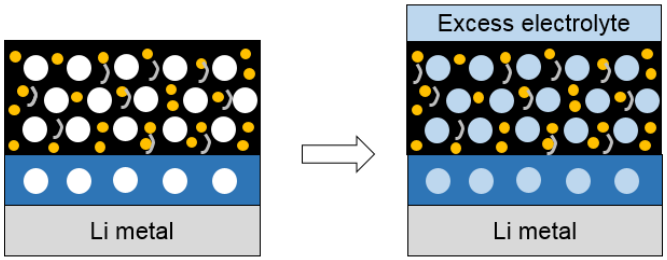
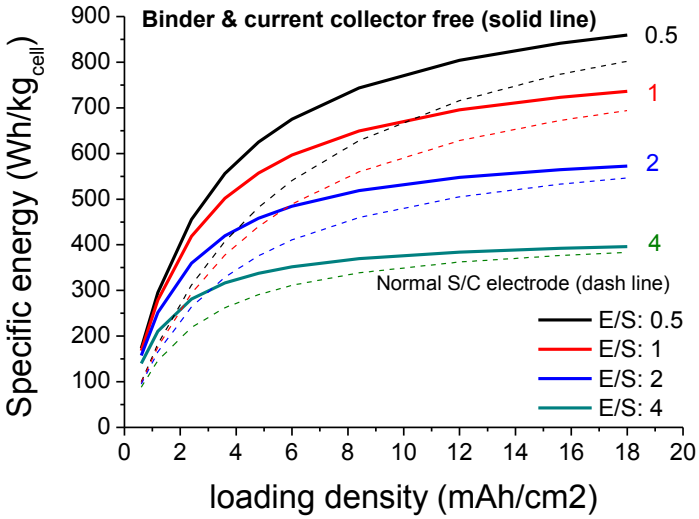
Practical a ratio of Electrolyte to Sulfur (El/S ratio)

❑ Both Physical & Chemical requirement NEEDS for practically available Li-S battery



1) Physical requirement
(electrolyte must fill all pore in a battery)

Just Physical
E/S ratio



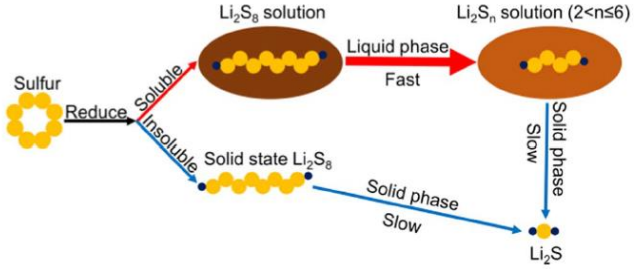
** Practical Specific energy density (Wh/Kg)

$$= \frac{cathode\ capacity\ (Ah) \times Norminal\ voltage\ (2.1V)[Wh]}{total\ weight_{\ cell}(=cathode+anode+electrolyte+Extra\ weight)[Kg]}$$

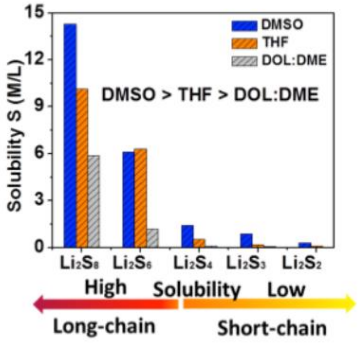
** N/P ratio>1

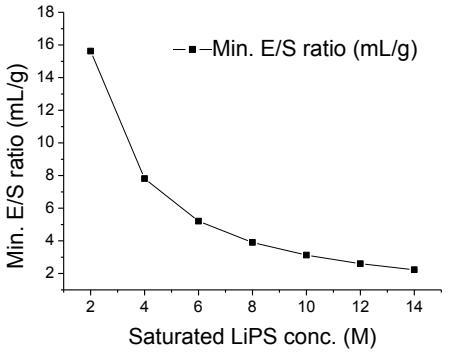
** Extra weight: Current collector, Tab, pouch

Feedback



Practical
E/S ratio





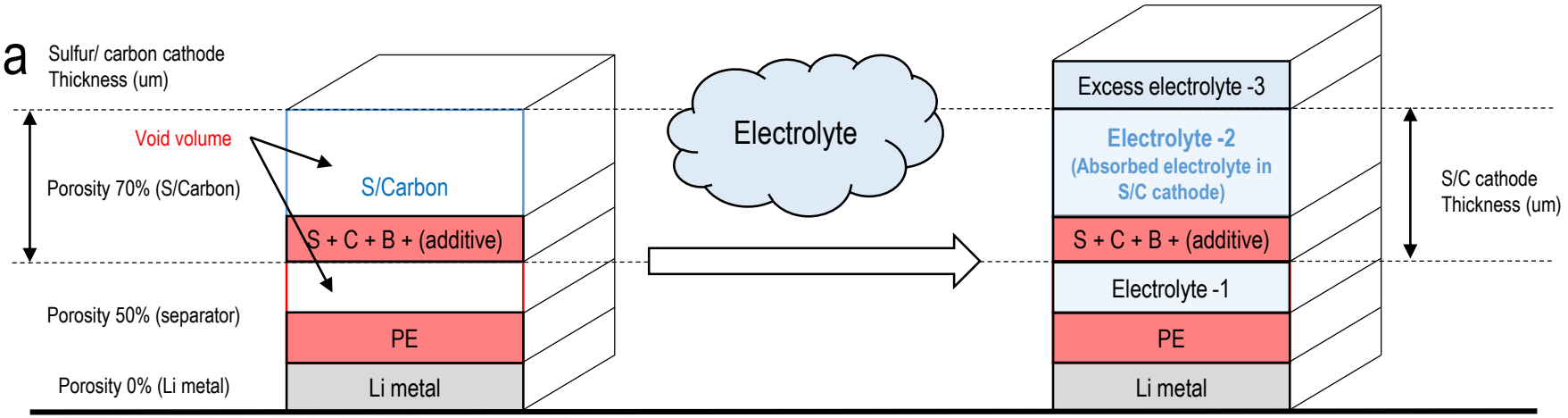
2) Chemical requirement: consider Li-Polysulfide (PS) solubility

** El/S ↑ → higher solubility of polysulfide → better reaction kinetics, but lower energy density

Practical a ratio of Electrolyte to Sulfur (El/S ratio)

❑ Both Physical & Chemical requirement NEEDS for practically available Li-S battery

a



<Previous concept of El/S ratio>

$$\frac{Total\ electrolyte\ 1+2+3}{Sulfur}$$

Which electrolyte can affect directly a solubility of Sulfur (or lithium polysulfide)

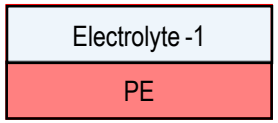
2 >>> 1 ≈ 3

<Modified concept of effective El/S ratio>

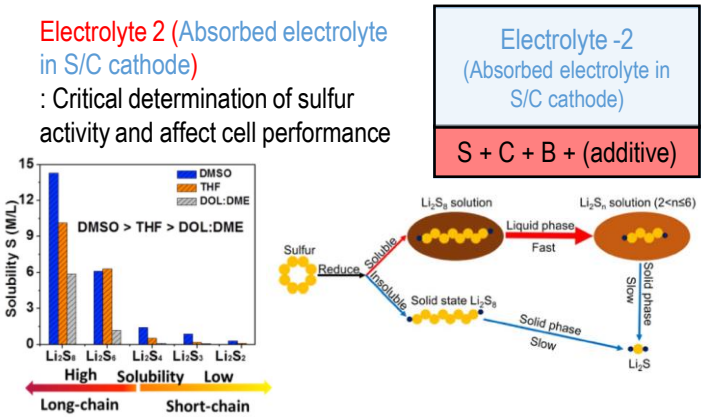
$$\frac{electrolyte\ 2}{Sulfur}$$

b

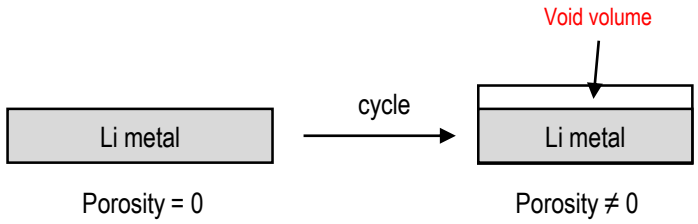
Electrolyte 1
: just occupy a void volume of separator



Electrolyte 2 (Absorbed electrolyte in S/C cathode)
: Critical determination of sulfur activity and affect cell performance



Electrolyte 3 (excess electrolyte)
: After cycling, Li metal becomes more porous and then extra electrolyte is consumed as new SEI layer onto fresh Li metal.
→ significantly affect a cycle life of Li-S cell

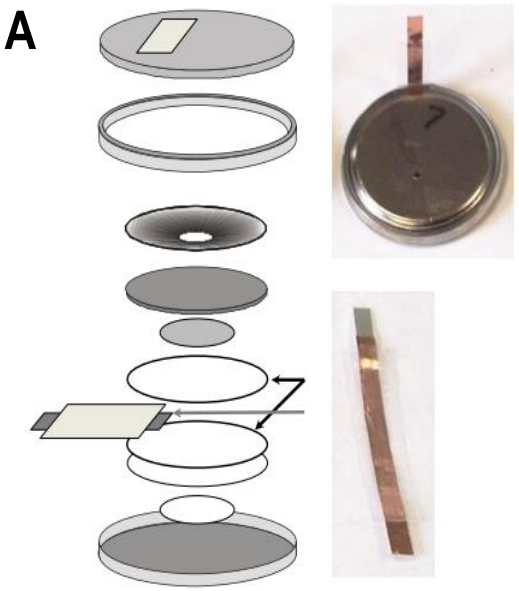


** New concept NEEDS for development of practically usable Li-S cell:

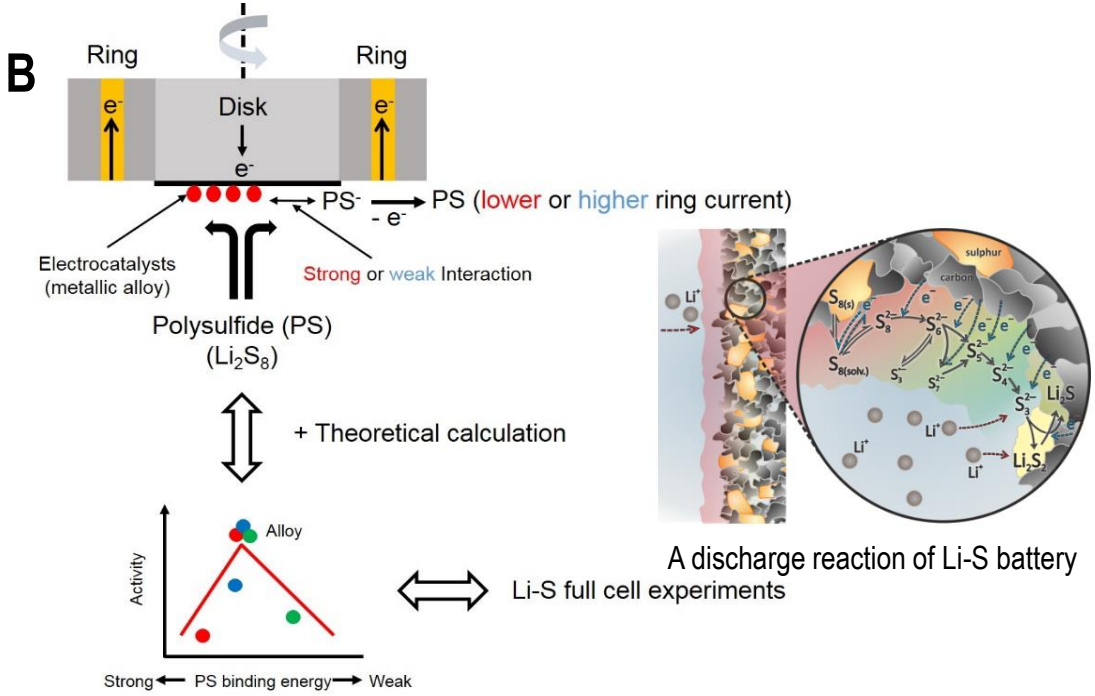
El/S & mAh/cm^2 → *effective* El/S ratio & volumetric loading density (mAh/cm^3) including filled electrolyte

In-situ Study on soluble lithium polysulfide (LiPS)

❑ Study on reaction mechanism related with LiPS



Introduce on Another working electrode to probe
Soluble lithium polysulfide under in-situ condition



Study on interaction between catalysts and soluble LiPS in terms of RRDE (rotating ring disk electrode) technique
→ Rational designed catalysts for LiPS for better Li-S cell

Development of in-situ analytical method in terms of electrochemistry
- Quantitative analysis of soluble LiPS with bi-potentiostat and 3-electrode cell
- Qualitative evaluation of stability of catalysts with interaction btw. Catalysts and LiPS

The rational design principle for advanced cathode materials for Rechargeable Li-Sulfur Batteries

Investigator

Dr. Jangsoo Lee

Objective

Managing soluble polysulfide is a significant issue for advanced Li-Sulfur battery because polysulfide degrade the battery performance. This soluble polysulfide is supposed to be deposited onto a carbon surface via redox reaction during discharge. Therefore, a fundamental understanding between polysulfides and carbon surface is highly required to improve the Li-S battery and studying this surface reaction is quite analogous to electrocatalytic reactions. The goal of this work is to propose the rational design principle for advanced sulfur cathode by studying an interaction between catalysts and long chain polysulfide. Researchers will synthesize a metallic alloy by carbonization of Prussian blue analogues and study its activity for polysulfide in terms of rotating ring disk electrode (RRDE) techniques. Different alloy could have different binding energy for polysulfide and then the amount of diffused species can be detected by ring current. With a clear mechanistic understanding, we hope to construct a rational design principle for advanced cathode materials for advanced rechargeable Li-Sulfur Batteries.

Background

Lithium–sulfur batteries have attracted a great attention due to its higher energy density compared to conventional Li-ion battery. During discharge, Lithium polysulfide (LiPS) dissolution is inevitable in ether electrolyte and then these intermediates are supposed to be deposited onto porous carbon surface reversibly. Carbon surface is not sufficiently polar so that it has a little interaction with polar LiPS, causing a degradation of battery. Affording polarity to carbon host in terms of hetero atom doping[1] or metal oxides[2] has been extensively studied. For example, N or O dopants enhances the interaction between carbon and LiPS, but B, F, S, P, and Cl is not satisfactory.[1] Even stronger interaction to catch LiPS effectively can be predicted by Co-doping strategy. However, Cui group point out balancing optimization between sulfide-adsorption and diffusion on the oxides.[2] It is still controversial issues and thus a clear mechanistic understanding and corresponding selection criteria are still lacking, which eventually impede the progress of advanced Li-S battery.

Approach

Studying a redox of polysulfides at the carbon surface is analogous to electrocatalytic reactions. Co-doping[1] or alloy[3] can significantly effect on its catalytic activity compared with monodopants or one metal composition. Therefore, different alloy could have different binding energy for polysulfide and yields different amount of reduced and diffused species. Thin film Rotating Ring Disk Electrode (RRDE) techniques is widely used to study an electrocatalysts for oxygen reduction or evolution reaction. With different metallic alloy coated disk as working

electrode, applying reduction potential of polysulfide, reduced long chain polysulfide at disk electrode could be strongly or weakly adsorbed onto catalysts and then different amount of diffused species can be oxidized in terms of ring current. Furthermore, theoretical calculation as well as Li-S full cell study can support aforementioned discussion. Therefore, we hope to construct a rational design principle for advanced cathode materials for advanced rechargeable Li-Sulfur Batteries (Figure 1).

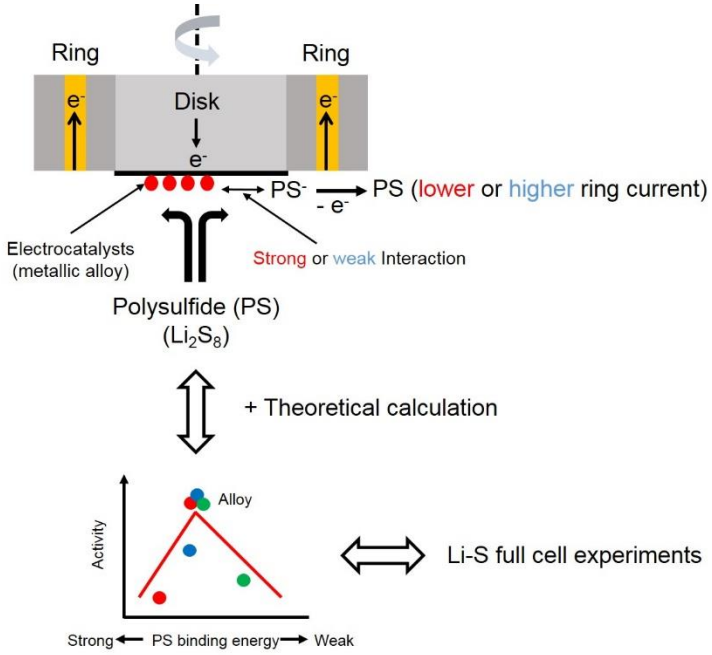
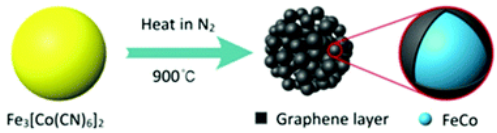


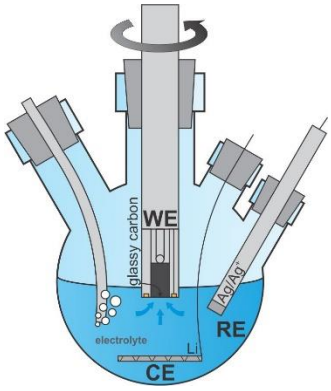
Figure 1: Proposed research to investigate an interaction between electrocatalysts and polysulfide in terms of rotating ring disk electrode (RRDE) technique. For example, different alloy could have different binding energy for polysulfide and thus it could be expected that a strong interaction between electrocatalysts and reduced PS^- cause slow diffusion of intermediates to ring electrode, resulting in low ring current.

Experimental sections and methods

Synthesis of bi-metallic alloy: Other $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) prussain blue analougue are synthesized in the previous literature[4] and then heat treated under inert atmospere to gain bi-metallic alloy. (***Experimentally, for example, we can grow carbon nanotube with Mn-Co alloy encapsulated by graphitic carbon shell by carbonization of $Mn_3[Co(CN)_6]_2$. above 700°C***) For example, synthesis of FeCo alloy is described following.[5]



Electrochemical characterization: The non-aqueous rotating ring disk electrode set-up was fully described in previous literatures.[6] Especially, stability of $S_3^{\cdot-}$ radical could be a key issues so that DMSO with high dielectric constant maybe used for this study. Schematic non-aqueous RRDE setup is described following.[6c]



References

1. Hou, T.-Z.; Chen, X.; Peng, H.-J.; Huang, J.-Q.; Li, B.-Q.; Zhang, Q.; Li, B., Design Principles for Heteroatom-Doped Nanocarbon to Achieve Strong Anchoring of Polysulfides for Lithium–Sulfur Batteries. *Small* **2016,** *12* (24), 3283-3291.
2. Tao, X.; Wang, J.; Liu, C.; Wang, H.; Yao, H.; Zheng, G.; Seh, Z. W.; Cai, Q.; Li, W.; Zhou, G.; Zu, C.; Cui, Y., Balancing surface adsorption and diffusion of lithium-polysulfides on nonconductive oxides for lithium–sulfur battery design. **2016,** *7*, 11203.
3. Li, J.; Stein, H. S.; Sliozberg, K.; Liu, J.; Liu, Y.; Sertic, G.; Scanley, E.; Ludwig, A.; Schroers, J.; Schuhmann, W.; Taylor, A. D., Combinatorial screening of Pd-based quaternary electrocatalysts for oxygen reduction reaction in alkaline media. *Journal of Materials Chemistry A* **2017,** *5* (1), 67-72.
4. Kaye, S. S.; Long, J. R., Hydrogen Storage in the Dehydrated Prussian Blue Analogues M3[Co(CN)6]2 (M = Mn, Fe, Co, Ni, Cu, Zn). *Journal of the American Chemical Society* **2005,** *127* (18), 6506-6507.
5. Hu, L.; Zhang, R.; Wei, L.; Zhang, F.; Chen, Q., Synthesis of FeCo nanocrystals encapsulated in nitrogen-doped graphene layers for use as highly efficient catalysts for reduction reactions. *Nanoscale* **2015,** *7* (2), 450-454.
6. (a) Herranz, J.; Garsuch, A.; Gasteiger, H. A., Using Rotating Ring Disc Electrode Voltammetry to Quantify the Superoxide Radical Stability of Aprotic Li–Air Battery Electrolytes. *The Journal of Physical Chemistry C* **2012,** *116* (36), 19084-19094; (b) Lu, Y.-C.; He, Q.; Gasteiger, H. A., Probing the Lithium–Sulfur Redox Reactions: A Rotating-Ring Disk Electrode Study. *The Journal of Physical Chemistry C* **2014,** *118* (11), 5733-5741; (c) http://www.emutoro.com/schematics.html.