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High Capacity Retention in Lithium Batteries Utilizing Nano Iron Sulfide Particles

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MRS Fall Meeting EN09.05: Metal Sulfides in Batteries III

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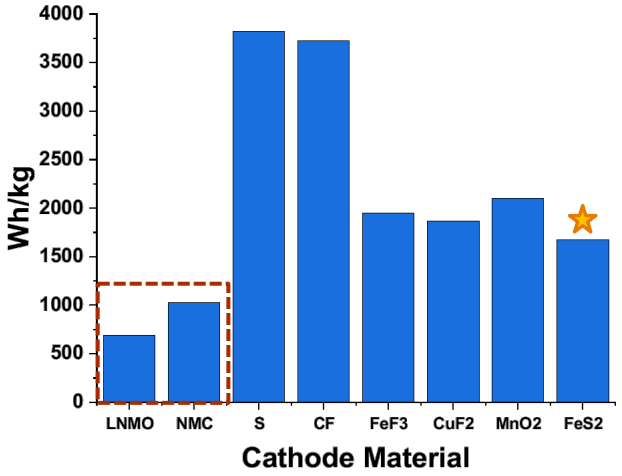
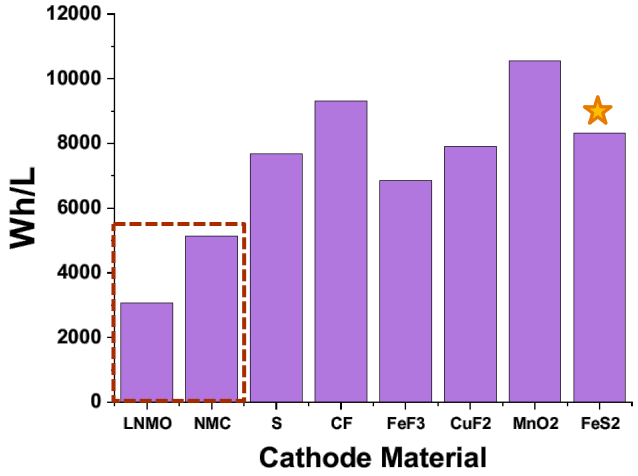
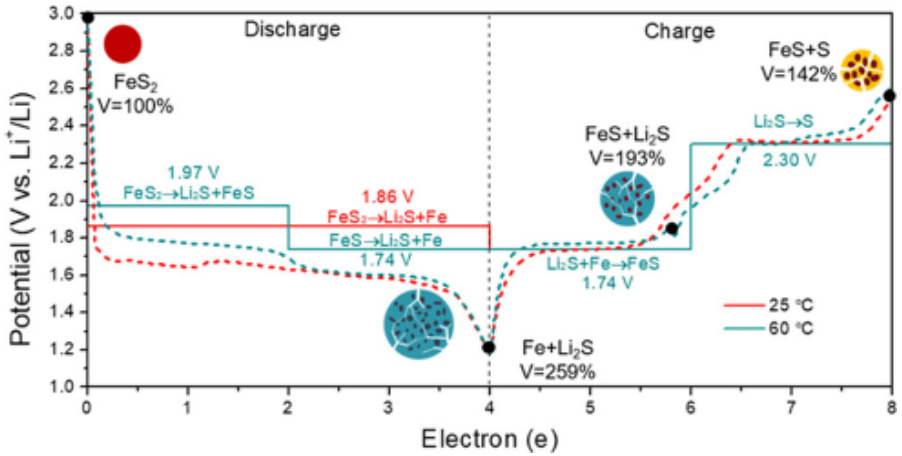
FeS_2 as a Cathode

- With a specific capacity of 894 mAh/g and a gravimetric energy of 1671 Wh/kg FeS_2 is an attractive choice for a conversion cathode for a Li battery
- The general reaction pathways leads to clues about how to improve cathode reversibility







Zou, J. et al. *ACS Appl. Mater. Interfaces* 2020, 12, 44850-44857

Initial Discharge

$$FeS_2 + 4Li^+ + 4e^- \rightarrow Fe + 2Li_2S$$

Subsequent Discharge

$$FeS_2 + 2Li^+ + 2e^- \rightarrow FeS + Li_2S$$

$$FeS + 2Li^+ + 2e^- \rightarrow Fe + Li_2S$$

Charge (low voltage)

$$Li_2S + Fe - 2e^- \rightarrow FeS + 2Li^+$$

Charge (High voltage)

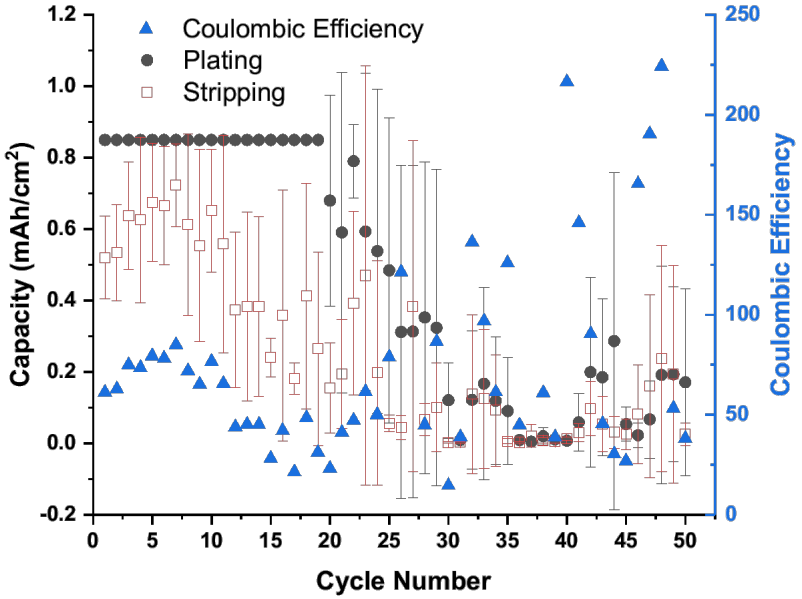
$$Li_2S - 2e^- \rightarrow 1/8S_8 + 2Li^+$$

Polysulfides generated during discharge after charging to 3 V will react with lithium, decreasing cell capacity

Making a Stable Li Metal Anode

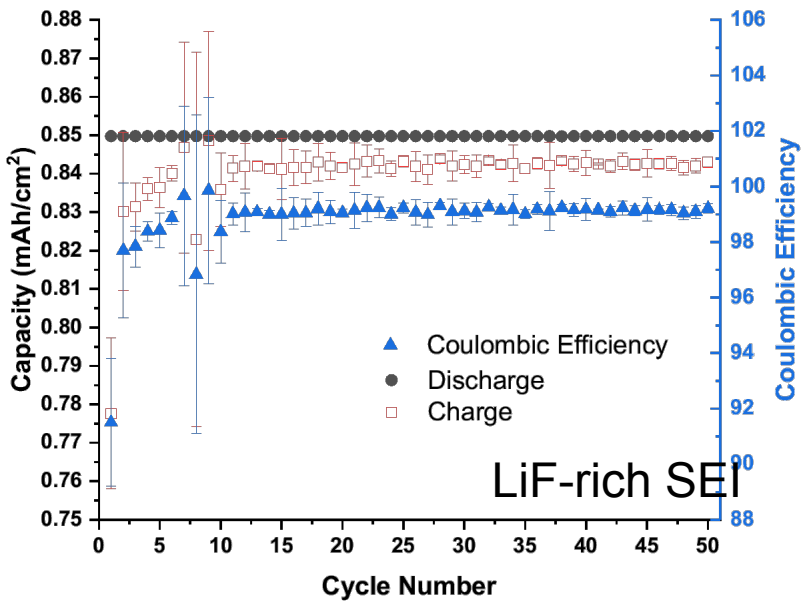
- A suitable commercial lithium-metal anode will not have extreme excess of mass and will require above 99% Coulombic efficiency
- Lithium metal plating and stripping on Cu foil completed over 50 cycles demonstrates electrolyte compatibility with Li anode

1M LiTFSI DOL:DME



Average Coulombic efficiency **56.20%**

1M LiTFSI : 2M LiFSI DOL:DME



Last 40 cycles average Coulombic efficiency is **99.1%** (98.8% all)

- Li-FeS_2 cells with 1 M LiTFSI in DOL/DME would be anode-limited and not cycle well
- $LiNO_3$ additive cannot be used in Li-FeS_2 batteries because $LiNO_3$ reacts with FeS_2 below 1.8 V

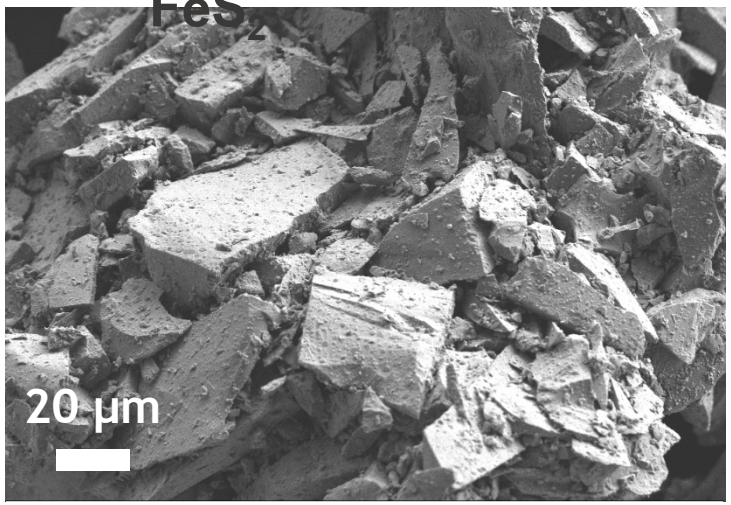
1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mA/cm² – 0.85 mAh/cm²;
Schorr, N.B. et al *ACS Appl Nano Mater*. **2021**, in press, DOI:10.1021/acsanm.1c02178

Error bars represent 95% confidence interval

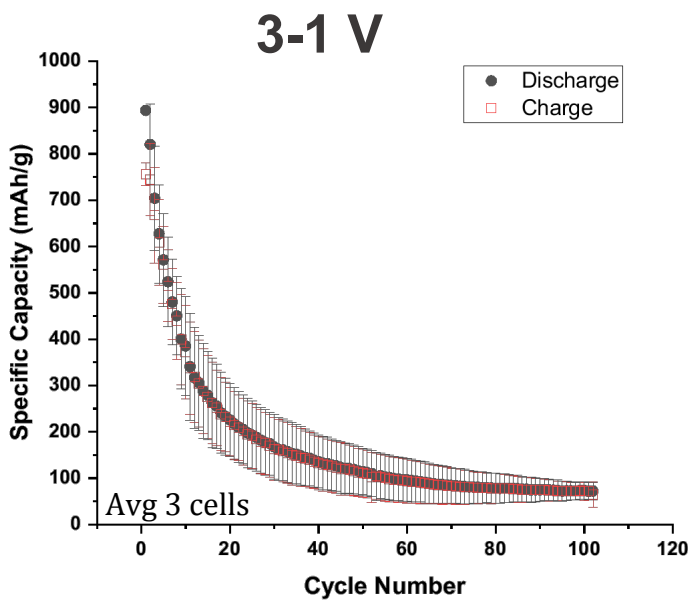
Commercial Iron Disulfide

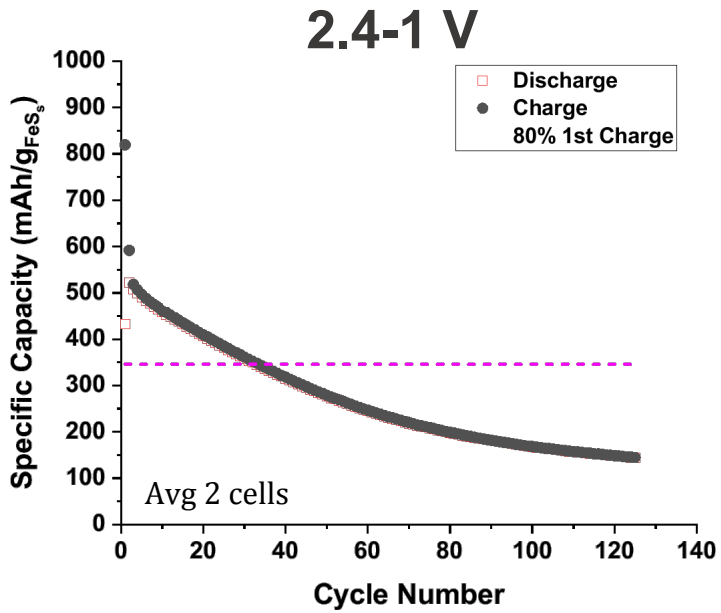
- Commercial FeS_2 (sigma) used as is in cathodes is insufficient, even with 1M LiTFSI : 2M LiFSI DOL:DME
- This is true regardless using a charging voltage limit that should impede formation of sulfur and subsequently polysulfides

SEM COTS FeS_2



Cycling cathodes made from COTS FeS_2





Rapid capacity fade is unsurprising given undesirable qualities of macro FeS_2, resistance, low Li^+ flux, more susceptible to stress and strain from volume changes

1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mA/cm^2; cathode 60:20:20 FeS_2:Super-P:PVDF

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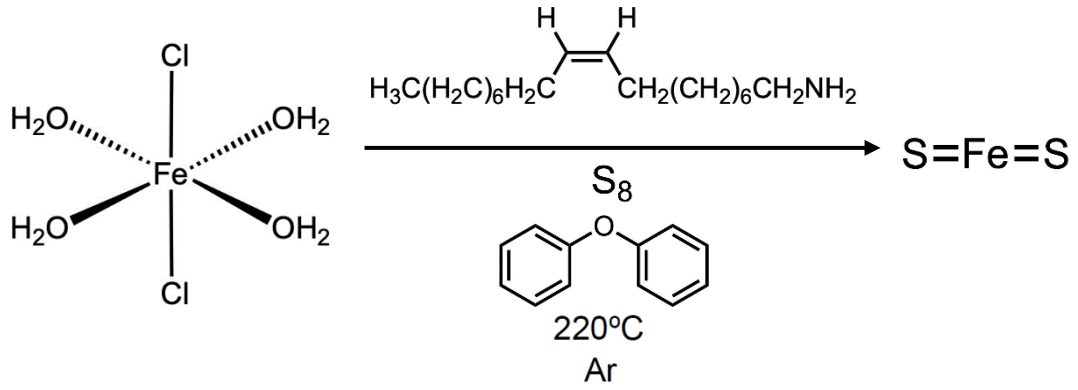
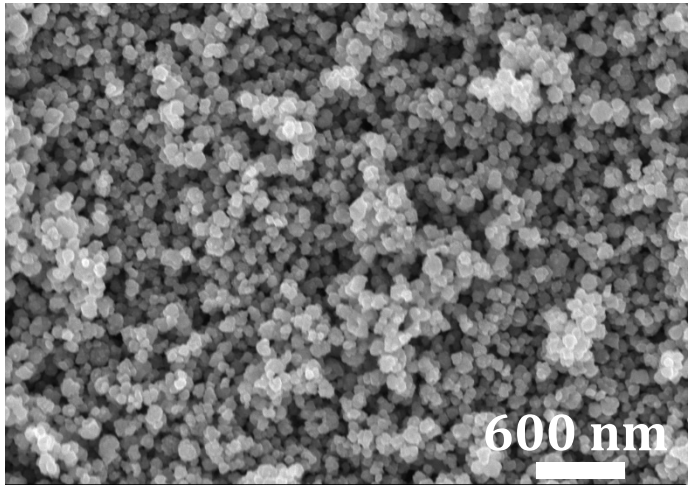
Synthesizing FeS_2 Nanoparticles

- Nano FeS_2 was synthesized to decrease particle size and to control particle size, improve kinetics, and lower resistance compared to macro

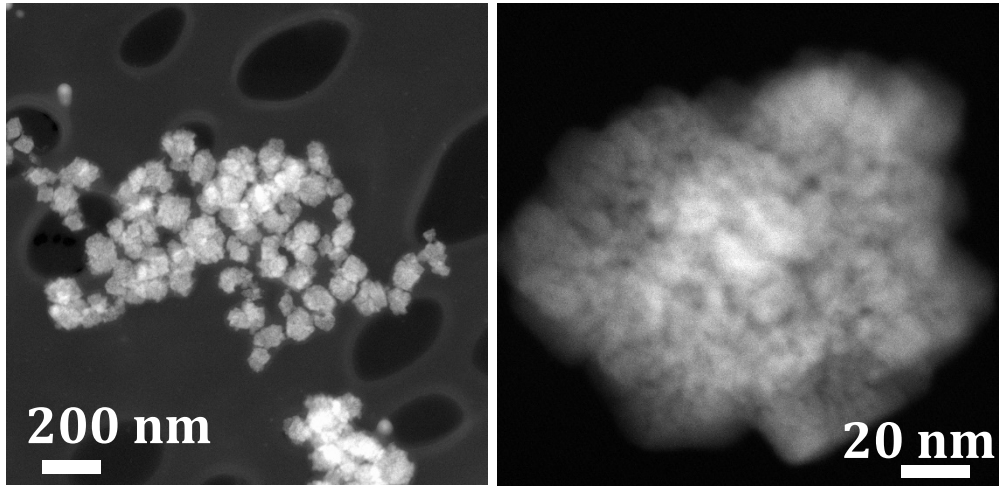


Iron disulfide with oleylamine ligand

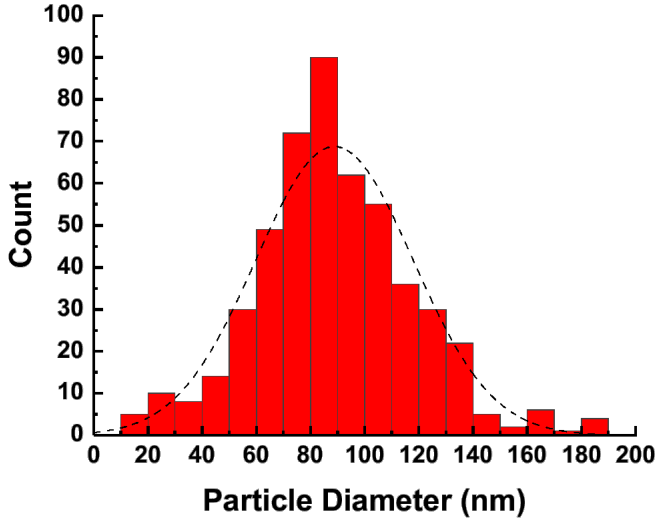
SEM



TEM



Avg. Diameter: ~89 nm

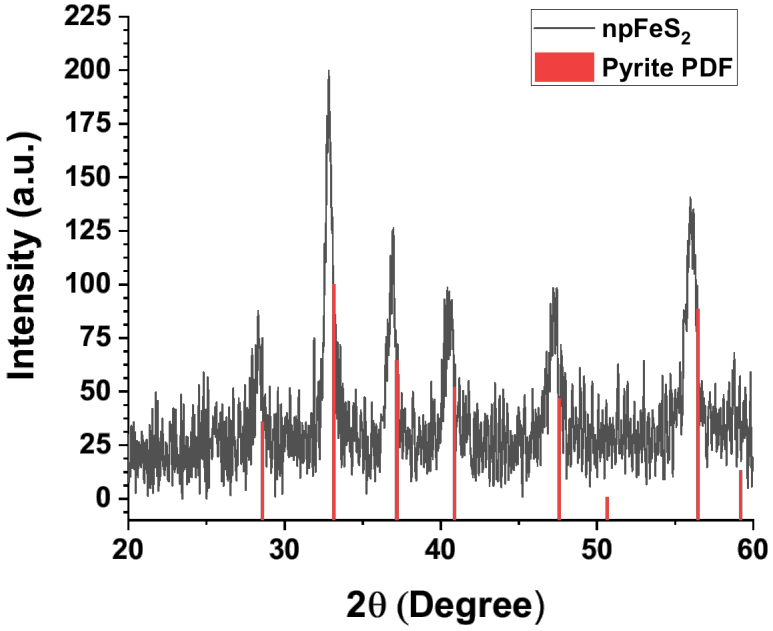


Schorr, N.B. et al *ACS Appl Nano Mater*. **2021**, in press, DOI:10.1021/acsanm.1c02178

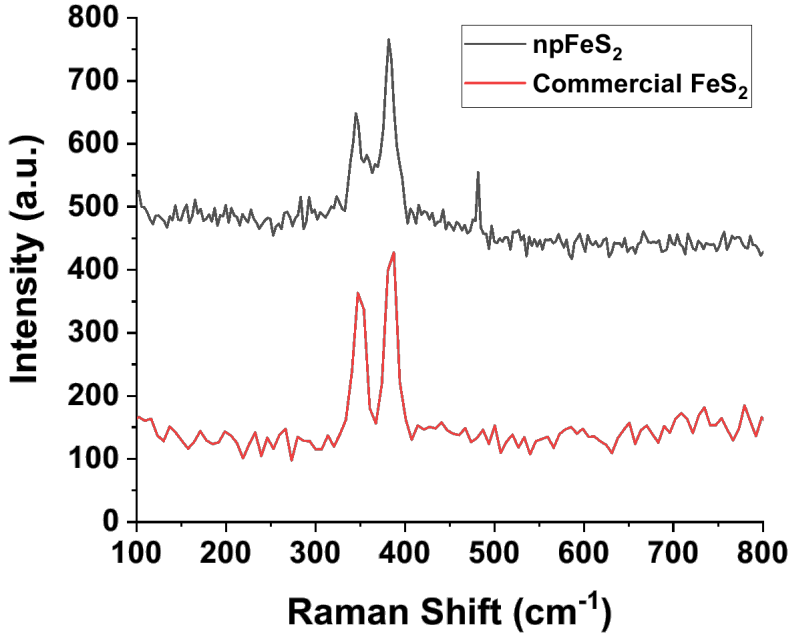
Nano FeS_2 Characterization

- FeS_2 product was confirmed through multiple techniques

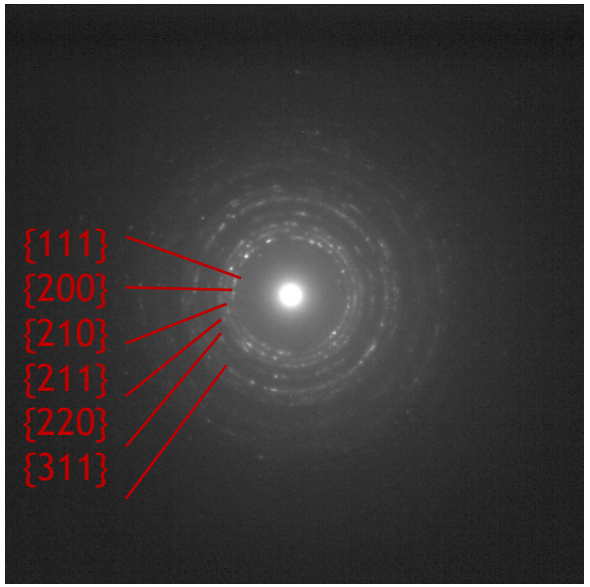
Powder XRD



Raman spectroscopy



Select-area electron diffraction (SAED)



Interplanar spacing values matched to pyrite PDF

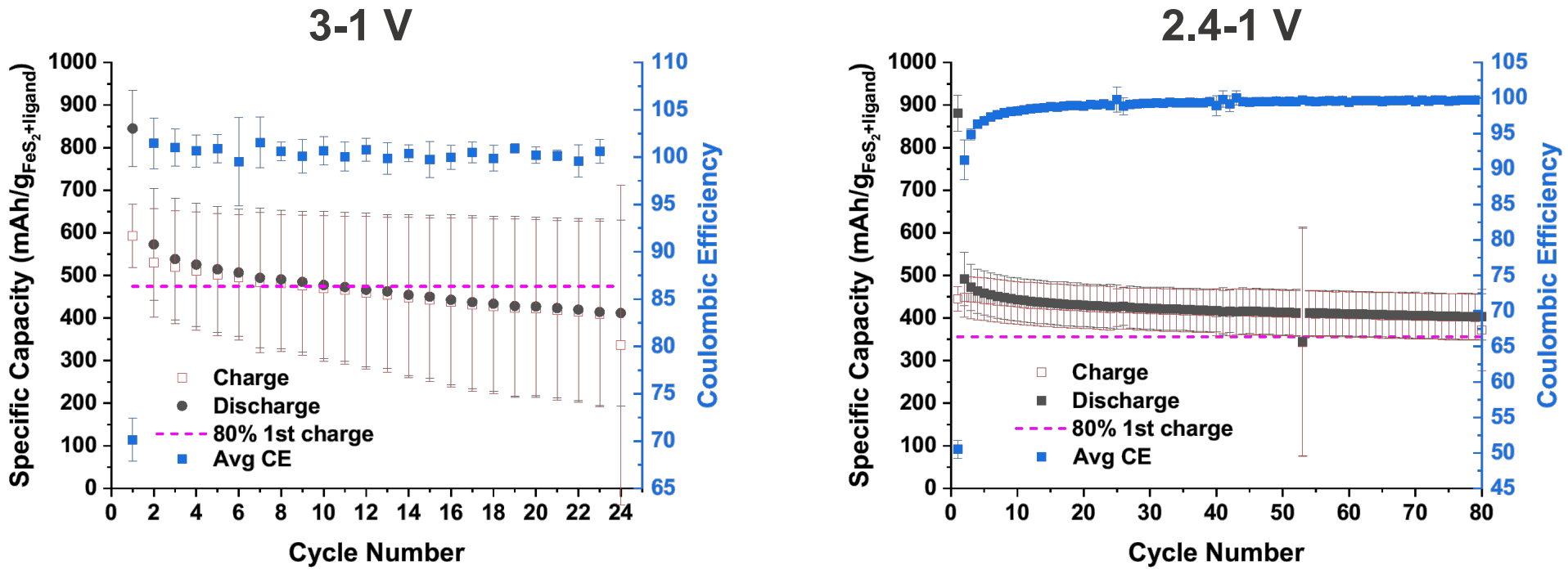
Ligand content was ~4 wt. % by EA and ~11% by TGA

Schorr, N.B. et al *ACS Appl Nano Mater*. **2021**, in press, DOI:10.1021/acsanm.1c02178

Voltage Window dependence of Nano FeS_2

- Cycling of nano FeS_2 vs Li in coin cells showed charging of the cathode to 3 V led to capacity decline, though not as rapid as commercial
- Limiting the charging voltage greatly increases cathode capacity stability

Cycling cathodes made from nano FeS_2



Average 421 mAh/g over 80 cycles

1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mA/cm^2; cathode 60:20:20 FeS_2:Super-P:PVDF

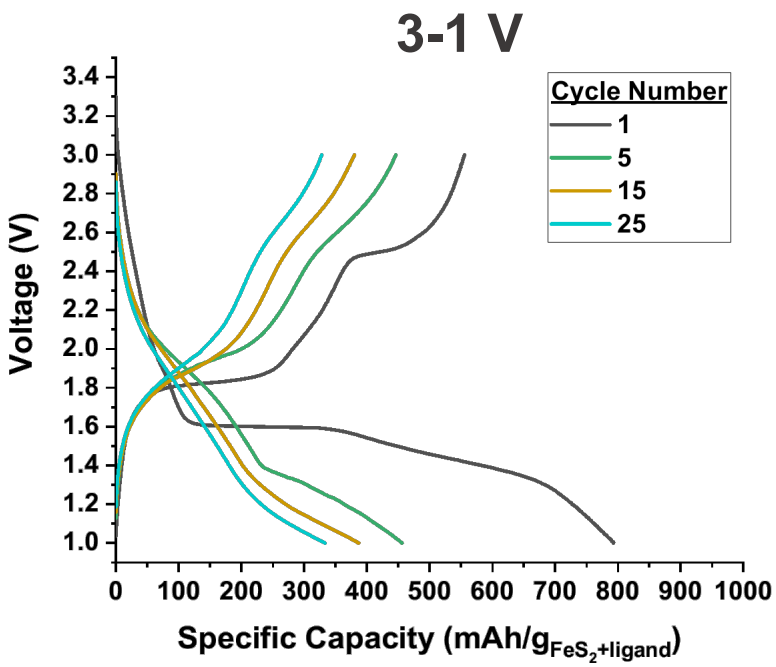
Schorr, N.B. et al *ACS Appl Nano Mater*. **2021**, in press, DOI:10.1021/acsanm.1c02178

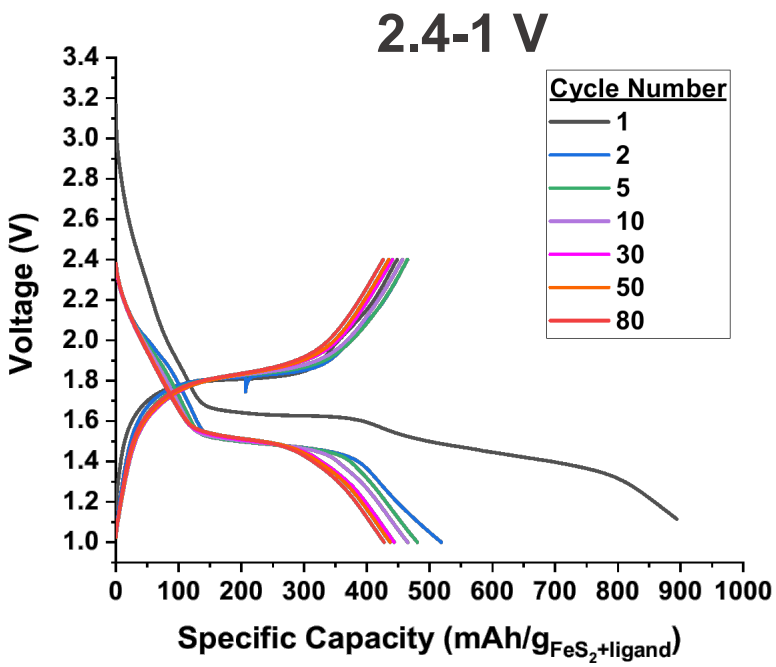
Error bars represent 95% confidence interval

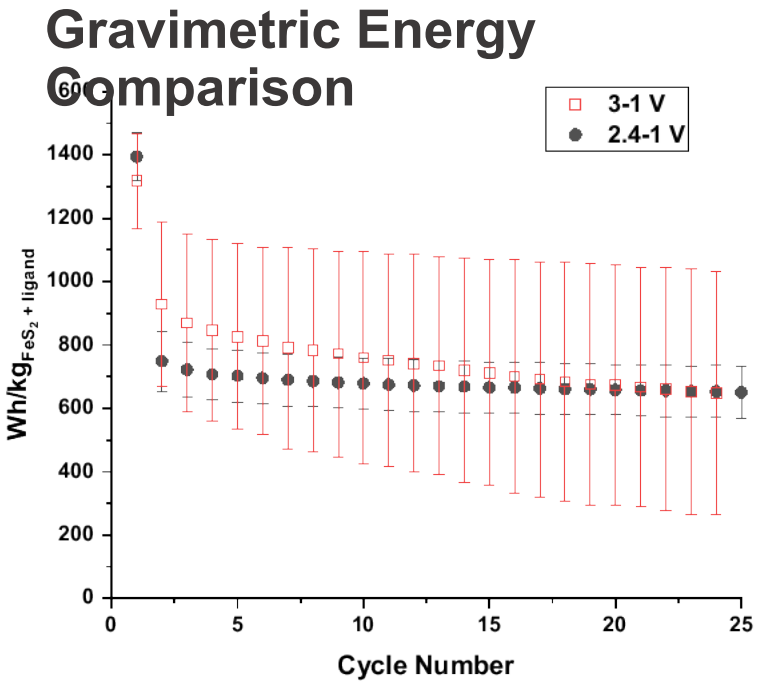
Voltage Window dependence of Nano FeS_2

- Benefits of larger voltage window is quickly nullified by capacity loss and lack of high voltage discharge

Cycling cathodes made from nano FeS_2







Also see better reproducibility between cells made with nano FeS_2

1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mA/cm^2; cathode 60:20:20 FeS_2:Super-P:PVDF

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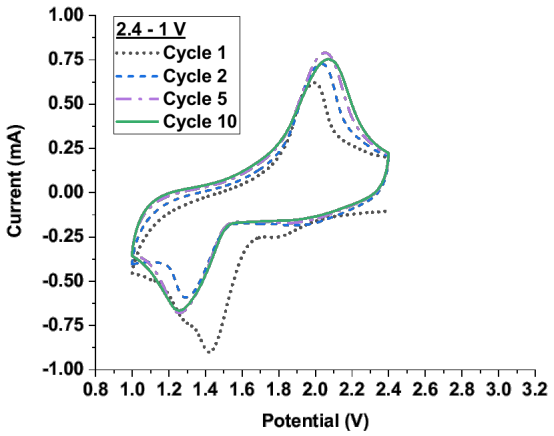
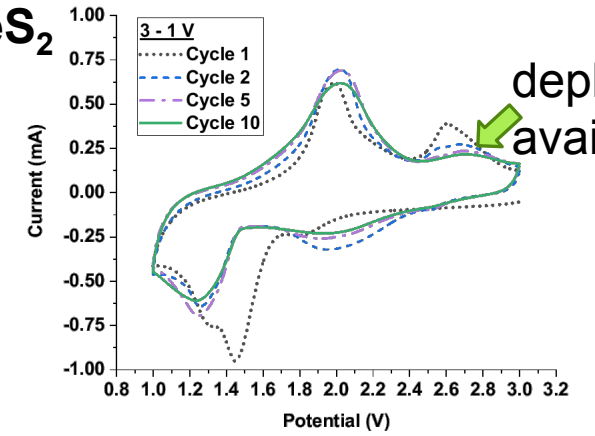
FeS_2 Comparison

- Cyclic voltammetry highlights the size-dependent electrochemistry of FeS_2.
- Polysulfides are still being produced in the limited voltage range for the COTS while absent in nano material

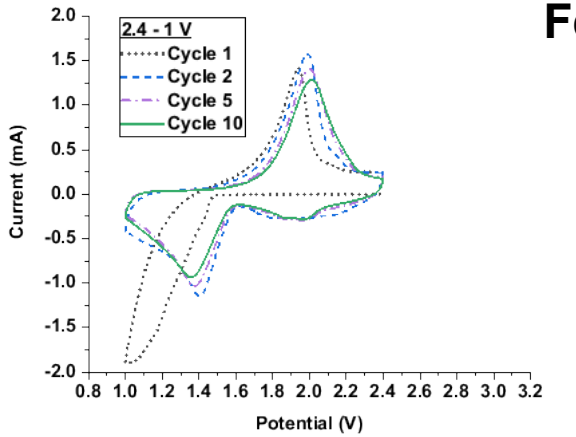
Nano FeS_2

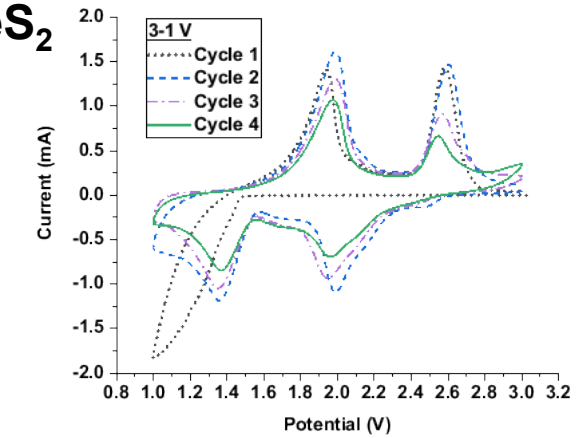




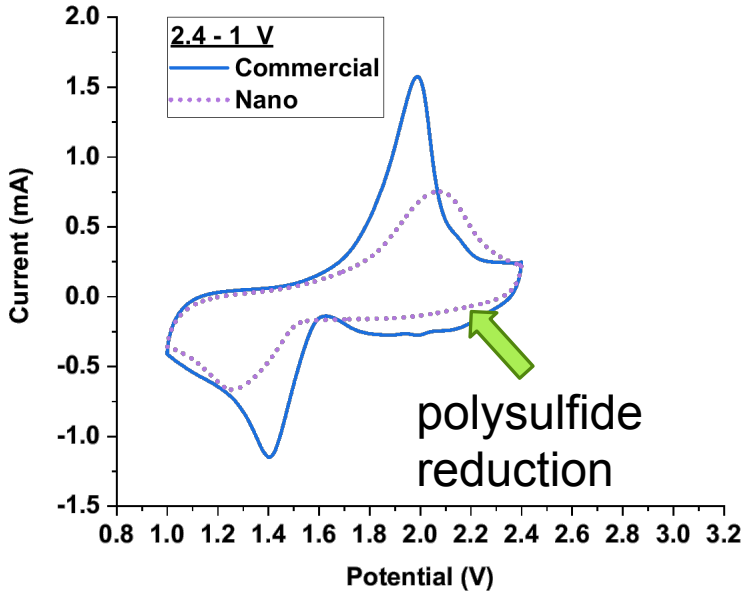
depletion of available Li_2S

COTS FeS_2





1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mV/s; cathode 60:20:20 FeS_2:Super-P:PVDF



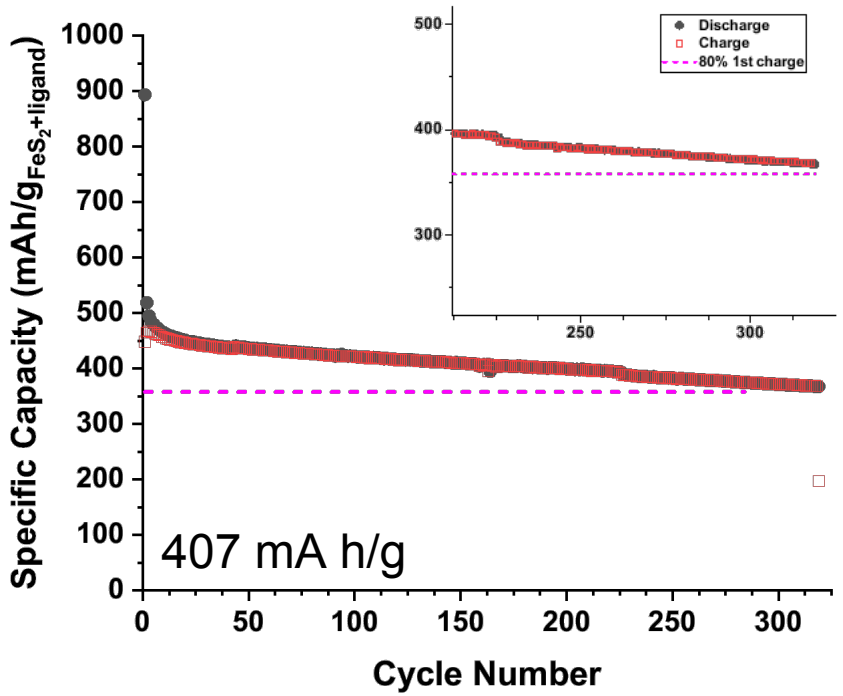
Surface-area-to-volume ratio of nano FeS_2 ensures a more uniform interface for the conversion reactions and an incentive for the uniform extent of the redox reaction in each particle.

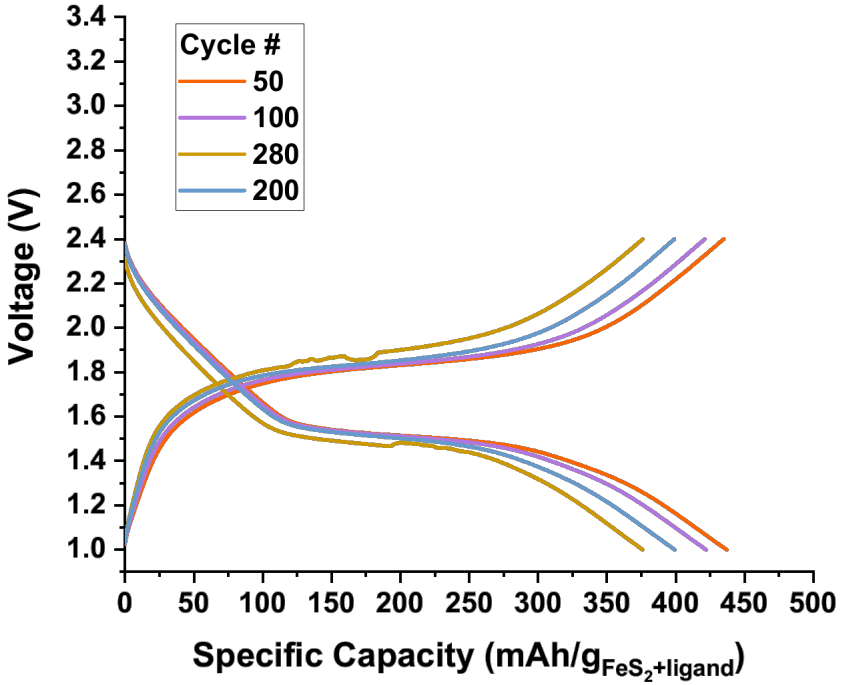
A voltage cutoff is not the only necessary step required to suppress polysulfide formation;

Nano FeS_2 Stability

- Cell cycled between 2.4-1 V capable of hundreds of cycles with good capacity retention and minimal change in voltage profile

Cycling cathodes made from nano FeS_2





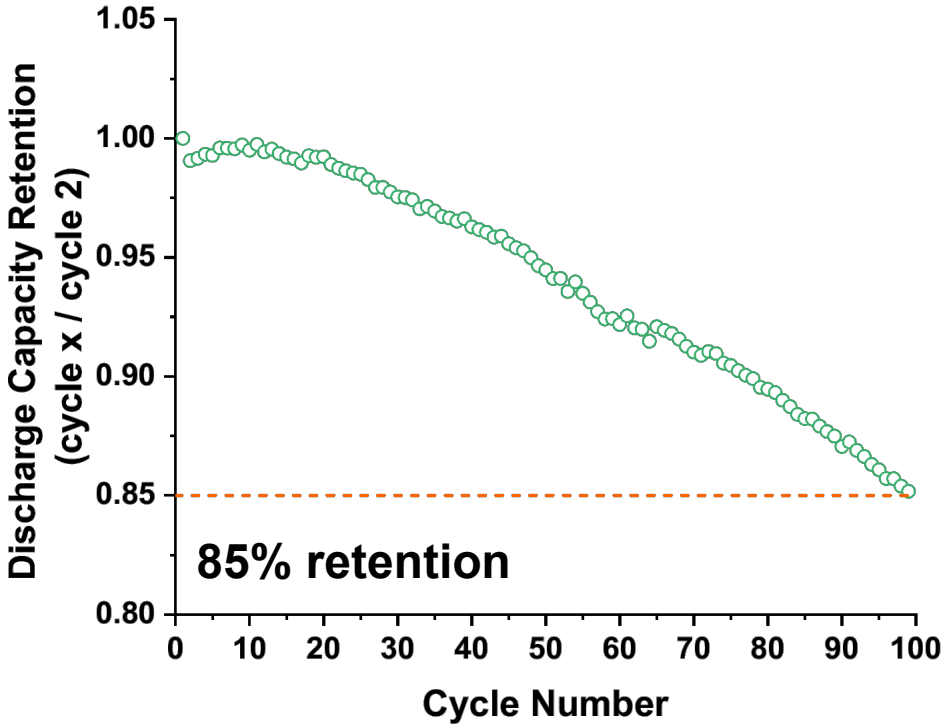
Capacity calculation includes mass of ligand

1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mV/s; cathode 60:20:20 FeS_2:Super-P:PVDF

Nano FeS_2 Stability

- Using limited Li anode with limited voltage window similarly shows cell with decent capacity retention

nano FeS_2 cathode vs 20 µm thick Li anode capacity retention



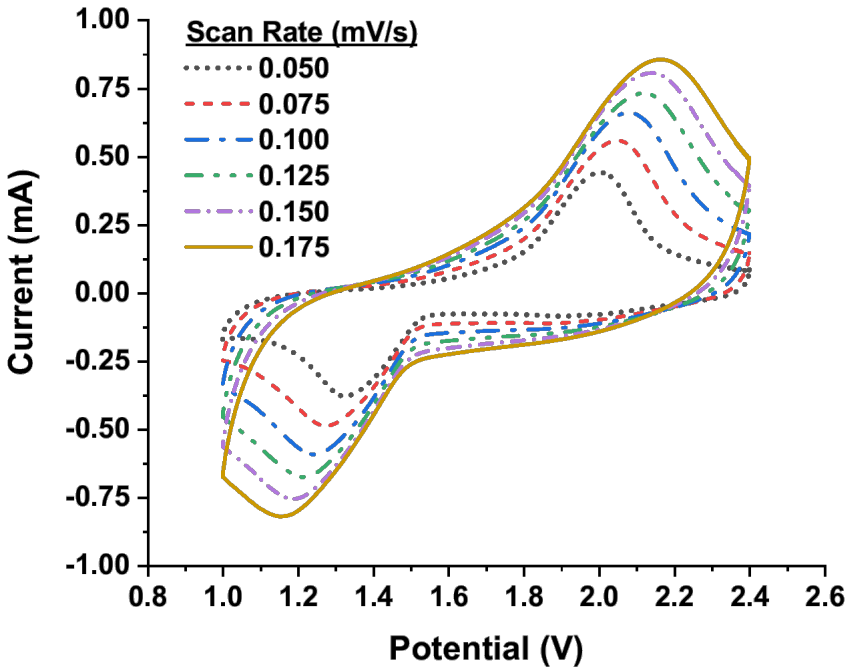
- Avg CE cell = 99.1%
- Li anode capacity = 4.671 mAh
- nanoFeS_2 cathode capacity = 3.052 mAh

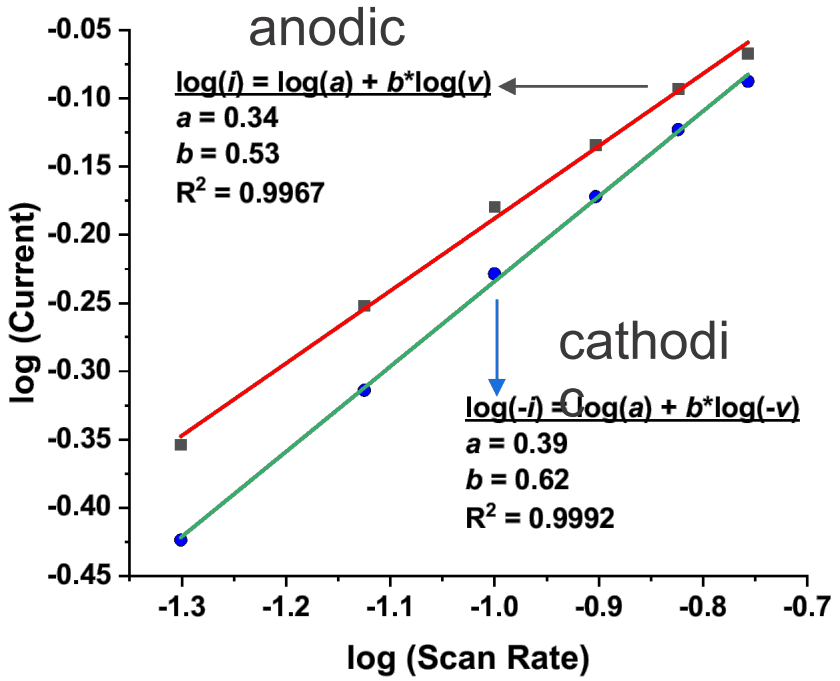
Cell stable with 1.5x Li capacity rather than 50x Li capacity

1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mV/s; cathode 60:20:20 FeS_2:Super-P:PVDF

Source of Current in Nano FeS_2

- Cyclic voltammetry scan rate dependence of nano FeS2 serves as a way to explore the source of current





Where $i_{peak}=ab^{v}$, and b values close to 0.5 calculated from the cathodic and anodic peaks indicates the majority of current is related to a diffusion-controlled process instead of psuedocapacitance

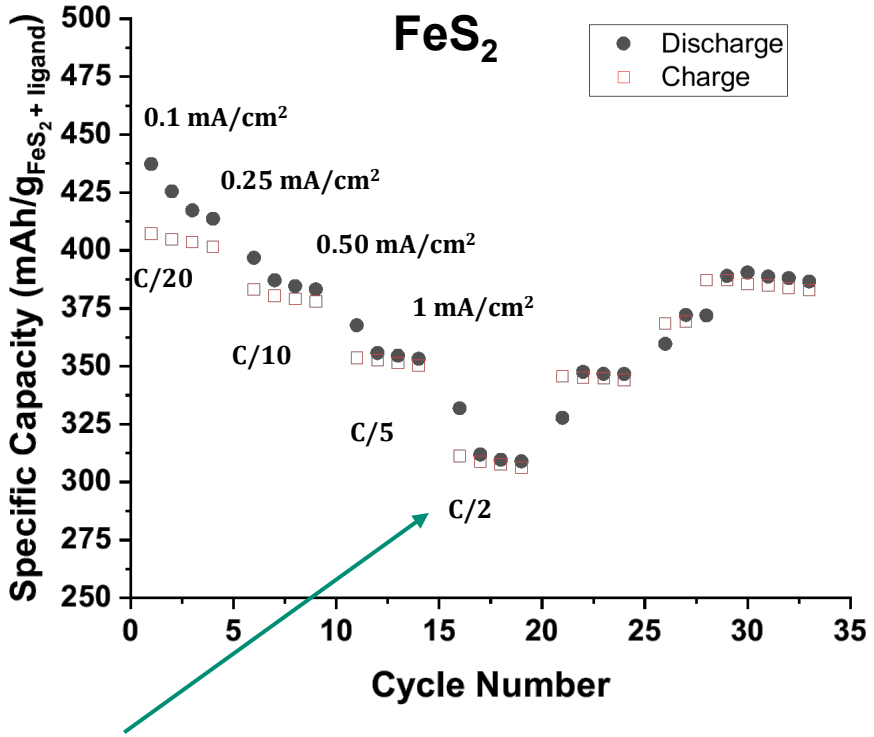
1M LiTFSI : 2M LiFSI DOL:DME; cathode 60:20:20 FeS_2:Super-P:PVDF

Nano

- Nano FeS2 also demonstrates better rate capabilities than COTS

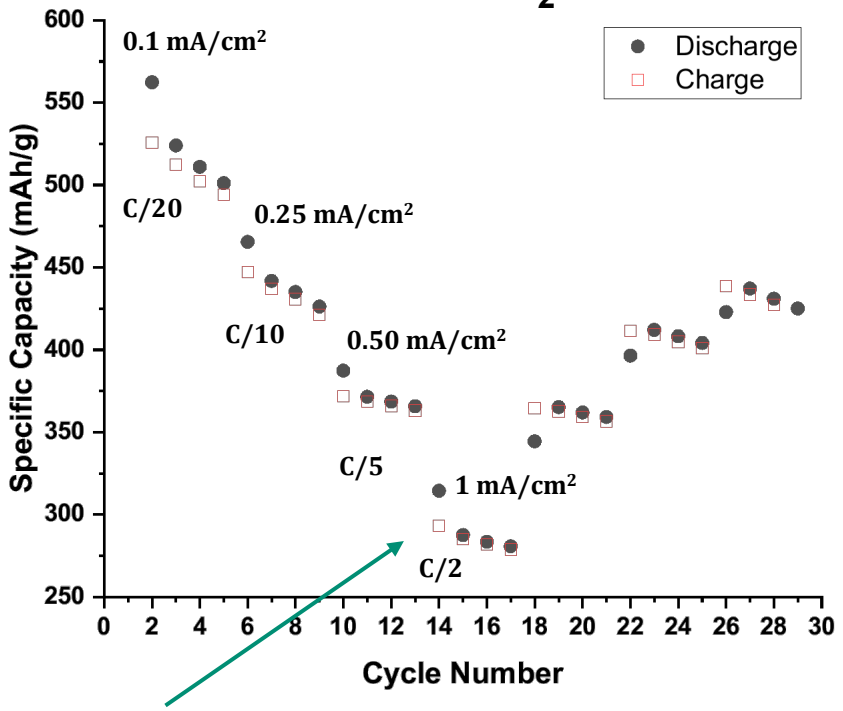
2.4 – 1 V cutoff

Nano FeS_2



75% average retention
from 0.1 mA/cm² cycling

COTS FeS_2



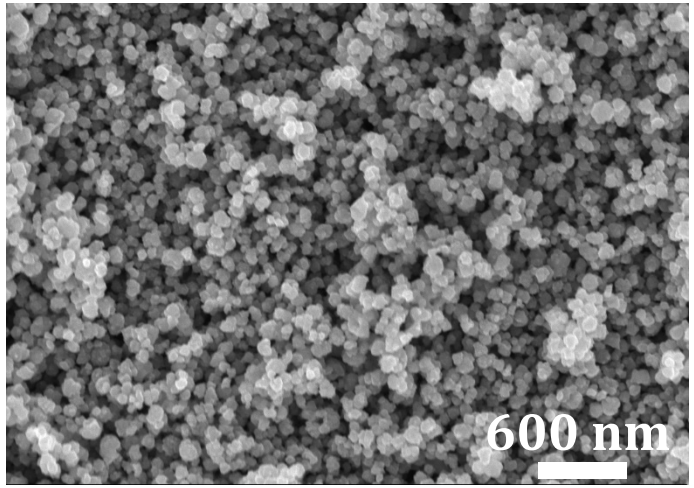
56% average retention
from 0.1 mA/cm² cycling

1M LiTFSI : 2M LiFSI DOL:DME; 0.1 mA/cm²; cathode 60:20:20 FeS_2:Super-P:PVDF

Conclusions

- Rechargeable FeS_2 with capacity retention and minimal complication from polysulfides is a difficult task.

  - Harmony between cathode and anode via electrolyte is of upmost importance
  - Size does mean something to FeS_2
  - Coupling nano FeS_2 to other polysulfide prevention methods could lead to use of full V window



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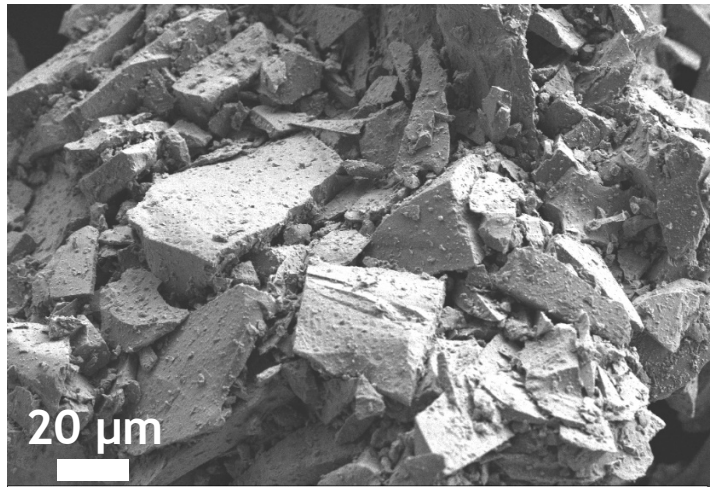
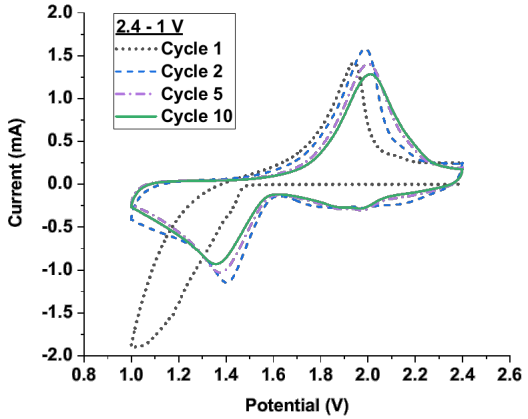
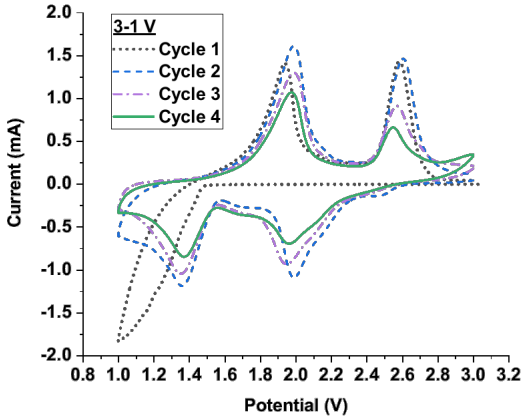
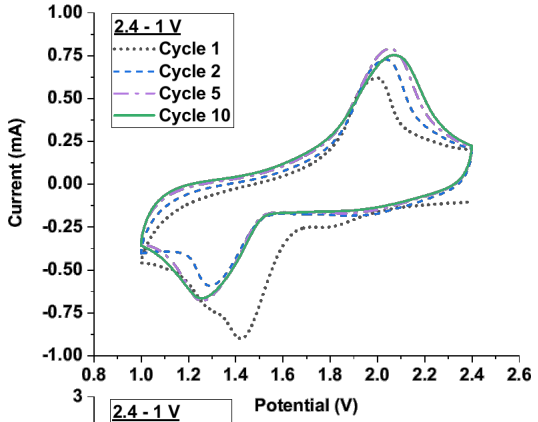
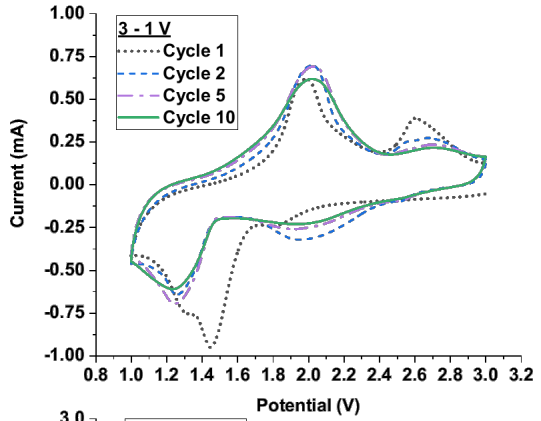


Acknowledgments

- Support
  - Igor V. Kolesnichenko, Laura C. Merrill, Katharine L. Harrison, Timothy N. Lambert

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This presentation describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the presentation do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Content slide

	2.4 – 1 V cutoff	3 – 1 V cutoff
Commercial		
Nano		
Ball Milled