Investigation of rechargeable lithium-sulfur batteries by in-situ techniques

Natalia A. Cañas[1,2], K. Andreas Friedrich[1,2], Norbert Wagner[1], Brigitta Pascucci[1], Renate Hiesgen[3]

[1] German Aerospace Center, Stuttgart, Institute of Technical Thermodynamics Pfaffenwaldring 38-40, 70569, Germany
[2] University of Stuttgart, Institute for Thermodynamic and Thermal Engineering, Pfaffenwaldring 6, 70569, Germany
[3] University of Applied Sciences Esslingen, Department of Basic Science, Kanalstrasse 33, 73728 Esslingen, Germany

The lithium-sulfur (Li-S) battery is currently of great interest for the research community. This battery promises with its high theoretical capacity (1675 mA h^{-1}) and energy density (2600 Wh kg^{-1}) to be one of the energy storage systems of the future. Impressive advances in capacity improvement and capacity stability have been reported recently, e.g. in [1,2]. Nevertheless, the electrochemical processes and degradation mechanisms of the cells need further investigation as the obtained information is mainly of indirect nature and a confirmation of proposed mechanism is required.

In this work, in-situ characterization methods were applied for the characterization of reaction products and changes in the electrode properties. By means of XRD, the formation of reaction products during charging and discharging were monitored in operando [3]. The formation of dilithium sulfide and the recrystallization of sulfur have been semi-quantitatively determined. The electrochemical behavior of the cell was also investigated using electrochemical impedance spectroscopy (EIS) at different depths of discharge and charge; and up to 50 cycles [4]. An electrical circuit is proposed to quantify the impedance contribution of the cell. Changes in the electrolyte resistance and charge transfer resistance due layer formation on the electrode are amongst others the analyzed processes in this research. With these in-situ measurements, a methodology is presented to understand the processes by direct evidence.

Furthermore, ex-situ atomic force microscopy (AFM) measurements provide information about changes in the electrical conductivity of the cathode surface. A comparison of their nanoscale electrical, electrochemical, and morphological properties at samples was performed. Morphological studies of the cathodes before and after the electrochemical tests were performed by scanning electron microscopy (SEM).

This work highlights the importance of in-situ studies and the combination of different spectroscopic and microscopic techniques to reveal new insights into the Li-S battery.

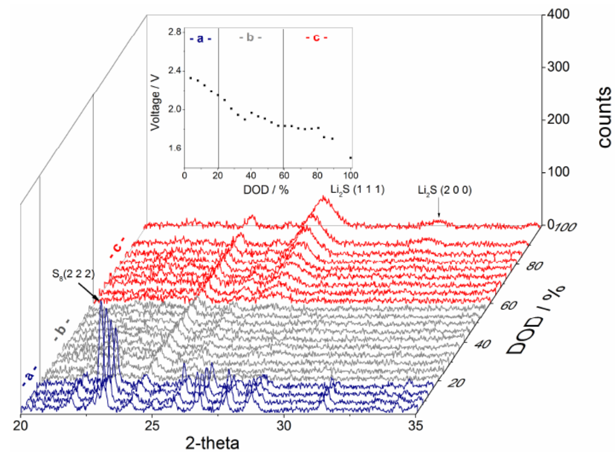

Fig. 1: In-situ X-ray diffraction data collected during discharging of Li-S battery at a rate of 300 A kg^{-1}. Three different regions are shown: a) reaction of sulfur to high order polysulfides (blue), b) reactions of high order polysulfides (gray) and c) formation of Li_2S (red). The discharge curve is shown on the top. The average discharge capacity is 1276 mAh $gsulfur^{-1}$.

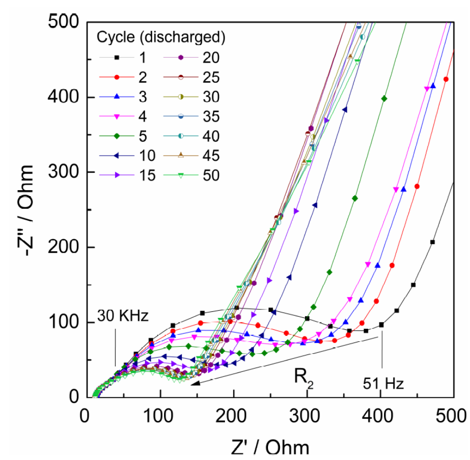

Fig. 2: Selected Nyquist plots in the frequency range of 60 mHz–1 MHz at different depth of discharge, DOD.

References
[1] M. Pasta, C.D- Wessells, R.A. Huggins,Yi Cui, Nat. Commun. 3 (2013) 1149.
[2] Y.-S. Su, A. Manthiram, Nat. Commun. 3 (2012) 1166
[3] N.A. Cañas, S. Wolf, N. Wagner, K.A. Friedrich, J. of Power Sources 226 (2013) 313-319.
[4] N.A. Cañas, K. Hirose, N. Wagner, B. Pascucci, N. Wagner, K.A Friedrich, R. Hiesgen, Electrochimica Acta 97 (2013) 42–51.
[5] K. Kumaresan Y. V. Mikhaylik, R. E. White, J. Electrochem. Soc. 155 (2008) A578.