

Sulfurized Polyacrylonitrile (SPAN) Cathodes in Lithium-Sulfur Batteries: Investigating the Influence of Cathode Microstructure and Electrolyte System on Electrochemical Performance

Martina Gerle^a, Robin Moschner^b, Timo Danner^a, Kathrin Küster^c, Peter Michalowski^b, A. Kwade^b, K. Andreas Friedrich^a, Maryam Nojabaei^a

^a German Aerospace Center (DLR e.V.), Institute of Engineering Thermodynamics, 70569 Stuttgart, Germany

^b Institute for Particle Technology, Technische Universität Braunschweig, 38104 Braunschweig, Germany

^c Max Planck Institute for Solid State Research, 70569, Stuttgart, Germany
Martina.Gerle@dlr.de

With their unmatched specific energy, lithium-sulfur batteries are an outstanding example for the potential of next-generation energy storage. However, major challenges such as the well-known polysulfide shuttle effect and the inherent insulating nature of sulfur stand in the way of widespread application. To combat these problems, numerous approaches have been explored, largely focusing on the cathode. [1] One of the most promising approaches is the application of covalently bound sulfur within an organic backbone, which leads to better cyclability by eliminating or suppressing sulfur dissolution. [2]

In this work, a promising organosulfur namely sulfurized polyacrylonitrile (SPAN) serving as the cathode in lithium-sulfur batteries is deeply studied. In particular, the effect of the cathode microstructure caused from varying degrees of calendaring as well as the influence from the electrolyte system on the redox pathways and electrochemical performance are investigated. To elucidate the impacts of morphology and electrolyte system variation, electrochemical impedance spectroscopy in a symmetrical two- or three-electrode system is employed. [3,4] Suitable impedance modelling, investigation of the distribution of relaxation times and fitting are deployed to differentiate between various processes on the cathode side. The results are further supported by mechanical characterization, galvanostatic cycling experiments, chemical analyses and numerical simulation.

Electrochemical analysis of the highly calendared SPAN cathodes indicates damage to the electronic conductive network while the active material does not appear to be affected during the calendaring process. Moreover, increased overpotentials are detected in the calendared cathodes, leading to incomplete charging and rapid capacity decay, which we have discussed in detail regarding the restriction of electronic and ionic percolation pathways caused by the calendaring process. Additionally, emphasis is placed on the effect of the electrolyte system, in particular ether and carbonate electrolyte, recognizing their capability to influence redox pathways and capacity retention. It is shown that SPAN cathodes are exhibiting high compatibility with the carbonate-based electrolyte. The differences in electrochemical stability and impedance response for these two electrolyte systems are being discussed in detail and the role of the generation of a cathode electrolyte interphase (CEI) layer is highlighted.

References:

- [1] M. Nojabaei: "Ultramicroporous carbon aerogels encapsulating sulfur as the cathode for lithium-sulfur batteries", J. Mater. Chem. A, 2021, 9, 6508-6519
- [2] X. Zhao: "Sulfurized polyacrylonitrile for high-performance lithium sulfur batteries: advances and prospects", J. Mater. Chem. A, 2021, 9, 19282
- [3] M. Gerle: "Identification of the Underlying Processes in Impedance Response of Sulfur/Carbon Composite Cathodes at Different SOC", J. Electrochem. Soc., 2022, 169, 030505
- [4] M. Gerle: "Impact of the Sulfurized Polyacrylonitrile Cathode Microstructure on the Electrochemical Performance of Lithium-Sulfur Batteries", Adv. Sci., 2025, 2415436