Polythiophene-Sulfur-Copolymers as Cathode-Active-Materials for Lithium-Sulfur-Batteries

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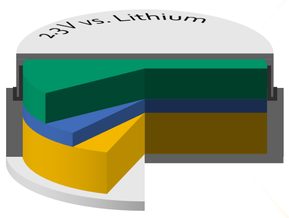
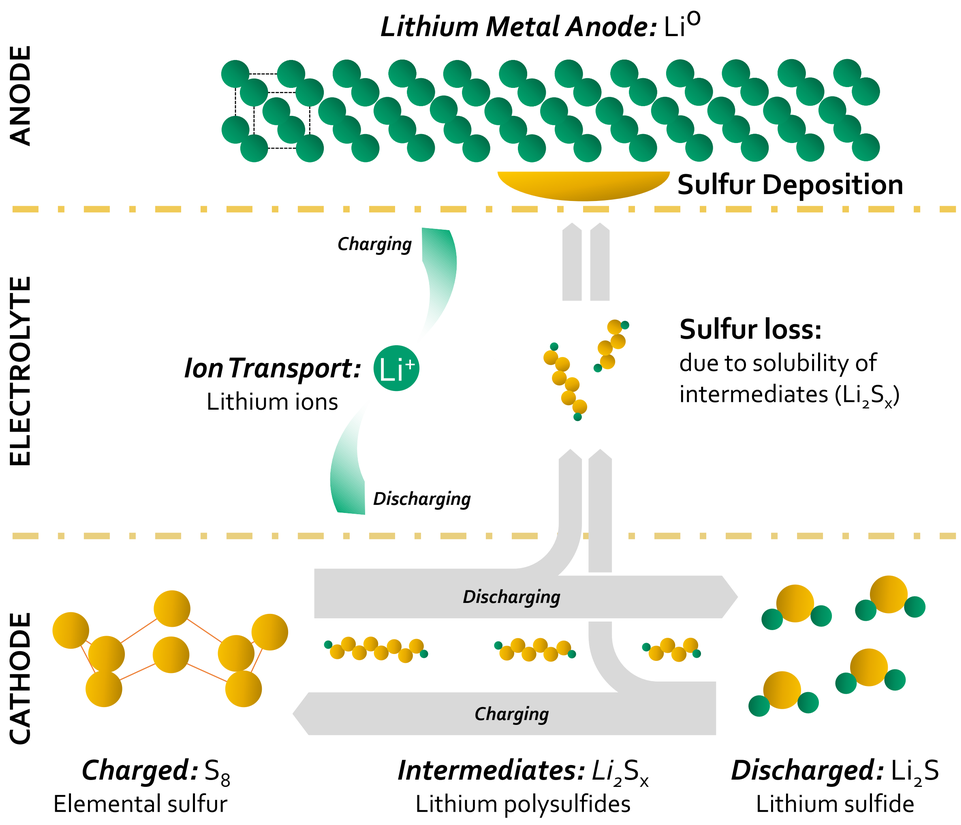
Motivation and Challenges

Pros
- ✓ high availability
- ✓ low prize of sulfur
- ✓ environmentally benign
- ✓ high specific capacity

Cons
- x low conductivity of sulfur
- x solubility of intermediates results in capacity decay
- x intermediates can form insulating layer on anode
- x high volume expansion

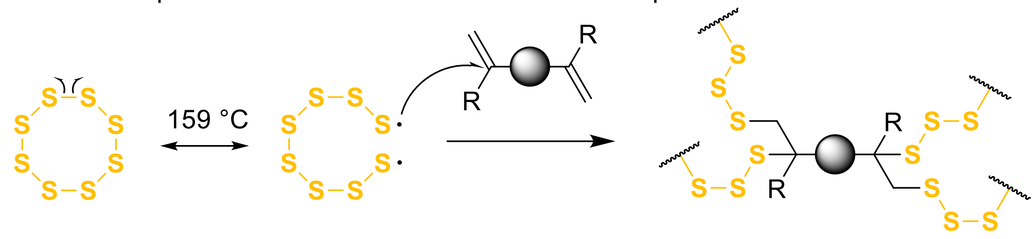




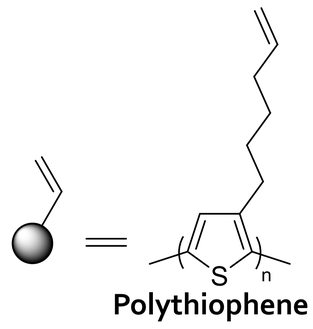
Concept

Inverse vulcanization

- ➢ reduction/prevention of sulfur loss/polysulfide dissolution
- ➢ improve sulfur distribution in cathode composite



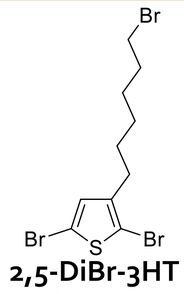
Semiconducting polymer backbone



- ➢ address low conductivity of sulfur
- ➢ improve charging rate limitations
- ➢ tunable polymer properties
- ➢ variable anchor moiety density

Material Synthesis and Characterization

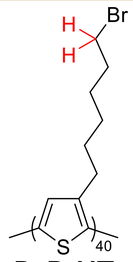
Monomers



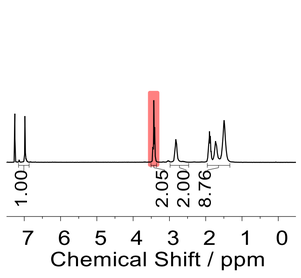
2,5-DiBr-3HT
2,5-dibromo-3-(6-bromohexyl)thiophen

Polymerization

a) 3.4 g (83%)

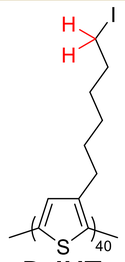


P3BrHT
poly(3-(6-bromohexyl)thiophene

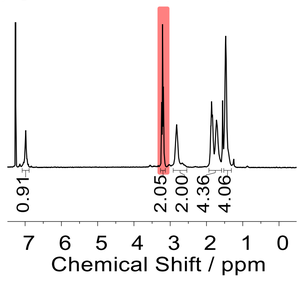


Polymeranalogeous Reactions

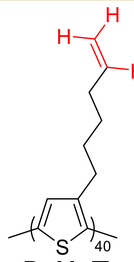
b)



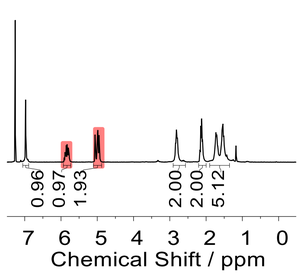
P3IHT
poly(3-(6-iodohexyl)thiophene



c) 300 mg (60%)

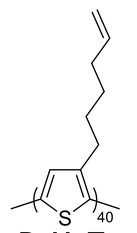


P3HeT
poly(3-(5-hexen-1-yl)thiophene



reaction conditions
a) tBuMgCl, Ni(dppp)Cl2, THF, HCl, 1h
b) KI, TBAB, H2O/Toluene, 3d
c) KOtBu, THF, 0°C, 8h
d) 1,2-DCB, 165 °C, 1h

Inverse Vulcanization



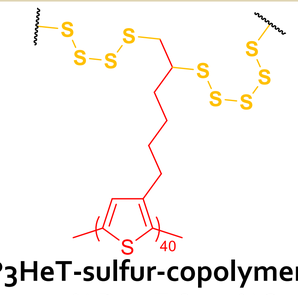
P3HeT

d)

carbon-carbon double bond is used to attach sulfur covalently to the polymer

cathode-active-materials (CAMs) are used to formulate cathode composites

Cathode-Active-Materials

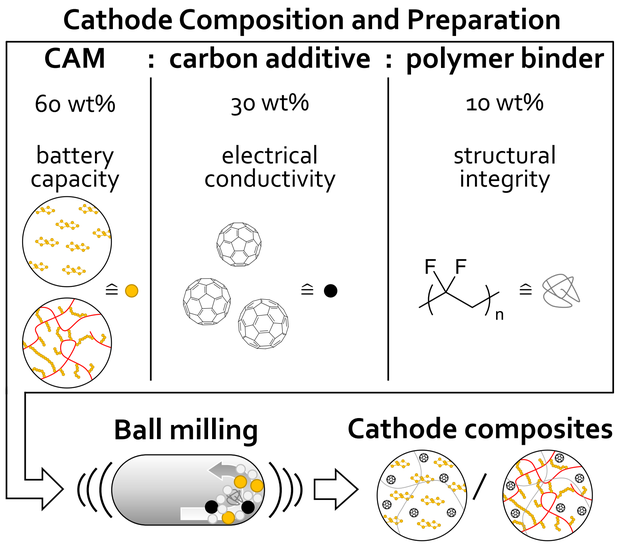


P3HeT-sulfur-copolymer
20 wt% P3HeT-80 wt% S

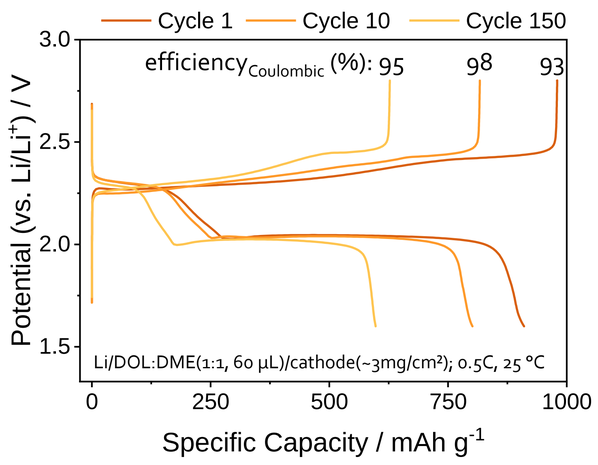
Elemental sulfur as reference

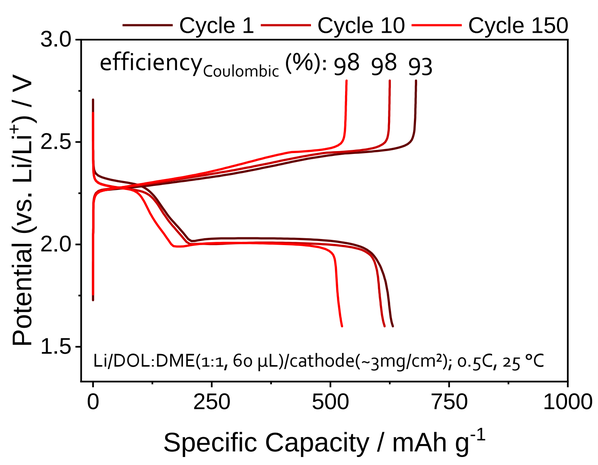
Electrochemical Studies

Cathode Composition and Preparation

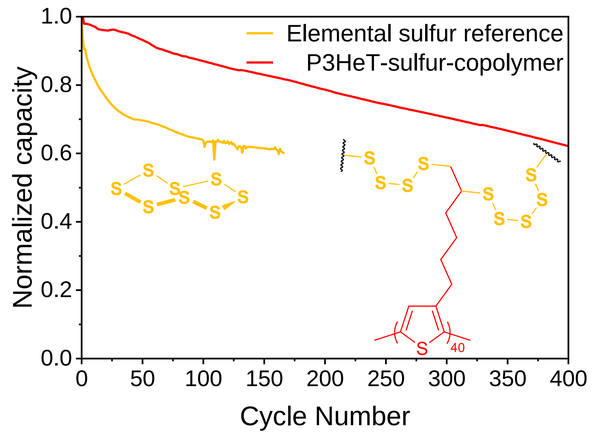


- cathode composites slurry is coated on conductive substrates by doctor blading



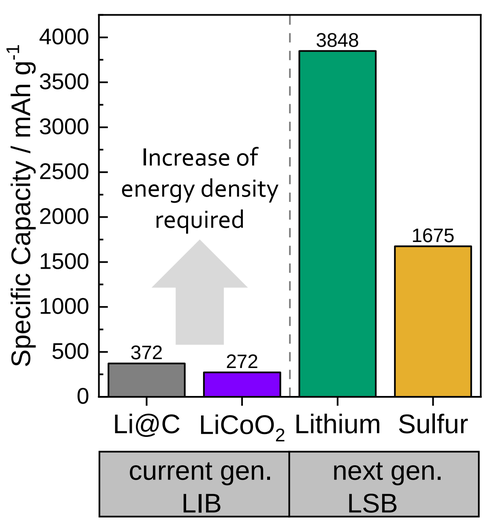


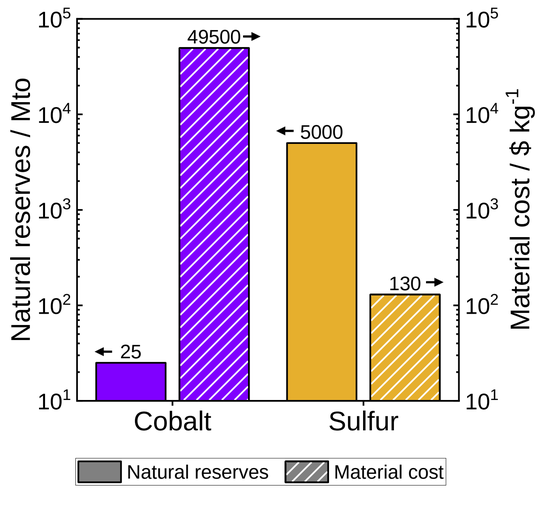
- sulfur exhibits a two-step reduction process (1st step: 2.4-2V; 2nd step: 2V plateau)
- low Coulombic efficiency during 1st cycle → interface formation reaction and sulfur loss
- overall higher discharge capacities for elemental sulfur cathodes



- capacity fading reduced in P3HeT-sulfur-copolymer compared to elemental sulfur
- 60% of initial capacity after 156 and 424 cycles for P3HeT-S and S, respectively

Lithium-Sulfur Batteries in Numbers





Conclusion and Outlook

- ✓ successful material synthesis of P3HeT and application in lithium-sulfur batteries
- ✓ covalent connection during inverse vulcanization improved cycling life → reduced sulfur loss
- ➢ optimization of cathode preparation to improve accessible discharge capacities
- ➢ variation of polymer compositions by copolymerization with other monomers
- ➢ doping experiments of P3HeT and influence on electrical conductivity in cathode composite

References

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