MOLECULAR ENGINEERING OF ORGANIC AND ORGANOMETALLIC MATERIALS FOR AQUEOUS REDOX FLOW BATTERY

ANUBHAV KUMAR

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

HAUZ KHAS, NEW DELHI-110016

APRIL 2024

MOLECULAR ENGINEERING OF ORGANIC AND ORGANOMETALLIC MATERIALS FOR AQUEOUS REDOX FLOW BATTERY

by

ANUBHAV KUMAR

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

Submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy to the

INDIAN INSTITUTE OF TECHNOLOGY

APRIL 2024

dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled "**Molecular Engineering of Organic and Organometallic Materials for Aqueous Redox Flow Battery**" being submitted by Mr. Anubhav Kumar to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

Prof. Bijay P. Tripathi
Associate Professor
Department of Materials Science & Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi - 110016

ACKNOWLEDGEMENTS

An undertaking of this kind would not have been realized without the collective efforts of many individuals. Firstly, I would like to express my sincere gratitude to my thesis supervisor, Prof. Bijay P. Tripathi. I am indebted to him for the guidance and opportunities which will help me throughout my career. He has always encouraged me to develop a deep understanding and carry out meaningful scientific research. I am grateful for his generosity in countless discussions, insightful suggestions and for giving me academic freedom to develop various skills. It is also necessary to mention his continuous availability and support throughout my Ph.D. and even during the trying times of COVID-19 lockdown, which were instrumental in an uninterrupted workflow.

I would also like to thank the SRC members, Prof. Josemon Jacob, Prof. Leena Nebhani, and Prof. Pravin P. Ingole, for their valuable suggestions, encouragement, and feedback from time to time. Sincere thanks to Prof. Anup K. Ghosh and all the faculty members of DMSE for the supportive and inspiring atmosphere in the department. Additionally, I would like to thank DRC (DMSE) for organizing half-yearly seminars, allowing me to disseminate my research findings and progress to a broader audience.

I am highly thankful to Prof. Nazia Tarannum (Department of Chemistry, CCSU, Meerut) for personally teaching me several experimental techniques and always motivating me to pursue doctoral studies. In addition, she helped me during the Ph.D. application process. I would like to acknowledge Prof. Mukesh C. Joshi (Kirori Mal College, DU) for his friendly teaching and several scientific discussions during my bachelor studies.

It is my pleasure to thank Mr. Surendra Sharma, Mr. Gajraj Singh, Mrs. Astha Sharma, Mr. E. Islam, Mr. Jitendra Kumar, Mr. Ashish Sharma, Mr. Brijesh Kumar, Mr. Ashok Kapoor, and Mr. Gyanendra Kr. Yadav, for tremendous support in performing various experimental characterizations. I especially thank Mr. Gajraj Singh for supporting infrastructural developments for the redox flow battery test setup. Additionally, Mr. Subhash Chand, Mr. Amit Kumar, Mr. Sudhir Pandey, Mrs. Jyoti, Mr. Ramesh, Mr. Narendra, Mrs. Shalini, and Mrs. Sunita Rani Arora have immensely helped and supported in various documentations, organizing seminars, and purchasing activities.

I extend my sincere thanks to all the colleagues in Functional Materials and Membrane Laboratory – Dr. Kanupriya Nayak, Harshit Jain, Biswajit Mishra, Supriya Maity, Sandeep Kumar, Pooja Dhami, Sandeep Kumar Aman, Sushant Bhardwaj, Avoy Mondal, Divya Gaur, Sai Krushna Jena, Swayam Prakash Biswal, and Ankit Rai. I especially thank Dr. Kanupriya Nayak and Pooja Dhami for stimulating academic and non-academic discussions. I acknowledge all the collaborators in FUNMEM for countless hours working together and doing impactful research. Working with all of them was a great pleasure and learning opportunity. I would also like to acknowledge the enlightening and insightful discussions with all the group members during the Saturday meetings. I thank Divya Gaur for proofreading my thesis.

During my doctoral studies, I have been fortunate to meet several individuals. Dr. Ifra Mirza and Mr. Amir Raiz have supported me immensely from the initial phase of my Ph.D. and provided me with a welcoming environment in the department. I want to mention Dr. Debarghya Saha for various thought-provoking discussions. My friends Aditya, Chandan, Hemant, Sakshi, and Sooryansh have been invaluable and supportive during this academically challenging and intellectually stimulating journey. Their presence has made this time genuinely memorable.

I greatly acknowledge the generous financial support from the Council of Scientific and Industrial Research, India, for my doctoral studies. I extend profound thanks to Prof. Bijay P. Tripathi for generous financial support from the RP04006G project after the completion of my CSIR fellowship. Additionally, I acknowledge travel support from the DST-TMD-MES-2K18-02 project for my attendance at the "VII-SEEC" conference.

Expressing my sincerest gratitude to my family for their unwavering support and love – my parents, Mr. Virendra Singh and Mrs. Mithlesh Devi; my sisters, Priyanka and Neetu; my brother-in-law Dr. Bhoodev Sisodia; and my nephews Athrava and Bhavarth. Their love and constant belief in me give me the strength to face challenges with utmost courage. I am always indebted to them for their continuous encouragement and tireless efforts, which have been indispensable to my success.

Anubhav

ABSTRACT

Using renewable solar and wind energy is a sustainable and benign approach to realizing a carbon-neutral economy by mitigating the adverse effects of burning traditional fossil fuels. However, the capricious nature of solar and wind energy requires energy storage devices to streamline the energy generation and supply of the electricity grid. Aqueous redox flow batteries are promising technologies for integrating renewable energy into the electricity grid because of their scalability, safety, low cost, and modular design. The aqueous vanadium redox flow batteries are currently state-of-the-art and most commercially viable technology. However, the price of vanadium-based redox active materials and environmentally hazardous electrolytes limits their widespread implementation. The aqueous organic and organometallic redox active molecules and polymers are low-cost and benign alternatives to traditional inorganic active materials. The composition of organic materials ensures their widespread availability and limited cost constraints due to geopolitical-driven trades. The volumetric capacity, redox potential, and chemical stability of organic materials are limited; however, they can be tuned by rational molecular engineering.

The primary efforts of this thesis are to synthesize derivatives of ferrocene, viologen, and aromatic imides with high water solubility, multi-electron storage, chemical stability, and low crossover using a molecular engineering approach. The ferrocene and viologen derivatives with multielectron storage capability were synthesized by judicially incorporating multiple viologen and ferrocene subunits in the molecules. The ferrocene and viologen-based polymers were designed to limit crossover in combination with a size exclusion membrane. The polymers were synthesized by combining two units responsible for redox activity and enhancing water solubility. In the next step, the molecular engineering of pyromellitic and naphthalene diimide derivatives was done by tailoring alkyl sulfonates with variable alkyl chain length, alkyl phosphonate, and zwitterionic functionalities in the molecular backbone. A systematic synthesis approach was adopted to study the effect of alkyl chain length, counterions, extended π-conjugation, and functional groups on electrochemical performance and the π-π stacking phenomenon of aromatic diimides.

The electrochemically active ferrocene, viologen, and aromatic diimide derivatives with desired properties were successfully synthesized using the molecular engineering approach. The electrochemical properties of the synthesized molecules and polymers were evaluated extensively with density functional theory calculations, cyclic voltammetry, and rotating disk electrode voltammetry measurements. Besides, we studied the water solubility mechanism using a combined framework of density functional theory calculations, nuclear magnetic resonance spectroscopic measurements, and molecular dynamics simulations. The mechanistic insights help in synthesizing highly water-soluble organic materials by polarizing the charge density on the molecular structure. The flow battery performance of synthesized molecules and polymers was evaluated comprehensively with ion exchange and size exclusion membranes, respectively. A maximum capacity retention of >99.997% per cycle, >90% energy and voltage efficiency, >95% capacity utilization, and >99.9% coulombic efficiency have been obtained. The elucidation of electrochemical stability post-battery cycling has provided an opportunity to improve the molecular structure and design the next generation of organic materials with superior battery performance.

सारांश

नवीकरणीय सौर और पवन ऊर्जा का उपयोग पारंपरिक जीवाश्म ईंधन जलाने के प्रतिकूल प्रभावों को कम करके कार्बन-तटस्थ अर्थव्यवस्था को साकार करने के लिए एक स्थायी और सौम्य दृष्टिकोण है। तथापि, सौर और पवन ऊर्जा की विशाल प्रकृति के लिए ऊर्जा उत्पादन और विद्युत ग्रिड की आपूत को कारगर बनाने के लिए ऊर्जा भंडारण उपकरणों की आवश्यकता होती है। जलीय रेडॉक्स फ्लो बैटरी उनकी स्केलेबिलिटी, सुरक्षा, कम लागत और मॉड्यूलर डिजाइन के कारण बिजली ग्रिड में अक्षय ऊर्जा को एकीकृत करने के लिए आशाजनक प्रौद्योगिकियां हैं। जलीय वैनेडियम रेडॉक्स प्रवाह बैटरी वर्तमान में अत्याधुनिक और सबसे व्यावसायिक रूप से व्यवहार्य तकनीक है। हालांकि, वैनेडियम-आधारित रेडॉक्स सक्रिय सामग्री और पर्यावरणीय रूप से खतरनाक इलेक्ट्रोलाइट्स की कीमत उनके व्यापक कार्यान्वयन को सीमित करती है। पानी में घुलनशील कार्बनिक और ऑर्गेनोमेटेलिक रेडॉक्स सक्रिय अणु और पॉलिमर पारंपरिक अकार्बनिक सक्रिय सामग्री के लिए कम लागत और सौम्य विकल्प हैं। कार्बनिक पदार्थों की संरचना भू-राजनीतिक संचालित व्यापार के कारण उनकी व्यापक उपलब्धता और सीमित लागत बाधाओं को सुनिश्चित करती है। कार्बनिक पदार्थों की आयतनमितीय क्षमता, रेडॉक्स क्षमता और रासायनिक स्थिरता सीमित है; हालांकि, उन्हें तर्कसंगत आणविक अभियांत्रिकी द्वारा परिवर्तित किया जा सकता है।

इस शोध प्रबंध के प्राथमिक प्रयास आणविक इंजीनियरिंग दृष्टिकोण का उपयोग करके उच्च जल घुलनशीलता, बहु-इलेक्ट्रॉन भंडारण, रासायनिक स्थिरता और कम क्रॉसओवर के साथ फेरोसीन, वायोलोजेन और एरोमेटिक इमाइड के यौगिक को संश्लेषित करना है। बहुविद्युदणु भंडारण क्षमता के साथ फेरोसीन और वियोलोजेन यौगिक को अणुओं में कई वियोलोजेन और फेरोसीन द्वितीया इकाइयां को न्यायिक रूप से शामिल करके संश्लेषित किया गया था। फेरोसीन और विओलोजेन-आधारित बाहुलक को आकार बहिष्करण झिल्ली के साथ संयोजन में क्रॉसओवर को सीमित करने के लिए बनाया गया था। पॉलिमर को रेडॉक्स गतिविधि और पानी की घुलनशीलता बढ़ाने के लिए जिम्मेदार दो इकाइयों के संयोजन से संश्लेषित किया गया था। अगले चरण में, पाइरोमेलिटिक और नेफ्थलीन डाइमाइड डेरिवेटिव की आणविक अभियांत्रिकी आणविक रीढ़ में परिवर्तनीय अल्काइल श्रृंखला लंबाई, एल्काइल फॉस्फोनेट और ज्विटेरियोनिक कार्यात्मकताओं के साथ अल्काइल सल्फोनेट को तैयार करके की गई थी। विद्युत रासायनिक प्रदर्शन पर एल्काइल श्रृंखला की लंबाई, काउंटरियन, विस्तारित π-संयुग्मन और कार्यात्मक समूहों के प्रभाव और एरोमेटिक डाइमाइड्स की π-π स्टैकिंग घटना का अध्ययन करने के लिए एक व्यवस्थित संश्लेषण दृष्टिकोण अपनाया गया था।

वांछित गुणों के साथ विद्युत रासायनिक रूप से सक्रिय फेरोसीन, वियोलोजेन और एरोमेटिक डाइमाइड यौगिक को आणविक अभियांत्रिकी दृष्टिकोण का उपयोग करके सफलतापूर्वक संश्लेषित किया गया था। संश्लेषित अणुओं और बाहुलक के विद्युत रासायनिक गुणों का मूल्यांकन घनत्व कार्यात्मक सिद्धांत गणना, चक्रीय वोल्टामेट्री और घूर्णन डिस्क इलेक्ट्रोड वोल्टामेट्री माप के साथ बड़े पैमाने पर किया गया था। इसके अलावा, हमने घनत्व कार्यात्मक सिद्धांत गणना, परमाणु चुंबकीय अनुनाद स्पेक्ट्रोस्कोपिक माप और आणविक गतिशीलता सिमुलेशन के संयुक्त ढांचे का उपयोग करके पानी की घुलनशीलता तंत्र का अध्ययन किया। यंत्रवत अंतर्दृष्टि आणविक संरचना पर चार्ज घनत्व को ध्रुवीकृत करके अत्यधिक पानी में घुलनशील कार्बनिक पदार्थों को संश्लेषित करने में मदद करती है। यंत्रवत अंतर्दृष्टि आणविक संरचना पर चार्ज घनत्व को ध्रुवीकृत करके अत्यधिक पानी में घुलनशील कार्बनिक पदार्थों को संश्लेषित करने में मदद करती है। संश्लेषित अणुओं और पॉलिमर के प्रवाह बैटरी प्रदर्शन का मूल्यांकन क्रमशः आयन विनिमय और आकार बहिष्करण झिल्ली के साथ व्यापक रूप से किया गया था। प्रति चक्र >99.998% क्षमता प्रतिधारण, >90% ऊर्जा और वोल्टेज दक्षता, अधिकतम >95% क्षमता उपयोग, और >99.9% कूलम्बिक दक्षता प्राप्त की गई है। बैटरी साइक्लिंग के बाद विद्युत रासायनिक स्थिरता के स्पष्टीकरण ने आणविक संरचना में सुधार करने और बेहतर बैटरी प्रदर्शन के साथ कार्बनिक पदार्थों की अगली पीढ़ी निर्माण करने का अवसर प्रदान किया है।

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

1

1-methyl-1′-[3-(trimethylammonio)propyl]-4,4′-bipyridinium trichloride

[(Me)(NPr)V]Cl_3

1',1''',1''''-(benzene-1,3,5-triyltris(methylene)) tris(dimethyl-ammoniomethyl) ferrocene trichloride

BTTAMF

1',1''',1''''-(benzene-1,3,5-triyltris(methylene))tris(1-(3-(trimethyl ammonio) propyl)-[4'',4'''-bipyridine]-1,1'-diium) nonachloride

BTTMPB

1,1'-disubstituted-4-4'bipyridnium ion

Viologen

(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn][3,8]phenanthroline-2,7-diyl)bis(ethane-2,1-diyl) bis(phosphate) tetra ammonium

NDI-PSEA-NH_4

2

2,2,6,6-tetramethyl-1-piperidinyloxy)

TEMPO

2-aminoethyl dihydrogen phosphate

PSEA

2,7-bis(3-(dimethylamino)propyl) benzo[lmn][3,8]phenanthroline-1,3,6,8 (2H,7H)-tetraone

NDI-DMAP

3

3-aminopropane-1-sulfonic acid

APSA

3-aminoethane-1-sulfonic acid

AESA

3-aminomethane-1-sulfonic acid

AMSA

3,3'-(((1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn][3,8]phenanthroline-2,7-diyl)bis(propane-3,1-diyl))bis(dimethylammoniumdiyl))bis(propane-1-sulfonate)

NDI-DMAPS

A

Aqueous organic redox flow battery

AORFB

Aqueous redox flow battery

ARFB

Aqueous polymer redox flow battery

APRFB

Area specific resistance

ASR

Attenuated total reflection Fourier transform infrared spectroscopy
ATR-FTIR

C

Compressed air energy storage
CAES

Cyclic voltammetry
CV

Coulombic efficiency
CE

Continuum conductor-like screening model
COSMO

D

Density functional theory
DFT

E

Electrical energy storage
EES

Energy efficiency
EE

Electrochemical impedance spectroscopy
EIS

F

(Ferrocenylmethyl) trimethylammonium chloride
FcNCl

Fourier transformed infrared
FTIR

G

Gel permeation chromatography
GPC

H

Highest occupied molecular orbital
HOMO

L

lowest unoccupied molecular orbital
LUMO

Lithium-sulfur
Li-S

linear sweep voltammetry
LSV

M

Methyl viologen
MV

Molecular dynamics
MD

Molecular weight cutoff
MWCO

N

Naphthalene diimide

NDI

N,*N*′-bis(glycinyl)naphthalene diimide

[K_2-BNDI]

Nuclear magnetic resonance

NMR

N',N'-dimethylpropane-1,3-diamine

DMAP

O

Open circuit potential

OCV

P

Pumped hydro storage

PHS

Poly(ferrocenylmethyl-2-methylpropenoate-co-[2-(methacryloyloxy) ethyl] trimethylammonium chloride)

Catholyte-P

Poly(1-4-vinylbenzyl-1'-1-(3-(trimethylammonio)propyl)-[4,4'-bipyridin]-1-1'-ium trichloride)

Anolyte-P

Pyromellitic diimide

PDI

R

Redox flow battery

RFB

Redox active material

RAM

Redox-active organic and organometallic material

ROM

Rotating disk electrode

RDE

Radial distribution function

RDF

S

Solid electrolyte interface

SEI

Sodium-sulfur

Na-S

Standard hydrogen electrode

SHE

Singly occupied molecular orbital

SOMO

State of charge

SOC

V

Voltage efficiency

VE

Vanadium redox flow battery

VRFB

LIST OF SYMBOLS

Symbol	Meaning
ΔG	Gibbs free energy change
z	Charge number
F	Faraday's constant
E	Cell voltage
C	Volumetric capacity
m	Mass
M	Molar mass
E	Energy density
μ_v	Volume fraction
η	Efficiency
Q	Charge
T	Time
n	Number of electron
A	Area
D	Diffusion coefficient
c_0	Concentration
ν	Kinematic viscosity
i_k	Mass transport independent kinetic current
i_0	Exchange current
k^0	Electron transfer rate constant
V_a	Amplitude of sine wave
ΔG_{Sol}	Solvation energy
Ps	Salt permeability
L	Membrane thickness
D_S	Diffusion coefficient of salt
R	Area resistance
$Đ$	Polydispersity index

M_w	Weight average molecular weight
M_n	Number average molecular weight