



# Sulfur Cathodes with Self-organized Cellulose Nanofibers in Stable Ah-Level, $>300 \text{ Wh kg}^{-1}$ Lithium-Sulfur Cells

--Cellulose-based Binders for High-Energy Density Lithium-Sulfur Batteries

**Dr. Yingyi Huang**

**Applications Scientist at ENSERV Australia**

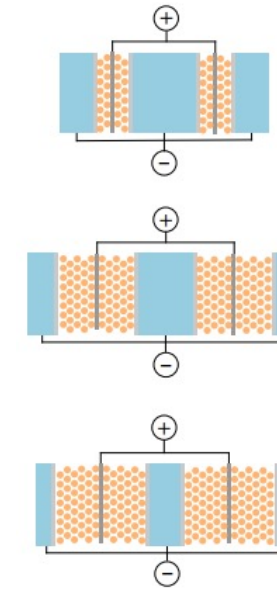
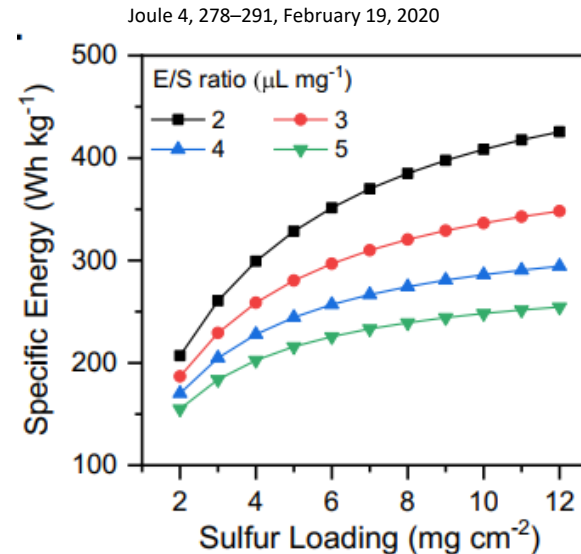
**29<sup>th</sup> October 2022**

# Sulfur cathode: Cheap and abundant with a large capacity to hold lithium but unstable

A lot of attention to “Polysulfides Shuttle”, little attention to “Mechanical Failure”

A simple estimation:

$$\begin{aligned} &\text{Li-ion} \quad \text{Li-S} \\ &3.5 \text{ mAh cm}^{-2} \times 3.7 \text{ V} \cong 6 \text{ mAh cm}^{-2} \times 2.10 \text{ V} \\ &1000 \text{ mAh g}^{-1} \times 6 \text{ mg cm}^{-2} \cong 6 \text{ mAh cm}^{-2} \\ &1400 \text{ mAh g}^{-1} \times 4.3 \text{ mg cm}^{-2} \cong 6 \text{ mAh cm}^{-2} \end{aligned}$$

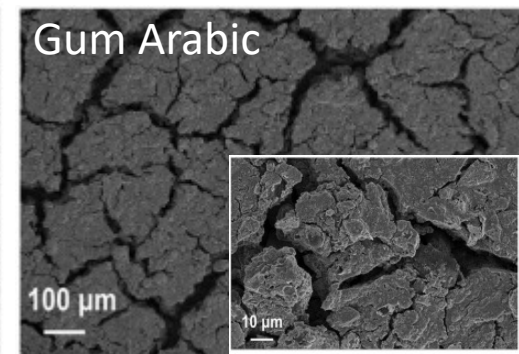
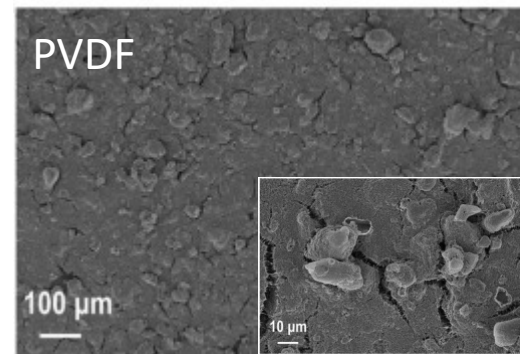


300 Wh kg<sup>-1</sup> Li-S battery  
 $m_{\text{sl}} \geq 4 \text{ mg cm}^{-2}$   
 $R_{\text{E/S}} \leq 2.7 \text{ } \mu\text{L mg}^{-1}$   
 $R_{\text{NP}} \leq 7$   
 $C_{\text{sulfur}} \geq 1,200 \text{ mAh g}^{-1}$

500 Wh kg<sup>-1</sup> Li-S battery  
 $m_{\text{sl}} \geq 10 \text{ mg cm}^{-2}$   
 $R_{\text{E/S}} \leq 2.4 \text{ } \mu\text{L mg}^{-1}$   
 $R_{\text{NP}} \leq 2.4$   
 $C_{\text{sulfur}} \geq 1,300 \text{ mAh g}^{-1}$

1,000 Wh kg<sup>-1</sup> Li-S battery  
 $m_{\text{sl}} \geq 12 \text{ mg cm}^{-2}$   
 $R_{\text{E/S}} \leq 1.2 \text{ } \mu\text{L mg}^{-1}$   
 $R_{\text{NP}} \leq 1.2$   
 $C_{\text{sulfur}} \geq 1,600 \text{ mAh g}^{-1}$

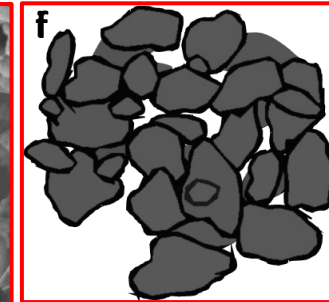
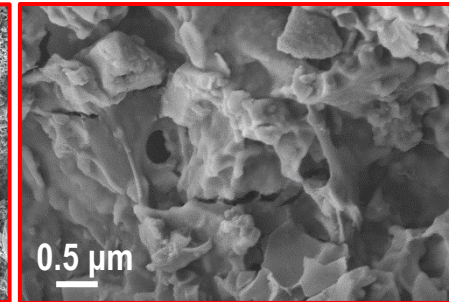
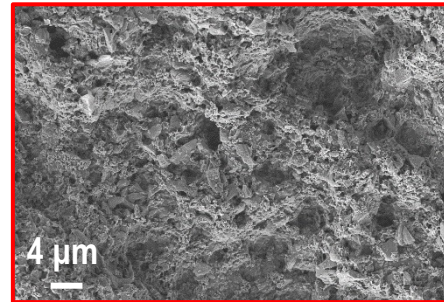
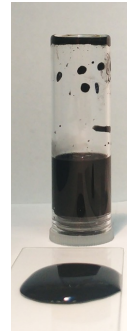
Fabrication of high-loading sulfur cathodes is a challenge itself!



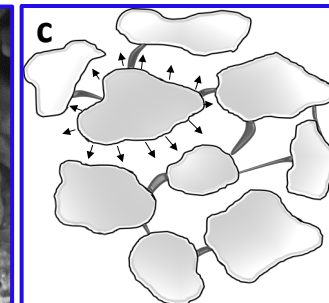
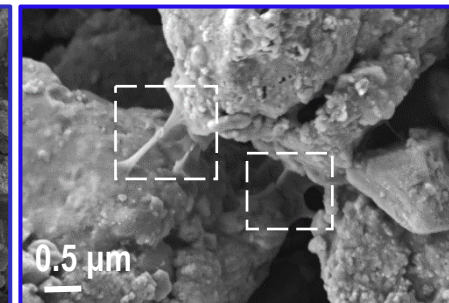
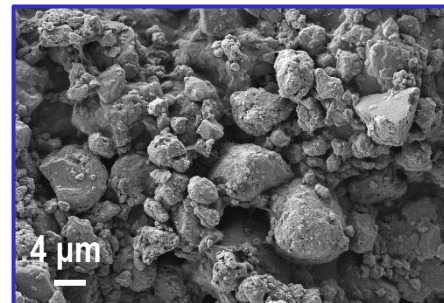
# Fabrication of Expansion-tolerant (ET) Cathodes using Prevalent Constituents

Controlling the dispersion of Carboxymethyl cellulose (CMC) binder enables the formation of mechanically strong bridging bonds between the particles, producing a unique segregated structure.

Wet mixing of C/S in a pre-dissolved CMC solution to form a slurry



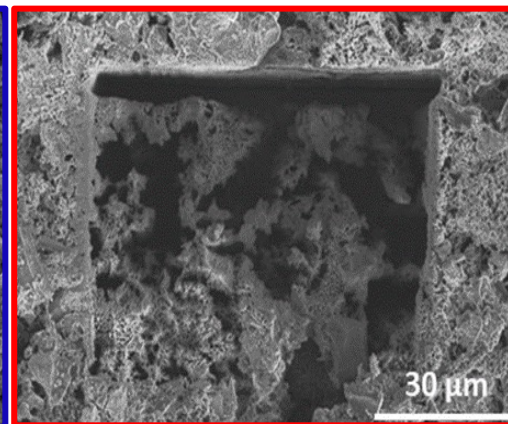
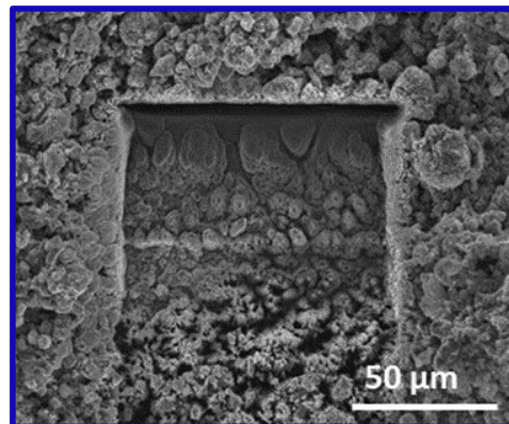
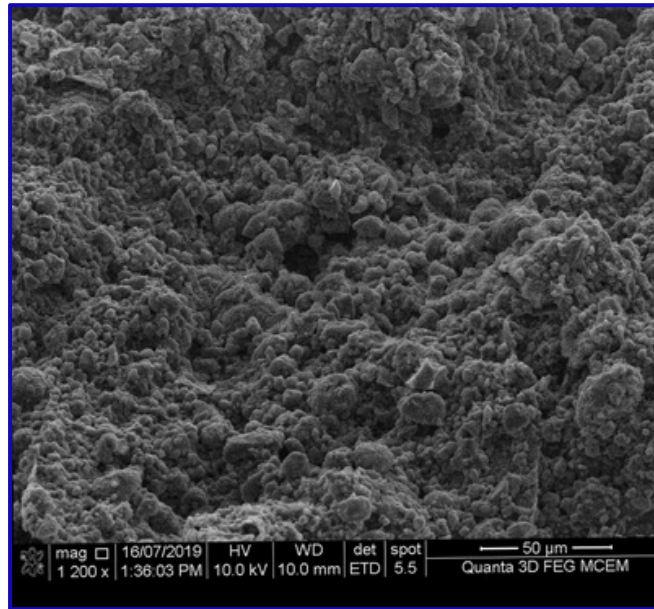
Dry mixing of all ingredients and minimal addition of water to obtain a castable paste



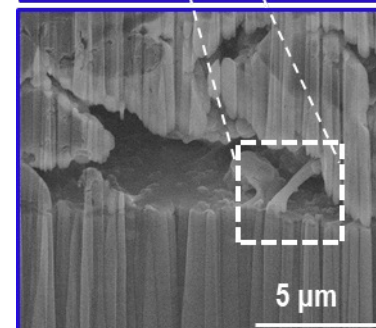
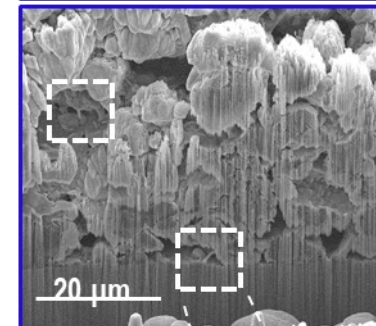
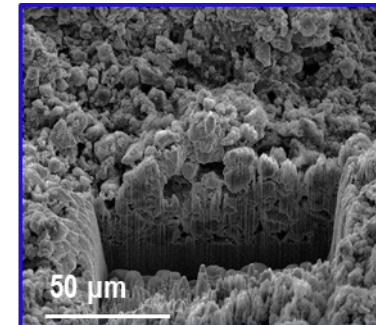
Bridging mechanism links the neighboring particles without covering them unduly, imparting:

- i. a high degree of freedom to the particles to expand,
- ii. an unimpeded collection of electrons,
- iii. and a facilitated uptake of the electrolyte.

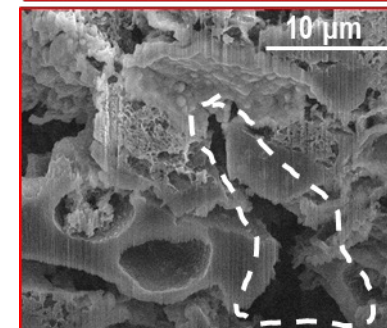
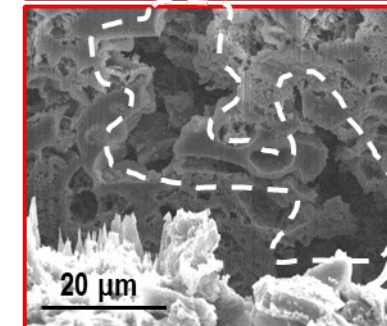
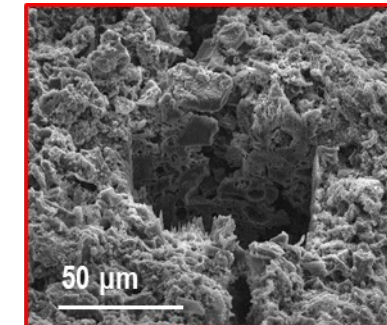
# After Cycling Observation of Cathodes – FIB Milling



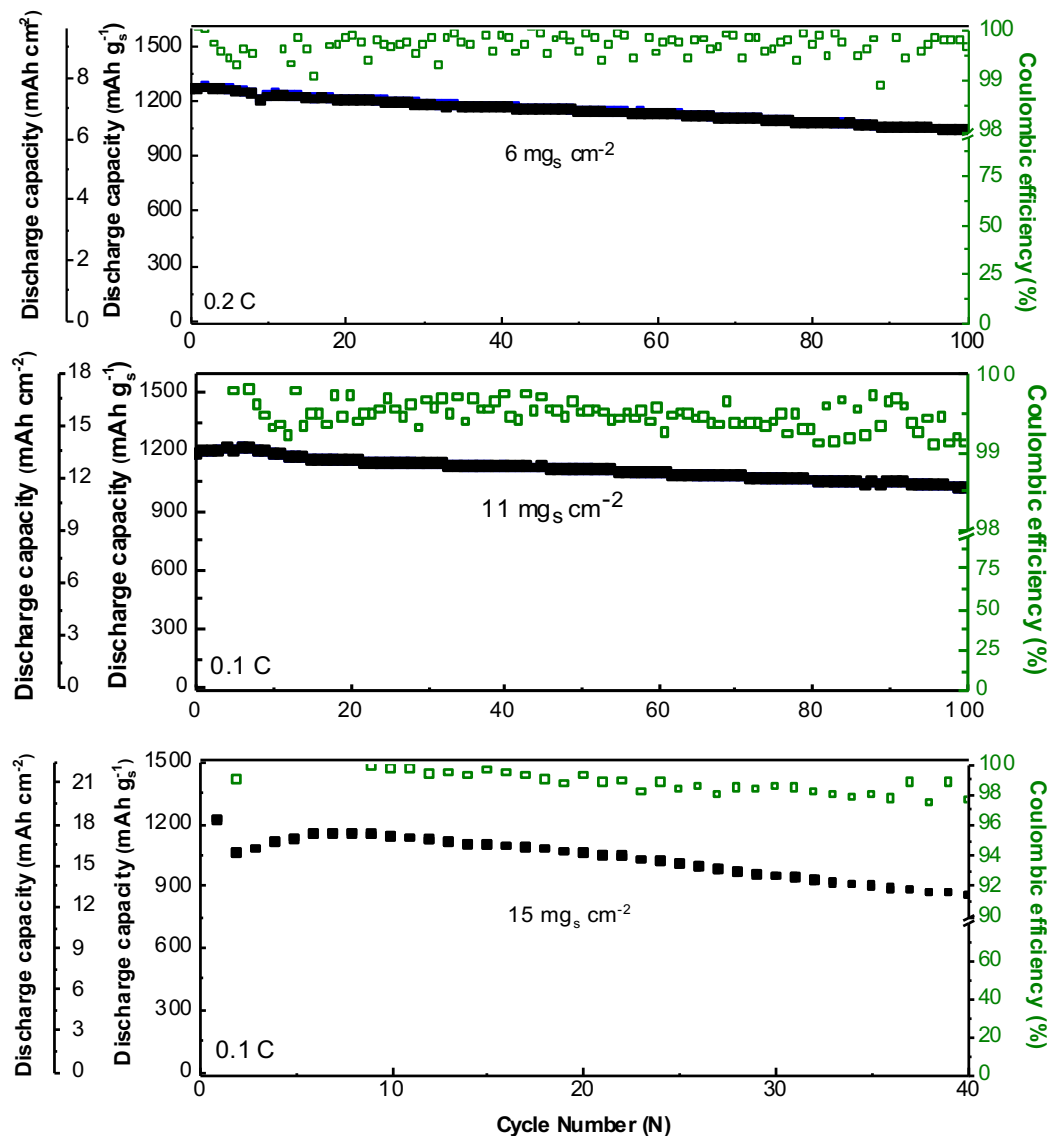
Dry mixing



Wet mixing

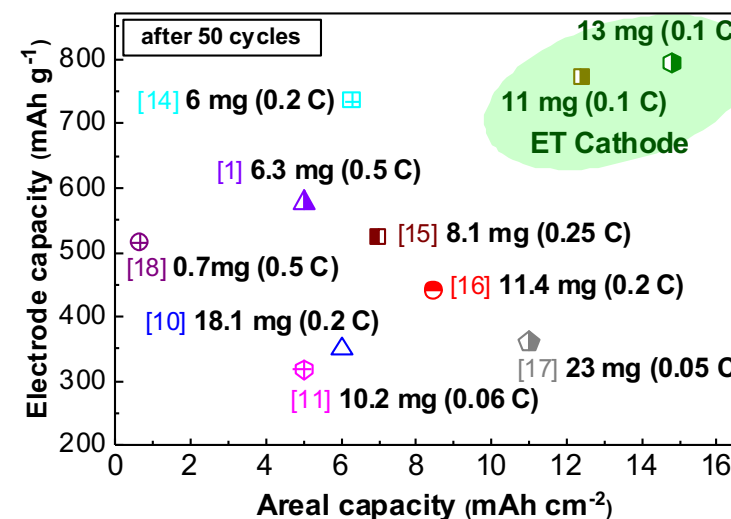


# Cycling Performance of our Thick Cathodes

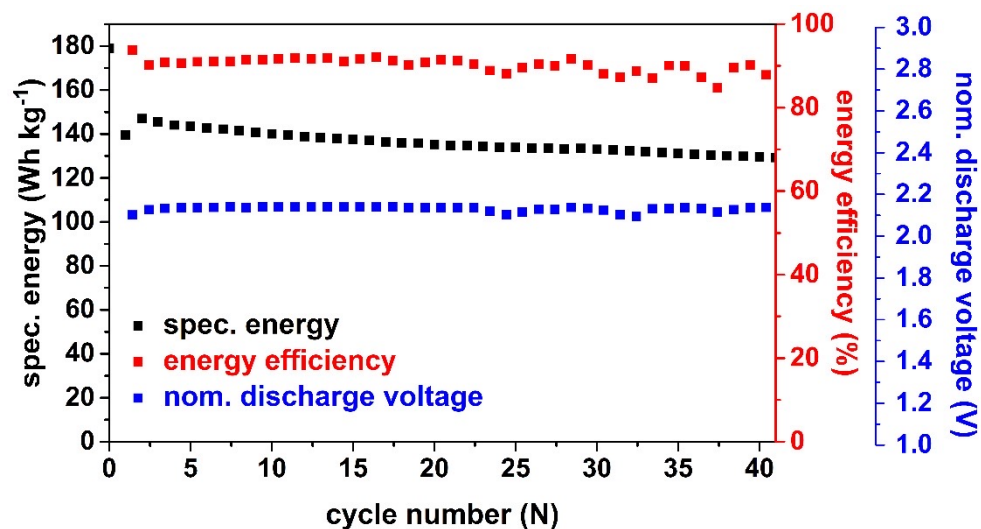
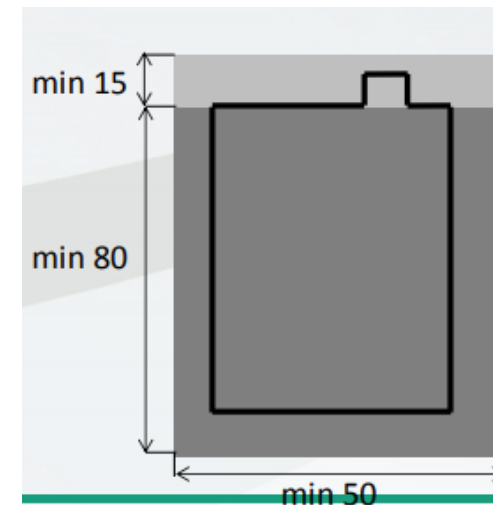
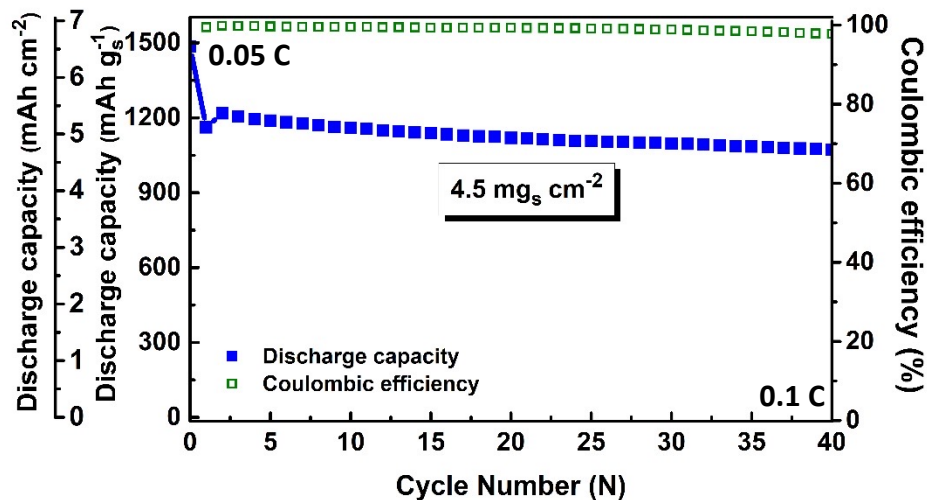


The expansion-tolerant architecture effectively:

- ✓ removes much of the cycling stress, and
- ✓ at the same time minimizes the limitations that conventionally deployed binders place on electronic conductivity and ion transport:
- ✓ the partial/full particle coverage with binder is minimised and,
- ✓ carbon pore filling with the binder solution is prevented.



# Translating Coin Cell to Pouch Cell in Collaboration with Fraunhofer IWS



# Glucose can help soil retain sulfur compounds

**Advances in Organic Geochemistry 1987**

*Org. Geochem.* Vol. 13, Nos 4–6, pp. 1087–1091, 1988

Printed in Great Britain

## Interaction of glucose and cellulose with hydrogen sulphide and polysulphides

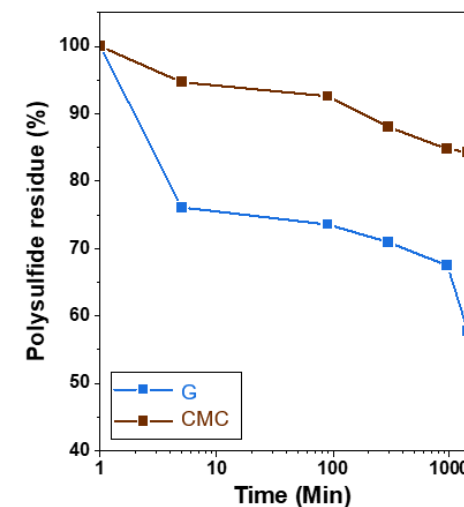
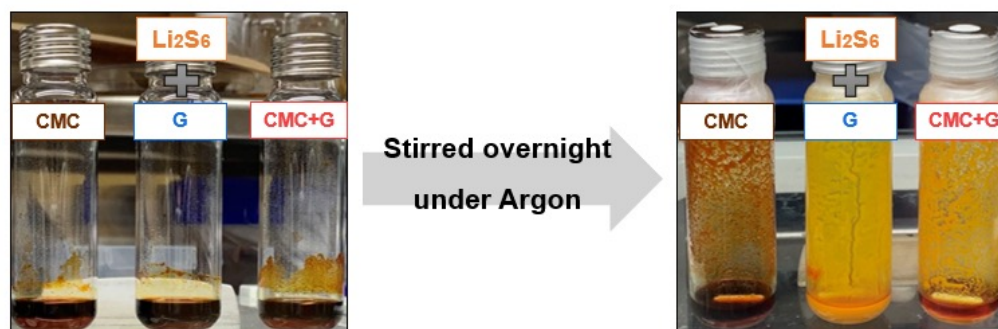
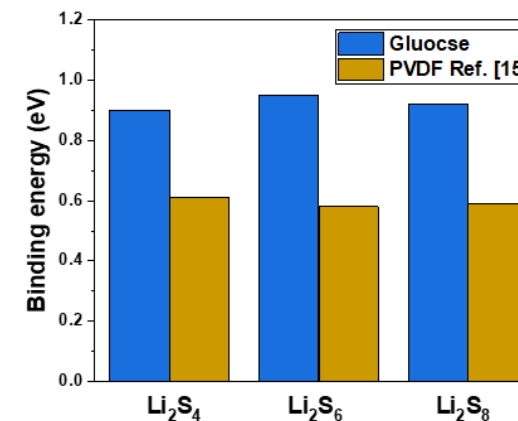
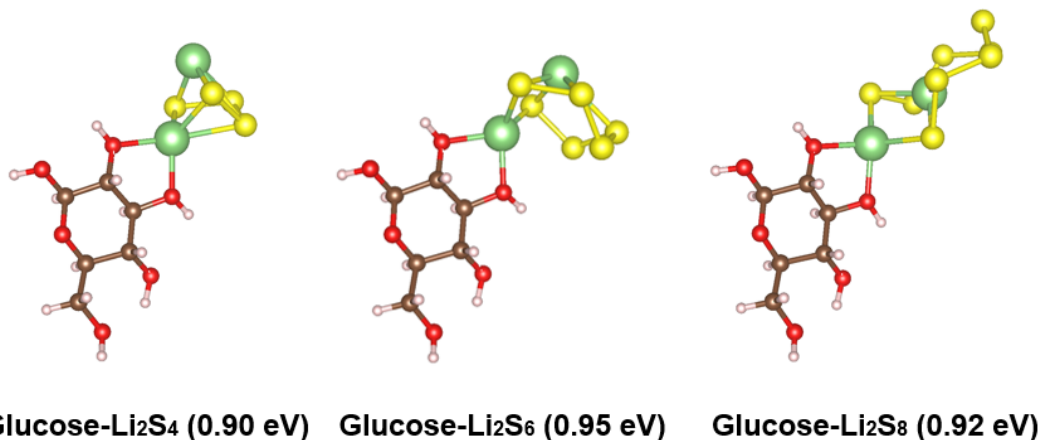
M. E. C. MOERS, J. W. DE LEEUW, H. C. COX and P. A. SCHENCK

Delft University of Technology, Organic Geochemistry Unit, de Vries van Heystplantsoen 2,  
2628 RZ Delft, The Netherlands

**Abstract**—This paper describes simulation experiments in which glucose and cellulose were reacted with polysulphide and hydrogen sulphide at ambient temperatures in an aqueous environment. Organic sulphur containing compounds were formed that yield several thiophenes upon pyrolysis/evaporation. The experiments show that interaction of carbohydrates with hydrogen sulphide or polysulphides is a possible way for carbohydrates to react in very recent sediments. From the results of this study it can be concluded that carbohydrate carbon can be preserved in sediments in a form that is resistant to microbial attack and that will have a greater potential for survival during diagenesis than the carbohydrate precursor.



# Glucose can help with retarding the “shuttle” in Li-S battery



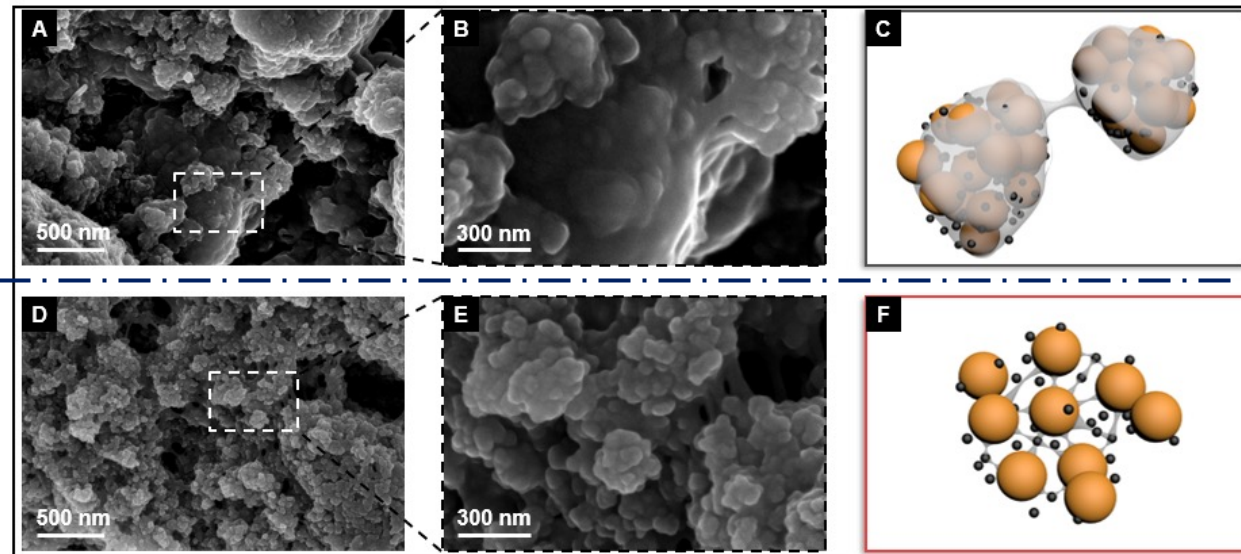
Illustrating the evolution of polysulfide in the presence of high concentrate lithium polysulfide

# Fabrication of mechanically robust cathode with a web-like architecture

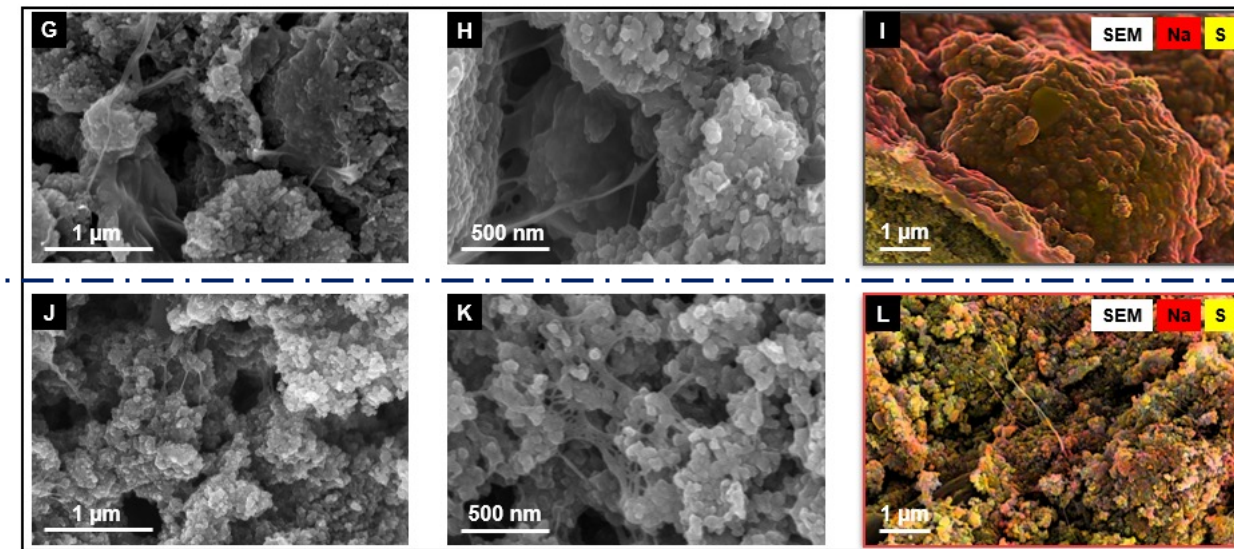
Pure CMC  
as binder

- ✓ Strong binding bridge
- × Limited sulfur exposure

- × Increased interfacial resistance
- × Instable bulky nonconductive phases



Top view



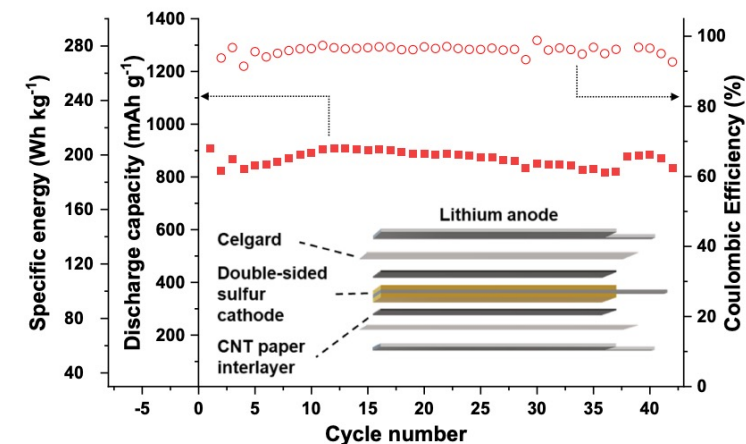
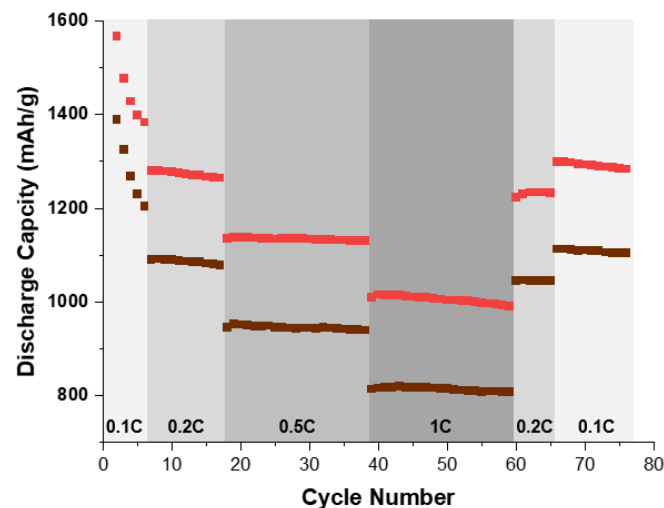
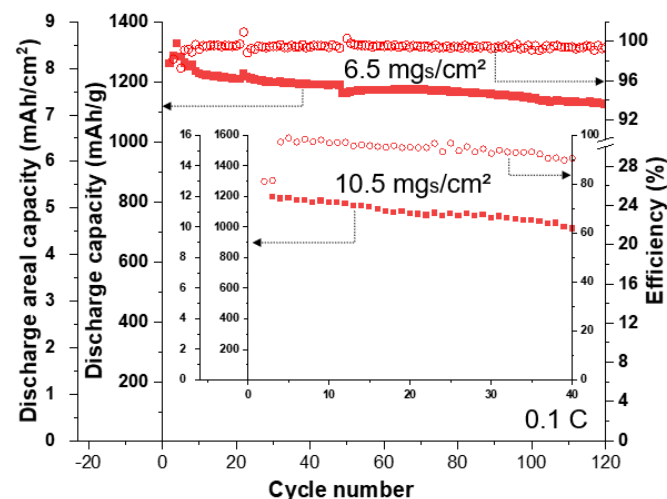
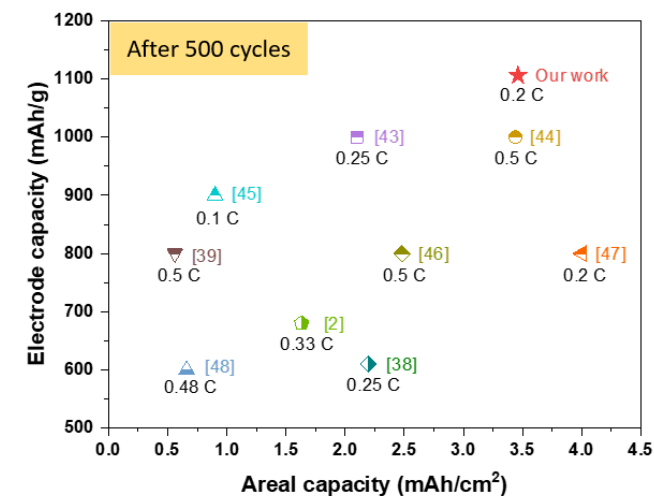
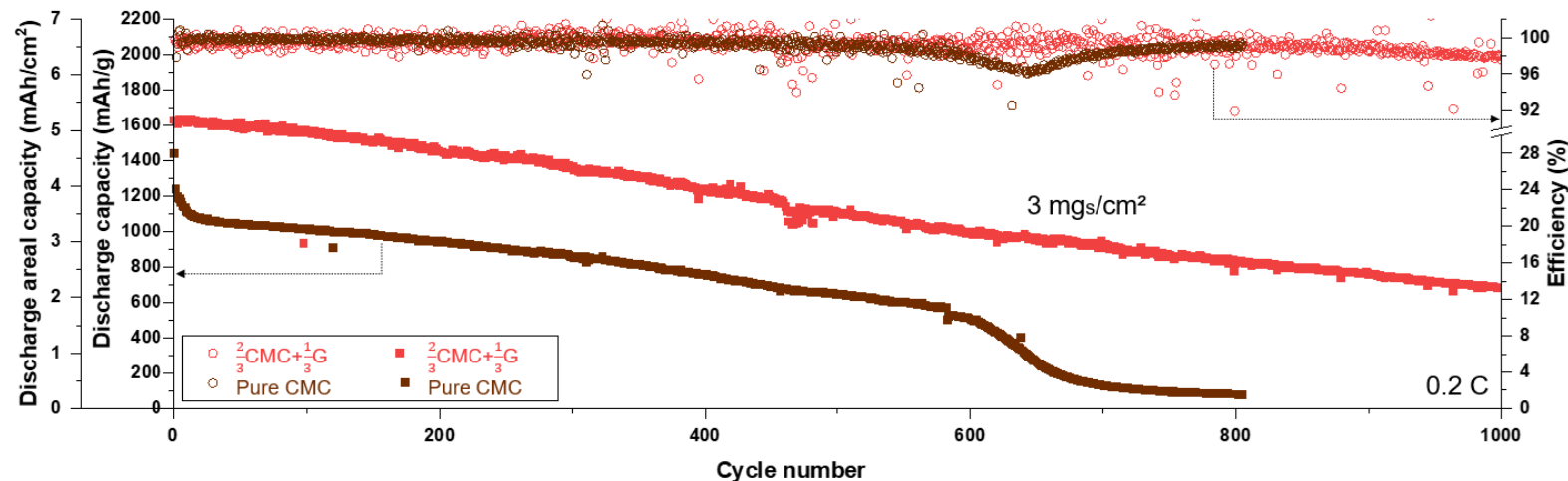
Cross-section

$\frac{2}{3}\text{CMC} + \frac{1}{3}\text{G}$   
as binder

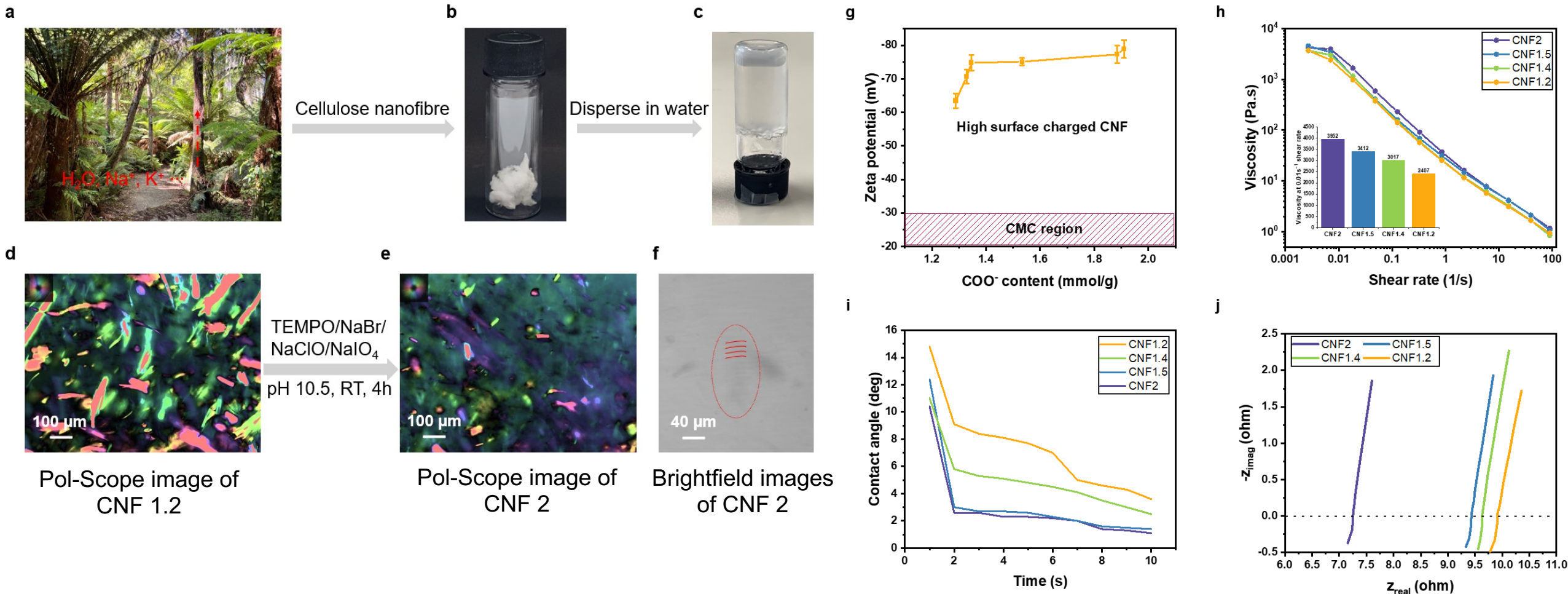
- × Relatively lower bonding strength
- ✓ Increased sulfur exposure

- ✓ Low-resistance internal pathways
- ✓ Enhanced electrolyte accessibility

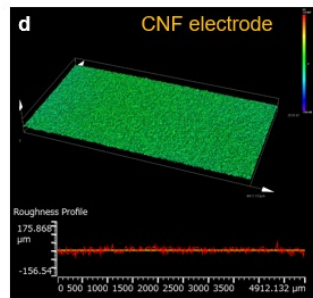
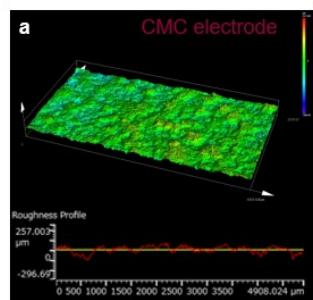
# Cycling performance at coin cell and pouch cell level



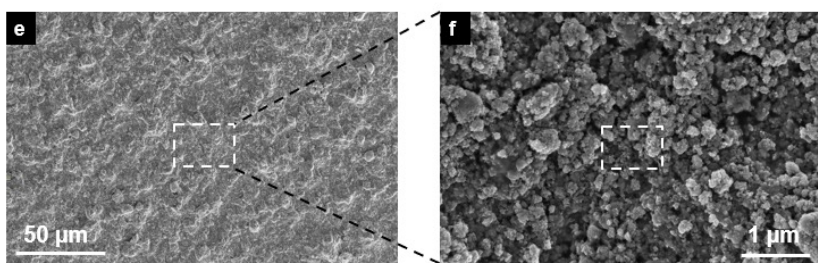
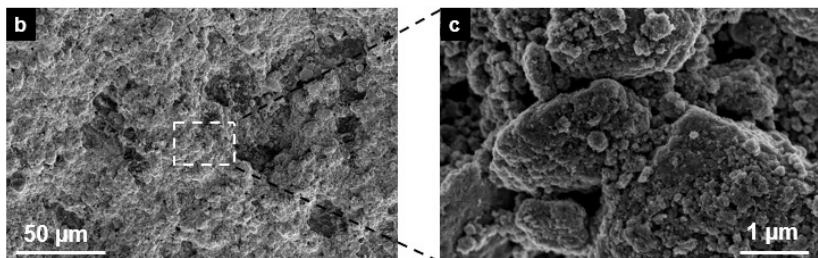
# Characterizations of cellulose nanofiber (CNFs) with different surface charges



# Morphology and architectonic study of cellulose nanofiber electrodes

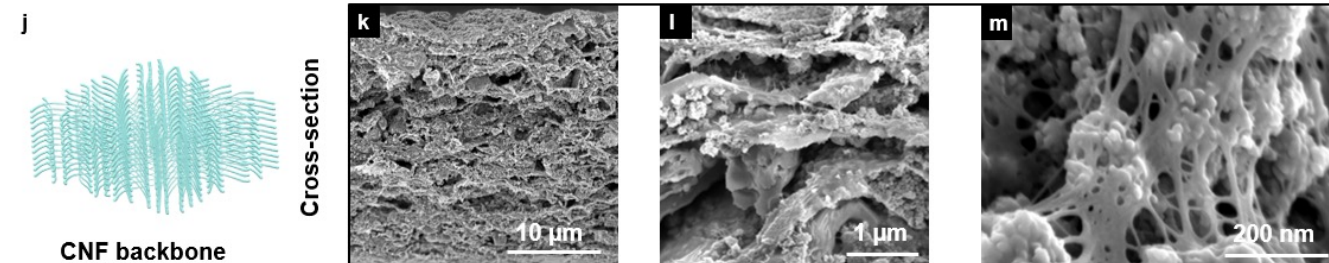
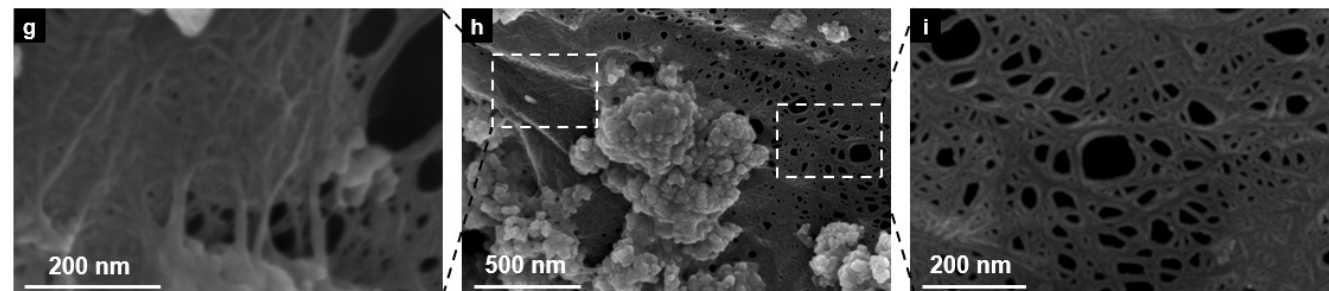


Profilometer examination



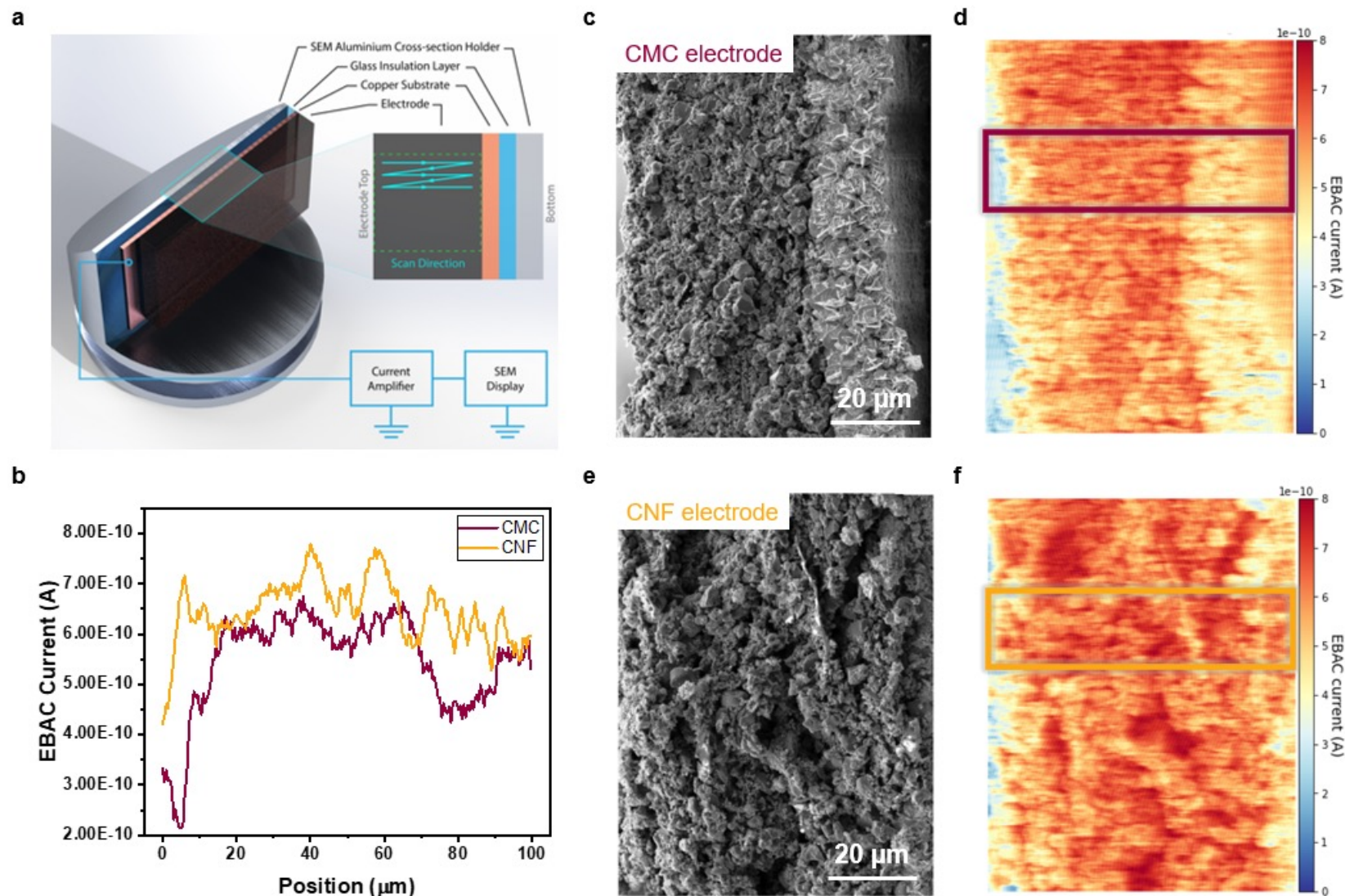
Top-view SEM images

Top-view SEM images of CNF electrodes

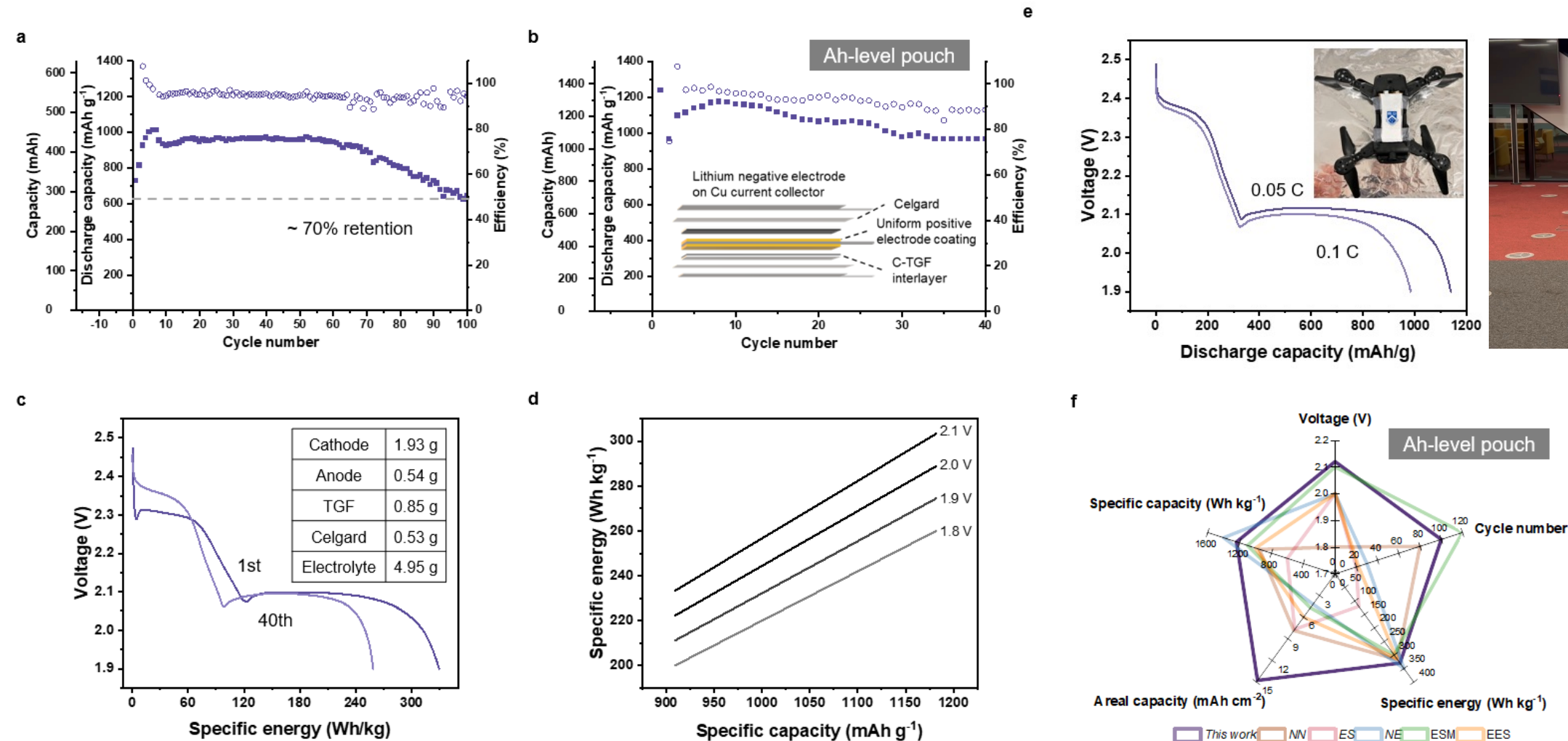


Cross-sectional SEM images of CNF electrodes

# Electron beam absorbed current (EBAC) test of sulfur cathode



# Pouch cell characterization





**R&D and Project Opportunities**

**Thank you for your attentions**