

Mechanism of Capacity Enhancement in Li–S Batteries via Oxygen Functional Groups in Microporous Carbon Pores for Sulfur Hosts

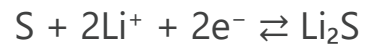
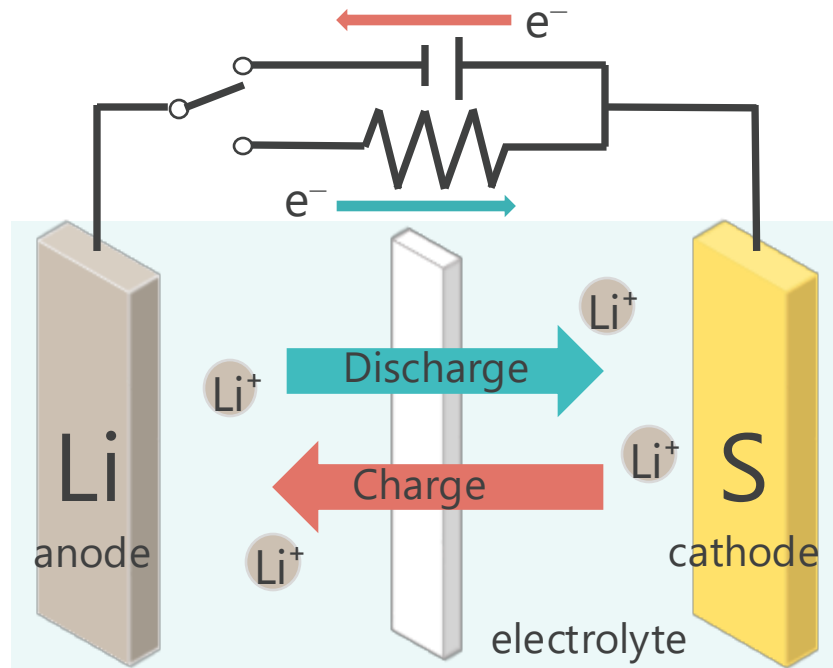
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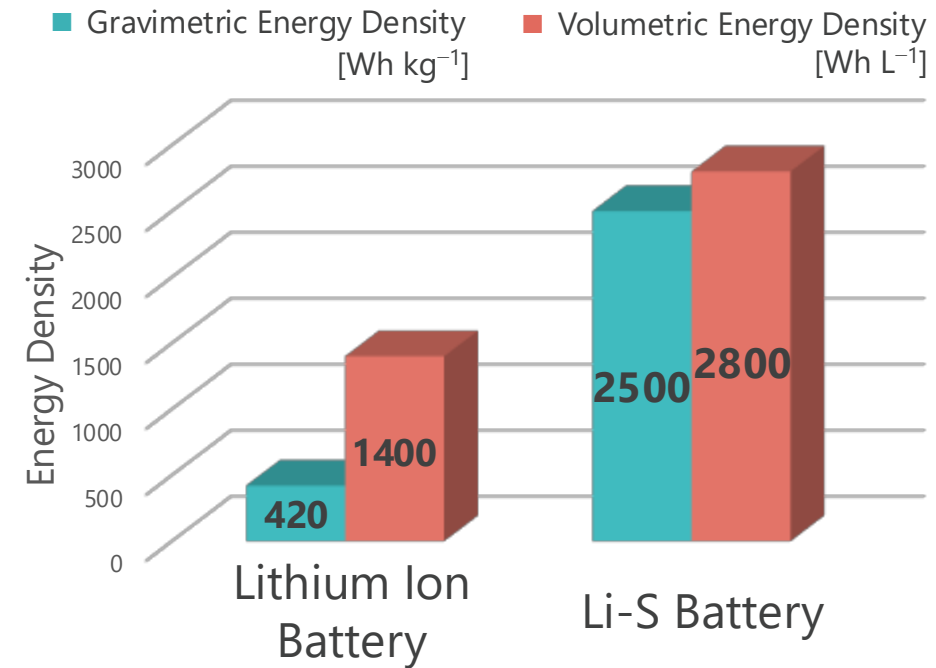
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Lithium-Sulfur Batteries (LSBs)

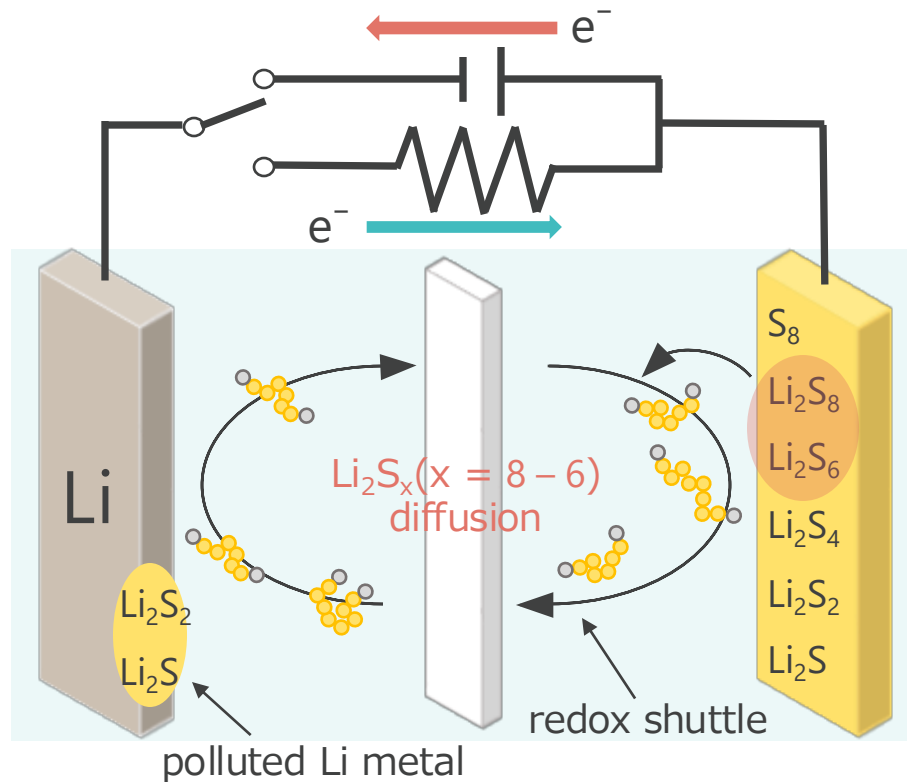


Specific Capacity of S and Li : 1672, 3860 mAh g⁻¹



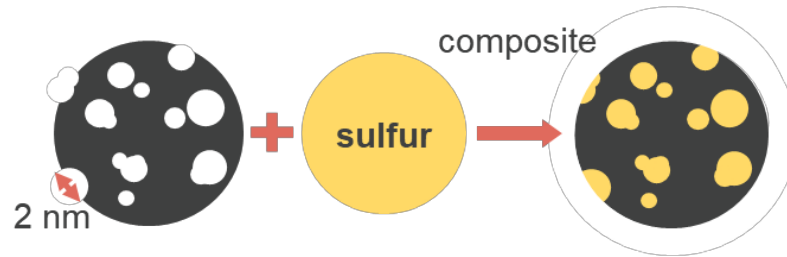
- 😊 high specific capacity of sulfur (1672 mAh g⁻¹)
- 😊 high energy density (2500 Wh kg⁻¹)
- 😊 abundant in resources
- 😊 inexpensive

LSBs have received significant attention as next-generation secondary batteries



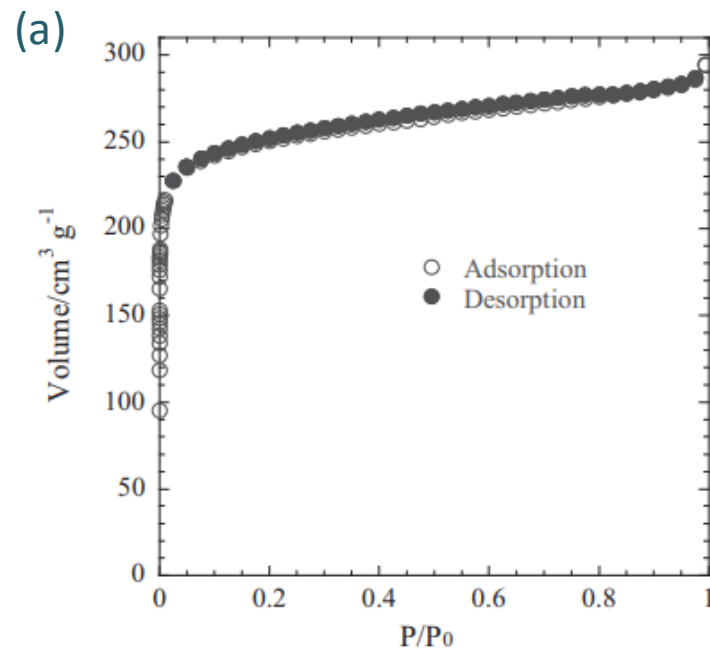
- ☹️ very low electronic conductivity of sulfur and Li_2S : insulator
 - much lower capacity than theoretical one
- ☹️ 1.8-fold volume expansion during reaction from sulfur
- ☹️ intermediate Li_2S_x ($x = 8 - 6$) are soluble in most electrolytes
 - loss of electronic contact
 - fatal capacity decay
- ☹️ redox shuttle
 - low coulombic efficiency, leak current
 - poor cycling stability

Li-S batteries with sulfur-only cathodes cannot be charged or discharged



S_8 ring molecule transforms into **1D chain sulfur** in spaces **less than 2 nm** in diameter, and the chain sulfur forms strong covalent bonds that stabilize in the pores and do not sublime. ¹⁾

Adsorption/desorption isotherm



Pore size distribution

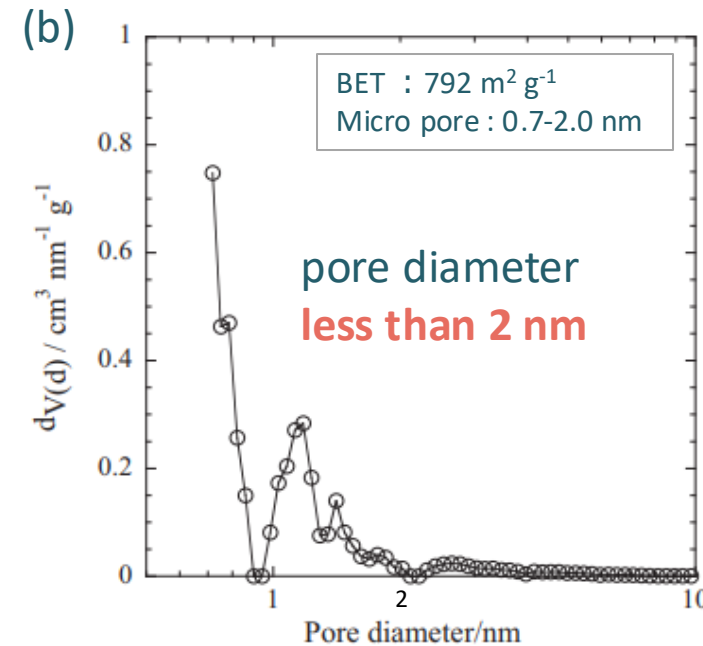
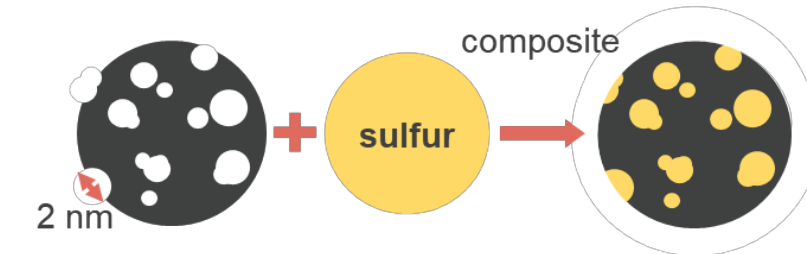


Fig. (a) N_2 adsorption-desorption isotherm and (b) pore-size distribution by the DFT method for microporous AC ²⁾

1) T. Fujimori et al., *Nat Commun.*, **4**, 2162 (2013)

2) T. Takahashi, M. Ishikawa et al., *Prog. Nat. Sci.*, **25**, 612 (2015)



- Preparation flow**
1. Sulfur + AC mixed
 2. Heated at 155°C for 5h
 3. 300°C for 2h
 4. Gradually cooled to R.T.

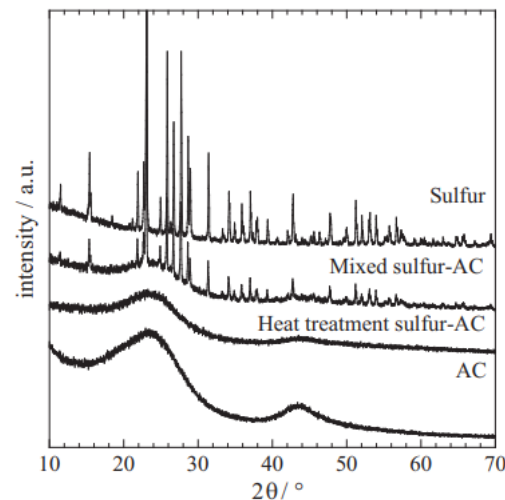
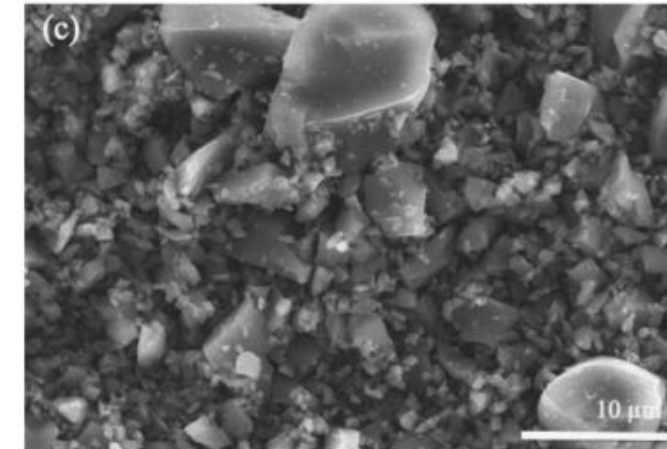
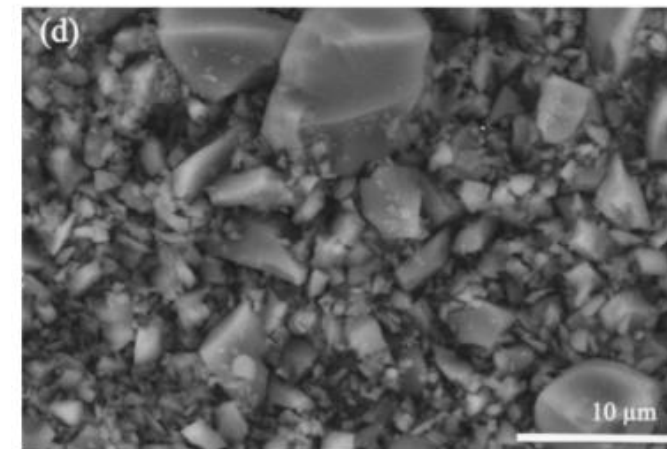


Fig.1 XRD patterns of sulfur, sulfur mixed with AC powder, heat treatment sulfur-AC, and AC powder.

After confinement



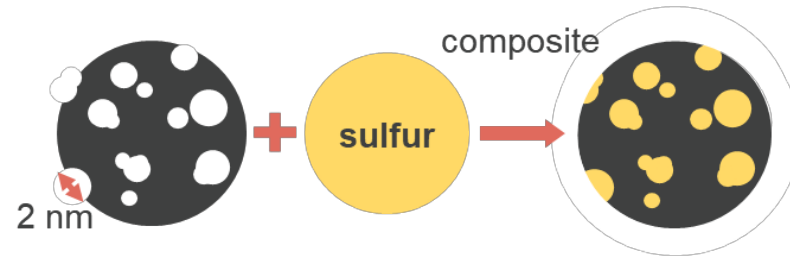
SE



BSE

Fig.2 SEM images of sulfur-AC composited by heat treatment; (c) SEM image, (d)BSE image.

No sulfur on surface ⇒ Completely confined



【Cathode】	S-AC(S-29%) : AB : CAC : SBR
【Anode】	Lithium
【Electrolyte】	LiTFSI/G4/HFE LiFSI/EMImFSI LiPF ₆ /EC:DMC

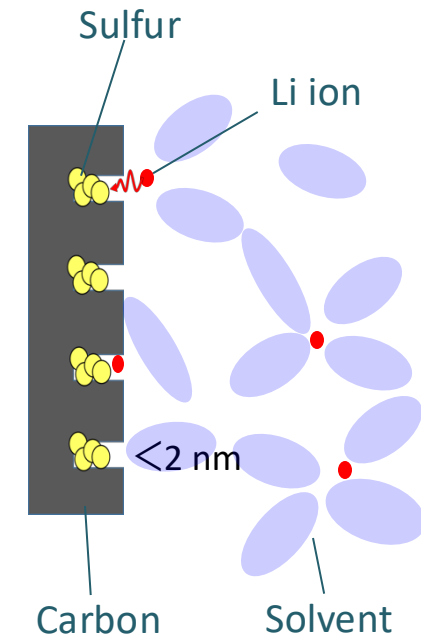
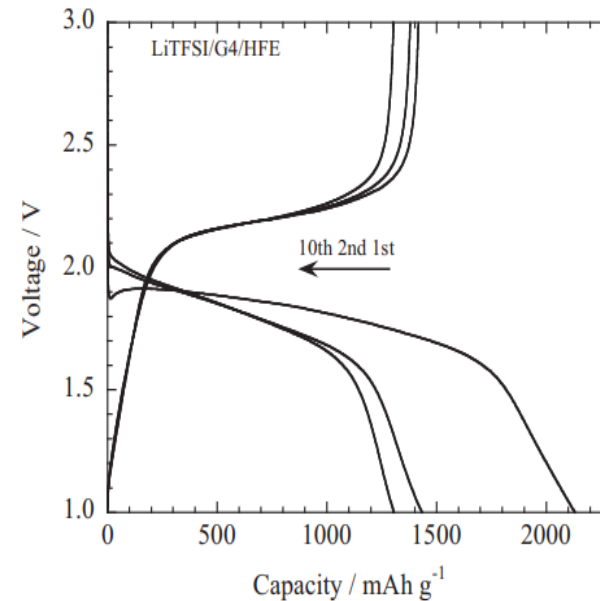
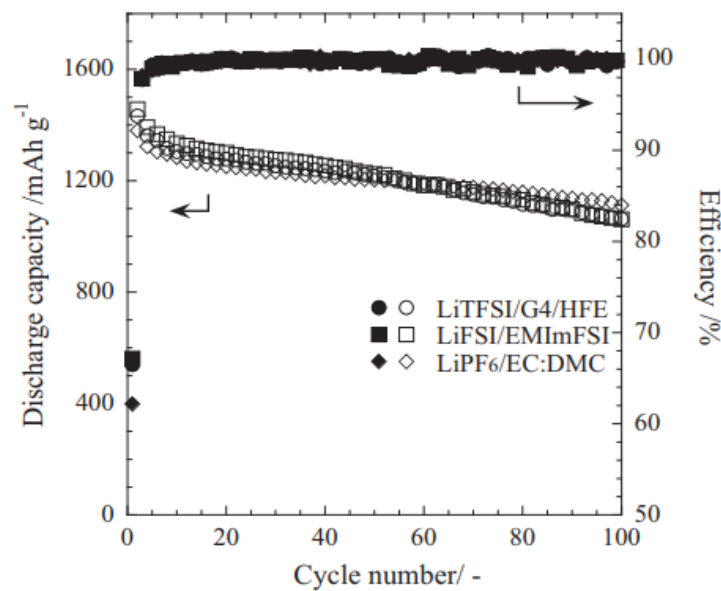
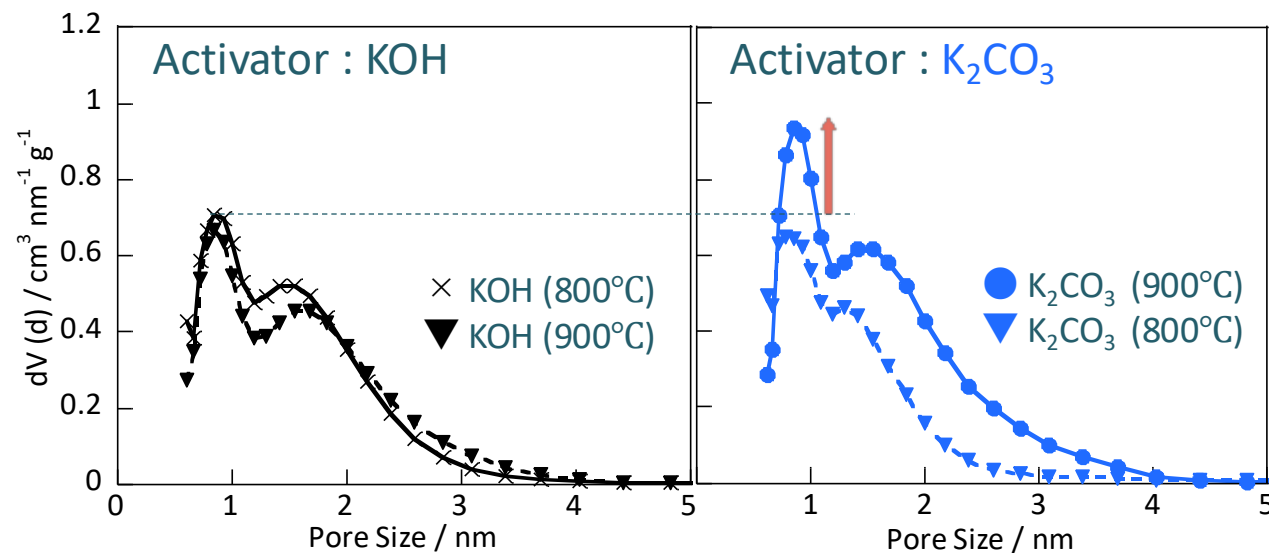


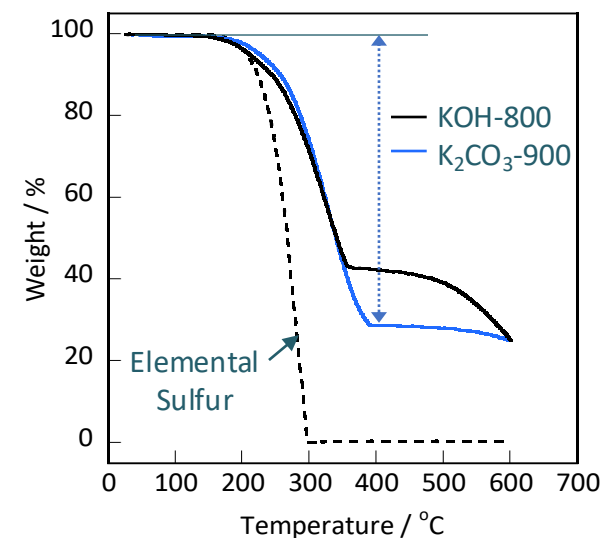
Fig. Discharge capacity after 2nd cycle(open) and charge-discharge efficiency (solid) of the sulfur-ball milled AC composite positive electrode with (●, ○) LiTFSI/G4/HFE, (■, □) LiTFSI/EMImFSI and (◆, ◇) LiPF₆ / EC:DMC electrolytes.

We successfully keeps S reaction sequence within microporous AC

Pore size distribution



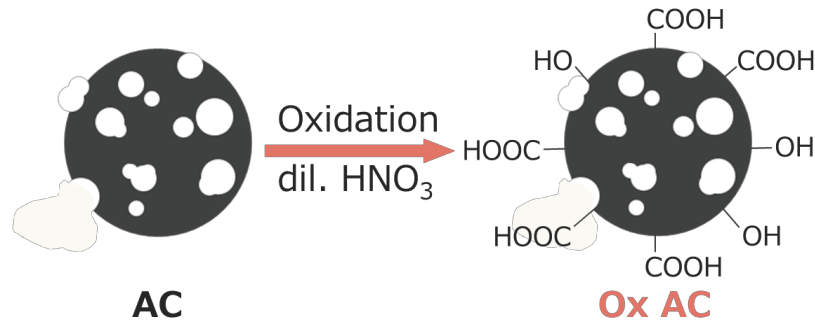
Thermogravimetric analysis



	KOH		K_2CO_3	
	800°C	900°C	800°C	900°C
Surface Area ($m^2 g^{-1}$)	2231	1846	1848	2633
Pore Volume ($cm^3 g^{-1}$)	1.059	0.994	0.827	1.286

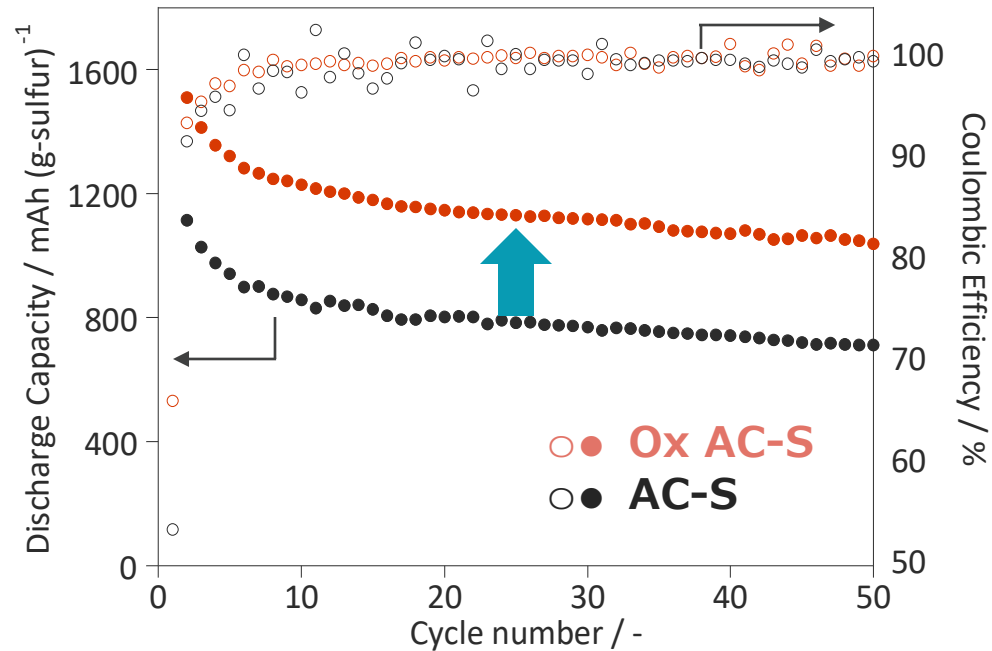
	KOH(800°C)	K_2CO_3 (900°C)
Sulfur content	62 wt.%	70 wt.%
Sublimation completion temperature of sulfur	350°C	400°C
Retention of sulfur in pores	Good	✓Excellent

The combination of K_2CO_3 activator and heating at 900°C promoted the best micropore development.
It was possible to **load 70 wt.%** of sulfur.



Improved lithium-sulfur battery performance by **oxidation treatment** to microporous carbon as sulfur matrix.

Oxidation treatment of AC

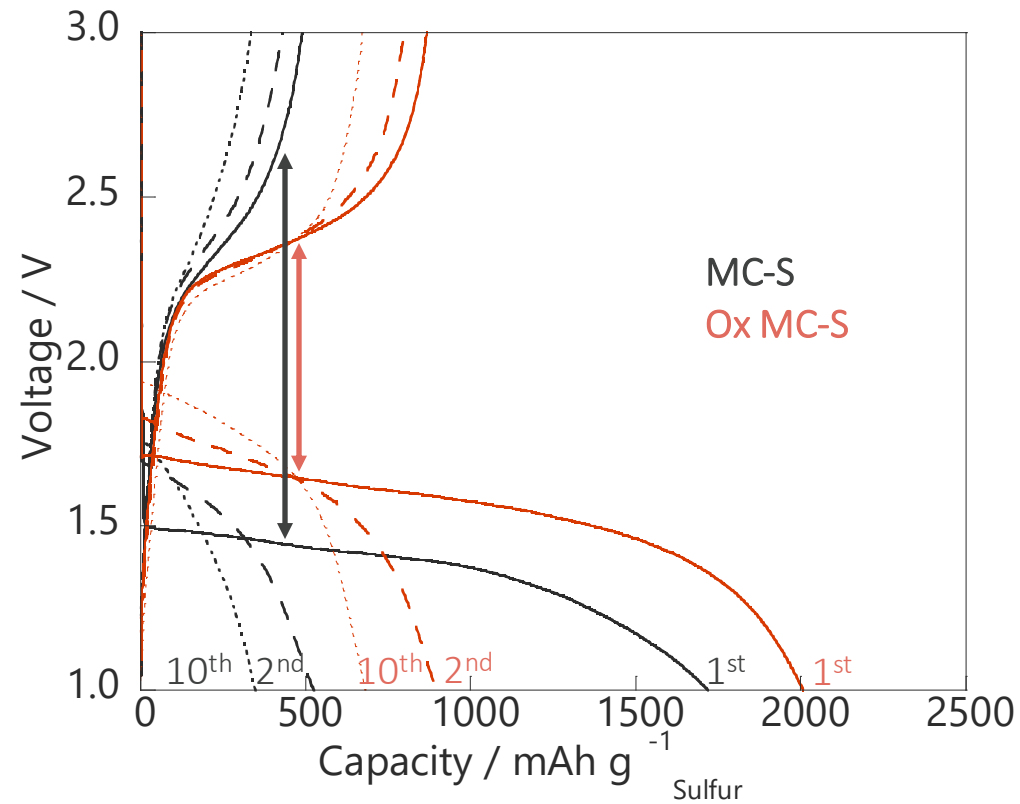


Treatment procedure

1. Mix with HNO_3 2 h at 120°C
2. Wash with pure water
3. Dry at 80°C under vacuum

【Electrolyte】 LiTFSI/G4/HFE

- improve discharge capacity
- stabilize coulombic efficiency



【Galvanostatic cycling】

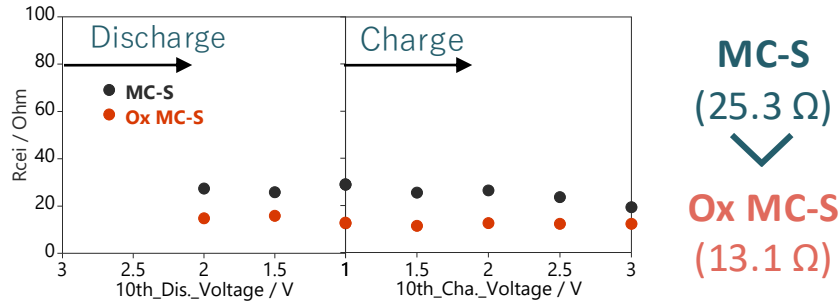
Voltage range: 1.0 – 3.0 V

Current density: 0.1 C (1 C = 1672 mA g⁻¹)

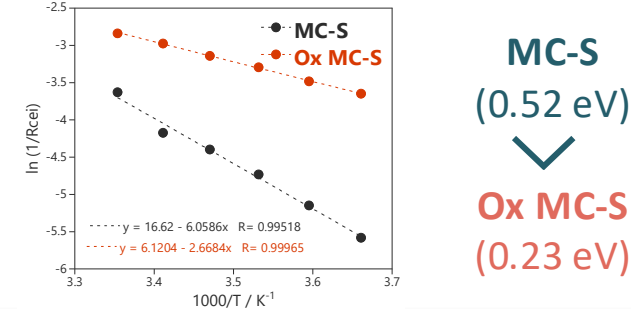
Overpotential: MC-S > Ox MC-S

■ Resistance of Cathode Electrolyte Interface (R_{cei})

Voltage dependence for Ave. R_{cei}



Arrhenius plot for Activation Energy



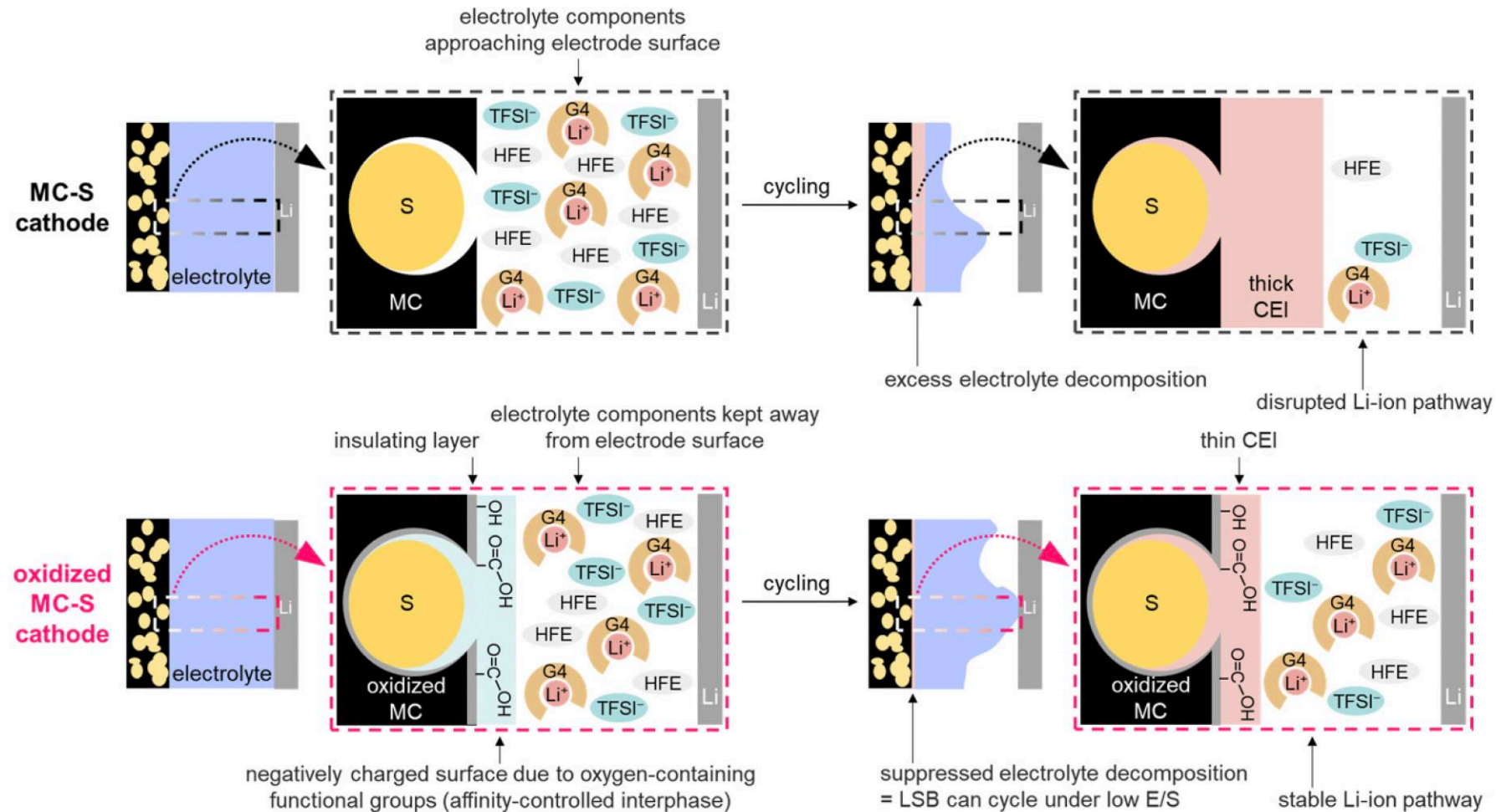
Oxidation treatment decreases R_{cei} and activation energy of reaction.

**The cathode taken out from the cell at 10th cyc. cha. 3.0 V was measured after washing and drying.

	C	O	S	F
	[wt.%]	[wt.%]	[wt.%]	[wt.%]
Pristine AC-S	61.5	2.16	36.2	-
Cycled AC-S	50.5	27.8	16.0	5.57
Pristine Ox AC-S	54.4	6.72	38.9	-
Cycled Ox AC-S	42.7	33.9	22.6	0.79

- O and F from electrolyte decomposition products (CEI) are detected after cycles.
- The weight gain ratio at **Ox MC-S** is lower.

Oxidation treatment suppresses the electrolyte decomposition and prevents excessive CEI formation.

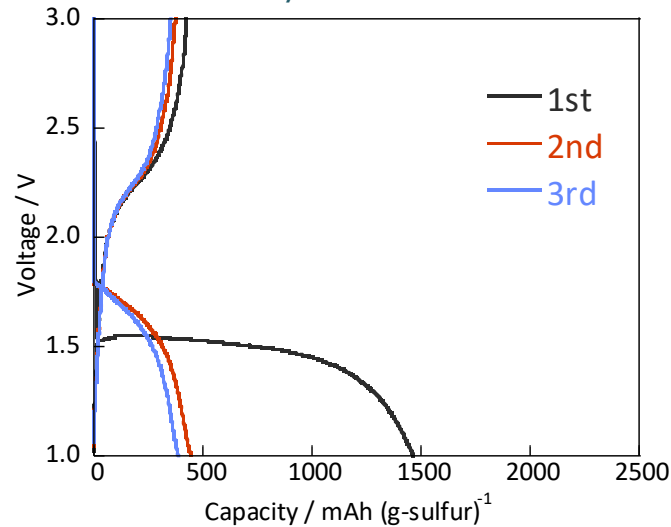
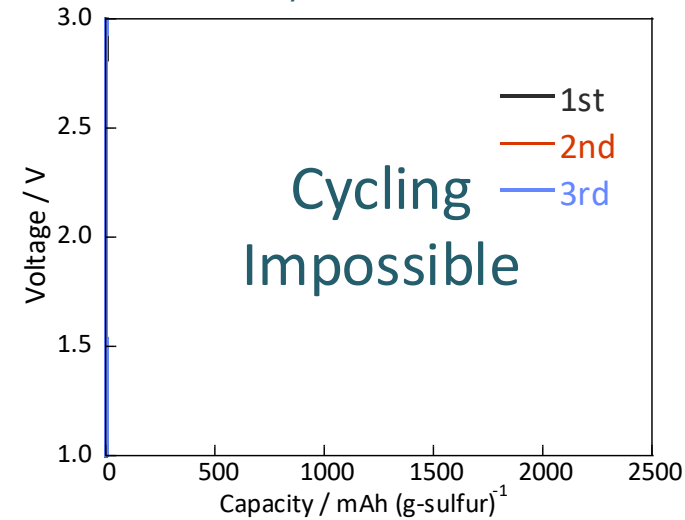


Scheme 2. Mechanism underlying the performance improvement of an LSB containing oxidized MC.

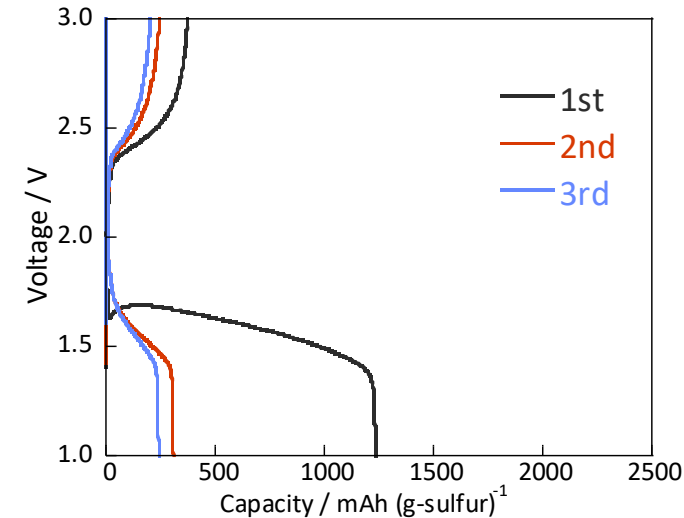
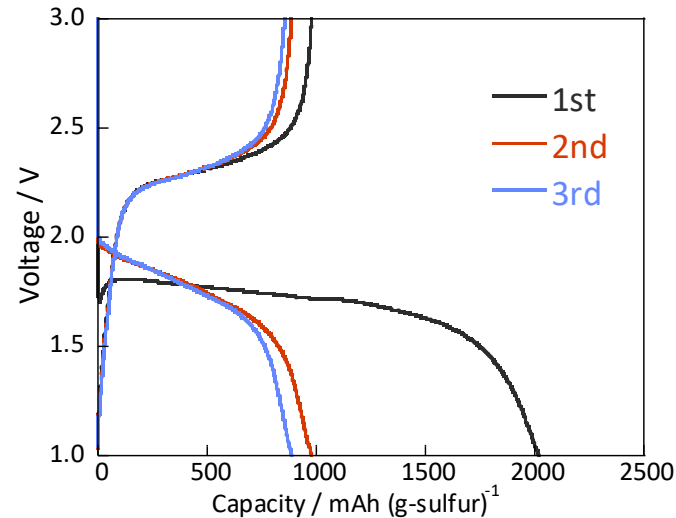
Without oxidation treatment, both CEI formation and electrolyte depletion occur due to electrolyte decomposition

$$*** E/S = \frac{\text{Volume of Electrolyte } [\mu\text{L}]}{\text{Weight of Sulfur } [\text{mg}]}$$

MC-S

 $E/S = 18.7$  $E/S = 2.01$ 

Ox MC-S

【Electrolyte】
LiTFSI/G4/HFE

LSB using the oxidized AC-S can cycle with less electrolyte without excess decomposition of electrolytes

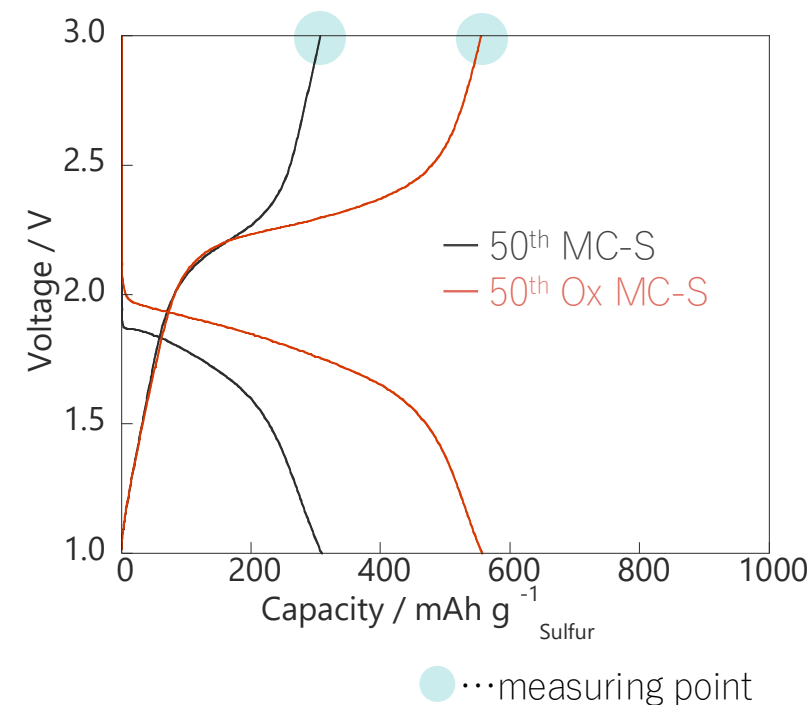
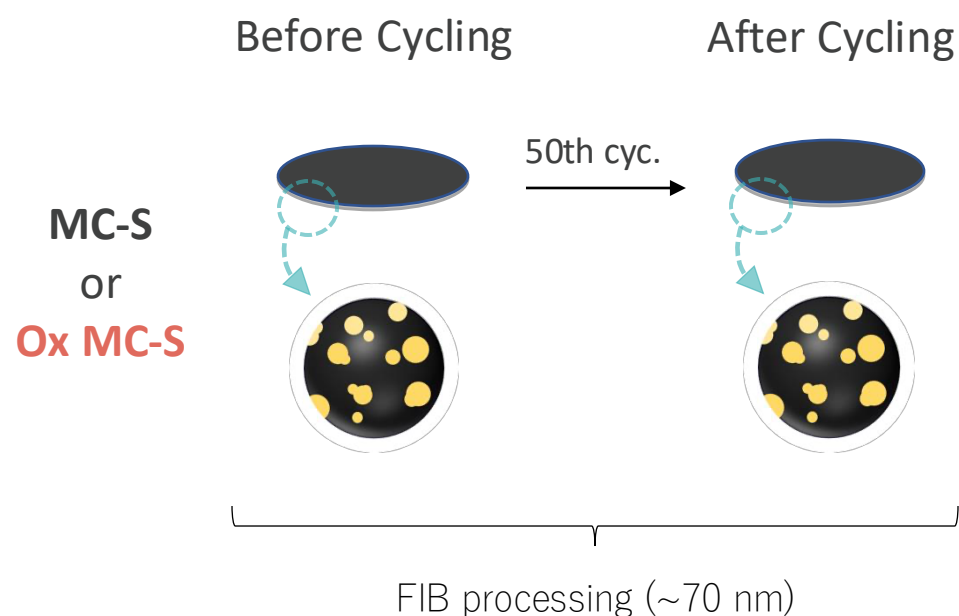
Surface oxidation of microporous carbon can actually control electrolyte affinity and suppress electrolyte decomposition.

So, are there oxygen functional groups inside the micropores? If so, what role do they play?



Internal observation of carbon-sulfur composite particles using STEM-EELS

Electrolyte: LiTFSI: G4: HFE = 10: 8: 40 (by mol)

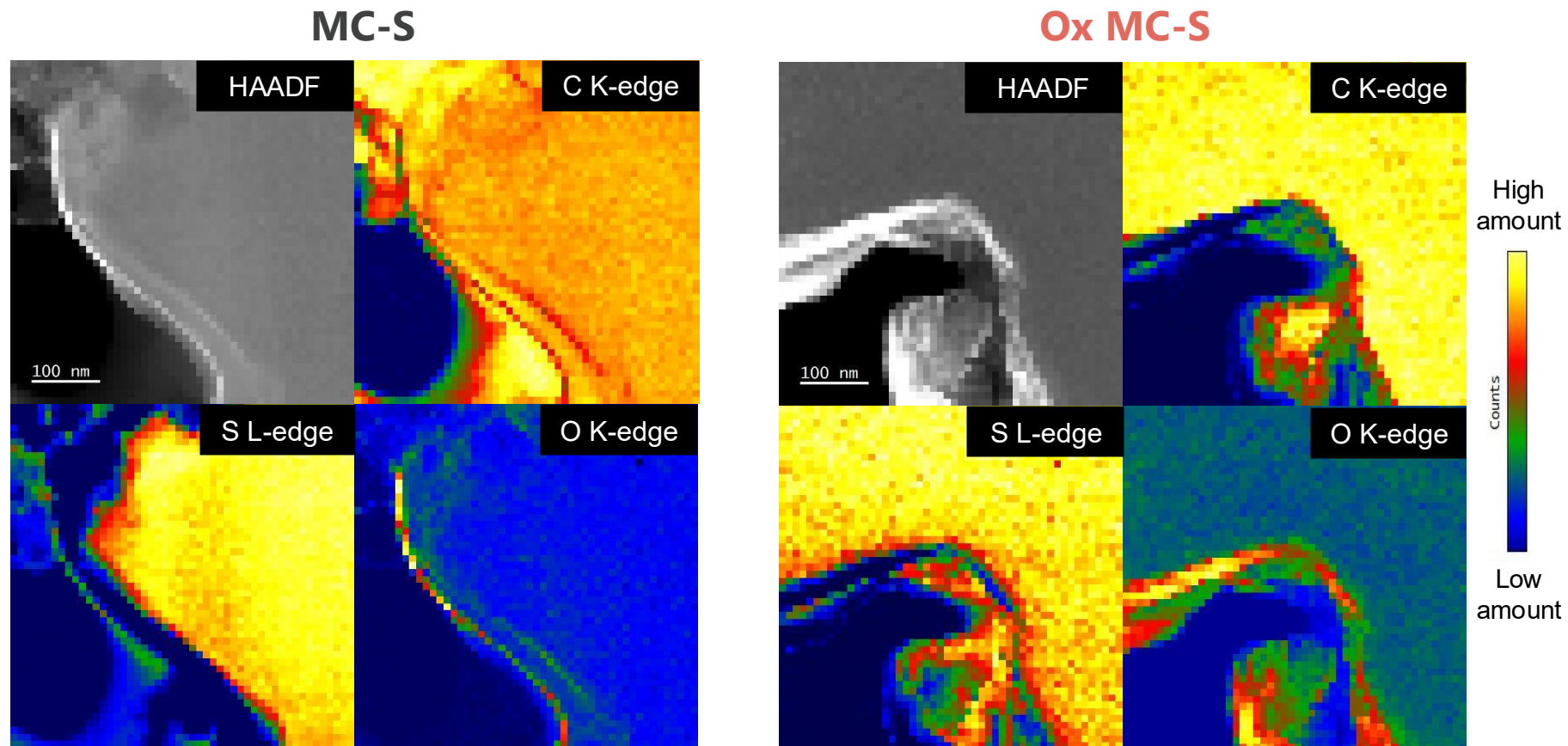


STEM-EELS observation of the above four samples was used to understand...

Influence of oxygen functional groups in carbon particles on cathode material behavior

Observation of the Internal Elemental Distribution of C–S Composite Particles by STEM–EELS

[EELS (Before Cycling)]

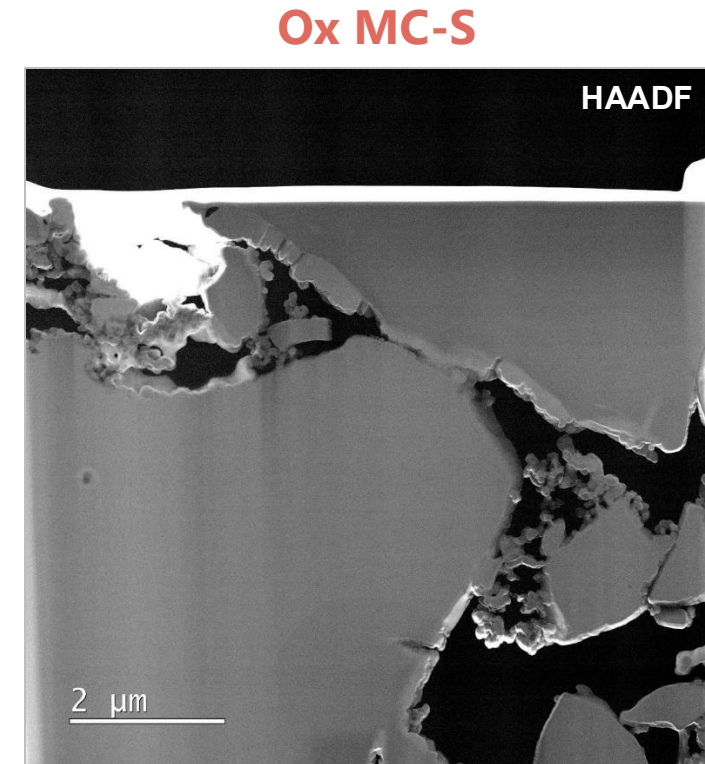
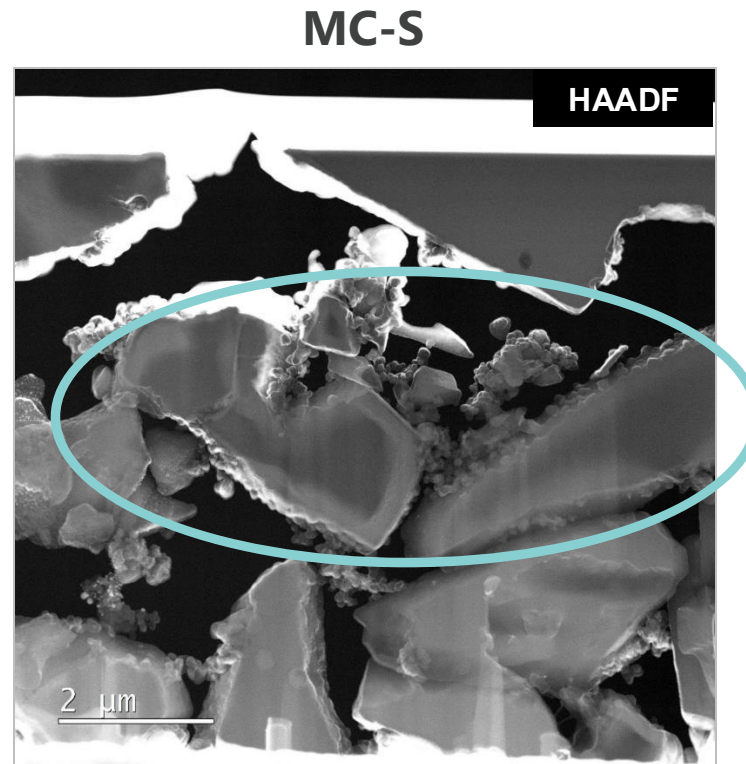


Sulfur was uniformly distributed regardless of the oxidation treatment.

Oxidation treatment increases the oxygen content inside the particles, that is, within the pores.

【STEM (After Cycling)】

Acc. V : 200 kV

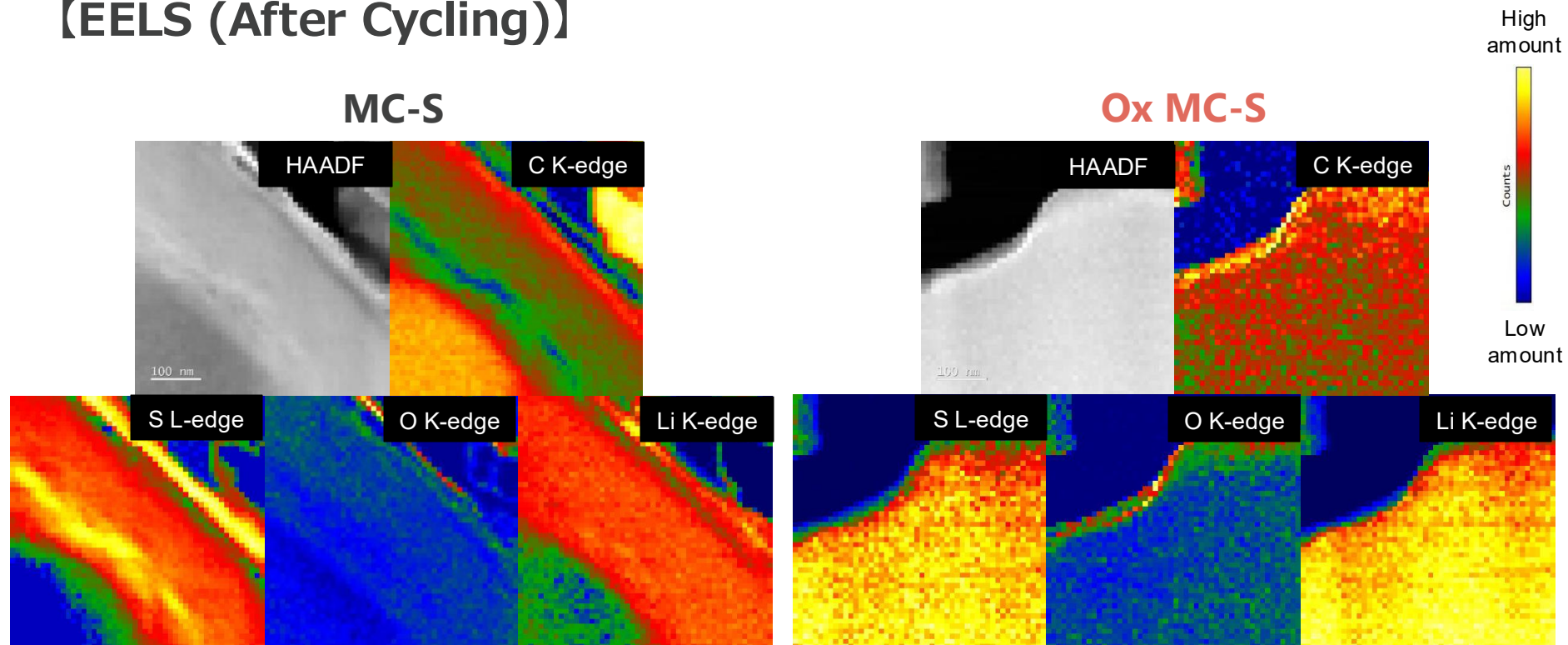


MC-S shows contrast inside the particle...

Light area suggests localization of heavier elements near particle surfaces, likely S relative to C

Observation of the Internal Elemental Distribution of C–S Composite Particles by STEM–EELS

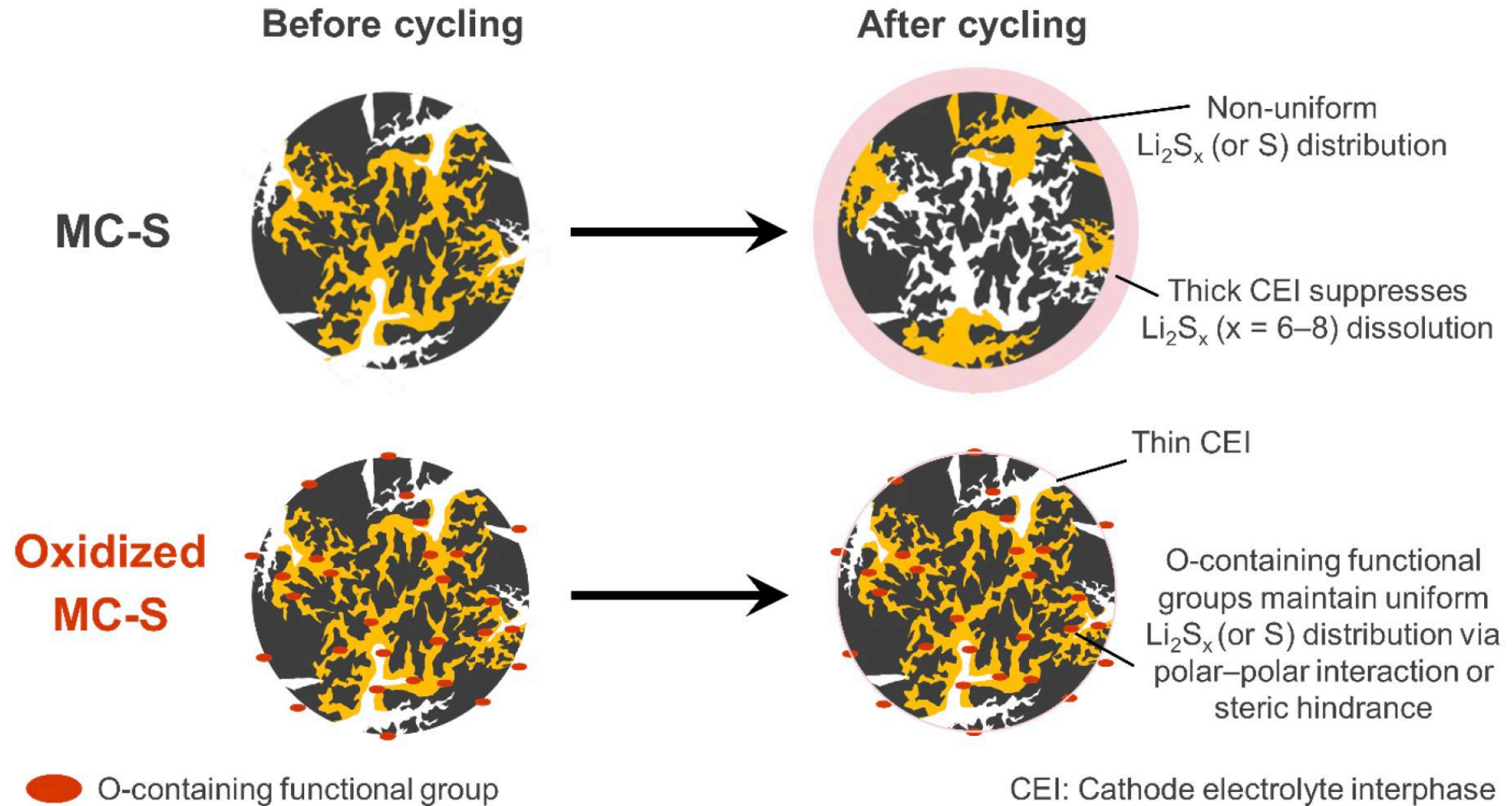
【EELS (After Cycling)】



Without oxidation, S or Li_2S_x moves and concentrates near the particle surface after cycling

Ox MC-S shows no elemental segregation within the particles...

Oxygen functional groups inside the particles suppress the migration and segregation of S or Li_2S_x



Oxidized AC-S cathode enables cycling with sulfur species uniformly retained in the pores.

Development of Lightweight, Compact, High-Capacity Batteries

R&D Project Title : Development of **lithium-sulfur batteries** with low environmental impact and high performance

Project Leader : Masashi Ishikawa
Professor, Department of Chemistry and Materials Engineering,
Faculty of Chemistry, Materials and Bioengineering, Kansai University

R&D Team : Kansai Univ, Yokohama National Univ, Keio Univ, Kyushu Univ, Waseda Univ, Hokkaido Univ, AIST, Niigata Univ, Japan Atomic Energy Agency, Kyoto Univ, Univ of Hyogo (11 org.)



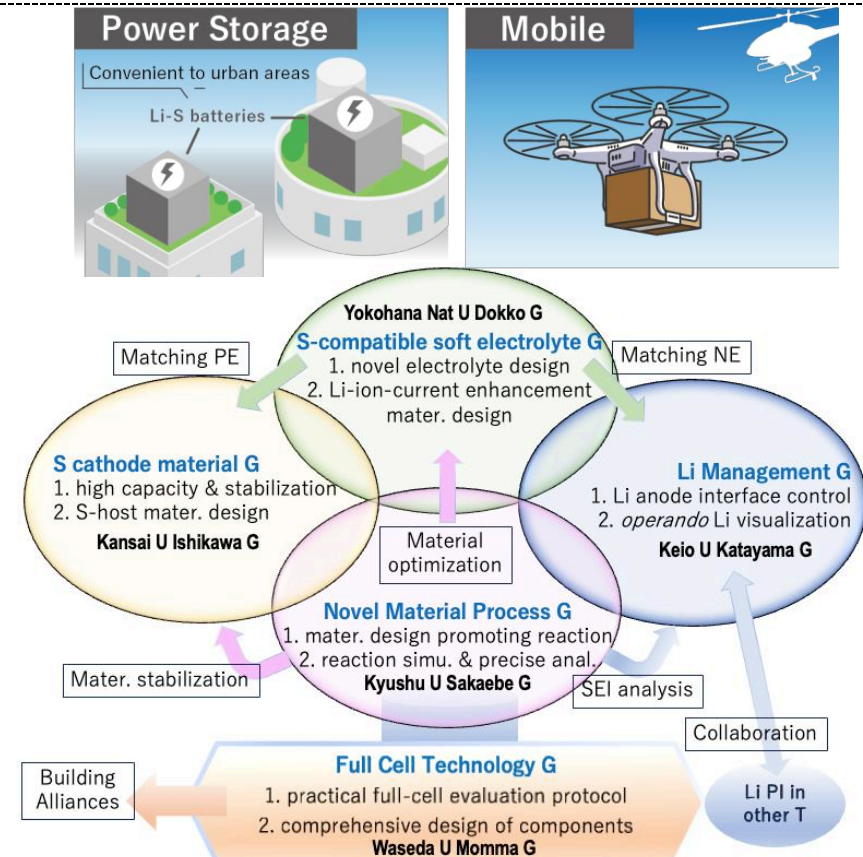
Summary :



The aim is to develop a **room-temp. operating lithium-sulfur (Li-S) battery** that uses a soft electrolyte such as an ionic solution to achieve a long life and high energy density twice that of current LIBs.

This battery is theoretically the lightest sealed battery available, and will enable **power storage in various locations**, such as on building rooftops and in homes. This will encourage the introduction of renewable electricity and contribute to the reduction of greenhouse gases. Another application is **power supply for drone and electric aircraft**.

The cathode requires virtually no rare metals, and its low environmental impact during production is also attractive. The world's most advanced R&D on Li-S is underway!



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Thank you for your attention 😊



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