In-Situ X-Ray Diffraction (XRD) and electrochemical characterization of cathodes for Li-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

In this work:

X-Ray Diffraction (XRD) and Electrochemical Impedance Spectroscopy (EIS) were applied to investigate the physical and chemical processes occurring in Li-S battery during cycling

Materials and Methods

Sulfur cathode composition

50 wt.% sulfur, 40 wt.% carbon black and 10 wt.% polyvinylidene fluoride

Cathode preparation

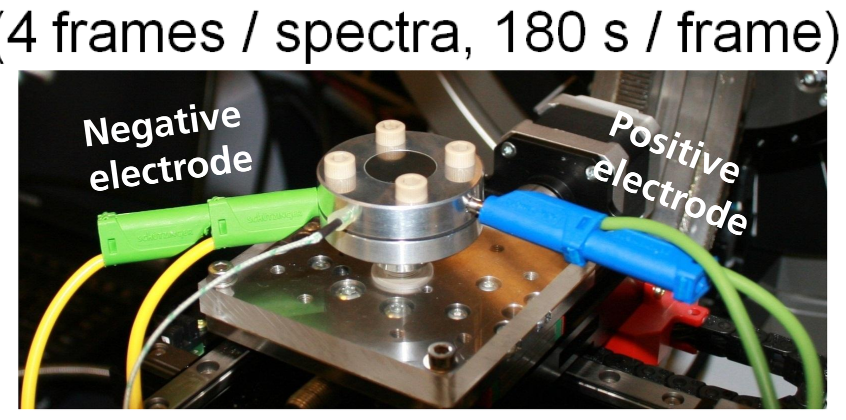
Suspension-spraying on carbon coated aluminum foil. Solvents: DMSO and ethanol 6:4.

Cycling of the battery

- Charge / Discharge Voltage (V): 2.8 / 1.5
- Specific discharge current: 300 mA/g S

XRD

- Equipment: Brucker D8 Discover with areal detector (VanTEC 2000)
- Measurements in reflexion mode: (4 frames / spectra, 180 s / frame)



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

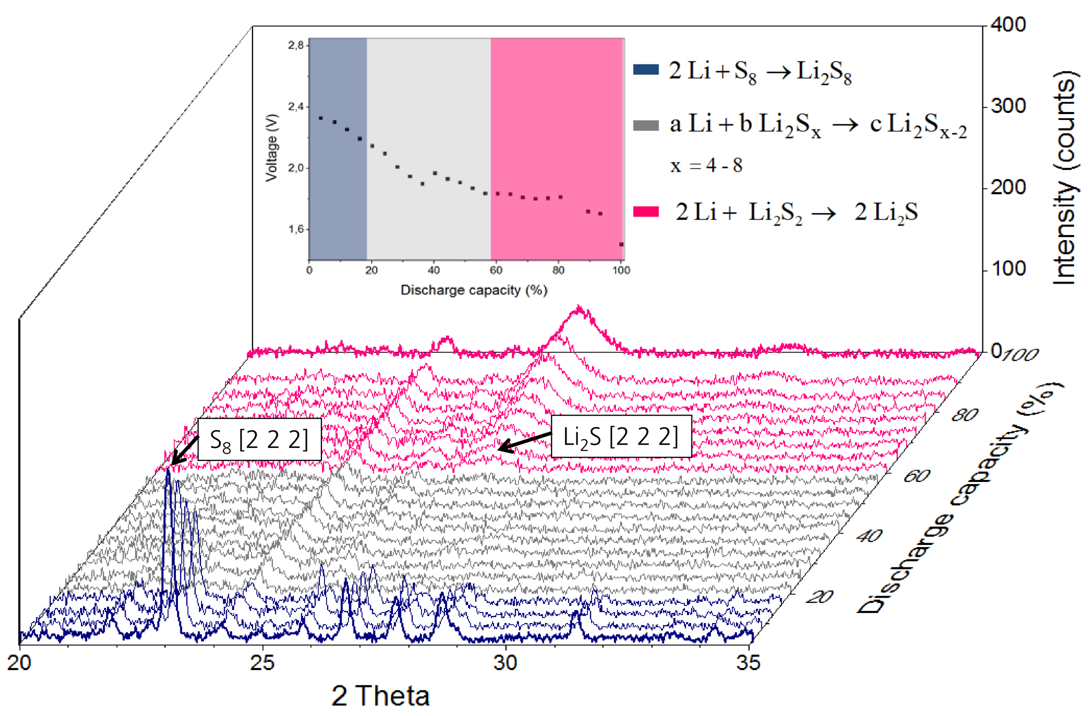
EIS

- Impedance spectra measured potentiostatic: 5 mV of amplitude in equidistant intervals of 50 mC
- Frequency range: 1 MHz to 60 mHz

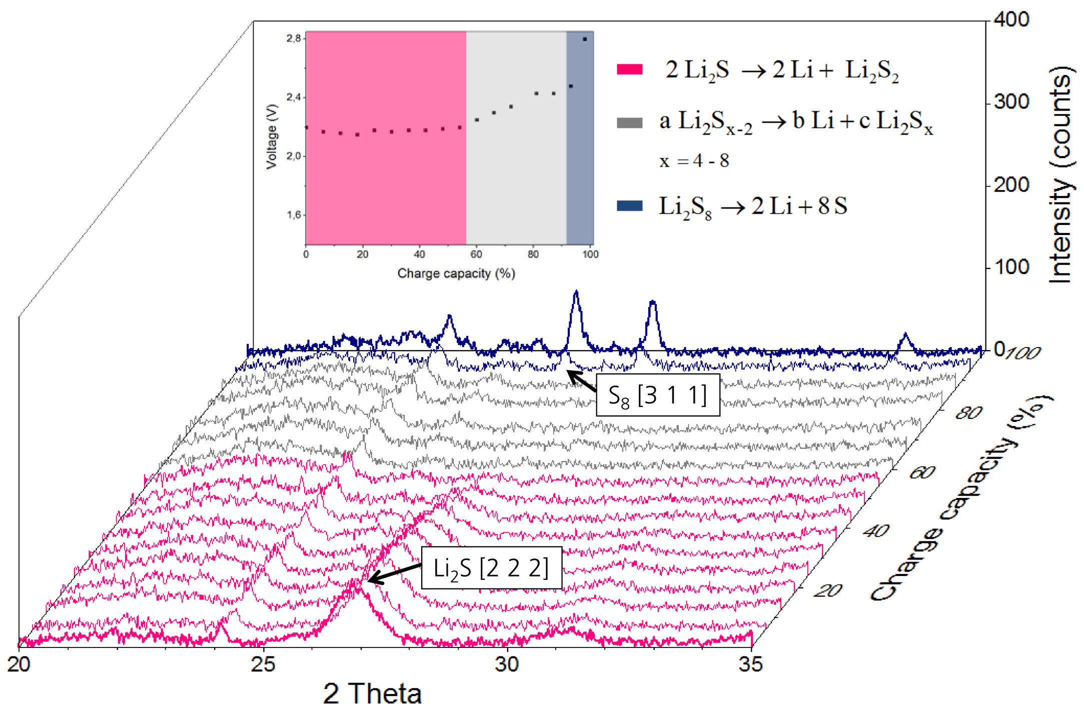
Results

X-Ray Diffraction

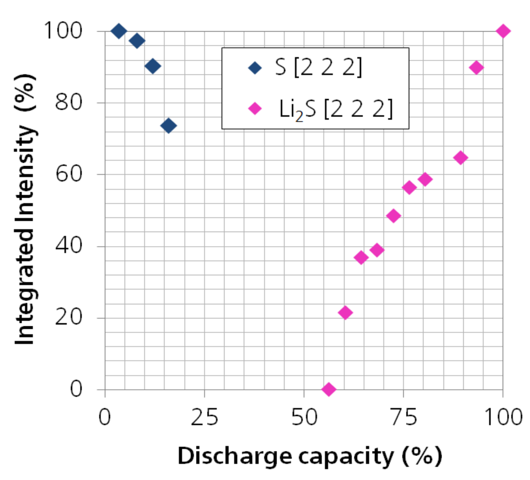
Discharge



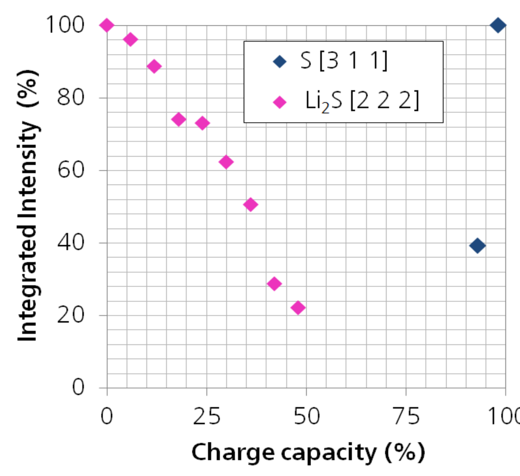
Charge



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

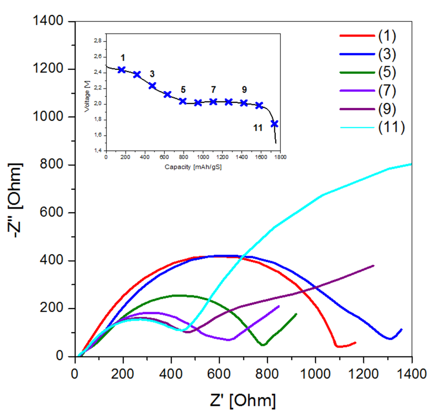


Semi-quantitative analysis

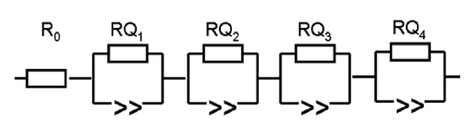


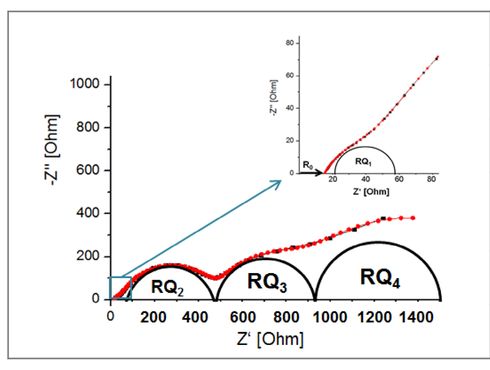
Integrated area of S [2 2 2], [3 1 1] and Li_2S [2 2 2] Bragg peaks.
Integrated Intensity (%) = integrated intensity $[x\ y\ z]_j$ / integrated intensity $[x\ y\ z]_{initial/final}$, j= state of charge.

Electrochemical Impedance Spectroscopy



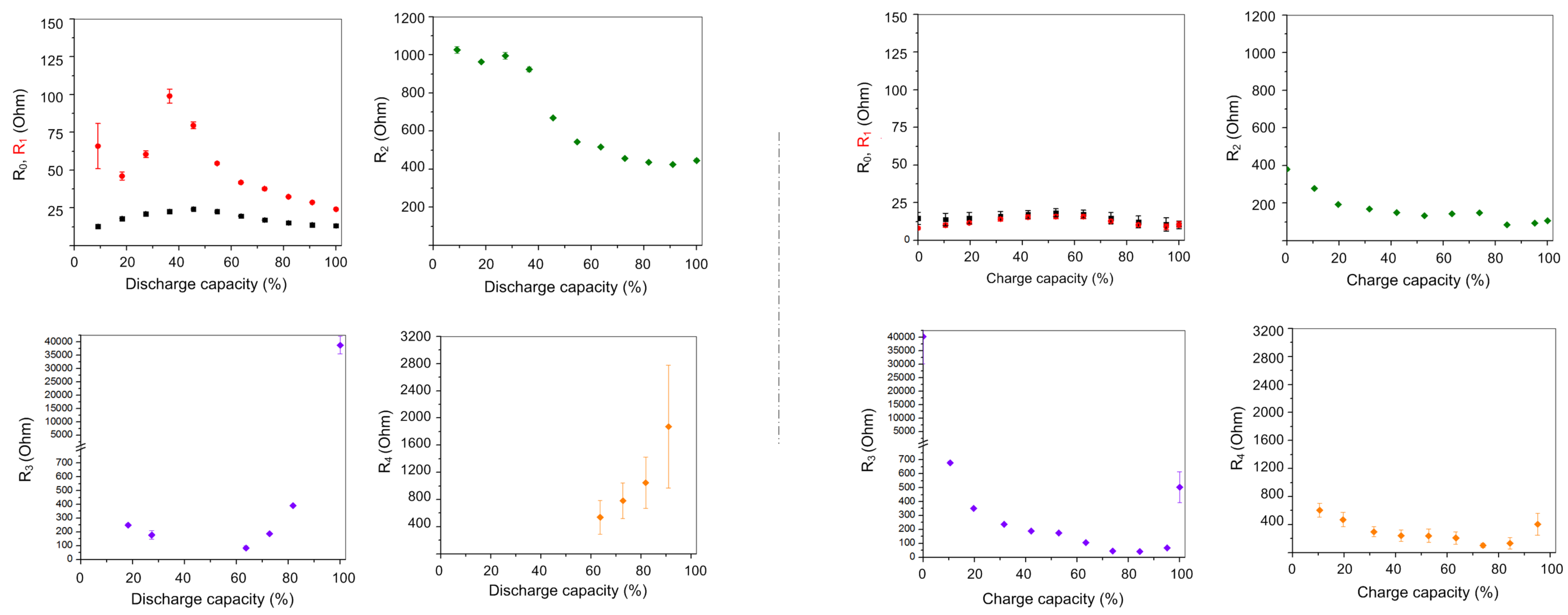
Equivalent electric circuit





Model	Chemical and physical cause
R_0	Ohmic resistance
RQ_1	Anode charge transfer
RQ_2	Cathode process: charge transfer of sulfur intermediates
RQ_3	Cathode process: reaction and formation of S_8 and Li_2S
RQ_4	Diffusion

Discharge **Charge**



Variation of the equivalent circuit elements during cycling determined by EIS analysis.

Summary and conclusion

- A suitable cell for in-situ X-ray diffraction analysis was designed and reaction products (S_8 and Li_2S) were monitored during cycling and semi-quantitatively determined.
- An equivalent electrical circuit for the cell was designed and evaluated by means of EIS. Variation of resistance contributions were studied in dependence with state of charge.
- This work highlights the importance of in-situ studies and the combination of XRD and EIS techniques to reveal new insights into Li-S batteries.

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