STRATEGIES TO STABILIZE THE SODIUM METAL ANODE FOR HIGHLY REVERSIBLE AND STABLE ROOM-TEMPERATURE SODIUM-SULFUR BATTERIES

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by

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Submitted

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Dedicated to my beloved parents

CERTIFICATE

I am satisfied that the thesis entitled **"Strategies to stabilize the sodium metal anode for highly reversible and stable room-temperature sodium-sulfur batteries"** submitted by **Chhail Bihari Soni** is an ethical work and worthy of consideration for the award of the degree of Doctor of Philosophy, and is a record of the original and bonafide research work carried out by him under my supervision. The thesis results have not been submitted in part or full to any other University or Institute for awarding any degree/diploma.

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cbsoni

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ABSTRACT

This thesis focuses on advancing the performance, stability, and safety of room-temperature sodium-sulfur (RT Na-S) batteries, addressing critical challenges related to the sodium metal anode, particularly dendrite formation, volume expansion during cycling, and the instability of the solid electrolyte interphase (SEI). The research employs a multi-faceted approach involving innovative material design, electrolyte optimization, and advanced characterization techniques to achieve significant improvements in battery performance.

The first objective aims to mitigate dendrite formation and manage volume changes in sodium metal anodes by developing a robust 3D host structure. A micro-architecture carbon nanotube (MACNT) framework design and integrate into the sodium metal anode to serve as a scaffold for sodium plating and stripping. This MACNT@SS anode demonstrates a substantial enhancement in cycling stability, achieving a Coulombic efficiency of over 98% across 300 cycles at a current density of 1 mA cm^{-2}. The 3D structure effectively accommodates the large volume changes associated with sodium metal, preventing the formation of harmful dendrites, which are a major cause of short circuits and capacity degradation in sodium metal batteries.

The second objective focuses on further stabilizing the sodium metal anode by enhancing the uniformity of sodium deposition. To achieve this, a patterned polypropylene interlayer (PPIL) introduces between the sodium metal anode and the separator. The PPIL features alternating dense and sparse fiber regions that effectively regulate sodium ion flux during cycling. This innovative interlayer design results in a significant improvement in the uniformity of sodium deposition, suppressing dendrite growth and thereby enhancing the battery's cycling stability. Symmetric cells with the PPIL demonstrate stable operation for over 1000 hours at a high current density of 5 mA cm^{-2}, with no evidence of short-circuiting, indicating the interlayer's effectiveness in preventing dendrite penetration and ensuring consistent anode performance.

The third objective targets to improve the SEI's mechanical integrity and ionic conductivity, which are critical for the long-term stability of sodium metal anodes. To address this, a novel organic molecule, 9F, employs as an electrolyte additive. The 9F additive facilitates the formation of a stable and robust SEI, composed of a mixture of organic and inorganic species, that effectively protects the sodium metal surface. Electrochemical tests reveal that cells with the 9F-modified electrolyte exhibit a Coulombic efficiency of approximately 99% and

maintained stable cycling performance for over 400 cycles at a current density of 1 mA cm^{-2}. The enhanced SEI suppresses dendrite formation and reduces the interfacial resistance, contributing to improve battery efficiency and longevity.

The fourth objective aims at controlling dendrite growth by altering the sodium-ion solvation environment within the electrolyte. This achieves by introducing a BiI_3 additive, which modifies the solvation structure of sodium ions, thereby reducing the occurrence of side reactions and promoting a more uniform sodium deposition. The introduction of BiI_3 into the electrolyte significantly improved the homogeneity of the SEI and reduces the likelihood of dendrite formation. Cells utilizing the BiI_3 additive demonstrates a Coulombic efficiency of 98.5% and stable cycling for over 500 hours at a current density of 3 mA cm^{-2}. This result highlights the effectiveness of solvation environment manipulation in enhancing the electrochemical stability of sodium metal anodes.

The final objective focuses on developing a multiphasic SEI that could provide both high mechanical stiffness and a low ionic diffusion barrier, ensuring long-term stability for RT Na-S batteries. Methylammonium iodide (CH_3NH_3I) introduces as a novel electrolyte additive, resulting in the formation of an SEI composed of NaF, NaI, and $NaNH_2$. The multiphasic nature of this SEI allows for a unique combination of properties: NaF provides high mechanical stiffness (~75 GPa), NaI contributes to enhance ionic conductivity, and $NaNH_2$ offeres the necessary ductility to accommodate volume changes. The SEI exhibits a remarkably low sodium ion diffusion barrier of 9.37 kJ mol^{-1}, facilitating efficient and reversible sodium plating and stripping. Symmetric cells equipped with this SEI maintain stability for over 3200 hours at a current density of 1 mA cm^{-2}. Additionally, in full-cell Na-S batteries, this SEI enables consistent operation over 500 cycles, with an initial discharge capacity of approximately 700 mA h g^{-1}, demonstrating its effectiveness in improving both capacity retention and cycling stability.

Throughout the thesis, advanced characterization techniques such as Field Emission Scanning Electron Microscopy (FESEM), X-ray Photoelectron Spectroscopy (XPS), Raman spectroscopy, and X-ray Diffraction (XRD) extensively utilizes to analyze the morphological, compositional, and structural changes in the SEI and electrode materials. These techniques provided critical insights into the mechanisms underpinning the improved performance, including the uniformity of sodium deposition, the chemical stability of the SEI, and the interaction between the electrolyte and electrode materials.

In conclusion, this thesis successfully meets its objectives by addressing the key challenges in RT Na-S battery technology. The development of innovative 3D host structures, patterned interlayers, electrolyte additives, and multiphasic SEI layers has led to significant advancements in cycling stability, Coulombic efficiency, and the safety of sodium-based batteries. These findings contribute valuable knowledge to the field of energy storage and offer promising pathways for the development of more efficient, reliable, and commercially viable RT Na-S batteries.

सार

यह थीसिस कमरे के तापमान पर सोडियम-सल्फर (RT Na-S) बैटरियों के प्रदर्शन, स्थिरता और सुरक्षा को आगे बढ़ाने पर केंद्रित है, जो सोडियम मेटल एनोड से संबंधित महत्वपूर्ण चुनौतियों, विशेष रूप से डेन्ड्राइट गठन, साइक्लिंग के दौरान वॉल्यूम विस्तार और ठोस इलेक्ट्रोलाइट इंटरफेस (SEI) की अस्थिरता को संबोधित करती है। अनुसंधान एक बहुआयामी दृष्टिकोण का उपयोग करता है जिसमें बैटरी के प्रदर्शन में महत्वपूर्ण सुधार प्राप्त करने के लिए अभिनव सामग्री डिजाइन, इलेक्ट्रोलाइट अनुकूलन और उन्नत लक्षण वर्णन तकनीक शामिल हैं।

पहला उद्देश्य एक मजबूत 3D होस्ट संरचना विकसित करके सोडियम मेटल एनोड में डेन्ड्राइट गठन को कम करना और वॉल्यूम परिवर्तनों का प्रबंधन करना है। एक माइक्रो-आर्किटेक्चर कार्बन नैनोट्यूब (MACNT) फ्रेमवर्क डिजाइन और सोडियम प्लेटिंग और स्ट्रिपिंग के लिए मचान के रूप में काम करने के लिए सोडियम मेटल एनोड में एकीकृत करता है। 3D संरचना सोडियम धातु से जुड़े बड़े आयतन परिवर्तनों को प्रभावी ढंग से समायोजित करती है, जिससे हानिकारक डेंड्राइट्स के निर्माण को रोका जा सकता है, जो सोडियम धातु बैटरी में शॉर्ट सर्किट और क्षमता में गिरावट का एक प्रमुख कारण है।

दूसरा उद्देश्य सोडियम जमाव की एकरूपता को बढ़ाकर सोडियम धातु एनोड को और अधिक स्थिर करने पर केंद्रित है। इसे प्राप्त करने के लिए, सोडियम धातु एनोड और विभाजक के बीच एक पैटर्नयुक्त पॉलीप्रोपाइलीन इंटरलेयर (PPIL) पेश किया है। PPIL में बारी-बारी से घने और विरल फाइबर क्षेत्र होते हैं जो साइक्लिंग के दौरान सोडियम आयन प्रवाह को प्रभावी ढंग से नियंत्रित करते हैं। इस अभिनव इंटरलेयर डिज़ाइन के परिणामस्वरूप सोडियम जमाव की एकरूपता में महत्वपूर्ण सुधार होता है, डेंड्राइट वृद्धि को दबाता है और इस तरह बैटरी की साइक्लिंग स्थिरता को बढ़ाता है। PPIL के साथ सममित सेल 5 mA cm^{-2} के उच्च धारा घनत्व पर 1000 घंटे से अधिक समय तक स्थिर संचालन प्रदर्शित करते हैं, जिसमें शॉर्ट-सर्किटिंग का कोई सबूत नहीं होता है, जो डेंड्राइट प्रवेश को रोकने और लगातार एनोड प्रदर्शन सुनिश्चित करने में इंटरलेयर की प्रभावशीलता को दर्शाता है।

तीसरा उद्देश्य SEI की यांत्रिक अखंडता और आयनिक चालकता में सुधार करना है, जो सोडियम धातु एनोड की दीर्घकालिक स्थिरता के लिए महत्वपूर्ण हैं। इसे संबोधित करने के लिए, एक नया कार्बनिक अणु, 9F, इलेक्ट्रोलाइट योजक के रूप में काम करता है। 9F योजक कार्बनिक और अकार्बनिक प्रजातियों के मिश्रण से बना एक स्थिर और मजबूत SEI के गठन की सुविधा देता है, जो सोडियम धातु की

सतह को प्रभावी ढंग से सुरक्षित रखता है। इलेक्ट्रोकेमिकल परीक्षणों से पता चलता है कि 9F-संशोधित इलेक्ट्रोलाइट वाले सेल लगभग 99% की कूलम्बिक दक्षता प्रदर्शित करते हैं और 1 mA cm^{-2} के वर्तमान घनत्व पर 400 से अधिक चक्रों के लिए स्थिर साइक्लिंग प्रदर्शन बनाए रखते हैं। बढ़ा हुआ SEI डेंड्राइट गठन को दबाता है और इंटरफेसियल प्रतिरोध को कम करता है, जिससे बैटरी की दक्षता और दीर्घायु में सुधार होता है।

चौथा उद्देश्य इलेक्ट्रोलाइट के भीतर सोडियम-आयन सॉल्वेशन वातावरण को बदलकर डेंड्राइट वृद्धि को नियंत्रित करना है। यह एक BiI_3 योजक को पेश करके प्राप्त किया जाता है, जो सोडियम आयनों की सॉल्वेशन संरचना को संशोधित करता है, जिससे साइड रिएक्शन की घटना कम हो जाती है और अधिक समान सोडियम जमाव को बढ़ावा मिलता है। इलेक्ट्रोलाइट में BiI_3 की शुरूआत ने SEI की समरूपता में उल्लेखनीय सुधार किया और डेन्ड्राइट गठन की संभावना को कम किया। BiI_3 एडिटिव का उपयोग करने वाली कोशिकाओं ने 3 mA cm^{-2} की वर्तमान घनत्व पर 98.5% की कूलम्बिक दक्षता और 500 घंटे से अधिक समय तक स्थिर साइकलिंग का प्रदर्शन किया। यह परिणाम सोडियम धातु एनोड की विद्युत रासायनिक स्थिरता को बढ़ाने में विलयन पर्यावरण हेरफेर की प्रभावशीलता को उजागर करता है।

अंतिम उद्देश्य एक बहु-चरणीय SEI विकसित करने पर केंद्रित है जो उच्च यांत्रिक कठोरता और कम आयनिक प्रसार अवरोध दोनों प्रदान कर सकता है, जिससे RT Na-S बैटरियों के लिए दीर्घकालिक स्थिरता सुनिश्चित होती है। मिथाइलमोनियम आयोडाइड (CH_3NH_3I) एक नए इलेक्ट्रोलाइट एडिटिव के रूप में पेश किया गया है, जिसके परिणामस्वरूप NaF, NaI और $NaNH_2$ से बना SEI बनता है। इस SEI की बहु-चरणीय प्रकृति गुणों के एक अद्वितीय संयोजन की अनुमति देती है: NaF उच्च यांत्रिक कठोरता (~ 75 GPa) प्रदान करता है, NaI आयनिक चालकता को बढ़ाने में योगदान देता है, और $NaNH_2$ आयतन परिवर्तनों को समायोजित करने के लिए आवश्यक लचीलापन प्रदान करता है। SEI 9.37 kJ mol^{-1} का उल्लेखनीय रूप से कम सोडियम आयन प्रसार अवरोध प्रदर्शित करता है, जो कुशल और प्रतिवर्ती सोडियम प्लेटिंग और स्ट्रिपिंग की सुविधा प्रदान करता है। इस SEI से सुसज्जित सममित सेल 1 mA cm^{-2} के वर्तमान घनत्व पर 3200 घंटे से अधिक समय तक स्थिरता बनाए रखते हैं। इसके अतिरिक्त, पूर्ण-सेल Na-S बैटरियों में, यह SEI लगभग 700 mA h g^{-1} की प्रारंभिक डिस्चार्ज क्षमता के साथ 500 चक्रों से अधिक तक लगातार संचालन को सक्षम बनाता है, जो क्षमता प्रतिधारण और साइकलिंग स्थिरता दोनों को बेहतर बनाने में इसकी प्रभावशीलता को प्रदर्शित करता है।

पूरे शोध प्रबंध में, फील्ड एमिशन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (FESEM), एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS), रमन स्पेक्ट्रोस्कोपी, और एक्स-रे विवर्तन (XRD) जैसी उन्नत लक्षण वर्णन तकनीकों का व्यापक रूप से उपयोग किया गया है। एसईआई और इलेक्ट्रोड सामग्रियों में रूपात्मक, संरचनागत और संरचनात्मक परिवर्तनों का विश्लेषण किया गया है। इन तकनीकों ने बेहतर प्रदर्शन को रेखांकित करने वाले तंत्रों में महत्वपूर्ण अंतर्दृष्टि प्रदान की, जिसमें सोडियम जमाव की एकरूपता, एसईआई की रासायनिक स्थिरता और इलेक्ट्रोलाइट और इलेक्ट्रोड सामग्रियों के बीच परस्पर क्रिया शामिल है।

निष्कर्ष में, यह थीसिस RT Na-S बैटरी तकनीक में प्रमुख चुनौतियों को संबोधित करके अपने उद्देश्यों को सफलतापूर्वक पूरा करती है। अभिनव 3D होस्ट संरचनाओं, पैटर्न वाली इंटरलेयर्स, इलेक्ट्रोलाइट एडिटिव्स और मल्टीफ़ेज़िक SEI परतों के विकास ने साइक्लिंग स्थिरता, कोलोम्बिक दक्षता और सोडियम-आधारित बैटरी की सुरक्षा में महत्वपूर्ण प्रगति की है। ये निष्कर्ष ऊर्जा भंडारण के क्षेत्र में मूल्यवान ज्ञान का योगदान करते हैं और अधिक कुशल, विश्वसनीय और व्यावसायिक रूप से व्यवहार्य RT Na-S बैटरी के विकास के लिए आशाजनक मार्ग प्रदान करते हैं।

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List of Acronyms

Acronyms	**Full name**
AFM	Atomic force microscopy
AIMD	Ab initio molecular dynamics
AIP	Aggregate ion pairs
ALD	Atomic layer deposition
BCC	Body-centered cubic
BI	Bismuth iodide
CE	Coulombic efficiency
CEI	Cathode electrolyte interphase
CIP	Contact ion pair
CNT	Carbon nanotubes
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DEC	Diethyl carbonate
DFT	Density functional theory
DME	Dimethyl ether
DMSO	Dimethyl sulfoxide
E/S	Electrolyte to sulfur ratio
EC	Ethylene carbonate
EDS	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EV	Electric vehicle
FEC	Fluoroethylene carbonate
FESEM	Field emission scanning electron microscopy
GAA	Generalized gradient approximation
HCE	High concentration electrolyte
HOMO	Highest occupied molecular orbital
HT Na-S	High-temperature sodium-sulfur battery

IPA	Iso-propylene alcohol
IRC	Intrinsic reaction coordinate
K	Potassium
LHCE	Localized high-concentration electrolyte
LIB	Lithium-ion battery
LUMO	The lowest unoccupied molecular orbital
MACNT	Microarchitecture of carbon nanotubes
Mg	Magnesium
MI	Methylammonium iodide
Na2O	Sodium oxide
NaF	Sodium fluoride
NaFSI	Sodium Bis(fluorosulfonyl)imide
NaOTf	Sodium triflate
$NaPF_6$	Sodium hexafluorophosphate
NMR	Nuclear magnetic resonance spectroscopy
PAW	Projector-augmented wave
PCM	Polarizable continuum model
PE	Polyethylene
PP	Polypropylene
PPIL	Polypropylene interlayer
PVDF	Polyvinylidene fluoride
RT Na-S	Room temperature sodium sulfur
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SMB	Sodium metal battery
SME	Sodium metal electrode
SPAN	Sulfurized polyacrylonitrile
SS	Stainless steel
TEGDME	Tetraethyl glycol dimethyl ether
TEM	Transmission electron microscopy
VASP	Vienna ab initio simulation program

VdW	Van der wall
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
9-F	9 Fluorenone