ENGINEERING THE SULFUR CATHODE TO REALIZE THE DEVELOPMENT OF LONG-LIFE ROOM-TEMPERATURE SODIUM-SULFUR BATTERIES

ABSTRACT

This thesis focuses on enhancing the performance, stability, and practicality of sulfur-based cathodes for room-temperature sodium-sulfur (RT-Na/S) batteries, addressing critical challenges such the inherent insulating nature of sulfur and its discharge moieties (i.e., polysulfides, polysulfide shuttling, sluggish redox kinetics, loss of sulfur species and large volume changes during cycling. The research adopts a comprehensive strategy that includes rational cathode material design, and conductive host engineering, supported by advanced structural and electrochemical characterization techniques, to realize substantial improvements in the electrochemical performance of RT-Na/S batteries.

The first objective aims to develop a sulfur composite cathode to enhance the chemical adsorption of sodium polysulfides for a reversible RT-Na/S battery. To achieve this, a hybrid system of covalently-bonded Sulfurized Polyacrylonitrile (SPAN) with a metal monosulfide such as zinc sulfide (ZnS) as the cathode additive was proposed. The obtained SPAN-ZnS cathode system could exhibit excellent rate performance (0.14C to 1C), outstanding cycling stability (over 450 cycles at 1C), and a capacity retention of 69%. The multifunctional property of ZnS allows expedited charge transfer kinetics, as well as conveniently alters the local surface chemistry of the matrix by shortening the sulfur-sulfur bond of the matrix.

The second objective focusses on further maximizing the utilization of sulfur in SPAN cathodes by incorporating a composite into the matrix. A rational design comprising an optimized weight ratio of carbon source, i.e., graphite (G), and carbonized Prussian blue (PB) incorporated into the SPAN framework to serve as the sulfur cathode. A proof-of-concept cell with cathode delivers a high initial discharge capacity of 1678 mAh g^{-1} while delivering a capacity of 834 mAh g^{-1} after 500 cycles at 2C, retaining a capacity of ~77%. The incorporation of G and PB in the SPAN matrix not only serves as an effective adsorption site to confine sulfur moieties and provide high electronic conductivity but also enables the catalyzation of sulfur conversion reactions towards fast sulfur electrochemistry.

The third objective aims at investigating a unique approach combining physical and chemical confinement to realize a stable and reversible Na/S battery. To address this, a localized

engineering of the sulfur host was achieved by fine-tuning nitrogen doping in microporous carbon at room temperature conditions. With varying etching time of 4 to 12 hours, the nitrogen doping could be successfully altered from 7-19%. An optimized content of nitrogen doping of ~18.2 % corresponds to 8 hours of etching. The as-developed nitrogen doped microporous carbon based on 8 hours of etching exhibits the best performance with a stable cycle-life for over 520 cycles at 1C, which is superior to most of the previous works. RT-Na/S cell could attain a high Coulombic efficiency of ~99.5% with a minimal decay of 0.28 mAh g^{-1} per cycle and 77% capacity retention at 1C. The etching time serves as a critical parameter for simultaneously tuning the nitrogen doping level and hierarchical pore distribution within the sulfur host tailored under room-temperature conditions, eliminating the need for energy-intensive, high-temperature treatments.

The final objective targets a unique sulfur host with a 3D robust structure with the incorporation of a graphitic carbon nitride structure into the metal-organic framework (MOF). The modified microporous carbon exhibits unique pore size distribution and nitrogen-site enrichment. As such, the hierarchical microporous structure effectively confines the sulfur species physically while facilitating the ionic transportation. Further modification with DCD introduces abundant nitrogen functionalities, which create strong chemical adsorption sites for sodium polysulfides and improve the overall performance of the host. A microporous carbon derived from a MOF, further modified with dicyandiamide (DCD) serves as the novel host for to confine sulfur and its moieties. The optimized cathode exhibits a high reversibility with about 90% of capacity retention over the first 500 cycles and extended cycle life of 2000 cycles at 2 C. The synergistic effects of optimized pore architecture and nitrogen site engineering effectively suppress polysulfide migration, accelerate redox kinetics, and enhance active material retention.

Throughout the thesis, advanced characterization techniques such as X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) analysis, and High-Resolution Transmission Electron Microscope (HRTEM) are utilized to gain the structural and morphological changes in the sulfur cathode. Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR) are used to monitor chemical bonding as well as the evolution of polysulfide species. Surface and chemical information are captured using Brunauer-Emmett-Teller (BET) and X-ray photoelectron spectroscopy (XPS), respectively. These techniques together provide a significant insight into the mechanisms of sulfur's performance.

In conclusion, this thesis successfully achieves its objectives by tackling the key challenges associated with sulfur cathodes in RT-Na/S batteries. The development of conductive sulfur hosts, catalytic additives, and optimized composite architectures has resulted in enhancing the redox kinetics, suppression of the polysulfide shuttle, improving the capacity retention and long-term structural stability. These advancements not only enhance the cycling performance and efficiency of Na/S batteries but also provide valuable insights for the rational design of high-performance cathode materials, paving the way toward practical and commercially viable RT-Na/S battery technology.