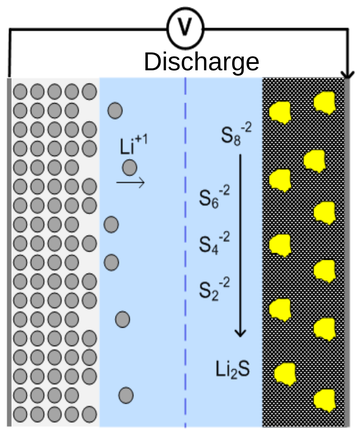
Investigation of rechargeable lithium-sulfur batteries by in-situ techniques

Natalia A. Cañas[1,2], Kei Hirose[1], Brigitta Pascucci[1], Norbert Wagner[1], K. Andreas Friedrich[1,2], Renate Hiesgen[3]

[1]German Aerospace Center, Stuttgart, Institute of Technical Thermodynamics Pfaffenwaldring 38-40, 70569, Germany
[2]University of Stuttgart, Institute for Thermodynamic and Thermal Engineering, Pfaffenwaldring 6, 70569, Germany
[3] University of Applied Sciences Esslingen, Department of Basic Science, Kanalstrasse 33, 73728 Esslingen, Germany

Lithium-sulfur battery



Electrochemical reactions

$Li \rightarrow Li^+ + e^-$

$S_{8(s)} \rightarrow S_{8(diss)}$

$^1/_2\ S_{8(diss)} + e^- \rightarrow {}^1/_2\ S_8^{-2}$

$^3/_2\ S_8^{-2} + e^- \rightarrow 2\ S_6^{-2}$

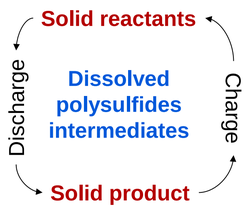
$S_6^{-2} + e^- \rightarrow {}^3/_2\ S_4^{-2}$

$^3/_2\ S_4^{-2} + e^- \rightarrow 2\ S_3^{-2}$

$S_3^{-2} + e^- \rightarrow {}^3/_2\ S_2^{-2}$

$^1/_2\ S_2^{-2} + e^- \rightarrow S^{-2}$

$2\ Li^{+1} + S^{-2} \rightarrow Li_2S_{(s)}$

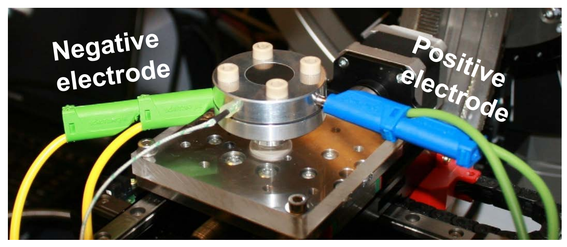


- high theoretical capacity (1675 Ah kg_{sulfur}^{-1})
- high energy density (2500 Wh kg^{-1})
- low cost and non-toxicity of sulfur

- high degradation due to loss of active material
- electrochemical processes and degradation mechanisms are still not well understood.

Materials and methods

In-situ XRD cell



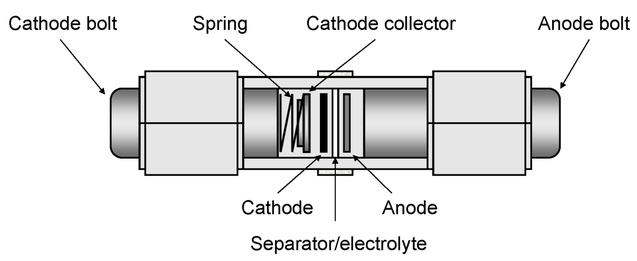
Cathode:
- Sulfur (50 wt. %)
- Carbon black (40 wt. %)
- PVDF (10 wt. %)

Electrolyte:
1 M $LiPF_6$/TEGDME

Separator: Celgard 2500

Anode:
Lithium

Swagelok- cell

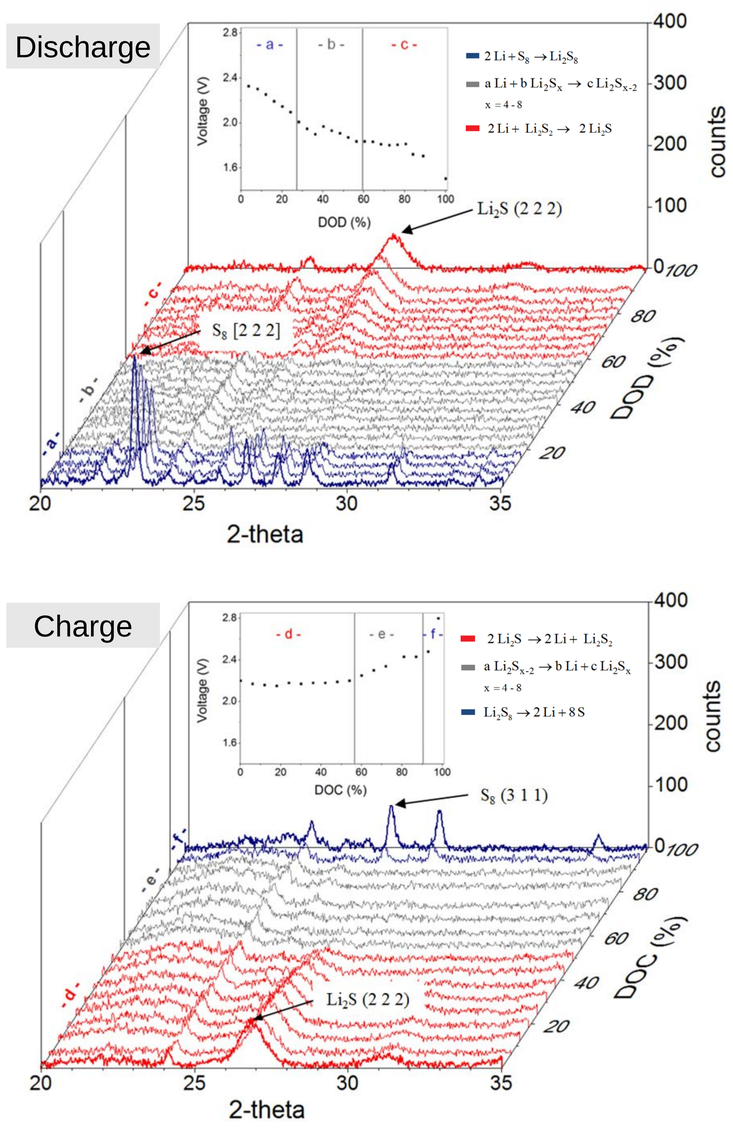


EIS

Potentiostatic: 5 mV amplitude
Equidistant intervals of 50 mC
Frequency range: 1 MHz to 60 mHz
End Voltages (V): 2.8/1.5
Discharge current: 300 A/kgS

Results

In-situ X-ray analysis



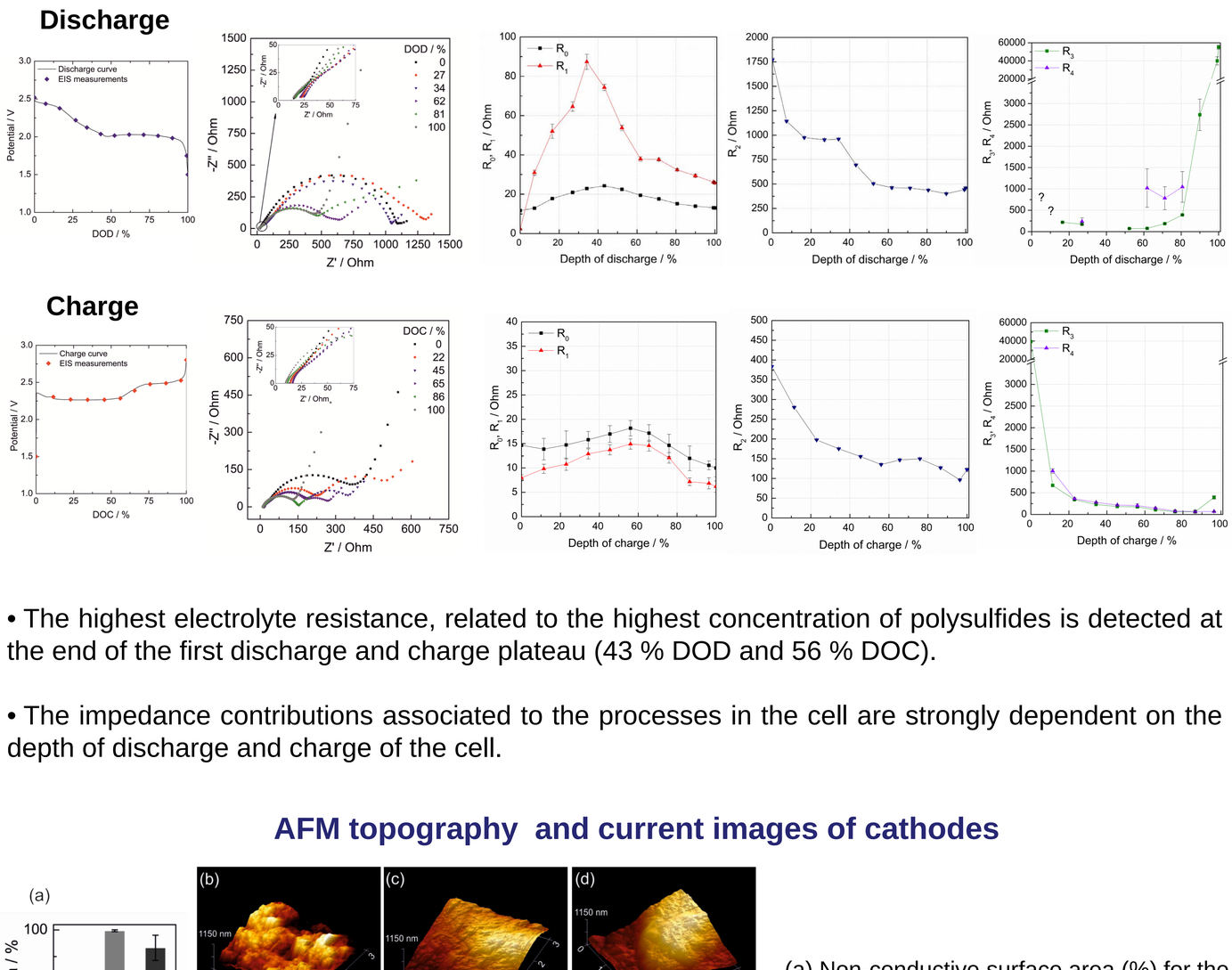
- At discharge rate of 300 mA g^{-1} sulfur reduces consecutively during the first discharge to Li_2S.

- The formation of Li_2S was observed for the first time at a depth of discharge of 60 % in the second discharge plateau at 1.8 V.

- During the charge cycle, Li_2S reacts entirely and sulfur recrystallizes with a different orientated structure and smaller particle size.

Electrochemical Impedance Spectroscopy

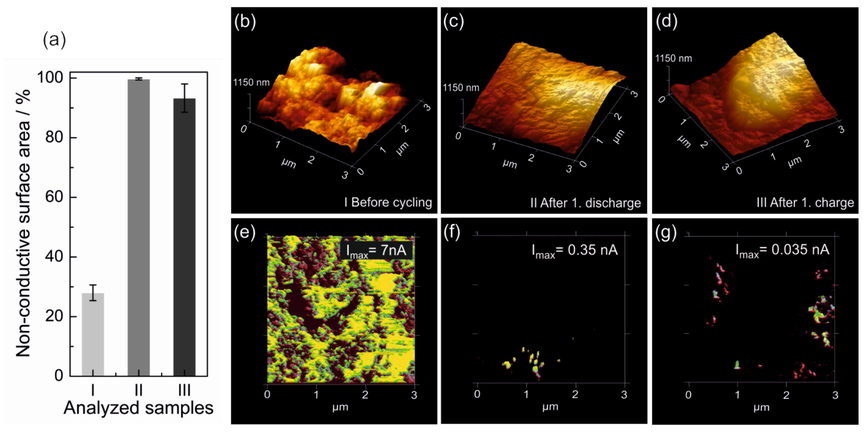
Variation of the equivalent circuit elements during cycling determined by EIS analysis.



- The highest electrolyte resistance, related to the highest concentration of polysulfides is detected at the end of the first discharge and charge plateau (43 % DOD and 56 % DOC).

- The impedance contributions associated to the processes in the cell are strongly dependent on the depth of discharge and charge of the cell.

AFM topography and current images of cathodes



(a) Non-conductive surface area (%) for the analyzed samples
I: cathode before cycling
II: cathode surface after the first discharge
III: cathode surface after the first charge.

The AFM results confirm the formation of an isolating layer in the cathode, which increases the surface resistance on the cathode, as observed through the analysis of the impedance at low frequencies (R_3)

References
[1] N. A. Cañas, S. Wolf, N. Wagner, K. A. Friedrich. J. of Power Sources, 226 (2013) 313-319.
[2] N. A. Cañas, K. Hirose, N. Wagner, B. Pascucci, K.A Friedrich, R. Hiesgen. Electrochimica Acta, 97 (2013) 42-51.

Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center

Correspondence to natalia.canas@dlr.de