

Unlocking the Potential of Calcium-Sulfur Batteries: Opportunities and Key Challenges for Practical Implementation

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Given the increasing global demand for advanced energy storage technologies, interest is growing in alternative battery chemistries beyond lithium-ion systems, driven by their potential advantages in terms of energy density, cost, sustainability and safety. The calcium-sulfur (Ca-S) chemistry stands out as a promising yet challenging systems. High theoretical energy density, abundance and low cost of materials as well as improved safety are among key benefits of this battery system. Despite growing research enabling limited cycling of Ca-S cells, the technology remains in its infancy, with major challenges like capacity fading from polysulfide shuttling and calcium anode passivation (Ref). Due to the low redox potential of calcium metal (-2.87 V vs. SHE), it is highly susceptible to reducing nearby species. This tendency leads to decomposition products from soluble sulfur intermediate's and electrolytes, which consequently limits the efficiency and long-term stability of the cell.

DLR has scanned the applicability of a series of separators and electrolyte systems enabling practical Ca-S batteries. Complementary techniques including galvanostatic cycling, impedance spectroscopy, SEM and XPS measurements have been implemented for this study. Thin polypropylene and cellulose-based separators demonstrate a significant reduction in voltage hysteresis in Ca-S cells. However, the shortened diffusion path associated with these separators leads to an enhanced polysulfide shuttle effect. This observation highlights the critical need for the development of strategies focused on sulfur retention and/or anode protection to improve the performance and stability of the cells. Therefore, on further attempts-, the polypropylene based separator was photochemically modified with a polymeric coating containing polar side chains. This modification effectively enhanced the cyclability of the Ca-S cell, improving both discharge and cycle life. Furthermore, the compatibility of different electrolyte systems varying the salt anion as well as the solvent have been investigated for the Ca-S batteries. Here the combination of $[B(hfip)_4]$ -based salt and monoglyme shows the best performance.

References:

- [1] Z. Li, S. Cui, J. Häcker, M. Nojabaee, M. Fichtner, G. Cui, Z. Zhao-Karger, *Angew. Chem. Int. Ed.* 64 (2025)