Theoretical and Spectroscopic Investigations on Ionogels

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Safna Hussan K.P.
Dr. Mohamed Shahin Thayyil

PREFACE

Ionic liquids (ILs) are salts with a melting point below 250^0C; they have been attracting electrochemists with their unique properties like non-volatility, thermal stability, non-flammability, and low vapor pressure with wide electrochemical window. ILs have emerged as a potential replacement for organic electrolytes. However, the liquid nature of ILs limits their application due to leakage. Thus there is incredible demand for the immobilization of ILs since it overcomes all the restrictions and opens up a new pathway to solid electronic gadgets like batteries, capacitors, super capacitors, fuel cells, sensors, etc. Among all the well-known strategies, entrapping ILs in the polymer matrix can be considered as a feasible, low-cost method for large scale production of ionogels. Ionogel consists of a non-conducting polymeric framework as the host and a conducting IL as the guest. Ionogel not only retains the properties of ILs but also shows the mechanical properties of a polymer matrix like flexibility, film-forming nature, etc. Thus ionogel will be a better choice for solid state electrolytes due to its appealing features of freestanding film and high thermal stability properties that allows us to design easily and cheaply with modularity and reliability in electrochemical devices. The versatility of both ILs and polymer chemistry allows us to develop an infinite number of ionogels. Every combination of ILs and polymer results in unpredictable behavior. Thus the field of ionogel membranes has yet to be explored.

This book is intended to report a complete characterization technique from theoretical prediction to the application level, including quantum mechanical predictions, synthesis method, characterization techniques, and molecular dynamics of the developed ionogel. This book will be useful for students, researchers, industrialists, etc., and whoever wishes to work in the field of ionogels, as well as in the application level of solid-state materials. As we said above, the field of ionogel membranes is yet to be explored, and this book can be used as reference material for upcoming innovations too.

This book covers ionogel membranes and their development, theoretical predictions, characterization, detailed thermal and electrical properties, molecular dynamics, and applications. It is written as a distinctive source taking the reader on a fantastic journey from quantum mechanical calculations to advanced research areas. Chapter 1 gives detailed information about ionic liquids and ionogel membranes and their preparations. The solution casting on glass technique was employed to develop ionogel by entrapping two highly conducting ILs, namely, 1-Ethyl-3-methyl imidazolium thiocyanate [EMIM] [SCN] and 1-Butyl-1-methyl pyrrolidinium bis (trifluoromethyl sulfonyl imide) [BMPyr] [TFSI], in two non-conducting polymers. Chapter 2 introduces a novel hybrid theoretical approach named ONIOM (n-layered integrated molecular orbital and molecular mechanics approach), which was implemented in the Gaussian 09 program package to study the interaction of ILs with complex polymer chains and subsequently to check the compatibility of the IL with two non-conducting polymers, namely polymethyl methacrylate and polyvinyl pyrrolidone matrix, to form an eco-friendly ionogel. This quantum mechanical approach helped us trace the most compatible pairs of ILs and polymer matrices among the chosen four combinations. Chapter 3 presents a detailed morphological characterization of ionogel membranes by means of the scanning electron microscope, Fourier transforms infrared spectroscopy, Fourier transforms Raman spectroscopy, and an X-ray diffractometer.

Chapter 4 delineates the influence of ILs in the polymer matrices and discusses the variations in phase transitions and thermal stability of the polymer matrices. Chapters 5 and 6 address the molecular dynamics, charge transport mechanism, conductivity relaxation in the ionogel membranes over broad frequency window, and wide temperature range to explore the molecular fluctuations and variations that happened in the ionogel membranes on varying weight ratios of the incorporated ionic liquid.

Chapter 7 discusses the specific properties and applications of the two developed ionogel membranes. This chapter covers the energy storage application of ionogel membranes and also emphasizes the CO_2 sensing and capturing properties of the developed one.

In summary, this will be a remarkable contribution toward the state of the art for material designing and development, morphology, structure, thermal and electrical properties, and applications of ionogel membranes. We hope that this will be very useful for academic and industrial purposes but also for fledgling students and newcomers in the field of solid state devices.

Safna Hussan K. P.
Dr. Mohamed Shahin Thayyil

ABSTRACT

Nowadays, an enormous research effort has been devoted to immobilize ionic liquid for electrochemical applications, since it can be used as an excellent substitute for liquid electrolytes. Among all the well-known strategies, entrapping ILs in the polymer matrix can be considered as a feasible, low-cost method for large scale production of ionogel. The versatility of both IL and polymer chemistry allows us to develop an infinite number of ionogels. Every combination of IL and polymer results in unpredictable behavior; thus the field of ionogel membranes is yet to be explored. This book is intended to report complete characterization techniques from theoretical predictions to the application level, including quantum mechanical predictions, synthesis method, characterization techniques, and molecular dynamics of the developed ionogel.

Moreover, a novel hybrid theoretical approach named ONIOM (n-layered integrated molecular orbital and molecular mechanics approach) was implemented to study the interaction of ILs with complex polymer chains in the ionogel. This book will be useful for students, researchers, industrialists, and so on, and for anyone who wishes to work in the field of ionogels as well as in the application level of solid-state materials. As we said above, the field of ionogel membranes is yet to be explored, and this book can be used as reference material for upcoming innovations too.

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Safna Hussan K. P. is a doctoral research scholar at the University of Calicut, Department of Physics, working with Dr. Mohamed Shahin Thayyil with a UGC-MANF fellowship. She earned her bachelors and master's degrees in physics from University of Calicut, Kerala, India in 2010 and 2012, respectively. She is currently involved in the research area of ionic liquids with two potential applications, namely, electrochemical and pharmaceuticals. She develops ionogel membranes by immobilizing ionic liquids in the non-conducting polymer matrices and makes it viable for application in solid-state devices. She is an internationally renowned scholar with many publications in international peer-reviewed journals. Safna Hussan has many collaborations at national and international levels.

Mohamed Shahin Thayyil is an Assistant Professor at the Dept. of Physics, University of Calicut (CU), India. He holds a Master's in Physics (CU), a PhD in Physics (Jawaharlal Nehru University, New Delhi, India) and pursued a Post-Doctoral Research at the Dept. of Physics, University of Pisa, Italy. Apart from teaching, he is involved in active research on amorphous materials, amorphous pharmaceuticals, ionic liquids, electrochemical studies. He has published more than 50 research papers and acted as reviewer for different journals. He has spent time and effort in developing amorphous materials from their crystalline counterparts and in understanding the molecular dynamics of such a system in the glassy state as well as in a supercooled liquid state. He made his signature in the area of pharmaceuticals and is currently interested in solid state electrolytes. He is also a specialist in broadband dielectric spectroscopy and differential scanning calorimeter analysis for a broad range of materials. He has published around 45 papers and acted as editor for one book. He has supervised PhD and MPhil theses and has had many collaborations across the world.

ABBREVIATIONS USED IN THIS BOOK

IL	: Ionic liquid
[EMIM] [SCN]	: 1-Ethyl-3-methylimidazolium thiocyanate
[BMPyr] [TFSI]	: 1-Butyl-1-methyl pyrrolidinium bis (trifluoromethyl sulfonyl imide)
PMMA	: Polymethyl methacrylate
PVA	: Polyvinyl alcohol
$E_{stretch}$	: The energy associated with bond stretching
$E_{bending}$	: The energy associated with bond bending
$E_{tortion}$	: Torsional energy
$E_{bonding}$	: The energy associated with bonding interactions
$E_{nonbonding}$	: The energy associated with nonbonding interactions
$E_{covalent}$	: The energy associated with covalent bonding
$E_{noncovalent}$	: The energy associated with non-covalent bonding
MM	: Molecular mechanics
QM	: Quantum mechanics
ONIOM	: Our N-layered integrated molecular orbital+ molecular mechanics
Sdf	: Standard data file
$k_{stretch}$	: Proportionality constant
L	: Length
l_{eq}	: Equilibrium length
H	: Hamiltonian energy operator
ψ	: Eigen function
E	: Eigenvalue
SM	: Semi-empirical method
DFT	: Density functional theory
TDFT	: Time-dependent density functional theory
E_{NN}	: Nuclear-nuclear repulsion energy
E_{v}	: Nuclear-electron attraction energy
E_{coul}	: Classical electron-electron Coulomb repulsion energy
E_{T}	: Kinetic energy of electrons
E_{ach}	: The non-classical electron-electron exchange energies

E_{corr}	: The energy from the correlated movements of electrons with different spins
PES	: Potential energy surface
FMO	: Frontier molecular orbital
HOMO	: Highest occupied molecular orbital
LUMO	: With lowest unoccupied molecular orbital
UV	: Ultra violet
IR	: Infrared
H	: Enthalpy
S	: Entropy
G	: Gibbs free energy
FTIR	: Fourier transform infrared
ATR-FTIR	: Attenuated total reflectance-Fourier transform infrared
NLO	: Nonlinear optical
IP	: Ionisation potentials
EA	: Electron affinity
H	: Hardness
S	: Softness
M	: Chemical potential
Ω	: Electrophilicity index
P	: Polarization
F	: Electric Field
A	: Polarizability
B	: First static hyperpolarizability
SEM	: Scanning electron microscope
FT-Raman	: Fourier transform Raman spectroscopy
DSC	: Differential scanning calorimetry
TGA	: Thermal gravimetry analysis
DTGA	: First derivatives thermal gravimetry analysis
Tg	: Glass transition temperature
Tm	: Melting point
X_1	: mass (weight) fraction
BDS	: Broadband dielectric spectroscopy
Z	: Impedance
ε	: Permittivity
σ	: Conductivity
M	: Modulus
IP	: Interfacial polarization
MWS	: Maxwell-Wagner-Sillars
G	: Conductance

CPE	: Constant phase element
CPE-T	: Pseudocapacitance
SCLC	: Space charge limited conduction
CV	: Cyclic voltammetry
Ag	: Silver
C	: Capacitance
SPE	: Solid polymer electrolyte
CO_2	: Carbon dioxide

CHAPTER 1

INTRODUCTION

1.1. Introduction

Material design is an art that plays a vital role in our day-to-day needs. Designing a material is the primary phase of any product development where the architect must focus on improving the properties of a material to overcome their limitations or to impart superior qualities. Quality and performance of material are assessed according to their structural, electrical, thermal, mechanical, chemical, and optical properties and by analyzing a wide variety of materials to reveal that a single material is not fulfilling all aspects of our requirements. Thus, in order to make a product viable for practical application, incorporation of diverse properties is essential within a feasible cost. Thus, material selection and design are the prominent stages of research keeping in view their practical applications.

Ionic liquids (ILs) offer a wide variety of properties that make them a prominent substitute for conventional organic electrolytes in many energy-related application fronts. The freedom to choose different cation-anion combinations make them unique with diverse properties like low volatility coupled with high electrochemical and thermal stability; significant ionic conductivity crafts the likelihood of designing an ideal electrolyte for batteries, super-capacitors, actuators, dye-sensitized solar cells, and thermo-electrochemical cells, etc. (1). Thus, the biggest charm of ionic liquids relies on the possibility to tune their properties by choice of the anion-cation combination. Moreover, a large family of them are air and water stable, as well as thermally stable even at temperatures higher than 570 K (2). Though ILs are used successfully as electrolytes in many gadgets, their leakage-causing fluid nature and high cost limit their large scale application (3–5).

Currently, enormous research efforts have been devoted to immobilize ILs for electrochemical applications, since they can be cast as an excellent substitute for liquid electrolytes. Chemical attachment with suitable ionic species and physical entrapment of an IL in non-conducting organic/inorganic matrices are the two strategies popularly used for immobilizing ILs, which are commonly named *ion-gels* or *ionogels*. Among them, polymers are an attractive platform considering their rich database and low cost for large scale production. The versatility of both ILs and polymer chemistry results in an infinite number of ionogels. Each combination of an IL with a polymer results in unpredictable behavior due to the possibility of diverse chemical bonding. Thus the field of ionogels is yet to be explored systematically.

This book is intended to report a complete overview of the development of ionogels to their application. It covers the characterization technique from theoretical predictions based on quantum mechanical calculations, structural and morphological studies, thermal behavior, molecular dynamics, and charge transport properties. Moreover, a novel hybrid theoretical approach named ONIOM (n-layered integrated molecular orbital and molecular mechanics approach) was introduced and implemented to study the interactions of ILs with complex polymer chains in the ionogels. It will be useful for readers, including students, researchers, and industrialists, who wish to explore the field of ionogels as well as their applications to solid-state materials. As we have said, the field of ionogel membranes is yet to be explored; this book can be used as reference material for upcoming innovations too.

1.2. Ionic liquids

Nowadays, ionic liquids (ILs) are considered as promising materials for electrochemical applications because of their unique characteristics compared with conventional molecular liquids (6). ILs are nothing but organic salts with either an asymmetric cation with a symmetric anion or vice versa or with both an asymmetric anion and cation. ILs are liquid at near room temperature with a shallow melting point precisely below 570 K (7) having negligible vapor pressure, non-flammability, and enhanced thermal and chemical stability. A most interesting feature of ILs is that they consist of ions with high ion density and conductivity.

Moreover, the physical and chemical properties of an IL can easily be tuned by introducing various kinds of ions in it. These unique properties of ILs have attracted worldwide attention for applying them in vast areas including green solvents, media for organic transformation, electrochemical applications, nanotechnology, biotechnology, pharmaceuticals, etc. These applications have already been reported in the literature, and hence we are more focused on their electrolytic applications alone.

Though electrodes play a vital role in electrochemical gadgets regarding their overall capacity, energy density, and cyclic-ability, electrolytes also have a crucial role in determining the current density, power density, time stability, and safety of the battery in electrochemical devices (8). Henceforth, ILs open up a new platform to improve the ion conductivity of electrolytes. The favorable properties of IL like non-volatility, high ionic conductivity (0.1–740 mS/cm), high thermal stability, and wide electrochemical window made it suitable for an ideal electrolyte. Further, ILs opens up an avenue for improving the properties of conducting materials. Thus ILs act as an excellent substitute for the legendary organic and non-organic electrolytes in the gadgets. A list of such ionic liquid with their characteristic properties is tabulated in Table 2.

Table 2. List of commonly used ionic liquids for the electrochemical application (9).

Ionic liquids	Conductivity	Electrochemical window
a) Highly conductive		
1-Ethyl-3-methylimidazolium dicyanamide	27 mS/cm	2.9 V
1-Ethyl-3-methylimdazolium thiocyanate	21 mS/cm	2.3 V
b) Electrochemically stable		
Triethylsulphonium bis(trifluoromethylsulfonyl)imide	8.2 mS/cm	5.5 V
N-Methyl-*N*-trioctylammonium bis(trifluoro-methylsulfonyl)imide	2.2 mS/cm	5.7 V
N-Butyl-*N*-methylpyrrolidinium bis(trifluoro-methylsulfonyl)imide	2.1 mS/cm	6.6 V
c) Combined properties		
1-Ethyl-3-methylimidazolium tetrafluoroborate	12 mS/cm	4.3 V
1-Ethyl-3-methylimidazolium trifluoromethylsulfonate	8.6 mS/cm	4.3 V

Generally, ILs with imidazolium cations exhibit higher conductivity while pyrrolidinium and sulphonium cations exhibit a wider electrochemical window. However, the liquid nature of ILs still limits their application as electrolytes in the current scenario, since safety had to be assured rather than their performance (10). A large number of works were already reported on the relevance of ILs and their effectiveness in electrochemistry. However, our main concern is devoted to overcoming the limitations of ILs owing to their liquid nature including leakage, gas formation from solvent decomposition, etc., and will not venture too much to other areas. This work is solely concentrated on two ILs with high conductivity, namely: 1-Ethyl-3-methylimidazolium thiocyanate and 1-Butyl-1-methyl pyrrolidinium bis (trifluoromethyl sulfonyl imide).

1.2.1. 1-Ethyl, 3-methylimidazolium thiocyanate

1-Ethyl-3-methylimidazolium thiocyanate [EMIM] [SCN], with the formula $C_7H_{11}N_3S$, is a room temperature IL with a molecular weight of 169.25 g/mol extensively used as an electrolyte in energy storage devices. The chemical structure of [EMIM] [SCN] is shown in Figure 1.

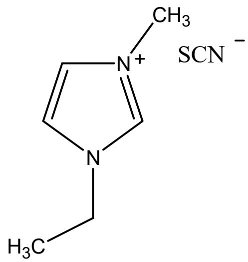

Figure 1. The chemical structure of 1-Ethyl-3-methylimidazolium thiocyanate.

[EMIM] [SCN] has a high conductivity of $2.1 Sm^{-1}$ and low viscosity at room temperature compared to other ILs, e.g. $[EMIm]BF_4$, $[BMIm]BF_4$, and organic electrolytes (11). The literature emphasizes that though the ionic conductivity of [EMIM] [SCN] is about 1/40 of that for 35 wt% H_2SO_4 and about five times that for 0.1M (CF_3SO_2) 2NLi in PC: DME (1:2, v/v), the electrochemical performance of [EMIM] [SCN] lie between the two specified electrolytes. Due to high capacitance, uncompromised performance, and stability, [EMIM] [SCN] can be used as a potential electrolyte in capacitors, double layer capacitors, supercapacitor, dye-sensitized solar cells, etc.

1.2.2. 1-Butyl-1-methyl pyrrolidinium bis (trifluoromethyl sulfonyl imide)

1-Butyl-1-methyl pyrrolidinium bis (trifluoromethyl sulfonyl imide) [[BMPyr] [TFSI]] with the formula $C_{11}H_{20}F_6N_2O_4S_2$ is also a room-temperature ionic liquid with a molecular weight of 422.41 g/mol with high conductivity and viscosity. The chemical structure of [BMPyr] [TFSI] is shown in Figure 2.