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High-energy sustainable Lithium Sulfur (Li/S) batteries for electrical vehicles and renewable energy applications

Development of innovative electrodes

This dissertation comprehensively speaks about the state of research in Li/S electrochemical system. Li-ion batteries are all over in gadgets, laptops and almost in every portable consumer electronics. But, future energy storage demand for electrical mobility and smart grids asking for much higher energy density, sustainable and cheaper solutions. Lithium-sulfur (Li/S) technology is one of the promising solutions to such demands as it can offer five times high energy density than that of state of art Li-ion technology. Li/S system can be potentially regarded as a sustainable and cheaper technology owing to abundancy and benignity of sulfur. However, the insulating nature of sulfur and Li_2S , free solubility of lithium polysulfide (LiPS) in the electrolyte, shuttling of LiPS across separator and use of metallic lithium as anode challenge the scientific community to offer some practical solutions for its commercialization (Figure 1). The effort can be done in various dimensions to realize stable and long-life Li/S batteries.

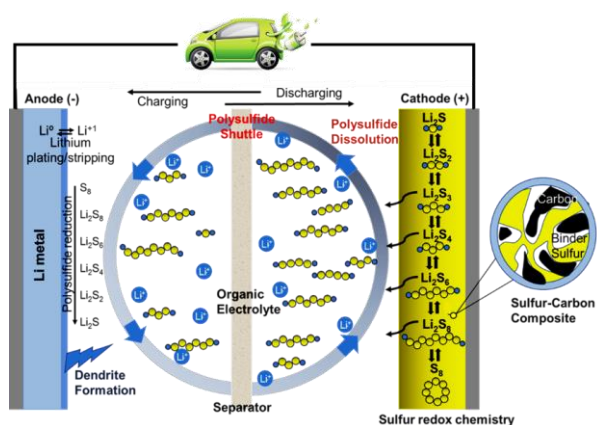


Figure 1: Schematic illustration of the working mechanism and limitations associated with Li/S system

In this dissertation, first, the focus is given to design cathode materials that can effectively host sulfur and its redox species. In addition to synthesizing effective host materials that can efficiently interact with LiPS, the emphasis is also maintained on practicability and industrial viability of the procedures. A broad spectrum of strategies has been presented to realize diverse sulfur host materials. Established processes, those already been practiced by industry, have been exploited to produce effective cathode and anode materials and electrodes. In the first three experimental chapters, diverse strategies have been exploited to reach stable sulfur cathodes. Later, the stable silicon anodes have also been realized to reach Li metal free full Li/S cell. Two practical approaches have been established to accomplish silicon anodes. In the last section, sulfur cathodes and silicon anodes have

been integrated in full cell configuration to accomplish lithium metal-free sulfur cells.

In the second chapter, two strategies have been put forth to produce microporous and hierarchical porous carbon matrices. The ultra-microporous carbon has been achieved by carbonization of β -cyclodextrin nanosponges that is acquired by polymerization of β -cyclodextrin with pyromellitic dianhydride. This preliminary work has laid the foundation to understand Li/S system. It has been observed that melt infusion of sulfur at $155\text{ }^\circ\text{C}$ is helpful in acquiring good carbon-sulfur composites. The cells with open spaces are not appropriate for Li/S system with liquid electrolyte. Performance of sulfur cathodes can be improved using interlayers but they add to dead mass especially for cathodes with low sulfur loading. The performance of as acquired cathodes has been demonstrated in Table 1. In the second strategy, elemental doped high surface area hierarchical porous carbons have been realized by KOH activation and carbonization of polypyrrole and polythiophene. Using these nitrogen or sulfur-doped hierarchical porous carbons; sulfur cathode has delivered highly stable capacities for more than 300 cycles. The high surface area, hierarchical pores, and elemental doping served together to reach such performances.

In the third chapter, three approaches have been proposed to prepare inorganic moieties decorated carbon structures. In one strategy, Magnéli phase TiO_x decorated carbon has been synthesized by simultaneous carbothermal reduction and carbonization from commercial TiO_2 powder. The porous carbon matrix serves to physically entrap sulfur and LiPS, while Magnéli Phases TiO_x nanoparticles assist to chemically bind LiPS on their surface. The novel architecture of host material offers better capacity retention (i.e.) 65% and 54% at 0.2C and 1C for more than 500 and 1000 cycles respectively. Moreover, the intensive characterization of the synthesized host material and aged cathodes provides an insight that sulfur species are adsorbed by the surface of TiO_x nanoparticles along with conventional physical entrapment by carbon. In another approach, electrochemically MnO_x deposited carbon structures have been exploited for high sulfur loading freestanding electrodes. It has been successfully demonstrated that achieving the right phase of MnO_x , which can interact with LiPS. It is possible to achieve high performing stable electrochemical performance even at high loading of sulfur 5 mg cm^{-2} . The role of carbon substrate is twofold; first, it is acting as a support to carry sulfur and MnO_x deposits, secondly, it acts as a matrix that physically traps LiPS. In the last approach, VN decorated nitrogen-doped carbon (VNNC) has been achieved by simultaneous in-situ ammonization and carbonization from commercial V_2O_5 powder. VNNC showed very strong interaction with LiPS. High rate capability is reported for sulfur cathodes assembled with this VNNC. Very stable performance has been recorded for hundreds of cycles at various C rates.

Both nitrogen-doped carbon and VN has imparted conductivity and ability to interact with LiPS. All three strategies exhibited promising stable cycling and rate capabilities performances with reduced capacity decay rate. In each case, as-synthesized materials have been physiochemically characterized for their distinct properties and ability to interact with LiPS.

In the fourth chapter, electroactive polymer covered carbon/sulfur composite has been suggested. In this section, a practical inadequacy of previous reports has been addressed where chloride-ion doped polyaniline had been proposed to limit LiPS solubility. We offered an alternative and trivial solution by accomplishing formate-ion doped polyaniline wrapped carbon/sulfur composite by in-situ oxidative polymerization. The as-prepared cathodes exhibited very stable performance around 800 mAh g⁻¹ for more than 500 cycles at 0.2C.

In chapter 5, two different approaches have been presented to realize stable silicon anodes. In the first strategy, electrospun silicon nanoparticles loaded carbon nanofibers have been produced via electrospinning and carbonization process. Simple HF washing of Si nanoparticle loaded CNF mats has induced void structures to accommodate the volume changes during lithiation and delithiation process. Citric acid crosslinked alginate network has been designated as a binder system. As prepared anodes showed stable electrochemical performances in an ether-based electrolyte (see Table 2). While in the second strategy, a simple approach is opted to reach well performing Si anodes. All in shelves chemicals

have been integrated into working Si anodes. Commercial nano-Si has been mixed with commercially available PEDOT:PSS electroactive polymer suspensions both as conductive and binding network with or without other conductive additives like CNT and rGO. With different types of electrolyte systems, as-prepared anodes exhibited some promising electrochemical performances.

In the last chapter, Si@void@CNF have been integrated with elemental doped hierarchical porous carbon/sulfur to reach lithium metal-free Li/S full cells. For the purpose, Si anode has been lithiated and balanced in areal density to the sulfur cathode. The assembled full cell has shown the promising capacity of 800 mAh g⁻¹ with 50% stabilized capacity retention for than 100 cycles at 0.15C. So, the rational design of porous carbon matrices has enabled to realize full Li/S cell.

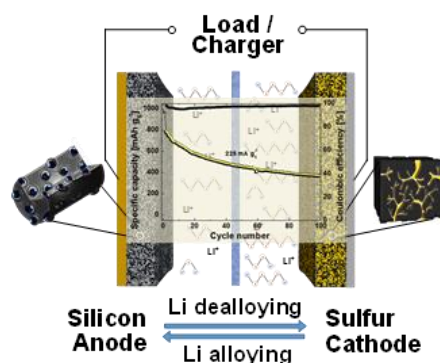


Figure 2: Realization of Li/S full cell using rationally designed carbon-based Si anodes and S cathode

Table 1: Performance matrix of manufactured S cathodes: their construction, sulfur content, loading, and electrochemical performance

	Cathode materials	Sulfur content (wt%) / sulfur loading	Electrolyte to sulfur ratio	Electrochemical performance [initial/final (mAh g⁻¹) (C-rate, cycles)]
Carbon	Microporous carbons form β-cyclodextrin nanosponges	60/2 mg cm ⁻²	15 μL/mg _s	1103/ 483 (0.2C, 100) GF 1108/ 723 (0.2C, 100) CFP
	Hierarchical porous nitrogen/sulfur doped carbons	66/1.5-2.2 mg cm ⁻²	10 μL/mg _s	1100/ 762 (0.2C, 250) N-doped C 800/ 631 (0.2C, 250) S-doped C
Inorganics	Magnèli phase Ti _n O _{2n-1} incorporated carbon matrix	60/ 2-2.3 mg cm ⁻²	6-7 μL/mg _s	1100/ 550 (0.2C, 500) 700/ 318 (1C, 1000)
	Vanadium nitride decorated nitrogen doped carbon	70/ 1.5 mg cm ⁻²	10 μL/mg _s	1013/ 630 (0.2C, 200) 814/ 530 (0.5C, 1200)
	Electrochemically MnO _x deposited carbon structures	50/ 5 mg cm ⁻²	8 μL/mg _s	800/ 770 (0.2C, 200) 750/ 660 (0.2C, 200)
Polymer	Formate-ion doped polyaniline wrapped carbon/sulfur	55/ 2 mg cm ⁻²	7-8 μL/mg _s	896/ 655 (0.2C, 500)

Table 2: Performance of manufactured Si anodes: construction, their loading, and electrochemical behavior

	Anode materials	Si content (wt%) / Si loading	Electrochemical performance [initial/final (mAh g⁻¹) (C-rate, cycles)]
Carbon	SiNP hosted in carbon nanofibers with void structures	18/ 0.5 mg cm ⁻²	3800/ 2200 (0.2C, 100) on Si wt% 3600/ 2000 (0.5C, 200) on Si wt%
Polymer	nSi/CNT/PEDOT:PSS composite anodes	50/ 0.2-0.8 mg cm ⁻²	2300/ 1500 (0.2C, 100) on Si wt%