

**DEVELOPMENT OF ENERGY STORAGE
MATERIALS FOR RECHARGEABLE AQUEOUS
ZINC-ION BATTERIES**

ABHAS ANAND



**DEPARTMENT OF CHEMICAL ENGINEERING
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DEVELOPMENT OF ENERGY STORAGE MATERIALS FOR RECHARGEABLE AQUEOUS ZINC-ION BATTERIES

by

ABHAS ANAND

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*For my late mother —
for her dreams that shaped me.*

Certificate

This is to certify that the thesis entitled “**Development of Energy Storage Materials for Rechargeable Aqueous Zinc-Ion Batteries**” submitted by **Mr. Abhas Anand** to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, have reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

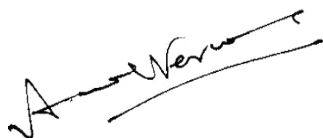


Prof. Siddhasatwa Basu

Supervisor

Department of Chemical Engineering

Indian Institute of Technology Delhi



Prof. Anil Verma

Supervisor

Department of Chemical Engineering

Indian Institute of Technology Delhi



Prof. Vijay K. Ramani

Supervisor

Department of Energy, Environmental and Chemical Engineering

Washington University in St. Louis, USA

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“If you fail, never give up because F.A.I.L. means ‘First Attempt In Learning’.”

— Dr. APJ Abdul Kalam

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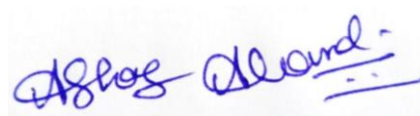
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Abhas Anand

Abstract

Rechargeable aqueous zinc-ion batteries (ZIBs) have attracted significant attention as next-generation energy storage systems for large-scale energy storage applications, owing to their low cost, enhanced safety, and promising electrochemical properties. However, the advancement of ZIB technology toward practical applications is hindered by several critical challenges, including the formation and growth of zinc (Zn) dendrites, short cycle life, limited operating voltage, reduced energy density, and complex charge storage mechanisms. The present work proposes a strategic approach focused on the development of stable electrodes by integrating sustainable material design and interface engineering to overcome key issues, such as dendrite formation, poor cycling stability, and sluggish ion kinetics. To suppress dendritic growth and enhance anode performance, activated carbon (AC) derived from corn husk biomass is incorporated into the Zn anode. At an optimal loading of 15 wt.% AC, the modified anode achieves a high initial discharge capacity of 211.67 mAh.g⁻¹ and retains 86.42% of its capacity after 125 galvanostatic charge-discharge (GCD) cycles, indicating improved electrochemical reversibility and cycling stability. Further enhancement is realized through surface engineering of the Zn anode using a metal-organic framework (MOF), specifically zeolitic imidazolate framework-8 (ZIF-8), electrodeposited onto a zinc-copper (Zn-Cu) structure. This interface-engineered structure promotes uniform Zn nucleation, minimizes dendritic growth, and enables stable plating/stripping of Zn²⁺ for 1000 hours in symmetrical cells. Post-cycling characterization confirms that the ZIF-8 layer effectively mitigates morphological degradation, contributing to extended anode lifespan in ZIBs. To gain quantitative insights into dendritic growth minimization, a mathematical model is developed that incorporates ion transport and electrochemical kinetics. The ZIF-8-modified electrode exhibits the highest Zn²⁺ transference number (t_+), the lowest dendritic current density, and a favorable steady-state Zn²⁺ concentration profile near the electrode surface. The developed

mathematical model suggests that while increasing the t_+ significantly reduce dendritic growth, it cannot be eliminated completely. Enhanced Zn^{2+} transport also reduces the charge transfer resistance, promoting more stable and uniform Zn deposition at the anode surface. On the cathode side, two multivalent transition metal oxide systems are studied: ZIF-67-derived $\text{Co}_3\text{O}_4/\alpha\text{-MnO}_2$ composite and mixed-valence spinel-type NiMn_2O_4 . $\text{Zn//Co}_3\text{O}_4/\alpha\text{-MnO}_2$ delivers a discharge capacity of $243.51 \text{ mAh.g}^{-1}$ at 0.4 C and 140.2 mAh.g^{-1} at 4 C, retaining 90.59% of its capacity after 2000 GCD cycles at 4 C, while maintaining high Coulombic efficiency and redox reversibility. $\text{Zn//NiMn}_2\text{O}_4$ delivers a discharge capacity of 146.4 mAh.g^{-1} at 1 C, with 88.5% capacity retention after 2050 GCD cycles with stable Coulombic efficiency. The findings of this work demonstrate that the use of biomass-derived porous AC and ZIF-based interface engineering effectively enhanced anode stability by minimizing Zn dendrite growth, while the development of mixed-valence spinel-type and tunnel-structured cathode materials improved capacity and cycling performance in ZIBs. The coupling of experimental validation with mathematical modeling provides a robust approach for the rational design of high-performance, sustainable, and safe energy storage systems.

Keywords: Zinc-ion battery, aqueous battery, zinc dendrite, metal-organic framework, spinel cathode, zinc dendrite modelling

सार

जैवभार-व्युत्पन्न पुनः रिचार्ज होने योग्य जलीय जिंक-आयन बैटरियाँ (ZIBs) अपनी कम लागत, बेहतर सुरक्षा तथा उत्कृष्ट विद्यरासायनिक गुणों के कारण बड़े पैमाने पर ऊर्जा भंडारण अनुप्रयोगों के लिए अगली पीढ़ी की ऊर्जा भंडारण प्रणालियों के रूप में विशेष आकर्षण का केंद्र बनी हैं। किंतु, ZIB तकनीक का व्यावहारिक उपयोग अभी भी कई महत्वपूर्ण चुनौतियों से बाधित है, जिनमें जिंक (Zn) डेंड्राइट्स का निर्माण एवं वृद्धि, अल्प चक्र-जीवन, सीमित परिचालन वोल्टेज, कम ऊर्जा घनत्व तथा जटिल चार्ज-संग्रहण तंत्र शामिल हैं। इन चुनौतियों को दूर करने के लिए प्रस्तुत शोधकार्य में टिकाऊ सामग्री डिज़ाइन और इंटरफ़ेस इंजीनियरिंग को सम्मिलित करते हुए स्थिर इलेक्ट्रोड विकसित करने की एक रणनीतिक पद्धति प्रस्तुत की गई है। डेंड्राइट निर्माण को दबाने और एनोड प्रदर्शन को सुधारने हेतु, मकई के भूसे से प्राप्त सक्रिय कार्बन (AC) को Zn एनोड में सम्मिलित किया गया। 15 wt.% AC के अनुकूलित स्तर पर संशोधित एनोड ने 211.67 mAh.g⁻¹ की उच्च प्रारंभिक डिस्चार्ज क्षमता प्रदर्शित की और 125 GCD चक्रों के बाद 86.42% क्षमता बनाए रखी, जो बेहतर चक्र-स्थिरता और विद्यरासायनिक पुनरावर्तनीयता को दर्शाता है। एनोड स्थिरता को और बढ़ाने के लिए, मेटल-ऑर्गेनिक फ्रेमवर्क (MOF), विशेष रूप से Zeolitic Imidazolate Framework-8 (ZIF-8), को Zn-Cu संरचना पर इलेक्ट्रोडिपोजिशन के माध्यम से कोट किया गया। यह इंटरफ़ेस-इंजीनियर्ड संरचना Zn का समान रूप से नाभिकीयकरण सुनिश्चित करती है, डेंड्राइटिक वृद्धि को न्यूनतम करती है तथा सममितीय कोशिकाओं में 1000 घंटे तक स्थिर Zn²⁺ प्लेटिंग/स्ट्रिपिंग को सक्षम बनाती है। चक्र-उपरांत विश्लेषण पुष्टि करता है कि ZIF-8 परत सतही अपक्षय को प्रभावी रूप से नियंत्रित करती है, जिससे एनोड का जीवनकाल बढ़ता है। डेंड्राइट वृद्धि में कमी के मात्रात्मक आकलन हेतु एक गणितीय मॉडल विकसित किया गया है, जिसमें आयन परिवहन और विद्यरासायनिक अभिक्रियात्मकता दोनों को शामिल किया गया है। ZIF-8 संशोधित इलेक्ट्रोड ने सर्वाधिक Zn²⁺ ट्रांसफरेंस संख्या (t_+), न्यूनतम डेंड्राइटिक करंट घनत्व तथा इलेक्ट्रोड सतह के समीप अनुकूल स्थिर-स्थिति Zn²⁺ सांद्रता प्रोफाइल प्रदर्शित की। मॉडल इंगित करता है कि t_+ में वृद्धि से डेंड्राइट वृद्धि में महत्वपूर्ण कमी आती है, किंतु इसे पूर्णतः समाप्त नहीं किया जा सकता। सुधरी हुई Zn²⁺ गतिशीलता चार्ज-ट्रांसफर प्रतिरोध को भी घटाती है, जिससे एनोड सतह पर अधिक स्थिर एवं समान Zn निक्षेपण सुनिश्चित होता है। कैथोड पक्ष में, दो बहुवैलेंट संक्रमण धातु ऑक्साइड प्रणालियों का अध्ययन किया गया: ZIF-67-व्युत्पन्न Co₃O₄/α-MnO₂ समिश्रण तथा मिश्रित-वलेन्सी स्पिनेल-प्रकार NiMn₂O₄।

Zn//Co₃O₄/α-MnO₂ ने 0.4 C पर 243.51 mAh.g⁻¹ तथा 4 C पर 140.2 mAh.g⁻¹ की डिस्चार्ज क्षमता प्रदान की, और 4 C पर 2000 GCD चक्रों के बाद 90.59% क्षमता को बनाए रखा। Zn//NiMn₂O₄ ने 1 C पर 146.4 mAh.g⁻¹ की क्षमता प्रदर्शित की तथा 2050 GCD चक्रों के बाद 88.5% क्षमता को स्थिर कूलॉम्बिक दक्षता के साथ बनाए रखा। समग्रतः, यह शोध दर्शाता है कि जैव-अवशेषों से निर्मित झरझरा AC तथा ZIF-आधारित इंटरफ़ेस इंजीनियरिंग Zn एनोड में डेंड्राइट वृद्धि को प्रभावी रूप से नियंत्रित करती है, जबकि मिश्रित-वलेंसी स्पिनेल एवं टनल-संरचित कैथोड सामग्रियाँ क्षमता तथा चक्र-जीवन में उल्लेखनीय सुधार लाती हैं। प्रायोगिक सत्यापन को गणितीय मॉडलिंग के साथ संयोजित करने से उच्च-प्रदर्शन, टिकाऊ तथा सुरक्षित ऊर्जा भंडारण प्रणालियों की तर्कसंगत डिजाइन हेतु एक सशक्त पद्धति प्राप्त होती है।

कुंजी शब्द: जिंक-आयन बैटरी, जलीय बैटरी, जिंक डेंड्राइट, मेटल-ऑर्गेनिक फ्रेमवर्क, स्पिनेल कैथोड, जिंक डेंड्राइट मॉडलिंग

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List of Abbreviations

BMT	Billion metric tons
GW	Gigawatts
MNRE	Ministry of new and renewable energy
EES	Electrochemical energy storage
LIB	Lithium-ion battery
HER	Hydrogen evolution reaction
SHE	Standard hydrogen electrode
RHE	Reversible hydrogen electrode
ZAB	Zinc-air battery
ZIB	Zinc-ion battery
SEI	Solid-electrolyte interphase
AC	Activated carbon
MOF	Metal-organic framework
ZIF	Zeolitic imidazolate framework
GC	Glassy carbon
GF	Glass fiber
NAC	Non-activated carbon
RDE	Rotating disk electrode
TGA	Thermal gravimetric analysis
XRD	X-ray diffraction
FESEM	Field-emission scanning electron microscopy
EDX	Energy-dispersive X-ray spectroscopy

List of Abbreviations

HRTEM	High-resolution transmission electron microscope
ICP-MS	Inductively coupled plasma mass spectrometry
BET	Brunauer-Emmett-Teller
PSD	Pore size distribution
NLDFT	Non-local density functional theory
BJH	Barrett-Joyner-Halenda
XPS	X-ray photoelectron spectroscopy
UHV	Ultra-high vacuum
FTIR	Fourier transform infrared
CV	Cyclic voltammetry
GCD	Galvanostatic charge-discharge
LSV	Linear sweep voltammetry
CA	Chronoamperometry
OCV	Open circuit voltage
EIS	Electrochemical impedance spectroscopy
GITT	Galvanostatic intermittent titration technique