CONTENTS

List of tables vii

List of figures viii

Preface xiii

Abstract xv

1 Introduction 1

1.1 Introduction on Solid State Ionics 1

1.2 Classification of Ion-Conducting Materials 3

1.2.1 Framework Crystalline / Polycrystalline Solid Electrolytes 3

1.2.2 Glassy /Amorphous Solid Electrolytes 4

1.2.3 Composite Solid Electrolyte 4

1.3 Polymer Electrolytes 5

1.3.1 Polymer-Based Electrolytes: An Overview 5

1.3.2 Classification of Polymer Electrolytes 8

1.3.2.1 Solvent-Free Polymer Salt Complexes Or Dry Solid Polymer Electrolytes 8

1.3.2.2 Plasticized Polymer Electrolytes 8

1.3.2.3 Rubbery Polymer Electrolytes OR Polymer-in-Salt Systems 9

1.3.2.4 Gel Polymer Electrolytes 10

1.3.2.5 Composite Polymer Electrolytes 11

1.4 Applications of Polymer Electrolytes 13

1.4.1 Electrochemical Batteries 13

1.4.2 Electrochemical Capacitor or Supercapacitor 15

1.4.3 Fuel Cell 16

1.4.4 Dye-Sensitized Solar Cell (DSSC) 17

1.4.5 Electrochromic Display Devices (ECDs) 18

1.4.6 Sensors 19

1.5 Motivation and Objective of The Present Work 19

References 23

2 Theoretical Details 30

2.1 Introduction 30

2.2 Theoretical models for Temperature Dependence of Ionic Conductivity 31

2.2.1 Arrhenius Theory / Arrhenius Model For Ion Transport 31

2.2.2 VTF Theory / Vogel – Tammann – Fulcher Theory 32
2.2.3 WLF (Williams – Landel – Ferry) Theory 32
2.3 Theoretical Models for DC Conductivity 33
2.3.1 Free Volume Model 33
2.3.2 Configurational Entropy Model 34
2.3.3 Static Bond Percolation Model 34
2.3.4 Dynamic Bond Percolation Model (DBP) 36
2.3.5 Space Charge Model 36
2.3.6 Amorphous Phase Model 37
2.3.7 Effective Medium Theory 38
2.4 Theories of Explaining Plasticization 39
2.4.1 The Lubricity Theory 39
2.4.2 Gel Theory 40
2.4.3 The Free-Volume Theory 40
2.5 Impedance Spectroscopy and Various Conductivity Formalisms. 41
2.5.1 Complex Impedance Spectroscopy (CIS) 41
2.5.2 Dielectric spectroscopy Techniques 49
2.5.3 Modulus Formalism 53
2.6 Frequency-Dependent Conductivity 54
2.6.1 Jonscher's Power Law 55
References 58

3 Experimental Details 63

3.1 Introduction 63
3.2 Sample Preparation 63
3.2.1 Materials 65
3.2.2 Preparation of Gel Polymer Electrolyte 69
3.3 Characterization Techniques 70
3.3.1 X-ray Diffraction (XRD) 70
3.3.2 Fourier Transform Infrared Spectroscopy (FTIR) 72
3.3.3 Differential Scanning Calorimetry (DSC) 76
3.3.4 Scanning Electron Microscope (SEM) 78
3.3.5 Atomic Force Microscopy (AFM) 80
3.3.6 Ionic Transport Number 81
3.3.6.1 Wagner Polarization Technique 82
3.3.6.2 Combined ac/dc Technique for Cation Transport Number (t_+) / DC Polarization Technique. 83

3.3.6.3 EMF method 84
3.3.7 Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) 85
3.3.8 Tensile Strength Characterization 86
3.3.9 Electrical Properties 88
References 91

4 Characterization Results 95

4.1 X-ray Diffraction Analysis 95
4.2 SEM Analysis 99
4.3 DSC Analysis 103
4.4 FTIR Analysis 107
4.5 AFM Analysis 113
4.6 Transport Number Measurement 115
4.7 Electrochemical Stability Window 117
4.8 Mechanical Strength 119
References 123

5 Electrical Properties 127

5.1 Introduction 127
5.2 Complex Impedance Analysis 131
5.3 Temperature-Dependent DC Ionic Conductivity 142
5.4 AC Conductivity 146
5.5 Dielectric Analysis 170
5.6 Modulus Analysis 185
References 202

6 Battery Study- Electrochemical Application 209

6.1 Introduction 209
6.2 Working Principle of The Battery 210
6.3 Preparation of Electrode Materials and Fabrication of Li^+ Ion Conducting Primary Cell 213
6.3.1 Preparation of Electrodes Materials 213
6.3.2 Gel Polymer Electrolyte Used As a Separator 214
6.3.3 Cell Configuration 214
6.4 Cell Characterization and Performance 215

6.4.1 Open Circuit Voltage (OCV) 215
6.4.2 Discharge Characteristics 215
References 220

7 Conclusions 221

List of Publications and Presented Papers in International/National Conferences 225