Sulfurized carbon as high performance cathode material for lithium/sulfur batteries

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Why sulfurized carbon (SC)?

- **Li/S battery faces great challenges that cannot be solved by a single solution**
  - Dissolution of long-chain lithium polysulfide (PS) in organic electrolytes, resulting in
    - Loss of sulfur active material
    - Redox shuttle (low energy efficiency, high self-discharge, Li corrosion)
  - Low power capability due to intrinsic insulating nature of S, PS and Li$_2$S
  - Poor safety due to PS dissolution and low melting point of sulfur (specially for hot-oven storage)

- **Complete solution to the problems present in the Li/S battery**
  - **Solid state electrolyte;** this however brings new challenges
    - Difficulty in making a large area electrolyte membrane
    - Insufficient ionic conductivity for high power applications (two factors: the bulk and thickness)
    - Electrolyte-electrode interface issues (chemical compatibility, contact resistance, grain boundary resistance)
    - High cost
  - **Sulfurized carbon (SC)**
    - No PS dissolution
    - High electronic conductivity for meeting high power applications
    - Excellent thermal stability for safety
    - Low cost and environmental friendliness

**SC materials provide a complete solution to the problems of Li/S battery**
What is a SC?

**Structural characteristics**
- A compound with short \(-S_n-\) chains covalently bound to carbon or polymeric backbone of a carbon precursor
- Sulfur cannot be removed through sublimation/evaporation and solvent extraction

**Preparation of SC (i.e., “sulfurization”)**
- Reaction of sulfur with carbon or carbon precursor at temperatures above 300 °C
  - Carbon source: A variety of carbons, polymers, organic compounds and even organic wastes
  - Sulfur source: Elemental sulfur, H$_2$S, SO$_2$, CS$_2$, and all other sulfur-containing organic compounds

**Primary application of SC**
- Enrichment & removal of heavy transition metal ions from water for environmental treatment

**SC compound vs. S-C composite**
- Thermally stable up to 700 °C, cannot be extracted by solvent, such as CS$_2$ and toluene
- Prefer carbonate-based electrolytes
- Only a single discharge voltage plateau at ~2 V
- High polarization and capacity loss in the first discharge
Stage 1 (early 1980s): Exxon Res. & Eng. Company


Stage 2 (2002-2009): Shanghai Institute of Microsystem and Information Technology, China

- J.L. Wang, J. Yang, J.Y. Xie, N.X. Xu, “A novel conductive polymer sulfur composite cathode material for rechargeable lithium batteries”, *Adv. Mater.*, 2002, 14, 963–9650: Prepared a SC by reacting sulfur with polyacrylonitrile (PAN) at 280-300 °C for 6 h, and tested Li/SC cell using a 1 M LiPF$_6$ 1:1 (vol.) EC/DMC electrolyte. The authors thought sulfur formed complex with the conductive polymer

Stage 3 (since 2009): Nankai University, China

Many kinds of SCs have been prepared mainly through two routes:
- Reaction of sulfur with carbonaceous materials, either commercial carbon or pyrolyzed carbon of natural or synthetic polymers.
- Reaction of sulfur with carbon precursor, either organic compounds or polymeric resins.

It has been recognized that except for a difference in specific capacity, all kinds of SCs have very similar electrochemical properties no matter the synthetic route and carbon source.

Both chemical structure and electrochemical mechanism are poorly understood and debated:
- SC compounds are often misunderstood to be S-C composites, for example, small sulfur molecules trapped within the pores of carbon.
- The Redox mechanism of SC remains unclear.

The chemical structure and electrochemical properties of SCs will be the focus of this presentation.
• **Mechanism of sulfurization**
  - Typically, two kinds of reactions are involved in the formation of S-C bonds
    - **Dehydrogenation** to produce >C=C< bonds
    - **Vulcanization**, in which S reacts with >C=C< bonds, to form S-C bonds
  - These two reactions take place together

• **As one of the most important SCs, sulfurized polyacrylonitrile (SPAN) is selected for further discussion. The synthesis of SPAN consists of [1]**
  - **Step 1:** Sulfur functions as a dehydrogenating agent to produce >C=C< bonds
  - **Step 2:** Sulfur vulcanizes >C=C< bonds to form C-S bonds
  - With an increase in the temperature of sulfurization, the length of –Sn– chains shortens and the content of sulfur decreases

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The form of sulfur in SPAN

Three forms have been proposed

**Small sulfur molecules trapped within the pores of carbon (X)**
- Sulfur should be extracted by CS$_2$ solvent or evaporated/sublimated by heating
- Small S molecules tend to form more stable S$_8$, breaking the structure of pores

**Small sulfur molecules doped into conjugated >C=C< polymer (X)**
- Conductivity of SPAN made at 350 °C was too low to be measured by Solartron instruments

**Short –S$_n$– chains covalently bound to carbon or polymeric backbone (V)**
- Sulfur cannot be completely removed even at 800 °C, the TG-MS spectrum shows strong CS$_2$ in the thermal decomposition of SPAN [1]
- Raman spectrum shows absorptions of C-S vibration at 305, 374, and 927 cm$^{-1}$ [2]
- XPS shows S$_{2p}$ double peak of C-S at 163.2 eV [3]

Based on the fact that the short \(-S_n-\) chains are covalently bound to carbon or a polymeric backbone, Structures A and B have been proposed, however, both structures do not match the results of elemental analysis (C/H=2.8–2.9) [1, 2].

A more reasonable structure would be C, namely the short \(-S_n-\) chains are covalently bonded onto cyclized, partially dehydrogenated, and ribbon-like polyacrylonitrile backbones [3].

Two stages of thermal decomposition: i.e., 300-410 °C and above 410 °C, corresponding to the breakage of S–S bonds and C–S bonds, respectively.

H₂S dominates low temp. region, and CS₂ dominates above 410 °C.

Based on the mass loss in two temp. regions and the sulfur content by elemental analysis, the length of –Sn– chains can be estimated. For example, the averaged n in the –Sn– chains of a SPAN containing 49.1% S is 3.37.

Typical electrochemical properties of SPAN

- Cyclic voltammogram shows only a pair of redox current peaks
- Discharge shows a single voltage plateau
- The first discharge suffers high polarization
- There is a large irreversible capacity loss from the 1st to 2nd discharge

The above behaviors indicate that the Li/SPAN cell operates more like an all-solid-state Li/S cell than a liquid electrolyte Li/S cell.
Comparison with S-C composites in liquid electrolyte Li/S cells

Cyclic voltammogram: One reduction current peak vs. two peaks
Discharge voltage profile: One plateau vs. two plateaus

Li/S-C cell
- two peaks in CV
- two plateaus in voltage profile

Li/SC cell
- one peak in CV
- one plateau in voltage profile

Both types of cells have only a discharge voltage plateau, suggesting that the conversion of the short $-S_n-$ chains in SC to Li$_2$S undergoes through a single phase transition (i.e., solid-to-solid, no polysulfide dissolution).

High polarization in the first discharge is due to the large grain boundary resistance (GBR), which can be observed from all conversion-type cells.

Electrolyte preference

- Li/SC cell performs better in a carbonate-based electrolyte than in an ether-based electrolyte

1 M LiPF$_6$-PC-EC-DEC  
1 M LiTFSI-DME-DOL

Advantages of Li/SC cell over conventional Li/S cell

- Compared with the conventional Li/S cells, a Li/SC cell shows
  - High specific capacity (1200-1500 mAh/g S) even at high SC loading (>6 mg/cm²)
  - Nearly 100% coulombic efficiency and very low self-discharge
  - Excellent capacity retention, most failures were found to be related to the Li anode, not the SC cathode
  - Excellent safety due to the thermal stability
  - Prefer carbonate-based electrolytes, enabling to design a low cost, metal-free, “all-carbon” Li-ion battery with a conventional graphite anode

- Examples of Li/SPAN cells

  SPAN was made by heating a mixture of S and PAN [1] and S and PAN-pyrolyzed carbon [2]

A proof-of-concept for “all-carbon” Li-ion battery

- A metal-free “all-carbon” graphite/SPAN cell [1, 2]
  - Used a SPAN made at 300-450 °C
  - SPAN was pre-lithiated using an electrochemical method
  - Resultant Li-ion cell showed excellent cyclability and over-discharge tolerance, having no issues of PS dissolution and self-discharge

• Reproducible observations
  – High polarization
  – Inevitable capacity loss from the 1\textsuperscript{st} to 2\textsuperscript{nd} discharge

• Understanding
  – High polarization is due to the grain boundary resistance (GBR), which is very common and can be observed from all conversion-type electrode materials
  – Initial capacity loss is unlikely to be the irreversible reduction of electrolyte solvents on the surface of carbon

• Established facts
  – Inevitable capacity loss from the 1\textsuperscript{st} to 2\textsuperscript{nd} discharge
  – Extra reversible capacities when being over-discharged
  – High specific capacity (typically 400-700 mAh/g SPAN or 1200-1500 mAh/g S) and excellent capacity retention

• Proposed redox mechanism [1]

• Explanation to the observations
  – \textbf{Initial capacity loss}: due to irreversible reduction of the short conjugated >C=C< chains
  – \textbf{Extra capacity by over-discharging}: due to reversible redox of the long conjugated >C=C< chains/planes
  – \textbf{High specific capacity and excellent capacity retention}: due to single solid-to-solid phase transition (no polysulfide dissolution) as well as the strong interaction (complex) between the conjugated >C=C< chain/plane and Li$_2$S$_n$

Both the potential and reversibility of reduction are changed with the delocalization degree of electrons, i.e., the length/size of carbon conjugation.

<table>
<thead>
<tr>
<th>&gt;C=C&lt; conjugation</th>
<th>Potential vs. Li/Li⁺</th>
<th>Reversibility</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single &gt;C=C&lt; bond</td>
<td>vinylene carbonate</td>
<td>1.4~1.5 V</td>
<td>irreversible</td>
</tr>
<tr>
<td>Long 1D chain</td>
<td>n-doped polyacetylene</td>
<td>~1.3 V</td>
<td>reversible</td>
</tr>
<tr>
<td>Large 2D plane</td>
<td>graphite</td>
<td>0.1~0.3 V</td>
<td>highly reversible</td>
</tr>
<tr>
<td>SPAN</td>
<td>short &gt;C=C&lt; bond</td>
<td>1.0~1.2 V</td>
<td>irreversible</td>
</tr>
</tbody>
</table>


It may conclude that:
- The initial capacity loss is due to irreversible reduction of the short conjugated >C=C< chains.
- The extra reversible capacities below 1 V are due to reversible reduction of the highly delocalized conjugated >C=C< bonds.

Challenges for the SC materials

- **Challenge for the requirements**
  - **High capacity**: requires high sulfur content, which however leads to the formation of long $-S_n-$ chains or even elemental sulfur. Currently limited to 40~45 wt.% for SPANs with excellent cyclability.
  - **High power (conductivity)**: requires high sulfurization temperature, which often results in low sulfur content.
  - **Long cycle life (stable capacity retention)**: requires short $-S_n-$ chain, which is often accompanied by low sulfur content.

- **Strategy/direction**: Increase the content of sulfur while retaining short $-S_n-$ chains ($n<4$) by maximizing the formation of C–S bonds.
  - Elimination of functional groups is often accompanied by the formation of $>C=C<$ bonds or radical intermediates, therefore, molecular design of the carbon precursor opens a promising direction for increasing the number of C-S bonds.
  - Strategies used for vulcanization in the rubber industry can be borrowed. Use of a vulcanization accelerator (VA) has proven to increase the content of sulfur from 28% to 36% [1].

Like an initiator in radical polymerization, the VA thermally decomposes to generate radicals, which subsequently initiate the vulcanization (forming C–S bond).

Conclusions

• Sulfurized carbon (SC) materials provide a complete solution to the problems of liquid electrolyte Li/S batteries
  – No PS dissolution and related problems
  – Excellent thermal stability for safety
  – Low cost and abundant resources for carbon and carbon precursors
  – Prefer carbonate-based electrolytes, making “all-carbon” Li-ion possible
  – Environmentally friendly without need of disposal

• Challenges still remain
  – How to increase the content of sulfur while retaining short –S\(_n\)– chains

• Focus for future research
  – Fundamental understanding on the SC materials and their electrochemical properties
  – Molecular design of carbon precursors and optimization of sulfurization conditions.