German Aerospace Center (DLR)

Institute of Engineering Thermodynamics

Performance and Mechanistic Comparison of Mg-S and Li-S batteries

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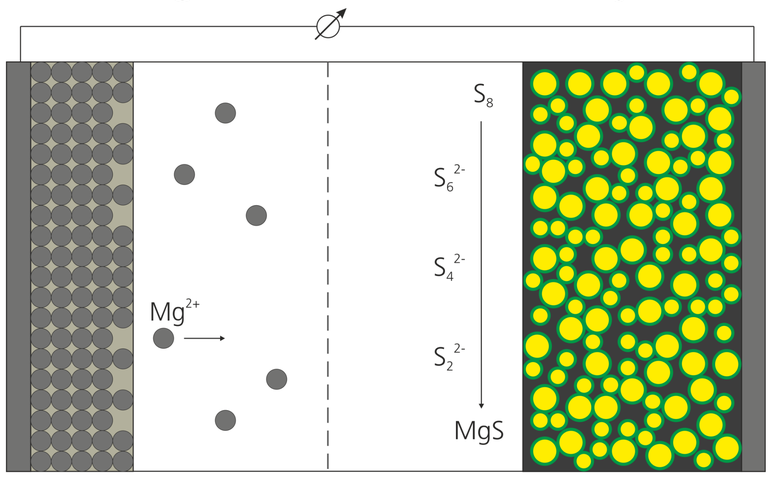
Magnesium-sulfur battery



Anode:
Mg foil (250 µm)
Li foil (750 µm)

Separator:
Glass fiber sheet (260 µm)
Electrolyte:
1.4 M $Mg(HMDS)_2$ / TEGDME:DEGDME
0.4 M $Mg(B(hfip)_4)_2$ / DME
1 M LiTFSI / TEGDME:DEGDME

Cathode:
Sulfur (50 wt.%)
Ketjenblack EC600 JD (40 wt.%)
PVDF (10 wt.%)

Electrochemical reactions

$$Mg_{(s)} \rightarrow Mg^{2+} + 2e^-$$
$$S_{8(s)} \rightarrow S_{8(diss)}$$
$$\tfrac{1}{2}\, S_{8(diss)} + e^- \rightarrow \tfrac{1}{2}\, S_8^{-2}$$
$$\tfrac{3}{2}\, S_8^{-2} + e^- \rightarrow 2\, S_6^{-2}$$
$$S_6^{-2} + e^- \rightarrow \tfrac{3}{2}\, S_4^{-2}$$
$$\tfrac{3}{2}\, S_4^{-2} + e^- \rightarrow 2\, S_3^{-2}$$
$$S_3^{-2} + e^- \rightarrow \tfrac{3}{2}\, S_2^{-2}$$
$$\tfrac{1}{2}\, S_2^{-2} + e^- \rightarrow S^{-2}$$
$$Mg^{2+} + S^{-2} \rightarrow MgS_{(s)}$$

$Mg(HMDS)_2$: Magnesium dihexamethyldisilazide
LiTFSI: Lithium-bistrifluoromethylsulfonylimide
TEGDME: Tetraethylene glycol dimethyl ether (tetraglyme)
DEGDME: Diethylene glycol dimethyl ether (diglyme)
DME: Dimethoxy ethane (monoglyme)
PVDF: Polyvinylidene fluoride

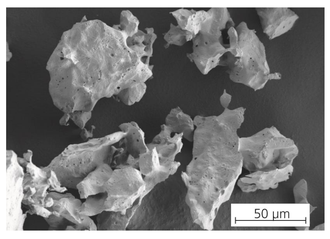
Features and Drawbacks of MgS batteries

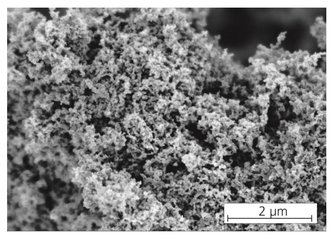
+ High theoretical capacity of sulfur (1672 mAh g^{-1}) and magnesium (2230 mAh g^{-1} and 3832 mAh cm^{-3}).
+ High theoretical energy density for a Mg-S cell (1330 Wh kg^{-1} and 2500 Wh l^{-1}, calculated based on second plateau at 1.4 V).
+ Low cost and non-toxicity of sulfur.
+ Abundancy, non-toxicity and high safety of magnesium (no dendrite formation).

– Slower diffusion and reaction kinetics due to bivalent nature of Mg^{2+}.
– Active material loss due to polysulfide shuttle.
– Passivation layer on Mg anode (SEI) non-permeable for Mg ions.
– Suitable electrolyte has to be non-nucleophilic, stable towards both electrodes, may not form a blocking layer and offer sufficient ionic conductivity.

Materials and Methods

Slurry preparation

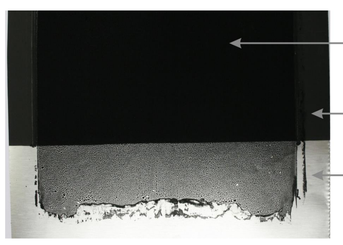




1. Sulfur powder dry ball-milled with Ketjenblack EC600 JD
2. Dispersion of S/C-composite in PVDF-solution (DMSO)

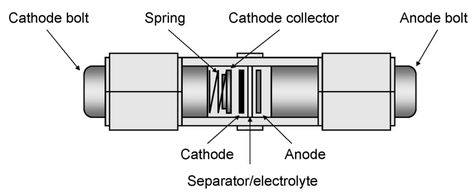
Easy scalable process without energy consuming infiltration step.

Coating



Doctor blading of slurry on C-primed Al-foil and drying at 60°C for 12 h.
Resulting sulfur loadings: 0.6 – 0.8 mg cm^{-2}.

Cell assembling



Battery assembling in Swagelok-cells (Ø 22mm) with defined cell pressure (45 N).

Characterization

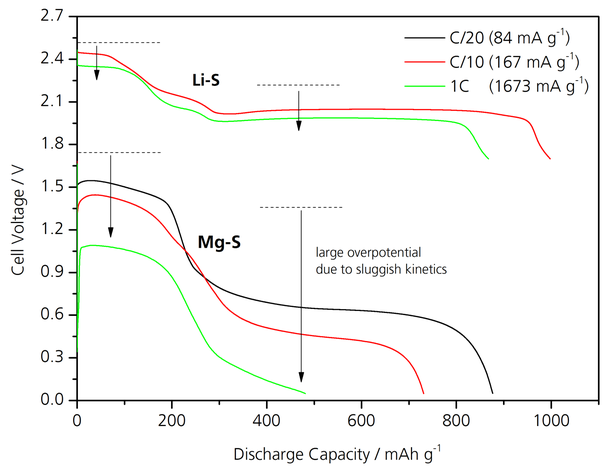
Thermogravimetric analysis of cathode composition (thermal stability).

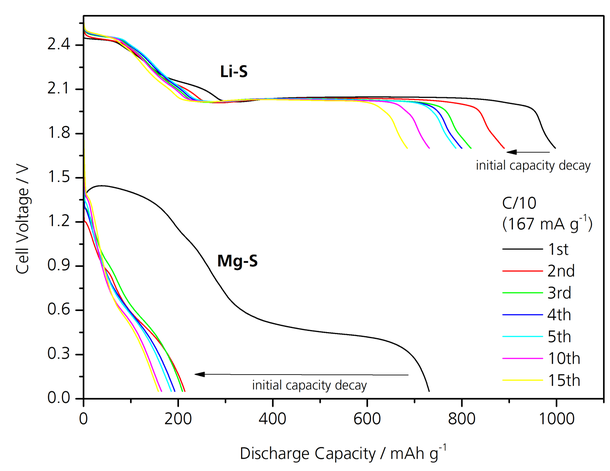
Battery cycling at RT with different C-rates (C/20 to 1C).

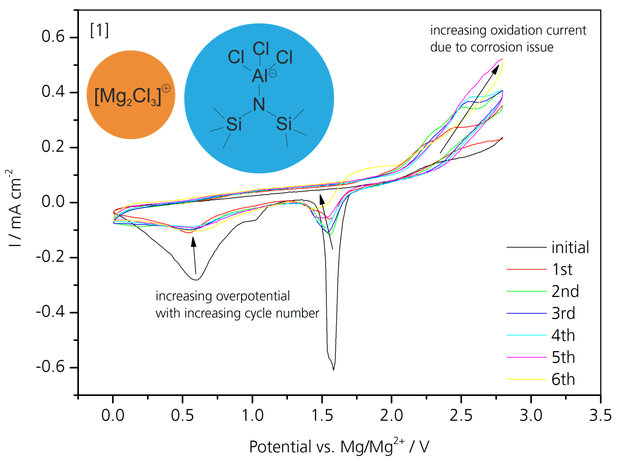
Electrochemical impedance spectroscopy (EIS) during battery cycling.

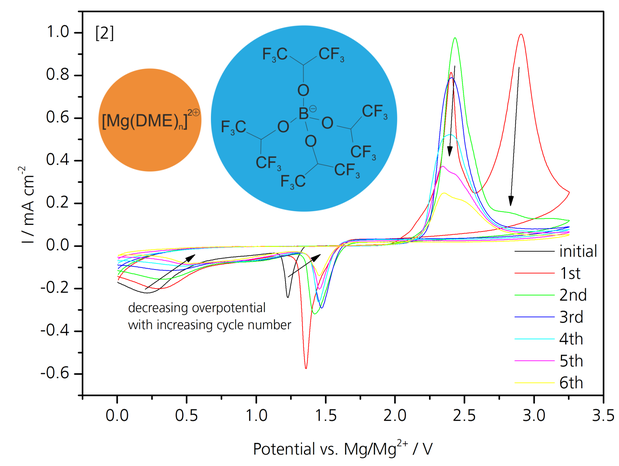
Cyclic voltammetry with Mg-reference ring (scan rate 100 µV/s).

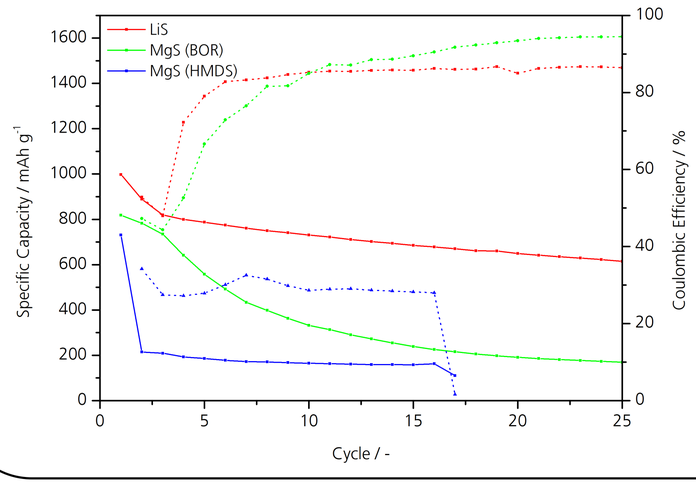
Experimental Results











- Mg-S system suffers from large overpotentials and initial capacity decay due to sluggish kinetics and Mg anode surface passivation, respectively (cf. individual discharge curves).
- Boron-centered Mg-electrolyte salt [2] displays decreasing overpotentials with increasing cycle number while being non-corrosive in contrast to the Chloride-based Mg-electrolyte [1] (cf. CV).
- In addition, the Boron-based electrolyte features better reoxidation resulting in an enhanced charging behaviour and reversibility (cf. Coulombic Efficiency).
- Despite a significant lower discarge capacity of Mg-S cells in comparison to the Li-S system, the development in the research field of Mg-electrolytes enhances the performance of Mg-S batteries successively.

[1] Zhao-Karger et al., *Adv. Energy Mater.*, 2015, **5**, 1401155

[2] Zhao-Karger et al., *J. Mater. Chem.* A, 2017, **5**, 10815

Conclusion

- Synthesis of S/C composite cathodes via **ball-milling** and **dispersion processes** followed by **doctor blading**. Kept easy and energy efficient (no melt infiltration step) for scale-up purposes.
- Initial discharge capacity of Mg-S similar to Li-S cells yet **fast capacity decay** in following cycles which can be attributed to an increased charge transfer resistance (most probably **passivation layer** on Mg anode surface).
- Despite displaying similar mechanisms, the Li-S and Mg-S system also feature significant differences mainly due to the **bivalent character** of Mg ions and the resulting **sluggish kinetics** and the **blocking behaviour of passivation layers**.
- HMDS-based Mg-electrolyte displays **corrosion** at high potentials and **irreversibility** due to chloride species and prominent polysulfide shuttle, respecitvely. In contrast the Boron-centered Mg-electrolyte features **decreasing overpotentials** and **enhanced reversibility (high Coulombic efficiency)**, which make it a promising electrolyte component for future Mg-S batteries.

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