# PJT.1: Development of advanced zinc-air battery with high energy density

School of Energy and Chemical Engineering
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**Duration**: 2010.03 ~ 2014.02 (Ph.D course)

**Role**:

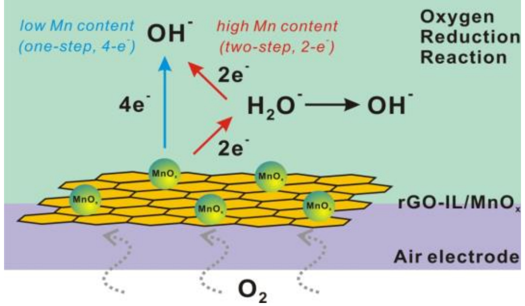
- Design and synthesis of non-precious metal catalysts for primary zinc-air battery
- Evaluation and analysis of as-prepared materials with zinc-air mono cell level.

**Technical Experiences:**

- Deep knowledge and background about Rational design of non-precious metal electrocatalysts
- Synthetic skills for desired nanostructures with functionality
- Hand on experience in overall zinc-air battery including air electrode architecture, zinc electrode, and physico and electrochemical evaluation

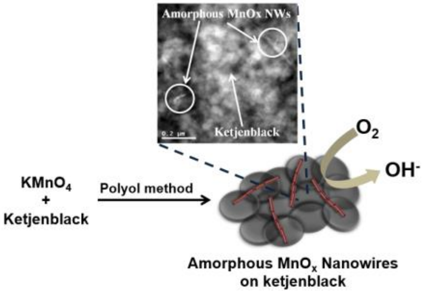
# 1.1 Previous Accomplishments on Electrocatalysts

### rGO supported $Mn_3O_4$



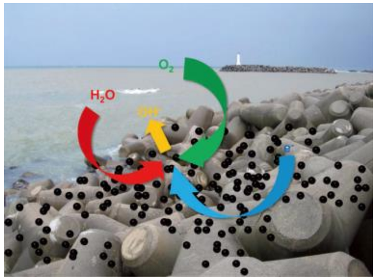
*Energy & Environmental Science*
4, 4148 (2011)

### KB supported $MnO_x$ nanowires



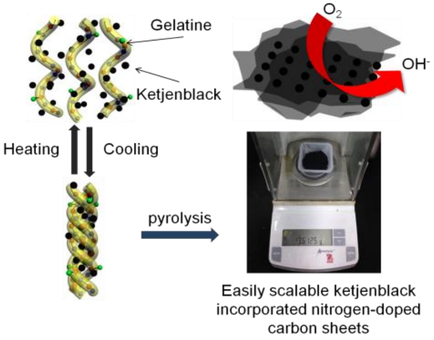
*Nano Letters* 11, 5362 (2011)

### Melamine foam supported $Fe/Fe_3C$



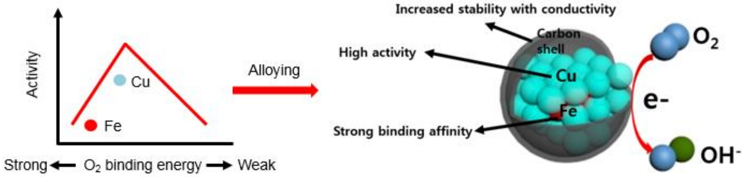
*Angewandte Chemie International Editions*
52, 1026 (2013)

### Gelatin/KB derived N-doped carbon



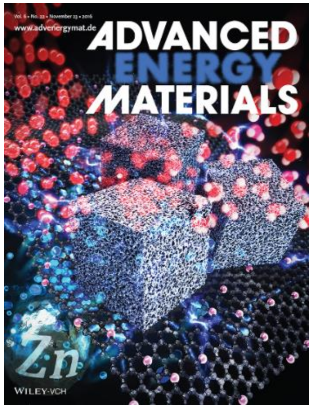
*Nano Letters* 14, 1870 (2014)

### Carbon coated Fe-Cu bi metallic alloy



*ACS nano* 9, 6493 (2015)

### Surface engineered Highly porous metal oxides



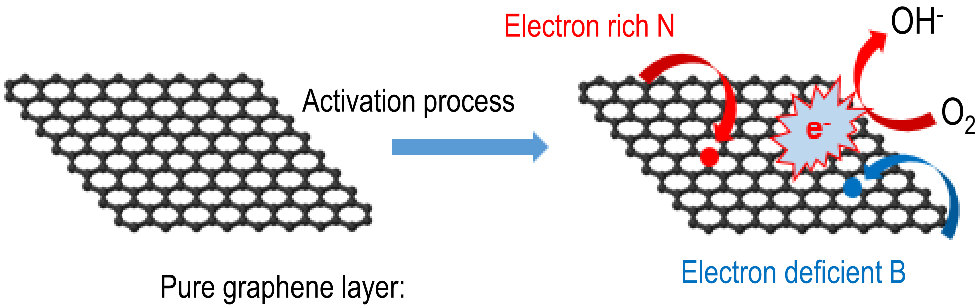
*Adv. Energy Mater.* 6, 1601052 (2016)

Improved mass trasnfer and kinetic and Scalable synthesis NEED!!!

# 1.1 Accomplishments 1) Scalable synthesis

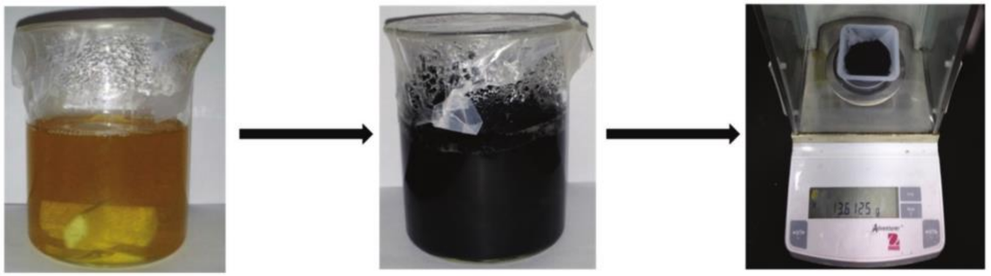
## Gelatin/KB derived N-doped carbon with Scalable synthesis

- *Material design:*
  *N doping → efficient for ORR*



Pure graphene layer:
Much e-, but conjugated π electrons
quite inert to use, not activated.

- *Scalable synthesis and more exposed carbon edge sites*

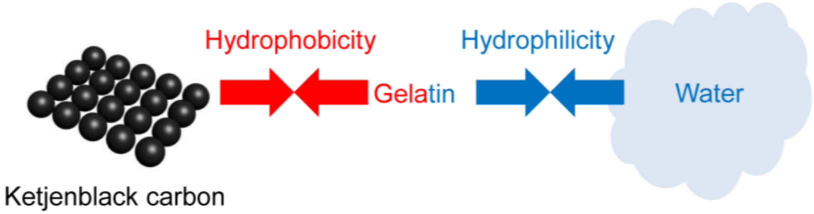


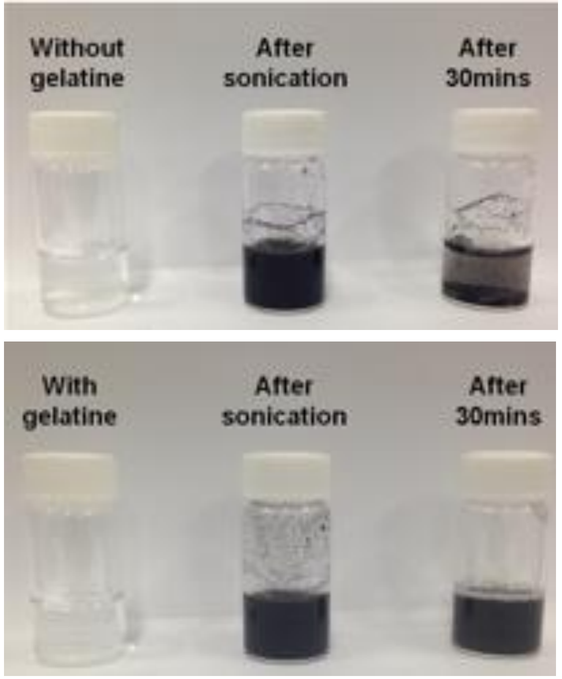
25g of Gelatine
in water

2g of Ketjenblack
in 25 of gelatine dissolved water

13.5g of GKs catalysts
after pyrolysis

- *Gelatin is hydrophobic& hydrophilic*





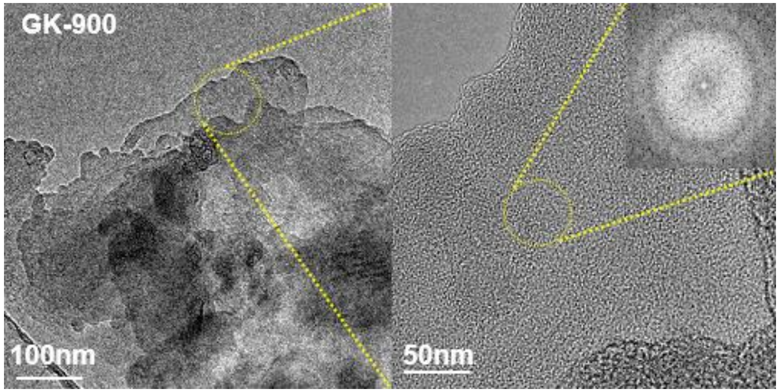
Stabilizer & 16% Nitrogen source

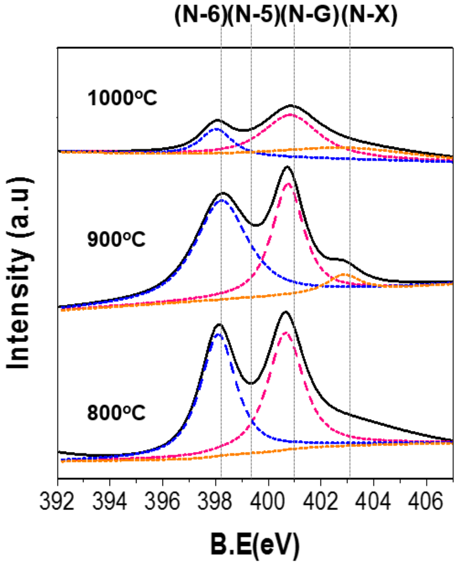
***Nano Letters*** 52, 1026 (2013)

# 1.1 Accomplishments 1) Scalable synthesis

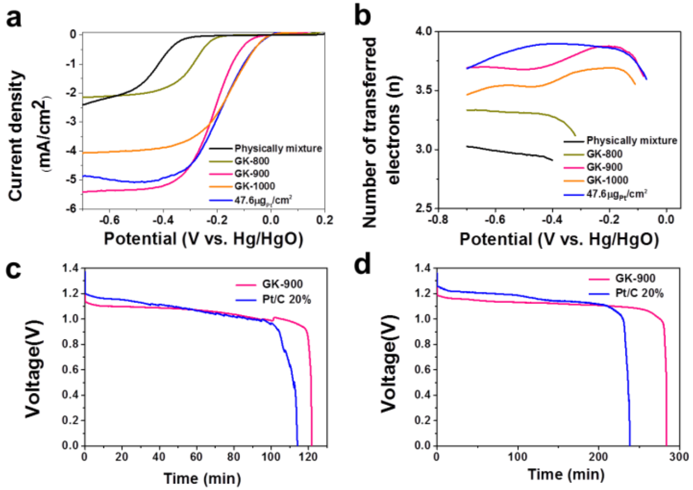
## Gelatin/KB derived N-doped carbon with Scalable synthesis

- ☐ Irregular stacked sheets with more edged sites and Pyridine or Graphitic-like N doping → efficient for ORR

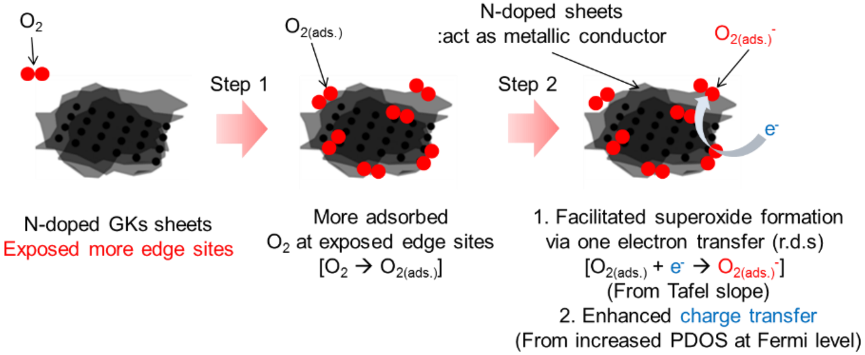




***Nano Letters*** 52, 1026 (2013)



Proper combination of graphitic and pyridinic N
→ the highest efficient ORR performance



N-doped GKs sheets
Exposed more edge sites

More adsorbed
$O_2$ at exposed edge sites
[$O_2 \rightarrow O_{2(ads.)}$]

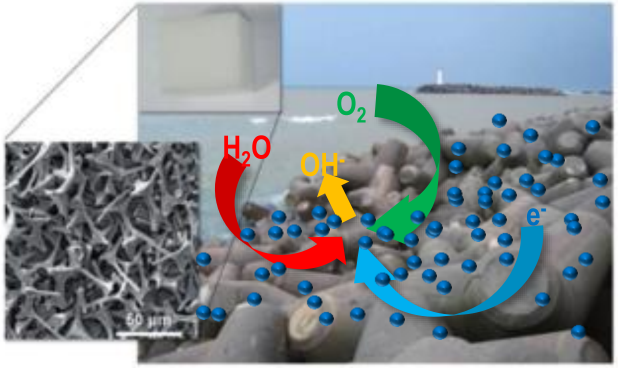
1. Facilitated superoxide formation via one electron transfer (r.d.s)
[$O_{2(ads.)} + e^- \rightarrow O_{2(ads.)}^-$]
(From Tafel slope)
2. Enhanced charge transfer
(From increased PDOS at Fermi level)

More adsorbed $O_2$ at exposed edge sites
[$O_2 \rightarrow O_{2(ads.)}$]

# 1.1 Accomplishments 2) Mass transfer

## Melamine foam supported Fe/$Fe_3C$ with improved power density

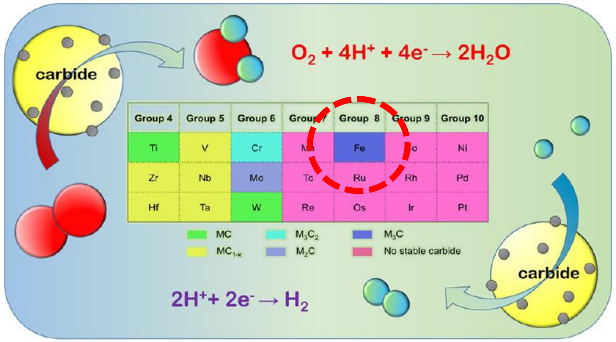
- ❑ *Material design:*
  *Inspiration from tetrapod structure of breakwater*



*Connecting pores where air and electrolyte can easily invade

+

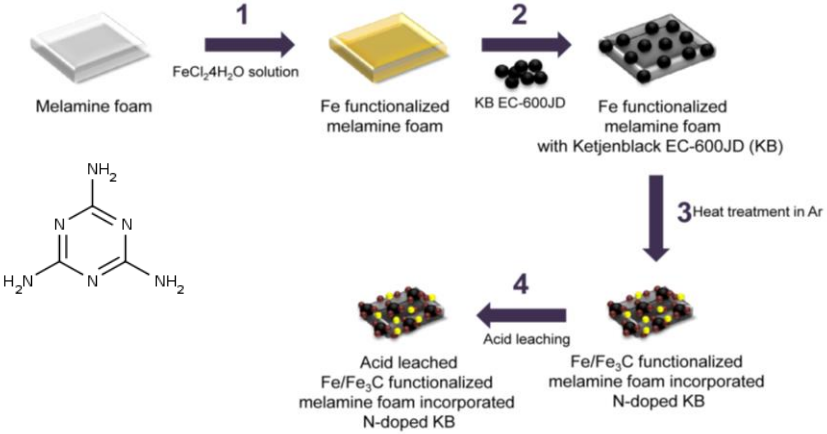
- ❑ *Further functionalization of melamine foam for better catalytic activity*



Mustain, W. E. et. al. , *ACS Catalysis* (2013)

*similar electronic structure of carbide to noble metals near the Fermi level

- ❑ *Synthesis of melamine foam and ketjenblack derived catalysts*



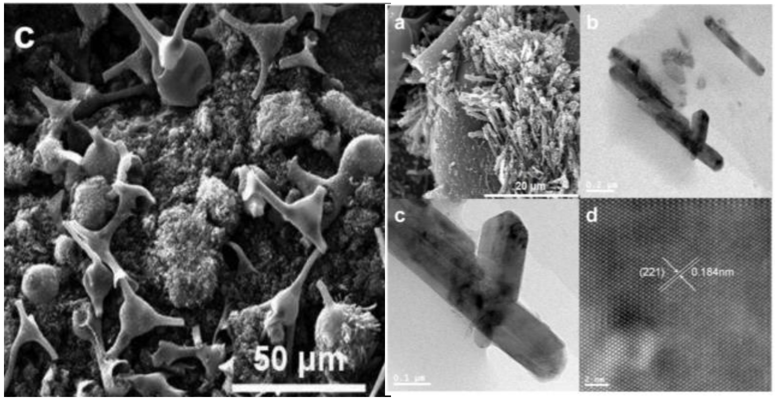
* Expected two types of active sites
1) Melamine foam derived N-doped carbon
2) $Fe_3C$ nanomaterials

***Angewandte Chemie International Editions*** 52, 1026 (2013)

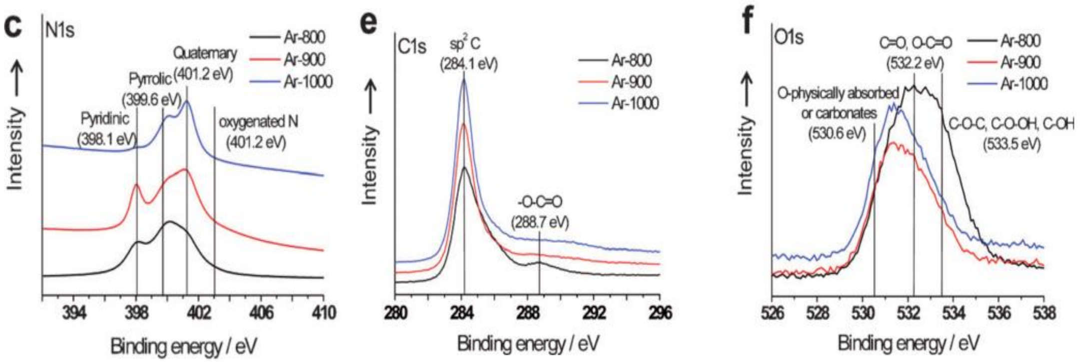
# 1.1 Accomplishments 2) Mass transfer

## Melamine foam supported Fe/$Fe_3C$ with improved power density

❑ *Physical and chemical characterization of as-prepared catalysts*

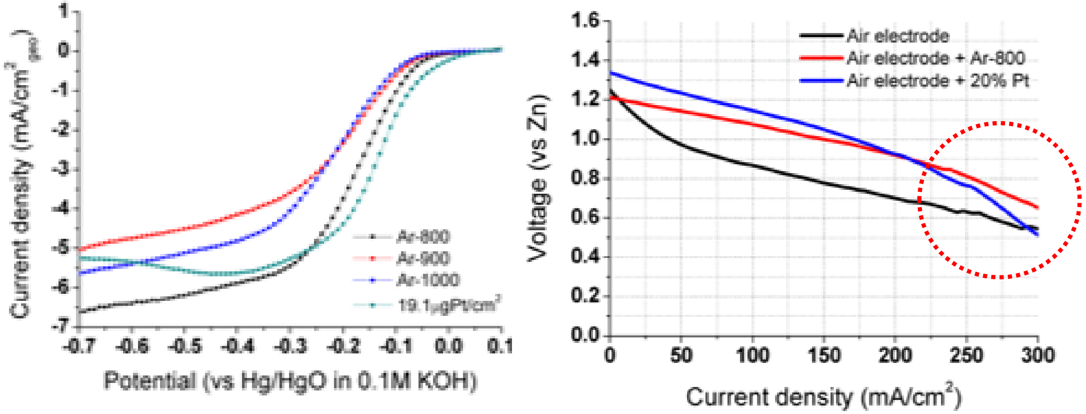


*Physical characterization of $Fe_3C$ nanorods



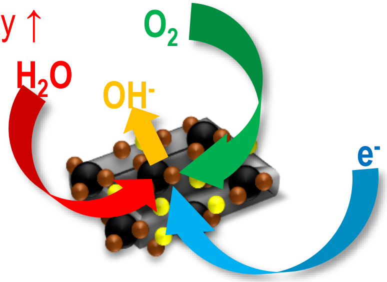
*Enhanced hydrophilicity for Ar-800 sample

❑ *Electrochemical characterization and discussion on enhanced mass transfer within catalysts*



*Better performance@ high current density than Pt/C catalysts

- Oxygen diffusion↑
- Hydrophilicity ↑



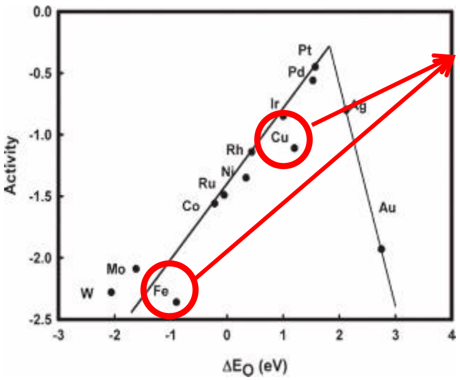
***Better mass transfer and increase in available active sites**

***Angewandte Chemie International Editions*** 52, 1026 (2013)

# 1.1 Accomplishments 3) binding energy

## Carbon coated Fe-Cu alloy with moderate binding energy

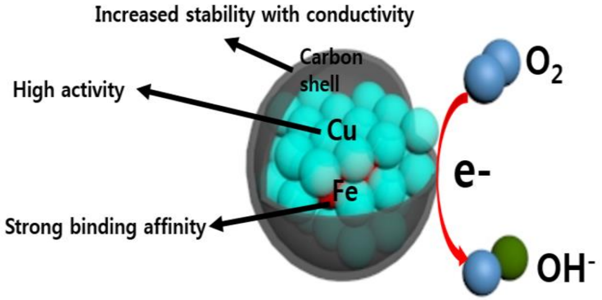
- ☐ *Material design: Trends in oxygen reduction activity vs. oxygen binding energy*



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

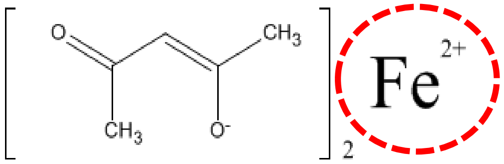
*With high activity of Cu and high absorptivity of Fe*
*→ Alloy could be solution!*

*But, Technical problems is possibility of metal oxides.*
*→ Carbon coating could be solution?*



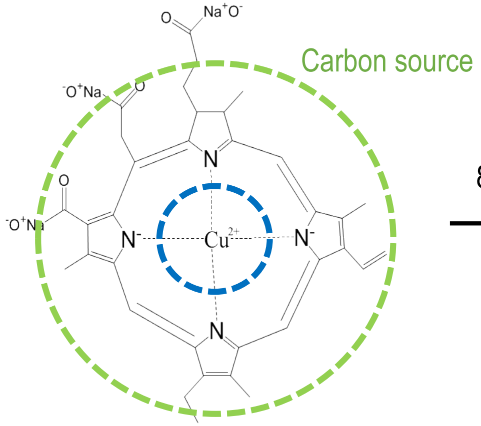
**Carbon coated Fe-Cu alloy**

- ☐ *Synthesis of carbon coated Cu-Fe alloy*



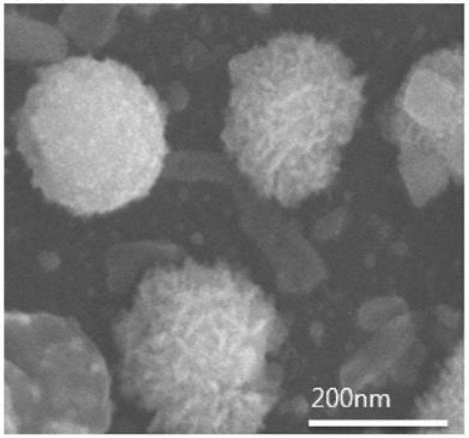
Iron(II) acetylacetonate

+



Chlorophyllin

800°C, Ar →

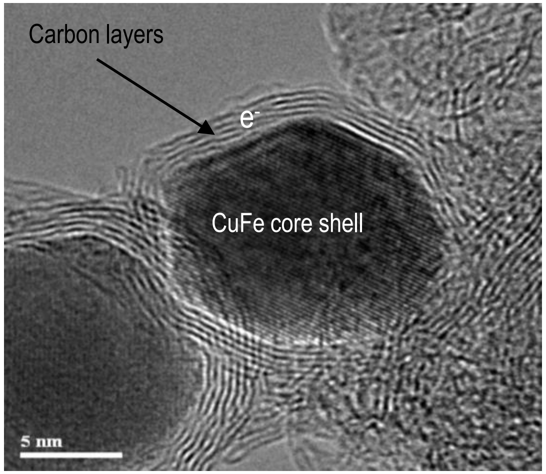


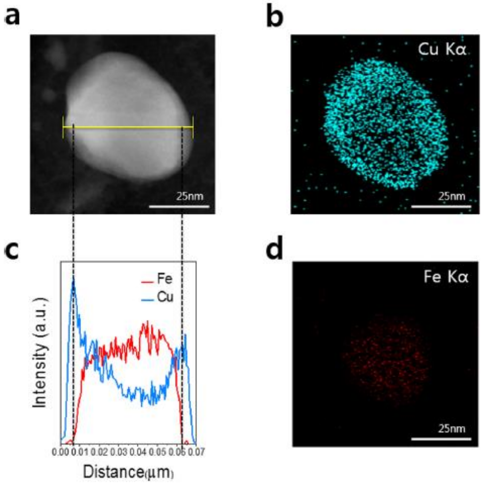
***ACS nano** 9, 6493 (2015)*

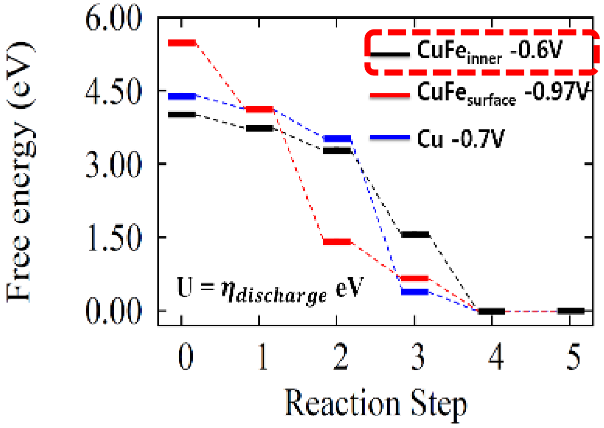
# 1.1 Accomplishments 3) binding energy

## Carbon coated Fe-Cu alloy with moderate binding energy

- ❑ *Physical and chemical characterization of bi-metallic CuFe core shell catalysts*



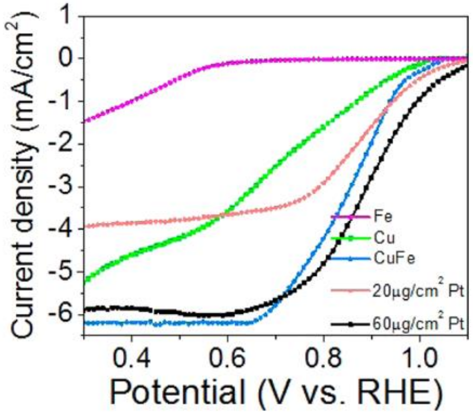


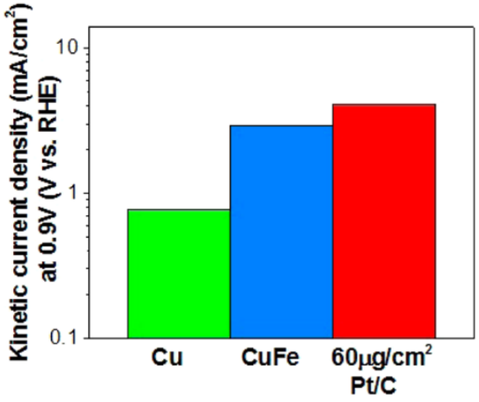


*Enhanced electrical conductivity

* DFT calculation on reaction pathway Cu-Fe$_{inner}$ model has the lowest overpotential

- ❑ *Bi-metallic outperformed catalytic activity compared to single*





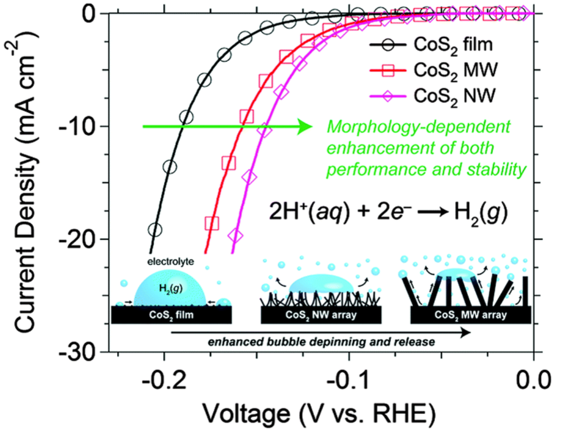
*Fe: Heat treated Iron(II) acetylacetonate at 800$^o$C under Ar
*Cu: Heat treated Chlorophyllin at 800$^o$C under Ar

***ACS nano*** *9, 6493 (2015)*

# 1.1 Accomplishments 4) Surface engineering

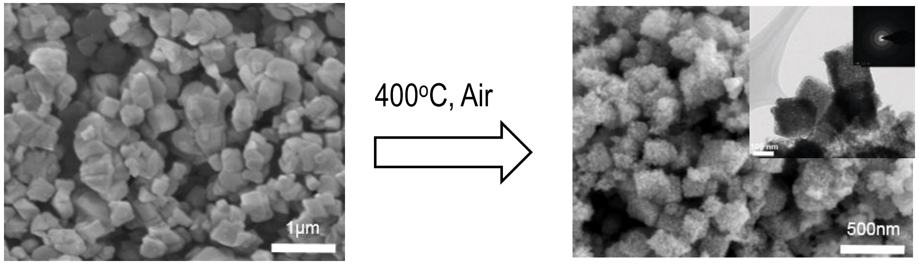
## Surface engineered Highly porous metal oxides

☐ *Surface modification for gas evolution electrode*



*Song Jin group, J. Am. Chem. Soc.(2014)*

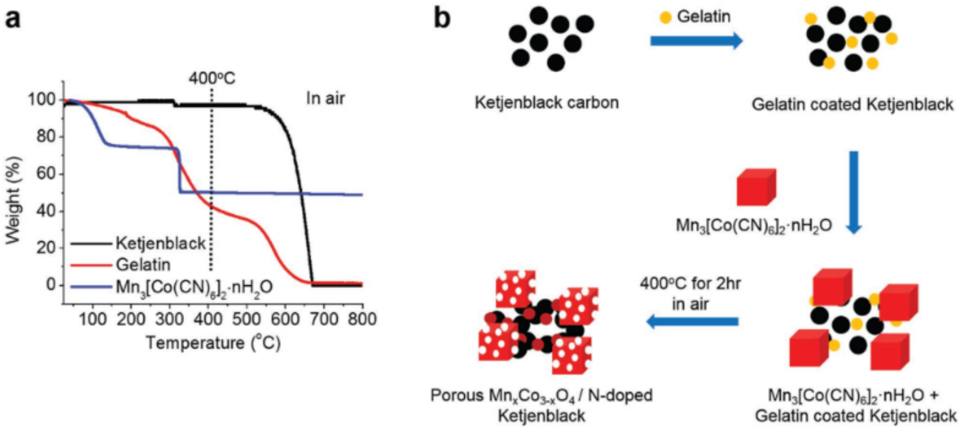
☐ Inter-connected hydrophobic pores and *rough surface for better oxygen diffusion*

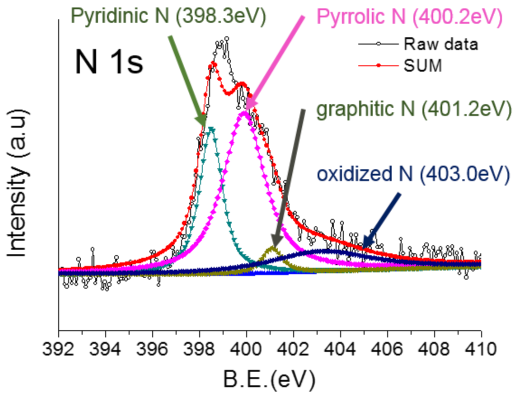


$Mn_3[Co(CN)_6]_2 \cdot nH_2O$

$Mn_{1.8}Co_{1.2}O_4$

☐ *Gelatin **also** thermally decomposed to pyrrolic N-rich carbon **at 400°C** and preparation of catalysts*



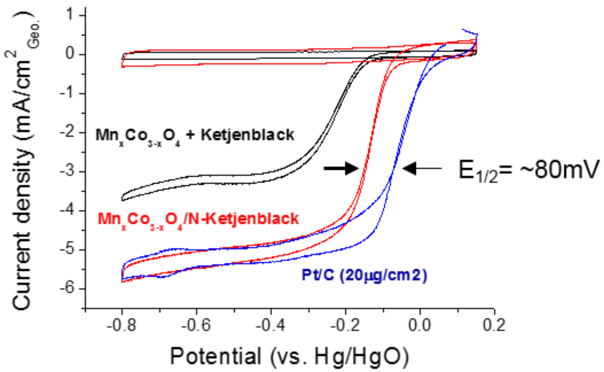


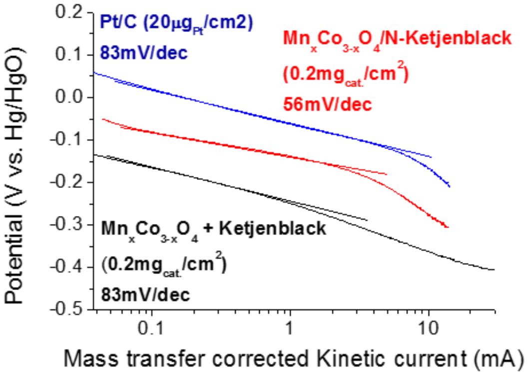
***Adv. Energy Mater.*** 6, 1601052 (2016)

# 1.1 Accomplishments 4) Surface engineering

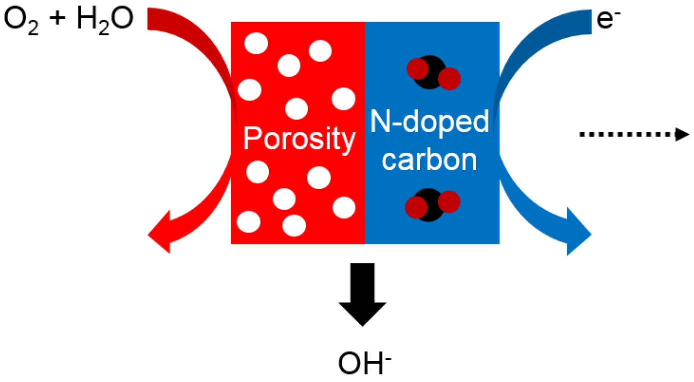
## Surface engineered Highly porous metal oxides

- *N-rich carbon affords another active sites for oxygen reduction*

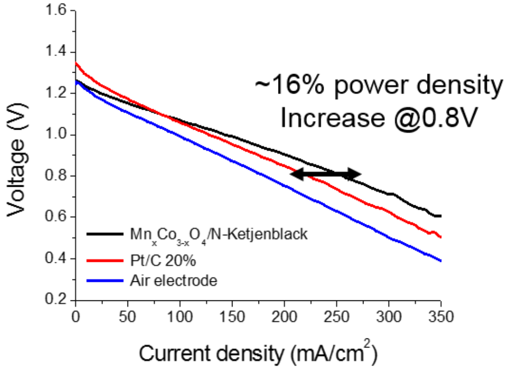


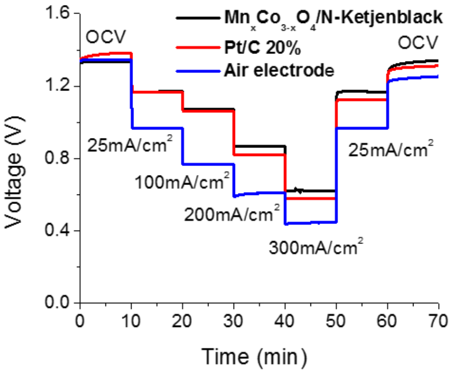


- *Combination of N-rich carbon and porous architectures give better performance at high current discharge*



Characteristics





Zn-air full cell performance

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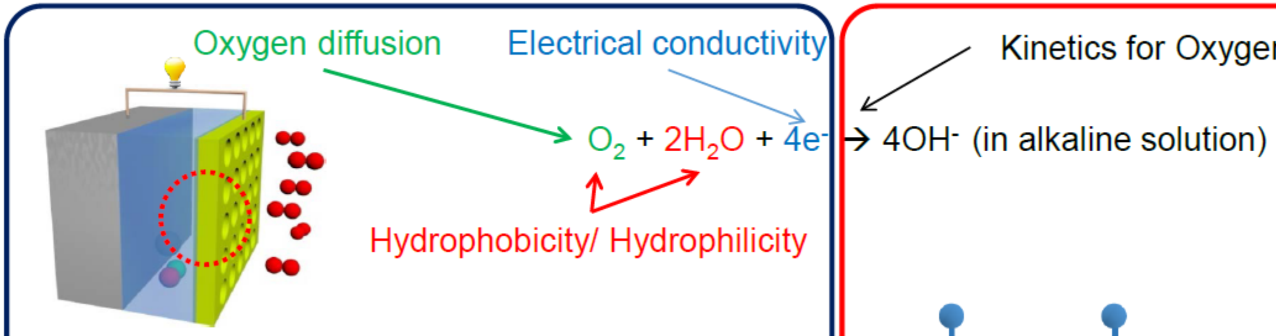
# 1.1 Summary: Electrocatalysts for ORR

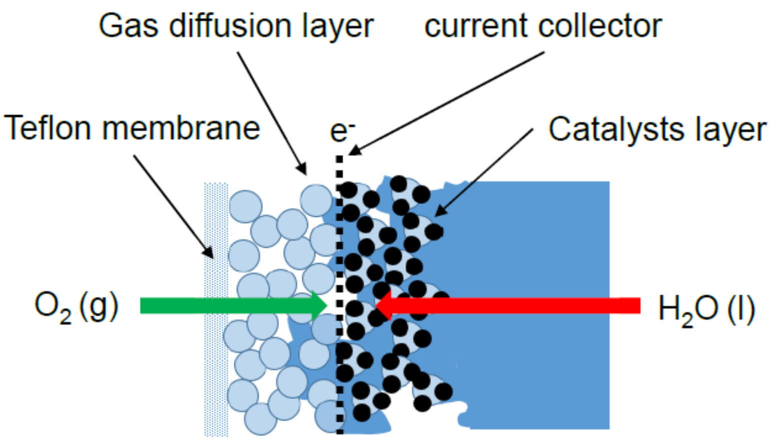
[Electrocatalysts]

*Reactants* → *Conversion* → *Products*

**Part I: Mass transfer (*at high j: single cell*)**

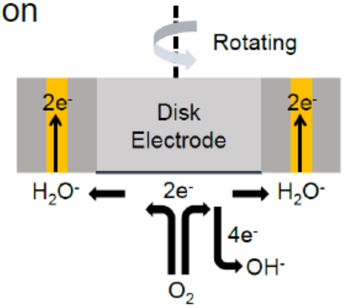


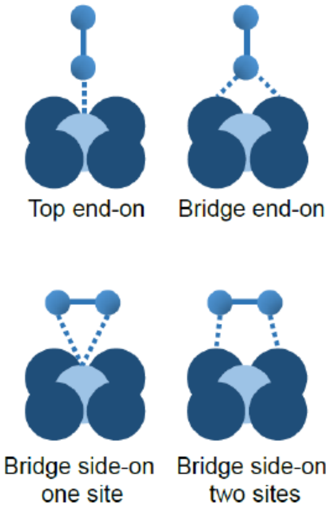
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (in alkaline solution)



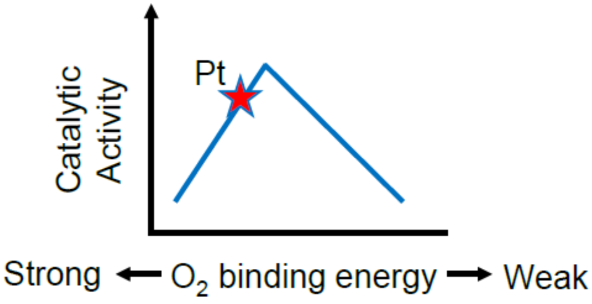
**Part II: Kinetics (*at low j: Half cell*)**

Kinetics for Oxygen Reduction





Ideal catalysts – Sabatier's Principle
- Not too strong & not too weak

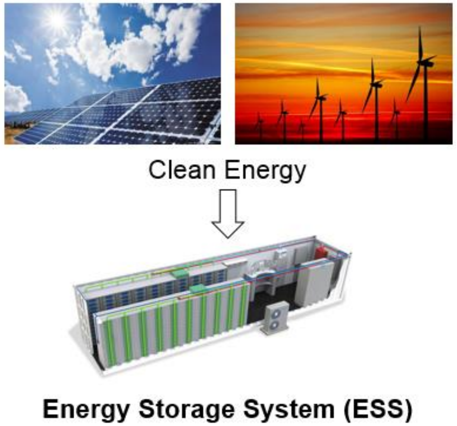


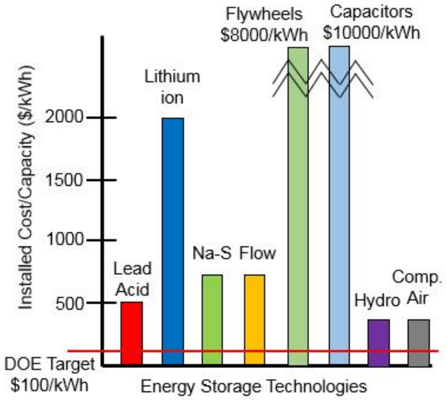
***Adv. Energy Mater.*** 6, 1601052 (2016)

# 2.1 Future Research plans: Post-Li ion battery project

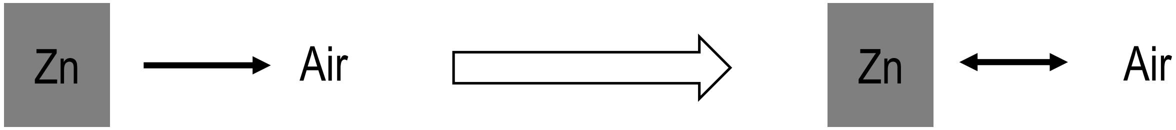
## Object 3: Rechargeable zinc-air battery

- ☐ Fluctuant & clean Energy source → cost-effective ESS NEEDS





Existing Electrochemical Energy Storage: Li-ion battery is too expensive!!



Make it Rechargeable with Tasks!!

**Project: Development of rechargeable zinc-air battery**

Task I: Reversible zinc electrode with proper aqueous electrolyte

Task II: Advanced bi-functional electrocatalysts for oxygen reduction and evolution reaction

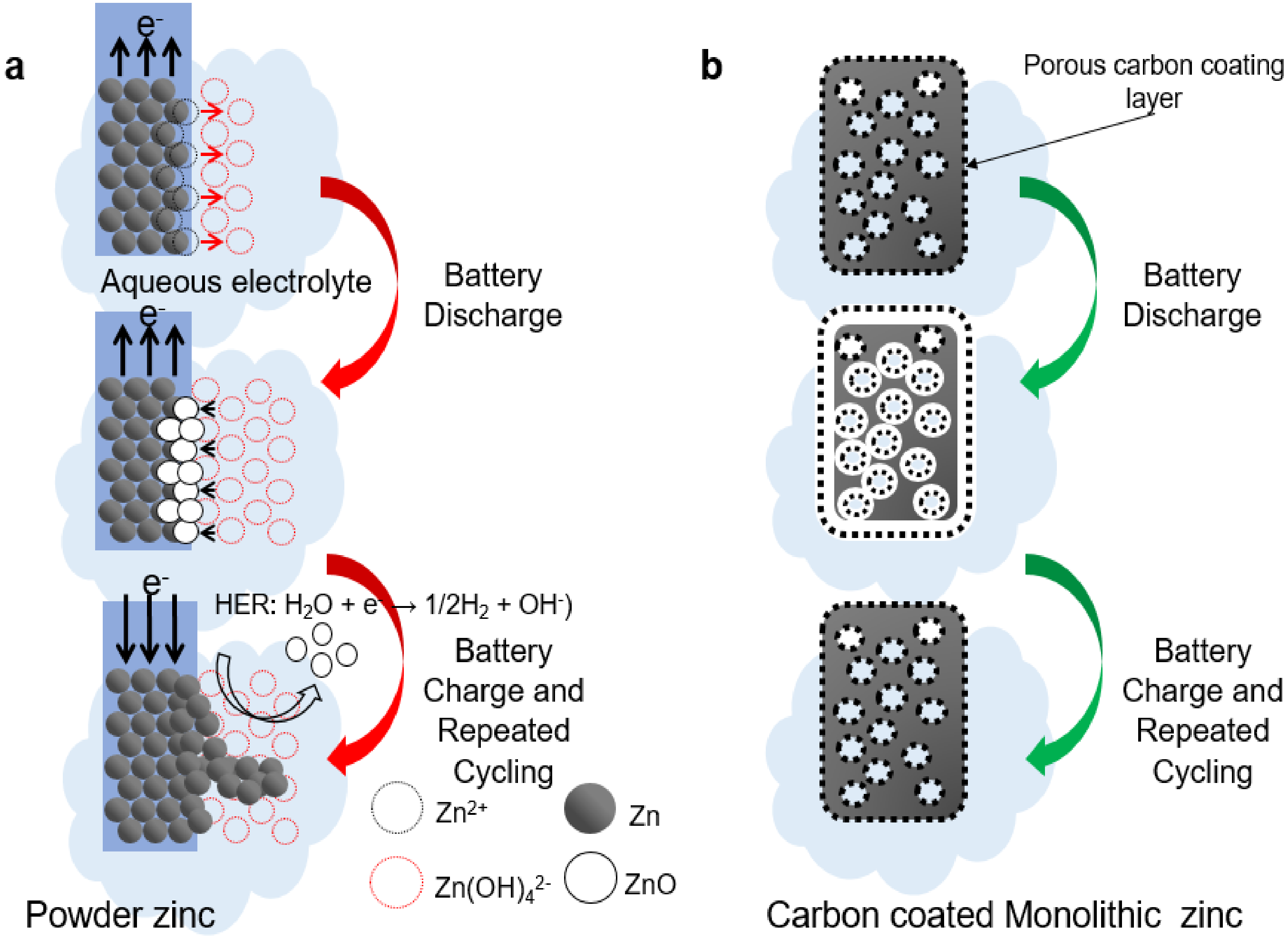
Task III: Development of hybrid cathodes functionalized with $MnO_2$, Sulfur, and air

Task IV: Study on reaction mechanism of zinc-sulfur battery

# 2.1 Future Research plans: Post-Li ion battery project

## Object 3: Rechargeable zinc-air battery

☐ Task I: Reversible zinc electrode for zinc metal based battery



Conventional powder based zinc electrode (a) carbon coated monolithic zinc electrode (b)

# 2.1 Future Research plans: Post-Li ion battery project

## Object 3: Rechargeable zinc-air battery

- ☐ Task I: Reversible zinc electrode for zinc metal based battery

Ni foam

Zinc It, 16 Oz, Net 13 oz
$7.54/EA

Zn spray coating

Zinc coated Ni foam

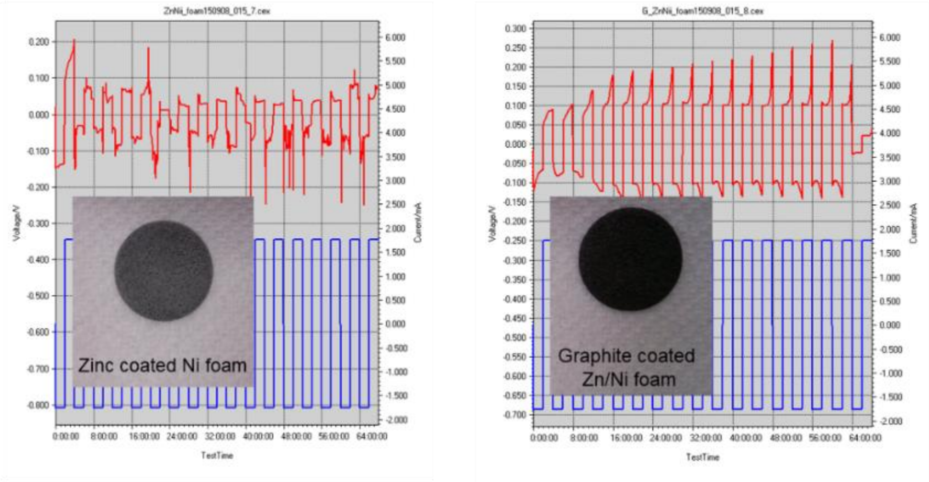
* Zn loading density:
~10mg/cm$^2$
→ 8.85mAh/cm$^2$

Graphite ink/
dip coating

PELCO® Conductive Graphite,
water base, 50g
$9.95/EA

Graphite coated
Zn/Ni foam

Heat
Treatment
at 200°C in air

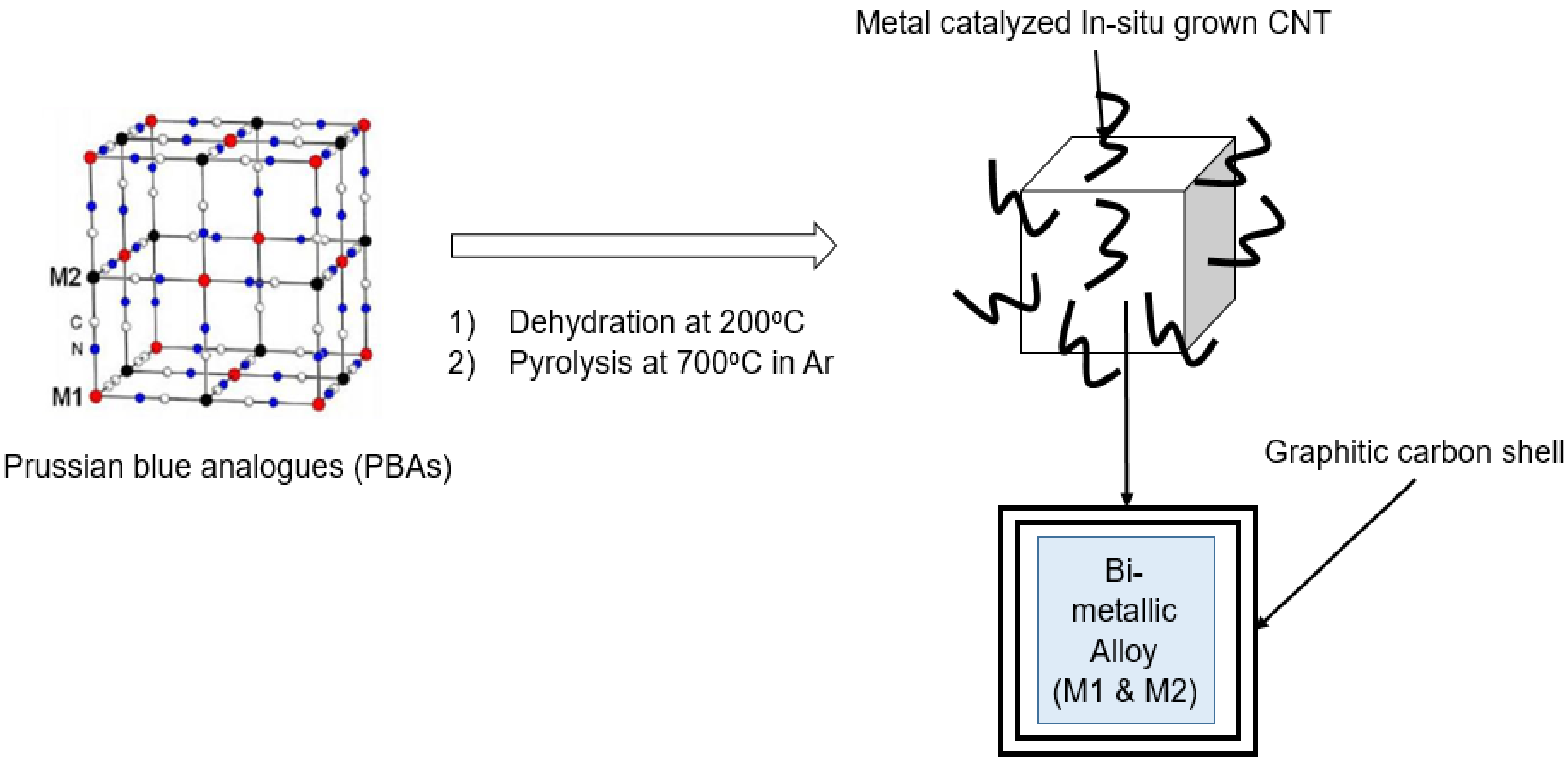


Possible preparation method for conducting carbon coated highly porous zinc electrode and corresponding Zn symmetric cell data. (Note that graphite coated Zn/Ni foam electrode has much more stable voltage profile than pristine zinc coated Ni foam electrode and heat treatment step at 200°C is required to remove organic additives without oxidation of zinc metal) (Unpublished data)

# 2.1 Future Research plans: Post-Li ion battery project

## Object 3: Rechargeable zinc-air battery

- Task II: Advanced bi-functional electrocatalysts for oxygen



Metal catalyzed In-situ grown CNT

Prussian blue analogues (PBAs)

1) Dehydration at 200ºC
2) Pyrolysis at 700ºC in Ar

Graphitic carbon shell

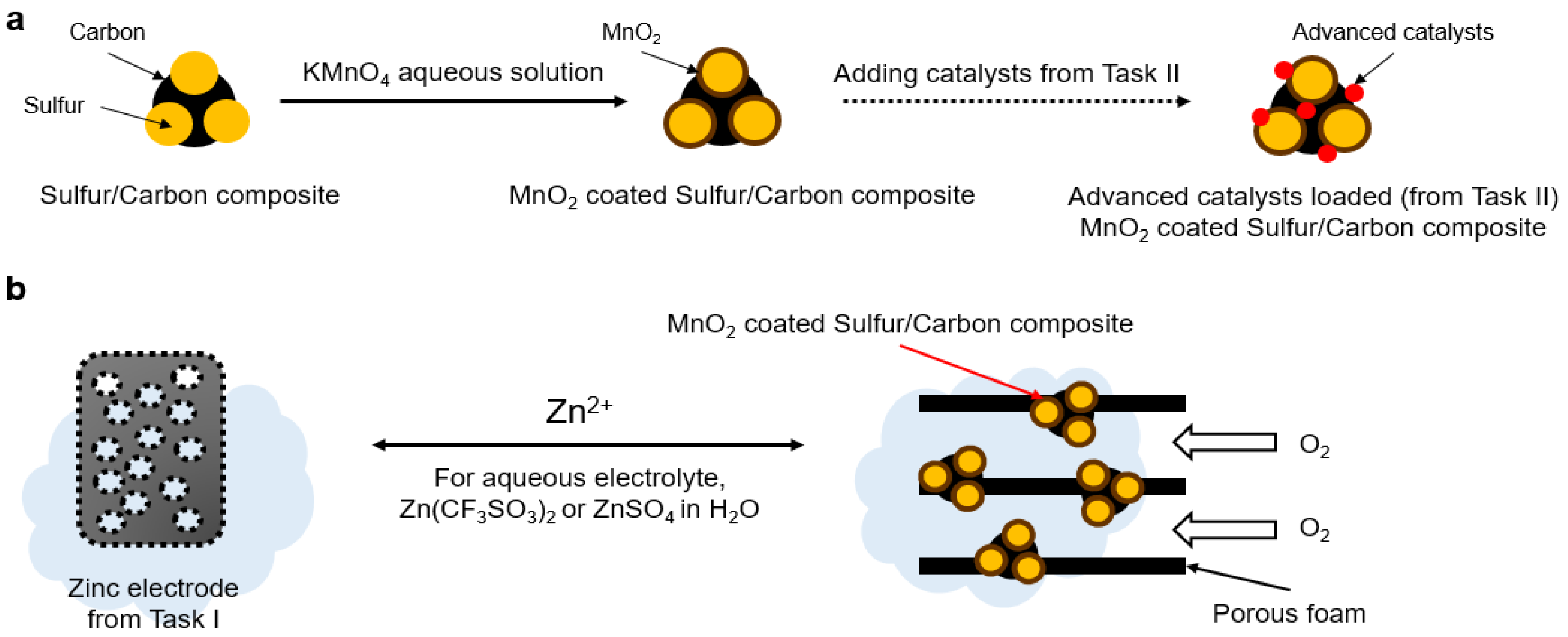
Bi-metallic Alloy (M1 & M2)

Schematic preparation of in-situ grown CNT/carbon coated bi-metallic bi-functional electrocatalysts for oxygen

# 2.1 Future Research plans: Post-Li ion battery project

## Object 3: Rechargeable zinc-air battery

### ❑ Task III: Development of multi functional hybrid cathodes



**Three key functions of $MnO_2$**
1) Active materials as itself
2) Bi-functional catalysts for ORR/OER
3) Catalysts/ adsorbent for polysulfide

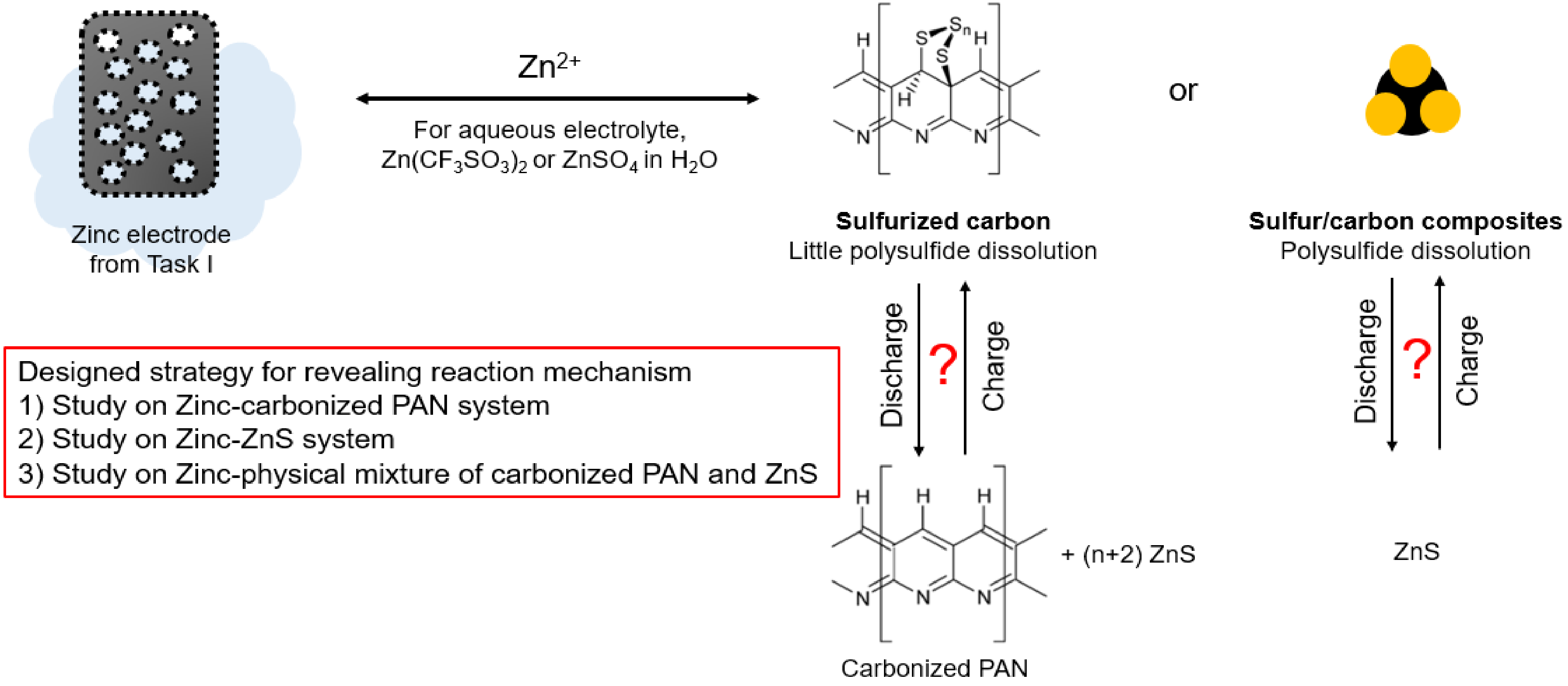
**During discharge at Noble hybrid cathode**
1) $MnO_2$ reduction with slope voltage profile (>1.5V vs. Zinc)
2) Oxygen reduction reaction with flat voltage (~1.1V vs. Zinc)
3) Sulfur reduction with slope voltage profile (<0.8V vs. Zinc)

Schematic preparation of $MnO_2$ coated Sulfur/Carbon composite (a) and configuration of advanced zinc-air battery with hybrid cathode for energy storage system

# 2.1 Future Research plans: Post-Li ion battery project

## Object 3: Rechargeable zinc-air battery

❑ Task IV: Study on reaction mechanism of zinc-sulfur battery



$Zn^{2+}$

For aqueous electrolyte,
$Zn(CF_3SO_3)_2$ or $ZnSO_4$ in $H_2O$

Zinc electrode
from Task I

or

**Sulfurized carbon**
Little polysulfide dissolution

**Sulfur/carbon composites**
Polysulfide dissolution

Discharge

Charge

+ (n+2) ZnS

ZnS

Carbonized PAN

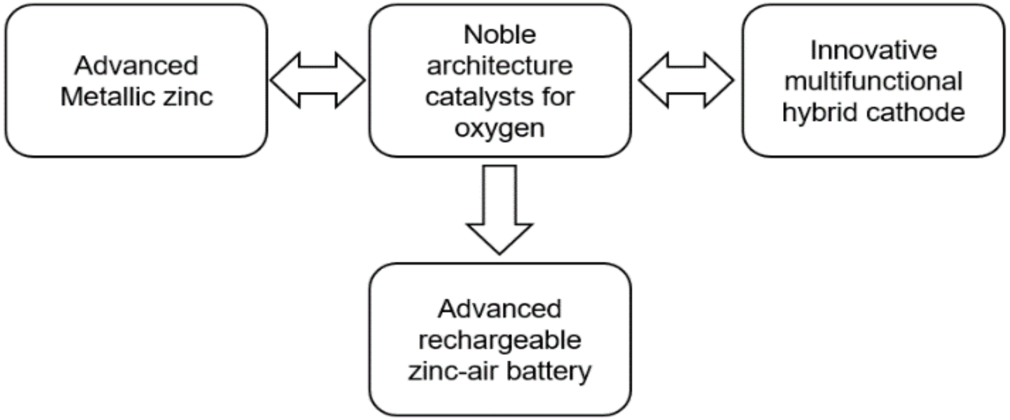
Designed strategy for revealing reaction mechanism
1) Study on Zinc-carbonized PAN system
2) Study on Zinc-ZnS system
3) Study on Zinc-physical mixture of carbonized PAN and ZnS

Schematic research plan for zinc-sulfur battery

# 2.1 Future Research plans: Post-Li ion battery project

## Object 3: Rechargeable zinc-air battery

- ❑ Conceptual framework, method and approaches & Timeline



Advanced Metallic zinc

Noble architecture catalysts for oxygen

Innovative multifunctional hybrid cathode

Advanced rechargeable zinc-air battery

| Tasks: Rechargeable zinc-air battery with hybrid cathode for a gird scale energy storage system | 1st year | | | | 2nd year | | | | 3rd year | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Development of highly stable and reversible zinc anode | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| 2. Study on rechargeable Zinc-Sulfur battery | ■ | ■ | | | | | | | | | | |
| 3. A noble Nano-structured electrocatalysts to promote a reduction or oxidation of oxygen | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| 4. Demonstration of advanced rechargeable zinc air battery with hybrid cathode technology | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| 5. Results report, publications and patent applications | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

# PJT.1: Development of advanced zinc-air battery with high energy density

- **Expected Results** (Ref. https://arpa-e.energy.gov/?q=slick-sheet-project/rechargeable-zinc-air-batteries)

If successful, zinc-air battery would provide 300-500% more power than a traditional EV battery at less than half the cost, facilitating the widespread adoption of EVs.

1) Actively solve to energy issue such as blackout by installing zinc based grid scale energy storage system (by cost down to <50$/KWh)
2) Active preparation for next-generation battery system and take the first-mover
3) Increased use of EVs would decrease U.S. dependence on foreign oil--the transportation sector is the dominant source of this dependence
4) Greater use of EVs would reduce greenhouse gas emissions, 28% of which come from the transportation sector.
5) This battery would enable an EV (300 miles) on a single charge, for less than $10 on average.

**Project Description**

**Principle Investigator: Jangsoo Lee Ph.D (linastar24@gmail.com)**

## 1. PROJECT TITLE

***Rechargeable zinc-air battery with hybrid cathode for energy storage system.***

Does riding electric vehicle powered by batteries really reduce carbon dioxide ($CO_2$) emission? How to produce electricity to charge overwhelming electric vehicles than ever before? Growing needs of electronic transportations will force us to use conventional power plant much more, naturally causing more $CO_2$ emission or some others means like more demands for common Lithium-ion batteries causes increasing in cost of rare metal based batteries. Therefore, to increase utilization of renewable and clean energy source such as solar, wind, and water is highly required and development of large scale energy storage system (ESS) is urgently needed. New nano-materials and battery chemistry beyond conventional Li-ion battery is required to meet customers' needs. Advanced rechargeable zinc-air battery with novel hybrid cathode developed from this project will be an ideal solution and this technology will be more feasible together with USA's abundant zinc mining and advanced solar cell technology. A successful outcome of this project will induce an interest within and beyond the academy and directly can be applied to ESS, thereby can be naturally employed in both households and industry, and strengthen the leading role in renewable energy research.

## 2. AIMS AND BACKGROUND

### 2.1 AIMS

Recently, the increasing demands for the deployment of renewable energy sources from the sun and wind has been an urgent need for energy storage system (ESS) which can store extra clean energy and supply it to home or industry immediately if needed in **Figure 1**. For an ideal large-scale ESS, long cycle life, safety, high energy and power densities, environmental benignity are necessary. Furthermore, achieving a cost of <\$100/kWh is so highly required for a successful commercialization of this system.[1] Rechargeable Lithium-ion batteries (LIBs) have been today's dominant energy-storage solution of choice for various applications such as transportation as well as even ESS. These Li based battery system, however, inevitably should use organic electrolytes, which is highly flammable, and thus having potential safety issues as well as low ionic conductivity. These safety risks cannot be clearly addressed yet even with advanced electrode materials and these risks can be amplified as loading more battery. Furthermore, a production cost of LiBs, however, depends on mainly rare metals such as Lithium, Cobalt, and Nickle and even a price of them is ever increasing as growing needs, and this situation can be accelerated if more and more people ride electric vehicles and it means that much more electricity to charge batteries will be need. It will force us to use conventional power plant much more, naturally causing more carbon dioxide ($CO_2$) emission. Obviously, it is not supposed to occur and this can be another aspect of growing needs for electric vehicles powered by the battery. Besides this environmental effect, its increasing cost is not appropriate for their application in especially large-scale energy storage and can be a critical challenge for targeting EES with <\$100/kWh. Therefore, new strategies and efforts are immediately required to address these problems such as cost and safety issues, thus, with advanced nanotechnology, advanced materials, and much more deep understanding, revisiting safer and cheaper zinc based battery chemistry is so worthwhile. ***The aim of this project is to develop a rechargeable zinc air battery with higher energy as well as high power density for a gird scale energy storage system.*** The key research objectives of this project will include:

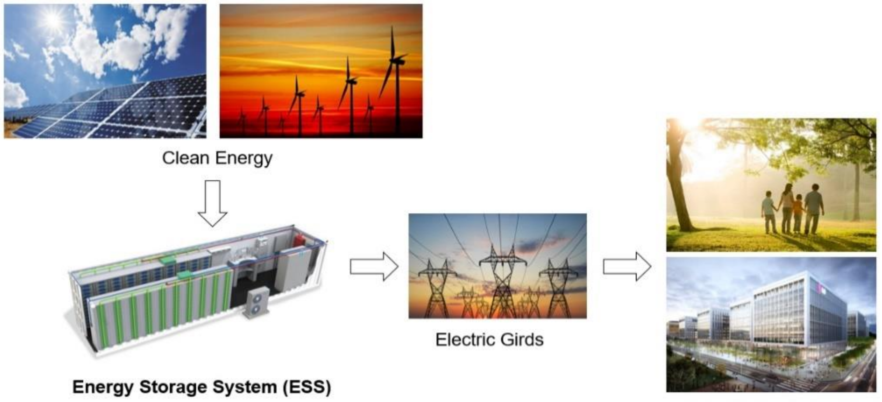


**Figure 1** A concept of Energy Storage System (ESS) to store extra clean energy and supply it to family or industry if needed**.**

- Development of highly stable and reversible zinc anode.
- A noble nano-structured electrocatalysts to promote a reduction or oxidation of oxygen.
- Demonstration of advanced rechargeable zinc air battery with hybrid cathode technology.

### 2.2 BACKGROUND

Needs for harvesting a clean and unlimited energy from nature efficiently are naturally increasing as needs to lower $CO_2$ emission, but its utilization has been significantly limited due to its challenging character, fluctuation. Therefore, it is urgently need to make a grid-scale energy storage system (ESS) commercialization. Up to now, ubiquitous Li ion battery (LIBs) has been a powerful and proper choice because it have already powered portable electronic devices as well as transportation. Its great success, however, has forced this battery to have higher energy density than ever before. This situation may be never imagined at that time that LiBs emerge into the market and it is so difficult to gain higher energy density within limited volume of batteries. This is why a working principle of LiBs is based on intercalation chemistry in which only limited Li ion can be inserted or extracted without collapsing host materials. The one way to gain a higher energy density with intercalating materials is to put more active materials in terms of minimizing non-electrochemically active materials. For example, using thinner separator or current collector can make more room to store active materials, but using thinner separator clearly causes more safety issues like an event of Samsung's battery recall. The second way is just to stack more batteries, but this approach increase a volume, weight, and, especially, cost of battery pack. For example, Tesla's Model S has ~500Km of driving range with 85KWh of battery pack, but it needs ~7000 cell of 18650 type cylindrical cell. Other approach is to increase Ni contents in NCM, which is a kinds of LiCoO cathode materials substituted some cobalt with Nickel and Manganese, to increase intrinsic specific capacity, but this material stability with high Ni contents is not sufficient for commercialization. Furthermore, most Li based battery use highly flammable organic electrolyte and a combination of $O_2$ generated from metal oxides cathode during over-charging can cause catastrophic failure via thermal runaway. In other words, Lithium based batteries still have sever concerns about safety, limited specific capacity, and cost although Lithium based batteries are ubiquitous up to now. Using chemical conversion chemistry renders a battery to have much higher energy density although severe volume expansion occurs during cycling compared to intercalating materials. For example, Li-$O_2$ or Li-Sulfur battery can afford much higher energy density and recently has been attracted as post Li-ion battery at academic as well as industry, but its battery chemistry is not well understood yet and there are several challenging issues for commercialization. Especially, these batteries use even metallic Lithium as anode so that it cannot be intrinsically free from safety issues and anode. Therefore, new strategies and efforts are immediately required to address aforementioned problems. To meet these requirements, a combination of chemical transformation chemistry and aqueous electrolyte enable us to revisit safer, yet performance-limited battery chemistry.

***Historically safer aqueous batteries*** have a great potential to meet the aforementioned requirements. Firstly, it is non-flammable and thus free from safety issues compared to flammable organic electrolyte. Secondly, a cost of electrolytes and assembly processes for aqueous battery are much cheaper than for LIBs. Furthermore, a battery with chemical transformation chemistry can significantly boost up its energy density compared to with intercalation chemistry although it has lower voltage window than organic electrolytes, thus its power density is lower than Li-based battery. Therefore, an aqueous battery with conversion chemistry can be so promising candidates due to its higher capacity, low cost, and much safer than current state of LiBs, and these outstanding advantages can enable aqueous batteries to fit a targeting large scale EES with <\$100/kWh. Several candidates including Lead acid, Na-S, and redox-flow battery have been extensively studied to date, but its battery technology does not corresponds to a grid scale energy storage. For example, recently developed Prussian blue analogue based battery has good cycle life as well as high rate capability, but its specific capacity is quite low, ~60mAh/g, which is not suitable for ESS.[2]

Zinc is one of the most plentiful and inexpensive metals and Metallic zinc have been used as anode materials for primary battery due to good compatibility to aqueous electrolyte, low cost, abundance, low equilibrium potential, environmental benignity and a long shelf-life. Furthermore, this battery has sufficient specific capacity to compensate its low voltage, thus can have higher energy density compared to conventional LiBs (<200Wh/Kg) including a zinc-sulfur (572Wh/Kg of theoretical specific energy density),[3] Zn-$MnO_2$ (336Wh/Kg), and Zn-air (1084 Wh/kg).[4] Among them, zinc air battery can deliver the highest energy density immediately if needs because there is no need to integrate a cathode reactant, but this system breath oxygen as active materials. Therefore, this system can save a space as well as cost and the only consumed materials is abundant metallic zinc, which render zinc-air battery to meet requirements for ESS. For example, EOS's aurora, commercial zinc-air battery technology, needs \$1000/kW as an initial price, but can have \$160/kWh, which is very close to target cost, <\$100/kWh. Besides, it has 30 calendar years of operation with No periodic replacement of components (e.g., membranes, cells, battery packs) required and, first of all, this system is totally environmentally benign and stable. This commercialization of zinc-air cell can be catalyzed in terms of using already proven technology of primary alkaline zinc-$MnO_2$ battery. For example, to produce zinc-air battery, the manganese dioxide ($MnO_2$) cathode is just replaced with a thin air electrode with as-prepared manufacturing facility. Zinc-air battery, however, has not yet applied fully to advanced technologies demanding extended cycling due to historically difficulty to make rechargeable. Several distinguishable approaches have been suggested and developed, but there is still much room to be further developed for advancing zinc-air battery technology.

## Metallic zinc as anode for battery

Recently, metallic lithium with 3860mAh/g of theoretical specific capacity has been extensively studied to increase energy density.[5] Compact lithium metal, however, becomes more porous as cycling, thus causing dendrite problems and dead lithium. Enhanced porosity with increasing surface area can react with more electrolyte and continuously consume Li metal as well as electrolyte, thus resulting in severe capacity fading for Li metal anode based battery. For example, this degradation mechanism is augmented in a Li-sulfur battery with low ratio of electrolyte to sulfur (E/S ratio).[6] Besides this fading problem, the most important thing is that using metallic lithium has always high potential risks. For example, Moly's, Canada's battery company, attempts using Li metal were absolutely failed and then industries are reluctant to introduce metallic lithium and produce Li metal-based battery to date. Therefore, the next generation of high-performance batteries should include alternative chemistries that are inherently safer to operate than non-aqueous lithium-based batteries.

Metallic zinc has been regarded as an ideal anode material for the aqueous batteries for its high theoretical capacity (820 mAh/g), low negative potential (-0.762 V vs. SHE), abundance, far less expensive than lithium, low toxicity, environmental benignity and a long shelf-life, but the most significant advantage is that zinc is highly compatible with non-flammable aqueous electrolyte. Recently, rechargeable batteries using zinc metal anode have been extensively exploited to maximize its potential application including energy storage system (ESS). Despite these important advantages, discharged product, ionically insulating ZnO is fully covered onto zinc metal[7] and thus core zinc metal cannot participate anymore and formed dendrites during charging results in increasing in its surface area, which can accelerate a corrosion of zinc metal via hydrogen evolution.[8] These processes it is not supposed to occur severely lower a utilization of metallic zinc as anode and columbic efficiency. Especially, the dendrite formation is a highly challenging and troublesome issue when studying zinc anode. For example, dissolved zinc ion is usually deposited on dislocated places during charging, facilitating to grow needle-shape dendrite. Eventually, continuously grown dendrite can reach the cathode, resulting in short circuit and a sudden drop in capacity although explosion is not occur unlike metallic lithium. Metallic zinc becomes porous structures and then increase in a surface area, which process is quite similar to metallic lithium. In this environment, a corrosion and other side reaction can be augmented, leading to a faster capacity fading of battery performance. Therefore, It has been a central issue that how to strip or plate zinc uniformly and how to suppress dendrite growth of zinc metal. This crucial task is closely related with a structure of zinc anode and this shape of zinc can significantly affect the performance of zinc-based batteries. For example, typical zinc anode is comprised of zinc powder held together with polymeric binder and gel type aqueous electrolyte so that electric field could localize on hot spot due to lack of long range electrical connection, which cause dendrite problems as well as low utilization of metallic zinc, typically <60% of theoretical capacity. Recently, interconnected metallic zinc architecture is developed to address aforementioned problems.[9] These three-dimensional (3D)-sponge typed electrode allows to discharge deeper with minimizing its original shape. For example, this porous, well-wired zinc electrode can increase overall electrified active area and decrease local current density, thus minimizing forming zinc dendrite. This monolithic zinc sponge can significantly enhance a reversibility of metallic zinc, but a newly deposited zinc is still exposed to aqueous electrolyte, causing a corrosion issues, thus these low columbic efficiency can hamper its application on targeting EES with long cycle-life.

## Electrocatalysts for oxygen reduction and evolution for metal air battery

Conventional rechargeable batteries such as Li-ion batteries are closed systems in which energy storage and conversion occur in the same compartment. As a result, they are not suitable for meeting the ever-increasing demands for higher energy densities. On the other hand, a notable characteristic of metal-air batteries is their open-cell structure, which allows oxygen to diffuse through the porous electrode and then diffused oxygen is reduced at cathode during discharge, oxygen reduction reaction (ORR). During charging, on the other hand, oxygen is generated from a porous air electrode, oxygen evolution reaction (OER). Therefore, energy storage, oxygen fuel, and energy conversion, at air breathing electrode, occur at different compartments in a metal-air battery, thus theoretically, it is possible to increase energy density much more. However, this oxygen gas related reaction, ORR and OER, is very sluggish reaction and it need more potential to occur, resulting in potential loss. Moreover, its voltage drop is much more severe when discharging or charging with high current. Therefore, the way to promote ORR/OER with catalysts including Pt-based,[10] non-precious,[11] and metal-free catalysts,[12] has been a key research topic to date, but most studies have focused on just kinetics, an interaction between oxygen and electrocatalysts (**kinetic part in Figure 2**).[13] These limited studies have produced a number of research papers in academic fields, but clearly, a metal-air battery is not yet commercialized. This means that much more efforts on how to enhance mass transfer of oxygen as well as electrolyte should be required for a success of metal-air battery. For example, the oxygen molecules must reach the surface of the catalyst through a porous electrode for

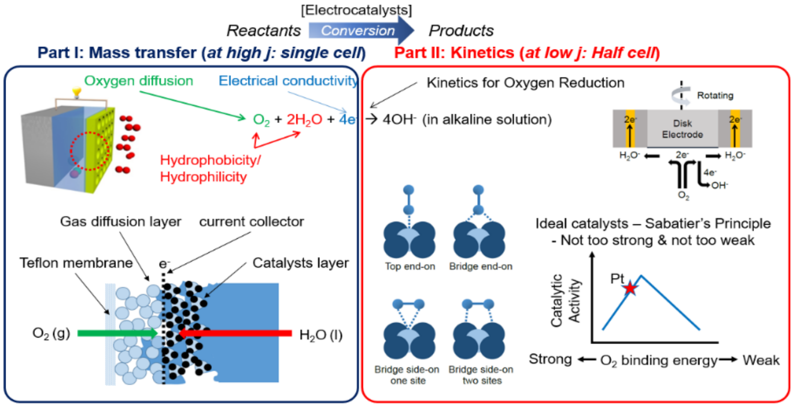


**Figure 2** Strategy summery for better non-precious metal electrocatalysts for oxygen reduction. It is noted that ORR equation can be divided into two parts: mass transfer and kinetics.[13]

discharge. If catalysts have too much hydrophobicity, aqueous electrolyte cannot access to active sites. On the other hand, if catalysts is totally surrounded by aqueous electrolyte due to too much hydrophilicity, gas phase oxygen molecules cannot reach the reaction sites. Therefore, proper combination of hydrophobicity and hydrophilicity should be maintained within desired catalysts. Diffused oxygen then have to form chemical bonds with the catalyst surface, resulting in their activation, O–O bond activation/cleavage with electron. This means that catalysts should have sufficient electrical conductivity and this process is very sluggish and high loading of precious metal catalysts (e.g., Pt-based catalysts) demands, which unfavorably increases the cost of these electrochemical energy conversion devices. During charging, generated oxygen molecules should be removed as fast as possible to expose fresh catalysts. Adsorbed oxygen onto catalysts, however, increase in additional polarization. Moreover, generated oxygen can collapse a porous architecture of air electrode. Therefore, when designing electrocatalysts for such batteries, the following two aspects should be taken into consideration: how to transfer oxygen to the active sites effectively (mass transfer)[14] and how to ensure that the binding energy is moderate (kinetics) (**Figure 2**).[15] In addition of reaction occurring at catalysts, generated oxygen gas bubble should be removed quickly, which means that proper surface engineering is need by maximizing three phase reaction sites.

### Rechargeable zinc-air battery

Recharging of zinc-air battery means regeneration of metallic zinc. Therefore, just refueling zinc metal can produce electricity until air electrode is degraded. Thus, it function as a power generator fueled by zinc and oxygen. This mechanical rechargeable battery, however, cannot store an energy from a nature such as sun or wind, thus it is not appropriate to our targeting ESS. Therefore, it is urgently need to make this primary battery electrically rechargeable. Many problems have hampered this goal. For example, severe dendrite and low columbic efficiency of zinc metal is not yet addressed. For breathing electrode, this air electrode is mainly composed of porous carbon materials for oxygen to diffuse, but these carbon materials can be corroded under high charging potential,[16] lowering its hydrophobicity. This lowered hydrophobicity increase polarization and then eventually degrade air electrode. To address these carbon corrosion, in-situ grown metal oxide onto metal foam was proposed as a carbon and binder free air electrode and render this zinc-air battery to have longer cycle life compared to a battery coupled with carbon based air electrode.[17] Severely lowered surface area, however, do not afford sufficient active sites for oxygen and cannot meet high drain current discharge. Based on aforementioned discussion, advanced zinc electrode and noble air electrode architecture with proper electrocatalysts have partially addressed these issues, but intrinsically it is extremely difficult to increase working voltage for high power cell without significant change in battery chemistry. Recently, chen group designed Ni based cathode decorated highly porous air electrode for high power density. In this system, under high drain current, Ni-based electrode can deliver higher voltage than ORR catalyzed carbon electrode, making high power possible.[18] On the other hand, ORR participates in mid or low current discharge with lower voltage compared to Ni based cathode. Intrinsic flat discharge voltage from zinc-air battery, however, makes estimating remaining capacity so difficult and this problem is still not addressed even with these kinds of hybridization. It means that there is still a room to upgrade this system in terms of applying other noble battery chemistry.

## 3. Proposed project quality and innovation

### 3.1 Significance

Riding electric vehicles powered by Lithium-ion batteries significantly reduce or eliminate $CO_2$, but charging a battery needs much more electricity as electric vehicles becomes popular. It means that more power plant should work and then produce more $CO_2$ than ever before. Therefore, storing a fluctuation energy coming from renewable and clean energy such as wind and solar is highly required and development of large scale energy storage system is urgently needs. For ideal grid scale energy storage, it should be low-cost (initial cost <\$100/kWh and life time cost < \$ 0.025/kWh cycle), scalable (~MW-GW/plant to TW), >5000 cycles life and 90%> round trip energy efficiency. Li ion battery, however, is too expensive and does not have enough cycle in **Figure 3**.[19] For example, Li-ion battery is not yet scalable because it needs around 30 years to get 1TW scale when considering world annual Li-battery production is around 40GW for 1hr. Furthermore, much more expensive cathode materials based on Cobalt and Nickel should be required to increase its energy density, causing high initial cost. This shortcoming will be augmented as demands for Li-ion batteries increases. It follows that new materials and

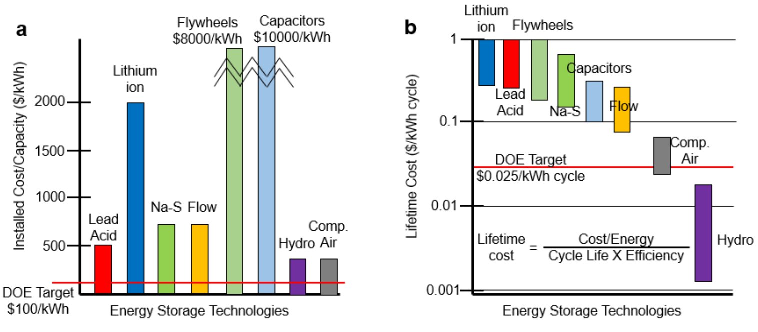


**Figure 3** Existing Electrochemical Energy Storage: Li-ion battery is too expensive (a) as well as Not Enough Cycle (b)[19]

battery chemistry for a desired energy storage system (ESS) should be required to meet ever-increasing customers' needs and to store clean energy effectively. ***In this regard, abundant zinc based aqueous battery, especially rechargeable zinc-air battery, can be efficient, cost-effective and reliable new clean energy sources and storage technologies and a goal of this project is to develop a highly rechargeable zinc-air battery technology with reversible zinc electrode, advanced catalysts, and hybrid and multifunctional cathode materials and is to increase in utilization of clean energy in terms of charging this battery with solar or wind energy, and thus is to reduce $CO_2$ emission.*** A successful implementation will induce an interest from industry as well as academic research area and then make these aqueous zinc metal based battery commercialization and finally, a developed technology directly can be applied to practical ESS in terms of coupling with solar cell. This can be naturally employed in both households and industry, and strengthen the leading role in renewable energy research.

## 3.2 Innovation

### Reversible and durable zinc electrode operated in aqueous electrolyte

During discharge, conventional power based zinc electrode generates zincate ion in alkaline electrolyte and these dissolved discharging produce is precipitated as ZnO onto a surface of metallic zinc. In this condition, inner zinc power cannot be further discharged so that a utilization of zinc anode becomes lower than what we expect based on its theoretical specific capacity. During charge, metallic zinc dendrite is formed and then being porous structure increase its surface area and then hydrogen evolution reaction can lower columbic efficiency (**Figure 4a**). ***In this project, a facile method of preparing porous carbon coated interconnected porous metallic zinc electrode will be developed to increase columbic efficiency as well as reversibility of metallic zinc.*** Firstly, highly porous zinc foam will be prepared via zinc spray coating onto 3D metallic current collector such as metal foam and then as-prepared zinc foam is coated with porous carbon in terms of using conventional carbon pastes. It is possible to achieve more uniform current distribution via long-range electronic conductivity and restrain shape change within pore volume within as-prepared metallic zinc foam, which can avoid dendrite formation effectively. Additionally, carbon coating can avoid direct contact between electrolyte and zinc metal, thus can minimize corrosion issues related with hydrogen gas evolution in aqueous electrolyte (**Figure 4b**). Especially, this coating layer can be further modified by introducing functional materials such as a stabilizer for zinc ion. Aforementioned approach is easily scalable and directly applied to all zinc metal based batteries.

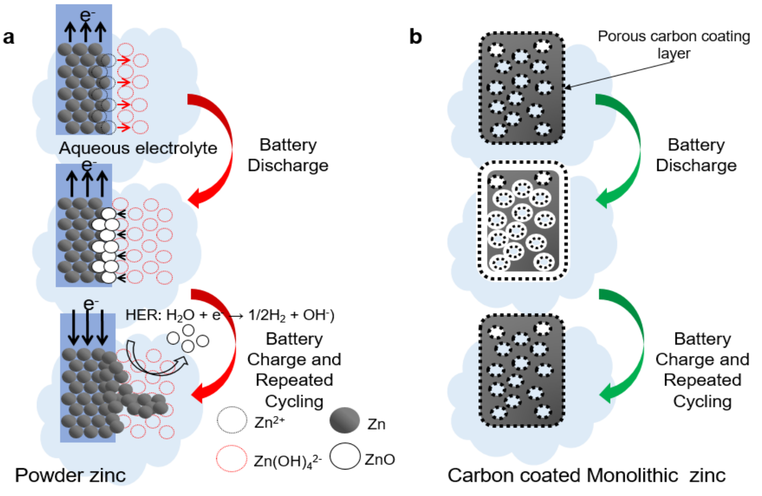


**Figure 4** Conventional powder based zinc electrode (a) carbon coated monolithic zinc electrode (b)

### Advanced electrocatalysts for oxygen reduction/evolution

To increase energy efficiency of rechargeable zinc-air battery, polarization gap between discharging, oxygen reduction, and charging, oxygen evolution, voltage should be minimized by using proper electrocatalysts. Moreover, this improvement should last longer. Therefore, an effort to develop advanced catalysts for oxygen reduction and evolution reaction has been a significant issue, but most studies at academic fields have focused on the way to increase a kinetic of oxygen related reaction, thus this approach cannot meet a needs for practical applications. In this project, highly efficient as well as durable electrocatalysts are prepared according to a design role suggested by the author, Dr. Lee. ***A key idea of this role is to combine proper binding energy and enhanced mass transfer. Moreover, a desired catalysts should be realized with innovate and scalable synthetic procedures for direct application on a grid-scale energy storage system.*** In this proposed catalysts, bi-metallic alloy can finely tune its electronic structure and then control a binding energy for oxygen. This moderate binding energy, not too strong and not too weak, will be beneficial to ORR as well as OER. In addition, this introduced transition metal can catalyze one-dimensional carbon nanotube (CNT) covered with defect less graphitic carbon layer, thus as-grown bundle type CNT can enhance oxygen diffusion with partially blocking access of aqueous electrolyte. In addition this 1-D shape, these defect-less carbon structure can act a shield layer and endure a strong oxidation environment during charging, thus enhancing durability. The most interesting thing is that aforementioned advantages can be realized by just one-pot high temperature pyrolysis of easily available Prussian blue analogues. Obviously, these scalable synthetic way is desired requirement.

### Advanced rechargeable zinc air battery with hybrid cathode chemistry

Homemade rechargeable zinc-air battery fabricated at academic fields usually has large electrolyte chamber and use excess electrolyte. In this structure, sufficient physical gap between zinc anode and air electrode enable metallic zinc electrode to be recharged without severe short circuit issues, but its volumetric energy density has overlooked to date and this is a reason why industry has a little interest in aqueous metal-air battery. Furthermore, ongoing research for zinc-air battery at academic field have mainly focused on development of bi-functional catalysts, not whole air electrode architecture, but its discharge voltage is slightly improved with even using a state of art electrocatalysts. Therefore, zinc-air battery technology intrinsically is not appropriate to high power application and needs. Furthermore, its flat discharge prevent us from estimating remaining capacity and this point makes battery management for ESS much more difficult. In this project, conventional zinc air battery will be advanced with hybridization of cathode chemistries to meet aforementioned requirements. For example, ***innovative metal oxide coated sulfur/carbon composites will be prepared and applied to this new system.*** Newly introduced metal oxides will function as other active materials as well as catalysts for oxygen reduction and evolution reaction and thus not only increase working potential for power capability, but also improve a performance of air electrode. In addition, this metal oxide will also catalyze polysulfide conversion while sulfur/carbon composites discharge. In other words, introduced metal oxides will be a key material affecting a performance of overall hybrid zinc-air battery. Moreover, sulfur/carbon composites will act as the other active materials and produce electricity by zinc-sulfur battery chemistry and its lower voltage than zinc-air enable us to confirm a remaining capacity. Eventually, this difference in working potential will be beneficial to manage battery pack for ESS.

### 3.3 Conceptual framework, method and approaches

In order to realize aforementioned knowledge, three key research objectives are proposed in this project (**Figure 5**), including 1) reversible and durable zinc electrode operated in aqueous electrolyte, 2) advanced electrocatalysts for oxygen reduction/evolution, 3) advanced rechargeable zinc air battery with hybrid cathode chemistry. This project will provide a sound scientific platform to maximize a potential of rechargeable zinc air battery with three innovative technology described. Proposed approaches necessarily need a combination of synthesis of materials, physico-chemical and electrochemical characterization of as-prepared metallic zinc anode, electrocatalysts, and metal oxide coated sulfur/carbon composites. Therefore, we will suggest a following research plans at laboratory.

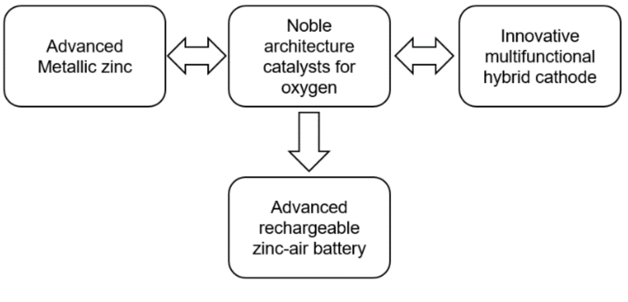


**Figure 5** Schematic flow chart for proposed objectives

### Task I: Reversible and durable zinc electrode operated in aqueous electrolyte

In this project, porous carbon coated interconnected zinc electrode will be prepared via designed scalable method (**Figure 6**). Firstly, highly porous zinc foam will be prepared via zinc spray coating on metal foam. Heating as-prepared zinc foam at 409°C under argon condition can enhance an interaction between zinc particles though slight melting of zinc. Then, calcination at 665 °C in air can wrap ZnO shell. Inner core zinc can further fuse and then yielding highly interconnected porous structure. Any organic materials from zinc spray can be totally removed during two heat treatment process. As-prepared Zn@ZnO foam will be coated with commercial carbon paste to prepare carbon coated Zn@ZnO electrode and then calcined at 450°C. This heat treatment process can totally remove any additives within carbon pastes and partially oxidize carbon shell, yielding lower conductivity where zinc ion cannot be reduced onto oxidized carbon surface instead of zinc metal core and this partially oxidized carbon shell enhance a compatibility with aqueous electrolyte as well as more ion can be conducting. This carbon layer can block a direct contact between electrolyte and zinc metal and more functional carbon materials will be introduced as a coating layer in the near future.

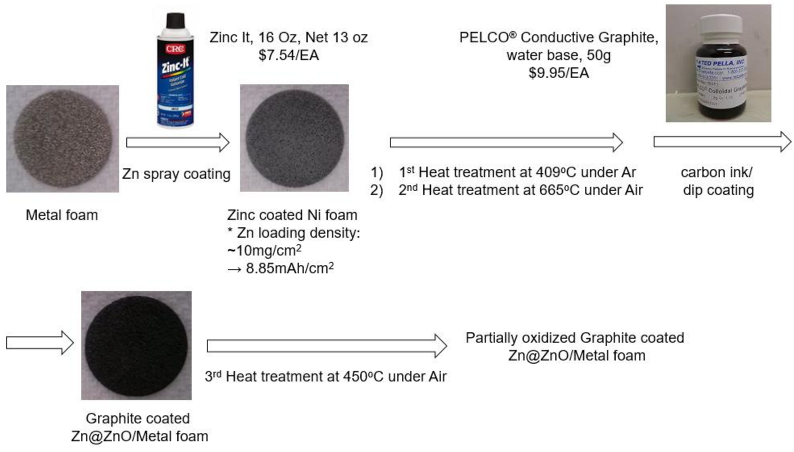


**Figure 6** Schematic preparation of carbon coated Zn@ZnO/Metal foam

### Task II: Advanced electrocatalysts for oxygen reduction/evolution

In this project, series of prussian blue analogues (PBAs), $M_3^{II}[M^{III}(CN)_6]_2 \cdot nH_2O$ ($M^{II}=M^{III}$ transition metal), will be synthesized using precipitation method and then dehydration process removing water molecules within PBAs is required to grow bundle type carbon nanotube (CNT). After that, high temperature pyrolysis above 700°C of dehydrated PBAs can produce graphitic carbon coated bi-metallic electrocatalysts with in-situ grown CNT. Described synthesis is facile and scalable so that it is possible to apply these developed catalysts directly. In this noble architecture, bi-metallic core can tune its electronic structures, thus controlling binding energy for oxygen molecules and in-situ carbon coating layer can prevent an oxidation of metallic phase and affords high durability even during charging process. More interestingly, surface exposed CNT can afford fast oxygen diffusion by partially impeding access of aqueous electrolyte (**Figure 7**).

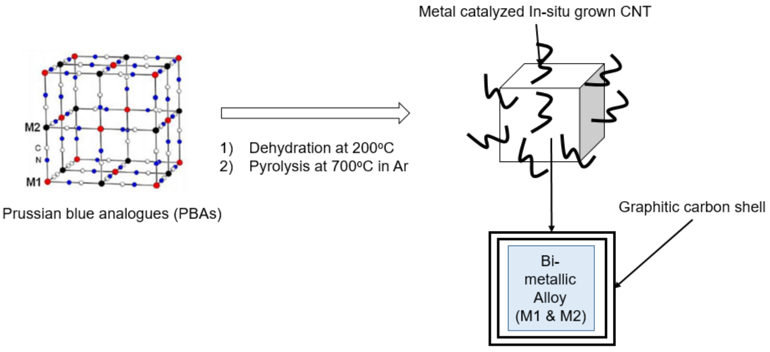


**Figure 7** Schematic preparation of in-situ grown CNT/carbon coated bi-metallic bi-functional electrocatalysts for oxygen

## Task III: Advanced rechargeable zinc air battery with sulfur cathode

This project will significantly improve a rechargeable zinc air battery with hybridization of novel cathode chemistry to meet power and energy density as well as roundtrip efficiency for desired energy storage system. In this task, new types of cathode will be developed, $MnO_2$ coated sulfur/highly porous carbon composites. For example, sulfur/carbon composites can be easily prepared in terms of conventional melt diffusion method and as-prepared sulfur/carbon composites will react with $KMnO_4$ aqueous solution to in-situ growth $MnO_2$ (**Figure 8a**), and then a desired cathode slurry will be coated onto metal foam for oxygen to diffuse easily. Final electrode will be prepared by attaching commercial hydrophobic film to as-prepared cathode and $MnO_2$, oxygen, and sulfur can participate in cathode reaction with different voltage (**Figure 8b**). For example, hybridization with $MnO_2$ makes Zinc-$MnO_2$ battery with higher and slope voltage profile than zinc-air battery with flat voltage and will meet high power application. Furthermore, $MnO_2$ also can catalyze oxygen reduction[20] as well as evolution reaction of zinc-air battery and sulfur will participate in a discharge reaction under ~1V with slope voltage profile and will meet a low power application. Besides, this slope voltage will help to monitor a remaining capacity because conventional zinc-air battery has flat voltage profile, which makes battery managements so difficult. More interestingly, dissolved polysulfide generated from a working of zinc-sulfur battery can be oxidized by $MnO_2$ and then these intermediates can be strongly adsorbed onto $MnO_2$ surface. During charge, higher reversibility of $MnO_2$ and sulfur, which is hybrid cathode, than oxygen evolution reaction will improve a rechargeability and efficiency of Zinc-air battery. Finally, this energy storage devices will be further improved in terms of using porous zinc electrode (Task I), advanced catalysts from Task II, and nano-structured sulfur/steam activated carbon composites.

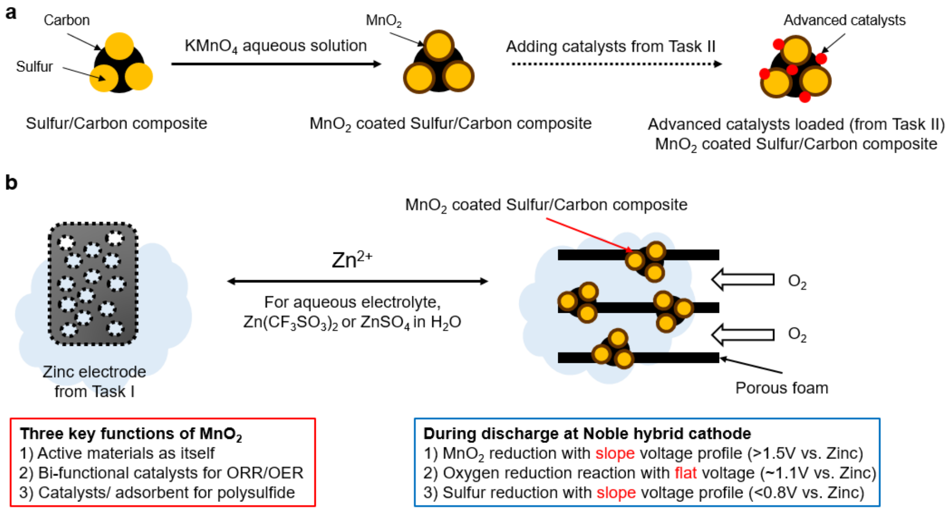


**Figure 8** Schematic preparation of $MnO_2$ coated Sulfur/Carbon composite (a) and configuration of advanced zinc-air battery with hybrid cathode for energy storage system.

Especially, zinc-sulfur battery chemistry is not yet confirmed so that before fabricating the described battery device, it is so reasonable to understand zinc-sulfur battery chemistry. The development of rechargeable Zn-S batteries, however, could be hampered by a passivation onto zinc anode resulting from polysulfide dissolution into electrolyte. To do this, firstly, sulfurized carbon such as sulfurized PAN polymer composites will be synthesized using pyrolysis of PAN polymer and sulfur, which is known for a little dissolution of polysulfide and then zinc-sulfur battery system will be prepared and

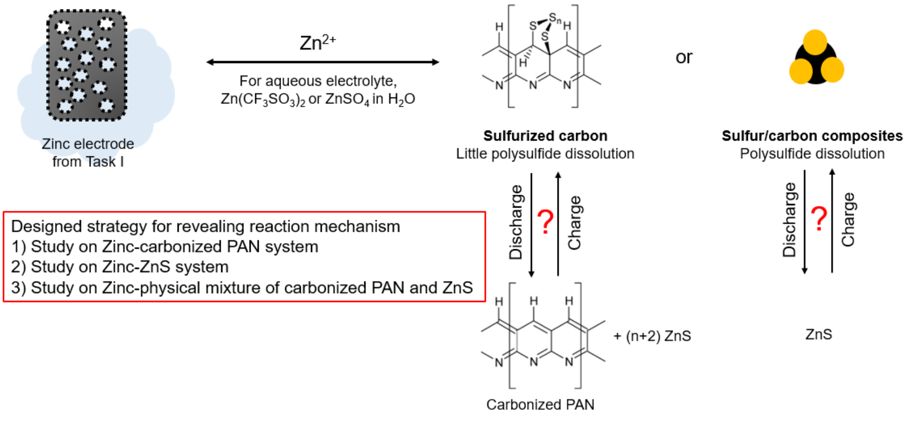


**Figure 9** Schematic research plan for zinc-sulfur battery

studied more detail. The working principle of electrochemically rechargeable Zn-S battery is described in **Figure 9**. This battery is composed with 3D monolithic Zn sponge anode (avoiding zinc dendrite and passivation, resulting in higher zinc utilization), sulfurized carbon as cathode (to minimize polysulfide dissolution into electrolyte), and proper aqueous or organic electrolyte. For development of advanced Zn-S battery, cathode and anode should be improved to increase overall voltage and efficiency. Firstly, it is required to understand a reaction mechanism of sulfurized carbon as cathode. Possible approaches are following. 1) Overdischarge of sulfurized carbon could insert more zinc ion into the short conjugated >C=C< chains of sulfurized carbon backbone so that zinc ionic conductivity could be significantly improved and thus increase its working voltage (Experimentally known fact when studying Li-sulfurized carbon battery). This experimental fact can be supported in terms of zinc ion diffusion coefficient calculated from Galvanostatic Intermittent Titration Technique (GITT) or electrochemical impedance spectroscopy (EIS). 2) Study on Zinc-ZnS system could reveal the critical role of short chain sulfur and its contribution on improved cycle life because this system has no sulfurized carbon species. 3) Study on Zinc-Physical mixture of carbonized PAN and ZnS could reveal a role of sulfurized carbon during discharge/charge because we can expect little interaction between carbonized PAN and ZnS as a discharge product. Furthermore, overdischarge effect on a physical mixture of carbonized PAN and ZnS could yield different a result compared with sulfurized carbon so that this approach could reveal an additional Zinc ion insertion into the short conjugated >C=C< chains of sulfurized carbon backbone, which is described in the approach 1. With a deep understanding of a reaction mechanism, the author will start synthesizing nano-architecture Sulfur/carbon composite and apply it to advanced zinc-air battery with hybrid cathode.

**Timeline.** This is a three-year project with the following activities.

| Tasks: Rechargeable zinc-air battery with hybrid cathode for a gird scale energy storage system | 1st year | | | | 2nd year | | | | 3rd year | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Development of highly stable and reversible zinc anode | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| 2. Study on rechargeable Zinc-Sulfur battery | ■ | ■ | | | | | | | | | | |
| 3. A noble Nano-structured electrocatalysts to promote a reduction or oxidation of oxygen | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| 4. Demonstration of advanced rechargeable zinc air battery with hybrid cathode technology | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| 5. Results report, publications and patent applications | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

## 4. REFERENCES

1. Dunn, B.; Kamath, H.; Tarascon, J.-M., Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011,** *334* (6058), 928-935.

2. Wessells, C. D.; Huggins, R. A.; Cui, Y., Copper hexacyanoferrate battery electrodes with long cycle life and high power. *Nature Communications* **2011,** *2*, 550.

3. Bendikov, T. A.; Yarnitzky, C.; Licht, S., Energetics of a Zinc−Sulfur Fuel Cell. *The Journal of Physical Chemistry B* **2002,** *106* (11), 2989-2995.

4. Lee, J.-S.; Tai Kim, S.; Cao, R.; Choi, N.-S.; Liu, M.; Lee, K. T.; Cho, J., Metal–Air Batteries with High Energy Density: Li–Air versus Zn–Air. *Advanced Energy Materials* **2011,** *1* (1), 34-50.

5. Lin, D.; Liu, Y.; Cui, Y., Reviving the lithium metal anode for high-energy batteries. *Nature Nanotechnology* **2017,** *12*, 194.

6. Fan, F. Y.; Chiang, Y.-M., Electrodeposition Kinetics in Li-S Batteries: Effects of Low Electrolyte/Sulfur Ratios and Deposition Surface Composition. *Journal of The Electrochemical Society* **2017,** *164* (4), A917-A922.

7. Horn, Q. C.; Shao-Horn, Y., Morphology and Spatial Distribution of ZnO Formed in Discharged Alkaline Zn / $MnO_2$ AA Cells. *Journal of The Electrochemical Society* **2003,** *150* (5), A652-A658.

8. Cho, Y.-D.; Fey, G. T.-K., Surface treatment of zinc anodes to improve discharge capacity and suppress hydrogen gas evolution. *Journal of Power Sources* **2008,** *184* (2), 610-616.

9. Parker, J. F.; Chervin, C. N.; Nelson, E. S.; Rolison, D. R.; Long, J. W., Wiring zinc in three dimensions re-writes battery performance-dendrite-free cycling. *Energy & Environmental Science* **2014,** *7* (3), 1117-1124.

10. (a) Debe, M. K., Electrocatalyst approaches and challenges for automotive fuel cells. *Nature* **2012,** *486* (7401), 43-51; (b) GreeleyJ; Stephens, I. E. L.; Bondarenko, A. S.; Johansson, T. P.; Hansen, H. A.; Jaramillo, T. F.; RossmeislJ; ChorkendorffI; Nørskov, J. K., Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. *Nat Chem* **2009,** *1* (7), 552-556.

11. Hong, W.; Risch, M.; Stoerzinger, K. A.; Grimaud, A. J. L.; Suntivich, J.; Shao-Horn, Y., Toward the rational design of non-precious transition metal oxides for oxygen electrocatalysis. *Energy & Environmental Science* **2015**.

12. (a) Qu, L.; Liu, Y.; Baek, J.-B.; Dai, L., Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells. *ACS Nano* **2010,** *4* (3), 1321-1326; (b) Nam, G.; Park, J.; Kim, S. T.; Shin, D.-b.; Park, N.; Kim, Y.; Lee, J.-S.; Cho, J., Metal-Free Ketjenblack Incorporated Nitrogen-Doped Carbon Sheets Derived from Gelatin as Oxygen Reduction Catalysts. *Nano Letters* **2014,** *14* (4), 1870-1876; (c) Park, G. S.; Lee, J.-S.; Kim, S. T.; Park, S.; Cho, J., Porous nitrogen doped carbon fiber with churros morphology derived from electrospun bicomponent polymer as highly efficient electrocatalyst for Zn–air batteries. *Journal of Power Sources* **2013,** *243* (0), 267-273.

13. Lee, J.-S.; Nam, G.; Sun, J.; Higashi, S.; Lee, H.-W.; Lee, S.; Chen, W.; Cui, Y.; Cho, J., Composites of a Prussian Blue Analogue and Gelatin-Derived Nitrogen-Doped Carbon-Supported Porous Spinel Oxides as Electrocatalysts for a Zn–Air Battery. *Advanced Energy*

*Materials* **2016,** *6* (22), 1601052-n/a.

14. Lee, J.-S.; Park, G. S.; Kim, S. T.; Liu, M.; Cho, J., A Highly Efficient Electrocatalyst for the Oxygen Reduction Reaction: N-Doped Ketjenblack Incorporated into Fe/$Fe_3C$-Functionalized Melamine Foam. *Angewandte Chemie International Edition* **2013,** *52* (3), 1026-1030.

15. Nam, G.; Park, J.; Choi, M.; Oh, P.; Park, S.; Kim, M. G.; Park, N.; Cho, J.; Lee, J.-S., Carbon-Coated Core–Shell Fe–Cu Nanoparticles as Highly Active and Durable Electrocatalysts for a Zn–Air Battery. *ACS Nano* **2015,** *9* (6), 6493-6501.

16. Maass, S.; Finsterwalder, F.; Frank, G.; Hartmann, R.; Merten, C., Carbon support oxidation in PEM fuel cell cathodes. *Journal of Power Sources* **2008,** *176* (2), 444-451.

17. Lee, D. U.; Choi, J.-Y.; Feng, K.; Park, H. W.; Chen, Z., Advanced Extremely Durable 3D Bifunctional Air Electrodes for Rechargeable Zinc-Air Batteries. *Advanced Energy Materials* **2013**, n/a-n/a.

18. Lee, D. U.; Fu, J.; Park, M. G.; Liu, H.; Ghorbani Kashkooli, A.; Chen, Z., Self-Assembled NiO/Ni(OH)2 Nanoflakes as Active Material for High-Power and High-Energy Hybrid Rechargeable Battery. *Nano Letters* **2016,** *16* (3), 1794-1802.

19. Cui, Y., Materials Design for Grid-Scale Energy Storage. **2012**.

20. (a) Lee, J.-S.; Park, G. S.; Lee, H. I.; Kim, S. T.; Cao, R.; Liu, M.; Cho, J., Ketjenblack Carbon Supported Amorphous Manganese Oxides Nanowires as Highly Efficient Electrocatalyst for Oxygen Reduction Reaction in Alkaline Solutions. *Nano Letters* **2011,** *11* (12), 5362-5366; (b) Lee, J.-S.; Lee, T.; Song, H.-K.; Cho, J.; Kim, B.-S., Ionic liquid modified graphene nanosheets anchoring manganese oxide nanoparticles as efficient electrocatalysts for Zn-air batteries. *Energy & Environmental Science* **2011,** *4* (10), 4148-4154.