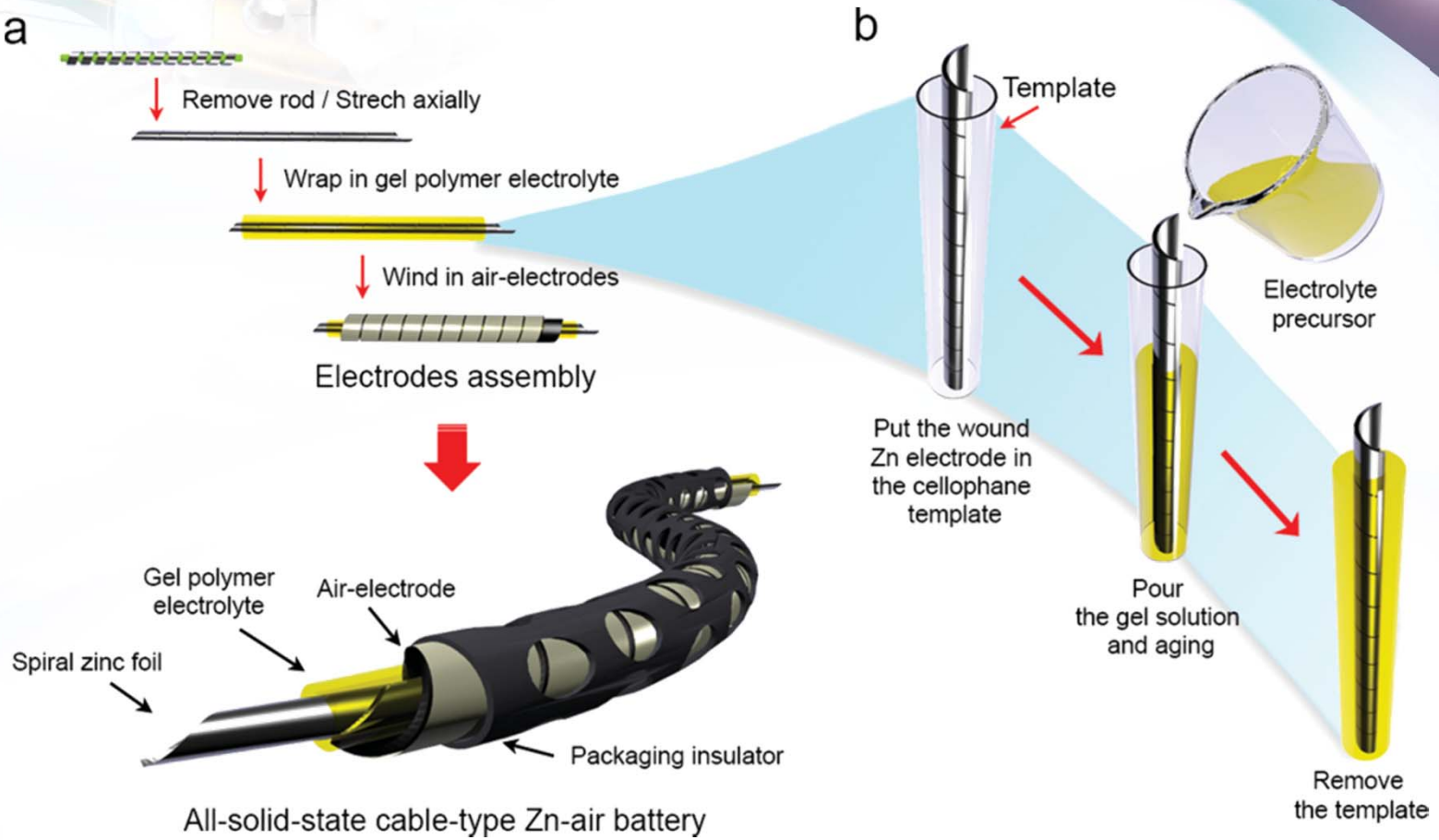
Still many dead space

35.7 Wh/kg

41.5 Wh/L

Unpublished

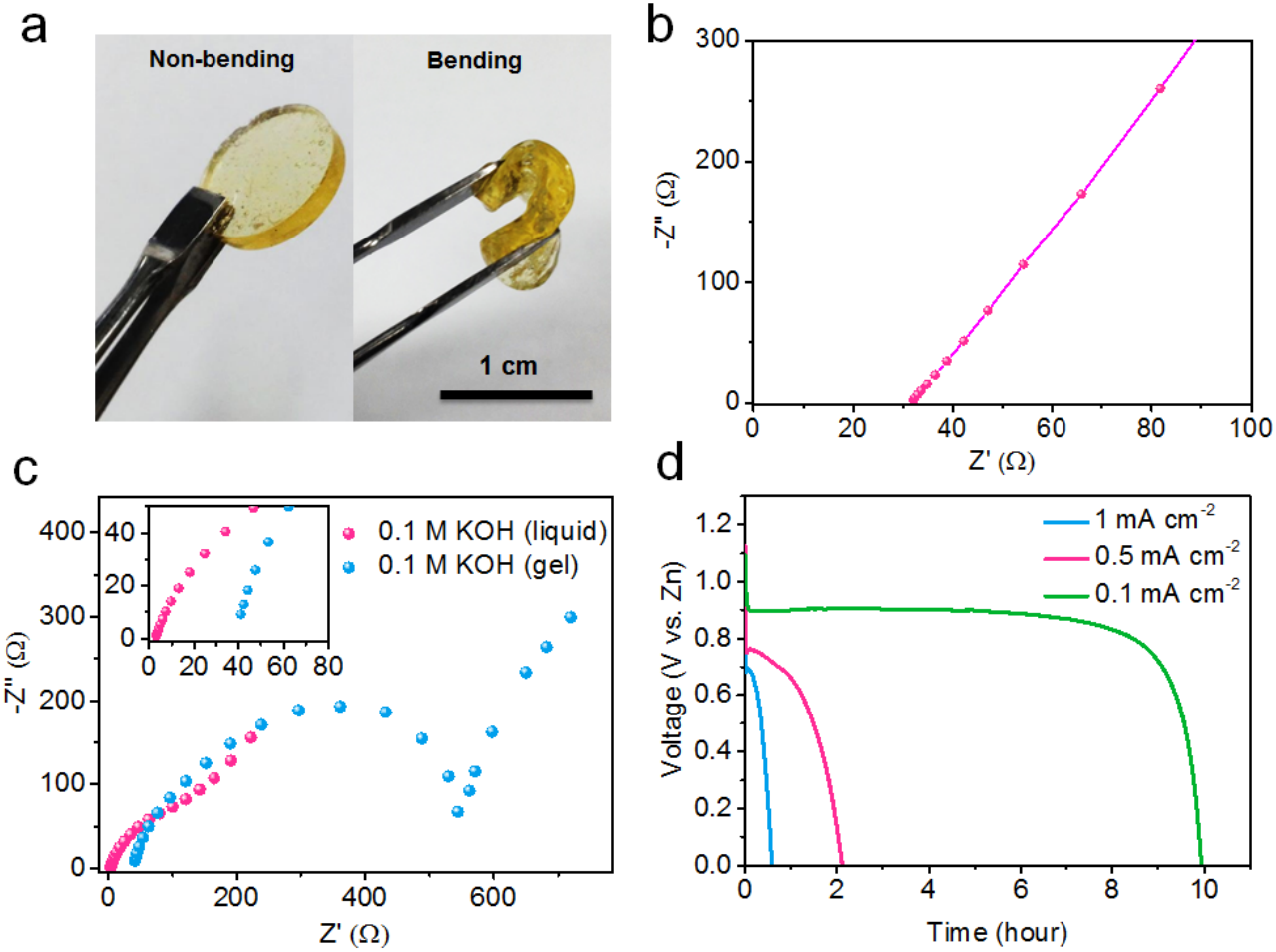
◆ All-Solid-State Cable-Type Flexible Zn-air Battery



Cable-type flexible Zn-air battery. (a) Schematic diagram of Cable-type flexible Zn-air battery assembly and (b) coating method of gel polymer electrolyte based on gelatin and 0.1 M KOH with zinc spiral metal.

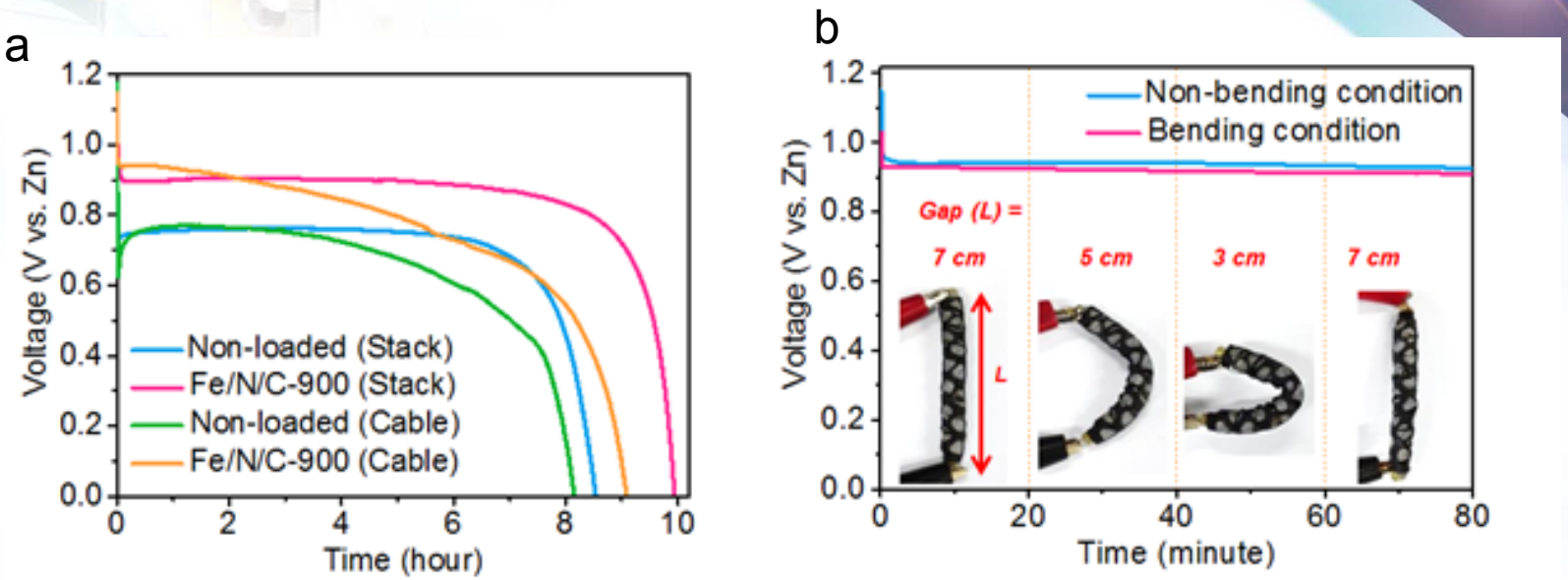
J. Cho., et al., Adv. Mat., 2015, 27, 1396

Free standing gel-type electrolyte



gelatin based gel polymer electrolyte (GGPE) with 0.1M KOH, showing an ionic conductivity of 3.1 × 10^{-3} S cm^{-1} at 24°C

◆ All-Solid-State Cable-Type Flexible Zn-air Battery



(a) Discharge curves of stack-type and cable-type Zn-air battery with the discharge current density was 0.1 mA cm^{-2}. (b) Discharge curves of cable-type Zn-air battery with variations in bending strain every 20 minutes. The discharge current density was 0.1 mA cm^{-2}. Catalyst: metal catalyst derived from silk fibroin

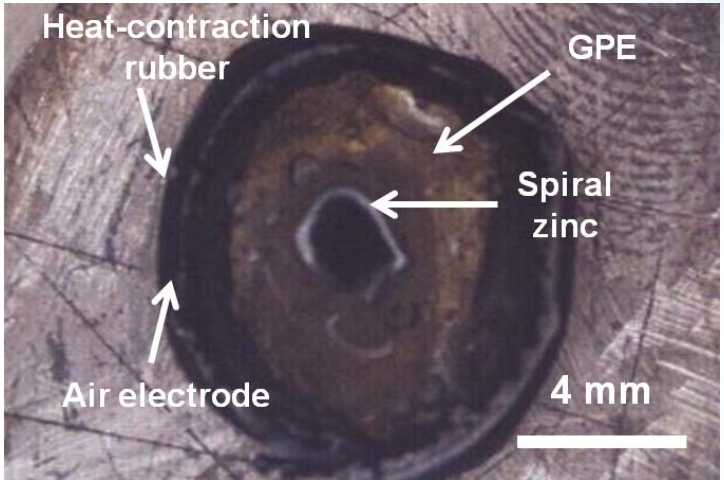
Different discharge curve shapes of stack and cable due to the pressure difference

Stable electrical performance of cable-type Zn-air battery during bending test

J. Cho., et al., Adv. Mat., 2015, 27, 1396

◆ All-Solid-State Cable-Type Flexible Zn-air Battery

Photograph of the cable-type flexible Zn-air battery



Cross-sectional image of the cable-type flexible ZAB

Specification of Cable-Type Flexible ZAB

Cell total weight : 6.5 g

[Dimension]

Diameter : 8 mm

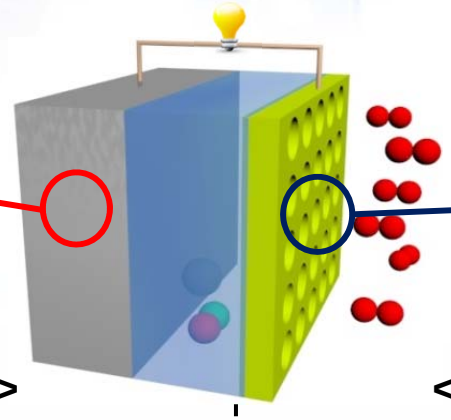
Length : 7 cm

1.9 kWh/kg

3.6 Wh/L

J. Cho., et al., *Adv. Mat.*, 2015, 27, 1396

6. Conclusions



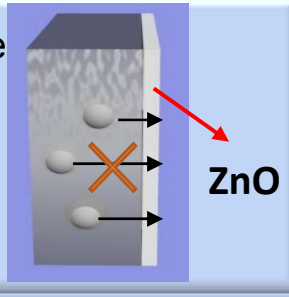
Fully immersed Zn electrode

Partially wetted air electrode

<Primary Zinc air battery>

Anode (Zinc electrode)

- ZnO passivation layer & volume expansion → low Zn utilization
- Electrolyte loss or low Zn utilization (from HER)

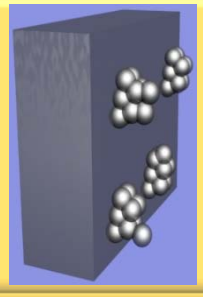


Cathode (Air electrode)

- Slow ORR/electrolyte infiltration → polarization ↑
- Pore clogging/lower ionic conductivity (from CO_2)
- Open cell structure → electrolyte evaporation

<Secondary Zinc air battery>

- High solubility of zincate
  → Zn dendrite
  → Low Zn utilization
  → Short circuit



- Carbon corrosion during OER → polarization ↑
- Large overpotential
- Air electrode architecture with different pore structure

6. Conclusion

◆ **Zn-air battery test protocol**

- **Use ambient air**
- **Do not separate electrode for ORR and OER**

↓

Two electrode ZAB system in ambient air is reliable

◆ **Perspective view for rechargeable Zn-air battery**

- **Zinc anode** : Scavenger reducing agent for ZnO
- **Air electrode** : New design, bi-functional catalyst
- **Electrolyte** : Zinc oxide blocking agent

↓

Electrically rechargeable Zn-air battery

ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY
NANO ENERGY STORAGE LABORATORY

Acknowledgement

ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

NESM MEMBERS

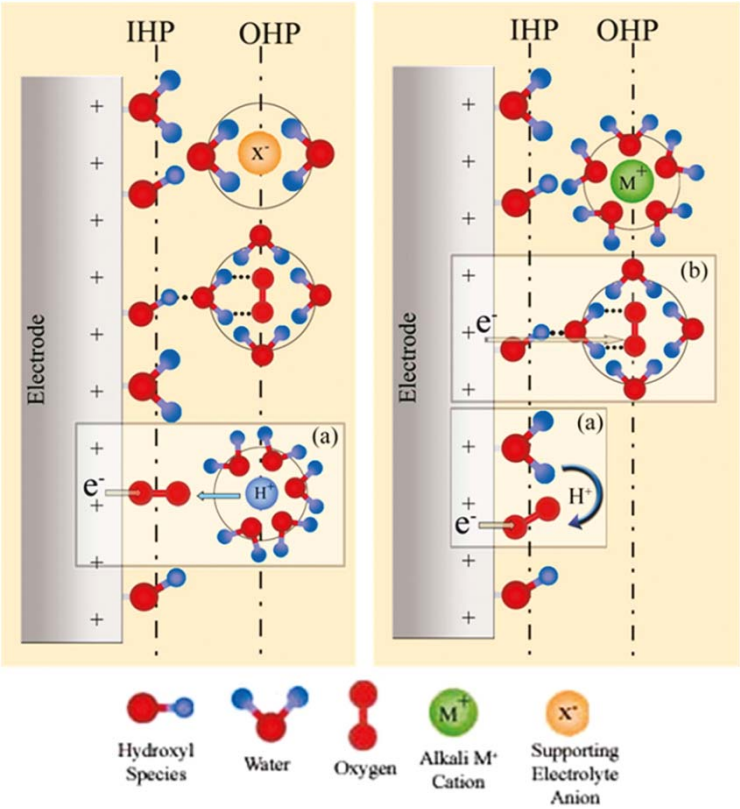
Website : www.jpcho.com

NANO ENERGY STORAGE LABORATORY

◆ Experimental for ORR based on RRDE method

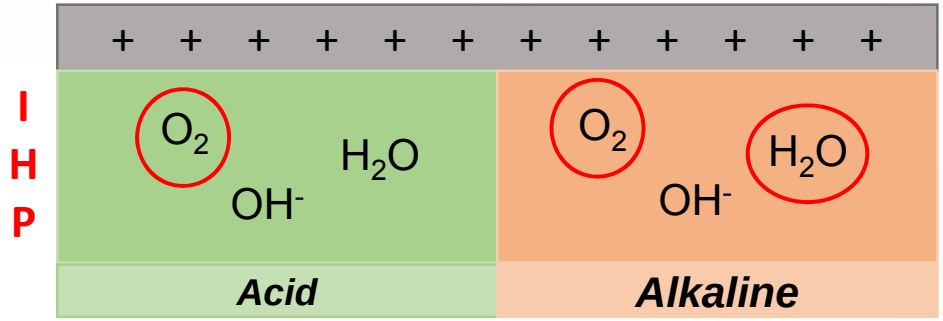
- **ORR in alkaline > acid** : Lower overpotential for first electron transfer step (O_2/O_2^-).

Acid **Alkaline**



Schematic illustration of the double-layer structure during ORR in acidic (left) and alkaline (right) conditions. Insets (a) and (b) illustrate the inner- and outer- sphere electron transfer processes.

- **Acid** : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
- **Alkaline** : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$



1.53 V > 0.7 V

High overpotential of acid medium compare to alkaline

Sanjeev Mukerjee et al., J. Phys. Chem. C, 2011, 115, 18015

Introduction: Oxygen reduction reaction (ORR)

Intrinsic kinetic and ORR mechanism based on Tafel plot[1]

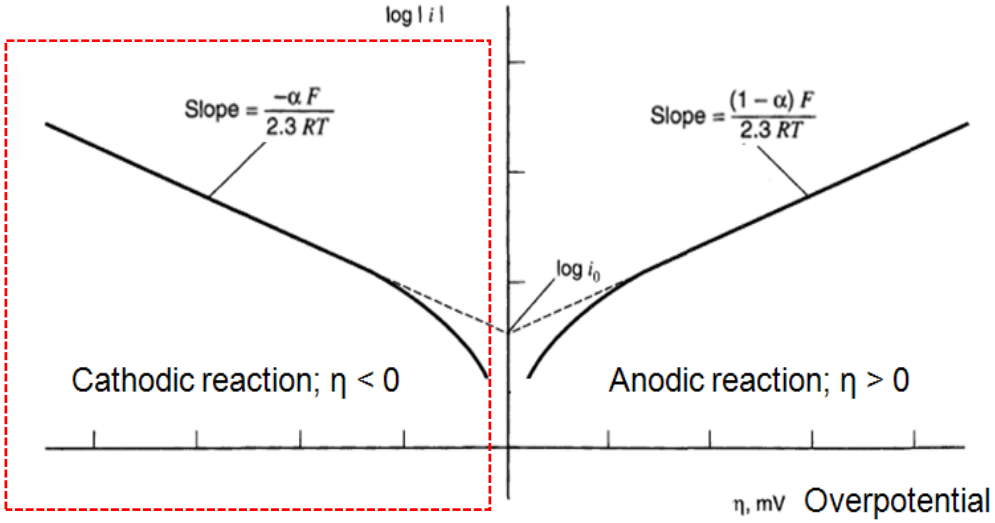


Fig. Schematic illustration of the Tafel plot of log| i | vs. overpotential (η) for the anodic and cathodic reactions of an electrode

Tafel slope:

η = a + b log I

$$b = \frac{RT}{\alpha n F} = \frac{60\ \text{mV decade}^{-1}}{\alpha}$$

$$\alpha = \frac{\gamma}{\nu} + \rho\beta$$

α (*assuming n=1*)	Tafel slope (mV/dec)
0.5	120
1	60
1.5 (=3/2)	40
2	30

- Difference in Tafel slope means different nature of the active ORR site.
- α (transfer coefficient) indicates that which step is rate determining step (r.d.s).

1. A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, New York, 2001.
2. William E. Mustain, Electrochimica Acta 52 (2007) 2102–2108

Introduction: Oxygen reduction reaction (ORR)

General r.d.s of Pt/C based on Tafel plot[1]

low

Overpotentials

High

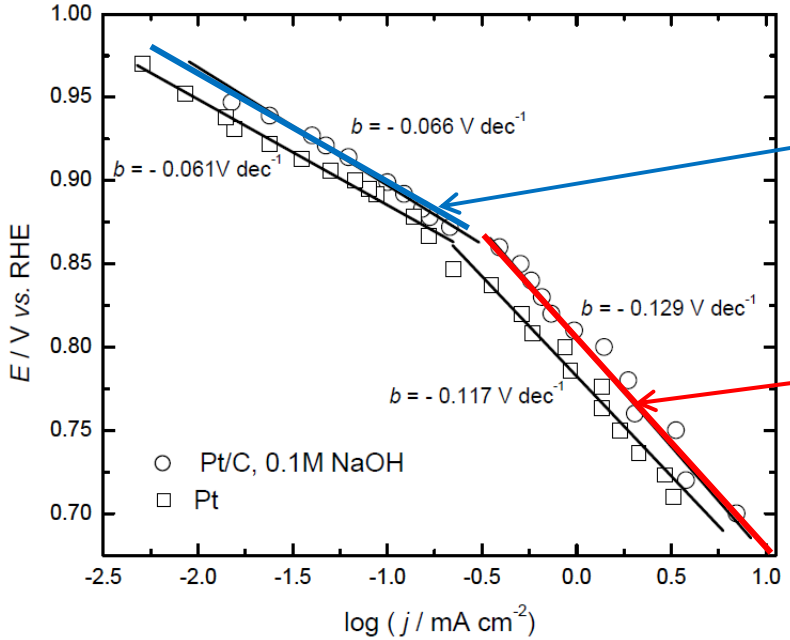


Fig.6. Tafel plots normalized to the electrochemically active surface area for O_2 reduction in 0.1 M NaOH solution at Pt and Pt/C electrodes.

Temkin adsorption (high O_2 coverage) at low overpotential (~60mV/dec.)

Langmuir isotherm (low O_2 coverage) at high overpotential (~120mV/dec.)

Leading to a coverage-dependent activation barrier for the ORR.

- The change in Tafel slopes is, generally, a consequence of a change in the r.d.s. (based on different α transfer coefficient).
- It is widely accepted that the different Tafel slopes arose from different adsorption conditions of the reaction intermediates and the same first charge transfer step was the r.d.s.

1. N.R. Elezovic et. al, J. Serb. Chem. Soc. 72(7) 699-708 (2007)

Exchange current density (i_0): intrinsic activity for ORR

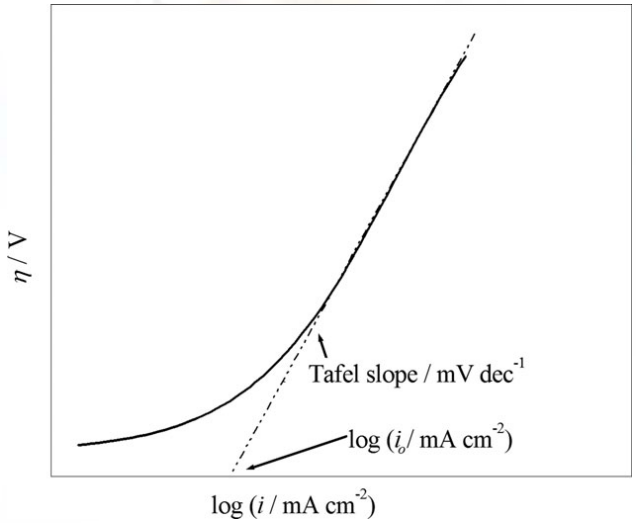


Fig. A typical Tafel plot for an electrode reaction[1]

Electrode materials/ Catalysts	ORR exchange current density, A/cm^2
Pt	2.8×10^{-7}
PtO/Pt	1.7×10^{-10}
FePc	1.3×10^{-7}
PtFe/C	2.15×10^{-7}
PtW_2C/C	4.7×10^{-7}
Ru_xSe_y	2.22×10^{-8}
$Ru_xFe_ySe_z$	4.47×10^{-8}

Table. ORR exchange current densities on various electrode materials[2]

- The magnitude of the exchange current density determines how rapidly the electrochemical reaction can occur.
- The exchange current density of an electrochemical reaction depends on the reaction and on the electrode surface

1. Feng Zhao et. al., Chem. Soc. Rev., 2009, 38, 1926–1939
2. Song, C. and Zhang, J., Electrocatalytic Oxygen Reduction Reaction. In PEM Fuel Cell Electrocatalysts and Catalyst Layers, Zhang, J., Ed. Springer London: 2008; pp 89-134.