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# Lithiation/De-Lithiation of a Unique C-S Species in Amorphous $FeS_x$/C Cathodes for Li Batteries

Bryan R. Wygant, Igor V. Kolesnichenko, Noah B. Schorr, Katharine L. Harrison, Timothy N. Lambert

Sandia National Laboratories, Albuquerque, NM

Electrochemical Society Spring Meeting, A02-0387

Vancouver, BC, Canada

June 1, 2022

SAND# Here



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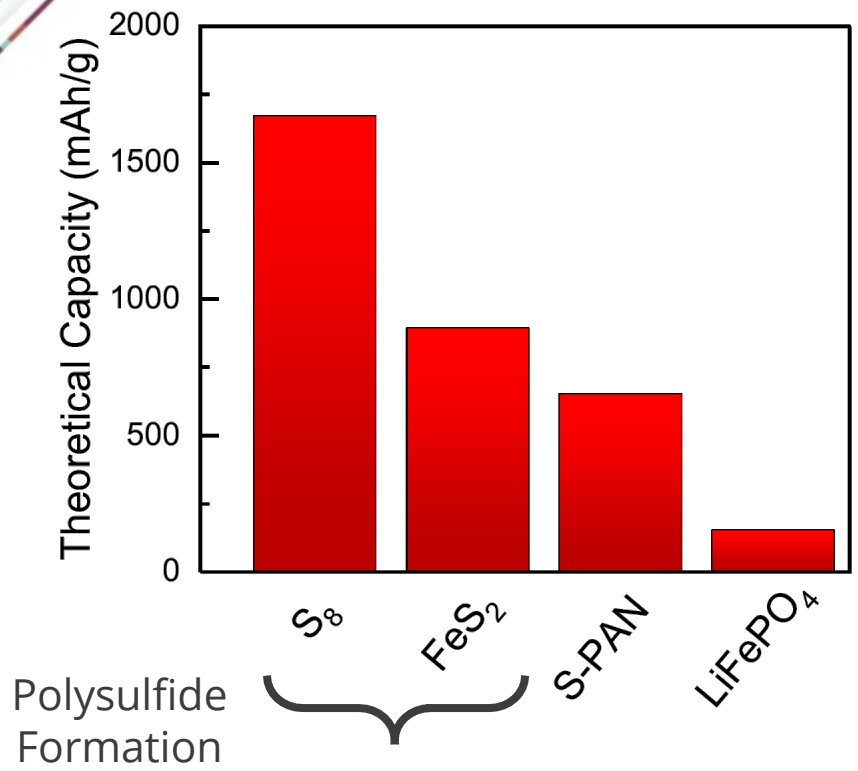
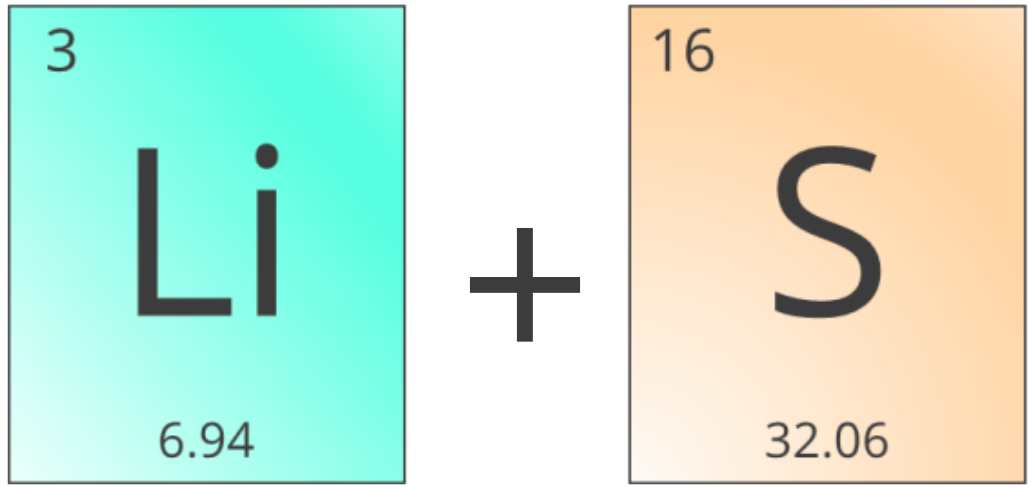
# Sulfur-based Cathodes for Li Metal Batteries




$$S_8 + Li^+ \rightarrow Li_2S_x \ (x = 4, 6, 8)$$

<u>Reduction in Battery Capacity</u>

1. Loss of active cathode material
2. Reaction with anode

Li *et al.*, *Chem. Mater*. **2019**, *31*, 2002-2009

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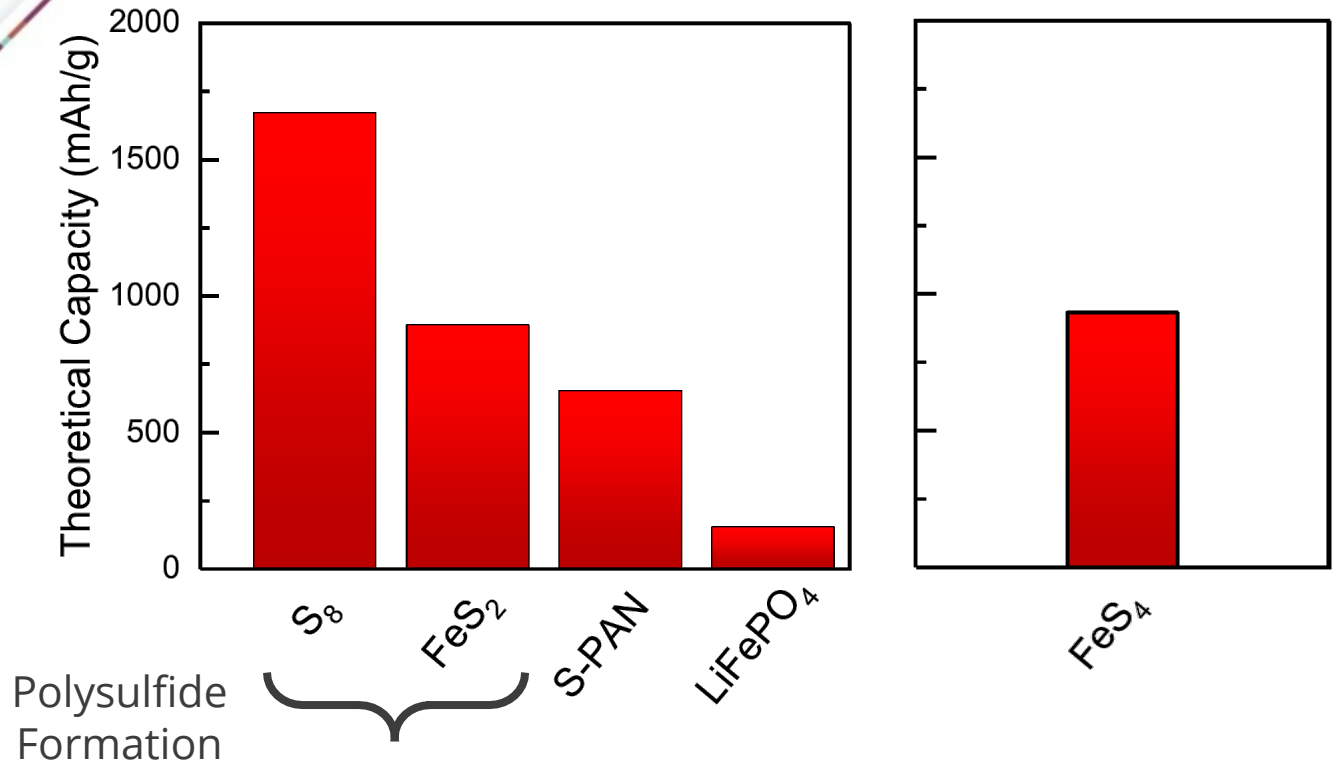


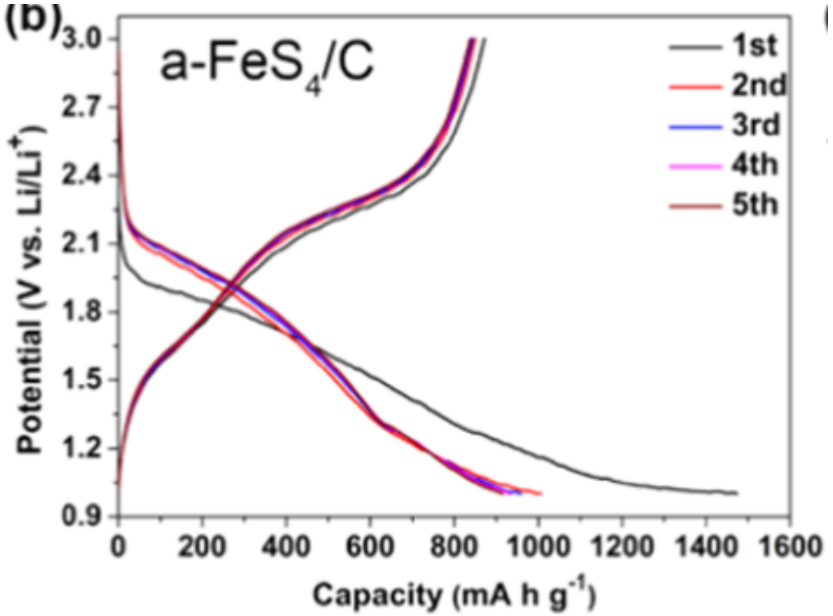


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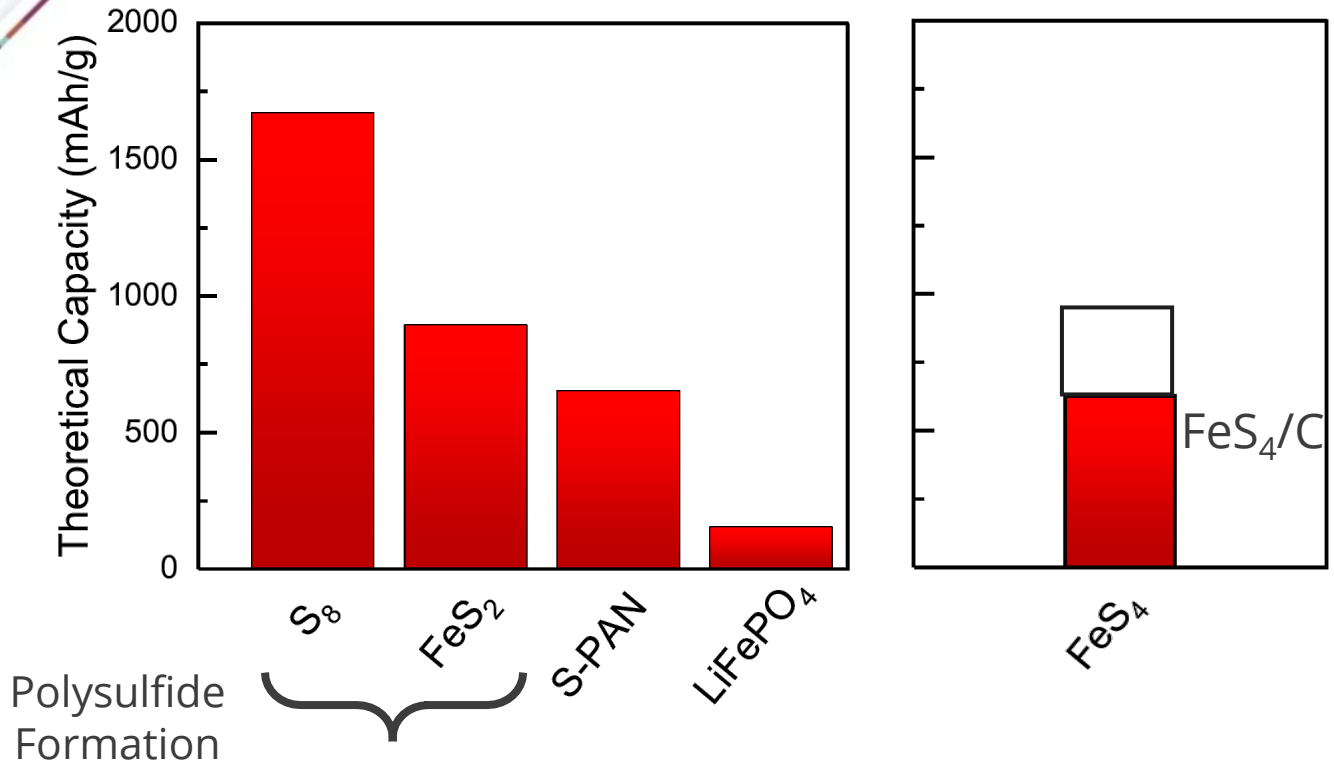


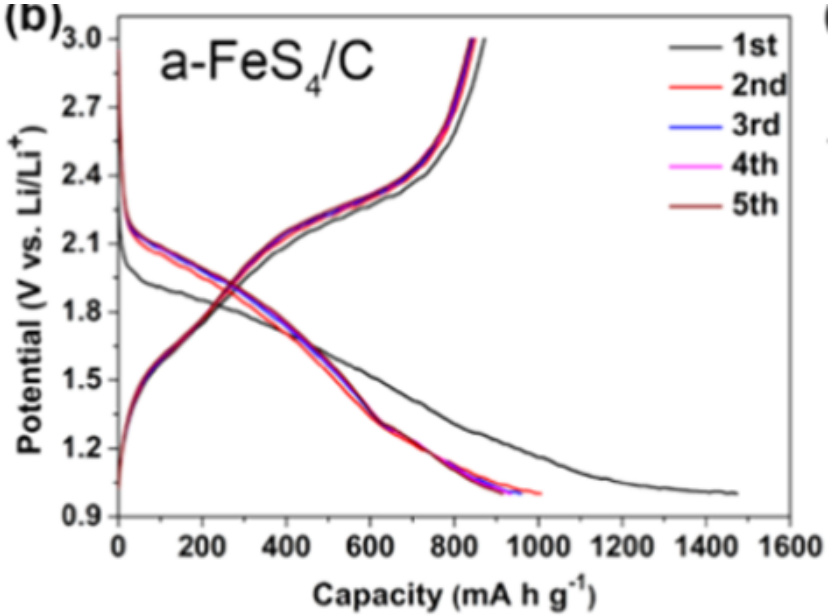


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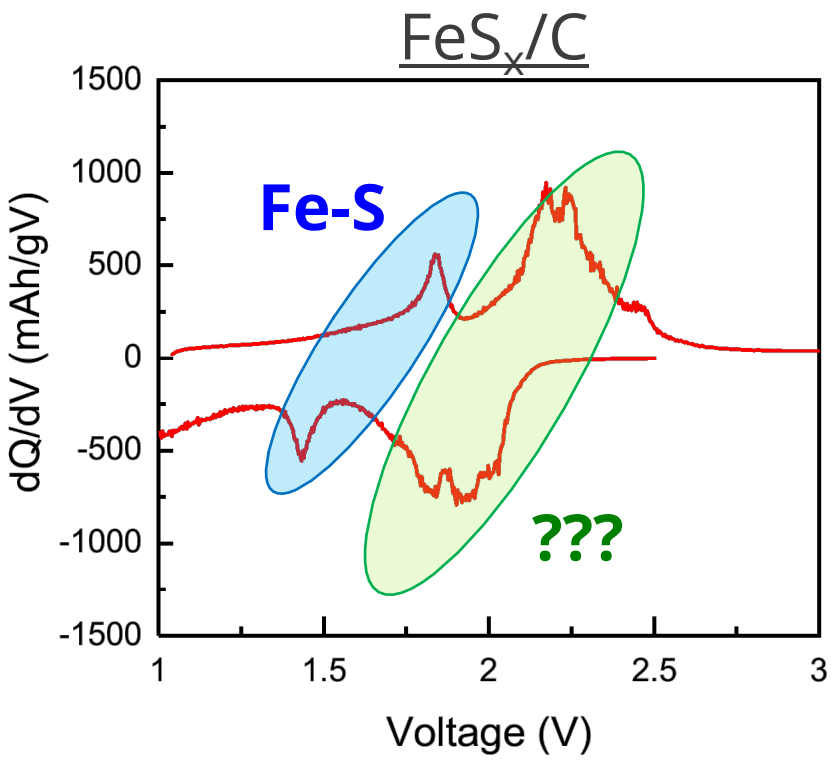
# What *is* the active material for these $FeS_x$/C composites?

- Evidence of non Fe-S related electrochemistry in the $FeS_x$/C indicates that $FeS_x$ may not be the **only** "active" material
- Conducted series of *ex situ* physiochemical analyses to better understand the electrochemistry of the material
  - Raman spectroscopy and X-ray photoelectron spectroscopy
- Find that the $FeS_x$/C system is a more complex cathode than previously reported




$$FeS_x + 2x\ Li^+ \rightarrow Fe^0 + x\ Li_2S$$

$$S_8 + 16\ Li^+ \rightarrow 8\ Li_2S$$

$$CS_x + 2x\ Li^+ \rightarrow C + x\ Li_2S$$

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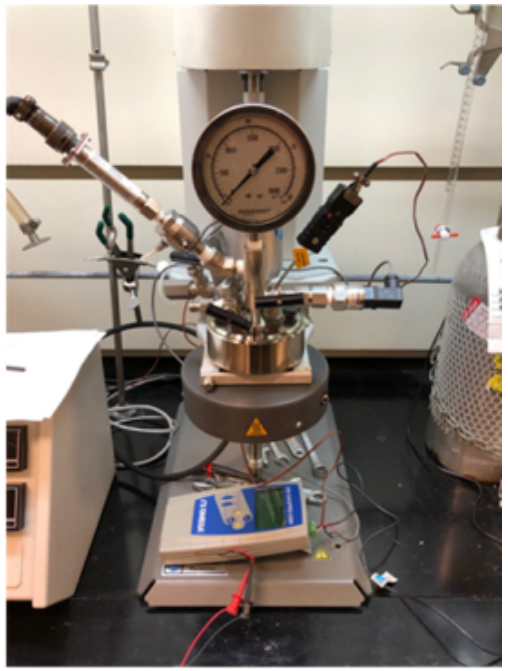
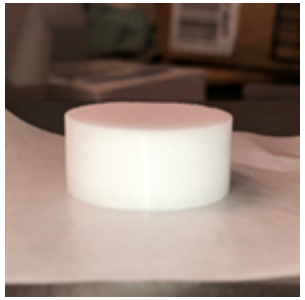
# Characterization of $FeS_x$/C shows Fe-S, $S^0$, and C-S moieties

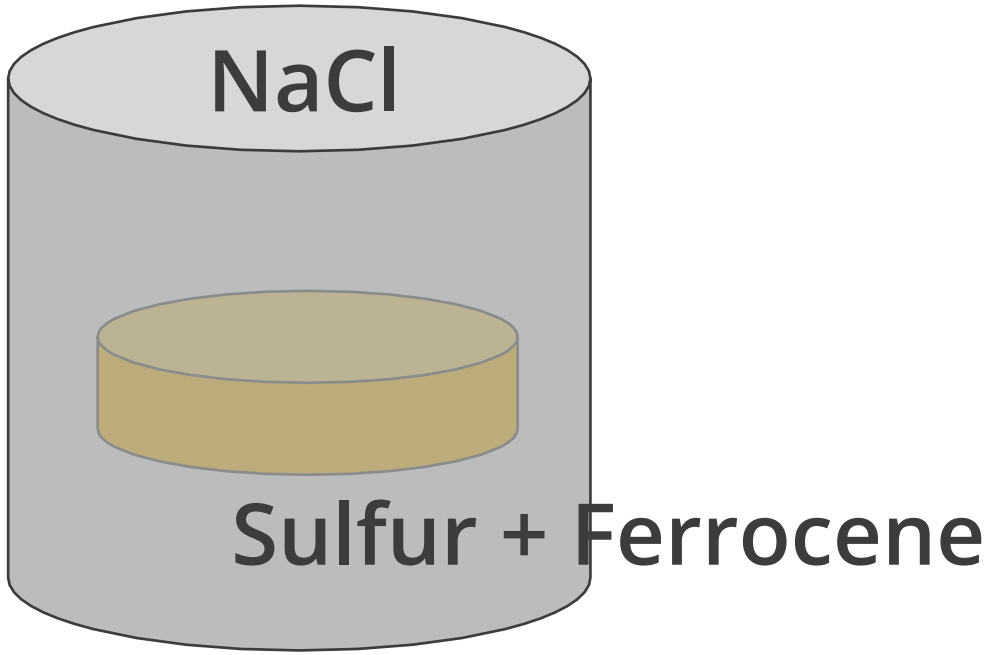
$FeS_x$/C is prepared using a “baked-in-salt” synthesis with ferrocene and S inside an NaCl pellet

**Pressurized Reactor**



**NaCl Pellet**



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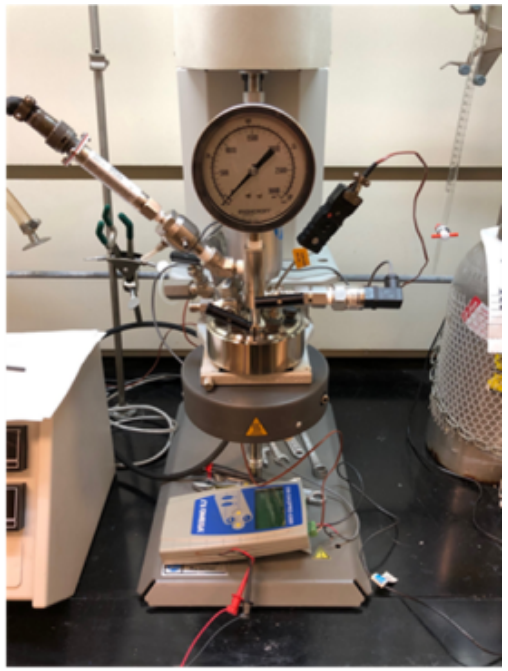

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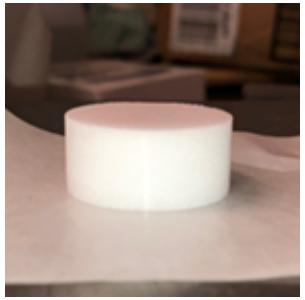
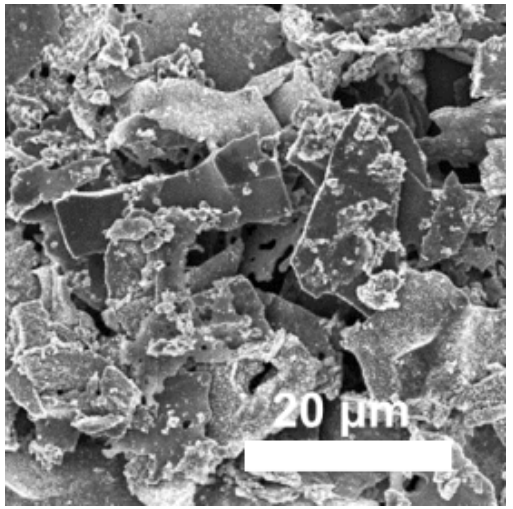
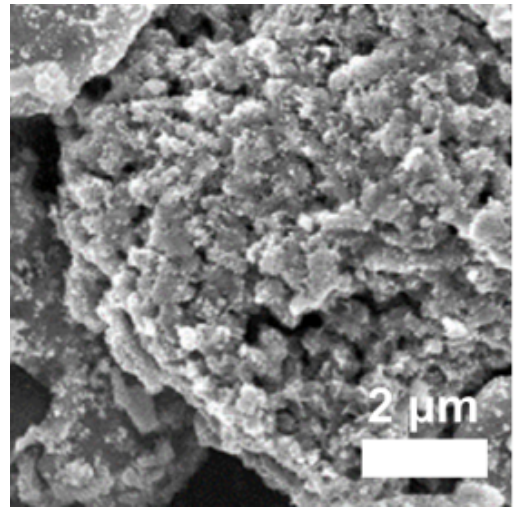
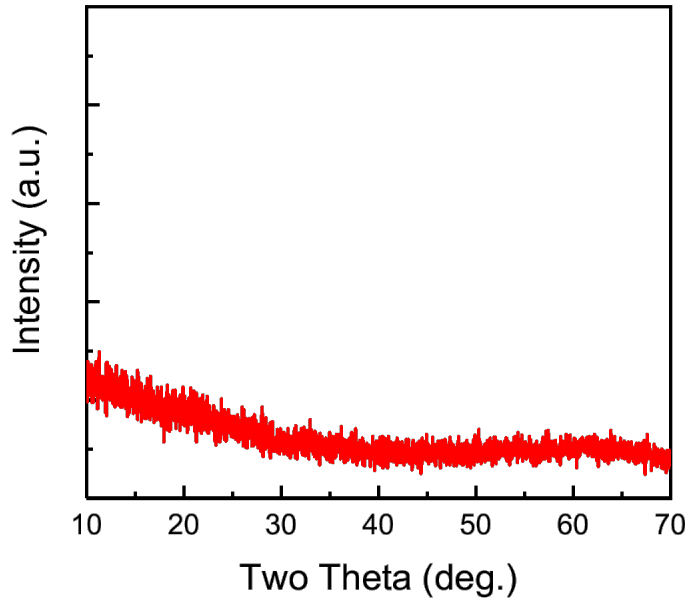


As-Synthesized Material

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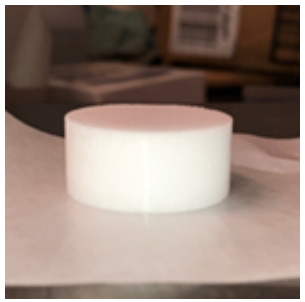

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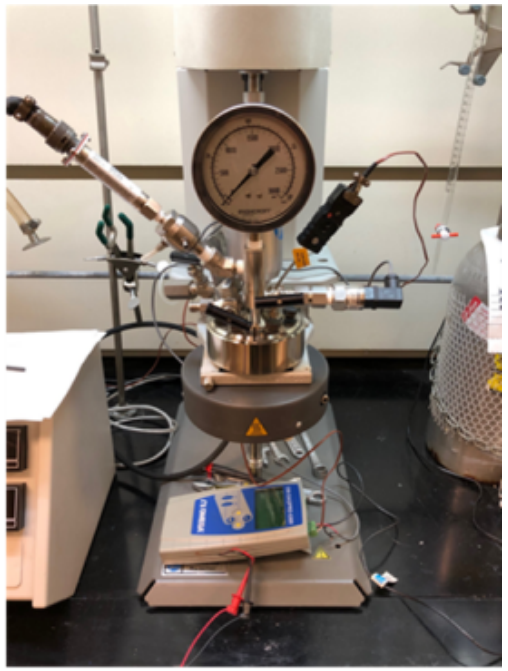

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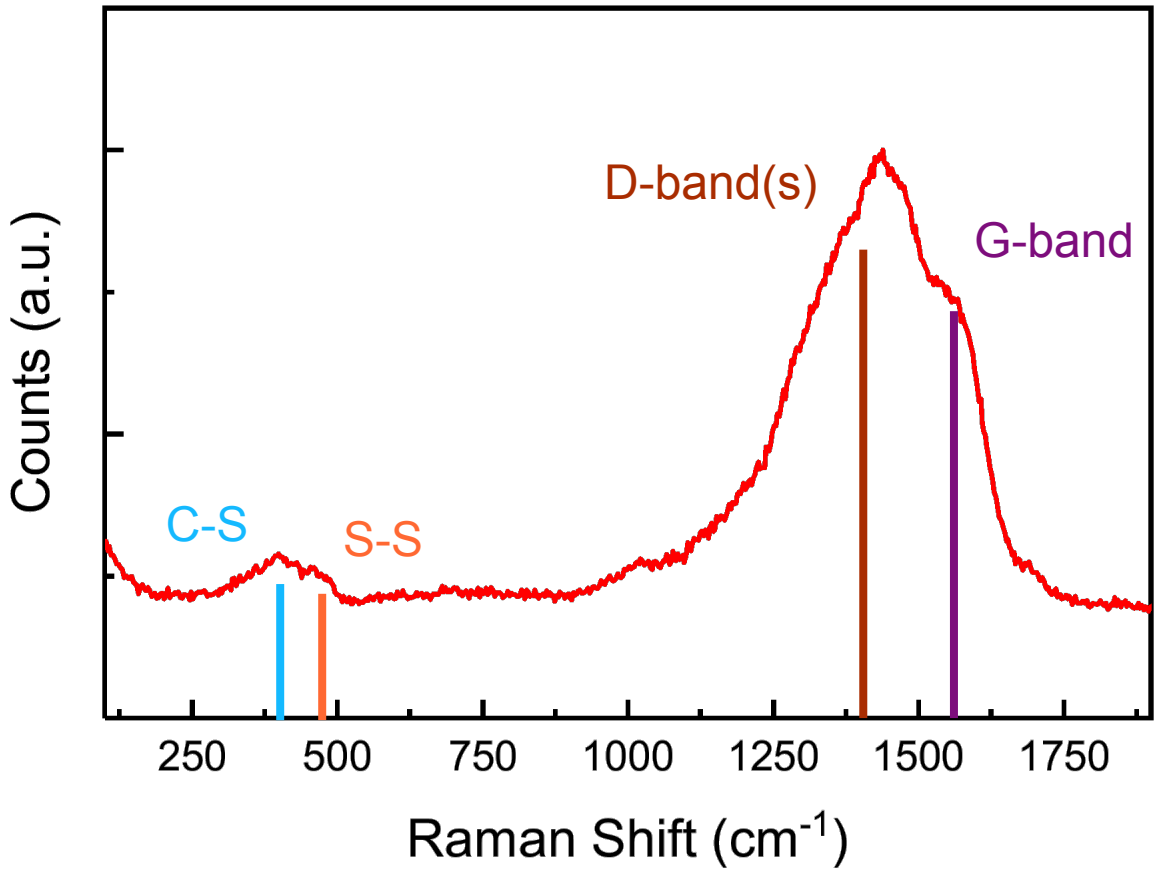


**Based on this, we clearly have an amorphous, disordered carbon with S-S/C-S bonding present**

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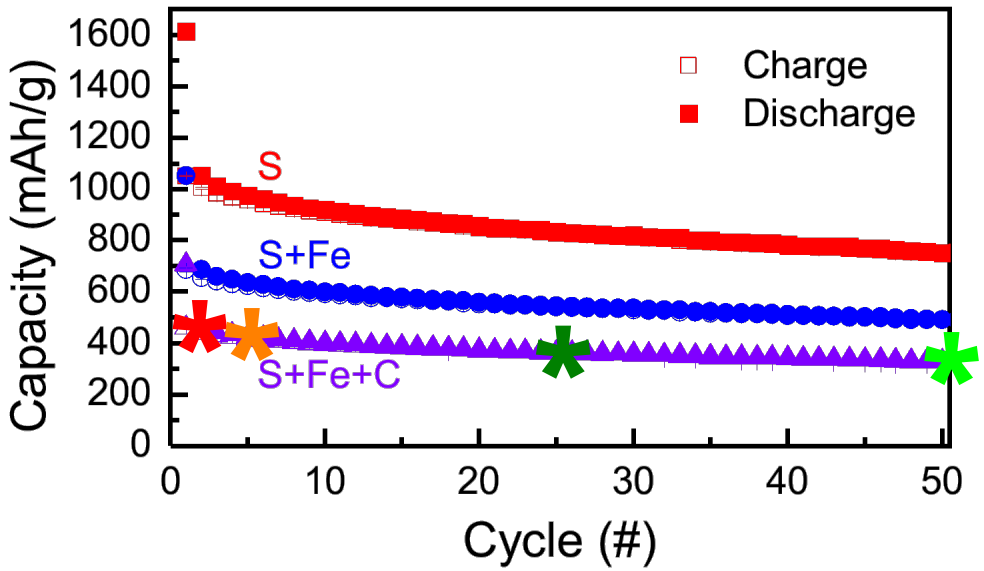
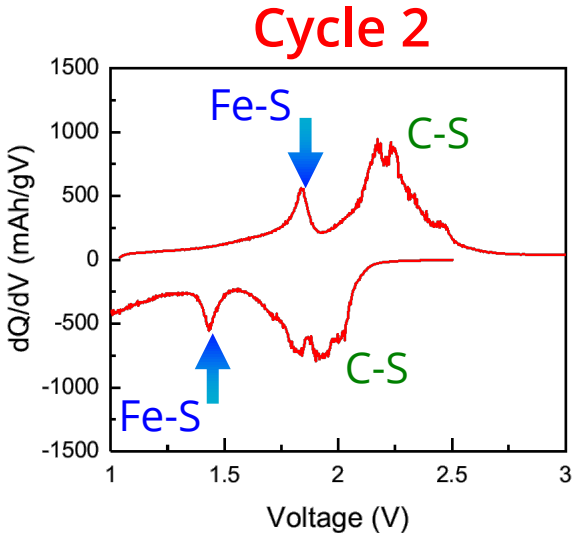
# Reasonable electrochemical performance… depending on the metric

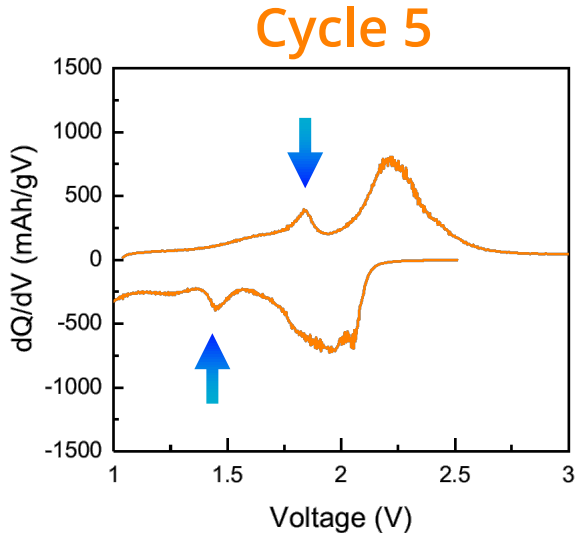
$FeS_x$/C cycles well against a Li anode in LiFSI/LiTFSI DOL/DME electrolyte, but it can be challenging to pick a metric for capacity

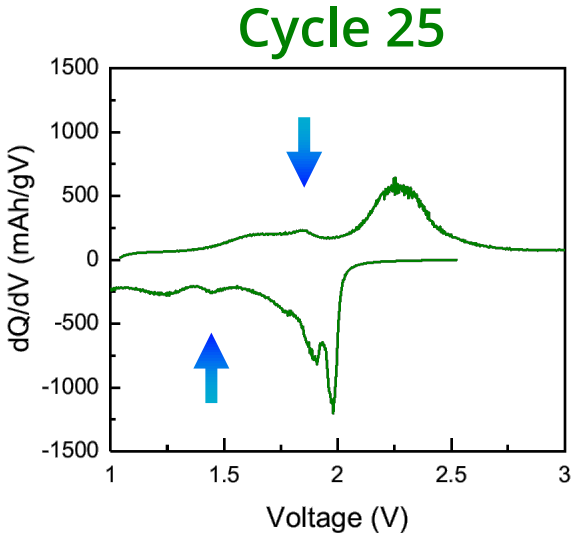
S = 1050 mAh/$g_S$
S+Fe = 690 mAh/g
S+Fe+C = 460 mAh/g

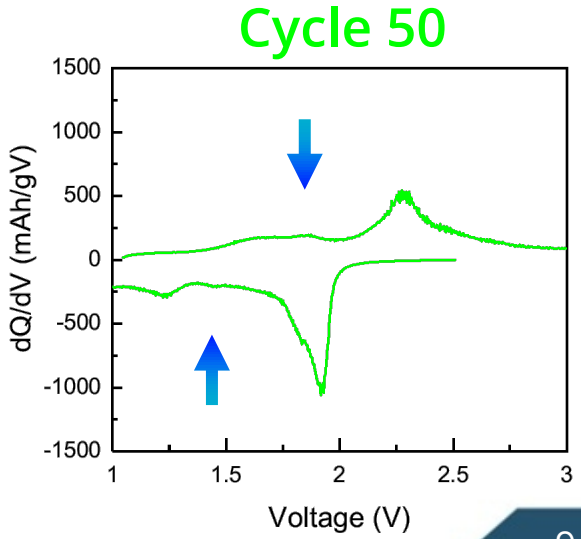



**Monitoring the dQ/dV behavior, it becomes apparent that you *must* include S+Fe+C when determining gravimetric capacity for $FeS_x$/C**




Wygant *et al.*, *J. Phys. Chem. C*. **2022**, 10.1021/acs.jpcc.2c01634

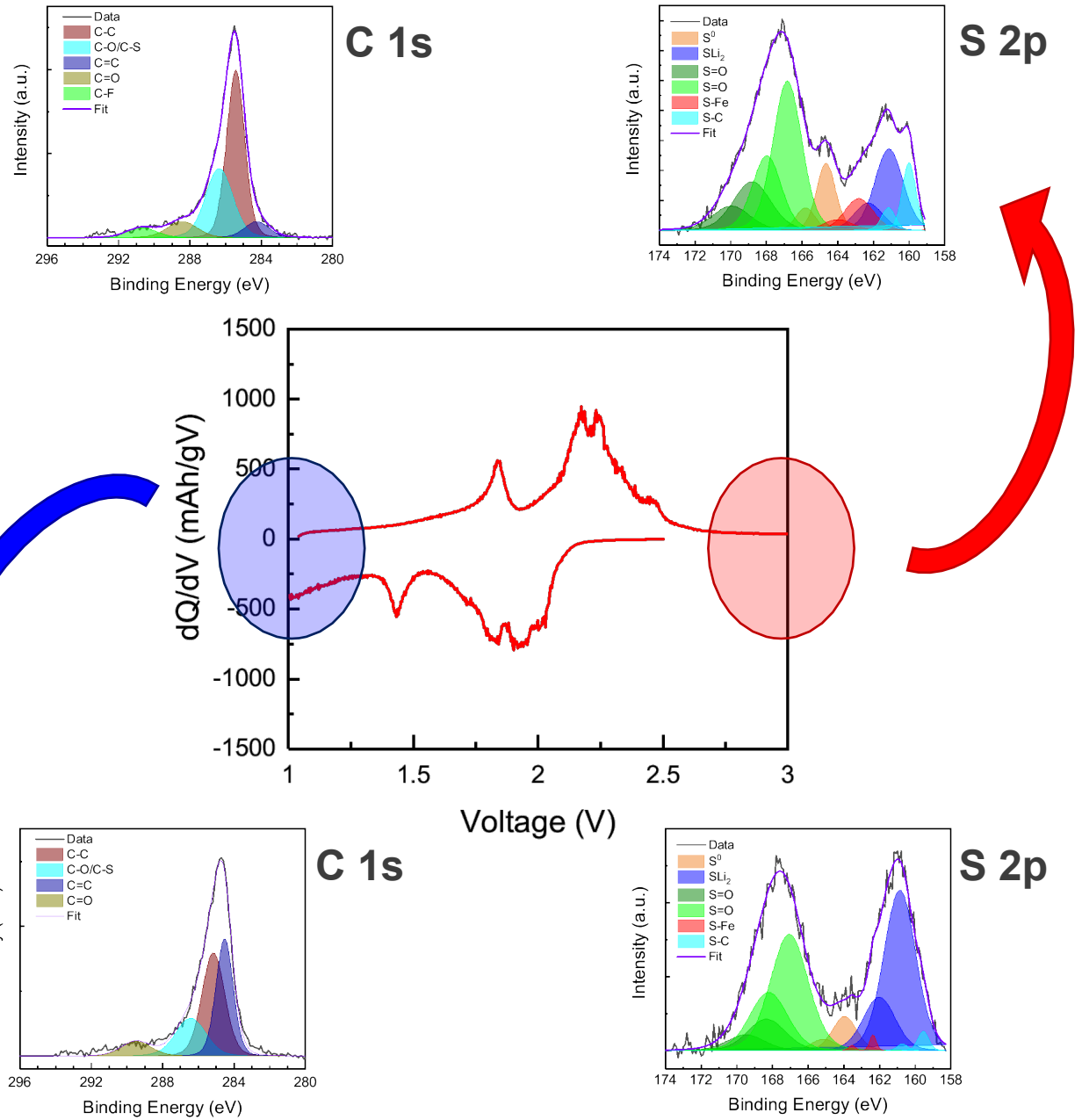
Chen *et al.*, *Nat. Commun*. **2019**, *10*, 1021

# XPS analysis provides additional evidence of C-S driven capacity

Compared XPS species present in samples at various states of charge to monitor changes with cycling

## Species

C-C ($sp^3$)
C=C ($sp^2$)
C-S
S-S
Fe-S
Li-S

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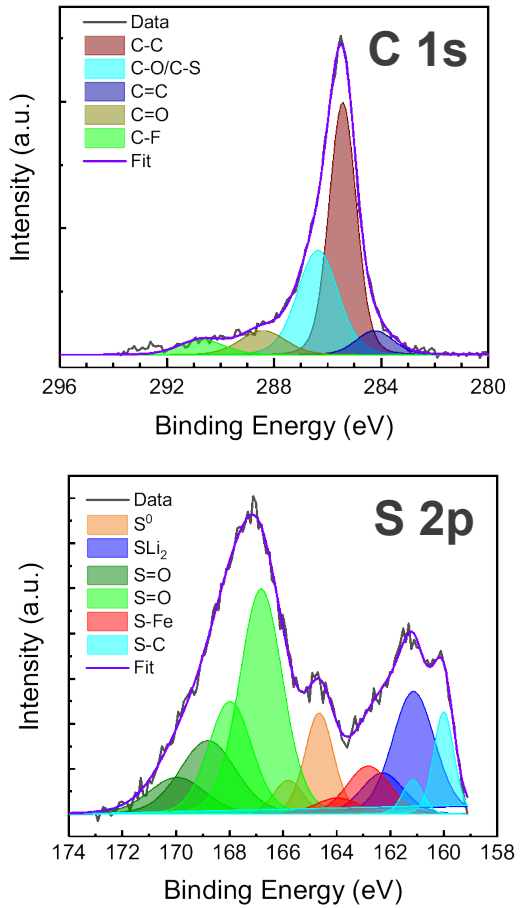
# XPS analysis provides additional evidence of C-S driven capacity

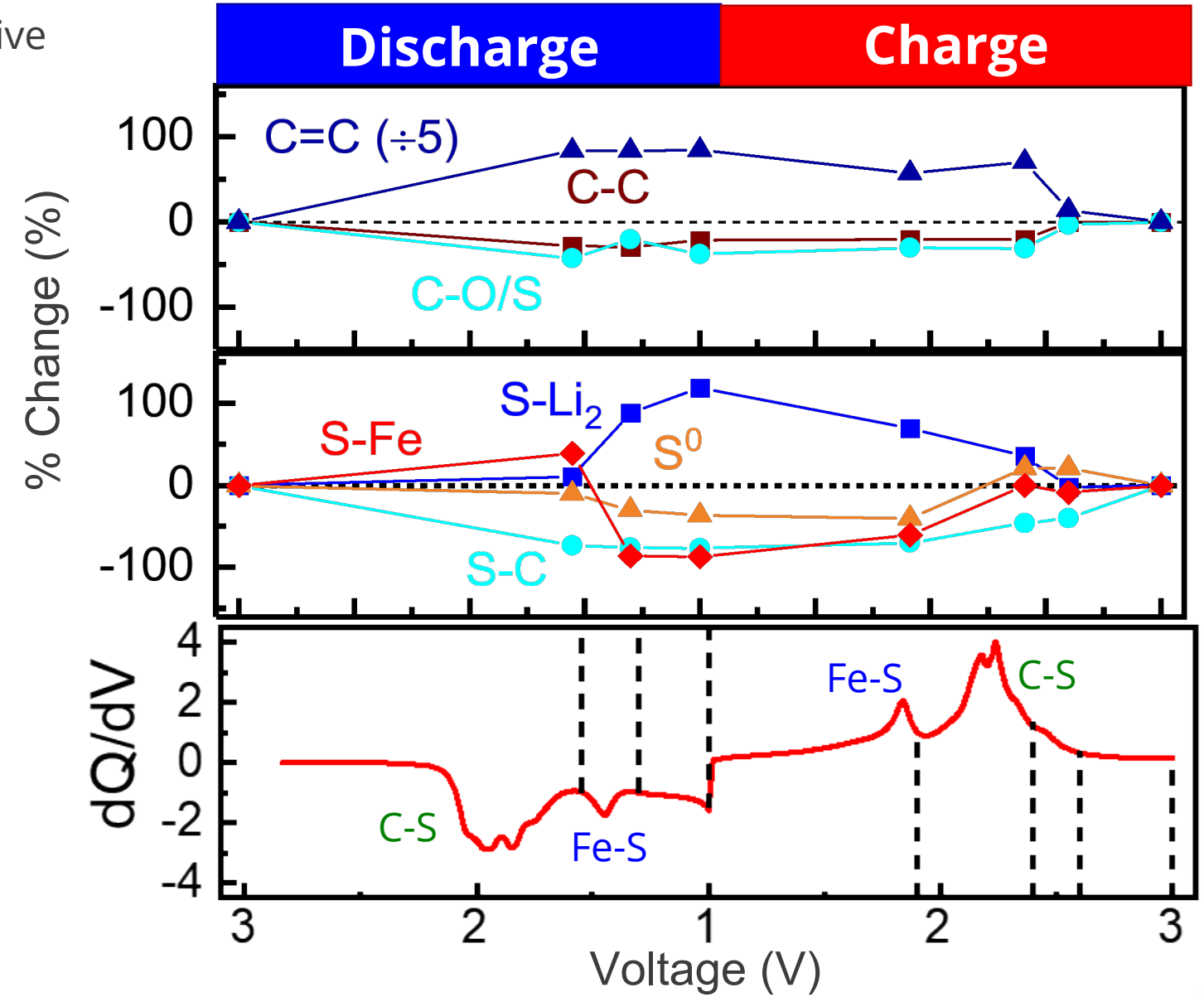
Cycle 2 shows all species are active

**Species**

C-C
C=C
C-S
S-S
Fe-S
Li-S

**Charge**

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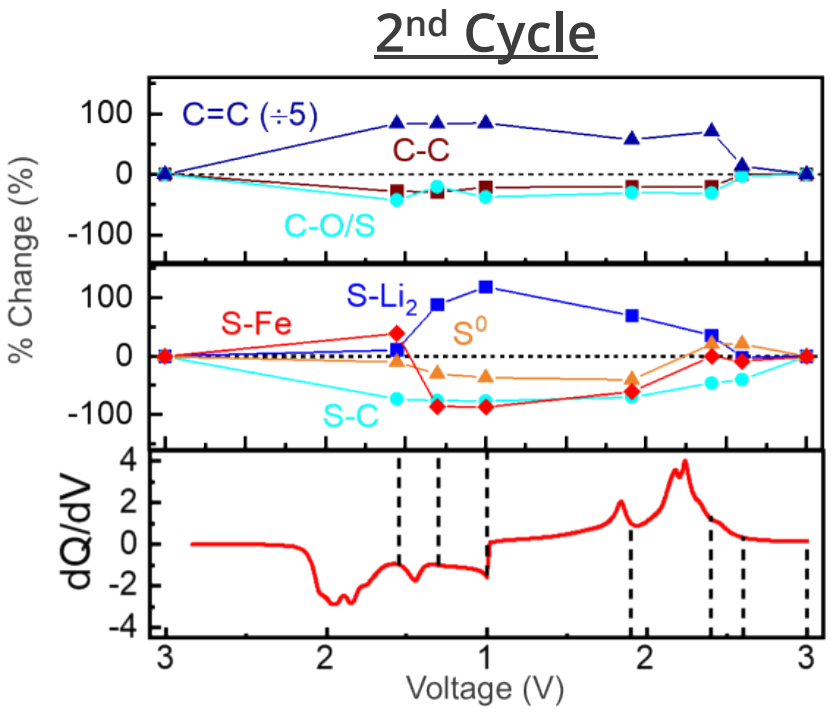
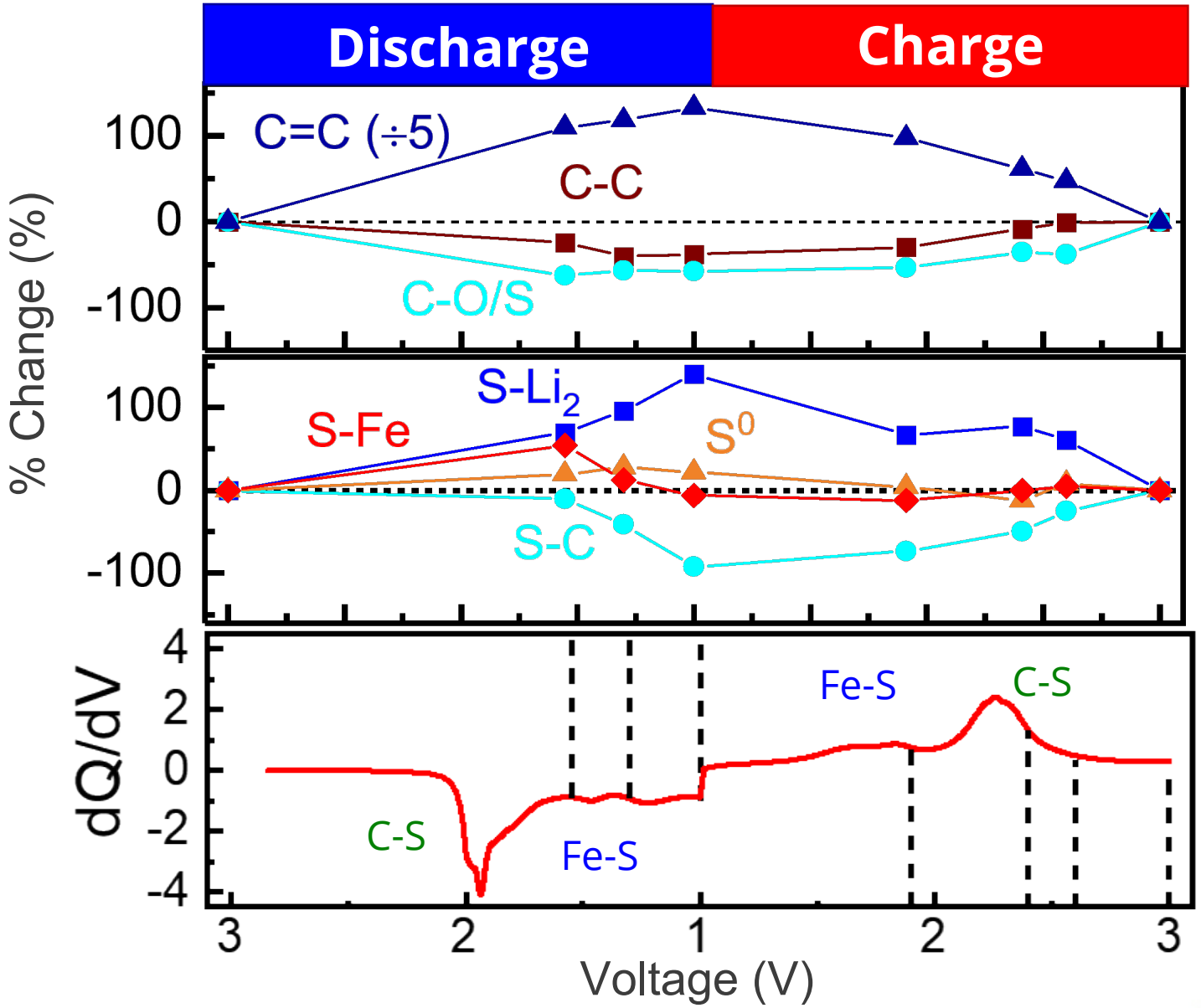
# 25th cycle XPS also clearly shows loss of Fe-S electrochemistry

**C-S shows similar behavior in 2nd and 25th cycles, while Fe-S no longer shows activity**

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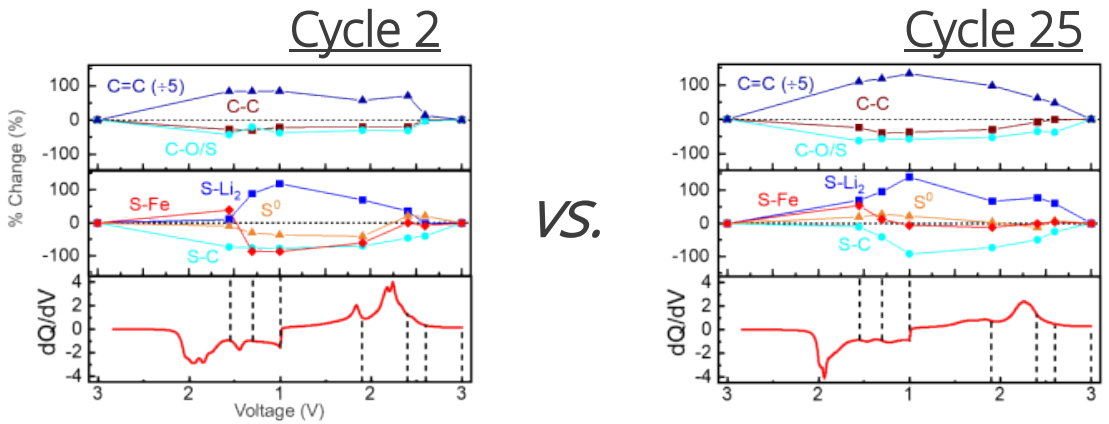
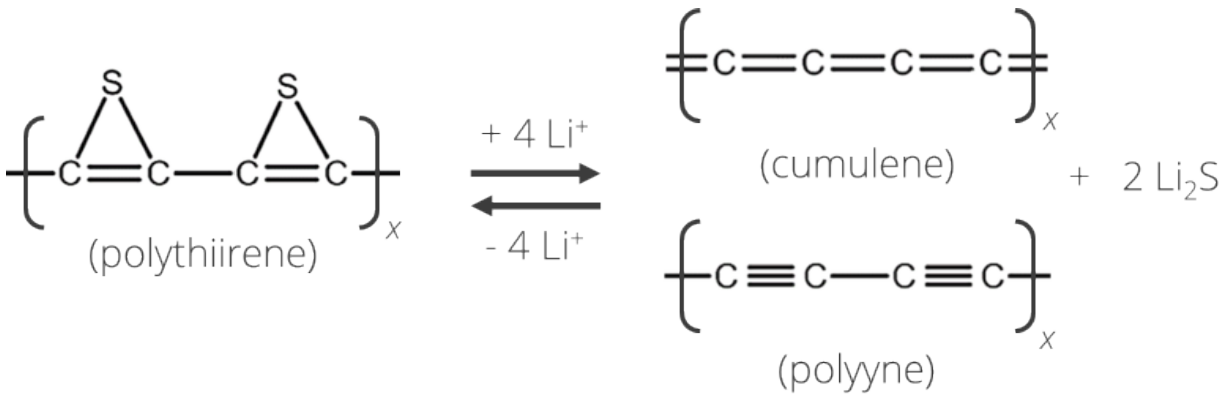
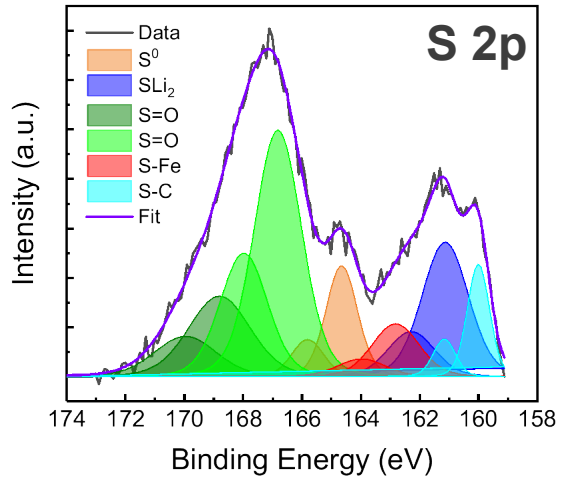
# Proposed C-S material and Summary

Our results clearly indicate that the $FeS_x$/C exhibits both Fe-S *and* C-S (de)lithiation



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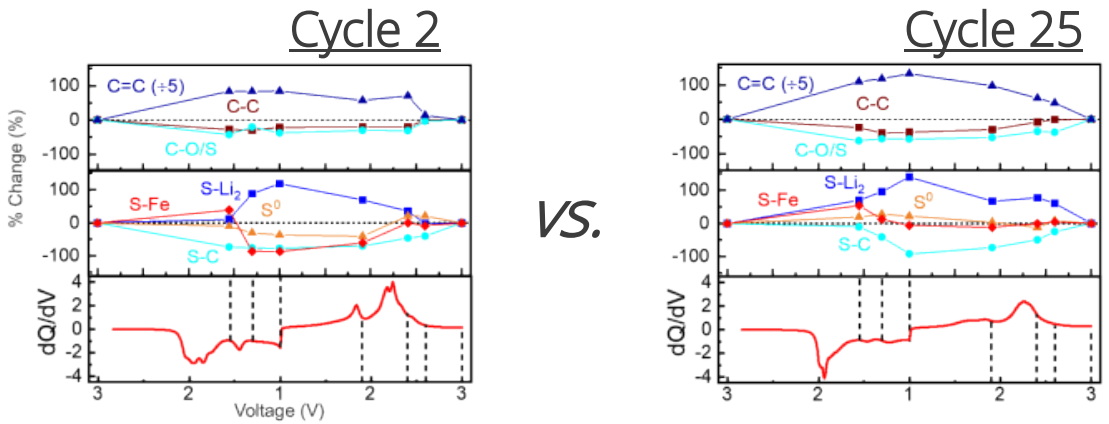
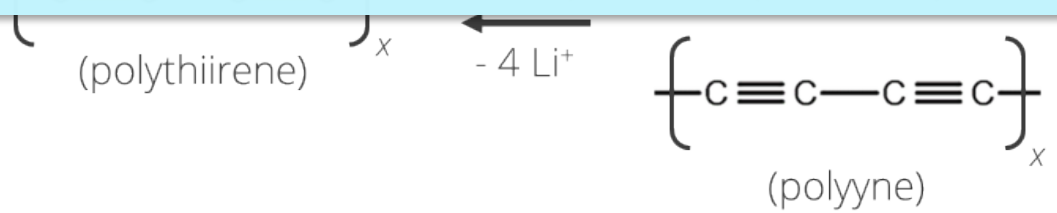
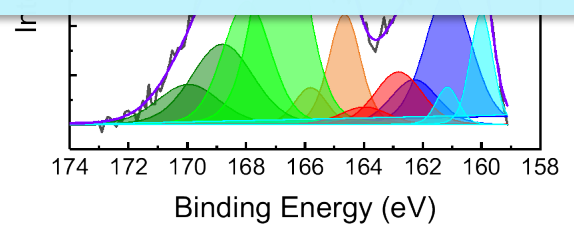



**In Conclusion:**

1) The considerations for gravimetric capacity should be carefully examined to ensure accuracy
2) Further study of $FeS_x$/C should be undertaken to better characterize the exact C-S species and its electrochemical properties



# Acknowledgements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  - Dr. Tim Lambert and Dr. Katie Harrison
- *Co-Authors*
  - Dr. Igor Kolesnichenko
  - Dr. Noah Schorr
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  - Dr. Samantha Rosenberg (XPS)
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Tim Lambert

Katie Harrison

Igor Kolesnichenko

Noah Schorr

Sandia National Laboratories

LDRD Laboratory Directed Research and Development


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