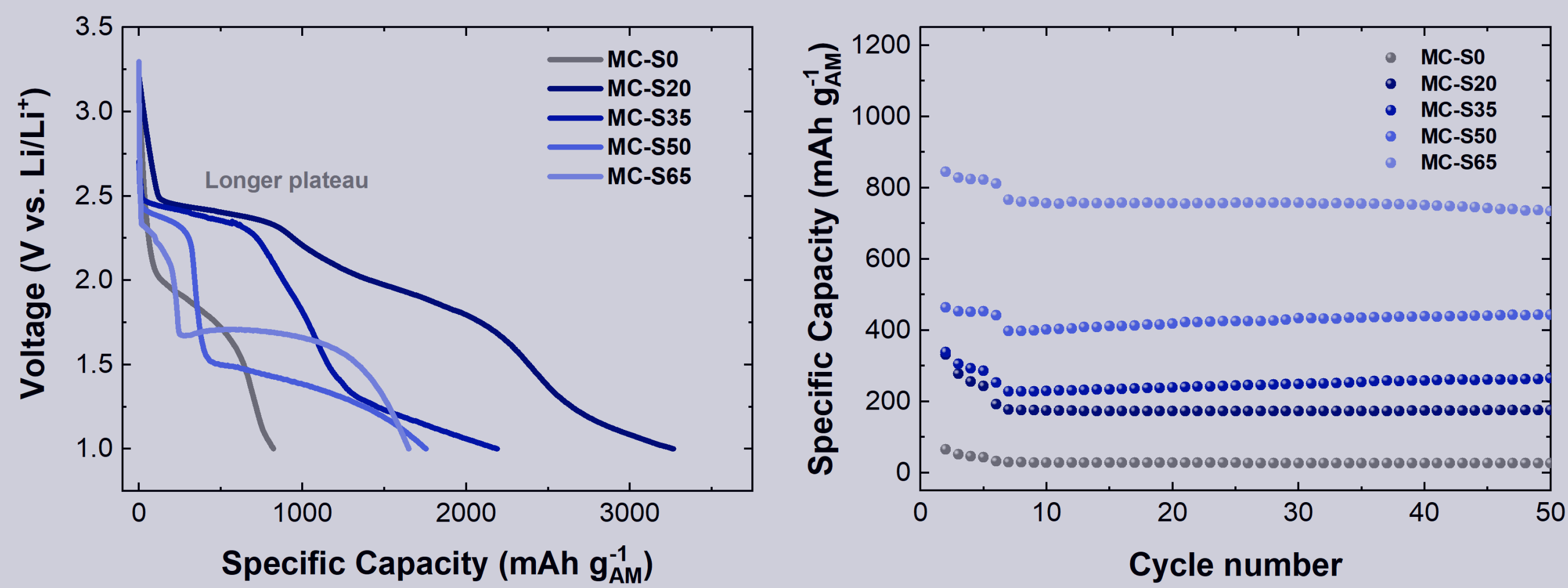


Decoding the First Discharge Plateau: CEI Formation in Li-S batteries & Carbonate-Based Electrolyte

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1. The Mystery

Puzzling Electrochemical Behavior



(Left) First discharge profile at C/20. (Right) Cycling stability at C/20 (cycles 2 to 5) and C/10 from cycle 6 onwards; Cathodes: MC-S:C65:PVDF (8:1:1) in C-coated Al foil (1 mg_S cm⁻²). Electrolyte: 20 ul mg_S⁻¹ 1M LiPF₆ DMC:FEC (4:1)

Observation:

Lower sulfur content → longer 2.4 V plateau

Higher sulfur content → Improved cyclability

Question 1:

Why does the **2.4V plateau** lengthen as the sulfur content **decreases**?

Question 2:

Why is this plateau **absent** in the bare carbon (MC-S0)?

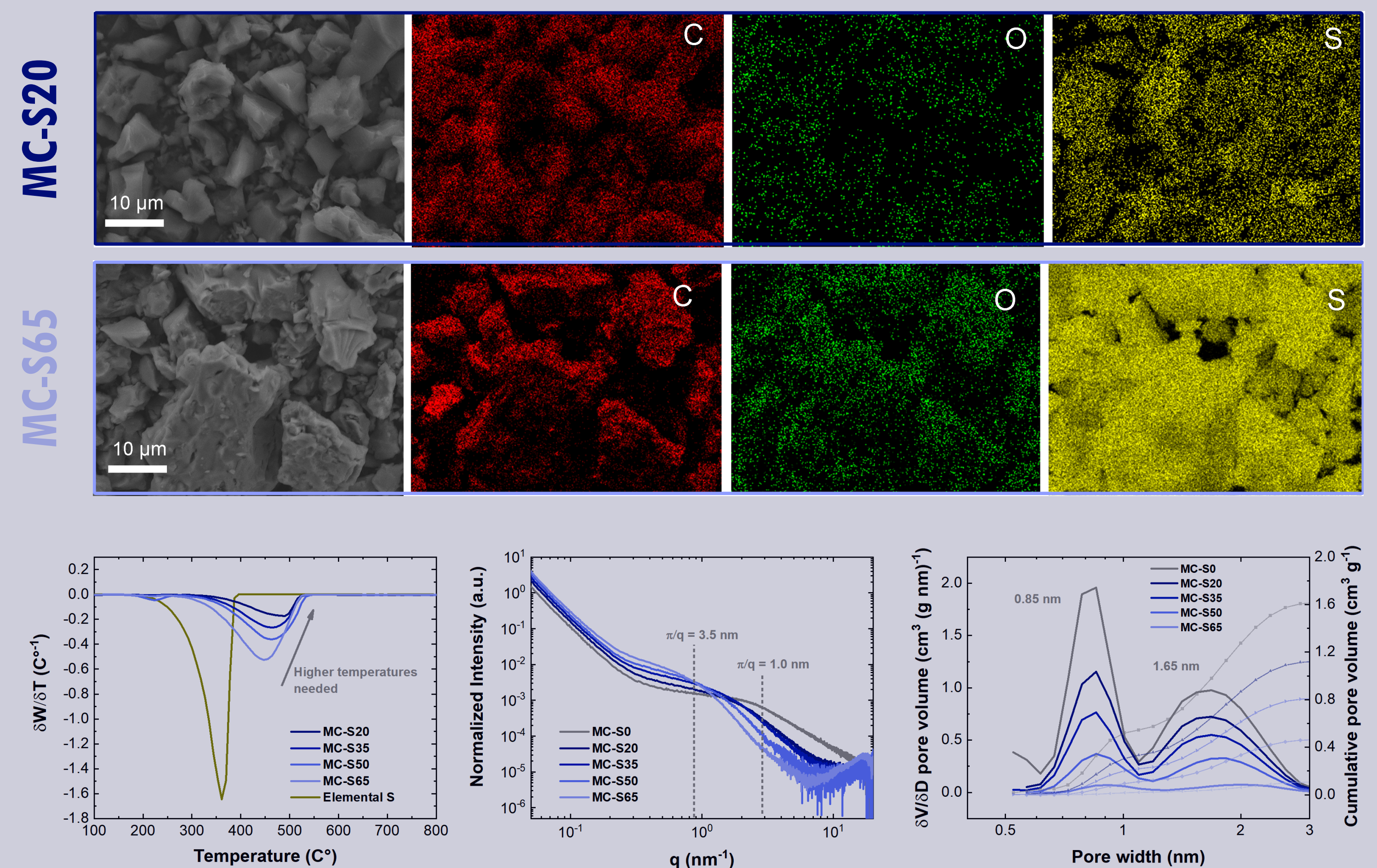
Question 3:

Plateau capacity > **209 mAh/g** exceeds PS formation limit. Are there other reactions?

Question 4:

Why does **MC-S65** show best cycling stability? (Opposite to ether-based systems!)

Carbon-Sulfur properties



✓ No external sulfur crystals:

TGA: no mass loss at 350°C - EDX: absence of localized sulfur enrichment

✓ Preferential filling of the 0.85 nm pores

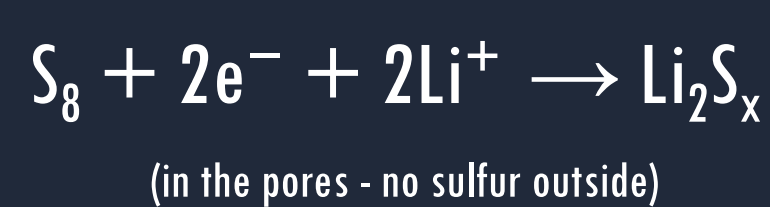
SAXS intensity analysis - GSA isotherms

2. The Solution

The Hidden Pathway: Electrochemical Nucleophilic Attack

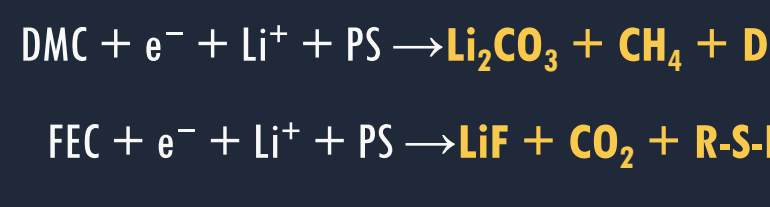
Step 1

Polysulfide Formation



Step 2

Nucleophilic Attack



Step 3

Pore Sealing

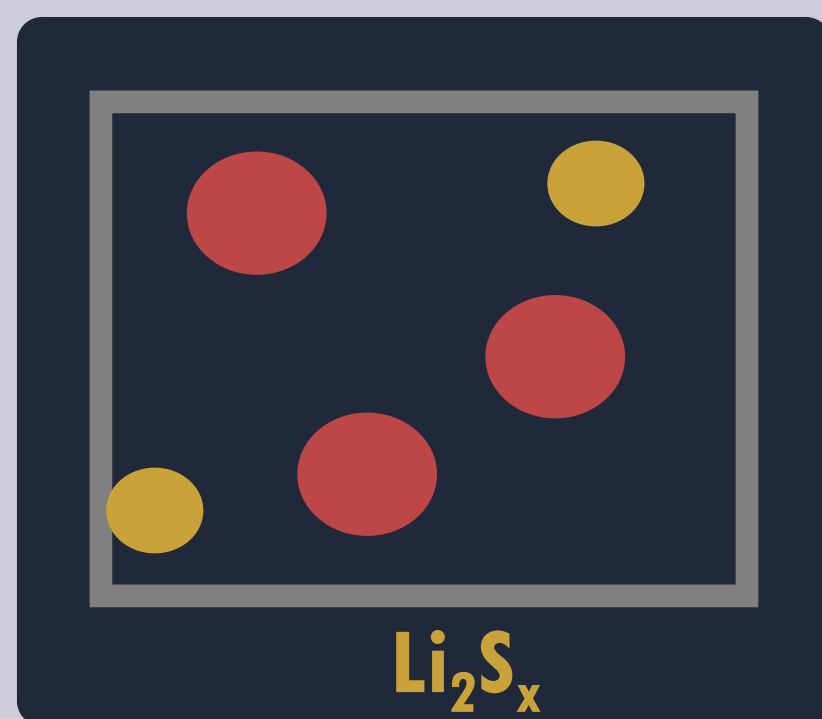
CEI Formation

LiF & Li₂CO₃ layer seals micropores
✓ Protects sulfur & Prevents dissolution

What Happens Inside the Micropores?



Before Discharge
S₈ + Electrolyte



At 2.4 V
PS + Electrolyte react



After CEI Forms
Sealed & Protected



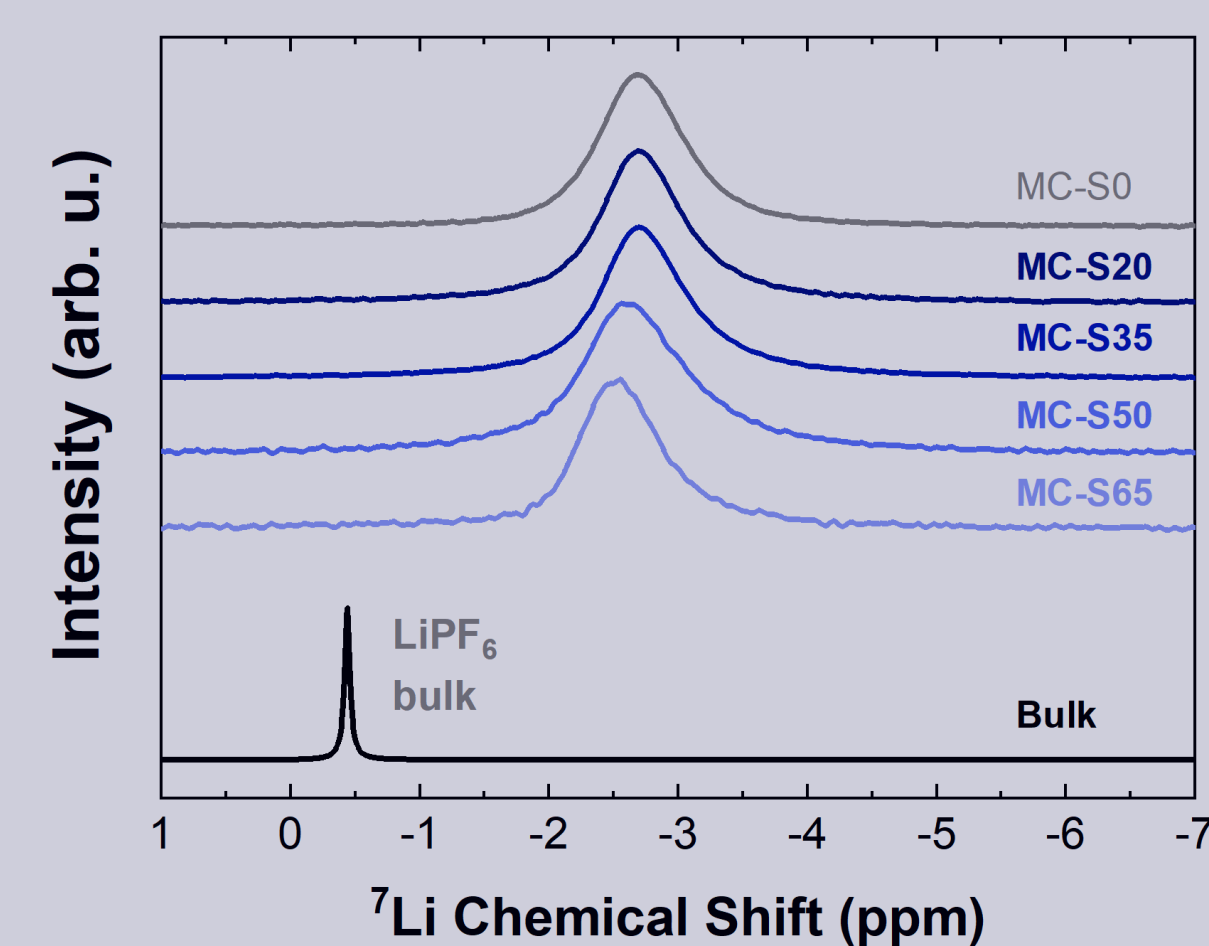
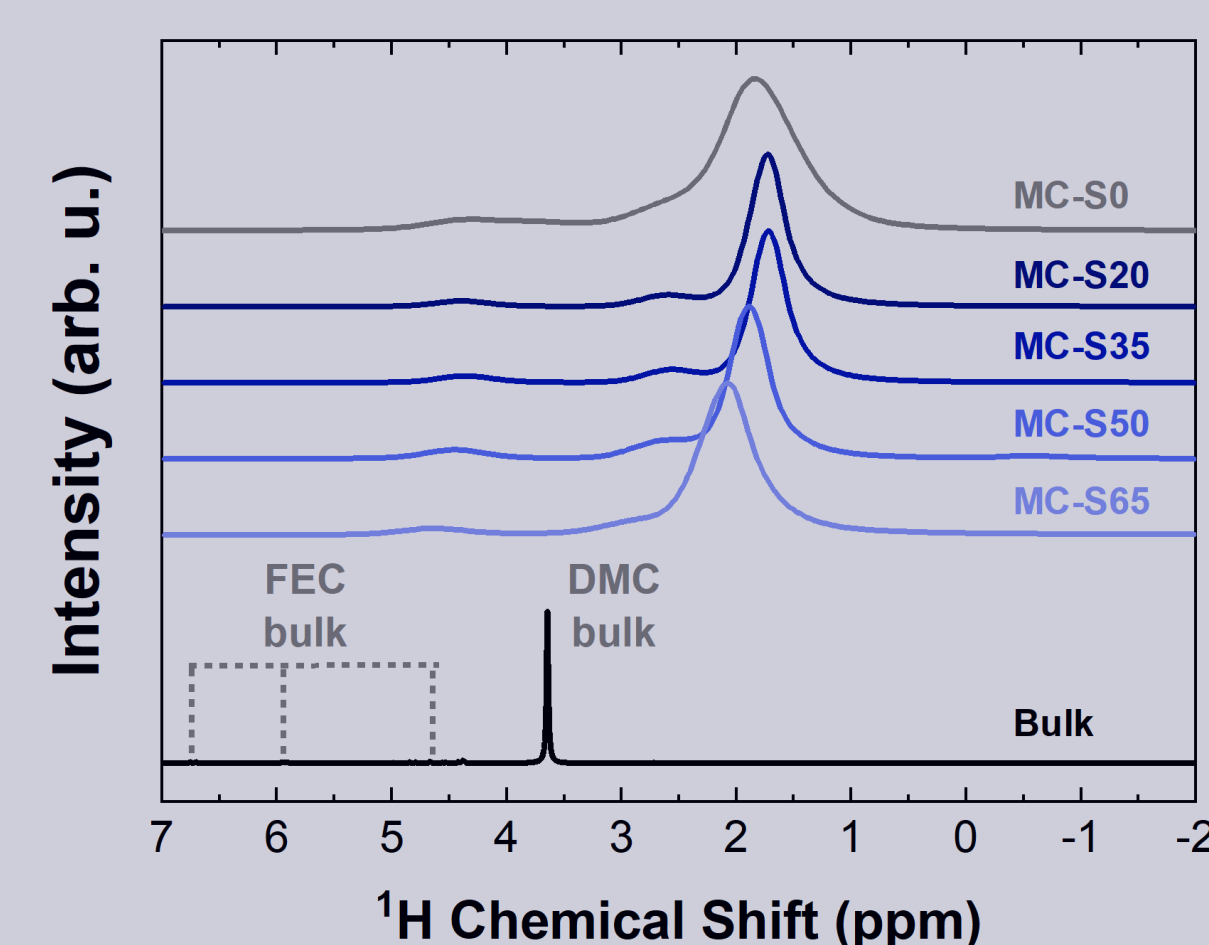
Key Innovation

Polysulfides act as **redox mediators**, enabling carbonate reduction at **2.4 V**

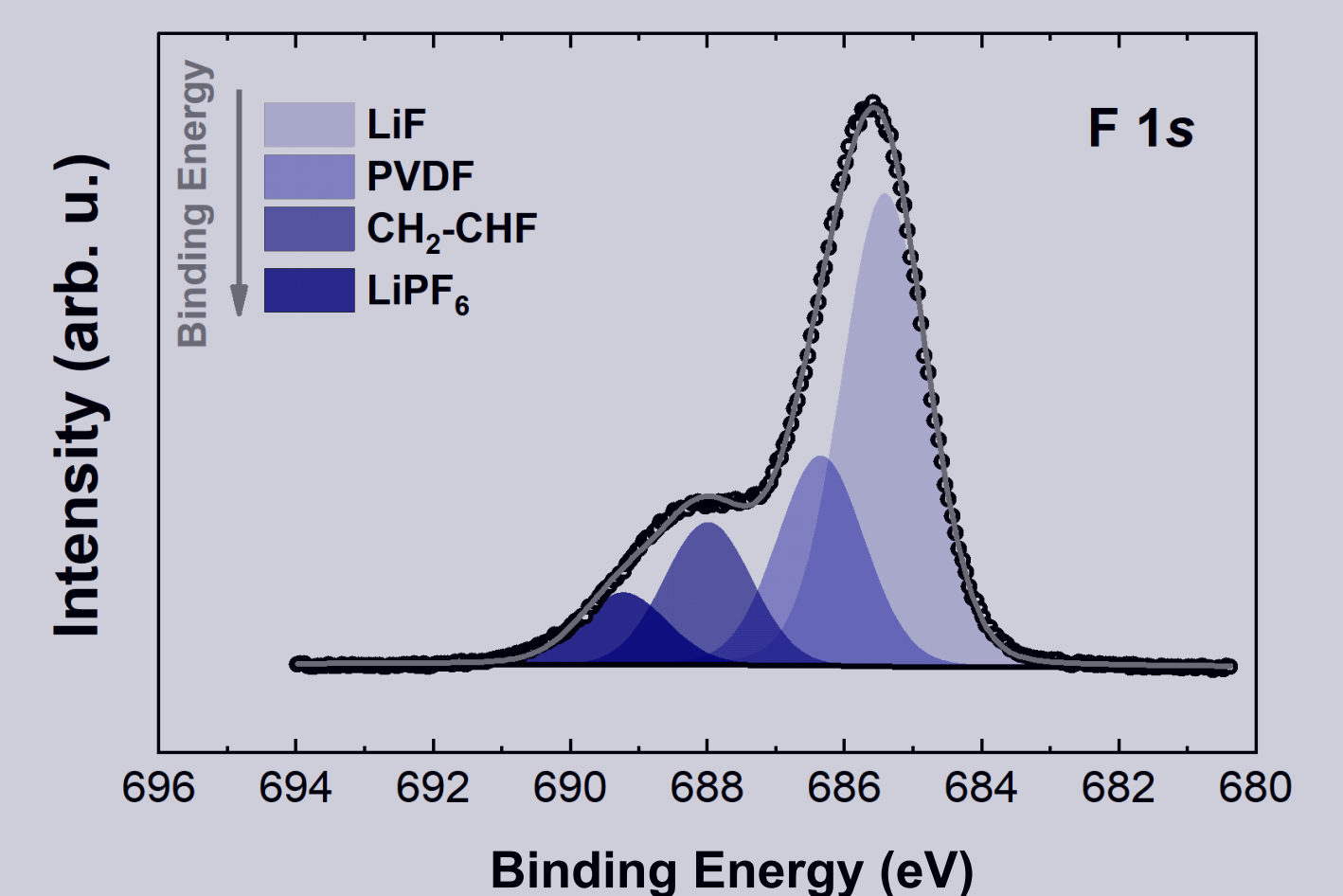
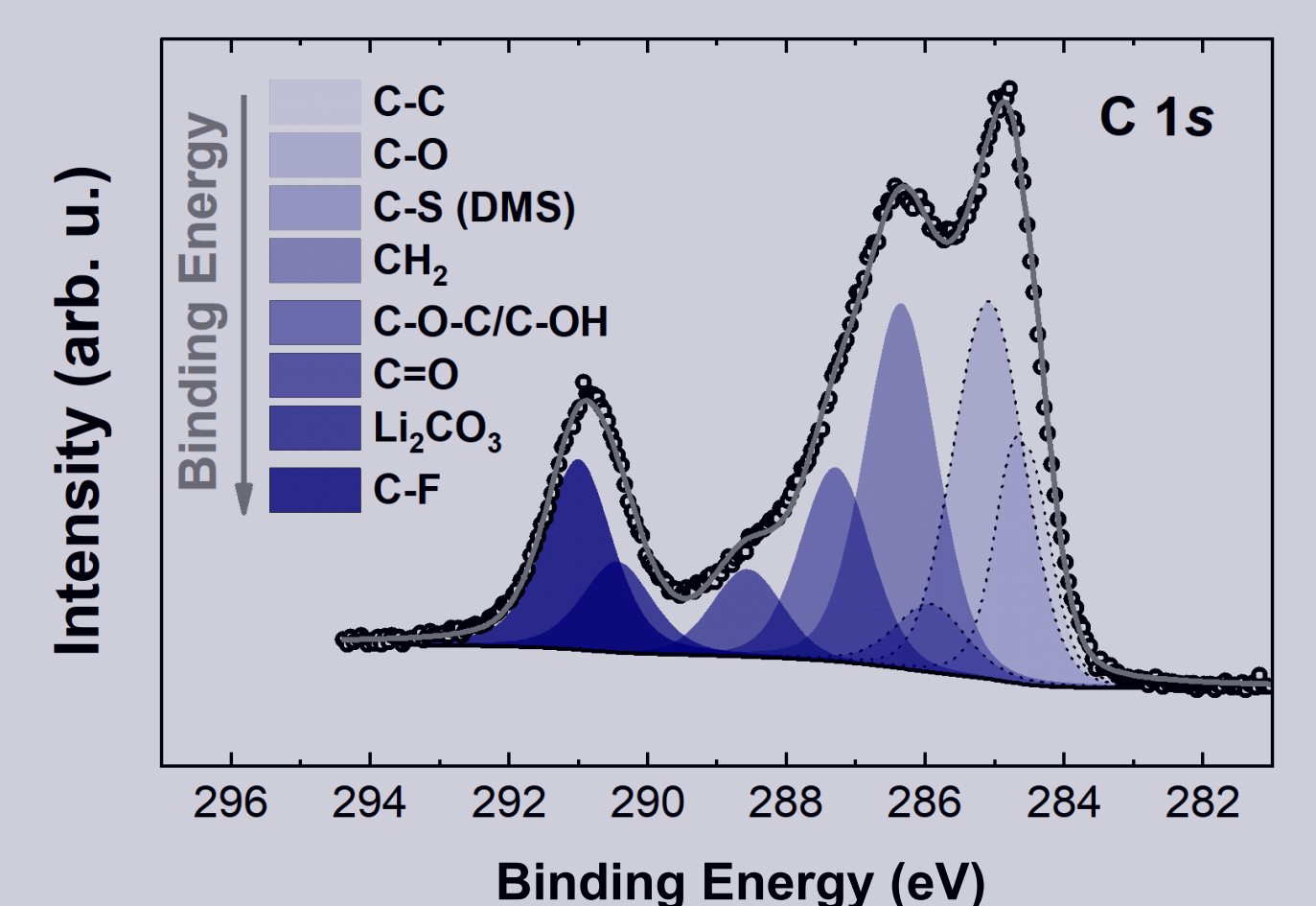
3. The Proof



NMR: Solvent in Pores



XPS: Chemical Proof (at 2.4 V)



✓ Chemical shift to lower ppm

✓ Shift increases with S loading

✓ Confinement of both ¹H and ⁷Li

Electrolyte **CAN** access micropores

✓ LiF detected at 685.4 eV

✓ Li₂CO₃ at 290.5 eV

✓ C-S bonds at 285.9 eV & 165.5 eV

Detection of the solid products

4. Answering the Questions

Q1: Why longer plateau at low S?

- More empty pore volume is accessible to electrolyte
- Greater surface area for reaction

Q2: Why absent in bare carbon?

- The reaction requires polysulfides as mediators
- No sulfur means no reaction

Q3: Why capacity > 209 mAh g⁻¹?

- Electrons are used for BOTH:
PS formation and solvent reduction

Q4: Why does MC-S65 perform best?

- The reaction is limited by accessible pore volume
- Higher pore volume enables the formation of a thicker CEI



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