

Porous Organic Polymers Containing Redox-Active Disulfide as Electrode Materials for High-Performance Lithium-Sulfur (Li-S) Batteries



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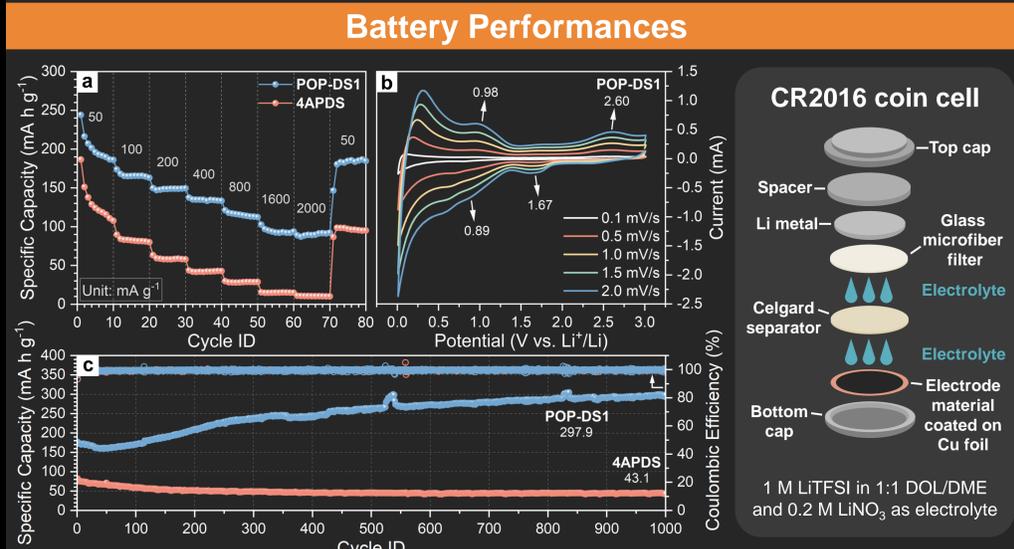
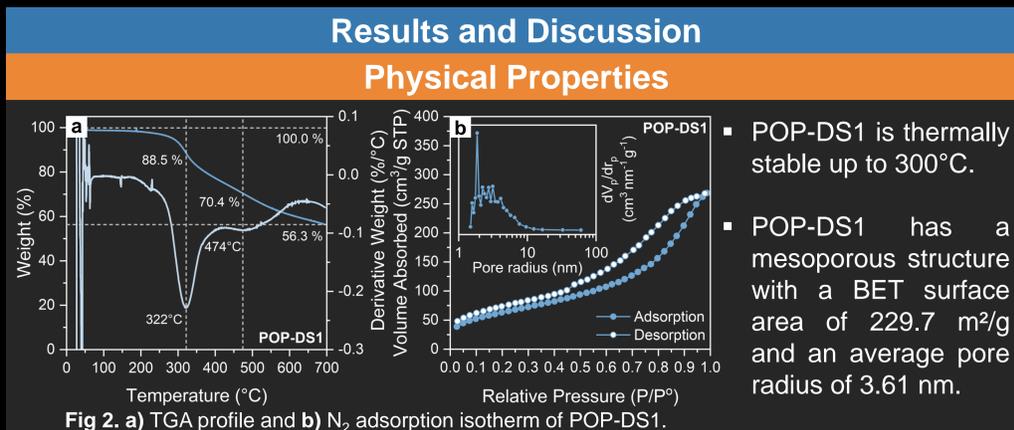
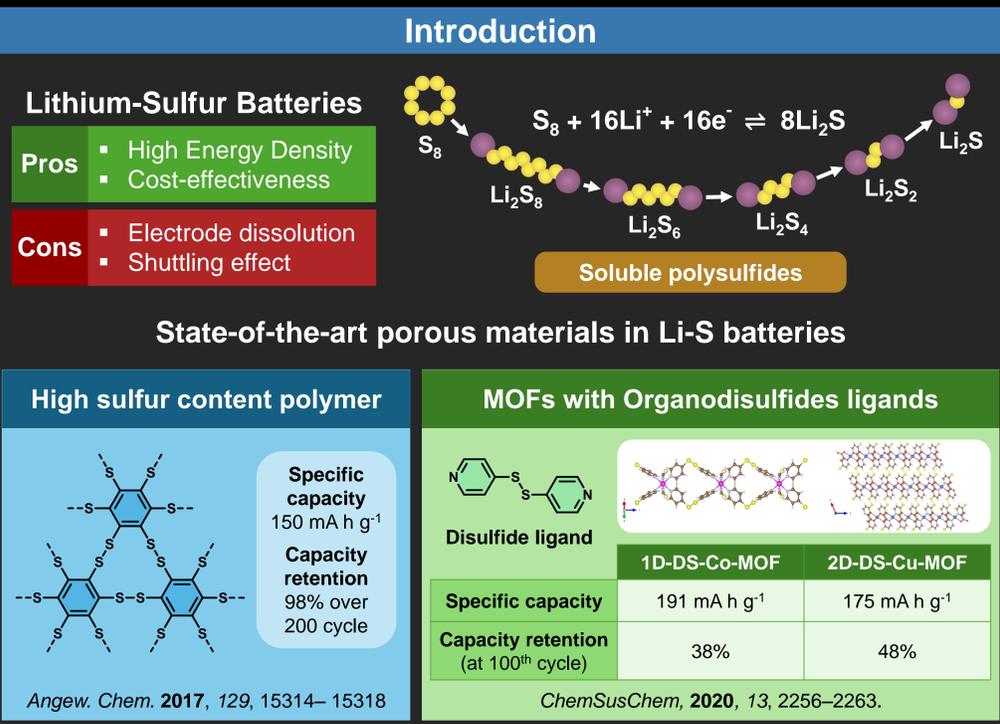
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Abstract

Using redox-active disulfide-containing polymers in lithium-sulfur (Li-S) batteries can reduce the shuttling effect, thereby improving battery performance. However, previous efforts in this area involved sophisticated synthesis to provide electrodes with inferior capacity performance and capacity retention. In this work, we anchored disulfide linkages in a porous organic polymer (POP), namely POP-DS1, via a simple azo coupling between 4,4'-aminophenyl disulfide (4APDS) and phloroglucinol. POP-DS1 was characterized by FT-IR, Raman, and ¹³C CP/MAS NMR spectroscopy. It was found that the battery performance of POP-DS1 demonstrated improved capacity (185 mA h g⁻¹ at a current density of 50 mA g⁻¹), good rate performance and better cycling stability than the 4APDS precursor. Interestingly, the capacities of POP-DS1 increased in long-term cycling studies, presumably due to material activation. We anticipated that our easily accessible POPs could effectively mitigate the polysulfide shuttle, providing high-performance organic electrodes comparable to the state-of-the-art materials for Li-S batteries.

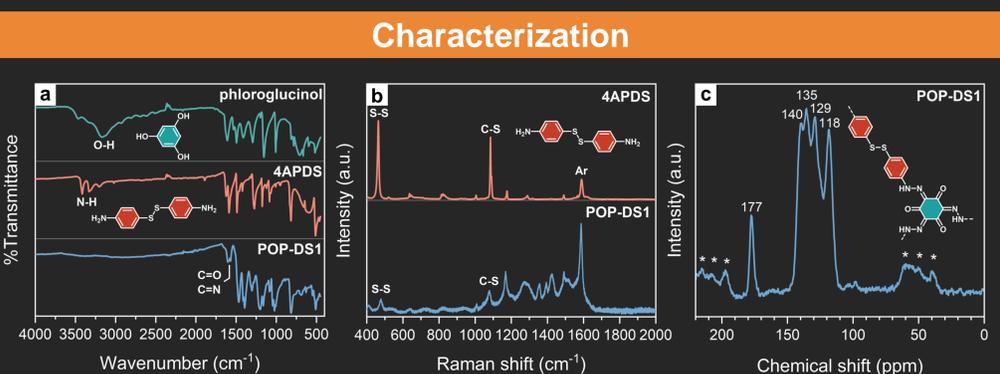
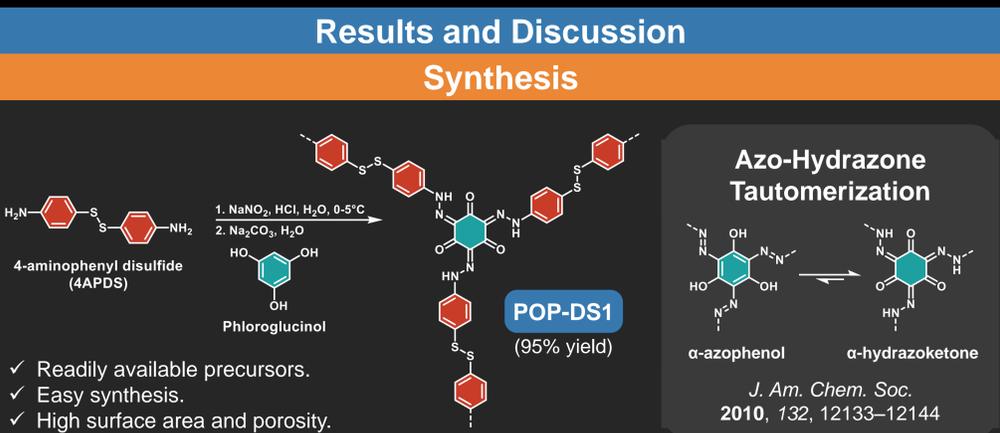


Research Objectives

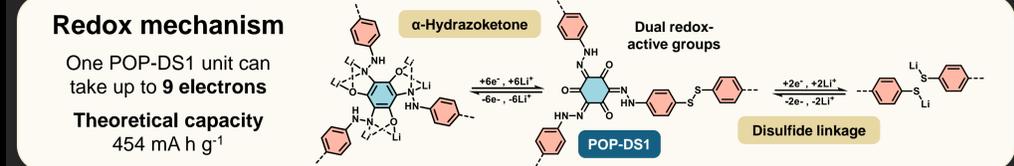
- To synthesize and characterize porous organic polymer containing disulfide linkage (POP-DS) through azo coupling reaction.
- To utilize as-synthesized POP-DS as an electrode material for Li-S batteries.

Research Methodology

Synthesis	Characterizations	Physical properties	Electrochemical studies
<ul style="list-style-type: none"> POP-DS Purification 	<ul style="list-style-type: none"> FT-IR Raman ¹³C CP/MAS NMR 	<ul style="list-style-type: none"> TGA N₂ sorption study 	<ul style="list-style-type: none"> Rate performance Cycling stability Kinetic study



- FT-IR and Raman spectra show characteristic signals from S-S and C-S stretching (464 and 1084 cm⁻¹). Signals near 1600 cm⁻¹ could be assigned to C=N and C=O stretching, which indicates that tautomerization is possible.
- ¹³C-NMR spectrum shows a signal at 177 ppm corresponding to C=O and C=N and aromatic signals around 118-140 ppm.



- POP-DS1 exhibits improved rate performance, with a specific capacity of 185 mA h g⁻¹ at 50 mA g⁻¹, which is on par with previously reported materials.
- POP-DS1 shows a steady increase in capacity, stabilizing at around 290 mA h g⁻¹ at >800 cycles, suggesting the material activation.
- A preliminary electrochemical kinetics study suggests that POP-DS1 stores charge through both capacitive and diffusion processes.

Conclusion

- POP-DS1 was successfully synthesized from a simple azo coupling reaction of 4APDS and phloroglucinol with excellent yield.
- FT-IR and Raman spectroscopy could verify the presence of disulfide bonds and α-hydrazoketone units in the polymers, while ¹³C CP/MAS NMR data provide additional confirmation of the structure of the synthesized polymers.
- POP-DS1 demonstrated good thermal stability and high porosity, which promotes electrolyte and ion infiltration suitable for battery applications.
- POP-DS1 exhibited improved rate performance and cycling stability, but the 4APDS precursor showed poor battery performance, suggesting that the effective incorporation of redox-active groups within the polymeric structure plays a key role in reducing electrode dissolution.

Acknowledgement

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