

# **SUSTAINABLE FIBROUS ELECTRODE MATERIALS FOR HIGH PERFORMANCE LITHIUM SULFUR BATTERIES**

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**SCHOOL OF INTERDISCIPLINARY RESEARCH  
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**September 2024**

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MATERIALS FOR HIGH PERFORMANCE  
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by

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**SCHOOL OF INTERDISCIPLINARY RESEARCH**

Submitted

in fulfilment of the requirements of the degree of

**Doctor of Philosophy**

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**September 2024**

*Dedicated to my parents*

# Certificate

This is to certify that the thesis entitled “*Sustainable Fibrous Electrode Materials for High Performance Lithium Sulfur Batteries*” being submitted by **Aashish Joshi** to the Indian Institute of Technology Delhi, for the award of **Doctor of Philosophy** degree, is a record of bonafide research work carried out by him. **Mr. Aashish** has worked under my guidance and supervision. He has fulfilled the requirements for submission of this thesis, which to my knowledge has reached the requisite standard.

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# Acknowledgements

First and foremost, I would like to express my heartfelt gratitude to my supervisors, Prof. Bhanu Nandan and Prof. Amit Gupta. I feel extremely fortunate to receive the opportunity to pursue my Ph.D. under their supervision. I express my deep gratitude to them for their continuous support, motivation and guidance through out my Ph.D. journey. Their constant belief in me imparted immense confidence which inspired me to achieve the aimed objectives. Also, I sincerely appreciate their encouragement to me for procurement of several experimental facilities during my Ph.D. tenure. I extend my gratefulness to the positive, productive and disciplined atmosphere created by them in their research groups known as “Functional Polymers and Functional Materials Group (FPFM)” and “Thermofluids and Energy Systems Laboratory (TESLA Lab)”, respectively.

I am thankful to the School of Interdisciplinary Research (SIRE) for offering me the opportunity to pursue my Ph.D. at SIRE. The collaboration of different departments presented great freedom to explore aspects from different branches of science and deliver my best in conducting productive research. I would like to thank Mr. Rahul Sharma for his helpful nature and constant assistance. I would like to thank the Department of Textile and Fibre Engineering for allowing me to utilize the infrastructure and research facilities to conduct my research work. I would like to express my gratitude towards my SRC members, Prof. Manjeet Jassal, Prof. Bijay P. Tripathi and Prof. Pravin Ingole for their valuable suggestions and inputs to my Ph.D. work. I would also like to thank Prof. Rajiv K. Srivastava for allowing me to avail the experimental facilities under him.

I am sincerely thankful to Central Research Facility (CRF) and Nano Research Facility (NRF) for providing the characterization facilities utmost important for completion of this work. Especially, I would like to thank Mr. Kuldeep Sharma, Ms. Aastha Sharma, Mr. Mahesh Soni, Mr. Dinesh Kumar, Mr. Akshey Kaushal and Mr. Rajesh Kumar. I am also thankful to Malaviya National Institute of technology (MNIT) Jaipur for helping with the XPS measurements.

I am thankful to Mr. R. Khattar, Mr. Amarjeet, Mr. R.K. Chikara, Mr. V. Khatkar and other members of the Department of Textile and Fibre Engineering for their support during my PhD.

I express my gratitude towards all my lab mates with great pleasure who have contributed significantly to the completion of this research work. I would like to express my gratitude to my seniors, Mr. Avinash Raulo, Mr. Sajan Singh, Mr. Sanchayan Pal and Mr. Anil Kumar. I sincerely thank my colleagues-cum-friends Mr. Pramod M. Gurave, Ms. Sumana Bandopadhyay, Mr. Sachidananda Mohapatra, Mr. Sagnik Ghosh for their constant support, motivation, and warm affection. I cherish the support from my colleagues Mr. Advitya Kumar, Mr. Dheeraj Kumar, Ms. Sweety Rani, Ms. Meenal Agrawal, Ms. Vanshika Handuja, Mr. Arvind Kumar. I am highly obliged to my friends Mr. Tejveer Singh Anand, Ms. Akshita Sharma and Ms. Jyotsana Kala for their constant support and assistance in completion of this work. I would also like to thank Mr. Rohit and Mr. Raghvendra from TESLA lab for their warm affection and support.

I thank the funding agencies Department of Science and Technology (DST), National Technical Textiles Mission (NTTM) and Industrial Research and Development (IRD), IIT Delhi. I would like to thank IIT Delhi for providing financial assistance under the Research Scholar Travel Awards (RSTA) that helped to attend “ACS Spring 2023 at Indianapolis, United States of America (USA)”.

Specially, I would like to express my soulful gratitude to my parents, my family and my friends for their love, affection, warmth, support, and motivation throughout my Ph.D. journey. And, I thank God for blessing me with such beautiful people and the patience for completing my Ph.D.

**(Aashish Joshi)**

# 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  $\text{TiO}_2$  nanofibers loaded with catalytic  $\text{Fe}_2\text{O}_3$  nanoparticles ( $\text{TiO}_2@\text{Fe}_2\text{O}_3$ ) are proposed as additives in synergy with carbon cloth collector. The hollow  $\text{TiO}_2$  nanofiber shell offers high specific surface area with abundant sites for trapping of polysulfides meanwhile the  $\text{Fe}_2\text{O}_3$  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.

## सारांश

लागत प्रभावशीलता, पर्यावरणीय सौम्यता और प्राकृतिक बहुतायत के साथ सुपीरियर मेट्रिक्स लिथियम-सल्फर बैटरी (एलएसबी) को अगली पीढ़ी के सबसे आशाजनक ऊर्जा भंडारण प्रणालियों के रूप में प्रस्तुत करता है। हालांकि, कैथोड पक्ष पर कई अंतर्निहित चुनौतियों के कारण बैटरी के प्रदर्शन में गिरावट व्यावहारिक अनुप्रयोग को बाधित करती है। सल्फर की रोधक प्रकृति, सक्रिय सामग्री के आयतन में परिवर्तन और इलेक्ट्रोलाइट में मध्यवर्ती प्रजातियों का विघटन होना प्रमुख चुनौतियां हैं। इन मुद्दों के संयुक्त प्रभाव के परिणामस्वरूप खराब विद्युत रासायनिक प्रदर्शन और एलएसबी की असामयिक विफलता होती है। इसलिए, एलएसबी की पूरी क्षमता का दोहन करने के लिए, इन चुनौतियों का समाधान करने वाली कार्यात्मक सामग्रियों के साथ कैथोड की उपयुक्त डिजाइन वास्तुकला महत्वपूर्ण है। उपर्युक्त के आधार पर, यह थीसिस कार्यात्मक रेशेदार सामग्रियों के निर्माण और इन सामग्रियों को कैथोड में एकीकृत करके एलएसबी का प्रदर्शन उच्च करने की खोज पर केंद्रित है।

इस थीसिस में, सरल, स्केलेबल और किफायती तकनीकों का उपयोग करके कार्यात्मक रेशेदार सामग्री तैयार की गई है। इन कार्यात्मक रेशेदार सामग्रियों के उपयोग से कैथोड वास्तुकला को तर्कसंगत रूप से निर्मित किया गया है। कार्बन माइक्रोफाइबर कपड़े को प्रत्येक अध्याय में इलेक्ट्रोड डिजाइन के निर्माण के लिए एक नींव के रूप में लागू किया गया है। अध्याय 4 में कपड़े का उपयोग विद्युत धारा कलेक्टर के रूप में किया जाता है, अध्याय 5 में, नैनोफाइबर को कार्बन कपड़े में इंटरलेयर के रूप में एकीकृत किया गया है। अध्याय 6 में खोखले नैनोफाइबर कार्बन क्लॉथ कलेक्टर के साथ एडिटिव्स के रूप में उपयोग किए गए हैं और अध्याय 7 में, कार्बन कपड़े का उपयोग अनौपचारिक कार्यात्मकता के लिए एक सबस्ट्रेट के रूप में किया गया है। यह थीसिस एलएसबी के लिए उपन्यास कार्यात्मक रेशेदार सामग्री के साथ तर्कसंगत कैथोड आर्किटेक्चर के निर्माण की रिपोर्ट करता है।

सबसे पहले, अपशिष्ट कपास कपड़े का उपयोग कार्बन कपड़ा तैयार करने के लिए किया गया है जहां 3-आयामी इंटरवॉवन नेटवर्क को सल्फर और पॉलीसल्फाइड के कारावास के लिए भौतिक मैट्रिक्स के रूप का समन्वेषण किया गया है। कार्बन कपड़े पर कार्बोनाइजेशन तापमान के प्रभाव का व्यवस्थित रूप से विश्लेषण किया गया है जहां उच्च कार्बोनाइजेशन तापमान बेहतर विद्युत गुणों को उत्पन्न करता है। भौतिक कारावास और बढ़ी हुई विद्युत चालकता के तालमेल के साथ प्रवाहकीय लंबी दूरी के इलेक्ट्रॉन परिवहन चैनलों से प्रारंभिक निर्वहन क्षमता के साथ-साथ एलएसबी के चक्र जीवन में सुधार आता है। इसके अलावा, कार्बन क्लॉथ की एक और परत को शामिल करके सेल आर्किटेक्चर को संशोधित किया गया है जो ऊपरी विद्युत धारा कलेक्टर और इंटरलेयर की दोहरी भूमिका निभाता है जो सेल प्रदर्शन को और बेहतर बनाता है। सारांश में, एल्यूमीनियम कलेक्टर का अपशिष्ट सूती कपड़े व्युत्पन्न कार्बन कपड़ा कलेक्टर से प्रतिस्थापन पर एलएसबी की विद्युत रासायनिक प्रदर्शन में वृद्धि होती है। दूसरे अध्याय में, शटल प्रभाव को प्रतिबंधित करने के लिए आसान इलेक्ट्रोस्पिनिंग तकनीक द्वारा उत्पादित पेरोव्स्काइट लीड जिंकोनेट टाइटेनेट (PZT) नैनोफाइबर प्रदर्शित किए गए हैं। पेरोव्स्काइट नैनोफाइबर पॉलीसल्फाइड को बांधने की भौतिक और रासायनिक क्षमता को दर्शाते हैं, इस बीच कार्बन कपड़ा शारीरिक कारावास प्रदान करता है। इसके अलावा, लिथोफिलिक परमाणुओं की उपस्थिति और PZT नैनोफाइबर द्वारा इलैक्ट्रोड सतह को क्लेदनीय बनाना आयन प्रसार को बढ़ावा देता है। PZT नैनोफाइबर को इस्तेमाल करके एक तर्कसंगत इलेक्ट्रोड डिजाइन तैयार किया गया है जहां कार्बन कपड़े के एक तरफ PZT के साथ लेपित होता है और सक्रिय सामग्री गारा को अनकोटेड पक्ष पर लेपित किया जाता है। पेरोव्स्काइट नैनोफाइबर की उपस्थिति के साथ तर्कसंगत इलेक्ट्रोड डिजाइन से प्रचारित प्रतिक्रिया कैनेटीक्स, उच्च सल्फर उपयोग और एलएसबी के

चक्र जीवन में महत्वपूर्ण सुधार प्राप्त किया जा सकता है। तीसरे अध्याय में, एलएसबी के विद्युत रासायनिक प्रदर्शन को बढ़ाने के लिए पॉलीसल्फाइड का विघटन रोकने के साथ साथ पॉलीसल्फाइड रूपांतरण की अवधारणा को दिखाया गया है। उत्प्रेरक  $Fe_2O_3$  नैनोकणों ( $TiO_2@Fe_2O_3$ ) से भरे खोखले  $TiO_2$  नैनोफाइबर को कार्बन क्लॉथ कलेक्टर के साथ तालमेल में एडिटिव्स के रूप में प्रस्तावित किया गया है। खोखले  $TiO_2$  नैनोफाइबर शेल पॉलीसल्फाइड को फंसाने के लिए प्रचुर मात्रा में साइटों के साथ उच्च विशिष्ट सतह क्षेत्र प्रदान करता है, इस बीच  $Fe_2O_3$  नैनोकण पॉलीसल्फाइड को फंसाने के साथ-साथ उनके रूपांतरण को प्रेरित कर सकते हैं। सैद्धांतिक अध्ययन भी प्रयोगात्मक परिणामों का समर्थन करते हैं जहां यह पता चला है कि समग्र नैनोफाइबर में मध्यम से मजबूत तक बाध्यकारी ऊर्जा होती है जो संतुलित बंधन के साथ साथ पॉलीसल्फाइड के रूपांतरण के लिए आवश्यक होती है। कार्बन कपड़े द्वारा पेश किए गए भौतिक कारावास और नैनोफाइबर एडिटिव्स द्वारा एक साथ कैप्चर-रूपांतरण का संयुक्त प्रभाव प्रतिक्रिया कैनेटीक्स के साथ एलएसबी चक्र जीवन को काफी बेहतर कर सकता है। अगले अध्याय में, कपास कपड़े को उपयुक्त धातु के साथ कोट करने के लिए एक स्केलेबल स्पटर जमाव तकनीक का पता लगाया गया है। कार्बोनाइजेशन उपचार के बाद यह धातु कोट करा हुआ कपास कपड़ा धातु ऑक्साइड सजाए गए कार्बन कपड़े के गठन की ओर जाता है। कार्यात्मक कार्बन कपड़े का उपयोग एलएसबी में विद्युत धारा कलेक्टर के रूप में किया गया है जो की कार्बन क्लॉथ कलेक्टर से बेहतर गुण प्रदर्शित करता है। 3-आयामी इंटरवॉवन नेटवर्क इलेक्ट्रॉन परिवहन के लिए लंबी दूरी के प्रभावी चैनलों के साथ भौतिक कारावास प्रदान करता है, इस बीच धातु ऑक्साइड के परिणामस्वरूप मजबूत सोखना और पॉलीसल्फाइड का कुशल परिवर्तन होता है। प्रयोगात्मक टिप्पणियों को सैद्धांतिक अध्ययनों का उपयोग करके पुष्टि की जाती है जहां दिखाया गया है कि धातु ऑक्साइड नैनोलेयर प्रतिक्रिया कैनेटीक्स को बढ़ावा देने के साथ-साथ घुलनशील पॉलीसल्फाइड के निक्षेपण के लिए ऊर्जा बाधाओं को काफी कम करता है। इसके अलावा, लिथियम धातु एनोड को नियंत्रित लिथियम मात्रा के साथ लेपित तांबे के विद्युत धारा कलेक्टर के साथ बदल दिया गया है जो कीमती लिथियम की बर्बादी को समाप्त करता है। एक पूर्ण सेल ज्यामिति को इकट्ठा किया गया है और एलएसबी सेल के बेहतर विद्युत रासायनिक प्रदर्शन को दर्शाया गया है।

संक्षेप में, यह काम एलएसबी की चुनौतियों का समाधान करने के लिए कार्यात्मक रेशेदार सामग्री का सफल निर्माण और उनका उपयोग कर उपयुक्त इलेक्ट्रोड डिजाइन करने की रिपोर्ट करता है। उपयोग की जाने वाली विधियां स्केलेबल, टिकाऊ और आर्थिक हैं जो उन्हें औद्योगिक विकास के लिए समीचीन बनाती हैं।

# Table of Contents

	<b>Content</b>	<b>Page no.</b>
	Certificate	i
	Acknowledgements	ii
	Abstract	iv
	Table of Contents	ix
	List of Figures	xv
	List of Tables	xxiii
	List of Symbols	xxiv
	List of Abbreviations	xxvi
<b>Chapter 1</b>	<b>Introduction and Motivation</b>	1-9
1.1	Introduction	1
1.2	Mechanism of operation of LSB	2
1.3	Inherent challenges of LSB	4
1.3.1	Sulfur cathode	4
1.3.1.1	Insulating nature of sulfur and its reaction products	4
1.3.1.2	Volume alteration of active material	4
1.3.1.3	Dissolution of lithium polysulfides (LiPS)	4
1.3.2	Challenges of lithium anode	5
1.4	Research objectives	5

<b>Chapter 2</b>	<b>Background and Literature Review</b>	10-42
2.1	Introduction	10
2.2	Conventional sulfur cathode	10
2.3	Carbon host for sulfur cathode	13
2.4	Heteroatom-doped carbon host	16
2.5	Metal compounds for LSB	18
2.6	Design of interlayer	27
2.7	Current collector	29
2.8	Full cell	30
2.9	Advantages of fibrous materials	31
2.10	Conclusion	31
<b>Chapter 3</b>	<b>Experimental Techniques</b>	43-52
3.1	Introduction	43
3.2	Materials	43
3.3	Fabrication of carbon cloth	44
3.4	Fabrication of nanofibers	44
3.5	Preparation of metal oxide nanofibers	45
3.6	Cathode preparation and cell assembly	46
3.7	Material Characterization	47
3.7.1	X-ray diffraction (XRD)	47
3.7.2	Scanning electron microscopy (SEM)	47

3.7.3	Transmission electron microscopy (TEM)	48
3.7.4	X-ray photoelectron spectroscopy (XPS)	48
3.7.5	Raman spectroscopy	49
3.7.6	Energy dispersive X-ray spectroscopy (EDX)	49
3.7.7	Thermogravimetric analysis (TGA)	49
3.7.8	UV-Vis spectroscopy	50
3.8	Electrochemical Characterization	50
3.8.1	Cyclic Voltammetry	50
3.8.2	Electrochemical Impedance Spectroscopy (EIS)	51
3.8.3	Galvanostatic cycling: charge and discharge	51
<b>Chapter 4</b>	<b>Fabrication of carbon cloth current collector with optimized electrical properties</b>	<b>53-70</b>
4.1	Introduction	53
4.2	Experimental	54
4.2.1	Preparation of carbon cloth	54
4.2.2	Preparation of sulfur cathode	54
4.2.3	Material characterization	55
4.2.4	LSB coin cell assembly and electrochemical characterization	55
4.2.5	Symmetric cell experiment	56
4.3	Results and Discussion	56
4.4	Conclusions	67

<b>Chapter 5</b>	<b>Application of perovskite lead zirconate titanate nanofibers as interlayer in LSB</b>	71-93
5.1	Introduction	71
5.2	Experimental	72
5.2.1	Preparation of PZT precursor solution	72
5.2.2	Preparation of PZT nanofibers	73
5.2.3	Material Characterization	73
5.2.4	Polysulfide adsorption experiment	73
5.2.5	Preparation of PZT interlayer	74
5.2.6	Preparation of sulfur cathode and electrochemical characterization	74
5.2.7	Transference number and ionic conductivity measurements	74
5.3	Results and Discussion	75
5.4	Conclusions	88
<b>Chapter 6</b>	<b>Fabrication of hollow metal oxide@metal oxide nanofibers and application in cathode of LSB</b>	94-116
6.1	Introduction	94
6.2	Experimental	95
6.2.1	Preparation of polymeric template	95
6.2.2	Preparation of metal oxide decorated polymeric template	95
6.2.3	Optimization of precursor solution concentration for preparation of hollow TiO <sub>2</sub> and TiO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub> nanofibers	96
6.2.4	Material characterization	96

6.2.5	Polysulfide adsorption experiment	96
6.2.6	Li <sub>2</sub> S precipitation and symmetric cell experiment	97
6.2.7	Cathode preparation and electrochemical characterization	97
6.2.8	Density functional theory calculations	98
6.3	Results and Discussion	98
6.4	Conclusions	113
<b>Chapter 7</b>	<b>Fabrication of functionalized carbon cloth current collector using physical vapor deposition</b>	<b>117-144</b>
7.1	Introduction	117
7.2	Experimental	118
7.2.1	Preparation of metal oxide decorated carbon cloth	118
7.2.2	Material characterization	119
7.2.3	Polysulfide adsorption experiment	119
7.2.4	Li <sub>2</sub> S precipitation and symmetric cell experiment	119
7.2.4	Preparation of sulfur cathode and electrochemical characterization	120
7.2.5	Electrodeposition of lithium and full cell assembly	120
7.2.6	Theoretical calculations	121
7.3	Results and Discussion	123
7.4	Conclusions	140
<b>Chapter 8</b>	<b>Summary and Outlook</b>	<b>145-147</b>
8.1	Summary	145

8.2	Outlook	147
	<i>Curriculum-Vitae</i>	148-150

# List of Figures

	<b>Figure caption</b>	<b>Page no.</b>
Figure 1.1	Schematic depicting components along with charging and discharging process of LSB.	2
Figure 1.2	Charge-discharge curve of LSB.	3
Figure 2.1	Schematic depicting carbon particles percolating network in sulfur cathode.	10
Figure 2.2	Initial discharge capacity with different carbon additives.	11
Figure 2.3	Cycle stability test with different carbon additives.	12
Figure 2.4	Capacity relation with carbon additive over 10 cycles.	13
Figure 2.5	(a) Schematic and mapping images of ordered mesoporous host with infused sulfur, (b) Initial discharge capacity for CMK-3/S mixture (b) without melt diffusion, (c) with melt diffusion, (d) cycle stability test.	14
Figure 2.6	Schematic showing different carbon-based host materials for sulfur cathode.	15
Figure 2.7	(a) Nitrogen doped carbon structure, (b) DFT calculations showing bonding of sulfur on nitrogen doped carbon and pure carbon.	17
Figure 2.8	(a) Schematic depicting binding ability of polar surfaces towards LiPs. (b) SiO <sub>2</sub> nanoparticles as additives in sulfur cathode.	19
Figure 2.9	(a) S-TiO <sub>2</sub> yolk-shell host. (b) Different metal oxides spheres as host for sulfur cathode.	20

Figure 2.10	Redox potentials of different metal oxides.	21
Figure 2.11	Perovskite materials as shuttle inhibitors.	25
Figure 2.12	(a) Schematic depicting function of metal oxide heterostructure in sulfur cathode. (b) Metal oxide heterostructure additives in sulfur cathode.	26
Figure 2.13	Design of interlayers for sulfur battery (a) physical barrier. (b) Separator coating.	27
Figure 2.14	Comparison of 2D aluminum current collector with 3D carbon-based collectors.	29
Figure 3.1	Schematic depicting tube furnace used for carbonization process.	44
Figure 3.2	Electrospinning setup used for preparing nanofibers.	45
Figure 3.3	Schematic depicting cathode preparation and coin cell assembly with the instruments used.	46
Figure 4.1	(a) Schematic of preparation process, (b) optical images of cotton and carbon cloth. SEM images of (c, g) cotton cloth, (d, h) CC800, (e, i) CC1100, (f, j) CC1300. Diameter plot of (k) Cotton cloth, (l) CC800, (m) CC1100 & (n) CC1300.	56
Figure 4.2	(a) XRD plots, (b, c) curve fitted XRD plots for CC800 and C1300, (d) crystallite size comparison, (e) Raman spectra of CC800, C1100 & CC1300 and (f) comparison of FWHM values for D and G band.	58
Figure 4.3	High resolution TEM images of (a) CC800, (b) CC1100 and (c) CC1300.	59

Figure 4.4	(a) I-V plots of CC800, CC1100 & CC1300, (b) electrical resistance values measured from slope of I-V curves.	60
Figure 4.5	(a) Top view of slurry coated collector (b) Cross-sectional view.	60
Figure 4.6	(a) CV profiles, (b) EIS spectra, (c) magnified EIS plot, (d) symmetrical cell CV.	62
Figure 4.7	(a) Rate capability test. Initial discharge capacity at different C-rates for (b) Al collector, (c) CC800, (d) CC1100 & (e) CC1300. (f) Cycle stability test at 0.2 C Rate.	64
Figure 4.8	(a) Schematic of cell assembly with upper current collector, (b) cycle stability test at 0.5 C rate, (c) long-term cycling test at 1 C rate, (d) higher loading cycling test.	65
Figure 4.9	SEM images of (a, b) cathode & (c, d) upper collector surface facing separator side after 200 cycles.	66
Figure 4.10	(a-d) Open-circuit potential of the cell under normal and stressed conditions, (e-g) optical image of LED lights powered by the cell under normal, bent and twisted conditions.	67
Figure 5.1	(a) Schematic illustrating preparation of PZT nanofibers. SEM images of (b, c) as spun fiber and (d, e) PZT nanofiber.	75
Figure 5.2	(a) XRD pattern, (b) HR-TEM image, (c) Lattice fringe image, (d) SAED pattern of PZT nanofiber.	77

Figure 5.3	(a) UV-vis spectra of blank $\text{Li}_2\text{S}_6$ and PZT- $\text{Li}_2\text{S}_6$ , (b) optical images of $\text{Li}_2\text{S}_6$ solution, high resolution XPS spectrum of Oxygen, Titanium, Zirconium in PZT (c-e) and after interaction with polysulfide solution (f-h).	78
Figure 5.4	H-tube diffusion test (a, b) PP separator. (c, d) PZT coated separator.	79
Figure 5.5	(a) TGA curve of PZT-CB coated carbon cloth, (b) EIS plot of symmetrical cells for ionic conductivity measurement.	80
Figure 5.6	EIS and current vs time plot for (a and b) Li/PZT-PP/Li symmetric cell, (c and d) Li/PP/Li symmetric cell.	81
Figure 5.7	Cyclic voltammetry plots at different scan rate ( $0.1\text{-}0.5\text{ mV s}^{-1}$ ), (a) PZT interlayer cell, (b) control cell. (c-e) Peak current vs square root of scan rate plots for reduction and oxidation peaks.	82
Figure 5. 8	(a) Comparison of CV plot for PZT interlayer and control cell, CV plot for 5 cycles (b) PZT interlayer cell, (c) Control cell, (d) Charge-discharge curve comparison at 0.1 C-rate, (e) rate capability test, (f) cycle stability test at 0.5 C-rate.	83
Figure 5.9	SEM images of cathode side facing separator before and after cycling (a, b) control cell and (c, d) PZT interlayer cell. (e, f) High magnification images for PZT interlayer cell.	85
Figure 5.10	Charge-discharge curves at 1 C-rate for (a) PZT interlayer cell, (b) control cell. (c) Cycle stability test at 1 C-rate for 140 cycles. Comparison of capacity obtained in plateaus in different cycles: (d) Upper plateau. (e) Lower plateau. (f-h) Long term cycling test with different sulfur loadings at 0.2 C-rate.	87
Figure 5.11	(a) Voltage of pouch cell with stacked configuration. (b) Green LED lights powered by the assembled pouch cell.	88

Figure 6.1	Schematic depicting preparation of hollow $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers.	98
Figure 6.2	SEM images of (a, b) PAN nanofibers, (c, d) 2 % Fe-PAN nanofibers, (e, f) 5 % Fe-PAN nanofibers, (g, h) 9 % Fe-PAN nanofibers.	99
Figure 6.3	SEM images of calcinated nanofibers obtained using precursor solution concentration of (a, b) 0.25 M, (c, d) 0.5 M, (e, f) 1 M, (g, h) 4 M. (i-l) SEM images of $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers using 4 M precursor solution.	100
Figure 6.4	HR-TEM images of (a-c) hollow $\text{TiO}_2$ nanofibers, (f, g) hollow $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers. (d, e) STEM-mapping images of hollow $\text{TiO}_2$ nanofibers. (h) dark and bright field image of $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers. (i) STEM-mapping images of hollow hollow $\text{TiO}_2$ nanofibers@ $\text{Fe}_2\text{O}_3$ . BET adsorption isotherms for (j) hollow $\text{TiO}_2$ nanofibers, (k) hollow $\text{TiO}_2$ nanofibers. (l) Comparison of specific surface area.	101
Figure 6.5	High magnification HR-TEM images of (a, b) hollow $\text{TiO}_2$ nanofibers, (c, d) hollow $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers. (e, f, g, h) Lattice fringe images. (i) Defect region in between different crystalline regions.	102
Figure 6.6	(a) XRD plots. Raman spectra of (b) $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers, (c) $\text{TiO}_2$ nanofibers.	103
Figure 6.7	XPS survey spectra (a) $\text{TiO}_2$ nanofibers, (d) $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofibers. High resolution XPS spectra of (b, c) Ti, (f) Fe and (c, g) O.	104
Figure 6.8	(a) Visual adsorption experiment, (b) UV-Vis spectra.	105
Figure 6.9	XPS after adsorption experiment (a-c) $\text{TiO}_2$ nanofiber, (d-g) $\text{TiO}_2@\text{Fe}_2\text{O}_3$ nanofiber.	106

Figure 6.10	(a) Polysulfide geometry after adsorption on anatase-TiO <sub>2</sub> , rutile-TiO <sub>2</sub> and Fe <sub>2</sub> O <sub>3</sub> . (b) Binding energy comparison on different surfaces.	107
Figure 6.11	Cyclic voltametric plot at different scan rates (a) Control cell, (b) TiO <sub>2</sub> nanofiber additive cell, (c) TiO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub> nanofiber additive cell. (d-g) Peak current vs square root of scan rate plots. (h) Symmetric cell experiment.	108
Figure 6.12	(a) Symmetric cell cyclic voltametric plot. Li <sub>2</sub> S precipitation plots for (b) carbon cloth, (c) TiO <sub>2</sub> nanofiber coated carbon cloth, (d) TiO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub> nanofiber coated carbon cloth.	109
Figure 6.13	(a) Cyclic voltametric plot comparison, (b) rate capability test. Charge-discharge curve for (c) control cell, (d) TiO <sub>2</sub> nanofiber additive cell, (e) TiO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub> nanofiber additive cell. (f) Comparison of overpotentials at different C-rates.	110
Figure 6.14	(a) Comparison of long-term cycling performance at 0.5 C-rate. (b) Cycling performance of TiO <sub>2</sub> @Fe <sub>2</sub> O <sub>3</sub> nanofiber additive cell at 2 C-rate.	111
Figure 6.15	Cycling performance with sulfur loading and E/S ratio (a) 2.1 mg cm <sup>-2</sup> , 20 μl mg <sup>-1</sup> , (b) 2.8 mg cm <sup>-2</sup> , 15 μl mg <sup>-1</sup> .	112
Figure 7.1	(a) Schematic depicting the complete fabrication process of metal oxide decorated carbon cloth. (b) Digital photograph of cotton cloth before and after sputter deposition. (c-e) SEM and elemental mapping images of cotton cloth. FESEM (f, i) and EDX (g, h, j, k) mapping images of cotton cloth after molybdenum deposition.	123
Figure 7.2	SEM images of carbon cloth (a-d), EDX mapping images of carbon cloth (f, g). SEM (h, i) and FESEM (j, k) images of metal oxide decorated carbon cloth. EDX mapping images of metal oxide decorated carbon cloth (m-o).	124
Figure 7.3	Cross-sectional SEM image of MoO <sub>2</sub> -CC.	125

Figure 7.4	(a) XRD plot comparison, (b) complete Raman spectra of MoO <sub>2</sub> -CC, (c) comparison of D-band and G-band in Raman spectra, (d) Adsorption isotherms.	126
Figure 7.5	(a) XPS survey spectra, high resolution XPS spectra of (b) Molybdenum and (c) Oxygen for metal oxide decorated carbon cloth.	127
Figure 7.6	HR-TEM images of carbon cloth (a-c), metal oxide decorated carbon cloth (d-f). (g). SAED pattern of carbon cloth. (h and i), lattice fringe image and SAED pattern for metal oxide decorated carbon cloth.	128
Figure 7.7	(a) Digital images of polysulfide adsorption before and after 24 hours. (b) UV-vis spectra.	129
Figure 7.8	(a) XPS survey spectra of MoO <sub>2</sub> -CC after adsorption experiment. (b and c), high resolution XPS spectra of Mo and O after adsorption experiment.	130
Figure 7.9	(a) Optimized (110) surface slab of MoO <sub>2</sub> . (b) Density of states plot. (c) Binding energies of different polysulfides calculated from DFT. (d) Optimized geometries of polysulfides. (e) Polysulfides geometries after adsorption on MoO <sub>2</sub> substrate.	131
Figure 7.10	(a) Comparison of CV plot, (b) CV peak separation voltage comparison, (c) CV peak current comparison. CV plot for 3 cycles (d) MoO <sub>2</sub> - (e) CC, (f) Tafel plot, (g) symmetric cell CV.	133
Figure 7.11	(a) EIS plot comparison, (b) Z <sub>real</sub> vs $\omega^{-1/2}$ plot.	134
Figure 7.12	CV plot with scan rate varying from 0.2 mV s <sup>-1</sup> to 0.5 mV s <sup>-1</sup> for (a) CC, (b) MoO <sub>2</sub> -CC. (c-f) Peak current vs square root of scan rate.	135

Figure 7.13	Free energy diagram (a) MoO <sub>2</sub> surface slab, (b) carbon surface slab. Li <sub>2</sub> S precipitation experiment (c) CC, (d) MoO <sub>2</sub> -CC. Sem images after precipitation experiment (e) CC, (f) MoO <sub>2</sub> -CC.	137
Figure 7.14	(a) Charge-discharge curve at 0.2 C rate, (b) zoomed region of charge-discharge plot showing voltage overpotential for Li <sub>2</sub> S precipitation, (c) rate capability test, (d) long-term cycle stability test at 0.5 C-rate.	138
Figure 7.15	(a) Typical LSB using excess lithium anode. (b) LSB full cell with lithium electrodeposited copper anode. (c) Electrodeposition curve for lithium plating on copper foil, (d and e) digital images of copper foil before and after electrodeposition. (f) CV plot of S-Cu/Li full cell. (g and h) Gravimetric and areal capacity plots of S-Cu/Li full cell.	140

# List of Tables

	<b>Table caption</b>	<b>Page no.</b>
Table 7.1	Diffusion Co-efficient values	139

# List of Symbols

min	Minute
h	Hour
cm	Centimeter
cm <sup>-1</sup>	Centimeter inverse
nm	Nanometer
μm	Micrometer
m <sup>2</sup> g <sup>-1</sup>	Meter square per gram
°C	Degree centigrade
°C min <sup>-1</sup>	Degree centigrade per minute
°	Degree
g	Gram
g cm <sup>-1</sup>	Gram per centimeter
mg	Milligram
mg cm <sup>-2</sup>	Milligram per centimeter square
mL	Milliliter
mL g <sup>-1</sup>	Milliliter per gram
mL min <sup>-1</sup>	Milliliter per minute
mL h <sup>-1</sup>	Milliliter per hour
μL mg <sup>-1</sup>	Microliter per milligram
μL cm <sup>-2</sup>	Microliter per centimeter square
M	Molar
mM	Millimolar

ppm	Parts per million
$S\text{ cm}^{-1}$	Siemens per centimeter
eV	Electron volt
$\Omega$	Ohm
C	C-rate
V	Volt
mV	Millivolt
kV	Kilovolt
$mV\text{ s}^{-1}$	Millivolt per second
$mA\text{ h g}^{-1}$	Milli ampere hour per gram
%	Percentage
$D_{Li^+}$	Diffusion Co-efficient
$Li^+$	Lithium-ion
$\eta$	Overpotential
$i$	Current
$\omega$	Angular Frequency
$Z_R$	Real impedance
$Z_{IM}$	Imaginary Impedance
$\sigma$	Warburg Co-efficient

# List of Abbreviations

Li	Lithium
S	Sulfur
LSB	Lithium sulfur battery
LiPS	Lithium polysulfide
CoC	Cotton cloth
CC	Carbon cloth
CB	Carbon black
KB	Ketjen black
LiTFSI	Lithium bis(trifluoromethane)sulfonamide
LiNO <sub>3</sub>	Lithium nitrate
DOL	1,3-dioxolane
DME	1,2-dimethoxymethane
NMP	N-methyl-2-pyrrolidone
PVDF	Polyvinylidene fluoride
SEM	Scanning Electron Microscopy
FESEM	Field Emission Scanning Electron Microscope
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscope
SAED	Selected Area Electron Diffraction
EDX	Energy Dispersive X-ray Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

TGA	Thermogravimetric Analysis
UV-Vis	Ultraviolet-Visible
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
$R_e$	Ohmic resistance
$R_{ct}$	Charge-transfer resistance
$Z_w$	Warburg resistance
$e^-$	Electron
LED	Light Emitting Diode
TTIP	Titanium tetra-isopropoxide
PVP	Polyvinylpyrrolidone
Pb	Lead
Ti	Titanium
Zr	Zirconium
O	Oxygen
SS	Stainless Steel
PP	Polypropylene
PZT	Lead Zirconate Titanate
E/S	Electrolyte to sulfur ratio
$Q_H$	Capacity in upper plateau
$Q_L$	Capacity in lower plateau
m	mass
Gsm	Grams per square meter
PAN	Polyacrylonitrile
Fe	Iron

C	Carbon
IPA	Isopropanol
DFT	Density Functional Theory
VASP	Vienna Ab-Initio Simulation package
GGA	Generalized Gradient Approximation
B.E.	Binding Energy
HCL	Hydrochloric Acid
$Q_{\text{disch}}$	Discharge Capacity
N	Number of Atoms
n	Number of Electrons
a	Area
d	Thickness
$N_A$	Avogadro Number
$M_w$	Molecular Weight
Cu	Copper
Mo	Molybdenum
DOS	Density of States