Abstract

Superior battery metrics along with cost effectiveness, environmental benignity, and natural abundance renders Lithium-sulfur batteries (LSB) as the most promising next generation energy storage systems. However, the practical application is restricted by degradation of battery performance due to several inherent challenges on the cathode side. The insulating nature of sulfur, volume alteration of active material and shuttling of intermediate species due to dissolution into electrolyte are the prime challenges. The combined effect of these issues results in a poor electrochemical performance and untimely failure of LSB. Therefore, to exploit the full potential of LSB, suitable design architecture of cathode with functional materials addressing these challenges is crucial. Based on the aforementioned, this thesis focuses on the sustainable development of functional fibrous materials and exploration of suitable architecture to integrate these materials into the cathode to achieve a high performance LSB.

In this thesis, fibrous materials have been prepared using facile, scalable, and economic techniques. The cathode architecture has been rationally modified by utilization of these fibrous materials. Carbon microfiber cloth has been implemented as a foundation for modification of the electrode design in each chapter e.g.in chapter 4, the cloth is used as current collector, in chapter 5, nanofibers are integrated into the carbon cloth as interlayer, in chapter 6, hollow nanofibers are used as additives with carbon cloth collector and in chapter 7, the carbon cloth is used as a substrate for unmediated functionalization. This thesis reports fabrication of novel functional fibrous materials with rational cathode architectures for LSB.

Initially, waste cotton cloth is used to prepare a carbon cloth where the 3-dimensional interwoven network is explored as a physical matrix for confinement of sulfur and polysulfides. The effect of carbonization temperature is systematically analysed where a higher carbonization temperature leads to better electrical properties. The enhanced electrical conductivity in synergy with physical confinement and conductive long range electron transport channels improves initial discharge capacity as well as the cycle life of LSB. Further, cell architecture is modified by incorporation of another layer of carbon cloth serving dual role of upper current collector and interlayer which further improves cell performance. In summary, the replacement of aluminium collector with the waste cotton cloth derived carbon cloth

collector leads to enhanced electrochemical performance. In the second part, perovskite lead zirconate titanate (PZT) nanofibers prepared using a facile electrospinning technique are demonstrated to restrict the shuttle effect. The perovskite nanofibers depict physical as well as chemical ability to bind the polysulfides meanwhile the carbon cloth offers physical confinement. Moreover, presence of lithophilic atoms with enhanced electrode wettability promotes ion diffusion. A pragmatic electrode design is devised where one side of the carbon cloth is coated with PZT nanofibers meanwhile the active material is coated upon the uncoated side. Benefitting from a rational electrode design with presence of perovskite nanofibers, higher sulfur utilization with promoted reaction kinetics and significant improvement in the cycle life of LSB can be achieved. In the subsequent work, the concept of simultaneous confinement-capture of polysulfides is shown to enhance the electrochemical performance of LSB. Hollow TiO_2 nanofibers loaded with catalytic Fe_2O_3 nanoparticles (TiO_2@Fe_2O_3) are proposed as additives in synergy with carbon cloth collector. The hollow TiO_2 nanofiber shell offers high specific surface area with abundant sites for trapping of polysulfides meanwhile the Fe_2O_3 nanoparticles can trap as well as propel the conversion of polysulfides. Theoretical studies further support the experimental results where it is revealed that the composite nanofibers possess binding energies varying from moderate to strong which are requisite for a balanced adsorption and conversion of polysulfides. The combined effect of physical confinement offered by carbon cloth and simultaneous capture-conversion by the nanofiber additives can significantly boost the reaction kinetics with improved cycle life of LSB. In the next chapter, a scalable sputter deposition technique is explored to coat cotton cloth with suitable metal followed by carbonization treatment which leads to formation of metal oxide decorated carbon cloth. The functionalized carbon cloth is utilized as a current collector in LSB and exhibits superior properties over a carbon cloth collector. The 3-dimensional interwoven network provides physical confinement with long range effective channels for electron transport meanwhile the metal oxide results in strong adsorption and efficient transformation of polysulfides. The experimental observations are corroborated using theoretical studies where is shown that the metal oxide nanolayer significantly lowers the energy barriers for precipitation of soluble polysulfides along with promotion of reaction kinetics. Further, the lithium metal anode is replaced with a copper current collector coated with controlled amount of lithium which eliminates wastage of precious lithium. A full cell geometry is assembled and promising electrochemical performance of LSB cell is demonstrated.

To summarize, this work reports successful fabrication of functional fibrous materials along with suitable electrode design to address challenges of LSB. The methods used are scalable, sustainable, and economic which renders them expedient to industrial development.