

**NOVEL IONIC LIQUID BASED SOLID
POLYMER ELECTROLYTES FOR LITHIUM
BATTERIES**

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by

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Dedicated to
The Grace of Almighty and My Family

CERTIFICATE

This is to certify that the thesis titled '*Novel Ionic Liquid Based Solid Polymer Electrolytes for Lithium Batteries*' being submitted by **Ms. Sumana Bandyopadhyay** 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 her. **Ms. Sumana** has worked under my guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.



(PROF. BHANU NANDAN)

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(SUMANA BANDYOPADHYAY)

ABSTRACT

All solid state lithium batteries are a promising prospect in the field of energy storage devices providing high energy density and safety. Presently, the rechargeable lithium battery technology stands at the pinnacle of the energy storage sector for powering a wide range of green technologies used in daily life. Besides the use of high capacity and high voltage cathode materials, the use of lithium metal as anode is considered advantageous in lithium batteries because of its high theoretical specific capacity, low density and the lowest electrochemical potential (-3.04 V vs. standard hydrogen electrode). Generally, lithium batteries suffer from various shortcomings associated with the electrochemical operation and design limitations which often get accelerated when lithium metal anode is used. Firstly, the conventional liquid electrolytes used in lithium batteries are predominantly based on a mixture of lithium salt in organic solvents that are highly toxic, flammable, and volatile with a narrow electrochemical stability window, and prone to liquid leakage. The uncontrolled dendrite growth on lithium metal surface in lithium batteries using liquid electrolytes brings additional safety issues, such as internal short circuits, thermal runaway, and, even causes explosion. “Solid state” batteries seek to resolve these limitations of current lithium battery technology by eliminating the need for a liquid electrolyte and replacing it with solid state electrolytes. Solid polymer electrolytes based on polymeric materials can promote safe and reliable solid state lithium batteries with several advantages like high flexibility, lightweight, good chemical stability, safety, and easy fabrication. The traditional solid polymer electrolytes suffer from reduced ionic conductivity due to the semi-crystalline nature of the polymers employed, as a result plasticizer addition or other modifications are required to reduce crystallinity and improve the ionic conductivity. A balanced solution for fabricating solid polymer electrolytes can involve ionic liquids as plasticizers with improved ionic conductivity and crosslinking or incorporation of fibrous frameworks as reinforcements. The prime objective of this research work is the synthesis and application of ionic liquid based solid polymer electrolyte systems for solid state lithium batteries. For this purpose, cage-like 1,4-Diazabicyclo [2.2.2] octane (DABCO) was selected to synthesize novel ionic liquids. In this thesis, attempts have been made to achieve excellent electrochemical performance of true solid state lithium batteries via the development of solid polymer electrolytes based on ionic liquids and poly(ionic liquids), that have remained relatively unexplored as lithium battery electrolytes.

Firstly, a simple solvent-free melt-diffusion method is presented to fabricate a free-standing solid electrolyte. A porous polymer host is infiltrated with a binary mixture composed of mono-quaternized DABCO based ionic liquid and a lithium salt. Next, DABCO is used to prepare backbone poly(ionic liquids) or ionenes with cationic moieties tethered to the backbone separated by oxyethylene spacers ($-\text{CH}_2\text{CH}_2\text{O}-$). The effect of spacer length on the electrochemical performance is investigated. Moreover, binary mixtures of the prepared ionene oligomers and lithium salt are used to coat poly(acrylonitrile) based electrospun fibrous mat to fabricate the flexible fibre reinforced solid polymer electrolytes. In this case, the soft ionene improves the interfacial contact and the cell operation in absence of any micro-wetting. In continuation to the previous work, a unique one-step fabrication approach is also tried where an all solid state polymer electrolyte is fabricated by uniaxial electrospinning of poly(acrylonitrile) blended with ionene oligomer and doped with lithium salt. Following heat-treatment, the ionene oligomer flows out of and around the nanofibers, closing the pores of the nanofibrous mat forming all solid state polymer electrolytes reinforced by fibrous framework. Therefore, to incorporate electrolyte in the fibrous mat an extra step involving coating or melt-diffusion gets eliminated in this case. Compared to the coating process this one step process can achieve greater mechanical strength and ionic conductivity. Lastly, DABCO is further used to synthesize cationic monomers with TFSI^- and FSI^- anions to form a semi-interpenetrating network-based polymer matrix that is incorporated within an electrospun fibrous poly(acrylonitrile) network. A two-fold reinforcement effect is achieved collectively from the semi-interpenetrating structure and the three-dimensional fibrous network. Further, a dual anion synergy is demonstrated by the formation of an ion conductive inorganic rich solid electrolyte interface layer when both TFSI^- and FSI^- anions are present. The fibre reinforced solid polymer electrolyte can remain stable at high temperatures of 150°C while the traditional polyolefin based commercial separator shrinks at such high temperature. The fabricated solid polymer electrolytes here in each case shows good electrochemical performance when evaluated in lithium metal batteries with high voltage cathodes like LiFePO_4 (LFP) and $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) or high-capacity sulfur/carbon cathodes in lithium sulfur batteries.

The knowledge from textile and fibre engineering proved to be valuable in designing flexible lithium batteries with the fabricated fibre reinforced solid polymer electrolytes that are shown to operate under bent, folded or cut states. In summary, this work can provide inspiring ways to fabricate flexible batteries that can be integrated to power next generation wearable technologies.

सार

उच्च शक्ति घनत्व और सुरक्षा प्रदान करने वाले ऊर्जा भंडारण उपकरणों के क्षेत्र में ऑल सॉलिड स्टेट लिथियम बैटरी एक आशाजनक संभावना है। वर्तमान में, दैनिक जीवन में उपयोग की जाने वाली हरित प्रौद्योगिकियों की एक विस्तृत श्रृंखला को बिजली देने के लिए रिचार्जबल लिथियम बैटरी टेक्नोलॉजी ऊर्जा समग्र भंडारण क्षेत्र के शिखर पर है। उच्च सैद्धांतिक विशिष्ट क्षमता, कम घनत्व, और सबसे कम इलेक्ट्रोकेमिकल क्षमता (-3.04 वोल्ट बनाम मानक हाइड्रोजन इलेक्ट्रोड) के कारण लिथियम बैटरी में एनोड के रूप में लिथियम धातु का उपयोग फायदेमंद माना जाता है। आम तौर पर लिथियम बैटरियां इलेक्ट्रोकेमिकल संचालन और डिजाइन सीमाओं से जुड़ी विभिन्न कमियों से ग्रस्त होती हैं, जो अक्सर लिथियम धातु एनोड का उपयोग करने पर तेज हो जाती हैं। सबसे पहले, लिथियम बैटरी में उपयोग किए जाने वाले पारंपरिक लिक्विड इलेक्ट्रोलाइट्स मुख्य रूप से कार्बोनेट द्रावक में लिथियम सॉल्ट के मिश्रण पर आधारित होते हैं जो एक संकीर्ण इलेक्ट्रोकेमिकल स्थिरता विंडो के साथ अत्यधिक जहरीले, ज्वलनशील और अस्थिर होते हैं, और तरल रिसाव की संभावना होती है। तरल इलेक्ट्रोलाइट्स का उपयोग करके लिथियम बैटरी में लिथियम धातु की सतह पर अनियंत्रित डेंड्राइट वृद्धि अतिरिक्त सुरक्षा समस्याएं लाती है, जैसे आंतरिक शॉर्ट सर्किट, थर्मल रनअवे, और यहां तक कि विस्फोट का कारण भी बन सकता है। "सॉलिड स्टेट" बैटरियां लिक्विड इलेक्ट्रोलाइट की आवश्यकता को समाप्त करके और सॉलिड स्टेट इलेक्ट्रोलाइट्स के साथ प्रतिस्थापित करके वर्तमान लिथियम बैटरी टेक्नोलॉजी की इन सीमाओं को हल करना चाहती हैं। पॉलिमरिक सामग्रियों पर आधारित सॉलिड पॉलिमर इलेक्ट्रोलाइट्स उच्च नमन्शील, हल्के वजन, अच्छी रासायनिक स्थिरता, सुरक्षा और आसान निर्माण जैसे कई फायदों के साथ सुरक्षित और विश्वसनीय सॉलिड स्टेट लिथियम बैटरी को बढ़ावा दे सकते हैं। पारंपरिक सॉलिड स्टेट पॉलिमर इलेक्ट्रोलाइट्स नियोजित पॉलिमर की अर्ध-क्रिस्टलीय प्रकृति के परिणामस्वरूप कम आयनिक वाहकता से पीड़ित होते हैं, जिसके कारण क्रिस्टलीयता को कम करने और आयनिक वाहकता में सुधार करने के लिए प्लास्टिसाइज़र या अन्य संशोधनों की आवश्यकता होती है। सॉलिड स्टेट पॉलिमर इलेक्ट्रोलाइट्स के निर्माण के लिए एक संतुलित समाधान में प्लास्टिसाइज़र के रूप में बेहतर आयनिक वाहकता के साथ आयनिक लिक्विड और सुदृढीकरण के रूप में क्रॉसलिंग या रेशेदार साँचे की तैयारी किया जा सकता है। इस शोध कार्य का मुख्य उद्देश्य सॉलिड-स्टेट लिथियम बैटरियों के लिए आयनिक लिक्विड आधारित सॉलिड पॉलिमर इलेक्ट्रोलाइट तंत्र का संश्लेषण और अनुप्रयोग है। इस उद्देश्य के लिए, नए मोनो-केटाएनिक या डाइ-केटाएनिक आयनिक लिक्विड को संश्लेषित करने के लिए केज की तरह 1,4-डायजेबीसाइक्लो [2.2.2] ऑक्टेन (DABCO) का चयन किया गया था। इस थीसिस में, आयनिक लिक्विड

और पॉली (आयनिक लिक्विड) पर आधारित सॉलिड पॉलिमर इलेक्ट्रोलाइट के विकास के माध्यम से वास्तविक सॉलिड स्टेट लिथियम बैटरी के उत्कृष्ट विद्युत रासायनिक प्रदर्शन को प्राप्त करने का प्रयास किया गया है, जो लिथियम बैटरी इलेक्ट्रोलाइट्स के रूप में अपेक्षाकृत अज्ञात रहे हैं।

सबसे पहले, एक मुक्त-स्थायी सॉलिड इलेक्ट्रोलाइट बनाने के लिए एक सरल विलायक-मुक्त पिघल-प्रसार विधि प्रस्तुत की जाती है। एक छिद्रपूर्ण पॉलिमर होस्ट को मोनो-क्वाटरनाइज्ड DABCO आधारित आयनिक लिक्विड और एक लिथियम सॉल्ट से बने बाइनरी मिश्रण अंदर से भर देता है। इसके बाद, DABCO का उपयोग ऑक्सीथिलीन स्पेसर्स ($-\text{CH}_2\text{CH}_2\text{O}-$) द्वारा अलग किए गए बैकबोन से जुड़े कैटायनिक अंशों के साथ बैकबोन पॉली(आयनिक लिक्विड) या आयोनीन को तैयार करने के लिए किया जाता है। इलेक्ट्रोकेमिकल प्रदर्शन पर स्पेसर लंबाई के प्रभाव की जांच की जाती है। इसके अलावा, तैयार आयनीन ऑलिगोमर्स और लिथियम सॉल्ट के बाइनरी मिश्रण का उपयोग फाइबर प्रबलित नमन्शील सॉलिड पॉलिमर इलेक्ट्रोलाइट्स को बनाने के लिए पॉली(एक्रिलोनिट्राइल) आधारित इलेक्ट्रोस्पन रेशेदार साँचा को कोट किया जाता है। इस मामले में, नरम आयनीन किसी सूक्ष्मतरंग गीलापन के अनुपस्थिति में भी अंतरापृष्ठीय संपर्क और सेल संचालन में सुधार करता है। पिछले कार्य को जारी रखते हुए, एक अद्वितीय एकपद निर्माण प्रक्रिया का भी प्रयास किया गया है, जहां एक ऑल सॉलिड स्टेट पॉलिमर इलेक्ट्रोलाइट को आयनीन ऑलिगोमर और लिथियम सॉल्ट के साथ मिश्रित पॉली(एक्रिलोनिट्राइल) के एकाक्षीय इलेक्ट्रोस्पनिंग द्वारा निर्मित किया जाता है। तापोपचार के बाद, आयनीन ऑलिगोमर नैनोफाइबर से और उसके आसपास बहता है, नैनोफाइबर साँचा के छिद्रों को बंद कर देता है और एक रेशेदार ढांचे द्वारा प्रबलित ऑल सॉलिड स्टेट पॉलिमर इलेक्ट्रोलाइट्स का निर्माण करता है। इसलिए, इस मामले में रेशेदार साँचा में इलेक्ट्रोलाइट्स को शामिल करने के लिए, कोटिंग या पिघल-प्रसार से जुड़ा एक अतिरिक्त कदम की आवश्यकता नहीं होता है। कोटिंग प्रक्रिया की तुलना में यह एकपद प्रक्रिया अधिक यांत्रिक शक्ति और आयनिक वाहकता प्राप्त कर सकती है। अंत में, DABCO का उपयोग अर्ध-इंटरपेनेट्रेटिंग नेटवर्क आधारित पॉलिमर मैट्रिक्स बनाने के लिए TFSI^- और FSI^- ऐनायनों के साथ कैटायनिक मोनोमर्स को संश्लेषित किया जाता है जो एक इलेक्ट्रोस्पून रेशेदार पॉली (एक्रिलोनिट्राइल) साँचे के भीतर शामिल होता है। अर्ध-इंटरपेनेट्रेटिंग संरचना और त्रि-आयामी रेशेदार नेटवर्क से सामूहिक रूप से दो गुना सुदृढीकरण प्रभाव प्राप्त किया जाता है। इसके अलावा, जब TFSI^- और FSI^- दोनों ऐनायनों मौजूद थे, तो आयन प्रवाहकीय अकार्बनिक समृद्ध सॉलिड इलेक्ट्रोलाइट इंटरफ़ेस परत के गठन से दोहरी ऐनायन का सहक्रिया प्रदर्शन किया जाता है। फाइबर प्रबलित सॉलिड पॉलिमर इलेक्ट्रोलाइट 150°C के उच्च तापमान पर मज़बूत रह सकता है जबकि पारंपरिक पॉलीओलेफ़िन आधारित वाणिज्यिक

विभाजक इतने उच्च तापमान पर सिकुड़ जाता है। जब LiFePO_4 (LFP) और $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) जैसे उच्च वोल्टेज कैथोड या लिथियम सल्फर बैटरी में उच्च क्षमता वाले सल्फर/कार्बन कैथोड के साथ लिथियम धातु बैटरी में मूल्यांकन किया जाता है, तो यहाँ प्रत्येक मामले में निर्मित सॉलिड पॉलिमर इलेक्ट्रोलाइट्स अच्छा इलेक्ट्रोकेमिकल प्रदर्शन दिखाते हैं।

निर्मित फाइबर प्रबलित सॉलिड पॉलिमर इलेक्ट्रोलाइट्स के साथ नमन्शील लिथियम बैटरी को बनाने में कपड़ा और फाइबर इंजीनियरिंग का ज्ञान मूल्यवान साबित हुआ, जो मुड़े हुए या कटे हुए अवस्था में संचालित होते हैं। संक्षेप में, यह कार्य नमन्शील बैटरी बनाने के प्रेरक तरीके प्रदान कर सकता है जिन्हें अगली पीढ़ी को पहनने योग्य प्रौद्योगिकियों को बिजली प्रदान करने के लिए प्रयोग किया जा सकता है।

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List of Symbols

cm	Centimeter
cm ⁻¹	Centimeter inverse
cP	Centipoise
°C	Degree centigrade
°C min ⁻¹	Degree centigrade per minute
eV	Electron Volts
g	Gram
g cm ⁻³	Gram per cubic centimeter
g mol ⁻¹	Gram per Mole
Hz	Hertz
h	Hour
J K ⁻¹ mol ⁻¹	Joules per Kelvin per Mole
K	Kelvin
kJ mol ⁻¹	Kilo Joule per Mole
kHz	Kilohertz
MHz	Megahertz
μL	Microliter
μm	Micrometer
mA h g ⁻¹	Milliampere-hour per gram
mAh cm ⁻²	Milliampere-hour per square centimeter
mg	Milligram
mg cm ⁻²	Milligram per centimeter square
mHz	Millihertz
mL	Milliliter
mL g ⁻¹	Milliliter per gram
mL h ⁻¹	Milliliter per hour
mL min ⁻¹	Milliliter per minute
mm	Millimeter
mm min ⁻¹	Millimeter per minute
Mmol	Millimole
Mmol g ⁻¹	Millimole per gram
mV	Millivolt
mV s ⁻¹	Millivolt per second
min	Minute
M	Molar
mol	Mole
nm	Nanometer

$\Omega \text{ cm}^{-2}$	Ohm per square centimetre
Pa s	Pascal second
M Pa	Mega Pascal
s^{-1}	Per second
s	Second
S cm^{-1}	Siemens per centimetre
$\text{K}^{1/2} \text{ S cm}^{-1}$	Square root Kelvin-Siemens per centimetre
V	Volt

List of Abbreviations

Li	Lithium
S	Sulfur
N	Nitrogen
O	Oxygen
C	Carbon
Cl	Chlorine
Br	Bromine
H	Hydrogen
DABCO	1,4-diazabicyclo [2.2.2] octane (DABCO)
BPO	Benzophenone
FSI	bis(fluorosulfonyl)imide
TFSI	bis(trifluoromethanesulfonyl)imide
LiFSI	Lithium bis(fluorosulfonyl)imide
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PEGDA	Polyethylene glycol diacrylamide
PEO	Polyethylene oxide
PP	Polypropylene
PVDF	Polyvinylidene fluoride
DME	1,2-dimethoxymethane
DOL	1,3-dioxolane
CNT	Carbon nanotube
DI	De ionized water
d6-CDCl ₃	Deuterated Chloroform
d6-DMSO	Deuterated Dimethylsulfoxide
EC	Ethylene carbonate
LiPF ₆	Lithium hexafluorophosphate
LFP or LiFePO ₄	Lithium iron phosphate
LiNO ₃	Lithium nitrate
NMP	N-methyl-2-pyrrolidone
DMF	N, N-dimethylformamide
NMC	Nickel manganese cobalt oxide
	Poly(3,4-
PEDOT:PSS	ethylenedioxythiophene):polystyrene sulfonate
[R ₄ N] ⁺	Quaternary ammonium cation
LiPS	Lithium polysulfide

LSB	Lithium sulfur battery
IL	Ionic liquid
PIL	Polymerized ionic liquid or Poly(ionic liquid)
SSE	Solid state electrolyte
ASSPE	All solid state polymer electrolyte
SPE	Solid Polymer Electrolyte
Semi-IPN	Semi-Interpenetrating network
SS	Stainless steel
OIPC	Organic ionic plastic crystal
DSC	Differential Scanning Calorimetry
T _g	Glass transition temperature
T _m	Temperature of melting
TGA	Thermogravimetric Analysis
CA	Chronoamperometry
CV	Cyclic Voltammetry
LSV	Linear Sweep Voltammetry
EIS	Electrochemical Impedance Spectroscopy
OCV	Open Circuit Voltage
SEI	Solid electrolyte interphase
PLOM	Polarized Light Optical Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
SEM	Scanning Electron Microscopy
XPS	X-Ray Photoelectron Spectroscopy
FTIR	Fourier Transform Infrared
ATR	Attenuated Total Reflection
IR	Infrared
NMR	Nuclear Magnetic Resonance
VFT	Vogel–Fulcher–Tammann
A	Area of electrolyte
ASR	Area specific resistance
N	Average number of ion coordination
E _a	Activation energy
a.u	Absolute Unit
σ or IC	Ionic conductivity
tLi ⁺	Lithium ion transference number
R	Resistance
R _b	Ohmic resistance
ρ	Resistivity
R _{ct}	Charge-transfer resistance
L	Length or thickness of electrolyte
Φ	Diameter

η	Eta (Viscosity)
v/v	Volume by volume
Zw	Warburg resistance
w/w	Weight by weight
e ⁻	Electron
wt. %	Weight percentage
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
$\pm$	Plus and minus
$\leq$	Less than equals to
$\geq$	Greater than equals to
$\sim$	Approximately