Recent Progress in Lithium-Sulfur-Batteries

Prof. Dr. S. Kaskel
Fraunhofer Institute for Material and Beam Technology IWS

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Progress in Lithium-Sulfur-Batteries

Overview

- Introduction
- Status of Li-S-technology
- Technology development
  - Cathode chemistry
  - Anode materials
  - Separator
  - Role of electrolyte
- Conclusion
Future potential: high energy plus cost savings

Sulfur as next generation battery material

**Theor. specific cathode energy**
(Voltage x capacity)
- NMC: ca. 630 Wh/kg
- Li$_2$S: 2.550 Wh/kg

**Costs**
- NMC: 23 €/kg
- Sulfur: << 1 €/kg

**Cathode materials**
- LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$
- LiFePO$_4$
- Li$_4$Ti$_5$O$_{12}$

**Anode materials**
- Hardcarbon
- Graphite
- Si/C-Komposite
- Si
- Li

Capacity (mAh/g)
Components of Li-S cell

- Electrolyte
- Separator
- Lithium Metal
- Current collector (+)
- Polymer-Binder
- Conductive additive
- Sulfur/carbon composite

Li-S-cell (~330 Wh/kg)
Li-S-Battery: Introduction
**Achievable energy density: Basic estimations on stack level**

**Cathode properties**
- 25 % cathode porosity (discharged)
- 47 % cathode porosity (charged)
- Electrolyte excess for volume change
- 1000 mAh/g (Li$_2$S), 2,1 V
- 65 wt-% Li$_2$S content in cathode
- Areal capacity: 5 mAh/cm$^2$
- Li-Anode: 100 % excess

**Energy density (charged state):** 672 Wh/kg / 840 Wh/L
Status of Li-S technology

Examples of existing prototype cells

- **Li-S-cell (~350 Wh/kg)**
- **Li-S-cell (up to 325 Wh/kg, 320 Wh/L)**
- **Li-S-cell (up to 330 Wh/kg)**

- Energy density is far from its theoretical limit
- Cycle life is limited to < **50 cycles** for the high energy cells
- However, applications are already there:

**High Altitude Pseudo-Satellite (HAPS)**

Main cause of low cycle life: Lithium anode surface reactions

Degradation mechanisms

- Depletion of org. electrolyte, cells dry out
- Dendritic or porous structure causes shortcuts
- Self-discharge and active material loss through polysulfide shuttle

Polysulfide Shuttle:
Chemical reduction of dissolved PS at anode surface

→ LiNO$_3$-Additive suppresses shuttle
Focus topic Li-S-Battery at Fraunhofer IWS, Dresden

Anodes

Cathodes

Electrolytes

Separators

Mixing

Coating

Tests

Laser-Cutting

Assembly
**Cathode Materials Development**

Reducing PS Shuttle by Tailoring porous carbons

**Up to**

SA = 3000 m²/g

PV = 3-4 cm³/g

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Anode materials development

- Hard carbons form stable SEI in ether electrolytes
- 4000 reversible cycles achieved
- Recommended for cathode evaluation

Projected: up to \textbf{190 Wh/kg}


Ion-selective separator coatings

- Nafion as cation-selective polymer coating to reduce polysulfide shuttle

I. Bauer et al., J. Power Sources, 2014 251, 417–422, DOI:10.1016/j.jpowsour.2013.11.090
Cathode mechanism in ether electrolyte requires dissolution of polysulfides

Most studies use >> 5 µl Electrolyte / mg S

Saturated PS-solution in DME/DOL

LiNO$_3$: SEI former

LiTFSI: salt

DOL  Gn (n ≥ 1); DME (n = 1)
The role of LiNO$_3$
Standard electrolyte additive in DME/DOL

### LiNO$_3$: Directing SEI formation in Li-S cells

- Surface film: inorganic and organic species (LiN$_x$O$_y$, ROLi + ROCO$_2$Li)
- Compact and homogenous surface film formed with LiNO$_3$
- Enhanced stability of lithium anode and improved cycle life

LiNO$_3$ is consumed during cycling

**Electrolyte content determines cycle life**

- Electrolyte depletion and **LiNO$_3$ consumption** is major cause for low cycle life
- Excess electrolyte can enhance cycle life drastically

\[
E/S = \frac{\text{Electrolyte Volume}}{\text{Sulfur Mass}}
\]

Most research papers use $E/S >> 5$ or not even mention it

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M. Hagen et al. „Lithium–Sulfur Cells: The Gap between the State-of-the-Art and the Requirements for High Energy Battery Cells”
DOI 10.1002/aenm.201401986
**Status of Li-S technology**

**Inactive materials dominate the mass of Li-S cells**

**Li-S cathode**
- Coating (S/C): 100 µm
- Areal capacity: 5 mAh
- Porosity: 65%
- Cell voltage: 2,1 V

**Li-Ion cathode**
- Coating (NCA): 100 µm
- Areal capacity: 5 mAh
- Porosity: 25%
- Cell voltage: 3,7 V

**Weight distribution**

**17,5 wt-% active material**
- Al
- S
- B+C
- E

**76 wt-% active material**
- Al
- NCA
- B+C
- E

Fraunhofer IWS Dresden
New Electrolytes with low PS solubility (without LiNO$_3$)

Reducing electrolyte content

- Li-S pouch cell with ref. cathode, IWS electrolyte
- 3.4 µL/mg$_S$ vs. 2.5 µL/mg$_S$
- New electrolyte shifts the limit for minimum electrolyte content!

![Graph showing electrolyte content and capacity over cycles](image-url)

- Real capacity ~ 2.5 Ah at 12 h rest
- Real capacity ~ 2.7 Ah at 36 h rest

Patent pending
Electrolytes with low PS solubility

- **Reduced anode degradation**
- **Improved safety**
  - Smooth Lithium deposition
  - Low flammability

1.5M LiTFSI / 0.25M LiNO₃ in DME/DOL

**IWS electrolyte**

Li anode, 89 cycles, DME/DOL

Li anode, 100 cycles, new El.

Work in progress
Safety Tests: Lithium-Sulfur Pouch Cell (IWS electrolyte)

- Standardized Tests by SGS Germany GmbH (München)
  - Thermal Stability (130 °C), Overcharge, Simulated Internal Short Circuit, Nail Penetration, Short Circuit
  - no „Thermal Runaway“
  - max. Hazard Level (according to EUCAR): HL 3
- Significantly improved safety of Li-S-Cells, as compared to Li-Ion-Cells with same cell format
- Li-Metal burning at $T > 190 \, ^\circ C$; only if externally heated

Work in progress
Status of Li-S technology

- Li-S-cells reach 350 Wh/kg → lightest accumulator today
- Volumetric energy density currently lower than Li-Ion
- Cycle life in high energy cells is limited today to 50-100 cycles
- Available cells not yet suitable for automotive
- Potential for step-change
  - Anode
  - Cathode
  - Electrolyte
  - Separator
- Niche markets are growing and may expand
Related projects

Thanks to co-workers, partners and funding agencies!

Li-S-Battery-Team at IWS
6th Workshop »Lithium-Sulfur Batteries«

- Annual conference in Dresden
- More than 150 participants from industry and academia

Save the date: November 6–7, 2017
Thank you for your attention!

Prof. Dr. S. Kaskel
Dr. Holger Althues
Fraunhofer IWS
Winterbergstraße 28
01277 Dresden, Germany

Phone +49 351 83391-3476
Fax +49 351 83391-3300
E-Mail holger.althues@iws.fraunhofer.de

www.iws.fraunhofer.de
### Status and Potential of Li-S-Technology

<table>
<thead>
<tr>
<th>SoA (LIB)</th>
<th>SoA (Sion-Li-S)</th>
<th>Prognosis (Li-S) – GM*</th>
<th>Prognosis (Li-S) BMW**</th>
<th>Prognosis (Li-S) - IWS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grav. Energy density (Cell)</strong></td>
<td><strong>140 - 250 Wh/kg</strong></td>
<td><strong>350 Wh/kg</strong></td>
<td><strong>550 Wh/kg</strong></td>
<td><strong>419 Wh/kg</strong></td>
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<tr>
<td><strong>Vol. Energy density (Cell)</strong></td>
<td><strong>280 - 670 Wh/L</strong></td>
<td><strong>320 Wh/L</strong></td>
<td><strong>620 Wh/L</strong></td>
<td><strong>644 Wh/L</strong></td>
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**Li-Ion-Cells (examples)**

- LG Pouch-Cell (Opel Ampera): 140 Wh/kg
- Panasonic 18650 (Tesla): 243 Wh/kg

**Li-S-cells**

- Sion-Power: 350 Wh/kg (cell) 260 Wh/kg (pack)
- Oxis-Energy: -5 – 80°C ULC: 300 Wh/kg, 200 Wh/L LLC: 180 Wh/kg, 170 Wh/L

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* T. Greszler, GM **Beyond Lithium Ion 5, Berkeley, CA 2012**
** Dr. P. Oberhumer, BMW **Li-S-Battery-Workshop 2013, Dresden**

ULC = Ultralight Cell
LLC = Long life cell