In-Situ X-Ray Diffraction (XRD) Studies of Lithium-Sulfur Batteries

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Introduction

Lithium-sulfur batteries:

+ high theoretical specific capacity
+ high energy density
+ sulfur is abundant, inexpensive and nontoxic

- High degradation during cycling
- Structural and morphological changes during electrochemical reactions are still not well understood

These changes were studied in Operando by X-ray diffraction

So far, there has been little application of this method in Li-S batteries [1,2].

Materials and Methods

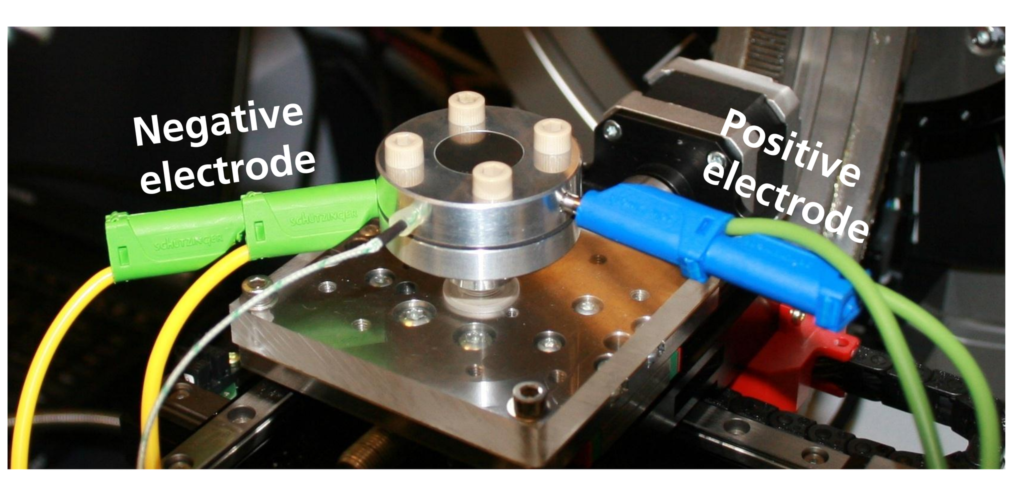
Sulfur cathode composition

- 50 wt.% sulfur
- 40 wt.% carbon black
- 10 wt.% polyvinylidene fluoride

Method of preparation

- suspension-spraying on carbon coated aluminum foil
- solvents: DMSO and ethanol 6:4

In-situ cell



In-situ cell connected to the potentionstat on the XRD-sample holder.

XRD

Equipment: Brucker D8 Discover with areal detector (VanTEC 2000)

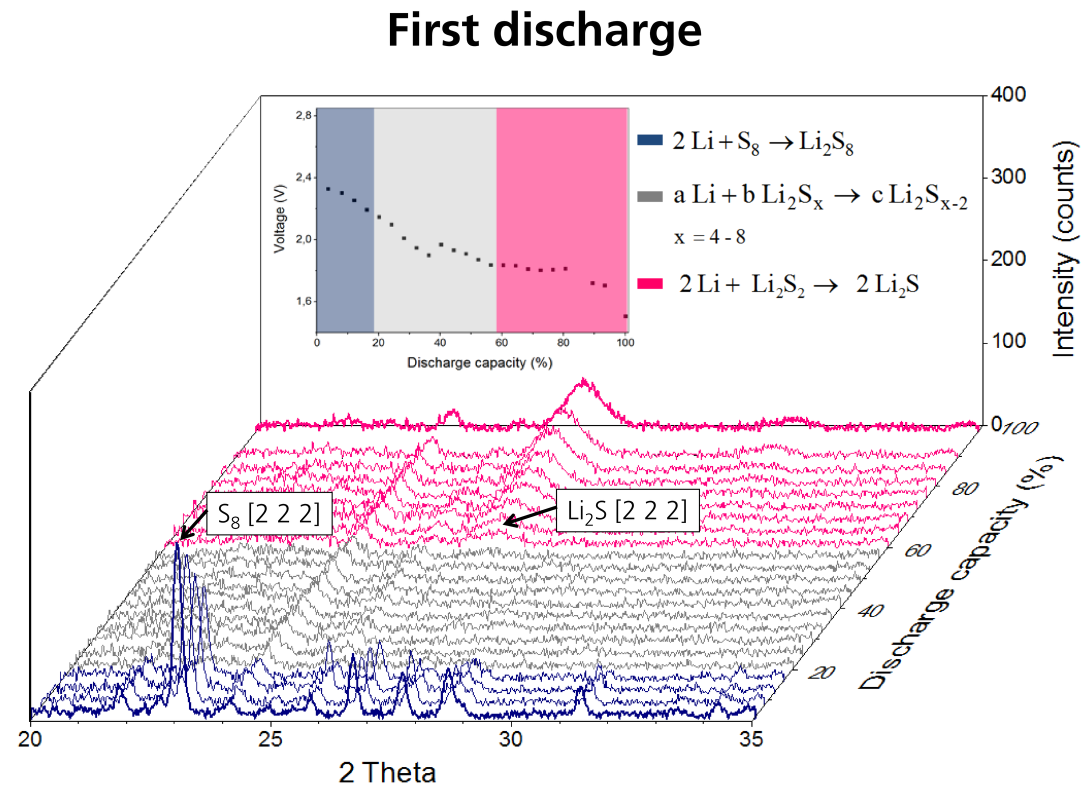
- measurements in reflexion mode
- four frames per spectra (180 s / frame)
- radiant beam: 45 KV, 650 mA

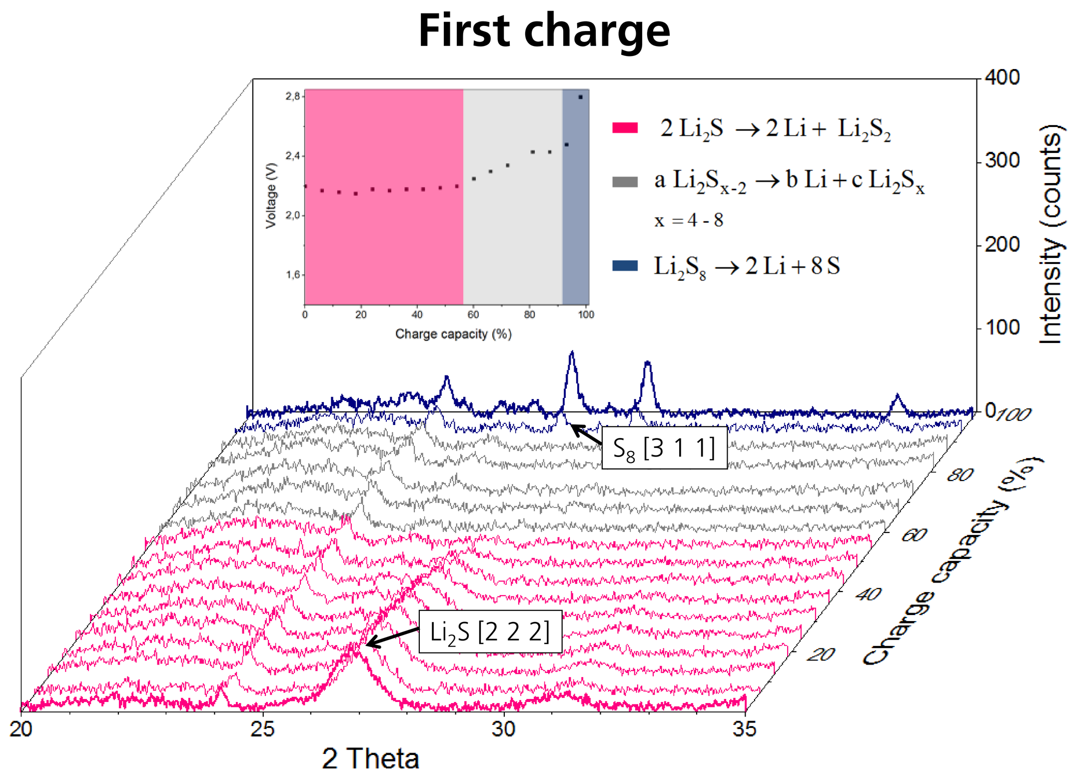
Cycling of the battery

Charge and discharge voltage	2.8 V – 1.5 V
Specific discharge current	300 mA/g $_{sulfur}$
Discharge current density	382 mA/cm^2

Results

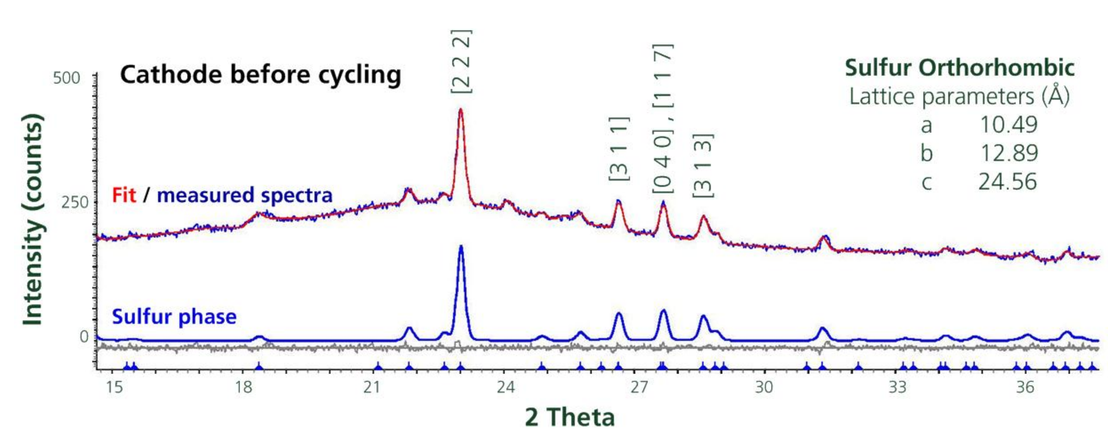
In-situ XRD Spectra



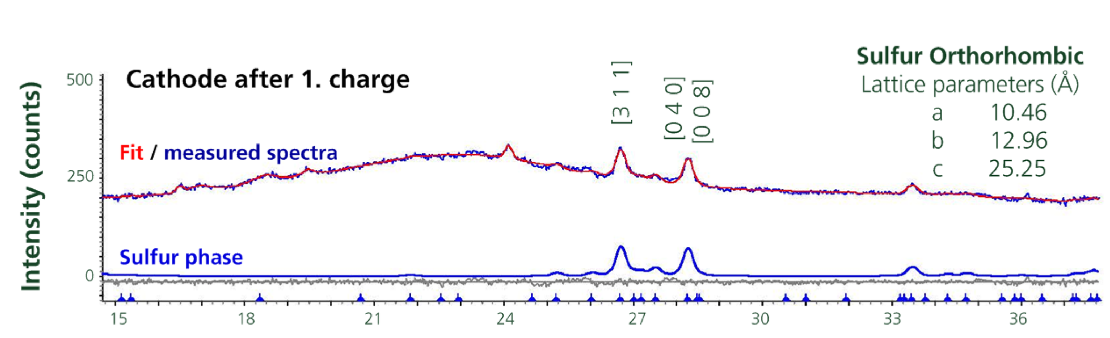


X-ray diffractograms of Li-S battery at various stages of discharge. Discharge and charge capacity: 1603 and 1575 mAh/ g_{sulfur} respectively.

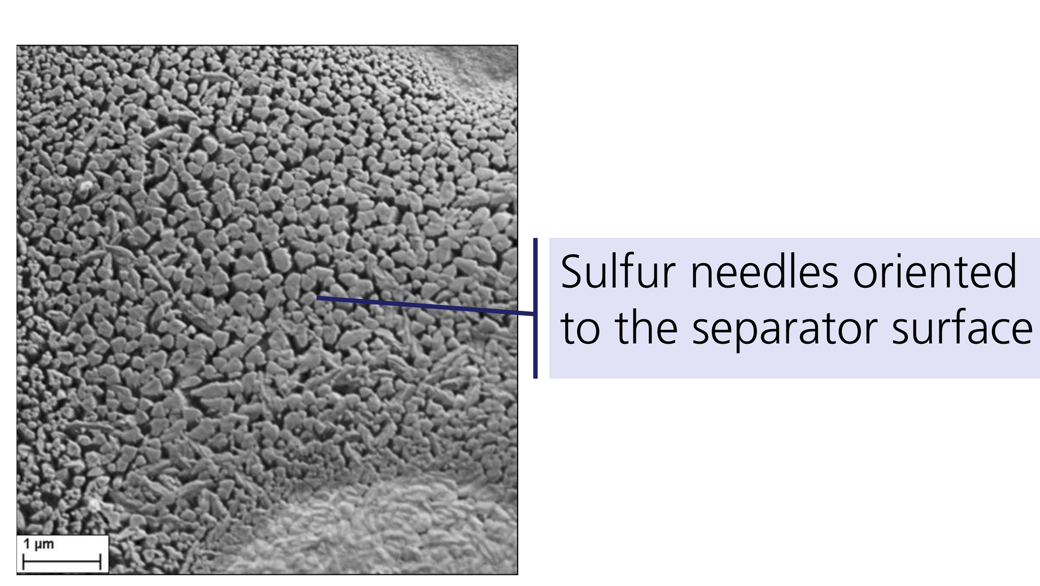
Structural changes in sulfur



After the first cycle crystalline sulfur phase diminishes and shows a different X-ray spectrum.

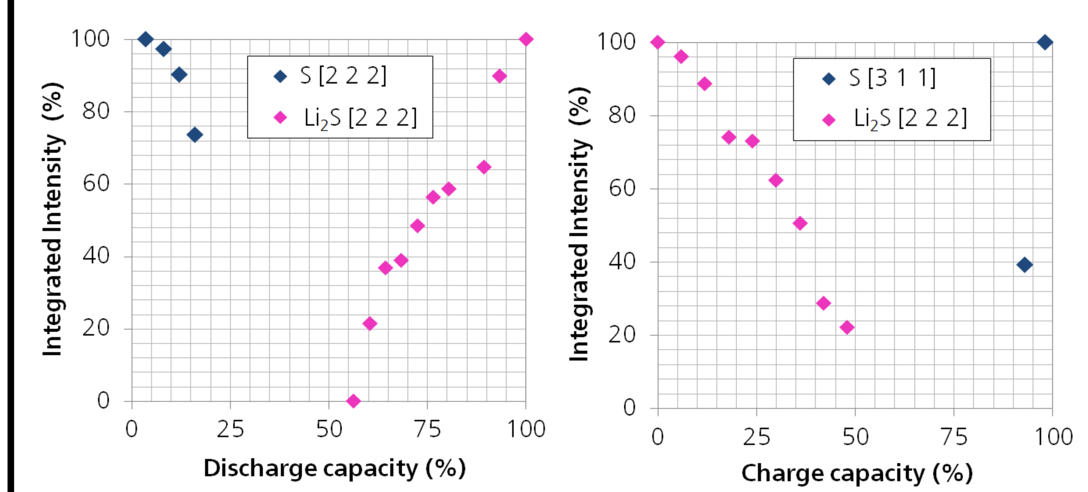


The sulfur particles crystallize with a preferred orientation:



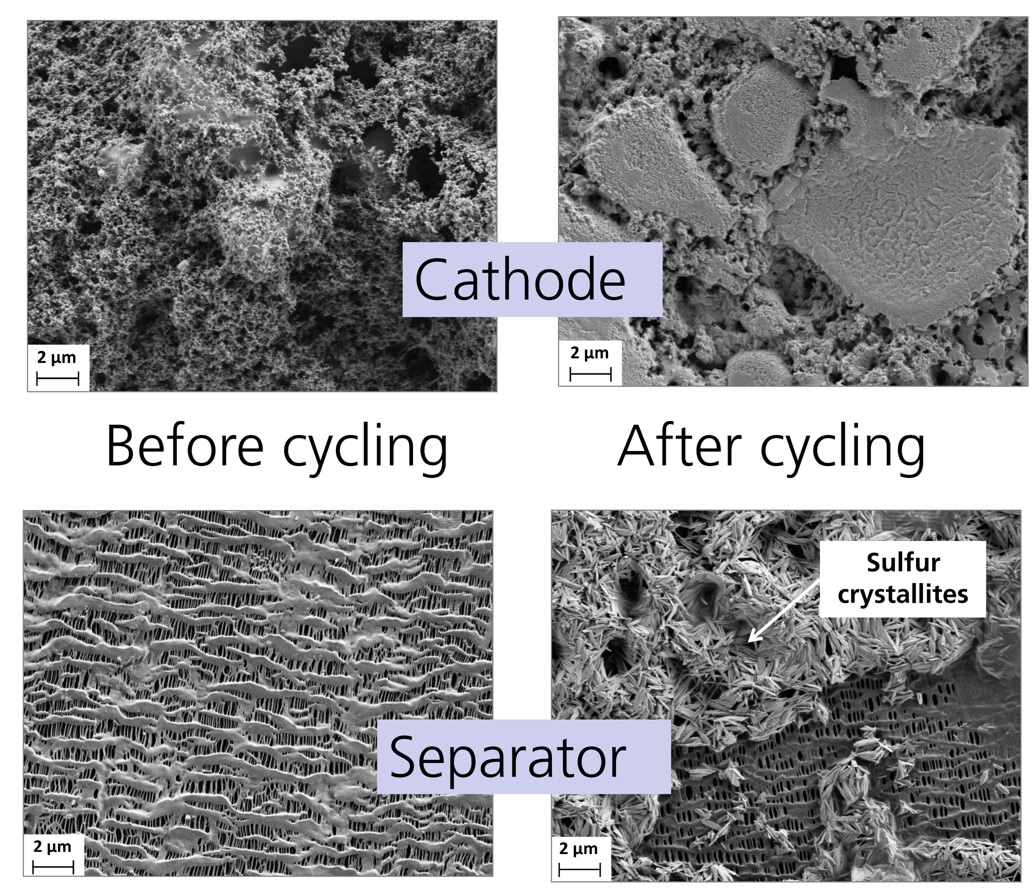
Ex-situ SEM micrograph of a cathode region after cycling.

Semi-quantitative XRD analysis



Integrated area of S [2 2 2], [3 1 1] and Li_2S [2 2 2] Bragg peaks. Integrated Intensity (%) = integrated intensity $[x\ y\ z]_j$ / integrated intensity $[x\ y\ z]_{initial/final}$, j= state of charge.

Morphological changes of the surface



SEM pictures of cathode surface and separator (Celgard 2500), before and after 10 cycles.

Summary and conclusion

- A suitable cell for in-situ X-ray diffraction analysis was designed and the cathode of Li-S Battery was monitored throughout cycling
- It was found that crystalline Li_2S does built up at the end of discharge
- Recrystallization of sulfur occurs after the first cycle with changes in the orientation and size of crystallites
- Crystalline sulfur phase diminishes continuously during cycling

Acknowledgment

We thank Werner Seybold for helping with the building of the in-situ cell.

References

[1] G. A. Roberts and D. H. Doughty, Sion Power Corporation, ECS 210th (2006) Meeting Abstract.

[2] Nelson et al. JACS (2012), 134, 6337-6343.

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