German Aerospace Center (DLR)

Institute of Engineering Thermodynamics

Synthesis and Characterization of S-C composite cathodes for Mg-S batteries

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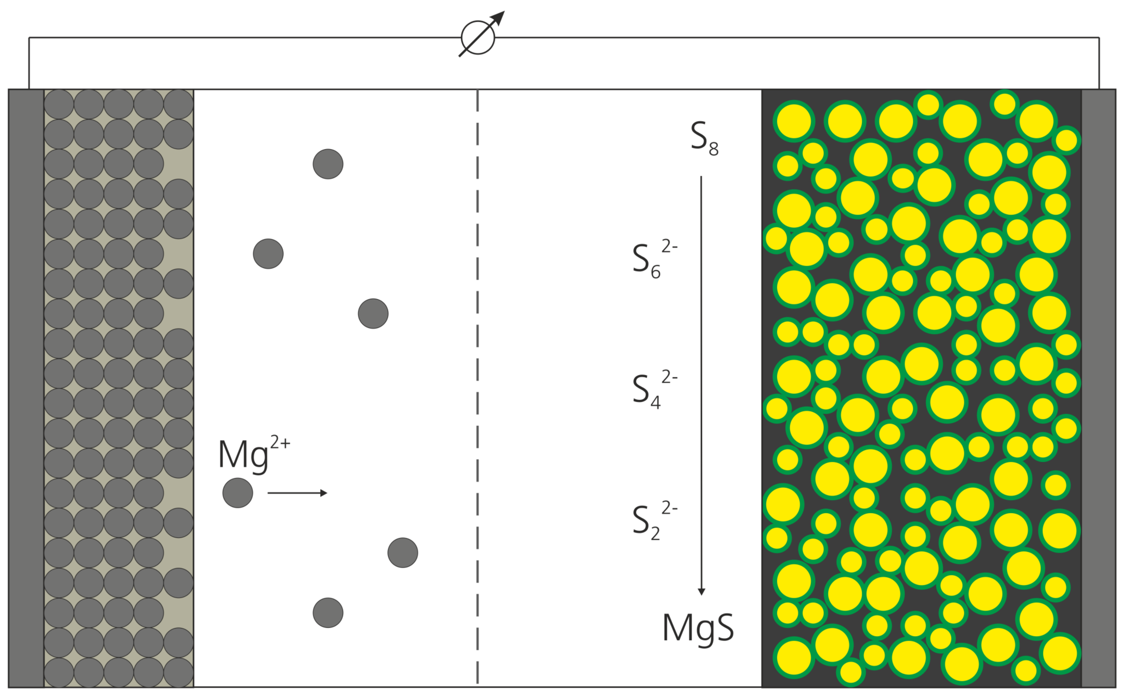
Magnesium-sulfur battery



Anode: Magnesium foil (250 µm) [Li foil (750 µm)]

Separator: Glass fiber sheet (260 µm)

Electrolyte: 1.4 M $Mg(HMDS)_2$ / TEGDME:DEGDME [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)
PVDF: Polyvinylidene fluoride

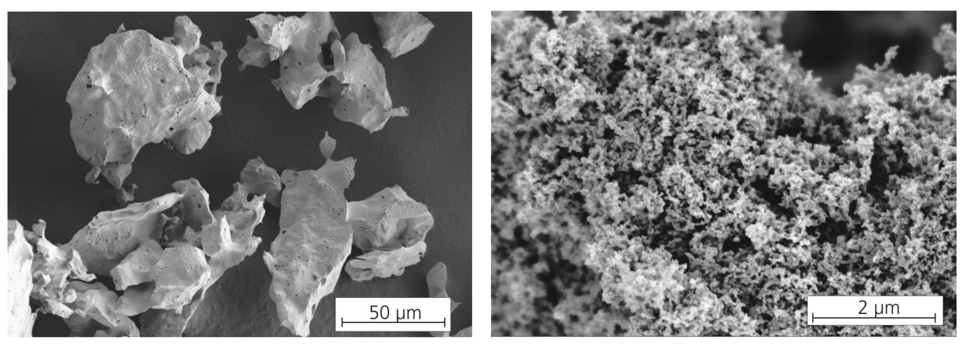
Features and Drawbacks

+ 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 (1600 Wh kg^{-1} and 3200 Wh l^{-1}).
+ 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.

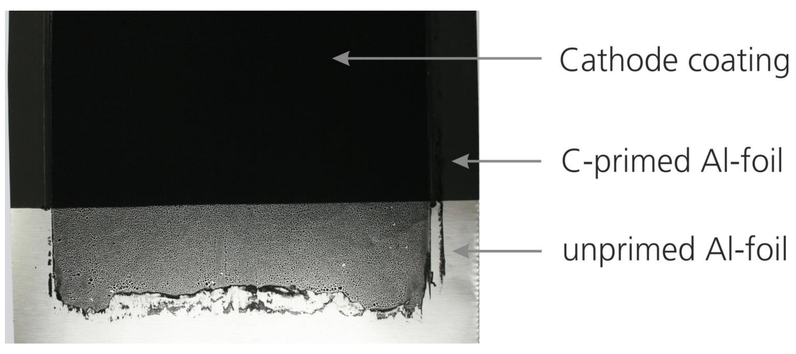
Materials and Methods

Slurry preparation



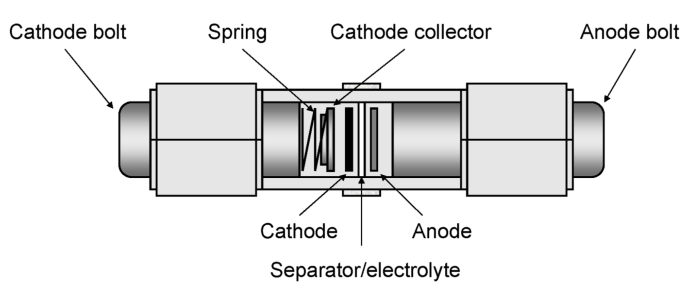
1. Sulfur powder dry ball-milled with Ketjenblack EC600 JD
2. Melt infiltration process at 155°C / 300°C
3. Dispersion of S/C-composite in PVDF-solution (DMSO)

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.

Characterization

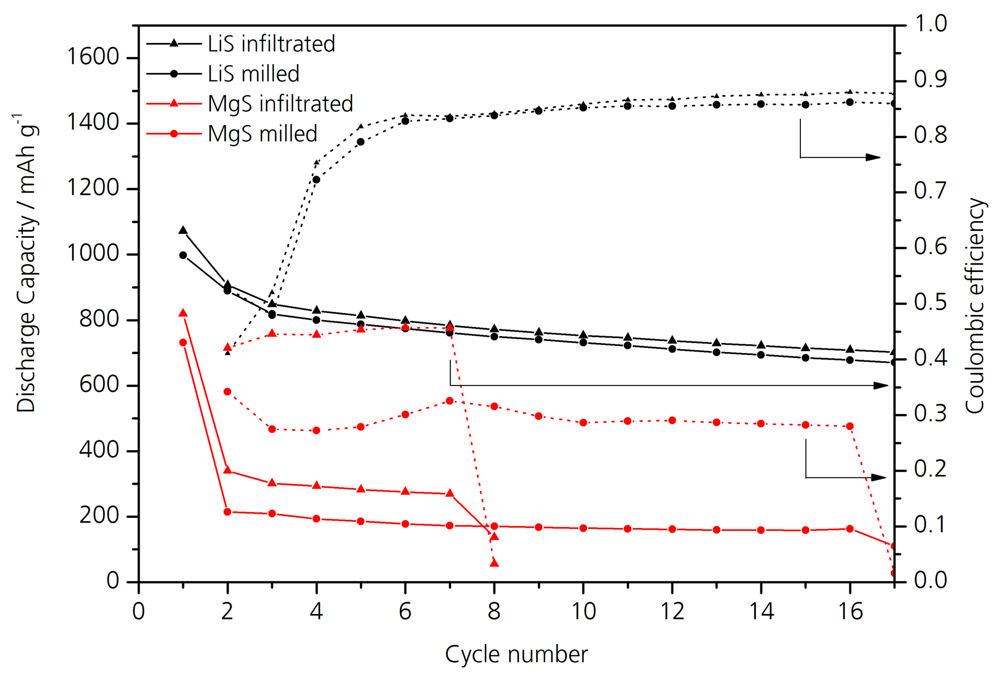
Thermogravimetric analysis of cathode composition (thermal stability).

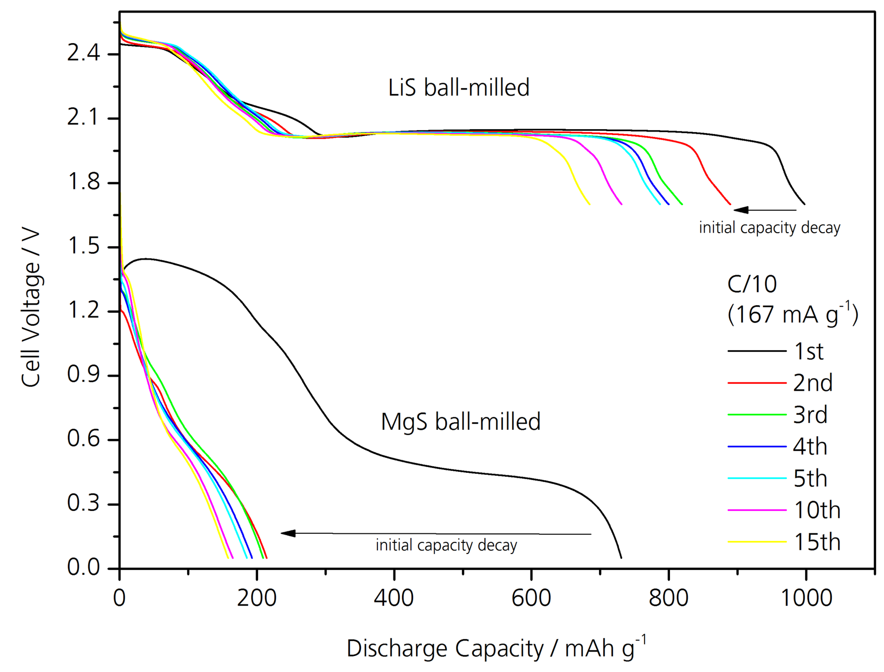
Battery cycling at RT with different C-rates (C/20 to 1C).

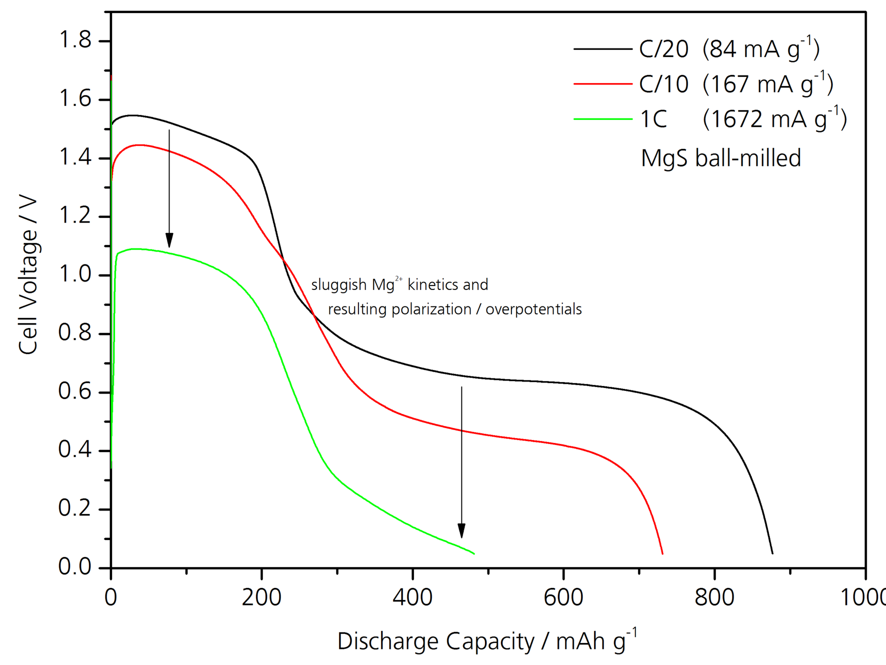
Electrochemical impedance spectroscopy (EIS) during battery cycling.

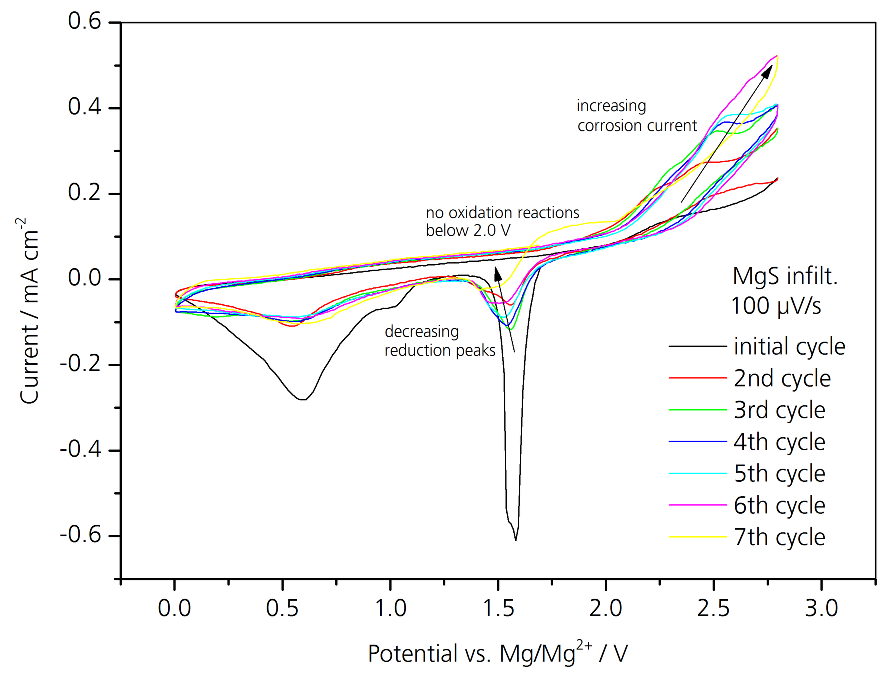
Cyclic voltammetry with Mg-reference ring (scan rate 100 µV/s).

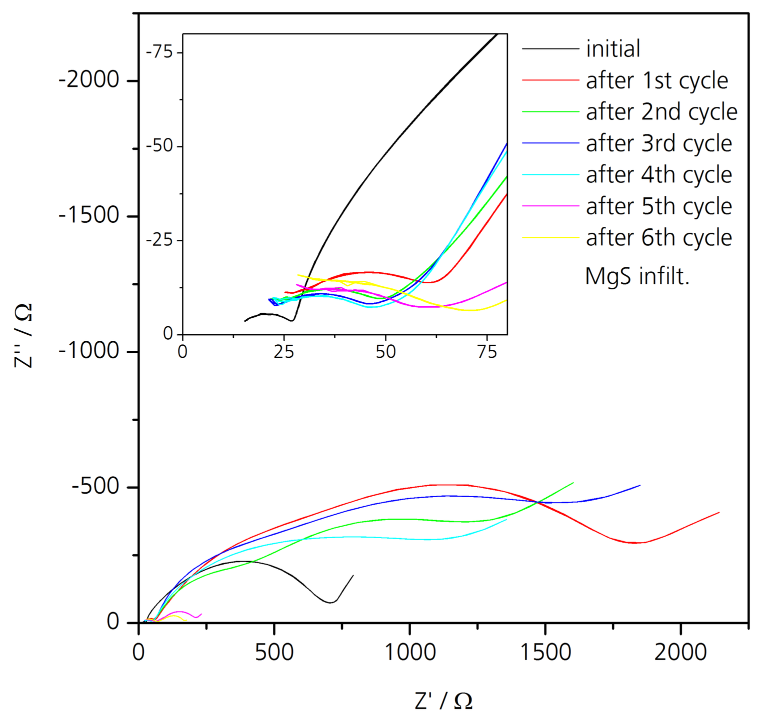
Experimental Results



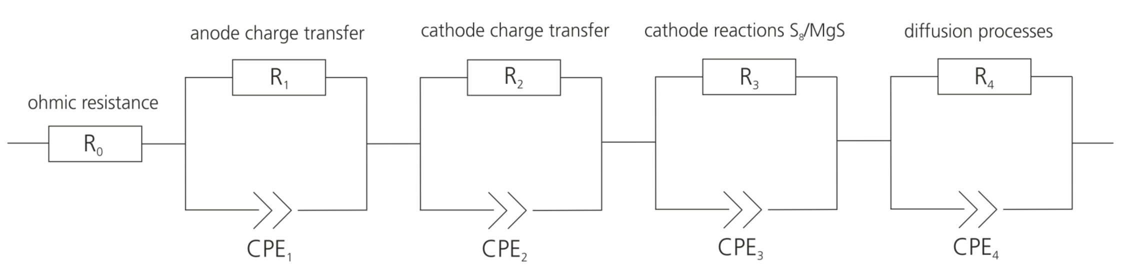








Equivalent Circuit Model (ECM) [1]



- Galvanostatic EIS measurement (1 MHz…30 mHz, 5 µA amplitude) after 1 h OCP and each complete discharge/charge cycle (prior 30 min rest).
- ECM was adapted from studies on LiS full cells by N. Cañas [1].
- Increase in electrolyte and charge transfer resistance after first cycle (yet no clear trend with increasing cycle number).
- After 5th cycle: cell failure and instant potential drop to 0.1 V (after 30 min rest) and decreased overall impedance.

[1] Natalia A. Cañas, Kei Hirose, Brigitta Sievert, Norbert Wagner, K. Andreas Friedrich Renate Hiesgen, Electrochimica Acta 97, 42– 51 (2013)

Conclusion

- Synthesis of S/C composite cathodes via **ball-milling** and **dispersion processes** followed by **doctor blading**. Kept easy for scale-up purposes. Only **small capacity gain due to sulfur infiltration** into porous carbon black matrix.
- Initial discharge capacity similar to Li-S cell yet **fast capacity decay** in following cycles which can be attributed to an **increased charge transfer resistance** (either passivation layer on anode or cathode).
- Low coulombic efficiency concludes that generated charge is intrinsically lost most probably due to **polysulfide shuttle.**
- Elongated charge behaviour with oxidation reactions beyond potentials of 2.0 V. Also non-prominent oxidation peaks in CV concluding an **incomplete reoxidation**. Increased **corrosion current at high potentials** with increasing cycle number due to chorine species in the electrolyte.
- EIS reveals **impedance increase after first cycle** and **impedance decrease after cell failure**. Underlying cell processes have to be further investigated via halfcell impedance measurements.

Knowledge for Tomorrow

Wissen für Morgen

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Bundesministerium für Bildung und Forschung

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