Use of Electrochemical Impedance Spectroscopy and in-situ XRD for characterization of cathodes for Li-Sulfur batteries

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DLR

Presentation outline

- Introduction and motivation: Lithium-Sulfur (Li-S) batteries
- Li-S battery at DLR: cathode fabrication
- Application of in-situ XRD and EIS during cycling
- Conclusion and outlook

Motivation

Why Li-Sulfur batteries?

- High theoretical capacity (1675 mAh/g) and specific energy density (2500 Wh/kg)
- Environmental friendliness
- Low cost and availability of sulfur
- Wide temperature range of operation
- Intrinsic protection mechanism from overcharge

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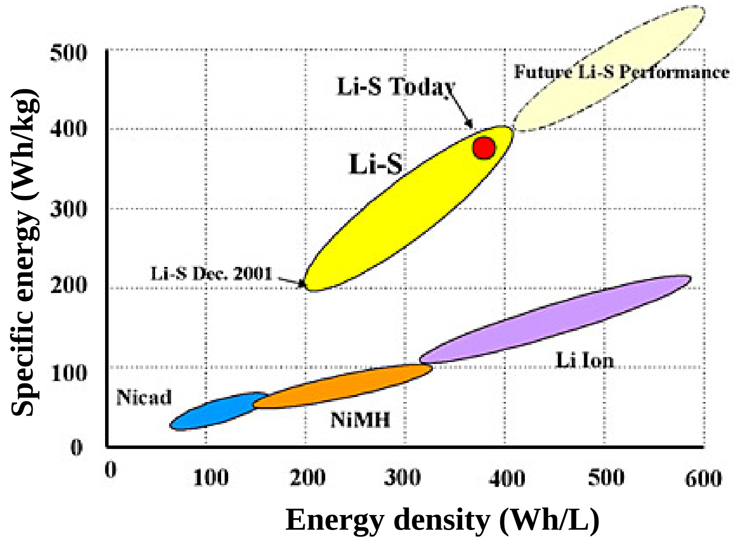
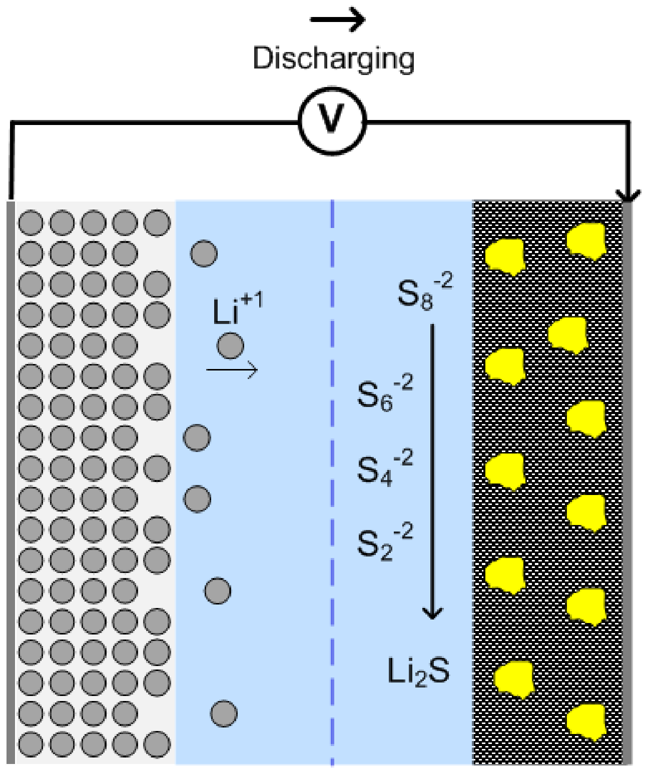


http://www.sionpower.com/technology.html

But still…

- High degradation during cycling
- No complete understanding of degradation mechanisms and structural modifications during charge and discharge

Schematic representation of a Li-sulfur battery



$$2\,\mathrm{Li} + S_8 \rightarrow \mathrm{Li}_2S_8$$

$$a\,\mathrm{Li} + b\,\mathrm{Li}_2S_x \rightarrow c\,\mathrm{Li}_2S_{x\text{-}2}$$

$$x = 4 - 8$$

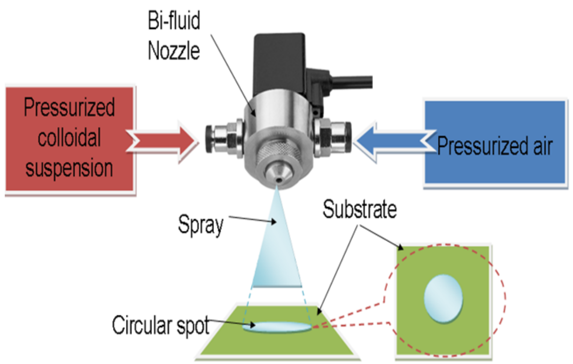
$$2\,\mathrm{Li} + \mathrm{Li}_2S_2 \rightarrow 2\,\mathrm{Li}_2S$$

Non soluble in electrolyte

- High order Li-polysulfides (Li_2S_x x = 4-8) are soluble in the electrolyte and migrate to the anode avoiding dendrite growth
- During recharging lithium ions are plated back onto the anode and sulfur oxidize back to S_8

Cathode production technique at DLR-TT

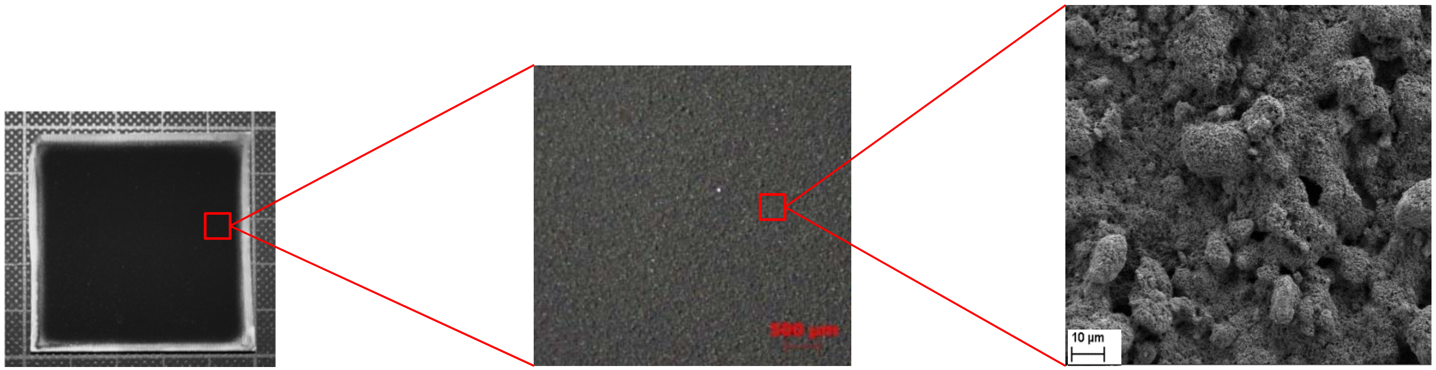
Suspension–spray machine



- Nozzle with extern mixing of air and suspension
- Cathode mixture: Sulfur, Carbon Black and PVDF (50:40:10, wt.%).

  Solvents: Ethanol and DMSO

Sprayed cathode

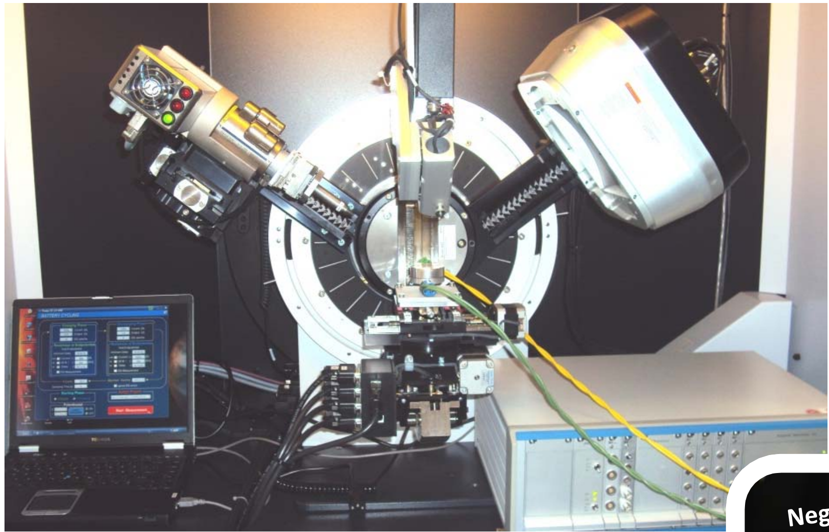


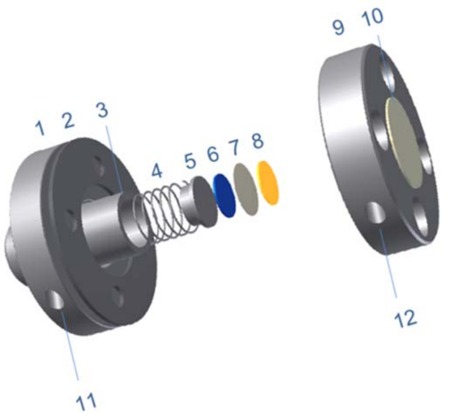
5 x 5 cm²

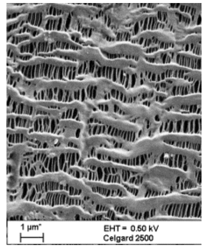
In-situ X-Ray diffraction

Objective:

To monitor the crystalline reaction products of the cathode and the structural changes during cycling



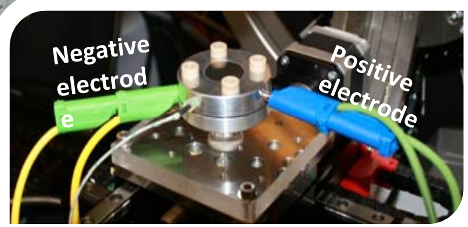




1) Anode plate
2) Polymer gasket
3) Insulator plastic tube
4) Spring
5) Al-anode collector

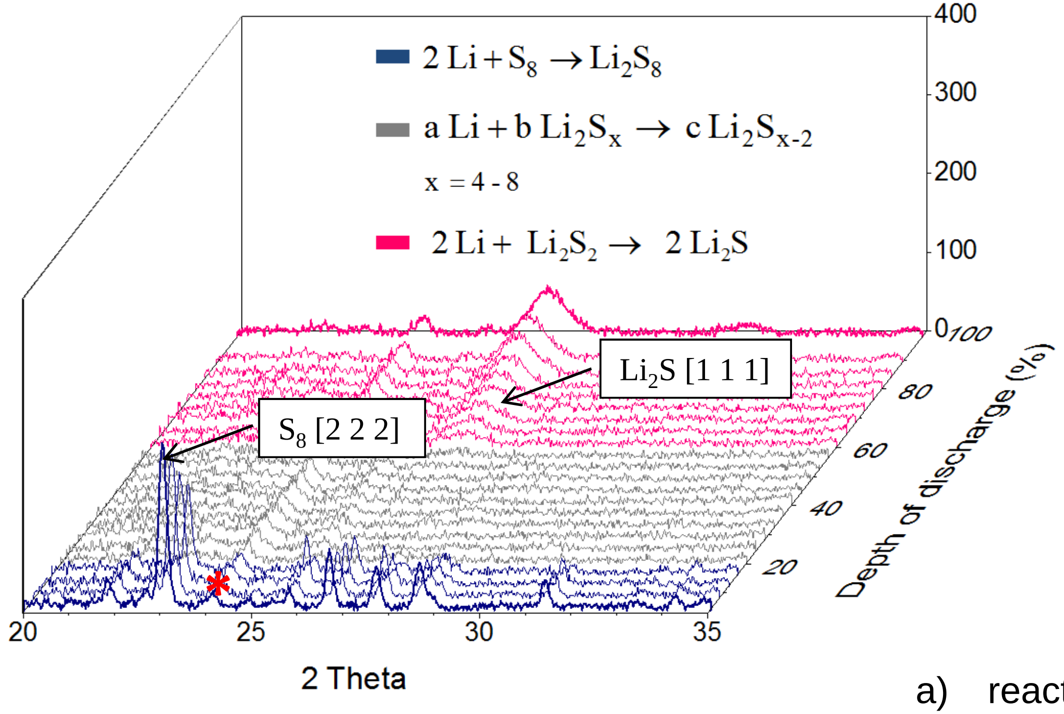
6) Anode: lithium
7) Separator (Celgard 2500) impregnated with electrolyte (1M $LiPF_6$ in TEGDME)
8) Cathode

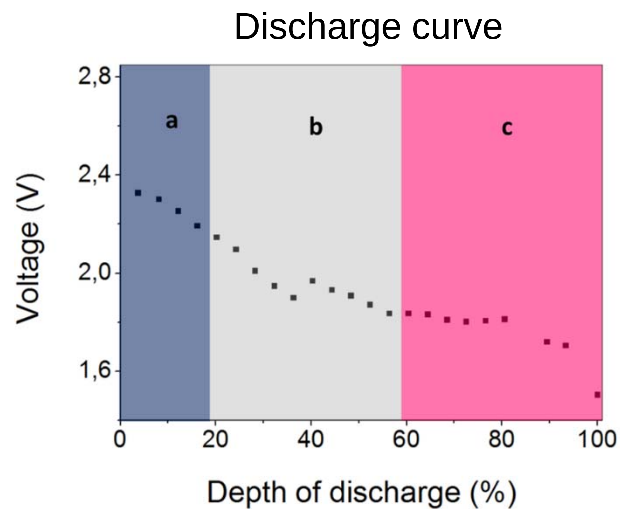
9) Cathode plate
10) Al- or Be-window
11-12) Holes for banana jacks



Experimental XRD results

First discharge step





In-situ X-ray diffraction data collected during discharging of Li-S battery at a rate of 300 mA g^{-1}

Average discharge capacity is 1276 mAh g_{sulfur}^{-1}

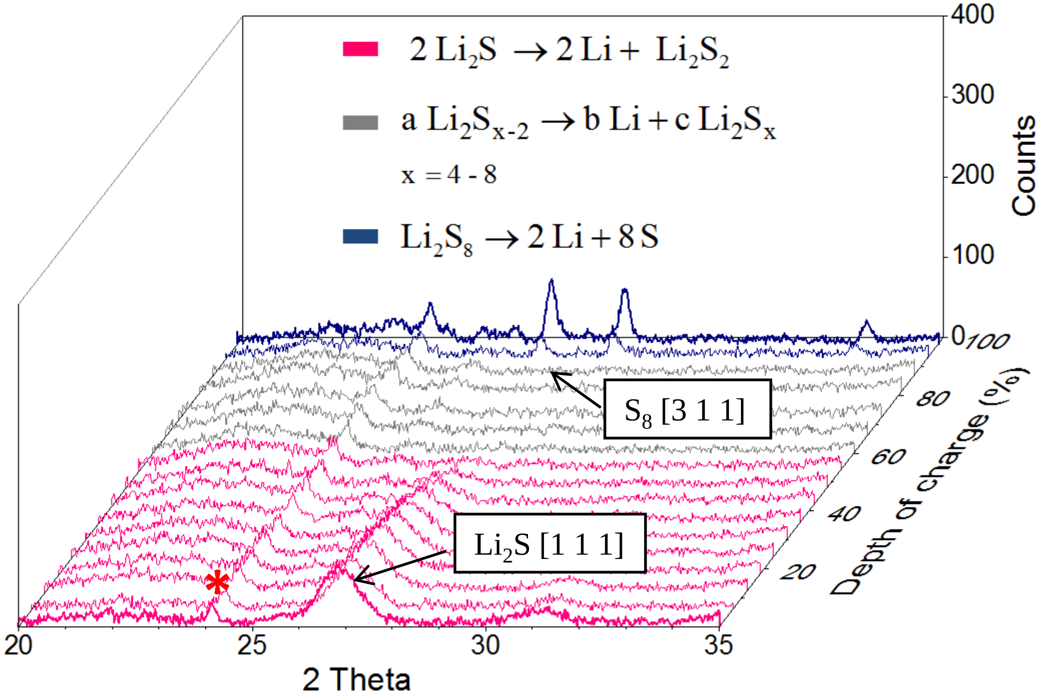
a) reaction of sulfur to high order polysulfides (blue)

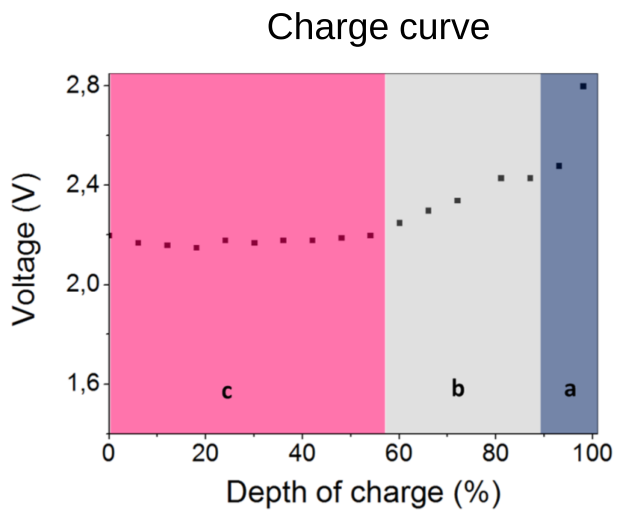
b) reactions of high order polysulfides (gray)

c) formation of Li_2S (red)

Experimental XRD results

First charge step





In-situ X-ray diffraction data collected during charging of Li-S battery at a rate of 300 mA g^{-1}

c) reaction of Li_2S (blue)

b) reactions of high order polysulfides (gray) and

a) formation of sulfur (red).

Average charge capacity is 1283 mAh g_{sulfur}^{-1}

EIS during cycling

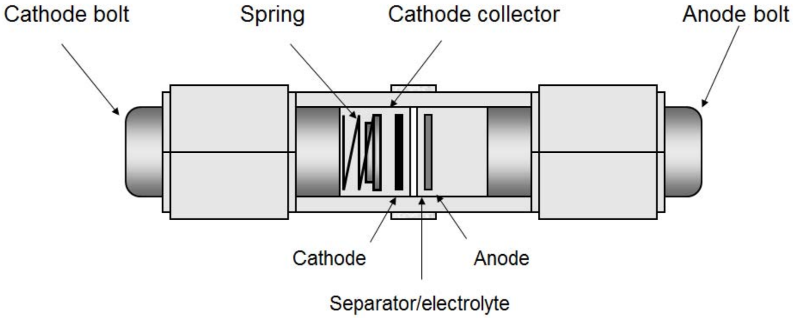
Objective: investigation of physical and chemical processes during cycling

Electrochemical cycling

- Galvanostatic
- Current density: 300 mAh g_{Sulfur}^{-1}
- Charge/discharge end potential:
  2.8 V und 1.5 V

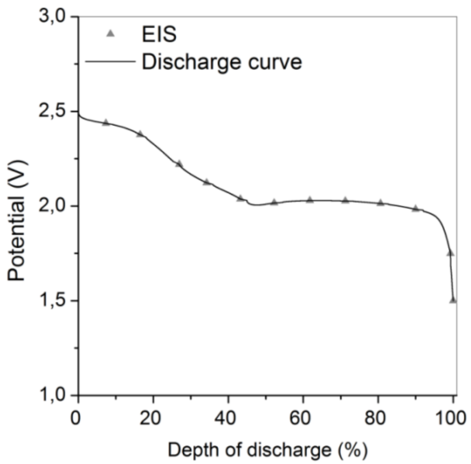
EIS:

- Frequences from 1 MHz to 60 mHz
- Potentiostatic excitation: 5 mV
- Impedance spectra were measured in 50 mC equidistant intervals
- 2-Electrodes configuration

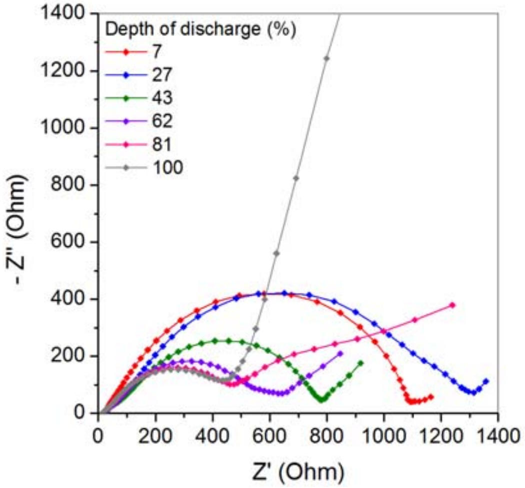


Swagelok-cell (EIS measurements)

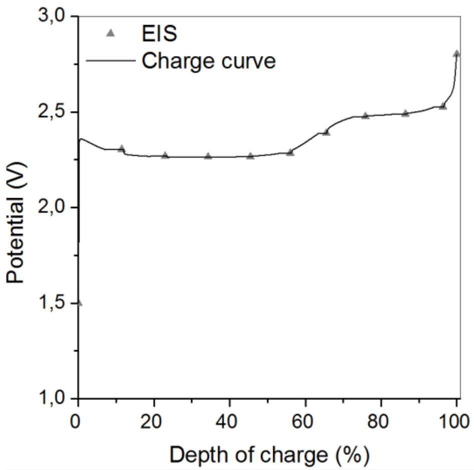
Overview EIS during first battery cycling



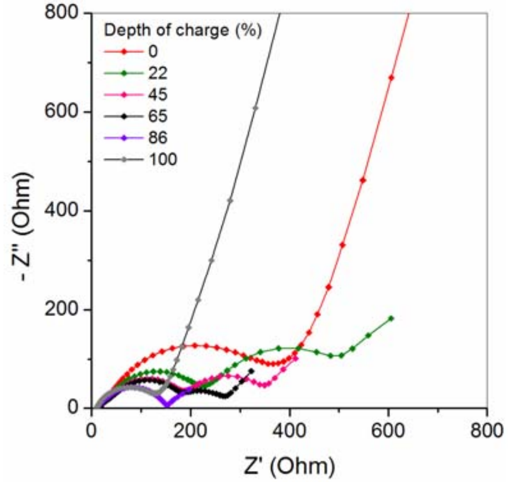
1. Discharge



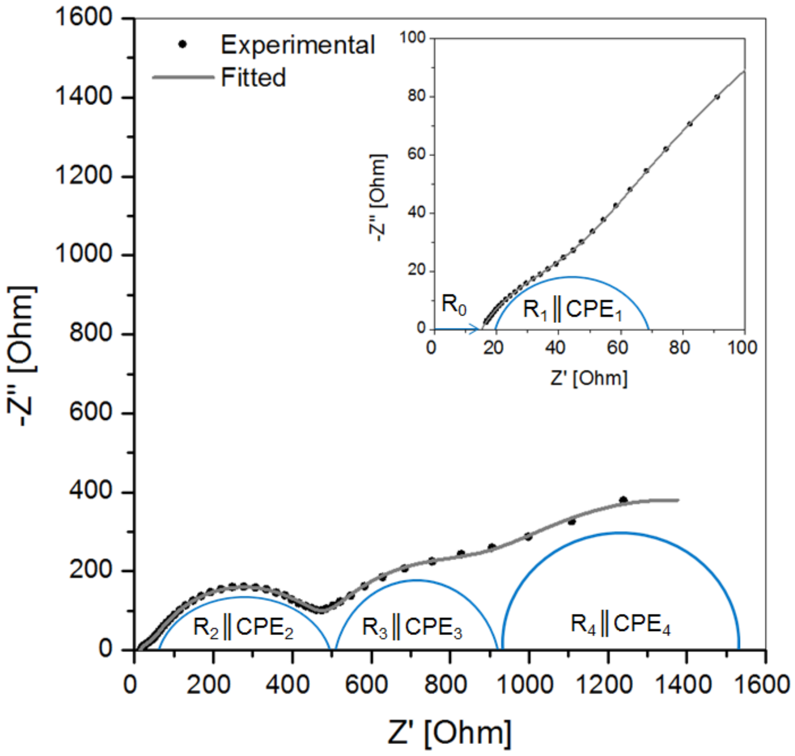
Changes in the resistances and the processes



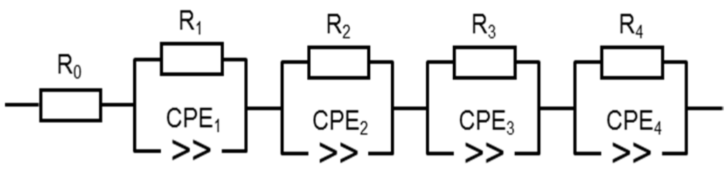
1. Charge



Model for Li-S Battery



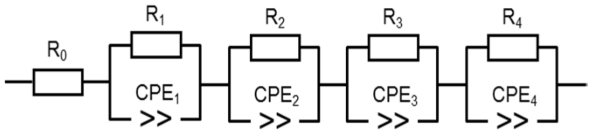
Equivalent circuit



Model	Chemical and physical cause
R_0	Ohmic resistance
R_1-CPE_1	Anode charge transfer
R_2-CPE_2	Cathode process: charge transfer of sulfur intermediates
R_3-CPE_3	Cathode process: reaction and formation of S_8 and Li_2S
R_4-CPE_4	Diffusion

First discharge step

Modelling results



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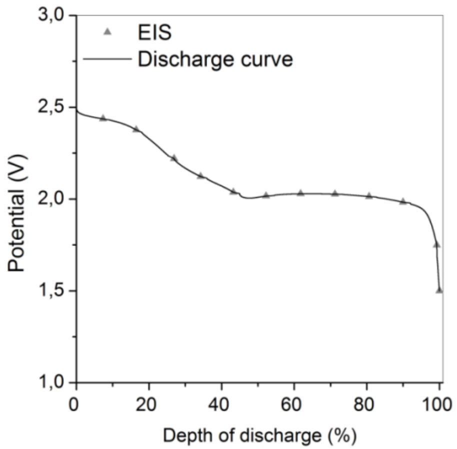

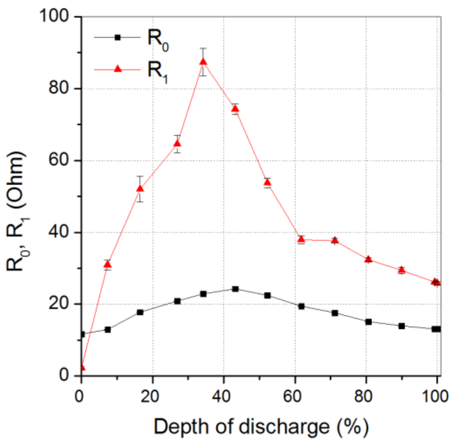

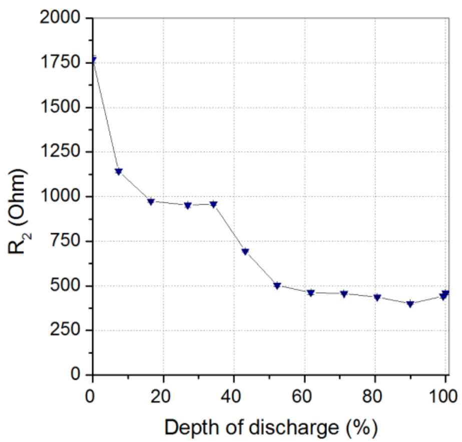

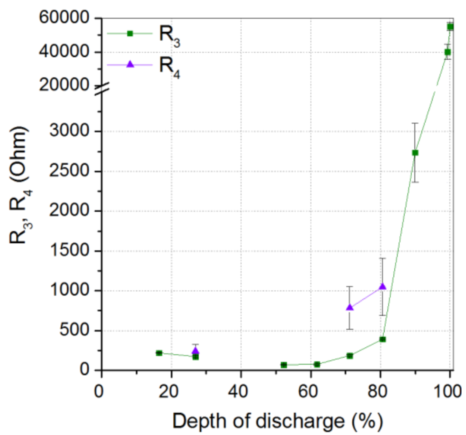

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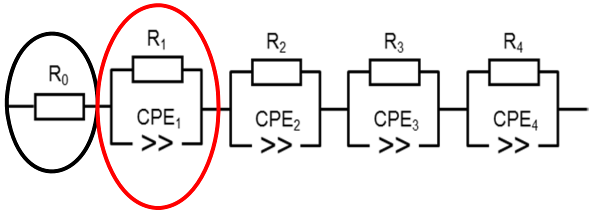

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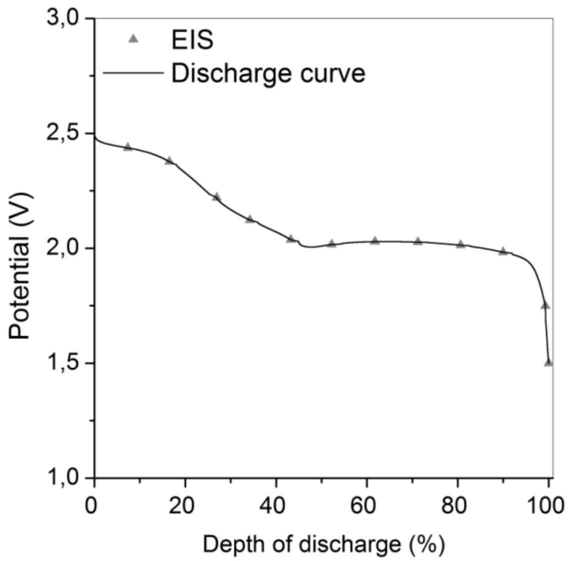
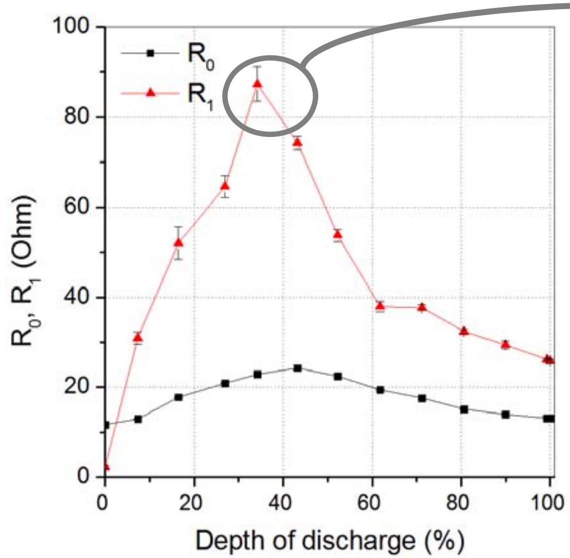


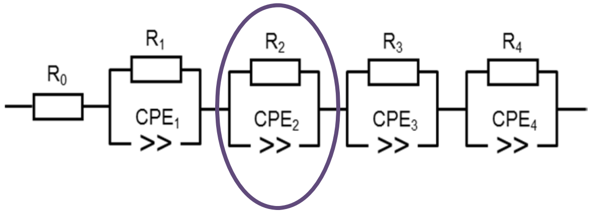


Maximum due to high concentration of soluble polysulfides

Ohmic resistance of the cell is influenced by the concentration of polysulfides

First discharge step

Modelling results



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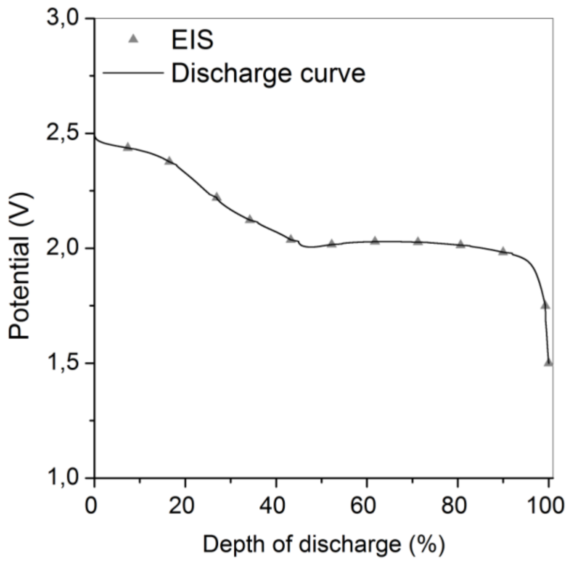
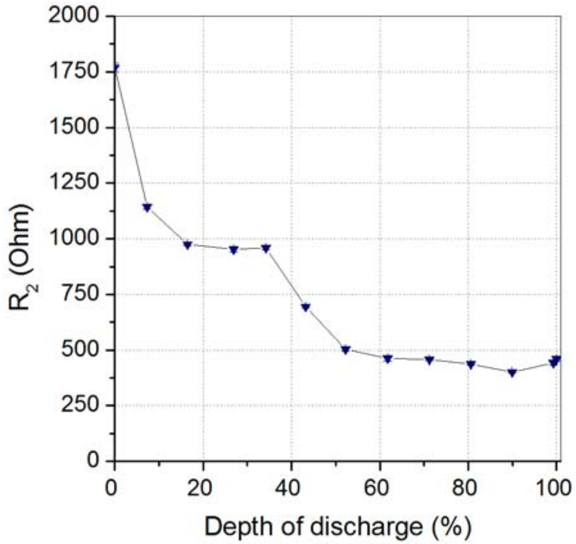




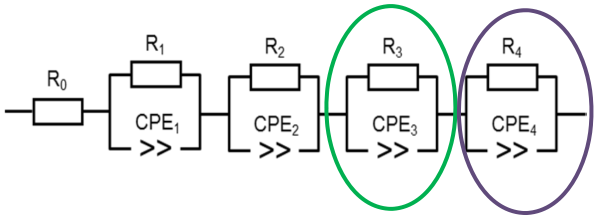
Decrease R_2

Charge transfer on the cathode surface is favored by decreasing order of polysulfides

Building of non conductive Li_2S avoid the further resistance decrease

First discharge step

Modelling results



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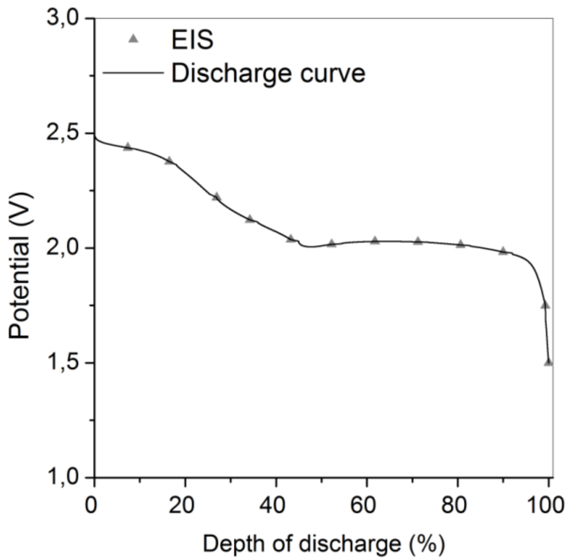
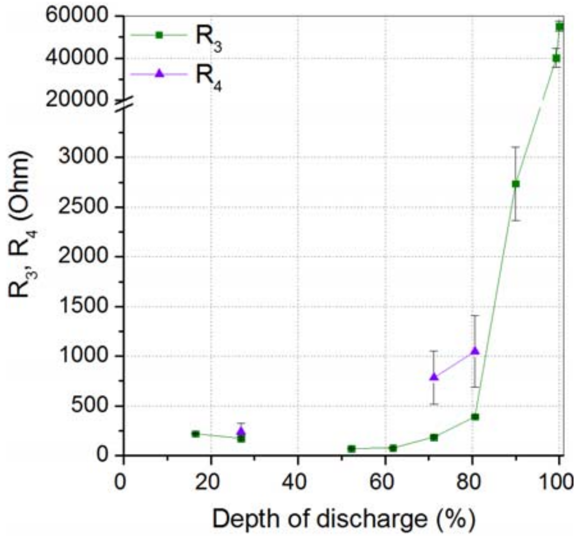




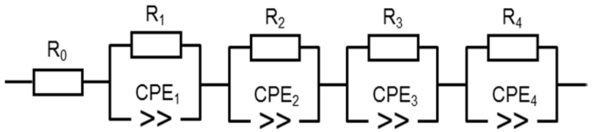
R_3: appears when:

- S_8 solid film disappears
- Li_2S solid film forms

R_4: the diffusion of species may be affected by R_3

First charge step

Modelling results



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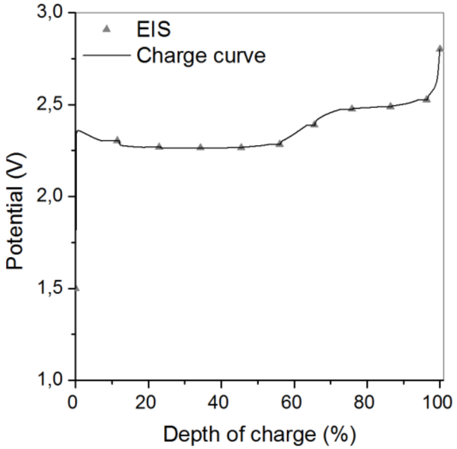
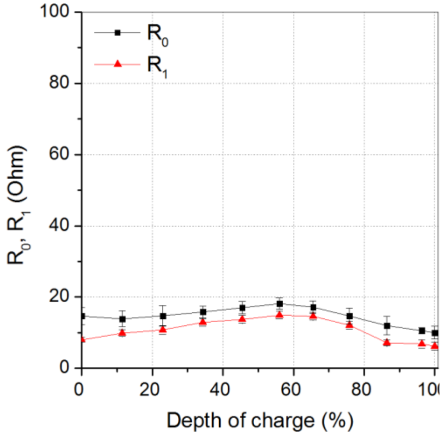
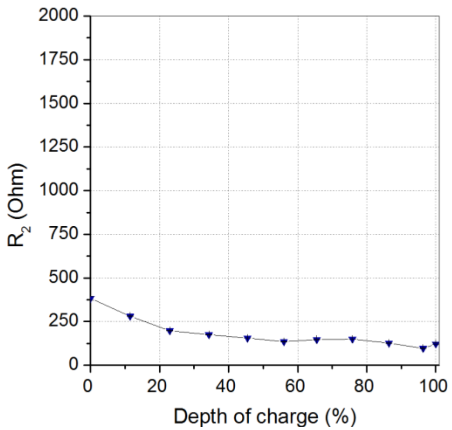
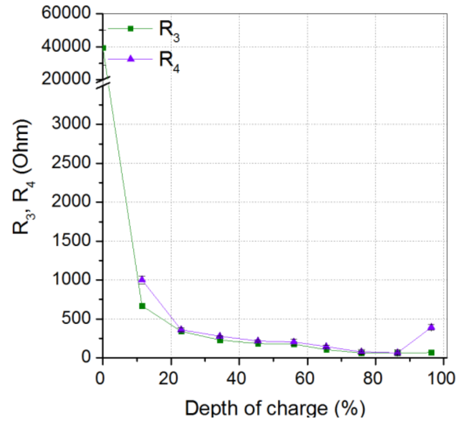








In general:

Lower resistances than by discharging

Maximum due to high concentration soluble polysulfides

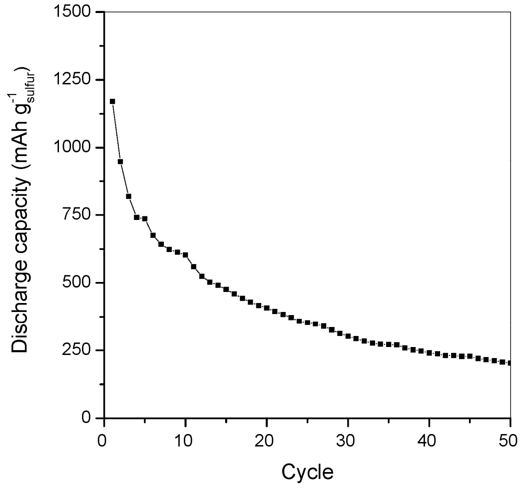
Decrease of charge transfer resistance due to reaction of non conductive Li_2S to high order polysulfides and S_8

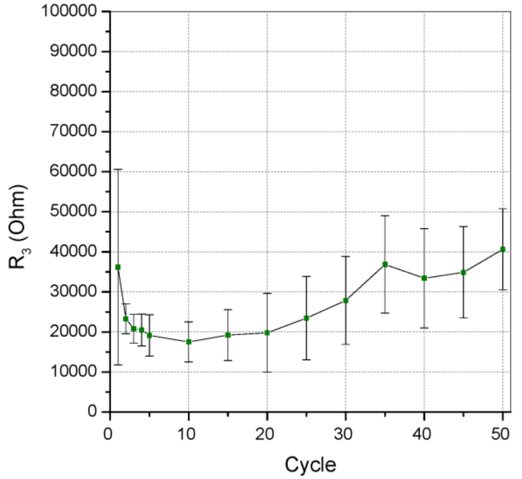
R_3: dissolution of Li_2S

Lower resistance at 100 % DOC due to low formation of S_8

DLR

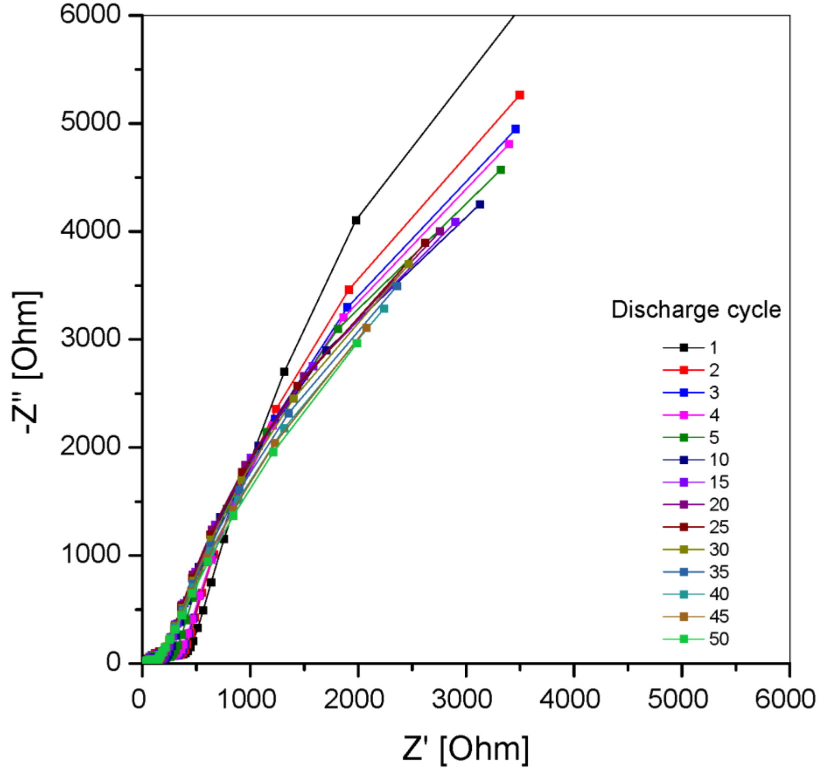
Cycling degradation (DOD=100%)





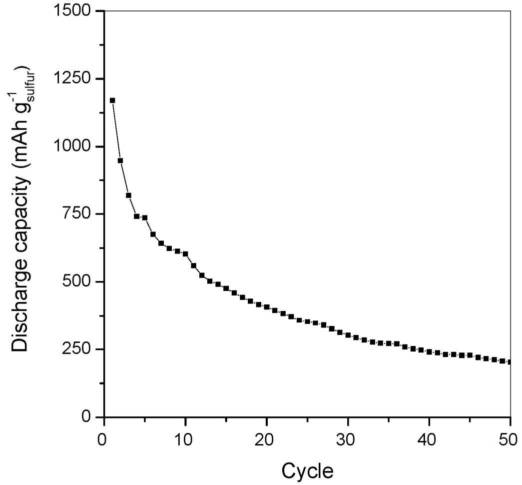
Resistance due to formation of Li_2S

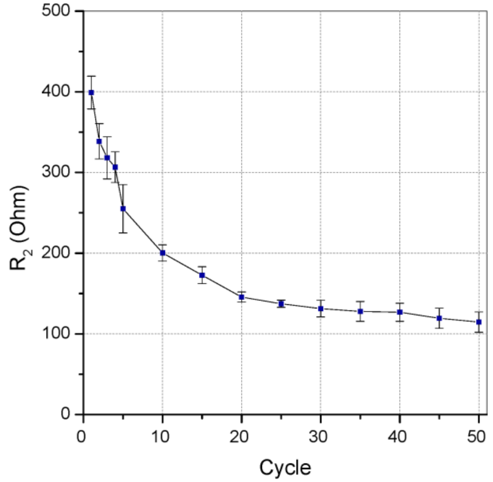
1 MHz – 60 mHz



1-20: decrease due to less formation Li_2S
20- 50: formation of stable isolated film?

Cycling degradation (DOD=100%)

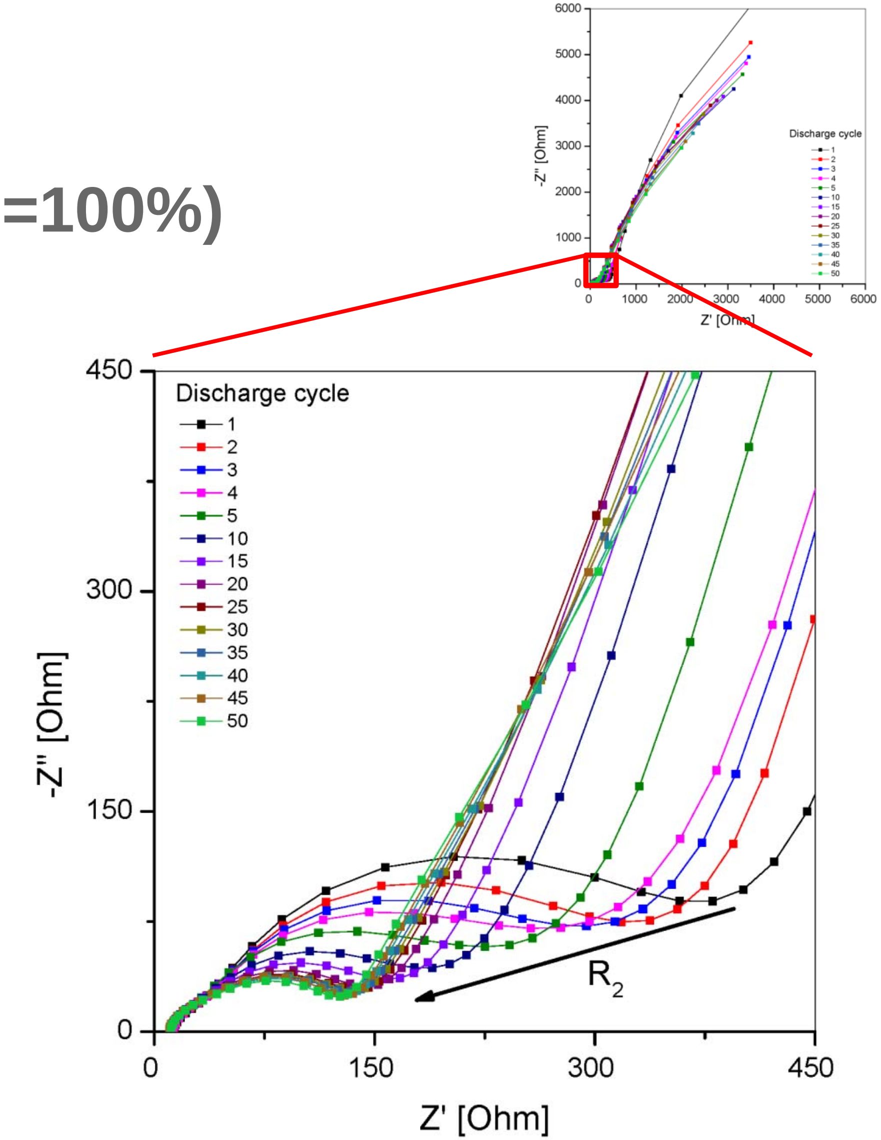




Decrease of discharge capacity

Reduction of charge transfer on cathode surface

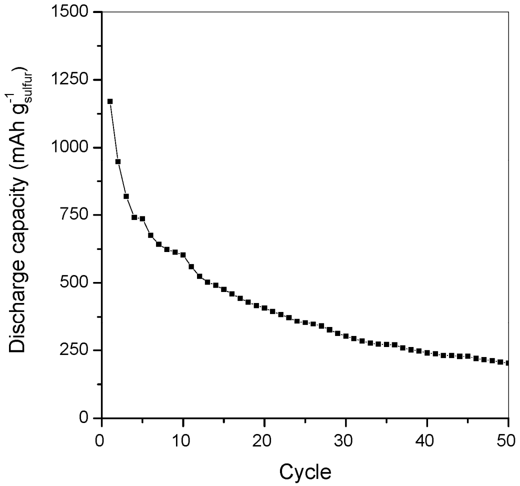
Uncompleted reaction to Li_2S

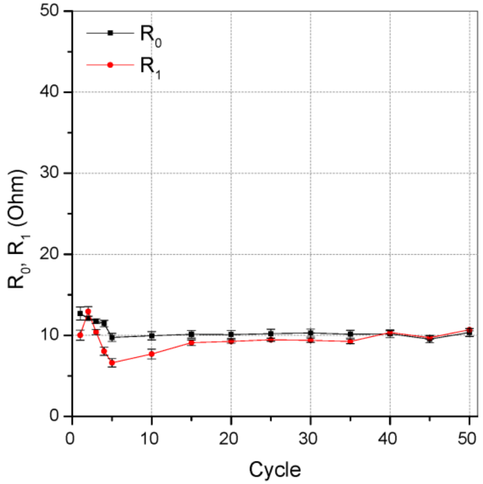


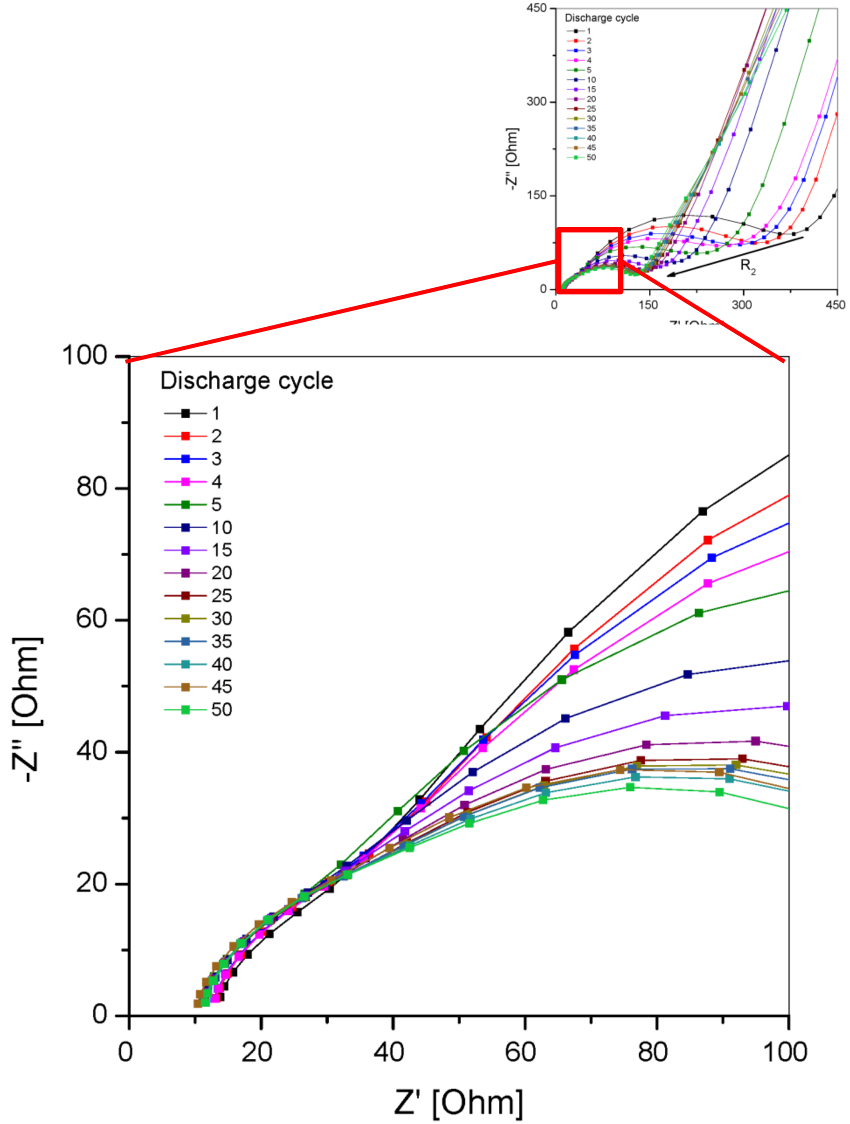
Morphological changes in the cathode: less non-conductive material

DLR

Cycling degradation



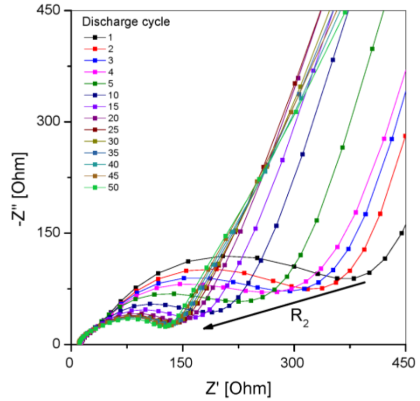


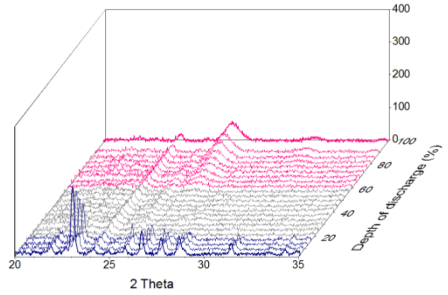


Ohmic resistance and anode charge transfer resistance stabilizes after approx.. 15 cycles

Conclusions and outlook

- EIS was performed at different depth of discharge and charge for the first cycle of lithium-sulfur (Li-S) batteries
- The mechanisms of Li-S battery aging during cycling were reviewed for fifty cycles
- An equivalent electrical circuit is proposed to simulate the electrochemical processes and to quantify their impedance contributions





- A suitable cell for in-situ XRD analysis was designed and reactions products (S_8 and Li_2S) were monitored during cycling

This works highlights the importance of in-situ studies and the combination of XRD and EIS techniques to reveal new insights into Li-S batteries

Thank you for your Attention !

EIS from 1 MHz – 1 mHz