FIBROUS CATHODE MATERIALS FOR ADVANCED LITHIUM SULFUR BATTERIES

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by

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Submitted in fulfilment of the requirements of the degree of **Doctor of Philosophy**

to the

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Dedicated to

My Parents, Brother, and Sister-in-law

CERTIFICATE

This is to certify that the thesis titled '***Fibrous Cathode Materials for Advanced Lithium Sulfur Batteries'*** being submitted by **Mr. Avinash Raulo** 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. Avinash** has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

Bhanu Nandan

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ABSTRACT

Lithium sulfur batteries (LSBs) are one of the most promising next-generation electrochemical energy-storage systems owing to their ultra-high energy density at low cost. However, there are several challenges that lead to the performance degradation of LSBs over repeated cycling. The challenges mainly arise from the insulating nature of sulfur, the dissolution of intermediate polysulfide into the electrolyte causing infamous "shuttle effect", and the volume variation of sulfur during repeated cycling. Therefore, the sulfur cathode, the most crucial component, and its architecture is the key parameter that directly affect the electrochemical performance of LSBs. Due to these challenges associated with the sulfur cathode, the practical application and commercialization of LSBs are seriously impeded. Based on these issues, this thesis mainly focuses on the development of various functional fibrous architectures, and their suitable employment as desired component in the cathode to develop a high-performance sulfur cathode for LSBs.

In this thesis, both nano and microfiber-based architectures are fabricated *via* simple and cost-effective methods. These fibrous materials are explored as functionalized components in the cathode with the adaption of bare sulfur as active material, e.g., the nanofibers as functional cathode additives in Chapter 4 and cathode matrix in Chapter 5, the microfibers as current collector and template for sulfur encapsulation in Chapter 6, and both nano and microfibers as additives and current collector, respectively in Chapter 7. Each chapter introduces novel cathode designs with the deployment of specifically designed fibrous material, followed by necessary modifications.

First, a simple method is presented to design a cathode with the incorporation of nanofibers as functional cathode additives. The nanofibers are featured with the in-situ grown sulfur particles embedded inside porous polyacrylonitrile shell and coated with poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT-S@PAN). They are able to trap the lithium polysulfides (LiPS) which results in their suppressed migration and ensure effective electronic conduction as well. Therefore, incorporation of such nanofibers in the sulfur cathode at minimal content can improve the electrochemical performance of LSBs. Second, a

sophisticated cathode design is proposed, in which a three-dimensional nanofiber matrix composed of α-Fe_2O_3 integrated carbon nanofiber (Fe-CNF) is demonstrated for the development of a collector-free and binder-free flexible self-standing sulfur cathode. With the aid of physical barrier effect by the interwoven nanofibrous architecture and the intense chemisorption by the combined effect of polar α-Fe_2O_3 and nitrogen-doped carbon present in Fe-CNF, it can restrict the LiPS dissolution into the electrolyte. Moreover, the α-Fe_2O_3 can accelerate the polysulfide conversion reactions. Benefiting from the nanofibrous cathode architecture, an improved sulfur utilization and thus high capacity, and better cycle performance can be achieved. Third, a sustainable and scalable route is demonstrated to develop a sulfur cathode by utilizing the carbon microfibers derived from waste cotton cloths. The replacement of a cotton derived carbon microfiber cloth as the current collector in the cathode instead of the conventional aluminum collector endow the LSB with much superior capacity. This is mainly due to the sufficient accessibility of electrolyte in the cathode owing to the interfiber pores and efficient electron transport by the long-length carbon microfibers. Furthermore, the encapsulation of sulfur inside the carbon fibers developed *via* the utilization of cotton microfiber cloth as the fiber templet and support substrate can not only restricts the LiPS shuttling but also improve the ionic and electronic accessibility to sulfur. As a result, the microfiber incorporated cathode can display superior cycle and rate performance as compared to the bare sulfur cathode. Inferring from the effect of each of the fibrous structures used in custom designed cathodes towards improving the performance of LSBs, finally a heterostructure constructed from $CoFe_2O_4$ and SnO_2 decorated over the carbon nanofiber framework (CoFe@SnCNF) is developed. A synergism between the multiple adsorptive and catalytic sites of the heterostructure enable an efficient LiPS entrapment and expedite their conversion, meanwhile the carbon nanofiber framework provides a long-range electrical conduction. Based on these merits, a cathode fabricated by using CoFe@SnCNF as a functional cathode additive and carbon microfiber cloth as the current collector with reasonably high sulfur loading and low electrolyte/sulfur (E/S) ratio showed a decent capacity and excellent cyclability.

In summary, the present thesis work has successfully developed high-capacity LSB by employing novel fibrous architectures fabricated through cost-effective and high-throughput techniques which have the ability to become industrially viable solutions.

सार

लिथियम सल्फर बैटरी (एलएसबी) सबसे आशाजनक अगली पीढ़ी के विद्युत रासायनिक ऊर्जा-भंडारण प्रणालियों में से एक हैं, जो कम लागत पर उनके अति-उच्च ऊर्जा घनत्व के कारण हैं। हालांकि, कई चुनौतियां हैं जो बार-बार चक्रण पर एलएसबी के प्रदर्शन में गिरावट का कारण बनती हैं। मुख्य रूप से सल्फर की रोधक प्रकृति, इलेक्ट्रोलाइट में मध्यवर्ती पॉलीसल्फाइड के विलयन हेतु कुख्यात "शटल प्रभाव", और बार-बार चक्रण के दौरान सल्फर की मात्रा में भिन्नता से चुनौतियां उत्पन्न होती हैं। इसलिए, सल्फर कैथोड सबसे महत्वपूर्ण घटक है, और इसकी वास्तुकला प्रमुख पैरामीटर है जो सीधे एलएसबी के विद्युत रासायनिक प्रदर्शन को प्रभावित करता है। सल्फर कैथोड से जुड़ी इन चुनौतियों के कारण, एलएसबी के व्यावहारिक अनुप्रयोग और व्यावसायीकरण गंभीर रूप से बाधित हैं। इन मुद्दों के आधार पर, यह थीसिस मुख्य रूप से विभिन्न कार्यात्मक रेशेदार वास्तुकला के विकास पर केंद्रित है, और एलएसबी के लिए उच्च प्रदर्शन सल्फर कैथोड विकसित करने के लिए कैथोड में वांछित घटक के रूप में उनके उपयुक्त सेवायोजन पर केंद्रित है।

इस थीसिस में, नैनो और माइक्रोतंतु-आधारित वास्तुकला दोनों को सरल और लागत प्रभावी तरीकों से निर्माण किया गया है। इन रेशेदार पदार्थों को सक्रिय सामग्री के रूप में अनावृत सल्फर के अनुकूलन के साथ कैथोड में कार्यात्मक घटकों के रूप में अन्वेषण किया है, उदाहरण के लिए, अध्याय 4 में नैनोतंतु को कार्यात्मक कैथोड एडिटिव्स के रूप में और अध्याय 5 में कैथोड मैट्रिक्स, अध्याय 6 में माइक्रोतंतु को सल्फर एनकैप्सुलेशन के लिए करंट कलेक्टर और टेम्पलेट के रूप में।, और नैनो और माइक्रोतंतु दोनों क्रमशः अध्याय 7 में एडिटिव्स और करंट कलेक्टर के रूप में। प्रत्येक अध्याय विशेष रूप से डिजाइन किए गए

रेशेदार सामग्री की तैनाती के साथ उपन्यास कैथोड डिजाइन पेश करता है, इसके बाद आवश्यक संशोधन करता है।

सबसे पहले, एक कैथोड को कार्यात्मक कैथोड एडिटिव्स के रूप में नैनोतंतु के समावेश के साथ रचना करने के लिए एक सरल विधि प्रस्तुत की जाती है। नैनोतंतु को यथास्थान उगाए गए सल्फर कणों के साथ विशेष रुप से प्रदर्शित किया जाता है जो छिद्रपूर्ण पॉलीएक्रिलोनिट्राइल शेल के अंदर अंतर्निहित होते हैं और पॉली (3,4-एथिलीन डाइऑक्सिथियोफीन):पॉलीस्टाइरीन सल्फोनेट (PEDOT-S@PAN) के साथ लेपित होते हैं । यह लिथियम पॉलीसल्फाइड (LiPS) को फंसाने में सक्षम हैं, जिसके परिणामस्वरूप उनका प्रवासन दबा हुआ है और यह प्रभावी इलेक्ट्रॉनिक चालन भी सुनिश्चित करता है। इसलिए, सल्फर कैथोड में न्यूनतम सामग्री पर ऐसे नैनोतंतु को शामिल करने से एलएसबी के विद्युत रासायनिक प्रदर्शन में सुधार हो सकता है। दूसरा, एक परिष्कृत कैथोड डिजाइन प्रस्तावित है, जिसमें α-Fe2O3 एकीकृत कार्बन नैनोतंतु (Fe-CNF) से बना एक त्रि-आयामी नैनोतंतु मैट्रिक्स एक कलेक्टर-मुक्त और बाइंडर-मुक्त लचीले स्व-स्थायी सल्फर कैथोड के विकास के लिए प्रदर्शित किया गया है। इंटरवॉवन नैनोतंतु वास्तुकला द्वारा भौतिक बाधा प्रभाव की सहायता से और Fe-CNF में मौजूद ध्रुवीय α-Fe_2O_3 और नाइट्रोजन-डॉप्ड कार्बन के संयुक्त प्रभाव से तीव्र रासायनिक अधिशोषण, यह इलेक्ट्रोलाइट में LiPS विघटन को प्रतिबंधित कर सकता है। इसके अलावा, α-Fe_2O_3 पॉलीसल्फाइड रूपांतरण प्रतिक्रियाओं को तेज कर सकता है। नैनोरेशेदार कैथोड वास्तुकला से लाभान्वित होकर, एक बेहतर सल्फर उपयोग और इस प्रकार उच्च क्षमता, और बेहतर चक्र प्रदर्शन प्राप्त किया जा सकता है। तीसरा, अपशिष्ट कपास कपड़े से प्राप्त कार्बन माइक्रोतंतु का उपयोग करके सल्फर कैथोड विकसित करने के लिए एक स्थायी और मापनीय मार्ग का प्रदर्शन किया जाता है। पारंपरिक एल्यूमीनियम कलेक्टर के बजाय कैथोड

में करंट कलेक्टर के रूप में एक कपास व्युत्पन्न कार्बन माइक्रोतंतु कपड़े का प्रतिस्थापन एलएसबी को बहुत बेहतर क्षमता प्रदान करता है। यह मुख्य रूप से कैथोड में इलेक्ट्रोलाइट्स की पर्याप्त पहुंच के कारण इंटरतंतु छिद्रों और लंबी लंबाई वाले कार्बन माइक्रोतंतु द्वारा कुशल इलेक्ट्रॉन परिवहन के कारण होता है। इसके अलावा, तंतु टेम्पल और सहयोग सब्सट्रेट के रूप में कपास माइक्रोतंतु कपड़े के उपयोग के माध्यम से विकसित कार्बन तंतु के अंदर सल्फर का एनकैप्सुलेशन न केवल LiPS शटलिंग को प्रतिबंधित कर सकता है, बल्कि सल्फर के लिए आयनिक और इलेक्ट्रॉनिक पहुंच में भी सुधार कर सकता है। परिणामस्वरूप, माइक्रोतंतु निगमित कैथोड अनावृत सल्फर कैथोड की तुलना में बेहतर चक्र और दर प्रदर्शन प्रदर्शित कर सकता है। एलएसबी के प्रदर्शन में सुधार के लिए कस्टम-डिज़ाइन किए गए कैथोड में उपयोग किए जाने वाले प्रत्येक रेशेदार संरचनाओं के प्रभाव का उल्लेख करते हुए, अंत में, कार्बन नैनोतंतु फ्रेमवर्क (CoFe@SnCNF) पर सजाए गए $CoFe_2O_4$ और SnO_2 से निर्मित एक हेटरोस्ट्रक्चर विकसित किया गया है। हेटरोस्ट्रक्चर के एकाधिक सोखने वाले और उत्प्रेरक साइटों के बीच तालमेल एक कुशल LiPS को फंसाने में सक्षम बनाता है और उनके रूपांतरण में तेजी लाता है, इस बीच कार्बन नैनोतंतु ढांचा एक दीर्घकालिक विद्युत चालन प्रदान करता है। इन गुणों के आधार पर, CoFe@SnCNF को एक कार्यात्मक कैथोड योज्य के रूप में और कार्बन माइक्रोतंतु क्लॉथ का उपयोग करके करंट कलेक्टर के रूप में यथोचित उच्च सल्फर लोडिंग और कम इलेक्ट्रोलाइट/सल्फर अनुपात के साथ निर्मित एक कैथोड ने एक उचित क्षमता और उत्कृष्ट चक्रीयता दिखाई।

संक्षेप में, वर्तमान थीसिस कार्य ने लागत प्रभावी और उच्च-साद्यांत तकनीकों के माध्यम से निर्मित कुलीन रेशेदार वास्तुकला को नियोजित करके उच्च क्षमता वाले एलएसबी

को सफलतापूर्वक विकसित किया है जो औद्योगिक रूप से व्यवहार्य समाधान बनने की क्षमता रखते हैं।

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List of Symbols

min	Minute
h	Hour
cm	Centimeter
cm^{-1}	Centimeter inverse
nm	Nanometer
mm	Millimeter
µm	Micrometer
$m^2\ g^{-1}$	Meter square per gram
°C	Degree centigrade
$°C\ min^{-1}$	Degree centigrade per minute
°	Degree
g	Gram
$g\ cm^{-1}$	Gram per centimeter
mg	Milligram
$mg\ cm^{-2}$	Milligram per centimeter square
mL	Milliliter
$mL\ g^{-1}$	Milliliter per gram
$mL\ m^{-1}$	Milliliter per minute
$mL\ h^{-1}$	Milliliter per hour
$\mu L\ mg^{-1}$	Microliter per milligram
$\mu L\ cm^{-2}$	Microliter per centimeter square
M	Molar

mM	Millimolar
ppm	Parts per million
$\mathrm{S\ cm^{-1}}$	Siemens per centimeter
eV	Electron volt
Ω	Ohm
C	C-rate
V	Volt
mV	Millivolt
kV	Kilovolt
$\mathrm{mV\ s^{-1}}$	Millivolt per second
$\mathrm{mA\ h\ g^{-1}}$	Milli ampere hour per gram
%	Percentage
≤	Less than or equal to
>	More than
±	Plus-minus

List of Abbreviations

Li	Lithium
S	Sulfur
LSB	Lithium sulfur battery
LiPS	Lithium polysulfide
SEI	Solid electrolyte interphase
CNF	Carbon nanofibers
CF	Carbon fiber
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate
PAN	Polyacrylonitrile
PS	Polystyrene
PMMA	Poly (methyl methacrylate)
PVDF	Polyvinylidene fluoride
DMF	N, N-dimethylformamide
DOL	1,3-dioxolane
DME	1,2-dimethoxymethane
NMP	N-methyl-2-pyrrolidone
CS_2	Carbon disulfide
LiTFSI	Lithium bis(trifluoromethane)sulfonamide
$LiNO_3$	Lithium nitrate
KOH	Potassium hydroxide
TMO	Ternary metal oxides
SEM	Scanning Electron Microscopy

FESEM	Field Emission Scanning Electron Microscope
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscope
EDX	Energy Dispersive X-ray Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
UV-Vis	Ultraviolet-Visible
FTIR	Fourier Transform Infrared
IR	Infrared
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
$Na_2S_2O_3.5H_2O$	Sodium thiosulfate pentahydrate
Na_2SO_4	Sodium sulphate
α-Fe_2O_3	Alpha Iron Oxide
$FeSO_4.7H_2O$	Ferrous sulfate (heptahydrate)
$FeCl_3$	Iron (III) chloride
$Sn(Oct)_2$	Tin(II) 2-ethyl hexanoate
$CoCl_2.6H_2O$	Cobalt(II) chloride hexahydrate
DI water	Deionized water
wt.%	Weight percentage
w/w	Weight by weight
v/v	Volume by volume

R_e	Ohmic resistance
R_{ct}	Charge-transfer resistance
Z_w	Warburg resistance
e^-	Electron
α	Alpha
λ	Lamba (wavelength)
η	Eta (Overpotential)
Φ	Diameter
C	Carbon
N	Nitrogen
O	Oxygen
Fe	Iron
Cu	Copper
Sn	Tin
Co	Cobalt