NOVEL NANOSTRUCTURED MULTI-FUNCTIONAL MATERIALS FOR HIGH-ENERGY LITHIUM-SULFUR BATTERIES

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by

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ABSTRACT

The realization of a highly developed society with zero-carbon emissions and advanced electrified transportation demands the emergence of batteries delivering superior energy density and charge storage capability. Conventional lithium batteries, which have persuaded deep into the social structure, failed to fulfill the increasing needs due to their energy limitations. Lithium-sulfur batteries, functioning in accordance with the electrochemical reaction between lithium and sulfur, can yield a theoretical capacity of 1675 mAh g^{-1}, and an attractive energy density has come up as a solution. Additionally, the abundance, cost-effectiveness, and non-toxic nature of sulfur add to its advantage as an electrode material. Nonetheless, the widespread development of lithium-sulfur batteries is held back because of some serious concerns. This thesis focuses on developing multifunctional nanostructures as electrode materials to overcome the challenges faced by Li-S batteries and improve the specific capacity. The detailed characterization of the developed materials and the elaborate description of the electrochemical results are presented in five chapters (chapters 2-6).

The first chapter provides a detailed introduction to LSBs comprising their basic electrochemistry, challenges, and the state of art literature survey. More emphasis is given to the aspects which are currently focused on the thesis.

In the second chapter, a grain-like lithium cobalt vanadate embedded graphene nanoplatelets (GLCVO) has been designed as a potent sulfur host in Li-S batteries. The composite cathode with preferable active sites is highly efficacious in capturing the polysulfides through strong chemical interaction and propelling the polysulfide conversion reaction kinetics. Furthermore, the graphene nanoplatelets render an interconnected pathway for electronic conduction. As a direct consequence, the GSLCVO cell evinces an initial discharge capacity of 982 mAh g^{-1} at 0.5 C rate and maintains excellent cyclability with a low attenuation rate of 0.031% over 800 cycles. Besides, the cell exhibits better static stability and attenuates the self-discharge

behaviour to a great extent. (This work was published in the *Journal of Electroanalytical Chemistry*, 2021)

Separator modification using polar materials exploiting its ability to entrap polysulfides has been demonstrated as an effective approach to deal with the conundrum of polysulfide shuttling. Metal sulfides are an interesting candidate found to exhibit stronger polysulfide confinement ability compared to carbon nanomaterials and possess better electronic conductivity than metal oxides. In the third chapter, a carbon nanotube-manganese sulfide (CMS) nanocomposite is designed for the first time as a separator modifier in lithium-sulfur batteries. The structural features of MnS provide specific sites for polysulfide capture and accelerate lithium-ion diffusion. Furthermore, the carbon nanotube network provides a continuous network for rapid electronic conduction, imparts structural stability, and acts as a secondary barrier for polysulfides. Consequently, the cell displays an initial discharge capacity of 876 mAh g^{-1} at 0.5C and sustains excellent stability with a retained capacity of 76% after 500 cycles. The self-discharge of the cell is also conspicuously reduced, maintaining a constant voltage for 100 hours under open-circuit conditions. (This work was published in *Energy & Fuels*, 2022)

The fourth chapter discusses a novel bayberry-like zinc sulfide-carbon nanotube composite harnessed as a polysulfide barrier in lithium-sulfur batteries for the first time. The material demonstrates effectual polysulfide entrapment property and catalyzes the sulfur reduction kinetics. Furthermore, the carbon nanotube imparts admirable electronic conductivity and assists physical polysulfide confinement. The better structural and functional features of the composite impart the system with a discharge capacity of 1105 mAh g^{-1} at 0.5C with superior cyclability for 500 cycles. A constant open circuit voltage is maintained for 100 hours, establishing the meager self-discharge behavior of the system. (This work was published in *New Journal of Chemistry*, 2023)

The mixed metal sulfides offer enhanced catalytic activity for the polysulfide conversion reaction compared to the single metal sulfides. In the fifth chapter, a nickel-cobalt sulfide-carbon nanotube composite was synthesized by a hydrothermal route and was employed as a separator coating to enhance the electrochemical output of LSBs. The superior ionic-electronic conductivity, strong polysulfide immobilization property, and better catalytic effect of the composite greatly enhanced the electrochemical results and accelerated the kinetics of the polysulfide conversion reaction. Consequently, the cell delivered an initial discharge capacity of 1152 mAh g^{-1} at 0.5 C rate and maintained a capacity retention of 82% after 500 cycles. (This work was published in *Energy Technology*, 2024)

Polymer binders play a crucial role in maintaining the structural stability and firmness of the electrode. However, conventional binders like PVDF, being electrochemically inactive, cannot provide any extra benefits other than acting as an inert binder. In the sixth chapter, a polyvinyl alcohol- poly 2- acrylamido 2-methyl 1-propane sulfonic acid blend was employed as a multi-functional aqueous binder for LSBs. The polymer binder revealed enhanced ionic conductivity and superior polysulfide confinement ability. As a result, the cell showed an initial discharge capacity of 1264 mAh g^{-1} at 0.1 C with 89% capacity retention after 100 cycles. Further, the cell also revealed a capacity of 815 mAh g^{-1} at 0.5 C rate with a retention capacity of 72% after 500 cycles.

The final chapter of the thesis includes the conclusion and future perspectives section, which combines the summary of the complete work done, a comparative study of the electrochemical results, and the future outlook of the study.