Optical Diagnostics of Lithium-Sulfur Batteries with Attenuated Total Reflection Spectroscopy

Cody Silva, Najmus Saqib, Dr. Jason Porter

Li-S Battery Fundamentals
Lithium anode, carbon/sulfur cathode
Electrolyte composed of a lithium salt in an organic solvent
Current is produced via the reduction of sulfur (S₄) to lithium polysulfides of decreasing order (pictured right)

Benefits:
- High specific capacity of lithium metal (3862 mAh/g vs. 372 mAh/g in lithium-ion batteries via LiC₆)
- High reduction energy of sulfur from S₄ to S²⁻ (1675 mAh/g, ~10 times higher than transition metal oxides used in lithium-ion batteries)
- Lithium and sulfur are lightweight active materials
- Sulfur is an earth-abundant choice for cathodic material

Challenges:
- Volume expansion of lithium polysulfides mechanically stresses cathode
- Dissolution of higher-order polysulfides causes irreversible loss of sulfur and unwanted side reactions with the anode
- Precipitation of Li₂S on cathode inhibits sulfur utilization

Prior to this study, no quantitative method existed for measuring polysulfides in Li-S batteries. Such a method would be indispensable in understanding the complex polysulfide shuttling in these batteries.

Polysulfide Characterization with ATR Spectroscopy
Lithium polysulfide samples were prepared in a glove box by the reaction of Li₂S and elemental sulfur in DMSO and TEGDME solvents, the amount of sulfur being varied to skew the polysulfide equilibrium around a specific polysulfide order.

Spectra were taken using the Nicolet™ iS™ 50 FT-IR Spectrometer with an ATR attachment (pictured below).

Full spectra were collected, with attention given to the far-IR region, where absorption features characteristic of the S-S bonds in the polysulfide chains are present.

Principles of ATR Spectroscopy
Attenuated Total Reflection (ATR) is a technique used in conjunction with IR spectroscopy that enables spectra to be taken directly in the solid or liquid phases with very minimal sample preparation.

An incident light beam is totally internally reflected in a crystal, producing an evanescent wave, an electromagnetic wave whose energy is concentrated in the vicinity of the reflection, in the medium adjacent to the crystal. If a sample is pressed against the reflecting crystal, a portion of the beam energy can be absorbed by the sample. The reflected beam is measured and an absorbance spectrum is obtained.

A New Optical Diagnostic Method for Li-S Batteries
The results of this research represent the first quantitative method to measure lithium polysulfide reduction.

Spectral analysis revealed that the peak position of the S-S absorption feature increased linearly with increasing polysulfide order (pictured right).

In addition, analysis showed that the area under the S-S absorption peak of a specific polysulfide increased linearly with respect to concentration (pictured left).

These phenomena were combined into a new optical diagnostic technique to determine the prevailing order and concentration of an unknown lithium polysulfide sample (pictured right).

Future Design Iterations
1. A porous carbon cathode will be incorporated, and in-situ spectroscopy will be performed to assess the optical and electrochemical performance of the cathode/spectrometer system.
2. The cathode will be doped with sulfur in order to form a true lithium-sulfur battery in which in-operando measurement of lithium polysulfide compounds may be performed.

Citations
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